NATURALLY OCCURRING ARSENIC IN THE CENTRAL OKLAHOMA AQUIFER

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INTRODUCTION

The Central Oklahoma aquifer is a major source of water in central Oklahoma. In the confined part of the aquifer, dissolved arsenic (As) concentrations commonly exceed the Federal drinking-water standard of 10 micrograms per liter (µg/L) (U.S. Environmental Protection Agency, 2001). This natural water-quality problem was investigated by the U.S. Geological Survey (USGS) as part of the Central Oklahoma aquifer National Water-Quality Assessment pilot project. The high concentration of As was found to be a function of: (1) The distribution of As in solid phases of the aquifer, (2) the oxidized nature of the aquifer, (3) the distribution of sandstone and mudstone in the aquifer, and (4) changes in water chemistry as water flows through the aquifer. This paper describes water-rock interactions that mobilize As. This report also describes the population of wells exceeding the new drinking water standard of 10 µg/L in 2001.

DESCRIPTION OF THE STUDY UNIT

The Central Oklahoma aquifer underlies about 8,000 square kilometers in central Oklahoma. It is composed of Quaternary alluvium and terrace deposits and underlying Permian sandstone and mudstone. The alluvium and terrace deposits generally do not contain water with high concentrations of As. Permian geologic units in the aquifer include the Garber Sandstone, the Wellington Formation, and undivided rocks of the Chase, Council Grove, and Admire Groups. These predominantly red Permian units dip to the west at about 50 feet per mile. The Permian Hennessey Group (fig. 1) confines the western one-third of the aquifer.
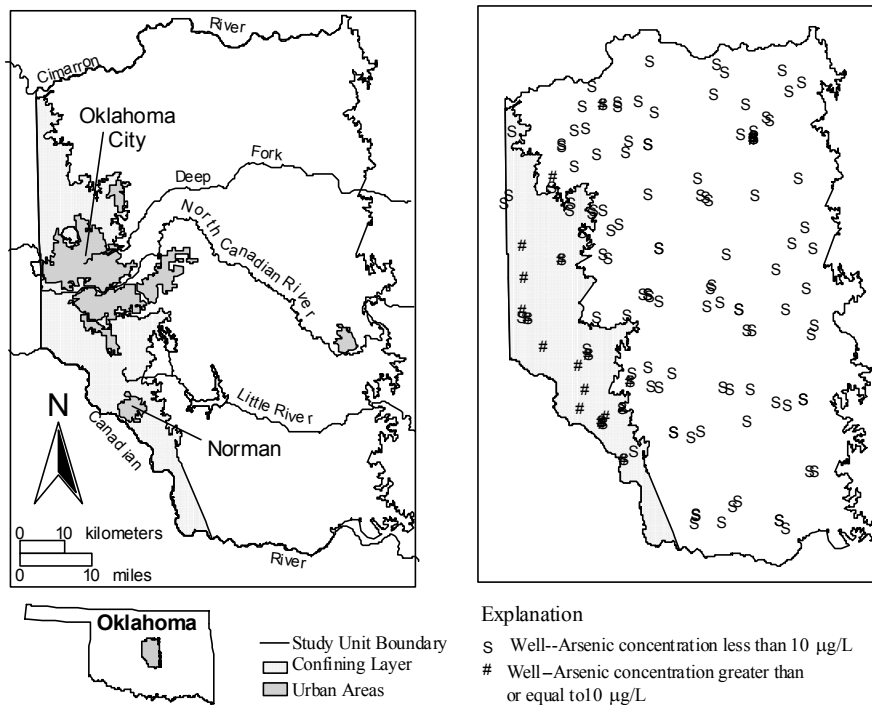

Figure 1. Major features of the study unit and distribution of arsenic in the Permian aged part of the Central Oklahoma Aquifer.

The base of the aquifer is defined to be the base of fresh water, where the bicarbonate-type waters transition to underlying sodium chloride brines. The depth to the base of fresh water is greatest in the west-central part of the aquifer where fresh water is as deep as 1,000 feet below land surface.

Recharge to the aquifer is predominantly from precipitation. Results of flow modeling (Parkhurst and others, 1993) indicate that some recharge flows west from the unconfined part of the aquifer into the confined part, then the water flow diverges to the north and

south under the confining layer to discharge into major streams. Flow in the unconfined part of the aquifer is generally from west to east and is controlled by local topography.

