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Naturally Occurring Arsenic in the Groundwater at the Kansas City Plant

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ENVIRONMENTAL SCIENCES DIVISION
PUBLICATION NO. 3501

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Environmental Sciences Division

NATURALLY OCCURRING ARSENIC IN THE GROUNDWATER
AT THE KANSAS CITY PLANT

N. E. Korte

Environmental Sciences Division

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ABSTRACT

This report describes an investigation concerning the presence of arsenic in concentrations exceeding 0.4 mg/L in the groundwater under the Department of Energy's Kansas City Plant (KCP). The study consisted of four distinct phases: a thorough review of the technical literature, a historical survey of arsenic use at the facility, a laboratory study of existing techniques for determining arsenic speciation, and a field program including water, soil, and sediment sampling. The historical survey and literature review demonstrated that plant activities had not released significant quantities of arsenic to the environment but that similar occurrences of arsenic in alluvial groundwater are widespread in the midwestern United States. Laboratory studies showed that a chromatographic separation technique was necessary to accurately determine arsenic speciation for the KCP groundwater samples. Field studies revealed that naturally occurring reducing conditions prevalent in the subsurface are responsible for dissolving arsenic previously sorbed by iron oxides. Indeed, the data demonstrated that the bulk arsenic concentration of site subsoils and sediments is ~7 mg/kg, whereas the arsenic content of iron oxide subsamples is as high as 84 mg/kg. Literature showed that similar concentrations of arsenic in sediments occur naturally and are capable of producing the levels of arsenic found in groundwater monitoring wells at the KCP. The study concludes, therefore, that the arsenic present in the KCP groundwater is the result of natural phenomena.

1. INTRODUCTION

The purpose of this report is to present an explanation for the arsenic found in the groundwater underlying the Department of Energy's (DOE's) Kansas City Plant (KCP).

Arsenic (As) geochemistry is complex. Thus, it is important that the reader have a basic understanding of As reactions in the environment. For that reason, discussions of As geochemistry and environmental abundance are included in this report. Section 2 provides an overview of As reactions in the environment. Section 3 provides a description of the data pertinent to the Kansas City facility. Section 4 presents results that show that the As present in the groundwater is the result of natural conditions.

2. OVERVIEW OF ARSENIC IN THE ENVIRONMENT

The purpose of this section is to demonstrate that

1. the geochemistry of As is very complex and not completely understood,
2. As is present in significant concentrations in all natural systems,
3. As in the environment is frequently associated with hydrous oxides--particularly those of iron, and
4. many factors affecting analytical and separation techniques of As have not been fully researched, and standard analytical procedures are inadequate for many types of samples.

2.1 GENERAL COMMENTS ON ARSENIC GEOCHEMISTRY

Arsenic in aquatic systems has an unusually complex chemistry in which oxidation-reduction, ligand exchange, precipitation, adsorption, and biologically mediated reactions are all taking place (Ferguson and Gavis 1972; Welch et al. 1988). Indeed, As may occur in four oxidation states (+5, +3, 0, -3) under redox conditions occurring in aquatic systems. Currently, the relationships governing these oxidation states are impossible to predict under many field circumstances. For example, Reimer et al. (1988) stated that "it is insufficient to assume that As(V) and As(III) will dominate in oxic and reducing environments respectively. Instead, both heterogenous and microbiological factors conspire to control the observed As(III)/As(V) values."

Figure 1 is an Eh-pH diagram [a graph of the chemical species present under given pH and redox conditions (Stumm and Morgan 1974)] for arsenic in water. This diagram demonstrates some complex relationships, but data are not available to include several other important factors that affect As mobility. For example, organic arsenicals (known to

occur in nature) are not included, the effects of solid surfaces such as iron and manganese oxides are neglected, and equilibrium is assumed. As we will subsequently discuss, organic arsenicals are not found at the Kansas City Plant (KCP), but hydrous oxides of iron do play a major role in As solubility. Furthermore, the assumption that the systems in Fig. 1 are in equilibrium may be erroneous, considering the lack of information concerning As reaction rates in water and the fact that redox reactions involving dissolved species in groundwater are often not reversible (Stumm and Morgan 1970). Little is currently known about the oxidation rate of arsenite to arsenate in natural waters (Aggett and Kriegman 1988). Although it is reportedly very slow at neutral pH values (such as those at the KCP), the As(III) to As(V) oxidation reaction, however, proceeds measurably in several days in strongly alkaline or acid solutions (Kolthoff 1921). Finally, note that the Eh-pH diagram (Fig. 1) shows the effect of sulfide species; Welch et al. (1988) report that data on As-sulfur interactions are suspect because of uncertain thermodynamic data. Thus, any Eh-pH diagram calculated for As can only be considered a conceptual model. Trends and general relationships are known with certainty, but many interrelationships important under environmental conditions have not been quantified.

2.2 NATURAL ABUNDANCE

Arsenic occurs in all geologic materials, as shown in Tables 1 and 2. These data demonstrate no obvious difference in As concentration among the various types of rocks (Welch et al. 1988). Arsenic does, however, concentrate in some minerals; for instance, As readily substitutes for silicon, ferric iron, and aluminum in crystal lattices of silicate minerals (Onishi and Sandell 1955).

Arsenic is naturally present in the atmosphere as well. Total atmospheric As emissions have been estimated to be 31×10^9 g/year. The major natural sources of atmospheric As appear to be volcanoes and the terrestrial biosphere (Walsh et al. 1979).

Arsenic is also present in all natural waters. For example,

Table 1. Abundance of As (ppm) in
geologic materials

Material	Missouri region ^a		International studies ^b		
	Range of geometric means	Maximum value	Range of means	Maximum value	Mean of means
Shale, clay	6.4, 9	27	3.2-32 ^{c, d}	60 ^d	11.5 ^c
Sandstone, sand	1.1, 4.3	25	1.2-17		6.5
Carbonates	0.7-2.5	39	0.1-14.6	23.5	3.1
Soil	5.5-13	170	5-10		
Loess	8.3	13			
Terra Rossa	15-21	61			

^aFrom Connor and Shacklette (1975).

^bFrom Onishi (1978).

^cIncludes data for recent marine muds and clays.

^dExcluding six samples with ≤ 100 ppm As.

Source: Fleischhauer 1988

Table 2. Arsenic concentrations in rocks

Type of rock	Arsenic (mg/kg)
<u>Igneous^a</u>	
Ultrabasic	
Periodotite, dunite, serpentinite	0.3-15.8
Basic	
Basalt (extrusive)	0.18-113
Gabbro (intrusive)	0.06-28
Intermediate	
Latite, andesite, trachyte (extrusive)	0.5-5.8
Diorite, granodiorite, syenite (intrusive)	0.09-13.4
Acidic	
Rhyolite (extrusive)	3.2-5.4
Granite (intrusive)	0.18-15
<u>Metamorphic rocks^a</u>	
Quartzite	2.2-7.6
Slate/phyllite	0.5-143
Schist/gneiss	0.0-18.5
<u>Sedimentary rocks^{b,c,d}</u>	
Marine	
Shale/claystone (nearshore)	4.0-25
Shale/claystone (offshore)	3.0-490
Carbonates	0.1-20.1
Phosphorites	0.4-188
Sandstone	0.6-9
Nonmarine	
Shales	3.0-12
Claystone	3.0-10

^aFrom Boyle and Jonasson (1973).

^bFrom Tourtelot (1964).

^cFrom Gulbrandsen (1966).

^dFrom Onishi (1978).

Source: Welch 1988.

As concentrations in rain derived from unpolluted oceanic air masses average 0.019 $\mu\text{g/L}$, and rain from terrestrial air masses averages 0.46 $\mu\text{g/L}$ (Andreae 1980). Boyle and Jonasson (1973) reported that natural groundwaters contain 0.01 to 800 $\mu\text{g/L}$ As. Many groundwaters, however, contain $<0.001 \mu\text{g/L}$.

Some As, therefore, will be found in all environmental samples, provided the techniques of analysis are sufficiently sensitive. Arsenic is always present to be mobilized or concentrated if the appropriate environmental conditions are achieved.

2.3 ARSENIC OCCURRENCE IN THE KANSAS CITY AREA

Arsenic is commonly found in alluvial groundwater in the Kansas City area. A 100-mile stretch of Missouri River alluvium from the Iowa state line to Kansas City contains several wells in which As concentrations range from 10 to 300 $\mu\text{g/L}$ (Fig. 2). The As is typically associated with clay soils and high concentrations of dissolved iron or manganese (Telephone conversation between R. Maley, Missouri Department of Health, Jefferson City, Missouri, and N. Korte, Oak Ridge National Laboratory, Grand Junction, Colorado, March 21, 1989). The use of lead arsenate as an insecticide in orchards has been considered a potential source of the As, but field evidence shows that some high-As wells are not located near orchards and that lead is not found in association with the As. The As occurrences in the Missouri River alluvium are analogous to the circumstances at the KCP, except that no lead arsenate was used at the KCP site. Lead contamination is found in the soil but is associated with plating wastes not containing As. (Section 3 contains further discussion of lead arsenate contamination in Missouri.)

