Occurrence of Arsenic in Ground Waters of Arkansas and Implications for Source and Release Mechanisms

By Tim Kresse and John Fazio
Arkansas Ambient Ground-Water Monitoring Program
Arkansas Department of Environmental Quality
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WATER DIVISION, PLANNING SECTION

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"Sir, if you were my husband, I would put arsenic in your tea."
"Madam, if you were my wife, I'd drink it."

> **Heated exchange between Lady Astor and Winston Churchill.**

"With all those kids in the tub, it's not arsenic in the water I'd be worried about."

> **George Bush, on displaying a picture of himself and his siblings in the bathtub with their father.**

"Let's say you have half a glass of arsenic. Now how would the optimist see it?

> **Tim O'Brien**

"They put arsenic in his meat
and stared aghast to watch him eat;
they put strychnine in his cup
and shook to see him drink it up."

> **A.E. Housman (A Shropshire Lad, 1896)**

Introduction

The U. S. Environmental Protection Agency recently revised the maximum contaminant level (MCL) for As from 50 µg/L to 10 µg/L. The final proposed rule was published in the Federal Register on January 22, 2001 (USEPA, 2001). Community water systems and non-community, non-transient water systems with As exceeding 10 µg/L in their drinking water will be required to reduce the As concentrations. Compliance with the 10 µg/L MCL is required 5 years after the publication of the final rule (i.e., January, 2006). The impact to municipal supply water systems in Arkansas is low based on analyses collected by the Arkansas Department of Health. However, a recent publication documenting water quality in the Bayou Bartholomew watershed (Kresse and Fazio, 2002), revealed that ground water from 21 of a total 118 irrigation wells completed in shallow Quaternary alluvial deposits, had As concentrations exceeding 10 µg/L. This information suggests that domestic wells completed in alluvial deposits may present risks to private well owners not protected by the Safe Drinking Water Act (SDWA).

The present report presents an introduction to As geochemistry and discusses the occurrence of As in ground water in Arkansas, the potential sources and transport mechanisms by which As enters ground water, and implications for water users supplied by either domestic or municipal water systems. Although much of the discussion is focused on the alluvial aquifer in Arkansas, which appears to have the highest detection rate and concentrations for As, a review of As is presented for other ground-water systems in Arkansas. Material was gathered from unpublished and published data collected by the Arkansas Department of Environmental Quality (ADEQ), compliance data from the Arkansas Department of Health (ADH) for water-supply systems, and data from the U. S. Geological Survey (USGS) National Water Information System (NWIS).

Occurrence and Sources of Arsenic in Ground Water

Arsenic is ubiquitous throughout the biosphere and occurs naturally in rocks, soil, water, air, plants and animals. Natural processes such as volcanic action, weathering and water-rock interactions, upwelling of geothermal water, and forest fires can release As into the environment. Anthropogenic sources include industrial products (wood preservatives, paints, dyes, metals, pharmaceuticals, pesticides, soaps and semiconductors), mining and smelting operations, burning of coal, agricultural activities, and waste disposal of As-containing products (EPA, 2002; Hem, 1989).

Based on information from EPA’s CERCLIS 3 database through 1999, As is the second most common contaminant of concern (COC) cited in Records of Decision (RODs) for sites on the Superfund National Priorities List (NPL). Arsenic is a COC at 568 (47%) of the 1,209 sites on the NPL (for which a ROD has been signed) for various media types. Arsenic is a COC for ground water at 380 sites (31%) of the same 1,209 sites (EPA, 2002). However, contamination at most of these sites is limited in extent, and natural sources account for most of the areas in the United States that experience widespread As contamination. In a review of As in ground water throughout the United States, release from iron oxide and sulfide oxidation were cited as the most prevalent causes of widespread, elevated (>10 µg/L) concentrations of As (Welch, 1999).

Arsenic occurs as a major constituent in more than 200 minerals, including elemental As, arsenides, sulfides, oxides, arsenates and arsenites; most of which are ore minerals or their alteration products. The most abundant As ore mineral is arsenopyrite (FeAsS), followed by realgar (AsS) and orpiment (As_2S_3). Arsenic is also present in varying concentrations in common rock-forming minerals including sulfide minerals (pyrite, chalcopyrite, galena, and marcasite) and in many oxide minerals and hydrous metal oxides, particularly where formed from oxidation of primary sulfide minerals (Smedley and Kinniburgh, 2002). Arsenic has been measured as high as 7-10 % by weight in pyrite (Westjohn et al., 2001; Kolker and Nordstrom, 2001) and can reach weight percent values in Fe oxides. Elevated levels of As in ground water have been associated with various rock types throughout the United States including sandstone containing pyrite (Westjohn et al., 2001), schist and/or gneiss with intrusive granitic veins (Peters and Blum, 1999; Mueller et al., 2001; Brown and Chute, 2001), metamorphosed marine sediments (Ayotte et al., 1999), tufaceous sedimentary rocks, tuffs and basalts (Hinkle and Polette, 1998), organic-rich carbonate rock (Warner, 2001), black shale (Vowinkel et al., 2001), volcanic ash (Carter et al., 1998) and alluvial deposits with iron-oxide coatings (White and Sevee, 1999; Stollenwerk, 2001; Stanton et al., 2001; Kent et al., 2001; Kresse and Fazio, 2002).

Arsenic Exposure and Health Effects

Arsenic is linked with toxic effects from both ingestion and inhalation exposure. Soluble inorganic arsenicals are generally recognized as more toxic than organic forms, with As(III) being more toxic than As(V). Most of the available information on toxicity has come from large exposed populations throughout the world, including parts of Bangladesh, Japan, Chile, Taiwan and Argentina. Short-term acute effects from large doses of As can occur within 30-60 minutes, resulting in vomiting, diarrhea, hypotension and hypoxia, and fatal As poisoning has been reported after exposure to concentrations exceeding 2 grams. Chronic exposure has been linked to adverse health effects, including skin pigmentation changes, hyperkeratosis and skin cancer, since the early part of the 19th century as a result of consumption of As in medicines and drinking water. By the early 1900s, reports of skin disorders attributed to As in drinking water were reported for parts of Argentina, Chile, Mexico and Taiwan. Blackfoot disease was perhaps the most notorious vascular disease from As poisoning, which was recognized in Taiwan as early as 1920 and characterized by coldness and numbness in the feet, followed by ulceration, black discoloration and dry gangrene of the affected parts (WHO, 2002).

Cases of cancer related to As exposure most notably include bladder, lung and liver cancer. Studies in Taiwan related to mortality rates for lung, liver, kidney and bladder cancer showed a significant dose-response increase in relation to drinking water concentrations, with median concentrations from three categories of classification ranging from <300 μg/L to >600 μg/L. Similar studies in other countries (Finland, Chile, Argentina and Japan) showed positive correlations of increased cancer risks from exposures to As at <100 μg/L up to values exceeding 1 mg/L. Studies in the United States, Belgium and Australia have had mixed results and have either failed to show a conclusive link between As and cancer risk, or have demonstrated contributing factors including smoking and diet. Skin cancer resulting from As exposure has been most intensively studied on exposed populations of Taiwan, South America, India, Mexico and the United States, with only the studies in the United States not showing any excess of skin disorders. Other deleterious effects generally accepted as caused by As poisoning include neurological effects and reproductive effects (WHO, 2002).

Although adverse effects from As poisoning are well documented, no clear consensus exists in the area of environmental levels and human exposure-related health risks. Arsenic concentrations in all environmental media are documented throughout the world (Smedley and Kinniburgh, 2002), and links between these concentrations and health effects are most often cited in toxicological studies. However, ingestion concentrations are complicated by the concentrations of As in foodstuffs worldwide, where both soil and water As concentrations contribute to the food concentrations. Additionally, the daily intake of total As will vary worldwide as a result of the differing diets, especially in the consumption of fish and shellfish, which are particularly high in As (WHO, 2002). The other difficulty in establishing the lowest As concentration in drinking water is the broad exposure categories used in the majority of epidemiological studies. While conceding that there is clear evidence that chronic exposure to inorganic As of at least several hundred μg/L may cause cancer and non-cancer effects, Brown and Ross (2002) argue that epidemiological data is inadequate to support the conclusion that adverse effects occur from As in drinking water below 50 μg/L. They additionally state that beneficial effects of arsenic as an essential nutrient may be at doses above the current 10 μg/L drinking water limit. Conversely, Smith (2001) questioned if the current 10 μg/L standard is sufficiently protective of human health, and cited publications other than those used by the EPA, which suggest low-dose cancer risks considerably higher than that reported by EPA. Applying linear regression analysis to dose-response data from Chile, Japan and Argentina, Smith (2001) suggests that the EPA may have underestimated cancer risks by a factor of 10. Smedley and Kinniburgh (2002) further state that if the standard basis for risk assessment applied to industrial chemicals were applied to As, the maximum permissible concentration would be lower than 10 μg/L. The World Health Organization (WHO) guideline for As in drinking water was reduced in 1993 from 50 μg/L to 10 μg/L, and many national authorities now are seeking to reduce their limits in line with the WHO guideline.

Arsenic Geochemistry and Transport Mechanisms

Arsenic is a metalloid or inorganic semiconductor and occurs most commonly with valence states of +3 (arsenite, As [III]) and +5 (arsenate, As [V]). Arsenic forms both inorganic and organic compounds including hydrides (e.g., arsine), halides, oxides, acids, and sulfides. The toxicity and mobility of As varies with its valence state and chemical form. As(III) is generally more toxic to humans and four to ten times more soluble in water than As(V). However, different As-containing chemical compounds exhibit varying degrees of toxicity and solubility (USEPA, 2002).

Arsenic can change its valence state and chemical form in the environment. Some conditions that affect As valence and speciation in ground water include pH, oxidation-reduction (redox) potential, presence of competing ions at sorption sites, microbial activity and adsorption-desorption reactions. Clays, carbonaceous materials, and oxides of iron, aluminum, and manganese are soil components that can participate in adsorptive reactions with As (USEPA, 2002). Kent et al. (2001) conducted field tracer experiments using Br, As(III) and As(V) and demonstrated the extent to which ground-water chemistry influences the mobility of As. Oxidation of As(III) to As(V) was observed in oxic and mildly reducing ground water, whereas reduction of As(V) to As(III) was observed in anoxic ground water with high concentrations of Fe(II). Recent studies have shown that Mn oxides can oxidize As(III) to As(V) on time-scales of minutes to hours.

Arsenate generally predominates under oxidizing conditions, whereas arsenite predominates when conditions become sufficiently reducing. Within the normal pH ranges for potable ground water, arsenate is present as negatively-charged oxyanions $H_2AsO_4^-$ (normally between pH of 3-7) or $HAsO_4^{2-}$ (between pH of 7-11), whereas arsenite is present as the uncharged species H_3AsO_3 (Hinkle and Polette, 1998; Hem, 1989). Both arsenate and arsenite adsorb to aquifer materials, and both adsorb strongly to iron-oxide surfaces in acidic and near-neutral pH water. However, desorption of arsenate from iron-oxide surfaces becomes favored as pH values increase, as related to the change in net surface charge of the iron oxide from low to high pH values. Where pH values are above 8, the negative net charge of iron oxide can repel negatively charged ions including arsenate. Arsenite adsorption to iron-oxide surfaces also tends to decrease as pH increases, at least between a range of pH 6 - pH 9 (Hinkle and Polette, 1998). Arsenate and arsenite adsorption and desorption reactions with common surfaces other than iron oxides are less well characterized; however, the EPA (Wilkin, 2001) recently has conducted experiments to evaluate sorption of arsenite onto iron monosulfides at near-neutral pH with an excess of ferrous iron (low sulfate reduction) or bisulfide (complete precipitation of iron). Additional laboratory and field-scale investigations, similar to that of Wilkin (2001) and Kent et al. (2001) are necessary for improving the current understanding of the sources, sinks, fate and transport characteristics for As in ground water.

Redox reactions are instrumental in controlling As concentrations by their effects on As speciation and reduction of metal oxides which adsorb or precipitate As. Reduction of arsenate to arsenite can promote As mobility because arsenite is generally less strongly adsorbed than is arsenate. Arsenic adsorption onto metal oxides can also be affected by the presence of competing ions, including PO_4 and oxyanions of Mo, Se, and V. The interplay of redox reactions and solid-phase precipitation and dissolution are critical with regard to aqueous As and solid-phase iron oxides and sulfide minerals (Hinkle and Polette, 1998). The dissolution of iron oxides has been cited as the source for elevated concentrations of As at many locations throughout the United States and in other countries (Nickson,et al., 2000; McArthur et al., 2001; White and Sevee, 1999; Stollenwerk, 2001; Mueller et al., 2001; Reeve et al., 2002; White and Scully, 1999; Hon et al., 2002). Conversely, the sorption of As to iron oxides acting as sinks for soluble As has been demonstrated to perform as a natural remediation mechanism downgradient from contaminated sites (Vlassopoulos et al., 1999; Carter et al., 1998; Goddard, 1987). Sulfide minerals generally are unstable under oxidizing conditions, and precipitate under reducing conditions. The occurrence and possible oxidation of sulfide minerals has been cited as a potential source of As in various portions of the United States (Westjohn et al., 2001; Lee and Goldhaber, 2001), although the release mechanisms have not been fully defined in these areas. Molecular oxygen is quantitatively the most important oxidant, and sulfide mineralization is limited by the amount of oxygen in recharging waters; however, raising and lowering of the water table and exposing these minerals to atmospheric oxygen can greatly increase oxidation (Welch and Ayotte, 2002). In addition to reductive dissolution of iron oxides, desorption of As from iron oxides occurs in high pH (and often highly oxic) waters, and has been cited for parts of the United States as a major release mechanism in these type of systems (Stanton, et al., 2001; Carter et al., 1998; Brown and Chute, 2001; Schlottmann, 2001; Peters et al., 2002).

Examples of widespread areas of elevated As in ground water as related to anthropogenic sources include mining operations (Queiroz et al., 2001; Goddard, 1987) and pesticide manufacturing plants (Vlassopoulos et al., 1999). Large areas of As contamination also have been associated with landfills (White and Sevee, 1999; Stollenwerk, 2001; White and Scully, 1999); however, the landfills were not identified as the primary source of As, but provided the elevated levels of dissolved and/or total organic carbon which drove the reductive dissolution of As-bearing minerals in the aquifer matrix. Organic carbon is critical in the microbial-mediated reduction of metal oxides. Nickson et al. (1998) listed sedimentary organic matter (peat) up to 6% as the driving force for reduction of iron oxides in the Ganges delta of Bangladesh.

