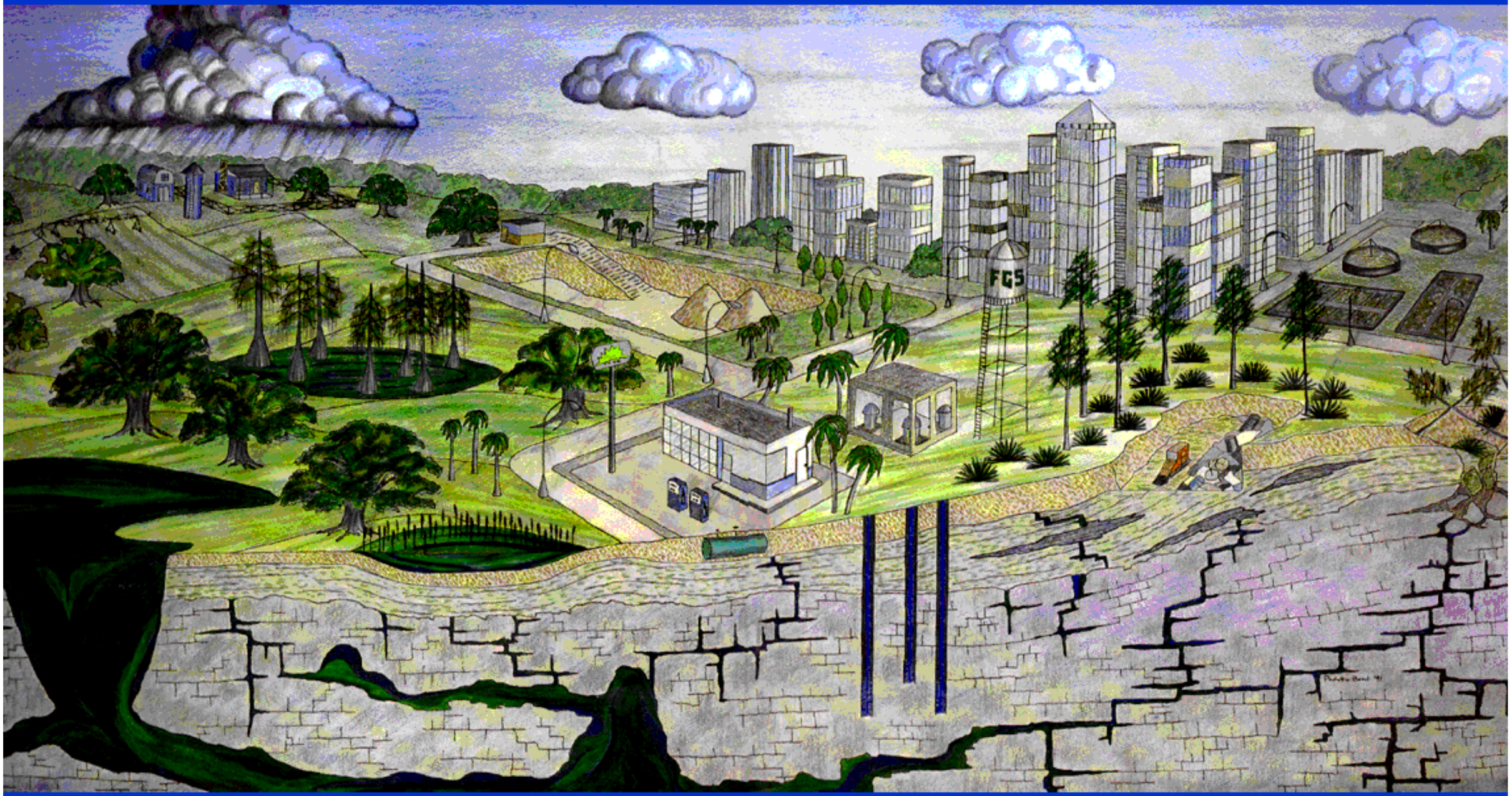
FLORIDA'S GROUND WATER QUALITY MONITORING PROGRAM



BACKGROUND HYDROGEOCHEMISTRY

DEPARTMENT OF NATURAL RESOURCES

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LETTER OF TRANSMITTAL

Florida Geological Survey
Tallahassee
October, 1992

Governor Lawton Chiles, Chairman
Florida Department of Natural Resources
Tallahassee, Florida 32301

Dear Governor Chiles:

The Florida Geological Survey, Division of Resource Management, Department of Natural Resources, is publishing, as its Special Publication 34, Florida's Ground Water Quality Monitoring Program - Background Hydrogeochemistry. This publication is the second in a series which will present the results of the ground water quality network program established by the 1983 Water Quality Assurance Act (Florida Statutes, Chapter 403.063). It is primarily a series of maps which provide the background hydrogeochemical parameters present within the principal aquifer systems of Florida. These results can be used by state and local governments, planners, and developers for land-use planning, conservation, and protection of Florida's valuable water resources.

Respectfully yours,

Walter Schmidt, Ph.D., P.G.
State Geologist and Chief
Florida Geological Survey

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FLORIDA GEOLOGICAL SURVEY SPECIAL PUBLICATION

FLORIDA'S GROUND WATER QUALITY MONITORING PROGRAM
BACKGROUND HYDROGEOCHEMISTRY

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Published for the
FLORIDA GEOLOGICAL SURVEY
Tallahassee
1992

ISSN 0085-0640

ACKNOWLEDGEMENTS

This publication is the result of contributions by a number of individuals and agencies associated with the Florida's Ground Water Quality Monitoring Program. The list of contributors below recognizes the many geologists, field technicians, computer specialists, draftsmen, secretaries and student assistants who aided in this effort.

Much of the work that resulted in the maps found in this volume was performed by the five water management districts and the county cooperators. These agencies have primary responsibility for maintaining and sampling the Ground Water Quality Monitoring Program well networks. Ground-water sampling of these networks has been conducted since 1984. Personnel of these agencies also contributed by providing interpretation of the hydrogeologic framework within their respective areas. Administration of the program has been provided by personnel of the Ground Water Quality Monitoring Section of the Department of Environmental Regulation (DER). Several individuals from Florida's State University System contributed valuable research, training and technical advice to the program. The U.S. Geological Survey has provided technical assistance from the early days of the program. The Florida Geological Survey (FGS) has contributed to the program by providing extensive geotechnical assistance and editing, and by publication of this report.

The editors of this volume each provided valuable and necessary expertise. Rick Copeland (DER) provided the leadership and central management necessary for the development and ultimate completion of this large scale project. Gary Maddox (DER) served as a central focal point for the interaction between DER, the water management districts and the FGS and provided computer expertise in the management of the massive data files generated by this effort. Sam Upchurch (University of South Florida) was the hydrogeochemical guru advising all the scientists involved in completing this research effort. Jacqueline Lloyd (FGS) and Tom Scott (FGS) edited the maps and text, supervised map digitization and correction, and compiled the volume for publication.

The following individuals and agencies contributed time, data and valuable expertise in the development of the Background Network and the preparation of this report:

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Chapter I
INTRODUCTION

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Over the past several decades, Florida has experienced phenomenal population growth, with approximately 300,000 new residents annually joining the 13 million who, in 1992, already call the "Sunshine State" their home. This trend will likely continue into the foreseeable future. The rapid influx of people, in addition to exerting acute pressures on existing social services and the infrastructural framework of many communities, has stressed the water resources of the state in two ways: a sharp increase in the demand for potable water supplies, and a corresponding increase in the volume of waste products generated.

Florida is blessed with the most abundant fresh ground-water resources of any state (McGuinness, 1963). Plentiful potable water is perhaps Florida's most important - and vulnerable - natural resource. As of 1980, approximately 87% of Florida's public drinking water supply came from underground sources (Fernald and Patton, 1984). The remaining 13% came from surface sources, such as rivers and lakes. In order to achieve potability, these surface sources generally require more extensive treatment than most ground-water sources. This is due in large part to pollutants introduced into surface waters by human activities. Without abundant ground water, there would not be enough clean fresh water to supply the current population, especially in the high growth areas of southern and central Florida.

Since all fresh ground water ultimately has a surface source, any pollution contained in rainfall, river or lake water can eventually turn up in our underground drinking water supplies. In Florida these two sources, ground and surface water, are intimately connected: most lakes and rivers in the state are fed at least partially from ground-water discharge through springs and seeps, and surface water bodies recharge aquifers. Changes in land use activity can supply potential contaminants: rainfall percolating into the subsurface can carry with it pesticides and herbicides from agricultural areas, metals and synthetic organic compounds from urban stormwater runoff, and hydrocarbons from leaking fuel storage tanks. Past waste disposal practices, coupled with the increasingly high volumes of waste generated, have resulted in movement of significant quantities of pollutants into portions of the state's aquifer systems. In many areas, Florida's ground-water resources are not well protected from surface infiltration of potential contaminants. Most of the state's ground-water supplies are derived from shallow aquifers, which begin at the top of the water table and extend downward. Often there is no protective overlying aquitard or aquiclude to attenuate the downward migration of potential contaminants. Where present, these protective low permeability formations are often locally breached by karst features, such as sinkholes and solution pipes, which allow surficial waters to rapidly infiltrate downward, carrying with them any pollutants picked up along the way. This provides little time for natural chemical and biological processes to break down potential contaminants before they reach the water table and enter aquifer systems.

Unlike visible contamination in surface waters, the effects of contaminant transport in underground aquifers are not easily observed. Delineation of subsurface contamination areas can involve the use of expensive technology, such as geophysical detection methods and the installation of monitoring wells. Cleanup of a contaminated site can easily cost millions of dollars. Even so, once contaminated, it is virtually impossible to remove all pollutants from the subsurface environment using current technology, making restoration of an aquifer to completely natural conditions unlikely. It is much easier (and cost-effective) to prevent, rather than clean up, ground- water contamination.

Floridians use more water per capita than any other state. As a result of this use, coupled with increasing population growth and development, the state's ground-water supplies are threatened by excessive overdraft and contamination. Increased demand means increased drawdown in the aquifer systems, and this can also cause water quality degradation. When withdrawal exceeds recharge, the aquifer systems are essentially being mined for water. Excessive withdrawal of fresh water within some areas causes the upwelling of underlying denser connate water, or lateral intrusion of seawater. This is particularly problematic in high volume withdrawal areas along the coast, such as in the vicinity of urban wellfields. In these and other susceptible areas, ground-water withdrawals must be carefully managed in order to preserve water quality; this is one reason why Florida's water management districts require permits for the installation of certain types of wells. In many areas, increased demand for potable ground water has resulted in water shortages and subsequent restrictions on water use.

In some areas of Florida, the amount of meteoric water entering the aquifer systems greatly exceeds the amount locally discharged; these areas are referred to as recharge zones. These areas are particularly sensitive to land uses which contribute contaminants to soil or surface waters, or restrict downward percolation of meteoric waters. Protecting these areas from large-scale human development preserves the quality and amount of water entering the aquifer, and thus the ground-water supply. Currently, Florida counties and municipalities are required to address the issue of protecting areas of high recharge through the state's Growth Management Act, particularly within the Natural Ground Water Recharge element of local Comprehensive Plans. While forcing some difficult decisions regarding growth management and land use, everyone ultimately benefits from the continued availability of abundant, safe drinking water.

HISTORY AND PURPOSE

Realizing the need to thoroughly study the effects of man's activities on our aquifer systems and to protect and more wisely manage our water resources, the Florida Legislature, in 1983, passed the Water Quality Assurance Act. This legislation required the Department of Environmental Regulation to "establish a ground water quality monitoring network designed to detect or predict contamination of the state's ground water resources" (Florida Statutes, Section 403.063). To facilitate this effort, the Act required the Department to work cooperatively with other federal and state agencies, including Florida's five water management districts, in the establishment of the network.

The three basic goals of the statewide Ground Water Quality Monitoring Program are:

1) To establish the background and baseline ground-water quality of major aquifer systems in the state;

2) To detect and predict changes in ground-water quality resulting from the effects of various land uses and potential sources of contamination;

3) To disseminate water quality data generated by the network to local governments and to the public.

The purpose of this report is to present the results of the initial quantification of background water quality in each of the state's major potable aquifer systems. Results are presented and interpreted in light of the influencing factors which locally and regionally affect ambient ground-water quality. This initial data will serve as a baseline from which future sampling results can be compared. Future sampling of the Network will indicate the extent to which Florida's regional ground-water resources are improving or declining in quality.

ORGANIZATION AND ESTABLISHMENT OF THE GROUND WATER QUALITY MONITORING NETWORK

The Florida Department of Environmental Regulation (DER) is the lead agency in establishment of the Ground Water Quality Monitoring

Network, determining goals and strategies, setting priorities and coordinating the overall effort. The Department works closely with the five water management districts (WMD's) (WMD boundary lines are shown in Appendix 3, figure 1), and several counties, which carry out most of the necessary field work and provide local technical expertise. The Florida Geological Survey (FGS) and the Water Resources Division of the U.S. Geological Survey (USGS) provide additional technical support, as have several studies funded through the State University System. The Ground Water Quality Monitoring Network is actually made up of three principal elements: two major sub- networks and one survey, each of which has unique monitoring priorities and goals. These are:

- **Background Network**, designed to help define background water quality through a network of over 1600 wells that tap all major potable aquifers within the state;

- **VISA (Very Intense Study Area) Network,** designed to monitor the effects of various land uses on ground- water quality within specific aquifers in selected areas. The VISA Network became operational in 1990, and results will be published in a subsequent volume;

- **Private Well Survey,** designed to analyze, on a one-time basis, ground- water quality from 50 private drinking water wells in each of Florida's counties. This data will supplement the Background Network by providing over 3000 additional sampling points, while indicating the general quality of water consumed by private well owners. This survey is a joint effort between the Florida Department of Health and Rehabilitative Services (HRS) and the DER. This long-term project began in 1986 and is ongoing.

This publication is a compilation of water quality data generated by the Background Network of Florida's Ground Water Quality Monitoring Program. The data used in this report were generated between 1984 and 1988. Future data generated by both the Background and VISA Networks will be compared to information contained in this report in an effort to quantify changes in ground-water quality over time.

BACKGROUND NETWORK

Before changes in ground-water quality can be detected, a baseline from which to compare future changes must be determined. Baseline refers to current regional ground-water quality, determined from statewide sampling from 1984-1988. This may or may not be synonymous with the pristine ground- water quality that existed before measurable human impact to the aquifer. A well in the Background Network is designed to monitor an area of the aquifer which is representative of the general ground-water quality of the region (for the purposes of this program, a region generally incorporates an area greater than or equal to the size of a county, and is defined by aquifer extent and, if possible, ground- water basin boundaries). It is not intended to indicate changes in aquifer chemistry associated with specific contamination sources; however, widespread changes in water quality associated with regional land use patterns (the accumulated effects of many sources) may be present.

USEFULNESS OF BACKGROUND NETWORK DATA

Data generated by the Ground Water Quality Monitoring Program can be used to evaluate regional ground-water quality. This has numerous practical applications in both the public and private sectors.

Local water quality can be compared to regional background water quality, where changes in quality are suspected. This data can provide upgradient information, against which the effects of a potential contamination source can be compared. It can also aid in quantifying temporal changes in ground-water quality brought on by sweeping land use changes, such as urbanization. Until background is defined, it is difficult to determine whether an unusual parameter concentration measured at a well is the result of natural or anthropogenic influences.

Background data will be useful for determining potential health risks to the public resulting from ground-water consumption. State and local agencies will find the data useful in land use planning and zoning decisions, the protection of public drinking water supplies, and in the development of state-mandated comprehensive growth planning. Water management districts can use the data to evaluate permit applications regarding water withdrawal and use. Regulatory agencies will find the data invaluable in implementing aquifer resource management strategies, such as wellhead protection, delineation of recharge and discharge areas, and surface water/ground water co-management. Mapping of physical aquifer extents and distribution (Scott et al, 1991), coupled with knowledge of chemical aquifer characteristics (this volume) helps to better define available resources. Future efforts involving the mapping of potential aquifer vulnerability, refinement of hydrostratigraphic units, and the development of data evaluation methods will all contribute to the body of information which will aid in the wise use of the state's ground-water resources.

The private sector will find the data particularly useful when preparing reports on such issues as contamination assessments, risk evaluations, water supply studies and waste disposal designs. Industry and agricultural interests will benefit by being able to identify appropriate water supply sources based on water quality.

The well and water quality data is available to the public via access to a computer bulletin board, or by contacting:

Florida Department Of Environmental Regulation
Bureau Of Drinking Water & Ground Water Resources
Ground Water Quality Monitoring Section
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Staff—(904) 488-3601 or SUNCOM 278-3601

FAX—(904) 487-3618 or SUNCOM 277-3618

GWIS BBS (Computer Bulletin Board) —
(904) 487-3592 or SUNCOM 277-3592

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Chapter II

DATA COLLECTION AND MANAGEMENT METHODS

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WELL SELECTION AND SAMPLING

Prior to selecting monitoring sites for inclusion in the Background Network, hydrogeologic data were evaluated in conjunction with land use information. Most of this information was of a general nature and was compiled by the state's five water management districts (Appendix 3, figure 1). The first volume of this series (Scott et al, 1991) contains a wealth of hydrogeological data collected during the initial phase of the program. This information was used to develop regional monitoring strategies, and aided in the selection of potential well sites. These wells were selected or drilled in order to achieve optimum areal and aquifer distribution.

The second phase of the program entailed locating existing wells suitable for inclusion in the monitoring network. An initial inventory of existing wells meeting these criteria was conducted by the U.S. Geological Survey and the water management districts. The following criteria were used to determine eligibility:

a) Depth of well and cased interval known;
b) Open hole interval taps only one aquifer or water-bearing zone;
c) Precise site location known;
d) Well owner cooperative; e) Future accessibility for sampling granted;
f) History of the site (prior land use, previous sampling results) known.

Other non-mandatory. but desirable criteria included:

a) Site ownership by local, state or federal agency;
b) Prior water quality data available;
c) Well diameter known;
d) Lithologic and geophysical logs available;
e) Hydrogeologic information available.

Over 1200 existing wells were initially selected through this process. Although optimal quality assurance and quality control could be more fully realized by drilling all monitoring wells expressly for use in the network, the associated costs prohibited such an approach. It was determined that useful data could be obtained using wells already in existence, if the selection criteria were strictly adhered to.

Subsequent to locating existing wells, correlating well depth with site hydrogeology and considering land use patterns, locations for additional monitoring wells were determined. Over 600 new wells were drilled in areas where no suitable existing wells could be found. Depending on the hydrostratigraphy at each new site, a single well or cluster of wells was installed, allowing each major water-bearing zone to be separately monitored. Geological information was obtained at each site during drilling. At many sites, a core from the uppermost significant confining bed was obtained for laboratory determination of permeability. Initial well placement was biased toward preferential monitoring of the most important potable aquifer within a region; current strategy emphasizes the uppermost aquifer system in an area. This latter philosophy is based on the notion that surface-introduced chemical changes (due to land use or meteorological considerations) would first be detected in the uppermost water- bearing unit. Figure 1 shows the general location of currently sampled wells by aquifer system in the Background Network.

The first sampling of each well in the network involved the measurement of a comprehensive set of field, chemical, microbiological, and naturally- occurring radioactive parameters (Table 1). These analyses, combined with historical data, can be used to estimate baseline ground-water quality. Once current baseline has been determined, data from future monitoring of the network will be continually evaluated to determine changes in water quality over time. This information is particularly useful for implementation of wellfield protection measures, water quality monitoring and land use planning.

After the initial samples are collected and analyzed, Background Network monitoring wells are resampled approximately every three to five years for all network parameters. A subset of Background Network wells, the Temporal Variability Subnetwork ("TV Net"), is sampled more frequently (monthly or quarterly), in order to detect variations in ground-water quality over time. Samples collected on a quarterly basis are analyzed for major ions and field parameters, while monthly data collection consists of the measurement of field parameters only **(see Table 1)**. ~Wells sampled monthly are a subset of the wells which are sampled quarterly. In addition, a pilot project is currently underway to define temporal variability on an even finer scale. Using dedicated probes and automatic sampling devices installed in a few wells, the goal of this "optimal frequency study" is to observe variations in ground-water quality on a weekly, daily, or hourly basis. Results from the Temporal Variability Subnetwork will be published in a future volume.

Development of the Background Network occurred in the following phases:

- **Phase I:** Data collection, compilation, and location of existing wells which could be incorporated into the Background Network;

- **Phase II:** Selection and drilling of initial monitoring wells;

-**Phase III:** Initial sampling of the Background Network to determine ground- water quality spatial trends and define baseline;

-**Phase IV:** Resampling of wells found to contain abnormal concentrations of one or more parameters;

-**Phase V:** Refinement of the network through removal of redundant wells and those found not to monitor representative background ground-water quality, as well as drilling of additional wells where needed;

- **Phase VI:** Ongoing periodic resampling to define variations in ground-water quality over time.

SAMPLING PROTOCOL

The history of sampling of the Background Network reflects an increasing awareness of the many difficulties encountered in collecting and analyzing a representative ground-water sample. Potential variability introduced by the use of different sampling personnel, techniques and equipment, sample transport from the field to the laboratory, environmental and laboratory contamination, concurrent use of several analytical laboratories, and varying methods of reporting results have all had an effect on the analyses discussed here. By working closely with personnel in the field and in the laboratory, and by developing standardized QA/QC procedures, sampling and analytical methods have steadily improved over the history of the program, with the goal of minimizing the potential variability introduced throughout the entire process.

Sampling of the Background Network began in mid-1985. A portion of the existing wells were sampled using permanently installed pumps. The remaining existing wells and all new wells were sampled using teflon bailers, dedicated bladder pumps or submersible pumps. Some monitoring wells have been fitted with semi-permanent internal standpipes, to facilitate purging and water sample collection. Sample collection protocol currently follows that established by the U.S. Environmental Protection Agency (EPA) (EPA, 1982,1991). The initial sampling episode included the collection of a comprehensive set of physical, chemical, biological and radiometric parameters (Table 1).

Initial sampling of the Background Network was overseen or performed by each water manage-

ment district. All sampling is currently conducted or supervised by a trained professional. Annual training of sampling personnel is funded by DER and provided by the staff of the USGS Ocala Quality of Water (QW) Service Unit. A rigorous quality control program has been established (see ANALYTICAL METHODS section below). Field, trip and laboratory blanks are submitted on a routine basis. Initially, all sampling agencies were required to have an individually-approved quality assurance/quality control (QA/QC) plan on file with the Department, and to submit periodic QA/QC reports. In order to standardize procedures, all sampling is now performed under a single "umbrella" QA/QC plan, authored by DER and signed by each sampling agency (DER, 1991). Agreement by each agency to use standardized sample collection methodology further minimizes sampling variability.

The determination of sampling frequency and the parameters to be monitored at each site were based on several factors, such as network designation, land use activity and the hydrogeologic sensitivity of the site. After initial sampling, several wells were dropped from the Background Network, based on analytical sample results which indicated that data from the wells were not representative of regional background water quality. In some instances, existing monitoring wells did not have good hydraulic connection with the aquifer to be monitored. In other instances, the quality of water from the well was impacted by poor well construction. Additional wells may be added to fill in gaps in areal or aquifer-specific coverages. This refinement process is ongoing.

Residual well construction materials and casing corrosion can significantly increase the volume of suspended solid material present within a well. Turbidity analysis can be used to evaluate well construction integrity for many wells. Redevelopment is often required in problem wells which were improperly installed, or have a tendency to accumulate residual solids, due to local hydrogeologic conditions (Aller et al., 1989). Prior to 1989, almost all samples were unfiltered in the field prior to laboratory analysis. Thus, the combined contribution of particulate matter, suspended (colloidal) solids, and the soluble fraction in each sample were measured with each analysis. This is representative of well water quality, but not necessarily aquifer water quality, since the well itself could possibly be the source for many of the particulates present in the samples (Nielsen, 1991). Since data on both aquifer and well water quality was desired, filtered and unfiltered samples are now collected for affected parameters at each site and separately analyzed.

ANALYTICAL METHODS

The initial chemical analyses of Background Network samples were performed by private laboratories, with some parameters analyzed by the water management district laboratories. Due to the magnitude of the program and the large initial number of samples, several different analytical laboratories were used. This caused concern about consistency and relative comparability of data from one lab to another. As a result, all inorganic analyses are currently performed by one lab, the USGS Ocala QW Service Unit, and organics are analyzed by the DER Central Laboratory or its designated overflow lab. Sample analysis protocol generally follows methods described by EPA, USGS or DER (American Public Health Association, 1980; Fishman et al., 1989; DER, 1981).

To assess laboratory accuracy and precision, duplicate samples and reference samples are anonymously submitted, along with trip, equipment and field blanks. These QA/QC samples currently constitute over 20% of the total number of samples analyzed. As a QA/QC check on procedures and efficiency, the laboratories are periodically audited by outside agencies. Frequent meetings are held among the Ground Water Quality Monitoring Program staff and laboratory personnel to discuss procedural problems as they arise.

Table 1 references the standard EPA laboratory methods initially used to analyze samples from the Background Network. These methods have and will change as better equipment and procedures become available. Major ions, metals, organics, radiometrics and microbiological parameters were all included in the analyses. Field parameters were measured in the field at the time of sample collection. **Table 2** lists the Primary and Secondary Drinking Water Standards for parameters sampled in the Background Network.

To assess methodology protocol and the performance of sampling personnel, periodic field audits are carried out by members of the DER program staff. These audits are supplemented by required QA/QC reports, submitted quarterly by each sampling agency, detailing real and potential problems encountered during sample collection. All agencies performing sampling or analytical services for the program are required to have an approved QA/QC plan on file with the Department, or to comply with the "umbrella" plan written by DER.

All water quality results are submitted to DER in both paper and electronic formats. In addition to the actual results, these data also include information on analytical method used, STORET code, (EPA, 1984), well, field and laboratory identification numbers, units, parameter name, project name, exceedances of existing standards, and data submitted by field personnel, such as sampling date and time, and remarks. This information is for the most part incorporated into the data bases discussed below.

DATA BASE SYSTEMS

A variety of data base and software systems have been developed to store, manipulate and display information related to the Ground Water Quality Monitoring Program. All water quality information collected by the program is uploaded to DER's mainframe "Central Repository", an archive of statewide environmental data available to DER and other state agencies. In the near future, Background Network data will also be written into an ORACLE database, for use with DER's ARC/Info geographic information system (GIS). Contact DER's Bureau of Information Systems for details on availability of these data formats.

Currently the most widespread system in use is the Generalized Well Information System (GWIS), a micro-computer database and retrieval system which houses all well and analytical water quality information generated by the program. It was developed on an IBM-PC compatible platform, and consists of two separate data bases: one containing physical well information and one containing analytical results. The two are linked by a USGS-format (latitude/longitude/sequence number) common well identifier. The data file format is currently fixed-field length ASCII, but will be changed to dBase format in the near future. The system was written in-house, to quickly and efficiently handle the large volume of data generated by the network, and is available to the public. GWIS water quality data retrievals run in three main steps:

1) Select wells of interest from physical well information database, using almost any combination of constraints);

2) Select parameters of interest (from sample database, individually or by predefined group);

3) Retrieve data.

The program also allows the user to constrain retrievals by sampling dates, or to only retrieve results above or below a given threshold value (these can correlate with exceedances of assigned standards). Output formats allow for row-and- column or tabular report generation and the calculation of summary statistics on multiple samples. Various utility programs allow the calculation of frequency distributions, water types, and statistical outliers. A direct interface with a popular off-the-shelf computer-aided drafting (CAD) package allows the user to plot well locations and data on a map, or define a region of interest graphically, for subsequent data retrieval.

AVAILABILITY OF DATA

The GWIS program and data files can be obtained from DER by contacting our Tallahassee office at the address or telephone numbers previously listed. The programs and data are also available via a computer bulletin board (BBS) run-

ning 24 hours a day, seven days a week, for anyone with an IBM-compatible personal computer and a modem. The entire Background Network database and GWIS programs are available for remote use or for down-loading. The bulletin board system can handle 300, 1200 and 2400 baud calls using industry standard communications parameters of no parity, 8 data bits, and 1 stop bit (n-8-1). These are the default settings for most major communications software packages. To connect, use your computer to call (904)487-3592 or SUNCOM 277-3592.

DATA VALIDATION PROCEDURES

Before network data is released to the public, raw laboratory and field data is converted into dBase format and then run through an extensive series of automated and manual screening procedures (Figure 2). Error checking programs detect parameter values outside allowable ranges. Data entry mistakes are often the cause for these errors. Charge balance checks are run, usually an indication of the integrity of laboratory analyses. Outlier programs use non-parametric estimation to flag values which, while within allowable ranges, seem not to fit regional trends. When outliers are found, sampling procedures are first checked. In addition to these automated checks, the data are inspected manually by staff to assure completeness of each data set and to remove QA data to another database. QA data includes field, trip and laboratory blanks submitted at regular intervals in the sampling process. After in-house editing and review, provisional data sets are released to sampling agencies for their review. Outliers are flagged, and samplers are asked to provide any data which may explain the anomalous values. Results are compared to trip and equipment blanks taken during sampling. In some instances, the well may be resampled, or laboratory procedures may be investigated. If circumstances surrounding the collection or analysis of the sample are suspect, the data may be left in the database but flagged with conditional provisions, or removed altogether. Other para- meter analyses from the same sample may or may not be affected. If no disqualifying problems are found, the outlier may not be rejected, and is included in the release database.

Ground-water quality data are constantly being received as ongoing sampling projects continue. The main GWIS distribution databases are updated three or more times a year.

ENDNOTES

[1]STORET is a water quality database management system established by the U.S. Environmental Protection Agency. Five-digit STORET codes are assigned for each parameter based on methods used during sample collection and analysis.

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Chapter III
HYDROSTRATIGRAPHY

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INTRODUCTION

Florida's ground-water resources occur in a complex lateral and vertical sequence of Cenozoic sediments comprised of both siliciclastics and carbonates which underlie the entire state. Hydrostratigraphically, the section consists of several major aquifer systems defined on lateral extent, degree of confinement, and hydrologic parameters of the sediments. The Southeastern Geological Society's ad hoc Committee on Florida Hydrostratigraphic Unit Definition (Southeastern Geological Society (SEGS), 1986), in an attempt to alleviate many of the nomenclatural problems surrounding Florida's hydrostratigraphic units, defined the framework of the various aquifer systems occurring in the state. Most of the geologic community have accepted these definitions and are using the suggested nomenclature. Aquifers of lesser importance have been recognized in some areas of the state and are discussed in the literature on specific areas. This text will define and characterize only the major aquifer systems discussed by the SEGS (1986). These systems include the surficial aquifer system, the intermediate aquifer system or intermediate confining unit, and the Floridan aquifer system including the Claiborne aquifer and the sub- Floridan confining unit. Figure 3 indicates which formations form portions of the various aquifer systems throughout the state. Miller (1986) provides an excellent, in-depth discussion of the Floridan aquifer system and the associated shallower strata. It is recommended that the reader review Miller's volume for a more detailed description of the ground-water system in Florida. Appendix 3, figure 2 delineates the distribution of aquifer systems in Florida.

References to Florida's geomorphic features are made in this and succeeding chapters. Appendix 3, figures 3 to 7 delineate these features in each district. For further discussion refer to Scott (1991).

Geologic Structures in Relation to Hydrostratigraphy

The occurrence, thickness and, to some extent, the aquifer characteristics are directly related to the structural features present in a given area. The major positive features affecting the various aquifer systems include the Ocala Platform, Chattahoochee Anticline,Sanford High and the St. Johns and Brevard Platforms (Figure 4a). The major negative features include the Gulf Basin, Apalachicola Embayment, Gulf Trough, Jacksonville Basin, Osceola Low and the Okeechobee Basin (Figure 4a). These structures affected the deposition and erosion of the later Cenozoic sediments. Older structures, including the Peninsular Arch and the South Florida Basin (Figure 4b), affected the lower portions of the Cenozoic section (see Scott (1991) for a discussion of the structural features in Florida).

The surficial aquifer system is thin to absent on the positive features. Its thickness increases off the positive structures reaching maximum thicknesses in the Okeechobee, Jacksonville and Gulf Basins and the Apalachicola Embayment.

The intermediate aquifer system and/or intermediate confining unit also thins onto the positive features. Sediments forming these units are erosionally absent from much of the Chattahoochee Anticline, Ocala Platform and the Sanford High. These units thicken off the highs, reaching the maximum thicknesses in the basinal areas. As the sediments of the intermediate aquifer system and confining unit thicken, permeable beds become more commonly interbedded with the impermeable strata, resulting in a more fully developed intermediate aquifer system.

Eocene and Oligocene carbonate sediments of the Floridan aquifer system are exposed to thinly covered on the Ocala Platform and the Chattahoochee Anticline. These sediments are covered by a thin intermediate confining unit on the flanks of the positive features. In these areas, the carbonates have been exposed to aggressive ground water, developing an extensive karstic terrain. In the basinal areas, the carbonate sediments have not undergone such extensive dissolution due to the thick protective cover provided by the intermediate aquifer system and intermediate confining unit.

AQUIFER SYSTEMS AND CONFINING UNITS

Surficial aquifer system

The SEGS (1986) defines the surficial aquifer system as the

> "permeable hydrologic unit contiguous with the land surface that is comprised principally of unconsolidated to poorly indurated, (silici)clastic deposits. It also includes well-indurated carbonate rocks, other than those of the Floridan aquifer system where the Floridan is at or near land surface. Rocks making up the surficial aquifer system belong to all or part of the Upper Miocene to Holocene Series. It contains the water table, and the water within it is under mainly unconfined conditions; but beds of low permeability may cause semi-confined or locally confined conditions to prevail in its deeper parts. The lower limit of the surficial aquifer system coincides with the top of the laterally extensive and vertically persistent beds of much lower permeability. "

The surficial aquifer system occurs throughout most of the state. In many areas, it is used for small yield domestic and agricultural water supplies. However, in the western panhandle the surficial aquifer system, referred to as the Sand and Gravel Aquifer, supplies important amounts of water for municipal and industrial supplies. In the southeastern part of the state, the surficial aquifer system is called the Biscayne Aquifer and provides enormous quantities of water for the coastal communities in this area. The surficial aquifer system is utilized for public water supply in southern Brevard, Indian River and St. Johns Counties. Elsewhere in the state, the surficial aquifer system is of limited importance. Throughout the extent of the surficial aquifer system, the thickness varies significantly from a feather edge to more than 350 feet in southeastern Florida and 500 feet in the western-most panhandle (Scott et al., 1991). The top of the surficial aquifer system is the natural land surface. The base occurs where impermeable beds of the intermediate confining unit and aquifer system begin or, in those areas where the intermediate is absent, at the top of the Floridan aquifer system carbonates.

In many areas of the state, the surficial aquifer system lies on a karstified erosional surface developed on Eocene to Miocene carbonates. Karst processes have also affected the surficial aquifer system by forming collapse features which filled with surficial aquifer system sediments and may be in direct hydrologic contact with the Floridan aquifer system. Karst features also perforate the surficial aquifer system developing open sinkholes on the present land surface.

NORTHWEST FLORIDA WATER MANAGEMENT DISTRICT

The surficial aquifer system in the Northwest Florida Water Management District (NWFWMD) occurs over most of the district. It is absent only in a limited portion of Wakulla, Leon and Jefferson Counties at the eastern edge of the district along the western flank of the Ocala Platform. It is thin to absent on part of the Chattahoochee Anticline in Jackson and Holmes Counties. Where the surficial is present it ranges in thickness from less than 10 feet in the east to more than 500 feet in the north-western corner of the area (Scott et al., 1991).

The siliciclastic sediments comprising the surficial aquifer system in NWFWMD are part of the Citronelle and Miccosukee Formations, "Coarse Clastics" and the undifferentiated sediments of Pleistocene-Holocene age (Marsh, 1966; Scott, 1991). These sediments are primarily quartz sands with varying percentages of clay. Where the clay content becomes great enough to inhibit

the transmission of ground water, localized impermeable beds may confine water creating artesian conditions within the surficial aquifer system. The surficial aquifer system yields greater quantities of water in the western panhandle where the Citronelle contains less clay and is thicker than in those areas where the clayey Miccosukee occurs.

SUWANNEE RIVER WATER MANAGEMENT DISTRICT

The surficial aquifer system in the Suwannee River Water Management District (SRWMD) is present in several areas of the district. According to Ceryak (SRWMD, personal communication, 1991), the surficial aquifer system is present in adjoining portions of southern Madison, eastern Taylor and western Lafayette Counties, eastern Suwannee County, much of Columbia, Hamilton and Union Counties, along the eastern edge of

Bradford County under Trail Ridge and under Waccasassa Flats in central Gilchrist County. Sediments equivalent to the surficial aquifer system are present throughout much of the district but are not utilized for water resources. Thicknesses of the surficial aquifer system range from 10 to 30 feet but may reach 50 to 60 feet under Trail Ridge (see Scott (1991) for discussion of the geomorphology of Florida).

The surficial aquifer system sediments in SRWMD are part of the undifferentiated sediments and in some areas, the upper Hawthorn Group sediments. These sediments are quartz sands with varying amounts of clay and carbonate. In localized areas the clay content of the sediments may form confining beds within the surficial system.

The base of the surficial aquifer system in the SRWMD occurs at the top of the impermeable sediments of the Hawthorn Group throughout much of the district. However, in the eastern portion of the district, the base may occur within the sediments of the upper Hawthorn Group. In other areas, the intermediate confining unit may be absent and the surficial aquifer system may lie directly on the carbonates of the Floridan aquifer system or be absent.

ST. JOHNS RIVER WATER MANAGEMENT DISTRICT

The surficial aquifer system in the St. Johns River Water Management District (SJRWMD) is an important source of potable water in Duval, Clay, St. Johns, Putnam, Brevard and Indian River Counties. The coastal counties utilize the surficial to varying degrees with St. Johns, southern Brevard and Indian River Counties, using it for public supply. Eastern Orange and eastern Alachua Counties also utilize the surficial aquifer system. In other areas of the district, the surficial aquifer system may be used for limited domestic supplies. The surficial aquifer system thickness is highly variable, ranging from a few feet to in excess of 100 feet.

Sediments forming the surficial aquifer system in SJRWMD are lithostratigraphically assigned to the undifferentiated sediments, Cypresshead and Nashua Formations, Caloosahatchee Formation-equivalent shell beds and the Coosawhatchie Formation of the Hawthorn Group. The undifferentiated sediments and the Cypresshead Formation consist of quartz sands with varying percentages of clay. The Nashua Formation and Caloosahatchee Formation-equivalent beds are composed of varying admixtures of quartz sand, clay, shells and shell debris. The Anastasia Formation is composed of sand and coquina. Quartz sands and varying amounts of clay make up the Coosawhatchie Formation with limestone becoming prominent in portions of Duval and Nassau Counties. Locally, the sediments contain sufficient clay to form impermeable beds creating artesian conditions in the surficial aquifer system.

The base of the surficial aquifer system in the SJRWMD occurs at or near the top of the Hawthorn Group or in the undifferentiated post-Hawthorn sediments when those sediments are relatively impermeable.

SOUTHWEST FLORIDA WATER MANAGEMENT DISTRICT

The surficial aquifer system occurs over much of the Southwest Florida Water Management District (SWFWMD). It is of generally limited value in the northern portions of the district and increases in importance to the south. SWFWMD data indicates that the surficial aquifer system is thin over much of the district (Scott et al., 1991). Thicknesses range from less than 25 feet in much of the northern part of the district on the Ocala Platform to 25 to 50 feet in the southern area and more than 250 feet under the Lake Wales Ridge.

Surficial aquifer system sediments in SWFWMD belong to the undifferentiated sediments in the northern half of the district. In the southern half of SWFWMD the sediments include the Tamiami, Caloosahatchee and Fort Thompson Formations. Along the Lake Wales Ridge, the surficial aquifer system is comprised of sediments belonging to the Cypresshead Formation and the undifferentiated sediments. In a limited area in central SWFWMD, the Bone Valley Member of the Peace River Formation, Hawthorn Group forms part of the surficial aquifer system. The sediments in these units generally consist of quartz sand with varying percentages of clay and shell except in the Bone Valley Member where phosphate forms a significant proportion of the sediment. Vacher et al. (1990) characterize the sediments as quartz sand with less than 10 percent clay over much of the district. They also show shell content of the surficial aquifer system increasing toward the coast and to the south in the southern half of the district.The base of the surficial aquifer system occurs at the top of the impermeable sediments overlying the carbonates of the Floridan aquifer system in the northern part of the district. When impermeable sediments of the Hawthorn Group are subjacent to the undifferentiated sediments they form the base of the surficial. The Hawthorn Group lies subjacent to the Cypresshead Formation under the Lake Wales Ridge and forms the base of the system. The Hawthorn Group sediments also form the base of the surficial aquifer system in southern SWFWMD where the Hawthorn underlies the Tamiami, Caloosahatchee and Fort Thompson Formations.

SOUTH FLORIDA WATER MANAGEMENT DISTRICT

The surficial aquifer system is widespread in the South Florida Water Management District (SFWMD) constituting an important water resource. Although the surficial aquifer system is present over much of the district, it is the most important source of ground water in the southeastern portion of SFWMD, in Dade, Broward and Palm Beach Counties. In Lee, Hendry and Collier Counties, the surficial provides significant quantities of potable water for domestic and agricultural uses. Throughout the district, the surficial aquifer system varies in thickness from a few feet to more than 400 feet thick.

The sediments comprising the surficial aquifer system are from several lithostratigraphic units. In the north-central SFWMD area, the surficial occurs in the undifferentiated sediments, Cypresshead Formation and shell beds of the Caloosahatachee/Fort Thompson Formations. In the western part of SFWMD, sediments of the Tamiami, Caloosahatchee/Fort Thompson Formations and the undifferentiated sediments make up the system. In the eastern area of SFWMD, the surficial aquifer system, in part referred to as the Biscayne Aquifer, consists of sediments from the Anastasia Formation, Miami and Key Largo Limestones, Fort Thompson Formation, and Caloosahatchee and Tamiami-equivalent sediments. In SFWMD, the base of the surficial system occurs at the first impermeable sediments in the Hawthorn Group. Occasionally, the upper Hawthorn Group sediments may form the basal portion of the surficial.

The lithostratigraphic units forming the surficial aquifer system consist of a complex array of facies. The sediments range from quartz sands to limestones with varying admixtures of shell and clay. As a result of the variability, the quality of the surficial aquifer system in SFWMD changes dramatically from place to place. Numerous investigations of these sediments have discussed the variable nature of the aquifer characteristics ffor example, Causaras, 1985; Wedderburn et al., 1982; Shaw and Trost, 1984; Knapp et al., 1986; Smith and Adams, 1988).

Intermediate Aquifer System and Intermediate Confining Unit

The SEGS (1986) defines the intermediate aquifer system or intermediate confining system as including

"all rocks that lie between and collectively retard the exchange of water between the overlying surficial aquifer system and the underlying Floridan aquifer system. These rocks in general consist of fine grained (silici)clastic deposits interlayered with carbonate strata belonging to all or parts of the Miocene and younger Series. In places poorly yielding to non-water-yielding strata mainly occur and there the term intermediate confining unit applies. In other places, one or more low to moderate-yielding aquifers may be interlayered with relatively impermeable confining beds; there the term intermediate aquifer system applies. The aquifers within this system contain water under confined conditions."

"The top of the intermediate aquifer system or intermediate confining unit coincides with the base of the surficial aquifer system. The base of the intermediate aquifer is at the top of the vertically persistent permeable carbonate section that comprises the Floridan aquifer system, or, in other words, that place in the section where siliciclastic layers of significant thickness are absent and permeable carbonate rocks are dominant."

The intermediate aquifer system or inter mediate confining unit occurs over much of the state. It is absent from those areas where it was removed by erosion and the surficial aquifer system sediments, if present, lie immediately suprajacent to the carbonates of the Floridan aquifer system. Springs are a common feature of these areas. Surrounding the areas where these sediments are missing, the intermediate aquifer system or intermediate confining unit is often perforated by karst features. Where this condition exists, the intermediate aquifer system and the intermediate confining unit allow water to pass through into the Floridan aquifer system or into the surficial aquifer system.

The regional significance of the intermediate aquifer system is quite limited. Statewide, this section is referred to as the intermediate confining unit. It serves to confine the Floridan aquifer system and forms the base of the surficial aquifer system. The sediments comprising this section are predominantly siliciclastic (quartz sand, silt and clay) with varying proportions of carbonates (limestone and dolostone) present. Much of the intermediate confining unit was deposited during the Miocene and Early Pliocene. It is interesting to note that in some areas Miller (1986) has included low permeability Oligocene and Eocene carbonates in contact with the Miocene sediments as part of the intermediate confining unit.

The top of the intermediate aquifer system or intermediate confining unit ranges from more than 350 feet below National Geodetic Vertical Datum (NGVD) to greater than 225 feet above NGVD. Miller (1986) cites thicknesses of the intermediate confining unit (his upper confining unit) ranging from very thin or absent to greater than 1000 feet.

NORTHWEST FLORIDA WATER MANAGEMENT DISTRICT

The intermediate confining unit occurs over much of the NWFWMD serving to effectively confine the Floridan aquifer system. It is thin to absent over the Chattahoochee Anticline in portions of Jackson and Holmes Counties. The intermediate confining unit is also thin to absent in eastern Wakulla, southeastern Leon and southern Jefferson Counties. The intermediate confining unit thickens dramatically under the western end of NWFWMD in Escambia County and in the Apalachicola Embayment under Gulf and Franklin Counties. Thicknesses range from less than 10 feet to greater than 1000 feet.

The ability of the intermediate confining unit to effectively confine the subjacent Floridan aquifer system is impaired in those areas where it has been breached by karst development. These areas include portions of Jackson, Holmes, Washington, Walton, Leon and Wakulla Counties (Sinclair and Stewart, 1985).

Siliciclastic sediments predominate in the intermediate confining unit in NWFWMD. Carbonate sediments are present in the sediments of the Apalachicola Embayment and east of the Apalachicola River. In western NWFWMD, the confining unit is the Pensacola Clay which grades eastward into the Alum Bluff Group. Further east, generally east of the Apalachicola River, the Hawthorn Group forms the intermediate confining unit. Within the Apalachicola Embayment, portions of the Intracoastal Formation form the intermediate confining unit.

The intermediate aquifer system is generally not an important water-bearing unit in NWFWMD. Permeable beds of limited extent are present locally and may provide limited amounts of water to small, domestic wells. The intermediate aquifer system/confining unit acts as an aquifer system primarily east of the Choctawhatchee River (Wagner, 1988). The permeable zones utilized for ground water are siliciclastic and carbonate beds in the Intracoastal Formation (Barr and Wagner, 1981), the Alum Bluff Group and, to a very limited extent, the Hawthorn Group.

SUWANNEE RIVER WATER MANAGEMENT DISTRICT

The intermediate confining unit is present in SRWMD under the Northern Highlands. This includes portions or all of Jefferson, Madison, Hamilton, Suwannee, Columbia, Baker, Bradford, Union and Alachua Counties. Within this area, the thickness of the intermediate confining unit may exceed 300 feet (Scott, 1988) and confined to semiconfined conditions exist. It is thin to absent on the Ocala Platform and thickens on its flanks reaching the greatest thickness in the Jacksonville Basin to the east of SRWMD. Karst features are common throughout this area except in the northeastern part of SRWMD (parts of Baker, Bradford, Columbia, Hamilton and Union Counties). Outliers and sinkhole fill consisting of the sediments of the intermediate confining unit are common in the areas where the unit is absent.

Siliciclastic sediments dominate the intermediate confining unit in SRWMD. These sediments most often are part of the Hawthorn Group or materials that are residual from it ("Alachua Formation").

The intermediate aquifer system is interbedded with the impermeable beds of the intermediate confining unit. The intermediate aquifer system is developed in the sands and carbonates of the Hawthorn Group (Ceryak et al., 1983). In the northeastern portion of the District, four discrete carbonate units have been identified, each of which is a separate intermediate aquifer. These aquifers are up to 40 feet thick, and are all confined, with the possible exception of the basal Hawthorn carbonate unit, which may be in hydraulic contact with the uppermost Floridan aquifer system.

ST. JOHNS RIVER WATER MANAGEMENT DISTRICT

The intermediate confining unit and intermediate aquifer system occur throughout the SJRWMD except along the western district boundary in parts of Marion and Alachua Counties on the Ocala Platform. The combined confining unit and aquifer system ranges in thickness from less than ten feet to more than 500 feet. It is thickest in the Jacksonville Basin in northeastern SJRWMD. It thins over the St. Johns Platform, Sanford High and Brevard Platform in the central portion of the district then thickens into the Osceola Low and the Okeechobee Basin in southern SJRWMD. In the SJRWMD the Hawthorn Group or undifferentiated post- Hawthorn sediments, where present, are considered to form the top of the intermediate aquifer system.

The intermediate confining unit and intermediate aquifer system consist primarily of interbedded siliciclastic and carbonate sediments of the Hawthorn Group and sand, clay and limestone of the undifferentiated post-Hawthorn sediments. The Hawthorn Group sediments are absent over much of the Sanford High and limited portions of the St. Johns and Brevard Platforms in southern Flagler County, much of Volusia County and northern Brevard County.

Karst conduits breaching the intermediate aquifer system and intermediate confining unit are common in much of the SJRWMD. Only in Baker, Nassau, Duval and parts of Clay and St. Johns Counties are karst features very few in number and the intermediate confining unit is not often breached (Sinclair and Stewart, 1985).

The intermediate aquifer system is utilized as a public water supply source in Flagler and eastern Indian River Counties. Elsewhere it is utilized for limited domestic and agricultural supplies. Permeable strata in the Hawthorn Group and the post-Hawthorn undifferentiated sediments often exhibit rapid lateral and vertical variability resulting in a limited areal distribution of water-producing units. The intermediate aquifer system is most often utilized in Nassau, Duval, Baker, St. Johns and Clay Counties where the Hawthorn Group or post-Hawthorn undifferentiated sediments are thickest, infilling the Jacksonville Basin.

SOUTHWEST FLORIDA WATER MANAGEMENT DISTRICT

The intermediate confining unit and intermediate aquifer system are present throughout most of SWFWMD (Buono et al., 1979). Although the sediments comprising this section are absent to very thin in the northern half of SWFWMD, they thicken to more than 650 feet in the southern end of the district (Buono et al., 1979). In the northern half of the district, the section is generally the intermediate confining unit and is thin to absent on the southern end of the Ocala Platform. In the southern half of SWFWMD, approximately from northern Polk and Hillsborough Counties south, the intermediate confining unit also contains permeable sediments forming the intermediate aquifer system. In this area, the sediments thicken to the south into the Okeechobee Basin (Buono et al., 1979; Scott, 1988).

Siliciclastic and carbonate sediments of the Hawthorn Group comprise the majority of the intermediate confining unit and intermediate aquifer system in SWFWMD. In addition, some post-Hawthorn siliciclastics may form a limited portion of the intermediate confining unit in the northern half of the district. In the northern portion of the district, clayey sediments lying on the Floridan aquifer system carbonates belong in part in the Hawthorn Group and in part may be reworked Hawthorn sediments along with residuum from dissolution of carbonates.

Breaching of the intermediate confining unit and the intermediate aquifer system by karst features is common in the northern half of the district and along the Lake Wales Ridge in Polk County (Sinclair and Stewart, 1985). The southern portion of SWFWMD has limited karst development (Sinclair and Stewart, 1985) and few karst conduits penetrate the intermediate confining unit and intermediate aquifer system.

The intermediate aquifer system is utilized in the southern half of SWFWMD and becomes most important at the southern end of the district where the Floridan aquifer system is deeply buried and highly mineralized. The permeable strata of the Hawthorn Group and portions of the Tamiami Formation form the water-producing horizons providing variable quantities of ground water (Sutcliffe, 1975).

SOUTH FLORIDA WATER MANAGEMENT DISTRICT

The intermediate confining unit and the intermediate aquifer system occur throughout SFWMD. However, the intermediate aquifer system is utilized in a limited number of counties along the western edge of the district. This section ranges in thickness from approximately 500 feet in the northern SFWMD area to more than 900 feet in the southernmost portion of the district (Scott, 1988). Much of the SFWMD area lies in the Okeechobee Basin.

Interbedded siliciclastic and carbonate sediments from the Hawthorn Group form the intermediate confining unit and intermediate aquifer system in SFWMD. Previously, some of the sediments currently included in the intermediate confining unit and intermediate aquifer system along the west coast were placed in the Tamiami Formation but are now considered part of the Hawthorn Group (Missimer, 1978; Wedderburn et al., 1982; Scott,1988). In the eastern part of the district, Tamiami-equivalent sediments may form the top of the intermediate confining unit (Causaras, 1985).

The importance of the intermediate confining unit and intermediate aquifer system in the western part of SFWMD has led to a number of studies in Charlotte, Lee, Hendry and Collier Counties (Sutcliffe, 1975; Wedderburn et al., 1982; Knapp et al., 1986; Smith and Adams, 1988). There are three principle producing zones within the intermediate aquifer system in this area, the "Sandstone aquifer" named by Boggess and Missimer (1975), the "mid-Hawthorn aquifer" of Wedderburn et al. (1982) and the "lower-Hawthorn aquifer" of Knapp et al. (1984). These producing zones have been very important to the development of southwestern Florida.

Floridan Aquifer System

The SEGS (1986) defines the Floridan aquifer system as a

> "thick carbonate sequence which includes all or part of the Paleocene to Early [sic] Miocene Series and functions regionally as a water-yielding hydraulic unit. Where overlain by either the intermediate aquifer system or the intermediate confining unit, the Floridan contains water under confined conditions. Where overlain directly by the surficial aquifer system, the Floridan may or may not contain water under confined conditions..."
>
> "The top of the aquifer system generally coincides with the absence of significant thicknesses of (silici)clastics from the section and with the top of the vertically persistent permeable carbonate section. For the most part, the top of the aquifer system coincides with the top of the Suwannee Limestone, where present, or the top of the Ocala Group (Limestone)."

In limited areas the Avon Park Formation forms the top of the aquifer system. Sediments of the Arcadia Formation (Hawthorn Group), the Bruce Creek Limestone, the St. Marks Formation or the Tampa Member of the Arcadia Formation may form the top of the Floridan aquifer system (SEGS, 1 986).

> "The base of the aquifer system in panhandle Florida is at the gradational contact with the fine-grained (silici)clastic rocks belonging to the Middle Eocene Series. In peninsular Florida, the base coincides with the appearance of the regionally persistent sequence of anhydrite beds that lies near the top of the Cedar Keys Limestone (Formation)." (SEGS, 1 986).

The Floridan aquifer system exhibits extreme variations in permeability resulting from a combination of original depositional conditions, diagenesis, structural features and dissolution of carbonates and evaporites (Miller, 1986). The system has been extensively altered by karst processes in some areas of the state. Dissolutional and diagenetic processes have been extremely important in the development of the Floridan aquifer system from carbonate sediments deposited during the Paleocene through Early Miocene.

The thickness and lithology of the sediments suprajacent to the Floridan determine the surficial expression of the karst processes. On the Ocala Platform from Hillsborough and Polk Counties north to the state line, then westward into Leon and Wakulla Counties and on the Chattahoochee Anticline in Jackson and Washington Counties, carbonate sediments of the Floridan aquifer system crop out or are covered by a thin layer of unconsolidated siliciclastics (Sinclair and Stewart, 1985). In these areas, the carbonates have been exposed to extensive dissolution by aggressive ground waters percolating downward from land surface. Often the karst geomorphology has reached a relatively mature stage of development resulting in numerous surface depressions which often coalesce. The Floridan aquifer system exhibits well developed cavernous porosity and conduit flow paths. Most of Florida's major springs occur in this zone including Wakulla and Silver Springs.

The carbonates of the Floridan aquifer system lie beneath a variable thickness of post-Floridan sili-

ciclastics and carbonates of the intermediate confining unit, intermediate aquifer system and the surficial aquifer system on the flanks of the Ocala Platform and the Chattahoochee Anticline. Although karst processes have affected the sediments of the Floridan in these areas, forming dissolutional conduits and caverns, the karst topography is not as well developed as in the areas of thin cover. However, in these areas the karst features are often of large diameter and depth due to overburden thickness (Sinclair and Stewart, 1985).

The Floridan aquifer system lies subjacent to a thick sequence of post-Floridan sediments in the Okeechobee Basin, Jacksonville Basin, Gulf Trough, Apalachicola Embayment and the Gulf Basin of the western panhandle. In these areas the carbonates of the Floridan have apparently not been subjected to extensive karstification. However, subsurface investigations of the limestones indicate some karstic modification of the sediments during subaerial exposure prior to the deposition of the sediments of the inter- mediate confining unit and intermediate aquifer system (U. Hamms and D. Budd, University of Colorado, personal communication, 1991).

The elevation of the top of the Floridan aquifer system varies significantly throughout the state. The top occurs at elevations in excess of 100 feet above NGVD on the Ocala Platform and Chattahoochee Anticline to depths greater than 1100 feet below NGVD in southern Florida and 1500 feet below NGVD in the western-most panhandle (Miller, 1986). The thickness of the Floridan varies from less than 100 feet in the western half of the panhandle to in excess of 3500 feet in southwestern peninsular Florida (Miller, 1986).

The base of the Floridan aquifer system, the sub-Floridan confining unit, varies stratigraphically throughout the state. The SEGS (1986) indicates that the base of the Floridan in the panhandle occurs in the Middle Eocene approximately at the top of the Claiborne Group. The base of the system in the peninsula generally is considered to occur within or near the top of the Paleocene Cedar Keys Formation (SEGS, 1986). Miller (1986) provides a more detailed picture of the variability of the stratigraphic positioning of the Floridan aquifer system base but indicates the same general regional trends.

NORTHWEST FLORIDA WATER MANAGEMENT DISTRICT

The Floridan aquifer system in NWFWMD supplies more than 90 percent of the water demand and is utilized in all the counties in the district except Escambia and part of Santa Rosa Counties (Wagner, 1988). It underlies the entire district but is too saline for potable water in the western end of the panhandle. The water quality over a broad area corresponding to the Apalachicola Embayment and the Gulf Trough and the coastal zone may be affected by the upconing of mineralized waters (Scott et al., 1991).

The top of the Floridan aquifer system in NWFWMD varies in elevation from 150 feet above NGVD in Jackson and Holmes Counties to greater than 1500 feet below NGVD in Escambia County (Miller, 1986; Scott et al., 1991). The thickness of the aquifer system ranges from approximately 100 feet thick in portions of Jackson and Holmes Counties on the Chattahoochee Anticline to more than 2800 feet thick in Franklin County in the Apalachicola Embayment (Scott et al., 1991).

