

Factors Controlling Elevated Lead Concentrations in Water Samples from Aquifer Systems in Florida

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U.S. GEOLOGICAL SURVEY

Water Resources Investigations Report 99-4020

Prepared in cooperation with
Florida Department of Environmental Protection

Tallahassee, Florida
1999



U.S. DEPARTMENT OF THE INTERIOR
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U.S. GEOLOGICAL SURVEY
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Conversion Factors, Abbreviations, and Acronyms

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
meter (m)	3.28	foot
kilometer (km)	0.62	mile

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
 $^{\circ}\text{F} = 1.8\ ^{\circ}\text{C} + 32$

- amu = atomic mass unit
- cm/yr = centimeters per year
- mg/kg = milligrams per kilogram, parts per million
- μg/L = micrograms per liter
- μS/cm = microsiemens per centimeter at 25 degrees Celsius
- yr = year
- ASTEX-MAGEX = Atlantic Stratocumulus Experiment-Marine Aerosol and Gas Exchange
- EPA = Environmental Protection Agency
- FDEP = Florida Department of Environmental Protec
- FGWQMN = Florida Ground Water Quality Monitoring Network
- MDL = method detection limit
- Mn = manganese
- Pb = lead
- TOC = total organic carbon
- USGS = U.S. Geological Survey
- WMW = Wilcoxon-Mann-Whitney

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Abstract

Concentrations of total lead (Pb) and dissolved Pb exceeded the U.S. Environmental Protection Agency action level of 15 micrograms per liter ($\mu\text{g/L}$) in approximately 19 percent and 1.3 percent, respectively, of ground-water samples collected during 1991-96 from a statewide network of monitoring wells designed to delineate background water quality of Florida's major aquifer systems. Differences in total Pb concentrations among aquifer systems reflect the combined influence of anthropogenic sources and chemical conditions in each system. A highly significant ($p < 0.001$) difference in median total Pb concentrations was found for water samples from wells with water-level recording devices that contain Pb-counterweights (14 $\mu\text{g/L}$) compared to non-recorder wells (2 $\mu\text{g/L}$). Differences between total Pb concentrations for recorder and non-recorder wells are even more pronounced when compared for each aquifer system. The largest differences for recorder status are found for the surficial aquifer system, where median total Pb concentrations are 44 and 2.4 $\mu\text{g/L}$ for recorder wells and non-recorder wells, respectively. Leaching of Pb from metal casing materials is another potential source of Pb in ground water samples. Median total Pb concentrations in water samples from the surficial, intermediate, and Floridan aquifer systems are higher from recorder wells cased with black iron than for recorder wells with steel and PVC casing material.

Stable isotopes of Pb were used in this study to distinguish between anthropogenic and natural sources of Pb in ground water, as Pb retains the

isotopic signature of the source from which it is derived. Based on similarities between slopes and intercepts of trend lines for various sample types (plots of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$) the predominant source of total Pb in water samples from the surficial aquifer system is corrosion of Pb counterweights. It is likely that only ground-water samples, not the aquifer, were contaminated with elevated Pb concentrations. Pb-isotopic ratios of water from the Floridan aquifer system plot between trend lines connecting the isotopic composition of Pb counterweights and the composition of acid leachates of material from the Floridan aquifer system, indicating that Pb in these waters most likely is a mixture of Pb derived from aquifer material and corrosion of Pb counterweights.

INTRODUCTION

Since the 1970's, significant reductions have been made in the major sources of lead (Pb) to the environment (including removal of Pb in paint, reducing the amount of Pb in solder and pipe fittings, and removal of tetraethyl and tetramethyl Pb in gasoline). In response to these reductions, Pb concentrations in air (transported as particulate material) have decreased 97 percent from 1977 to 1996 (U.S. Environmental Protection Agency (EPA), 1997). Mean blood levels of Pb in humans in the United States also have been decreasing; however, guidelines for acceptable Pb levels have been reduced in response to growing evidence that even very low levels of Pb can produce harmful health effects (Reese, 1995). Humans receive about 15 to 20 percent of their total Pb intake from drinking water (EPA, 1994). Therefore, it was particularly dis-

concerting to find that approximately 20 percent of the ground-water samples collected from wells in a state-wide monitoring network in Florida (fig. 1) contained total Pb concentrations that exceeded the EPA action level of 15 micrograms per liter ($\mu\text{g/L}$) for Pb in drinking water (EPA, 1996). Less than 2 percent of these samples contained concentrations of dissolved Pb (operationally defined as material in water that passes through a 0.45 micron (μm) membrane filter) above the action level. During 1986-96, approximately 5,080 water samples were collected from 2,180 wells that are

part of the Florida Ground Water Quality Monitoring Network (FGWQMN), a multiagency cooperative effort among the Florida Department of Environmental Protection (FDEP), the five water management districts in Florida, other State and county agencies, and the U.S. Geological Survey (USGS). The monitoring network was designed to define background or baseline concentrations of major ions, nutrients, selected trace elements and organic compounds in Florida's major aquifers and aquifer systems: the sand-and-gravel aquifer, Biscayne aquifer, and the surficial, inter-

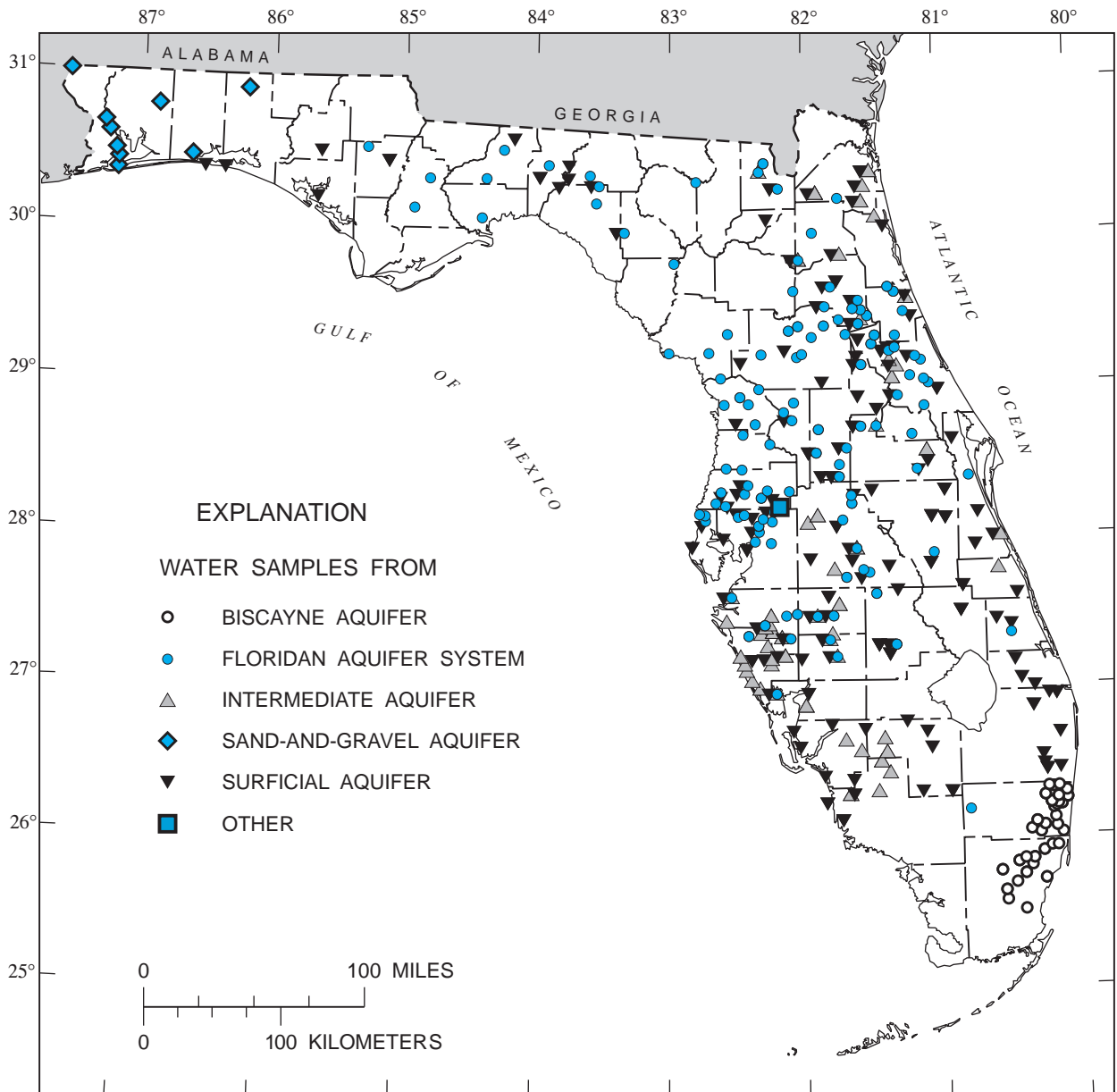


Figure 1. Location of wells with total Pb concentrations in water samples greater than 15 $\mu\text{g/L}$.

mediate, and Floridan aquifer systems (Maddox and others, 1992). Ground water is the major source of supply in Florida, and knowledge of the sources of Pb contamination is of critical importance in protecting and managing this valuable resource.

Little is known about the source(s) of Pb in Florida ground water and its mode of transport in these major aquifer systems. Lead concentrations above background levels in ground water could originate from several anthropogenic and natural sources, including atmospheric deposition, casing materials used in constructing wells, Pb counterweights used in water-level recording devices in monitoring wells, and ground-water sampling methodology (Upchurch, 1992). Pb also is present naturally in soils and rocks.

Accurate identification of the major sources of Pb in ground water is difficult to accomplish using only Pb concentration data. Therefore, to overcome the problem of Pb-source definition, stable isotopes of Pb are used in this study to distinguish between various environmental Pb sources. The composition of the four stable isotopes of Pb (^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb) can vary significantly in different Pb-sulfide ore bodies due to geochemical cycling of ^{238}U , ^{235}U , and ^{232}Th (the parent isotopes of ^{206}Pb , ^{207}Pb , and ^{208}Pb , respectively) and the geologic character of the ore body (Faure, 1986). As a result, each potential source of Pb in ground water (such as metallic weights, natural Pb in aquifer material, atmospheric deposition of Pb) could have a distinct Pb-isotopic signature depending on the isotopic composition of the original lithogenic source from which these anthropogenic and natural sources were derived. By comparing ratios of stable Pb isotopes in ground water with Pb-isotopic ratios of atmospheric deposition, Pb counterweights, and aquifer material, discrimination of dominant source(s) of Pb in ground water is possible. Isotopic ratios of Pb, such as $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$, have been used for source discrimination in various media, including soils (Gulson and others, 1981; Erel and others, 1997), grassland (Bacon and others, 1996), seawater (Shen and Boyle, 1987; Sherrell and others, 1992), alpine ground water (Erel and others, 1990), estuarine sediments (Gobeil and others, 1995), and atmospheric aerosols (Flegal and others, 1989; Hopper and others, 1991; Hamelin and others, 1997; Veron and Church, 1997).