2.4 ADSORPTION REACTIONS

The most important environmental reaction of As is adsorption by hydrous oxides of iron, aluminum, and manganese. This adsorption behavior contrasts many trace inorganic species, such as divalent lead

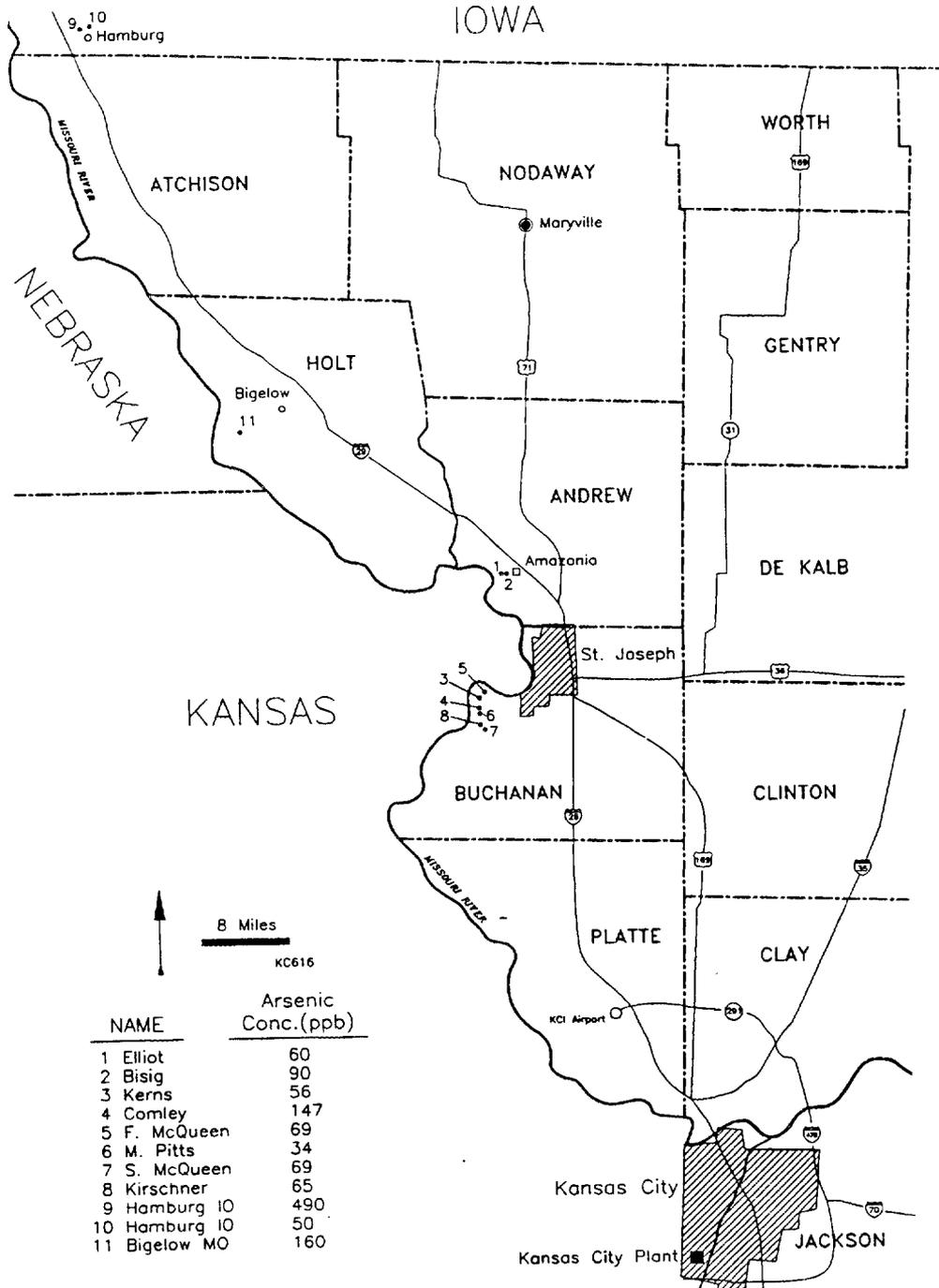


Figure 2. Locations of 11 private wells in the Missouri River alluvium that contain As.

or copper whose solubility in the environment is generally controlled by precipitation reactions.

Arsenic adsorption reactions have been studied by numerous authors (Jacobs et al. 1970; Elkhatib et al. 1984; Wagemann 1978; Livesey and Huang 1981). These authors indicate that As in natural waters is generally present as either arsenate ($H_n As O_4^{3-n}$) or arsenite ($H_n As O_3^{3-n}$) or both. Arsenic never exists as a free cation. It cannot complex directly with humic and fulvic acids and, as far as known, it forms no complexes with other common ions that would maintain it in solution. Indeed, Pierce and Moore (1980) demonstrated that an increase in background electrolyte did not affect the extent of adsorption of As.

The adsorption reaction is the result of the positive charge associated with the hydrous oxides or originating from exposed crystal edges of micas, vermiculites, and similar materials present in the clay fraction of soils. The work of Pierce and Moore (1980) also shows that arsenite adsorption on amorphous iron oxide is not a simple reaction because the mechanism contains elements of specific adsorption as well as electrostatic interactions. The complexity of these reactions indicates that the rate and extent of adsorption in a complex environment cannot be quantitatively predicted by available techniques. Figure 3, which compares adsorption reactions of several soils, demonstrates that the rate and extent of adsorption is variable. In a relative sense, however, the extent of the reactions varies predictably (Korte et al. 1976).

As a final complicating factor, evidence shows that the adsorption mechanism is controlled by the amount of As in solution at certain concentration ranges (Livesey and Huang 1981). Furthermore, Elkhatib et al. (1984) showed that adsorption of As(III) to soils was correlated to iron oxide content at high As(III) concentrations but was correlated to clay content at low arsenic concentrations.

The conclusion that can be drawn from this discussion is that arsenic adsorption reactions are well understood in a qualitative sense. Much additional research is needed, however, before quantitative predictions are possible for natural systems.