In the western part of the district, the Floridan aquifer system is subdivided into an upper and lower aquifer separated by a confining unit, the Bucatunna Clay. The confining unit thins and pinches out towards the east in Okaloosa County, where the Floridan becomes a single aquifer (Marsh, 1966; Scott et al., 1991).

Carbonate sediments dominate the Floridan aquifer system with minor occurrences of siliciclastics. The siliciclastics generally occur intimately mixed with the carbonates and are more common in the upper portion of the aquifer system. Within the district, the Floridan aquifer system is composed of the Ocala, Marianna, Suwannee, Chickasawhay, and Bruce Creek Limestones and the St. Marks and Chattahoochee Formations.

Stratigraphically, the base of the Floridan aquifer system varies significantly throughout NWFWMD. In the Pensacola area, the base occurs within the Upper Eocene Ocala Limestone (Miller, 1986). Under the eastern end of the district, the base falls within the Paleocene Cedar Keys Formation. The depth to the base of the Floridan varies from -100 NGVD on the Chattahoochee Anticline to -3100 feet NGVD in the Apalachicola Embayment (Miller, 1986).

The Claiborne aquifer has been recognized within the sub-Floridan confining unit. The total extent of this aquifer is not known and it is not often utilized (Allen, 1987). It is composed of carbonate and siliciclastic sediments of the Claiborne Group.

The effects of karstification are most intense on and surrounding the Chattahoochee Anticline in Jackson, Holmes and Washington Counties and on the flank of the Ocala Platform in Leon and Wakulla Counties. In these areas, the aquifer system has been extensively altered by dissolution and often has many direct conduits from the surface into the Floridan. An extensive, underwater conduit mapping project of the Woodville Karst Plain by the Woodville Karst Plain Project (Parker Turner, Florida State University, personal communication, 1991) is currently documenting the length and complexity of the dissolutional features of the area.

SUWANNEE RIVER WATER MANAGEMENT DISTRICT

The Floridan aquifer system occurs throughout the SRWMD providing the vast majority of the water supplies. The top of the Floridan ranges from greater than 100 feet above NGVD in Jefferson County to more than 300 feet below NGVD in Bradford County (Scott et al., 1991). The thickness ranges from approximately 1100 feet in northern Jefferson County to 2200 feet in southern Jefferson County (Miller, 1986). The thicknesses of the Floridan aquifer system sediments in SRWMD show the effects of the Apalachicola Embayment and Gulf Trough in Jefferson County. These sediments also exhibit the thicker carbonate sequence deposited in the peninsular area.

Carbonate sediments deposited during the Paleocene through the Early Miocene comprise the Floridan aquifer system in SRWMD. The base of the system occurs near the top of the Paleocene Cedar Keys Formation (Miller, 1986). Carbonates of the Oldsmar and Avon Park Formations, the Ocala and Suwannee Limestones and the St. Marks Formation comprise the Floridan aquifer system in the district. The Suwannee Limestone forms a portion of the Floridan in approximately one half of the district while the St. Marks Formation occurs in limited areas. When the Suwannee Limestone and the St. Marks Formation are absent, the Ocala Limestone forms the top of the system. In the southern portion of the district, the Ocala Limestone is absent due to erosion and the Avon Park Formation forms the top of the system.

The top of the sub-Floridan confining unit generally occurs within the Cedar Keys Formation throughout SRWMD (Miller, 1986). The position- ing of the permeability barrier shifts locally within the upper part of the Cedar Keys Formation from the top of the unit to some distance below the top. The depth to the sub-Floridan confining unit varies from -1200 feet NGVD on the Ocala Platform to -2100 feet on the flank of the Gulf Trough (Miller, 1986).

The sediments of the Floridan aquifer system throughout SRWMD have been greatly affected by karstification. Sinkholes a~e very common in most areas and numerous springs are scattered across the district. The only area of minor karstification is in northernmost Columbia and Baker Counties.

ST. JOHNS RIVER WATER MANAGEMENT DISTRICT

The Floridan aquifer system is present throughout the SJRWMD containing potable water supplies in most areas. Salt water intrusion or upwelling is a concern in many of the coastal areas and along the St. Johns River Valley (Scott et al., 1991).

The top of the Floridan aquifer system in SJR-

WMD occurs at the highest elevations on the flank of the Ocala Platform in Alachua and Marion Counties. In this area, the uppermost Floridan sediments range from 50 to more than 100 feet above NGVD. The upper surface of the system dips into the Jacksonville Basin, in the northern part of SJRWMD, where it may be more than -550 feet NGVD. To the south, the top of the Floridan reaches more than -350 feet NGVD (Scott et al., 1991). The thickness of the system ranges from approximately 1500 feet in Baker County (northwestern SJRWMD) to 2900 feet in southern Brevard County (Miller, 1986).

Carbonate sediments dominate the Floridan aquifer system within the district. Siliciclastic sediments, when present, occur mixed in with carbonate lithologies and predominantly in the uppermost portion of the Floridan. The Ocala Limestone forms the top of the aquifer system over the majority of the district. In very limited areas of Volusia and Orange Counties, the Avon Park Formation occurs at the top of the Floridan. Sediments of Oligocene age occur at the top of the aquifer system along the east coast in southernmost Brevard County and in Indian River County. Miller (1986) shows small outliers of Suwannee Limestone at the top of the Floridan in the northern portion of the district. The majority of the aquifer system is comprised of the Avon Park and Oldsmar Formations.

The sub-Floridan confining unit occurs within the Cedar Keys Formation throughout the district. The positioning of the base of the Floridan varies from the top of the Cedar Keys Formation to within the upper portion of the formation (Miller, 1986). The top of the sub-Floridan confining unit varies from -1600 feet NGVD on the flank of the Ocala Platform to -3200 feet NGVD in the Jacksonville Basin and the Okeechobee Basin (Miller, 1986).

Karst processes have significantly altered the carbonates of the Floridan aquifer system in much of the SJRWMD. Karst features are common in much of the central and western portions of the district (Sinclair and Stewart, 1985). The karstification in these areas is related to dissolution of the Ocala Limestone. In the southern half of the district, dissolution of the carbonate fraction of the Plio-Pleistocene sediments is responsible for the development of some of the karst features.

SOUTHWEST FLORIDA WATER MANAGEMENT DISTRICT

The Floridan aquifer system underlies the entire SWFWMD area and contains plentiful, potable water supplies throughout most of the district. Areas of mineralized water along the coast and in portions of Charlotte and Sarasota Counties limit the availability of fresh water from the Floridan in these areas (Scott et al., 1991).

The top of the Floridan aquifer system in the SWFWMD displays two distinct elevational trends. The northern two thirds of the district (from central Polk and Hillsborough Counties northward) is relatively flat with elevations varying from sea level to between 100 and 150 feet above NGVD. The top of the Floridan in the southern one third of the district dips distinctly to the south dropping from sea level to more than 750 feet below NGVD along the southern district boundary (Scott et al., 1991). These trends are related to the positions of the Ocala Platform and the northern edge of the Okeechobee Basin.

The thickness of the aquifer system also displays distinct trends. The Floridan is more than 1400 feet thick in the northernmost portion of the district and thins southward across the northern one third of SWFWMD to approximately 600 feet thick (Wolansky and Garbode, 1981). From the thinnest point of the Floridan aquifer system, it thickens into the Okeechobee Basin southward, reaching more than 2400 feet thick in the SWFWMD part of Highlands County (Wolansky and Garbode, 1981).

As in the rest of the peninsula, carbonate sediments dominate the Floridan aquifer system in SWFWMD. Siliciclastic-bearing carbonates and siliciclastic units in the basal Hawthorn Group may form the upper portion of the Floridan in part of the southern portion of SWFWMD. In much of the district, the Suwannee Limestone forms the top of the Floridan. In the northern most portion of SWFWMD, the Ocala Limestone and, in limited areas, the Avon Park Formation comprise the top of the aquifer system. The Avon Park and oldsmar Formations form the main body of the Floridan in the district. The sub-Floridan confining unit occurs in the upper Cedar Keys Formation and varies from -1900 feet NGVD on the Ocala Platform to -4100 feet NGVD in the Okeechobee Basin (Miller, 1986).

Karstic alteration of the Floridan aquifer system has occurred throughout much of the district. In the southern portion of SWFWMD, where the Hawthorn Group thickens in the Okeechobee Basin, karst features are not as abundant (Sinclair and Stewart, 1985). In the northern two-thirds of the district and along the Lake Wales Ridge, karst features are quite common. Surficial karst features in much of southern SWFWMD are the result of dissolution of carbonate sediments and shell material in the Miocene through Pleistocene units.

SOUTH FLORIDA WATER MANAGEMENT DISTRICT

Potable water supplies within the Floridan aquifer system in SFWMD are limited to the northern part of the district. The sediments of the Floridan occur throughout the district but in many areas do not contain acceptable quality water.

The top of the Floridan aquifer system occurs at elevations ranging from sea level in the northern most edge of the district (Orange County) to greater than 1100 feet below NGVD in southwestern SFWMD (Miller, 1986). Most of this area lies in the Okeechobee Basin. The thickness of the Floridan ranges from less than 2300 feet in Orange County to more than 3400 feet under parts of Palm Beach and Martin Counties and more than 3500 feet under western Lee County (Miller, 1986).

A thick sequence of carbonate sediments containing some beds of siliciclastics and siliciclastic-rich carbonates form the Floridan aquifer system in SFWMD. The majority of the sediments comprising the Floridan are carbonates with little to no siliciclastics. However, in southwestern Florida, sand beds have been noted in the Ocala Limestone (Missimer, personal communication, 1991). Siliciclastic-bearing carbonates and a few siliciclastic beds from the basal Hawthorn Group may form the upper beds of the Floridan aquifer system in some areas of the district. In general, the Suwannee Limestone forms the upper unit of the aquifer system with the Ocala Limestone and the Avon Park, Oldsmar and upper Cedar Keys Formations comprising the main mass of the system. The base of the Floridan aquifer system, the top of the sub-Floridan confining unit, occurs within the upper portion of the Cedar Keys Formation (Miller, 1986). The top of the sub-Floridan confining unit ranges from -3000 feet NGVD on the northern edge of the Okeechobee Basin to -4400 feet NGVD in the deeper portion of the Okeechobee Basin.

The development of karst features in the sediments of the Floridan aquifer system in SFWMD has not been extensive. Throughout much of the district, the Floridan contains saline waters and has not been flushed by fresh water. The Floridan aquifer system is also buried by as much as 1100 feet of confining beds and other aquifer systems under much of SFWMD.

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Chapter IV

QUALITY OF WATER IN FLORIDA'S AQUIFER SYSTEM

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INTRODUCTION

Scope

This chapter discusses the quality of water in Florida's aquifer systems. The database used is the Background Network developed by DER and the water management districts. Some data have been omitted from the maps and analyses because they either do not meet quality-assurance standards in terms of ion balance[1] [Note: endnotes are located at the end of each chapter] or they are radically different from data collected at nearby wells and, therefore, cannot be proven to reflect background water quality.

Three aquifer systems[2] are included in the report: (1) surficial aquifer system, (2) intermediate aquifer system and intermediate confining unit (hereafter termed the intermediate aquifer system), and (3) Floridan aquifer system. The distributions of these aquifer systems in Florida are discussed in Chapter 111 of this volume and in Scott et al. (1991).

The discussion and maps are arranged by water management district[3]. Alachua County participated as a separate entity during parts of the data collection and analysis phases of the data. For convenience, the Alachua County data are included with the SRWMD. The tables contain data on the number of samples collected, not number of wells. Surficial aquifer system results are divided into (1) Sand and Gravel Aquifer, (2) Biscayne Aquifer, and "Other", which includes all of the samples not classified as coming from either the Sand and Gravel or Biscayne Aquifers.

The data presented below can be used in a number of ways. They can be used as a baseline for evaluation of the condition of water quality in the aquifer systems of the state as they existed between 1985 and 1988, and for monitoring water- quality changes in the future, which is part of the intent of the 1983 Florida Water Quality Assurance Act. While there is not sufficient data for site specific determinations, the data can also be used to assess general background conditions for permitting, risk assessment, and contamination evaluation. Finally, the data can be used to evaluate ground-water flow systems, ability of the aquifer systems to tolerate contamination, and potential best uses of the waters. These last uses require some understanding of how ground-water chemical systems behave. To this end, the following discussions summarize some of the chemical behaviors of the aquifer systems, and it discusses some ways that the aquifer systems adjust chemically to contamination and mixing of waters with different compositions.

Throughout this chapter, references to various geomorphic features and surface-water basins are made when discussing ground-water quality. Appendix 3, figures 3 to 12 show the locations of these features.

Chapter Organization

The discussions of individual analytes in this report are organized into four major topics:

- *General Descriptors* - the variables that describe the conditions under which the chemicals occur, specifically temperature and pH;
- *Cations* - including calcium, magnesium, sodium, potassium, iron, mercury, and lead;
- *Anions* - including bicarbonate and carbonate, chloride, sulfate, fluoride, nitrate, and phosphate; and
- *Other Constituents* - including total dissolved solids, conductivity, total organic carbon, and synthetic (man-made) organics.

The discussions for each analyte are broken down into aquifer system and then into regions (water management districts), as needed.

Comparison of Map and Table Data

Comparison of the analyte-distribution maps and tables in the following text will indicate some discrepancies. These discrepancies are a result of the dual goals of the Background Network. The maps represent the program's best interpretations of analyte distribution, while the tables reflect GWIS database and an uncritical review of the data contained therein.

The maps were prepared from the best available data. Outliers and data that failed the nearest-neighbor criteria were excluded from the maps. As a result, many of the "bulls eye" contour lines typical of representations on unevaluated data are avoided. The map contours represent the best assessment of data distributions, although some of the maxima and minima represented in the tables are not displayed. The maps, therefore, represent conservative assessments of the distributions of analytes.

The tables reflect the distribution of data in the GWIS database at the time of report preparation. Maximum and minimum values are reported regardless of whether they fit the nearest-neighbor and outlier criteria. Unreasonable maxima and minima are evaluated in the text in the context of how valid they are. In most cases, they can be shown to represent well-construction problems or values that cannot be considered until confirmed by re-sampling and analysis. The tables give the reader a "feel" for the range of data in the GWIS database.

Use of median and quartile population descriptors avoids problems with inclusion of the outliers and represents the best possible indications of water quality. Users are cautioned to examine the GWIS database and be selective in use of these data until confirmations are made with the second round of sampling.

VARIABLE DESCRIPTION CONVENTIONS

Nature of Data Distributions

Environmental, geochemical data are seldom normally distributed (Ahrens, 1954a,b). That is, they normally do not reflect the classic "bell- shaped" curve for which the standard distribution descriptors (mean, standard deviation, variance, etc.) are intended. Geochemical data are typically characterized by a large number of samples with low concentration values and a few samples with high concentrations. This leads to a distribution that is skewed. That is, the distribution is asymmetrical, with a long tail that extends towards the high concentrations. If mean and standard deviation were used to describe a skewed distribution, the mean would be high relative to the most abundant concentrations, thus giving a false impression of the quality of water in the aquifer system.

Distribution Descriptors

In order to better represent the distributions of variables, the median, quartiles, minima, and maxima are used, where appropriate. The median is the 50th percentile. Half the samples are below the median in concentration, the other half above. The median is used in this report to compare water quality between aquifer systems and regionally.

The quartiles represent 25 and 75 percent of the samples. The 25th percentile (lower quartile or ↓Qrtile in the tables) represents the value below which 25 percent of the samples occur. Conversely, the 75th percentile (upper quartile or ↑Qrtile on the tables) represents the value above which only 25 percent of the samples occur. The maximum and minimum are also given in the tables, so a complete representation of the distribution is available. Where a standard or guidance concentration is available, the number of samples that exceeded that value is also represented in the tables.

AQUIFER CONTROLS ON GROUNDWATER CHEMISTRY

Factors That Control Ground-Water Chemistry

Before discussing the water chemistry of Florida aquifer systems it is important to briefly discuss the factors that affect ground-water chemistry. These factors include:

- Precipitation chemistry,
- Surface conditions at the site of recharge,
- Soil type in the recharge area,
- Mineralogy and composition of the aquifer system,
- Nature of aquifer system porosity and structure,
- path in the aquifer system
- Residence time of water in the aquifer system,
- Mixing with other waters in the aquifer system, and
- Aquifer microbiology.

Precipitation Chemistry

The first major factor that affects the chemical composition of ground water is the chemical composition of precipitation. Precipitation, which recharges the aquifer systems, is important as a source of dissolved chemical species and as an acid that induces chemical reactions in the aquifer systems.

Natural rainfall is affected by reactions with atmospheric gases and particulates and by proximity to the sea. Natural rainfall is slightly acidic. It gains acidity by the reaction of water (H_20) with carbon dioxide ($C0_2$) to form carbonic acid (H_2C0_3) according to the reactions:

$$C0_2 + H_20 = H_2CO_3 \qquad (1)$$

$$H_2C0_3 = H^+ + HC0_3\text{-}.$$

As shown in reaction 1, carbonic acid dissociates into hydrogen ion (H^+), which is the source of acidity, and bicarbonate ($HC0_3$-). If rainwater is fully equilibrated with atmospheric carbon dioxide, the resulting pH4 is approximately 5.5 to 5.7 at 25°C. If atmospheric moisture has not completely equilibrated with atmospheric carbon dioxide, pH will be somewhat greater than 5.5. This is the same level of acidity as soda pop, and this moderately acidic precipitation has been responsible for rock weathering over geologic time.

"Acid rain" is a problem caused by introduction of sulfur and nitrogen gases into the atmosphere as fossil fuels are consumed. These gases react with water in reactions similar to reaction 1 to form nitric acid ($HN0_3$) and sulfuric acid (H_2S0_4) and further lower the pH of rainfall (Table 3). Acid rain has been produced in the U.S. for less than 200 years. Because of the long times involved with ground-water transport and the high buffering capacities of limestone- and dolostone- rich aquifers, only a small amount of Florida's ground water has been affected by acid rain. The data presented in this report suggest that the surficial aquifer system and near-surface portions of the intermediate and Floridan aquifer systems have been locally affected by acid rain where recharge is rapid and buffering capacities are minimal. The effects of acid rain on aquifer water quality cannot yet be evaluated because no suitable background water-quality database for comparison has existed until this time.

Florida's climate can be classified as a "maritime climate". The proximity of all parts of the state to the sea has a profound affect on rainfall chemistry. Sea spray is generated by the wind and transported inland as an aerosol. This aerosol is mixed with precipitation so that Florida rainfall is a very dilute mixture that has the ionic proportions of sea water (Figure 5).

Table 3 summarizes the chemical quality of rainfall in Florida (National Atmospheric Deposition Program (IR-7)/National Trends Network, 1990). Note that there is a small amount of all of the major ground-water chemicals in average rainfall. These data also show that there is some nitrate and sulfate presently being introduced as acid rain.

The last column in Table 3 is the deviation (difference) of the sodium to chloride mole ratio from that of average sea water. The coastal and near-coastal stations (Quincy, Kennedy Space Center, Verna Well Field, and Everglades National Park) have average deviations from sea-water composition of five percent or less. More inland sites (Austin-Cary Forest, Bradford Forest) have average deviations from sea water compositions of 54 and 20 percent, respectively. The significance of these larger deviations should not b.e exaggerated, however, as the individual data points show a significant grouping near the sea-water ratio. The means are skewed because of a few data points that may reflect anomalous conditions or analyses.

Therefore, as a general rule, newly fallen precipitation, uncontaminated surface runoff, and uncontaminated soil waters in Florida have the initial compositions of dilute sea water. Based on the differences in chloride concentrations, these waters average about 0.009 percent (1.66 mg/L in precipitation, 19,350 mg/kg in sea water) sea water. While the total dissolved solids contents are low, the ratios of dissolved metals to chloride, especially sodium to chloride, are nearly constant and reveal an origin as marine aerosols.

As this dilute sea-water solution evaporates from the land surface and vadose zoneS soils or is transpired by plants, the chemicals dissolved in the water are concentrated. Evaporation also occurs from the water table, especially where it is shallow and in porous and permeable aquifers. As will be shown below, the increase in dissolved solids content by evapotranspiration is an important starting point in the evolution of aquifer waters.

Surface Conditions

Surface conditions have a pronounced effect on ground-water chemistry, especially in the surficial aquifer system and in unconfined portions of the Floridan aquifer system. Land use, for example, can have a dramatic effect, including introduction of waste heat and contaminants. The effects of human activities have been avoided, where possible, in design of the Background Network. However, natural conditions can also affect ground-water quality.

Natural surface features that can have significant effects on ground water include: (1) lakes, swamps, and marshes, (2) sinkholes and sinking streams, and (3) proximity to the sea and tidal influences. Lakes, swamps, and marshes can serve as sources of natural organics, metals, and low pH water. Sinkholes, sinking streams, and other karst features can introduce surface waters into deeper portions of the aquifer system (Ceryak, 1977). The sea is a source of sodium, chloride and other constituents, which can enter the ground water through canals, river mouths, and other regions where the fresh-water potential is insufficient to prevent intrusion. Saline water can also intrude laterally and vertically when fresh-water potential is reduced by human activity.

Soil Type in Recharge Area

As precipitation percolates into the soil and aquifer environment, the weak acids react with the minerals of the soil or rock and with organics. The uppermost soil zone, where plant growth is active, is characterized by an accumulation of plant debris (humus), which is decomposed by soil microbes. If the soils are aerated, these microbes produce carbon dioxide ($C0_2$), which combines with water according to reaction 1 to form additional carbonic acid and further lower pH. In addition, the partly decomposed organic material often includes water-soluble fractions, including fulvic acids. These organics contain abundant hydrogen as acid radicals. The added carbonic and organic acids lower the water pH to values that are commonly less than four. If the soils are wet and chemically reducing, the microbes produce organic acids and methane gas (CH4), rather than carbon dioxide. Under wet, reducing conditions, microbial destruction of humus is retarded, and peats and mucks form as soil components.

Therefore, recharge through wet, lowland or dry, upland soils will affect local ground-water chemistry differently. The nature of plant cover, supply of humus, moisture content, and soil temperature affect both the availability, quantity, and chemistry of humic substances and the microbial populations that feed upon these substances.

Soil and Aquifer Mineralogy

Once water has passed through the humus zone, it is characteristically acidic, and it can react with minerals in the soil or rock. The reaction (modified from Goldich [1938] and assuming that the reaction is with carbonic acid) can be generalized as

$$\text{Mineral} + H_2C0_3 = \text{Cations} + HC0_3\text{-} + \text{Residue}. \quad (2)$$

Cations6 are the metals found in the soil or aquifer minerals, and bicarbonate is the dominant anion. The residue forms if the mineral contains aluminum or oxidized iron (Fe3+), which are often relatively immobile in ground and soil waters.

To illustrate these reactions, we can compare the reaction of acidic soil water with calcite, the primary mineral in limestone, to a reaction with potassium feldspar, a common, aluminum-bearing mineral that is present in small amounts in Florida quartzose sands. The reaction with calcite is

$$CaC0_{3\,calcite} + H_2C0_{3aq.} \leftarrow Ca^{2+}{}_{aq} + 2HC0_3\text{-}_{aq.}. \quad (3)$$

In this reaction, dissolved calcium and bicarbonate are produced. There is no residue because neither aluminum nor iron is present in the mineral. In reality, natural limestones usually contain other minerals that may leave residues upon rock weathering. →

Potassium feldspar ($KAlSi_3C0_3$) reacts with carbonic acid according to

$$2KAlSi_3C0_{8\ K\text{-}feldspar} + 2H_2CO_{3\ carbonic\ acid} + 9H_2C0 = A1_2Si_2O_5(OH)_{4\ kaolinite} + 2K+_{aq.} + 4H_4SiO_{4\ aq.} + 2HC0\text{-}_{3\ bicarbonate}\ . \quad (4)$$

In this reaction, aluminum and some silica remain to form the common soil clay mineral kaolinite ($Al_2Si_2C0_5(OH)_4$). Silica is also mobilized as silicic acid (H_4SiO_4), and potassium (K^+) is a dissolved ion cation. The H^+ in reaction 4 comes from carbonic acid through reaction 1, so bicarbonate is also produced. In tropical to subtropical climates, kaolinite can be further weathered according to

$$A1\ {}_2Si_2O_5(OH)_{4\ Kaolinite} + 5H_2C0 = A1_2C20_3.3H_2C0_{gibbsite} + 2H_4SiO_{4\ aq\ .} \quad (5)$$

with release of additional silica as silicic acid. Gibbsite ($Al_2C0_3.3H_2C0$) is one of several common aluminum oxyhydroxides found in Florida soils. Both kaolinite and gibbsite are residues in the Goldich weathering reaction (reaction 2). Aluminum can also be mobilized in ground water if the waters are acidic or organic rich.

Iron and aluminum oxyhydroxides, sulfide and sulfate minerals, and a few other minerals are weathered by different processes, which are discussed with the individual analytes below. Clay minerals and some of the oxyhydroxides are also important as sites for ion exchange, which may also affect ground-water quality.

When water sequentially passes through rocks with different mineral compositions, the chemistry of the resulting water reflects the compositions of all previous contact, not just the rock type from which the water was sampled. For example, water from the Floridan aquifer system that has passed through the confining beds of the Hawthorn Group contains fluoride, magnesium, silica, and other constituents that were derived by weathering of Hawthorn minerals (Lawrence and Upchurch, 1976).

Table 4 lists the compositions of common minerals found in Florida aquifer systems and confining beds, and their dissolved weathering products according to the weathering reaction (reaction 2). Most of these minerals are weathered slowly, so an important factor in determining how much of the weathering product enters the ground water is the length of time the water is in contact with a particular rock type (e.g., the residence time).

Table 5 lists the most common minerals found in Florida aquifer systems and confining beds. The surficial aquifer system is composed predominantly of sand from the south-central part of the peninsula to the western end of the panhandle. This sand is primarily composed of the mineral quartz, which is essentially chemically inert (Table 4). The surficial aquifer system in coastal areas contains varying amounts of shell and sand- to silt-sized calcite and aragonite. The calcite/aragonite content of the aquifer system increases to the south, and the Biscayne Aquifer of southeastern Florida is predominantly carbonate. The surficial aquifer system contains highly variable amounts of clay, oxyhydroxides, and humic material (Table 5), all of which are reactive and have the ability to sorb metals and some anions. Iron oxide coatings, which have some sorption capacity, are common on the sands. In all, the sand-rich surficial aquifer system has the ability to sorb moderate amounts of metals and anions. In addition, the carbonate-rich portions of the aquifer system have the ability to consume (buffer) acidity by reactions similar to reaction 3.

The intermediate aquifer system and confining beds comprise a complex array of materials (Table 5) with important consequences for ground-water quality. Strata of the Hawthorn Group include interfingering beds of clay, sand, dolostone, limestone, and phosphorite (Scott, 1988).

The clays include a predominance of magnesium- and iron-rich smectite, palygorskite, and sepiolite (Weaver and Beck, 1977; Reik, 1982; Scott, 1988). Weathering of these minerals releases iron, magnesium, and silica, and produces kaolinite as a residue (Table 4). Clay-rich horizons often contain opaline material (opal-A and opal-CT; Jones and Segnit, 1971), which also releases silica upon weathering. The clays have very high sorption capacities and can effectively bind most metals. As a result of chemical weathering, the Hawthorn Group introduces numerous constituents into the ground-water system.

Dolostone and limestone contain the minerals dolomite and calcite (Table 4). Reactions with these carbonate minerals (e.g., reaction 3) buffer the acidity of ground water and release calcium and magnesium into the system (Table 4).

The primary phosphorite deposits are composed of carbonate-fluorapatite, while weathered and reprecipitated deposits contain carbonate-hydroxylapatite (Table 4). These apatite minerals contain fluoride, phosphate, and small amounts of uranium (Altschuler et al., 1958), which are released upon weathering.

Finally, the Hawthorn contains a number of trace constituents that may be locally important. It contains widespread but small quantities of pyrite (Table 4), which release iron and sulfur as sulfate or sulfide to ground water. The sulfate may be in the form of sulfuric acid (H_2S0_4), and the sulfide may be as hydrogen sulfide (H_2S), which imparts a "rotten egg" odor to water. Pyrite, and possibly other sulfide minerals, can release small quantities of trace metals and arsenic (which is present in some metal sulfides) upon weathering. The Hawthorn also contains gypsum, a source of sulfate (Table 4), at scattered localities[7]. This gypsum has not been previously described, nor has its origin been determined. Rosette-shaped clusters of gypsum, especially those which have been replaced by chalcedonic quartz, are probably a primary deposit indicative of playa lake or coastal, evaporitic basin conditions. The other occurrences do not have diagnostic crystal forms, but the nature of their occurrence suggests that the gypsum may have formed as a result of pyrite oxidation.

The mineral assemblage of the Floridan aquifer system is less complex than the other aquifer systems (Table 5). The predominant minerals are calcite in limestone and dolomite in dolostone (Table 4). Dolomite is widespread. Significant portions of the Floridan in the SRWMD and SFWMD are dolomitic. Also, large sections of Middle Eocene to Paleocene strata (particularly the Avon Park and Oldsmar Formations) of the Floridan aquifer system are dolomitic. Where the lower Hawthorn Group carbonates are part of the Floridan (Scott et al., 1991) dolostone is likely to be significant. Calcite predominates in the

Suwannee and Ocala Limestones elsewhere. Water which has equilibrated with the Floridan aquifer system, therefore, includes calcium, magnesium, and bicarbonate as dominant chemical species. The pH of Floridan aquifer system water is buffered by dissolution of carbonate minerals and generally ranges from 7 to 8.

The base of potable water in the Floridan is variable. The base of the aquifer system, which varies from the lower Avon Park Formation, through the Oldsmar Formation, to the top of the Cedar Keys Formation (Scott et al., 1991) is usually dolomitic. The base of the aquifer system is characterized by reduced permeability, partly as a result of the presence of intergranular gypsum and anhydrite **(Tables 4, 5)**. Therefore, water that has come in contact with the base of the aquifer system contains sulfate as a major constituent.

Nature of Aquifer System Porosity and Structure

Porosity, the nature and amount of pore space in an aquifer system, and structure, the distribution of large-scale fractures, joints, faults and karst features affect the ability of water to react with rock materials. This is because the size and geometry of the pore space controls the amount of reactive mineral surface area with which the water comes in contact. Where faults, fractures, and large caverns exist, contact of water with rock is minimized and water can travel through an aquifer system without significant changes in composition.

INTERGRANULAR POROSITY

All of Florida's aquifer systems contain significant intergranular porosity. Intergranular porosity dominates in coarse siliciclastic aquifers, such as occur in the sands and gravels of the surficial and parts of the intermediate aquifer systems. With intergranular porosity, the pores through which water passes are the spaces between sand grains. The passages (pore throats) between adjacent pores are often small, and sandy aquifers can be excellent mechanical filters for microbes, and small particles of humic material, oxyhydroxides, and clays. When the pore throats become plugged, permeability is reduced. Fine to medium sand aquifers have moderate areas of mineral surface in contact with the water, and, while quartz is inert, coated sand grains, interstitial clays, or interstitial oxyhydroxides can chemically interact with the water.

Where the surficial aquifer system is composed of quartz sand and gravel, porosity is intergranular. White, loose, "sugar sands" have little interstitial material or grain coatings, so they have little ability to sorb and bind dissolved chemicals. Brown, coated sands and clayey sands have moderate sorption capacities which can improve water quality to a limited extent. As the clay and carbonate contents of the surficial aquifer system increase, porosity remains intergranular, but permeability is reduced. The clays and carbonates are reactive and the low water/mineral surface area ratio suggests that chemical interactions are increased in comparison to pure sands.

The siliciclastic beds of the Hawthorn Group constitute part of the intermediate aquifer system. These sands contain significant intergranular clay and phosphatic sediments that range from gravel to clay sizes. The phosphate minerals (carbonate-fluorapatite and carbonate-hydroxylapatite) are sources of weathering products (Table 4), such as dissolved phosphate and fluoride. The clays are also subject to weathering, and they also have high sorption capacities, which assist in retarding the movement of certain metals in ground water (Upchurch et al., 1991). The clays yield magnesium and silica upon weathering.

Intergranular porosity in the carbonate- mineral-rich Biscayne Aquifer and the Floridan aquifer system is between carbonate grains, which are chemically reactive. These aquifer systems are doubly porous, with both primary, intergranular porosity and secondary, fracture- or karst-related porosity. Due to the presence of secondary dissolution features and fractures, the intergranular porosity of these aquifer systems may be significantly less important in terms of water flow than the larger openings. As a result, these aquifer systems may contain blocks of rock where water quality is dominated by the reactions associated with the high grain-surface areas characteristic of intergranular flow systems. These blocks are separated by zones of cavernous or fracture porosity that have distinctly different water compositions.

CAVERNOUS, VUGGY, AND FRACTURE POROSITY

The Biscayne Aquifer, carbonate aquifers of the intermediate aquifer system and limestone and dolostone of the Floridan aquifer system are doubly porous. That is, they contain two types of porosity at two different scales. Intergranular porosity is present in most areas, but the permeability associated with intergranular porosity is significantly less than that characteristic of larger, interconnected cavities, such as caverns, vugs, fossil molds, and fractures. Therefore, unless a well is located in the middle of a block of rock that is affected only by intergranular porosity or in which the larger pores are unconnected, water quality in the well reflects the more productive, larger interconnected pore space. When water passes through larger cavities, the water may not come in contact with rock, or it may have a short time in contact with the rock. The water has little opportunity for chemical interactions with the rock and it retains its chemical character inherited from precipitation, soils and human impacts, or earlier rock contacts. For example, Upchurch and Lawrence (1984) were able to identify a plume of surface water within the Floridan aquifer system that originated from Alligator Lake in Lake City, Columbia County. The plume extended several kilometers south of the lake along a prominent fracture trace.

Structure of the clay-rich confining beds of the Hawthorn Group is also important. Vertical leakage through the confining beds is most efficient where these beds are breached by sinkholes or where the clays have developed blocky fractures.

Aquifer System Flow Path and Residence Time

The length, depth, and tortuosity of the flow path a body of water follows in an aquifer system profoundly affect the quality of water. In general, shallow, short flow paths, which are characteristic of the surficial aquifer system, result in low residence times for chemical reactions to go to completion. Also, short flow paths result in contact with a limited number of different aquifer minerals and less opportunity for chemical composition to be altered. Consequently, total dissolved solids contents are less than those anticipated for longer flow-path systems. By the same reasoning, short flow-path systems are more vulnerable to contamination because of lack of (1) contact with reactive aquifer minerals or (2) sufficient time for chemical reactions to occur.

If the flow path is long (on the order of tens of kilometers), reactions between rock and water become more probable and the total dissolved solids content of the water increases as a result of continued rock weathering. Flow paths of the Floridan aquifer system in central Florida are characteristically long, and changes in composition along the flow paths reflect chemical maturation9 as reactions occur.

Residence time is, therefore, the length of time the water has been in contact with a particular rock type. Residence time is a function of hydraulic head, bulk permeability, and flow path length. Residence time decreases if either head or permeability increases. If water passes through rock rapidly, there may not be sufficient time for the rock to interact with the water. On the other hand, a long residence time may allow sufficient time for full chemical equilibration of the water and rock. In the first instance, the rock will have little effect on the water; in the second, the effect may be considerable.

Typical residence times range from days to thousands of years depending on the nature of the flow system. Residence times in the surficial aquifer system range from days to perhaps hundreds of years. The flow systems are short (Toth, 1962, 1963), with primary discharge to local wetlands, lakes, streams, and canals. It is not possible to predict residence times in the intermediate aquifer system because of the complexity of pathways through the lithologically diverse Hawthorn Group. Water that passes through sinkholes, fractures, and karst conduits that penetrate the Hawthorn may have brief residence times.

Conversely, water that passes along the tortuous pathways in the clay-rich horizons may have residence times of thousands to tens of thousands of years. Residence times in the Floridan aquifer system also cover a wide range of time. Short times have been recorded for some sinking streams and resurgences in north and central Florida (e.g., Ceryak, 1977). These short residence times are associated with conduit flow over distances of a few kilometers. In contrast, Hanshaw et al. (1965) used 14C dating methods to approximate residence times in the regional flow system of the Floridan aquifer system in the west-central part of the state. They found residence times in excess of 30,000 years for flow from northern Polk County to coastal Sarasota County. This long residence time is associated with ground-water velocities as high as 2 to 8 meters per year (Hanshaw et al, 1965).

Mixing with Other Waters in the Aquifer System

Mixing of waters in aquifers is common. Most of the time mixing is of little consequence. When, however, the mixing is between waters that differ significantly in chemistry, important changes in composition and reactivity of the mixture may result (Runnels, 1969). There are two situations in Florida where natural mixing (as opposed to mixing of contaminated water with native water) is known to be important. These are (1) mixing along the fresh-water/sea-water transition zone'° in coastal areas and (2) mixing of fresh and saline waters near the base of the upper Floridan aquifer system.

In both of these settings the mixtures have been shown to have increased ability to react with the host limestones and dolostones. Hanshaw and Back (1971a,b), Badiozomani (1973), and Plummer (1975), for example, showed that mixing in the transition zone can cause dissolution of calcite and, under certain circumstances, precipitation of dolomite. The dissolution of calcite can lead to development of karstic features (caverns, enlarged fractures, etc.) and formation of collapse breccias. Precipitation of dolomite in the space created by dissolution of calcite is thought by many (Hanshaw and Back, 1971 a,b; Badiozomani, 1973) to be an important dolomitization mechanism.

Aquifer Microbiology

All aquifers contain microbes (bacteria, fungi, and other organisms) that play important roles in the chemistry of the water. To survive, these microbes require sources of organic carbon, nitrogen, phosphorus, sulfur, iron, and other nutrients. Because these nutrients are normally introduced into the aquifer systems near the land surface, the microbes are most abundant there, and they decline in abundance with depth. Microbial utilization of these nutrients results in a number of changes in aquifer chemistry. These changes are discussed in detail with the individual analytes (below). The most important roles microbes play in maintaining aquifer chemistry deal with transformation of nitrogen, iron, and sulfur species. For example, sulfate-reducing bacteria transform sulfate (SO_4^{2-}) to hydrogen sulfide (H_2S) according to

$$SO_4^{2-} + 2C_{organic} + 2H_2O \quad (6)$$

microbial
→
activity

$$H_2S + {}_2HCO^-_3.$$

By this reaction, organic carbon and sulfate are consumed and hydrogen sulfide and bicarbonate produced. Since bicarbonate is also a product of weathering of calcite, addition of bicarbonate through sulfate reduction will tend to drive reaction 3 to the left and may induce calcite precipitation. Thus, microbial activity may result in a complex array of "spin off" reactions that affect major and minor element compositions of ground water.

DEFINITION OF HYDROCHEMICAL FACIES

The net result of the factors discussed above is that the composition of ground water reflects its recharge and flow history. Shortly after recharge the chemistry may be highly variable, but with chemical maturation, as a result of increasing residence time, the compositions become more uniform. The final compositions reflect interactions with the major rock types along the flow paths.

Part of this complex hydrochemical history of ground water can, therefore, be determined by examining the regional composition and variability of the water. Broad regions of an aquifer system that can be shown to contain water with relatively uniform major-element compositions are represented by a particular hydrochemical "facies"[11]. Methods of identification and mapping of hydrochemical facies have been described by Back (1961, 1966). As an example, waters of the Floridan aquifer system which have been in contact with limestones are likely to belong to the calcium-bicarbonate facies as a result of limestone weathering. Water in a quartzose portion of the surficial aquifer system may belong to a sodium-chloride facies derived from the marine aerosols that give precipitation its chemical character.

PREVIOUS WORKS

The aquifer systems of Florida have been intensely studied for over 50 years. Previous studies have largely been directed toward aquifer systems that are heavily used. As a result, large areas of the state that are characterized by low populations and aquifer systems with little use have been neglected. With the exception of the Biscayne Aquifer and, to some extent, the Sand-and-Gravel Aquifer, very few studies have been directed toward the surficial aquifer system. The intermediate aquifer system has also been somewhat neglected. In contrast, the Floridan aquifer system, which is one of the most productive aquifer systems in the world and the major source of public supply for much of the state, has been widely studied.

Surficial Aquifer System

The surficial aquifer system is not a major source of water in most of the state. This report is the first statewide synthesis of its ground-water quality. Many of the individual county and water management district water-supply reports published by the Florida Geological Survey, U.S. Geological Survey, and the water management districts contain minor amounts of chemical data on the surficial aquifer system.

The sand and sand-and-shell portions of the surficial aquifer system in northern and northeastern Florida are used for public water supply, notably in St. Johns County. Elsewhere in eastern NWFWMD, SRWMD, SJRWMD, and SWFWMD, scattered domestic wells supply potable water from the surficial aquifer system, but otherwise its main use has been for irrigation, waste disposal, and maintenance of surface-water features. There are a few studies that characterize water quality in the surficial aquifer system of north and central Florida. These include Hutchinson (1978), Causey and Phelps (1978), Hayes (1981), Duerr and Wolansky (1986), Duerr et al. (1988), and Upchurch et al. (1991). In general, the emphasis of these papers has been to simply describe water quality in the surficial aquifer system. Upchurch et al. (1991) included reduction-oxidation potentials and radionuclides in their study of surficial aquifer system waters in, and near, interaquifer recharge wells in Polk County.

The Sand and Gravel Aquifer of Escambia County is a major source of public and private supply for western NWFWMD. It had been somewhat neglected until recent years, when the U.S. Geological Survey began a comprehensive study of the aquifer, including water quality. Significant papers on the chemistry of the Sand and Gravel Aquifer include Katz and Choquette (1991) and Roaza et al. (1991).

The Biscayne Aquifer has been extensively studied because it is the major source of potable water for southeast Florida. Early work on the physical aspects of the aquifer includes Parker (1951) and Parker et al. (1955). More recent papers that include important summaries of Biscayne Aquifer water quality include Klein and Hull (1978) and Radell and Katz (1991). The latter report includes some of the Background Network data. A major U.S. Geological Survey report on the chemistry of surficial aquifer system water in southwest Florida is in review (Berndt and Katz,

pers. comm., 1991). Salt-water intrusion in the Miami area has been a major concern since the 1950's. Several landmark papers on the salt-water transition zone were written on the transition zone in the Miami area. These include Kohout (1960 a,b) and Cooper et al. (1964).

Intermediate Aquifer System

Southwestern Florida (portions of Charlotte, Lee, and Collier Counties) and portions of Flagler and Indian River Counties in east-central Florida are the only areas where the intermediate aquifer system is a major water-supply aquifer. The quality of water in the intermediate aquifer system in this area has received some attention. Elsewhere, little interest has been shown in water quality of the system. Duerr and Enos (1991) discussed the hydrogeology of the intermediate aquifer system in Hardee and DeSoto Counties. Duerr and Wolansky (1986) described the intermediate aquifer system in central Sarasota County, and Duerr et al. (1988) described the intermediate aquifer system in southwest Florida. Wedderburn et al. (1982) described the geologic framework of the intermediate aquifer system in Lee County, and they included some water quality data. Upchurch (1986) used uranium-series isotopes and major element chemistry to establish inter-aquifer connections between the surficial, intermediate and Floridan aquifer systems in Lee County.

Floridan Aquifer System

Because of its importance as a water-supply aquifer, the Floridan aquifer system has been extensively studied. Important papers that discuss water-quality data include Stringfield (1966), Stringfield and LeGrand (1966), Back et al. (1966), Kaufman and Dion (1967), Back and Hanshaw (1970, 1971), Plummer (1977), Wilson (1977), Hull and Irwin (1979), Ceryak et al. (1983), Crane (1986), Sprinkle (1989), Duerr and Enos (1991), and 1. Jones (1991). A major review of the hydro- chemistry of the Floridan by Katz (pers. comm., 1991) using data from the Background Network is in review by the U.S. Geological Survey.

GENERAL DESCRIPTORS

Temperature

IMPORTANCE

Temperature of ground water is controlled by climatic conditions, cultural activities, heat flow from the earth's interior, and chemical reactions in the aquifer system. Water temperature affects the nature and rate of chemical reactions and microbial activity in aquifers. It can also be used to evaluate the residence time of water in aquifer systems and depth to which ground water has moved.

In shallow aquifers, water temperature is usually controlled by climatic conditions, as opposed to other possible causes. Water that has recently entered the aquifer system normally reflects atmospheric temperature at the time of recharge. Therefore, temperature can often be used to identify recently recharged ground water. If the temperature of the water source is modified by human activity, including such activities as industrial processing, power generation, and some forms of waste-water disposal, temperature can be an excellent parameter to identify affected water in the aquifer system. In karst systems, actively recharging sinkholes can sometimes be identified because the water they introduce is at a different temperature from the ambient ground water. As the water moves away from local recharge areas and enters local flow, water temperature in shallow aquifer systems approaches mean annual atmospheric temperature. Because of the local nature of shallow aquifer systems, it may be difficult to correlate temperatures from one well to another.

In deeper aquifer systems, temperature can be affected by recharge from shallow environments, earth heat flow, and chemical reactions. Of these, heat flow has received the most attention in Florida (Smith and Griffin, 1977). Rock is an excellent thermal insulator, so water temperatures change slowly. As water passes downward into deeper parts of an aquifer system, it is warmed by heat generated nearer the earth's interior. In Florida this warming is slight because of the dynamic circulation within the deeper aquifer systems (Smith and Griffin, 1977).

If deep-flow-system water moves upward without sufficient time to cool, such as might occur in large conduits near the coastal salt-water transition zone, warm springs may result. Few warm springs exist in Florida. The most notable are Warm Mineral Springs and Little Salt Springs in Sarasota County (Rosenau et al., 1977). Warm Mineral Springs has waters ranging from 23 to 37°C (Clausen et al., 1975; Rosenau et al., 1977). In general, therefore, warm waters are attributed to discharge of the regional flow system and relatively cold waters to recharge. Deviations from this large-scale regional pattern are generally caused by rapid, local recharge, conduit flow, or contamination .

STANDARD OR GUIDANCE CRITERION

There is no standard or guidance criterion for temperature in ground water (Florida Department of Environmental Regulation, 1989).

DISTRIBUTION IN GROUND WATER

Temperature data from shallow aquifer system environments (e.g., the surficial aquifer system and shallow, unconfined portions of the intermediate and Floridan aquifer systems) are locally variable. Water from local recharge areas is likely to reflect conditions at the time of sampling. Temperature of recently recharged water and of very shallow water varies with seasons, so these data do not represent long-term conditions. Temperatures in deeper portions of the aquifer systems do not vary significantly with time, and the data are better indicators of long-term conditions.

Surficial Aquifer System

Since the surficial aquifer system is, by definition, unconfined or poorly confined, water temperature often reflects the most-recent recharge and seasonal temperatures. Consequently, water temperatures within a region vary considerably. In addition, temperatures vary with latitude and aquifer system type **(Table 6)**. Median water temperatures are slightly less in northern portions of the state, and higher in the south. Where the aquifer system is sandy and permeable, water temperature should fluctuate with recharge. Clayey portions of the aquifer system have less exchange with the surface and respond to recharge events less rapidly.

Figure 6 shows the distribution of temperature in the surficial aquifer system, by district. With the exception of the surficial aquifer system in the SFWMD, the data are not contoured due to the lack of continuity between data points. The inability to contour these data reflects the localized nature of the flow systems and temperature variations over the time of sampling. The variability of the data, therefore, reflects time of sampling, local weather conditions, recharge events, and depth in the aquifer system.

Intermediate Aquifer System

In many areas of the state the intermediate aquifer system is more isolated from surficial conditions than the surficial aquifer system. However, there is still considerable variability in the data (Table 6; Figure 7). Median temperature in the intermediate aquifer system is 24.6°C statewide, with a quartile range of about two degrees (Table 6). As with the surficial aquifer system, there is an increase in water temperature to the south, which reflects an increase in mean annual atmospheric temperatures.

Floridan Aquifer System

Temperature data for the Floridan aquifer system are summarized in Table 6 and Figure 8. The regional data clearly illustrate flow-system- related patterns. Water temperatures are cooler inland, where recharge is likely, and warmer near the coasts, where discharge after passing along a deep flow path occurs. Cooler waters are often present near drainage divides. Note that water temperatures in excess of 28°C occur along the Peace River lineament (G. Jones, 1991) and in coastal Sarasota County (Figure 8d). The wells along the Peace River tap the lower portions of the aquifer system in an area characterized by

upwelling (Healy, 1975; Kaufman and Dion, 1967; Lehman, 1978). The coastal wells are in the coastal upwelling zone in the vicinity of Florida's warm springs (Warm Mineral Springs, Little Salt Springs; Clausen et al., 1975; Rosenau et al., 1977).

Median ground-water temperature in the Floridan aquifer system is 24.0°C. There is an increase in temperature toward the south, and the median temperatures by district reflect atmospheric temperatures.

Acid-Base Relationships (pH)

IMPORTANCE

The variable pH reflects the potential for acid-base reactions in water. As such, it is often treated as a variable that determines the reactions in the aquifer system, rather than as the product of those reactions. The pH of aquifer water is, in fact, a result of past chemical reactions, and it is also a measure of the potential for reactions, if chemical equilibrium between the water and surrounding rock has not been established. It is included in this section because of its importance in predicting reactions that affect both cationic and anionic constituents discussed below.

The hydrogen-ion concentration in water is reported as pH, which is defined as the negative logarithm of the hydrogen-ion activity. Waters with a pH of 7 are neutral, while values less than 7 are acidic and those greater than 7 are basic, or alkaline. Hydrogen ion (H^+) is generally the cause of acidity, and bicarbonate ($HC0_3$-) is the most abundant source of alkalinity in natural waters. Acidity can also be generated by other proton donors, notably organic acids, and alkalinity can be created by proton receptors, such as phosphate ($P0_4^{3-}$) and nitrate ($N0_3$).

The pH in aquifer systems is normally controlled by chemical reactions with the atmosphere and rock framework. For example, ground water becomes acidic by dissolving carbon dioxide gas ($C0_2$). The carbon dioxide is produced by equilibration with the atmosphere and with carbon dioxide produced by microbial decay of humus in the soil. The reaction forms carbonic acid (H_2C0_3) by the reactions given in reaction 1.

Equilibration of water with atmospheric $C0_2$, which has an average partial pressure (gas concentration) of $10^{-3.5}$, results in a pH in rainfall of about 5.5. Once the precipitation infiltrates, the water reacts with the $C0_2$ in the soil atmosphere, and the pH drops even more. The partial pressure of $C0_2$ in the soil can be as high as $10^{-2.0}$, which is 10 to 50 times the $C0_2$ in the open atmosphere. The high $C0_2$ partial pressure in soil atmosphere is a result of $C0_2$ production by soil microbes as they metabolize humus. Dissolved organic acids are also a by-product of the microbial decay of humus. Therefore, the pH's of soil waters and shallow, surficial aquifer system waters are commonly in the range of 3-5 from the carbonic and organic acids.

The acids may then react with aquifer minerals, during which acidity is consumed and alkalinity is produced. Quartz is inert **(Table 5)** and has no affect on pH. Carbonate minerals are highly reactive, and buffer the pH through consumption of acidity and production of $HC0_3$-. For example, the major mineral in the Floridan aquifer system is the carbonate mineral calcite ($CaC0_3$). It reacts with carbonic acid according to reaction 3. The resulting pH increases to approximately 7.0-7.5, depending on temperature and $C0_2$ concentrations.

In recharge areas, waters that have not equilibrated with carbonate minerals tend to be more acidic due to the presence of carbonic and organic acids. In Florida, water from mid-flow and discharge areas has come in contact with carbonates and other minerals, so pH values tend to be higher. In other words, pH is an excellent indicator of the history of reactions of the water with aquifer minerals.

STANDARD OR GUIDANCE CRITERION

The guidance criterion for pH in Florida ground waters is established by the Secondary Drinking Water Standards (Chapter 17-550.310-320 F.A.C.), and is legally enforceable under Florida statutes (Florida Department of Environmental Regulation, 1989). The pH of water must fall within the range of 6.5 to 8.5 according to the standard.

Water less than 6.5 is likely to be corrosive, have high iron and high phosphate, and cause transport of undesirable metals, such as lead. Above 8.5, the waters may also be corrosive to certain alloys and boiler scale and turbidity may result from precipitation of carbonate minerals.

It is unlikely that natural pH values greater than 8.5 will occur in most Florida aquifer systems. Where pH values of aquifer water are this high, well construction problems are usually indicated. This is because drilling fluids and poorly cured cements and grouts are highly alkaline. Natural, aquifer water in siliciclastic aquifers is likely to fall below the minimum of 6.5 due to the carbonic and organic acid contents.

Table 7 lists the number of samples in which the standard was not met. Note that 93 percent of the surficial aquifer system samples in the NWFWMD failed to meet the standard, while only 27 percent failed in SFWMD. Statewide, water samples from the surficial aquifer system failed to meet the standard 37 percent of the time. Some of these failures represent the high alkalinities shown in Table 7 and are a result of well construction problems. Most, however, fail the standard because they are low, which is a result of natural causes. Failure to meet the standard in the intermediate aquifer system averages 16 percent of the samples, while 14 percent failed in the Floridan aquifer system. The lower failure rates in the intermediate and Floridan aquifer systems result from buffering with host-rock carbonates. The high failure rate for samples from the Floridan aquifer system in the SRWMD results from high organic acid content of waters from the poorly confined Coastal Rivers Basin (Taylor, Dixie, and Lafayette Counties). This problem is discussed below and in the Total Organic Carbon section.

DISTRIBUTION IN GROUND WATER

Table 7 summarizes the distribution of pH measurements. The aquifer systems that are characterized by high carbonate-mineral contents have median water pH values that are slightly over 7, while siliciclastic aquifer waters have pH values of 5 to 6, depending on the amount of admixed carbonate mineral material.

Surficial Aquifer System

The surficial aquifer system in the panhandle and north-central Florida is predominantly quartz sand, which is not reactive with carbonic or organic acids. As a result, pH values are generally low (Table 7), and the median pH values of surficial aquifer system water in NWFWMD and SRWMD are less than 6.0. Elsewhere, median pH values are somewhat higher because of equilibration of the waters with carbonate materials, especially calcite and aragonite, in the aquifer system. Carbonates are found in the surficial aquifer system near the coast in all districts, and throughout the south half of SWFWMD and all of SFWMD. These result in higher median pH values in these districts. For example, compare the median pH of the Sand and Gravel Aquifer of NWFWMD with the pH of the Biscayne aquifer of SFWMD. Minimum pH values are in the 3 to 4 range, which reflects waters from sandy aquifers in which no equilibration with carbonate minerals has occurred.

Figure 9 illustrates the distribution of pH of surficial aquifer system waters, by district. Note that there is considerable local variability, which reflects variations in well depth, aquifer mineralogy, and local production of carbonic and organic acids. In the SJRWMD (Figure 9c) the effect of coastward increase in shell content of the surficial aquifer system on pH is particularly well demonstrated. Inland, pH values are 6.0 or less, and near the coast the water may exceed 7.5. In south Florida (Figure 9e), pH is usually in excess of 6.5 due to the high carbonate mineral content of the Biscayne Aquifer and related rocks. All pH values above 8.8 in the SFWMD came from

newly constructed wells. These samples may reflect incomplete removal of well-construction materials (grout, drilling mud) prior to sampling.

Intermediate Aquifer System

The high range in pH values in the intermediate aquifer system **(Table 7)** reflects the mixed lithology of the Hawthorn Group and related sediments. Both siliciclastic and limestone and dolostone horizons serve as aquifers in the Hawthorn. Carbonate units have higher water pH values, while siliciclastic units may have low pH's, if the water has not come in contact with carbonate minerals. Median pH of waters from the intermediate aquifer system is 7.3, which reflects buffering by reactions with carbonate materials in many portions of the aquifer system.

Figure 10 illustrates the distributions of pH within the intermediate aquifer system. Note that there is considerable variability in pH at a local scale. This reflects the nature of the aquifer horizons within the intermediate aquifer system. Carbonate aquifers near the base of the system are the most productive, and these waters have pH values near 7 as a result of reactions with limestone and dolostone. The upper and middle parts of the system include siliciclastic horizons that yield somewhat acidic ground waters.

The amount of carbonate material and lateral continuity of aquifer horizons increase southward within the Hawthorn. This can be seen by comparing Figures 10a and 10b with 10e. The pH data from the intermediate aquifer system in NWFWMD and SRWMD (Figures 10a,10b) cannot be contoured due to high local variability and lack of stratigraphic continuity between production zones. The pH values vary by as much as one unit (one order of magnitude in hydrogen ion activity) between adjacent wells. In SFWMD, the intermediate aquifer system becomes more deeply buried and individual water-producing horizons become more continuous. With more isolation from the land surface and more lateral continuity, pH data are less variable and more continuous. As a result the data can be contoured.

Floridan Aquifer System

Table 7 depicts the distribution parameters for pH in the Floridan aquifer system. Median pH's are uniformly near 7.4 with the exception of a 7.1 in the SRWMD. pH values range from 4.9 to 12.5 in the SRWMD. The high range in Floridan aquifer system water pH in SRWMD is a result of well construction problems and high recharge of acidic waters.

The high values (12.5 in SRWMD, 12.2 in SJRWMD, 10.7 in SWFWMD; Table 7) reflect alkalinities that are a result of residual drilling fluids or well cements or grouts that have cured improperly. pH values within the upper and lower quartiles (Table 7) are natural and represent equlibration with the carbonates of the Floridan.

The minimum pH of 4.9 in the SRWMD reflects water that contains carbonic and/or organic acids that have not yet reacted with the Floridan carbonate minerals (Lawrence and Upchurch, 1976). This is locally common in recharge areas characterized by conduit flow. Because of the large amount of rock surface area to which non- conduit (intergranular) flow water is exposed, equilibration of water and rock is much faster in intergranular-flow than in conduit-flow water and low pH values are not expected. Low pH values are widespread in the Coastal Rivers Basin (Taylor, Dixie, and Lafayette Counties) of the SRWMD, where the Floridan is poorly confined and the surface is predominantly swampy and poorly drained .

Figure 11 illustrates the distribution of measured pH in the Floridan aquifer system. In general, there is little variation in pH data, which is a common occurrence in carbonate-rock aquifers due to buffering. The patterns of pH in each of the maps appear to be characterized by closed areas of high or low pH within an overall distribution of little or no variation. For the most part, these closed areas reflect differences in depth of well penetration and sampling. Shallow wells usually have somewhat lower pH values and deeper wells have somewhat elevated pH values. Several local areas show data with pH values less than 6.5. These are from shallow wells that are near swamps in unconfined, or poorly confined, areas. In these areas, high concentrations of dissolved organic acids lower pH. Comparison of these areas with the distribution of total organic carbon suggests a close correspondence.

