# Characterization of Ground-Water Chemistry in the Area of an Alcohol Production Facility in Western Kansas

A report for the
Kansas Department of Health and Environment
and an Alcohol Production Facility

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# EXECUTIVE SUMMARY

Monitoring of ground-water quality in the area of an alcohol production facility in Wichita County, Kansas, found arsenic concentrations in the ground water of >100 µg/L that substantially exceeded the maximum contaminant level for drinking water (10 µg/L). The Kansas Department of Health and Environment and the alcohol facility requested the assistance of the Kansas Geological Survey in interpreting the source of and processes controlling the arsenic in the ground water. Wastewater from the alcohol facility placed in surface ponds at the site has seeped into the subsurface to the underlying High Plains aquifer as indicated by the higher chloride concentration in the wastewater and ground water than background for the aquifer. The arsenic content of the wastewater is not large enough to be the source of the high arsenic concentration in the contamination plume downgradient of the wastewater ponds.

The high-arsenic ground-water plume has a near neutral pH and contains low or undetectable concentrations of sulfate and nitrate and relatively high concentrations of dissolved iron and manganese. Although the pH of the wastewater influent is acidic, the buffering capacity of the soil moisture and soil or sediment in the unsaturated zone and the ground water is large enough to neutralize infiltrating wastewater. The source of the high dissolved arsenic in the ground water is interpreted as primarily arsenic released from ferric oxyhydroxide coatings on precipitates in sediments within the saturated zone while these oxyhydroxides were chemically reduced and dissolved, as indicated by the high positive correlation between dissolved arsenic and iron contents and negative correlation of dissolved arsenic with sulfate and nitrate contents of the ground water. Some additional arsenic could be derived from reduction and dissolution of manganese oxides. Biochemical oxidation of dissolved organic matter in the wastewater seeping into the subsurface is interpreted as the driving mechanism producing the chemically reducing conditions. When the dissolved oxygen in the unsaturated zone and in the ground water was largely consumed, further biochemical oxidation of the dissolved organic matter derived its oxygen from the reduction of sulfate and nitrate dissolved in the ground water and iron and manganese oxyhydroxide in the sediment. The acidic pH of the wastewater infiltrating through the unsaturated zone before neutralization could possibly have initially contributed to the leaching of arsenic from the oxyhydroxides in the sediment. Another possible mechanism releasing arsenic from the sediment to the ground water is exchange of dissolved phosphate from the wastewater with arsenic adsorbed on the subsurface sediment. However, there were no available data for the phosphate content of the wastewater or the contaminant plume.

The arsenic contents of the surface soil and subsurface sediment at the alcohol facility are in the typical ranges for soils and unconsolidated sediments. The dissolved arsenic and iron concentrations in the contaminated ground water amount to substantially less than one percent of the total arsenic and iron contents of the subsurface sediment. The arsenic, iron, and aluminum contents of the subsurface sediment suggest that most of the arsenic was released from iron oxyhydroxides associated with the sandier parts of the strata.

The plume of high-arsenic ground water should continue to migrate as long as a chemically reducing environment exists along the front of the plume. This will depend on the amount of degradable, dissolved organic matter remaining in the plume front relative to the rate of essentially complete degradation of the dissolved organics. If the amount of degradable

organic matter becomes very small and the rate of mixing of precipitation recharge containing dissolved oxygen is great enough to maintain a high oxidation potential at the front of the plume, then the dissolved iron and manganese will oxidize and precipitate as oxyhydroxides in the sediment. This would then allow readsorption of the arsenic on the sediments and decrease the dissolved arsenic concentration.

The results of this study suggest that the generation of high arsenic concentrations in ground water may not be unusual where wastewaters with large amounts of dissolved organic matter are applied at the surface in sufficient quantities to substantially increase recharge to unconsolidated aquifers If enough dissolved organic matter is introduced to appreciably decrease the oxidation potential of the ground water and reduce and dissolve iron oxyhydroxides in the sediment, then bound arsenic can be released. High-arsenic ground waters could also potentially be generated under other sources of organic matter such as landfills and spills and leaks of organics such as hydrocarbons. Sediments of the High Plains and alluvial aquifers in which volcanic ash was deposited could have higher arsenic contents and possibly release more arsenic to ground waters under chemically reducing conditions than sediments without ash.