METHODS

During 1987–89, 146 wells penetrating the Permian part of the aquifer were sampled. Major and trace elements, and radioisotopes were analyzed by the U.S. Geological Survey National Water-Quality Laboratory. Selected samples were analyzed for tritium, stable hydrogen isotopes of water, or carbon-14 and carbon-13 for the purpose of estimating the recharge age of water. Common field parameter values were determined at the sampling site (Ferree and others, 1992). Samples from five wells were not used in this report because they are not representative of the general water-quality characteristics of the aquifer due to high concentrations of sulfate or chloride or unacceptable variance between duplicate samples (fig. 2).

Eight test-holes were drilled in the aquifer to provide additional information about As and other toxic trace elements in the ground water, and were sampled to determine rock and water chemistry and associated mineralogy. Two holes were drilled near wells having high concentrations of As. One test hole was drilled as a control in an area known to produce water with only low concentrations of As and other toxic trace elements (fig. 2). Water-producing sandstone layers in the test holes were isolated using inflatable packers, and water samples were collected and analyzed in the same manner as the samples from the 146 wells. Additional determinations of As oxidation state were made on selected samples (Schlottmann and Funkhouser, 1991). Rock core was collected for the entire depth of each test hole, was described at the site, and then analyzed for chemistry and mineralogy. Determination of cation-exchange capacity was made on clay-sized separates from 18 samples. Methods used and results are summarized by Breit and others (1990), and by Mosier and others (1990).

RESULTS AND DISCUSSION

The greatest concentrations of As [up to 62 micrograms per gram (μg/g)] were in rocks containing abundant yellow-brown goethite grain coatings. No discreet As-mineral phases were recovered, although two grains of iron pyrite isolated by heavy separation did contain some As. Pyrite is rare in the aquifer. Mudstone in the aquifer generally contains greater concentrations of As than does sandstone and may be an important source of As.

The aquifer is composed primarily of fine- and very fine-grained quartz-litharenite sandstone lenticularly interbedded with mudstone. The mudstone is predominantly composed of mixed-layer illite-smectite. Important authigenic minerals in the aquifer include hematite, goethite, and dolomite. The most notable diagenetic feature of the aquifer is the pervasive red color, which is caused by abundant grain-coating iron oxides indicating the generally oxidized nature of the rocks. Locally, yellow-brown goethite grain coatings color thick sequences of sandstone.

Sandstones interbedded with mudstones in the clay-rich eastern part of the aquifer contain more clay than sandstones in the sand-rich central part of the aquifer. Mudstones in the aquifer generally contain 35 to 50 milliequivalents/100 grams (meq/100g) of exchangeable cations, predominantly calcium and magnesium, with 3.5–20 percent sodium. Sodium was the dominant exchangeable cation below the base of fresh water. Clay-size separates from sandstones in the aquifer contain 22–40 meq/100g exchangeable cations with 0.25–10 percent sodium. The lowest percentages of exchangeable sodium were in samples from the sand-rich part of the aquifer. Mixed layer illite-smectite is the dominant ion exchange substrate.

The amount of cation exchange that water had undergone was estimated assuming that the only sources for sodium in the aquifer are the underlying sodium-chloride brines and exchange of sodium bound to mixed layer clays for dissolved calcium and magnesium. The amount of cation exchange in millimoles per liter (mmol/L) exchanged sodium was estimated by subtracting mmol/L chloride

from mmol/L sodium in solution, thereby subtracting sodium contributed by brine. Estimated cation exchange in the aquifer ranges from -4 to 12.5 mmol/L sodium with a median value of 1.1 mmol/L. The largest amounts of cation exchange between clays and water occurred in the confined and the clay-rich parts of the aquifer.

Predominant water types in the aquifer range from calcium magnesium bicarbonate to sodium bicarbonate. High concentrations of chloride or sulfate are rare. The pH of water in the Permian part of the aquifer ranges from 6.0 to 9.6.