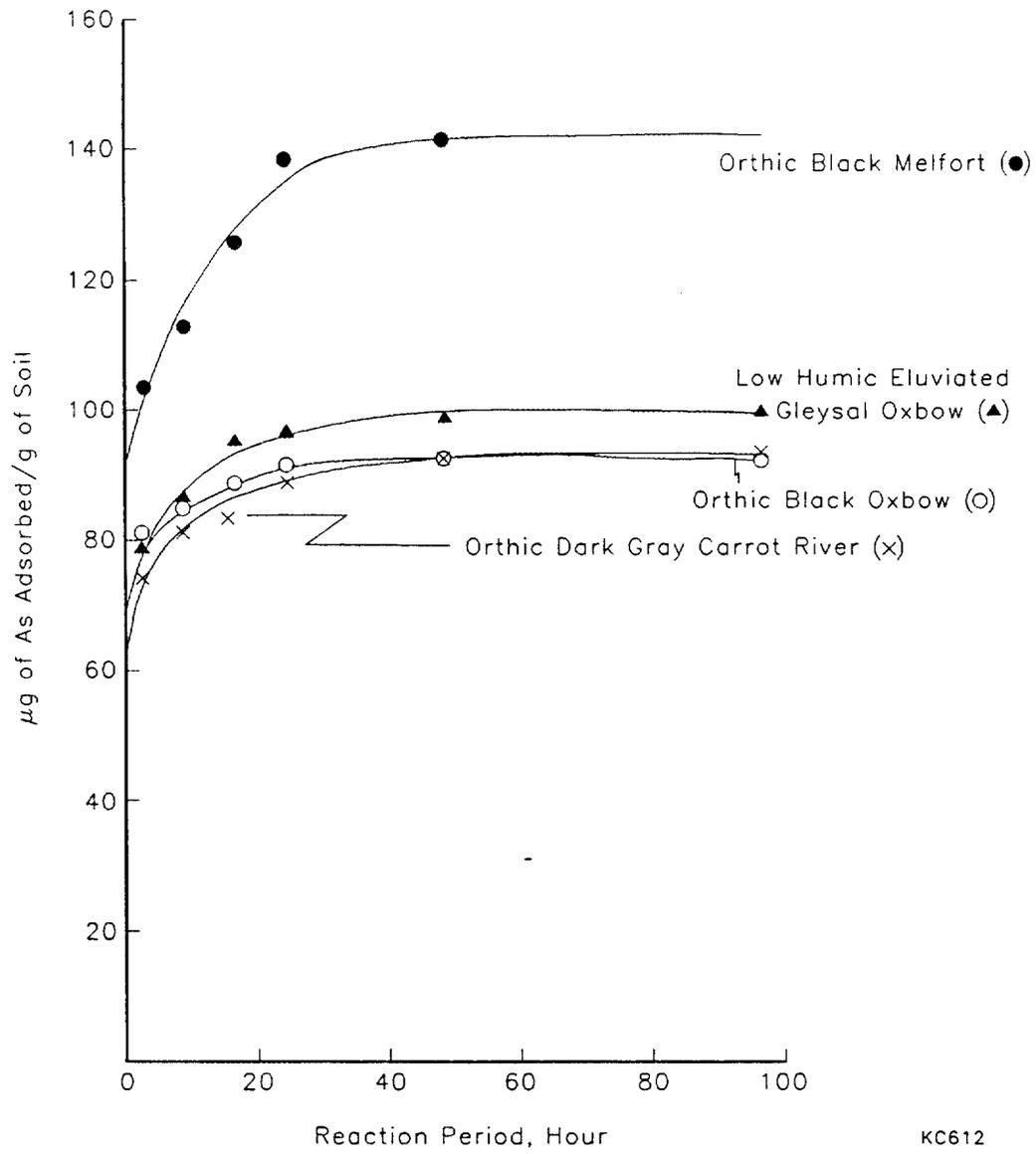


Figure 3. The removal of As from solution by selected soils as a function of time.

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2.5 ANALYTICAL CHEMISTRY OF ARSENIC

The technical literature is replete with methods for determining As. Unfortunately, many of the results reported by various authors are contradictory, the reason for which is explained in a recent paper by Van Wagenen et al. (1987). These authors studied the kinetic control of peak shapes in the commonly used arsine generation technique for As analysis and found that the solubility of arsine in solution played an important role in the analysis. Although the technique had been in use for nearly two decades, this effect had never been reported. The relationship between the acid concentration, the sodium borohydride concentration, and the rate of removal of dissolved arsine by the evolved hydrogen gas was also previously unrecognized although the effects of varying these individual parameters had been reported. Furthermore, the effects of gas flow rates, dead-space volume, and residence time of the As atoms in the optical path of the atomic absorption spectrophotometer are additional factors examined separately by various workers, but their interrelationships have not been deduced. Similar problems apparently exist with furnace atomic absorption methods (Korte et al. 1984; Korte and Hollenbach 1985).

The discussion in the preceding paragraph accounts only for variables in measurement by atomic absorption. It does not account for As solution chemistry, which must be correctly managed to ensure that all the As is actually measured, a particularly important step when attempting to perform analyses of specific As species. For example, most laboratories use reduction of As species to arsines at selective pH to achieve separation of various As compounds. The technique, however, is subject to incomplete recoveries and numerous interferences. Tedious and expensive column chromatographic techniques are apparently necessary to ensure that the As species are adequately separated (Grabinski 1981). Finally, it must be emphasized that the measurement of As species is never routine but is only attempted by a few laboratories that are supporting specific research objectives.

3. ARSENIC AT THE KANSAS CITY PLANT

The purpose of this section is to demonstrate that

1. As in groundwater at the KCP occurs sporadically and is not associated with a spill site or anthropogenic effect,
2. As concentrations in soil at the KCP are not elevated and demonstrate no soil contamination, and
3. all As in KCP groundwater is present as As(III).

3.1 HISTORICAL INFORMATION

A historical survey of plant operations began in 1984 and still continues. The initial survey included questionnaires to over 300 past and present employees and follow-up interviews with many of these (Korte and Kearl 1984). Employees were selected based on their involvement with maintenance, waste management, or buildings and grounds activities at the plant. Over the following 2 years, extensive field work conducted at the site resulted in a wealth of additional employee contacts. Thus, a revised historical survey was produced in 1986 (Korte et al. 1986). Simultaneously and independently, the U.S. Department of Energy's (DOE's) Albuquerque Operations initiated a site review and produced a historical survey (DOE 1986), although many of the same sources were consulted. Finally, DOE headquarters retained outside consultants to perform still another historical review of the site and its operations (DOE 1988). These surveys identified nearly 40 sites or practices that may have resulted in contamination of the environment.

None of these surveys, however, identified a source of As contamination at the KCP. A current raw materials list, compiled in an attempt to delist the South Lagoon, listed only one material, BDT 200 Brightener with 0.005% As as containing any As whatsoever (personal communication from H.L. Fleischhauer, UNC Geotech, Grand Junction, CO., to Mary Robison, NUS Corporation, Pittsburgh, PA., June 26, 1987). The

failure of the surveys to find As is especially significant because high As levels were noted in the first set of samples collected from monitor wells installed in 1984. Thus, an explanation for the As has been sought by all of the auditors and reviewers since that time.

The historical reviews revealed that As compounds were purchased for the plant. Some coolants reportedly contained As and small quantities have been purchased for laboratory usage. There is no evidence, however, that these compounds were present in sufficient quantities to contaminate the environment if, in fact, they were ever released.

In addition, the overall results of the historical surveys with respect to what has actually been found at the plant should be considered. Many sites and potential contaminants were identified, and except for the As finding, all other contaminants eventually found on-site had been identified in the historical surveys.

3.2 ABSENCE OF ARSENIC IN THE LAGOONS

Figure 4 shows that the wells surrounding the former site of the KCP wastewater lagoons contain As. As will be demonstrated however, this appearance of As is not the result of lagoon operation but to the large number of wells installed in appropriate geology in a small area. The absence of As in the lagoons themselves is demonstrated by the data presented here in. Most of these data are taken from the Exposure Information Report (DOE 1986) for the lagoons.

Tables 3 and 4 present typical influent analyses for the two lagoons. Arsenic is not present, but the other metals found in the lagoon sludge (Cd, Cr, Cu, Pb, Ni, and Zn) are frequently present in significant concentrations. Likewise, lagoon effluent results, as shown in Table 5, are very similar. Of course, influent/effluent data only show the results for a brief period of time and do not represent the entire period of lagoon operation. The results are noteworthy, however, because they support the historical information with regard to plant operation and are consistent with results obtained for lagoon sediments. Arsenic analyses of ten sediment samples (five from each lagoon)