Occurrence of As in the Alluvial Aquifer of Eastern Arkansas

The recent revision of the As standard from 50 µg/L to 10 µg/L has presented new concerns for water-supply systems throughout the country. The new standard is estimated to affect approximately 10% of the ground-water supplies in the United States (Welch, 1999). The costs of new treatment technologies will vary widely depending on the size of the system and the concentration of As and other metals in the water. A review of As data for public water-supply systems currently serving Arkansans reveals that the impact of the new rule will be minimal for current public ground-water supply systems (Robert Hart, Arkansas Department of Health, written communication). Only one system out of all systems supplying both small and large communities in Arkansas had an As concentration equaling 10 µg/L. However, results of a recent investigation of ground-water quality in the Bayou Bartholomew watershed in southeastern Arkansas (Kresse and Fazio, 2002), together with a review of data from the ADEQ and the USGS, revealed elevated levels (>10 µg/L) of As in water from wells completed in the alluvial aquifer of eastern Arkansas. Although municipal water-supply wells in eastern Arkansas are advanced predominantly into deeper Tertiary formations, because of the problems associated with the high concentrations of Fe and Mn in the alluvial aquifers, many private well owners obtain water for drinking and other uses from the shallow alluvial deposits. Domestic wells are not regulated under the SDWA, and private well owners potentially are exposed to unsafe levels of As in their drinking water supply.

As part of the investigation of non-point sources of contamination in the Bayou Bartholomew watershed, ground-water samples were collected from 118 wells completed in shallow (~100 feet in thickness) Quaternary alluvial deposits (Kresse and Fazio, 2002). Arsenic concentrations in 21 of the 118 wells (18 %) exceeded 10 µg/L with a maximum concentration of 50 µg/L (Figure 1). Twenty five of the 118 wells were drilled in upland terrace deposits, where silviculture is the typical land use, whereas the remaining 93 wells were drilled in the flat-lying delta portion of the watershed, where land use is dominated by row-crop agriculture. Because the 21 wells with elevated As were in the delta portion of the watershed, this results in a higher percentage of contaminated wells (22%) when accounting only for wells completed in the delta region of the watershed. A detailed geology of the Bayou Bartholomew watershed is found in Kresse and Fazio (2002).

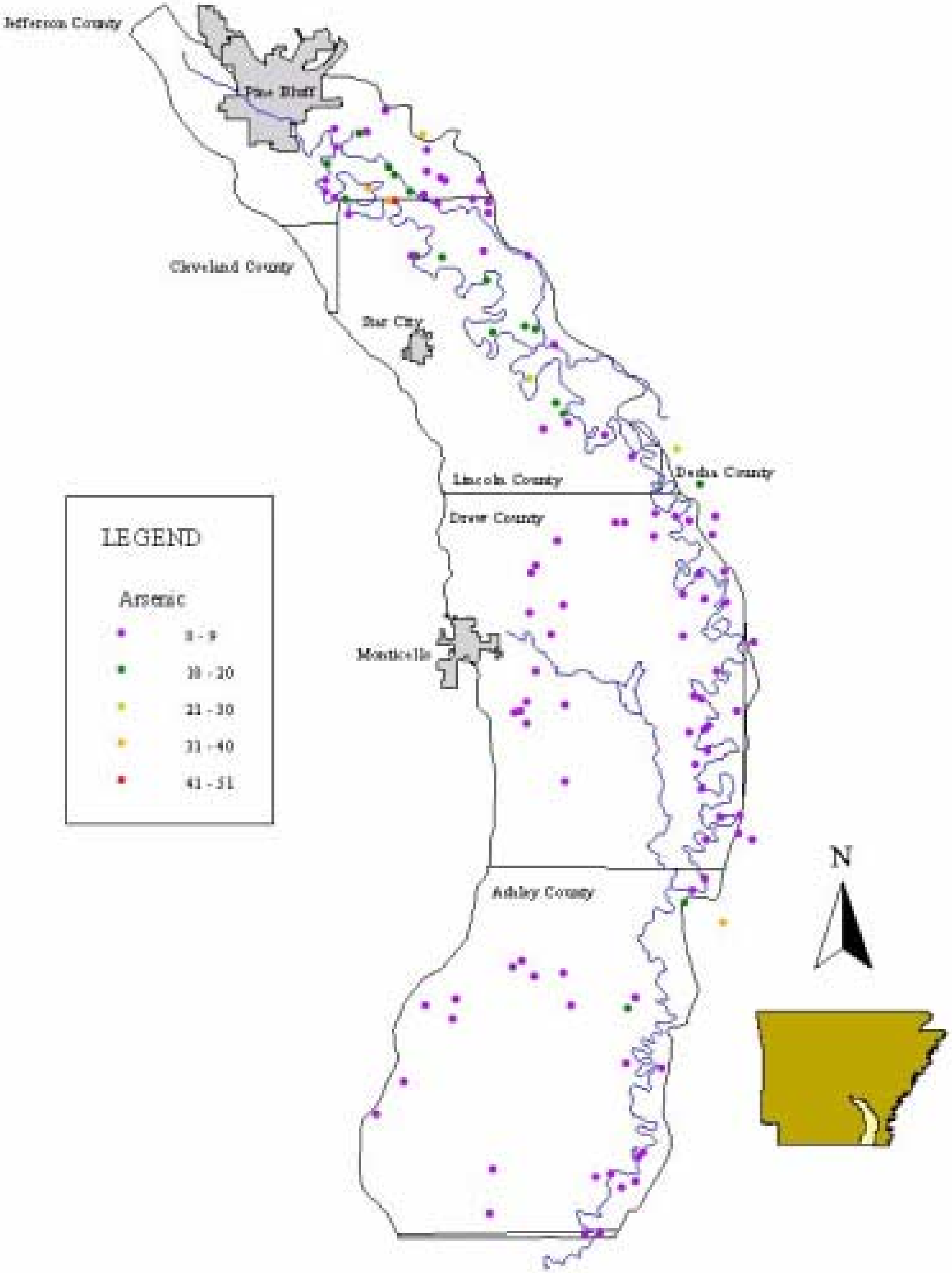

Figure 1. Map of arsenic concentrations (µg/L) for the Bayou Bartholomew watershed study area**.** Boundary of watershed includes only portions of identified counties.

Focazio et al. (1999) produced a retrospective analysis on the occurrence of As in ground-water resources throughout the U.S. and showed an area in eastern Arkansas that contained elevated (>10 μg/L) As concentrations. Because the USGS NWIS data base and a public water-supply data base from the USEPA were listed as the source of the data, a review was performed on the arsenic point data base from the USGS Arkansas District (Dave Freiwald, USGS Arkansas District, written communication) and the public water-supply data from the ADH (Robert Hart, ADH, written communication) for correlation to the map produced by Focazio et al. (1999). A review of the ADH data revealed no As concentrations exceeding 10 μg/L; however, a review of the USGS data produced 18 wells exceeding 10 μg/L. All of the wells from the USGS data set were completed in the alluvial aquifer, and an inspection of the location of these wells (Figure 2) compared favorably to the general location (east-central Arkansas) provided in Focazio et al. (1999). Arsenic concentrations for the USGS data set ranged upward to 80 μg/L.

Because of the elevated As concentrations in the alluvial aquifer, a review was performed of data from Tertiary aquifers underlying the alluvial aquifer (ADEQ, unpublished data), including over 200 wells completed in both the Sparta and Cockfield formations; two important aquifer systems in eastern Arkansas used extensively for the purpose of domestic, municipal, industrial and some irrigation supply. Most of the As concentrations were less than the detection limit of 1 μg/L and none exceeded 10 μg/L, which indicates that As problems in eastern Arkansas are confined to water in the shallow alluvial deposits.

Source of As in the Alluvial Aquifer

Because As was of little concern under the old standard of 50 μg/L, very little research has occurred with respect to sources of As in the alluvial aquifer. Although arsenical pesticides (i.e., lead arsenate, MSMA, etc.) were used in the past, Kresse and Fazio (2002) discounted pesticide use based on the low-leaching potential and competition with phosphorus in the formation of insoluble salts, and cited Fe oxides as the potential source of dissolved As in the ground water. Preliminary evidence for Fe oxides as a source of As was z-test analyses which revealed large, statistically-significant differences for elevated Fe ($p = 0$), Mn ($p = 2.5$ E-4), As ($p = 2.2$ E-10) and Ba ($p = 1.1$ E-19) in the delta deposits versus low to non-detect concentrations in the terrace deposits. Additional evidence is presented within this section to support Fe oxides as the source and reductive dissolution as the release mechanism for Fe, Mn and As within the alluvial aquifer.

A detailed review of ground-water quality data from the Bayou Bartholomew watershed revealed two populations with different geochemical trends. The first population of points, ranging from TDS concentrations of <100 mg/L to approximately 350 mg/L, denotes an evolution toward a strongly Ca-HCO_3 water type at the upper TDS range, with Ca and HCO_3 ions composing over 65% and 95% of the total cations and total anions, respectively. Values for pH increase from approximately 5.9 at the lower TDS concentrations to approximately 7.4 near the upper TDS values in the first population, reflecting the consumption of H^+ ions with the dissolution of carbonate material. However, Ca and HCO_3 percentages decrease with increasing TDS in the second population of data points, which are characterized by increasing concentrations of Na, Cl and SO_4 and decreasing pH values at TDS concentrations between 350 - 750 mg/L. Calculation of saturation indices demonstrated that samples in the first population are undersaturated (-0.11 to -0.98) with respect to calcite, whereas samples from the second population are supersaturated (+0.01 to +0.18) with respect to calcite, which may explain the decreasing pH, Ca and HCO_3 values in the second population of data points (Kresse and Fazio, 2002).

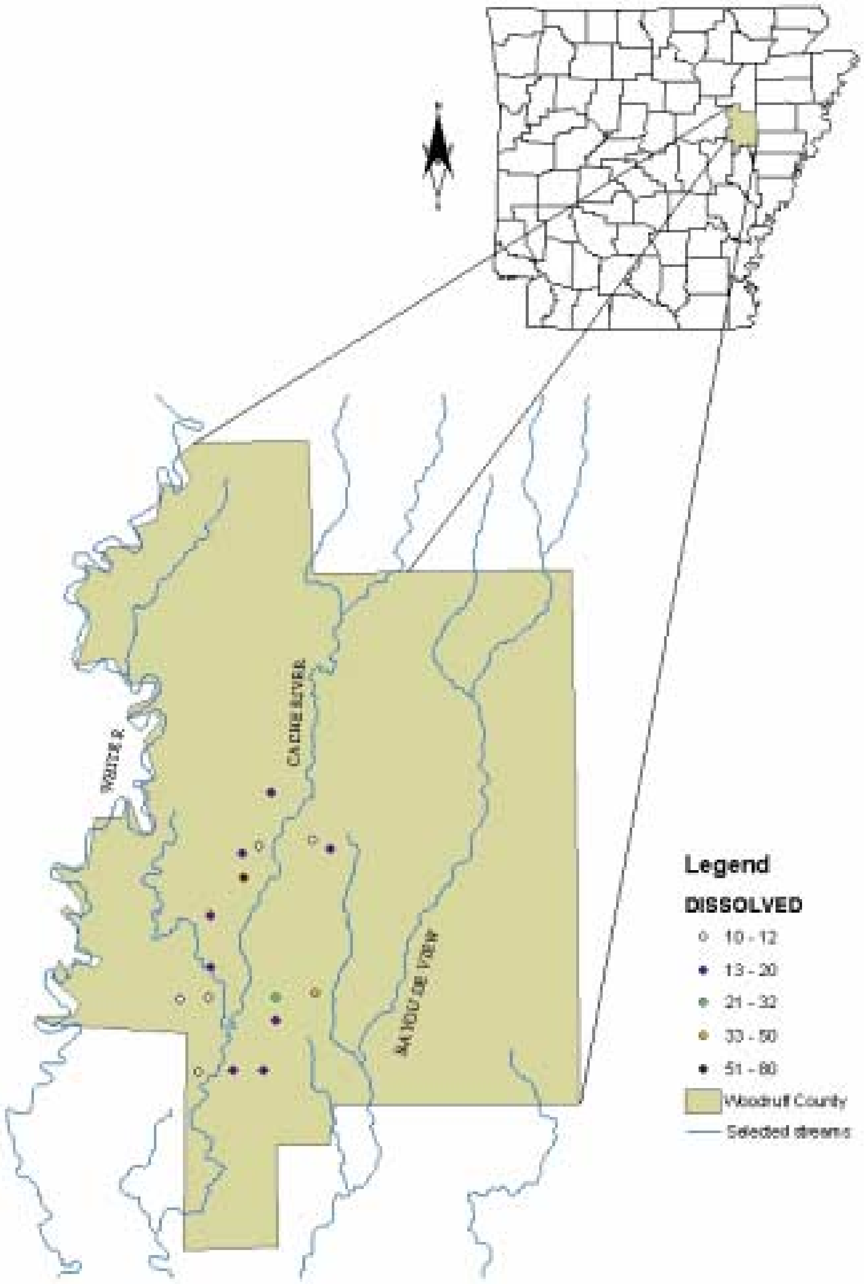

Figure 2. Arsenic concentrations greater than 10 µg/L for USGS alluvial well data**.**

Figure 3 depicts As versus TDS concentrations for the Bayou Bartholomew data. Arsenic concentrations are <10 µg/L at TDS concentrations <175 mg/L, and subsequently rise to a maximum of 50 µg/L at a TDS concentration of approximately 325 mg/L. Maximum arsenic concentrations are below 10 µg/L for all TDS concentrations >400 mg/L, which possibly reflects mixing with a water lower in As concentrations. Figure 4 depicts Fe versus TDS concentrations, and shows a similar trend as that noted in Figure 3 for As versus TDS. Except for one anomalous point, Fe concentrations are all below 10,000 µg/L for all TDS concentrations less than approximately 175 mg/L. Fe concentrations rapidly increase beyond 175 mg/L TDS, reaching a maximum concentration exceeding 40,000 µg/L. All Fe concentrations >10,000 µg/L occur approximately between TDS concentrations of 175 mg/L and 325 mg/L. Samples having Fe and As concentrations near zero (along the x-axis) on both graphs dominantly are represented by samples retrieved from wells completed in the upland terrace deposits.