There is an area of high pH that extends from southeast to northwest through Alachua and southern Columbia Counties in the SRWMD (Figure 11b). This high pH water may reflect somewhat "stagnant" flow under the Northern Highlands physiographic province (Lawrence and Upchurch, 1976,1982; Upchurch and Lawrence, 1984), which allows equilibration with the carbonate minerals. This is a common phenomenon where the Floridan is highly confined and the hydraulic gradient is low.

Regional flow in the Floridan is such that waters from coastal discharge regions are likely to have somewhat higher pH's due to the multiplicity of reactions that have affected the water along the flow path. This is illustrated in scattered coastal zones through the state. However, there is a surprising amount of low pH water in coastal areas. Some of this low pH water in coastal areas reflects local recharge, which may be acidic due to organic acids or carbonic acid.

Water from areas where the Floridan is unconfined and near the mouths of rivers, such as near the mouth of the Suwannee River (Figure 11b), shows low pH values, which appears inconsistent with the regional discharge pattern. These low pH waters may reflect local recharge from the rivers or flux of lower pH waters on the salt-water transition zone.

Finally, there are minor indications (isolated wells with low pH water) near some urban areas that may reflect use of drainage wells. Drainage wells are utilized in many areas of the state where urban and suburban development is in karst terrain. Drainage wells are installed to carry storm-water runoff into the host aquifer. The effects of these wells have been studied by Hull and Yurewicz (1979), Kimrey and Fayard (1982), Schiner and German (1983), and Bradner (1991). The sampling plan for the Background Network was established to avoid urban areas with similar, known sources of contamination, but suburban and rural drainage wells were not avoided. Low pH water near Orlando (Orange County, Figures 11c,e), Live Oak (Suwannee County, Figure 11b), and elsewhere may reflect this storm-water disposal practice.

CATIONS

Classification

Cations are positively charged ions that are generated by loss of electrons. Cations can be grouped into three categories according to their abundance in the natural environment.

MAJOR CATIONS

Major cations are the dominant elemental cations in an aqueous solution. They are usually present in concentrations in excess of 1.0 mg/L. The major cations in Florida waters are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), and strontium (Sr^{2+}). With the exception of strontium, which is often less than 1 mg/L in Florida, all of the major cations are discussed below.

MINOR CATIONS

Minor elemental cations occur in concentrations of 0.001 to 1.0 mg/L. Important minor cations include iron (Fe^{2+}, Fe^{3+}), barium (Ba^{2+}), and manganese (Mn^{2+}, Mn^{3+}). Iron is included in this report because of its importance as a regulated water-quality constituent. Barium and manganese have not been included. Ammonium (NH_4^{+}) is a trace cation. However, for convenience it is discussed in the Anion section with its negatively charged counterpart nitrate (NO_3^{-}).

TRACE METALS

Trace metals include elemental cations that are characteristically present at concentrations less than 0.001 mg/L. Trace metals are usually present in very low concentrations in natural ground water due to (1) low abundance in aquifer rock materials, (2) low mineral solubilities, (3) high probability of adsorption on mineral surfaces and particulate organics, and (4) precipitation as a metal oxide or sulfide. If present, trace metals are usually in the ,µg/L concentration range. Some of the important trace metals that occur in aqueous systems are lead (Pb^{2+}), mercury (Hg^{2+}), cadmium (Cd^{2+}), chromium (Cr^{6+}), and cobalt (Co^{2+}). In Florida, lead and mercury are of concern due to the widespread occurrences of these metals in aquatic organisms. For this reason, lead and mercury are discussed below. The other metals are not included because they are rare in natural Florida ground waters.

The chemical controls on cations are discussed under the individual constituents. Common processes that affect cation abundances include mixing of water masses, mineral dissolution and precipitation, reduction/oxidation reactions, cation exchange on clays, oxyhydroxides and organics, and chemical complexing.

Calcium

IMPORTANCE AND SOURCES

In many aquifer systems, calcium is the dominant cation. It is dominant because of weathering of the calcite (or aragonite) and dolomite **(Table 4)**, the minerals that constitute limestone and dolostone, respectively. Calcite and aragonite are abundant in shelly portions of the surficial aquifer system. Dolomite and calcite constitute the carbonate-rock horizons and are abundant as clasts in the siliciclastic horizons of the intermediate aquifer system. The Floridan aquifer system is composed of calcite and dolomite.

The reaction for weathering of limestone is given in reaction 3. Dolomite is weathered according to

$$CaMg(CO_3)_{2\ dolomite} + 2H^{+} \rightleftarrows Ca^{2+} + Mg^{2+} + 2HCO_3^{-}. \quad (7)$$

In both reactions, calcium is released as a dissolved cation. Therefore, calcium is expected to be a widespread and important cation in carbonate-rich aquifers. Weathering of limestones and dolostones consumes acidity (reactions 3 and 7), so calcium concentrations are highest in alkaline waters that are fully equilibrated with the host rock.

Calcium is also released upon weathering of gypsum and anhydrite (Table 4). Gypsum is occasionally found in the Hawthorn Group, and both gypsum and anhydrite are common at the base of the Floridan aquifer system, in the Avon Park and Oldsmar Formations.

Sea water contributes calcium to the aquifer systems in two ways. Precipitation that contains marine aerosols introduces minor amounts of calcium to the land surface. Average precipitation throughout Florida contains approximately 0.1-0.3 mg/L Ca^{2+} **(Table 3)**. Calcium is also important where mixing with sea-water-derived ground water along the salt-water transition zone occurs **(Table 8)**.

Weathering of silicates in siliciclastic aquifer zones is generally an insignificant source of calcium in Florida ground waters. Calcium-rich silicates are rare in Florida sands and carbonate rocks. An important exception results from weathering of the clays in the intermediate aquifer system. Smectite **(Tables 4, 5)** is a major component in the Hawthorn Group and although it contains more magnesium than calcium, weathering can be shown to contribute some calcium to intermediate and Floridan aquifer system waters (Lawrence and Upchurch, 1982).

Calcium is removed from the aquifer systems by mineral precipitation and ion exchange. Calcite cements and void fillings are common in sandstones and carbonate rocks throughout the state (see for example, Vernon (1951) and Puri and Vernon (1964) for descriptions of calcite-cemented strata). These cements are a result of evaporation of calcium-bicarbonate-rich waters or by degassing of carbon dioxide. However, Jones et al. (in press) have argued that there is little regional cementation in the Floridan aquifer system from mass-balance calculations.

Calcite precipitates as a result of carbon dioxide degassing according to the reaction

$$Ca^{2} + 2HCO_3^{-} \rightarrow CaCO_{3\ solid} + CO_{2\ gas} + H_2O. \quad (8)$$

Carbon dioxide degassing is the common process for calcite cementation in caves (White, 1988) and shallow ground-water systems. Little work has been done on carbon dioxide mobility in Florida ground waters. Starks (1986) has shown that degassing of carbon dioxide occurs on the upward-flow portion of the Floridan aquifer system near springs on the middle Gulf Coast. This degassing provides potential for calcite precipitation in coastal environments. On-going research at the SWFWMD (Upchurch, Jones, and DeHaven, 1992, pers. comm.) indicates that carbon dioxide partial pressures in shallow Floridan aquifer system water can be used to identify local recharge areas.

Precipitation of calcite as a result of evaporative concentration is common in the surficial aquifer system. Calcite "sand crystals"'2 have been found growing in the quartzose, barrier- island sands of Dade County and in dolomitic silts in Citrus and Levy Counties. Calcitic nodules are widespread in the surficial aquifer system and barrier islands throughout the state. Vadose pisolites occur in soil-filled caverns at the top of the Floridan aquifer system in Hernando, Citrus, and Alachua Counties. Evaporative precipitation has also been shown to form calcrete crusts on rocks of the Biscayne Aquifer in south Florida and the Keys (Multer and Hoffmeister, 1968).

Ion exchange is a widespread phenomenon in aquifer systems deposited in coastal plain environments (Foster, 1950). Clays, particularly smectites, have high ion-exchange capacities. The ion-exchange reactions of sodium and calcium with a clay sorption (ion exchange) site can be characterized as follows

$$\begin{matrix} Na \\ Na \end{matrix} \diagdown\!\diagup \text{-clay} + Ca^{2+}_{aq.} \rightleftarrows \text{Ca-clay} + 2Na^{+}_{aq.}. \quad (9)$$

If deposited in sea water, these clays are initially saturated with sorbed sodium, which is loosely held on clay-mineral surfaces. Calcium and magnesium have a higher affinity than does sodium

for clay surfaces, so when calcium- or magnesium-rich ground waters bathe the Na- clays, ion exchange is likely to occur. Calcium or magnesium exchange for sodium, and the clay becomes a Ca-and/or Mg-saturated clay, while the water is enriched in sodium. The reverse reaction occurs upon salt-water intrusion into Ca- or Mg- rich clays. Even though the sorption potential of sodium is low relative to calcium or magnesium, the high concentrations of sodium in sea water cause exchange with a release of calcium and magnesium and a loss of sodium in the ground water.

STANDARD OR GUIDANCE CRITERION

There is no standard or guidance criterion for calcium in ground water (Florida Department of Environmental Regulation, 1989). Calcium is not considered a hazardous component in potable water.

The calcium plus magnesium content of water is called "hardness". Durfor and Becker (1964) classified waters according to their hardness **(Table 9)**. Hardness is of concern because calcium and magnesium interfere with the function of soaps and certain detergents. Hard waters are also a problem because they form calcium- and magnesium-carbonate mineral residues ("scales") in hot-water heaters, boilers, and humidifiers. Evaporation of hard waters leads to scale on swimming pool walls, bathroom and kitchen fixtures, and dishes. For these reasons, a large industry selling and supporting water softeners has evolved. Care should be taken, however, in consumption of softened water due to increased sodium content. Additionally, calcium-rich waters provide dietary calcium. Hardness of waters in the Floridan aquifer system has been described by Shampine (1965) and Sprinkle (1982a).

DISTRIBUTION IN GROUND WATER

Calcium concentrations in ground water in Florida are a direct result of aquifer contact, residence time, and flow path. **Table 10** compares the calcium contents of aquifer systems, by district. Comparison of the surficial, intermediate, and Floridan aquifer systems illustrates the role of calcite and dolomite dissolution in aquifer chemistry. Calcium concentrations are generally higher in the intermediate and Floridan aquifer systems than in the surficial aquifer system (Table 10). This is a result of interaction of the water with limestone and dolostone horizons in both aquifer systems and with carbonate clasts in siliciclastic horizons of the intermediate aquifer system.

Surficial Aquifer System

Calcium concentrations are least in the surficial aquifer system, especially in NWFWMD and SRWMD, where the aquifer system is predominantly siliciclastic in composition. The surficial aquifer system in the SJRWMD and SWFWMD includes carbonate minerals in coastal environments and in the southern half of the SWFWMD. The surficial aquifer system in SFWMD is predominantly carbonate.

The distribution of calcium in the surficial aquifer system is shown in Figure 12. It is difficult to reconcile some of the calcium concentrations in the surficial aquifer system with known compositions of aquifer materials. For example, the surficial aquifer system in the interior of the state in north Florida is predominantly a siliciclastic aquifer system. As such, calcium concentrations should be relatively low. Most analyses in NWFWMD and SRWMD are low (<10 mg/L; Figure 12a,b), however a few of the analyses are in excess of 20 mg/L. These may reflect calcium derived from (1) cements used in well construction, (2) weathering of carbonate minerals or rock fragments reworked into the surficial sands and gravels from the underlying Hawthorn Group or residual from the original shell content, (3) fugitive dust from unpaved roads, quarries, or nearby construction sites, or (4) application of calcium-rich soil amendments, such as gypsum, calcite, or dolomite. All of these sources can locally affect the chemistry of the surficial aquifer system. Also, since the samples were not filtered, the presence of suspended particles may affect some analytical results.

In coastal areas and the southern half of the Florida peninsula, the surficial aquifer system contains shell, marl, and limestone. In these areas, calcium will naturally be relatively high and local influences, such as discussed above, will be masked. Calcium increases toward the coast in the SJRWMD (Figure 12c) indicating the increased importance of calcite and aragonite in the surficial aquifer system near the coast. A similar pattern is present in northern and central SWFWMD, but there is also a net southerly increase in calcium along the southern district boundary (Figure 12d). This increase in calcium is continued in western SFWMD (Figure 12e), and reflects increased importance of shell to the south.

Intermediate Aquifer System

The intermediate aquifer system includes abundant beds of limestone and dolostone, and the siliciclastic horizons include fragmental limestone and dolostone that have been reworked by waves and currents into and mixed with the quartz sand and clays. As a result, calcium content of the water is uniformly high relative to the surficial aquifer system (cf. Table 10 and Figures 12 and 13).

Calcium concentrations are highly variable because of the heterogeneous nature of composition in the Hawthorn Group and wide range of contact times between rock and water (Figure 13 a,b, and c). There is a minor increase in calcium content towards the coast in the SJRWMD (Figure 13c), which reflects salt-water intrusion and increased carbonate content and water residence times.

In southwestern SWFWMD (Figure 13d) and western SFWMD (Figure 13e) there is a second process operating. Upwelling along the salt-water/fresh-water transition zone brings deep Floridan aquifer system water into the intermediate aquifer system (Upchurch et al., 1991). This water has some of the longest and deepest flow paths of any aquifer system water in Florida. As a result of having traveled along the base of the Floridan, where it picked up calcium from the dissolution of gypsum, calcium is present in excess of 100 mg/L.

Floridan Aquifer System

The Floridan aquifer system is almost entirely limestone or dolostone. Waters that are in equilibrium with the host aquifer rock, therefore, have high calcium content. Much of the variability shown in Figure 14 is a result of well depth or position of highly productive zones in long open-hole wells. Water from deeper wells often has higher calcium and sulfate concentrations due to contact with gypsum and anhydrite at the base of the Floridan, long flow paths, and long residence times. Wells that have long reaches of open hole cannot be quantified as to depth of the water sample. It is clear that highly productive horizons near the base of the aquifer system in central and south Florida (the "boulder zones" of Puri and Winston, 1974)) are often characterized by high calcium and sulfate. Due to the high transmissivities of these zones, wells that tap them are characteristically dominated by these deeper waters.

Lawrence and Upchurch (1976; 1982) found somewhat elevated calcium concentrations in the highly confined Floridan in north-central Florida, where flow systems are apparently sluggish and equilibration thereby enhanced. Upchurch and Lawrence (1976) also suggested that high calcium in the Floridan aquifer system in the vicinity of the Cody Escarpment, a zone of high recharge at the transition between the unconfined Floridan of the Coastal Lowlands and the highly confined Floridan of the Northern Highlands in north Florida, is a result of complexing with natural organics. Brown (1989) confirmed that organic complexing enhances transport of calcium, but failed to show a strong spatial correlation with all of the high calcium regions in the escarpment environment. The location of these studies is within the >200 mg/L zone in southern Columbia County (Figure 1 4b).

Back and Hanshaw (1971) studied the distribution of calcium and degree of saturation of aquifer water with respect to calcite and dolomite in central Florida. They found that calcium concentration and saturation state of the water with respect to the minerals increase along the flow paths radiating from the vicinity of the Green Swamp in northern Polk County (Figure 1 4d).

The data from SJRWMD (Figure 14c) and SWFWMD (Figure 14d) support this conclusion, although the pattern is not as apparent as indicated by Back and Hanshaw (1971). There is a minor increase in calcium toward the coast in the SJRWMD, but most of the higher calcium concentrations appear to be a result of saline- water upconing in central Flagler and Volusia Counties (Figure 14c). Sea water, which averages 411 mg/kg **(Table 8)**, is locally a potential source of calcium at the transition zone throughout the state.

Calcium is lowest in recharge areas in central Pasco County and in the upper Withlacoochee and Hillsborough River watersheds in the SWFWMD. The region associated with the Withlacoochee and Hillsborough Rivers coincides with the margin and western half of the Green Swamp and suggests that recharge is most effective on the margin of the swamp as opposed to its center. A similar conclusion has been drawn by Swancar and Hutchinson (1992) from isotopic data. Concentrations increase radially from these regions according to the Back and Hanshaw (1971) model. The high calcium in the vicinity of the Peace River (southern Hardee, Desoto, western Sarasota, and northern Charlotte Counties; Figure 14d) coincides with upwelling of calcium-sulfate-rich waters at the salt-water transition zone. G. Jones (1991) has suggested that this upwelling is enhanced by the presence of a fracture system along the axis of the Peace River and also along the Myakka River, which coincides with a re-entrant in the transition zone in coastal Sarasota County. Culbreth (1988) has documented some of these fracture systems. The width of the reentrant, which occupies a zone a few kilometers in width along the Peace River, is too wide to correspond to a single fracture. These fracture traces must reflect a concentration of multiple fractures or extensive modification of a fracture zone by rock dissolution. The width of the reentrant in the water-quality data is most likely an artifact of upconing along the fracture-trace system and lateral transport of deep, calcium- sulfate waters in the "boulder zones" in response to heavy pumpage.

Finally, since the samples were not filtered, high calcium may be a result of particulate calcite or dolomite in the samples. Unusually high calcium concentrations most likely represent drilling-fluid or particulate contamination in poorly developed wells.

Magnesium

IMPORTANCE AND SOURCES

Due to chemical similarities, many of the factors that govern the distribution of calcium in Florida aquifer systems may also be applied to magnesium. Magnesium has several sources and some possible sinks (pathways by which it is removed from the water).

Mean magnesium concentration in precipitation ranges from 0.07 mg/L in north Florida to 0.2 mglL in the south **(Table 3)**. Evapotranspiration may raise the concentration in surface and soil waters by a factor of ten. Sea water averages 1,290 mg/kg magnesium (Table 8), so the waters in the transition zone may be magnesium rich.

The Hawthorn Group contains significant sources of magnesium **(Table 5)**, including magnesium-rich clays (Weaver and Beck, 1977; Miller, 1978; Reik, 1982; Strom and Upchurch, 1983, 1985; Scott, 1988), and dolomite (Wilson, 1977; Prasad, 1985; Scott, 1988). Weathering of any of these minerals adds to the load of magnesium in the intermediate and Floridan aquifer systems (Lawrence and Upchurch, 1976, 1982). The Floridan aquifer system also contains abundant dolomite, especially within the Suwannee Limestone and Avon Park Formation (Randazzo and Saroop, 1976; Randazzo et al., 1977; Randazzo and Hickey, 1978; Randazzo et al., 1983). The dolomite in the intermediate and Floridan aquifer systems may be either a source or sink for magnesium. Finally, particulate dolomite in the unfiltered samples may cause a strong correlation of magnesium with dolostone.

One of the most important models for dolomite formation in Florida is based on chemical equilibrium conditions that exist in the salt-water transition zone. Back and Hanshaw (1970), Hanshaw and Back (1971a,b), and Hanshaw et al. (1971) first postulated that dolomites may be forming in coastal portions of the Floridan aquifer system at the present time. Runnels (1969) offered an explanation for this phenomenon. His argument is that mixing of two water masses that are saturated with respect to calcite will result in a new water mass that is out of equilibrium with respect to calcite. In coastal mixing zones, the mixture is under-saturated with respect to calcite and limestone dissolution is predicted. Badiozomani (1973), Plummer (1975), and Wigley and Plummer (1976) expanded the concept and showed that mixtures of calcium-bicarbonate-rich Floridan aquifer system water and sea water, both of which may be saturated with respect to calcite and dolomite before mixing, become undersaturated with respect to calcite in the approximate range of 4 to 45 percent sea water. The water is over saturated with respect to dolomite in this same salinity range. Thus, in the landward "half" of the salt-water transition zone, the equilibrium models predict that calcite would be either dissolved, thereby producing karstic porosity, or replaced by dolomite. Hanshaw and Back (1980) have documented calcite dissolution in the mixing zone in the Yucatan, but the possibility of dolomitization remains controversial. Hardie (1987) has reviewed the mixing zone model and noted possible flaws. If the model is possible, dolomitization of limestones within transition zones along the coast and at the base of the Floridan may constitute a significant sink for magnesium.

Dolomite precipitation within the intermediate and Floridan aquifer systems is a highly debated topic. Dolomite is less soluble than calcite or aragonite, and the mixing-zone dolomitization model is a possible mechanism for magnesium removal from aquifer water. Randazzo and Saroop (1976), Randazzo et al. (1977), Randazzo and Hickey (1978) and Randazzo et al.(1983) have extensively studied the origins of dolomite in Florida aquifer systems from core petrography. These studies concluded that much of the dolomite in the Avon Park Formation and Suwannee Limestone can be attributed to depositional conditions at, or shortly following, the time of deposition. Prasad (1985) concluded that dolostones and dolomitic clays and silts in the Hawthorn resulted from replacement of aragonitic or calcitic muds at the transition zone. However, Randazzo and Bloom (1985) and Randazzo and Cook (1987) found dolomites in the Floridan aquifer system that can be attributed to dolomitization in the transition zone. While modern dolomitization cannot be documented, they found that modern, transition-zone ground waters are thermodynamically saturated with respect to dolomite and dolomite precipitation is predicted. One of the problems with correlation of existing dolostone horizons to modern ground-water chemistry is that Cenozoic sea-level fluctuations have been sufficiently rapid to prevent formation of well-defined dolostone horizons or transition-zone karst at the present positions of the transition zones (Fanning et al, 1981).

STANDARD OR GUIDANCE CRITERION

There is no standard or guidance criterion for magnesium (Florida Department of Environmental Regulation, 1989). The problems with hardness that were discussed under **Calcium** (above) are valid for magnesium.

DISTRIBUTION IN GROUND WATER

Surficial Aquifer System

The median magnesium concentrations in the surficial aquifer system **(Table 11)** are low (<10 mg/L) throughout the state. Maximum values in SJRWMD, SWFWMD, and SFWMD probably reflect either intermediate or Floridan aquifer system water that has been introduced through irrigation or upward discharge or weathering of magnesium-rich minerals reworked into the sediments of the surficial aquifer system from underlying strata.

Magnesium concentrations are characteristically less than 2 mglL in north Florida (Figure 15a- c). High magnesium concentrations in NWFWMD and SRWMD are in areas where the Hawthorn is present beneath the surficial aquifer system. These high magnesium values may reflect wells that inadvertently tap the intermediate aquifer system or horizons where Hawthorn sediments

have been reworked into the surficial aquifer system. The highest magnesium concentrations in SJRWMD are in an area of coastal intrusion in Flagler County and upconing in Seminole and southeast Orange Counties. In SWFWMD, high magnesium concentrations are also coastal (Figure 15d), with minor highs in the interior. Highest magnesium concentrations in SFWMD are in Lee, Highlands, and Glades Counties. Much of this region is characterized by clay-rich, shelly sands, which contain reworked material from the Hawthorn. The Biscayne Aquifer is low in magnesium, but a few wells on the western margin of the aquifer show minor increases in magnesium (Figure 15e).

Magnesium concentrations in marine aerosols **(Table 3)** are less than 0.4 mg/L magnesium, while magnesium in the surficial aquifer system in much of the northern part of the state is less than 1 mg/L (Figure 15). These concentrations are on the same order of magnitude as precipitation with minor evaporative concentration. In the southern part of the state magnesium concentrations are higher indicating more evaporative concentration, additions of irrigation waters from deeper aquifer systems, and possible mixing with residual marine waters trapped within the Plio-Pleistocene sediments.

Intermediate Aquifer System

Intermediate aquifer system water characteristically has higher magnesium concentrations **(Table 11)** than the surficial or Floridan aquifer systems due to the presence of magnesium-rich minerals (clays, dolomite; Table 5). There is an increase in median and maximum magnesium to the south, indicating a southward increase in clay and dolomite content and in aquifer system thickness, water residence times, and permeabilities.

In the NWFWMD, the magnesium increases to the east (Figure 16a), where the Hawthorn Group magnesian clay deposits occur (Scott, 1988). The trend continues into the SRWMD and western SJRWMD (Figure 16b,c). Concentrations in the interior of the SWFWMD (Figure 16d) are similar to those of north Florida. However, magnesium increases to concentrations in excess of 50 mg/L in the coastal transition zone and lower Peace River basin. The concentrations in Lee, Highlands, and Glades Counties (Figure 16e) are in excess of 25 mg/L as a result of extensive dolostones that constitute major aquifers in the area.

Floridan Aquifer System

Median magnesium concentrations in the Floridan aquifer system fall between those of the surficial and intermediate aquifer systems (Table 11). This is an artifact of two processes. First, much of the water in the Floridan aquifer system has passed through the intermediate aquifer system and has inherited magnesium from that system (Lawrence and Upchurch, 1976, 1982). This magnesium is diluted by directly recharged waters that are low in magnesium. Second, some portions of the Floridan aquifer system (notably near the base of the aquifer system in the Avon Park Formation and Oldsmar Limestone, near the top in the Arcadia Formation (Hawthorn Group), and in the Suwannee Limestone in central SRWMD) contain dolomite. Maximum magnesium contents are in coastal transition-zone environments where sea water (mean magnesium concentration = 1,290 mg/kg; Table 8) intrudes the aquifer system.

The distribution of magnesium in the Floridan aquifer system (Figure 17) reflects several of the processes mentioned above. Magnesium increases in a seaward direction in NWFWMD (Figure 17a). This increase reflects maturation along the direction of regional flow and interaction with dolostones within the aquifer system. Magnesium concentrations are in excess of 20 mg/L in the Apalachicola River delta as a result of coastal upwelling. The corridor of low magnesium along the lower Ocklockonee River reflects displacement of the transition zone by riverine waters, while the complex pattern in Wakulla County reflects the complex flow patterns associated with the large springs there.

The region of high magnesium in the northeastern part of the SRWMD (Figure 17b), in the Northern Highlands of Hamilton, Columbia, Union, Bradford, and Alachua Counties, represents the influence of weathering of the magnesium-rich minerals in the Hawthorn, through which Floridan aquifer system waters pass during recharge. The large area of high magnesium concentrations in Taylor, Lafayette, and Madison Counties corresponds to an area of dolomitic Suwannee Limestone. High values in coastal environments reflect the transition zone, which exhibits large reentrants up several rivers.

Floridan aquifer system water in the SJRWMD is generally low in magnesium, with highest concentrations near the coastal transition zone (Figure 17c). There is a reentrant near Daytona Beach (Volusia County) that reflects intrusion as a result of well pumpage. There is a similar area with high magnesium concentrations near Hastings (St. Johns County). Highs in northern Lake County, near Lake George, and in southern Seminole County underlie the St. Johns River. Leve (1983) has shown that upwelling from the Floridan aquifer system along faults occurs elsewhere on the St. Johns River.

There is a trend of increasing magnesium towards the coast in SWFWMD (Figure 17d). The transition zone is well delineated by the 10 mg/L isoline in the northern part of the district. The 10 mg/L isoline crosses the District from west to east where the Hawthorn Group ceases to be an effective confining unit. That is, south of the 10 mg/L isoline the Floridan is confined, and north it is semi- to unconfined. Therefore, confinement, long flow paths, and proximity of the overlying Hawthorn result in higher magnesium concentrations. There are significant re-entrants that parallel both the Peace and Myakka River axes. These re-entrants were attributed to upwelling along major lineaments by G. Jones (1991).

Data from SFWMD (Figure 17e) are limited and cannot be used to draw many conclusions. The absence of data in the central and south portions of the District reflect poor water quality in the Floridan aquifer system. Magnesium concentrations are high here as reflected by the 100 mg/L isoline that skirts the northern shore of Lake Okeechobee.

Sodium

IMPORTANCE AND SOURCES

The primary sources of sodium in Florida aquifer systems are marine aerosols and mixing with sea water in the transition zone. Concentrations of sodium in rainfall average from 0.44 in north Florida to 1.58 mg/L in south Florida (Table 3). The range of sodium concentrations measured in precipitation is 0.02 to 29.3 mg/L. Evapotranspiration of meteoric water can cause increases in sodium concentrations above those of the rainfall itself. The mole ratio of sodium to chloride in sea water is 0.857, and in Florida rainfall it ranges from 0.85 to 0.92. These ratios persist throughout the surficial aquifer system in Florida and reflect the importance of precipitation as a source of sodium.

Connate, saline waters that are residual from the Plio-Pleistocene marine transgressions also constitute a signficant source of sodium inland. Connate waters may be present in isolated pores within the fresh-water portions of the aquifer systems. They may also occur at the base of the Floridan aquifer system in northern and central Florida and throughout much of the Floridan aquifer system in southern Florida, where deep circulation has not been able to sweep the water out of the system. Minor sea water is also present as "bubbles" trapped in unconnected primary porosity that ranges in size from cavities up to a few centimeters between grains to cavities less than a millimeter within marine shells and authigenic minerals; however, the volume of this water is likely to be low.

Sorption sites on clays deposited in a marine environment are usually saturated with sodium. When bathed in calcium- or magnesium-rich waters, the calcium and magnesium is exchanged for the sodium in a form of natural "water softening" (reaction 9; Foster, 1950). This sodium is not from connate water, although it is left over from previous marine transgressions. Sodium released from clays by ion exchange can be recognized by comparison of sodium and calcium to chloride concentrations. Since meteoric waters have a

sodium to chloride ratio similar to that of sea water (mole ratio = 0.857), increases in the ratio which are accompanied by a decrease in the calcium to chloride ratio can be attributed to ion exchange. The large amount of sodium- bicarbonate water in the aquifer systems (see **Hydrochemical Facies** section) indicates that ion exchange is an important process in Florida.

The reverse exchange reaction occurs where sea water intrudes into an aquifer system that contains potable, calcium- or magnesium-rich waters. Here, calcium- or magnesium-saturated clays are bathed in sodium-rich solution and the exchange reaction (reaction 9) goes to the left. This results in a calcium- or magnesium-chloride facies, which has been documented in this report along the inner margin of the transition zone.

An excellent example of widespread ion exchange occurs in Taylor County, where a near-surface, Plio-Pleistocene clay (the "San Pedro clay") appears to be releasing sodium to the ground water. The mole ratio of sodium to chloride in adjacent counties, where the clay is not present, is essentially the same as sea water (0.857) due to the influence of marine aerosols. In Taylor County the prevalent ratio is approximately 1.3, indicating that there is approximately fifty percent more sodium as a result of exchange for calcium .

Finally, weathering of sodium-rich minerals, such as feldspars or clays, can be a source of sodium in ground water. Sodium feldspars (sodic plagioclase, (Na,Ca)Al(Al,Si)Si2O8) and sodium- rich clays (montmorillonite and nontronite; Table 4) are found in siliciclastic horizons of the surficial and intermediate aquifer systems. Minor amounts occur in the Floridan aquifer system. The weathering reaction is similar to reaction 4, with release of sodium, other cations, silicic acid, and bicarbonate (Table 4).

STANDARD OR GUIDANCE CRITERION

Sodium is regulated under the Primary Drinking Water Standard (Ch. 17-550.310-320, F.A.C.; Florida Department of Environmental Regulation, 1989). The standard is 160 mg/L. The standard is based on the possibility of adverse health effects, including heart disease and hypertension. Table 12 includes the number of samples that exceeded the standard by district. The samples that exceed the standard are characteristically in the coastal transition zone or in regions of upconing of deeper waters.

Statewide, four percent of the samples from the surficial aquifer system exceeded the 160 mg/L criterion. The proportion of samples that exceeded the standard ranged from zero in SRWMD to 16 percent in SJRWMD. The samples from the SJRWMD are coastal and reflect the transition zone.

Twenty-three percent of the samples from the intermediate aquifer system exceeded the standard. The range in proportion of samples that exceeded the standard ranged from zero to 45 percent. The proportion that exceeded the standard was low in all districts except the SFWMD, where connate waters are common in the intermediate aquifer system.

Seventeen percent of the samples from the Floridan aquifer system exceeded the standard. The proportion ranged from one percent in NWFWMD to 59 percent in SFWMD. Again, connate waters in the Floridan in southern Florida and in coastal regions elsewhere, and the coastal transition zone account for these high concentrations.

DISTRIBUTION IN GROUND WATER

The distribution of sodium in Florida's aquifer systems is summarized in **Table 12**. Care should be taken in interpreting these data as the design of the Background Network includes coastal, sea water intruded zones, regions affected by connate water, and areas of upconing of deeper waters. In addition, there are no wells in the central Everglades region of SFWMD. The distribution of wells is not in proportion to the areal extents of these regions of the aquifer systems, so neither the distributions nor the number of samples exceeding the 160 mg/L standard can be taken to literally characterize the aquifer systems. The maps (Figures 18-20) provide a better synthesis of the conditions present in the aquifer systems.

Note that Table 12 suggests that there is a general increase in median and maximum sodium contents of aquifer system waters to the south. These increases are, in part, a result of the increased importance of marine aerosols in precipitation in the peninsula as opposed to the northern part of the state, especially with respect to the surficial aquifer system and shallow wells in the unconfined parts of the Floridan aquifer system. The large increases in SFWMD are a result of low hydraulic gradients, which have not caused complete flushing of the aquifer systems, especially near the coast, and to human-induced salt-water intrusion.

Surficial Aquifer System

The median sodium concentration in the surficial aquifer system statewide is 17.0 mg/L. The range of values is 0.7 to 3,730 mg/L (Table 12). The majority (samples within the upper quartile) of the sodium concentrations are within the range of marine-aerosol enriched precipitation that has been concentrated by evapotranspiration. The higher concentrations reflect wells that are near the coastal transition zone or that are inland and are influenced by connate water or introduction of deeper aquifer system water through irrigation or other interaquifer transfer.

Examination of Figure 18 reveals the influence of the coast and these "pockets" of high sodium inland. There is a weak coastal influence in the Sand and Gravel Aquifer (Figure 18a) in the NWFWMD, but highest sodium values near the coast appear to reflect upconing of saline water under pumping stresses. The influence of the coastal transition zone and, possibly, incomplete flushing is well displayed in the SJRWMD (Figure 18c). Here, large re-entrants from the coast have developed where pumpage has induced intrusion. The data from the southern half of SWFWMD also indicate a well-developed transition zone (Figure 18d). Note that well-developed re-entrants of sodium-rich water extend inland along the axes of the Peace, Myakka, and Little Manatee Rivers. In SFWMD (Figure 18e) the Biscayne Aquifer illustrates the coastward increase in sodium. This is one of the classic and most studied transition zones in the world (Kohout, 1 960a,b; Cooper et al., 1964). A major management effort of the SFWMD is to minimize landward intrusion and restore water quality in the Biscayne Aquifer. High sodium concentrations inland, especially in southwestern Glades County, are probably a result of interaquifer transfer through irrigation and remnant connate water.

Intermediate Aquifer System

Sodium in the intermediate aquifer system statewide ranges upward from 1.0 mg/L (Table 12), with a median concentration of 41.0 mg/L. The wide range in sodium concentration reflects a diversity of processes, including marine aerosols, connate water, coastal, saline waters, and weathering of Hawthorn Group minerals. The influence of Hawthorn Group weathering has been discussed by Lawrence and Upchurch (1976, 1982).

The majority of the inland samples (Figure 19), particularly in the NWFWMD and SRWMD, are equivalent to the sodium contents of the surficial aquifer system, and marine aerosols; so they reflect simple recharge. Near the coast, upwelling along the transition zone results in higher sodium concentrations, especially where pumping or the presence of large rivers cause the lowering of hydraulic heads.

There is a high sodium area at the south- western corner of Glades and northeastern corner of Lee Counties (Figure 19e). This is the only area in the intermediate aquifer system sample set where the sodium standard is significantly exceeded. This high corresponds with the high noted in the same area in the surficial aquifer system (Figure 18e). The high is located near the Caloosahatchee River and coincides with a re-entrant in the Floridan aquifer system potentiometric surface (Healy, 1962). This area appears to be characterized by both natural upwelling and heavy pumpage, and coincides with the location of improperly abandoned wells that were initially installed for petroleum exploration purposes.

Floridan Aquifer System

Sodium in the Floridan aquifer system is greatest along the coast, where the salt- water/fresh-water transition zone is clearly delineated (Figure 20). Elsewhere, minor sodium highs appear to be a result of ion exchange in the overlying Hawthorn clays, connate water, and sampling of deeper, more mature waters. **Table 12** summarizes the sodium-distribution data for the Floridan throughout the state. The median sodium concentration for the state is 11.0 mg/L; and the range in concentrations is from a minimum of 0.2 mg/L to a maximum of 7043 mg/L.

In the NWFWMD (Figure 20a) the transition zone is well defined, although few of the samples exceeded the standard. A major re-entrant occurs in Walton County, which reflects major withdrawals in Okaloosa and Walton Counties (Wagner et al, 1984). Wagner et al. (1984) attributed the large re- entrant in southern Bay and Gulf Counties to pumpage. The re-entrant in Wakulla County is a result of discharge from the large spring complex surrounding Wakulla Springs and by pumpage.

Re-entrants in the SRWMD (Figure 20b) reflect intrusion towards coastal cities and industries. Re- entrants on the transition zone include one in Taylor County that is a result of high pumpage near Perry and a large re-entrant in Levy County that corresponds with the Waccasassa River and swamp. Minor sodium highs in Hamilton and Alachua Counties correspond with areas of withdrawal near White Springs and Alachua. The high sodium in Bradford County corresponds to withdrawals near Starke.

Data from the SJRWMD (Figure 20c) indicate that the coastal transition zone is well-developed throughout the District. A major re-entrant exists in St. Johns County, and smaller, inland features exist along the St. Johns River. Much of this high sodium water is believed to be connate in origin (Boniol, 1992, pers. comm.). Leve (1983) has attributed similar features to upwelling along fault-controlled regions of high permeability in the St. Johns River. The upwellings are, in some areas, apparently natural and associated with springs. In other areas the upwellings are associated with pumpage.

The coastal transition zone is apparent in the SWFWMD (Figure 20d), with re-entrants in Manatee County and along the axes of several of the major rivers. These features have been previously discussed.

Most of central and south SFWMD (Figure 20e) has no data. This region is characterized by low potentiometric heads and little flushing action. Consequently, Floridan aquifer system water in the District is saline and unfit for most uses. If there were data in this region, sodium contours would indicate high concentrations, with most areas in excess of the standard. The contoured data delineate this region of poor quality with increasing sodium to the south.

Potassium

IMPORTANCE AND SOURCES

Potassium is primarily derived from sea water, which averages 399 mg/kg **(Table 8)**. Therefore, coastal regions, where the fresh-water/salt-water transition zone is present, are expected to contain the highest potassium concentrations. Elsewhere, potassium is derived in trace concentrations (usually less than 0.2 mg/L) from marine aerosols in precipitation and from minor weathering of clays and feldspars. Weathering of potassium feldspars and clays (see reaction 4) is not considered a dominant process in Florida due to the scarcity of these minerals in aquifer sediments and slow weathering reaction rates. Inland, potassium is rarely present in quantities over a few milligrams per liter. This is because there is not a great quantity of potassium-rich sediment in the aquifer system and because potassium is immobilized as a nutrient by plants and sorbed onto clays.

Potassium is an excellent indicator of the integrity of newly installed wells because potassium is a major constituent of drilling fluids and cements used in well construction. High potassium in a potable-water well often indicates that either the well cement is poorly cured, the well has been poorly developed and drilling fluids are still present, or the well cements are deteriorating.

STANDARD OR GUIDANCE CRITERION

There is no standard or guidance criterion for potassium. Potassium is an essential nutrient, and is considered beneficial in low to moderate quantities.

DISTRIBUTION IN GROUND WATER

Median potassium content in all districts and aquifer systems is low indicating minor contributions from aerosols and weathering. The values that fall below the upper quartile **(Table 13)** are well within the expected concentrations from evaporative concentration of precipitation and rock weathering. Very high concentrations (>100 mg/L inland, >400 mg/L in coastal areas) are suspect. These probably represent well construction problems.

Surficial Aquifer System

The median potassium concentration for the surficial aquifer system statewide is 1.2 mg/L (Table 13). There is no significant difference in potassium concentration medians or quartiles within the state. Maxima do vary significantly, but the highest values represent either sea water or well-construction problems.

Potassium concentrations in excess of 100 mg/L inland may be considered artifacts of well construction. These highs are found in several districts (Table 13, Figure 21) and their distribution appears to be random and uncorrelated to adjacent wells.

Potassium concentration in sea water is approximately three percent of the sodium concentration. Therefore, potassium in meteoric waters should be in the range 0.1-0.3 mg/L, if derived from marine aerosols and not concentrated by evapotranspiration. Most samples should remain near three percent of the sodium concentration unless weathering, plant uptake, or sorption change the partitioning of sodium and potassium. Most of the samples from the surficial aquifer system are within or near this concentration range, or they are in proper proportions with sodium to indicate meteoric

The data from SJRWMD and SWFWMD (Figures 21c,d) illustrate the influence of the transition zone on potassium. Note that many of the coastal re-entrants mentioned above are represented in the potassium data. The high in central Hardee County (Figure 21d) coincides with a zone of upconing saline water in the underlying Floridan (Dalton, 1978; Lehman, 1978). Dalton (1978) documented the flux of Floridan aquifer system water into the surficial aquifer system in Hardee County and showed that it is a result of irrigation practices. Other highs in the surficial aquifer system, therefore, may reflect irrigation waters pumped from the underlying Floridan aquifer system. The high potassium on the east side of the SWFWMD roughly coincides with the Lake Wales Ridge. Similar highs are not present in the SFWMD data (Figure 21e), so SWFWMD data are suspect at present.

Intermediate Aquifer System

The arguments that were given for potassium in the surficial aquifer system hold for the intermediate aquifer system. Median potassium concentration statewide is 4.4 mg/L. Most of the data are well within expected concentrations for meteoric water, but high potassium concentrations that result from weathering of the Hawthorn and possible well constnuction problems exist (Figure 22).

Floridan Aquifer System

The distribution of potassium in the Floridan aquifer system (Table 13; Figure 23) clearly illustrates the influence of the transition zone. There is a coastward increase in potassium in the Floridan aquifer system in the districts (Figure 23). Re-entrants along the coast were previously discussed under **Sodium**. Scattered occurrences of high potassium concentrations inland probably reflect residual potassium in newly constructed wells. Large areas characterized by minor highs in potassium concentration in the regions where the Hawthorn Group overlies the Floridan aquifer system reflect rock weathering in the siliciclastic

section of the Hawthorn (Lawrence and Upchurch, 1976, 1982). Elsewhere, the data are consistent with marine aerosols accompanied by minor concentration as a result of evaporation in the near surface environment.

Iron

IMPORTANCE AND SOURCES

Iron has two valence states, Fe^{2+} and Fe^{3+}, and is highly susceptible to reduction/oxidation (redox) reactions. Hem (1976) summarized the stability relationships of iron in sulfur-rich systems. In general, the sources of iron in ground waters include (1) oxidation of pyrite (FeS_2), (2) oxidation of organic compounds, and (3) dissolution of iron oxide and silicate minerals **(Table 4)**.

Upchurch et al. (1991) characterized the surficial and Floridan aquifer systems in central Florida in terms of reduction/oxidation (redox) potentials (Figure 24). They found that the surficial aquifer system ranges from slightly oxidizing to slightly reducing. The Floridan aquifer system is generally reducing, although areas of rapid recharge are likely to be oxidizing. The waters of the intermediate aquifer system are similar to the Floridan in redox potentials. Data from surficial and Floridan aquifer system water samples from Polk County were plotted on Eh-pH diagrams for iron species, and they indicate that Fe^{2+} is generally the stable form of iron in central Florida ground waters (Figure 24).

In general, Fe^{2+} is the stable iron phase in acidic, reducing waters (Figure 24). Iron should remain in solution in acidic, oxidizing waters. In basic, reducing waters, pyrite (FeS_2) and siderite ($FeC0_3$) are stable solids that may precipitate depending on the sulfide and bicarbonate contents of the water; whereas, in basic, oxidizing waters, amorphous ferric hydroxide ($Fe(OH)_3$) should precipitate.

Ferric hydroxides form colloidal and larger particles that generally do not travel long distances in intergranular aquifers. Travel distances depend on sizes of the colloids and of pore throats. These colloids have been documented to travel distances up to a few meters, but not kilometers. The particles are more likely to travel as suspended sediment in karst conduits. Ferric hydroxide is the reddish to yellowish scale or stain that is so commonly found where iron-rich waters are utilized. Ferric hydroxide forms rapidly when water is heated in hot water heaters or aerated in the vicinity of well pumps, sinks, toilets, and other environments where oxidation of Fe^{2+} to Fe^{3+} is possible. In soils and rocks ferric hydroxide slowly crystallizes as the mineral goethite (Table 4).

Iron is closely associated with bacterial activity in ground waters. In oxidizing environments, bacteria induce colloidal ferric hydroxide precipitation. These iron colloids and the associated bacteria cause clogging of well screens and aquifer pore throats. They also result in violations of color and turbidity standards. For example, in a water quality survey of the central Florida phosphate district, Gordon Palm and Associates (1983) found that 16 percent of the shallow-well samples from mine areas violated the water-quality standards for color and 20 percent violated standards for iron. In deep wells, 13 percent violated the color standard and 10 percent violated iron standards. Recharge wells utilized by the phosphate industry are particularly susceptible to iron, color and turbidity problems. The well screens plug with bacterial mats and ferric hydroxides; and dislodging these encrustations from the well bore during sampling causes color and iron standards to be violated (Upchurch et al, 1991).

Ferrous iron (Fe^{2+}) is a minor, but prevalent, constituent in organic- (humic-substance) rich waters. Because organic-rich waters include a source of carbon, microbial activity tends to cause strongly reducing conditions, which encourage reduction of ferric iron (Fe^{3+}) to the ferrous state and transport with the water. Ferrous iron is known to move moderate to long distances in reducing, karstic aquifers. Given the presence of sulfide or phosphate, ferrous iron may precipitate as pyrite (FeS_3), vivianite ($Fe_3(P0_4)_2\ 8H_20$), or other mineral species.

Filtration, mode of sampling, and well environment may greatly affect reported iron concentrations. Iron analyses reported in this study are total iron, and no attempt is made to differentiate the two oxidation states. Since Fe^{3+} tends to precipitate as ferric hydroxide, it is probable that iron concentrations in well- developed wells are predominantly Fe^{2+}. Samples from poorly developed wells probably contain both iron species, especially since the metals samples were not filtered. Also, iron-bearing well casing material may "rust" or otherwise prejudice iron concentrations. For this study, only data from non-metal cased wells were used, so the sample density is much reduced over other analytes.

STANDARD OR GUIDANCE CRITERION

Iron is subject to the Florida Secondary Drinking Water Standards, and the maximum allowed concentration is 0.30 mg/L (300 µg/L; Florida Department of Environmental Regulation, 1989). This is because of the potential for discoloration and turbidity in waters with excess iron.

Table 14 summarizes the proportions of samples that exceeded the standard. Because of possible contamination from iron and steel casing, only samples taken from wells with non-metallic casing are listed in the table. Statewide, 75 percent of the surficial aquifer system samples exceeded the standard. The range in the proportion that exceeded the standard was from 70 to 90 percent. The proportion that exceeded the standard in the intermediate aquifer system was 42 percent statewide, with a range of 14 to 86 percent. The proportion that exceeded the standard in the Floridan aquifer system was 49 percent, statewide. The proportion ranged from zero to 70 percent. Clearly, there is a high probability that any aquifer system water sample from Florida will violate the standard for iron, especially if it is an unfiltered sample.

DISTRIBUTION IN GROUND WATER

Iron distribution data are summarized in Table 14. Note that median iron concentrations are characteristically highest in the surficial aquifer system. This is a result of proximity to sources of iron in the siliciclastic portion of this aquifer system, including iron minerals, ferric iron- and organic-rich soil horizons, and dissolved humic substances. Median iron concentrations are low in all of the aquifer systems. High values (concentrations > 5 mg/L) are probably a result of using unfiltered samples. These high concentrations represent particulate ferric hydroxides that were washed from the aquifer system under the turbulent conditions characteristic of well pumping.

Surficial Aquifer System

Median iron concentrations reported by district from the surficial aquifer system range from 0.88 to 2.14 mg/L (Table 14). The statewide median is 1.08 mg/L. Normally, the surficial aquifer system is high in iron because of the presence of organics and reduction-oxidation reactions that can mobilize iron.

Lack of physical continuity between sample sites prevents contouring of data (Figure 25). The high degree of variability reflects local well conditions and surface conditions.

Intermediate Aquifer System

The statewide median iron concentration is 0.07 mg/L in the intermediate aquifer system. There is a high range in median iron concentrations (<0.05-1.17 mg/L; Table 14) due to the diversity of environments in the Hawthorn Group. Iron is abundant in the Hawthorn Group as a constituent in clays, pyrite, goethite, and related iron oxyhydroxides. Figure 26 illustrates the distrbutions of iron in the districts.

Floridan Aquifer System

The distribution of iron in the Floridan aquifer system (Figure 27) suggests that high iron waters may occur near the coast. In SRWMD and northern SWFWMD this reflects swampy conditions overlying the unconfined Floridan. Elsewhere, high iron near the coast and along the re-entrants previously discussed indicates mobilization of iron in the aquifer systems. Median concentration of iron, statewide, is 0.21 mg/L. Comparison of this median with average sea water, which has an

average concentration of 2 mg/kg **(Table 8)** indicates that iron concentrations are increased in the wells by a factor of over 50.

Iron is present in waters directly affected by the Hawthorn Group. There is also a strong correspondence of iron and total organic carbon in many areas of the state as a result of iron complexing by humic substances (Young and Comstock, 1986) (compare Figure 27 and the distribution of TOC in Figure 55).

It is important to note that small iron anomalies are evident in the aquifer system near areas where rivers discharge water through swallow holes into the Floridan at the Cody Escarpment in SRWMD (Figure 27b). These anomalies suggest that areas where rivers flow directly into karst conduits in the Floridan aquifer system should be closely monitored because of their sensitivity to rapid ground-water quality deterioration, if water quality in the rivers deteriorates.

Mercury

IMPORTANCE AND SOURCES

Mercury is included in this report because of recent concerns about mercury in surface waters and aquatic biota. There is considerable debate as to the source of mercury in surface waters, and discovery of mercury in the ground-water data would have been of great assistance in determining the origin of the mercury in surface waters. The ground-water data do not indicate any sources of mercury in the surface waters.

Elemental mercury is stable under Earth surface conditions. It is slightly soluble in water (~25 µg/L; Hem, 1985), but if the water is open to the atmosphere, the mercury is sufficiently volatile that much of it will escape as a gas. Mercury forms chemical complexes with chloride and hydroxide in high ionic strength solutions.

Metallic mercury (Hg°) can be oxidized to either Hg_2^{2+} (mercurous) or Hg^{2+} (mercuric) valence states. Both ions can form strong chemical complexes with humic substances (Jenne, 1970; Jonasson, 1970; Cline and Upchurch, 1973). In addition, methanogenic bacteria have the capability of forming methyl mercury ($HgCH_3^+$) from metallic mercury in organic-rich environments (Wood et al., 1968). Methylated mercury is readily soluble in body tissues resulting in bioaccumulation of mercury and its entrance into the food chain.

Mercury minerals are unknown in Florida's sediments. Sea water, which averages 0.03 ,µg/kg Hg, is an important natural source of mercury. Assuming that the average chloride in precipitation is 1.66 mg/L **(cf. Table 3)**, the equivalent mercury concentration in rainfall is estimated to be approximately 0.05 parts per trillion, which is not detectable. Marine aerosols may, therefore, transport very small amounts of mercury inland. Quaternary marine transgressions may constitute an additional source of natural mercury in Florida. Mercury forms strong chemical complexes with sedimentary organics and clays. Marine transgressions place sea water in juxtaposition with these sorption media, and sorbed or complexed mercury may remain as the sea retreats.

Human activity has undoubtedly contributed to the availability of mercury in the environment. Draining peat- and muck-rich sediments may allow oxidation of the organics, and any sorbed or chemically complexed mercury has the potential for release into surface waters and the surficial aquifer system. Atmospheric fallout is another possible source of mercury. Burning of fossil fuels (coal, oil) and municipal and industrial wastes has the potential of introducing variable amounts of mercury into the atmosphere and, ultimately, onto the land surface as either dry fallout or precipitation (Hem, 1985). Finally, many pesticides that have been widely used contain mercury compounds (Grier, 1968). Organomercuric compounds were used as seed grain treatments prior to the 1960's. Phenylmercury salts and other mercury compounds have been widely distributed for bactericides and fungicides. These pesticides may also constitute a source of mercury in surface environments. The relative importances of these sources are unknown for Florida ground waters at the present time.

Due to the small natural amounts of mercury in Florida's aquifer systems and the strong affinity of mercury for sorption and/or chemical complexing with natural organics it is unlikely that mercury would be naturally present in detectable amounts. Any mercury detected in the aquifer systems as part of the Background Network is most likely a result of human activity, including atmospheric fallout or agricultural use of mercury-containing pesticides.

STANDARD OR GUIDANCE CRITERION

Mercury is subject to the Florida Primary Drinking Water Standards (Florida Department of Environmental Regulation, 1989), and the maximum allowed concentration is 0.002 mg/L (2 µg/L). This is because of the potential for accumulation in the food chain and serious toxicity problems in humans. Mercury intake in humans has been associated with chronic and acute toxicity, especially mental illness and gastric and respiratory distress (Grier, 1968).

Table 15 summarizes the samples that were found to exceed the 2 µg/L standard. Many of these detections have not yet been confirmed by resampling. As might be expected, mercury in excess of the standard is most common in the surficial aquifer system. Statewide, two percent of the samples exceeded the standard. The proportion of samples that exceeded the standard ranged from zero to ten percent.

It is somewhat surprising that three percent of the samples from the intermediate aquifer system exceeded the standard. Given the reducing conditions and clay and organic content of the intermediate aquifer system, one would expect mercury to be immobile. The range in proportions of samples within the districts is zero to 13 percent. The district with 13 percent of its intermediate aquifer samples exceeding the standard is the SJRWMD.

As might be expected, few samples from the Floridan aquifer system exceeded the mercury standard. Statewide, the proportion was 0.9 percent, with a range of zero to two percent.

DISTRIBUTION IN GROUND WATER

The concentration data indicate that there is minimal opportunity for mercury to enter surface waters from the ground-water system and that the risk of exposure to humans from state ground waters is minimal. A few wells in each aquifer system have detectable amounts of mercury. Since the samples that did have detectable quantities of mercury are widely scattered, and because many of the incidences of detection have not been confirmed by resampling, maps showing the locations of these detections are not included in this report.

Surficial Aquifer System

Mercury concentrations are generally quite low in the surficial aquifer system (Table 15). Median concentrations are below detection limits in the surficial aquifer system. With the exception of data from the NWFWMD, at least 75 percent of all samples were below detection limits. The SJRWMD had a sample with 52 µg/L.

Intermediate Aquifer System

Similar results exist in the intermediate aquifer systems. The medians are below detection limits, and only SJRWMD had more than 25 percent of the samples with detectable concentrations.

Floridan Aquifer System

The median concentration in the Floridan aquifer system is also below detection limits. At least 75 percent of the sample sets from all districts were below detection limits, as well. Statewide, there were only six samples from the Floridan aquifer system with mercury in excess of the standard.

Lead

IMPORTANCE AND SOURCES

Lead minerals are very rare, but trace quantities of lead are present in feldspars and other minerals. Average sea water contains 0.03 µg/kg lead (Table 8), so Plio-Pleistocene marine transgressions may have resulted in deposition of trace

quantities of lead in peats and mucks, clay beds, and other favorable sites. As with mercury, marine aerosols can be expected to transport lead into the interior, but only in concentrations of fractions of a part per trillion concentration. Because of the lack of an obvious source, any occurrence of lead in Florida ground water is probably a result of human activities.

Dissolved lead is divalent (Pb^{2+}; Garrels and Christ, 1964; Hem, 1985) in most natural waters. If carbonate is present, lead carbonate (cerussite, $PbC0_3$) is relatively insoluble and precipitation of cerussite may control the solubility of lead in carbonate aquifers. Lead sulfate (anglesite, $PbSO_4$) and lead sulfide (galena, PbS) are also relatively insoluble and are likely to precipitate in sulfur-rich, oxidizing and reducing environments, respectively. None of these minerals have been found in Florida, but sorption isotherm experiments by Upchurch et al. (1991) indicate that trace amounts of cerussite should precipitate where lead-rich waters encounter Florida carbonate rocks.

Lead is also strongly bound to organics, colloidal oxyhydroxides, and clay surfaces by sorption and/or chemical complexing mechanisms (Hem, 1976; Moore and Ramamoorthy, 1984; Upchurch et al., 1991). Sorption isotherms (Upchurch et al., 1991) of lead on surficial aquifer system quartz sand (a ferric hydroxide-coated sand), Hawthorn Group clay (montmorillonite, palygorskite), and Floridan aquifer system limestone indicate that all three media are able to fix lead, but the limestone and sand have less sorption capacity than the Hawthorn clays. In this experiment, 99.6 percent of the lead was removed on the clay, while both the sand and the limestone were responsible for removal of 97.8 percent.

The absence of a strong source and the affinity of lead for both mineral precipitation and sorption or complexing suggest that ground-water samples from Florida's aquifer systems should not contain detectable lead. Lead concentrations in natural systems are expected to be in the order of 2 µg/L or less (Hem, 1985).

Human influences, alternatively, do contribute lead to the land surface. Fallout from fossil fuel combustion (e.g., leaded gasoline, coal and fuel oil); disposal of lead-containing wastes (e.g., batteries, paints); widespread use of lead solders, flashings, paints; use of lead weights and solder in well or water systems; past uses of lead in pesticides by the agriculture industry; and spent bullets are among the many potential sources of lead in Florida environments. Many of the wells that were used in this study have had lead weights on water-level recorders installed at one time. This may be a reason for some of the detections of lead mentioned below.

STANDARD OR GUIDANCE CRITERION

Lead is subject to the Florida Primary Drinking Water Standards (Florida Department of Environmental Regulation, 1989), and the maximum allowed concentration is 0.050 mg/L (50 µg/L). Lead compounds are highly toxic to animals and humans. Accumulation in the food chain has been documented. Lead intake in humans has been associated with chronic and acute toxicity, and children are particularly at risk (Harris, 1968; Hem, 1985).

Table 16 summarizes the samples found to exceed the standard in Florida's aquifer systems. Many of these exceedances have not been confirmed by resampling. There is a large number of samples that exceed the standard. The very high values (>500 µg/L) almost certainly represent some contamination problem. All samples with concentrations above detection limits probably reflect local contamination. Given that local contamination as a result of land use cannot be documented for these wells from which the samples came, a probable source for the lead is the use of lead weights in the wells. According to SFWMD staff (J. Herr, 1991, pers. comm.) many of the high lead concentrations in that district are a result of use of lead weights on water-level recorders in the wells. A similar situation apparently exists in the SWFWMD, where intermediate and confined Floridan aquifer system samples have reported lead.

