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Comparison of Water Chemistry in Spring and Well Samples from Selected Carbonate Aquifers in the United States

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ABSTRACT

Water chemistry in samples from 226 wells and 176 springs were assessed to determine if samples from springs and wells have similar concentrations of selected properties such as dissolved solids, dissolved oxygen, nitrate, and calcite and dolomite saturation indices. Samples were collected in seven carbonate aquifers–Edwards-Trinity, Floridan, Mississippian, Basin and Range, Valley and Ridge, Springfield Plateau, and Ozark. Comparisons were made between concentrations of inorganic constituents in water samples from springs and from wells within the same aquifer. Results were variable, but showed that concentrations were not significantly different between samples from springs and wells for most properties. Nitrate and dissolved solids concentrations were only significantly different between spring and well samples in one or two of the seven aquifers; however, dissolved oxygen concentrations were significantly different between well and spring samples in four of the seven aquifers. Median calcite and dolomite saturation index values were significantly different between well and spring samples in three of the seven aquifers. Spring samples probably represent water from shallower parts of the aquifer flow systems and thus represent parts of the flow system that are most susceptible to contamination from land-use practices. These results indicate that the collection of water from springs should be considered critical to adequately characterize water quality in carbonate aquifers.

INTRODUCTION

About 20 percent of the ground water withdrawn for drinking water in the United States is from carbonate aquifer systems (M.A. Maupin, U.S. Geological Survey, written commun., 2004). Understanding the factors that control water quality in these systems requires information on water chemistry from the aquifer matrix, fractures, and from secondary porosity features (e.g., solution conduits). Comprehensive monitoring strategies that include the sampling of both springs and wells (Quinlan, 1989) have been used to interpret geochemical variability that arises from ground-water flow through different parts of a carbonate aquifer system (Scanlon, 1990; Adamski, 2000).

Water samples were collected from 226 wells and 176 springs in seven carbonate aquifers from 1993 through 2003 as part of the U.S. Geological Survey's National Water-Quality Assessment Program. This number of samples from carbonate aquifers around the United States represents an opportunity to explore the differences in major-ion chemistry between samples collected from wells and from springs. Limestone and dolomite units were sampled within the following aquifers: Edwards-Trinity, Floridan, Mississippian, Basin and Range, Valley and Ridge, Springfield Plateau, and Ozark (fig. 1). These limestone and dolomite units range in age from Cambrian to Quaternary (Adamski, 2000; Miller, 1990; Maclay, 1995) and some are interlayered with sandstone or chert layers (Dettinger and others, 1995; Johnson, 2002; Kingsbury and Shelton, 2002).

COMPARISON OF SAMPLES FROM SPRINGS AND WELLS WITHIN SELECTED AQUIFERS

Spring and well water samples were collected from seven aquifers—Edwards-Trinity, Floridan, Mississippian, Valley and Ridge, Basin and Range,

