

Arsenic and Uranium in Four Aquifer Settings: Occurrence, Distribution, and Mechanisms for Transport to Supply Wells

Craig J. Brown, Bryant C. Jurgens, Brian G. Katz, Matthew K. Landon, Sandra M. Eberts
U.S. Geological Survey

Abstract

A U.S. Geological Survey (USGS) study of the transport of anthropogenic and natural contaminants to public-supply wells (PSWs) in four aquifer systems documents the occurrence and distribution of arsenic and uranium, and determines some of the mechanisms for their mobilization and movement. The study areas include a glacial aquifer system in Woodbury, Connecticut (referred to herein as CT); the Floridan aquifer system and overlying units in Tampa, Florida (referred to herein as FL); the High Plains aquifer in York, Nebraska (referred to herein as NE); and the Central Valley aquifer system in Modesto, California (referred to herein as CA).

Chemical analyses of solid-phase material indicated geologic sources of arsenic and uranium, but did not always correspond to their relative concentrations in ground water. In CT, low extracted concentrations of arsenic and uranium in most glacial deposits corresponded to low concentrations in ground water. Arsenic and uranium concentrations in sediment were highest in NE and among the lowest in CA, yet dissolved concentrations at both sites were similar. The predominance of calcium-uranyl-carbonate complexes, which can inhibit uranium adsorption, probably contributes to uranium mobility in NE, CA, and FL. Shallow, high-bicarbonate water is drawn downward by pumping and irrigation recharge at both sites. Arsenic correlates well with orthophosphate in shallow ground water in both areas, possibly indicating a tendency for competitive desorption of arsenic by phosphate. In FL, the highest concentrations of arsenic and uranium in depth-dependent samples from the public supply well were found in a highly transmissive zone in the Suwannee Limestone. The arsenic likely results from reactions between oxic water from the surficial aquifer system and arsenic-rich pyrite in parts of the limestone. Evidence of short-circuit pathways were observed in all four aquifer systems, and those in FL, NE, and CA result in sporadic exceedances of drinking-water standards for arsenic and (or) uranium in PSWs. At the FL, NE, and CA sites, these pathways resulted from human-induced changes in the flow system.

Introduction

About 10 percent of arsenic analyses in ground water in the U.S. exceeded the 10 $\mu\text{g/L}$ USEPA MCL (Welch and others, 2000) and large concentrations of dissolved radium and uranium have been detected in many ground-water supplies across the United States (Zapczka and Szabo, 1988). To safeguard public health, a better understanding is needed of geochemical processes associated with the occurrence of natural contaminants in public-supply wells (PSWs) because they provide drinking water to about one-third of the U.S. population. Understanding PSW contamination also is an economic issue

because of the expense and difficulty in remediating ground water from aquifers that are vulnerable to high levels of arsenic or uranium, or changing the locations of supply wells.

In 2001, the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program began a multi-scale study to assess the vulnerability of PSWs to contamination from a variety of compounds (Eberts and others, 2005), including arsenic and uranium. The Transport of Anthropogenic and Natural Contaminants to Supply Wells (TANC) study focuses on sources of contaminants and processes related to the mobilization and transport of contaminants within those parts of ground-water systems contributing water to PSWs. Sources, mobilization, and pathways for arsenic and uranium differ among aquifers, so the threat of these naturally occurring compounds to water quality in PSWs varies even where similar contaminant sources exist. This study identifies and compares these differences, as well as similarities, in a complementary set of aquifer systems, land-use settings, and public-water systems, on the basis of data that were collected and analyzed using consistent methods.

The TANC study began with eight regional study areas that represent a variety of hydrologic, physiographic, and climatic conditions. Hinkle and others (2006) used TANC study ground-water-flow-model particle-tracking results and geochemical data together with statistical methods to determine the feasibility of using such data to screen for public-supply well vulnerability to contamination from arsenic and uranium at the regional scale (tens to thousands of square kilometers). More detailed study of contaminant sources, and mobilization and transport processes that control the movement of arsenic and uranium to a PSW on a more local scale are the focus of this paper.

Description of Study Areas

Local-scale studies were conducted within the contributing area (less than 100 square kilometers) of a single, representative PSW in Woodbury, Connecticut, in a glacial aquifer (CT); Tampa, Florida, in the Floridan aquifer system (FL); York, Nebraska, in the High Plains aquifer (NE); and Modesto, California in the Central Valley aquifer system (CA) during 2003-2006. These four aquifer systems are shown on the principal aquifers map (fig. 1; USGS, 2003), and the state abbreviations used in this paper refer only to the study area. Conceptual illustrations of the aquifer systems in the four study areas are shown in figure 2. The study areas are described briefly below.

The glacial aquifer system study area in Woodbury, Connecticut (CT) is located near the eastern edge of the glaciated region of the U.S. The study area is in the Pomperaug River Basin where most water for public supply is obtained from wells completed in glacial aquifer deposits that are mostly less than 30 m thick. Characteristics of the selected aquifer system are similar to many glacial aquifer systems in the region that encompasses much of the populated parts of New England, northern New Jersey, and eastern New York. The primary inflow to the aquifer system is direct recharge from precipitation, and the primary outflow is discharge to streams (fig. 2A). Upland surface and shallow subsurface runoff also are important sources of water to this glacial aquifer system. Inflow from underlying Mesozoic bedrock of relatively low permeability is a

minor source of water. High recharge rates, high permeability, and relatively thin sand units result in relatively rapid ground-water travel times through the aquifer--nearly all ground water sampled in the local-scale study area had an apparent mean age of less than 25 years, based on age tracers. Water in the glacial aquifer is generally oxidic with localized zones of reducing conditions. Water in the underlying till and fractured bedrock is typically anoxic.