## INTRODUCTION

Monitoring of ground-water quality in the area of an alcohol production facility nearby and to the east of Leoti in Wichita County, Kansas, found arsenic concentrations in the ground water sampled at some well locations that substantially exceeded the maximum contaminant level (MCL) for drinking water (10 µg/L). The Kansas Department of Health and Environment (KDHE) and the alcohol facility requested the assistance of the Kansas Geological Survey (KGS) in interpreting the geochemistry of the ground water because of uncertainties in determining the source of and processes controlling the arsenic in the ground water. The alcohol facility, a consultant for the facility, and the KDHE provided data for water and soil analyses and other information related to monitoring and water-supply wells at the facility and nearby area. This report discusses the water chemistry and explains the most probable source of the arsenic found in the ground water and the processes expected to govern the arsenic fate. Chemical data from QWAL Laboratories for samples prior to 2002 and included in the information provided to the KGS were not used in this report because the laboratory lost its certification in Kansas.

Wastewater from the alcohol production facility is placed in surface ponds at the site. The wastewater can slowly seep into the subsurface and enter the ground water in the underlying High Plains aquifer as indicated by chemical data for samples from water-supply and monitoring wells in the downgradient direction of ground-water flow from the ponds.

## CHARACTERISTICS OF GROUND WATER IN THE GENERAL STUDY AREA

The alcohol production facility is located in Sec. 17, T. 18 S., R. 36 W. over the High Plains aquifer, which provides water supply for the facility operation. The ground water is used for irrigation and municipal purposes in the region. The depth to bedrock within the 9 mi$^2$ area surrounding the facility ranges from 160 to 193 ft below land surface based on water-well logs available on the KGS WWC-5 web site (http://www.kgs.ku.edu/Magellan/WaterWell/index.html). The depth to bedrock at the alcohol facility is 155 to 175 ft.

Water levels have slowly declined in the High Plains aquifer in the region during the last few decades from the consumptive pumping of ground water. Most of the water use in the region is for irrigation. Water levels in long-term monitoring wells within three miles of the facility have declined from over 22 ft to almost 60 ft from the mid-1960s up to 2007 based on winter measurements (KGS WIZARD online database, http://www.kgs.ku.edu/Magellan/WaterLevels/index.html). The depth to the water table underlying the alcohol facility was between 137 and 144 ft below land surface in the fall of 2005. Thus, the current saturated thickness of the High Plains aquifer at the facility is generally in the range of 20-30 ft. Water-well logs of the aquifer sediments penetrated by monitoring wells at the site primarily show zones of fine to coarse sand and some gravel alternating with layers of sandy clay to clay. The general direction of ground-water flow in the region is towards the east (Bohling and Wilson, 2006).

Ground water in the general area around the alcohol facility is fresh, with a total dissolved solids concentration in the range of 260-400 mg/L based on values computed from the analyses of water sampled from domestic, municipal, and irrigation wells listed in Table 1. The chemical type is calcium-bicarbonate to calcium, magnesium-bicarbonate. Chloride and sulfate concentration ranges for the well-water samples in Table 1 are 12-76 mg/L and 29-101 mg/L, respectively. The Kansas Department of Health and Environment determined arsenic in samples from municipal wells of the City of Leoti to the west of the alcohol facility; the arsenic content range was 1.4-4.8 µg/L, which is below the MCL of 10 µg/L for drinking water.

## CHEMICAL CHARACTERISTICS OF FACILITY INFLUENT WATER

Mash water from the alcohol facility has been placed in settling ponds next to the alcohol generation operation. The ponds were initially unlined but later lined with clay. The water influent to the ponds has been moderately acidic as indicted by a pH range of 3.6-4.4 units measured from 2002 to 2007 (Table 2). The cells in the table in which values are not listed for sodium, chloride, and sulfate concentrations represent data that were deemed to have too high an error to be representative based on comparison to the rest of the values and sodium/chloride and sulfate/chloride ratios that did not fit those for the other analyses. The chloride and sulfate concentration ranges in the influent for 2002-2007 were 100-413 mg/L and <1-208 mg/L, respectively. The chloride content of the influent has been greater than expected for uncontaminated ground waters from the High Plains aquifer surrounding the facility area (Table 1). The influent sulfate concentration has often been in the general range of uncontaminated ground water in the area, although it sometimes has been lower and higher than the values in Table 1. Ranges for ammonium ion and nitrate in the influent during the sampling period in Table 2 have been <1-29.8 mg/L and <1-27.8 mg/L, respectively. The presence of both ammonium ion and nitrate together suggests that the oxidation potential of the water has been transitional between reducing and oxidizing; either the oxidation potential has been more reducing and ammonium ion was being oxidized to nitrate or vice versa.