While the widespread nature of lead is a matter of concern at this time, it is important to recall that the samples were not filtered, many of the wells have had lead weights on water-level recorders in the past. Also, most of the analytical results have not been confirmed by subsequent sampling. If the high proportion of wells with detectable lead continues after the second round of sampling and analysis of the Background Network data, which will include filtered and unfiltered samples, has been completed, then it will be necessary to determine the cause of lead mobilization in Florida's aquifer systems.

Samples from the surficial aquifer system that exceeded the standard made up eight percent of the samples statewide. This is a high number, but the range of proportions of wells in which lead was detected varied from zero percent in the SRWMD to 21 percent in SWFWMD. The proportion of samples that exceed the standard in the intermediate aquifer system averages eight percent statewide, with a range of two to 24 percent by district. Again, this proportion is high and suspect. Finally, the proportion in the Floridan aquifer system is nine percent statewide. NWFWMD had zero percent above the standard, and SJRWMD and SWFWMD had 19 and 20 percent, respectively.

DISTRIBUTION IN GROUND WATER

The distribution of lead in Florida's aquifer systems is summarized in Table 16. Several rather startling trends are apparent in the lead data.

First, lead appears to be widespread, although usually in quantities less than the standard. The widespread nature of the metal, combined with the large number of samples that exceeded the standard, suggest the need for additional study and a potential problem.

Second, it is somewhat surprising that detectable lead is present in the carbonate- and clay-rich aquifer systems. The intermediate aquifer system is rich in clays and lead should be adsorbed, rather than mobile. Lack of sample filtration is likely to result in analysis of the sorbed- lead fraction, however. In the carbonate aquifer systems (Floridan aquifer system and portions of the intermediate and surficial aquifer systems), lead is likely to precipitate as cerussite. Comparison of filtered to unfiltered samples in the second Background Network sampling will indicate the presence of sorbed or precipitated lead.

Since the samples that did have detectable quantities of lead are widely scattered, and because many of the incidences of detection have not been confirmed by resampling, maps showing the locations of these detections are not included in this report.

Surficial Aquifer System

Median lead content of samples from the surficial aquifer system statewide was 2 µg/L. This is a high value, which is subject to concern. The medians ranged from less than <2 µg/L in SFWMD to below 10 µg/L in the NWFWMD and SRWMD to 36 µg/L in the SWFWMD. The upper quartiles (75th percentiles) for lead concentration in the SJRWMD exceeded the standard. Maximum concentrations exceed 1,000 µg/L lead in two districts. The three wells in SFWMD with the highest measured lead concentrations had once contained either water-level recorders with lead weights or had casings perforated by bullet holes.

One would expect that the surficial aquifer system might be the most susceptible to lead contamination through fallout or local land uses. The low clay content, low carbonate content, high acidity, and high organic content of surficial aquifer system waters can lead to lead mobility. However, the large proportion of samples with detectable lead, and the high concentrations detected in many wells, seems too great, even with these potential transport conditions.

Intermediate Aquifer System

Median lead concentrations in the intermediate aquifer system vary from below detection limits in three districts (Table 16) to <43 µg/L in the SWFWMD. Maximum and upper quartile concentrations are not as high as in the surficial aquifer system, but they are still high. Given that the intermediate aquifer system includes the clay-

and organic-rich sediments, as well as carbonate-rock horizons, the incidence of lead should be lower. The SWFWMD samples show the highest lead concentrations, which reflects, in part, use of lead weights on water-level recorders in some wells.

Floridan Aquifer System

Lead concentrations from the Floridan aquifer system are roughly equivalent to those in the intermediate aquifer system. The statewide median concentration is below detection limits, but two districts had upper quartile samples above detection limits, and two are near the standard.

ANIONS

Classification

Anions are negatively charged species in aqueous solutions. They form by taking on electrons given up by cations. Unlike the cations, many of the naturally occurring anions are not elemental (e.g., Cl-), they are compound radicals (e.g., $P0_4^{3-}$). Anions can be classified according to their abundances in the natural environment.

MAJOR ANIONS

Anions that are present in aqueous systems in concentrations greater than 1.0 mg/L are said to be major anions. Major anions in ground-water systems usually include bicarbonate ($HC0_3$-), sulfate ($S0_4^{2-}$), and chloride (Cl^-). These anions are used to classify hydrochemical facies and are discussed in the following section.

MINOR ANIONS

Minor anions range in concentration from 0.001 to 1.0 mg/L. The important minor anions in Florida ground waters include fluoride (F^-), nitrate ($N0_3^-$), sulfide (S^{2-} and HS^-), and orthophosphate ($P0_4^{3-}$). With the exception of sulfide, the minor anions are discussed in separate sections. Sulfide data are limited, so the anion is discussed in conjunction with sulfate.

TRACE ANIONS

Trace anions normally occur in concentrations less than 0.001 mg/L. Carbonate ($C0_3^{2-}$), nitrite ($N0_2^-$), and organic nitrogen (total Kjeldahl nitrogen [TKN]) are included in this group and discussed below. Carbonate is discussed with bicarbonate. Nitrite and TKN are discussed in conjunction with nitrate. While ammonium (NH_4^+) is a positively charged cation, it is included with nitrate for convenience.

Bicarbonate, Carbonate, and Alkalinity

IMPORTANCE AND CONTROLS

The importance of the carbonate system as an agent in weathering reactions has been previously discussed. Bicarbonate and carbonate are dissociation products of the reactions between carbon dioxide and water. Carbon dioxide and water react to produce carbonic acid (reaction 1). Carbonic acid dissociates to bicarbonate and hydrogen ions (reaction 1), which are represented by pH. The hydrogen reacts with rock materials in the weathering reaction (reaction 2), and bicarbonate remains as the anionic constituent in the water. Bicarbonate can further dissociate to carbonate according to the reaction

$$HC0_3^- \rightleftarrows H^+ + CO_3 \qquad (10)$$

Thus, pH, bicarbonate, and carbonate are closely related.

Bicarbonate - Bicarbonate ($HC0_3$-) is the dominant carbonate species in the pH range of 6.4 to 10.3 at 25°C. Bicarbonate is the primary anionic weathering product (reactions 2 and 3), so it is an important indicator of chemical maturity in an aquifer. Because of its role in the weathering reaction, bicarbonate is usually the dominant anion in potable ground waters.

Carbonate - Carbonate ($C0_3^{2-}$) does not become an important anion in water unless pH values are in excess of 8 to 8.5. In most natural systems, carbonate is not an important anionic constituent, and concentrations are small compared to bicarbonate. Depending on the method of analysis, carbonate concentrations are unlikely to be reported.

In order for carbonate to be a dominant anion in water, extraordinary conditions that cause high pH must exist. Such conditions occur in saline, arid-environment lakes where pH is greater than 9. Buffering of the pH through rock-water interactions limits natural carbonate activities in groundwater systems in Florida.

Cements, grouts, and some drilling fluids used in well construction are highly alkaline. If the cements are not properly cured and if wells are not properly developed, the pH of the resulting well water may be alkaline and carbonate may be present. Therefore, in Florida's aquifer systems, where highly alkaline environments are not considered normal, carbonate can be used as a possible check on well development and construction.

Alkalinity - Total alkalinity is determined by titrating all of the anions in a solution with strong acid. The variable is, therefore, a measure of the ability of a water to consume, or buffer, acid, and it is a measure of the total anionic concentration in the water that can be titrated with an acid. The anions that are neutralized by titration with strong acid include $HC0_3$-, $C0_3^{2-}$, $B(OH)_4$, $H_3SiO_4^-$, HS^-, $P0_4^{3-}$, and some organic ligands. **Total alkalinity** includes all of these acid-neutralizable anions. In most natural systems, bicarbonate is the major anion, and concentrations of the other anions are minor. As such, bicarbonate is the dominant constituent of alkalinity of the water. If the analysis of alkalinity includes only bicarbonate and carbonate, then the alkalinity is called the **carbonate alkalinity**. The other components can, however, significantly contribute to total alkalinity in some waters. **Non-carbonate alkalinity** is the total amount of the non-carbonate species that can be titrated. Of the non-carbonate components listed above, $H_3SiO_4^-$, HS^-, and $P0_4^{3-}$ are likely to be significant in Florida waters.

The districts varied in how alkalinity and concentrations of carbonate and bicarbonate were measured. Some measured bicarbonate and carbonate, others carbonate alkalinity, and yet others total alkalinity. In some cases the districts measured more than one analyte. Consequently, the tables and maps that follow indicate the nature of the variable reported.

DATA INTERPRETATION

Three tables are used to indicate the variety of alkalinity and carbonate-species measurements. **Table 17** reports bicarbonate concentrations, **Table 18** gives carbonate concentrations,and **Table 19** reports total alkalinity. Note that the method of reporting total alkalinity includes both calcium carbonate alkalinity and alkalinity in milliequivalents per liter[13].

Wide ranges in bicarbonate content (Table 17) reflect different levels of "chemical maturity" of the ground waters. In general, high bicarbonate concentrations indicate that the waters have undergone significant equilibration with the rock matrix. Low values indicate that little equilibration has occurred.

The bicarbonate concentration ranges reported in Table 17 are indicative of some of the problems associated with bicarbonate analyses in aquifer systems. For example, in the surficial aquifer system, zero bicarbonate concentrations are possible due to the acidity of waters in siliciclastic aquifer materials, especially those characterized by organic acids. High bicarbonate concentrations reflect shelly siliciclastic or limestone aquifers in which equilibration with a carbonate mineral has occurred. The same relationships are possible, but less likely, in the intermediate aquifer system. Here, carbonate clasts are mixed with the siliciclastics and there are widespread horizons of limestone and dolostone.

Significant aqueous carbonate concentrations are unusual in natural systems. They are usually

caused by improper well installation or development. Low bicarbonate concentrations **(Table 17)** associated with high pH **(Table 7)** values may reflect high alkalinity in the form of carbonate ion ($C0_3^{2-}$). Obvious problem data have been omitted from this analysis, yet some data remain that suggest influences from well construction. Carbonate concentrations are summarized in Table 18. Comparison of the bicarbonate and carbonate concentrations in the database, or the bicarbonate and pH values on the maps in this report, should suffice to differentiate between natural carbonate and well-related carbonate. In the Floridan aquifer system, zero bicarbonate concentrations should not occur. Newly recharged water located in a large, karst conduit and, therefore, not in contact with the host carbonate rock may still be acidic and have low bicarbonate. Mixing and partial equilibration with the host rock should occur in most cases.

The bicarbonate content of the aquifer water can be used as a very rough indicator of the ability of the aquifer system to tolerate acidic wastes. Low bicarbonate waters, such as occur in siliciclastic aquifers, have little or no tolerance, while high bicarbonate aquifers have some tolerance.

STANDARD OR GUIDANCE CRITERION

The carbonate species do not constitute a health hazard per se; therefore, there are no standards or guidance criteria for the carbonates. To an extent, carbonate concentrations are represented in criteria for pH. There is a maximum pH criterion of 8.5, which is about the pH where $HC0_3^-$ concentration begins to decline and $C0_3^{2-}$ begins to grow in importance.

DISTRIBUTION IN GROUND WATER

Most Florida ground-water samples have low to non-detectable carbonate contents **(Table 18)**. Wells with detectable carbonate, especially those wells with carbonate contents in excess of 1 mg/L, are likely to be newer wells that have not been thoroughly developed or in which cements and grouts have not yet cured.

Available alkalinity data for the aquifer systems **(Table 19)** are inconsistent. Some of the districts reported alkalinities in milligrams per liter as CaC03, others reported it in milliequivalents per liter, others did not report it at all. In spite of the inconsistent data, alkalinity is included in this report because it is a common analyte in ground-water contamination studies. Note that, where available, the alkalinity data closely follow the bicarbonate concentrations, indicating that the primary source of alkalinity is bicarbonate.

Surficial Aquifer System

Median bicarbonate (Table 17) and total alkalinity (Table 19) in the surficial aquifer system increase to the south in response to increasing calcium-carbonate content of the aquifer system. Statewide, the median bicarbonate concentration is 138 mg/L, no carbonate is present, and total alkalinity is approximately 111 mg/L as CaC03.

Bicarbonate concentrations are generally low in the surficial aquifer system in northern Florida (Figure 28a,b) as a result of lack of carbonate minerals in the aquifer system. These low bicarbonate concentrations are associated with low pH's and often with high total dissolved carbon. Comparison of Figure 28 with Figure 9 illustrates the relationship between low pH and low bicarbonate content.

Shell and limestone content of the surficial aquifer system increases to the south. As a result, rock weathering becomes more important and bicarbonate content increases. The southward gradient is well illustrated in the SWFWMD (Figure 28c). The increase in bicarbonate content toward the coast and along the Peace River axis is an artifact of a general increase coastward in ionic strength of the water associated with increased shell contents in coastal, Plio-Pleistocene sediments.

A similar coastward increase in total alkalinity is weakly shown in the data from the northern portion of the SFWMD (Figure 28d). Waters along the Kissimmee River valley and adjacent parts of the Lake Wales Ridge and along the Caloosahatchee River axis have low alkalinities, while waters elsewhere have high alkalinities. There are no wells in the surficial aquifer system in the majority of the Everglades and Big Cypress drainages. Available data indicate that alkalinities are low in these regions, which are characterized by organic-rich waters and direct interconnection between the surficial aquifer system and surface water. The SFWMD well with the 2,260 mg/L concentration probably represents contamination by grout or drilling mud. Subsequent samples from this well have produced much lower alkalinity concentrations.

Carbonate was only detected in wells in the SRWMD (Table 18), where well construction is known to have been a problem. In SRWMD and SWFWMD, the median and quartiles are below detection limits.

Intermediate Aquifer System

The Hawthorn Group and associated strata contain abundant carbonate material. Dolostone and limestone beds are widespread and often constitute major water-producing zones. Silici- clastic horizons contain carbonate clasts reworked from these beds. Also, the Hawthorn contains beds of silt-sized, unconsolidated dolomite (Scott, 1988). These fine-grained "dolosilts" are highly reactive with ground water. Water in contact with either source of carbonate gains bicarbonate alkalinity as a result of weathering. Consequently, ground waters in the intermediate aquifer system generally have higher bicarbonate alkalinities than do waters in the surficial aquifer system. The median bicarbonate concentration in the intermediate aquifer system, for example, is 143 mg/L as compared to 138 mg/L in the surficial aquifer system. This difference is particularly distinct in north Florida, where the surficial aquifer system waters contain little bicarbonate (compare Figures 28 and 29).

Bicarbonate content in the intermediate aquifer system is highly variable due to the heterogeneous nature of the Hawthorn Group and related sediments. Samples with lower bicarbonate contents are either from karstic zones or from siliciclastic horizons. Samples with higher bicarbonate concentrations are from carbonate- rich beds, including the dolostones, limestones, or dolosilts.

Carbonate (Table 18), converted to mg/L bicarbonate gives similar concentrations. Carbonate was detected in SRWMD and in a few SWFWMD wells, where well development problems have been reported.

Floridan Aquifer System

The Floridan is almost entirely limestone or dolostone, so bicarbonate concentrations are characteristically high and variability is less than in the other aquifer systems. Statewide, the median concentration is 146 mg/L, and the quartile range is 96 mg/L.

A weak coastward increase in bicarbonate is present in the Floridan aquifer system throughout the state (Figure 30a, b, and d). This increase is a result of chemical maturation along ground-water flow lines. Chemical maturation within the Floridan aquifer system is characterized by increases in ionic strength accompanied by dissolution of carbonate minerals (Runnels, 1969; Drever, 1988). Where deeper waters rise to the surface at springs, this increase in bicarbonate is pronounced. For example, the large re-entrant in Liberty, Wakulla, and Franklin Counties (NWFWMD, Figure 30a) is a result of upwelling of deeper waters on the inner margin of the transition zone. Note that average sea water contains about 142 mg/L bicarbonate **(Table 8)**, so bicarbonate concentrations higher than 200 mg/L are a result of maturation along the flow path, not salt-water intrusion.

The pattern of bicarbonate in SRWMD (Figure 30b) is complicated because of the presence of flow systems east and west of the Suwannee River. The highest bicarbonate values are near springs and areas of regional discharge. High bicarbonate concentrations also exist along the Cody Escarpment, in Columbia and Alachua Counties, and in the Northern Highlands, where flow is thought to be relatively stagnant and recharge is limited due to the presence of thick confining strata (Lawrence and Upchurch, 1976).

Total alkalinity in the Floridan aquifer system in the

SJRWMD (Figure 30c) suggests a weak re- entrant that follows the St. Johns River. Many of the higher alkalinity concentrations reflect deeper wells.

Bicarbonate concentrations in the SWFWMD (Figure 30d) reveal two significant patterns. The data from the northern half of the district show an irregular distribution of bicarbonate. Part of this irregular pattern is a result of variations in well depth, but much of it reflects the unconfined to poorly confined nature of the Floridan aquifer system in the area. Local flow systems and regions of direct discharge result in the irregular pattern. The data from the southern half of the district show a simpler distribution pattern due to the confined nature of the aquifer system.

Data from the SFWMD (Figure 30e) are insufficient to provide much information. Total alkalinities are low in the Kissimmee River valley and Lake Wales Ridge area. The Lake Wales Ridge is a region of recharge, which suggests that the low alkalinities are a result of a low level of chemical maturation. In contrast, Floridan aquifer system waters near the coast contain higher alkalinities, which reflect maturation. As indicated below, there is an abundance of sulfate in Floridan aquifer system water in coastal and the central and southern parts of the SFWMD. This sulfate replaces bicarbonate as a major anion, and thereby reduces akalinities.

Sulfate

IMPORTANCE AND CONTROLS

Sulfur occurs in several oxidation states, depending upon the reduction/oxidation potential of the water. Two are of major importance in aquifer systems. These are the oxidized form, sulfate (SO_4^{2-}), in which sulfur has a valence of +6, and the reduced form, sulfide (S^{2-} or HS^-), which has a valence of -2.

SOURCES AND SINKS OF SULFUR

There are many potential sources of sulfur in Florida's aquifer systems. Sulfate is directly introduced to the system by marine aerosols **(Table 8)** and by acidic precipitation from airborne sulfur oxides. Deposition of significant quantities of airborne sulfur oxides is a recent phenomenon related to the acid-rain problem. Waters that recharged Florida's aquifer systems prior to the late 1800's should contain little or no anthropogenic sulfur. Recently recharged waters may contain significant amounts of this sulfur. Modern precipitation contains an average of 1.75 mg/L sulfate statewide **(Table 3)**. The highest sulfate concentration recorded in the precipitation data (Table 3) was almost 23 mg/L, which is well within the range of concentrations recorded from Florida's various aquifer systems.

Rock weathering is the most important natural source of sulfur in aquifers. Most rocks contain at least trace quantities of pyrite (FeS_2) and other metal sulfides. These sulfide minerals can be oxidized according to the reaction

$$R\text{-}S_2 + 3.5O_2 + H_2O \rightleftarrows R^{2+} + 2S0^{2-}_4 + 2H^+, \quad (11)$$

where $R\text{-}S_2$ is a metal-sulfide compound, such as pyrite, containing reduced sulfur, and R^{2+} is a metal, such as iron, that is simultaneously involved in the oxidation reaction

$$R_2 + 0.25O_2 + 2.5H_20 \rightleftarrows R^{3+}(OH)_3 + 2H^+ \quad (12)$$

If the reaction involves pyrite, R^{2+} is Fe^{2+}, which is oxidized to Fe^{3+}. Thus, oxidation of metal sulfide minerals results in the production of sulfate and hydrogen ion, which reduces the pH. Reactions 11 and 12 are the "acid-mine drainage" reactions. Pyrite is found in all of Florida's aquifer systems and aquitards. It is especially abundant in clay-rich horizons of the Hawthorn Group **(Table 5)**.

Dissolution of gypsum and anhydrite at the base of the Floridan is also an important source of sulfur as sulfate. The dissolution of gypsum has been documented by Rightmire et al. (1974) and Rye et al. (1981). This sulfate is brought upward along the coastal transition zone, so that much of the coastal Floridan aquifer system can contain high sulfate concentrations.

Sulfur is a necessary element for life. Plants contain sulfur in amino acids and other organic components. They obtain this sulfur by reducing dissolved sulfate, and they pass the sulfur on to heterotrophs, including humans and other animals. Because sulfur is stored in tissues, decomposition of organic materials constitutes another possible source of sulfur as sulfide. Sulfur constitutes about one percent dry weight in organisms. Decomposition of humic substances by microbes involves chemical reduction, so the released sulfur is usually in the form of sulfide. Oxidation may follow rapidly.

Sea water is an important source of sulfate in coastal environments. Average sulfate concentration in sea water is 2,710 mg/kg (Table 8), so the transition zone should contain a concentration gradient that increases toward the coast regardless of any contributions from the deep flow system.

Finally, a number of agricultural, waste disposal, and industrial activities release sulfur compounds to ground water. Gypsum **(Table 4)** is used as a soil amendment to acidify soils. Landfill leachate can be high in sulfates and/or sulfides. Many industries, such as fertilizer, battery, and plating plants, release sulfates, usually as sulfuric acid. Phosphogypsum disposal at agrichemical plants in central and north Florida has been shown to contribute sulfate to ground water in the immediate vicinity of the gypsum disposal areas (Miller and Sutcliffe, 1982, 1984). Hutchinson (1978) included analyses of seven surficial aquifer system water samples in the Alafia River basin. He found calcium-sulfate water in two wells that are distant from the phosphochemical plants. Therefore, high sulfate concentrations in the general area of phosphochemical plants may not be a direct product of those fertilizer plants.

Sulfate is removed from surficial aquifers by plant metabolism. It can also be removed by aquifer microbe metabolism, including reduction to sulfide. Precipitation of sulfate as gypsum can occur at high ionic strengths, such as occur in evaporative lakes and desert soils. Although there is no evidence of sulfate mineral precipitation in Florida today, sulfate-rich evaporite minerals are common at the base of the Floridan aquifer system and locally in the Hawthorn Group. Sulfides are removed from ground water by oxidation to sulfate, metal-sulfide mineral precipitation, degassing of H_2S_{gas}, and microbial fixation.

Sulfide - Given prevailing reducing conditions, sulfide is the thermodynamically favored species (Figure 31) in most Florida aquifer system environments. Upchurch et al. (1991) studied the Eh-pH conditions of surficial and shallow Floridan aquifer systems in Polk County. They found that surficial aquifer system water is reducing (-300 to O mV) and, given a pH range of 4 to 6, H_2S is the most probable sulfur species. Water samples from the Floridan aquifer system were influenced somewhat in their study by interaquifer recharge. Eh ranged from -250 to O mV, and the pH was near 7 (Figure 31). Under those Eh and pH conditions, the Floridan aquifer system water samples fell near the intersection of the $S0_4^{2-}$, H2S, and HS^- stability fields. It appears that, outside of regions of immediate recharge, Floridan aquifer system water is reducing and H_2S is the stable sulfur species. Hydrogen-sulfide odor (the familiar "rotten egg" odor) is detectable in many wells in all aquifer systems of the state, supporting the conclusion of Upchurch et al. (1991).

Much of the H_2S in aquifer systems is a result of sulfate reduction. The conversion of sulfate to sulfide is usually accomplished by aquifer or soil microbes, and follows a reaction such as shown in reaction 6. Note that a source of organic carbon must be present for sulfate reduction. Rightmire et al. (1974) and Rye et al. (1981) used isotopic analysis of sulfur to determine the origins of sulfate and sulfide in Floridan aquifer system waters. Sulfide in shallow portions of the Floridan near recharge areas was shown to be a result of

sulfate reduction.

Unfortunately, sulfide was not determined throughout the Background Network, so only the role of sulfate can be documented in this report. There are some sulfide data from the SWFWMD that allow a partial understanding of sulfide concentrations in Florida's aquifer systems. Sulfide in the surficial aquifer system averages 0.55 mg/L (σ^2 = 1.09 mg/L, range = 0.00-5.50, n = 82). There are no data for the intermediate aquifer system. In the Floridan aquifer system, sulfide averages 0.44 mg/L (σ^2 = 0.63, range = 0.00-2.43, n = 136). These concentrations are consistent with concentrations in equilibrium with H_2S at the Eh and pH ranges found by Upchurch et al. (1991).

Sulfate - If the water is oxidizing (Figure 31), sulfides may be oxidized to sulfates. This reaction can be driven either inorganically or microbially. The reactions can be characterized by reactions 11 and 12. Note that the product is $S0_4^{2-}$ plus H^+, in other words a dilute sulfuric acid solution. While sulfide oxidation is a widespread reaction in Florida's aquifer systems, the dominant source of sulfate is dissolution of gypsum and anhydrite near the base of the Floridan aquifer system. These minerals, which are interstitial in the Eocene Avon Park Formation and lower horizons, are dissolved into deep flow systems in the Floridan. The result is that Floridan aquifer system water that upwells near the coastal transition zone has an inner "belt" of sulfate-rich water. Rightmire et al. (1974) and Rye et al. (1981) showed that dissolution of the sulfate minerals, rather than oxidation of sulfides, is the dominant cause of the deeper and coastal sulfate-rich waters.

Microbial Activity - Microbial processes and chemical kinetics determine the rates of conversion from one species to the other (Connell and Patrick, 1968; Rye et al., 1981). The ability of the microbes to function in an aquifer system is dependent upon a complex array of conditions and, if these are not met, the sulfur may not be altered regardless of Eh and pH. For example, if there isn't a source of organic carbon (reaction 6), aquifer microbes may not be able to reduce sulfate to sulfide. Therefore, metastable sulfur species may be present in the water samples.

The abundance of sulfate in the deep Floridan aquifer system is an example of a potentially metastable sulfur species. The deep Floridan is chemically reducing, and sulfide is generally the stable species. While there is some sulfide in deep Floridan aquifer system waters, microbes appear to be unable to effectively reduce all of the sulfate derived by dissolution of gypsum or anhydrite near the base of the aquifer system. The inability of the microbes to reduce the sulfate may be a result of a lack of an organic carbon source (Watrous and Upchurch, in prep.). Consequently, sulfate persists for many years and many kilometers along the flow path.

STANDARD OR GUIDANCE CRITERION

Even though sulfur is necessary for life, adverse effects arise if it is present in hazardous forms or concentrations. Formation of sulfate through aqueous sulfide oxidation (reactions 11 and 12) or equilibration of sulfur oxides with water in the atmosphere both result in acidic, sulfate-rich waters that have the potential of being corrosive and hazardous to aquatic organisms. Sulfate-rich waters are potentially toxic to plants and deposition of high sulfate water on plant foliage may cause crop losses. Sulfate-rich water has a laxative effect on humans and may produce adverse taste in drinking water, as well. As a result of the latter effects, the Secondary Drinking Water standard for sulfate has been set at 250 mg/L (Florida Department of Environmental Regulation, 1989).

Sulfides are much more undesirable than sulfates in ground water. Hydrogen sulfide gas (H_2Sgas) is a persistent problem in ground water, although Florida suffers less than some regions. This gas produces the familiar "rotten egg" odor, which can be detected in water at dissolved concentrations of just a few milligrams per liter. While some persons treat H_2S- and sulfate-rich water ("sulfur water" in the vernacular) as a health- giving resource which one drinks to "clean out" the alimentary system or in which one bathes for therapeutic reasons, most consider this common phenomenon as a liability. In high concentrations, hydrogen sulfide is irritating to the eyes and lungs. It is highly toxic as an atmospheric gas. There is no standard or guidance criterion for sulfide in ground or drinking water for two reasons: (1) the odor can be eliminated by degassing and is unpleasant enough to serve as its own limitation, and (2) there is usually sufficient aeration and oxidation in public water supplies that any sulfide is converted to sulfate, for which there is a standard.

DISTRIBUTION IN GROUND WATER

It is interesting to note that, while maps and spatial studies of the distribution of sulfate clearly show an increase with depth and towards the coast, **Table 20** suggests that there is little difference in sulfate concentrations between the three aquifer systems. This is in part because (1) sea water affects all systems equally, (2) there is significant interaquifer transfer of water in both upward and downward directions, and (3) the sample set is somewhat biased toward the more potable, low sulfate waters. Maximum concentrations do suggest that the deep Floridan aquifer system is prone to higher sulfate concentrations than are the other aquifer systems.

Surficial Aquifer System

The distribution of sulfate in the surficial aquifer system (Table 20) reflects local geology and flow system dynamics. Median sulfate concentrations (Table 20) are low in NWFWMD and SRWMD for three reasons: (1) the surficial aquifer system, especially the Sand and Gravel Aquifer of Escambia County, is well flushed, (2) there is limited upward flux of deeper, sulfate-rich waters, and (3) few wells in the sample set are coastal. The maps of sulfate distribution (Figure 32a,b) in these districts show minor coastal increases in sulfate concentrations. The causes of high sulfate concentration inland are unknown, but oxidation of pyrite-containing peats, upward transfer of intermediate or Floridan aquifer system water by pumpage, and evaporative concentration of sulfate-rich precipitation are possible causes.

Median sulfate concentrations in the other three districts (Table 20) are relatively high because the surficial aquifer system includes regions of natural and irrigation-related upward flux of deeper, sulfate-rich waters and of mixing with sea water in the coastal transition zone. Atlantic Coastal Ridge portions of the surficial aquifer system often contain sulfide-rich organics and pyrite. These are locally important aquifers in the SJRWMD and SWFWMD, and they are well represented in the data set. Zones of local upconing are evident in western Indian River County, Volusia County, and Orange County and the coastal interface is well demonstrated in SJRWMD (Figure 32c). Sulfate upconing is also present in Hardee and DeSoto Counties, and there is a large re-entrant along the Peace River axis (Figure 32d; Kaufman and Dion, 1967). In SFWMD, the sulfate concentrations in the Atlantic coastal ridge portions of the surficial aquifer system are low due to the dynamic circulation in the aquifer systems. Few sulfate data exist from the Everglades portion of the SFWMD (Figure 32e). Andrejko and Upchurch (1978) have shown that the peats of the Everglades contain sulfur that is converted to anhydrite during peat fires. This anhydrite is then dissolved in surface waters, which, in turn, recharge the surficial aquifer system. One can conclude, therefore, that sulfate concentrations in the surficial aquifer system should be moderately high.

Comparison of the Eh-pH conditions of the surficial aquifer system (Figure 31) indicates that, at 25°C, the water falls at or below the boundary between SO_4^{2-} and H_2S, with the majority of the samples well within the H_2S stability field. The kinetics of equilibrium reactions between the two sulfur species are dominated by bacteria, and metastable species can exist if bacterial action is inhibited. Connell and Patrick (1968) investigated the stability of sulfate and sulfide in waterlogged soils, such as the surficial aquifer system. They found that microbial sulfate reduction is inhibited and sulfide formation is minimized at redox potentials above -150 mv and at pH's outside the range of 6.5 to 8.5. Since optimal conditions for microbial sulfate reduction may not be present in the surficial aquifer system (low pH values and Eh

values that tend to be above -150 mv), sulfate, not sulfide, may predominate as a metastable species.

Intermediate Aquifer System

The intermediate aquifer system contains abundant pyrite, and gypsum has been found in a number of regions of the state. Low permeabilities in the clays and the presence of particulate humic substances limit oxidation of the pyrite, but the potential for oxidation and aqueous sulfate production exists. Red, orange, and yellow tints from ferric hydroxides and goethite in exposures of the Hawthorn Group and in immediately underlying limestones along the flanks of the Ocala Platform document oxidation of pyrite in the past.

With the exception of Flagler and Indian River Counties (SJRWMD), the intermediate aquifer system is neither widespread nor widely used in the northern districts (NWFWMD, SRWMD, and SJRWMD; **Table 20)**; consequently, few data are available. Where data are present, it appears that flow systems are restricted and sulfide oxidation is limited. Sulfate concentrations are characteristically low and variable (Figure 33a,b, and c).

In contrast, the intermediate aquifer system is highly utilized in southwestern SWFWMD and in western SFWMD. Here, the circulation system is better developed, and connection with the underlying Floridan aquifer system is present in many coastal areas (Upchurch, 1986). As a result, sulfate is widespread and abundant (Table 20). Re-entrants along the Peace and Myakka River axes (Figure 33d) reflect upconing and intrusion along lineaments that extend through the Hawthorn Group (G. Jones, 1991). These regions are a result of natural discharge, exacerbated by pumping. There is a region of high sulfate that apparently reflects upconing in northeast Lee County, as well (Figure 33e).

Floridan Aquifer System

Sulfate concentrations increase with depth in the Floridan aquifer system throughout the state.The data set summarized in Table 20 and Figure 34 has not been stratified by depth, so some of the higher sulfate concentrations represent deeper wells. Lowest sulfate concentrations are in recharge regions where meteoric waters have not accumulated sulfate. This lack of sulfate results from (1) residence times that are too brief for pyrite oxidation, (2) pyrite or other sulfate sources have either been depleted or were never present, or (3) pyrite oxidation is not thermodynamically favored. Highest concentrations are in deep wells where contact with the underlying gypsum and/or anhydrite has enriched the water with sulfate.

In general, sulfate concentrations are least in NWFWMD and SRWMD. Large, coastal re-entrants occur in Walton County and along the Apalachicola River in NWFWMD (Figure 34a). These are a result of natural discharge along the river and to pumpage. The pattern in SRWMD is more complicated due to the local flow system between the Suwannee River and the coast. Coastal re-entrants exist along many of the coastal rivers and in the vicinity of the Suwannee River. High sulfates are also present in the confined, sluggish flow system under the Northern Highlands in the northeast part of the SRWMD (Figure 34b; Lawrence and Upchurch, 1976).

High sulfate concentrations in SJRWMD and SWFWMD (Table 20) reflect longer flow paths in the Floridan that contact the gypsum and anhydrite at the base of the aquifer system and bring that water near the surface along the inner, coastal- transition zone. Characteristically, sulfate concentrations increase towards the coast. There is a region of high sulfate along the St. Johns River (Figure 34c), which has been attributed to upconing along a fracture or fault by Leve (1983). Similar re-entrants along the Peace and Myakka Rivers (Figure 34d) have also been attributed to upconing along lineaments by G. Jones (1991). The coastward increase in sulfate is best illustrated in the SWFWMD (Figure 34d). Localized areas of upconing of sulfate-rich water are found throughout both districts.

The Floridan aquifer system in the SFWMD is very poorly flushed and sulfate-rich. The data given in Table 20 are somewhat biased in that no wells are represented from the southern portion of the district (Figure 34e), where sulfate concentrations are the highest.

Eh-pH relationships (Figure 31) indicate that either sulfate or sulfide can be stable in the Floridan aquifer system. Low concentrations of sulfate in much of the upper Floridan aquifer system in the center of the state indicate that sulfate reduction, sorption/precipitation reactions, and dilution reduce sulfate in comparison with the surficial aquifer system. The Eh-pH range in the deep Floridan is suitable for microbial sulfate reduction according to the criteria of Connell and Patrick (1968). Limitations of available organic carbon apparently inhibits sulfate reduction and accounts for the persistence of sulfate.

Chloride

IMPORTANCE AND CONTROLS

Chloride (Cl^-) is a conservative ion. That is, it is not reactive in most ground-water chemical systems. It does not participate in sorption, mineral precipitation, microbial metabolism, or other processes. The only processes that lower chloride concentrations in Florida ground water are dilution and dispersion. The only common circumstance in which chloride is chemically removed from an aquifer is mineral precipitation under intense evaporation, which occurs only in desert environments, not in Florida. Because it is not reactive, chloride travels at the rate of the ground water, so it is an excellent tracer of ground- water flow.

Chloride can be added to aquifer environments in three ways. The most widespread process is addition of chloride in marine aerosols that enter the ground water through rainfall. Florida precipitation averages 1.66 mg/L chloride **(Table 3)**. Mean chloride concentrations in precipitation range from 0.75 mg/L in north Florida to 2.81 mg/L in the south. Lawrence and Upchurch (1982) documented the origin of sodium and chloride in the Floridan aquifer system in an unconfined, high recharge area of north Florida as having been derived from rainfall.

Chloride is the dominant anion in sea water **(Table 8)**. Sea water averages 19,350 mg/kg (Table 8), so chloride content of water on the coastal transition zone can be quite high. Because of the water quality standard for chloride, the coastal transition zone is often defined as the 250 mg/L isochlor. While the transition zone is actually a broad belt, the position of this isochlor, which defines a surface, has incorrectly led to the concept of the transition zone as being an interface, the "salt-water interface". Connate water'4 can be a minor source of chloride. The potentiometry of the Floridan aquifer system in south Florida is insufficient to flush the Floridan aquifer system completely. As a result, connate waters remain in much of the aquifer system, where they render the water non-potable. Connate waters also occur in southern St. Johns, north-central Flagler, Brevard, and Indian River Counties. Elsewhere, minor connate waters may be present in "dead" spaces in the aquifer system. Dead spaces may include portions of the aquifer system with poor to nonexistent circulation or low permeability. Exploration of the Eocene and older strata below the lower confining beds of the Floridan aquifer system for deep-well disposal of wastes and oil and gas exploration indicates the widespread presence of connate water and brines. These high chloride waters may upwell locally into the potable portion of the Floridan if the confining sequence is inadequate or where withdrawal is too great.

Once chloride enters the aquifer systems, it is subject to several factors that can cause increases in chloride concentrations. Near the land surface, evaporation and transpiration may increase chloride content. Evaporation occurs both at the land surface, in lakes, streams, and other water bodies, and within permeable and porous aquifers. Plant roots extract moisture from the vadose, capillary, and phreatic zones, as well. The net result is that chloride content increases in near- surface environments. Comparison of Tables 3 and 21 shows that median chloride concentrations in surficial aquifer system waters range from four to over 30 times the chloride concentrations in precipitation within the respective water management districts. In the same data, the mole ratio of sodium to chloride remains relatively constant and near that of sea water (0.87 to

1.25 in precipitation; 0.71 to 1.42 in ground water), so it appears that much of this increase in chloride concentration is a result of evaporation or transpiration .

The observed increases in chloride concentration with depth can be explained by three hypotheses. One explanation is that connate water trapped in sealed pore spaces or below the sub-Floridan confining sequence is added to the aquifer system water by rock dissolution and/or opening of pore throats. Another explanation is that hydration of minerals removes water from the aquifer system, thus increasing the residual chloride content. The most plausible explanation is that the chloride is a result of incomplete flushing subsequent to the Plio-Pleistocene marine transgressions.

STANDARD OR GUIDANCE CRITERION

Chloride is associated with taste and electrolytic corrosion problems. As a result, the Secondary Drinking Water standard for chloride has been set at 250 mg/L.

DISTRIBUTION IN GROUND WATER

The distribution of chloride statewide reflects proximity to connate waters and recharge by meteoric waters. The surficial aquifer system contains waters with low median chloride concentrations **(Table 21)**. Median concentrations in the intermediate aquifer system are high, largely as a result of low permeability zones in the Hawthorn Group. Median concentration in the Floridan is low, but this reflects the bias in sampling towards potable water masses. The maximum chloride content recorded is in the Floridan and, at 20,500 mg/L, this concentration is slightly greater than average sea water (19,350 mg/kg, Table 8). Thus, the Floridan aquifer system contains the highest concentrations of chlorides.

Surficial Aquifer System

The distribution of chloride in the surficial aquifer system (Table 21) closely mirrors precipitation **(Table 3)**. Median chloride concentrations are lowest in north Florida (NWFWMD, SRWMD) where continental influences on precipitation are greatest. Peninsular Florida has highest median concentrations of chloride in both precipitation and ground water. The difference in concentration between precipitation and surficial aquifer system water can be attributed to evaporation and transpiration.

Characteristically, chloride concentrations are lowest inland (Figure 35). Monitor wells in NWFWMD and SRWMD are generally inland, so the median and maximum chloride concentrations are low. The coastal transition zone is reflected in a few wells in NWFWMD (Figure 35a).

SJRWMD data include a number of wells near the transition zone, hence the higher median concentration (Table 21). As Figure 35c indicates, coastal re-entrants with high chloride concentrations exist in Flagler and, to some degree, St. Johns Counties. A high chloride zone centered on western Brevard and Indian River Counties coincides with the upper St. Johns River and wetlands to the south. Intense evapotranspiration accompanied with possible upconing or upward transfer of water from deeper aquifer systems along fractures and through irrigation can account for this area of high chloride concentration.

The coastal transition zone and associated salt-water intrusion are well represented in the SWFWMD (Figure 35d). The high in Hardee County has been attributed by Dalton (1978) to up- ward transfer from the Floridan aquifer system by irrigation. The re-entrant along the Peace River has been attributed by G. Jones (1991) to upconing and intrusion along a major lineament.

Chloride concentrations in the Biscayne Aquifer (Table 21, Figure 35e) are generally low, with a small, intrusion-related re-entrant in the Miami (Dade County) area. Chloride concentrations in the northern part of the district are also generally low, but irrigation with deeper, more saline waters has resulted in a few high chloride zones. Data from the SFWMD indicate an increase in chloride toward the Everglades, which reflects the presence of connate water and upconing of poorer quality water from underlying aquifer systems. Reduced permeability of the surficial aquifer system has prevented thorough flushing of connate water beneath the Everglades. In addition, drainage of wetlands for agriculture has significantly lowered the water table and induced upconing.

Intermediate Aquifer System

Median chloride concentrations in the intermediate aquifer system show the same pattern as in the surficial aquifer system (Table 21). Chloride concentrations are low in the continental-climate-dominated northern part of the state and high in the more maritime climate of the south.

The intermediate aquifer system, which includes the Hawthorn Group, contains significant clay deposits (Scott, 1988), which have high porosity and low permeability. These clays apparently contain some connate water. As a result, one would intuitively expect that chloride concentrations would be somewhat more variable and the median would be higher than surficial aquifer system waters. This pattern is supported by data from the Background Network (Table 21). The medians and ranges of chloride in the surficial and intermediate aquifer systems are generally not significantly different in the northern part of the state. However, the central and southern portions, where the Hawthorn is thick, are characterized by high chloride concentrations. One should not be surprised, therefore, if somewhat elevated chloride concentrations are encountered in the intermediate aquifer system inland.

Distributions of chloride in the intermediate aquifer system in NWFWMD, SRWMD, and SJRWMD (Figure 36a-c) reflect evaporative concentration. There is considerable local variability, and increases toward the coast can be seen. The causes of the local variability cannot be identified from the data set, but interaquifer transfer through irrigation is likely.

The coastal transition zone is well documented in SWFWMD (Figure 36d). Local re-entrants reflect salt-water intrusion due to pumpage and lowering of potentials by other medians. The large re-entrant along the Peace River axis is also well documented.

The transition zone appears as a broad surface with a relatively shallow dip in the SFWMD (Figure 36e). Highs in northern Collier and eastern Lee Counties are a result of upconing caused by natural upward discharge and by pumpage.

Floridan Aquifer System

With the exception of the data from SFWMD, the Floridan aquifer system is similar in chloride distribution to the other aquifer systems of the state (Table 21). Chloride concentrations are generally low in shallow wells, inland, and in recharge areas. They are highest near the coast, in deeper wells, and in areas of pumpage-induced intrusion .

The transition zone is well defined in the NWFWMD (Figure 37a). Areas of intrusion include Escambia County, southern Walton County, southern Bay County, and isolated spots in Franklin and Wakulla Counties. All of the re-entrants west of the Apalachicola River are associated with well fields and pumpage. The isolated highs in Franklin and Wakulla Counties are near small communities and a large spring complex, both of which can lead to intrusion. The transition zone is relatively narrow in most of the SRWMD (Figure 37b). Re-entrants exist along some coastal rivers (Steinhatchee, Aucilla, Waccasassa), and re-entrants in Taylor and Dixie Counties can be attributed to pumpage associated with small towns and industry. Inland highs include an upconing at the Ichetucknee Springs group (the high at the Suwannee-Columbia County boundary and the Santa Fe River).

The data from SJRWMD (Figure 37c) illustrate the coastal transition zone, with a re-entrant in Volusia County. Other high chloride areas in St. Johns and central Flagler Counties; along the St. Johns River in Putnam, Volusia, and Seminole Counties; and in Brevard and Indian River Counties are thought to be connate water (Stringfield, 1966; Boniol, 1981, pers. com.). The re-entrant that extends from the coast in St. Johns County, through Putnam County, and into Marion County is probably due to upconing.

Comparison of the potentiometric map of the

Floridan aquifer system (Figures 35 and 36 in Scott et al., 1991) with chloride data from SWFWMD (Figure 37d) and SFWMD (Figure 37e) clearly illustrates the effects of poor flushing and intrusion where the hydraulic potentials are low15. The southern third of SWFWMD and the southern two thirds of SFWMD have lower potentials. As a result, chloride content of the aquifer system is higher and the transition zone is broader and flatter. In the central and northern thirds of SWFWMD, hydraulic potentials are high, chloride concentrations are low, and the transition zone is steep and narrow. Scattered areas with chloride concentrations in excess of 10 mg/L in the northern third of the SWFWMD reflect somewhat deeper wells. In general, this area is characterized by recharge, and chloride contents are near those of precipitation.

Phosphate

IMPORTANCE AND CONTROLS

Phosphate, as reported here, is ortho- phosphate ($P0_4^{3-}$). Phosphate is of concern because it is an essential nutrient of all living things. Because is it an essential nutrient, excess phosphate can cause run-away plant growth and eutrophicationl6 of surface waters. Therefore, control of phosphate in surface water has been a national priority since the late 1960's. Control was established as a priority of the Federal Water Pollution Control Administration, and its successor the U.S. Environmental Protection Agency, because it was felt that phosphate was the limiting nutrient'7 in most waters of the nation. It is questionable whether phosphate is a limiting nutrient in surface water in many areas of the state due to the abundance of apatite-group minerals in late Tertiary and Quaternary sediments.

The most important sources of phosphate in Florida are the phosphate-bearing sediments found throughout the Hawthorn Group. Two apatite group minerals predominate in the phosphatic sediments: carbonate-fluorapatite [$Ca_5(P0_4,C0_3)_3F$, or"francolite"16] and carbonate-hydroxylapatite [$Ca_5(P0_4,C0_3)3(0H)$, or "dahlite"].

Weathering of both minerals introduces phosphate into ground and surface waters (Lawrence and Upchurch, 1982). The widespread occurrence of these phosphate minerals (see the discussion of the distribution of the Hawthorn Group in Scott [1988]) suggests that phosphate is locally, naturally available throughout much of the state.

Carbonate-fluorapatite is the primary phosphate mineral in the Hawthorn Group. It was precipitated from the Miocene sea throughout the eastern and southern sides of the Ocala Platform. Subsequent erosion of the Hawthorn on the crest of the Ocala Platform and elsewhere, led to transport of dissolved and particulate phosphate into contemporary sediments, where the phosphate accumulated as extremely rich ore deposits. These deposits are mined in central Florida (Polk, Hillsborough, Hardee, DeSoto, and Manatee Counties) and in north Florida (Hamilton County). Ore-quality deposits occur at depth in St. Johns and Brevard Counties and other areas. The deposits that contain these phosphate-rich horizons constitute portions of the intermediate aquifer system. Carbonate-fluorapatite was also reworked during subsequent marine transgressions and regressions into younger, Quaternary deposits that constitute the surficial aquifer system.

Carbonate-fluorapatite is a source of several other environmentally important constituents in Florida ground water. Carbonate-fluorapatite is the primary source of fluoride in the aquifer systems (see Fluoride below). Carbonate- fluorapatite also contains trace quantities of uranium (Cathcart, 1956; Altschuler et a/., 1958). The uranium undergoes a series of decay events that result in radium, radon, and polonium, all of which have been shown to be problems in Florida's aquifer systems (e.g., Kaufmann and Bliss, 1977; Cowart *et al*., 1978; Burnett *et al.*, 1988; Upchurch *et al*., 1991).

Carbonate-hydroxylapatite is a result of re- precipitation of phosphate following weathering of carbonate-fluorapatite. The phosphate ion (PO_4^{3-}) is soluble in acidic waters, such as occur in siliciclastic horizons of the surficial aquifer system. The ion is insoluble in alkaline aquifers, such as occur in the Floridan aquifer system. The reactions are as follows. In the acidic surficial and intermediate aquifer system waters, carbonate-fluorapatite is dissolved according to

$$Ca_5\,(PO_4,\,C0_3)_3F_{solid} + 7.5H^+ \rightarrow 5Ca^{2+}{}_{aq}.+ + 1\ .5H_3PO_{4aq.} + 1.5H_2C0_{3aq.} + F^-, \quad (13)$$

where the phosphate and carbonate are written as phosphoric and carbonic acids for simplicity and phosphate and carbonate are present in equal mole proportions in the apatite. Upon encountering an alkaline environment, the phosphoric and carbonic acids are neutralized and carbonate- hydroxylapatite precipitates according to

$$5C^{2+}{}_{aq.} + 1.5H_3P0_4 + 1.5H_2CO_{3aq.} + H_20 \rightarrow Ca_5\,(PO_4,\,CO_3)_3\,(OH)_{solid} + 8.5H^+. \quad (14)$$

The hydrogen released by the precipitation reaction is consumed by alkalinity and/or dissolution of calcite (reaction 3). If it is consumed by dissolution of calcite, carbonate-hydroxylapatite is likely to replace limestone.

The crest of the Ocala Platform was stripped of Hawthorn sediments in Late Miocene, Pliocene, and Quaternary times. While most of the weathering products of this erosion were swept into adjacent rivers, estuaries, and the sea, some of the dissolved phosphate (H3P04in reaction 13) migrated downward into the underlying Floridan aquifer system. Upon contact with the limestones of the Floridan, phosphate precipitated according to reaction 14. Upchurch and Lawrence (1984) document an area in Columbia County where this process is taking place today.

Deposition of carbonate-hydroxylapatite in significant ore bodies occurred in a belt along the eastern flank of the Brooksville Ridge (Hernando, Citrus, Marion, Levy Counties) and elsewhere. The deposits are commonly preserved in paleosinkholes, where the carbonate-hydroxylapatite lines the sinkholes and partially replaces the adjacent limestone. Economically important deposits are termed "hard-rock" phosphate. Hard- rock phosphate was mined in Citrus, Gilchrist, Marion, and Levy Counties from the 1890's to the mid-1960's. The process of carbonate- hydroxylapatite precipitation continues today in the Floridan aquifer system, and dissolution of the resulting hard-rock deposits may constitute an additional source of phosphate in ground water.

Marine aerosols constitute a small, but significant, source of phosphate. Based on an average chloride concentration of 1.66 mg/L in precipitation **(Table 3)**, and chloride and phosphate concentrations in sea water of 19,350 mg/kg and 0.05 mg/L (50 µg/kg, Table 8), respectively, the concentration of phosphate in precipitation should be 1.6 µg/ml. Measurements of phosphate in precipitation (Table 3) average 0.03 mg/L statewide, and suggest that the atmosphere is enriched four orders of magnitude over the predicted aerosol concentrations. This is partly because the monolayer of sea water at the atmosphere/water contact (the source of aerosols) is enriched in phosphate, and partly a result of organics and particulates in the atmosphere. At any rate, precipitation is an important source of phosphate for plants. The concentration of phosphate in precipitation is similar to that in the surficial aquifer system.

Other sources of phosphate include inorganic and organic fertilizers, organic tissues, animal wastes, human waste effluent, and industrial effluent. Phosphate is an abundant constituent of household waste. In the areas of the state represented in the Background Network, this waste is usually released to the environment by means of on-site treatment systems (septic-tanks) and small, land-application treatment facilities. Should such systems fail to properly function, phosphate may enter the aquifer system. Since septic-tank systems, fertilizer use, and animal wastes are com-

mon in rural areas, especially in agricultural areas, phosphate is a likely constituent in near-surface aquifers in the Background Network. Phosphate is removed from ground water by several processes. In carbonate-rich aquifers, the removal is by precipitation of carbonate-hydroxylapatite (reaction 14). This reaction is effective as a mechanism for orthophosphate precipitation, and alkaline waters seldom have detectable phosphate as a result. Should phosphate be detected in ground water, it is safe to conclude that (1) the phosphate has not yet encountered sufficient alkalinity to cause precipitation (a common phenomenon in karst conduits and siliciclastic aquifer horizons) or (2) the phosphate is either complexed with a metal or present as some form other than aqueous orthophosphate.

Phosphate is strongly adsorbed by ferric hydroxides and certain other colloids in soils and aquifers. This sorption is an important mechanism for phosphate removal from ground water, especially where on-site and land-application sewage treatment release phosphate to the environment. Childs et al. (1974) documented orthophosphate sorption reactions on ferric hydroxide-coated sand grains and on clays below the water table in a siliciclastic aquifer. They showed that phosphate fixation in septic-tank drain fields is very nearly quantitative, with concentration factors on the host soils in excess of 1000 times. Rea and Upchurch (1980) studied orthophosphate fixation on a ferric hydroxide- coated fine sand in the surficial aquifer system. They found that minor amounts of ferric hydroxide (< 3 weight percent) removed large quantities of phosphate.

STANDARD OR GUIDANCE CRITERION

There is no standard or criterion for phosphate in ground water (Florida Department of Environmental Regulation, 1989). The U.S. Environmental Protection Agency and the state both have standards for total phosphorus in surface waters. These standards vary with classification of the surface water body. The use of a standard for surface water, but not for ground water, is a result of recognition of natural sources of phosphorus in ground water and the importance of phosphorus as a limiting nutrient in surface water.

DISTRIBUTION IN GROUND WATER

The districts measured phosphate in several ways **(Table 22)**. SRWMD measured ortho- phosphate in unfiltered samples. NWFWMD and SJRWMD measured total phosphorus, which includes minor amounts of condensed and organic phosphorus, as well as orthophosphate. SWFWMD analyzed for total phosphate (ortho- phosphate, condensed phosphates, and other phosphate compounds), and SFWMD measured dissolved (filtered) orthophosphate. Differences in these measurements are not considered significant.

The distribution of orthophosphate in Florida ground waters is summarized in Table 22. In general, median phosphate concentrations follow chemical controls rather than the distribution of sources. That is, highest median and maximum concentrations are in the surficial aquifer system, where the water is acidic and reaction 13 predominates. Water from the intermediate aquifer system, which contains the majority of the phosphate mineralization, contains less phosphate because of buffering with alkalinity derived from the associated carbonates (reaction 14). Water from the Floridan aquifer system is characteristically low in phosphate due to the relatively high alkalinities.

Surficial Aquifer System

Phosphate in the surficial aquifer system can come from several sources, including natural weathering of phosphate minerals reworked into the aquifer sediments from the underlying Hawthorn Group, leaching of natural phosphates from organic sediments and decomposing plant materials, use of agricultural fertilizers, and septic tank systems and other waste-disposal practices. The widespread occurrence of phosphate in the surficial aquifer system suggests that geologic conditions produce a strong "overprint" on the aquifer system and that local sources (swamps, human activities) build on that background overprint. Because the human sources are local, they cannot be identified on the maps, and the main thrust of the following discussion is the geologic overprint.

Statewide, the median orthophosphate concentration is 0.06 mg/L and the maximum recorded is 4.00 mg/L (Table 22). Maxima are generally lower, however, and indicate that phosphate mobility is not a widespread problem in the state.

Phosphate concentrations are highly variable and generally low in NWFWMD and SRWMD (Figure 38a,b). Higher concentrations are found in siliciclastic portions of the aquifer system where pH's are low. The sources of the phosphate range from natural apatite reworked into aquifer sediments, especially in eastern SRWMD, to animal and human wastes and fertilizers. In SJRWMD (Figure 38c) the phosphatic portion of the Hawthorn Group, especially in St. Johns County, is accompanied by higher phosphate concentrations in ground water.

The data from SWFWMD (Figure 38d) indicate a region of moderately high phosphate concentrations (>0.5 mg/L) in southern Polk and Hardee Counties, where phosphate mining of the underlying Hawthorn Group is underway. There is also a belt of moderate phosphate concentrations (>0.1 mg/L) that parallels the coast and reflects the inner margin of the transition zone.

The Biscayne Aquifer (Table 22; Figure 38e) is generally low in phosphate due to the absence of phosphate-bearing minerals (apatite) and to the high alkalinity of the water. Where present, phosphate can be attributed to land uses. In western SFWMD (Figure 38e), the Hawthorn is present near land surface, and phosphatic rock has been reworked into the surficial aquifer system sediments. This reworked phosphate is accompanied by organics, which may also be a source of phosphorus.

Intermediate Aquifer System

The distribution of phosphate in waters of the intermediate aquifer system is variable (Figure 39). Phosphate tends to be below detection limits in carbonate-rich portions of the system. In siliciclastic horizons the phosphate ranges up to 2.28 mg/L (Table 22). It is not possible to discern large patterns in the distribution maps due to the localized nature of dissolution/precipitation reactions and the sparsity of data.

Floridan Aquifer System

Phosphate concentrations should be at or below detection limits in the Floridan aquifer system due to high water alkalinity. As Table 22 indicates, median concentrations are near detection limits, and they are generally low. The sample from the SRWMD that has 21.00 mg/L is suspect. The value is either an incorrect chemical analysis or the sample, which is unfiltered, contained particulate apatite. The median concentration in the Floridan aquifer system is 0.04 mg/L.

Maximum phosphate concentrations in the Floridan aquifer system are somewhat higher than expected (Table 22). This is an artifact of the "plumbing" of the karstic and fractured aquifer system. Dissolved phosphate requires alkaline waters in order to precipitate. In recharge areas, much of the water moves in conduits (fractures or caverns) under laminar flow conditions. Under these conditions, equilibration is slow and phosphate can persist for some distance within the Floridan aquifer system. Lawrence and Upchurch (1976) illustrated an example of dissolved phosphate persistence in cavernous flow near Lake City, Columbia County. There, phosphate enters the Floridan through karst features. Upon recharge, the dissolved phosphate persists as a well organized "plume" for several kilometers with minimal dilution, dispersion, or precipitation.

The pattern of dissolved phosphate in the Floridan aquifer system in the NWFWMD (Figure 40a) shows several regions of modest phosphate concentrations. Phosphate is elevated along the inner transition zone in Okaloosa and Gulf Counties. Phosphate is also slightly elevated in a broad belt that originates near the coast in Franklin and Wakulla Counties and extends westward, through the center of the district, into Okaloosa County. This belt roughly coincides with the Beacon Slope, New Hope Ridge, and southern Western Highlands, and with the edge of the Hawthorn Group and equivalent units to the west (Scott et al., 1991). Lawrence and Upchurch (1976, 1982) and Upchurch and Lawrence (1984)

have shown that phosphate is introduced with recharge in a similar context to the east, in the SRWMD. An area of low phosphate concentrations occurs along the northern boundary of the district. This region includes recharge areas where confinement is limited and flow along karst conduits occurs. All of the data from the NWFWMD are near the detection limit (0.04 mg/L).