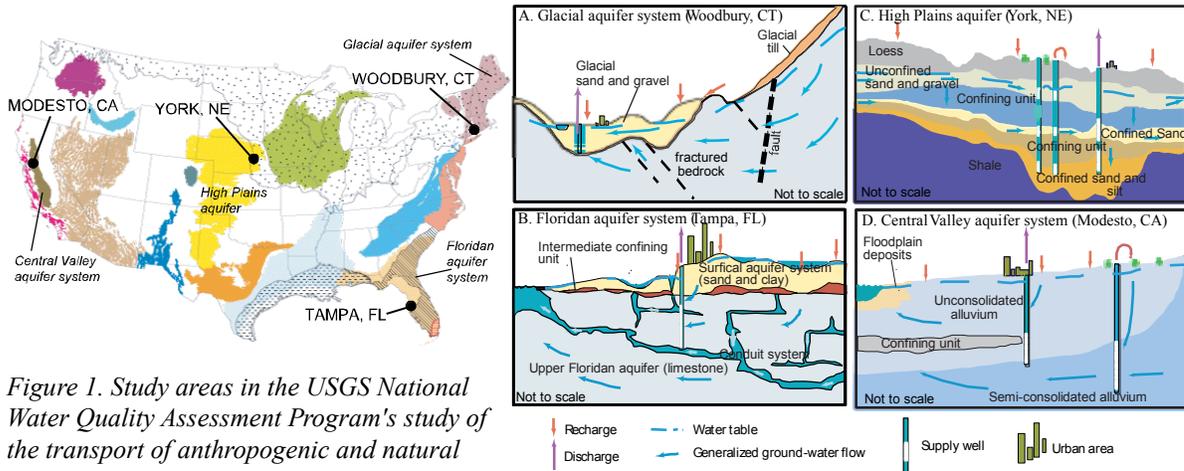


Figure 1. Study areas in the USGS National Water Quality Assessment Program's study of the transport of anthropogenic and natural contaminants to supply wells.

Figure 2. Conceptual models for ground-water flow in four aquifers in the USGS study of the transport of anthropogenic and natural contaminants to supply wells.

The TANC study area in the Floridan aquifer system (FL) is in west-central peninsular Florida in the central Tampa Bay region (fig. 1). The Tampa metropolitan area, and a considerable part of the southeastern U.S., rely heavily upon the Floridan aquifer as a source of drinking water. The Upper Floridan aquifer at the FL study area consists of karst limestone and dolomite and is overlain by unconfined sand and clayey-sand deposits known as the surficial aquifer system (fig. 2B). A clay-rich, intermediate confining unit, where present, separates these aquifers, although dissolution of the Upper Floridan aquifer limestone can result in sinkhole collapse and breaches in the overlying confining unit that can serve as preferential flow paths to the underlying Upper Floridan aquifer (Fig. 2B). Solution-enlarged fractures are common in the Upper Floridan aquifer and yield large quantities of water to wells (Stewart and others, 1978). The presence of younger water (apparent mean age less than 12 years, based on age tracers) in the PSW and in the surficial aquifer indicates the high vulnerability of PSWs associated with highly transmissive zones in the Upper Floridan aquifer (apparent mean age greater than 23 years) that are directly connected to the surficial aquifer. Water in the Upper Floridan aquifer is typically sulfate-reducing, whereas water in the surficial aquifer system is typically oxidic.

The TANC study area in the High Plains aquifer is in east-central Nebraska near the city of York (NE). The aquifer serves as an important source of water for agricultural irrigation and drinking-water supply throughout the region and constitutes the sole source of drinking water for the entire population. The aquifer is composed locally of layered Quaternary alluvial deposits with unconfined and confined sands as the primary water-bearing units (fig. 2C). The upper confined sand layer, which is directly overlain by a silty, clayey till confining unit, is the principal unit providing drinking water for public supply in the area. Many irrigation and some commercial and older supply wells are

screened in the unconfined and confined layers. Irrigation withdrawals from confined layers result in large downward hydraulic gradients, creating conditions where water can move downward across the confining unit (fig. 2C). On the basis of age tracers and a piston flow model assumption, apparent ages in the unconfined layer range from 7 years at shallow depths to 48 years near the bottom of the layer. Age-tracer data for the upper confined layer and the PSW were consistent with mixing of “old” water (not containing modern tracers) and exponentially-mixed young water from the overlying unconfined layer. Water in most of the unconfined layer is oxic, whereas water in most of the confined layers is nitrate- to iron- to sulfate-reducing.

The Modesto, CA, study area (CA) in the Central Valley aquifer system (fig. 2D) is typical of areas in the eastern San Joaquin Valley that have high population-growth rates and a gradual urbanization of adjacent farmlands. The aquifer sediments in the study area are comprised of a series of overlapping, stacked alluvial-fan sequences deposited by streams during Pleistocene glacial cycles (Burow and others, 2004). Percolating irrigation water is the primary form of ground-water recharge, and irrigation pumpage is the primary form of ground-water discharge. As a result, ground water is drawn vertically downward within the regional and local flow systems, and water moving laterally may be pumped and reapplied at the surface multiple times (fig. 2D). Ground-water age increases logarithmically with depth in this aquifer system and reaches ages greater than 1,000 years. Most ground water in this study area is oxic, although anoxic conditions may occur in localized areas.

Methods

The four study areas represent a range of settings, sources, sinks, and pathways for naturally occurring arsenic and uranium. Criteria used to select the PSWs for investigation included representative and well-understood hydrogeologic, land-use, and operational conditions and detectable anthropogenic and natural compounds of concern. A network of short-screened monitoring wells was installed throughout the areas contributing recharge to the selected PSW, including one well nest adjacent to each supply well. The areas contributing recharge to the four selected PSWs were estimated using ground-water flow models and particle-tracking routines (Kauffman, 2006).

Core samples were collected and analyzed using x-ray diffraction, elemental analysis of coating extractions, and organic carbon analysis. The mineralogy of bulk samples and clay separates was determined by powder x-ray diffraction. The abundances of elements in grain coatings or other mineral phases were determined using different acids and reagents, including (1) 10-percent (%) nitric acid (HNO₃), (2) 6Normal (N) hydrochloric acid (HCl) extraction, (3) 0.5N-HCl-hydroxylamine (HA)-extractable iron, and (4) acid-volatile and chromium-reducible sulfides (K. Conko, 2006, U.S. Geological Survey, written communication). The coating extraction (HCl and HNO₃ extractions) methods were primarily intended to target extraction of ferric oxyhydroxides and their associated trace elements, but they also can extract other oxides and clay, carbonate, and sulfide phases to varying degrees. Leachate derived from the 10% HNO₃ extractions was analyzed by ICP-OES. Analysis of the 6N-HCl extractants required dilution to 1.6N-HCl

prior to analysis by ICP-MS. The 0.5N-HCl-HA and 6N-HCl extractions were performed according to Lovley and Phillips (1987) and analyzed by ICP-MS. The 0.5N-HCl-HA extracts were analyzed using the ferrozine method (HACH, 2002).

