Naturally Occurring Arsenic in Groundwaters of the Midwestern United States[1]

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ABSTRACT / High concentrations of naturally occurring arsenic are present in alluvial groundwater systems in the midwestern United States. These occurrences tend to be sporadic because the arsenic is mobilized only under a narrow range of redox conditions. The reducing conditions must be sufficient to reduce and dissolve iron and manganese but not to produce sulfide. Typically, the affected aquifers are relatively high in clay content and of relatively low yield. For that reason, many of these arsenic occurrences are in aquifers supplying single families. The mechanism by which the arsenic is mobilized begins with the deposition of iron oxides during streamflow while the alluvium is being deposited. The oxides have a strong affinity for dissolved arsenic and adsorb it from the streamwater. As the alluvium is buried, it eventually becomes subject to slow groundwater movement. As conditions become more reducing, ferric oxides are reduced to soluble ferrous oxides, resulting in mobilization of the adsorbed arsenic.

Introduction

A recent investigation of the groundwater at an industrial facility in the state of Missouri, U.S.A, revealed the presence of arsenic in concentrations significantly greater than the United States Environmental Protection Agency's drinking water standard of 0.05 mg/l (Korte 1990). Extensive reviews of the site's history revealed no arsenic usage. More puzzling was the fact that the arsenic concentrations were not correlated to other groundwater parameters. For example, many wells at the site contained tens of parts per million of iron and manganese. Because of the ability of iron and manganese oxides to adsorb arsenic (Pierce and Moore 1980), a direct correlation of iron and/or manganese content and arsenic content might have been expected. Instead, water samples containing elevated arsenic typically exhibited elevated levels of iron and manganese, but relative concentrations were so variable that no direct correlation existed.

Discussions with state agencies revealed that high concentrations of arsenic occur in aquifers in at least five states in the midwestern United States: Missouri, Iowa, Illinois, South Dakota, and Ohio. In most cases, the appearance of the arsenic could not be correlated with waste disposal, chemical usage, or with site geochemical and geologic features. Data collected at the Missouri site, however, and a review of information from the various states revealed that similar geochemical conditions prevailed wherever elevated concentrations of arsenic were found in groundwater. A review of some of the data suggested that one reason there had not been much study of this phenomenon is that the arsenic-contaminated water-supply aquifers were relatively low-yield—sufficient for single families but not municipalities. The purpose of this article, therefore, is to describe a common set of hydrogeologic conditions that yield elevated levels of naturally occurring arsenic in groundwaters of the midwestern United States.

Arsenic in Groundwater

Relatively high concentrations of naturally occurring arsenic are common in the United States. Most published sites occur in the west and result from weathered volcanic rocks, geothermal areas, irrigation practices, or mineral deposits (Thompson 1979; Welch and others 1988; Sonderegger and Ohguchi 1988). Most of these studies describe regional occurrences.

The circumstances at the Missouri study site are very different. The aquifer under investigation is quaternary alluvium underlain by Pennsylvanian strata—mostly limestones and shales. Furthermore, as shown in Figure 1, the occurrences of arsenic within the site are somewhat sporadic. Well 9 is hydraulically upgradient of the facility and contains the highest concentration (70.2 mg/l) found on site. Indeed, seven years of intensive site characterization have demonstrated that the industrial operations were not a source of arsenic contamination.

The wells at the facility are multiple completions, such that up to three piezometers are nested in one borehole. The piezometers are screened at 5-ft intervals