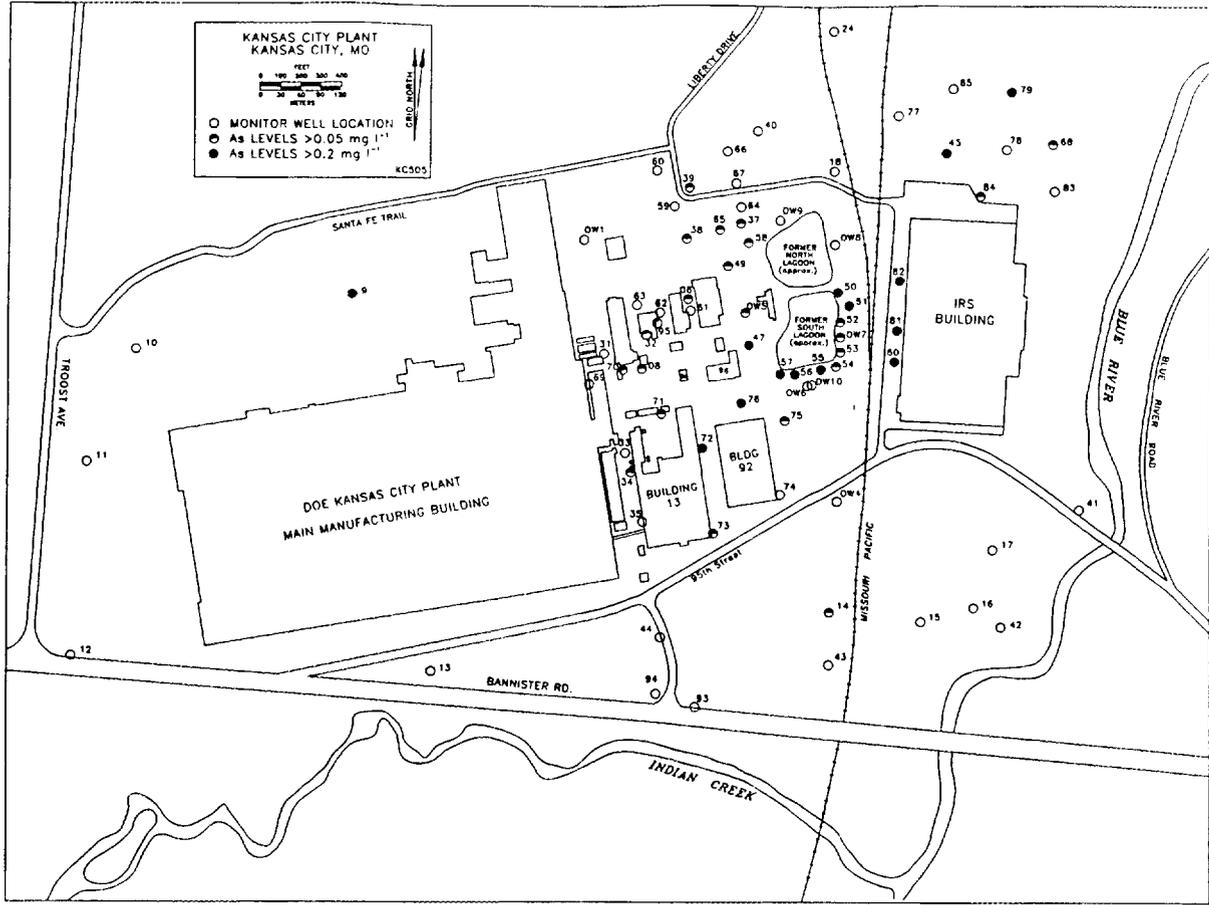


Figure 4. Relative locations of wells containing >0.05 and >0.2 mg/L As.

Table 3. North Lagoon influent analysis^a

Hazardous constituents	Concentration range (mg/L)		Average concentration (mg/L)
Arsenic	<0.001	0.0035	0.0003
Beryllium	0.0001	0.0102	0.001
Cadmium	<0.001	0.009	0.003
Chlorinated hydrocarbons	<0.001	0.51	0.106
Chromium (total)	0.017	0.730	0.198
Copper	0.063	22.500	3.600
Cyanide	<0.001	0.018	0.005
Lead	0.011	0.419	0.085
Mercury	<0.001	0.0015	0.0001
Nickel	<0.010	0.590	0.134
Phenol	<0.001	0.049	0.013
PCBs	<0.0001	0.430	0.038
Selenium	<0.001	<0.001	0.001
Silver	<0.001	0.006	0.001
Zinc	0.015	0.444	0.0787

^aData collected April 1984 through March 1985.

Table 4. South Lagoon influent analysis^a

Hazardous constituents	Concentration range (mg/L)		Average concentration (mg/L)
Arsenic	<0.001	<0.001	<0.001
Beryllium	<0.001	<0.001	<0.001
Cadmium	<0.001	0.008	0.003
Chlorinated hydrocarbons	<0.001	1260	105.490 (0.487) ^b
Chromium (total)	0.033	3.28	0.607
Copper	0.036	0.460	0.252
Cyanide	<0.001	0.034	0.0087
Lead	<0.010	0.126	0.0306
Mercury	<0.001	<0.001	<0.001
Nickel	0.045	0.498	0.180
Phenol	<0.001	0.034	0.008
PCBs	<0.0001	0.002	0.0003
Selenium	<0.0001	0.001	0.00009
Silver	0.001	0.009	0.003
Zinc	0.013	0.683	0.096

^a Data collected March 1984 through April 1985.

^b Average concentration excluding the reading of 1260 mg/L is 0.487 mg/L.

Table 5. South Lagoon effluent data from samples
collected May 1985 through April 1986

Hazardous constituents	Concentration range (mg/L)		Average concentration (mg/L)
Arsenic	<0.001	<0.001	<0.001
Beryllium	<0.001	<0.001	<0.001
Cadmium	<0.001	0.015	0.004
Chlorinated			
hydrocarbons	<0.001	11.28	0.002
Chromium (total)	0.105	2.02	0.587
Copper	0.088	5.42	0.859
Cyanide	<0.001	0.008	0.002
Lead	<0.001	0.224	0.086
Mercury	<0.001	<0.001	<0.001
Nickel	0.018	1.85	0.33
Phenol	<0.001	0.053	0.009
PCBs	<0.001	0.007	0.004
Selenium	<0.001	<0.001	<0.001
Silver	<0.001	0.008	0.003
Zinc	0.01	1.065	0.164

collected in 1984, for example, demonstrated that the As concentration of the sediments was less than the facility background average (Table 6). Table 7 presents data from yet another suite of sediment samples--from the North Lagoon. These samples were subjected to the EP/toxicity test, and the results showed no detectable As in the sediment. Another set of samples was collected from the North Lagoon and subjected to the the EP/toxicity later that year. These samples were collected and analyzed by a different laboratory, and once again, As was not detected (Table 8). Finally, Table 9 presents data from samples collected from the South Lagoon. Once again, the EP/toxicity test demonstrated no detectable As.

Tables 10 and 11 present additional data supporting low As concentrations. Table 10 shows the results of a south lagoon sludge sample, a composite used to test a dewatering program used for remedial action. The raw sludge had an As concentration of 1.08 mg/kg, less than the site average. Similarly, the filtrate of the dewatered sludge contained no detectable As which indicates that little or no dissolved As was present (Table 11).

3.3 GROUNDWATER OCCURRENCE OF ARSENIC

Figure 4 shows the location of all wells containing As in concentrations exceeding the drinking water standard of 0.05 mg/L and, also, those exceeding 0.2 mg/L. Most other wells on-site contain As in concentrations from 0.01 to 0.05 mg/L. It can be observed that As is associated with virtually every area of the KCP including upgradient locations. Well 9 is of particular interest. One of 14 that typically contains more than 0.2 mg/L, it is hydraulically upgradient of the plant as shown by the potentiometric surface for the alluvial groundwater (Fig. 5) at the site.

The contamination pattern provides additional evidence that the As found is not the result the lagoon operations. First, As is associated with other areas of the plant. Second, the only lagoon well containing significant contamination with organics is well 51, located on the east side. Yet, high As levels are as likely to be found on the south side.

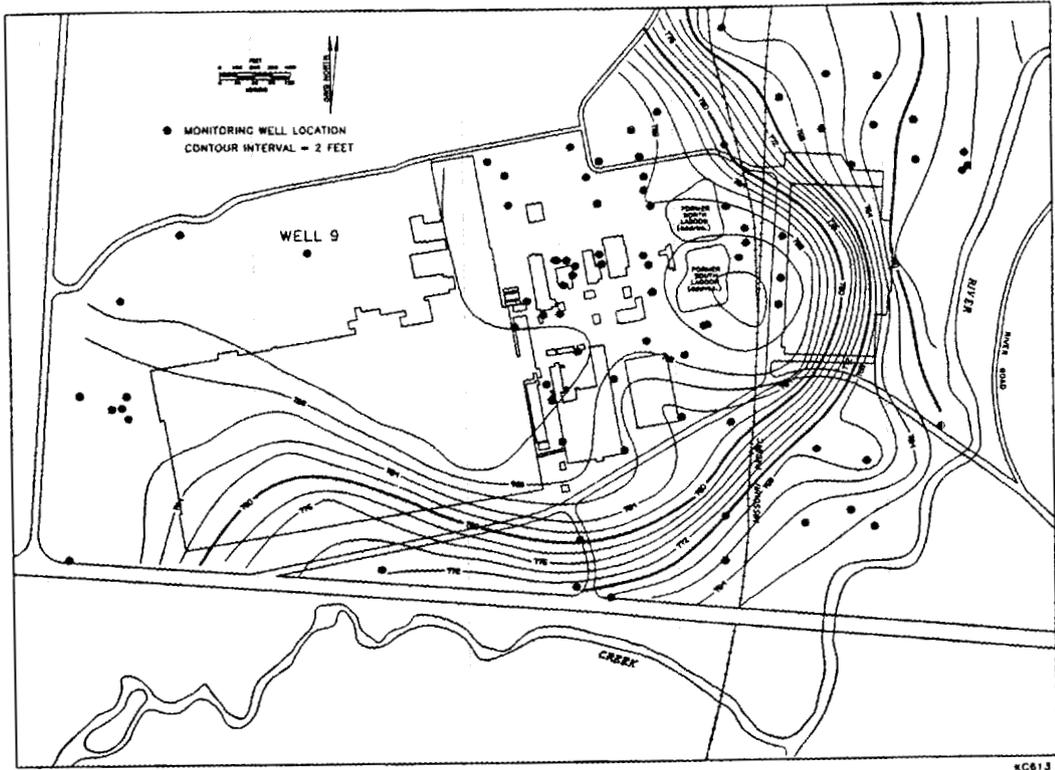


Figure 5. Potentiometric surface map of the basal gravel unit of the alluvial aquifer.