A similar pattern is present in the SRWMD (Figure 40b), where a center of high phosphate concentrations occurs in southern Columbia and Union Counties. This center is situated on the Cody Escarpment, which is characterized by large sinkholes and sinkhole lakes that drain into the Floridan aquifer system. It is within this center that Lawrence and Upchurch (1976, 1982) and Upchurch and Lawrence (1984) documented recharge of phosphate-rich, intermediate and surficial aquifer system water, and surface water, into the Floridan. Their studies show that high phosphate waters in the Floridan aquifer system represent local recharge and conduit flow. A similar high occurs in southeastern Madison County. Highs in Levy and Gilchrist Counties are on the flanks of the Brooksville Ridge and of Bell Ridge. Both represent similar situations to the Cody Escarpment. It is interesting to note that there is high phosphate in the Floridan aquifer system along the coast in Levy and Dixie Counties. The concentrations reported here are too high for sea water **(Table 8)**, and most probably reflect the influence of organic-rich surface water from the coastal swamps.

Phosphate concentrations in the Floridan aquifer system in the SJRWMD are generally near detection limits (Figure 40c). Highs exist in north- western Volusia and in Flagler Counties. The Flagler County high is apparently related to withdrawals near Bunnell, an area characterized by extensive fern cultivation. This higher phosphate water is probably a result of induced recharge from the overlying intermediate aquifer system. The Volusia County high is less easily explained. It is associated with a minor recharge area (Figure 74, Scott et al., 1991) and may reflect downward movement of intermediate aquifer system water as well.

Phosphate in the Floridan aquifer system in the SWFWMD (Figure 40d) is associated with local recharge through the Hawthorn Group. The belt that extends from southeast to northwest in Sumter and Citrus Counties cannot be readily explained. This belt is in roughly the same area as the hard-rock phosphate district, but the belt of high phosphate and the mining district do not coincide. Additional work is needed to explain this distribution. Many of the local highs in Hillsborough County coincide with karst terrains (Upchurch and Littlefield, 1988) that are urbanized or agricultural in use. These phosphate concentration highs, therefore, may reflect the influences of local use of on-site waste treatment, animal wastes, and/or crop and lawn fertilization. The re- entrant that extends up the Hillsborough River reflects an unconfined part of the aquifer system that is immediately overlain by swamps and moderate cultural development.

Phosphate is generally low in the Floridan aquifer system in SFWMD (Figure 40e). The Floridan is confined by the Hawthorn Group, and there appears to be little recharge to the Floridan aquifer system. Upward hydraulic potentials and the high alkalinities of the Floridan aquifer system also result in precipitation of any significant phosphate introduced to the aquifer system.

Fluoride

IMPORTANCE AND CONTROLS

Like chloride, fluoride (F^-) is a halogen anion. It is somewhat more reactive than chloride, and it forms dissolved chemical complexes. These complexes remain soluble in Florida ground water, so fluoride essentially behaves as a conservative ion.

Marine aerosols can contribute small amounts of fluoride to ground water. Assuming that the concentration of chloride in precipitation is 1.66 mg/L **(Table 3)** and that the ratio of fluoride to chloride is constant in sea water (Table 8) and in marine aerosols, precipitation should contain approximately 0.00022 mg/L F^-, which is three orders of magnitude less than median concentrations in Florida's aquifer systems **(Table 23)**.

Most of the fluoride in Florida ground water is derived from weathering of carbonate-fluorapatite in the Hawthorn Group (reaction 13). Consequently, the presence of fluoride is an excellent indicator of waters that have come in contact with the Hawthorn Group at some time in the past.

Cook et al. (1985) described fluorite (CaF_2) in gypsum nodules at the base of the Floridan aquifer system (Eocene Avon Park Formation) in Hernando County. The surrounding water was found to be undersaturated with respect to gypsum and fluorite, so dissolution of fluorite at the base of the aquifer system may constitute a second source of fluoride for the deep flow system. To date, only one core has been found to contain fluorite, so it is uncertain as to whether the fluorite constitutes a major source of fluoride.

Intrusion of sea water can also be a minor source of fluoride (Table 8). With the exception of the coastal transition zone, sea water is an unimportant source.

The Florida phosphate industry is one of the nation's most important producers of fluoride and fluorine products. The fluoride is extracted from the carbonate-fluorapatite as hydrofluoric acid (HF). Some of this fluoride is lost to ground water near the phosphochemical plants, where it may present a problem. Upchurch *et al.* (1982) characterized the effects of fluoride-rich effluent that had been introduced from a phosphochemical plant into sea water in Tampa Bay. The minerals fluorite (CaF_2) and pachnolite ($NaCaAlF_6.H_20$) were found precipitated in a delta at the outfall. Similar processes may be occurring in calcium- and sodium-rich ground water near other agrichemical plants. At the present time, there is little evidence that this process is wide- spread or important.

There is little indication that any natural process is responsible for actively removing fluoride from ground water in Florida. Most of the reduction in concentration is a result of dilution and dispersion.

STANDARD OR GUIDANCE CRITERION

In small amounts (< 1 mg/L), fluoride is considered beneficial as a preventative for dental caries. The fluoride reacts with the apatite in teeth to form a fluorapatite that is resistant to cavity- causing microbes. In excess of 2 mg/L, fluoride begins to cause unsightly darkening and mottling of the teeth, a condition termed dental fluorosis. Severe mottling requires concentrations in excess of 12-14 mg/L. Extreme doses can induce toxicity, including excess calcification of bones, stiffness, and, under some circumstances, death.

Standards for fluoride have been set to control toxicity and fluorosis. The Primary Drinking Water Standard, which addresses toxicity, is 4 mg/L. The Secondary Drinking Water Standard, which addresses fluorosis, is 2 mg/L.

Due to weathering of carbonate-fluorapatite in the Hawthorn Group, fluoride is widespread in Florida's aquifer systems. Concentrations that exceed the Drinking Water Standards are occasionally found, especially in the SWFWMD and SFWMD (Table 23). Statewide, only 0.1 percent of the samples in the surficial aquifer system exceeded the Primary Drinking Water Standard. Four tenths of a percent of the samples from the intermediate aquifer system exceeded the standard, and 0.1 percent exceeded it in the Floridan aquifer sample set.

In most areas of the state, ground water does not contain concentrations sufficient to serve as a preventative for caries, so many public water supplies have opted to augment natural fluoride for the sake of public health.

DISTRIBUTION IN GROUND WATER

The median concentrations of fluoride in the aquifer systems (Table 23) reflect the source. Fluoride is lowest in the surficial aquifer system, with a median of 0.17 mg/L. The intermediate and Floridan aquifer systems contain median concentrations of 0.39 and 0.20 mg/L respectively. The intermediate aquifer system is highest in fluoride

concentration because the source carbonate-fluorapatite is present in the aquifer system. Concentrations are somewhat lower in the Floridan because of dilution and dispersion of waters that have passed through the Hawthorn sediments, and because the data set includes waters that have not come in contact with these sediments.

Surficial Aquifer System

As **Table 23** indicates, fluoride concentrations in the surficial aquifer system are generally lower than in the other two aquifer systems. The low concentrations are a result of limitations on the sources of fluoride. While the relative importances of the following sources have not been quantified, the data presented in this report clearly indicate that some of the fluoride is from precipitation, with the concentrations enhanced by evapo-transpiration. Most of the fluoride in the surficial aquifer system, however, is derived either from weathering of reworked carbonate-fluorapatite or from deeper waters that are introduced to the aquifer system by natural discharge and by pumpage (Dalton, 1978).

The pattern of fluoride in the surficial aquifer system in north Florida (Figure 41 a,b) is characteristic of a local flow-system aquifer. Data are variable, and concentrations are generally low.

The data from SJRWMD (Figure 41c) suggest a coastal source of fluoride. High fluoride occurs in the transition zone in Nassau and Duval Counties, and in St. Johns County. These highs coincide with regions of well-field development. The plume of dissolved phosphate that crosses Flagler County into northwestern Volusia County (Figure 38) is also represented in the fluoride data. This suggests that the chemistry of the plume is somehow influenced by the weathering of carbonate-fluorapatites in the Hawthorn Group.

Two regions of high fluoride can be seen in SWFWMD (Figure 41d). One is in central and southern Polk County, a phosphate mining area. High fluoride probably occurs in this area because it is associated with waters derived from within the phosphatic deposits, not because of mining. The Hawthorn Group, especially the Bone Valley Member of the Peace River Formation, in central and southern Polk County is characterized by enriched deposits of carbonate-fluorapatite. Some of this apatite has been reworked into the surficial aquifer system here, and the uppermost part of the Bone Valley Member is in direct hydraulic connection with the sands of the surficial aquifer system. Thus, this region of high fluoride directly reflects mineralization and hydraulics of the aquifer system. The coastal high fluoride zones in Hillsborough County and in the southwestern part of the district reflect the transition zone. The outer part of the transition zone is directly influenced by sea water, the inner part reflects fluoride-rich waters upwelling after following long, deep flow paths and mixing with the sea water.

Fluoride is somewhat high in coastal areas in the surficial aquifer system in SFWMD (Figure 41e). The coastal parts of the Biscayne Aquifer contain over 0.2 mg/L, as do coastal parts of the aquifer system in Lee and northern Charlotte Counties. Fluoride is low in the central part of the district.

Intermediate Aquifer System

Given that the intermediate aquifer system in the eastern panhandle and the peninsula generally coincides with the phosphatic Hawthorn Group, one would expect that fluoride concentrations would be high compared to the other aquifer systems. This is the case (Table 23), but concentration differences are not significant. Fluoride is highest in SWFWMD and SFWMD, where the intermediate aquifer system is thick and used as a potable water source.

Data from NWFWMD, SRWMD, and SJRWMD (Figure 42a-c) show similar patterns to other analytes. The concentrations range from below detection limits to maximum of 1.75 mg/L. The data do not reveal systematic patterns because of the complex, local nature of production zones.

High fluoride concentrations are evident in SWFWMD and northwest SFWMD (Figure 42d,e) near the coastal transition zone. Note especially the well-defined re-entrant along the Peace River lineament (Figure 42d).

Floridan Aquifer System

While there are no known significant sources of fluoride in the Floridan aquifer system, water that has passed through the Hawthorn Group contains fluoride (Lawrence and Upchurch, 1982), as does water in the coastal transition zone. The median concentration in the Floridan aquifer system is 0.2 mg/L (Table 23). The maximum concentration found was 6.9 mg/L in the NWFWMD. The location of this high is near the coast in Gulf County. The concentration is higher than expected for sea water **(Table 8)**.

The distribution of fluoride in NWFWMD (Figure 43a) shows a strong coastward gradient. A large re-entrant in Gulf and Bay Counties can be attributed to pumpage and discharge along the Apalachicola River. To the east, the pattern in Wakulla and Liberty, and Franklin Counties is irregular, probably in response to local flow systems associated with the extensive conduit flow system there.

High fluoride concentrations occur along the erosional margin of the Hawthorn Group at the Cody Escarpment and in the Northern Highlands in the SRWMD (Figure 43b). These reflect recharge of intermediate and surficial aquifer system waters in the large sinkhole complexes that characterize the escarpment. Other areas of elevated fluoride concentration exist in Hamilton County. The eastern area is near a phosphate-mining and agri-chemical complex. The western one is associated with the recharge of intermediate aquifer system waters near the Alapaha River (Ceryak, 1977). High fluoride concentrations in Taylor and Lafayette Counties appear to be associated with the San Pedro clays which overlie the partly confined Floridan aquifer system. Coastal transition zone fluoride is also evident.

Fluoride concentrations are generally low in the Floridan aquifer system in SJRWMD (Figure 43c). High concentrations exist in Flagler and Volusia Counties. There are minor indications of the coastal transition zone. Since most of the coastal communities in Flagler County utilize the intermediate aquifer system, the transition zone in the Floridan is not well represented.

The Floridan aquifer system in SWFWMD can be divided into domains based on fluoride (Figure 43d). The northern half of the District contains low fluoride concentrations. This region is unconfined and there is little, or no, Hawthorn to act as a source. The coastal transition zone is well developed in this area. The southern half of the map clearly indicates that fluoride, derived from waters passing through the Hawthorn, slowly increases in concentration along the flow paths. With the exception of the re-entrant along the Hillsborough River, the 0.2 mg/L isoline closely approximates the northern edge of the Hawthorn Group. Fluoride uniformly increases to the south and west from this isoline. The coastal transition zone is delineated by a steepened gradient near the coast and by a re-entrant along the Peace River lineament.

Little can be said about fluoride in SFWMD (Figure 43e). There are indications that fluoride content increases to the south, into the non-potable portions of the aquifer system where connate water predominates. There is a high in Lee County, where pumpage and free-flowing wells induce upconing of deeper waters along the transition zone.

Nitrate

IMPORTANCE AND CONTROLS

Nitrate ($N0_3^-$) is one member of a sequence of related nitrogen compounds that includes nitrogen gas (N_2), nitrogen dioxide gas ($N0_2$) and other oxides, ammonia and ammonium (NH_3, NH_4^+), nitrite ($N0_2$), a number of other inorganic compounds, and many organics. The gaseous phases exist in the atmosphere and in soil atmospheres, but are not of importance in the saturated zones of aquifers. Ammonia gas also escapes into the atmosphere. Ammonia is present in ground water as the ammonium ion (NH_4^+) because of prevalent pH and reduction-oxidation potentials. The complex organic compounds can occur as soluble

organic molecules and as particulates. Concentrations of dissolved, organic- nitrogen compounds, including amino acids and proteins, are reported as Total Kjeldahl Nitrogen (TKN) in samples from aqueous systems and soils.

Organic nitrogen, ammonium, nitrite, and nitrate are the compounds considered important in ground-water systems. These compounds are related through a sequence of reduction and oxidation reactions as indicated below

Organic Nitrogen (TKN)

$NH_4^- \rightarrow NO_2^- \rightarrow NO_3^-$ (1 5)

----Oxidation--→

←-- Reduction --

with oxidation being the normal sequence in ground-water systems. The reduction/oxidation transformations between the compounds indicated in reaction 15 can be driven by inorganic processes, but the primary mechanisms for the reactions are microbial.

The largest reservoir of nitrogen is the atmosphere, which is 78.93 percent nitrogen, mostly as N_2 gas. NH_3 and $N0_3^-$ occur naturally in the atmosphere as a result of releases by terrestrial plants (Stallard and Edmond, 1981). Atmospheric nitrogen is also converted to NO_x[19] by lightning. Modern precipitation contains increased nitrogen oxides as a result of combustion of fossil and modern organic fuels. The oxides of nitrogen are then converted by oxidation and hydrolysis to nitric acid (HNO_3), which dissociates to H^+ and NO_3^-. Consequently, precipitation is a source of nitrate and ammonium derived from both natural and anthropogenic causes. Nitrate in precipitation in Florida ranges from 0.00 to 10.32 mg/L (Table 3), and the statewide mean is 0.97 mg/L. Ammonium ion ranges from 0.00 to 17.12 **(Table 3)** and the mean is 0.17 mg/L.

Clearly, conversion of nitrogen compounds in the atmosphere followed by precipitation introduces nitrogen to the ground-water system. Modern rainfall, however, cannot be used as an argument for high nitrogen in most aquifers. This is because of the long time intervals involved in ground-water flow. Waters in surficial environments, including the surficial aquifer system and shallow, unconfined portions of the Floridan aquifer system, may be affected by high-nitrogen precipitation. Deeper waters were recharged as meteoric waters before the advent of the industrial revolution. These older waters entered the aquifer system with some natural nitrogen content, but at much lower concentrations than the present.

Certain microbes can fix nitrogen gas in soils. These microbes, in conjunction with plants such as the legumes, directly convert nitrogen into tissues and nitrogenous by-products. Plants require nitrate as a major nutrient, and they are responsible for removal of much of the nitrate that is taken from soils and ground water. Average nitrogen content of living organisms is 16 percent. These living tissues contain amino acids and other nitrogen compounds that can be released back into the environment upon death or waste elimination.

Animal wastes and decaying plant tissues release ammonia and ammonium, nitrite, nitrate, urea20, and a number of nitrogenous organic molecules. Soil and aquifer microbes metabolize these according to the reduction-oxidation potential (reaction 15) of the soils and aquifers. Under reducing conditions, microbes convert these compounds to ammonium, and other reduced nitrogen species. Under oxidizing conditions, they are converted to nitrate, often with an intermediate nitrite step.

Therefore, in reducing environments, such as water-saturated, reducing soils and aquifers, ammonium may persist and become a part of the ground-water system. Under these circumstances, ammonium can travel considerable distances before sorption, microbe metabolism, dilution, or dispersion reduce concentrations to below detection limits. Ammonium tends to sorb onto clays and soil particles, so some soil and aquifer materials mitigate ammonium migration. Septic-tank systems, land-application waste- treatment systems, and feed-lot wastes can, under circumstances of overloading or failure of sorption systems, cause widespread ammonium contamination.

Oxidizing conditions are necessary for microbes to produce the complex reactions required to make the nitrogen useable for plants. These aerobic microbes convert the ammonium and complex organic nitrogen molecules to nitrite and then nitrate. Ammonium and organic-nitrogen compound concentrations are low in most aquifers because oxidizing conditions are widespread near the land surface, where these nitrogen compounds are generated. Oxidizing conditions occur in oxygenated soils, vadose environments and shallow, oxygenated portions of aquifers.

If nitrates are available in small amounts near the land surface, plants will utilize the nitrates. There are also microbes that denitrify soils by conversion of nitrate to nitrogen gas. If nitrate production from ammonium and more complex nitrogen compounds is not completed within the root zone, if the nitrate is unavailable to plants and denitrifying microbes, or if nitrate is produced in quantities too great for biological agents to fix, nitrate migrates with the ground water. With the exception of plant and microbial activity, there are few mechanisms for nitrate removal in aquifers. Once nitrate enters the aquifer and is isolated from environments where denitrification and plant fixation occur, nitrate behaves more-or-less conservatively and can move long distances in aquifers.

Ideal, land-based, waste-disposal practices include sufficient vadose zone and biomass to convert nitrogen compounds to nitrate and then to utilize the nitrate. Unfortunately, high water tables, plugging of soils by particulate matter, underdesign of treatment facilities, crowding of waste-disposal facilities or animals on too small a tract of land, and many other factors tend to lead to failures of natural nitrogen-removal mechanisms. Under such circumstances, nitrate, ammonium, and other nitrogen compounds may enter the ground-water system and travel long distances.

Swamps and organic horizons in soils can contribute natural ammonium and/or nitrates to aquifers. Under most circumstances, however, decay of the organics is sufficiently slow that the nitrogen compounds are utilized within the wetland and adjacent aquifers. High nitrate and ammonium concentrations in aquifers are more likely to be caused by inadequate soil and aquifer conditions and contamination by human or animal wastes.

For microbial decomposition of nitrogenous compounds to occur, there must be a source of organic carbon, and other nutrients. The role of nitrogen-utilizing microbes in deep aquifers has not been adequately evaluated. It appears that microbial transformations analogous to sulfate reduction may occur. Availability of organic carbon and nitrogen compounds is limited in deeper portions of the Floridan aquifer system, so nitrogen-utilizing microbes are probably ineffective in the same way as are sulfate-reducing microbes. Our present concepts suggest that the majority of nitrogen fixation occurs in shallow, oxidizing aquifers and soils.

The presence of nitrate, and the other nitrogenous compounds in ground water, is not considered in Florida to be a result of interaction of aquifer system water with surrounding rock materials. Nitrate in ground water is a result of specific land uses. If the land use is widespread, a body of nitrate-enriched water that is large enough to be contoured may result. Otherwise, detection of nitrate is an isolated phenomenon.

Nitrate contamination of ground water is of concern in Florida. Numerous areas of the state have reported nitrate problems. These are associated with areas of intense agriculture use and suburban housing. Some of the areas where nitrates are of concern include dairies and cattle ranches in the Suwannee and the Kissimmee River valleys, crop lands in the northern Everglades, and suburbs served by on-site waste treatment (septic tanks) throughout the state.

Finally, Barcelona (1984) has pointed out that drilling fluids can serve as sources of organic carbon and nitrogen compounds. Care should be taken to validate any high nitrate concentrations reported below, especially if the data come from

newly drilled wells.

STANDARD OR GUIDANCE CRITERION

The only compound for which there is a standard or guidance criterion in ground water is nitrate. Nitrate is subject to the Primary Drinking Water Standard (Florida Department of Environmental Regulation, 1989). The limit under the Primary standard is 10 mg/L as N, or 44 mg/L as $N0_3^-$. There is a health advisory for nitrate at 1 mg N/L (4.4 mg NO_3^-/L), as well. The major cause of concern is methemoglobinemia, an excess of methemoglobin[21], which causes oxygen deprivation. This condition is especially hazardous in infants and young children, where it produces a condition known as "blue baby syndrome" (Hersh, 1968; Hem, 1985). There are no standards for ammonium or other nitrogenous decay products in ground water (Florida Department of Environmental Regulation, 1989).

Table 24 lists the number of samples in which the 10 mg/L N standard was exceeded. Given the notoriety of nitrate contamination problems in the state, the Background Network detected surprisingly little nitrate contamination above the water-quality standard. Statewide, 0.6 percent of the samples from the surficial aquifer system exceeded the standard. No samples from the intermediate aquifer system exceeded the standard, and one percent of the samples from the Floridan aquifer system exceeded it. This does not mean that there are no problems, only that the problems are localized.

DISTRIBUTION IN GROUND WATER

With the exception of the SJRWMD all districts analyzed for nitrate. SJRWMD analyzed its samples for nitrate plus nitrite[19]. Unless stated otherwise, all concentrations given below are reported as nitrogen.

Surficial Aquifer System

The only nitrogen species widely measured in the surficial aquifer system in the Background Network is nitrate. Other analytes have been included in a few samples. In all cases, most samples have no detectable nitrogen compounds. Detection of nitrate, ammonium, and other compounds is unusual.

Ammonium - SFWMD analyzed 577 samples and found a mean concentration of 0.437 mg/L (standard deviation = 0.341, range = 0.000 - 1.550). No other surficial aquifer system analyses are available. Characteristically, if ammonium is present at all, it should occur near the land surface and waste sources. Given the high organic contents of soils and water in the central portion of the SFWMD, moderate ammonium concentrations are not unexpected.

TKN - Total Kjeldahl Nitrogen (TKN) represents the nitrogen included in complex, nitrogen- containing organics and some ammonia. The SFWMD found an average of 0.775 mg/L (standard deviation = 0.679 mg/L, range = 0.000 - 2.660, number of samples = 20) in the surficial aquifer system. TKN is closely related to ammonium in the oxidation/reduction sequence (reaction 15). Therefore, high TKN should be related to the land surface and proximity to organic nitrogen sources.

Nitrate - Nitrate is relatively widespread in the surficial aquifer system. This is a result of application of fertilizers and wastes on the land surface, which is the upper boundary of this aquifer system. Animal wastes are generated in range lands, feed lots, and dairies. Human wastes also contaminate the surficial aquifer system in some areas as a consequence of septic-tank use in rural areas. The distribution of nitrate is summarized in Table 24. Nitrates are characteristically at or below detection limits statewide. The median nitrate concentration statewide is below detection limits (Table 24), and only the Sand and Gravel Aquifer in the NWFWMD shows significant nitrate concentrations.

The distribution of nitrate in the northern districts (NWFWMD, SRWMD; Figure 44a,b) illustrates the "point-source" nature of nitrate. The data are highly variable, and they cannot be correlated from point to point. It is important to note that there are many nitrate "hits", indicating that nitrate contamination of the surficial aquifer system is widespread.

There are 64 NO_x analyses from the surficial aquifer system in the SJRWMD (Table 24). The maximum concentration found was 7.50 mg/L. The median concentration in the SJRWMD is <0.01 mg/L. Given data from other districts and studies, most of the NO_x is nitrate, and nitrite is rare as a constituent. Therefore, most of the concentrations reflected in the map (Figure 44c) represent nitrate. Nitrate in the SJRWMD is at or below detection limits throughout much of the district. Moderate nitrate concentrations occur in agricultural areas along the St. Johns River corridor.

The SWFWMD and SFWMD nitrate data (Figure 44d,e) also reflect enrichment of surficial aquifer system waters under large agricultural areas. There is some indication of elevated nitrates in the upper Everglades and along portions of the Kissimmee River valley.

Intermediate Aquifer System

Because of the confining properties of clay- rich horizons in the intermediate aquifer system, one would not expect nitrogen species to be a problem.

Ammonium and TKN - One hundred and fifty- five samples from the SFWMD have an average ammonium concentration of 0.32 mg/L (standard deviation = 0.17 mg/L, range = 0.00-0.78 mg/L). No other ammonium or TKN data are available.

Nitrate - Table 24 illustrates the distribution of nitrate in the aquifer system. With the exception of NWFWMD, the median nitrate concentrations are below detection limits. Maximum nitrate concentrations are low compared to the other aquifer systems, and three samples were found to exceed the 10 mg/L N standard.

Nitrate concentrations are moderately high throughout the NWFWMD (Figure 45a), but correlations between the wells are impossible. Concentrations are variable, indicating local sources. In contrast, nitrate concentrations in the intermediate aquifer system in the SRWMD, SJRWMD, SWFWMD, and SFWMD (Figure 45b-e) are generally low, with a few widely scattered detections.

Floridan Aquifer System

The distribution of nitrogen species in the Floridan aquifer system is related to proximity to the land surface and karst conduits. Lawrence and Upchurch (1982) attributed nitrates in the poorly confined Floridan aquifer system near Live Oak (Suwannee County) to local recharge through drainage wells and sinkholes and transport in karst conduits. The waters with nitrates were subject to relatively rapid infiltration. Elsewhere, nitrogen species should be absent or rare.

Ammonium - There is not enough ammonium data to draw conclusions.

Nitrate - The distribution of nitrate reflects characteristically low concentrations. With the exception of the NWFWMD (Table 24), median nitrate concentrations are at detection limits. Maximum concentrations are high (>10 mg/L) and reflect near-surface conditions and flow through karst conduits.

A belt of moderate nitrate concentrations occurs in central Okaloosa and Walton Counties (Figure 46a). This belt is large and includes a variety of land uses, such as silviculture and a U.S. Air Force base. A similar belt occurs from northeastern Bay through Leon Counties. This area includes a karst terrain, which has been shown by Lawrence and Upchurch (1982) to be subject to recharge of nitrate-rich surface waters. Additional work is needed to determine the reasons for the extensive nitrate occurrences in the district.
The most extensive area of nitrate in waters of the Floridan aquifer system in the SRWMD (Figure 46b) is centered on Suwannee County. This is an area known to have contributions of nitrates from agriculture (Upchurch and Lawrence, 1984) and from surface waters recharged through storm- water drainage wells (Hull and Yurewicz, 1979). Lawrence and Upchurch (1982) described the mechanisms of

recharge of ammonium and nitrate to the Floridan aquifer system in this area. They found three chemical influences: (1) slowly recharged waters that were affected by contact with the Hawthorn Group, (2) high nitrate waters, which were attributed to rapid infiltration through sinkholes, and (3) ammonium-rich waters that rapidly infiltrated through drainage wells and sinkholes. Other areas of moderate to high nitrate concentrations with similar origins occur in portions of Lafayette, Alachua, Gilchrist, and Dixie Counties. The Floridan is unconfined to poorly confined in all of the areas indicated, and surface runoff drains directly into sinkholes that penetrate the Floridan aquifer system.

Similar arguments can be made for the spotty distribution of nitrate in waters of the Floridan aquifer system in the SJRWMD (Figure 46c). High nitrate concentrations occur under the agricultural areas that extend across the center of the district from St. Johns and Flagler Counties to Marion County. The western and central portions of this belt have high recharge potentials (Scott et al., 1991), but the eastern third does not. The sources of nitrates in the high recharge areas are similar to those of the SRWMD, while the causes of high nitrates in the eastern part of the district are less easily identified. It is possible that recharge is being induced by pumpage in the eastern area.

Nitrates in the SWFWMD (Figure 46d) also reflect differences in recharge potential. The northern half of the district, which is characterized by high recharge potential, has a spotty pattern of nitrate concentrations that reflects local land uses. The Floridan is better confined in the southern half of the district, and nitrate concentrations are characteristically lower.

There is little data for the distribution of nitrate concentrations in the Floridan aquifer system in the SFWMD (Figure 46e). Most values are at or below detection limits.

OTHER CONSTITUENTS

The constituents discussed in this section include the general descriptors of water quality (Total Dissolved Solids and Specific Conductance) and the organic chemistry of the state's aquifer systems. The discussions of organic compounds in the aquifer systems are divided into three subjects: Total Organic Carbon, Synthetic Organics, and Pesticides. Total Organic Carbon is a measure of the natural organic content of the water, while Pesticides and Synthetic Organics reflect anthropogenic compounds.

Total Dissolved Solids

IMPORTANCE

Total dissolved solids (TDS) is a measure of the total mass of ions dissolved in water. The procedure for determining total dissolved solids involves weighing the mass of salts deposited after the water is evaporated. Volatile materials may be lost in this procedure, and there is some difficulty in obtaining a moisture-free environment for weighing. Consequently, total dissolved solids is, at best, a general estimator of the total load of chemicals dissolved in the water.

The more reactive a rock is, the higher the total dissolved solids content of waters within that rock are likely to be. For example, total dissolved solids are likely to be higher in a limestone aquifer than in a siliciclastic aquifer. Total dissolved solids also tends to increase with residence time and as water progresses along a flow path. An important consequence of this is that waters in the Floridan aquifer system that go deep into the aquifer system and contact the reactive, gypsum- and anhydrite-bearing lower confining beds may contain high total dissolved solids due to dissolved calcium and sulfate **(Table 4)**. Therefore, total dissolved solids can be used to understand the chemical maturation and flow history of certain aquifer systems.

Total dissolved solids in the Floridan aquifer system have been discussed by Shampine (1975), Kaufman and Dion (1967, 1968), Hull and Irwin (1979), Sprinkle (1989), and others. Sprinkle (1982b) presents a map of the distribution of total dissolved solids in the Floridan aquifer system. Sprinkle's map agrees in general with the data presented below, although the level of detail of his map is less.

STANDARD OR GUIDANCE CRITERION

The Florida Secondary Drinking Water standard for total dissolved solids is 500 mg/L (F.A.C. CH. 17-550.310-320; Florida Department of Environmental Regulation, 1989). This standard is based on a number of concerns. Waters with high total dissolved solids content have an unpleasant taste. The high total dissolved solids may result in development of scale and precipitates in water, especially in boilers, hot water heaters, and other heated-water systems. Finally, persons who consume high total dissolved solids water are at risk of developing kidney and gall stones.

Table 25 summarizes the samples found to exceed the 500 mg/L standard. Since the Background Network includes wells that are located in the salt-water transition zone, the number of samples found to exceed the standard largely reflects deeper wells, that sample the transition zone near the lower confining beds, and coastal wells. Statewide, 22 percent of samples from the surficial aquifer system exceeded the standard. Most of the samples that exceeded the standard came from the SFWMD (Table 25), where upconing of connate water and coastal intrusion are widespread. Samples from the intermediate aquifer system include 37 percent that exceed the standard. These exceedances are largely located in southwest SWFWMD and western SFWMD, where the Hawthorn Group is extensive and utilized as a water source. The high total dissolved solids waters are located in coastal areas and regions of upconing. Thirty-one percent of the samples from the Floridan aquifer system exceeded the standard. These samples are uniformly distributed through the districts and reflect coastal and upconing areas in the aquifer system. Given the purposeful location of wells in transition zones, little significance can be attached to the high proportion of samples that exceeded the standard. Examination of the maps discussed below is a better way of evaluating the total dissolved solids content of the potable portions of the aquifer systems.

DISTRIBUTION IN GROUND WATER

The distribution of total dissolved solids in Florida ground waters is summarized in Table 25. Note that, while several important trends are apparent, the data reflect all samples from within a district. Some districts utilized monitor wells that are either near the coastal salt-water transition zone or the base of the aquifer system. These wells yield high total dissolved solids waters and bias the summary statistics.

The most significant patterns in total dissolved solids data (Table 25) reflect equilibration with carbonates and poor flushing of aquifer systems. In the surficial aquifer system, total dissolved solids tends to increase southward, which reflects the increase in reactive carbonate minerals in the surficial and intermediate aquifer systems southward. Total dissolved solids data from the Floridan aquifer system show similar medians for all districts except the SFWMD. The high total dissolved solids concentrations in the SFWMD reflect low quality of water in the Floridan over much of the district. This is a result of incomplete flushing of the aquifer system due to low hydraulic heads.

Surficial Aquifer System

Figure 47 illustrates the distribution of total dissolved solids in water of the surficial aquifer system. Total dissolved solids concentrations are quite low, indicating minimum weathering of the siliciclastic host rock materials in NWFWMD and SRWMD. There is an increase in total dissolved solids towards the coast and Escambia Bay within the Sand and Gravel Aquifer (Figure 47a). There are a few coastal wells that exhibit high total dissolved solids in SJRWMD (Figure 47c), but most inland wells have low total dissolved solids waters. The high total dissolved solids coastal wells are in areas of both connate water and heavy pumpage, which may have induced some salt-water intrusion. Coastal salt-water intrusion is well documented in SWFWMD (Figure 47d),

where the 250 mg/L total dissolved solids isoline in the surficial aquifer system parallels the coast and major embayments. The high total dissolved solids content of waters in the re-entrant along the Peace River axis result from calcium-sulfate rich waters that are released to the surficial aquifer system by irrigation and natural upwelling.

The reverse is somewhat true in SFWMD (Figure 47e). SFWMD can be divided into three zones (Figure 47e): the Kissimmee and Caloosahatchee watersheds, the Everglades and Big Cypress Swamp, and the Atlantic Coastal Ridge. In the Kissimmee and Caloosahatchee watersheds, the total dissolved solids concentrations range from below 250 mg/L to over 500 mg/L. Highest total dissolved solids waters seem to follow the rivers and most likely represent upwelling and discharge of deeper waters. This upwelling has been documented in Lee County by Wedderburn et al. (1982) and Upchurch (1986). While few data are present from the surficial aquifer system in the Everglades and Big Cypress Swamp, total dissolved solids concentrations are elevated there as well. This is a result of poor flushing of connate waters and of upconing subsequent to draining wetlands to enhance agriculture. Finally, the Biscayne Aquifer, which comprises the Atlantic Coastal Ridge, has waters with total dissolved solids concentrations in the range of 250 to 500 mg/L. This water is locally recharged, and it represents the highest quality ground water in southeast Florida.

Intermediate Aquifer System

Total dissolved solids in the intermediate aquifer system ranges from 18 mg/L to 6,892 mg/L **(Table 25)**. This wide range is a result of the diversity of lithologies represented in the Hawthorn Group, as well as the influences of the coastal transition zone. Where water has been in contact only with siliciclastic materials, the total dissolved solids content is low. Where it has been in contact with carbonates and chemically unstable silicates (clays, opal; **Tables 4,5**), total dissolved solids content is high. Highest total dissolved solids concentrations are in south Florida, where saline water is present in the aquifer system.

The intermediate aquifer system data cannot be contoured in north and central Florida due to the heterogeneity of the aquifer system units (Figure 48a,b,c). The data can be contoured in southern SWFWMD and western SFWMD (Figure 48d,e), where the aquifer system is moderately deep and continuous. Where the intermediate aquifer system is near the coast, the salt-water transition zone is characterized by high total dissolved solids (Figure 48d,e).

In areas where the intermediate aquifer system contains abundant carbonate horizons, fracture traces appear to affect water quality. For example, re-entrants of salty water can be delineated in Sarasota County (Figure 48d). These coincide with major lineaments that can be identified from satellite imagery (Culbreth, 1988). There is also local upconing of deeper, high total dissolved solids water along a lineament which is occupied by the Peace River (Figure 48d; G. Jones, 1991). These areas of upconing follow zones of high vertical permeability. In some areas the relative head distribution of the aquifer systems will encourage upconing, in other areas pumpage is the cause.

Floridan Aquifer System

The pattern of total dissolved solids in waters of the Floridan aquifer system is directly related to the salt-water transition zone and regional flow systems (Figure 49). High total dissolved solids concentrations in the Floridan aquifer system are a result of long contact times with soluble limestones and dolostones of the Floridan and mixing with high total dissolved solids, saline waters at the base of the aquifer system and at the coast. Lowest total dissolved solids concentrations are in the interior, where recharge is prevalent and residence times in the aquifer system are too short for effective equilibration with the aquifer system.

The potentiometric surface of the Floridan aquifer system controls the position of the transition zone (see the potentiometric maps in Scott et al., 1991). Where head is high near the coast, the salt-water transition zone beneath the land surface is narrow, or it may be offshore. The transition zone also slopes steeply inland where potentials are high. Re-entrants occur near river mouths, where the potential is lowered. These re-entrants can be seen near the Escambia and Apalachicola Rivers (Figure 49a), and the Hillsborough, Manatee, and Peace Rivers (Figure 49d). Other re-entrants along the coast are related to intrusion caused by pumpage. Where the potential is low, such as occurs in the Everglades and Big Cypress Swamp areas of the SFWMD, the total dissolved solids content of the Floridan aquifer system is high, and the coastal transition zone is broad, with a shallow slope (Figure 49e).

The 500 mg/L isoline defines the extent of potable water in the Floridan aquifer system. Note that it crosses the state from Sarasota County (Figure 49d), north of Lake Okeechobee (Figure 49e), to southern Brevard County (Figure 49c). South of the 500 mg/L isoline the flow system in the Floridan aquifer system is weak, and high total dissolved solids waters have not been flushed from the aquifer system by fresh-water flow.

Locally, waters high in total dissolved solids content in the interior of the state (Figure 49) represent wells that either are deep enough to reach high-sulfate concentrations near the base of the Floridan aquifer system or are in regions of upconing as a result of pumpage.

Specific Conductance

IMPORTANCE

Specific conductance is a measure of the ability of material to conduct electrical currents. The American Society of Testing and Materials (1980) has defined specific conductance as the "reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of an aqueous solution at a specified temperature". The inverse of the ohm (the measure of electrical resistance) is the mho. Natural waters are moderately resistive, so specific conductance is measured in micromhos/cm (µmhos/cm). The micromho is equivalent to the microSiemen (µS) in SI notation.

The ability of water to conduct electricity is primarily a function of the concentration of electrical charges in the water and of water temperature (Miller et al., 1988). When an electrical potential is applied to water, cations tend to migrate to the cathode, while anions migrate to the anode. It is this potential for ionic migration that specific conductance measures. Therefore, specific conductance is sensitive to the concentrations and types of ions in the water. Miller et al. (1988) have discussed the effects of mixtures of ions on specific conductance. All of the ions previously discussed contribute to the electrolytic properties of water.

Specific conductance roughly reflects the same processes as total dissolved solids, and there is a good statistical correlation between the two variables. However, specific conductance is dependent upon the specific combinations and concentrations of the electrolytes in the solution, so two water samples with the same total dissolved solids contents may not have the same conductivities (Miller et al., 1988). As a rule of thumb, at equal TDS concentrations, the following anions can be ranked according to ability to conduct electricity

$$Cl^- > SO_4^{2-} > HCO_3^-, \quad (16)$$

←High Conductivity
Low Conductivity→

where chloride-rich waters are more conductive than sulfate-rich waters, and so on. Because specific conductance and total dissolved solids are correlated, specific conductance can be utilized to evaluate chemical maturity along a flow path and salt-water intrusion.

STANDARD OR GUIDANCE CRITERION

There are no standards or guidance criteria for specific conductance. Specific conductance, per se, does not constitute a water-quality hazard to water users. It is commonly used as a field analyte for evaluation of gross water quality, so it is included in this report. Given certain assumptions about the composition of the water, specific con-

ductance can be correlated with salinity, and many aquifer salinity measurements given in the literature are based on specific conductance uncorrected for water chemical speciation. Consequently, it is not safe to assume that high specific conductance waters are necessarily in violation of standards for important electrolytes for which standards exist, such as sodium and chloride.

DISTRIBUTION IN GROUND WATER

The distributions of specific conductance data in Florida ground waters are summarized in **Table 26**. Since specific conductance is correlated with total dissolved solids, the arguments concerning the distribution of dissolved solids data (see Total Dissolved Solids) hold for specific conductance.

In Florida's aquifer systems, high chloride waters cause highest specific conductance anomalies. For this reason, conductivities tend to increase towards the coast and estuaries.

High conductivities inland reflect several factors, including upconing of deeper, more saline waters into shallow wells; release of deep Floridan aquifer system water on the land surface as irrigation water, which is then recharged to the surficial aquifer system; increases of chlorides due to evaporation of meteoric water in unconfined portions of aquifer systems; and residual (or connate) waters from earlier high sea-level stands that have yet to be flushed from the aquifer systems.

Surficial Aquifer System

Specific conductance of water from the surficial aquifer system is characteristically low due to the low concentrations of electrolytes. Median conductivities increase southward (Table 26), indicating an increase in total dissolved solids as aquifer carbonate content and influence of salt water increase. The median specific conductance for the surficial aquifer system, statewide, is 475 µmhos/cm, while the district medians range from 50 µmhos/cm in the NWFWMD to 619 µmhos/cm in the SFWMD.

Increases in specific conductance have been documented towards the coast and estuaries in NWFWMD (Figure 50a) and SWFWMD (Figure 50d). Specific conductances in the SRWMD (Figure 50b) are relatively uniform, indicating that over its limited extent water from the surficial aquifer system has a relatively homogeneous composition. The surficial aquifer system in the SJRWMD (Figure 50c) has several good examples of high specific conductance waters inland. Many of these are associated with areas of irrigation, where deeper waters or evaporative concentration elevate specific conductance. Floridan aquifer system water is widely used to irrigate pastures and crops in the area, where it recharges the surficial aquifer system (Dalton, 1978). Increased specific conductances in central SFWMD (Figure 50e) are caused by contamination of irrigation waters from deeper aquifer systems, upconing of more mineralized water, and salt-water intrusion.

Intermediate Aquifer System

Specific conductance in the intermediate aquifer system is generally higher than in the surficial aquifer system (Table 26). These specific conductances are higher in response to increased anion concentrations that result from chemical weathering of the host rock. Inland, where chlorides are of minimal importance, sulfates produced by the oxidation of pyrite **(Table 4)** contribute most significantly to the specific conductance. The southward increase in specific conductance as a result of increased total dissolved solids is evident (Table 26).

Figure 51 illustrates the distribution of specific conductance in the intermediate aquifer system. In south Florida (Figure 51d,e), where data can be contoured, it is evident that specific conductance increases toward coasts and estuaries. This same pattern is present in the other districts; however, it is not contourable (Figures 51a,b,c). Upconing along the Peace River lineament (G. Jones, 1991) is evident (Figure 51d), as is a zone of high specific conductance waters along the Caloosahatchee River (Figure 51e).

Floridan Aquifer System

Figure 52 illustrates the distribution of specific conductance in the Floridan aquifer system. Specific conductance values away from the coast are low in north and central Florida. Specific conductances tend to increase toward the coast (Figure 52a), which reflects maturation along long flow paths and mixing with salt water near the transition zone.

The Suwannee River divides the SRWMD (Figure 52b) into two flow systems, east and west of the river. Both flow systems illustrate the increase in specific conductance along flow paths. Lowest conductivities are near surface-water drainage divides. Highest specific conductance waters are in the coastal transition zone both in the western and eastern flow systems, and near the Suwannee River in the eastern system. High specific conductances are also found in the Northern Highlands physiographic province in the SRWMD. These result from equilibration of the water with the host rock under nearly stagnant flow conditions. Note that there are several, isolated, "plume-like" water masses, such as in Alachua County. These appear to be related to slightly elevated chloride levels near karst recharge areas along the Cody Escarpment (Lawrence and Upchurch, 1976, 1982).

Specific conductance data from the SJRWMD (Figure 52c) indicate relatively low specific conductances inland. There is a large re-entrant centered on St. Johns and Flagler Counties, which can be attributed to connate waters and intrusion under pumping stress. There are also several centers of high specific conductance along the St. Johns River which appear to reflect upconing along faults and fractures (Leve, 1983).

The influence of coastal salt water is well illustrated by specific conductance of waters of the Floridan aquifer system in the SWFWMD (Figure 52d). A strong specific conductance gradient is shown at the salt-water transition zone. Re-entrants occur along the axes of the Withlacoochee, Hillsborough, Manatee, Peace, and Myakka Rivers.

In south Florida (Figure 53e) the Floridan has high sulfate, chloride, and bicarbonate contents. This causes the Floridan water to have conductivities in excess of 4,000 µmhos/cm south of the line from Lee to Brevard Counties. Again, this high anion content is a result of poor flushing-of the aquifer system under low hydraulic head-conditions.

Total Organic Carbon

IMPORTANCE

Total organic carbon (TOC) in aquifers and-monitor wells can have three sources: (1) natural-humic substances, (2) synthetic organic-contaminants, and (3) drilling fluids. Data-presented below (see sections on Synthetic-Organics and Pesticides) indicate that the-concentrations of anthropogenic organics are-orders of magnitude less than the total organic-carbon concentrations. Barcelona (1984) suggests-that the concentrations to be expected from drilling-muds are also much less than the TOC-concentrations reported herein. Therefore, the-TOC concentration data discussed in this section-reflect naturally occurring organics, or humic-substances.

Humic Substances - Most of the total organic-carbon reported in ground water is composed of-humic substances (humic and fulvic acids) which-are derived from microbial decay of leaf litter, soil-organics, and soil biota waste products. Humic-substances are complex molecules with a wide-range in molecular weights (Thurman, 1985). Since they are decomposition products, humic-substances can include a number of different-molecular structures and functional groups, such-as carboxyl, amino, and carbonyl groups. Humic--substance molecules have flexible structures, large-sizes, and a diversity of functional groups, so they-are effective chemical complexing agents,-especially for metals. They are capable of conforming to clay surfaces and of flocculation as-particulates in their own right.

The wide range in molecular weight, diversity-of molecular structures, and large number of-functional groups make characterization of humic-sub-

stances difficult. As a result, a common-method of classification is by their response to the-pH of surrounding water (Thurman, 1985). Humic-acids are humic substances that are soluble in-basic solutions and insoluble in acidic solutions-(pH < 2) or ethanol. Humic acids include large,-complex molecules with molecular weights of-2,000 to >5,000 daltons (24,000 to 60,000 a.m.u.;-Thurman, 1985). Because of their low solubility in-acidic solutions, humic acids tend to flocculate in-acidic, siliciclastic soil zones and contribute to the-formation of organic hard pans. In alkaline-carbonate aquifers humic acids can migrate until they flocculate or are decomposed. Fulvic acids are less complex than humic acids (molecular weights of 500 to 2,000 daltons [6,000 -24,000-a.m.u.; Thurman, 1985]), and they are soluble under both acid and alkaline conditions. The smaller fulvic acid molecules do not color water, while humic acids may. Humins are insoluble in both acids and bases. The particulates and colloids that constitute the majority of organics in soils, especially organic hard pans, and sediments are humins.

Three processes affect the mobility of organic-acids: (1) microbial decay, (2) pH of the host water, and (3) total dissolved solids content of the host water (Thurman, 1985).

Microbial Decay - Microbial decay of organic-rich material is associated with many of the processes previously discussed. Iron, sulfur, and nitrogen transformations are associated with soil-microbes, especially bacteria. Reaction 6 is an example of a microbially driven reaction in which organic carbon and sulfate are metabolized. Therefore, bacteria require a source of organic-carbon, as well as the other nutrients. The bacteria form mats composed of a number of different species, all of which support each other in a complex community.

In order for microbial mats to thrive, they require (1) a solid substrate for attachment and (2) a constant bath of water rich in organic carbon and other nutrients. In intergranular aquifers, there is abundant substrate and particulate organic materials (particulate humic substances and dead microbes) are mechanically filtered from the water. In karstic flow systems, the caverns and karst-conduits provide less substrate per unit volume of water, so microbial activity may be reduced and TOC may persist. In karstic aquifers, therefore, dissolved and particulate organic carbon can travel some distance before suitable conditions for microbial decay or mechanical trapping can be realized. While they are produced in most soils, humic substances are best preserved in water -saturated, reducing soils and aquifers where complete oxidation and aerobic microbial decay are inhibited.

Transformation Mechanisms and Carbon Fixation Organic carbon can be fixed in a soil or aquifer as a particle or as organic tissue, or it can be released as a gas. The gas can then be lost to the atmosphere, or it can become involved in inorganic reactions. Most organic carbon is consumed by microbial activity with a sequence of degradation steps leading to the ultimate production of carbon dioxide ($C0_2$) or methane (CH_4)

Microbes have the capability of converting organics into CO_2 under aerobic conditions[22], and CH4 under anaerobic conditions. Both gases can pass out of the soil and aquifer by degassing. Carbon dioxide released by microbes in the soil contributes to the production of carbonic acid in soil and aquifer waters. Partial pressures of CO_2 characteristically rise from $10^{-3.5}$ to approximately $10^{-2.0}$ as a result of $C0_2$ production in soils. This results in a drop in water pH from around 5.5 to pH values of 3.5-4.5. In aerobic, intergranular flow systems, microbial decay may occur over a short distance, in which case the resulting ground water will become relatively free of total organic carbon. In anaerobic systems, microbial activity is somewhat inhibited, and total organic carbon can persist.

Soluble organic acids can be removed from ground water by flocculation (Thurman, 1985). Flocculation of organic acids takes place when chemically reactive sites on the organic molecule become saturated with cations. If abundant, hydrogen ions are sufficient to cause flocculation of humic acids, which results in a loss of solubility in acidic solutions. Both organic acid groups can flocculate if they come in contact with high total dissolved solids waters, such as occurs when meteoric waters enter a carbonate-rock aquifer or sea water.

Transport of Trace Metals - Humic and fulvic acid molecules include numerous sites (carbonyl, carboxyl, amino-, and similar sites) where chemical complexing[23] can occur. Because of these sites, these acids are capable of binding metals and inducing their transport. For this reason, water high in total organic carbon is usually high in iron and trace metals (Young and Comstock, 1986). At contaminated sites humic and fulvic acids may cause undesirable movement of large amounts of metals.

Sources of TOC - Most organic material is derived from the land surface. Swamps and organic zones in soils are widespread and contribute total organic carbon to ground water. Thus, in most places total organic carbon decreases in concentration with depth (Watrous and Upchurch, in prep.). This is not to say that there are not other sources of total organic carbon. Clays in the Hawthorn Group contain organics that can be decomposed to produce soluble total organic carbon. Limestones and dolostones in the Avon Park Formation contain widespread organic- rich zones that may also contribute total organic carbon.

Trace organic contamination of ground water by synthetic organics is rarely represented in total organic carbon data because the small concentrations that are usually present are below the detection limits of the total organic carbon analytical method. None of the total organic carbon data reported herein can be shown to be primarily a result of anthropogenic, synthetic organics.

Many muds used in well drilling contain organics as emulsifiers, binders, and/or coagulation- control additives. These can contaminate poorly developed wells and result in spurious total organic carbon concentrations (Barcelona, 1984). The latter is a known problem in the Background Network data set, and isolated reports of high total organic carbon must be considered as probable contamination[24] by drilling fluid until confirmed by further sampling. For example, in the SRWMD the original data set of 24 surficial aquifer system wells contained 11 wells (46%) with over 10 mg/L total organic carbon. When the wells that had known or suspected drilling-fluid contamination or excess particulates are removed from the data set, the number with high total organic carbon drops to 4 out of 15 (27%).

STANDARD OR GUIDANCE CRITERION

There are no standards or criteria for naturally occurring organic carbon. Where synthetic organics constitute all or part of the organic carbon, individual criteria would be in effect.

Natural organic carbon is not harmful to humans. It may cause discoloration of water and may stain porcelain fixtures. Because humic substances can complex and transport trace metals, which may be hazardous, organic carbon may be of secondary concern.

Considerable attention has been given to organic carbon in public water supplies in southeast Florida because of the potential for formation of trihalomethane (or THM) compounds. When organic-rich water is sterilized by chlorination, chlorine may substitute for hydrogen on methane radicals. An example of this reaction is the formation of trichloromethane (or chloroform), which has the structure

H
½
Cl ¾ C ¾ Cl.
½
Cl

The trihalomethanes are known to be carcinogenic, and considerable effort is expended to avoid formation of THM's in drinking water.

DISTRIBUTION IN GROUND WATER

The total organic carbon data are among the most interesting and important data in this report. No other known study has compiled a data set of

organic carbon in aquifer systems that is as extensive. It is also of interest that the total organic carbon levels are so high. Hem (1985) noted that all natural waters contain organic carbon because of the intimate relationship of water and living matter. His review of total organic carbon data from aquifers indicates, however, that total organic carbon concentrations can be expected to be less than 20 mg/L as carbon. Thurman (1985) summarized the distribution of dissolved humic substances in filtered ground and surface waters. He reported the concentration range in ground water to be 0.03 to 0.10 mg/L as carbon. The samples described in this section were not filtered, so one would expect higher concentrations.

Florida total organic carbon data indicate that organic carbon is very widespread and concentrations range as high as 380 mg/L **(Table 27)**. The statewide median concentrations in mg/L as carbon are: surficial aquifer system - 14.0, intermediate aquifer system - 4.8, and Floridan aquifer system - 2.2 mg/L. All of the medians exceed Thurman's (1985) expected concentration range, and they are near the upper level cited by Hem (1985).

Total organic carbon is distributed throughout all aquifer systems, but is highest in the surficial aquifer system (Table 27). Given the regional extent and continuity of the total organic carbon concentrations, it is clear that most of the organic carbon in Florida's aquifer systems is a result of local recharge of humic substances.

Surficial Aquifer System

The surficial aquifer system should contain the highest total organic carbon concentrations because it contains humus in spodic zones and upper soil horizons, and it is in shallow soils that most microbial decay of plant material occurs. The surficial aquifer system median concentration is 14.0 mg/L total organic carbon (Table 27), with the SFWMD having the highest median total organic carbon. The highest maximum concentration is 380 mg/L, which must include considerable colloidal and particulate humic material. Given the wet and highly vegetated nature of many areas of the state, one would expect high concentrations of total organic carbon in the surficial aquifer system. The median and maximum concentrations increase to the south, also indicating the prevalence of organic-rich, wetland environments to the south.

The pattern of total organic carbon in the surficial aquifer system is largely controlled by proximity to organic-rich surficial environments, such as wetlands, rivers, or peat deposits. Total organic carbon declines with depth in the aquifer system due to microbial decay and flocculation.

Surficial aquifer system wells that are high in total organic carbon in NWFWMD and SRWMD (Figure 53a,b) are closely associated with marshes, swamps and riverine drainage. High TOC is also associated with swamps and other surficial sources of organics in the SJRWMD (Figure 53c). High total organic carbon occurs in some coastal wells in all three districts in regions where coastal swamps and marshes abound. Sediments of the coastal ridges include peats and disseminated organics which may also contribute to the total organic carbon concentrations in the aquifer system waters. Total organic carbon in the surficial aquifer system in SFWMD (Figure 53e) is generally low in the Atlantic Coastal Ridge, where highly oxidizing environments have reduced the organic content. Elsewhere, total organic carbon is high in waters related to the Everglades and Big Cypress drainage systems and portions of the Caloosahatchee and Kissimmee River drainages, which are characterized by extensive swamps, marshes, and peat deposits.

Intermediate Aquifer System

Total organic carbon in the intermediate aquifer system can result from rapid recharge of surface and surficial aquifer system waters, or it may be derived from decomposition of organics in the Hawthorn Group (Miller, 1978). Median total organic carbon concentration in the system is 4.8 mg/L (Table 27). The highest TOC concentration is 71.0 mg/L in the SFWMD (Table 27).

The high total organic carbon concentrations throughout the northern and central portions of the state are generally related to rapid recharge environments, such as in karst terrains and the vicinity of drainage well systems. Total organic carbon in intermediate aquifer system waters of southern Florida (southern SWFWMD, Figure 54d; western SFWMD, Figure 54e) are probably not related to rapid recharge. These high concentrations, including the highest in the aquifer system, may be related to disseminated organics in the Hawthorn Group. Figure 54e indicates that most of the areas characterized by high total organic carbon concentrations in the intermediate aquifer system water are inland from the coastal salt-water transition zone, so total organic carbon may also be derived from local recharge of surficial, organic-rich waters.

Floridan Aquifer System

Total organic carbon in the Floridan aquifer system (Table 27, Figure 55) ranges from below detection limits to over 80 mg/L within the state. While the median total organic carbon concentration is relatively low (2.2 mg/L) compared to other Florida aquifer systems, it is high compared to data from aquifer systems outside of Florida (Hem, 1985; Thurman, 1985).

The highest total organic carbon concentrations in northwest Florida are in areas where the Floridan aquifer system is either unconfined or characterized by poor confinement in a well- developed karst terrain. In NWFWMD (Figure 55a), highest total organic carbon concentrations are in areas where the Floridan is unconfined and overlain by thin, organic-rich, sandy soils, such as in the lower Wacissa and Aucilla drainage basins. These areas are dominated by fresh-water swamp communities and poorly drained pine flatwoods, both of which are excellent sources of humic substances. Lowest total organic carbon concentrations are in areas where the Floridan is well confined by the overlying Hawthorn Group. High total organic carbon concentrations also occur in the limestone outcrop belt (Suwannee Limestone and Ocala Limestone) in Walton, Holmes, Washington, and Jackson Counties. In this area the Floridan aquifer system is unconfined and is characterized by karst drainage.

High total organic carbon concentrations are found in scattered wells along the karstic Cody Escarpment in the SRWMD (Figure 55b). High total organic carbon concentrations have been noted in the Live Oak and Lake City areas by Upchurch and Lawrence (1984) and Brown (1989). Brown found two sources of total organic carbon in the Lake City area (Columbia County). She concluded that total organic carbon concentrations in the Coastal Lowlands and Cody Escarpment are a result of direct recharge of the Floridan by organic-rich surface waters. The moderately high total organic carbon concentrations in the Floridan aquifer system beneath the Northern Highlands, where the aquifer system is confined by the Hawthorn Group, were attributed to leaching of organics found in the Hawthorn (Miller, 1978).

An extensive area of high total organic carbon occurs in the Coastal Rivers Basin (Figure 55b), the coastal drainage system west of the Suwannee River in Taylor, Lafayette and Dixie Counties. This area is characterized by a thin clay (the "San Pedro clay") that overlies the Floridan aquifer system. The Floridan is exposed at a number of sites in the embayment and the clay is penetrated by many sinkholes. The land surface is characterized by extensive woodlands and swamps. The large area of organic-rich water in the Coastal Rivers Basin is remarkable because it so accurately defines the extent of the basin. Total organic carbon in this basin appears to be controlled by the local flow system and is most likely a result of local recharge through swamps and other areas with highly organic surface waters and organic-rich soils. The large re-entrant of water with less than 3 mg/L total organic carbon in Taylor County roughly corresponds to the Fenholloway River and possible upconing of deeper Floridan water near Perry and Foley. Discharge of low total organic carbon water in the Aucilla and Suwannee basins appears to limit the lateral extent of the higher total organic carbon water.