In 1995, the USGS began a study in cooperation with FDEP to evaluate the factors controlling elevated Pb concentrations in ground water samples from the statewide monitoring network in Florida. Two main goals of this study were to determine the source(s) of dissolved and total Pb concentrations in water from the Florida's major aquifer systems, and to determine the mode of Pb transport in these aquifer systems.

Purpose and Scope

This report presents results of detailed statistical analyses of total and dissolved Pb concentrations in water samples collected from the major aquifer systems in Florida for the FGWQMN to determine the influence of anthropogenic factors on elevated Pb concentrations. In addition, Pb isotopic data are presented for water samples collected from a subset of 13 wells in the monitoring network, samples of aquifer material, rainfall, and Pb counterweights. The Pb-isotope data provide a better understanding of the relative contributions of anthropogenic and natural sources of Pb in ground water samples from Florida's major aquifer systems.

Hydrogeology of Major Aquifer Systems in Florida

The main distinguishing hydrogeologic characteristics are described briefly in this paper for the major aquifers and aquifer systems in Florida. More detailed information on the hydrogeology of these systems is in Franks (1982), Vecchioli and Foote (1985), Miller (1986), and Southeastern Geological Society (1986).

The surficial aquifer system consists of the permeable hydrogeologic unit contiguous with the land surface and is composed mainly of unconsolidated to poorly indurated clastic deposits (Southeastern Geological Society, 1986). Water in the surficial aquifer system is under mainly unconfined conditions; however, beds of low permeability may cause semiconfined or locally confined conditions in some deep parts of the aquifer system. In some parts of Florida, aquifers within the surficial aquifer system constitute a major source of supply and have been given distinctive names. For example, the sand-and-gravel aquifer is the major source of water supply in the western part of the Florida panhandle. This aquifer consists of surficial sediments that are thickest in northwestern Florida and

thin to the south and east. Water in the aquifer is under both unconfined and semiconfined conditions, depending on the presence of discontinuous clay layers of low permeability that are interbedded with the more permeable sand-and-gravel sediments. The Biscayne aquifer underlies the extreme southeastern part of the Florida peninsula and supplies the densely populated Miami-Palm Beach coastal area. The aquifer is mainly composed of highly permeable limestone, but is also interbedded with less permeable sands. Water in the Biscayne aquifer is under unconfined conditions, and is hydraulically connected to the many canals that cross the area. Due to its highly permeable nature, vulnerability to contamination, and use as the source of water to more than 3 million people, the Biscayne aquifer has been designated as a "sole-source" aquifer by the U.S. Environmental Protection Agency.

The intermediate aquifer system includes all rocks that lie between the overlying surficial aquifer system and the underlying Floridan aquifer system. Rocks that comprise the intermediate aquifer system generally consist of fine-grained clastic deposits interlayered with carbonate strata that are Miocene and younger in age. The intermediate aquifer system typically contains one or more low to moderate-yielding aquifers that may be interlayered with relatively impermeable confining beds. Water in the intermediate aquifer system is under confined conditions. Water from the aquifer system is a major source of supply in parts of southern and southwestern Florida.

The Floridan aquifer system consists of a thick carbonate sequence that includes all or part of the Paleocene to early Miocene Series (Southeastern Geological Society, 1986). Water in the Floridan aquifer system is under confined conditions where it is overlain by the intermediate aquifer system. Water is generally under unconfined conditions where the aquifer system is overlain directly by the surficial aquifer system or where the carbonate rocks crop out. Even in these areas, deeper zones may contain water under confined conditions. The Floridan aquifer system is one of the most productive sources of ground water in the United States, and many large cities tap this aquifer system for public supply, including Jacksonville, Orlando, Clearwater, St. Petersburg, and Tallahassee. The aquifer system extends across the entire State, but nonpotable water (high salinity) is present in the southern one-third of the peninsula (Vecchioli and Foose, 1985).

Acknowledgments

The authors greatly appreciate the assistance with ground water sampling from personnel with the Southwest Florida, Suwannee River, and St. Johns River Water Management Districts. The authors gratefully acknowledge T.R. Kraemer and J.B. Martin for their comments and suggestions that significantly improved earlier versions of this paper.

METHODS

Wells included in the FGWQMN are located in pristine areas or areas where no known sources of contamination are believed to exist (Maddox and others, 1992). Water samples from network wells therefore should be representative of background conditions (no anthropogenic influence) in aquifer systems.

Data Screening, Sample Collection and Analysis Procedures

Ground-water samples for Pb have been collected from 1986 through 1996; however, Pb data collected prior to 1991 were not used in this study because of inconsistent sampling and analytical procedures. For instance, various types of sampling equipment and procedures were used for well purging and water-sample collection, sample preservation, and measurement of ground-water chemical characteristics in the field. Also, analytical methods prior to 1991 were not consistent among laboratories that were analyzing ground-water samples collected from the monitoring network. Detection limits varied considerably from one laboratory to another, ranging from 1 to 50 µg/L. Beginning in 1991, FDEP instituted an extensive training program on sampling methodology to standardize sampling procedures statewide (ground-water sampling is conducted by personnel from five water management districts, and county and local agencies). From 1991 to 1995, ground-water samples were analyzed for dissolved (filtered, 0.45 µm) and total Pb concentrations by a USGS laboratory (Ocala, Fla.) using graphite furnace atomic-absorption spectrophotometric techniques with a reported method detection limit (MDL) of 1 µg/L (Fishman, 1993). From October 1995 to present, ground-water samples are analyzed for dissolved and total Pb by the FDEP Central Laboratory (Tallahassee, Fla.) using three methods (U.S. EPA,

1994): Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) (EPA method 200.8; MDL ranges from 0.1 to 5 $\mu\text{g/L}$); ICP-Trace (EPA method 200.7; MDL 2-3 $\mu\text{g/L}$); and ICP (EPA method 200.7; MDL 12 $\mu\text{g/L}$, used only for high lead concentrations). A rigorous quality assurance/quality control program was established in 1991 that included laboratory analysis of equipment blanks and field blanks, standard reference samples, and replicate samples for dissolved and total Pb (Hansard, 1993).

Statistical Analyses of Pb in Ground Water

Data for the concentrations of total and dissolved Pb in Florida ground water are highly censored with numerous values below reported analytical detection limits, but greater than zero. Summary statistics of total and dissolved Pb concentrations in ground water were calculated based on nonparametric analysis techniques (Helsel and Cohn, 1988; Helsel and Hirsch, 1992). These robust nonparametric methods were used to calculate summary statistics and to compare median concentrations of total and dissolved Pb by aquifer system, type of casing material, and water-level recorder status. The Wilcoxon-Mann-Whitney (WMW) test was used for hypothesis testing of sample populations where multiple left-censored data exist (Helsel and Hirsch, 1992). Spearman's Rho nonparametric statistic was used to determine the degree of correlation between dissolved and total Pb concentrations with selected chemical characteristics and species in ground water and depth of the sampled well (Iman and Conover, 1983).

Two other modifications were made to the database to improve data consistency for statistical analysis of total and dissolved Pb concentrations: (1) data with reported analytical detection limits that were less than 1 $\mu\text{g/L}$ for dissolved and total Pb concentrations were censored at 1 $\mu\text{g/L}$ to insure comparability of data below method detection limits from USGS and FDEP laboratories, and (2) only the most recent data were included for wells that were sampled more than once during 1991-96. The calculation of a median value for each well would have been preferred. However, in many cases it was not possible to calculate median values; numerous wells were sampled twice with one water sample typically having a Pb concentration below the analytical detection limit, the other sample having a measurable concentration of total Pb.

Stable Lead Isotopes

To evaluate possible sources of Pb in ground water, four stable isotopes of Pb (^{208}Pb , ^{207}Pb , ^{206}Pb , and ^{204}Pb) were analyzed in samples from laboratory experiments and field sampling studies. Ratios of radiogenic isotopes of Pb (^{206}Pb , ^{207}Pb , and ^{208}Pb) relative to the nonradiogenic isotope, ^{204}Pb , are typically used by geochemists to study ore genesis and related topics (for example, Faure, 1986). However, ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ generally have been adopted as the most sensitive to change in environmental studies (Bacon and others, 1996). Also, better analytical precision has been reported for radiogenic Pb isotopes compared to the analysis of ^{204}Pb , due to its relatively minor abundance (Monna and others, 1997). In this report, plots are presented for ratios of radiogenic isotopes of Pb ($^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$) and isotopic ratios of radiogenic to nonradiogenic Pb ($^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$) because both types of plots yield unique information about sources of Pb in ground water. Lead retains the signature of the source from which it is derived, providing a powerful tool that can be used to differentiate between anthropogenic and natural sources of Pb in ground water.

Laboratory experiments consisted of leaching metallic Pb counterweights (used in water-level recording devices) and samples of aquifer material. The Pb-isotopic composition of leachates of water-exchangeable and acid-exchangeable Pb was determined in clay-size material ($<2\ \mu\text{m}$), obtained by pulverizing samples of sediment ($<2\text{mm}$) and rock from the surficial and Floridan aquifer systems, respectively. Water leachates were obtained by reacting 1 g of pulverized material in 10 mL of deionized water at 25 $^{\circ}\text{C}$ for 24 hr. Acid leachates were obtained by reacting 1 g of material with 10 mL of 0.1N HCl at 25 $^{\circ}\text{C}$ for 24 hr.

Samples of ground water for Pb-isotope analyses were collected from seven wells screened in the surficial aquifer and six wells tapping the Upper Floridan aquifer (fig. 2) using ultra-clean sampling protocols described by Ivahnenko and others (U.S. Geological Survey, written commun., 1998). In addition to analyses of stable Pb isotopes, ground-water samples were analyzed for total and dissolved Pb ($<0.10\ \mu\text{m}$), major ions, pH, dissolved oxygen, specific conductance, and dissolved organic carbon (Fishman, 1993).

Monthly-composite samples of atmospheric deposition (wetfall only) for Pb-isotope analyses were obtained from Aerochemetrics wet/dry atmospheric deposition collectors at three sites in the

Florida peninsula (fig. 2): (1) Rocky Hill, (2) Ft. Myers, and (3) Lake Barco. The two latter sites are part of the Florida Atmospheric Mercury Study network and methods of sample collection are described by Landing and others (1995).