Table 6. Total concentrations of organic and inorganic parameters in sediment samples collected June 11, 1984, from the waste water lagoons

Parameter	Range ^a (mg/kg)		
	North Lagoon	South Lagoon	Site Background ^b
Arsenic	<5-6	<5-7	7.2
Barium	540-720	650-720	N/A ^c
Cadmium	67-89	<2-13	0.75
Chromium	1080-2140	123-370	66.6
Lead	457-1820	27-75	23.8
Mercury	1-3	<1-2	<0.5
Silver	8-8	<5-17	N/A
Selenium	<5	<5	N/A
Beryllium	<5-6	<5	2.8
Copper	2829-7850	162-722	21.4
PCBs	<1.0-12.6	<1	

^a Based on five samples from each wastewater lagoon.

^b Average background concentrations for the KCP (personal communication from H. L. Fleischhauer, UNC Geotech, Grand Junction, CO., to Mary Robison, NUS Corporation, Pittsburgh, PA., June 26, 1987).

^c Not available.

Table 7. EP/toxicity analysis of North Lagoon
sediment samples collected
February 1984^a

Parameter	Concentration (mg/L)					Toxicity (mg/L)
	1	2	3	4	5	
Arsenic	N/D ^b	N/D	N/D	N/D	N/D	5.0
Barium	N/D	N/D	N/D	N/D	N/D	100.00
Cadmium	0.81	0.44	0.26	0.26	0.09	1.0
Chromium (total)	N/D	N/D	N/D	N/D	N/D	5.0
Chromium VI	N/D	N/D	N/D	N/D	N/D	5.0
Lead	N/D	N/D	N/D	N/D	N/D	5.0
Mercury	N/D	N/D	N/D	N/D	N/D	5.0
Selenium	N/D	N/D	N/D	N/D	N/D	1.0
Silver	N/D	N/D	N/D	N/D	N/D	5.0
Copper	N/D	0.06	0.05	0.06	0.05	
Nickel	14.0	8.3	5.2	4.4	3.1	
Endrin	N/D	N/D	N/D	N/D	N/D	0.2
Lindane	N/D	N/D	N/D	N/D	N/D	0.4
Methoxychlor	N/D	N/D	N/D	N/D	N/D	10.0
Toxaphene	N/D	N/D	N/D	N/D	N/D	0.5
2,4-D	N/D	N/D	N/D	N/D	N/D	10.0
2,4,5-TP Silvex	N/D	N/D	N/D	N/D	N/D	1.0

^a EP/toxicity is a test to determine if metals are leachable under environmental conditions. Test conditions are specified by the Environmental Protection Agency under the Resource Conservation and Recovery Act (RCRA). If standards established for certain metals are exceeded, the waste is considered hazardous under RCRA.

^b N/D - not detected.

Table 8. EP/toxicity analysis of North Lagoon
sediment and soil collected
June 11, 1984

Parameter	Detection limit (mg/L)	EP/ toxicity (mg/L)	Concentration (mg/L)						
			1	2	3	4	5	12 ^a	
Arsenic	0.25	5.0	N/D ^b	N/D	N/D	N/D	N/D	N/D	N/D
Barium	5.0	100.00	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Cadmium	0.05	1.0	0.13	0.07	0.07	0.08	N/D	N/D	N/D
Chromium	0.25	5.0	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Lead	0.25	5.0	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Mercury	0.01	5.0	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Selenium	0.05	1.0	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Silver	0.25	1.0	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Endrin	0.001	0.2	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Lindane	0.02	0.4	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Methoxychlor	0.5	10.0	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Toxaphene	0.025	0.05	N/D	N/D	N/D	N/D	N/D	N/D	N/D
2,4-D	0.5	10.0	N/D	N/D	N/D	N/D	N/D	N/D	N/D
2,4,5-TP									
Silvex	0.05	1.0	N/D	N/D	N/D	N/D	N/D	N/D	N/D

^aSample 12 is soil collected midway between the waterline and crest of berm for reference. All other samples are of lagoon sediment.

^b N/D = not detectable.

Table 9. EP/Toxicity analysis of South Lagoon
sediment and soil collected
June 11, 1984

Parameter	Detection limit (mg/L)	EP/ toxicity	Concentration (mg/L)					
			6	7	8	9	10	11 ^a
Arsenic	0.25	5.0	N/D ^b	N/D	N/D	N/D	N/D	N/D
Barium	5.0	100.00	N/D	N/D	N/D	N/D	N/D	N/D
Cadmium	0.05	1.0	N/D	N/D	N/D	N/D	N/D	N/D
Chromium	0.25	5.0	N/D	N/D	N/D	N/D	N/D	N/D
Lead	0.25	5.0	N/D	N/D	N/D	N/D	N/D	N/D
Mercury	0.01	5.0	N/D	N/D	N/D	N/D	N/D	N/D
Selenium	0.05	1.0	N/D	N/D	N/D	N/D	N/D	N/D
Silver	0.25	5.0	N/D	N/D	N/D	N/D	N/D	N/D
Endrin	0.001	0.2	N/D	N/D	N/D	N/D	N/D	N/D
Lindane	0.02	0.4	N/D	N/D	N/D	N/D	N/D	N/D
Methoxychlor	0.5	10.0	N/D	N/D	N/D	N/D	N/D	N/D
Toxaphene	0.025	0.05	N/D	N/D	N/D	N/D	N/D	N/D
2,4-D	0.5	10.0	N/D	N/D	N/D	N/D	N/D	N/D
2,4,5-TP								
Silvex	0.05	1.0	N/D	N/D	N/D	N/D	N/D	N/D

^a Sample 11 is soil collected midway between the waterline and crest and berm for reference. All other samples are of lagoon sediment.

^b N/D = not detectable.

Table 10. Composite sludge sample from the South Lagoon
collected March 21, 1988

Analysis	Results (mg/kg)
Aluminum	3,550
Antimony	<1.0
Arsenic	1.08
Barium	65.1
Beryllium	0.31
Boron	105
Cadmium	11.8
Chromium	400
Cobalt	38.1
Copper	946
Iron	5,850
Lead	49.8
Magnesium	985
Manganese	144
Manganese	144
Mercury	0.81
Molybdenum	<1.0
Nickel	379
Selenium	<0.1

Table 11. Filtrate from South Lagoon sludge sample after dewatering

Analysis	Results (mg/L)
Arsenic	<0.003
Cadmium	0.003
Chromium	0.025
Copper	0.021
Lead	0.045
Nickel	0.014
Zinc	0.090
PCBs	<1

Most important, the principal organic contaminant found associated with the lagoon, 1,2-dichloroethane, is hydrophobic and conservative (probably not retained by the soil), whereas As is probably adsorbed to some extent. Thus, 1,2-dichloroethane would be expected to move faster and be more likely than As to have contaminated the groundwater in all directions. Instead, the opposite appears to be the case. Finally, well 47, which is sufficiently upgradient of the lagoon to be unaffected by lagoon seepage, also contains high levels of As.

Driller's logs for the monitoring wells provide an explanation for the lower As concentrations associated with wells along the river and west of the plant. A complete review of the logs is beyond the scope of this report, but suffice it to say that the wells containing low levels of As apparently contained little of the green reduced-clay/limonite environment prevalent elsewhere at the plant. Much of the alluvium consists of a clay described as gray, blue, or green. Such a description indicates reducing conditions and the presence of reduced iron (Bohn et al. 1979). In contrast, at some portions of the site, the clays were brown or tan, indicating more-oxidizing conditions.

For example, the lower zone of well 9, containing high levels of As, is described as "clayey silt, dark-blue gray," whereas the clayey silt in nearby well 10, which does not contain As, is described as "tan." Both descriptions were written before As was identified in the plant's groundwater. Later descriptions are more revealing. Well 81, which has high As levels, is described as "silty clay: greenish gray," whereas well 83, which has low As levels, is described as "silty clay: very dark gray, mottled with brown." Thus, mobile As is associated with reduced green or blue clay zones.