Floridan aquifer system water in the SJRWMD is comparable to the other northern districts (Table 27), with a median of 3.3 mg/L and a maximum of 29.0 mg/L. The majority of the high total organic carbon samples came from a large area centered

on Flagler County (Figure 55c). It appears from other data that this water has a significant connate component, and the high total organic carbon may reflect organics in the sediments of the aquifer system.

Total organic carbon in the SWFWMD (Figure 55d; **Table 27**) is high relative to the remainder of the state. The median concentration is 16.8 mg/L and the maximum concentration is 78.8 mg/L. High total organic carbon concentrations are consistently high throughout the district, but the highest concentrations occur in regions where wetlands and riverine systems overlie unconfined, or poorly confined portions of the aquifer system.

Total organic carbon concentrations are relatively low in the Floridan aquifer system of the SFWMD (Table 27; Figure 55e). Median concentration is 1.9 mg/L, but the maximum concentration is the highest recorded in the Floridan at 80.6 mg/L. Subsequent sampling of this well yielded total organic carbon concentrations of 1.0 and 3.5 mg/L, indicating that the initial, high concentration may be anomalous. High concentrations are associated with the Kissimmee River corridor and with an area in western Lee County.

Synthetic Organics

DEFINITION AND ANALYTES

Synthetic organics include a list of 142 **(Table 28)** anthropogenic organic compounds. This list includes most of the compounds on the U.S. Environmental Protection Agency priority list. These compounds range from primary compounds used in manufacturing and energy industries to degradation products produced by microbial decay and hydrolysis. Many of the synthetic organics have been utilized as pesticides, and inclusion in Synthetic Organics, as opposed to Pesticides, is based on common uses. For additional information on these and other synthetic organics, refer to Montgomery and Welkom (1990).

Only those compounds that have been tentatively found in Florida aquifer systems are discussed below. Many of the occurrences reported herein are near the detection limit, so they may represent "false positives". Most of these occurrences have not been confirmed by resampling .

Table 29 lists the number of samples in which any of the compounds in Table 28 were found and the number of samples found to exceed the standards. The table includes unconfirmed occurrences. Care should be taken in interpreting these data because the data are unconfirmed. The discussions that follow list the compounds tentatively detected and some important concerns about each. The proportions of samples that contain each analyte are given in the text.

No maps are given for this and the following Pesticides sections because of the uncertainties encountered in confirmation by resampling, analytical procedures (many of the positive results are too near the practical quantitation limit25), and attribution to causes.

IMPORTANCE AND CONTROLS

The synthetic organics have a diversity of sources. They range from heavy industry to local, household uses. Some are solvents, others are lubricants. None are of natural origins. The densities of the organics vary with respect to water, as do the solubilities. As a result, they may exist dissolved in water or, locally, as an non-aqueous phase. None of the samples in this study are of free product; all are dissolved in water. Several factors affect the mobility of synthetic organics. These include (1) advection, (2) dilution and dispersion, (3) volatization, (4) density stratification, (5) dissolution, (6) sorption, and (7) biological conversion and hydrolysis.

Advection - Advection is the term used to describe transport with the flow of water in the aquifer system. All constituents in ground water are subject to advective transport.

Dilution and Dispersion - Dilution and dispersion are caused by individual packets of water following flow paths of different lengths. Dilution and dispersion are highly effective in reducing the concentration of synthetic organics in intergranular flow systems, but less effective inconduit flow. Here, flow paths are less tortuous and dispersion is limited. Dilution within the conduit may significantly reduce the concentration, however.

Volatization - Many of the synthetic organics listed herein are volatile. That is, given proper conditions, the organic may go to a gaseous state and pass out of the system. This process is especially important in unconfined, water-table aquifers where the gaseous phase can pass directly into the soil or aquifer atmosphere. **Table 30** gives the classification utilized in discussing volatility below. This classification (Lyman et al., 1990) is based on the Henry's Law constant, or the air-water partition coefficient. Henry's Law constant is defined as the ratio of the partial pressure of the organic vapor in air to the concentration in water. At 1 atmosphere the Henry's Law constant is calculated by

$$H = \frac{P \bullet FW}{760S} \qquad (17)$$

where H = Henry's Law constant (atm m^3/mol), P = partial pressure (mm Hg), S = solubility (mg/L), and FW = gram formula weight of the compound (Montgomery and Welkom, 1990).

Density Stratification - Many of the compounds found in Florida waters are liquids with densities that differ significantly from water. If free product is present in the aquifer system, it will come to density equilibrium with the water. If it is less dense than water, the product floats on the water surface and forms a Light, Non-Aqueous Phase Liquid (LNAPL). If it is more dense, the liquid sinks and forms a Dense, Non-Aqueous Phase Liquid (DNAPL). In either case, sampling may miss the non-aqueous phase and detect only that portion of the organic dissolved in the water. Given the design of the Background Network sampling plan, it is unlikely that non-aqueous phase liquids are present at most of the sample sites.

The compounds in the following discussion are classified on the basis of their relative density (specific density) as defined by

$$P_{SP} = \frac{P_S}{P_w}$$

where P_{SP} = the specific density (dimensionless), P_S = density of the organic (g/mL or g/cm^3), and P_w = density of water at 4°C (g/mL or g/cm^3). Compounds with P_{SP} significantly less than 0.7 are said to be light, while compounds with P_{SP} greater than 1.3 are said to be dense.

Solubility - All of the organics exhibit some solubility in water. This ability to dissolve into water encourages transport. The solubilities of the organics are highly variable, and inversely related to sorption onto soil or aquifer particulate organics.

Sorption - One of the governing principles of synthetic organic transport is the octano/-water partition coefficient (K_{OW}). This coefficient is a ratio of the solubility of a synthetic organic in octanol, a representative organic solvent, and water. Low K_{OW} organics are more soluble in water than in organic solvents. High K_{OW} compounds are more soluble in organic solvents than in water. In aquifer systems, one of the possible places where high K_{OW} organics can be fixed is particulate organics (humins, see Total Organic Carbon). There is some debate as to whether the high K_{OW} organics actually dissolve into the particulate humin (true absorption) or simply adsorb onto available surface sites. At any rate, given the presence of humins in the soil or aquifer, high K_{OW} organics are likely to be fixed on the particles and thereby retarded from advective transport. Domenico and Schwartz (1990) present an excellent discussion of the sorption process.

The octanol-water partition coefficient is determined by laboratory experiments and data are readily available for many compounds (see Montgomery and Welkom, 1990). A more realistic coefficient for use in ground-water systems is the organic-carbon partition coefficient (K_{OC}). The organic-carbon partition coefficient is the ratio of sorbed chemical per unit mass of humin (as C) to solubility in water. Many equations have been developed to relate K_{OC} to K_{OW}. For example,

Kenaga and Goring (1980) related the two partition coefficients by

$$\log K_{OC} = 1.38 + 0.54 \log K_{OW} \quad (19)$$

Other equations are discussed in Freeze and Cherry (1979) and Domenico and Schwartz (1990). Care should be taken in choosing which of the equations (e.g. equation 19) to use because there is no general agreement as to which is most appropriate. In a sense, therefore, solubility in water and retardation on humins are related and the synthetic organics can be classified on the basis of either solubility in water or by K_{OC}. **Table 31** gives the mobility classification of Fetter (1988). In this classification mobility is classified on the basis of solubility in water, which is approximately inversely proportional to the K_{OC} .

Biological Transformations and Hydrolysis - Many of the synthetic organics can serve as sources of organic carbon for soil and aquifer microbes. As a result, some of the chemicals listed in Table 28 are degradation products, not primary contaminants. Microbial degradation behaves chemically much like hydrolysis, with cleaving of radicals and substitution of water or OH^-. The rate of degradation has been likened to radioactive decay as biodegradation and hydrolysis in ground-water systems follow an exponential decay rate.

STANDARD OR GUIDANCE CRITERION

Table 28 gives the standards or guidance concentrations for the synthetic organics. Only the hazards or health consequences of analytes detected in the Background Network are discussed below.

Use of the term "mdl" in Table 28 signifies that the standard for the organic compound is the detection or practical quantitation limit. In these cases, there is no specific standard, but the water is subject to the "free from" provisions of Florida's water quality statutes (Ch. 17-550 F.A.C.). Under this provision, the water must be "free from" deleterious contaminants, including compounds that harm biota, use of the water, or humans. Harm to humans includes toxicity, mutagenicity, carcinogenicity, or teratogenicity.

Given the large number of samples from Florida's aquifer systems and the fact that the detections have not been confirmed, it is remarkable that so few samples had detectable synthetic organics. Many of the analytes that were found to be present were from a single sample, so the areal distribution of "problems" is highly limited. Most of the samples are from wells near urban, industrial, or heavy agriculture areas, which sugaests that it is unlikely that any significant problem of wide extent exists.

In all cases, the median and upper quartiles of synthetic organic data **(Table 29)** are detection limits. The proportions of samples with detected synthetic organics are as follows:

Surficial aquifer system

NWFWMD	2.8%
SRWMD	0.0%
SJRWMD	6.9%
SWFWMD	2.4%
SFWMD	8.9%
Statewide	6.6%

Intermediate aquifer system

NWFWMD	0.0%
SRWMD	0.0%
SJRWMD	0.0%
SWFWMD	0.0%
SFWMD	2.8%
Statewide	1 .3%

Floridan aquifer system

NWFWMD	0.0%
SRWMD	1.3%
SJRWMD	4.5%
SWFWMD	7.1 %
SFWMD	3.8%
Statewide	3.1 %

As one might expect, the highest proportions of samples with detectable synthetic organics are from the surficial aquifer system and unconfined portions of the Floridan aquifer system. This indicates the susceptibility of those aquifer systems to contamination from surficial sources. The intermediate aquifer system contains little indication of contamination, which is due to the confined nature of the water-producing zones in the aquifer system. Areas at greatest risk include the unconfined Floridan aquifer system in west- central Florida (SRWMD, SWFWMD) and in SJRWMD, and the surficial aquifer system, especially the Sand-and-Gravel Aquifer in NWFWMD and the Biscayne Aquifer in SFWMD.

DISTRIBUTION IN GROUND WATER

Rather than divide this discussion into aquifer systems and districts, the following discussion deals with the specific chemicals found or suspected in the aquifer systems. The chemicals are in alphabetical order for ease in location, as opposed to being placed in order of origin or chemical similarities. Unless stated otherwise, the Henry's Law constants, K_{OC}'s, and uses of the following chemicals are from Montgomery and Welkom (1990).

Care should be taken in placing importance on the occurrences reported below. At this time there is question as to whether the chemical is actually in the water or is spurious[26]. The following list should be utilized in two ways: (1) to show that, even at the worst case, there is little background contamination of Florida's aquifer systems and (2) to identify chemicals that may be present and require further study.

As this discussion continues, it will be apparent that many of the compounds detected in Florida's aquifer systems have been used in the past as pesticides. Many are no longer licensed for use in Florida and the Background Network is detecting residual contamination. Also, note that most of the chemicals are only moderately volatile, which is consistent with the residual occurrences. Very highly volatile compounds ($H > 10^{-2}$ atm m^3/mol) are suspect because the Background Network actively avoided sites likely to have active releases and older releases should have previously volatized. There is also an absence of highly mobile or immobile compounds. Immobile compounds do not spread widely, which reduces the probability of detection. Highly mobile compounds are diluted and dispersed to concentrations below detection limits.

Acrylonitrile

Acrylonitrile (C_3H_3N) is copolymerized with other organic compounds to produce acrylics, ABS (acrylonitrile-butadiene-styrene), and other plastics. It is used as a grain fumigant, and in pharmaceuticals, antioxidants, dyes, and surfactants. It is a light compound with moderate volatility ($H = 1.1x10^{-4}$ atm m^3/mol). Based on a K_{OC} of 0.074, the compound is very mobile. According to literature cited in Montgomery and Welkom (1990), acrylonitrile can be photo-oxidized. The practical quantitation limit, the guidance concentration, is 2.5 µg/L based on cancer risks (Florida Department of Environmental Regulation, 1989).

One sample out of 29 from the surficial aquifer system in the SFWMD contained possible acrylonitrile. The chemical was not detected in other districts or aquifer systems.

Benzene

Benzene (C_6H_6) is widely utilized by the energy and manufacturing industries. It is an additive in automotive fuels, paints, plastics, and resins. It is one of the most widely used solvents, and is a common contaminant in ground water. It is a common contaminant in plumes from leaky underground gasoline storage tanks. The Henry's Law constant for benzene is $5.5x10^{-3}$ atm mVmol, which categorizes it as highly volatile. Benzene is very mobile in ground water (K_{OC} = 49.0 -1 00). Soil microbes can break down benzene to catechol and other products. The Primary Drinking Water Standard for benzene is 1 µg/L.

Benzene was detected, but has not yet been confirmed, in a number of samples around the state. In the surficial aquifer system eight out of 98 from

the NWFWMD contained possible benzene. One out of 81 from the SWFWMD and 12 out of 575 from the SFWMD also contained possible benzene. In the intermediate aquifer system, three out of 52 samples from SWFWMD and two out of 136 from SFWMD contained possible benzene. Benzene was detected by most districts in the Floridan aquifer system, as well. The occurrences were: one out of 101 (NWFWMD), one out of 302 (SRWMD), six of 161 (SWFWMD) and three of 153 (SFWMD).

Bromodichloromethane

Bromodichloromethane ($CHBrC1_2$) is a component in fire extinguisher fluids and a solvent for fats, waxes, and resins. It is used as a degreaser and flame retardant. It is dense and moderate to highly volatile (H = $2.1x10^{-4}$ to $2.4x10^{-3}$ atm m^3/mol). It is mobile in ground water (K_{OC} = 62). Bromodichloromethane is a trihalomethane, and the Primary Drinking Water Standard for total concentration of trihalomethanes is 100 µg/L.

No bromodichloromethane was detected in the surficial or intermediate aquifer system samples. One sample in 302 from the Floridan aquifer system in the SRWMD and one of 100 in the SWFWMD contained possible bromodichloromethane.

Bromoform

Bromoform (CHBr3) is a dense liquid. It is moderately volatile (H = $5.3\text{-}5.6x10^{-4}$ atm m^3/mol), and is mobile in ground water (K_{OC} = 110 - 280). It is used as a solvent for waxes, greases, and oils and as a component of fire-resistant chemicals. Bromoform is a trihalomethane, and the Primary Drinking Water Standard for total concentration of trihalomethanes is 100 µg/L.

Bromoform was reported from one sample out of 532 from the surficial aquifer system in the SFWMD. It was not reported elsewhere.

Chlorobenzene

Chlorobenzene (C_6H_5Cl) is used in the manufacture of a number of organic chemicals. It is also utilized as a solvent, insecticide, pesticide, and heat transfer agent. Chlorobenzene is highly volatile (H = $3.6\text{-}3.9x10^{-3}$ atm m^3/mol) and moderately mobile to mobile in ground water (K_{OC} = 48 - 330). It can be photodegraded to phenol and chlorophenol under certain circumstances. There is an Environmental Protection Agency Health Advisory on chlorobenzene, and it is organoleptic (it imparts taste or odor problems to water) (Florida Department of Environmental Regulation, 1989). As a result the guidance concentration in Florida is 10 µg/L.

Chlorobenzene was detected in the surficial aquifer system in one sample out of 57 from the SJRWMD and in 16 out of 652 in the SFWMD. It was not detected in the intermediate or Floridan aquifer systems.

Chloroform

Chloroform ($CHCl^3$) is a dense liquid. It is highly volatile (H = $2.9\text{-}3.4x10^{-3}$ atm m^3/mol), and very mobile in ground water (K_{OC} = 44). Chloroform has been shown to be microbially degraded in anaerobic environments to methyl chloride and other products. It is a member of the trihalomethane group, and the Primary Drinking Water Standard for total concentration of trihalomethanes is 100µg/L.

Chloroform was widely detected in the Background Network data set. In the surficial aquifer system, one sample of 98 in the NWFWMD, one of 57 from SJRWMD, and three of 632 from SFWMD contained chloroform. None was detected in the intermediate aquifer system. One sample of 302 from the Floridan aquifer system in the SRWMD and two samples of 160 from the SWFWMD contained probable chloroform.

Chloromethane

Chloromethane or methyl chloride (CH^3Cl) is a highly volatile liquid (H = $6.6\text{-}8.8x10^{-3}$ atm m^3/mol). The K_{OC} value of 25 estimated by Montgomery and Welkom (1990) indicates that chloromethane is very mobile in ground water. U.S. Environmental Protection Agency draft preliminary protective concentration limit data (Florida Department of Environmental Regulation, 1989) have resulted in a guidance concentration of 3,800 µg/L.

Chloromethane was not detected in the surficial or intermediate aquifer system. It was detected in two of 16 samples from the Floridan aquifer system in the SJRWMD.

Dibromochloromethane

Dibromochloromethane ($CHBr_2Cl$) is utilized in the manufacture of fire extinguishing agents and propellants. It has been used as a refrigerant and as a pesticide. It is moderate to highly volatile (H = $9.9x10^4$ to $7.8x10^3$ atm m^3/mol), and mobile in ground water (K_{OC} = 83). It is a member of the trihalomethane group, and the Primary Drinking Water Standard for total concentration of trihalomethanes is 100 µg/L.

Dibromochloromethane was not detected in the surficial or intermediate aquifer systems. It was detected in the Floridan aquifer system in one sample out of 160 from the SWFWMD.

1,2 Dibromoethane

1,2 Dibromoethane is better known as ethylene dibromide or EDB. It has the composition $C_2H_4Br_2$, and has been widely used in the state of Florida as a soil fumigant. It is dense and essentially insoluble in ground water. EDB had been considered immobile. However, EDB was detected in a number of wells in Florida in the 1980's and this apparent mobility made EDB a chemical of major concern. The Drinking Water Standard for EDB is 0.02 ,µg/L.

No EDB was detected in the surficial or intermediate aquifer systems, statewide. Two out of 55 samples from the Floridan aquifer system in SWFWMD had possible EDB.

1,2 Dichlorobenzene

1,2 Dichlorobenzene (o-Dichlorobenzene, $C_6H_4Cl_2$) is moderately dense and highly volatile (H = $1.2\text{-}1.9x10^{-3}$ atm m^3/mol). It has mobilities that are moderate to low in ground water (K_{OC} = 180 - 1,700). The compound has been detected to be biodegraded with a number of possible transformation products. 1,2 Dichlorobenzene is widely used as a solvent for organic compounds and nonferrous metals, and as a fumigant and insecticide, degreaser for hides and wools, metal polish, among others. The compound imparts taste and odor to water and there is a U.S. Environmental Protection Agency Health Advisory for it (Florida Department of Environmental Regulation, 1989). The guidance criterion is 10 µg/L.

Three samples out of 632 from the surficial aquifer system in the SFWMD contained possible 1,2 dichlorobenzene. None of the intermediate aquifer samples contained 1,2 dichlorobenzene. One sample out of 160 from the Floridan aquifer system in the SWFWMD and one out of 175 from the SFWMD contained the compound.

1,3 Dichlorobenzene

1,3 Dichlorobenzene (m-dichlorobenzene, $C_6H_4Cl_2$) is highly volatile (H = $2.63.6x10^{-3}$ atm m^3/mol), and has a mobility that is low to moderately low in ground water (K_{OC} = 170 - 1,700). It is used as a soil fumigant and insecticide, as well as in organic synthesis. The guidance concentration, based on taste and odor problems and a Health Advisory from the Environmental Protection Agency, is 10 ,µg/L (Florida Department of Environmental Regulation, 1989).

Two samples out of 570 from the surficial aquifer system in the SFWMD contained possible 1,3 dichlorobenzene. No samples from the intermedi-

ate or Floridan aquifer systems contained the compound.

1,4 Dichlorobenzene

1,4 Dichlorobenzene (p-1,4 dichlorobenzene, $C_6H_4Cl_2$) is highly volatile (H = 2.7-3.1x10^{-3} atm m3/mol). It can be photodegraded to chlorophenol or phenol. It is moderately mobile in ground water (K_{OC} = 160). 1,4 Dichlorobenzene is utilized as a moth repellent and general insecticide, fumigant, and germicide; soil fumigant; and disinfectant. The Primary Drinking Water Standard is 75 ,µg/L.

Ten samples out of 572 from the surficial aquifer system in the SFWMD contained possible 1,4 dichlorobenzene. One sample out of 52 from the intermediate aquifer system in the SWFWMD and one out of 138 from the SFWMD also contained possible traces of the chemical. One sample of 162 from the Floridan aquifer system in the SWFWMD also contained possible 1,4 dichlorobenzene.

Dichlorodifluoromethane

Dichlorodifluoromethane (Freon-12, CCl_2F_2) is widely utilized as a refrigerant and aerosol propellant. It is also used in plastics and as a low temperature solvent. Dichlorodifluoromethane can occur as either a gas or a liquid, and the liquid is very highly volatile (H = 4.3x10^{-1} to 3 atm m^3/mol). The estimated K_{OC} is 360, which makes it moderately mobile in ground water. The guidance concentration in ground water is 1,400 µg/L, based on the Integrated Risk Information System (Florida Department of Environmental Regulation, 1989).

One sample out of 116 from the Floridan aquifer system in the SJRWMD contained possible dichlorodifluoromethane. Elsewhere, it was not detected.

1,1 Dichloroethane

1,1 Dichloroethane has the formula $C_2H_4Cl_2$. It is highly volatile (H = 4.3-5.9x10^{-3} atm m^3/mol), and slightly mobile (Koc = 30). It is used as an extraction solvent; insecticide and fumigant; preparation for vinyl chloride; finish remover; solvent for plastics, oils, and fats; and other applications. Under anaerobic conditions 1,1 dichloroethane can be microbially converted to vinyl chloride. The guidance concentration is 2,400 µg/L (Florida Department of Environmental Regulation, 1989), based on toxicant profiles prepared by the Center for Biomedical and Toxicological Research at Florida State University.

1,1 Dichloroethane was detected in the surficial aquifer system in the SWFWMD in one sample out of 57. Three samples out of 632 in the SFWMD also may contain the compound. None was detected in the intermediate aquifer system or the Floridan aquifer system.

1,2 Dichloroethane

1,2 Dichloroethane (ethylene dichloride, $C_2H_4Cl_2$) is moderately volatile (H = 9.1-9.8x10^{-4} atm m3/mol). It is very mobile in ground water (K_{OC} = 14 -19). It is used as a vinyl chloride solvent; lead scavenger in certain leaded gasolines; paint and varnish remover; degreaser; wetting and penetrating agent; tobacco flavoring; and as a soil and food fumigant. The Primary Drinking Water standard for 1,2 dichloroethane is 3 µg/L because of its carcinogenicity.

No 1,2 dichloroethane was detected in samples from the surficial or intermediate aquifer systems. One sample out of 116 from the Floridan aquifer system in the SJRWMD and one out of 176 from the SFWMD may have contained 1,2 dichloroethane.

trans-1,2 Dichloroethene

The primary uses of trans-1,2dichloroethene (trans-1,2 dichloroethylene, $C_2H_2Cl_2$) are as solvents for fats, phenols, and other compounds. It is an ingredient in perfumes, and is used as a low- temperature solvent and refrigerant. The compound is highly volatile (H = 5.3x10^{-3} to 0.38 atm m^3/mol) and mobile in ground water (K_{OC} = 59). Transformation in methanogenic (anaerobic) aquifers is to vinyl chloride and other compounds. The guidance concentration is based on organoleptic properties (taste and odor) and recommended protective concentrations suggested by the Center for Biomedical and Toxicological Research at Florida State University. The guidance concentration is 4.2 µg/L (Florida Department of Environmental Regulation, 1989).

Four samples out of 632 from the surficial aquifer system in the SFWMD contained possible trans-1,2 dichloroethene. One sample of 302 from the Floridan aquifer system in the SRWMD also contained the compound. It was not detected elsewhere.

1,2 Dichloropropane

1,2 Dichloropropane ($C_3H_6Cl_2$) is a dense compound. It is highly volatile (H = 2.3-2.9x10^{-3} atm m3/mol), and it is very mobile in ground water (K_{OC} = 27 - 51). It is used as a scavenger in certain leaded gasolines; metal cleaner and degreaser; soil fumigant for nematodes; and a solvent for oils, fats, waxes, and other organics. The guidance concentration is 1 µg/L, which is the practical quantitation limit, based on an Environmental Protection Agency Health Advisory for cancer risks.

Only one sample out of 81 from the surficial aquifer system in the SWFWMD contained possible 1,2 dichloropropane. The chemical was not detected in samples from any other districts or aquifer systems.

Ethylbenzene

Ethylbenzene (C_8H_{10}) is a highly volatile liquid (H = 6.4-6.6x10^{-3} atm m^3/mol). It is mobile to moderately mobile in ground-water systems (K_{OC} = 95 - 260). Ethylbenzene is an additive to gasoline products and a widely used solvent. It is utilized in the manufacture of plastics and other organics. The guidance concentration is 2 µg/L (Florida Department of Environmental Regulation, 1989), which is the practical quantitation limit. The guidance concentration is based on toxicant profiles from the Center for Biomedical and Toxicological Research at Florida State University.

Ethylbenzene was detected in one sample out of 79 from the surficial aquifer system and two out of 48 from the intermediate aquifer system in the SWFWMD. It was also detected in one sample of 151 the Floridan aquifer system in SWFWMD and in one sample of 154 in SFWMD.

Hexachlorobenzene

Hexachlorobenzene (HCB, C_6Cl_6) is used as a seed fungicide and wood preservative. It is highly volatile (H = 1.3-1.7x10^{-3} atm m^3/mol), and, even though there is a wide range of Koc values (360 - 35,000) in the literature (Montgomery and Welkom, 1990), apparently relatively immobile. The guidance concentration is based on the practical quantitation limit and Environmental Protection Agency cancer risk evaluations (Florida Department of Environmental Regulation, 1989). It is set at 10 ~lg/L. Hexachlorobenzene was possibly detected in the surficial aquifer system in one sample out of 79 from the SWFWMD. One of nine samples from the Floridan aquifer system in the SWFWMD also contained hexachlorobenzene.

Methylene chloride

Methylene chloride (dichloromethane or Freon 30; CH_2Cl_2) is a highly volatile, dense liquid. The Henry's Law constant is 2.0-3.2x10^{-3} atm m^3/mol. It is very mobile in ground water (K_{OC} = 8.7). Methylene chloride is a widely used solvent. It is used in paint and varnish removers and as a degreaser and drying agent. It is also used as a fumigant and refrigerant. It has been shown to be converted to methyl chloride, methanol, formic acid, or formaldehyde by hydrolysis and oxidation/reduction reactions. The guidance concentration is based on an Environmental Protection Agency Health Advisory. The guidance concentration is 5 µg/L.

Two surficial aquifer system samples out of 57 in the SJRWMD and one of 81 from the SWFWMD contained possible methylene chloride. No sam-

ples from the intermediate aquifer system were detected to contain methylene chloride. In the Floridan aquifer system, ten of 116 samples from the SJRWMD and one of 160 from the SWFWMD contained methylene chloride.

PCB-1016

PCB-1016 (polychlorinated biphenyl-1016, Arochlor 1016) is a dense liquid used as an insulating fluid in electric condensers and as an additive in high-pressure lubricants. It is volatile (H = 750 atm/mol fraction) and immobile in groundwater systems (K_{OC} = 50,000). The guidance concentration is set at the practical quantitation limit for all polychlorinated biphenyl compounds, which is 0.5 µg/L. The guidance concentration is based on U.S. Environmental Protection Agency Health Advisories.

PCB-1016 was not detected in the surficial or intermediate aquifer systems. One sample of Floridan aquifer system water of two analyzed by the SJRWMD contained possible PCB-1016. Given the low sample size (n = 2) and lack of confirmation by resampling, plus the improbability of PCB-1016 in the Floridan aquifer system, this detection of PCB-1016 is considered to be false.

1,1 ,2,2 Tetrachloroethane

1,1,2,2 Tetrachloroethane ($C_2H_2Cl_4$) is dense and moderately volatile (H = 3.8-4.6x10^{-4} atm m3/mol). It is very mobile to mobile in ground water (K_{OC} = 46-118). It serves as a solvent for chlorinated rubber, and is utilized as a paint, varnish, and rust remover; degreaser, drying agent, and cleaner for metals; denaturant in ethyl alcohol; insecticide and weed killer; fumigant; and herbicide. The guidance concentration is 1 µg/L based on the practical quantitation limit and recommendations of the Center for Biomedical and Toxicological Research at Florida State University.

Two samples out of 57 from the surficial aquifer system in the SJRWMD contained possible 1,1,2,2 tetrachloroethane. It was not detected elsewhere in the surficial, intermediate or Floridan aquifer systems.

1,1,1 Trichloroethane

1,1,1 Trichloroethane has the formula $C_2H_3Cl_3$. It is dense, highly volatile (H = 1.3-1.8x10^{-2} atm m3/mol), and mobile to moderately mobile (K_{OC} = 104-151) in ground water. It is used in organic syntheses and as a solvent for metal cleaning. It is also used in textile processing, as a pesticide, and as an aerosol propellant. The maximum concentration standard is 200 ,ug/L, based on the Primary Drinking Water Standards.

1,1,1 Trichloroethane was detected in three out of 57 surficial aquifer system samples in the SJRWMD. One out of 632 samples from the surficial aquifer system in SFWMD also contained possible 1,1,1 trichloroethane. None of the samples from the intermediate aquifer system contained 1,1,1 trichloroethane. Three samples out of 116 from the Floridan aquifer system in SJRWMD contained the compound.

Tetrachloroethene

Tetrachloroethene (tetrachloroethylene, PERC; C2C14) is a dense liquid used as a cleaning fluid, degreaser and drying agent, solvent for waxes, greases, fats, and oils, and in manufacturing of inks, paint removers, and fluorocarbons. It is very highly volatile (H = 1.3-1.5x102 atm m3/mol). It is also moderately mobile (Koc = 210 - 360). The Primary Drinking Water Standard for tetrachloroethene is 3 llg/L.

Tetrachloroethene was detected in the surficial aquifer system in two districts, NWFWMD ffive of 98 samples) and the SFWMD (four of 632 samples). It was not detected in the intermediate aquifer system. Two districts detected tetrachloroethene in the Floridan aquifer system. These were the SJRWMD (one of 110 samples) and the SWFWMD (three of 160 samples).

Toluene

Toluene (C7H~) is a highly volatile liquid (H = 6.7x10-3 atm m3/mol). It is mobile in ground water (Koc = 115 -151). Toluene is widely used as a solvent for paints and coatings, gums, resins, rubber, oils, and vinyl compounds. It is an adhesive solvent in plastic toys, a diluent in some lacquers and high octane gasolines. It is a common solvent in manufacturing processes. Toluene is common in plumes from leaky underground petroleum tanks. The guidance concentration for toluene is 24 ,ug/L, based on taste and odor concerns and toxicant profiles of the Center for Biomedical and Toxicological Research at Florida State University (Florida Department of Environmental Regulation, 1989).

Toluene was detected in a small number of samples in the Background Network. In the surficial aquifer system, it was detected in the NWFWMD (one of 97 samples), SRWMD (one of 20 samples) and SFWMD (12 of 558 samples). It was detected in the intermediate aquifer system in the SJRWMD (one of 26 samples) and SWFWMD (one of 19 samples). In the Floridan aquifer system, it was detected in the SRWMD (one of 293 samples), SWFWMD (two of 152 samples), and SFWMD (one of 150 samples). The preponderance of single detection events in the district samples suggests that many of these are questionable.

Trichloroethene

Trichloroethene (trichloroethylene, TCE; C_2HCl_3) is a dense liquid. It is highly volatile (H = 9.1x10^{-3} to 1.7x10^{-2} atm m^3/mol). It is mobile in ground water (Koc = 65 - 130). TCE is used as a dry-cleaning fluid; degreasing and drying agent; solvent for fats, oils, and waxes; refrigerant; fumigant; diluents in paints and adhesives; and many other uses. It was previously used as a degreaser in septic-tank cleaners. The Primary Drinking Water Standard for TCE is 3 µg/L.

Trichloroethene was detected in samples from the surficial aquifer system in the SJRWMD (one of 57 samples) and the SFWMD (seven of 632 samples). It was not detected in the intermediate or Floridan aquifer systems.

Trichlorofluoromethane

Trichlorofluoromethane (Freon 11; CCl^3F) is a dense liquid. It is highly volatile (H = 5.8x10^{-3} to 1.1x10^{-1} atm m^3/mol) and mobile in ground water (K_{OC} = 140 - 160). The primary uses of trichlorofluoromethane are as a propellant and refrigerant. It is also used as a solvent and a "blowing agent" in polyurethane foams. The guidance concentration is 2,400 ,µg/L, based on Environmental Protection Agency draft preliminary Protective Concentration Limits (Florida Department of Environmental Regulation, 1989).

Trichlorofluoromethane was detected in the surficial aquifer system in one sample out of 57 from the SJRWMD. It was not detected in the intermediate aquifer system. One Floridan aquifer system sample out of 302 from the SRWMD possibly contained it. Two samples of 116 from the SJRWMD also contained possible trichlorofluoromethane.

Vinyl Chloride

Vinyl chloride (chloroethylene; C_2H_3CI) is normally a gas at earth surface temperatures and pressures. It is available as a liquified compressed gas. It is highly volatile (H = 2.2x10^{-2} to 2.8 atm m^3/mol). Montgomery and Welkom (1990) estimated the Koc to be 2.5, which indicates that it is very mobile in ground water. Vinyl chloride is a degradation product of other chlorinated organics as well as being an ingredient in the manufacture of polyvinyl chloride and other copolymers. It is used as an adhesive for plastics, a refrigerant, and an extraction solvent. The Primary Drinking Water Standard is 1 µg/L.

One sample out of 57 from the surficial aquifer system in the SJRWMD contained possible vinyl chloride. It was not detected in the intermediate aquifer system. Vinyl chloride was detected in samples from the Floridan aquifer system in the SRWMD (one of 302 samples) and SWFWMD (one of 115 samples).

Pesticides

IMPORTANCE

Pesticides are widely used in Florida by agriculture, the government, and individuals to control unwanted plants and insects. Their use is closely regulated by the state. Pesticide use in the past has not necessarily been well regulated and persistent pesticides remain as an environmental concern.

Pesticides are subject to the same physical and chemical factors that control the fixation or movement of Synthetic Organics, and in fact many of the synthetic organics have been used as pesticides. Physical factors that affect pesticide concentrations include advection, dispersion, dilution, and volatization. Chemical controls include sorption, decomposition, and biological transformation. Modern pesticide design and application criteria emphasize minimization of exposure to the pesticide. For example, the pesticide may be approved if it sorbs onto soil mineral or organic matter, thereby minimizing mobility. It may also be approved for use in Florida if it can be shown to be destroyed by photo- oxidation, biological transformation, or some other means of neutralization of hazardous effects.

The Background Network samples in the SWFWMD and SFWMD were scanned for 172 pesticides **(Table 32)**. Samples from the NWFWMD, SRWMD, and SJRWMD were scanned for arsenic only, and no organic pesticide analyses were made in these districts. For details of many of the organic pesticides, see Montgomery and Welkom (1990).

STANDARD OR GUIDANCE CRITERION

Standards and guidance criterion of the common pesticides are listed in Florida Department of Environmental Regulation (1989). Others are subject to the "free from" criteria.

Given the heavy use of pesticides in Florida, the number of samples in which standards or guidance concentrations were exceeded is small.

Table 33 summarizes the distribution of pesticides in the state's aquifer systems. The table reflects the first sampling and detections have not been confirmed by resampling. The median and upper quartiles are at or below detection limits, with one exception, for all aquifer systems.

As might be expected, the maximum concentrations are highest in the surficial aquifer system, where most pesticide application occurs. Maxima in the intermediate aquifer system are lowest of the three aquifer systems, the maxima in the Floridan aquifer system are intermediate between the two. The high concentrations detected in the Floridan aquifer system reflect pesticide application where the Floridan is either unconfined or poorly confined. The individual pesticides that are responsible for these maxima are discussed in detail below.

The proportions of samples that exceed the standards or guidance concentrations are given below:

Surficial aquifer system

NWFWMD	1.2%
SRWMD	0.0%
SJRWMD	0.0%
SWFWMD	18.1 %
SFWMD	0.3%
Statewide	3.2%

Intermediate aquifer system

NWFWMD	0.0%
SRWMD	0.0%
SJRWMD	0.0%
SWFWMD	41.2%
SFWMD	0.0%
Statewide	6.7%

Floridan aquifer system

NWFWMD	0.0%
SRWMD	0.0%
SJRWMD	3.8%
SWFWMD	21.0%
SFWMD	0.0%
Statewide	4.6%

Recall that arsenic is the only pesticide analyzed in samples from the NWFWMD, SRWMD, and SJRWMD. Therefore, the low number of detections in these districts probably reflects sampling as much as any other factor. In the SFWMD, the proportions of samples in which pesticides were detected and detected to exceed standards are low and consistent with the synthetic organic data. The high proportion in the SWFWMD must be studied further. These detections have not been confirmed by resampling. In many cases, these detections include several pesticides in one sample, so the number of wells that are believed to be affected is less than the number of detections.

DISTRIBUTION IN GROUND WATER

As Table 33 indicates, the surficial aquifer system appears to be more highly impacted by pesticide application than the other aquifer systems. The intermediate aquifer system is least affected, largely because it is the most isolated of the three aquifer systems. There is no large scale pattern in the data, except that the maximum concentration was detected in the SFWMD, which is a major cropland area.

The following discussions include only those pesticides detected or suspected in Florida's aquifer systems. Samples reported to contain pesticides, but not confirmed by resampling and analysis are included. This is to indicate the nature of probable pesticide contaminants. Recall that, with the exception of arsenic, only data from the SWFWMD and SFWMD are summarized below.

Aldrin ($C_{12}H_8Cl_6$) is a widely used insecticide and fumigant. Pure Aldrin is a solid. It has a low Henry's Law constant (1.4-5.0x10-6 atm m^3/mol) and is only slightly volatile. In solution, it is moderately mobile, with a K_{OC} of 407. The guidance concentration is set at the practical quantitation limit of 0.05 ,µg/L, based on toxicant profiles from the Center for Biomedical and Toxicological Research at Florida State University (Florida Department of Environmental Regulation, 1989).

Aldrin was detected in seven samples out of 30 from the surficial aquifer system in the SFWMD. One sample out of 30 from the intermediate aquifer system in the SWFWMD contained possible Aldrin. It was not detected in the Floridan aquifer system.

Unlike the other analytes discussed in this section, arsenic is not an organic compound, although it is often formulated into organics. Some characteristic arsenic-bearing compounds used as pesticides are listed in Table 34. Arsenic occurs in two valence states (As^{5+} and As^{3+}), which combine with oxygen to form arsenates (AsO_4^{3+}) and arsenites(AsO_2^-). According to Hem (1985), the monovalent arsenate anion ($H_2AsO_4^-$) predominates at pH values of 3 to 7 and positive Eh's. At pH 7 to 11 $HAsO_{42-}$ predominates. Under mildly reducing conditions arsenite ion ($HAsO_2^0$) forms. Arsenates sorb or co-precipitate with ferric hydroxides and metal sulfides. Arsenic compounds are involved in biological transformations, including methylation. Dimethyl arsenic and methyl arsonic acids [$(CH_3)_2AsOOH$ and $CH_3AsO(OH)_2$, respectively] have been synthesized by microbial methylation.

Given the above data from Hem (1985), it appears that both siliciclastic and carbonate aquifers may have conditions conducive for aqueous transport of arsenic compounds. Organic-rich waters may be characterized by methylation and transport as an organic complex.

In the 1920's there was a statewide infestation of the Texas tick. Cattle ranchers were required to dip their cattle to control the tick. Dipping was done in thousands of unlined pits filled with arsenic solutions as pesticides. The locations of most of these pits have been lost. Today, arsenic remains in soils and may contaminate the aquifer systems. Environmental audits are turning these contaminated sites up, and today's land owners will have to clean up the sites.

Arsenic is highly toxic, and is regulated under the Primary Drinking Water Standards at a maximum concentration limit of 50 µg/L. As indicated by **Table 33**, arsenic was detected in the surficial aquifer system. One sample out of 84 from the surficial aquifer system in NWFWMD and one surficial aquifer system sample of 324 in the SFWMD contained possible arsenic. The single sample from the SFWMD containing 1,100 µg/L is by far the highest concentration detected in the data set. This sample is from a well installed to monitor a closed landfill. Therefore, the sample may not represent true background conditions inthe area. Two samples out of 53 from the Floridan aquifer system in the SJRWMD also contained possible arsenic.

a-BHC

α-BHC (benzene hexachloride-α−isomer, α-Lindane, α-hexachloro-cyclohexane; $C_6H_6Cl_6$) is not produced in the U.S. and its sale is not allowed (Montgomery and Welkom, 1990). It was used as an insecticide in the past, however. α-BHC is a solid. It is slightly volatile in water (H = $5.3x10^{-6}$ atm m^3/mol) and mobile (K_{OC} = 1,900). α-BHC is subject to microbial decomposition in aerobic and anaerobic conditions (Montgomery and Welkom, 1990), although it is slow to react. The guidance concentration is set at the practical quantitation limit of 0.05 ,µg/L due to U.S. Environmental Protection Agency recommendations to minimize cancer risks (Florida Department of Environmental Regulation, 1989).

α-BHC was only detected in the surficial aquifer system in the SFWMD. There, one sample out of 29 contained possible traces of the insecticide.

b-BHC

β-BHC (β-Lindane, β-hexachloro-cyclohexane; C6H6C16) is a solid utilized as an insecticide. β-BHC has low volatility in water (H = $2.3x10^{-7}$ atm m^3/mol). The chemical exhibits low mobility in aquifers, as well. The K_{OC} ranges from 2,100 to 3,600. The guidance concentration is set at the practical quantitation limit of 0.05 llg/L due to U.S. Environmental Protection Agency recommendations to minimize cancer risks (Florida Department of Environmental Regulation, 1989). β-BHC was detected in one of 29 surficial aquifer system samples in the SFWMD.

2,4-D

2,4-Dichlorophenoxyacetic acid, or 2,4-D, is a synthetic auxin, or plant hormone-like compound, used as a selective weed killer. It is slightly mobile in ground water. 2,4-D is regulated by the Primary Drinking Water Standards at 100 llg/L (Florida Department of Environmental Regulation, 1989). Two samples out of 58 from the surficial aquifer system and four of 138 from the Floridan aquifer system in the SWFWMD possibly contained 2,4-D.

4,4 '-DDE

1, 1 '(Dichloroethenylidene)bis(4-chlorobenzene), or 4,4'-DDE ($C_{14}H_8Cl_4$) is a solid utilized as an insecticide. It is also a transformation product of DDT. In water, 4,4'-DDE is slightly volatile (H = $2.3x10^{-5}$ atm m^3/mol). It is immobile in ground water (K_{OC} = 240,000 -1,000,000). It may degrade in water, and it can be photo-oxidized in ultraviolet light. The guidance concentration is the minimum detection level (0.01 µg/L; Florida Department of Environmental Regulation, 1989).

One out of 29 surficial aquifer system samples from the SFWMD contained possible 4,4'-DDE. Two Floridan aquifer system samples out of 134 from the SWFWMD may also have contained the pesticide.

4,4'-DDT

1 , 1'-(2 ,2,2-Trichloroethylidene)bis[4-chlorobenzene] or 4,4'-DDT ($C_{14}H_9Cl_5$) was formerly used throughout the world as an insecticide. Use in the U.S. is now prohibited. It is moderately volatile in water (H = 3.8-$4.9x10^{-5}$ atm m^3/mol). It is immobile in ground water (K_{OC} = 140,000-1,800,000). 4,4'- DDT can be transformed aerobically and anaerobically to DDD, DDE and other metabolites. The guidance concentration is 0.1 µg/L, based on the practical quantitation limit and Environmental Protection Agency recommendations to minimize cancer risks (Florida Department of Environmental Regulation, 1989). One sample out of 134 from the Floridan aquifer system in the SWFWMD contained possible 4,4'-DDT.

Dieldrin

Dieldrin ($C_{12}H_6Cl_6O$) is an insecticide. It has a slight to low volatility in water (H = $3.2x10^{-5}$ to $2x10^{-7}$ atm m^3/mol). It is slightly mobile in ground water

(K_{OC} = 12,000 - 35,000). The guidance concentration is 0.05 µg/L, based on the practical quantitation limit and Environmental Protection Agency Health Advisories (Florida Department of Environmental Regulation, 1989). One surficial aquifer system sample out of 29 from the SFWMD, and one out of 134 Floridan aquifer system samples from the SWFWMD contained possible dieldrin. Endrin

Endrin ($C_{12}H_8Cl_6O$) is an insecticide that is slightly volatile in water (H = $5.0x10^{-7}$ atm m^3/mol). It has low mobility in ground water (Koc =1,900). Endrin is microbially degraded. The Primary Drinking Water Standard for Endrin is 0.2 µg/L (Florida Department of Environmental Regulation, 1989). Only one sample out of 29 surficial aquifer system samples from the SFWMD contained possible Endrin.

Methoxychlor

Methoxychlor ($C_{16}H_{15}Cl_3O_2$) is used to control mosquito larvae and house flies. It is utilized as a stock dip to control ectoparasites. It is immobile in ground water (K_{OC} = 79,000 - 89,000). Methoxychlor is microbially transformed in aerobic and anaerobic environments. It is also subject to hydrolysis. The Primary Drinking Water Standard for methoxychlor is 100 µg/L (Florida Department of Environmental Regulation, 1989). Two samples out of 29 from the surficial aquifer system were detected to contain methoxychlor in the SFWMD.

Mirex (cyclodiene group) was used for fire ant control. It is no longer used since one of its breakdown products is dioxin. The guidance concentration for Mirex is 3.5 µg/L, based on toxicant profiles from the Center for Biomedical and Toxicological Research at Florida State University (Florida Department of Environmental Regulation, 1989). One sample out of 134 from the Floridan aquifer system in the SWFWMD contained Mirex.

HYDROCHEMICAL FACIES AND PREDOMINANT WATER TYPES

Introduction

As ground water moves along a flow path, it encounters different rock types with different mineral assemblages and porosity/permeability configurations. The residence time of the water in contact with the rock varies with the nature of the rock porosity, flow velocity, tortuosity of the flow path, and hydraulic gradient. The water may also come in contact and mix with sea water, connate water, or water that has a different chemistry from following a different flow path. All of these events affect the chemistry of the water. The result is that the water can be classified on the basis of its chemical composition.

For the purposes of this report, the water-type classification that is used is modified from Davis and DeWiest (1966). They utilized two standard trilinear diagrams - one for the dominant cations and the other for dominant anions in water. Each diagram was subdivided into fields that represent different proportions of the ions. These diagrams are represented on the predominant water type maps that follow (Figures 56-58). **Table 35** explains the proportions of constituents in each field. The proportions are based on conversion of the concentrations to milliequivalents per liter (meq). The cation proportions are based on the following equation

$$X_{c,\%} + \frac{X_{c,\,meq}}{Na_{meq} + K_{meq} + Ca_{meq} + Mg_{meq}} \bullet 100 \qquad (20)$$

where $X_{c,\%}$ is the equivalent percent of cation X. Cation X includes the following cations: sodium plus potassium, calcium, or magnesium. $X_{c,\,meq}$ is the equivalent concentration of X, and Na_{meq}, K_{meq}, Ca_{meq} and Mg_{meq} are the equivalent concentrations of the major cations. The proportions of anions are calculated in the same fashion. Anion groupings are: (1) bicarbonate *plus* carbonate, (2) sulfate, and (3) chloride.

The arrangement of ions on the trilinear diagrams is based on logical combinations expected in ground-water chemistry. For example, sodium and chloride are paired because of their common association in marine aerosols and sea water and calcium and bicarbonate are paired because they are common weathering products of limestones and a number of other rock types.

The predominant water type is designated by the dominant ions present. A water mass that is predominantly calcium and magnesium (area B on the trilinear cation diagram) and bicarbonate (area 1 on the anion trilinear diagram), the water is said to be a calcium-magnesium-bicarbonate water mass (or Ca-Mg-HCO_3 water type; B1 symbol on the maps).

Once the predominant water type is identified for an aquifer system, hydrochemical facies can be attributed to areas within that aquifer system that can be characterized by a single predominant water type or by a specific mixture of water types. Hydrochemical facies are interpretational, and result from assigning a common origin, history, or composition to a volume of water within an aquifer system. For example, if a large volume of water within the Floridan aquifer system has a common calcium-magnesium-bicarbonate composition, one could interpret that water mass to reflect a facies controlled by dissolution of dolomite.

In the following discussions, predominant water types are attributed to hydrochemical facies where possible. The symbol used on the predominant water type maps is given as well.

Predominant Water Types

Some water types are highly unlikely and are not discussed below. These include magnesium-bicarbonate, magnesium-chloride, and magnesium-sulfate waters. Also, many samples from the Background Network have complex histories and thoroughly mixed compositions. A number of samples, for example, have a mixed composition (G7), where all major ions are present in subequal proportions. These samples are characteristically transitional between better defined water types, and they are not discussed below.

Calcium-Bicarbonate (A1) - Calcium-bicarbonate waters are among the most widespread in Florida. They are derived from dissolution of calcite or aragonite in limestone and shelly siliciclastic sediments.

Calcium-Magnesium-Bicarbonate (B1) -Calcium-magnesium-bicarbonate waters are either derived by dissolution of dolomite in dolomitic limestones and dolostones or mixing of magnesium-rich waters derived from clay weathering in the Hawthorn Group with calcium-bicarbonate waters. Facies attribution is largely based on interpretation of local geology and hydrology. If the water is from a dolomitic aquifer, it is attributed to a facies characterized by dolomite weathering. If it is near an area of active weathering of the Hawthorn Group sediments or if the intermediate confining zones are highly leaky, the facies is said to reflect weathering of the clays.

Calcium-Sulfate (A3), Calcium-Magnesium-Sulfate (B3), and Calcium-Magnesium-Bicarbonate-Sulfate (B2), Calcium-sulfate, calcium-magnesium-sulfate, and calcium-magnesium-bicarbonate-sulfate waters are characteristically derived by interaction with the gypsum and anhydrite at the base of the Floridan aquifer system. The mixed waters result from mixing of calcium or calcium-magnesium- bicarbonate waters with calcium-sulfate waters derived from dissolution of the gypsum.

Sodium-Chloride (E5) - Sodium-chloride waters are found in two environments. Marine aerosol dominated waters in the surficial aquifer system may have a sodium-chloride composition if little or no reaction with calcite or aragonite has occurred. Also, Na-Cl water masses are common in the salt- water transition zone.

Sodium-Bicarbonate (E1 or E6), Calcium-Chloride (A5 or A6), and Calcium-Magnesium-Chloride (B5 or B6) - When cation exchange (see the **Calcium** and **Sodium** sections) occurs sodium-bicarbonate and calcium-chloride waters may result. Sodium-bicarbonate waters are most common in Florida. In areas where Na-HCO_3 waters predominate, calcium has exchanged with sodium on the clays. This phenomenon develops when sodium- saturated marine clays are bathed in calcium- bicarbonate waters. Calcium-chloride or calcium- magnesium-chloride waters are less common. They result from salt-water intrusion into aquifer systems that contain calcium or magnesium- saturated clays.

Sodium-Sulfate (E4) - Sodium-sulfate waters have been found in the surficial aquifer system in central Florida (Hutchinson, 1978). These waters are difficult to explain, but may result from addition of sulfate through oxidation of organics or pyrite to a sodium-rich water. Upchurch et al. (1991) found similar water types near phosphogypsum waste disposal areas in Polk County.

Uses of Predominant Water Type and Hydrochemical Facies Maps

The maps that follow can be used in a number of ways, largely related to predicting the outcomes of water-use options. Grouping the predominant water type data into areally extensive hydrochemical facies allows interpolation between data points and prediction of background water quality throughout the state. The following are just some of the benefits from hydrochemical facies analysis.

Water History - Since the composition of the water reflects the sequence of rocks and sediments through which it has passed and any anthropogenic modifications that have occurred, the water composition reflects, in a broad way, the history of the water. While this history is largely of academic interest, it can allow deduction of flow paths, vulnerability of aquifer systems to contamination, and potentials for degradation by changing the flow paths, especially through upconing .

Buffering Capacity - Buffering capacity is the ability of water to neutralize acids or bases. Within the aquifer systems, buffering capacity involves interactions with rock as well as water. The buffering reactions have been discussed previously (reactions 1-7). When the water is removed from the aquifer system, its buffering capacity depends only on reactions within the water.

Calcium- and calcium-magnesium-bicarbonate water masses have relatively high buffering capacities. In other words, application of acids and bases will result in some degree of neutralization. Sodium-chloride waters in siliciclastic aquifers have little buffering capacity and cannot tolerate addition of acids or bases. As an example of the application of the principle, consider the acid rain problem. Lakes fed by buffered (calcium- bicarbonate) ground waters have much higher tolerances for acidic precipitation than do lakes fed by sodium-chloride waters in siliciclastic soils. Similar arguments can be made for waste disposal impacts on aquifer systems.

Water Use and Treatment Requirements - Development of ground-water resources for water supplies requires considerable sensitivity to the constraints placed on that development by water quality. The state of Florida has developed a ground-water classification system that reserves water utilization to its highest uses. G-I and G-II designations are utilized for waters that are potable and can be used for water-supply aquifer systems[27]. The designations G-III and G-IV[27] are reserved for aquifer systems that contain non-potable water that is more compatible with land uses that may degrade G-I and G-II waters. While designation of ground water by this scheme

requires knowledge of the TDS concentration, number of aquifer systems, and degree of confinement, knowledge of the hydrochemical facies can be of assistance as well.

In addition, the chemical composition of the water will dictate treatment alternatives. Calcium- and calcium-magnesium-bicarbonate waters are likely to be hard and require softening to prevent boiler scale, taste, and soap effectiveness problems. Low TDS, sodium-chloride waters are likely to be soft and require little treatment other than color removal and disinfection. Sulfate-rich waters may have odor and taste problems from included sulfides.

Finally, use of underground injection wells for disposal of storm runoff and waste water is widespread in Florida (Hull and Yurewicz, 1979; Kimrey and Fayard, 1982; Schiner and German, 1983; Hickey and Veccioli, 1986; Bradner, 1991). Knowledge of the general water type into which injection occurs will allow prediction of reactions between the host and injection waters. Also, treated drinking water is stored for later retrieval (aquifer storage and recovery or ASR) in several locations throughout the state (Merritt et al., 1983). The facies maps can be used to identify injection zones and predict reactions between host and injection waters. Recovery of brackish waters for treatment by reverse osmosis is becoming common in coastal regions of the state. The maps can assist in locating potential supply wells and the level of treatment necessary for conversion to potable water.

Ion Exchange - Aquifer systems in many areas of the state can be shown to have waters that have been affected by ion exchange. These areas may be useful for certain types of waste disposal. For example, it is possible that movement of trace metals can be more effectively retarded in these areas. While considerable additional information is necessary, the maps can assist in locating these areas.

One engineering aspect of ion exchange has been extensively studied elsewhere in the country, but has not been widely applied in Florida is the Sodium Absorption Ratio. Smectitic clays, such as are common in the surficial and intermediate aquifer systems, have the ability to expand and contract (swell and shrink) depending on the chemical composition of the surrounding water. The clays swell in sodium-rich waters and shrink in calcium- or magnesium-rich solutions. The ability of clays to shrink or swell is predicted by the Sodium Absorption Ratio (SAR)

$$SAR = \frac{Na_{meq}}{\sqrt{\frac{Ca_{meq} + Mg_{meq}}{2}}} \qquad (21)$$

where Na_{meq}, Ca_{meq}, and Mg_{meq} are the concentrations in milliequivalents per liter. If the SAR > 8-10, smectites can be expected to swell (Bouwer, 1978). It can be assumed that the clays are in equilibrium with the surrounding water. Changing the quality of water can induce shrinking or swelling of the clays. For example, if the clays are calcium- or magnesium-saturated and high sodium water is introduced, swelling will occur. This could occur where septic-tank effluent, landfill leachate, or other high sodium waters are introduced to the aquifer systems. Sodium- saturated clays that are bathed in calcium- or magnesium-rich water can shrink. This can happen when sodium-saturated clays in siliciclastic soils and aquifers are flooded with calcium-rich, Floridan aquifer system water, such as might occur when lawns are irrigated or wastewater is applied. Shrinking or swelling of clays could, therefore, cause failures of landfill liners, foundations, and other structures. It can also dramatically change the permeability of the soil or aquifer system and reduce its effectiveness as a water-supply or waste-disposal medium.

Water Types in Florida Aquifer Systems

SURFICIAL AQUIFER SYSTEM

There is a general change in predominant water type from north to south. In the north, the surficial aquifer system is largely siliciclastic, and shell content is limited to coastal areas. Therefore, water types are mixed, with sodium-chloride waters near the coast as a result of the coastal transition zone and inland as a result of precipitation of marine aerosols. To the south, the carbonate content of the aquifer system increases and the water types become less variable and dominated by calcium-carbonate water types.

Water from the Sand and Gravel Aquifer in western NWFWMD (Figure 56a) is predominantly sodium-chloride in composition. There is calcium-bicarbonate and sodium-bicarbonate water mixed with it, indicating a complicated history, different well depths, and minor carbonate sources. The sodium-chloride water results from the coastal transition zone and marine aerosols. There is insufficient data to speculate on predominant water type in central and coastal portions of the district. However, sodium-chloride and calcium-sulfate waters do occur along the coast. There is a region centered on Jackson and Gadsden Counties where calcium-bicarbonate water predominates. This region is characterized by exposures of limestones of the Floridan aquifer system, and surficial aquifer system waters undoubtedly reflect this influence.

The surficial aquifer system is poorly developed in the SRWMD (Figure 56b). Waters are largely calcium-bicarbonate due to influences of Floridan aquifer system water. Magnesium- bicarbonate water reflects the magnesium-rich clays of the Hawthorn Group, and sodium- bicarbonate waters reflect ion exchange. In general, surficial aquifer system waters in the district are calcium-bicarbonate facies derived from the influences of underlying intermediate and Floridan aquifer systems.

The surficial aquifer system in the SJRWMD (Figure 56c) includes some regions of mixed water type inland. There is a large area characterized by calcium-bicarbonate facies along the St. Johns River. This may reflect the upconing described by Leve (1983), or shelly horizons in the aquifer system. Elsewhere sodium-chloride facies predominate along the river. There is a coastal sodium-chloride facies, with large re-entrants that probably reflect connate sea water rather that active intrusion.