Ground-water samples were collected and analyzed for a broad suite of analytes, including water temperature, specific conductance, pH, dissolved oxygen (DO), major and trace elements, nutrients, volatile organic chemicals (VOCs), pesticides, age tracers, radium isotopes and radon, arsenic species, and stable isotopes of oxygen, hydrogen, nitrogen, sulfur, carbon, and uranium. The reporting levels for arsenic and uranium analyzed in samples were 0.2 µg/L and 0.04 µg/L, respectively. The age tracers sampled and analyzed among the study areas varied depending on local conditions, but included chlorofluorocarbons (CFCs 12, 11, 113), sulfur hexafluoride (SF₆), and ratios of helium (³He) isotopes derived from radioactive decay of tritium (³H) to helium. Nonparametric methods were used for statistical analysis of correlations between variables. The significance level (p) used for hypothesis testing for this paper was 5 percent ($\alpha=0.05$). Correlations were investigated using Spearman's method, where the rank order correlation coefficient (rho) was calculated.

Different approaches for collecting depth-dependent flow and chemistry data in or near the PSWs were used to help determine where and how contamination-susceptible water enters the PSWs (Landon and others, 2006). Approaches for determining flow profiles in the PSWs included the tracer pulse method of Izbicki and others (1999) used at the NE and CA sites, and geophysical methods used at the FL site, as described in Landon and others (2006). Depth-dependent samples could not be collected in CT because of well access limitations and a short well screen (4.6 m long), making it difficult to resolve vertical differences in chemistry within the PSW. Samples from the adjacent PSW monitoring-well nests were used to help understand vertical changes in chemistry near the PSW.

Results and Discussion

Arsenic and Uranium in the Aquifer Matrix

Mineralogic analysis by x-ray diffraction yielded mostly quartz, plagioclase, potassium feldspar, clay, mica, and minor amounts of hornblende in the bulk fractions of unconsolidated deposits in CT, NE, and CA, and in the surficial aquifer at the FL site. Calcite was the dominant mineral in samples from the Floridan Aquifer and was present in small amounts in NE and in underlying bedrock in CT. Calcite also is known to be present in surficial soils of CA and NE, but was not analyzed for this study. The clay fractions contained smectite, illite, kaolinite, chlorite, hornblende, and goethite, in that general order of abundance.

Ferric oxyhydroxide coatings were extracted from core samples to help determine redox conditions and potential adsorption sites for arsenic or uranium. The fractions of the 0.5N-HCl-HA-extractable iron and 6N-HCl-extractable iron (fig. 3A and B) and 10%-HNO₃-extractable arsenic and uranium (figs. 3C and D) were compared between the

four sites. The 0.5N-HCl-HA extractable iron fraction at the CT site, which is mostly oxic, had the highest median concentration of 970 $\mu\text{g/g}$, but the upper range of 1,500 $\mu\text{g/g}$ was much lower than that of the FL and NE samples. The aquifer at the CA site, which also is mostly oxic, generally had the highest concentrations of extractable iron; the 6N-HCl-extractable fraction had a median of 6,600 $\mu\text{g/g}$, and was an order of magnitude greater than the poorly crystalline 0.5N-HCl-HA-extractable fraction, which had a median of 620 $\mu\text{g/g}$. Median concentrations of 10%-HNO₃-extractable arsenic and uranium were highest in the NE samples (0.37 $\mu\text{g/g}$ and 1.0 $\mu\text{g/g}$, respectively), and CA samples had comparably high median concentrations of uranium (0.83 $\mu\text{g/g}$; fig. 3C and D). Uranium also is abundant in shallow soils of NE and CA (Phillips and others, 1993), but these sediments were not sampled for this study. Extractable arsenic and uranium concentrations generally were lowest in samples from the CT and FL study areas. However, high arsenic and uranium concentrations were found in one CT sample collected from glacial deposits that were derived from an organic-rich shale; this outlier helps to illustrate that sediment-core data derived from heterogeneous aquifer material represent discrete points in space and may not always reflect sources of naturally occurring constituents in ground water (Brown and Zielinski, 2004). Similarly, a sample from the deposits that overlie the Floridan aquifer in FL had high arsenic (1.4 $\mu\text{g/g}$) and uranium (19 $\mu\text{g/g}$) concentrations in the 10%-HNO₃ fraction.

Arsenic and Uranium in Ground Water

Median dissolved arsenic concentrations in ground water in CT, FL, NE, and CA were less than 0.2, 1.9, 6.0, and 6.5 $\mu\text{g/L}$, respectively; those for uranium were 0.07, 1.6, 4.4, and 10 $\mu\text{g/L}$. Major and minor ion chemistry can affect arsenic and uranium concentrations through changes in pH and bicarbonate concentrations, cation exchange, and through possible complexation with carbonate and phosphate. Chemical sources and processes, including differences in mineral sources and weathering, as well as anthropogenic factors such as road salting and septic leachate, are reflected in proportions of major cations and anions in water samples plotted on figure 4. Ground waters in FL have higher proportions of calcium and lower magnesium, while dominant anions range from sulfate to bicarbonate. Ground-water samples in CA have proportionately high bicarbonate, as do many of the samples from NE, and reflect carbonate-rich shallow sediments that are leached by intensive irrigation in both study areas.

Time-of-travel and other ground-water-flow-model-based variables such as redox-zonation fluxes have not yet been computed using the local-scale ground-water-flow models of the four study areas; however, arsenic and uranium concentrations were shown to be significantly correlated with time-of-travel variables derived using the regional-scale ground-water-flow models (Hinkle and others, 2006). Arsenic concentrations in samples from FL and NE wells showed an increase with depth (fig. 5A), and the correlation in NE samples is significant (spearman's rho = 0.31, p = 0.023). Uranium concentrations at the NE and CA sites decreased with depth (fig. 5B). Processes associated with variations in arsenic and uranium chemistry with depth are discussed below.