Figure 5 depicts As versus Fe concentrations. A positive, weakly-linear trend is noted for all As concentrations >10 µg/L versus Fe concentrations ($R^2 = 0.02$ for all points). However, the lack of a strong correlation does not diminish the potential of iron oxides as the primary source of As. McArthur et al. (2001) cited reductive dissolution of Fe oxides as the source of elevated (>1,000 µg/L) As concentrations in Bangladesh in a similar geologic setting (alluvial plain) and also noted poor co-variance between As and Fe, which was attributed to the possibility that (1) Fe and As are sequestered differently into diagenetic pyrite, (2) dissolved Fe may also be derived from weathering of biotite, (3) As/Fe ratio in dissolving FeOOH is variable, and (4) Fe may be removed from solution into vivianite, siderite, or mixed-valency hydroxycarbonates. Smedley and Kinniburgh (2002) suggest that chromatographic separation of As(III) and As(V) during transport affects the As versus Fe relationship, thus complicating the interpretation of ground-water quality data. Whatever the reason for the weak correlation, both As and Fe increase beyond 175 mg/L TDS, and the highest concentrations for each are within a similar range of TDS concentrations. Figure 6 additionally reveals a weakly-positive correlation between As versus Mn concentrations similar to that for As versus Fe (Figure 5). The weakly linear correlation of As to both Fe and Mn may simply reflect both the spatial variability and composition of the As-bearing metal complexes.

Figure 7 depicts total P versus TDS concentrations. Total P concentrations increase from <0.3 mg/L at TDS concentrations <175 mg/L to values exceeding 1 mg/L at TDS concentrations >175 mg/L, similar to the sharp increases noted for As (Figure 3) and Fe (Figure 4) at the same approximate TDS concentration of 175 mg/L. A fairly linear and positive correlation between total P and Fe concentrations is revealed in Figure 8, suggesting a common diagenetic origin for both parameters. Orthophosphate, the most stable form of P, strongly sorbs or coprecipitates onto Mn and Fe oxy-hydroxides, similar to As, which acts as a major solubility control in natural waters (Hem, 1989). This explanation for the positive correlation between total P and Fe concentrations is substantiated by a cursory review of the composition and concentration of total suspended sediments (TSS) in the alluvial water samples. Production wells typically have low turbidity water for all aquifer systems in Arkansas, and the authors rarely note TSS concentrations exceeding 10 mg/L (>600 samples). However, unfiltered samples from the alluvial aquifer extracted for purposes other than for dissolved metals (filtered in the field with 0.45 micron filters) frequently will turn a strong orange color within an hour or so after sampling in the presence of high dissolved Fe concentrations. Visible settling of oxides occurs by the time of delivery to the laboratory, and account for TSS concentrations ranging upwards to 70 mg/L for the Bayou Bartholomew samples.

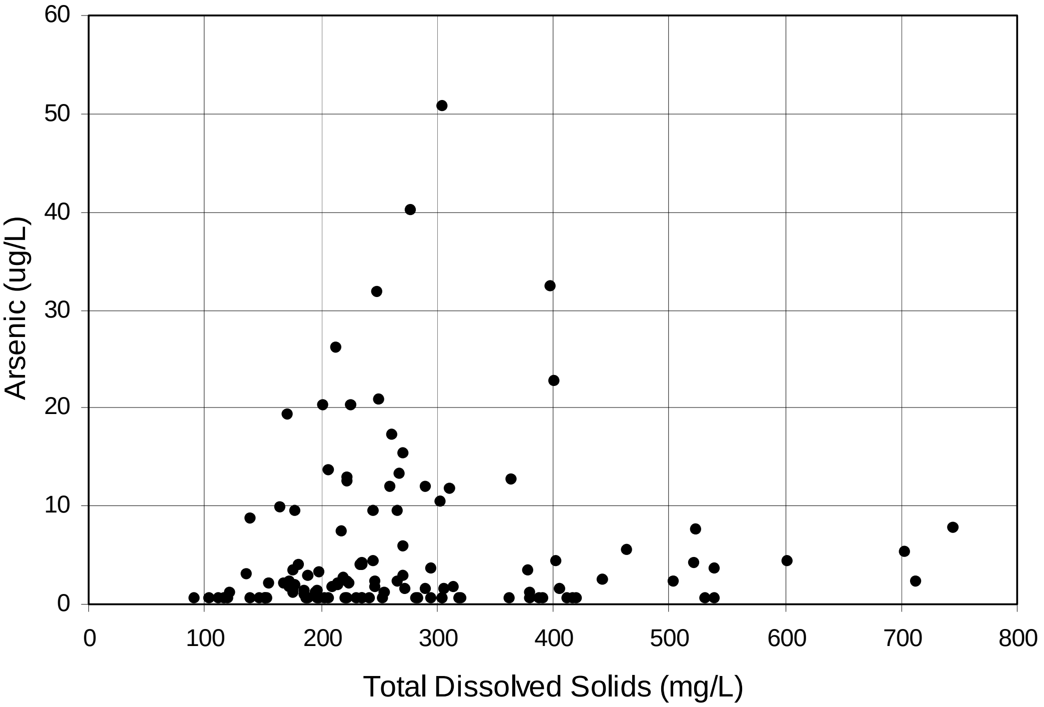

Figure 3. Arsenic versus total dissolved solids concentrations.

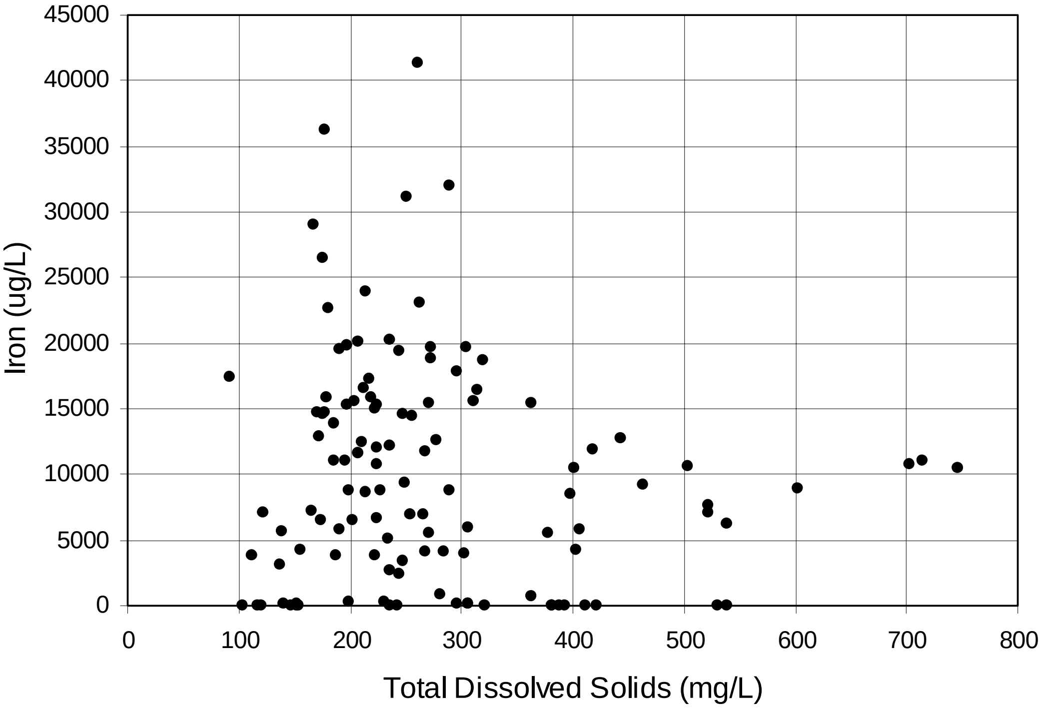

Figure 4. Iron versus total dissolved solids concentrations.

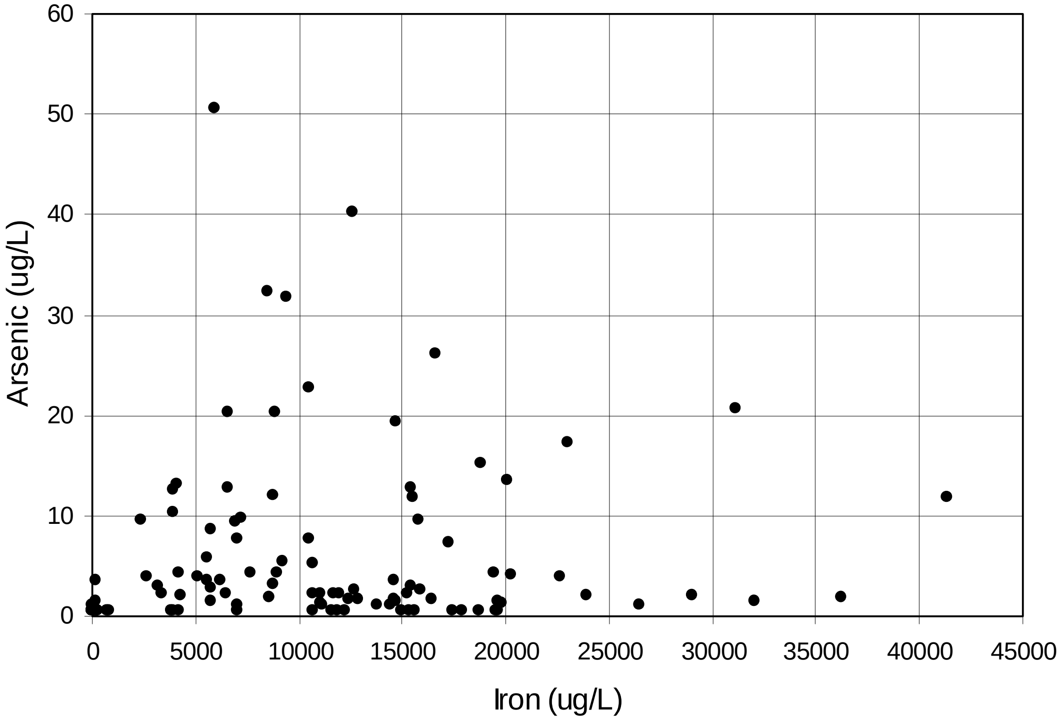

Figure 5. Arsenic versus iron concentrations.

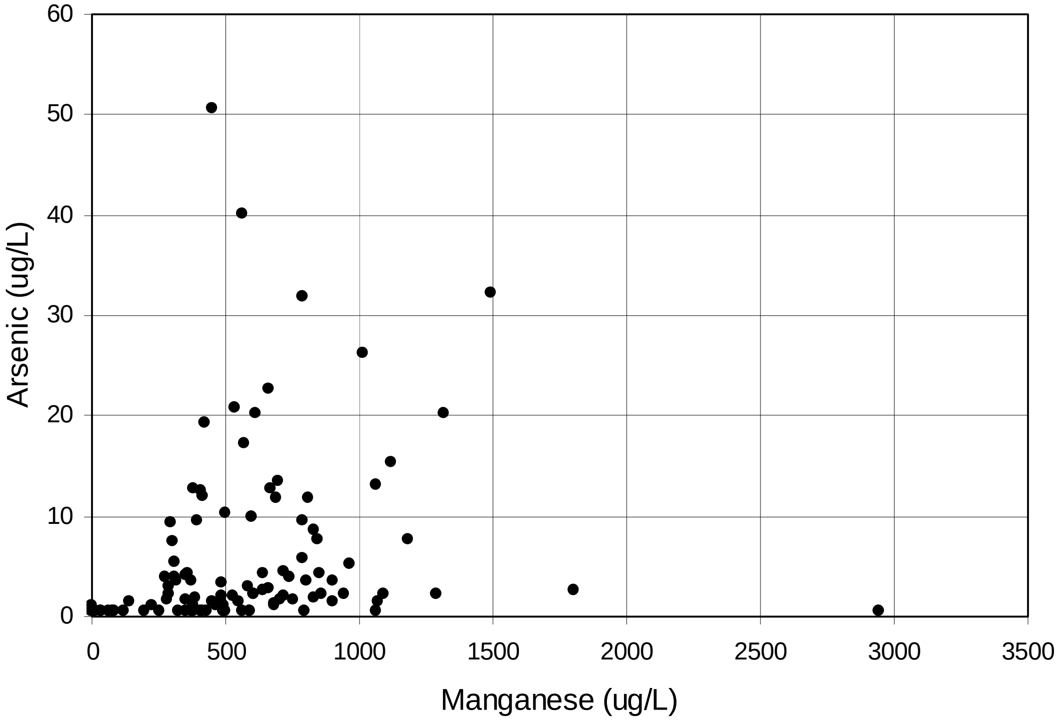

Figure 6. Arsenic versus manganese concentrations.

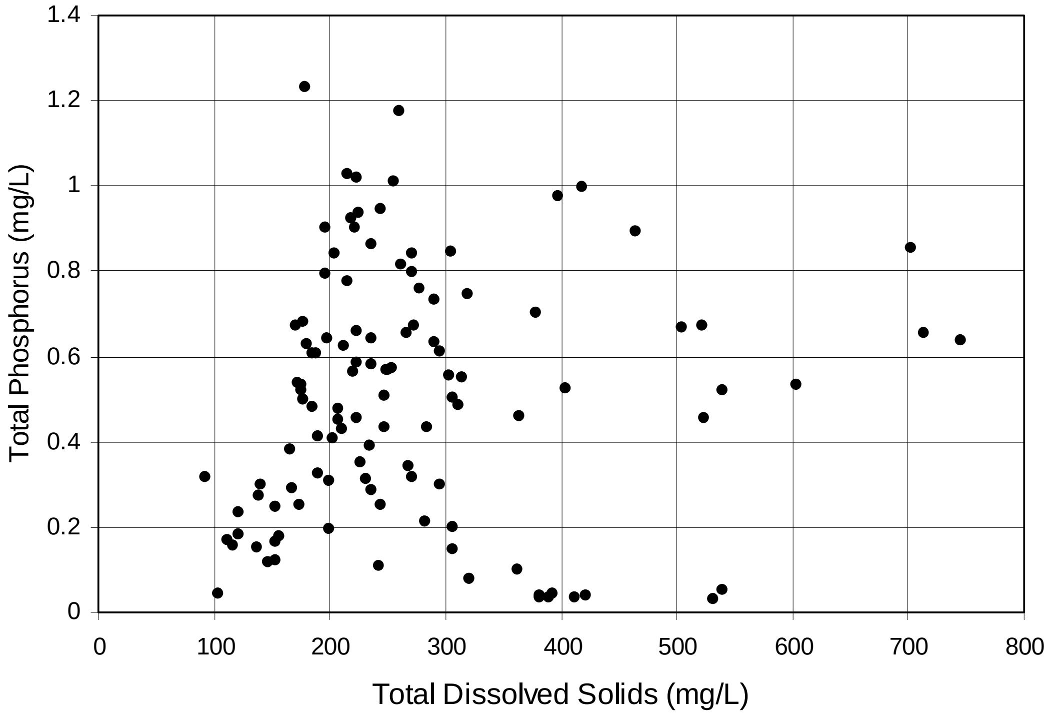

Figure 7. Total phosphorus versus total dissolved solids concentrations.