Procedures for Pb-isotope analyses involved the use of Teflon labware and Teflon-distilled reagents. Water samples and leachates of aquifer sediment and Pb weights were taken to dryness in Teflon beakers in a clean hood. The residues were redissolved in 0.6N HBr, and the Pb was separated from the other cations and anions using AG1-X8 strong acid anion resin. For mass

spectrometric analysis, the Pb fractions were converted to nitrate form and loaded onto Re filaments with 40 μL of 0.5N H_3PO_4 and 10 μg of colloidal silica. Pb isotopes were analyzed on a Finnigan-MAT 261 multi-collector mass spectrometer at the USGS Water Resources Division isotope laboratory in Menlo Park, California. Analyses were made using both static faraday cup multi-collector and peak-hopping ion counter routines depending on signal intensity. Analyses were corrected for thermal fractionation effects by repeated reference to values obtained for the NBS981 Pb reference metal. Corrections are approximately 0.11 percent per amu.

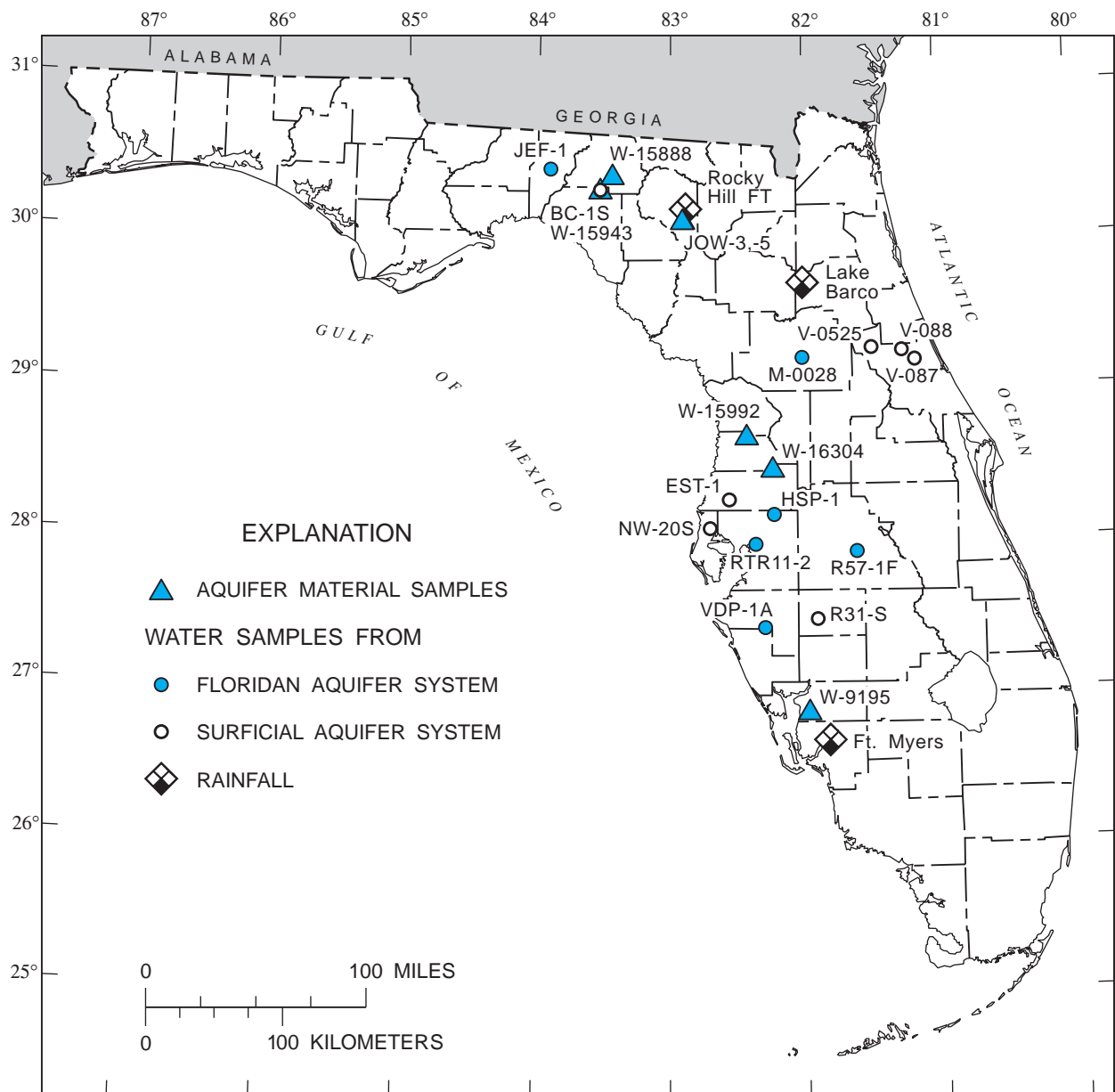


Figure 2. Location of sampling sites for Pb-isotope analyses.

Table 1. Descriptive statistics for total lead concentrations, $\mu\text{g/L}$, in major aquifers and aquifer systems of Florida

[N denotes number of observations]

Aquifer	Casing	N	Median	Mean	Standard deviation	Maximum
Biscayne	All	97	8.2	27.4	70.8	510
Surficial	All	398	3.9	67.1	425	7400
Sand-and gravel	All	63	1.5	7.2	20.3	150
Intermediate	All	194	2.0	24.9	101	1100
Floridan	All	777	1.0	13.2	79.6	1700
All	Galvanized	37	1.2	64	228	1100
	Wrought iron	11	20	23.3	23.1	75
	Black iron	259	1.0	29.2	185	2800
	PVC	924	2.0	22.6	109	2000
	Steel	249	2.0	50.6	482	7400
	Other	49	2.0	25.0	125	880

FACTORS CONTROLLING ELEVATED LEAD CONCENTRATIONS IN GROUND-WATER SAMPLES

Total Pb concentrations vary considerably among aquifer systems, with the lowest median and mean concentrations of total Pb in the sand-and-gravel aquifer (1.5 and 7.2 $\mu\text{g/L}$, respectively), and highest median total Pb concentrations in the Biscayne aquifer (8.2 $\mu\text{g/L}$) and highest mean total Pb concentrations in the surficial aquifer system, 67 $\mu\text{g/L}$ (table 1). Median total Pb concentrations are significantly higher ($\alpha < 0.05$) in water samples from the Biscayne aquifer than samples from other aquifer systems (table 1). Statistically significant differences (WMW, $\alpha < 0.05$) for total Pb concentrations were found between most combinations of aquifers and aquifer systems (table 2). No statistically significant differences in total Pb concentrations were found between the sand-and-gravel aquifer and the intermediate aquifer system, and between the sand-and-gravel aquifer and the Floridan aquifer system (table 3).

Table 2. Descriptive statistics for total lead concentrations, $\mu\text{g/L}$, in Florida aquifers grouped by status of water-level recorder and casing material

[N denotes number of observations]

Aquifer	Casing	N	Median	Mean	Standard deviation	Maximum	Lead Weight Recorder Status				
							Yes			No	
							N	Median	Mean	Standard deviation	Maximum
All	All	263	14	85.5	2800	483	2.0	26.8	7400		
Biscayne	All	20	15	18.9	15.3	45	15	2.7	6.6	8.3	28
Surficial	All	64	44	214	490	2800	233	2.4	43.3	485	7400
Intermediate	All	44	18	59.7	124	720	74	1.6	9.1	22.3	150
Floridan	All	135	9.1	42.9	166	1700	161	1.0	12.8	78.0	890
All	Black iron	40	14	120	448	2800	31	2.0	10.5	18.6	96
	PVC	155	16.6	86.6	247	2000	337	2.0	8.0	22.5	300
	Steel	51	8.1	60.5	241	1700	83	1.0	103	812	7400
Biscayne	Black iron	6	12.1	18.7	13.8	38	4	2.7	8.6	10.0	28
	PVC	5	31	43.3	9.1	45	2	2.1	2.1	0.71	2.6
	Steel	7	4.6	12.8	16.6	39	6	6.6	8.8	8.2	22
Surficial	Black iron	10	104	424	855	2800	7	19.7	26.5	32.2	96
	PVC	44	47.5	201	425	2000	205	2.0	9.2	26.3	300
	Steel	5	30	100	168	400	13	16	601	2043	7400
Intermediate	Black iron	1	32	32	--	32	1	1.0	1.0	--	1.0
	PVC	31	20	76.5	144	720	57	2.0	7.0	20.1	150
	Steel	9	5.7	19.6	29.4	93	8	1.0	10.8	19.5	57
Floridan	Black iron	23	11.0	18.5	23.6	91	19	2.0	5.4	8.4	32
	PVC	75	8.0	27.3	45.8	210	73	1.7	5.4	8.8	48
	Steel	30	9.9	77.3	307	1700	56	1.0	11.1	58.9	440

Table 3. Summary of Wilcoxon-Mann-Whitney rank sum test for total Pb concentrations by aquifer systems, and by subgroups of wells with water-level recorders (R) and without recorder (N) and by well casing type

[BI denotes the Biscayne Aquifer, FAS the Floridan aquifer system, IAS the Intermediate aquifer system, SAS the Surficial aquifer system, and SG the sand-and-gravel aquifer. Values are p-values, level of significance is < 0.05]

Aquifer							
	BI	FAS	IAS	SAS	SG		
BI							
FAS	0.0001						
IAS	0.0001	0.0001					
SAS	0.0011	0.0001	0.0112				
SG	0.0001	0.4352	0.0915	0.0004			

Aquifer-recorder status							
	BI - R	BI - N	FAS - R	FAS - N	IAS - R	IAS - N	SAS - R
BI - R							
BI - N	0.0111						
FAS - R	0.4371	0.0447					
FAS - N	0.0001	0.0555	0.0001				
IAS - R	0.3305	0.0035	0.0094	0.0001			
IAS - N	0.0001	0.2248	0.0001	0.2203	0.0001		
SAS - R	0.0062	0.0001	0.0001	0.0001	0.0608	0.0001	
SAS - N	0.0001	0.5688	0.0001	0.0003	0.0001	0.142	0.0001

Analyses of dissolved Pb were fewer in number and concentrations of dissolved Pb were much lower than total Pb concentrations. Eighty percent of the 1,468 analyses for dissolved Pb were less than 1 µg/L, compared to 34 percent of the 1,529 analyses for total Pb concentrations. Statistical analyses of dissolved Pb concentrations by aquifer, recorder status, and casing material were not meaningful because of the high percentage of water samples with censored data. Median dissolved Pb in samples from wells with black-iron casing material is 1.5 µg/L, the only group of samples with a median concentration above the analytical detection limit. The highest maximum dissolved Pb concentrations are found in water samples from the surficial aquifer system, which is not surprising given the highly corrosive conditions (typically low pH, high DOC concentrations, low dissolved oxygen levels) compared to conditions in the intermediate and Floridan aquifer systems.

Lead Counterweights Used in Water-Level Recording Devices

Differences in total Pb concentrations among aquifer systems reflect the combined influence of anthropogenic sources and chemical conditions in each system. One potential source of Pb contamination in ground-water samples is the use of metallic Pb as a float counterweight in a water-level recording device.