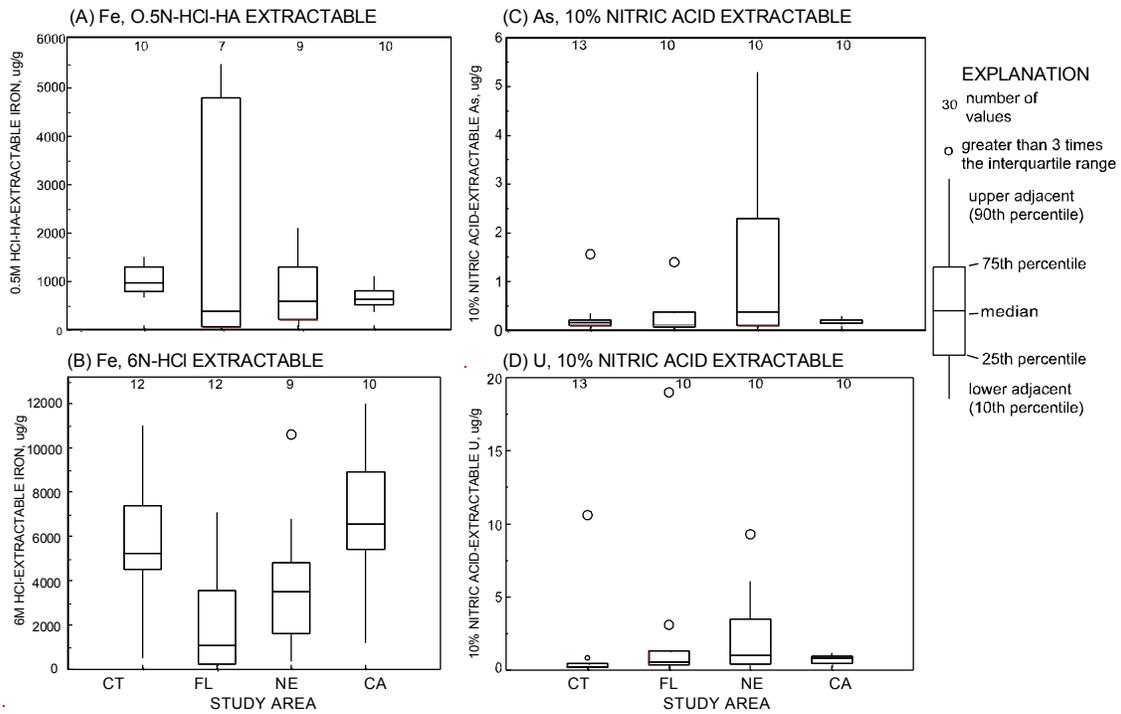


Figure 3. Box plots showing elements extracted from core samples at the CT, FL, NE, and CA study areas, including (A) Total iron in 0.5N HCl-hydroxylamine (HA) extractions, (B) Total iron in 6N HCl extractions, and (C) Arsenic, and (D) Uranium, in 10% nitric acid extractions.

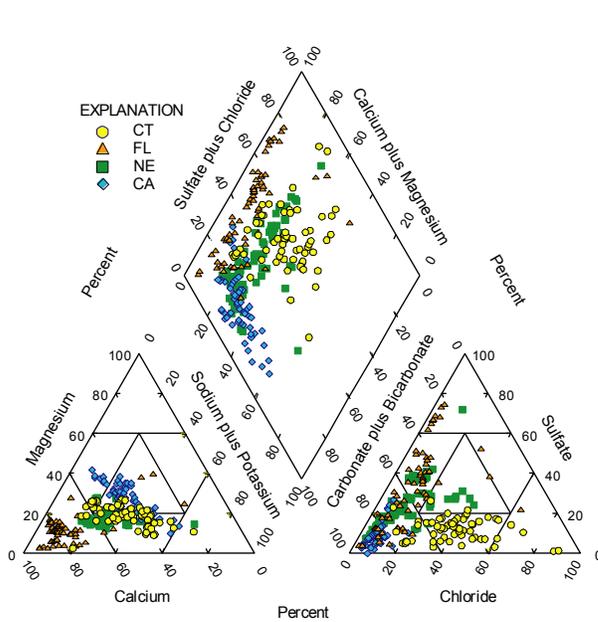


Figure 4. Concentrations of major cations and anions in ground-water samples in the four study areas plotted on trilinear diagrams and projected onto a common diamond plot (Piper diagram).

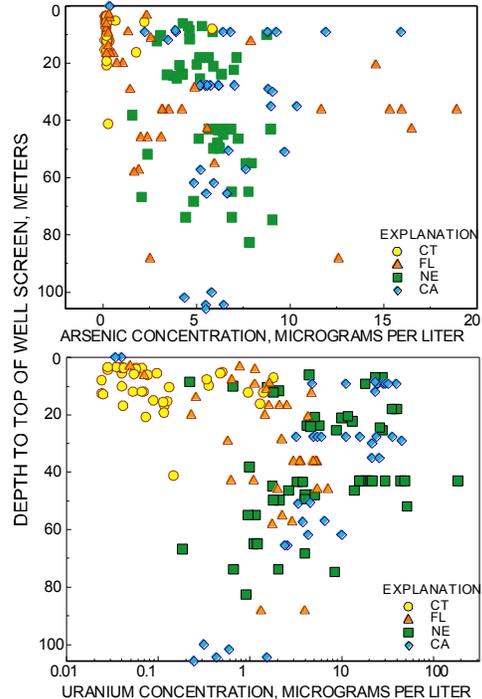


Figure 5. Concentrations of (A) Arsenic and (B) Uranium, plotted with depth to the top of well screen at the four study areas.

Water samples from the CT area had the lowest arsenic concentrations, and appear to reflect, in part, the low source concentrations in the aquifer (fig. 3C). However, relatively high concentrations (6 $\mu\text{g/L}$) of arsenic were found in a water sample from one well that also had high concentrations in the solid phase. This well is screened in reduced, organic-rich glacial aquifer sediments, as described previously, and reductive dissolution of ferric oxyhydroxides and the subsequent release of associated arsenic is likely the source of the high dissolved arsenic concentrations. A study of arsenic concentrations in rocks, sediments, and ground water in New England showed that the distribution of bedrock type closely correlates with areas of elevated arsenic in ground water, stream sediments, and bedrock (Ayotte and others, 2006; Robinson and Ayotte, 2006). Arsenic concentrations are highest in ground-water samples from most wells with low DO concentrations in the FL and NE study areas, and at one site in CT (fig. 6D). Arsenic is mobilized under reducing conditions through reductive dissolution of iron and manganese oxyhydroxides, and the subsequent release of sorbed or co-precipitated arsenic (Smedley and Kinniburgh, 2002), and through the reduction of sorbed arsenate to less strongly sorbed arsenite (Stollenwerk, 2003). Redox conditions affect the speciation of As in NE, but, do not appear to have a major effect on concentrations. The oxic conditions prevalent in CA ground water (fig. 6D) did not appear to inhibit the mobility of arsenic, probably due to competitive exchange and complexation processes. The relation between arsenic concentrations and redox indicators can be complex and suggests that other mechanisms influence arsenic mobility in addition to redox conditions.