3.4 ARSENIC SPECIATION AT THE KANSAS CITY PLANT

A knowledge of the As(III)/As(V) ratio is important because it may provide information on the source and mechanism of As migration. The As(III)/As(V) ratio at the KCP was expected to be stable for

several reasons. Site geology is relatively uniform, notwithstanding small local variations in iron oxide content and overall texture. The appearance of the subsurface soils obtained during drilling indicated that reducing conditions prevailed across the site. The slow groundwater flow [5 to 15 m/year (Madril et al. 1986)] indicated that there should be little variation in redox conditions. The depositional environment for the area was uniform, stable, and low-energy. Thus, one would expect the redox conditions to be stable. Indeed, measurements of dissolved oxygen (Table 12) indicated that the entire aquifer is low in dissolved oxygen and that reducing conditions do prevail throughout the site. The high levels of iron and manganese found in the groundwater (Table 12) offers other evidence of reducing conditions. Indeed, water samples collected without acidification typically showed iron precipitate within a few minutes of collection. Note, however, that conditions are not sufficiently reducing to form sulfide, which was not detected in any of the water samples.

Because of the difficulty in analyzing for As (see Sect. 2 and Appendix A), two laboratories were requested to determine the As(III)/As(V) ratios. The laboratories were selected, in part, because they used different analytical techniques. Each laboratory's samples were filtered without air contact, cooled to 4 °C, and shipped by overnight express. Table 13 compares the results. The results do not agree: one laboratory reported only As(V), and greatly underestimated the amount of As present; the other laboratory reported accurate results for total As (based on several years of monitoring and analytical results from more than one analytical method), but the data indicated that the As(III)/As(V) ratio varied across the site.

The results were troubling because both laboratories used published techniques and analyzed splits of the same sample. One explanation that might be consistent with the failure of the analytical methods was that organic arsenicals were present. To investigate this possibility, arrangements were made to have analyses performed by a research group (Van Wagenen et al. 1987) that recently described the many pitfalls in hydride generation analyses of As. This laboratory employs an exhaustive chromatographic separation (Appendix B) to ensure that the actual As species will be quantified. These data demonstrated that

Table 12. Dissolved oxygen, iron, and manganese concentrations for selected As-containing wells at the KCP

Well No. ^a	Depth-to-water (ft)	DO (mg/L)	Fe (mg/L)	Mn (mg/L)
8U	10.52	<0.5	N/A ^b	N/A
32L	10.63	<0.5	0.2	7.2
34U	8.61	<0.5	N/A	N/A
45L	8.80	<0.5	40.1	3.9
47L	7.67	<0.5	16.8	3.3
72L	19.64	<0.5	7.8	0.4

^a Most wells at the KCP are dual-completions. "U" refers to an upper completion, and "L" refers to a lower completion.

^b N/A = no analysis performed.

Table 13. Comparison of As(III)/As(V) results (mg/L) reported by two laboratories using conventional techniques

Well	Laboratory A ^a		Laboratory B ^b		
	As III	As V	As III	As V	As (total) ^c
32L	<.025	0.038	0.002	0.001	<0.005
32L(dup)	<.025	<.025	0.002	0.000	0.003
8U	<.025	<.025	0.068	0.015	0.076
Blank	<.025	<.025	<0.001	<0.001	<0.001
45L	<.025	0.033	0.200	0.011	0.202/0.239
45L(dup)	<.025	0.026	0.124	0.026	0.206/0.175
47L	<.025	0.035	0.327	0.035	0.374/0.340
57L	<.025	0.029	0.451	0.055	0.500/0.564
9L	<.025	0.099	0.240	0.002	0.290

^a Laboratory A analyses were performed by electrochemistry (Powell 1987).

^b Laboratory B analyses were performed by selective reduction and hydride generation (Shaikh and Tallman 1978).

^c Laboratory B As-total was performed by graphite furnace atomization atomic absorption spectrometry (Hollenbach 1988).

the organic arsenicals monomethylarsonic acid and dimethylarsinic acid were not present and that all of the As was present in the reduced form of As(III), or arsenite. The fact that all of the As is As(III) is proof that the redox conditions at the KCP are reducing and that they have been so for an extended period of time (see Table 1).

3.5 SOIL ANALYSIS OF ARSENIC

Arsenic background concentrations in the soils at the facility had not been formally described until 1988 (Fleischhauer 1988). To determine the arsenic background at the KCP, data from a reconnaissance grid (Korte et al. 1985), construction sites, the E lateral, and the Old 002 Outfall sample sets were compiled. The samples in the data set included both surface and subsurface samples. Of these, one below-detection value was excluded, giving a total of 99 values for computations. The As data range from 2 to 23 ppm.

The cumulative distribution of the combined sample sets is shown in Fig. 6. This plot indicates a lower threshold of ~10 ppm. To refine this estimate, the threshold was examined over the interval of 10 to 15 ppm, and statistics were calculated on all data less than or equal to these values. A threshold of 13 ppm gives a background distribution that is approximately normally distributed (skewness and kurtosis near zero and nonsignificant). Data less than or equal to the standard threshold average 7 ppm. Statistics for background data are given in Fleischhauer (1988). The development of the background value was conservative in that it included some As values above the threshold without including an explanation.

Published data on As abundance were presented in Tables 1 and 2. The estimated KCP background of 7 ppm is comparable with estimates for shale, soil, and loess in the Missouri region (Tidball 1984). Note that the regional maximum concentrations measured in earth materials are generally higher than the maximum As concentration obtained on the KCP (23 ppm). Therefore, the KCP estimates appear to be reasonable in light of the abundance data.

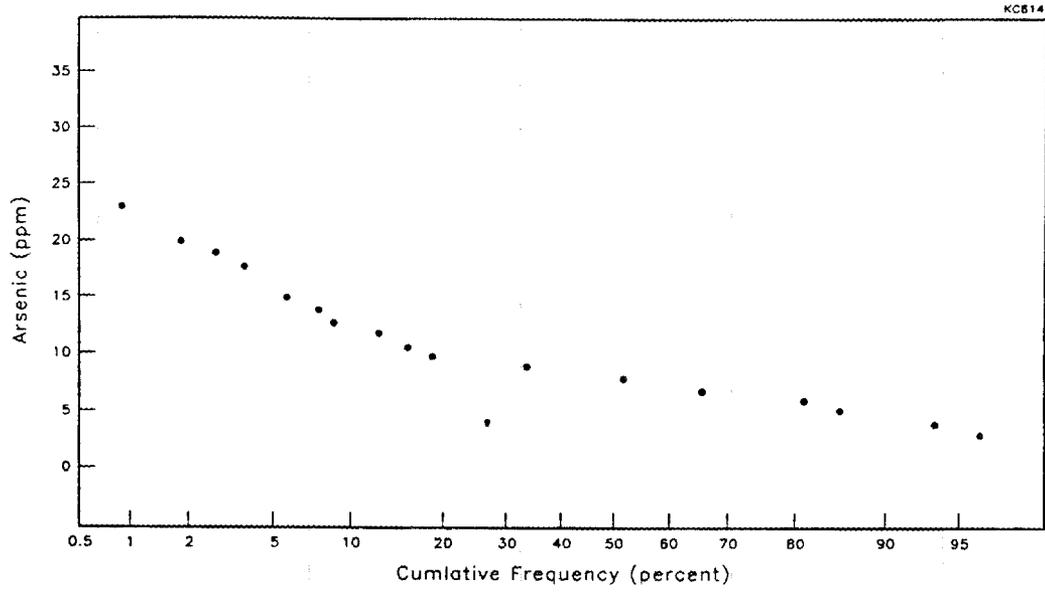


Figure 6. Plot of cumulative distribution of As in soils data from the KCP.

The fact that As is not found in elevated concentrations in the surface soil (Korte et al. 1985) is significant evidence that the presence of As is not the result of disposal at the plant. Hess and Blanchar (1976) studied the fate of As compounds, including lead arsenate, that were applied to soils in nearby Independence, Missouri, and found that As accumulated in the soil although reducing conditions had the ability to mobilize As as As(III). Boyle and Jonasson (1973) also reported that "soils sprayed with arsenicals tend to retain their arsenic contents." Thus, some accumulation in KCP soils should be evident if surface disposal was responsible for the As in the groundwater.

3.6 EXPLANATION FOR SPORADIC HIGH VALUES FOR ARSENIC IN SOIL

The analyses of the limonite (Table 14) show that limonite is an accumulator of As and can account for occasional higher values observed in some of the bulk soil samples. Geologists installing wells at the site noted the presence of limonite stains on the subsoils. Often, the presence of the limonite was striking because it was part of an assemblage of dark-green reduced clay stained with the orange, oxidized limonite. Because the limonite was such a minor constituent, not all of the geologists noted it in their logs, but all who performed much drilling at the site remembered seeing it from time to time. Because limonite might adsorb arsenic, an attempt was made to collect limonite from subsequent borings. These borings were not representative of the entire site, and the limonite was separated by physical means (e.g., using a tweezers under a microscope).