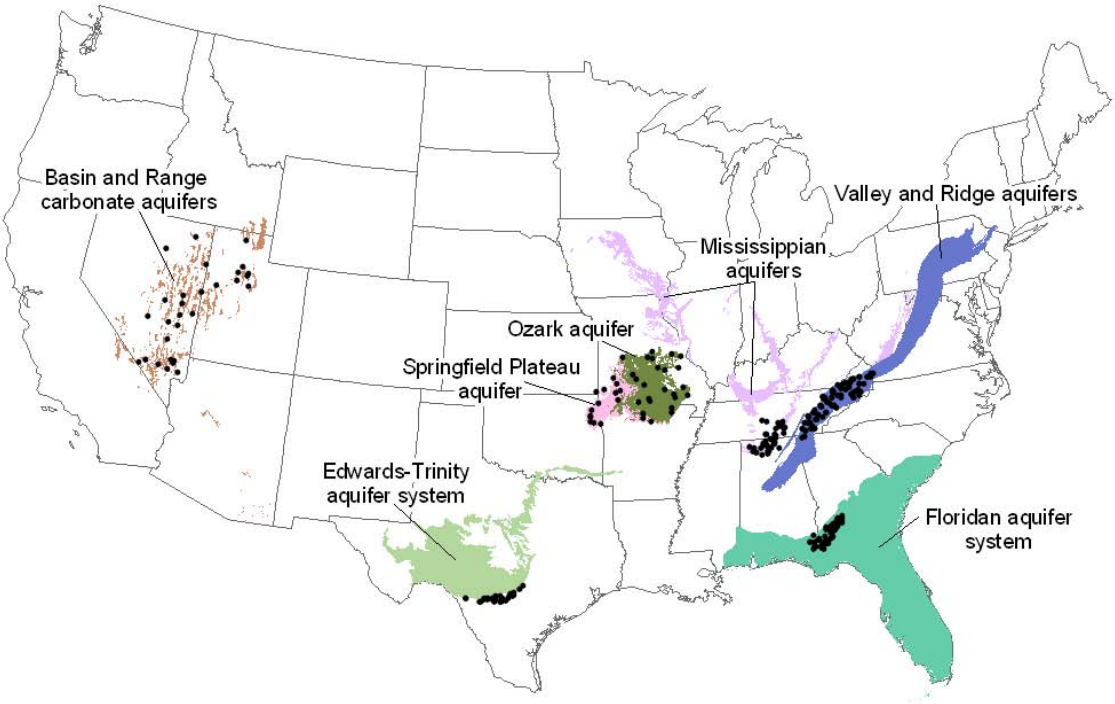

Figure 1. Location of spring and well sites sampled from 1993-2003.

Springfield Plateau, and Ozark. Within each aquifer, the number of water samples collected from springs ranged from 6 to 58 samples and the number of samples from wells ranged from 18 to 57 (fig. 2). In the Floridan aquifer system, samples were collected exclusively from the Upper Floridan aquifer, thus Upper Floridan will be used for the remainder of this discussion. Comparisons were made only between

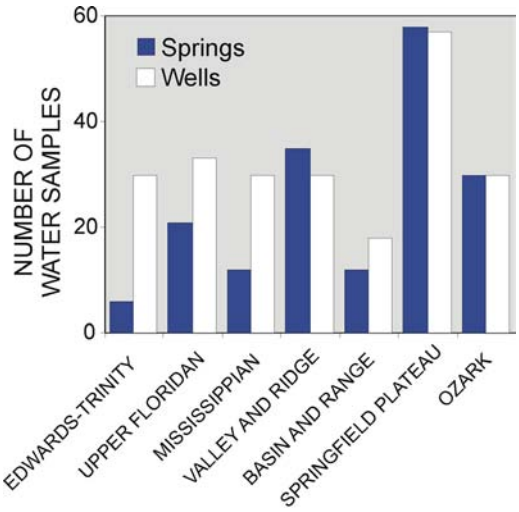

Figure 2. Number of spring and well samples collected from selected aquifers.

the water samples from springs and wells within a given hydrogeologic setting in each aquifer.

For example, in the Upper Floridan aquifer, samples were collected from throughout the extent of the aquifer, but spring water samples were collected only in southwestern Georgia; thus, these spring water samples were compared only to well samples collected in the same hydrogeologic setting in southwestern Georgia. The nonparametric Wilcoxon rank-sum test (Helsel and Hirsch, 1992) was used to determine if concentrations of constituents were significantly different (level of significance 0.05) between water samples collected from wells and springs.

Major Dissolved Species

Calcium-bicarbonate is the dominant water type for all of the aquifers and aquifer systems; however, the chemical composition of water samples from the springs and wells in the Basin and Range aquifer system was highly variable. In most aquifers, fewer than half of the 14 inorganic constituents examined showed significant differences in

Table 1. Summary of p-values from Wilcoxon rank-sum test comparing concentrations between samples from springs and wells.

[P-values lower than the level of significance, 0.05, are shaded gray; <, less than]