Uranium typically exists in the (VI) oxidation state under oxic conditions and forms the oxyanion uranyl (UO_2^{2+}), which adsorbs to iron oxyhydroxides and clay-mineral surfaces. However, carbonate and phosphate complexes can inhibit the attraction of uranyl to mineral surfaces, leading to an increase in the mobility of dissolved uranium concentrations through aqueous complexes with carbonate species, including uranyl di- and tri-carbonate complexes in neutral and alkaline solutions (Langmuir, 1997; Curtis and others, 2006) at some sites (figs. 6B and 6C). As conditions become more reducing, uranium is reduced to the (IV) state, and dissolved concentrations generally decrease as a result of adsorption to iron oxyhydroxides and clay-mineral surfaces, or precipitation. Consequently, uranium concentrations are positively correlated to oxic conditions, such as represented by dissolved oxygen in some samples at each study area (fig. 6D).

The pH values of ground-water samples in the study areas are related to the concentrations of bicarbonate and competitive exchange of arsenate and uranium. Arsenic concentrations in the FL, NE, and CA study areas were much higher in the pH range between 6.6 and 7.7, the same range at which bicarbonate concentrations are highest. Anions may effectively compete for sorption sites with arsenic if sorption sites are limiting. At pH values above about 7.5, arsenate and arsenite adsorb more weakly to aquifer sediments due to deprotonation (Stollenwerk, 2003; fig. 6a). At all sites, uranium concentrations were greater than 1 $\mu\text{g/L}$ in most samples between pH 6.5 and 8.5, although were much higher in NE and CA samples with a pH range from 6.7 to 7.8 (fig. 6B).

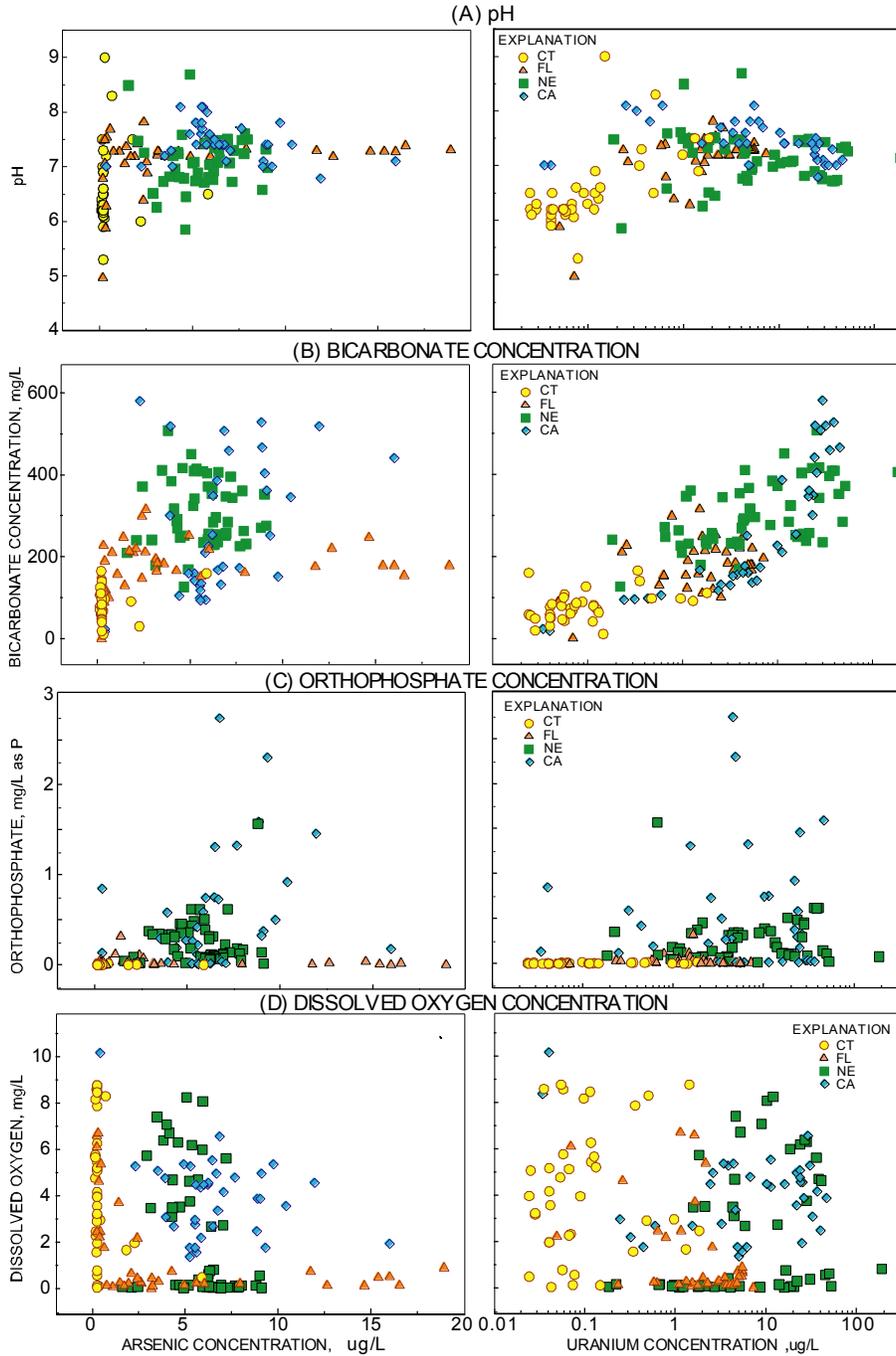


Figure 6. Arsenic and uranium concentrations plotted with (A) pH, and concentrations of (B) bicarbonate, (C) orthophosphate, and (D) dissolved oxygen for the four study areas.

Concentrations of uranium were correlated positively with bicarbonate concentrations in ground water at the CT, NE, and CA study areas. Calculations of uranium speciation with PHREEQC (Parkhurst and Appelo, 1999) using a modified thermodynamic database for uranium species from Lawrence Livermore National Laboratory, indicate that the most abundant uranium species present in FL, NE, and CA ground water is a calcium-uranyl-carbonate complex, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$. Median uranium concentrations in the FL study area were higher in water samples from the anoxic Upper

Floridan aquifer than from the oxic surficial aquifer system or intermediate confining unit, despite the lower mobility of uranium under reducing conditions. The microbially mediated reduction of U(VI) in anoxic water has been shown to decrease significantly when Ca-UO₂-CO₃ complexes are present (Brooks and others, 2003).