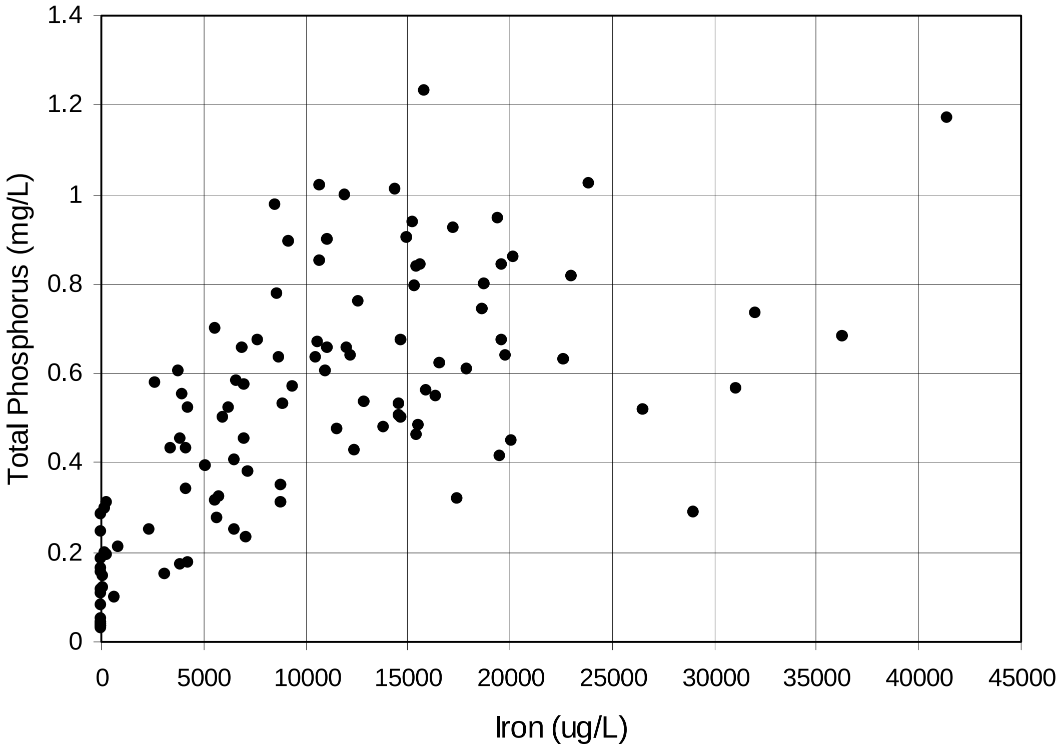

Figure 8. Total phosphorus versus iron concentrations.

Figure 9 reveals a strong linear relationship between TSS and Fe concentrations, and additionally indicates that Fe accounts for the bulk of the TSS composition. Total P concentrations also exhibit a strong linearity with TSS (Figure 10), and provide evidence for removal of phosphorus from solution by precipitation of Fe phosphate and/or sorption to Fe oxides. Because production wells are typically low in suspended solids, dissolved orthophosphate (ortho-P) generally constitutes most of the total P in water samples, and the concentrations of ortho-P typically are equivalent to total P concentrations. Table 1 provides an example of the similarity noted between total P and ortho-P concentrations in ground-water samples from both Quaternary terrace deposits and the Sparta Formation, which have typical Fe concentrations in the low µg/L range. However, a large increase in total P over that of ortho-P (over an order of magnitude for each descriptive statistical value), is noted for delta samples, in addition to larger total P concentrations for delta samples compared to terrace and Sparta total P concentrations. Table 2, which lists the results of a statistical comparison (Mann-Whitney) of delta versus terrace sample analyses, reveals statistically higher total P concentrations in the delta compared to terrace ground water samples.

Table 1, together with Figures 9 and 10, provide evidence for sorption of ortho-P to Fe oxides and/or precipitation of Fe-phosphate minerals as the dominant source of total P concentrations in water from the delta deposits. The lower ortho-P concentrations in the delta samples as compared to the values for the terrace and Sparta samples (Table 1), also appear to be the result of P sorption and/or precipitation in the sample bottle, and no inference can be made as to ortho-P concentrations at the time of sampling. However, based on the experience of the authors, and data from Table 1, the ortho-P concentrations in the ground water penetrated by the sampling wells were probably much higher than listed values and essentially equal to the concentrations represented by the total P concentrations. Figure 11 reveals a strongly inverse relationship between ortho-P and total P, and provides additional evidence for the precipitation of P from solution as the cause for the lower ortho-P concentrations. Arsenic has a strongly inverse relationship with ortho-P (Figure 12) and a weakly positive correlation with total P, similar to that for As versus Fe concentrations (Figure 13). A somewhat better correlation is noted between As concentrations >10 µg/L versus total P, with the exception of one As concentration. Similar to the correlation of As versus Fe (Figure 5) and Mn (Figure 6), the relationship of As to total P is potentially affected by source variability and geochemical processes controlling sorption, precipitation and transport rates. Regardless of the lack of specific information in regard to aquifer geochemistry, most of the above correlations strongly suggest an underlying link between the increases in Fe, Mn, As and P concentrations in the alluvial aquifer.

Based on the increasing Fe, As, and total P concentrations beyond an approximate TDS concentration of 175 mg/L, Fe appears to be dissolving under changing conditions along the flow path. Because dissolved oxygen was not measured, as a result of the uncertainty introduced by physical mixing associated with the large capacity pumps in the irrigation wells (upwards to 2500 gpm), reducing conditions within the aquifer cannot be defined based on dissolved oxygen concentrations. However, redox-sensitive parameters provide valuable, more robust information concerning reducing conditions within the aquifer. In fact, many researchers now use classification systems, such as that of Berner (1981), which divide redox environments in terms of indicative redox species, because of the problems with interpretation of *Eh* measurements. The following discussion combined with xy graphs of various ion-pair relationships provides geochemical evidence for reducing conditions along the flow path.

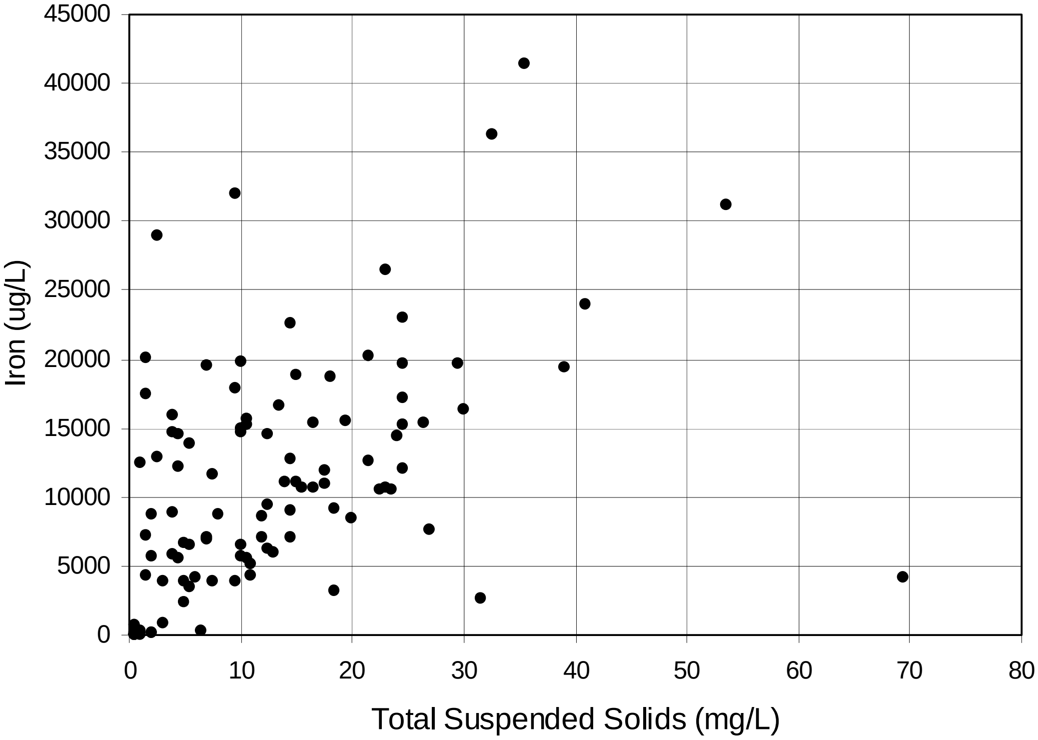

Figure 9. Iron versus total suspended solids concentrations.

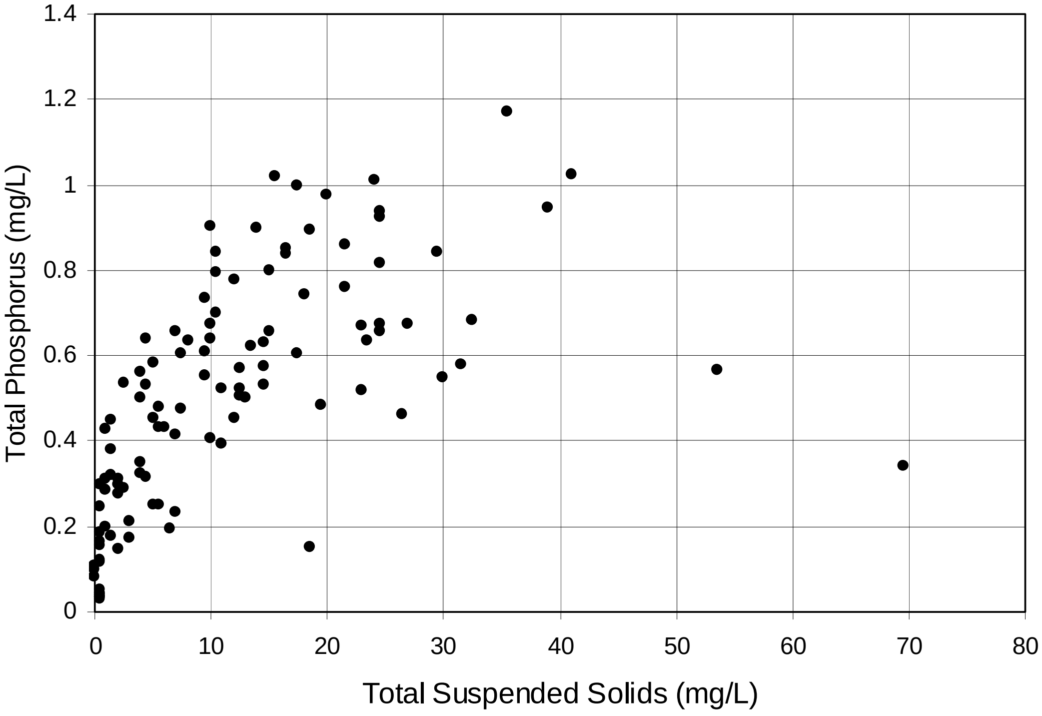

Figure 10. Total phosphorus versus total suspended solids concentrations.

Table 1. Comparison of ortho-phosphate and total phosphorus concentrations for ground-water samples taken from Quaternary terrace deposits, Quaternary alluvium (delta) deposits and the Sparta Formation.

Aquifer System	Ortho-Phosphate (mg/L)				Total Phosphorus (mg/L)			
	Min.	Max.	Mean	Median	Min.	Max.	Mean	Median
Delta[1]	0.003	0.136	0.037	0.023	0.099	1.232	0.600	0.580
Terrace[2]	0.048	0.404	0.190	0.156	0.030	0.310	0.141	0.121
Sparta[3]	0.003	0.531	0.141	0.123	0.010	0.533	0.198	0.185

[1] 93 samples from the Bayou Bartholomew watershed in southeastern Arkansas.

[2] 25 samples from the Bayou Bartholomew watershed in southeastern Arkansas.

[3] 56 samples taken from eastern Arkansas.

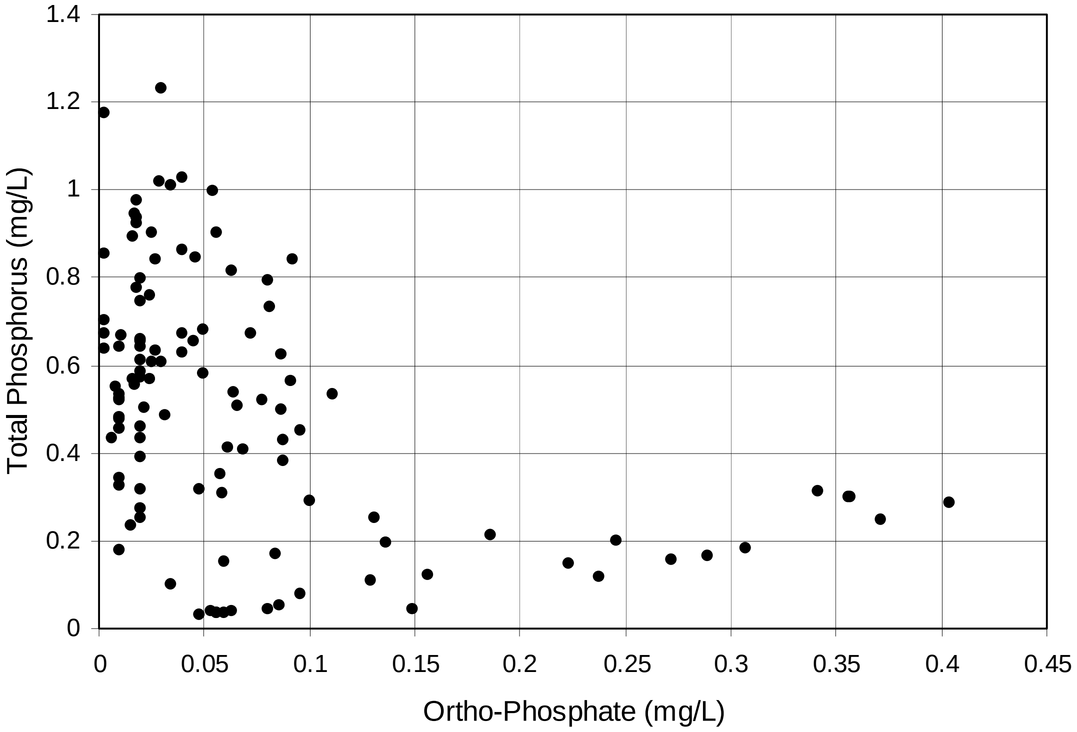

Figure 11. Total phosphorus versus ortho-phosphate concentrations.