In most of the aquifer, pH and cation exchange are related. Mass balance geochemical modeling (Parkhurst and others, 1993) indicates that the major reactions controlling water chemistry in the aquifer are uptake of carbon dioxide (CO_2) gas, dolomite dissolution, and cation exchange. Water in the unconfined sand-rich part of the aquifer generally is of a calcium magnesium bicarbonate type with detectable dissolved oxygen, a near-neutral pH, and little exchanged sodium. When water enters the aquifer in this area, it takes up CO_2 gas in the vadose zone and eventually equilibrates with dolomite. As water moves into either the confined or clay-rich part of the aquifer, interaction with mixed-layer clays results in the exchange of some of the calcium and magnesium for sodium. The resulting depletion of calcium and magnesium in the water allows dissolution of more dolomite. Deep in the aquifer, where the water is isolated from vadose-zone CO_2, dolomite dissolution causes a large increase in pH. This pH increase may be limited by the availability of clays, exchangeable sodium in the clays, and by the decreasing solubility of carbonate minerals at greater pH.

The data indicate a strong relation between dissolved As and pH and the amount of cation exchange the water has undergone (fig. 3). Arsenic occurs at concentrations greater than 50 µg/L only in water with a pH at or above 8.5. Twenty-six samples with As concentrations exceeding 10 µg/L had a pH of 8.5 or greater. One sample with a concentration greater than 10 µg/L of As had a lower pH, which may be explained by mixing of water in the borehole.

Figure 2—Relation of arsenic to pH and cation exchange

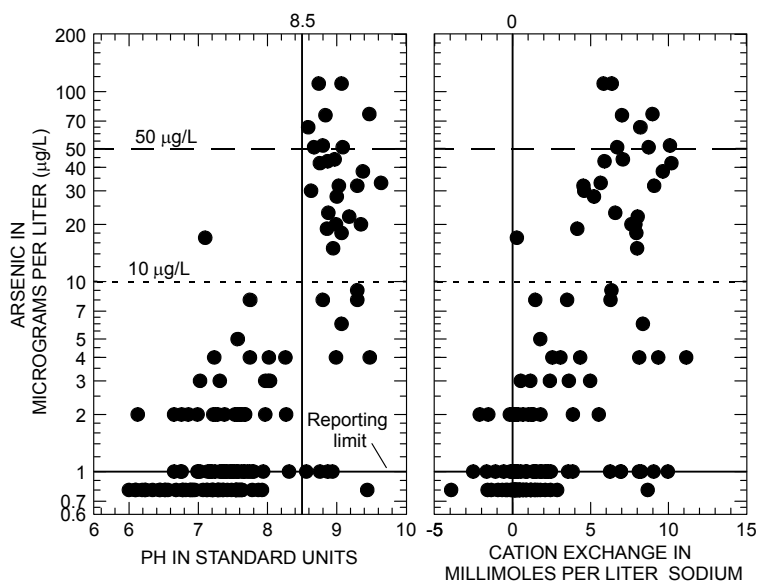Detectable dissolved oxygen greater than 1 milligram per liter (mg/L) is present in most water in the aquifer, indicating an oxic environment (Berner, 1981). Water without detectable oxygen commonly contains As, selenium, or uranium, which are generally only mobile in post-oxic or oxic environments, and are not mobile in sulfidic and methanic environments. Determination of As oxidation state in this water and in some oxic water indicated that As was present as As(V), the highest oxidation state. This indicates most water in the aquifer resides in post-oxic or oxic environments, which should allow As to be in an oxidation state [As(V)], which enhances mobilization of the element in high-pH water. As(V) is stable as the arsenate ($HAsO_4^{2-}$) oxyanion in waters with pH greater than about 7.0.

Arsenate tends to sorb on positively charged iron oxide surfaces (Davis and Kent, 1990). Iron oxides are abundant in this red-bed aquifer, and analyses of the rock cores indicated that arsenic is associated with yellow-brown goethite. Desorption of arsenate from iron-oxide surfaces is enhanced by increasing pH, which may explain the positive association between As and pH in the aquifer. Water with a pH below 8.5 tends to contain only low concentrations of As. High-pH water

concentrations of arsenic greater than 10 μg/L are common in the confined part and at depth in the unconfined clay-rich part of the aquifer and are rare in the unconfined sand-rich part of the aquifer.

The high arsenic concentrations in the aquifer are of concern because most ground-water city drinking-water supplies are produced from the confined part of the aquifer. Our results indicate the change in the arsenic maximum contaminant level to 10 μg/L will cause about 37 percent of wells greater than 90 meters deep (which typically are public-supply wells) to exceed drinking-water standards. Historical public-supply well arsenic data from other agencies increases the percentage of wells exceeding the arsenic standard to about 50 percent of public supply wells in the aquifer.

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