Orthophosphate concentrations in the CA study area were positively correlated with arsenic concentrations (spearman's rho = 0.5, p-value = 0.02) and suggest that phosphate, which is structurally similar to arsenate, may be competing with arsenic (fig. 6c). Phosphate has been identified as an anion that can compete with arsenic for sorption sites on oxides, resulting in desorption of arsenic when phosphate is present (Welch and Stollenwerk, 2003). Arsenic and phosphate (rho = 0.79; p = 0.001) and arsenic and chloride (rho = 0.55; p = 0.024) were correlated in NE samples from shallow wells in the unconfined layer and indicated a possible septic-leachate source for phosphate. This is supported by an association of orthophosphate with nitrogen isotope values that suggests a manure source in this urban area. Although concentrations of orthophosphate are relatively high in samples from NE and CA study areas (fig. 6C), complexation with phosphate is probably not significant in samples with elevated uranium concentrations due to the comparatively high concentrations of bicarbonate. Concentrations of orthophosphate in CT and FL samples were below 0.4 mg/L as P and did not correlate with arsenic or uranium.

Arsenic and Uranium in Public Supply Wells

CT study area. The PSW is completed to a depth of 18.3 m and is pumped at about 270 L/min (72 gal/minute, or gpm). Dissolved arsenic and uranium concentrations at the PSW and at most monitoring wells in the contributing area were near the reporting levels and reflected the generally low source concentrations and oxic conditions throughout much of the aquifer. Using geophysical methods and water quality profiles in an adjacent continuous-screen monitoring well, together with sampling results, two discrete zones of coarse-grained sand and gravel were located near the top and bottom of the PSW screen. These high-permeability zones are very thin (<0.1 m) and may not be adequately assessed with monitoring wells alone, but are likely the primary pathways for ground-water flow to the PSW. Although vertical variations in arsenic and uranium near the PSW were unremarkable, anthropogenic contaminants showed a distinct relationship with a relatively high-permeability zone of aquifer sediments.

FL study area. The PSW has an open borehole completed in the Upper Floridan aquifer from 36-53 m below land surface (bls), and is pumped at a rate of about 2,500 L/min (660 gpm). Caliper and televiewer logs collected for this study revealed large solution cavities at depths of 49-53 m. Geophysical logs were used to identify three zones of high ground-water inflow to the well and water samples were collected during pumping and non-pumping conditions at three depth intervals (38, 43, and 49 m bls) to evaluate the effect of pumping on the quality of the water produced. Samples represented a composite of water that entered the well at and below each sampling interval. The chemistry indicates that a highly transmissive zone at 49 to 53 m bls likely is hydraulically connected to the surficial aquifer system, and receives a mixture of water

from the surficial aquifer system and the Upper Floridan aquifer (Katz and others, 2006). Arsenic concentrations in the PSW ranged from 3.2 $\mu\text{g/L}$ to 3.5 $\mu\text{g/L}$ at the well head, but arsenic levels were notably higher in some samples from selected intervals. The highest concentrations of arsenic, uranium, and radon were found in samples collected from the highly transmissive, 49- to 53-m-depth zone during pumping (stressed) conditions. Concentrations of arsenic up to 19 $\mu\text{g/L}$ and higher ratios of arsenate/arsenite in samples from this zone likely result from oxic water in the surficial aquifer system that interacts with arsenic-rich pyrite present in parts of the Suwannee Limestone. This enhanced transport of arsenic is consistent with a study of arsenic release from pyrite in the Suwannee Limestone, which tends to be most abundant in high porosity zones (Price and Pichler, 2006). Geochemical mass-balance models indicate that the proportion of surficial aquifer system water produced by the PSW was somewhere between 50 to 70 percent (Katz and others, 2006). Uranium concentrations in samples from the PSW were consistently below the USEPA MCL of 30 $\mu\text{g/L}$, and ranged from 3.0 $\mu\text{g/L}$ to 5.4 $\mu\text{g/L}$.

NE study area. The PSW selected for study in the NE aquifer system is screened from 42.7 m to 61.0 m bls in the upper confined sand layer, and is pumped at about 1,900 L/min (500 gpm). Chemical and isotopic data reveal that samples from unconfined and confined layers of the aquifer are chemically distinct (Landon and others, 2006). However, flow profiles and depth-interval samples from the PSW reveal that water entering the bottom half of the screened interval contains a substantial fraction of unconfined layer water, whereas water entering the top part of the screen is primarily background upper confined waters. Water from the middle of the screen contains about 50 percent unconfined layer water. A small number of upper confined-layer monitoring-well samples also have chemical compositions intermediate between unconfined and confined water samples, and show evidence of mixing of unconfined and confined water. Samples from some upper confined-layer monitoring wells upgradient of the PSW represented mixtures of up to 85 percent unconfined-layer water. This evidence of mixing throughout the PSW contributing area, suggests that the presence of unconfined-layer water in the PSW is not likely a result of cross-wellbore flow in the supply well itself, but through irrigation, commercial, and older supply wells that are screened in both the unconfined and upper-confined layers. Large vertical downward hydraulic-head gradients are present between the unconfined and confined layers as a result of confined-layer withdrawals, particularly during summer irrigation.

The highest concentration of arsenic (9 $\mu\text{g/L}$) in samples collected from the PSW was in the deepest depth interval sample. Although the predominant arsenic species in the upper-confined aquifer is arsenite, the arsenic in this sample was predominantly arsenate, the dominant species in the unconfined layer. Uranium concentrations in the unconfined layer ranged from 0.22 to 40 $\mu\text{g/L}$ and generally were greater than concentrations in background confined layer monitoring wells. Concentrations in samples from the PSW wellhead were consistently between 15 and 20 $\mu\text{g/L}$. Concentrations of uranium in some depth-interval samples from the PSW, however, had concentrations as high as 184 $\mu\text{g/L}$. Such concentrations could not result from conservative mixing of unconfined and background upper confined layer waters. Elevated concentrations of uranium were consistently associated with samples from the upper confined layer with evidence of

mixing of unconfined layer and upper-confined layer waters under iron-reducing conditions. The exact mechanism for release of uranium during mixing was not confirmed, but one possible explanation that is consistent with observed conditions is the release of uranium during reduction (dissolution) of iron oxyhydroxides on colloids moving down well bores from the unconfined layer into the reduced upper confined layer. The uranium-234/uranium-238 ratio (1.35) for PSW samples is consistent with leaching of uranium from sediments or colloids from oxic shallow unconfined layer sediments.