To evaluate the influence of Pb counterweights on elevated Pb concentrations, data from all aquifer systems were separated into two subgroups, one subgroup consisting of wells coded in the database as having water-level recorders (R, fig. 3), the other subgroup consisting of wells coded as never having a water-level recording device (N, fig. 3). Unfortunately, information on recorder status was unavailable for the sand-and-gravel aquifer and was available for only 35 of 97 wells sampled in the Biscayne aquifer. The effect of recorder status on total Pb concentrations was investigated only for the surficial, intermediate, and Floridan aquifer systems and for the Biscayne aquifer. A highly significant difference in median total Pb concentrations ($p < 0.0001$) is observed for water samples from wells with recorders, 14 µg/L, compared to non-recorder wells, 2 µg/L (table 2).

Differences between total Pb concentrations for recorder and non-recorder wells are even more pronounced when compared for each aquifer system (fig. 3). The largest differences for recorder status are found for the surficial aquifer system, where, median total Pb concentrations are 44 and 2.4 µg/L for recorder wells and non-recorder wells, respectively (table 2). It is worth noting that median total Pb concentrations exceed 15 µg/L in water samples from recorder wells for all aquifer systems, except the Floridan aquifer system, which has a median concentration of 9.1 µg/L (table 2).

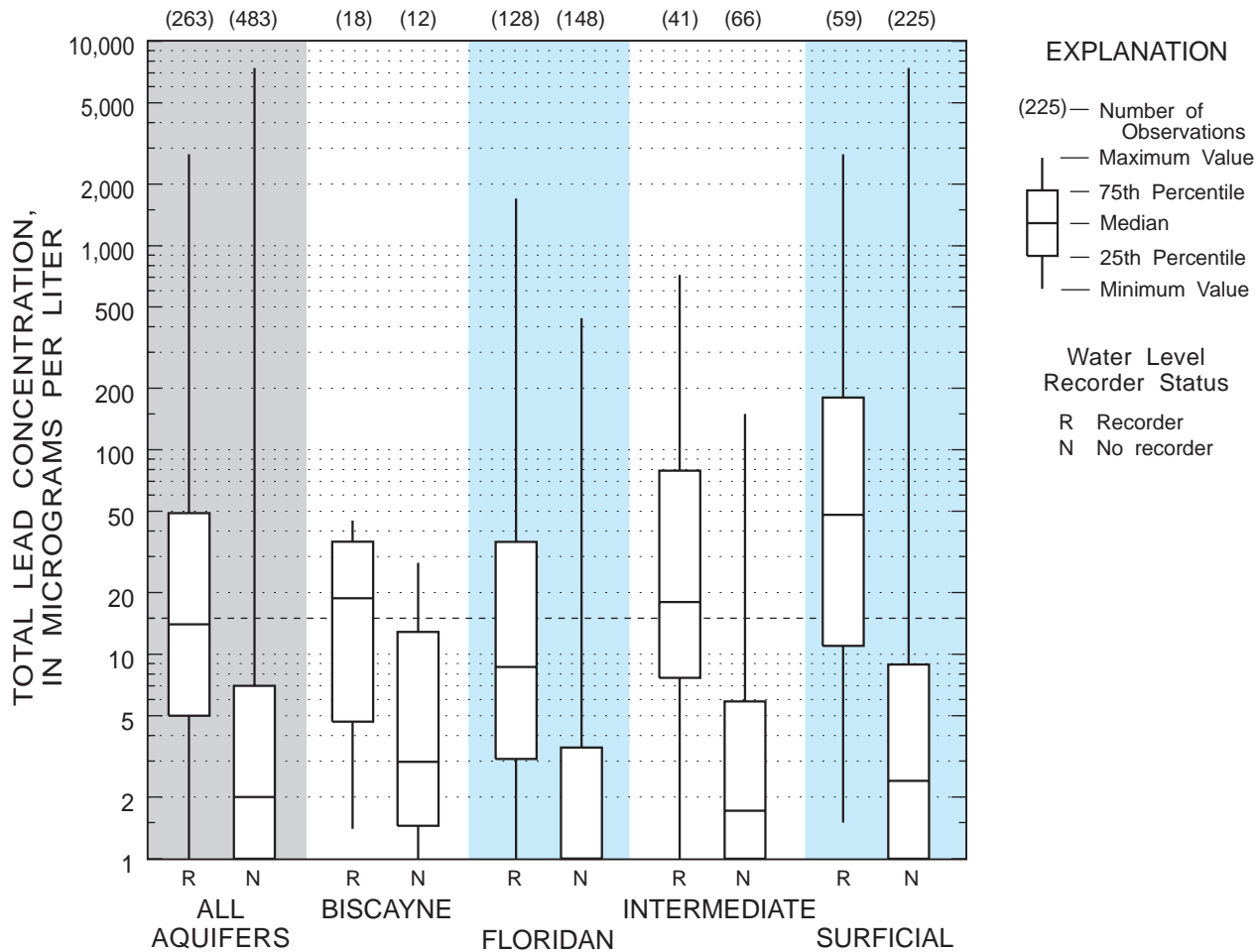


Figure 3. Boxplot showing distribution of total Pb concentrations in ground water by recorder status and aquifer.

Some of the significant differences noted in total Pb concentrations between aquifers (table 3) likely are related more to recorder status than to aquifer differences. For example, total Pb concentrations were significantly different between samples from the Biscayne and the Floridan, between the Biscayne aquifer and the intermediate aquifer system, and between the intermediate and the surficial aquifer systems. But when samples were separated into groups based on recorder status, there were not significant differences in total Pb concentrations between these same aquifers. For example, total Pb concentrations in samples from recorder wells between the Biscayne aquifer and Floridan aquifer system showed no significant difference, and no significant differences were noted for water samples from non-recorder wells between the Biscayne and Floridan (table 3), indicating that most of the difference in total Pb concentrations between these two aquifers was between the water samples from recorder wells and non-recorder wells. Similar findings were noted between recorder and non-recorder wells in the Biscayne aquifer and intermediate aquifer system, and

between recorder and non-recorder wells from the intermediate and surficial aquifer systems (table 3).

On the basis of a subset of water samples collected from the major aquifer systems in northeast Florida, total Pb concentrations were higher in water from wells that contained water-level recorders with Pb counterweights than non-recorder wells; however, even wells without Pb counterweights had total Pb concentrations much greater than 15 µg/L, (Osburn and Boniol, 1997) indicating the potential for high Pb concentrations even in the absence of water-level recorders.

Well Casing Materials

Leaching of Pb from metal casing materials is another potential source of Pb in ground water samples (Parker and others, 1990). To evaluate the influence of casing material on Pb concentrations, data for non-recorder wells were subdivided into the three most common casing-material types: black iron, PVC, and steel. No statistically significant differences were

found among the three casing materials when data for all aquifers are combined for non-recorder wells. In fact, median total Pb concentrations are 2.0 µg/L or less for all three casing-material types. However, median total Pb concentrations in water from non-recorder wells in the surficial aquifer system are significantly higher from black-iron and steel-cased wells (19.7 and 16 µg/L) than for PVC-cased wells (2.0 µg/L). The combined effect of casing material and active water-level recorder on elevated total Pb concentrations in water from each aquifer system also is worth noting. Median total Pb concentrations in water samples from the surficial, intermediate, and Floridan aquifer systems are higher from recorder wells cased with black iron than for recorder wells with steel or PVC casing material (table 2). The largest differences among casing material and wells with active recorders are found for water samples from the surficial aquifer system, with median total lead concentrations of 104, 48, and 30 µg/L for water from wells with black iron, PVC, and steel casing materials, respectively. In the Biscayne aquifer, median total Pb concentrations are higher in water samples from wells with active recorders and PVC casing material; however, the small number of samples in each group (7 or less) may not provide an accurate assessment of the influence of casing material on total Pb concentrations.

Casing and screen materials typically are selected for use in construction of water wells based on their tensile strength, and chemical resistance to corrosive subsurface environments (Lapham and others, 1997). Laboratory experiments have shown that PVC and stainless steel leach Pb to ground water (Hewitt, 1989); however, amounts and rates of leaching of Pb can vary widely within each major class of material. For instance with PVC, Hewitt (1989) reports a decreasing trend in Pb concentrations leached with time of exposure, from 2.5 µg/L after 1 day to 0.78 µg/L at 40 days (pH 7.8, specific conductance 24 uS/cm). Stainless steel 316 (SS316) has less tendency to leach Pb than another type, stainless steel 304 (SS304) (Hewitt, 1989). However, SS316 also had a greater ability to sorb Pb than SS304. Black iron or wrought iron material was commonly used in constructing older monitoring wells. During installation of well casing, sections of black-iron pipe commonly were joined together by welding with a Pb-based solder (J. Baker, South Florida Water Management District, 1998, personal commun.). Some water wells constructed prior to the mid-1980's also may contain a seal constructed of Pb above the screen and/or a Pb plug at the bottom of the screen (Lege and others, 1993).

Previous studies in Florida have indicated that the concentration of Pb in ground-water samples is related to the type of casing material. Median concentrations of dissolved Pb were higher in water samples from wells with black-iron and steel-cased material (4.6 and 5.2 µg/L) compared to wells with PVC casings (1.4 µg/L) in the Biscayne aquifer (Radell and Katz, 1991). Water from wells with black-iron (surficial aquifer system), galvanized steel (intermediate aquifer system), and steel casing material (Floridan aquifer system) had significantly higher total Pb concentrations than water from PVC-cased wells in these aquifer systems in northeast Florida (Osburn and Boniol, 1997).

Sampling Methods

Another possible source of Pb in ground-water samples is contamination introduced by sampling methods (equipment, preservatives, sample handling). This source of Pb in ground-water samples is unlikely. Based on an analysis of 342 equipment-blank samples (1994-97), 97.1 and 98.8 percent of dissolved and total Pb concentrations, respectively, were less than reported MDLs. Total Pb concentrations that were above the MDL were all less than 10 µg/L in the small number of samples in which total Pb was detected. Sampling methods may affect total Pb concentrations; sampling with a bailer may yield higher Pb concentrations because more particulates are collected than using high-volume purging prior to sampling (Kain and others, 1984).