Aquifer	Calcium	Magnesium	Sodium	Potassium	Iron	Manganese	Bicarbonate	Sulfate	Chloride	Nitrate	Silica	pH	Dissolved oxygen	Dissolved solids
Edwards-Trinity	0.20	0.78	0.46	0.36	1.00	0.51	0.01	0.63	0.52	0.98	0.75	0.98	0.63	0.38
Upper Floridan	0.68	0.69	0.58	0.59	0.01	0.01	0.45	0.37	1.00	0.16	0.80	<0.01	0.12	0.52
Mississippian	0.70	0.61	0.05	0.72	0.14	0.44	0.74	0.38	0.08	0.36	0.18	0.11	<0.01	0.40
Valley and Ridge	0.36	0.18	0.17	0.06	<0.01	<0.01	0.16	0.01	0.29	0.09	0.10	0.08	<0.01	0.05
Basin and Range	0.08	0.85	0.25	0.44	<0.01	<0.01	0.25	0.24	0.92	0.98	1.00	0.09	0.66	0.25
Springfield Plateau	0.34	0.08	0.54	<0.01	0.33	0.10	<0.01	0.16	<0.01	<0.01	<0.01	<0.01	<0.01	0.05
Ozark	<0.01	<0.01	0.04	0.51	0.45	0.09	0.05	0.12	0.23	0.95	0.94	0.05	<0.01	<0.01

concentrations between springs and well samples (table 1). The greatest number of inorganic constituents with significant differences in concentration was seven in the Springfield Plateau aquifer. In three aquifers—Edwards-Trinity, Mississippian and Basin and Range—significant differences in concentrations were noted for only one or two properties, indicating that samples collected from springs and wells were collected from ground water from similar locations within the aquifer flow systems.

The range in dissolved solids concentrations among the seven aquifers provides some information about the relative residence times and flow path lengths in the aquifers. Aquifers with greatest median dissolved solids concentrations in spring and well samples, the Edwards-Trinity aquifer (322 and 294 milligrams per liter (mg/L), respectively) and the Basin and Range aquifer (410 and 364 mg/L, respectively), also had the greatest median well depths—1,270 feet (Edwards-Trinity) and 940 feet (Basin and Range). The median well depths for wells in the other aquifers ranged from 87 to 227 feet. Water from the deeper wells with greater dissolved solids concentrations may indicate that longer flow paths and older ground water are being sampled in these aquifers. Dissolved solids concentrations were only significantly different between spring and well samples in the Valley and Ridge and Ozark aquifers (fig. 3).

Median dissolved oxygen concentrations ranged from 2.5 mg/L in water samples from the Basin and Range aquifer wells to about 8 mg/L for springs in several of the aquifers (fig. 4). In four of the seven aquifers, dissolved oxygen concentrations were significantly different between samples from springs and wells (fig. 4). In each aquifer where significant differences in dissolved oxygen were noted, the spring samples have the greater dissolved oxygen concentrations, indicating generally younger waters and more dynamic flow systems. The median dissolved oxygen concentration in water samples from wells was greater than that for springs in the Edwards-Trinity aquifer. Deeper, more regional circulation of ground water may account for lower dissolved oxygen concentrations in some springs in the Edwards-Trinity aquifer.

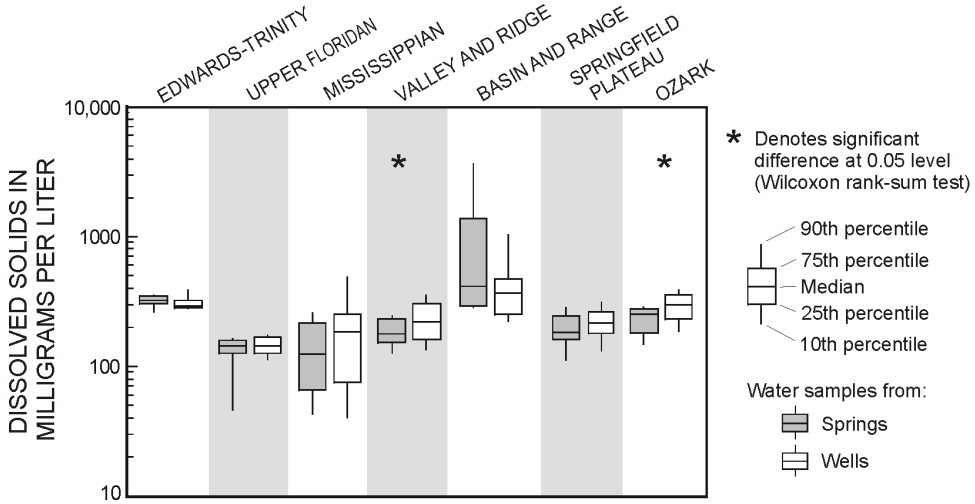

Figure 3. Distribution of dissolved solids concentrations in samples from springs and wells.