Table 2. Mann Whitney statistical analysis of ground water from terrace versus delta deposits in Bayou Bartholomew watershed.

Parameter	Null Hypothesis	Alternate Hypothesis	Median Concentration		Confidence Level	Significance Level
			Delta	Terrace		
Arsenic	Delta = Terrace	Delta > Terrace	2.82 µg/L	0.50 µg/L	99 %	1 x 10^{-5}
Barium	Delta = Terrace	Delta > Terrace	234 µg/L	61 µg/L	99 %	1 x 10^{-5}
Iron	Delta = Terrace	Delta > Terrace	11,600 µg/L	8 µg/L	99 %	1 x 10^{-5}
Manganese	Delta = Terrace	Delta > Terrace	573 µg/L	3.5 µg/L	99 %	1 x 10^{-5}
Silica	Delta = Terrace	Delta < Terrace	32.4 µg/L	46.3 µg/L	99 %	1 x 10^{-5}
Boron	Delta = Terrace	Delta < Terrace	10.5 µg/L	17.8 µg/L	99 %	0.0033
Calcium	Delta = Terrace	Delta ≠ Terrace	41.7 mg/L	55.7 mg/L	99 %	0.841
Magnesium	Delta = Terrace	Delta ≠ Terrace	9.6 mg/L	9.0 mg/L	99 %	0.228
Sodium	Delta = Terrace	Delta ≠ Terrace	20.2 mg/L	24.3 mg/L	99 %	0.057
Potassium	Delta = Terrace	Delta ≠ Terrace	1.9 mg/L	1.7 mg/L	99 %	0.177
Sulfate	Delta = Terrace	Delta > Terrace	5.5 mg/L	3.4 mg/L	99 %	0.267
Chloride	Delta = Terrace	Delta ≠ Terrace	16.4 mg/L	20.2 mg/L	99 %	0.603
Ammonia-N	Delta = Terrace	Delta > Terrace	0.26 mg/L	0.003 mg/L	99 %	1 x 10^{-5}
Nitrate-N	Delta = Terrace	Delta < Terrace	0.022 mg/L	0.063 mg/L	99 %	0.001
Ortho-Phosphate	Delta = Terrace	Delta < Terrace	0.024 mg/L	0.156 mg/L	99 %	1 x 10^{-5}
Total Phosphorus	Delta = Terrace	Delta > Terrace	0.58 mg/L	0.12 mg/L	99 %	1 x 10^{-5}
Total Dissolved Solids	Delta = Terrace	Delta ≠ Terrace	236 mg/L	282 mg/L	99 %	0.963
Total Suspended Solids	Delta = Terrace	Delta > Terrace	12.5 mg/L	0.50 mg/L	99 %	1 x 10^{-5}
Total Organic Carbon	Delta = Terrace	Delta > Terrace	1.93 mg/L	0.50 mg/L	99 %	1 x 10^{-5}

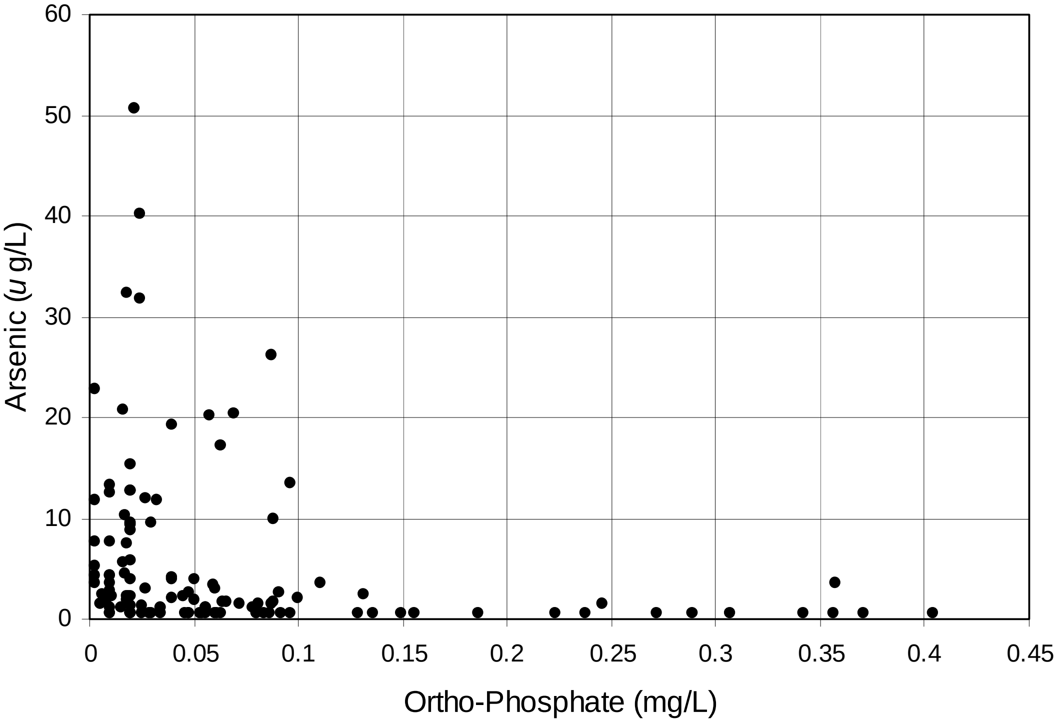

Figure 12. Arsenic versus ortho-phosphate concentrations.

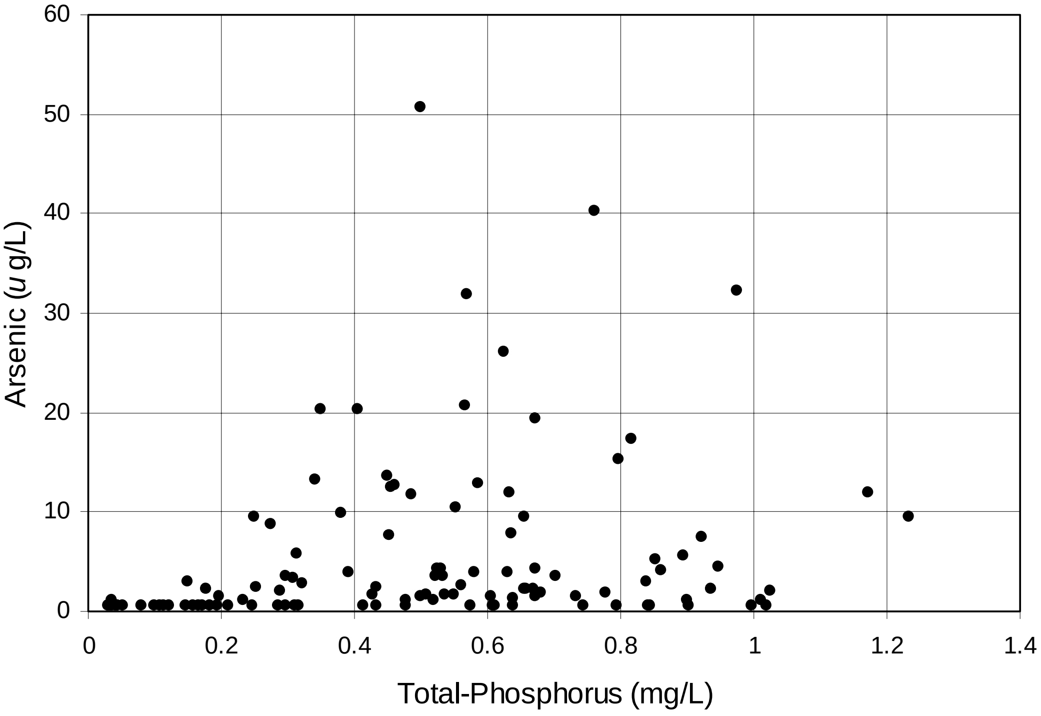

Figure 13. Arsenic versus total phosphorus concentrations.

Figure 14 reveals an inverse relationship between NO_3-N and NH_4-N concentrations. NH_4-N concentrations >0.5 mg/L are typified by NO_3-N concentrations approaching zero. Figure 15 additionally reveals that NH_4-N concentrations, similar to Fe and As, increase sharply at approximately 175 mg/L TDS. Because NO_3 and NH_4 represent the most oxidized and reduced forms of inorganic nitrogen, respectively, in a reduction series, the sharp increase of NH_4-N strongly suggests the removal of nitrate through reductive processes at TDS concentrations approaching 175 mg/L. Figure 16 reveals an inverse relationship between NO_3-N and As concentrations, similar to that observed for NO_3-N versus NH_4-N in Figure 14. All but three data points with As >5.0 µg/L have corresponding NO_3-N concentrations $\leq$ 0.05 mg/L. The fact that As exhibits a strongly inverse relationship with NO_3-N provides additional evidence for the redox constraints on the mobility of As in the alluvial aquifer. Furthermore, the relationship of Fe, As, NO_3-N and NH_4-N concentrations to TDS concentrations indicate that reductive processes become important along the flow path at a TDS concentration of approximately 175 mg/L.

There has been very little documented research into the concentration of organic carbon in the alluvial aquifer. The authors have documented large amounts of particulate organic matter (low-grade lignite to peat) and wood fragments in well logs taken during monitoring well installation in the alluvial aquifer. The well logs (ADEQ, unpublished data) often contain entries of "...sand peppered with lignite" and "...peat and/or lignite and large wood fragments." Various publications by the Arkansas Geological Commission address the occurrence and economic value of lignite in eastern Arkansas. These are mainly in reference to beds of lignite normally found in Tertiary-aged strata underlying the Quaternary deposits (Holbrook, 1980; Clardy, 1979; and Clardy, 1978). However, a review of well logs from these reports in eastern Arkansas note lignite (probably extremely low-grade and/or peat) fragments in the Quaternary deposits based on location and depth of the well logs. Based on these observations, it is sufficient to state that an abundance of organic matter is available to drive the reduction process in the alluvial aquifer.

Further evidence for the oxidation of organic matter is found in Figure 17, which depicts the total inorganic nitrogen (NH_4-N + NO_3-N) versus TDS. Except for a few outliers, resulting from elevated NO_3-N concentrations in some of the low TDS ground water, the highest density of points suggest that nitrogen is increasing with increasing TDS from lows nearing zero for the combined NH_4-N + NO_3-N, to values consistently above the mean and median values of 0.32 and 0.26 mg/L, respectively. Because both NH_4 and NO_3 are expressed as nitrogen, the increased concentration cannot be accounted for through the reduction of NO_3-N to NH_4-N, and is theorized to be the result of the oxidation of organic nitrogen. Additionally, because the dominant reduction product of NO_3 is N_2 (Appelo and Postma, 1999), the increase in total inorganic nitrogen seems more likely a result of the oxidation of organic nitrogen. Table 2 reveals that NH_4-N concentrations are significantly higher in the delta ground-water samples as compared to the terrace samples, which suggests that reducing conditions occur only in the delta portion of the watershed as a result of either increased organic matter or insufficient flushing.

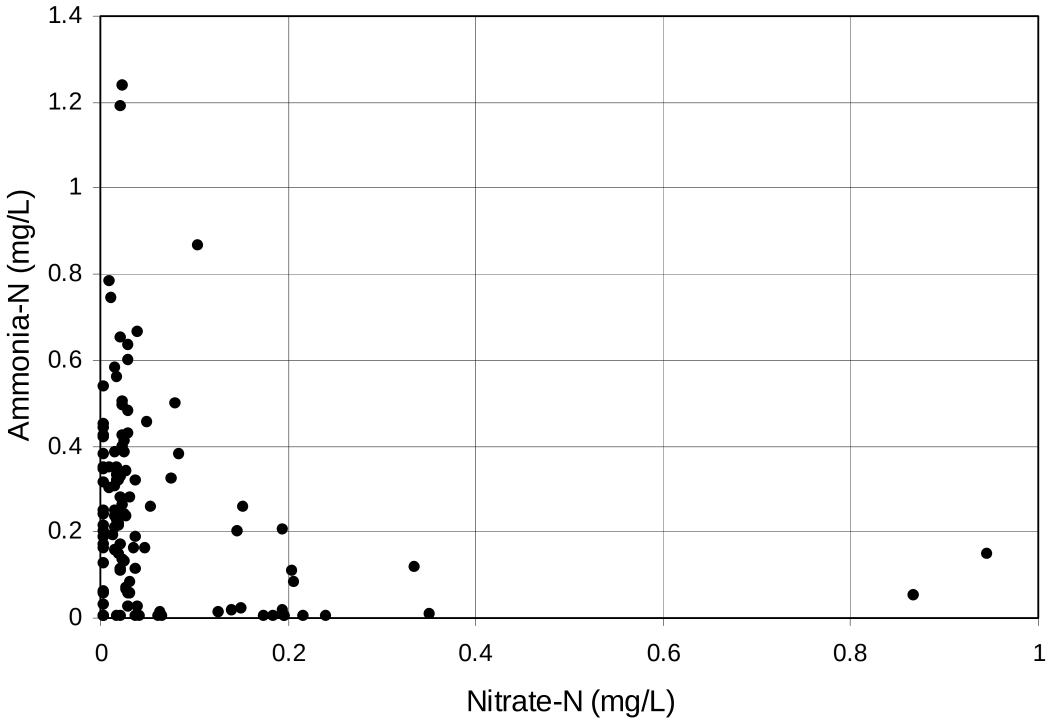

Figure 14. Ammonia-N versus nitrate-N concentrations.