Arsenic was not measurable in the pond influent samples collected since January 2002. However, the detection limit for the samples for which arsenic was determined ranged substantially. In general, the analyses suggest that the arsenic content in the influent has probably been <50 µg/L and could have been as low as <10 µg/L. The iron and manganese concentrations in the influent have been high (ranges of 743-26,700 µg/L and 763-2,240 µg/L, respectively). However, much of this iron and manganese could have been associated with particulates included in the chemical analysis. The one sample for which iron and manganese values exist and that was filtered had substantially lower iron and generally lower manganese concentrations than the other samples. Although not determined, a substantially greater amount of organic matter is expected to have been dissolved in the influent than naturally present in the ground water in the High Plains aquifer underlying the site. Dissolved phosphate would also be expected to be higher in the mash water than in the natural water of the High Plains aquifer.

Table 1. Chemical data for ground water from supply wells in the general area of the Leoti alcohol facility. Explanations for selected column headings are Sp.C. (specific conductance), Ca (calcium), Mg (magnesium), Na (sodium), $HCO_3$ (bicarbonate), Cl (chloride), $SO_4$ (sulfate), $NO_3$-N (nitrate-nitrogen), Al (aluminum), As (arsenic), Fe (iron), Mn (manganese), mg/L (milligram per liter), and µg/L (microgram/liter).

| T-R-S Location | Well type | Well number | Well depth, ft | Date | Data source | Sp.C. µS/cm | pH, lab | Ca mg/L | Mg mg/L | Na mg/L | $HCO_3$ mg/L | Cl mg/L | $SO_4$ mg/L | $NO_3$-N mg/L | Al µg/L | As µg/L | Fe µg/L | Mn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 18S-37W-13DDC | Domestic | | 98 | 10/14/47 | KGS | | | 56 | 22 | 23 | 189 | 40 | 42 | 5.2 | | | 30 | |
| 18S-37W-13CCA | Public supply | Leoti #11 | 173 | 04/25/95 | KDHE | 768 | 7.69 | 71.8 | 24.8 | 21.0 | 172 | 64.6 | 94.0 | 5.0 | 1.6 | 2.4 | 17 | 1.3 |
| 18S-37W-13ACA | Public supply | Leoti #8 | 187 | 04/25/95 | KDHE | 555 | 8.05 | 47.9 | 16.9 | 18.4 | 166 | 33.8 | 35.1 | 6.2 | 2.1 | 3.9 | 28 | <1 |
| 18S-37W-13CBA | Public supply | Leoti #7? | 174 | 04/25/95 | KDHE | 766 | 7.67 | 70.7 | 24.7 | 21.1 | 179 | 56.8 | 98.2 | 6.9 | 1.3 | 1.4 | <10 | <1 |
| 18S-37W-14DDC | Public supply | Leoti #10 | 174 | 04/25/95 | KDHE | 564 | 7.65 | 52.2 | 17.1 | 16.1 | 167 | 30.3 | 55.7 | 4.0 | 6.0 | 2.5 | 38 | <1 |
| 18S-37W-24ADD | Public supply | Leoti #5 | 165 | 04/25/95 | KDHE | 796 | 7.60 | 72.8 | 25.1 | 21.0 | 169 | 76.2 | 87.8 | 5.9 | 2.7 | 1.8 | 17 | <1 |
| 18S-37W-24BAC | Public supply | Leoti #14 | 107 | 04/25/95 | KDHE | 673 | 7.64 | 60.3 | 26.1 | 17.7 | 254 | 31.2 | 59.3 | 1.4 | 3.5 | 4.8 | 42 | <1 |
| 18S-37W-03CCC | Irrigation | | | 07/30/74 | KGS | 660 | 7.3 | 55 | 26 | 32 | 185 | 33 | 101 | 5.2 | | | 40 | 7 |
| 18S-36W-02DCB | Irrigation | | | 07/30/74 | KGS | 500 | 7.6 | 38 | 19 | 27 | 195 | 12 | 50 | 2.3 | | | 26 | 2 |
| 18S-36W-09BBB | Irrigation | | | 07/30/74 | KGS | 620 | 7.4 | 51 | 25 | 30 | 227 | 22 | 76 | 3.4 | | | 69 | 3 |
| 18S-36W-15DAD | Irrigation | | | 07/30/74 | KGS | 525 | 7.8 | 46 | 20 | 25 | 184 | 22 | 46 | 4.7 | | | 999 | 4 |
| 18S-36W-29ABB | Irrigation | | | 07/30/74 | KGS | 430 | 7.4 | 38 | 14 | 20 | 181 | 12 | 29 | 3.4 | | | 8 | 1 |
| 18S-36W-18BBA | Irrigation | | | 1988 | KGS | 510 | 7.65 | 47.8 | 20.5 | 22.3 | 184 | 28.5 | 51.4 | 4.9 | | | | |
| 18S-36W-18BBB | Irrigation? | | | 1999 | KGS | 530 | 7.45 | 50.4 | 21.9 | 23.3 | 182 | 32.2 | 50.9 | 5.4 | | | | |