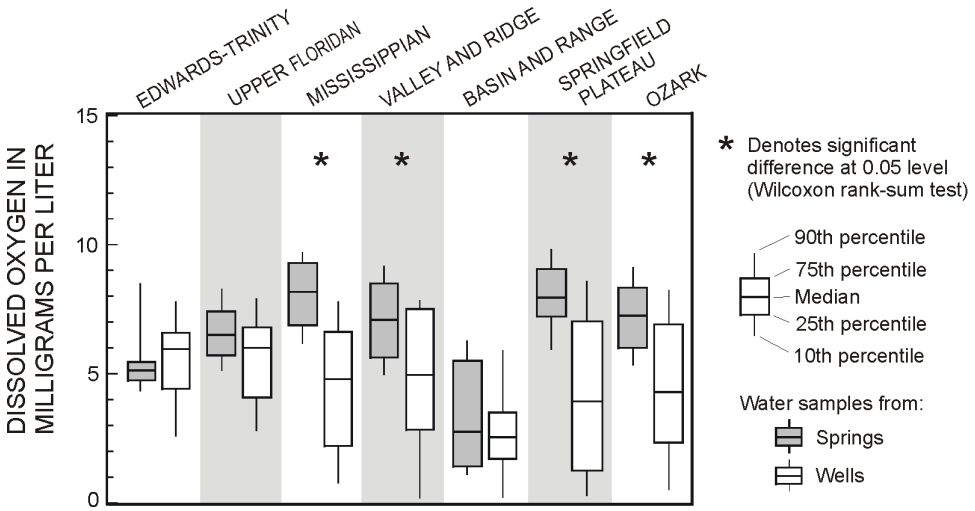

Figure 4. Distribution of dissolved oxygen concentrations in samples from springs and wells.

Saturation Indices with Respect to Calcite and Dolomite

Saturation indices were calculated for calcite and dolomite using the program PHREEQC (Parkhurst and Appelo, 1999). In most aquifers, the calcite saturation index values for the spring and well samples were at or near equilibrium (values of 0 +/- 0.2 are considered to represent equilibrium) (fig 5a). Most water samples were undersaturated with respect to calcite (values less than -0.2) for the Mississippian aquifer. Minerals in these aquifer materials may be less soluble than the aquifer materials in most of the other carbonate aquifers sampled.

Calcite saturation index values were significantly different between water samples from springs and wells in three of the seven aquifers—Upper Floridan, Springfield Plateau Ozark aquifers (fig. 5a). In each aquifer where the calcite saturation index values were significantly different (and in three of the other aquifers where significant differences were not noted), the significantly lower values were in the spring samples, indicating waters from