Chemical Conditions in Aquifer

A ground-water quality monitoring network designed to measure background or baseline conditions ideally would not contain wells that have known anthropogenic sources of lead. Based on the documented effects of Pb counterweights and metal casing materials on elevated Pb concentrations, a subset of non-recorder wells containing PVC casing material was selected to be more representative of background conditions for Pb in the major aquifer systems. For water samples from this subset of wells, there was no statistically significant difference in total Pb concentrations among aquifers (WMW test). Median total Pb concentrations are essentially equivalent and are 2.1, 1.7, 2.0, and 2.0 µg/L for the Biscayne aquifer, and the Floridan, intermediate, and surficial aquifer systems, respectively (table 2). Total Pb concentrations in 57 percent of the 338 water samples in this subset are less than 1 µg/L, although they exceed 15 µg/L in 11 percent of samples. Chemical conditions in each aquifer system also affect the dis-

tribution of total Pb concentrations. This effect is particularly evident for the surficial aquifer system, where the highest total Pb concentration in this subset was 300 µg/L. Median total Pb concentrations in the surficial aquifer system are higher than other aquifer systems even though 83 percent of wells in this system are cased with PVC material and 59 percent are coded as never having a recorder.

Using this subset of wells that best approximates background conditions for Pb in ground water, it is possible to determine the influence of other water-chemistry constituents on total and dissolved Pb concentrations without any known anthropogenic influence. There was a statistically significant (0.05 significance level) positive correlation between total Pb and total Fe, dissolved Fe, and total organic carbon (TOC). The strong correlation between total Pb and Fe can be attributed to two factors: (1) Pb tends to adsorb onto iron oxyhydroxides that can exist as mobile particulate matter (colloids), which results in Pb transport in aquifer systems (Jenne, 1977; Wells and others, 1989); and (2) nonsolute Pb can be present in ground water as undissolved particles of Pb-carbonate, oxide, hydroxide, and organic compounds (Hem, 1976; Wells and others, 1989). Statistically significant negative correlations were found between total Pb concentrations and concentrations of SO₄ and Cl. Total Pb concentrations also were inversely related to well depth. Sulfate and chloride concentrations tend to increase with depth in the Floridan aquifer system, so the negative correlation between total Pb concentrations and SO₄ and Cl probably results from the lower Pb concentrations in deeper parts of the aquifer. Other studies have found that the concentrations of Pb and Cl are positively correlated, which may result from landward migration of saltwater that contains soluble Pb-Cl complexes. Pb can accumulate in estuarine and riverine bottom sediments and in areas where saltwater intrusion has occurred, and as a result Pb concentrations in ground water can be elevated above background levels (Pucci and others, 1989). Even with the high percentage of censored data, dissolved Pb showed a significantly positive correlation with SO₄ and TOC, which indicates the importance of Pb-SO₄ and organic-Pb complexes on the aqueous solubility of Pb. The high degree of censored data may account for the lack of expected correlation of dissolved lead with pH and alkalinity. Other studies have reported decreased solubility of Pb with increasing pH and carbonate alkalinity due to the formation of Pb-carbonate and Pb-hydroxide compounds, which have low solubility (Hem, 1976; Harter, 1983).

Pb Transport in Ground Water

Pb most likely is transported in ground water by mobile particulate matter (McDowell-Boyer and others, 1986; Wells and others, 1989). Pb deposited on the land surface by atmospheric deposition (industrial sources of Pb) infiltrates through soils attached to colloids in soil moisture films, including iron (Fe)-hydroxides and large organic molecules such as humic material (Erel and Patterson, 1994). Erel and others (1990) estimate that up to 15 percent of the industrial Pb deposited from atmospheric deposition is incorporated in water that infiltrates through soils to ground water. Other studies have demonstrated a downward migration of Pb through soils and into aquifers, which depends on the mobility of organic matter and sequioxides because of the high stability of Pb-organic matter and Pb-sequioxide complexes (Erel and others, 1991; Erel and Morgan, 1992). In forest floors, Pb residence times were estimated to range from 17 to 80 years (Miller and Friedland, 1994). Based on changes in the isotopic composition of sorbed (extractable) Pb with soil depth, anthropogenic Pb can migrate downward into soil at approximately 0.5 cm/yr (Erel and others, 1997). Also, Bullen and Kendall (1998) show that soil zone Pb can be mobilized to streamflow during flushing events. Any dissolved Pb that is present (for example, low pH waters) in ground water would tend to form complexes with several anionic ligands and the migration of dissolved Pb in ground water would be dependent on its form (the predominant Pb species) in solution. For example, free divalent Pb ion (Pb²⁺), which is the predominant species of Pb in low-ionic strength waters, tends to sorb on negative sites of clays and other minerals and aquifer material (Saether and others, 1988).

LEAD-ISOTOPIC COMPOSITION OF GROUND WATER, AQUIFER MATERIAL, AND LEAD WEIGHTS

Water samples were collected from a subset of 13 wells from the FGWQMN to evaluate Pb sources in ground water using Pb isotopes. These 13 wells tap zones in the surficial and Floridan aquifer systems that represent the range of geochemical conditions in these systems. Also, total Pb concentrations have been high in water samples from most of these wells in the past, and most of these wells had active water-level recording devices with Pb counterweights at the time of sampling or have had a recorder in the past. Total and dissolved Pb concentrations in water from 7 sampled wells in the surficial aquifer system were considerably

Table 4. Physical characteristics of wells sampled for lead isotope ratios, dissolved and total lead concentrations, and chemical characteristics of selected water samples collected during study

[Casing depth, well depth, and depth to water are in meters below land surface. Well casing material denoted by P for PVC, P-A for ABS plastic, S for steel, and G for galvanized steel; Water-level recorder status is denoted by: N, no active recorder; but may have been one in past; A, active recorder with lead counterweight; I, no recorder present during sampling but one likely in past; S, water-level recorder with stainless-steel or other material as counterweight; O, water-level recorder present but has no counterweight. Dissolved and total lead concentrations are in micrograms per liter. Concentrations of dissolved organic carbon (DOC), iron (Fe) and dissolved oxygen (O₂diss) are in milligrams per liter. Depth to water is in meters below land surface; SAS and FAS denote the surficial and Floridan aquifer systems, respectively; Dec and Inc denote decreasing and increasing trends in total lead concentrations over time]

Site name	Sample date	Casing depth (m)	Well depth (m)	Casing material	Water-level recorder status	Depth to water (m)	Aquifer	Pb (diss.)	Pb (total)	Trend in total Pb conc	pH	DOC	Fe	O ₂ diss
V-087	4/23/96	5.5	6.1	P	I	1.80	SAS	230.0	340.	Dec	4.28	30.	2.7	2.0
V-088	4/23/96	5.5	6.1	P	O	1.20	SAS	50.0	5300.	Inc	5.25	1.3	0.65	0.2
V-0525	4/23/96	1.2	4.3	P	A	1.18	SAS	160.0	610.	Dec	4.79	19.	3.6	0.1
NW-20S	2/27/96	0.61	3.4	P	A	1.35	SAS	81.7	193.	Inc	4.54	38.	0.68	0.3
EST-1	2/27/96	3.0	6.1	P	S	1.14	SAS	5.0	16.6	Dec	4.96	25.	1.27	0.0
R31-S	2/26/96	1.5	4.6	P	S	1.99	SAS	30.8	905.	Inc	6.26	19.	1.12	1.5
BC-1S	3/19/96	1.2	4.3	P	S	1.75	SAS	12.0	29.	Dec	6.54	17.	0.15	2.2
HSP-1	2/27/96	0	7.3	G	N	2.66	FAS	16.6	28.5	Dec	6.91	4.9	1.0	0.2
R57-1F	2/28/96	49	193	P-A	A	8.56	FAS	0.34	1.91	Dec	7.06	2.5	0.23	0.0
RTR11-2	2/28/96	91	96	P	I	2.32	FAS	0.20	1.39	Dec	7.22	0.7	0.02	0.0
JEF-1	3/19/96	72	78	P	I	50.6	FAS	0.8	2.60	Dec	8.58	1.1	0.07	0.4
VDP-1A	2/26/96	126	146	S	A	15.6	FAS	0.33	24.2	Dec	7.46	9.2	0.52	2.2
M-0028	4/24/96	38	47	S	I	7.10	FAS	1.1	<1.0	Dec	7.78	4.1	0.15	0.0

higher than water samples from 6 wells tapping the Floridan aquifer system (table 4). Higher Pb concentrations reflect the more corrosive conditions in the surficial aquifer system (lower pH, higher dissolved organic carbon concentrations) compared to the Floridan aquifer system (table 4). Higher total Pb concentrations also correspond to higher dissolved Fe concentrations in water samples from the surficial aquifer system (table 4) and confirm the association of Pb with colloidal Fe oxyhydroxides that was previously mentioned. Concentrations of total and dissolved Pb decreased during 1991-1996 in water from all sampled wells that tap the Floridan aquifer system, but showed an increasing trend in 3 of 7 samples from the surficial aquifer system during this period. Reasons for the increase in total Pb concentrations are not known at this time; however, the increasing trend cannot be attributed to the presence of Pb counterweights at the time of sampling because both V-088 and R31-S contained recorders without Pb counterweights (table 4).

Corresponding to higher total Pb concentrations, ratios of radiogenic (²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb) relative to ²⁰⁴Pb are generally higher for ground water from the surficial aquifer system compared to the Floridan aquifer system (table 5). Also, the median value of the ²⁰⁶Pb/²⁰⁷Pb ratio is higher for water samples from the surficial aquifer system (1.207) compared to the Floridan aquifer system (1.192), although there is no statistically significant difference between these median values. The considerable variations among the ratios of radiogenic Pb isotopes in ground water, rainfall, aquifer material, and Pb counterweights are much greater than the uncertainties in the isotopic analysis measurement. The relative importance of anthropogenic and natural sources that contribute to differences in Pb-isotopic composition and concentrations of Pb in these systems are discussed in subsequent sections.