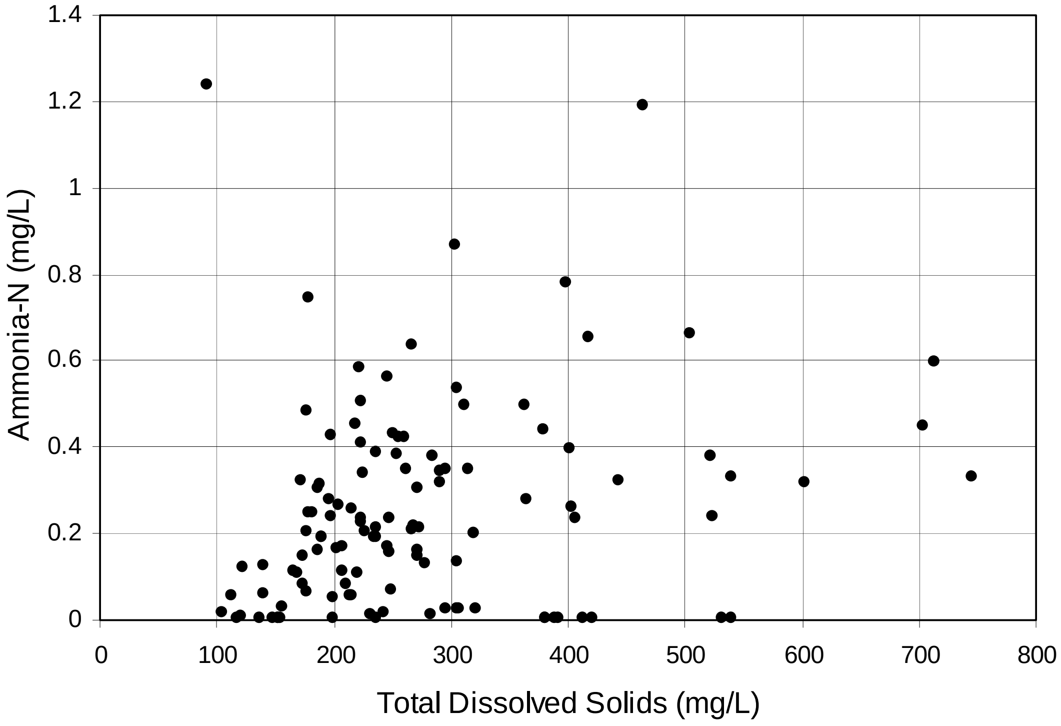

Figure 15. Ammonia-N versus total dissolved solids concentrations.

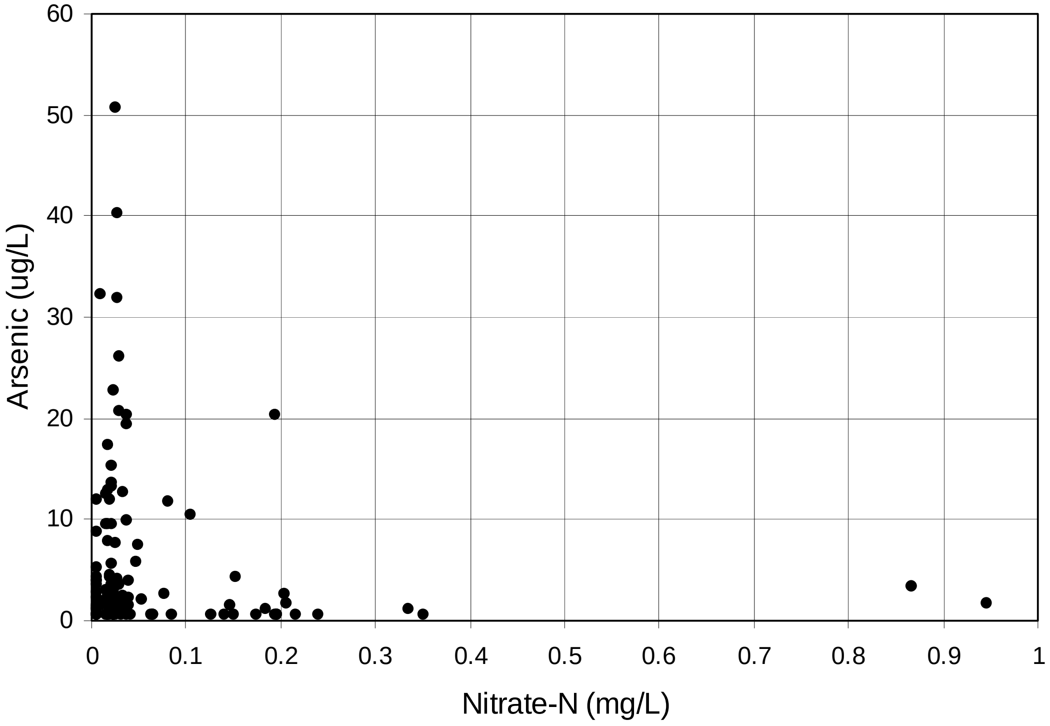

Figure 16. Arsenic versus nitrate concentrations.

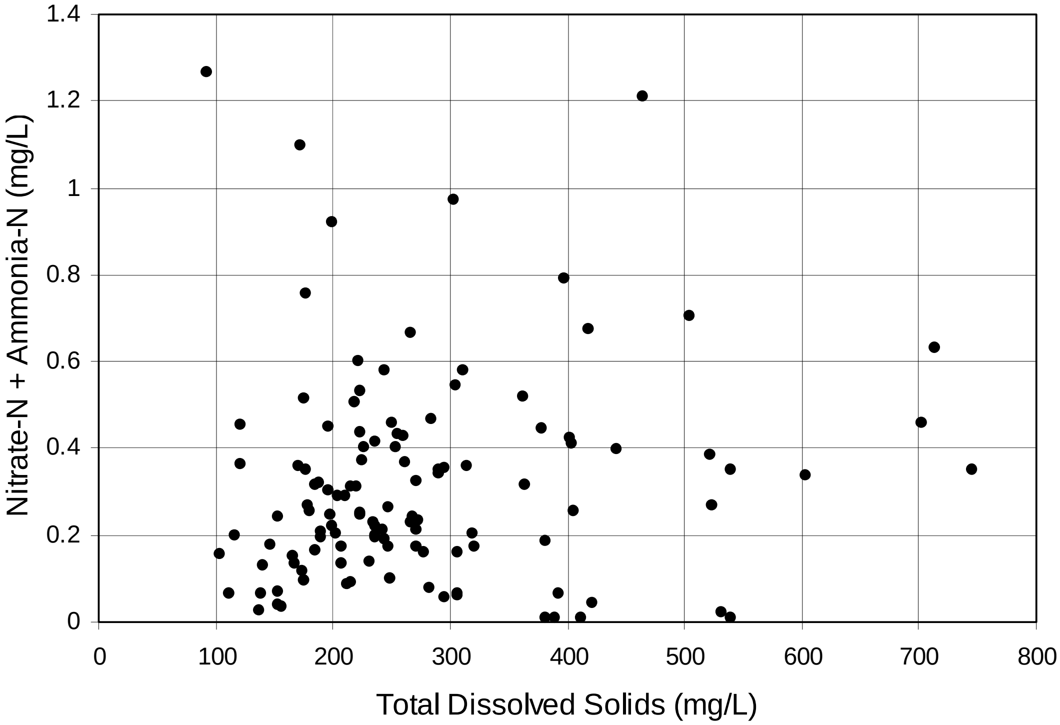

Figure 17. Nitrate-N + ammonia-N versus total dissolved solids concentrations.

Total organic carbon (TOC) concentrations also were evaluated for evidence of organic material within the aquifer matrix. Increasing TOC concentrations are interpreted to be the result of oxidation of organic matter leading to reducing conditions in the aquifer. Figure 18 depicts TDS versus TOC concentrations, and reveals that for TDS concentrations <175 mg/L, with the exception of one sample, TOC concentrations are <2 mg/L. The TOC concentrations increase sharply beyond 175 mg/L, to a maximum concentration of 11.4 mg/L at a TDS concentration of 261 mg/L. Figure 19 reveals a concomitant increase in Fe concentrations with TOC concentrations >2.0 mg/L. Similar trends are noted for TOC versus Mn (Figure 20), NH_4-N (Figure 21), and PO_4 (Figure 22). These trends are consistent with the hypothesis that reducing conditions develop as a result of oxidation of organic matter. Table 3 compares TOC values between ground-water samples taken from Quaternary alluvial (delta) deposits, Quaternary terrace deposits and the Sparta Formation, similar to the comparisons in Table 1 for ortho-P and total P concentrations. The maximum TOC concentration out of 25 samples from the terrace deposits is 3.0 mg/L, whereas 15 of 86 samples from the delta deposits are >3.0 mg/L, and Table 2 reveals significantly higher TOC concentrations in the delta as compared to terrace samples. Also, the maximum TOC concentration of 11.4 mg/L for delta ground-water samples is nearly four times greater than the maximum for either the terrace or Sparta ground-water samples (Table 3).

In view of the strong correlation between elevated (>2.0 mg/L) TOC concentrations and concomitant increases in Fe, Mn, NH_4-N and total P concentrations, As concentrations might be expected to show a similar positive correlation with TOC concentrations >2.0 mg/L. However, Figure 23 reveals an inverse relationship between TOC and As; i.e., As concentrations >10 µg/L occur at TOC concentrations <2.0 mg/L. In view of the above arguments for dissolution of As-bearing Fe oxides as a source of As in the alluvial aquifer, Figure 20 appears to present evidence contrary to these arguments. Possible reasons for the inverse relationship include the formation of organic complexes with As (i.e., dimethylarsinate and monomethylarsonate) in the presence of elevated dissolved TOC concentrations. Formation of stable organic As complexes in the presence of dissolved natural organic matter (NOM) from river water has been performed under laboratory conditions, with documentation of reduction of arsenate to arsenite under a variety of oxic conditions in the presence of NOM (Redman, 2002). However, investigators typically report organic As forms as quantitatively unimportant in ground-water systems relative to the inorganic forms of As(III) and As(V) (Smedley and Kinniburgh, 2002). Many questions remain unanswered with regard to the chemistry, solubility, speciation, and other retardation factors associated with the release and transport of As in aquifer systems, which could affect ion-pair relationships and statistical analysis. Variability in the occurrence and concentration of As within the aquifer minerals additionally may complicate or account for much of the poor co-variation in many of the ion-pair relationships. Site specific investigations are required to further test hypotheses associated with statistical and graphical interpretation of existing data.

One explanation for the poor co-variance of As with other redox-sensitive parameters, including Fe, Mn, total P, and TOC, is found in the construction of reactions that occur along the transition from a highly oxidized to highly reducing conditions in the alluvial aquifer. A review of data from the alluvial aquifer for this report has demonstrated that reduction of Fe and Mn occurs at TDS concentrations exceeding approximately 175 mg/L. Sequences of reduction reactions occur according to their redox potential, and examples of coupled reduction/oxidation reactions are

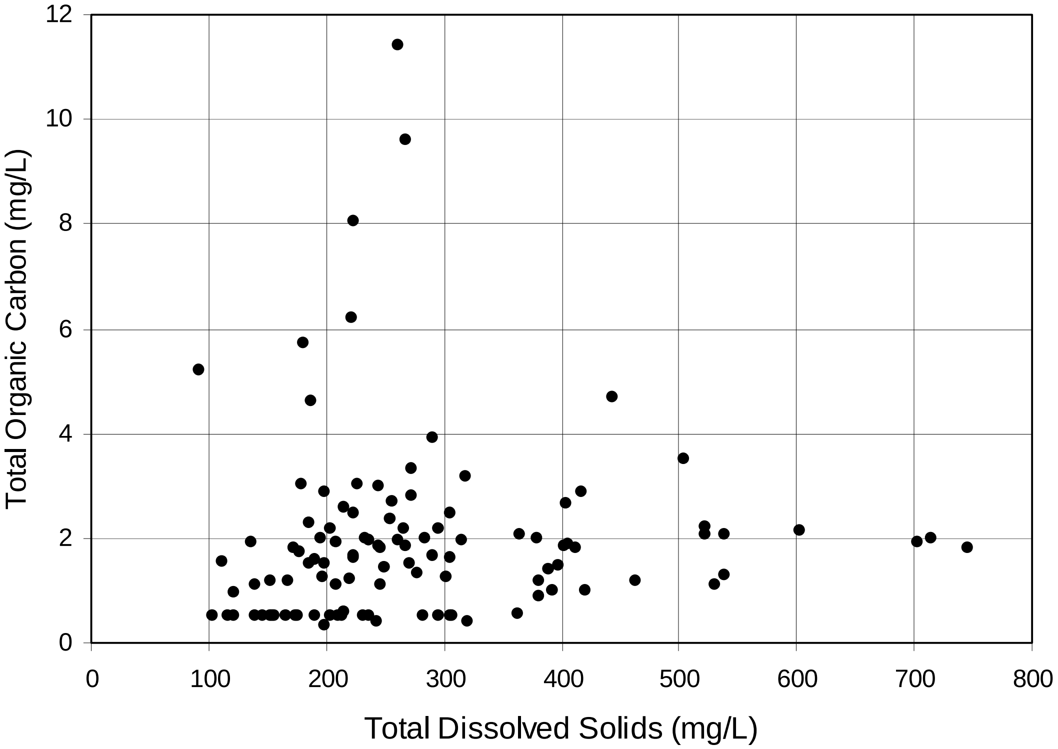

Figure 18. Total organic carbon versus total dissolved solids concentrations.