CA study area. The PSW selected for study at the CA site is screened from 28 m to 111 m bls with an open bottom, and is pumped at about 5,700 L/min (1,500 gpm). Discharge from this well is a mixture of water from three depth zones: shallow-intermediate, deep-intermediate, and deep zones within the aquifer. Eighty percent of the water produced by this PSW is from the deep-intermediate and deep zones. Arsenic concentrations were below 6.2 µg/L in samples collected from the PSW. Uranium concentrations in samples from the wellhead of the PSW ranged from 16 to 24 µg/L. The shallow-intermediate depth-interval sample had the highest uranium concentration (35 µg/L) at the PSW. The median concentration of uranium in monitoring wells near the water table was 24 µg/L and that in the shallow-intermediate zone was 21 µg/L. Median concentrations for uranium in the deep-intermediate zone and deep zones were 4.3 µg/L and 0.5 µg/L, respectively. Uranium appears to be advancing from the water table to depths greater than 50 m as a result of downward movement of high-alkalinity, oxygen-rich ground water. The continued downward movement of high-alkalinity, oxygen rich ground water, which is facilitated by the pumping stresses in the surrounding aquifer, will likely continue to liberate uranium from the sediment and increase uranium concentrations in the PSW over time. However, PSW depth-interval samples combined with adjacent monitoring well samples, indicate that the highest concentrations of uranium from the wellhead of the PSW are likely a consequence of PSW operation. It is hypothesized that the long-screened interval of the PSW acts as a conduit for flow from the shallow-intermediate aquifer zone to the deep aquifer zone during periods of low or no pumping (Burow and others, 2005). When pumping is increased during summer to meet greater demand, the stored water with its higher concentrations of uranium is evacuated from the deep aquifer zone surrounding the PSW and combines with water that is pumped from the shallow-intermediate zone. This results in a temporary increase in concentrations of uranium and other constituents. For the remainder of the summer, water from the shallow-intermediate zone is diluted by inflow of unaffected water from the deeper zones and overall concentrations in the PSW decrease.

Conclusions

Naturally occurring contaminants are ubiquitous in many aquifer systems of the U.S., and identification of the processes that control their mobilization and transport could help water managers meet compliance standards. Solid-phase chemistry data were useful in understanding arsenic and uranium sources, but did not always correspond to their relative concentrations in ground water. The mobilization of arsenic in the four study areas appears to be facilitated by (1) competitive sorption processes where arsenic

adsorbed onto iron or manganese oxides could be desorbed by bicarbonate or phosphate, and (2) release of arsenic related to reductive dissolution of ferric and manganese hydroxides under reducing conditions, or oxidative dissolution of arsenic-rich pyrite caused by reaction with oxic water. Mobilization of uranium in the four study areas appears to be facilitated by (1) the predominance of calcium-uranyl-carbonate complexes, which can inhibit uranium adsorption, and (2) oxic redox conditions.

Several types of preferential flow paths to PSWs are common in all four areas and can result in faster travel times and higher concentrations of naturally occurring constituents in public supply wells. These include zones of high permeability in sand and gravel aquifers, conduit flow in karst aquifers, downward well-bore flow in the PSW during periods of low or no pumping, and short-circuit pathways through wells and boreholes open to multiple aquifer layers. The study of naturally occurring contaminants to PSWs using geophysical methods, depth-dependent sampling, and sampling of monitoring wells adjacent to the PSW, improves understanding of the factors such as redox chemistry, competing ions, and preferential pathways that affect the movement of naturally occurring contaminants to PSWs.

References

- Ayotte J.D., Nolan, B.T., Nuckols, J.R., Cantor, K.P., Robinson, K.W., Jr., Baris, D., Hayes, L., Karagas, M., Bress, W., Silverman, D., and Lubin, J., 2006, *Modeling the probability of arsenic in groundwater in New England as a tool for exposure assessment*, Environmental Science & Technology, v. 40, no. 11, p. 3578 -3585.
- Brooks, S., Fredrickson, J., Carroll, S., Kennedy, D., Zachara, J., Plymale, A., Kelly, S., Kemner, K., and Pendorf, S., 2003. *Inhibition of bacterial U(VI) reduction by calcium*: Environmental Science and Technology, v. 37, p. 1850-1858.
- Brown, C.J., and Zielinski, R.A., 2004, *Occurrence and distribution of arsenic and uranium in the Pomperaug Aquifer, Woodbury, Connecticut* (abst.), in Geology of Long Island and Metropolitan New York, April 17, 2004, Program with Abstracts: Stony Brook, N.Y., Long Island Geologists.
- Brown, C.J., McMahan, Peter, and Starn, J. Jeffrey, 2006, *Effects of organic carbon distribution on redox chemistry in a glacial aquifer, Woodbury, Connecticut*, in National Water Quality Monitoring Council's (NWQMC) 5th National Water-Quality Monitoring Council meeting, May 7-11, 2006 in San Jose CA.
- Burow, K.R., Jurgens, B., Dalgish, B.A., and Shelton, J.L., 2005, *Effects of well operation on quality of water from a public-supply well in Modesto, California* [abs.]: GSA Annual Meeting, Oct. 16th-19th, 2005, Salt Lake City, Utah.
- Burow, K.R., Shelton, J.L., Hevesi, J.A., and Weissmann, G.S., 2004, *Hydrogeologic characterization of the Modesto area, San Joaquin Valley, California*: U.S. Geological Survey Scientific Investigations Report 2004-5232, 54 p.
- Curtis, G.P., Davis, J.A., and Napftz, D.L., 2006, *Simulation of reactive transport of uranium (VI), in groundwater with variable chemical conditions*: Water Resources Research, v. 42, no. 4.