The surficial aquifer system is well developed in the southern third of the SWFWMD, and it is spotty in the middle third (Figure 56d). It is poorly developed to not present in the northern third. In the central third of the district, the surficial aquifer system is largely quartz sand. The water types present are mixed, with a slight predominance of calcium-bicarbonate over calcium-sulfate and sodium-chloride. Much of the calcium- bicarbonate water is Floridan water introduced by irrigation. The sodium-chloride water is a result of marine aerosols. The calcium-sulfate water is problematical. Water near agrichemical plants is likely to be either sodium-sulfate or calcium-sulfate in composition. Water some distance from the chemical plants may reflect atmospheric fallout, sulfates from oxidation of peats and pyrite, or other causes. Waters in the southern third of the district are predominately calcium - magnesium-bicarbonate inland and sodium-chloride near the coast. The surficial aquifer system is shelly which results in calcium-bicarbonate waters. Upconing and irrigation pumpage in many areas of the southern third result in introduction of deeper, sulfate- and chloride-rich water.

Figure 56e reflects the surficial aquifer system water types and facies in the SFWMD. The Biscayne Aquifer is composed of predominantly calcite and aragonite. The resulting facies is a calcium-bicarbonate water. The salt-water intrusion near Miami (northern Dade County) is well shown by a re-entrant of sodium-chloride water. On the west coast the waters are derived from shelly sands and limestones and belong to the calcium-bicarbonate facies. Local sodium- chloride in Collier County may reflect upconing of connate water. The Kissimmee River corridor is predominantly characterized by calcium- bicarbonate water. The scattered areas of a sodium-

chloride facies are an artifact of the depth of completion of the surficial aquifer wells. The wells in the Kissimmee corridor that exhibit a sodium-chloride facies contain low ionic strength waters recharged by precipitation.

INTERMEDIATE AQUIFER SYSTEM

Waters of the intermediate aquifer system in the NWFWMD (Figure 57a) are predominantly calcium-bicarbonate type. This reflects the carbonates in the intermediate aquifer system and the absence of magnesium suggests that calcite dissolution controls water quality. Water from the intermediate aquifer system throughout the entire eastern half of the district area can be said to belong to a single calcium-bicarbonate facies that originates from limestone dissolution.

The intermediate aquifer system is very limited in extent in the SRWMD (Figure 57b). Where it is present, the predominant water type is calcium- or calcium-magnesium-bicarbonate, which reflects the dolostones and limestones of the aquifer system.

There is not much data on the intermediate aquifer system in the SJRWMD (Figure 57c). Where data are present, there is an inland calcium- bicarbonate facies and a coastal sodium-chloride facies.

The intermediate aquifer system is extensive and utilized in southern SWFWMD (Figure 57d). It is spotty to non-existent in the central third of the district and absent in the northern portion. Waters are characteristically calcium-magnesium- bicarbonate due to the dolostone and magnesium- saturated clays of the Hawthorn Group. To the south and west calcium-bicarbonate-sulfate and calcium-sulfate facies develop as a result of addition of sulfate during upward flow on the coastal transition zone. The outer coastal transition zone is characterized by sodium-chloride facies derived from sea water.

The intermediate aquifer system is well developed on the west coast of the SFWMD (Figure 57e). Elsewhere there is no information as to facies or water types. The intermediate aquifer system in Lee County includes sandstone cemented by calcite and limestone and dolostone aquifers. There is considerable clay in the aquifer system. The facies represented show the "chromatographic" effect in a different way. There is less sulfate than in the SWFWMD (Figure 57d, 58d), so the sulfate-rich belt is absent. There is, however, a sodium-bicarbonate belt derived by ion exchange. The clays of the aquifer system are sodium-rich and, as calcium-rich water upwells along the inner transition zone, exchange releases the sodium and fixes the calcium. There is a re- entrant along the Caloosahatchee River.

FLORIDAN AQUIFER SYSTEM

Waters in the Floridan aquifer system of the NWFWMD (Figure 58a) can be subdivided into three facies. The majority of the district is characterized by calcium-bicarbonate waters that reflect dissolution of aquifer calcite. Scattered magnesium-bicarbonate water masses reflect dissolution of dolomite. Near the coastal transition zone the predominant water types are mixed. Sodium-chloride and sodium-bicarbonate waters predominate. The sodium-chloride waters result from sea water on the transition zone. The sodium-bicarbonate waters are a result of ion exchange. Where the samples are predominantly sodium-chloride type, the resulting facies is a sea- water or sodium-chloride facies. Where several water types exist because of ion exchange and local calcium-bicarbonate waters, a mixed facies results. Near Gulf County there is a magnesium- bicarbonate facies, which reflects magnesium enrichment, probably from magnesium-rich clays.

The SRWMD can be subdivided into three facies. Most of the district (Figure 58b) is dominated by calcium-bicarbonate water. Local calcium-magnesium-bicarbonate samples reflect dissolution of dolomite or additions of magnesium from the overlying Hawthorn. Most of the facies is characterized, however, by limestone dissolution. Near the coast there is a sodium-chloride facies, which reflects the coastal transition zone. In central Taylor County there is a calcium- magnesium-bicarbonate facies which reflects extensive dolomitization in the Floridan aquifer system.

Figure 58c shows the facies and predominant water types for samples from the Floridan aquifer system in the SJRWMD. There are large re-entrants in the sodium-chloride facies near the coast. These reflect connate waters and modern intrusion. Scattered sodium-bicarbonate samples indicate ion exchange. The St. Johns River region includes two areas where the sodium-chloride facies exists. These reflect upconing as described by Leve (1983).

The Floridan aquifer system in the SWFWMD (Figure 58d) is characterized by three facies. Inland the water is calcium-magnesium- bicarbonate from dissolution of dolomite and calcite in the aquifer system and magnesium from the Hawthorn Group clays. Along the coast there is a sodium-chloride facies that reflects the coastal transition zone. In between, there is a calcium-sulfate facies that reflects upward flow of sulfate-rich water along the inner transition zone. This is an excellent example of the "chromatographic" effect produced by upwelling of deeper waters along the coasts of Florida. The inner margin of the transition zone is sulfate rich because of dissolution of gypsum and anhydrite at depth in the aquifer system. The outer belt is sodium- chloride-rich due to mixing with sea water.

There are no data from the Floridan aquifer system in most of the SFWMD (Figure 58e). Samples from the west coast, in Lee County, suggest a sodium-chloride facies as a result of poor flushing and/or salt-water intrusion. The northern and central Kissimmee River corridor is characterized by calcium-bicarbonate waters, while the southern portion is characterized by calcium- sulfate and the sodium-chloride facies. This is the extension of the "chromatographic" belts discussed in the previous paragraph. The calcium-sulfate facies is the inner half of the transition zone, while the sodium-chloride facies is the outer portion. The sodium-chloride facies persist into the Everglades because of little of no flushing of connate waters.

ENDNOTES

[1] In order to maintain electrical neutrality of water, the sum of negative charges on anions must equal the sum of all positive charges on cations. The samples described in this report were not filtered prior to analysis for metals. Consequently, some of the analyses had excess cationic constituents because particulates were dissolved during sample preservation. In other words, the analyses do not reflect electrical neutrality, and the number of positive charges exceeds negative. The ion-balance criterion for validating the analytical results of a sample is based on the requirement of electrical neutrality. In order to accept an analysis for this report and the Background Network database, the charge-balance error cannot be more that 30%.

[2] The nomenclature used in this report follows that of the Southeastern Geological Society's (SEGS) Ad Hoc Committee on Florida Hydrostratigraphic Unit Definition (1986). When a local, named hydrostratigraphic horizon is discussed, the unit is called an aquifer (e.g., Biscayne Aquifer, Sand and Gravel Aquifer). Major, statewide aquifers, especially those which contain several different aquifer horizons, are termed aquifer systems (e.g., surficial aquifer system, intermediate aquifer system)." In this context the term facies is used in the same fashion as in stratigraphy. Facies ffrom the Latin for face or appearance of a object) refers to entities with similar attributes which can be used to identify and distinguish them. Thus, hydrochemical facies represent water masses with similar chemical compositions and origins.

[3] For convenience, the district names are abbreviated in tables and text as follows: Northwest Florida Water Management District (NWFWMD), Suwannee River Water Management District (SRWMD), St. Johns River Water Management District (SJRWMD), Southwest Florida Water Management District (SWFWMD), and South Florida Water Management District (SFWMD).

[4] pH is a measure of the degree of acidity of waters. Neutral water has a pH of 7, acid waters have pH values <7, and basics, or alkaline, waters have a pH >7. The pH is defined as pH = $-\log^{10} a_H+$, where a_H+ is the activity (thermodynamic concentration) of hydrogen ion. Therefore, a change in concentration of the hydrogen ions by a factor of 1 0 results in a change in pH by a factor of 1.

[5] The vadose zone is the unsaturated zone above the water table. The capillary zone is the partially wetted zone just above the water table that results from the interaction of surface tension of water and soil or rock materials. The phreatic zone is the water-saturated soil or rock below the water table or the confining beds of a confined aquifer.

[6] Cations have net positive charges, while anions have negative charges.

[7] The Pious Museum at the University of South Florida, Geology Department, has gypsum (selenite) rosettes in its collection from the Hawthorn Group in northern St. Petersburg (Pinellas County) and chalcedonic casts of selenite rosettes from Tampa (Hillsborough County) and New Port Richey (Pasco County). Single and twinned gypsum crystals from near Ocala (Marion County) are also in the collection.

[8] Siliciclastic sediments are sediments that consist of quartz, silicate minerals and silicate rock fragments that have been mechanically transported. Characteristic siliciclastic sediment types include quartz sand and clay beds.

[9] Chemical maturation is a term that reflects the changes in chemical composition along a flow path. These changes typically include increases in total dissolved solids content and changes in specific chemical composition

[10] The salt-water/fresh-water transition zone is the zone of mixing of discharging fresh water with salty water near the coast or at the base of the aquifer system. This broad zone is sometimes called the salt-water interface, although it is a diffuse zone, not an interface. For simplicity, the salt-water/fresh-water transition zone will henceforth be called the "transition zone".

[11] In this context the term facies is used in the same fashion as in stratigraphy. Facies (from the Latin for face or appearance of an object) refers to entities with similar attributes which can be used to identify and distinguish them. Thus, hydrochemical facies represent water masses with similar chemical compositions and origins.

[12] "Sand crystal" are crystal of calcite that have grown in the pore space of a sand matrix and include the sand grains in their original depositional fabric within the body of the crystal. The crystal lattice is typically distorted in sand crystals, and crystal faces are convex. In this report, the term sand crystal is used in a more loose sense to include calcite crystals that have grown around and included any pre-existing material (quartz sand and silt-sized dolomite).

[13] Milliequivalents per liter (meq/L) is a measure of charge concentration in water (Hem, 1985). Milligrams per liter concentrations are divided by combining the weights of the appropriate ions to obtain milliequivalents per liter. Conversion tables are provided in Hem (1985). Calcium carbonate alkalinity is the carbonate alkalinity recalculated as if it were calcium carbonate. To convert mg/L bicarbonate to mg/L calcium carbonate, multiply the concentration by 0.8202. One meq/L is equal to 0.02 times mg/L as $CaC0_3$ (Hem, 1985).

[14] Strictly speaking, connate water is water of deposition. That is, it is water trapped in sediments at the time they were deposited. Since the Floridan Platform has been repeatedly inundated by marine transgressions during the late Tertiary and Quaternary, one cannot rule out the possibility of sea water trapped in the aquifer system as a result of more recent inundations. Therefore, connate water is herein defined as sea water trapped in the aquifer system as a result of any prior transgression.

[15] Hydraulic potentials represent the driving forces that cause water to circulate in an aquifer system. Their spatial distributions are represented by potentiometric-surface maps. Water tends to flow from areas of high potential (high elevations on the potentiometric surface map) to low. Potentials are low in south Florida, and there isn't a nearby high to force circulation and flush the aquifer systems.

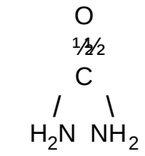
[16] Eutrophication is over enrichment of a water body with food. An eutrophic water body is characterized by over abundance of autotrophs (green plants, such as algae). Plant and animal diversity are limited due to loss of oxygen as the plant material decays and to imbalances in the species and abundances of elements of the food chain.

[17] Limiting nutrients are those nutrients that are in shortest supply and, therefore, inhibit primary production and over population in a water body.

[18] Mineral names are those presently accepted by the International Mineralogical Association Commission on New Minerals and Mineral Names (Fleischer, 1987). Names in quotes have been discredited, but are widely used within the phosphate industry.

[19] The combination of $N0_3$ and $N0_2^-$ is collectively termed NO_x in this report.

[20] Urea is an excretory product manufactured in the livers of animals. It is the primary excretory product of terrestrial animals and the excretory product of metabolism of ammonium, amino acids, and proteins. The structure of urea is



[21] Methemoglobin (ferrihemoglobin) is the equivalent of hemoglobin with the exception that the iron is oxidized to the ferric state. Methemoglobin is, therefore, incapable of carrying oxygen in the circulatory system.

[22] When a chemical system is capable of supporting chemical oxidation, it is said to be aerobic and assumed to contain an available source of oxygen. In reality, oxidation is possible at reduction/oxidation (Eh) potentials as low as approximately -200 mV. Below -200mV, chemical reduction occurs, oxygen sources are absent, and the system is said to be anaerobic.

[23] Chemical complexing includes the binding of dissolved anions or cations into a soluble molecule. Complexing occurs in waters with high total dissolved solids contents or in waters with humic substances. An example of an inorganic complex is $CaS0_4°$, which is present in high sulfate and TDS waters. This dissolved compound removes calcium and sulfate from availability to react with rock and other chemicals. An example of an organic complex is the formation of lead-humic acid pairs. In basic solutions, this complex is soluble and can transport lead rather that allowing it to sorb or precipitate.

[24] This is especially true if the sample also has high pH, alkalinity (especially as CO_3^{2-}), or high potassium.

[25] The Practical Quantitation Limit (PQL) is the minimum limit of detection of a chemical that can be expected from a laboratory under routine analytical conditions. The U.S. Environmental Protection Agency has the PQL to be five times the minimum detection limit.

[26] Most of the detections of synthetic organics and pesticides discussed herein have not been confirmed by re-sampling. The term "detected" is used to indicate the uncertainty present as to the presence of these compounds.

[27] G-I ground water is intended for potable uses and single source (the only available) aquifers. TDS is less than 3,000 mg/L, and Primary and Secondary Drinking Water Standards apply. Zones of discharge are restricted to domestic waste water and storm-water discharges, and are limited to the lesser of 100 ft. or the property line.

G-II ground water is also reserved for potable uses, but the designation is given to areas where multiple, potable water supply aquifers exist. TDS is less than 10,000 mg/L Primary and Secondary Drinking Water Standards apply, and zones of discharge are restricted to the lesser of the property line or 100 ft., unless discharge is beneficial to the aquifer.

G-III ground water is not potable, with TDS concentrations greater than 10,000 mg/L. The designation is given to unconfined aquifers, and the zones of discharge are the same as G-II.

G-IV ground water is reserved for confined, non-potable aquifers. TDS is greater than 10,000 mg/L, and zones of discharge are allowed on a case-by-case basis.

Chapter V
CONCLUSIONS AND RECOMMENDATIONS

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INTRODUCTION

The Water Quality Assurance Act of 1983 (Chapter 403.063 Florida Statutes) required the Florida Department of Environmental Regulation to assess the quality of water in the aquifer systems of Florida. This report is the second of a series that will discuss the aquifer systems of Florida. The first (Scott et al 1991) deals with the hydro- stratigraphic framework of Florida aquifer systems. This report is an assessment of the quality of water in Florida's three aquifer systems. Water quality reports that will follow include (1) a study of the temporal variability of water quality in the three aquifer systems, (2) a comparison of background water quality to the quality of water underlying areas of specific land uses with the goal of developing models for predicting changes in ground- water quality, and (3) a second evaluation of statewide water quality that will discuss changes in quality and provide comparisons of concentrations of metals in filtered and unfiltered samples.

Goals

This report discusses ambient water quality in Florida's aquifer systems statewide. It was written to meet four goals:

- Evaluation of background ground- water quality in all of Florida's aquifer systems,
- Development of ground-water-quality prediction techniques through application of hydrochemical facies maps and fundamental hydrogeochemical concepts,
- Discussion of the factors that affect regional ground-water quality so that the user can understand and anticipate controls on natural ground-water quality in the state, and
- Provide information for understanding the chemical consequences of water use.

The primary goal of this report is to present and evaluate the quality of water in the state's aquifer systems. Analytes were selected with two purposes in mind—identification of regional contamination and establishment of the hydrogeochemical framework of the aquifer systems. Many of the analytes described in this report are not subject to water-quality standards or guidance criteria, but their inclusion is necessary in order to understand the geochemical processes that govern reactions in the aquifer systems. Other analytes are subject to regulation and their inclusion is necessary in order to evaluate health risks and restrictions on ground-water use. Major and minor constituents, temperature and specific conductance were selected so that the geochemical framework of the state's aquifer systems can be identified. Understanding this framework allows us to conceptualize how chemical complexing, sorption reactions, reduction-oxidation reactions, and dissolution- precipitation reactions affect gross water chemistry and microchemical reactions in the aquifer systems. It is these reactions that mitigate contamination in the aquifer systems and allow us to utilize soils and aquifer systems for both water supply and waste disposal. This report, therefore, attempts to provide a minimum of information that will allow the user to understand the whys and hows of water-quality transformations in the aquifer systems.

The assessment of water quality includes contour maps where appropriate. These maps allow interpolation of water quality into areas not represented by samples. Care should be taken, however, in extrapolating beyond the data. Use of hydrochemical facies maps is a better approach for extrapolation because of the more general nature of these maps. While specific concentrations cannot be determined from the hydrochemical facies maps, general predictions as to the chemical constituency and reactions in an aquifer system can be made. These maps also allow recognition of regions of salt-water intrusion and connate water, and they allow prediction of general water-treatment alternatives for water- supply development.

The trace constituents (i.e., trace metals, trace nutrients, synthetic organics, and pesticides) are typically regulated analytes. Inclusion of these constituents allows direct assessment of statewide ground-water quality as affected by human activity. By comparing the distribution of these and other regulated constituents to the hydrogeochemical framework, we can understand tolerance levels of the aquifer systems to use and the mechanisms that mitigate introduction of these anthropogenic constituents into aquifer system environments.

The concentrations of trace chemicals are normally highly discontinuous, so they cannot be contoured. As a result, this assessment is best used, not to identify specific areas of contamination, some of which have been identified but not confirmed, but to develop predictive concepts of the probability of encountering a trace contaminant.

The data presented in this report assist greatly in identification of recharge and discharge areas, and of flow systems. They provide information that supports vulnerability evaluation, and they allow delineation of a number of specific problem areas that merit further investigation.

Finally, information as to how one can predict the prospects and outcomes of water uses is provided. These predictions range from locating brackish waters for reverse-osmosis treatment to prediction of the amount of boiler scale that will be developed by use of hard water to understanding the ion exchange and sorption reactions that may affect migration of metals and anthropogenic chemicals in waste-disposal scenarios.

We caution the user of this report that the concepts presented are general in nature. Attempts at using these concepts in a site-specific context should be undertaken only by those who thoroughly understand the geochemistry of aquifer systems. Even though this report summarizes the most comprehensive ground-water quality survey ever undertaken in Florida, the sample distribution is still insufficient for site-specific evaluations. Neither the authors nor the Departments of Environmental Regulation or Natural Resources can take responsibility for misuse of the data included in this report or the GWIS database from which the data were drawn.

Evaluation of Health and Use Risks

Major, minor, and trace constituents were determined according to standard protocols of the American Public Health Association (1980), U.S. Environmental Protection Agency (1982) and Florida Department of Environmental Regulation (1981). These protocols include use of unfiltered samples for metals. Since the samples may contain particulate as well as dissolved metals, factors other than ambient water quality are represented in the chemical analyses.

The consequence of use of unfiltered samples for metals analyses is that the sample reflects water produced by the well, not necessarily the chemicals dissolved in aquifer system water. There are two justifications for use of unfiltered samples. First, there is a growing body of evidence to indicate that particulates travel in aquifer systems. In transport through intergranular porosity, mechanical filtration reduces the probability of particulate movement, with colloids being most likely to move. Conduit flow in fractured and karstic aquifer systems is conducive to particulate transport. Second, users with domestic wells usually do not filter the water before consumption. Therefore, use of unfiltered samples in this report constitutes an evaluation of exposure upon consumption of the water rather that a simple discussion of natural water chemistry. A comparison of filtered and unfiltered samples is underway and will be published as part of the evaluation of the second statewide background analysis at a later date.

In many areas of the state, particularly in the surficial aquifer system, water quality criteria are exceeded by natural causes. These are predictable and have been discussed in Chapter IV.

DATA INTERPRETATION AND USE

Data have been interpreted in each section as to the causes and controls on the distribution of each chemical. It is possible to use these data in a much larger context, however. The data constitute a variety of evidence as to aquifer system flow paths, recharge and discharge areas, and land uses. Use of the data to assist in identification of these features will facilitate development of knowledgeable growth management, zoning, and land-use management decisions. This section notes some of the ways that the data can be utilized to understand aquifer system behavior and impacts of land use on aquifer system water quality.

Recharge Areas

A number of programs at state and local levels require identification of aquifer system recharge areas. Recharge areas are sensitive to ground-water contamination. Maintenance, or enhancement, of recharge is necessary to insure the long-term water supply. Recharge areas may also represent potential for optimal development of municipal well fields and unique industries that require low total dissolved solids water, such as the bottled-water industry.

The water-quality data presented in this report assist in identification of recharge areas in several ways **(Table 36)**. Recharge areas are typically characterized by lack of equilibration of the water with aquifer system materials and widespread evidence of surficial conditions, such as atmospheric temperatures, human activities, and wetlands. While there are many exceptions to the criteria listed in Table 36, the data do provide a starting point for identification of recharge areas.

It may also be possible to recognize recharge areas by vertical continuity of water chemical quality. If water-quality, for example hydrochemical facies, present in the surficial aquifer system persists downward into the Floridan aquifer system, there is indication of interconnection. This interconnection can be the result of downward or upward flow, so other water quality criteria and hydraulic head relations (Scott et al, 1991) must also be considered.

Discharge Areas

The arguments above can be reversed to identify some regional discharge areas. Table 36 summarizes some of the water quality criteria that might be useful in identifying discharge areas. Typically, water-quality data are less variable, chemicals reflective of surficial conditions more masked, and water more highly buffered (high bicarbonate and pH) in discharge areas.

Coastal discharge areas may be represented by a calcium- or calcium-magnesium-sulfate hydrochemical facies if the water has followed a deep flow path and come in contact with gypsum- and anhydrite-bearing strata at the base of the Floridan aquifer system.

Flow Systems

Flow systems can be recognized within the Floridan aquifer system by examining the analyte maps. Analytes that reflect equilibration with aquifer system rocks (i.e., total dissolved solids, pH, calcium, bicarbonate) typically increase along a flow path. Orthogonals to the concentration isolines should roughly indicate flow paths.

Some analytes allow identification of specific, conduit-flow systems. For example, phosphate may form plumes along karst conduits and indicate a rapid recharge and local flow system. Fluoride, nitrate, temperature, total organic carbon, and sulfate may allow recognition of these more local flow systems.

Surface-Water Features

The effects of several interesting surface-water features appear in the data set. For example, there is evidence in the Floridan aquifer system of disappearing streams along the Cody Escarpment. Several large wetland areas were mirrored by high total organic carbon, low pH, and other analytes.

Lakes, streams, and wetlands affect aquifer systems through introduction of organic carbon and nutrients. Several major rivers, notably the Peace and St. Johns Rivers, follow linear features that appear to be fractured lineaments. Upconing, and possibly preferential recharge, along these features provides clear evidence of the inter- relationship of surface features and ground water. These linkages between surface-water features and regional ground-water quality represent possible areas of further study, perhaps as Very Intense Study Area (VISA) projects.

Land Uses

Two of the requirements of the Water Quality Assurance Act are to detect and predict contamination in Florida's aquifer systems. It is not possible to detect a significant number of areas of contamination because of the high costs of an exhaustive well network. One can, however, predict water-quality degradation if one can establish correlations with specific land uses and ground-water quality. The VISA program is designed to do this. By comparison of the data collected in areas specifically selected to represent a given land use with the Background Network data, these correlations can be drawn. Results of the VISA study will be published in the future.

The data presented in this report indicate that there is a high chance of success for the VISA studies. A number of regions characterized by specific land uses do have anomalous ground-water quality. Some agricultural areas have high concentrations of nitrate, pesticide, or other constituents. Synthetic organics were found in industrial and suburban, as well as agricultural, areas. Considerably more study is required before confidence can be placed on the correlations, but it appears that we may be able to anticipate the contaminants and a probable level of contamination for a given land use.

GENERAL SUMMARY OF THE QUALITY OF FLORIDA GROUND WATER

General Quality of Florida's Ground Water

In general, the quality of ground water in Florida is excellent and has been little affected by humans. However, many local areas of the state's aquifer systems have been affected by human activities. Water quality is consistent with the lithologies of the aquifer systems. Part of the reason that water quality has not been adversely affected is the slow rate of recharge and flow in the aquifer system. Much of the water is simply too old to have been exposed to human impacts at the time of recharge.

Siliciclastic Aquifers

In very general terms, siliciclastic aquifers, such as the Sand and Gravel Aquifer of northwest Florida and the surficial aquifer system in the interior of north and central peninsular Florida are characterized by water quality associated with precipitation composition. The water usually has low total dissolved solids content, and is rich in sodium and chloride as opposed to calcium and bicarbonate. Water from these aquifers often contains high total iron and organic carbon concentrations.

Due to the lack of carbonate minerals in siliciclastic horizons, buffering capacity is low and the aquifers are vulnerable to contamination. Clay minerals, iron and aluminum oxyhydroxides, and humins range from non-existent to abundant in siliciclastic horizons. These particles give these aquifers a wide range in sorptive capacity and make it difficult to generalize as to ability of siliciclastic aquifers to tolerate waste loading. Since much of the flow in these aquifers is intergranular, mechanical filtration and sorption are enhanced.

Carbonate-Rich Siliciclastic Aquifers

Carbonate-rich siliciclastic aquifers, such as the shelly portions of the surficial aquifer system and the sand- and gravel-rich horizons in the interme-

diate aquifer system (especially in the Hawthorn Group) are intermediate between true siliciclastic and limestone/ dolostone aquifers. The presence of carbonate minerals provides buffering capacity, while abundant clays and organics provide sorption capacity.

Mechanical filtration is still important because flow is through intergranular porosity. Siliciclastic horizons in the Hawthorn Group usually occur between clay-rich strata which provide both confinement and isolation from anthropogenic chemicals.

Limestone and Dolostone Aquifers

Limestone and dolostone aquifers are doubly porous. While they exhibit intergranular porosity, which can be locally important, much of the flow is through fracture and cavernous porosity. There fore, carbonate-rock aquifers have lower mechanical filtration capabilities than siliciclastic aquifers, and wastes and particles are capable of travel through conduit flow for some distance.

Because of the presence of abundant carbonate minerals, buffering capacities are high and the waters of these aquifers are usually alkaline and calcium, magnesium, and bicarbonate rich. Sorption capacities vary. There is little clay or organic material in the rock, and much of that present is isolated from the conduits by low permeability rock. Detrital clays and other particles in the conduits may provide sorption capacity.

Floridan aquifer system water contains surprisingly high total organic carbon concentrations. This high organic carbon may reflect particulate organics, particularly in the Avon Park Formation, and some sorption capacity for anthropogenic organics. There is also a risk of development of halogenated hydrocarbons, especially trihalomethanes, upon chlorination of these waters. In general, it appears that dilution and dispersion are more important than sorption once water enters limestone/dolostone aquifers.

DEFINITION OF BACKGROUND WATER QUALITY

Pristine Water

Pristine water is water that has not been affected by human activity. After several hundred years of human activity in Florida, it is difficult to assess how much pristine water remains. Surely, water deep in the Floridan aquifer system and far away from injection and water-producing wells is pristine, but much of it may not be potable for natural causes. Shallow waters may or may not be pristine.

Since this is the first ground-water quality survey of its kind, we have little or no data with which the Background Network data can be compared. The baseline for comparison began with the development of the Background Network. Therefore, determinations of degradation of ground-water quality begin with this data set and go forward. In a large sense, we are constrained to monitoring and enforcing changes from the present status of ground-water quality. This data set constitutes the baseline against which future changes will be gauged. Background Network wells were chosen from or drilled in locations believed to be minimally affected by human activities.

Background Water

The quality of water today reflects background, not pristine, conditions. For some of the state, we can surmise that background water quality is near pristine conditions. However, large portions of the state's aquifer systems have been affected by human activity. Salt-water intrusion, upconing of deeper waters, interaquifer transfers, waste disposal, water withdrawals, land drainage, and other activities have induced change. Background water quality is, therefore, a mixture of human and natural conditions.

High Salinity Water

This report delineates a number of regions where water with high total dissolved solids content adversely impairs use. By volume, most of this water is naturally "contaminated", and the only human impact is causing that water to move into potable-water horizons. Suitable uses for this water include augmentation of potable water supplies by reverse-osmosis or other treatment, waste disposal, and certain industrial applications, such as cooling water. Care must be taken not to induce migration of this lower quality water into higher quality waters.

Not all of the high salinity water in Florida aquifer systems is derived from the modern sea. Connate water (sea water residual from previous marine transgressions) is present in many areas. In addition, sulfate-rich water in deep flow systems pose a water-quality problem.

Coastal Intrusion

All of Florida's aquifer systems contain salt water near the coasts. Salt-water intrusion along the coasts is an historical problem in Florida. The sampling plan was not constructed to identify the transition zone and it has not been mapped everywhere in the state. Likewise, these data do not allow differentiation of natural intrusion and intrusion caused by human activities. The data included in this report do give indication of the extent of the transition zone, which will help in planning and management of our ground-water resources.

In the 1990's we are concerned with global change, especially global warming. Should global warming cause a rise of sea level, baseline data are needed to evaluate the resulting loss of potable water and salt-water intrusion. These data are present in this data set. Those data from rural coastal areas where anthropogenic intrusion is unlikely will be especially helpful for evaluating the effects of sea-level rise.

Another important consequence of this study has been documentation of the slope of the transition zone and its chemical zonation. The chemical data clearly indicate that the slope of the transition zone is directly related to hydraulic head. The data indicate that regions where the transition-zone slope is gentle are associated with minimal flow and low hydraulic potential. Regions where the transition zone is steep are associated with more dynamic flow and higher potentials. These data can be used to assist in locating well fields. Regions where the transition zone slopes gently are much more susceptible to intrusion that are regions with steep transition zones.

Connate Water

Connate water (salt water) is present in all aquifer systems in regions where hydraulic potentials are insufficient to flush the aquifer systems with fresh water. This is particularly a problem in the Everglades/Big Cypress Swamp regions of SFWMD and in some portions of the SJRWMD. Not all of the horizons with connate waters have been identified in this report. Many have been recognized, and this experience should assist in predicting the locations of others.

Deep-Flow-System Water

Waters that recharge the Floridan aquifer system near the center of the state and that follow deep flow paths which skim along the top of the gypsum-and anhydrite-rich, lower confining units gain significant sulfate concentrations. As a result, water deep in the Floridan aquifer system and along the inner (landward) margin of the coastal transition zone are often sulfate rich. These waters may include sulfate in excess of the standards due to natural causes.

The quality of ground water in the Floridan aquifer system generally decreases with depth. This drop in water quality results from the cumulative history of chemical reactions along lengthy flow paths (Jones et al., in press) and also from mixing with sulfate-rich waters at the base of the aquifer system. A number of regions of sulfate- rich water have been attributed in this report to upconing under heavy pumpage stress. In most cases, the production wells were not completed in the sulfate-rich waters. Reduction of hydraulic potentials by pumping has, instead, induced flow upward along fractures and karst conduits. Therefore, it is important to anticipate where the naturally degraded waters are relative to production wells, karst conduits and fractures, and pumping stresses or well locations and depths adjusted accord-

ingly. The experiences described in this report should assist in identifying conditions where upconing of deep water may occur. The depths of sampling for each well in the Background Network are contained in the GWIS database management system. This database can be used to assist in predicting depths to lower quality waters.

Interaquifer Transfer

There are many areas of the state where upconing and interaquifer transfer bring low quality (high total dissolved solids) water into aquifer systems that otherwise would have higher water quality. Upconing because of natural, upward flow is common near the coasts and along some proposed fracture systems, such as along the St. Johns and Peace River axes. Elsewhere, upconing because of pumping stress is a common local problem. One of the most dramatic artifacts of human activity documented in this study is the transfer of calcium-magnesium-bicarbonate water from the Floridan aquifer system to the surficial aquifer system through irrigation.

NATURE OF ANTHROPOGENIC CONTAMINATION

There are numerous, minor exceptions to the conclusion that human impacts, other than upconing and salt-water intrusion, are minimal. Scattered occurrences of anthropogenic contaminants were detected, but most are unconfirmed by re-sampling. It is inappropriate at this time to conclude that these scattered detections are real because of the design of the Background Network, lack of confirmation, and high probability that some detections are a result of field or laboratory problems.

Users of the Generalized Well Information System (GWIS) are advised that caution must be used when interpreting the data contained therein. Until such time as contamination is confirmed, the data must be considered to represent a "worst- case scenario" for planning and management purposes.

There are a number of examples of possible contamination. Nitrate contamination is wide- spread in some areas, lead and mercury were found in the sample set, and there is some indication that synthetic organics and pesticides are present in limited areas of the state. Point-Source Contamination

The Background Network was designed to avoid known point-source contamination. Because of the spacing of wells, it cannot be assumed that single wells that detect anomalous concentrations of an analyte reflect a point source. That determination must be made upon further investigation of activities near the well and of the lateral extent of the anomaly.

Non-Point Source Contamination

Non-point source contamination is contamination caused by a widespread activity. Typical non-point sources include application of fertilizers and pesticides in agriculture, widespread use of on-site septic systems, and widespread application of animal wastes.

The Background Network data clearly indicate several regions that have been affected by non-point source contamination. For example, high nitrate concentrations in the Floridan aquifer system in Suwannee and Flagler Counties reflect widely dispersed agricultural practice. This report suggests the locations of many regions where non- point source contamination has impaired water quality.

It must be noted here that, while non-point sources are suggested in a number of aquifer systems and locations, the overall water quality of the state's aquifer systems cannot be shown to have been significantly impacted by non-point source contamination.

STATEWIDE LEVELS OF CONTAMINATION

Table 37 summarizes the proportion of the total sample set in which samples exceeded water-quality standards. The data were taken from preceding sections and the reader is cautioned to refer to those sections for a sense of the extent of contamination. In most cases, the proportions are high, not because the problem is widespread, but because an area with a problem has several wells.

The second most widespread violation of a water-quality standard is for pH. The Secondary Drinking Water standard requires the pH of water to fall between 6.5 and 8.5 s.u. Thirty-seven percent of the surficial aquifer system samples failed these criteria, largely because of low pH's. These low pH values are generally natural and a result of carbonic and organic acid content of the water. Intermediate and Floridan aquifer system water samples contained 16 and 14 percent, respectively, that failed the criteria. Many of these failures are a result of samples that exceeded the upper pH limit of 8.5. Some of these exceedances are natural, most appear to reflect high pH values associated with drilling fluids and cements, especially in the SRWMD.

Sodium

The Primary Drinking Water Standard for sodium is 160 mg/L. Only 4 percent of the samples from the surficial aquifer system exceeded the standard. However, 23 percent of samples from the intermediate and 17 percent of sample from the Floridan aquifer system exceeded that standard. The high levels of exceedance in the intermediate and Floridan aquifer systems reflects salt water in coastal and deep wells. Most of the intermediate aquifer system wells that exceeded the standard are located in southwest Florida (Lee, Charlotte, Collier Counties) where the intermediate aquifer system is used for public water supplies. Wells in the Floridan are generally located in the coastal transition zone.

The most widespread violation of water quality standards is for iron. Only wells cased in non- ferrous materials were used in this analysis, so the samples reflect dissolved and particulate iron, not well construction. The Secondary Drinking Water standard for iron is 0.3 mg/L. Seventy-five percent of all surficial aquifer system samples exceeded the standard. Forty-two percent of the intermediate aquifer system and 49 percent of the Floridan aquifer system samples violated the standard. There is no reason to believe that iron violations are anthropogenic. Iron is a natural constituent, and chemical conditions are conducive to transport of the iron. Iron sources are widespread in aquifer systems. It is present as ferric iron in deeper portions of the aquifer systems and is highly mobile. Mercury

The Primary Drinking Water Standard for mercury is 2 µg/L. Mercury is of concern in Florida because of recent discoveries of the metal in the aquatic food chain. Two percent of surficial aquifer system samples and three percent of intermediate aquifer system samples contained possible mercury in excess of the standard. Only 0.9 percent of Floridan aquifer system samples contained possible mercury. Occurrences of mercury are dispersed throughout the state, and there is no obvious area of concentration. The surficial and intermediate aquifer systems may be sources of mercury since both aquifer systems contain particulate organics. The abundance of organic carbon in Florida ground water is conducive for transport of mercury. An exceedance level of four to five percent of the samples seems high, given the abundance of sorption sites in Florida aquifer systems. Given that the sample were unfiltered and detections have not been confirmed by re-sampling, additional work should be done to confirm the occurrences and determine their origins.

Lead

A relatively large number of samples detected lead in excess of the 50 llg/L Primary Drinking Water standard. Lack of sample filtration and confirmation by re-sampling clouds interpretation of the extent of any lead problem. Eight percent of samples from the surficial aquifer system, eight percent of intermediate aquifer system samples, and nine percent of Floridan aquifer system samples detected excess lead. There is a good chance that some of these detections are a result of well or plumbing materials or of use of lead weights on water-level recorders. Lead mobility should be limited through sorption on clays and organics and precipitation of lead carbonates. The

large proportion of samples with lead suggests a possible problem, and additional work is needed to determine if the threat is real or an artifact.

Sulfate

The Secondary Drinking Water standard for sulfate is 250 mg/L. The proportions of samples that exceeded the standard are as follows: surficial aquifer system - two percent, intermediate aquifer system -13 percent, and Floridan aquifer system - 13 percent. These exceedances are typically related to high sulfate waters in regional discharge zones along the coasts, or to local upconing.

Chloride

Chloride is the dominant anion in sea water. The Secondary Drinking Water Standard is 250 mg/L. Exceedances are related to the coastal transition zone and to upconing in areas of pumping stress.

Fluoride

Exceedances of the 4 mg/L Primary Drinking Water Standard are low. Fluoride is derived from weathering of Hawthorn Group phosphate minerals, and is not considered a problem in Florida.

Nitrate

The Primary Drinking Water Standard for nitrate, as nitrogen, is 10 mg/L. The proportion of samples with excess nitrate is low. The exceedances reflect a small percentage of samples (0.6 percent - surficial aquifer system, zero percent - intermediate aquifer system, one percent - Floridan aquifer system) and does not reflect the findings of this report. While there are few samples that exceed the standard, there is a health advisory for nitrate concentrations of 1 mg/L N. Samples with concentrations in the 1 mg/L range are widespread. They usually occur in clusters that reflect local land use, especially agricultural uses. Nitrates are becoming a subject of concern at the time of the writing of this report because of the potential for eutrophication of surface water bodies. Several coastal springs (i.e. the Kings Bay spring complex in Citrus County and Lithia and Buckhorn Springs, Hillsborough County) have been subjected to significant increases in nitrates in recent years. A state-funded U.S. Geological Survey study in the Suwannee River Basin has shown high nitrate concentrations (up to 140 mg/L) in monitoring wells associated with dairy operations. Additional work is needed to determine the origins of the nitrates and means of mitigating what appears to be a growing problem.

Total Dissolved Solids

Total dissolved solids content of ground water reflects the presence of saline waters, such as occur in the coastal transition zone, at depth in the Floridan aquifer system, and in poorly flushed, connate water zones. The exceedances reflect these naturally "contaminated" regions and regions of induced degradation through pumpage and land drainage. The Secondary Drinking Water Standard is 500 mg/L.

Synthetic Organics

The group of chemicals defined as synthetic organics in this study includes 142 organic chemicals. Some of these chemicals are organic solvents, plastics components, and degradation products of other chemicals. Many of the chemicals detected are, or have been, utilized as pesticides, as well. All are either carcinogenic, teratogenic, toxic, or mutagenic. Standards vary with compound and the reader is referred to Table 28 for a list of compound included in this group and the associated standards. It is important to note that the presence of these organics has not been confirmed by re-sampling.

Table 37 lists the percentage of samples in which exceedances for any of the 142 chemicals were found. Most of these were not confirmed by re-sampling. Seven percent of the surficial aquifer system samples contained possible synthetic organics in excess of standards. It is not unexpected that a proportion of the surficial aquifer system samples would contain synthetic organics given that the surficial aquifer system supports much of the state's agriculture. One and three percent of the samples from the intermediate and Floridan aquifer systems, respectively, contain excess synthetic organics. These proportions of detections are relatively low and suggest relatively little human impact on these aquifer systems. While the level of contamination, statewide, is low, surveillance must continue given the pandemic use of synthetic organics.

Pesticides

The 172 chemicals included in the Pesticides group **(Table 32)** were analyzed for in the SWFWMD and SFWMD. Only arsenic was tested for in NWFWMD, SRWMD, and SJRWMD. Table 37 summarizes the percentage of samples in which the standards were exceeded. Arsenic is not a widespread problem, although a few samples contained excess arsenic in several districts. The proportions given in Table 37 largely represent detections in SWFWMD, and to a lesser extent in SFWMD. Most of these were not verified by confirmation re-sampling. If these proportions are representative of the other districts, then a problem may exist. Additional work, especially screening of the other districts is needed before firm conclusions can be drawn.

Total Organic Carbon

There is no standard for total organic carbon, and it has not been considered a problem in the past. Within the last few months the U.S. Environmental Protection Agency has indicated that it intends to set controls on the use of water high in organic carbon for public water supplies because of the widespread occurrence, nationally, of trihalomethanes and other halogenated hydrocarbons in finished drinking water. These compounds result from sanitization of water with chloride and other strong oxidants in treatment plants.

Florida aquifer systems have an extraordinary amount of total organic carbon in water. The distribution of total organic carbon is summarized in **Table 27**.

Need for Additional Work

Additional work needs to be done on several specific problem areas. First of all, it is necessary to re-sample and confirm or reject the detections of contaminants in this first round of sampling. Filtered and unfiltered samples need to be compared so that mobility of these suspected contaminants can be evaluated.

Nitrate contamination is much more wide- spread than anticipated. A study of the origins of this nitrate and means of mitigation of the problem should be undertaken in an organized way. Lead may not be a ground-water quality problem (sensu stricti). Lead in the sample set may result from choice of wells sampled, not aquifer system conditions. The widespread occurrence of lead must be further investigated and a determination made as to the source. Mercury was detected in a number of samples and, given the current problems with mercury in surface waters, its origin and distribution need to be studied. Finally, the synthetic organics and pesticides found include a number used in the agricultural industry. These occurrences need to be confirmed and the origins of the contaminants identified.

The second round of Background Network sampling, including filtered and unfiltered metals samples, will assist in answering some of these questions. The VISA and Temporal Variability studies will address others. Specific studies will be warranted in the future as the water-quality problems become better defined.

MANAGEMENT IMPLICATIONS

It is important that the data reported in this publication be utilized in every way possible. These data are useful for water management, including monitoring of water-quality change, location of water-use facilities, and establishing cause and effect relationships from aquifer system use. We have attempted to provide some basic concepts to allow the reader to understand how aquifer systems work in a chemical sense and to anticipate the consequences of water-management options. The following is a summary of some of the ways that the data can be utilized.

Comparison to Background

The concept of background water quality allows wise resource management at two scales, local

and regional. At the local scale, all contamination assessments, environmental impact studies, environmental audits, and many consumptive-use applications require development of an evaluation of background water quality for comparison to on site water-quality impacts. The person preparing a local study should not expect to use the data presented herein to support a site-specific application or evaluation, but these data can be used to determine what to expect when background water quality deter-minations are made. If local background water quality differs greatly from that predicted by this report, one should not take alarm, but an investigation as to the reason for the difference is appropriate. The water-resources manager can also utilize the Background Network data in evaluating permit applications and environmental assessments. These data provide a basis for comparison with the local background quality in the submission and for determination of any degradation of water quality.

On the regional scale, background ground- water quality takes on another meaning. Water resources are finite and, in a state with a growing population, one must anticipate and protect future water supplies. Data from the Background Network allow delineation of these future resources and monitoring of threats to them. Consultants and water-supply authorities can utilize the data in well field siting and design. Managers can evaluate well field sitings in the regional context and evaluate potentials for upconing or other adverse effects.

Sensitivity to Contamination

Recharge areas, aquifer systems with low buffering, sorption, or microbial degradation capacities, and aquifer systems with conduit flow are sensitive to contamination. The data presented herein identify these conditions and allow a qualitative judgement of sensitivity to contamination. More importantly, the data collected include all major and minor constituents necessary to model equilibrium, sorption, and certain types of biological reactions. It may be possible, therefore, to calculate the carrying capacity of the aquifer system. In other words, proper use of the data may allow one to quantify how much effluent an activity, such as waste disposal, can release to an aquifer system before water quality adversely changes.

Effects of Consumptive Use

Coastal intrusion, upconing or recharge, and induced lateral flow of contaminants may result from heavy pumpage of ground water. These data provide a basis for detecting proximity to low quality water and, by comparison with regions where adverse movement of water exists today, one may be able to anticipate degradation of local or regional water quality by pumpage.

Long-Term Resource Evaluation

It is clear that the intent of the Legislature when it adopted the Water Quality Assurance Act in 1983 was to begin a program that will allow water-resource managers to closely monitor future changes in water quality and resulting loss of the resource. The Background Network provides a baseline for evaluating the future of our aquifer systems. It allows us to identify change, but it does not allow us to predict it with any confidence. The VISA and Temporal Variability Networks will help with our ability to predict, but only continued monitoring will allow confidence in identification of change and successful management and enforcement.

Need to Continue the Program and the Future

The Ground-Water Quality Monitoring Program has begun the process of assessing the quality of ground water in Florida. This report is the first statewide assessment of all aquifer systems, ever. Re-sampling of the Background Network has begun, and this time both filtered and unfiltered metals analyses will be included. When this survey is completed, we will be able to compare the data to the data reported in this document to identify any changes in water quality. In addition, we will be able to evaluate the concentrations of dissolved and particulate metals. This re-sampling will assist in evaluation of the reality of the detections of synthetic organics and pesticides. It will also allow confirmation of the lead and mercury problems mentioned above.

Sampling of the VISA Network is nearing completion, and comparisons will be made with the Background Network to develop predictive models concerning the impacts of specific land uses. This comparison will comply with the charge of the Water Quality Assurance Act to predict contamination.

Finally, the Temporal Variability Network data is being analyzed as this report is being written. This data base indicates that water quality changes on short-and long-term time frames do occur. The data will allow one to place the conclusions of this report into perspective with respect to both spatial and temporal changes. It will also assist managers to evaluate the context of reports that include only one sampling event.

Several additional studies are suggested by the findings of this report. First, a study of the mechanisms by which fracture systems affect water quality should be undertaken. These fractures are widespread, and water-management policy should include potential for migration of low- quality water within them. Second, the origin of the lead and mercury reported in Florida's aquifer systems should be identified. Third, the origin, transport, and biochemical transformations of nitrogen species should be undertaken. There are several large regions where non-point source nitrate is abundant. While we may understand the sources of the nitrate, we must understand how those sources result in nitrate contamination. If the synthetic organic and pesticide problems are confirmed, then additional study will be required to determine the origins and fates of these compounds. Fourth, efforts should be made to develop demonstration projects to show how the data can be used to calculate aquifer system carrying capacities, identify recharge and discharge areas, and predict water-quality degradation as a result of a variety of land uses.

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Table 1. - Ground Water Quality Monitoring Network Parameters

PARAMETER GROUP	NETWORK					STANDARD METHOD[1,2]
Parameter Name	Background	VISA	HRS	Quarterly	Monthly	
MAJOR IONS						
Bicarbonate	B	V		Q		406
Carbonate	B	V				406
Chloride	B	V	H	Q		407A, 407B, or 407D
Cyanide	B	V				412B, 412C, or 412D
Fluoride	B	V	H	Q		413A, 413B, 413C, or 413E
Nitrate	B	V	H	Q		418C or 418F
Phosphate	B	V	H	Q		424F or 424G
Sulfate				Q		426A or 426C
METALS						
Arsenic	B	V	H			303E
Barium	B	V	H			303C
Cadmium	B	V	H			303A or 303B
Calcium	B	V	H	Q		303A or 311C
Chromium	B	V	H			303A or 303B
Copper	B	V	H			303A
Iron	B	V	H	Q		303A OR 315B
Lead	B	V	H			303A or 303B
Magnesium	B	V	H	Q		303A or 319B
Manganese	B	V	H	Q		303A or 319B
Mercury	B	V	H			303F
Nickel	B	V				303A or 322B
Potassium	B	V		Q		303A or 322B
Selenium	B	V	H			303E
Silver	B	V	H			303A or 303B
Sodium	B	V	H	Q		303A OR 325B
Strontium		V				
Zinc	B	V	H	Q		303A or 303B
FIELD PARAMETERS						
Conductivity	B	V		Q	M	205
pH	B	V		Q	M	423
Eh					M	
Dissolved Oxygen (DO)					M	
Temperature	B	V		Q	M	212
Water Levels	B	V		Q	M	
Odor			H			
MICROBIOLOGICAL						
Fecal Coliform	B	V				908C or 909C
Total Coliform	B	V				908A or 909A
ORGANICS AND PESTICIDES						
Total Organic Carbon	B	V		Q		505
Volatile Organic Carbon	B					EPA 601 & 602, OR EPA 624

PARAMETER GROUP	NETWORK					STANDARD METHOD[1,2]
Parameter Name	Background	VISA	HRS	Quarterly	Monthly	
Aldicarb & related compounds		V				EPA 531
Purgeable Halocarbons		V				EPA 601
Purgeable Aromatics		V	H			EPA 602
Pesticides		V				EPA Alt. 614
PCB's, Chlorinated Pesticides		V	H			EPA Alt. 617
Pesticides		V				EPA Alt. 619
Organophosphate Pesticides			H			EPA 622
Mixed Purgeables			H			EPA 624
Base/Neutral/Acid Extractables		V	H			EPA 625
Carbamate Pesticides		V	H			EPA 632
Pesticides		V				EPA 644
Herbicides			H			
Fumigant Pesticides		V	H			
RADIOMETRICS						
Gross Alpha		B	V			703
Gross Beta		B	V			703
Radon		B*				
Radium		B*				
OTHERS						
Total Dissolved Solids (TDS)		B	V		Q	209B
Ammonia			V			
Silica			V			

[1] Methods are from the American Public Health Association's Standard Methods for the Examination or Water and Wastewater, 15th edition, or from the Florida Department of Environmental Regulation's Supplement "A" to Standard Operating Procedures and Quality Assurance Manual (1981).

[2] Other approved methods with the same or better minimum detection limits, accuracy and precision are also acceptable.

* A subset of approximately 100 Background wells is being sampled for radon and/or radium.

Table 2. - Florida Primary and Secondary Drinking Water Standards for Selected parameters (from F.A.C. 17-22)***

PARAMETER GROUP	MAXIMUM CONTAMINANT LEVEL (µg/L unless otherwise noted)	
Parameter Name	Primary DWS	Secondary DWS
Major Ions		
Chloride		250,000
Fluoride	4,000	2,000
Nitrate	10,000	
Sulfate	250,000	
METALS		
Arsenic	50	
Barium	1,000	
Cadmium	10	
Chromium	50	
Copper		1,000
Iron		300
Lead	50	
Manganese		50
Mercury	2	
Selenium	10	
Silver	50	
Sodium	160,000	
Zinc		5,000
FIELD PARAMETERS		
pH		<6.5, >8.5 s.u.*
Odor		3 T.O.N**
MICROBIOLOGICAL		
Total Coliform	4 col/L (see rule)	
ORGANICS		
Endrin	0.2	
Lindane	4	
Methoxychlor	100	
Toxaphene	5	
2,4-D	10	
2,4,5-TP (Silvex)	10	
Tetrachloroethylene	3	
Trichloroethylene	3	
Carbon Tetrachloride	3	
Vinyl Chloride	1	
1,1,1-Trichloroethane	200	
1,2-Dichloroethane	3	
Benzene	1	
Ethylene Dibromide	0.02	
Trihalomethane	100	
RADIOMETRICS		
Gross Alpha	15 pCi/L	
Gross Beta	4 mrem/yr	
Radium 226, 228	5 pCi/L	
OTHERS		
Total Dissolved Solids		500,000

*** s.u. = standard units**

T.O.N. = Threshold Odor Number

***** Source: Florida Ground Water Guidance Concentrations, Florida**

Table 3. - Summary of the chemical composition of precipitation from selected sites in Florida. Based on data from the National Atmospheric Deposition Program (IR/7)/National Trends Network (1990).

Stat.	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)	NH_4 (mg/L)	NO_3 (mg/L)	Cl (mg/L)	SO_4 (mg/L)	PO4 (mg/L)	pH (field)	Cond. (field)	Na/Cl mole Ratio	Ratio dev. from water sea
Quincy, Gadsden County													
x	0.14	0.07	0.06	0.44	0.15	1.05	0.75	1.77	0.02	4.68	17.7	0.90	0.05
s	0.17	0.08	0.18	0.53	0.24	1.05	0.89	1.84	0.09	0.41	15.9	0.22	0.22
n	179	179	179	179	179	179	179	179	179	160	162	179	179
Min.	0.01	0.01	0.00	0.03	0.00	0.00	0.06	0.10	0.00	3.57	4.0	0.40	-0.45
Max.	1.15	0.53	2.12	3.23	1.53	6.19	5.58	12.78	0.78	5.90	132.5	2.90	2.05
Austin-Cary Forest, Alachua County													
x	0.28	0.09	0.09	0.78	0.15	1.00	0.96	2.03	0.00	4.79	17.87	1.39	0.54
s	0.28	0.07	0.16	0.85	0.85	0.88	0.99	1.47	0.00	0.53	12.09	1.01	1.01
n	92	92	92	92	92	92	92	92	92	89	92	92	92
Min.	0.02	0.00	0.00	0.02	0.02	0.07	0.10	0.10	0.00	3.49	3.70	0.13	-0.73
Max.	1.33	0.39	0.95	4.87	4.87	4.70	8.88	8.88	0.00	6.70	66.70	6.04	5.19
Bradford Forest, Bradford County													
x	0.26	0.11	0.07	0.80	0.16	1.04	1.19	1.96	0.01	4.70	16.77	1.05	0.20
s	0.44	0.26	0.22	2.13	0.24	0.95	3.16	2.13	0.07	0.46	12.82	0.64	0.64
n	367	367	367	367	367	367	367	367	367	340	337	366	366
Min.	0.01	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	3.22	2.20	0.31	-0.54
Max.	5.40	4.31	3.81	29.30	1.92	6.60	52.62	22.80	1.19	6.60	99.00	6.17	5.32
Kennedy Space Center, Brevard County													
x	0.28	0.20	0.09	1.58	0.10	1.05	2.81	1.93	0.02	4.92	23.15	0.87	0.02
s	0.34	0.25	0.10	2.03	0.17	1.13	3.64	1.71	0.07	0.37	14.99	0.14	0.14
n	229	229	229	229	229	229	229	229	229	208	201	229	229
Min.	0.01	0.00	0.00	0.09	0.00	0.00	0.15	0.20	0.00	3.73	0.80	0.37	-0.48
Max.	3.28	1.70	0.80	13.82	1.18	10.12	12.81	12.81	0.58	5.72	85.80	1.91	1.06
Verna Well Field, Sarasota Florida													
x	0.31	.014	0.23	0.81	0.21	1.00	1.39	1.53	0.05	4.85	15.02	0.90	0.05
s	0.42	0.25	1.40	1.50	0.63	1.15	2.62	1.47	0.39	0.54	10.70	0.22	0.22
n	202	202	202	202	202	202	202	202	202	159	177	202	202
Min.	0.02	0.01	0.00	0.07	0.00	.000	0.14	0.15	0.00	3.39	3.00	0.51	-0.34
Max.	3.49	1.93	17.40	13.31	7.30	10.32	24.53	13.64	4.98	7.30	85.30	2.31	1.46
Everglades National Park, Dade County													
x	0.36	0.20	0.20	1.32	0.22	0.73	2.31	1.14	0.07	4.98	15.98	0.88	0.03
s	0.73	.31	1.03	1.89	1.12	0.85	3.21	1.62	0.63	0.57	13.90	0.13	0.13
n	304	304	304	304	304	304	304	304	304	261	269	304	304
Min.	0.01	0.01	0.00	0.05	0.00	0.00	0.12	0.00	0.00	3.00	3.50	0.56	-0.30
Max.	7.68	2.66	12.60	15.91	17.12	8.37	26.89	15.42	9.98	7.27	141.50	2.22	1.37
State-wide													
x	0.28	0.14	0.13	1.00	0.17	0.97	1.66	1.75	0.03	4.77	17.58	0.96	0.11
s	0.48	0.25	0.74	1.80	0.61	1.01	2.98	1.80	0.34	0.50	13.80	0.47	0.47
n	1373	1373	1373	1373	1373	1373	1373	1373	1373	1217	1231	1373	1373
Min.	0.01	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	3.0	0.80	0.13	-0.73
Max.	7.68	4.31	17.4	29.3	17.2	10.32	52.62	22.8	9.98	7.3	141.5	6.17	5.32

x = arithmetic mean
s = standard deviation
n = number of samples

Table 4. - Common minerals in Florida aquifer systems and confining beds, and their dissolved weathering products. Mineral formulae from Fleischer (1987).