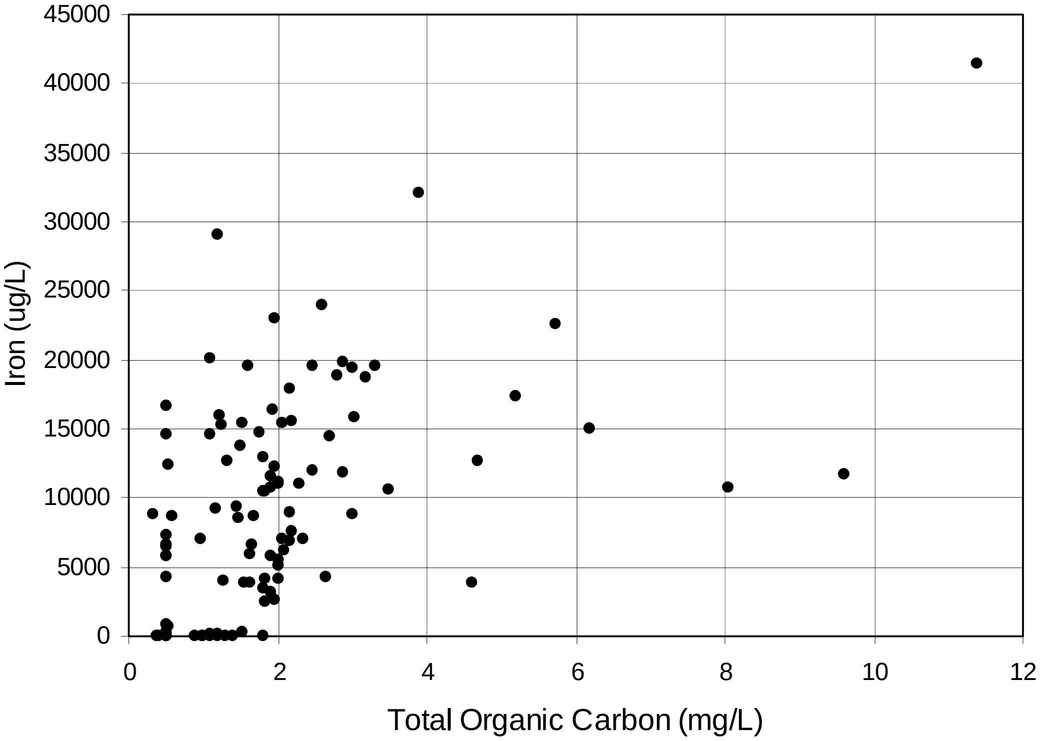

Figure 19. Iron versus total organic carbon concentrations.

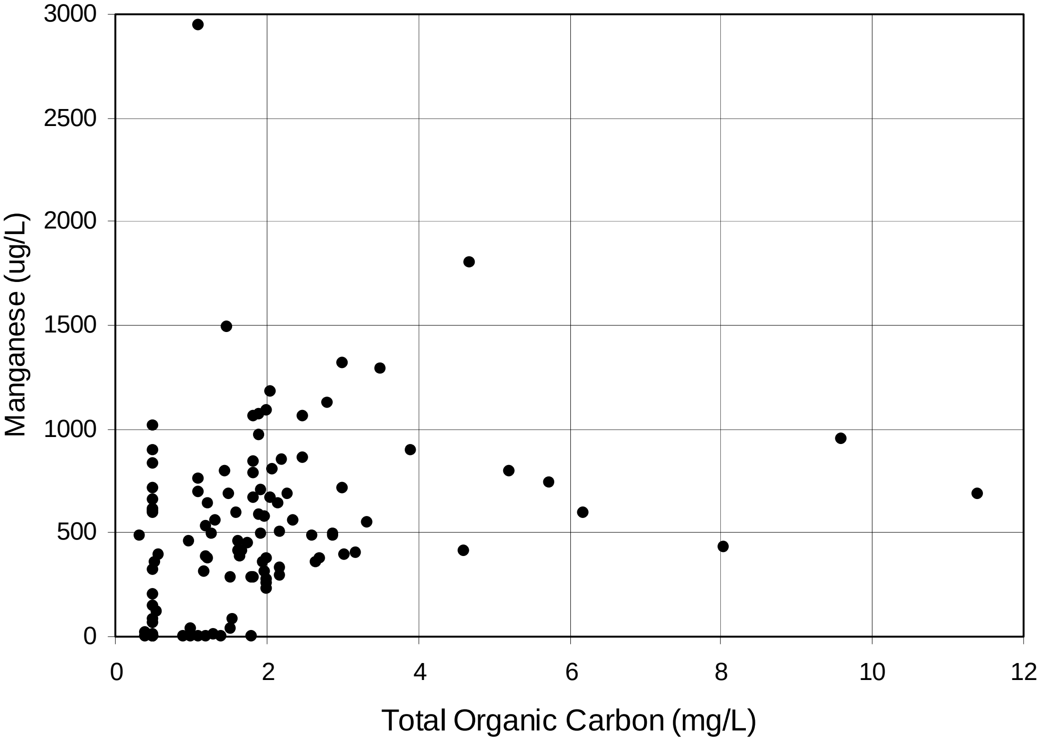

Figure 20. Manganese versus total organic carbon concentrations.

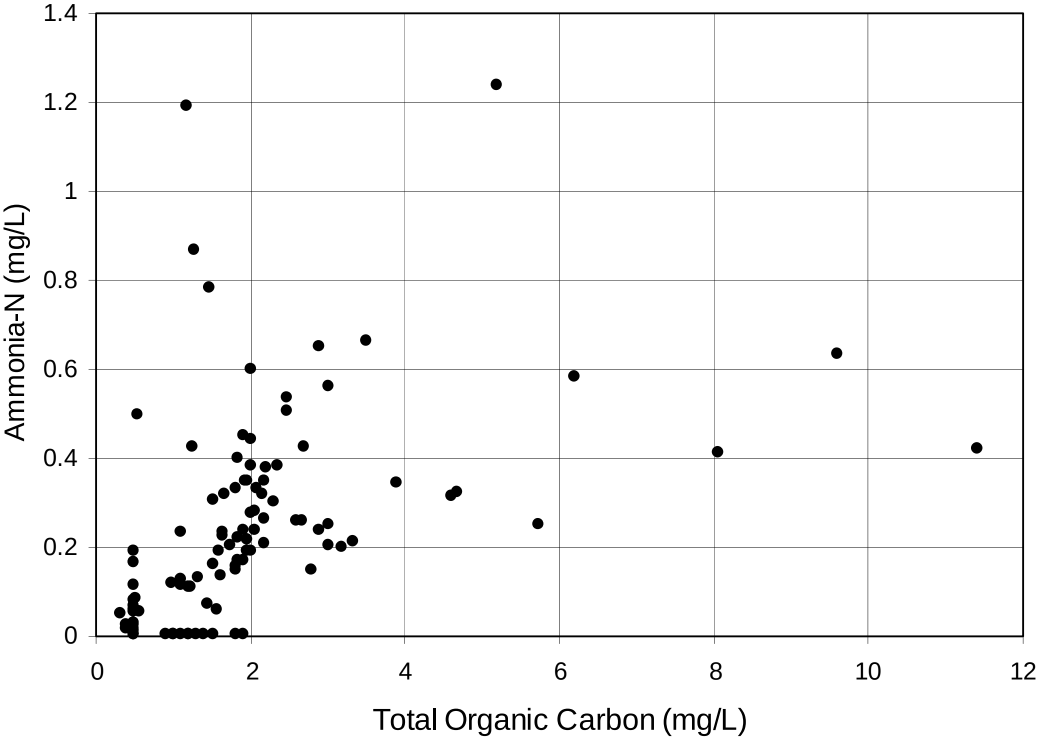

Figure 21. Ammonia versus total organic carbon concentrations.

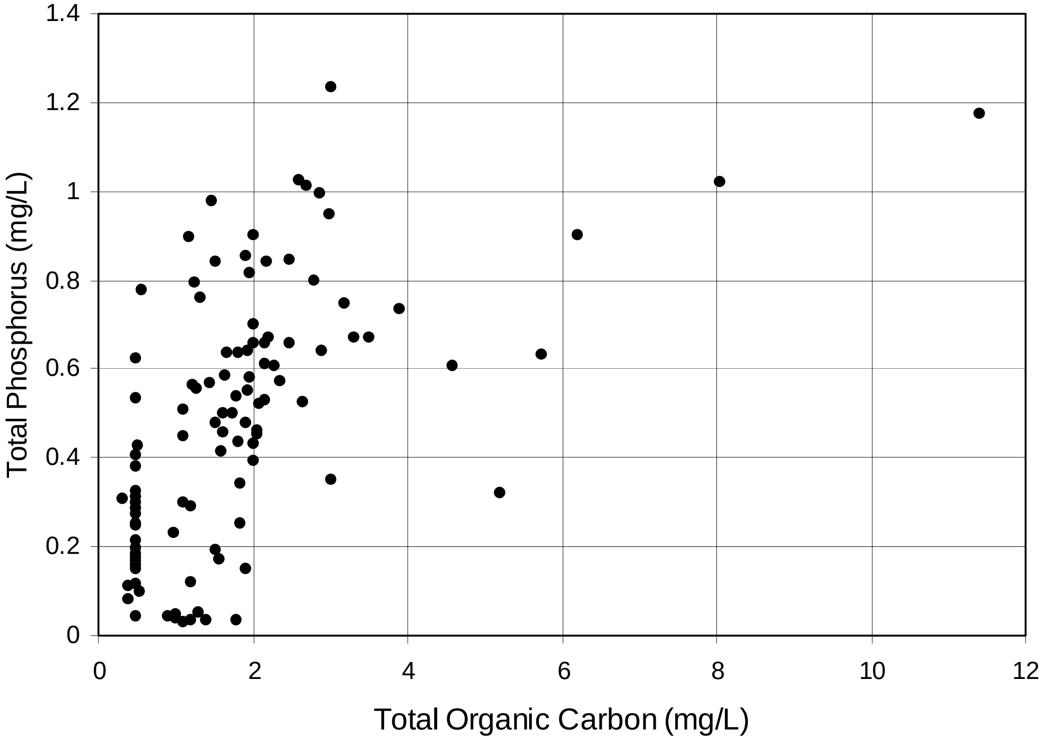

Figure 22. Total phosphorus versus total organic carbon concentrations.

Table 3. Comparison of total organic carbon concentrations in ground-water samples from three aquifer systems: Quaternary terrace deposits, Quaternary alluvial (delta) deposits, and the Sparta Formation.

Aquifer System	Total Organic Carbon (mg/L)			
	Min.	Max.	Mean	Median
Delta[1]	0.33	11.4	2.25	1.91
Terrace[2]	0.39	3.01	0.77	0.50
Sparta[3]	0.44	2.7	1.42	1.35

[1] 93 samples from the Bayou Bartholomew watershed in southeastern Arkansas.

[2] 25 samples from the Bayou Bartholomew watershed in southeastern Arkansas.

[3] 56 samples taken from eastern Arkansas.

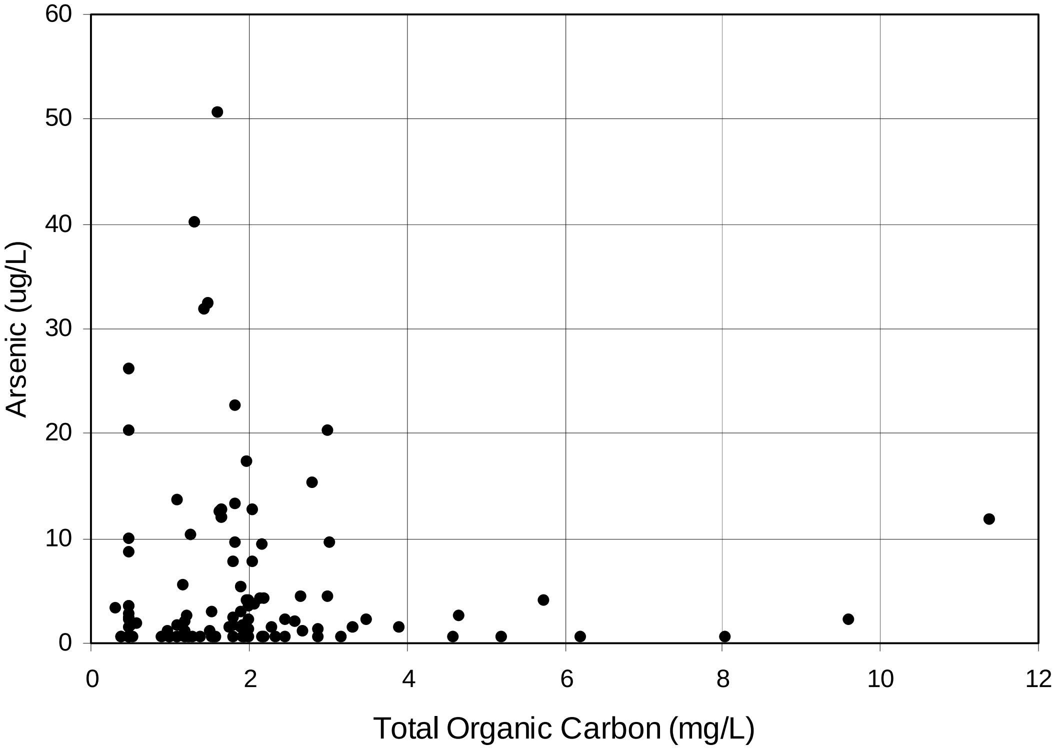

Figure 23. Arsenic versus total organic carbon concentrations.

provided in Appelo and Postma (1999). Berner (1981), as previously stated, proposed a classification of redox environments in terms of the presence or absence of indicative redox species, because of the inherent problems associated with interpretation of Eh measurements. Berner's classification distinguished between *oxic* and *anoxic* based on measurable amounts of dissolved O_2, and subdivided anoxic into *post-oxic*, dominated by reduction of NO_3, Mn oxide, and Fe oxide, *sulfidic*, where SO_4 reduction occurs and finally the *methanic* zone (production of methane). If redox conditions in the alluvial aquifer progress beyond Mn- and Fe-oxide reduction to sulfate reduction, then formation of As-containing Fe sulfides is possible, resulting in decreasing As concentrations along the flow path. Very small amounts of Fe and S are necessary to significantly reduce As concentrations, which would have little effect on Fe or SO_4 concentrations. Figure 24 revisits the Fe versus As relationship and graphically illustrates the net effect of Fe sulfide formation on As concentrations. Figure 24 presents the various As species as related to interpreted redox conditions in the aquifer. Arsenic is originally sorbed to FeOOH in the aquifer matrix, is desorbed under Fe-reducing conditions, and ultimately co-precipitated with the formation of Fe-sulfide minerals (represented by FeAsS in Figure 24) under sulfate-reducing conditions.