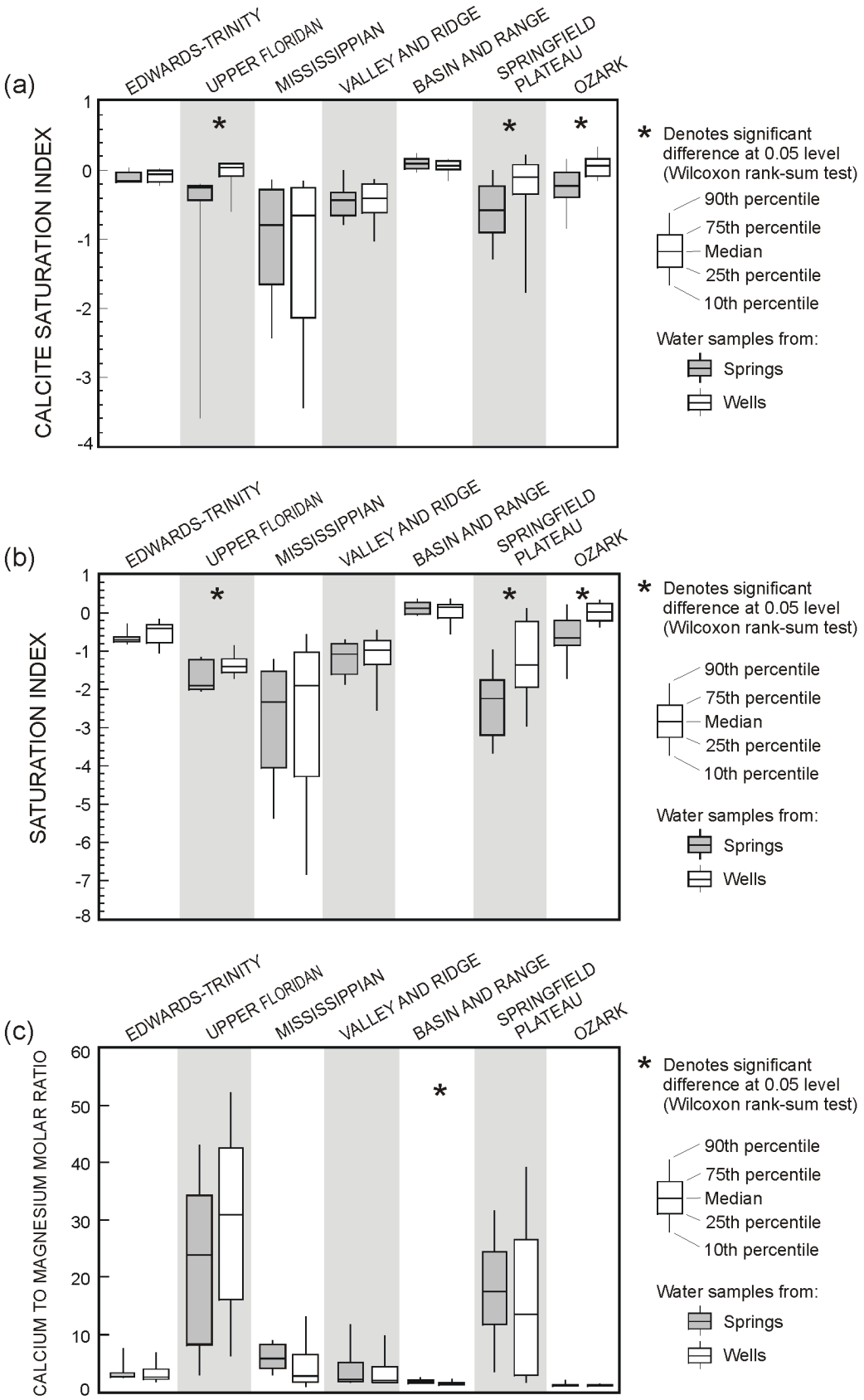

Figure 5. Distribution values for (a) calcite saturation index, (b) dolomite saturation index, and (c) calcium to magnesium molar ratio in samples from springs and wells.

springs were more undersaturated with respect to calcite than water from wells. The lower calcite saturation index values also indicate that spring waters may originate from shallower parts of the flow systems than the water withdrawn from wells.

Spring and well water samples for most of the aquifers were undersaturated with respect to dolomite (fig 5b). Only spring and well samples from the Basin and Range aquifer and well samples from the Ozark aquifer were at or near equilibrium with respect to dolomite (values mostly between -0.2 to 0.2) (fig 5b). Dolomite saturation index values for the spring and well samples were significantly different in three of the seven aquifers—Upper Floridan, Springfield Plateau, and Ozark (fig. 5b)—the same three aquifers where significant differences were noted for calcite saturation index values. In each of the three aquifers where dolomite saturation index values were significantly different (and in the four aquifers where significant differences were not noted), the significantly lower values were in the spring samples indicating that the spring samples were more undersaturated with respect to dolomite than the samples from wells.

The molar ratio of calcium to magnesium was calculated for each sample to determine if this ratio correlates with the relative amount of dolomite in the carbonate aquifers. Results show that in five of the aquifers, calcium-magnesium molar ratios were less than about 5, and are consistent with the reported mineralogy for the Edwards-Trinity, Mississippian, Valley and Ridge, Basin and Range, and Ozark aquifers (fig. 5c) (Maclay, 1995, Kingsbury and Shelton, 2002, Johnson, 2002, Dettinger and others, 1995, and Adamski, 2000). The three aquifers where the most dolomite is indicated (where the calcium-magnesium ratios were lowest), Edwards-Trinity, Basin and Range and Ozark aquifers, were also the aquifers where dolomite saturation index values were highest (greater than -1.0) (figs. 5b and 5c).