- Eberts, S.M., Erwin, M.L., and Hamilton, P.A., 2005, *Assessing the vulnerability of public-supply wells to contamination from urban, agricultural, and natural sources*: U.S. Geological Survey Fact Sheet 2005-3022, 4 p.
- Hach Company, 2002, *DR/2400 Spectrophotometer Procedures Manual*, Loveland, CO, 450 p.
- Hinkle, S., Kauffman, L., Thomas, M.A., Brown, C., McCarthy, K., Eberts, S., Rosen, M., and Katz, B., 2006, *Flow Modeling to Assess Public Supply Well Vulnerability to Natural Contaminants* [abs.] National Water Quality Monitoring Council's (NWQMC) 5th National Water-Quality Monitoring Council meeting, May 7-11, 2006, San Jose, CA.
- Izbicki, J.A., Christensen, A.H., and Hanson, R.T., 1999, *U.S. Geological Survey combined well-bore flow and depth-dependent water sampler*: U.S. Geological Survey Fact Sheet 196-99, 2 p.
- Katz, B.G., Crandall, C.A., McBride, W.S., and Berndt, M.P., 2006, *Use of Multiple Tracers and Geochemical Modeling to Assess Vulnerability of a Public Supply Well in the Karstic Upper Floridan Aquifer* [abs.]: 2006 National Monitoring Conference: Concurrent Session F: F3-Assessing Ground Water Vulnerability Through Mechanistic Methods II, May 7-11, 2006, San Jose, CA.
- Kauffman, L., 2006, *Comparison of intrinsic susceptibility of public-supply wells to contamination among selected regional aquifer systems* [abs.]: 2006 National Monitoring Conference: Concurrent Session F: F3-Assessing Ground Water Vulnerability Through Mechanistic Methods II, May 7-11, 2006, San Jose, CA.
- Landon, M.K., Eberts, S.M., Jurgens, B.C., Katz, B.G., Burow, K.R., Crandall, C.A., Brown, C.J., and Starn J.J., 2006, *Knowledge of Where and How Contamination-Susceptible Water Enters Public-Supply Wells Can Be Used To Improve Monitoring Strategies and Protection Plans*: Ground Water Protection Council Annual Forum 2006, Sept. 30 – Oct. 4, 2006, Miami Beach, FL, 15 p.
- Langmuir, D., 1997, *Aqueous environmental geochemistry*: Prentice Hall, NJ, 600 p.
- Lovley, D.R. and Phillips, E.J., 1987, *Rapid assay for microbially reducible ferric iron in aquatic sediments*: Applied Environmental Microbiology, v. 53, no 7, p. 1536-1540.
- Parkhurst, D.L. and Appelo, C.A.J., 1999, *User's guide to PHREEQC (Version 2) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*: U.S. Geological Survey Water Resources Investigations Report 99-4259, 310 p.
- Phillips, J.D., Duval, J.S., and Ambroziak, R.A., 1993, *National geophysical data grids: Gamma-ray, gravity, magnetic, and topographic data for the conterminous United States*: U.S. Geological Survey Digital Data Series DDS-9, URL: <http://crustal.usgs.gov/geophysics/gamma.html>, last accessed January 12, 2006.
- Price, R.E., and Pichler, T., 2006. Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): Implications for arsenic release during water-rock interaction: Chemical Geology, v. 228, p. 44-56.
- Robinson, G.R., Jr., and Ayotte, J.D., 2006, *The influence of geology and land use on arsenic in stream sediments and ground waters in New England, USA*: Applied Geochemistry, v. 21 p1482-1497.
- Smedley, P.L., and Kinniburgh, D.G., 2002, *A review of the source, behavior and distribution of arsenic in natural waters*: Applied Geochemistry, v. 17, p. 517-568.

- Stewart, J.W., Goetz, C.L., and Mills, L.R., 1978, *Hydrogeologic factors affecting the availability and quality of ground water in the Temple Terrace area, Hillsborough County, Florida*: U.S. Geological Survey WRIR 78-4, 38 p.
- Stollenwerk, K.G., 2003, *Geochemical processes controlling transport of arsenic in groundwater: a review of adsorption*, in *Arsenic in Groundwater*, A.H. Welch and K.G. Stollenwerk, ed., Boston: Kluwer Academic Publishers, 475 p.
- U.S. Geological Survey, 2003, *Principal aquifers of the 48 conterminous United States, Hawaii, Puerto Rico, and the U.S. Virgin Islands*, available online at <http://www.nationalatlas.gov/mld/aquifrp.html>
- Welch, A., Westjohn, D., Helsel, D., and Wanty, R.B., 2000, *Arsenic in ground water of the United States—occurrence and geochemistry*: *Ground Water*, v. 38, p. 589-604.
- Zapecza, O.S., and Szabo, Z., 1988, *Natural radioactivity in ground water—a review*: US Geological Survey Water Supply Paper 2325, 57 p.

Author Biographical Information

Craig J. Brown, Ph.D., is a hydrologist with the USGS. His research interests include aquifer geochemistry and processes associated with the mobilization and transport of trace elements in aquifer systems. He is currently working on studies of transport of anthropogenic and natural contaminants to public supply wells for the National Water-Quality Assessment Program, and the geochemical implications of Aquifer Storage and Recovery. USGS, 101 Pitkin St., East Hartford, CT 06108; Phone: (860) 291-6766; email: cjbrown@usgs.gov.

Bryant C. Jurgens has been a hydrologist with the USGS since 2002. His interests include aquifer geochemistry, tracers of ground-water age, and processes that affect the transport and fate of trace elements in ground-water systems. USGS, 6000 J St, Placer Hall, Sacramento, CA 95619; Phone: (916) 278-3275; email: bjurgens@usgs.gov.

Brian G. Katz, Ph.D., is a research hydrologist with the USGS. He has conducted numerous geochemical studies of processes that control the composition of natural and contaminated waters. His current research involves the use of isotopic and other chemical tracers to quantify hydrochemical interactions between ground water and surface water, determine sources and chronology of contamination in karst aquifers, and assess flow-system dynamics in complex aquifer systems. USGS, 2010 Levy Avenue, Tallahassee, FL 32310; Phone: (850) 942-9500; email: bkatz@usgs.gov.

Matthew K. Landon, a hydrologist with the USGS since 1990, has conducted studies of ground-water hydrology and ground-water quality in Minnesota, Nebraska, and California. He is currently working on studies of transport of anthropogenic and natural contaminants to public supply wells for the National Water-Quality Assessment Program and the California Ground Water Ambient Monitoring and Assessment program. USGS, 4165 Spruance Road, San Diego, CA 92101; Phone: (714) 508-4706; email: landon@usgs.gov.

Sandra M. Eberts, P.H.G., has been a hydrologist with the USGS for more than 20 years. Currently, she is team leader of the USGS National Water-Quality Assessment program Transport of Anthropogenic and Natural Contaminants to Supply Wells (TANC) study. Prior to her work on the TANC study, Sandra spent 8 years as a technical liaison to the U.S. Air Force for the clean-up of ground-water contamination at weapons manufacturing facilities nationwide. USGS, 6480 Doubletree Ave, Columbus, OH 43229; Phone: (614) 430-7740; email: smeberts@usgs.gov.