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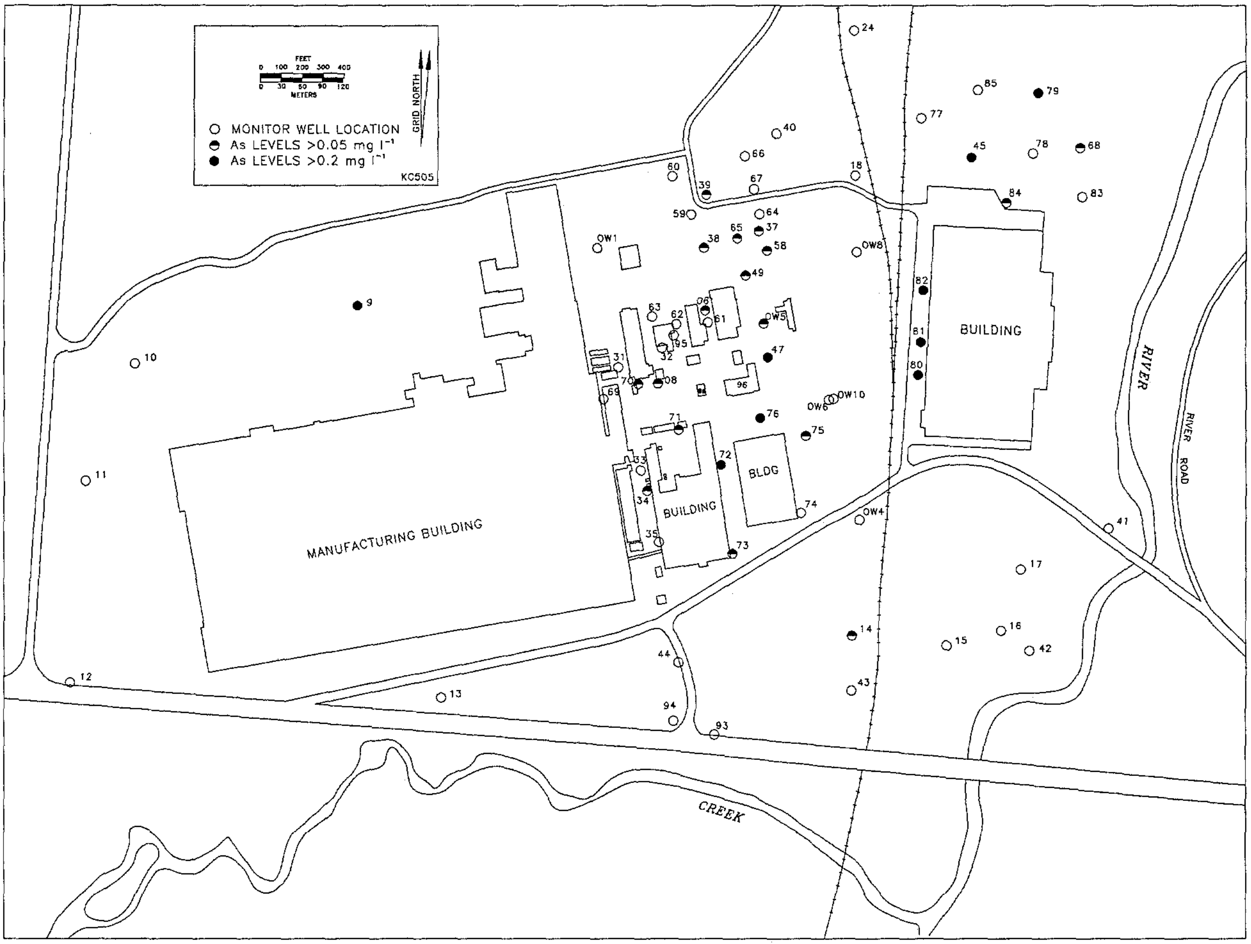

Figure 1. Relative locations of wells containing more than 0.05 mg/l and 0.2 mg/l of arsenic.

at the water table (typically 10–15 ft below ground surface), at a more permeable intermediate zone (20–25 ft), and at a basal gravel (38–43 ft). Although the highest arsenic concentrations typically were found in the basal zone, some wells had high concentrations in the upper and middle zones (Table 1). Moreover, the contamination patterns did not vary even after several years of monitoring.

Arsenic Speciation

The initial phase of the investigation focused on determining the arsenic species present in the groundwater. Such information was deemed important because: (1) the presence of organic arsenicals might indicate prior usage of pesticides or herbicides, and (2) a determination of arsenic oxidation states would provide additional insight into the redox conditions in the aquifer. In addition, As(III) is generally more toxic than As(V) (EPA 1986).

Because of controversy concerning the stability of As(III) in natural waters (Aggett and Kriegman 1987), several precautions were taken in the collection, shipment, and storage of the groundwater samples. Following purging of stagnant water, samples were collected with a bladder pump and filtered in-line to prevent air contact. Samples were pumped through a 0.45-μm filter directly into polyethylene bottles. No air bubbles were permitted to remain in the bottle. Samples were immediately stored at 4°C and shipped by overnight courier to the analytical laboratory. Samples were stored at 4°C until analyzed.