Changes in Lead-Isotopic Ratios with Depth in the Surficial Aquifer System

²⁰⁶Pb/²⁰⁷Pb ratios showed a slight decreasing trend (statistically not significant) with depth (fig. 4) in the surficial aquifer system (correlation coefficient -0.449, p= 0.31). No trend in isotopic ratios were observed for the ²⁰⁶Pb/²⁰⁷Pb ratio for aquifer material leachates; therefore, changes in the isotopic signature of ground water may reflect temporal changes in the Pb-isotopic composition of recharge water or contamination from Pb counterweights. For example, the

Table 5. Pb-isotope ratios of ground water, rainfall, lead weights, and leachates of aquifer material

[SAS and FAS denote surficial aquifer system and Floridan aquifer system, respectively; --- denotes not applicable]

Site name	Aquifer	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$
Ground water samples							
V-087	SAS	18.780	15.840	38.932	2.458	2.073	1.186
V-088F	SAS	18.423	15.597	38.139	2.445	2.070	1.181
V-088R	SAS	18.424	15.589	38.132	2.446	2.070	1.182
V-0525	SAS	19.219	15.682	38.649	2.465	2.011	1.226
NW-20S	SAS	19.064	15.795	38.862	2.460	2.039	1.207
EST-1	SAS	18.983	15.698	38.547	2.456	2.031	1.209
R31-S	SAS	18.974	15.833	38.980	2.462	2.054	1.198
BC-1S	SAS	18.987	15.714	38.592	2.456	2.033	1.208
HSP-1	FAS	18.507	15.657	38.124	2.435	2.060	1.182
R57-1F	FAS	18.917	15.647	38.417	2.455	2.031	1.209
RTR11-2	FAS	18.964	15.648	38.402	2.454	2.025	1.212
JEF-1	FAS	18.598	15.615	38.373	2.457	2.063	1.191
VDP-1A	FAS	17.861	15.602	38.047	2.439	2.130	1.145
M-0028	FAS	18.674	15.635	38.268	2.448	2.049	1.194
Rainfall samples							
RH-1	---	18.585	15.621	38.198	2.445	2.055	1.190
LAKE BARCO	---	18.977	15.690	38.604	2.460	2.034	1.210
FT. MYERS	---	18.640	15.641	38.238	2.445	2.051	1.192
Lead Counterweights							
SJRWMD1	---	19.237	15.766	38.887	2.467	2.021	1.220
SJRWMD2	---	19.183	15.699	38.670	2.463	2.016	1.222
SWFWMD1	---	18.395	15.586	38.237	2.453	2.079	1.180
SWFWMD2	---	18.383	15.570	38.183	2.452	2.077	1.181
DI water leachates of aquifer material							
W15992A	SAS	18.642	15.640	38.272	2.447	2.053	1.192
JOW-3A	SAS	19.204	15.676	38.568	2.460	2.008	1.225
JOW-5A	SAS	18.848	15.640	38.469	2.460	2.041	1.205
W15943A	SAS	18.837	15.630	38.314	2.451	2.034	1.205
JOW-3B	SAS	18.714	15.628	38.384	2.456	2.051	1.198
W15943C	FAS	18.833	15.625	38.311	2.452	2.034	1.205
JOW-5B	FAS	18.780	15.612	38.319	2.455	2.040	1.203
JOW-5C	FAS	18.555	15.548	38.124	2.452	2.055	1.193
JOW-3C	FAS	18.771	15.654	38.456	2.457	2.049	1.199
W16304	FAS	18.933	15.643	38.356	2.452	2.026	1.210
W15888	FAS	18.674	15.619	38.202	2.446	2.046	1.196
0.1N HCl leachates of aquifer material							
W15992A	SAS	18.838	15.675	38.753	2.472	2.057	1.202
JOW-3A	SAS	18.830	15.648	38.698	2.473	2.055	1.203
JOW-5A	SAS	19.120	15.669	38.941	2.485	2.037	1.220
W15943A	SAS	18.977	15.683	38.792	2.474	2.044	1.210
JOW-3B	SAS	19.435	15.646	38.650	2.470	1.989	1.242
W15943C	FAS	20.720	15.696	38.474	2.451	1.857	1.320
JOW-5B	FAS	18.726	15.564	38.120	2.449	2.036	1.203
JOW-5C	FAS	18.663	15.580	38.107	2.446	2.042	1.198
JOW-3C	FAS	18.662	15.590	38.180	2.449	2.046	1.197
W16304	FAS	19.841	15.730	39.024	2.481	1.967	1.261
W15992C	FAS	19.146	15.662	38.687	2.470	2.021	1.223
W9195	FAS	17.922	15.533	37.249	2.398	2.078	1.154

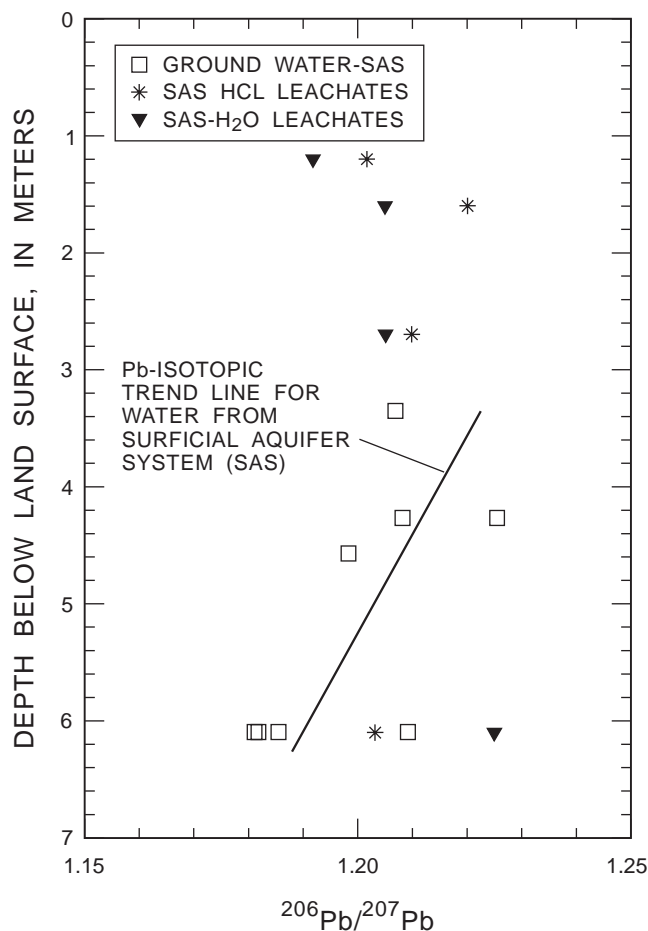


Figure 4. Plot showing ratio of $^{206}\text{Pb}/^{207}\text{Pb}$ by depth below land surface in water samples from the surficial aquifer system.

$^{206}\text{Pb}/^{207}\text{Pb}$ ratio in urban air in the United States increased from about 1.14 in the 1960's to about 1.224 in the 1980's because of a shift in major use from geologically old ores to much younger ores from Missouri that were especially radiogenic (Erel and Patterson, 1994). Thus, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in more shallow water from the surficial aquifer system may indicate more recent recharge of rainfall with a higher $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. Ground-water ages of water from the surficial aquifer can vary considerably, but in areas of moderate recharge (12 to 25 cm/yr), ground water ages typically range from about 15 to 30 years (Katz and others, 1995). Large differences in ground-water ages from one area to another; however, can result from variable amounts of recharge, which are related to factors such as temporal changes in rainfall patterns and thickness of confining layers. Since 1984, the phasing out of leaded gasoline has resulted in a decrease of Pb concentrations in the atmosphere and an decrease in

$^{206}\text{Pb}/^{207}\text{Pb}$ ratios from 1.22 to 1.20 (Veron and others, 1992). Other studies have shown diminished Pb levels in surface Atlantic Ocean water near Bermuda that have been accompanied by a decrease in the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio from 1.195 to 1.210 in 1983-84 to 1.177 to 1.188 in 1989 (Sherrell and others, 1992). These rapid shifts in isotopic ratios were attributed to changes in tropospheric input resulting from the reduction in the contribution from North American gasoline Pb (mined from highly radiogenic ores), and a relative increase in the contribution of Pb from less radiogenic sources (such as iron and steel production in the United States, coal combustion, waste incinerators, and metal smelting (Sherrell and others, 1992). The influence of atmospheric sources on the Pb-isotopic signature of ground water is very difficult to resolve due to changes in sources of atmospheric Pb over the past 50 years that may lead to a homogenized signature in ground water (Bacon and others, 1996). Another complicating factor is the Pb-isotopic signature from Pb originating from corrosion of Pb counterweights, which is discussed in more detail in a forthcoming section. Analyses of stable Pb isotopes along with ^{210}Pb dating of sediments (Keinonen, 1992) from seepage lakes in Florida, which receive most of their Pb influx from atmospheric deposition, might help to resolve changes in industrial sources of lead from atmospheric deposition.

Acid and Water Leachates of Aquifer System Material

The Pb-isotopic composition of material from the surficial and Floridan aquifer systems (table 6) was determined by leaching with two different solutions. Deionized water leachates provide information on Pb present in the aquifer matrix in a highly exchangeable form. Leaching with acid (0.1N HCl) facilitates the release of cations from all mineral surfaces. This treatment also dissolves Fe oxyhydroxides releasing bound metals and organic matter. Pb and other metals are released from a "labile reservoir" (Erel and others, 1990) whose composition consists mainly of Fe hydroxides, manganese (Mn) hydroxides, and organic material in which Pb is chelated. Acid-leachable Pb would exist in a highly-exchangeable form and could be released from moderately soluble minerals that contain Pb (such as calcite, dolomite, iron hydroxyl coatings on quartz grains, and soluble clay minerals).

Table 6. Lithology and clay mineralogy of aquifer material samples

[Sampling depth interval denotes meters below land surface; SAS and FAS denote surficial aquifer system and Floridan aquifer system, respectively]

Site name	Sampling depth interval	Lithology	Aquifer
JOW-3A	6.0-6.1	sand	SAS
JOW-3B	13-14	sandy clay	SAS
JOW-5A	1.5-1.6	sand	SAS
W-15992A	0.6-1.2	sand	SAS
W-15943A	2.4-2.7	clay	SAS
W-15888	26-27	calcarenite	FAS
W-15943C	15-18	dolomite	FAS
W-15992C	33-34	calcilutite	FAS
W-16304	29-30	calcite	FAS
W-9195	299-360	limestone	FAS
JOW-3C	30-31	limestone	FAS
JOW-5B	18.0-18.5	limestone	FAS
JOW-5C	27.0-27.5	limestone	FAS

Distinct differences in Pb-isotopic ratios were found between the acid and water leachates of aquifer material. A larger range of radiogenic Pb-isotope ratios was observed for acid leachates than for water leachates of material from both aquifer systems. For material from the surficial aquifer system, acid leachates generally yielded higher values of $^{206}\text{Pb}/^{207}\text{Pb}$ (with the exception of JOW-3A) than water leachates. Ratios of radiogenic to nonradiogenic Pb isotopes ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$) generally were higher for acid leachates than for water leachates with the exception of JOW-3A (table 5). Large variability in isotopic ratios for water and acid leachates of surficial aquifer system material indicate that Pb is present in a highly exchangeable form, possibly sorbed on iron-hydroxyl surface coatings on quartz grains (Coston and others, 1995). The acid leach (0.1N HCl) may preferentially remove Pb from minerals that contained ^{238}U (parent radionuclide of ^{206}Pb) and some nonradiogenic Pb.