Based on the above information, the authors postulate that the source of As in the alluvial aquifer is As-bearing iron and/or iron and manganese oxides in the form of coatings on the sand grains serving as the aquifer matrix material. Evidence in the form of redox-sensitive parameters suggests that microbial oxidation of organic matter and reduction of nitrate within the aquifer is

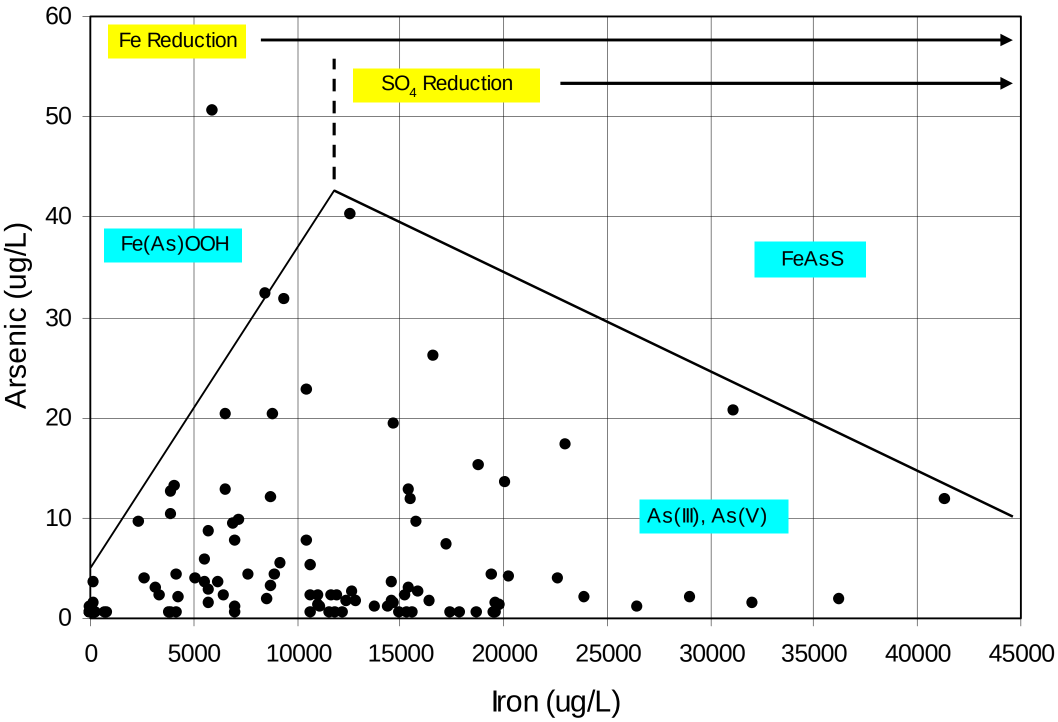

Figure 24. Phase diagram for speciation of arsenic and iron under interpreted redox conditions in the alluvial aquifer.

active at depths along the flow paths beginning at TDS concentrations of approximately 175 mg/L. At concentrations lower than 175 mg/L, NO_3-N predominates over NH_4-N, Fe concentrations are below 10,000 µg/L, total P concentrations are approximately <3.0 mg/L, and As is near or below the detection limit of 1 µg/L. Arsenic and Fe concentrations also decrease at TDS concentrations exceeding 350 mg/L. These decreases are accompanied by a decrease in pH, decreases in the Ca and HCO_3 molar percentage of the total cations and anions, respectively, and an increase in the concentration and molar percentage of Cl and SO_4 of the total anions. The absence of As together with overall changes in the geochemistry in ground water exceeding 350 mg/L possibly reflects mixing with a low-As source water or chemical reactions along the flow path.

Although strong corollary evidence exists for the reductive dissolution of Fe oxides as the source of As in the alluvial ground water of eastern Arkansas, additional work is necessary to document specific mineral assemblages within the aquifer, to identify the As species, to quantify the concentration of dissolved oxygen, Eh and dissolved and total organic matter, and to identify the implications for and conditions favorable to As mobility through various extraction processes similar to work by Keon et al. (1999), Bhattacharya et al. (1998), Breit et al. (2001) and Hein and Koschinsky (2001). Collaborative efforts by the U of A at Fayetteville, the USGS and the ADEQ currently are underway to secure funding for site-specific studies of sources of elevated Cl and As in identified areas of impact in the alluvial aquifer.

Occurrence of Arsenic in the Ozark Region of Northwest Arkansas

Ground water is extracted dominantly from two aquifer systems in the Ozark region of Arkansas: the Springfield Plateau aquifer and the Ozark aquifer. The Springfield aquifer comprises the Mississippian-aged Boone Formation, which attains a maximum thickness of approximately 375 feet and is generally unconfined. The Ozark aquifer comprises several formations of Ordovician age, which are dominantly dolomite and dolomitic sandstone units (Table 1). In northwest Arkansas, this aquifer system is almost always confined and domestic wells derive water from the more shallow (generally <1000 feet) and younger units (i.e., Cotter, Powell and Everton) (Imes and Emmett, 1994; Leidy and Morris, 1990). The Roubidoux Formation (Lower Ordovician) supplies water to several community-supply systems, and reaches depths of over 3000 feet in northwestern Arkansas (Prior et al., 1999).

A review of USGS arsenic data for over 250 wells in the Ozark region (David Freiwald, USGS, written communication) and over 150 wells in both published (Huetter et al., 1997) and unpublished data sets from the ADEQ for the Ozark region, revealed that most As concentrations are below the detection limit of 1 µg/L, and none exceeded 10 µg/L. Lee and Goldhaber (2001) described the behavior of As in aquifers of the Ozark Plateau region of Missouri, Arkansas, Oklahoma and Kansas, and also found no As concentrations exceeding 10 µg/L. Their study focused on areas of Mississippi Valley-Type (MVT) mineralization along major fault systems dominantly in Arkansas and southwestern Missouri. Chemical analyses on over 17,500 rock samples from 300 cores demonstrated that elevated As concentrations in rocks coincide with major structural zones. Epigenetic pyrite in the mineralized zones contained anomalous concentrations of MVT metals, including As. Whole rock As concentrations range upwards to 1500 ppm, and the insoluble residues of rocks (that contain the As-bearing sulfides) contain up to 10,000 ppm As. In spite of widespread and elevated As in the rocks, Lee and Goldhaber (2001) revealed that dissolved As in over 400 analyses of ground water is typically <1 µg/L. Sporadic occurrences of slightly higher As concentrations (from 2-10 µg/L) were associated with elevated dissolved concentrations of other MVT-related metals, and sulfate, along faults and fractures of the Chesapeake Tectonic Zone in northern Arkansas and southwestern Missouri. Mass-balance and reaction-path modeling of ground water showed that the elevated dissolved As along the fault zone is related to the oxidation of an increased proportion of sphalerite, relative to pyrite, in a system open to influxes of atmospheric oxygen.

Occurrence of As in the Ouachita Mountain Region of West-Central Arkansas

The Ouachita Mountains are made up of Paleozoic age sedimentary rocks that have been mildly to severely deformed by Late Paleozoic compressional forces, and Late Cretaceous intrusions are found in scattered locations within the mountain range (McFarland et al., 1997). Most wells in the Ouachita Mountains are less than 100 feet deep, but the larger yield wells generally range from 100 to over 650 feet deep. Ground water in the mountains principally occurs in secondary openings such as joints, fractures, and separations along bedding planes, and the best locations for wells are on the flanks of anticlines (in synclinal valleys) and off the noses of plunging anticlines (Albin, 1965). A search of well data from the USGS data base (David Friewald, USGS, written communication), reveal that wells dominantly are completed in formations ranging from Mississippian to Ordovician-aged rocks.

Table 4. Generalized Stratigraphic Column of Northern Arkansas and Geohydrologic Units (after Imes and Emmett, 1994).

Era	System	Formation	Geohydrologic unit	Geohydrologic system
Paleozoic	Pennsylvanian	McAlester Formation Hartshorne Sandstone Atoka Sandstone Bloyd Shale Hale Formation		Western Interior Plains Confining System
	Mississippian	Pitkin Limestone Fayetteville Shale Batesville Sandstone Moorefield Formation		
		Boone Formation -Reeds Spring Member -St. Joe Limestone Member	Springfield Plateau Aquifer	Ozark Plateaus Aquifer System
	Devonian	Chattanooga Shale	Ozark Confining Unit	
		Clifty Limestone Penters Chert	Ozark Aquifer	
	Silurian	Lafferty Limestone St. Clair Limestone Brassfield Limestone		
	Ordovician	Cason Shale Fernvale Limestone Kimmswick Limestone Plattin Limestone Joachim Dolomite St. Peter Sandstone Everton Formation Smithville Formation Powell Dolomite Cotter Dolomite Jefferson City Dolomite Roubidoux Formation Gasconade Dolomite Van Buren Formation - Gunter Sandstone Member		
	Cambrian	Eminence Dolomite Potosi Dolomite		
		Doe Run Dolomite Derby Dolomite Davis Formation	St. Francois Confining Unit	
		Bonneterre Dolomite Reagan Sandstone Lamotte Sandstone	St. Francois Aquifer	
Precambrian Igneous and Metamorphic Rocks			Basement Confining Unit	

McFarland et al. (1997) collected 700 rock samples from both natural and culturally-produced bedrock outcrops in the Ouachita Mountains for analysis of trace metals, although only 24 samples were analyzed for As concentrations. Because zones of metallic mineralization associated with major faults were purposely avoided, there is no manner by which to identify and/or quantify As-containing diagenetic minerals in the mineral-rich zones. Analysis of whole rock revealed As concentrations ranging from 0.1 to 4.1 ppm, with a mean of 2.2 ppm. Nix et al. (1996) sampled numerous locations along the Ouachita River, which drains the Ouachita Mountains, as part of the objectives set forth by the Arkansas Mercury Task Force. A total of 56 sediment and 233 water samples were analyzed for As concentrations. Sediments ranged from 0.1 μg/L to 41 μg/L, with a mean concentration of 5.5 μg/L. Water samples ranged from 2.0 μg/L to 34 μg/L, with a mean concentration of 6.0 μg/L. However, the water samples were unfiltered and total metals along with turbidity increased downstream along the river stretch.

Ground water from wells tapping formations within the Ouachita Mountain region ranges widely in quality, and analyses from an early reconnaissance study demonstrated that some well water contained Fe, Mn, Cl, NO_3, and TDS, which exceeded that recommended by the U.S. Public Health Service (Albin, 1965). Unfortunately, very little work has been performed to document water quality in the Ouachita Mountain region as compared to other regions of the state. Arsenic concentrations in water samples from 18 wells in the USGS arsenic-point data base were less than the detection limit of 1 μg/L. The ground-water As concentrations are somewhat surprising in view of the extensive mineralization along the fault zones, and whole rock As concentrations ranging upwards to 4.1 ppm. Additional work is required to validate the early results from the limited ground-water sampling in the area. The low As concentrations may be the result of a limited oxygen supply required for oxidation of the As-bearing minerals and/or precipitation and reaction with the extensive shale layers within the geologic profile in a reducing zone. However, both the sources and mechanisms of transport for As are poorly understood at the present date.

Summary and Conclusions

A review of ground-water-quality data for Arkansas reveals that As concentrations >10 μg/L have been found solely in ground water within the Quaternary alluvial sediments in eastern Arkansas. Although As concentrations in samples from mineralized fault zones and whole-rock demonstrate the potential for ground-water contamination in the Ozark and Ouachita Mountain regions of Arkansas, no As concentrations >10 μg/L have been documented in ground-water samples from these regions of the state. The increased attention to As in ground water as a result of the lower MCL for As in drinking-water supply systems should result in increased study and an increased As data base in the future for all regions of Arkansas.

Elevated levels of As in the alluvial ground water of eastern Arkansas are attributed to As-bearing Fe and/or Fe- and Mn-oxide coatings on the sand grains serving as the aquifer matrix material. Reductive dissolution of the Fe oxides appears to be the mechanism of release for the As based on geochemical trends of reduction-sensitive parameters including As, NO_3-N, NH_4-N and Fe. The oxidation of low-grade lignite and peat appears to be the reduction driver in the alluvial aquifer. The past use of arsenical pesticides were ruled out as a potential source based on the low-leaching potential, competition with phosphorus in the formation of insoluble salts, the lack of As concentrations in ground water with TDS concentrations <175 mg/L, and the inverse relation of As with NO_3-N and ortho-P concentrations.

The new As standard of 10 µg/L presently has little impact on Arkansas' community water supplies from a review of data from the ADH. However, production of ground water from the Quaternary deposits for drinking water purposes must be performed with the awareness of the potential for elevated As concentrations. Treatment technologies for removal of As in water-supply systems are well documented and include (1) precipitation/coprecipitation, (2) adsorption, (3) ion exchange, and (4) membrane filtration (EPA, 2002). Low-cost alternatives for household and small suppliers have been tested in various countries and include oxidation (followed by coagulation and filtration through sand filters), adsorption through activated carbon, and adsorption onto locally available iron materials such as laterite (Chadha, 2000; Bundschuh, 2000; Bhattacharya et al., 1998). The selection of treatment versus alternate sources of drinking water will depend largely on costs for the private user and availability of alternate water sources.

It is important to stress that the sources and release mechanisms attributed to the elevated (>10 µg/L) As concentrations in this report are based entirely on corollary evidence from existing water-quality data. Although there is compelling evidence based on distribution and concentration of redox-sensitive parameters along a flow path defined by an increase in TDS concentrations, much additional work is necessary for identification of the source, distribution and mechanisms responsible for elevated As concentrations in the alluvial aquifer. Specifically, the following activities would contribute to an increased understanding of the occurrence of dissolved As in the alluvial aquifer, including: (1) a detailed study of the mineralogy, sedimentology and chemical composition of aquifer materials through visual inspection, X-ray diffraction and other means, (2) laboratory extraction and leaching studies to investigate the ability of aquifer materials to release As under reducing conditions, especially in examining very fined-grained minerals, poorly identified through direct examination, (3) the identification of aquifer redox conditions by measurement of O_2, *E*h, As speciation, and gasses such as N_2O, N_2, CH_4, SO_2, H_2S and CO_2, (4) identification of the concentration, type and distribution of organic matter in the alluvial aquifer, and (5) the identification of As distribution as related to the spatial variability of hydrologic conditions (confined conditions, stagnant zones, age of ground water, etc.), sediments (variability in texture, mineralogy and chemistry), concentration of organic matter, and redox conditions. Although the alluvial aquifer has been identified as having the greatest number of well-water samples with elevated As concentrations, additional data pertaining to As in other aquifer systems is necessary to validate the absence of elevated As concentrations in these formations.

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