Determinations of As(III), As(V), monomethylarsonic acid, and dimethylarsinic acid were performed at the University of Arizona Department of Chemistry by ion exchange chromatography followed by arsine generation and atomic absorption (Maiorino and Aposhian 1985; Van Wagenan and others 1987). These analyses revealed that essentially all of the arsenic at the site was As(III), as arsenite. Such results are not typical of other

Table 1. Dissolved oxygen (DO), iron and manganese concentrations for typical arsenic-containing wells at the Missouri site

Well no.[a]	Depth to water (ft)	DO (mg/l)	Fe (mg/l)	Mn (mg/l)	As(III) (mg/l)
8U	10.52	<0.5	5.38	5.65	0.03
34U	8.61	<0.5	29.2	6.45	0.08
45L	8.80	<0.5	37.18	3.65	0.13
47L	7.67	<0.5	14.7	2.8	0.4
72L	19.64	<0.5	8.4	0.48	0.3

[a] Most wells at the Missouri site are dual completions. U refers to an upper completion, and L refers to a lower completion.

published data. For example, speciation data presented by Welch and others (1988) and by Holm and Curtiss (1988) showed that of more than 60 wells, only a few arsenic-containing wells contained no detectable As(V).

Site Geochemical Conditions

The presence of As(III) without detectable As(V) was evidence that conditions at the site were strongly reducing. Other evidence included high concentrations of iron and manganese and little or no dissolved oxygen in the groundwater (Table 1). However, no simple correlation existed between the arsenic content and the concentrations of iron, manganese, or oxygen. Sulfide was not present, but ample evidence of anaerobic biodegradation (based on transformations undergone by chlorinated solvents present in some portions of the aquifer) was present (Garland and others 1989). This information is important because arsenic is precipitated by sulfide (Gulens and others 1979) and may be reduced by microorganisms (Braman and Foreback 1973).

Extensive soil sampling on site provided data from more than 100 samples and demonstrated that the bulk soil contained approximately 7 mg/kg of arsenic, a value typical for the region (Tidball 1984). Concentrations ranged from 2 to 23 mg/kg and were normally distributed. Most of these samples, however, were collected from the surface or shallow subsurface, not in the zones where the high arsenic concentrations are found.

A review of drilling records revealed that an orange iron oxide stain (described as limonite) was frequently noted on the lithologic logs. Typically, the limonite was noted as a stain on a dark-green reduced clay. The literature contains much discussion of the scavenging of arsenic by iron oxides. For example, Boyle and Jonasson (1973) reported finding arseniferrous limonite in sediments in Canada and Alaska. Thus, in subsequent drilling operations, some of the limonite was collected and separated from the clay. Analysis of the limonite subsamples showed that some contained as much as 84 mg/kg of arsenic (Table 2). This finding was significant because a laboratory study (Clement and Faust 1981) demonstrated that sediments having arsenic concentrations similar to those in the limonite could support aqueous concentrations as high as those observed at the study site.

Table 2. Arsenic in limonite separates

Location	As (mg/kg)	Fe (mg/kg)
Well 83	4.4	29,200
Well 79A	31	76,200
Well 79B	10	18,300
Well 80	84	58,200
Well 82	26	28,800
Well 84	26	57,900

Other Midwestern Occurrences

Results similar to those for the Missouri site were obtained at a site in central Ohio. A single-family drinking water supply well contained arsenic in concentrations exceeding the drinking water standard (0.05 mg/l). No drill log was available for the well, but it was installed in an alluvial aquifer. There was no history of agricultural or industrial use of arsenicals in the area. A new water well was drilled, and the site geology was described as shown in Figure 2. Based on the results at the Missouri site, the soil was intentionally sampled where an accumulation of reduced iron was evident. The highest iron concentration coincided with a highly reduced, high-arsenic zone. A new well was screened above the reduced, high-arsenic zone, and repeated sampling demonstrated that the water contained less than 0.01 mg/l of arsenic.