3.7 SEDIMENT ANALYSIS OF ARSENIC

A stream sediment survey (Fleischhauer et al. 1987) conducted around the plant and its environs also demonstrates that there is no As contamination from the KCP. Maximum As values from quarterly samples at

Table 14. Arsenic in limonite separates from the KCP

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

a number of locations (shown in Fig. 7) range from 12 to 37 mg/kg (ppm), within the range of values found for the limonite samples. Also, some of the highest results were found upgradient of the KCP; the 37-mg/kg sample was taken from a small tributary to Indian Creek upstream of the KCP. The background site on the Blue River also exceeded the contaminant threshold estimated for soil samples (14 mg/kg vs 13 mg/kg).

Seven of the sediment sampling locations were located along surface-drainage/storm-water ditches on the KCP. The maximum As values ranged from 12 to 22 mg/kg. Not unexpectedly, some of these numbers are slightly elevated over the soil results because iron oxides in streams scavenge As. Wauchope and McDowell (1984) demonstrated that Mississippi River sediments had a very large capacity, usually unfilled, to act as arsenical sinks. Indeed, Boyle and Jonasson (1973) report that "sediments ... contain the largest amount of arsenic." These authors also reported finding arseniferous limonite in sediments in Canada and Alaska. Similarly, Moore et al. (1988) reported that an aquifer had been contaminated by As from iron oxide in sediments.

4. MECHANISM FOR ARSENIC MOBILIZATION AT THE KANSAS CITY PLANT

The purpose of this section is to demonstrate that As in the groundwater is the result of the reduction of ferric oxides that had previously scavenged the As during streamflow.

The discussion to this point has demonstrated that iron oxides may be found throughout the alluvium at the KCP. These iron oxides were formed during streamflow as the alluvium was deposited and adsorbed dissolved As. As the alluvium was buried and became subject to slow groundwater movement, redox conditions became increasingly reducing, resulting in the reduction of ferric oxides to ferrous oxides and mobilization of some of the adsorbed As.

Evidence for this mechanism is available in the literature. Duell and Swoboda (1972) studied the solubility of As as conditions became more reducing. Figure 8 is reproduced from their report and shows that

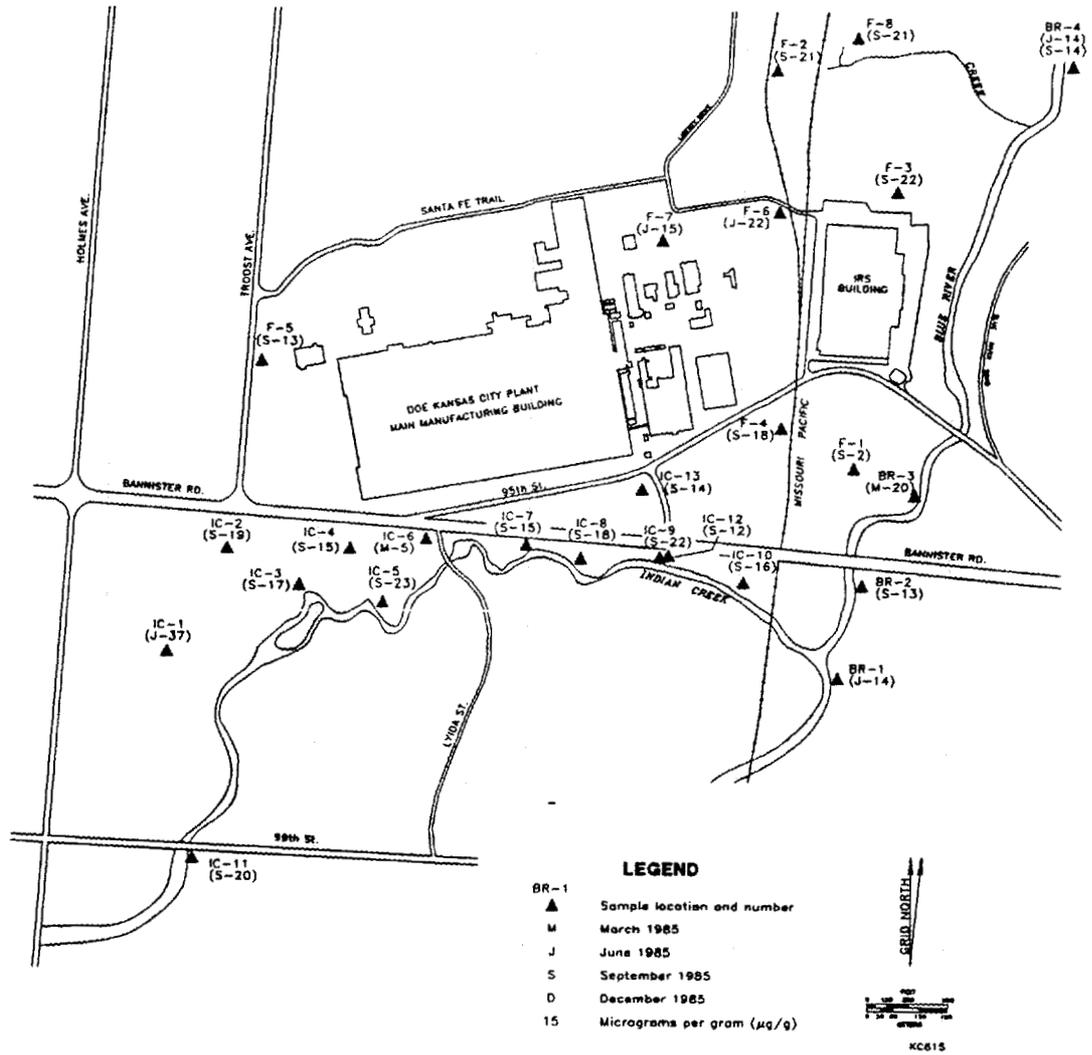


Figure 7. Maximum As concentrations in sediments surrounding the KCP.

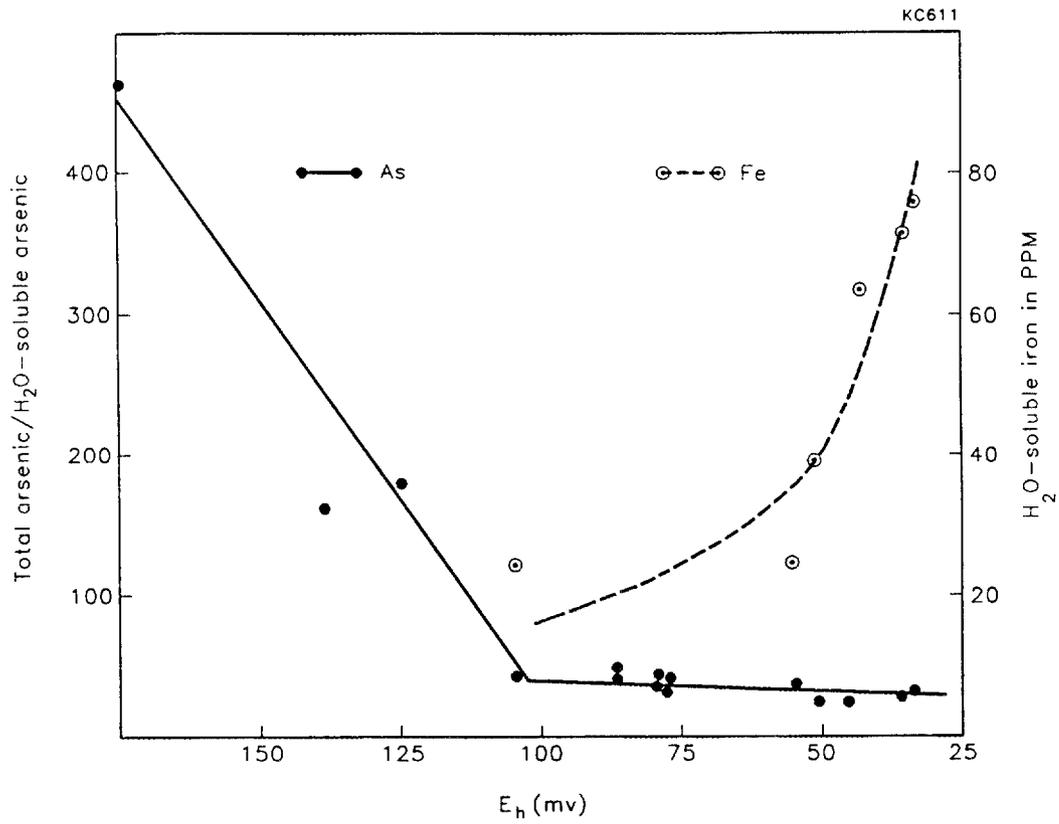


Figure 8. Ratio of the total As to soluble As as a function of the reduced environment in soil samples.

as the system becomes more reducing, the As in solution increases until an Eh of about 100 mV, when the amount of As dissolution levels off. It is important to note that the iron concentration continues to increase. Thus, one would not expect to find a direct correlation of iron content in groundwater with As in groundwater, even though the reducing conditions caused both to be mobilized. These are, in fact, the circumstances at the KCP as shown by the high iron and manganese contents in many wells (Table 4).