Acid leachates of carbonate material from the Floridan aquifer system generally had higher values of $^{206}\text{Pb}/^{207}\text{Pb}$ (with the exception of JOW-3C) than radiogenic Pb-isotopic ratios for water leachates (table 5). Acid leachate ratios of radiogenic to nonradiogenic Pb isotopes ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$) were higher than for water leachate ratios in three samples, W15943C, W16304, and JOW-5C, but lower than water leachate ratios in two samples, JOW-3C and JOW-5B (table 5). The lack of consistently higher

Pb-isotopic ratios for the acid leachates compared to the Pb-isotopic ratios for the water leachates indicates that total Pb may exist in a highly exchangeable form in the carbonate matrix. Average values of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios for acid leachates (1.222 ± 0.54) and water leachates (1.201 ± 0.0063) for Eocene carbonates that comprise the Floridan aquifer system are similar to Pb-isotopic ratios (1.198) for Jurassic limestones in southern France (Monna and others, 1995) and for the carbonate fraction (1.24-1.29) of Cretaceous limestone in Israel (Erel and others, 1997).

Anthropogenic and Natural Sources of Pb in Ground Water

On a plot of $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ (fig. 5a), Pb-isotope ratios of ground water, rainfall, leachates of aquifer material and Pb counterweights cluster along a linear trend line (slope -0.68; $r^2=0.95$). Slopes and intercepts of best-fit (linear least squares) regression lines for the Pb-isotopic composition of each sample type are very similar, ranging from -0.58 to -0.97, and 2.39 to 3.18, respectively (table 7). It is difficult to discriminate between Pb counterweights and aquifer material as a source of Pb in ground water from the surficial aquifer system because of similar slopes and intercepts of trend lines for Pb counterweights, ground water from the surficial aquifer system, and water leachates of surficial aquifer material (table 7). Acid leachates of surficial aquifer material samples plot along a line with a slightly gentler slope (-0.59) than ground water samples from the surficial aquifer system, Pb counterweights, or water leachates. The Pb-isotopic composition of water from the Floridan aquifer system plots along a line with a slightly lower slope (-0.64) than that for Pb counterweights (-0.68) and in between slopes of trend lines for water (-0.58) and acid (-0.71) leachates of aquifer material. Again, discriminating between an anthropogenic (Pb-counterweight) source and a natural source of Pb is equivocal using ratios of radiogenic Pb isotopes. Two possible exceptions are water samples from wells RTR11-2 and JEF-1, which plot along or very close to the line segment for the Pb counterweights. Both of these wells have PVC casings and did not have active water-level recorders (table 6); however, both of these wells have had water-level recording devices with Pb counterweights in the past.

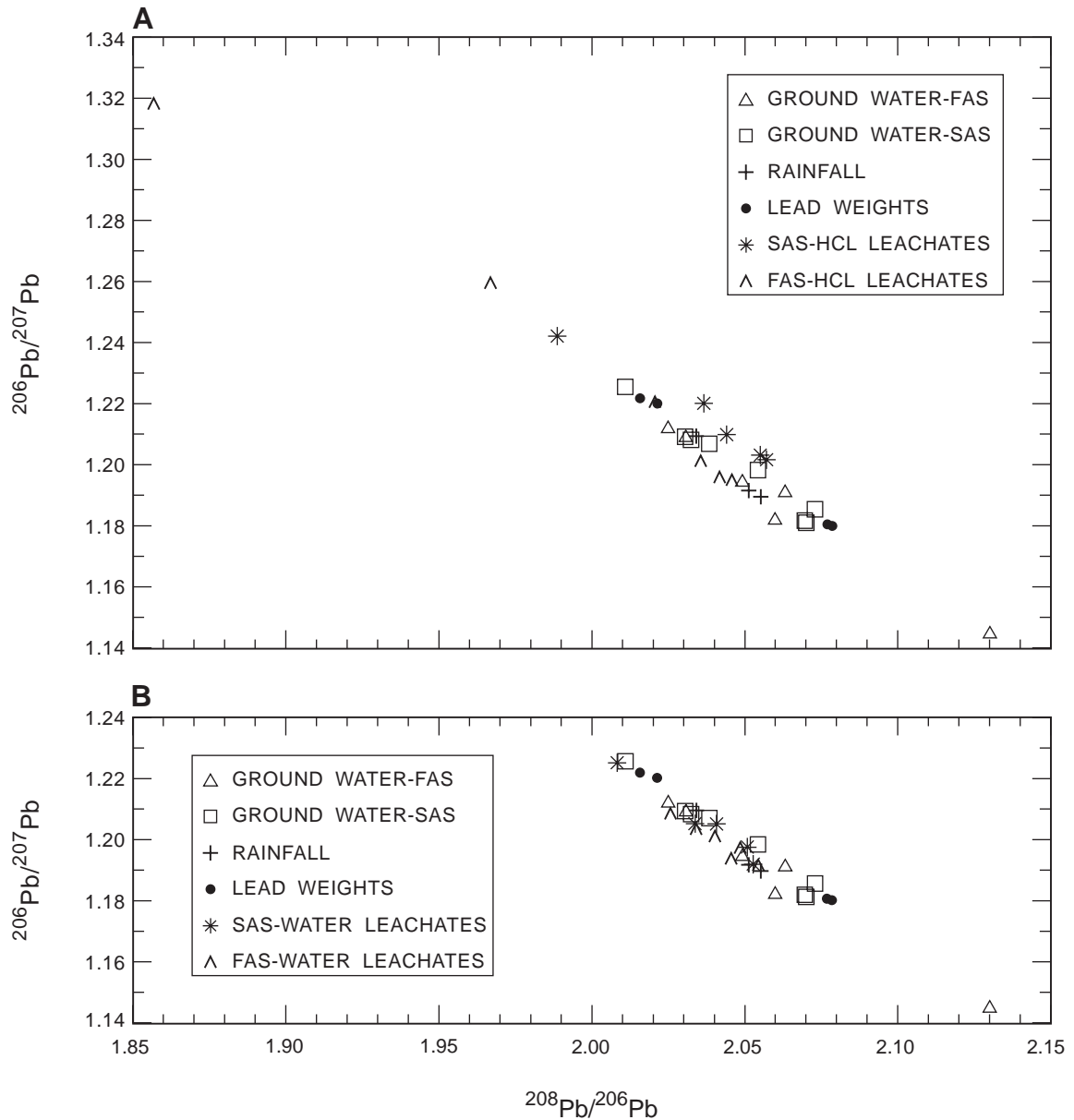


Figure 5. Plots showing ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$ for ground water, rainfall, Pb counterweights, and 0.1N HCl leaches of aquifer material and deionized water leachates of aquifer material. SAS and FAS denote surficial aquifer system and Floridan aquifer system, respectively.

Even though ratios of $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ are commonly used in environmental studies to discriminate between atmospheric sources of industrial Pb, plots of Pb-isotope ratios relative to non-radiogenic ^{204}Pb reveal much more detailed information on sources of Pb in ground water. For example, ratios of $^{206}\text{Pb}/^{204}\text{Pb}$ plotted against $^{207}\text{Pb}/^{204}\text{Pb}$ for water from wells with active water-level recorders fall along or cluster near a trend line connecting the isotopic composition of Pb counterweights. Water from wells that have had water-level recorders in the past

also plot near the isotopic composition of Pb counterweights, with the exception of water from V-087, which has a higher radiogenic signature, and water from VDP-1A, which has a lower radiogenic signature than Pb-isotopic compositions that plot along this line. Best-fit linear trend lines connecting the Pb-isotopic composition of leachates of surficial aquifer material (DI water and HCl) both have much lower slopes than that the trend lines for Pb counterweights and ground water (from the surficial aquifer system). Based on the similarity between the slopes and intercepts from plots

Table 7. Slope (m), intercept (b), and regression coefficients (r^2) for linear best-fit regression lines for different sample types from plots of Pb isotope ratios

[SAS and FAS denote surficial aquifer system and Floridan aquifer system, respectively]

Sample type	$^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$			$^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$			$^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$		
	m	b	r^2	m	b	r^2	m	b	r^2
Pb counterweights	-0.68	2.60	0.99	0.70	25.3	0.95	0.19	12.1	0.94
SAS ground water	-0.68	2.60	0.97	0.81	23.2	0.51	0.19	12.2	0.31
FAS ground water	-0.64	2.50	0.98	0.34	31.9	0.78	0.039	14.9	0.53
SAS DI water leachates	-0.69	2.60	0.97	0.48	29.4	0.75	0.078	14.2	0.75
SAS HCl leachates	-0.59	2.41	0.97	-0.066	40.0	0.02	-0.027	16.2	0.17
FAS DI water leachate	-0.58	2.39	0.92	0.67	25.7	0.56	0.23	11.4	0.64
FAS HCl leachate	-0.71	2.65	0.96	0.45	29.7	0.54	0.071	14.3	0.78
Rainfall	-0.97	3.18	0.99	1.05	18.6	0.99	0.17	12.6	0.98
Atlantic Ocean aerosols (Veron and Church, 1997)	-0.97	3.19	0.96	1.17	17.0	0.94	0.12	13.6	0.66

of $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ (fig. 5) and $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ (table 7), the source of Pb in ground water samples from the surficial aquifer system most likely originates from Pb counterweights. Additional Pb-isotopic analyses are needed to verify that metallic Pb counterweights can produce ratios of $^{207}\text{Pb}/^{204}\text{Pb}$ that are greater than 15.85.

Ratios of $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ of water from wells R57-1F and RTR11-2 (Floridan aquifer system) plot between the regression lines for the Pb-isotopic composition of Pb counterweights and the Pb-isotopic composition of acid and water leachates of material from the Floridan aquifer system, indicating that the Pb in these waters probably is a mixture of Pb derived from aquifer material and corrosion of Pb counterweights (fig. 6). Pb can substitute for Ca in calcite (CaCO_3), the predominant mineral in limestone that comprises the matrix of the Floridan aquifer system, the Biscayne aquifer, and parts of the intermediate aquifer system. Median and mean concentrations of naturally occurring Pb in samples of limestone and dolomite are 4 and 12 milligrams per kilogram (mg/kg; ppm), respectively (Lovering, 1976); and Drever (1988) reports 9 mg/kg as a typical concentration for Pb in limestone. Other evidence for a natural source of Pb in water from the Floridan aquifer system comes from Pb-isotopic data ($^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$) for spring waters. Springs integrate large parts of the Floridan aquifer system both vertically and laterally and their Pb-isotopic compositions (J. McCullough, 1998, University of Florida, written commun.) are sim-

ilar to those of acid and water leachates of carbonate aquifer material found in this study.