Nitrate

Median nitrate concentrations in the seven aquifers ranged from 0.32 to 2.5 mg/L (fig. 6). Median concentrations were lowest (less than 1.0 mg/L) in the spring and well water samples from the Basin and Range and the Ozark aquifers. Although median nitrate concentrations did not exceed the maximum contaminant level of 10 mg/L, several median nitrate concentrations ranged from 1 to 4 mg/L, which may indicate anthropogenic inputs. Nitrate concentrations were only significantly different between spring and wells samples in the Springfield Plateau aquifer. The significantly higher concentrations in nitrate in water samples from springs relative to wells in the Springfield Plateau was noted by Adamski (2000) who attributed the higher nitrate concentrations to the greater susceptibility of

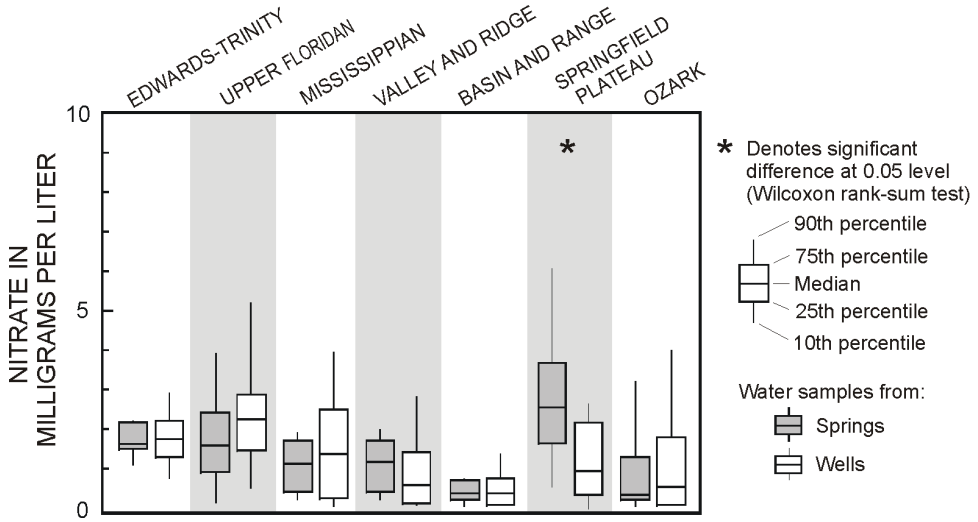

Figure 6. Distribution of nitrate concentrations in samples from springs and wells.

springs to surface sources of contamination. The land use in the area overlying the Springfield Plateau aquifer is predominantly agriculture (Adamski, 1996).

IMPLICATIONS FOR USE OF SPRINGS IN THE CHARACTERIZATION OF WATER QUALITY IN CARBONATE AQUIFERS

Differences in chemistry between spring waters and well water reflect ground-water movement in distinct parts of the flow system. Higher dissolved oxygen concentrations, lower saturation indices with respect to calcite and dolomite, and lower dissolved solids concentrations relative to water from wells, indicate that springs discharge ground water mainly from shallow parts of most of the studied aquifer systems. Exceptions are the Basin and Range and the Edwards-Trinity aquifers, where deeper circulation of ground water may occur prior to discharge from springs. Chemical differences between water from springs or wells also are related to the hydrologic conditions at the time of sampling. Rainfall patterns should be evaluated along with spring discharge at the time of sampling to characterize the contribution of recent recharge to the aquifer and its impact on ground-water chemistry.

There were no consistent patterns when comparing nitrate concentrations in spring waters and well water. Nitrate concentrations were significantly higher in spring water than in ground water in the Springfield Plateau aquifer, but not in the adjacent Ozark aquifer. Nitrate concentrations were higher in spring waters than in well waters from the Valley and Ridge aquifer, but nitrate concentrations in spring waters were similar or lower than nitrate concentrations in well waters from the Edwards-Trinity, Upper Floridan, Mississipian, and Ozark aquifers. These differences likely reflect the complex relation between nitrate concentrations in ground water and various nitrogen sources, and include past and present land-use and waste-management practices, and hydrologic and climatic variability.

Spring samples most likely represent water from shallower parts of the aquifer flow systems, and flow through large solution openings in carbonate aquifer systems. These parts of the flow system are also the parts of the aquifer systems most susceptible to contamination from land-use practices. For these reasons, obtaining water samples from springs, in addition to wells, may be necessary for adequate characterization of water quality in carbonate aquifers and for addressing their susceptibility to contamination.

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