The proposed mechanism for As mobilization is also supported by Aggett and Kriegman (1988), who studied the dissolution of As(III) in interstitial water in the sediment of a New Zealand lake and showed that the mobilization of As in the sediments was accompanied by dissolution of iron and manganese initiated by the reduction of oxyhydroxides.

The discussion presented in Sect. 3 showed that the ratio of As in solution to adsorbed As can be a function of the amount of As present. This finding also means that any simple correlation of solution properties with As content will fail. For example, the presence of the limonite stains demonstrates that on a microscale, at least, As present in the soil is subject to some significant variations. These results are consistent with laboratory studies reported by Brannon and Patrick (1987), who found no relationship between total As sediment concentrations and As released by the sediment.

Clement and Faust (1981) have also studied the mobility of As under reducing conditions. They attributed the As mobility to the reduction of ferric iron to ferrous and also stated that the amount of As in solution was found to be controlled by more complicated phenomena than simple dissolution. These authors concluded that the amount of soluble As depends on adsorption-desorption equilibria and the amount of available As. A consideration of these facts and the variations caused by small local changes in Eh and the observed As concentration at the KCP can be attributed to natural geochemical conditions.

Finally, Clement and Faust (1981) studied some As levels in soils and sediments to determine what level of As in water might be supported. They showed that 53 ppm As in soil could produce 270 ppb As in water.

This sediment concentration is within the range of concentration of some of the limonite samples and the amount of As in solution at the KCP.

In summary, the As in groundwater at the KCP is the result of natural conditions because

1. no evidence of As contamination from facility operations exists other than the appearance of the As itself in the groundwater and
2. the sporadic appearance of the As, the relative concentration, and the oxidation state can all be explained by the geochemical behavior of As.

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Appendix A

METHOD FOR THE SEPARATION,
IDENTIFICATION, AND DETERMINATION OF
ARSENIC SPECIES IN GROUNDWATER

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REAGENTS

A 1000-ppm arsenite stock solution was prepared from Gold Label arsenic(III) oxide, 99.999% (Aldrich Chemical Co.). A weighed amount of the As_2O_3 was dissolved in ~14-mL of 15% NaOH then transferred quantitatively into a 1-L volumetric flask. The solution was then diluted to ~800-mL with distilled, deionized water, the pH adjusted to 5.1 with concentrated H_3PO_4 (85%) and diluted to the mark with distilled, deionized water.

A 1000-ppm arsenate stock solution was prepared from arsenic(V) oxide, 99% (Fisher Scientific Co.). A weighed amount of As_2O_5 was dissolved in 7.5-mL of 2.5 M NaOH, transferred quantitatively to a 500-mL volumetric flask, and diluted to ~400-mL, and the pH adjusted to 8.1 with 6 M HCl; the solution was then diluted to the mark with distilled, deionized water.

A 1000-ppm arsenate stock solution of the disodium salt of methylarsonic acid, $\text{CH}_3\text{AsO}_3\text{Na}_2 \cdot 6\text{H}_2\text{O}$, (Pfatz and Bauer) and the sodium salt of dimethylarsinic acid, $(\text{CH}_3)_2\text{AsO}_2\text{Na} \cdot 2\text{H}_2\text{O}$, (Sigma Chemical Co.) were prepared in 0.2 M H_2SO_4 .

The 1000-ppm stock solutions were stored in polypropylene bottles at 4°C, except for the arsenite standard, which was stored at room temperature.

Sodium borohydride pellets (5/16 in. diam., 98% purity) were obtained from Alfa Products. All other chemicals were reagent grade unless specified otherwise.

ION EXCHANGE COLUMN

The ion exchange column was prepared from a 10-mL plastic serological pipet by removing the narrowed top 2 cm using a heated metal spatula. The column was clamped in a vertical position and a small plug

of glass wool was placed in the tapered end of the column. A slurry of 20- to 50-mesh Dowex 1-X8 strong anion exchange resin in deionized water was packed into the column to a height of 4.5 cm and secured with a small plug of glass wool. A slurry of 80- to 100-mesh Dowex 50W-X8 resin in deionized water was then packed into the column to a height of 12 cm above the anion exchange resin. The combined height of the cation and anion exchange resins in the column was 16.5 cm. A small plug of glass wool was placed at the top of the resin column to prevent any disturbance of the resin.

The column was washed with 20 mL 0.5 M HCl followed by 25-mL deionized water at a flow rate of 2 mL/min. The column was then equilibrated with 20 mL of 0.0058M trichloroacetic acid (TCA) at a flow rate of 2 mL/min. The flow rate of the solution through the column was controlled by a peristaltic pump that was attached to the end of the column. A 4-mL groundwater sample was loaded onto the column at a flow rate of 1 mL/min. The column was then eluted with 28 mL of 0.0058 M TCA followed by 4-mL of 0.187 M TCA, both at a flow rate of 2 mL/min. Two-milliliter fractions of the eluate were collected in graduated plastic vials. The column was eluted next with 28-mL of 1.5 M NH_3 , followed by 28-mL of 0.187 M TCA, both at a flow rate of 3 mL/min. Four-milliliter fractions of the eluate were collected until a total of 32 fractions were obtained.

The column can be regenerated by successive elution with 20-mL of 1.5 M NH_3 , 20-mL of 1.0 M HCl, 20-mL of 0.0058 M TCA. This method of regeneration may be used up to three times before repacking the column. In this work, however, a freshly packed column was used for each sample.

DIGESTION OF SAMPLE FRACTIONS

The contents of each of the vials was washed into 25-mL Erlenmeyer flasks with a minimum amount of 3.0 M HCl. One milliliter of 1% v/v sulfuric acid (0.20 M) and 2 mL 5% w/v potassium persulfate were added to each flask, and the volume of the solution in the flask was reduced

to 2- to 1-mL by heating the flasks on a hot plate. Care was taken to avoid bringing the solution to a boil. The flasks were removed from the hot plate and allowed to cool before analysis.

ANALYSIS OF SAMPLE FRACTIONS

The As(V) in each Erlenmeyer flask was reduced to As(III) by the addition of 1 mL of 20% w/v KI solution to each flask. The flasks were allowed to stand for about 30 min to ensure that the As(V) was completely reduced to As(III). The analysis was completed by reduction of the As(III) to AsH₃ using sodium borohydride, and the generated AsH₃ was converted to As atoms in a hydrogen-argon flame and determined by atomic absorption spectrophotometry.

The hydride generator consisted of a 100-mL three-neck round bottom flask, fitted with a drain tube and a stopcock. One neck of the hydride generator was fitted with a stopper into which a glass plunger was inserted. The plunger provided a means of introducing a sodium borohydride pellet (0.3 g) into the solution in the hydride generator. Nitrogen gas was bubbled through a sintered glass frit at the end of a tube that was inserted through the top neck in the hydride generator. The generated arsine gas was swept out through an exit tube, also in the top neck of the hydride generator into the hydrogen-argon flame of a Thermo Jarrel-Ash Video 12E atomic absorption spectrophotometer equipped with a Hamamatsu R166 solar blind detector. The burner used in this work had a standard three-slot burner head, and the hydrogen and argon flow rates to the burner were maintained at 4 and 6 L/min respectively, by a Matheson flowmeters. The As hollow cathode lamp was operated at 5 mA, and the transmittance was monitored at 193.7 nm at a slit width of 1.0 mm.

The concentration of As(III) in each of the samples was determined as follows. After the wet digestion and reduction with KI solution, the solution in the Erlenmeyer flask was transferred into the hydride generator with the aid of two 5-mL aliquots of 3 M HCl. The nitrogen gas was bubbled continuously at 2 L/min through the sintered glass

frit, which was positioned just below the surface of the solution. The NaBH_4 pellet was dropped into the solution using a plunger, and the arsine gas formed was swept into the flame. The detector response was monitored on the video display and recorded on a strip-chart recorder.

A calibration curve for arsenic(III) standards was obtained by employing this procedure. The linear portion of the calibration curve lies between 20- and 500-ppb As. A standard solution containing 200 ppb of all four As species was separated by using the ion exchange column followed by digestion, reduction with KI, and analysis using the hydride generation technique. Although it was possible to separate all four As species by this method, an overlap existed between the As(III) peak and the monomethyl arsonic acid peak.

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