Mineral	Composition	Dissolved Weathering Products (excl. H_2O, * = plus residual solids)
Anhydrite	$CaSO_4$	Ca^{2+}, SO_4^{2+}
Aragonite	$CaCO_3$	Ca^{2+}, HCO_3^-
Calcite	$CaCO_3$	Ca^{2+}, HCO_3^-
Carbonate-hydroxylapatite	$Ca_5(PO_4,CO_3)_3(OH)$	Ca^{2+}, PO_4^{3-}, HCO_3^-, plus trace $U^{4+,6+}$
Carbonate-fluorapatite	$CA_5(PO_4,CO_3)3F$	Ca^{2+}, PO_4^{3-}, F^-, HCO_3^-, plus trace $U^{4+,6+}$
Dolomite	$CaMg(CO_3)_2$	Ca^{2+}, Mg^{2+}, HCO_3^-
Ferric hydroxide	$Fe(OH)_3$	$Fe^{2+,3+}$
Gibbsite (G), bohmite and diaspore (BD)	G: $Al(OH)_3$ or $Al_2O_3•3H_2O$ BD: AlO(OH)	Al^{3+}
Goethite	FeO(OH)	$Fe^{2+,3+}$
Gypsum	$CaSO_4•2H_2O$	Ca^{2+}, SO_4^{2+}
Hematite	Fe_2O_3	$Fe^{2+,3+}$
K-feldspar	$KAlSi_3O_8$	K^+, H_4SiO_4, *
K-mica	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	K^+, F^-, H_4SiO_4, *
Kaolinite	$Al_2Si_2O_5(OH)_4$	Al^{3+}, H_4SiO_4, *
Opal (-A, -CT)	$SiO_2•nH_2O$	H_4SiO_4
Palygorskite	$(Mg,Al)_2Si_4O_{10}(OH)•4H_2O$	Mg^{2+}, Al^{3+}, H_4SiO_4, *
Pyrite	FeS_2	$Fe^{2+,3+}$, SO_4^{2-}
Quartz	SiO_2	Essentially inert
Sepiolite	$Mg_4Si_6O_{15}(OH)_{12}•6H_2O$	Mg^{2+}, H_4SiO_4, *
Smectite, v. Montmorillonite	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2•nH_2O$	Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, H_4SiO_4, *
Sectite, v. Nontronite	$Na_{0.3}Fe_2(Si,Al)_4O_{10}(OH)_2•nH_2O$	Na^+, Fe^{2+}, Al^{3+}, H_4SiO_4, *

Table 5. - Common minerals in Florida aquifer systems. See Table 4 for mineral compositions and weathering products. Volumetrically or chemically important minerals indicated in bold.

AQUIFER/MINERAL FRACTION	Surficial aquifer system	Intermediate aquifer system	Floridan aquifer system
Silicate Fraction	**Quartz** **Potassium feldspar** **Potassium feldspar** Kaolinite Chlorite Smectite	**Quartz** **Potassium feldspar** **Potassium mica** **Palygorskite** **Sepiolite** **Smectite** Kaolinite	Quartz
Carbonate Fraction	**Calcite** **Aragonite**	**Dolomite** Calcite	**Calcite** **Dolomite** Aragonite (?)
Oxyhydroxides, sulfides	**Ferric hydroxide** **Goethite** Gibbsite, boehmite, diaspore Pyrite	**Pyrite** **Ferric hydroxide** **Goethite**	Pyrite Ferric hydroxide Goethite
Other	**Humic substances***	**Carbonate-fluorapatite** **Carbonate-hydroxylapatite** Opal-A Opal-CT Gypsum	**Gypsum** **Anhydrite**

*** Humic substances refer to particulate organics, including organics concentrated in peats and mucks, and disseminated in other sediments.**

Table 6. - Summary of temperature distribution (EC), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	22.0	21.0	23.1	84	18.0	25.1
SRWMD	24.0	22.0	25.0	23	21.0	27.0
SJRWMD	24.0	22.3	25.0	44	19.0	29.0
SWFWMD	25.0	24.0	25.5	99	21.0	31.5
SFWMD	24.8	23.3	26.0	671	18.5	30.0
Statewide	24.4	23.0	25.9	921	18.0	31.5
Sand & Gravel	22.0	21.0	23.1	75	18.0	25.1
Biscayne	25.0	24.0	26.0	313	18.5	30.0
Other	24.2	23.3	25.2	533	19.0	31.5

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	23.2	22.2	24.0	24	21.0	26.0
SRWMD	22.0	21.0	23.0	27	18.0	24.0
SJRWMD	24.0	22.0	25.0	21	18.0	25.5
SWFWMD	25.0	24.0	26.0	60	23.0	30.0
SFWMD	25.1	24.4	25.6	102	22.3	27.5
Statewide	24.6	23.5	25.4	234	18.0	30.0

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	23.0	22.0	24.9	101	19.0	28.9
SRWMD	23.0	21.0	24.0	157	15.0	29.0
SJRWMD	23.0	22.0	24.0	77	18.0	27.0
SWFWMD	25.0	24.0	26.0	191	21.5	30.5
SFWMD	26.3	24.8	27.1	131	22.2	30.5
Statewide	24.0	23.0	25.5	657	15.0	30.5

Table 7. - Summary of pH distribution (s.u.), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	4.9	3.8	5.6	84	78	3.0	10.2
SRWMD	5.6	5.1	6.0	25	22	4.5	9.5
SJRWMD	6.6	5.9	7.2	53	24	3.5	9.9
SWFWMD	6.5	5.5	7.2	97	52	3.9	8.6
SFWMD	6.9	6.5	7.2	809	219	3.9	13.2
Statewide	6.8	6.3	7.1	1068	395	3.0	13.2
Sand & Gravel	4.9	3.8	5.6	75	70	3.0	10.2
Biscayne	6.9	6.6	7.2	477	103	5.6	10.5
Other	6.7	6.0	7.1	516	222	3.4	13.2

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	7.2	6.7	7.9	24	7	4.3	9.5
SRWMD	6.5	5.2	6.8	36	21	4.0	9.3
SJRWMD	7.1	7.0	7.5	29	3	5.1	11.3
SWFWMD	7.5	7.3	7.7	56	4	6.7	10.5
SFWMD	7.3	7.0	7.5	94	4	6.1	8.5
Statewide	7.3	6.9	7.6	239	39	4.0	11.3

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	7.5	7.1	7.8	101	3	6.6	8.8
SRWMD	7.1	6.6	7.9	220	63	4.9	12.5
SJRWMD	7.3	7.0	7.7	100	10	6.2	12.2
SWFWMD	7.5	7.3	7.8	172	16	6.0	10.7
SFWMD	7.4	7.1	7.6	125	8	5.6	8.9
Statewide	7.4	7.0	7.8	718	100	4.9	12.5

*** Number of samples which exceeded Florida Secondary Drinking Water Standards for pH (< 6.5 or > 8.5 s.u.).**

Table 8. - Concentrations of selected constituents in average sea water, ranked by abundance. Data compiled from various sources by Drever (1988). The predicted concentration in Florida precipitation is determined by multiplying the mole ration in sea water times the state-wide average concentration of chloride in precipitation (1.66 mg/L, Table 3).

Constituent	Conc. in Sea Water (mg/kg)	Mole ratio to Cl in Sea Water	Predicted Conc. in Avg. Florida Precipitation (mg/L) (NOTE 1)
Chloride	19,350	1.000	1.66
Sodium	10,760	0.857	1.42
Sulfate	2,710	0.052	0.09
magnesium	1,290	0.097	0.16
Calcium	411	0.019	0.03
Potassium	399	0.019	0.03
Bicarbonate	142	0.0043	0.0071
Fluoride	1.3	0.00013	0.00022
Trace Constituents	**(µg/kg)**		**(µg/L)**
Nitrate	5 - 2,000	1.5×10^{-7} - 5.9×10^{-5}	0.25 - 98
Phosphate	1 - 50	1.9×10^{-8} - 9.7×10^{-7}	0.032 - 1.6
Dissolved Organic Carbon	300 - 2,000	NA	NA
Iron	2	6.6×10^{-8}	0.11
Mercury	0.03	2.7×10^{-10}	0.00046
Lead	0.03	2.7×10^{-10}	0.00044

NOTE 1: The predicted concentration in precipitation assumed that the only sources of chemicals in rainfall are marine aerosols. The predicted concentration is calculated by

$$X_{precip.} = \left(\frac{X_{seawater}}{19{,}350}\right) \bullet 1.66 = 8.57\times10^{-5} X_{seawater}$$

Xprecip is the predicted concentration in precipitation, in mg/L. Xsea water is the concentration of the chemical in sea water (mg/kg, Table 8). Chloride concentrations are: 19,350 mg/kg in sea water and 1.66 mg/L in precipitation (Table3).

Table 9. - Classification of water hardness (from Durfor and Becker, 1964).

Hardness Range (mg/L as $CaCO_3$)	Description
0 - 60	Soft
61 - 120	Moderately hard
121 - 180	hard
More than 180	Very hard

Table 10. - Summary of total calcium distribution (Ca^{2+}, mg/L), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	3.7	1.6	8.8	84	< 0.1	38.0
SRWMD	11.0	5.2	40.0	25	0.4	240.0
SJRWMD	43.0	12.0	94.0	64	< 1.0	857.0
SWFWMD	22.3	7.5	58.8	84	0.2	763.0
SFWMD	98.0	73.3	124.0	610	< 1.0	756.0
Statewide	85.6	27.7	118.0	867	< 0.1	857.0
Sand & Gravel	3.6	1.6	8.9	75	< 0.1	38.0
Biscayne	97.4	79.4	125.0	248	1.4	260.0
Other	85.6	25.6	119.4	544	0.2	857.0

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	37.5	19.0	60.0	24	3.7	270.0
SRWMD	28.0	9.4	46.0	36	1.5	220.0
SJRWMD	52.0	27.0	133.0	33	1.6	336.0
SWFWMD	61.0	43.6	106.0	52	2.3	397.0
SFWMD	70.5	43.2	100.0	103	2.5	478.0
Statewide	58.0	36.0	100.0	248	1.5	478.0

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	34.0	21.0	46.0	101	2.2	143.0
SRWMD	82.0	51.0	150.0	220	0.6	1000.0
SJRWMD	41.0	24.0	64.0	125	4.0	546.0
SWFWMD	68.1	41.7	98.0	165	3.6	639.0
SFWMD	67.2	42.1	94.1	138	5.9	227.0
Statewide	51.9	28.5	84.1	749	0.6	1000.0

Table 11. - Summary of total magnesium distribution (Mg^{2+}, mg/L), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	0.9	0.6	2.0	84	0.2	20.0
SRWMD	1.6	1.2	3.2	25	0.1	44.0
SJRWMD	3.2	1.7	7.5	64	0.3	138.0
SWFWMD	3.5	1.1	11.5	85	< 0.1	401.0
SFWMD	3.9	2.7	6.5	229	0.1	51.9
Statewide	3.1	1.6	6.4	487	< 0.1	401.0
Sand & Gravel	0.9	0.6	2.0	75	0.2	13.0
Biscayne	3.9	2.7	6.5	229	0.1	51.9
Other	3.0	1.3	8.8	183	< 0.1	401.0

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	2.5	1.2	5.4	24	0.4	59.0
SRWMD	8.7	1.0	21.0	37	< 0.1	52.0
SJRWMD	4.8	2.6	14.0	33	0.1	255.0
SWFWMD	24.0	13.9	47.2	52	< 0.1	135.0
SFWMD (f)	26.6	19.4	67.6	103	2.2	465.6
Statewide	17.7	9.5	40.9	249	<0.1	465.6

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	6.4	3.0	12.0	101	0.3	60.0
SRWMD	6.3	2.6	19.0	220	< 0.1	430.0
SJRWMD	11.0	5.0	32.0	125	0.4	521.0
SWFWMD	7.0	2.2	23.0	166	0.1	180.0
SFWMD (f)	46.4	20.7	84.7	137	< 0.1	264.2
Statewide	14.6	6.3	33.1	749	< 0.1	521.0

(f) - Dissolved (filtered) Magnesium, mg/L.

Table 12. - Summary of total sodium distribution (Na^+, mg/L), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	5.0	3.2	8.2	84	1	1.2	310.0
SRWMD	5.0	2.6	7.0	25	0	0.8	30.0
SJRWMD	17.5	8.0	47.0	64	10	2.0	868.0
SWFWMD	6.4	3.4	15.5	85	2	0.7	3730.0
SFWMD	21.1	11.9	45.2	610	25	1.6	620.0
Statewide	17.0	7.0	39.0	868	38	0.7	3730.0
Sand & Gravel	5.0	3.2	8.6	75	0	1.3	160.0
Biscayne	18.0	11.1	31.0	248	7	2.1	420.0
Other	19.4	7.3	48.3	545	31	0.7	3730.0

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	4.5	3.3	20.0	24	0	1.0	78.0
SRWMD	4.3	3.7	7.4	37	0	2.3	23.0
SJRWMD	14.0	8.7	31.0	33	5	5.8	2585.0
SWFWMD	31.7	12.9	73.5	52	6	2.9	357.0
SFWMD	108.6	51.8	369.0	103	46	11.4	1264.0
Statewide	41.0	9.6	136.2	249	57	1.0	2585.0

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	6.0	2.9	27.0	102	1	0.7	350.0
SRWMD	6.3	3.7	12.0	220	5	0.2	3200.0
SJRWMD	20.0	7.9	80.0	125	22	1.0	7043.0
SWFWMD	7.4	4.3	28.9	165	18	1.8	1450.0
SFWMD	220.5	42.1	490.0	138	81	2.7	2500.0
Statewide	11.0	4.5	84.6	750	127	0.2	7043.0

*** - Number of samples which exceeded Florida Primary Drinking Water Standards for Sodium (> 160 mg/L).**

Table 13. - Summary of total potassium distribution (K^+, mg/L), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	1.2	0.7	2.6	84	0.2	31.0
SRWMD	1.5	0.5	3.4	25	< 0.1	19.0
SJRWMD	2.0	0.9	4.4	64	0.2	601.6
SWFWMD	0.8	0.3	2.3	85	< 0.1	29.7
SFWMD	1.3	0.7	2.8	610	< 0.1	159.2
Statewide	1.2	0.7	2.8	868	< 0.1	601.6
Sand & Gravel	1.4	0.7	2.5	75	0.2	31.0
Biscayne	1.1	0.7	2.2	248	< 0.1	69.0
Other	1.3	0.6	3.0	545	< 0.1	601.6

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	2.2	0.9	4.2	24	0.4	78.0
SRWMD	0.6	0.5	0.8	37	< 0.1	19.0
SJRWMD	2.3	1.2	8.4	33	0.2	85.0
SWFWMD	2.7	1.3	6.2	52	0.3	22.4
SFWMD	9.6	6.8	19.2	103	0.4	46.9
Statewide	4.4	1.3	11.0	249	< 0.1	85.0

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	1.6	0.6	4.7	101	0.2	76.0
SRWMD	1.1	0.4	4.2	220	0.1	320.0
SJRWMD	1.7	0.9	4.2	125	0.2	251.0
SWFWMD	1.0	0.4	3.2	166	< 0.1	145.0
SFWMD	9.5	2.5	20.8	138	0.5	99.0
Statewide	1.8	0.7	6.7	750	< 0.1	320.0

Table 14. - Summary of total iron distribution (Fe^{2+}+Fe^{3+}, mg/L), by region and aquifer system. Data from non-metal cased wells.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	2.05	0.78	6.75	80	72	0.07	95.00
SRWMD	1.09	0.32	2.85	23	18	< 0.01	18.00
SJRWMD	4.09	0.61	9.73	51	45	0.09	56.21
SWFWMD	2.14	0.32	8.39	39	30	< 0.03	43.90
SFWMD	0.88	0.20	2.58	376	263	< 0.01	41.50
Statewide	1.08	0.24	2.94	569	428	< 0.01	95.00
Sand & Gravel	2.00	0.79	6.30	73	66	0.07	95.00
Biscayne	1.19	0.27	2.46	155	120	< 0.01	8.46
Other	0.89	0.24	4.75	341	242	< 0.02	56.21

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	0.60	0.23	2.40	22	14	0.02	35.00
SRWMD	1.17	< 0.23	3.10	14	12	< 0.05	15.00
SJRWMD	0.46	0.33	1.72	21	16	< 0.01	4.61
SWFWMD	0.13	0.05	0.54	19	7	< 0.02	12.10
SFWMD	< 0.05	< 0.05	0.10	63	9	0.03	26.60
Statewide	0.07	< 0.05	0.43	139	58	< 0.01	35.00

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	0.23	0.05	0.87	34	16	< 0.01	2.50
SRWMD	0.61	0.17	1.60	135	95	< 0.01	17.00
SJRWMD	0.19	0.06	0.89	48	24	< 0.01	24.92
SWFWMD	0.13	0.05	0.35	70	21	< 0.01	55.70
SFWMD	< 0.05	< 0.05	< 0.05	32	0	< 0.02	0.29
Statewide	0.21	< 0.05	1.00	319	156	< 0.01	55.70

*** - Number of samples which exceeded Florida Secondary Drinking Water Standards for Iron (> 0.30 mg/L).**

Table 15. - Summary of total mercury distribution (Hg^{2+}, µg/L), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	< 0.5	< 0.5	< 0.5	84	8	< 0.5	7.3
SRWMD	< 0.2	< 0.2	< 0.2	23	1	< 0.2	3.0
SJRWMD	< 0.5	< 0.5	< 0.5	58	2	< 0.5	52.0
SWFWMD	< 0.1	< 0.1	< 0.1	67	3	< 0.1	3.1
SFWMD	< 0.2	< 0.2	< 0.2	424	0	< 0.1	0.6
Statewide	< 0.2	< 0.2	< 0.5	656	14	< 0.1	52.0
Sand & Gravel	< 0.5	< 0.5	< 0.5	75	8	< 0.5	7.3
Biscayne	< 0.2	< 0.2	< 0.2	333	0	< 0.2	<1.0
Other	< 0.2	< 0.1	< 0.5	248	6	< 0.1	52.0

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	< 0.5	< 0.5	< 0.5	37	1	< 0.3	2.2
SRWMD	< 0.2	< 0.2	< 0.2	27	0	< 0.2	2.0
SJRWMD	< 0.5	< 0.5	< 0.5	32	4	< 0.5	8.0
SWFWMD	< 0.1	< 0.1	< 0.1	45	0	< 0.1	1.3
SFWMD	< 0.1	< 0.1	< 0.1	10	0	< 0.1	<0.3
Statewide	< 0.5	< 0.1	< 0.5	151	5	< 0.1	8.0

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	< 0.5	< 0.5	< 0.5	209	4	< 0.3	6.5
SRWMD	< 0.2	< 0.2	< 0.2	157	0	< 0.2	2.0
SJRWMD	< 0.5	< 0.5	< 0.5	113	2	< 0.5	4.7
SWFWMD	< 0.1	< 0.1	< 0.1	154	0	< 0.1	1.3
SFWMD	< 0.1	< 0.1	< 0.1	18	0	< 0.1	0.2
Statewide	< 0.5	< 0.1	< 0.5	651	6	< 0.1	6.5

*** - Number of samples which exceeded Florida Primary Drinking Water Standards for Mercury (> 2.0 :g/L).**

Table 16. - Summary of total lead distribution (Pb^{2+}, µg/L), by region and aquifer system. Data from non-metal cased wells.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	< 10	7	15	80	10	< 1	190
SRWMD	< 10	< 10	< 10	23	0	< 10	40
SJRWMD	23	< 10	58	46	18	< 10	4300
SWFWMD	36	< 30	< 50	53	11	< 20	1630
SFWMD	< 2	< 1	3	440	9	< 1	173
Statewide	2	< 1	< 10	642	48	< 1	4300
Sand & Gravel	< 10	8	16	73	10	< 1	190
Biscayne	< 2	< 2	2	218	2	< 1	87
Other	7	1	30	351	36	< 1	4300

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	< 10	< 10	< 10	22	1	3	63
SRWMD	< 10	< 10	<10	14	1	< 10	56
SJRWMD	< 10	< 10	13	21	2	< 4	192
SWFWMD	< 43	< 30	< 50	25	6	< 30	530
SFWMD	1	< 1	5	59	1	< 1	71
Statewide	< 10	< 10	24	141	11	< 1	530

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc *	Min	Max
NWFWMD	< 10	< 10	< 10	35	0	1	50
SRWMD	< 10	< 10	< 10	135	4	< 10	100
SJRWMD	< 10	< 10	31	47	9	4	260
SWFWMD	< 30	< 30	< 36	69	14	< 20	470
SFWMD	< 1	< 1	< 1	30	0	< 1	9
Statewide	< 10	< 10	25	316	27	< 1	470

*** - Number of samples which exceeded Florida Primary Drinking Water Standards for Lead (> 50 :g/L).**

Table 17. - Summary of total bicarbonate distribution (HCO_3^-, mg/L), by region and aquifer system. (n.d. = not determined)

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	5	< 1	16	84	< 1	232
SRWMD	27	13	62	25	4	140
SJRWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SWFWMD	34	< 5	136	84	< 1	322
SFWMD	263	229	314	169	64	637
Statewide	138	10	260	362	<1	637
Sand & Gravel	5	< 1	13	75	< 1	134
Biscayne	263	229	314	169	64	637
Other	27	8	101	118	< 1	322

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	137	116	183	24	16	1463
SRWMD	90	24	150	36	< 1	490
SJRWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SWFWMD	173	118	213	53	4	306
SFWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Statewide	143	95	200	113	< 1	1463

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	158	122	207	101	29	451
SRWMD	150	76	230	220	< 1	770
SJRWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SWFWMD	144	116	181	162	3	646
SFWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Statewide	146	110	206	483	< 1	770

Table 18. - Summary of total carbonate distribution (CO_3^{2-}, mg/L), by region and aquifer system. (n.d. = not determined)

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SRWMD	< 1	< 1	< 1	23	< 1	70
SJRWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SWFWMD	< 1	< 1	< 1	71	< 1	1
SFWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Statewide	< 1	< 1	< 1	94	< 1	70
Sand&Gravel	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Biscayne	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Other	< 1	< 1	< 1	94	< 1	70

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SRWMD	< 1	< 1	< 1	27	< 1	22
SJRWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SWFWMD	< 1	< 1	< 1	44	< 1	116
SFWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Statewide	< 1	< 1	< 1	71	< 1	116

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SRWMD	< 1	< 1	< 1	157	< 1	650
SJRWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SWFWMD	<1	< 1	< 1	152	<1	46
SFWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Statewide	< 1	< 1	< 1	309	< 1	650

Table 19. - Summary of total bicarbonate alkalinity distribution (mg/L), by region and aquifer system. (n.d. = not determined)

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	4	< 1	13	84	< 1	190
SRWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SJRWMD**	147	70	238	59	1	508
SWFWMD++	42	16	97	18	5	251
SFWMD**	251	202	312	581	3	2260
Statewide	111	72	165	742	< 1	2260
Sand & Gravel	4	< 1	11	75	< 1	110
Biscayne**	242	212	294	219	64	637
Other	244	160	315	448	< 1	2260

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	113	95	150	24	< 1	1200
SRWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SJRWMD**	238	169	290	30	17	561
SWFWMD++	234	70	259	7	< 1	284
SFWMD**	234	177	271	102	111	445
Statewide	205	128	243	163	< 1	1200

C. Floridan aquifer system

DISTRICT	MEDIAN	QRTILE	QRTILE	# SAMPLES	MINIMUM	MAXIMUM
NWFWMD	130	100	170	101	24	370
SRWMD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
SJRWMD**	145	99	188	103	11	866
SWFWMD**	168	114	215	10	106	530
SFWMD**	130	95	162	138	10	287
Statewide	143	102	184	352	10	866

** - Calcium Carbonate Alkalinity, mg/L.
++ - Data reported in meq/L.

Table 20. - Summary of total sulfate distribution (SO_4^{2-}, mg/L), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	3.3	1.5	6.0	84	2	< 1.0	380.0
SRWMD	4.3	< 1.0	13.0	23	0	< 0.1	33.0
SJRWMD	12.0	3.0	30.0	61	4	< 1.0	597.0
SWFWMD	8.1	< 1.0	50.6	85	9	< 0.1	1480.0
SFWMD	11.8	< 5.0	24.0	614	4	< 1.0	431.0
Statewide	17.0	7.0	39.0	867	15	< 0.1	1480.0
Sand&Gravel	3.6	1.4	5.5	75	2	0.8	380.0
Biscayne	14.0	< 2.0	26.0	257	0	< 1.0	185.0
Other	10.0	< 5.0	24.5	535	13	< 0.1	1480.0

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	< 1.0	< 1.0	1.9	38	0	< 1.0	49.0
SRWMD	< 1.0	< 1.0	4.7	27	0	< 1.0	27.0
SJRWMD	< 1.0	< 1.0	4.0	33	1	< 1.0	408.0
SWFWMD	36.9	< 1.5	299.0	56	19	< 0.1	1590.0
SFWMD	52.3	14.4	182.0	97	13	2.0	1754.0
Statewide	5.4	< 1.0	65.5	251	33	< 0.1	1754.0

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	< 1.0	< 1.0	4.4	147	1	< 1.0	310.0
SRWMD	6.7	1.7	16.5	157	2	< 1.0	2200.0
SJRWMD	8.5	< 1.0	83.5	122	13	< 1.0	2040.0
SWFWMD	3.0	< 1.0	63.5	169	33	< 0.1	3102.0
SFWMD	176.4	49.3	308.4	135	46	3.3	713.1
Statewide	5.4	< 1.0	53.0	730	95	< 0.1	3102.0

*** - Number of samples which exceeded Florida Secondary Drinking Water Standards for Sulfate (> 250 mg/L).**

Table 21. - Summary of total chloride distribution (Cl^-, mg/L), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	7.0	5.0	11.5	84	1	1.8	410.0
SRWMD	6.0	3.0	8.2	25	0	1.4	32.0
SJRWMD	28.0	13.0	91.0	62	12	4.0	1790.0
SWFWMD	12.9	7.0	37.8	86	3	0.6	8520.0
SFWMD	48.3	26.2	83.0	857	48	< 0.4	1100.0
Statewide	40.5	16.0	74.3	1114	64	< 0.4	8520.0
Sand & Gravel	7.1	5.0	11.0	75	0	2.3	220.0
Biscayne	58.0	34.0	79.0	493	33	4.8	700.0
Other	30.5	13.0	74.7	546	31	< 0.4	8520.0

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	5.3	3.0	8.9	24	0	1.7	58.0
SRWMD	4.5	3.7	21.0	36	0	3.1	54.0
SJRWMD	18.5	12.5	42.5	32	4	7.0	4480.0
SWFWMD	50.0	13.2	204.0	56	13	2.7	940.0
SFWMD	172.0	61.1	580.0	103	42	15.2	2092.5
Statewide	61.9	18.0	334.5	251	59	1.7	4480.0

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	6.3	3.8	23.0	101	2	1.7	300.0
SRWMD	8.9	5.0	19.0	220	4	< 1.0	5200.0
SJRWMD	28.0	12.0	203.0	122	27	1.0	16270.0
SWFWMD	11.3	7.3	35.4	169	24	1.7	20500.0
SFWMD	419.6	58.6	922.5	136	84	3.5	3785.0
Statewide	21.0	7.6	276.0	748	141	< 1.0	20500.0

*** - Number of samples which exceeded Florida Secondary Drinking Water Standards for Chloride (> 250 mg/L).**

Table 22. - Summary of total ortho-phosphate distribution (PO_4^{3-} as P, mg/L), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD (P)	0.09	0.05	0.23	84	< 0.05	1.20
SRWMD	< 0.10	< 0.10	< 0.10	25	< 0.01	0.20
SJRWMD (P)	0.11	0.05	0.32	64	< 0.01	1.82
SWFWMD (t)	0.07	0.02	0.27	82	< 0.01	1.84
SFWMD (f)	0.01	< 0.01	0.02	357	< 0.01	4.00
Statewide	0.06	0.02	0.17	612	< 0.01	4.00
Sand & Gravel	0.09	0.05	0.22	75	0.01	1.20
Biscayne (f)	< 0.01	< 0.01	< 0.01	19	< 0.01	0.06
Other	0.07	< 0.05	0.06	518	< 0.01	4.00

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD (P)	< 0.05	< 0.01	0.11	29	< 0.01	1.20
SRWMD	< 0.10	< 0.01	< 0.10	36	< 0.01	2.00
SJRWMD (P)	0.11	0.03	0.21	33	< 0.01	0.43
SWFWMD (t)	0.11	0.04	0.16	52	< 0.01	1.20
SFWMD (f)	< 0.01	< 0.01	< 0.01	103	< 0.01	2.28
Statewide	0.04	0.01	0.10	253	< 0.01	2.28

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD (P)	0.04	0.02	0.06	116	< 0.01	1.60
SRWMD	< 0.10	< 0.10	< 0.10	220	< 0.01	21.00
SJRWMD (P)	0.04	0.01	0.11	122	< 0.01	0.75
SWFWMD (t)	0.10	0.05	0.17	152	< 0.01	0.80
SFWMD (f)	< 0.01	< 0.01	< 0.01	115	< 0.01	0.15
Statewide	0.04	0.02	0.07	725	< 0.01	21.00

(P) - Total Phosphorus (P), mg/L.
(t) - Total Phosphate as PO_4, mg/L.
(f) - Dissolved (filtered) ortho-phosphate, mg/L.

Table 23. - Summary of total fluoride distribution (F^-, mg/L), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	0.04	0.03	0.07	84	1	< 0.02	5.90
SRWMD	< 0.20	< 0.20	< 0.20	25	0	< 0.02	0.79
SJRWMD	< 0.10	< 0.10	0.14	63	0	< 0.01	1.75
SWFWMD	0.10	0.04	0.25	84	0	< 0.01	1.95
SFWMD	0.20	< 0.10	0.30	608	0	0.02	3.73
Statewide	0.17	< 0.10	0.28	864	1	< 0.01	5.90
Sand & Gravel	0.04	0.03	0.07	75	1	< 0.02	5.90
Biscayne	0.20	0.15	0.25	279	0	0.06	0.93
Other	< 0.20	< 0.10	0.31	510	0	< 0.01	3.73

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	0.19	0.13	0.23	25	0	< 0.05	0.53
SRWMD	< 0.20	0.20	0.30	36	0	< 0.01	1.00
SJRWMD	0.12	< 0.10	0.30	33	0	< 0.10	1.75
SWFWMD	0.89	0.30	1.15	53	0	0.07	4.00
SFWMD	0.82	0.43	1.30	103	1	< 0.10	4.78
Statewide	0.39	< 0.20	0.97	250	1	< 0.01	4.78

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	0.13	< 0.05	0.37	122	1	< 0.10	6.90
SRWMD	< 0.20	< 0.20	< 0.20	220	0	< 0.02	2.50
SJRWMD	0.16	< 0.10	0.26	124	0	< 0.10	1.28
SWFWMD	0.16	0.10	0.36	162	0	0.01	2.32
SFWMD	0.81	0.40	1.26	131	0	< 0.10	3.70
Statewide	0.20	0.12	0.41	759	1	< 0.02	6.90

*** - Number of samples which exceeded Florida Primary Drinking Water Standards for Fluoride (> 4.00 mg/L).**

Table 24. - Summary of total nitrate distribution (NO_3^-, mg/L as N), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	0.81	0.29	2.00	84	3	0.07	28.00
SRWMD	< 0.05	< 0.05	< 0.05	25	0	< 0.05	1.10
SJRWMD **	< 0.01	< 0.01	0.03	64	0	< 0.01	7.50
SWFWMD ++	< 0.01	< 0.01	0.18	84	1	< 0.01	52.52
SFWMD	< 0.01	< 0.01	< 0.01	571	1	< 0.01	44.80
Statewide	< 0.01	< 0.01	0.01	828	5	< 0.01	52.52
Sand & Gravel	0.95	0.37	2.30	75	3	0.07	28.00
Biscayne	< 0.01	< 0.01	< 0.01	239	1	< 0.01	44.80
Other	< 0.05	< 0.01	0.03	514	1	< 0.01	52.52

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	0.11	< 0.01	1.20	35	0	< 0.01	6.70
SRWMD	< 0.05	< 0.05	< 0.05	36	0	< 0.01	7.10
SJRWMD **	< 0.01	< 0.01	< 0.01	33	0	< 0.01	0.03
SWFWMD ++	0.01	< 0.01	0.02	52	0	< 0.01	3.50
SFWMD	< 0.01	< 0.01	< 0.01	100	0	< 0.01	0.19
Statewide	< 0.01	< 0.01	< 0.05	256	0	< 0.01	7.10

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	0.90	< 0.01	1.50	123	7	< 0.01	74.00
SRWMD	< 0.05	< 0.05	< 0.05	220	0	< 0.01	8.40
SJRWMD ##	< 0.01	< 0.01	0.03	123	1	< 0.01	18.40
SWFWMD ++	0.01	< 0.01	0.05	153	0	< 0.01	4.64
SFWMD	< 0.01	< 0.01	< 0.01	120	0	< 0.01	1.97
Statewide	< 0.01	< 0.01	0.05	739	8	< 0.01	74.00

* - Number of samples which exceeded Florida Primary Drinking Water Standards for Nitrate as N (> 10.00 mg/L) or Nitrate as NO_3 (> 43.00 mg/L).

** - Reported as Nitrate + Nitrite (NO_x), mg/L.

++ - Reported as Nitrate as NO_3, mg/L.

Table 25. - Summary of total dissolved solids concentrations (TDS, mg/L), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	74	46	125	84	3	15	1000
SRWMD	70	45	110	23	0	27	320
SJRWMD	300	151	472	63	14	63	3821
SWFWMD	187	80	336	83	11	1	17700
SFWMD	388	296	513	656	170	26	2537
Statewide	346	181	474	909	198	1	17700
Sand & Gravel	74	45	110	75	2	15	1000
Biscayne	392	316	468	288	55	108	1712
Other	339	160	512	546	141	1	17700

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	165	130	260	24	0	36	390
SRWMD	100	57	190	27	0	18	350
SJRWMD	355	241	397	33	6	38	6892
SWFWMD	525	286	943	54	28	40	2340
SFWMD	508	417	1427	103	55	47	4188
Statewide	390	219	871	241	89	18	6892

C. Floridan aquifer system

District	Median	Qrtile	Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	200	160	310	101	10	42	810
SRWMD	220	160	300	157	21	40	10200
SJRWMD	342	183	598	123	37	47	24092
SWFWMD	257	176	656	161	47	55	5990
SFWMD	1138	414	2045	138	97	58	7425
Statewide	277	176	715	680	212	40	24092

*** - Number of samples which exceeded Florida Secondary Drinking Water Standards for Total Dissolved Solids (TDS) (> 500 mg/L).**

Table 26. - Summary of specific conductance distribution (:mhos/cm), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	50	35	88	84	15	1522
SRWMD	90	50	160	25	20	500
SJRWMD	335	140	625	49	40	3900
SWFWMD	255	105	450	100	30	24000
SFWMD	619	450	894	378	41	8281
Statewide	475	138	743	636	15	24000
Sand & Gravel	50	34	85	75	15	747
Biscayne	517	415	587	19	383	687
Other	540	220	805	542	15	24000

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	229	193	348	24	41	593
SRWMD	160	80	270	36	25	500
SJRWMD	575	390	650	22	150	8000
SWFWMD	600	410	1200	61	50	3325
SFWMD	947	703	2324	100	245	6920
Statewide	650	319	1500	243	25	8000

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	274	216	470	101	81	1542
SRWMD	310	240	450	220	50	15000
SJRWMD	500	282	899	96	70	14500
SWFWMD	378	255	800	194	100	46000
SFWMD	1787	624	3305	131	120	12204
Statewide	385	251	1000	742	50	46000

Table 27. - Summary of total organic carbon distribution (TOC, mg/L), by region and aquifer system.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	6.8	4.2	9.7	84	1.9	42.4
SRWMD	5.9	< 1.0	17.5	23	< 1.0	50.0
SJRWMD	9.0	4.3	16.9	58	< 0.1	257.3
SWFWMD	11.4	3.4	22.1	82	< 0.1	122.0
SFWMD	17.0	9.5	31.1	548	< 0.1	380.0
Statewide	14.0	7.0	27.0	795	< 0.1	380.0
Sand & Gravel	6.6	4.1	8.4	75	1.9	25.2
Biscayne	14.3	8.4	22.7	258	1.0	73.0
Other	16.9	7.8	36.0	462	< 0.1	380.0

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	6.1	2.1	8.9	26	< 1.0	31.0
SRWMD	<1.0	< 1.0	2.8	27	< 1.0	12.0
SJRWMD	5.5	3.9	7.7	32	1.4	26.4
SWFWMD	9.8	< 1.0	21.6	52	< 0.1	52.3
SFWMD	6.3	2.0	19.0	91	< 0.1	71.0
Statewide	4.8	< 1.0	13.1	228	< 0.1	71.0

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samples	Minimum	Maximum
NWFWMD	< 1.0	< 1.0	3.2	178	< 0.1	39.0
SRWMD	2.0	< 1.0	6.2	157	< 1.0	34.0
SJRWMD	3.3	1.5	5.4	111	< 0.5	29.0
SWFWMD	16.8	10.4	27.1	150	< 0.1	78.8
SFWMD	1.9	0.5	3.5	114	< 0.1	80.6
Statewide	2.2	< 1.0	7.9	710	< 0.1	80.6

Table 28. - List of synthetic organics analyzed in the Background Network, with guidance concentrations or standards (Florida Department of Environmental Regulation, 1989).

Parameter Number	Parameter Name	Units	Guidance Concentration
11	METHYL BLUE ACTIVE SUBSTANCES	mg/L	500
86	CIS/TRANS-1,2-DICHLOROETHYLENE	µg/L	mdl
87	METHYL ISOCYANATE	µg/L	mdl
88	CIS/TRANS-1,2-DICHLOROETHYLENE	µg/L	mdl
89	1,2-BENZISOTHIOZOLE	µg/L	mdl
90	PETROLEUM HYDROCARBONS	µg/L	mdl
91	METHY-TERT-BUTYL-ETHER	µg/L	mdl
92	METHYL N-BUTYL KETONE	µg/L	mdl
93	TOTAL TRIHALOMETHANE	mg/L	100
94	METHYL IOS-BUTYL KETONE	µg/L	350
95	4,6 DINITRO O-CRESOL	µg/L	50
96	1,3-DIBROMO-2-CHLOROPROPANE	µg/L	mdl
97	P-CHLORO M-CRESOL	µg/L	3,000
98	HEXACHLOROBUTADIENE	µg/L	10
99	2-METHYL-4,6-DINITROTOLUENE	µg/L	mdl
100	DICHLORODIFLUOROMETHANE	µg/L	mdl
101	DIBENZO(A,H)ANTHRACENE	µg/L	mdl
102	1,3-DICHLOROPROPENE	µg/L	mdl
103	TRICHLOROFLUOROMETHANE	µg/L	mdl
104	1,1 DICHLOROETHANE	µg/L	2,400
105	1,1 DICHLOROPROPANE	µg/L	mdl
106	1,1 DICHLOROETHENE	µg/L	7
107	HEXACHLOROBENZENE	µg/L	mdl
108	PCB-1254	µg/L	0.5
109	TRICHLOROPHENOL ISOMERS	µg/L	mdl
110	PCB-1242	µg/L	0.5
111	1,1,1 TRICHLORORTHANE	µg/L	200
112	CIS-1,2-DICHLOROETHANE	µg/L	mdl
113	1,1,2 TRICHLOROETHANE	µg/L	1
114	METHYL ETHYL KETONE	µg/L	170
115	1,1,2,2 TETRACHLOROETHANE	µg/L	1
116	XYLENE	µg/L	50
117	BENXO(G,H,I)PERYLENE	µg/L	mdl
118	DICHLOROBENZENE	µg/L	75
119	PCB-1232	µg/L	0.5
120	4-CHLORO-3-METHYL PHENOL	µg/L	mdl
121	TRICHLOROETHENE	µg/L	3
122	PHENANTHRENE	µg/L	mdl
123	BENZIDINE	µg/L	mdl
124	DI-N-BUTYL PHTHALATE	µg/L	mdl
125	VINYL CHLORIDE	µg/L	1
126	TRIMETHYLBENZENE	µg/L	10
127	BIS(2-ETHYLHEXYL)PHTHALATE	µg/L	mdl
128	PYRENE	µg/L	mdl
129	ETHYL BENZENE	µg/L	2

Parameter Number	Parameter Name	Units	Guidance Concentration
130	TETRACHLOROETHENE	µg/L	3
131	CHLOROTOLUENE	µg/L	mdl
132	VINYL ACETATE	µg/L	mdl
133	BIS(2-CHLORO-1-METHYL) ETHER	µg/L	mdl
134	CIS 1,3 DICHLOROPROPENE	µg/L	1
135	HEXACHLOROETHANE	µg/L	10
136	NAPHTHALENE	µg/L	mdl
137	PHENOL	µg/L	mdl
138	TRANS 1,3 DICHLOROPROPENE	µg/L	1
139	1,2-DIBROMOETHANE (EDB)	µg/L	0.2
140	INDENO(1,2,3-CD)PYRENE	µg/L	10
141	1,2,4 TRIETHYL BENZENE	µg/L	mdl
142	BENZO(B)THIOPHENE	µg/L	mdl
143	N-BUTYLBENZENE	µg/L	mdl
144	N-PROPYLBENZENE	µg/L	mdl
145	BROMOMETHANE	µg/L	20
146	M XYLENE	µg/L	50
147	CHLOROMETHANE	µg/L	3,800
148	STYRENE	µg/L	1
149	PCB-1016	µg/L	0.5
150	BROMODICHLOROMETHANE	µg/L	100
151	TOTAL PCB'S	µg/L	0.5
152	METHYLENE CHLORIDE	µg/L	100
153	BROMOFORM	µg/L	100
154	N-NITROSODI-N-PROPYL AMINE	µg/L	10
155	CHLOROFORM	µg/L	100
156	N-NITROSODIPHENYLAMINE	µg/L	10
157	TOTAL PHENOLS	µg/L	mdl
158	N-NITROSODIMETHYLAMINE	µg/L	20
159	BENZENE	µg/L	1
160	NITROBENZENE	µg/L	mdl
161	ACENAPHTHENE	µg/L	20
162	ACROLEIN	µg/L	110
163	ACRYLONITRILE	µg/L	2.5
164	ANTHRACENE	µg/L	10
165	P XYLENE	µg/L	50
166	BENZO(K)FLUORANTHENE	µg/L	10
167	BENZO(A)PYRENE	µg/L	10
168	D-BHC	µg/L	0.05
169	BIS(2-CHLOROETHYL)ETHER	µg/L	10
170	BIS(2-CHLOROETHOXY)ME. ETHER	µg/L	10
171	BIS(2-CHLOROISOPROPYL) ETHER	µg/L	10
172	BENZYL BUTYL PHTHALATE	µg/L	1,400
173	CHLOROBENZENE	µg/L	10
174	CHLOROETHANE	µg/L	6,300
175	DIETHYLPHTHALATE	µg/L	5,600
176	2,6-DINITROTOLUENE	µg/L	mdl
177	PCB-1248	µg/L	0.5
178	1,2 DIPHENYLHYDRAZINE	µg/L	10
179	2,4,6-TRICHLOROPHENOL	µg/L	mdl

Parameter Number	Parameter Name	Units	Guidance Concentration
180	2,4-DINITROPHENOL	µg/L	mdl
181	2,4-DINITRITOLUENE	µg/L	mdl
182	2,4-DIMETHYLPHENOL	µg/L	mdl
183	ETHYLBENZENE	µg/L	2
184	FLUORANTHENE	µg/L	42
185	FLUORENE	µg/L	10
186	PCB-1262	µg/L	0.5
187	1,1,2TRICL.1,2,2TRIF. ETHANE	µg/L	mdl
188	ACETONE	µg/L	700
189	2,3,7,8-TETRACHLORODIBENZOPDIOXIN	µg/L	200
190	PCB-1221	µg/L	0.5
191	PCB-1260	µg/L	0.5
192	CARBON TETRACHLORIDE	µg/L	3
193	DIBROMOCHLOROMETHANE	µg/L	100
194	BENZOFURAN	µg/L	mdl
195	BENZO(A)ANTHRACENE	µg/L	mdl
196	ACENAPHTHYLENE	µg/L	10
197	1,2 DICHLOROETHANE	µg/L	3
198	BENZO(B)FLUORANTHENE	µg/L	10
199	1,2-DICHLOROBENZENE	µg/L	mdl
200	4-BROMOPHENYL ETHER	µg/L	mdl
201	1,2 DICHLOROPROPANE	µg/L	1
202	DIMETHYLPHTHALATE	µg/L	mdl
203	TRANS 1,2 DICHLOROETHENE	µg/L	4.2
204	HEXACHLOROCYCLYPENTANE	µg/L	10
205	1,2,4-TRICHLOROBENZENE	µg/L	mdl
206	O-XYLENE	µg/L	50
207	CARBON DISULFIDE	µg/L	mdl
208	TOLUENE	µg/L	24
209	4-NITROPHENOL	µg/L	mdl
210	4-CHLOROPHENYL PHENYL ETHER	µg/L	mdl
211	3,3'-DICHLOROBENZIDINE	µg/L	mdl
212	DI-N-OCTYL PHTHALATE	µg/L	mdl
213	2-NITROPHENOL	µg/L	mdl
214	2,4-DICHLOROPHENOL	µg/L	mdl
215	1,3-DICHLOROBENZENE	µg/L	mdl
216	1,4-DICHLOROBENZENE	µg/L	mdl
217	2 CHLOROETHYL VINYL ETHER	µg/L	1
218	2-CHLORONAPHTHALENE	µg/L	mdl
219	2-CHLOROPHENOL	µg/L	mdl
228	CHRYSENE	µg/L	10
281	CHLOROFORM	µg/L	100
282	TRICHLOROETHYLENE, DISSOLVED	µg/L	3
283	VINYL CHLORIDE	µg/L	mdl
284	M-XYLENE	µg/L	50
289	PHENANTHRENE, DISSOLVED	µg/L	mdl
297	PCNB	µg/L	mdl

Table 29. - Summary of total synthetic organics concentrations (:g/L), by region and aquifer system. Most detections were not confirmed by resampling.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	0.00	0.00	< 0.00	109	3	0.00	190.00
SRWMD	0.00	0.00	0.00	22	0	0.00	1.00
SJRWMD	< 0.50	< 0.50	< 0.50	58	4	< 0.50	128.00
SWFWMD	< 1.00	< 1.00	< 1.00	83	2	< 1.00	6.70
SFWMD	0.00	0.00	< 1.00	392	35	0.00	995.00
Statewide	0.00	0.00	< 1.00	664	44	0.00	995.00
Sand & Gravel	0.00	0.00	< 1.00	93	3	0.00	190.00
Biscayne	< 10.00	< 1.00	< 10.00	21	2	< 1.00	12.00
Other	0.00	0.00	< 1.00	550	39	0.00	995.00

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	0.00	0.00	< 1.00	26	0	0.00	3.50
SRWMD	0.00	0.00	0.00	24	0	0.00	0.00
SJRWMD	0.00	0.00	0.00	27	0	0.00	0.92
SWFWMD	< 1.00	< 1.00	< 1.00	52	0	< 1.00	1.60
SFWMD	< 1.00	0.00	< 1.00	107	3	0.00	2.10
Statewide	0.00	0.00	< 1.00	236	3	0.00	3.50

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD	0.00	0.00	0.00	118	0	0.00	2.70
SRWMD	0.00	0.00	0.00	301	4	0.00	14.00
SJRWMD	< 0.50	< 0.50	< 0.50	110	5	0.00	20.20
SWFWMD	< 1.00	< 1.00	< 1.00	168	12	0.00	70.01
SFWMD	0.00	0.00	0.00	133	5	0.00	3.90
Statewide	0.00	0.00	0.00	830	26	0.00	70.01

Table 30. - Classification of anthropogenic organics according to volatility in water. Modified from Lyman *et al.* (1982).

Henry's Law Constant (atm m^3/mol)	Volatility
< 10^{-7}	Low
10^{-7} - 10^{-5}	Slight
10^{-5} - 10^{-3}	Moderate
> 10^{-3}	High

Table 31. - Classification of synthetic organic mobility in water. Modified from Fetter (1988).

Mobility	Solubility (mg/L)	K_{OC}
Very mobile	miscible	≈ 1
Very mobile	> 4,000	1 - 50
Mobile	4,000 - ≈ 1,000	50 - 150
Moderately mobile	≈ 1,000 - ≈ 100	150 - 500
Low mobility	≈ 100 - ≈ 10	500 - 2,000
slight mobility	≈ 10 - ≈ 0.25	2,000 - 20,000
Immobile	< ≈ 0.25	> 20,000

Table 32. - List of pesticides analyzed in the Background Network as of 1989, with guidance concentration or standards.

Parameter Number	Parameter Name	Units	Guidance Concentration*
220	CHLOROPICRIN	µg/L	7.3
221	PROPAZINE	µg/L	mdl
222	AZINPHOS METHYL	µg/L	mdl
223	ENDRIN-ALDEHYDE	µg/L	0.1
224	ENDOSULFAN I	µg/L	0.4
225	ENDOSULFAN II	µg/L	0.4
226	ENDOSULFAN-SULFATE	µg/L	0.3
227	ETHOPROP	µg/L	mdl
229	ALACHLOR	µg/L	1.5
230	CHLORPYRIFOS	µg/L	mdl
231	NORFLURAZON	µg/L	mdl
232	ISOFENPHOS	µg/L	mdl
233	DICAMBA	µg/L	mdl
234	CHLOROTHALONIL	µg/L	mdl
235	METHYL PARATHION	µg/L	mdl
236	ISOPHORONE	µg/L	1050
237	CARBARYL	µg/L	mdl
238	METAM-SODIUM	µg/L	mdl
239	ETHYL PARATHION	µg/L	mdl
240	KELTHANE	µg/L	mdl
241	NALED	µg/L	mdl
242	OXAMYL	µg/L	mdl
243	DALAPON	µg/L	mdl
244	TERBUTRYN	µg/L	mdl
245	DICHLORAN	µg/L	mdl
246	TRIADEMEFON	µg/L	mdl
247	METHIOCARB	µg/L	mdl
248	METHAMIDOPHOS	µg/L	mdl
249	PROPOXUR	µg/L	mdl
250	FENAMIPHOS	µg/L	mdl
251	CHLORPYRIFOS	µg/L	mdl
252	BENFLURALIN	µg/L	mdl
253	1,2-DIBROMO-3-CHLOROPROPANE	µg/L	mdl
254	STROBANE	µg/L	mdl
255	HEXAZINONE	µg/L	mdl
256	PENTACHLOROPHENOL	µg/L	mdl
257	DALAPON	µg/L	mdl
258	ATRAZINE	µg/L	mdl
259	PCNB	µg/L	mdl
260	PERTHANE	µg/L	mdl
261	2,4-DB	µg/L	mdl
262	METALAXYL	µg/L	mdl
263	LINURON	µg/L	22
264	TERBUTHYLAZINE	µg/L	mdl
265	DINOSEB	µg/L	mdl
266	METHOMYL	µg/L	mdl
267	ALDICARB	µg/L	mdl
268	SIMAZINE	µg/L	mdl
269	PROMETON	µg/L	mdl
270	PROMETRYN	µg/L	mdl
271	DIQUAT DIBROMIDE (REGLONE)	µg/L	mdl
272	TRIFLURALIN	µg/L	mdl
273	PENDIMETHALIN	µg/L	mdl
274	PERMETHRIN	µg/L	mdl
275	DIBENZOFURAN	µg/L	mdl
276	O,P DDE	µg/L	mdl
277	O,P DDT	µg/L	0.1
278	4,4'-DDD	µg/L	mdl
279	DIELDRIN	µg/L	mdl
280	ALDRIN	µg/L	mdl
281	ENDRIN	µg/L	mdl
282	β-BHC	µg/L	mdl
283	ETHION	µg/L	14

Parameter Number	Parameter Name	Units	Guidance Concentration*
284	CHLORDANE	µg/L	mdl
285	TOXAPHENE	µg/L	mdl
286	4,4'-DDT	µg/L	mdl
287	α–BHX	µg/L	mdl
288	β-BHC	µg/L	mdl
289	O,P DDD	µg/L	mdl
290	4,4'-DDE	µg/L	mdl
291	HEPTACHLOR	µg/L	mdl
292	HEPTACHLOR EPOXIDE	µg/L	mdl
293	ISODRIN	µg/L	mdl
294	CHLOROBENZILATE	µg/L	mdl
295	METHOXYCHLOR	µg/L	100
296	CARBOFURAN	µg/L	36
297	METRIBUZIN	µg/L	200
298	ALDICARB SULFOXIDE	µg/L	10
299	ALDICARB SULFONE	µg/L	40
300	3-HYDROXYCARBOFURAN	µg/L	mdl
301	DISULFOTON	µg/L	mdl
302	MIREX	µg/L	3.5
303	2,4-D	µg/L	100
304	MALATHION	µg/L	mdl
305	PARATHION ETHYL	µg/L	mdl
306	2,4,5-TP (SILVEX)	µg/L	10
307	DIAZINON	µg/L	10
308	DCPA	µg/L	4000
309	ATRAZINE	µg/L	mdl
310	DICOFOL	µg/L	mdl
311	DIURON	µg/L	10
312	LINDANE	µg/L	4
313	PICLORAM	µg/L	mdl
314	TRITHION	µg/L	12
315	DEMETON	µg/L	mdl
316	CAPTAN	µg/L	mdl
317	CARBOPHENOTHION	µg/L	mdl
318	GUTHION	µg/L	mdl
319	TEDION	µg/L	mdl
320	MEVINPHOS	µg/L	mdl
321	DIQUAT	µg/L	mdl
322	TERBUFOS	µg/L	mdl
323	AMETRYN	µg/L	mdl
324	BROMACIL	µg/L	90
325	PARAQUAT	µg/L	30
373	TOTAL ARESENIC	µg/L	50
374	ARSENIC, DISSOLVED	µg/L	50
391	BENTAZON, TOTAL	µg/L	mdl
392	SEVIN, TOTAL	µg/L	mdl

*** mdl = Method Detection Limit**

Table 33. - Summary of total pesticide concentrations (:g/L), by region and aquifer system. Most detections were not confirmed by resampling.

A. Surficial aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD*	< 2.00	< 2.00	< 2.20	84	1	< 1.00	100.00
SRWMD*	< 10.00	< 10.00	< 10.00	22	0	< 10.00	50.00
SJRWMD*	< 1.00	1.00	4.00	22	0	< 1.00	27.00
SWFWMD	< 1.00	< 1.00	< 1.00	83	15	< 1.00	32.40
SFWMD	0.00	0.00	< 1.60	327	1	0.00	1100.00
Statewide	< 0.01	0.00	< 0.50	538	17	0.00	1100.00
Sand & Gravel	< 2.00	< 2.00	< 2.40	71	1	< 2.00	100.00
Biscayne	< 0.03	< 0.03	< 0.03	13	0	0.00	1.40
Other	< 1.50	< 0.50	< 2.00	454	16	0.00	1100.00

B. Intermediate aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD*	< 2.00	< 2.00	< 2.00	31	0	< 1.00	9.20
SRWMD*	0.00	0.00	0.00	24	0	0.00	0.00
SJRWMD*	0.00	0.00	1.00	27	0	< 1.00	5.00
SWFWMD	< 0.01	< 0.01	< 0.01	34	14	0.00	1.80
SFWMD	< 1.20	< 0.90	< 1.50	92	0	< 0.01	< 30.00
Statewide	< 0.50	0.00	< 0.50	208	14	0.00	9.20

C. Floridan aquifer system

District	Median	↓Qrtile	↑Qrtile	# Samps	# Exc*	Min	Max
NWFWMD*	< 2.00	< 2.00	< 2.00	171	0	< 1.00	14.00
SRWMD*	< 10.00	<10.00	< 10.00	299	0	< 1.00	30.00
SJRWMD*	< 1.00	< 1.00	< 1.00	53	2	< 1.00	66.00
SWFWMD	< 0.01	< 0.01	< 0.01	167	35	0.00	70.01
SFWMD	< 1.30	< 0.90	< 1.60	108	0	< 0.70	4.20
Statewide	< 0.01	< 0.01	< 0.50	798	37	0.00	70.01

*** - Total Arsenic values only (no organic pesticides sampled).**

Table 34. - Some arsenic based pesticides and their uses (from data in Carapella, 1968).

Pesticide	Use
Calcium arsenate	Insecticide, herbicide
Lead arsenate	Insecticide
Sodium arsenite	Herbicide, fungicide Aquatic weed control Animal dips for tick control
Sodium arsenate	Wood preservative
Disodium methylarsonate	herbicide
Ammonium methane arsonate	Herbicide

Table 35. - Proportions of major ions within the trilinear-diagram fields on the Predominant Water Type Maps. Based on the classification of Davis and DeWiest (1966). Percentages are based on total major ion content, in milliequivalents per liter.

Cation Trilinear Diagram

Water Type	Cation Percentage			
	Calcium	Magnesium	Sodium	Dominant Ion
A	60 - 100	0 - 40	0 - 40	Ca
B	40 - 60	40 - 60	0 - 20	Mixed Ca-Mg
C	0 - 40	60 - 100	0 - 40	Mg
D	0 - 20	20 - 60	20 - 60	Mixed Mg-Na
E	0 - 40	0 - 40	60 - 100	Na
F	40 - 60	0 - 20	20 - 60	Mixed Ca-Na
G	20 - 60	20 - 60	20 - 60	Mixed Ca-Mg-Na

Anion Trilinear Diagram

Water Type	Anion Percentage			
	Bicarbonate	Sulfate	Chloride	Dominant Ion
A	60 - 100	0 - 40	0 - 40	HCO_3
B	40 - 60	40 - 60	0 - 20	Mixed HCO_3-SO_4
C	0 - 40	60 - 100	0 - 40	SO_4
D	0 - 20	20 - 60	20 - 60	Mixed SO_4-Cl
E	0 - 40	0 - 40	60 - 100	Cl
F	40 - 60	0 - 20	20 - 60	Mixed HCO_3-Cl
G	20 - 60	20 - 60	20 - 60	Mixed HCO_3-SO_4-Cl

Table 36. - Some possible criteria for identification of aquifer flow system components. Assumes that water comes in contact with carbonate minerals along the flow path.

Analyte	Recharge Area	Discharge Area
Temperature	Locally variable, relatively cool	Low variability, relatively warm
pH	Generally acidic, locally variable	Slightly basic, low variability
Calcium, magnesium, bicarbonate	Concentrations relatively low, highly variable	Concentrations relatively high, low variability
Iron	Concentrations relatively high	Concentrations may be low
Nitrate	May be present	Normally absent
Phosphate	May be present	Normally absent
Synthetic organics, pesticides	May be present	Normally absent
Sulfate	Low in most areas, possible high near wetlands	High when deep flow system water discharge in coastal areas
Sodium:chloride ratio	Near that of sea water	May differ greatly from sea water
Total organic carbon	Concentrations often high	Concentrations often low

Table 37. - Percent of samples that exceeded water quality standards in Florida aquifers.

Analyte	Surficial Aquifer System	Intermediate Aquifer System	Floridan Aquifer System
pH	37	16	14
Sodium	4	23	17
iron	75	42	49
Mercury	2	3	0.9
Lead	8	8	9
Sulfate	2	13	13
Chloride	6	24	19
Fluoride	0.1	0.4	0.1
Nitrate	0.6	0	1
Total Dissolved Solids	22	37	31
Synthetic Organics	7	1	3
Pesticides[1]	3	7	5

[1] Summary is for 172 different pesticides in SWFWMD and SFWMD only. Only arsenic was determined in other water management districts