Pb-isotope ratios of rainfall samples plot along regression lines with higher slopes than trend lines for other sample types in plots of $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (table 7), but a lower slope than trend lines for Pb counterweights and ground water samples from the surficial aquifer system on a plot of $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ (table 7). The slopes and intercepts of the trend lines for rainfall samples on all three plots of Pb-isotopic ratios closely match slopes and intercepts for best-fit trend lines of Pb-isotopic ratios in aerosols collected during an Atlantic Ocean scientific cruise that transited between Miami and the Azores (Atlantic Stratocumulus Transition Experiment-Marine Aerosol and Gas Exchange, ASTEX-MAGEX) in 1992 (Veron and Church, 1997; Hamelin and others, 1997). For example, from a plot of $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$, the slope and intercept of Atlantic Ocean aerosols was -0.97 and 3.19 ($r^2=0.96$) compared to -0.97 and 3.18 ($r^2=0.99$) for rainfall samples collected in Florida. Pb-isotope data (analyzed at Florida State University) for rainfall samples from several sites in south Florida also plot along a best-fit trend line with a similar slope (-1.03) and intercept (3.32) (W.M. Landing, 1998, Florida State University, written commun.). Based on the similarity between the isotopic composition of rainfall from sites in Florida and data collected from ASTEX-MAGEX (Veron and Church, 1997), it is hypothesized

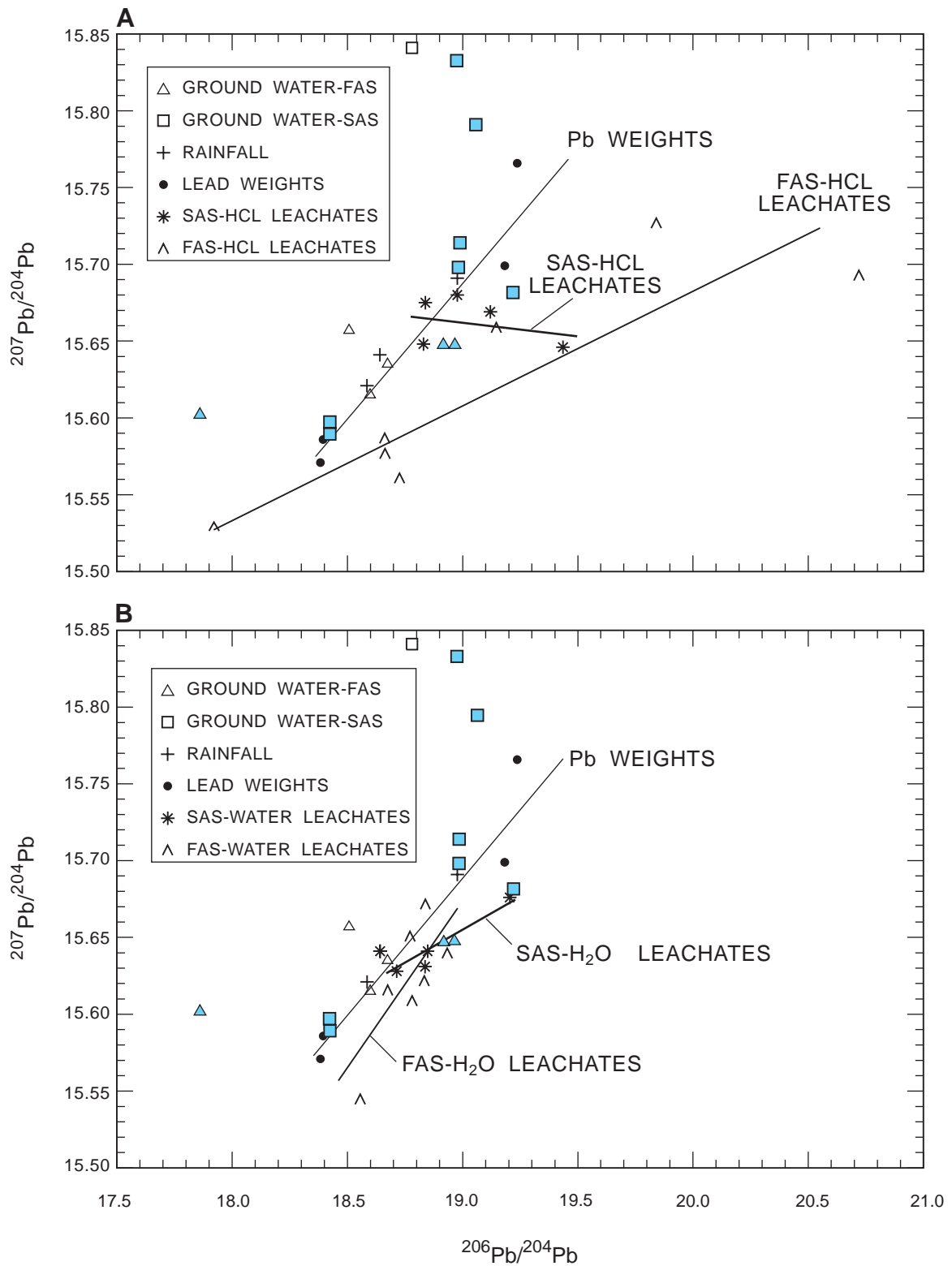


Figure 6. Plots showing ratios of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ for ground water, rainfall, Pb counterweights, and 0.1N HCl leachates of aquifer material, and deionized water leachates of aquifer material. SAAS and FAS denote surficial aquifer system and Floridan aquifer system, respectively. Filled triangles and squares denote wells that have a water-level recording device.

that Pb in Florida rainfall most likely originates from a mixture of air masses from North America and Europe. It is important to emphasize that the trend lines for the Pb-isotopic composition of rainfall is based on a limited number of samples; additional Pb-isotope analyses of rainfall are needed to test this hypothesis and to determine short-term variations of continental air-mass sources of Pb (seasonal influences). Pb concentrations in rainfall in Florida are greatly elevated above what one would predict based on crustal abundance relative to aluminum (Landing and others, 1995). Differences in isotopic composition between rainfall and samples of ground water (plots of $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$; table 7) indicate that the isotopic composition of Pb in ground water is probably not influenced by present-day rainfall.

There does not appear to be any appreciable difference of Pb-isotopic ratios between dissolved and particulate phases, based on Pb-isotopic analyses of dissolved (0.1 μm filter) and total Pb in water from a shallow well. The Pb-isotopic composition of dissolved (V-088F) and total Pb (V-088R) was nearly identical (table 5). Other studies also have found no significant difference in Pb-isotopic composition between dissolved and particulate phases and attributed this similarity to a rapid isotopic homogenization of both phases (Monna and others, 1995). Sherrell and others (1992) found that the Pb-isotopic composition of small particles in seawater match that of the upper 2,000 meters of the water column in the western Atlantic Ocean. Based on $^{206}\text{Pb}/^{207}\text{Pb}$ and $\text{Pb}/^{210}\text{Pb}$ ratios, Sherrell and others (1992) conclude that dissolved and particulate Pb equilibrate on a short time scale relative to the particle residence time in seawater.

SUMMARY AND CONCLUSIONS

Based on 2,745 samples of ground water collected during 1991-96 from a statewide network of 1,529 wells tapping the principal aquifers and aquifer systems in Florida, 19 percent had total Pb concentrations that exceeded the USEPA action level of 15 $\mu\text{g}/\text{L}$ for Pb in drinking water. Only 1.3 percent of 2,687 water samples collected from 1,468 wells had dissolved Pb concentrations that exceeded the action level. Lead concentration data were highly censored, with approximately 33 and 84 percent of the total and dissolved Pb concentrations in ground-water samples below the reported analytical detection limit. Wells sampled are part of a statewide network designed to

monitor background or baseline water quality conditions in the surficial, intermediate, and Floridan aquifer systems, and the sand-and-gravel and Biscayne aquifers. Differences in total Pb concentrations among aquifer systems reflect the combined influence of anthropogenic sources and chemical conditions in each system. A highly significant difference in median total Pb concentrations ($p < 0.001$) was found between water samples from wells with water-level recording devices that contain Pb-counterweights, 14 $\mu\text{g}/\text{L}$, compared to non-recorder wells, 2 $\mu\text{g}/\text{L}$. Differences between total Pb concentrations for recorder and non-recorder wells are even more pronounced when compared for each aquifer system. The largest differences for recorder status are found for the surficial aquifer system, where, median total Pb concentrations are 44 and 2.4 $\mu\text{g}/\text{L}$ for recorder wells and non-recorder wells, respectively. Leaching of Pb from metal casing materials is another potential source of Pb in ground water samples. Median total Pb concentrations in water samples from the surficial, intermediate, and Floridan aquifer systems are higher from recorder wells cased with black iron than for recorder wells with steel and PVC casing material. The largest differences among casing material and wells with active recorders is found for water samples from the surficial aquifer system, with median total lead concentrations of 104, 48, and 30 $\mu\text{g}/\text{L}$ for water from wells with black iron, PVC, and steel casing materials, respectively.

Pb concentrations in ground water are related to differences in chemical conditions among aquifers and aquifer systems. Analyzing a subset of wells that best represents natural conditions (PVC-cased wells that never had a water-level recording device), there was a statistically significant (0.05 significance level) positive correlation between total Pb and total Fe, dissolved Fe, and total organic carbon. These findings indicate that Pb is transported in ground water by sorption onto iron oxyhydroxides and organic material that can exist as mobile particulate matter (colloids).

Stable isotopes of Pb were used in this study to distinguish between anthropogenic and natural sources of Pb in ground water as Pb retains the isotopic signature of the source from which it is derived. Based on similarities between slopes and intercepts of trend lines for various sample types (plots of $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$) the predominant source of Pb in water samples from the surficial aquifer system is corrosion of Pb counterweights. It is likely that only ground-water samples, not the aquifer, were contaminated with elevated Pb

concentrations. Pb-isotopic ratios of water from the Floridan aquifer system plot between trend lines connecting the isotopic composition of Pb counterweights and the composition of acid leachates of material from the Floridan aquifer system, indicating that the Pb in these waters most likely is a mixture of Pb derived from aquifer material (radioactive decay of parent nuclides) and corrosion of Pb counterweights.

While median total Pb concentrations are near or below analytical detection limits for non-recorder wells with PVC casing material (sampling water that represents background conditions in the aquifer systems), there are isolated instances of elevated Pb concentrations in water samples from PVC-cased wells that have never had water-level recorders. A possible source of Pb in water from these wells could originate from the use of Pb weights or other materials, such as brass that contain soluble Pb, attached to the end of calibrated tapes that are used to measure ground-water levels. Anecdotal information indicates that these weights occasionally break off the tape and drop to the bottom of the well bore. In many instances, this information is not recorded and corrosion of these materials at the bottom of a monitoring well can release Pb to samples of ground water.

Wells that yield water with elevated Pb concentrations above background levels should be investigated for contamination from Pb weights or other alloys that contain Pb, particularly in corrosive chemical environments (low pH, high dissolved organic carbon concentrations, low dissolved oxygen levels). Also, in these environments, water samples for Pb and other trace elements from older monitoring wells with metal casing materials, such as black iron and galvanized steel, should be qualified because these samples probably do not represent background concentrations of metals in ground water. Present water sampling procedures of PVC monitoring wells that have been contaminated by anthropogenic sources of Pb also may not produce representative samples of ground-water quality with respect to background concentrations of Pb even after purging at least three casing volumes of water from the well.

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