Sporadic occurrences of arsenic in alluvial wells also have been reported in northern Missouri and southern Iowa (R. Maley, Missouri Department of Health, Jefferson City, Missouri, unpublished data). Concentrations in single-family water supply wells were as high as 0.49 mg/l (Korte 1990). Available information indicates

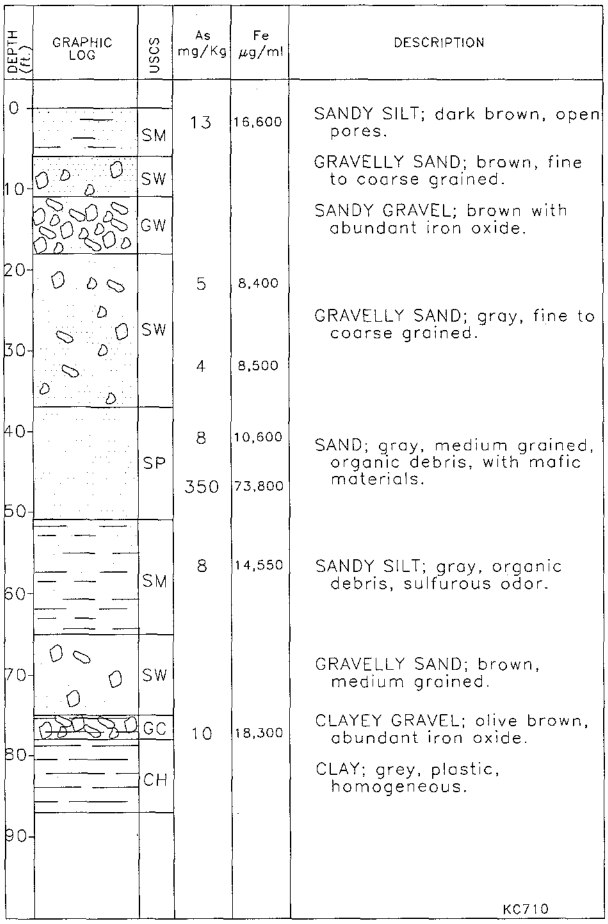

Figure 2. Lithologic log showing arsenic and iron content for water-supply well in Ohio.

that geochemical conditions are similar to those at the study site, but no arsenic speciation data were available. These wells, as at the study site, typically contained high levels of both iron and manganese.

Holm and Curtiss (1988) reported elevated (>0.05 mg/l) arsenic in east-central Illinois but did not describe local geologic conditions. These authors found both As(V) and As(III) in the groudwaters, with As(V) dominant in most of the wells. Finally, Matisoff and others (1982) theorized that a shift from oxidizing to reducing conditions caused arsenic contamination of well waters in northeastern Ohio. It appears, therefore, that the phenomenon of high arsenic in alluvial systems is not uncommon throughout the midwest.

Mechanism for Appearance of Arsenic(III) in Alluvial Wells

The mechanism for elevated arsenic concentrations in midwestern alluvial groundwater systems probably begins with the deposition of iron oxides during streamflow while the alluvium is being deposited. These oxides have a strong affinity for dissolved arsenic and adsorb it from the streamwater. The amount of arsenic adsorbed by the iron oxides is apt to be extremely variable because deposition occurs over a long period of time. Variations in redox conditions, concentrations of dissolved species, and position in the stream all effect the amount of adsorbed arsenic. As the alluvium is buried, it eventually becomes subject to slow groundwater movement. As redox conditions become increasingly reducing, the ferric iron is reduced to ferrous iron, resulting in mobilization of some of the adsorbed arsenic. If conditions are sufficiently reducing long enough, essentially all of the arsenic may be reduced to As(III) (Aggett and Kriegman 1988).

Support for this mechanism is available in the literature. Deuel and Swoboda (1972) showed in a laboratory study that as conditions became more reducing, ferric iron reduces to ferrous and previously sorbed arsenic is reduced and mobilized. Their experiment demonstrated that the arsenic in solution increased until the Eh reached about 100 mV, at which point no more arsenic was mobilized but the iron content continued to increase. This may explain why, at the study site, little correlation existed between the iron and arsenic concentrations in the groundwater. Clement and Faust (1981) reported similar effects and also stated that the amount of arsenic in solution depended on adsorption/desorption equilibria and on the amount of available arsenic. Thus, local variations in Eh and arsenic content demonstrate why the arsenic concentration in midwestern alluvial groundwaters may be significantly elevated yet sporadic and does not correlate with commonly measured groundwater parameters.

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