Table 2. Chemical data for influent water to the settling ponds in the Leoti alcohol facility. Explanations for selected column headings not given in the caption for Table 1 are $NH_3$-N = ammonia-nitrogen and TKN – total Kjeldahl nitrogen (sum of organic and ammonia nitrogen). Cells with an asterisk indicate that the original values appear to be erroneous and are not listed.

| Date | Filtered | Lab | pH lab | Na mg/L | Cl mg/L | Na/Cl ratio | $SO_4$ mg/L | $NH_3$-N mg/L | $NO_3$-N mg/L | TKN mg/L | As µg/L | Fe µg/L | Mn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 01/15/02 | | Pace | 3.56 | 26.8 | 99.7 | 0.269 | 44.0 | 22.7 | 36.8 | 4,790 | <5 | 3,370 | 896 |
| 03/29/02 | | Pace | 3.98 | 55.5 | 175 | 0.317 | 208 | 8.3 | <1 | 4,970 | <10 | 5,200 | 1,920 |
| 06/26/02 | | Pace | 3.57 | 44.2 | 264 | 0.167 | 61.9 | 15.5 | <1 | 2,070 | <5 | 26,700 | 1,760 |
| 09/17/02 | | Pace | 3.65 | 64.2 | 222 | 0.289 | 61.1 | 16.7 | <20 | 4,480 | <500 | 8,390 | 1,380 |
| 01/07/03 | | Pace | 3.74 | 91.8 | 220 | 0.417 | 113 | 13.3 | <1 | 702 | <1000 | 2,160 | 1,730 |
| 04/07/03 | | Pace | 3.71 | 59.6 | 124 | 0.481 | 221 | 17.9 | 5.31 | 607 | <100 | 4,850 | 859 |
| 07/17/03 | Yes | Pace | 3.69 | 95.4 | 239 | 0.399 | 72.3 | 7.6 | <1 | 566 | <500 | 743 | 1,370 |
| 10/01/03 | | Pace | 4.32 | * | * | | <1 | 7.3 | <1 | 4,940 | <10 | 10,400 | 1,610 |
| 12/18/03 | | Pace | 3.86 | 123 | 228 | 0.539 | 206 | 26.2 | <20 | 2,600 | <500 | 2,970 | 1,230 |
| 03/18/04 | | Pace | 3.94 | 74.1 | 274 | 0.270 | 93.8 | 9.2 | <1 | 670 | <10 | 1,660 | 1,860 |
| 06/10/04 | Yes | Pace | 4.40 | 129 | 189 | 0.683 | 53.5 | 13.4 | 2.11 | 375 | | | |
| 10/20/04 | | Pace | 4.35 | 120 | 216 | 0.556 | <1 | | <1 | 621 | <10 | 908 | 763 |
| 12/29/04 | No | Pace | 3.97 | 47.0 | 196 | 0.240 | 84.6 | 16.7 | <1 | 712 | | | |
| 03/17/05 | | Pace | 4.15 | 487 | 413 | 1.179 | 158 | 17.4 | 2.47 | 2,150 | <50 | 1,920 | 1,830 |
| 04/08/05 | | Pace | 3.61 | 42.6 | 361 | 0.118 | 106 | <4 | 1.17 | 214 | | | |
| 06/20/05 | | Pace | 3.76 | 77.6 | 269 | 0.288 | * | 12.3 | <50 | 2,530 | <50 | 2,450 | 2,240 |
| 09/12/05 | No | Pace | 3.93 | 138 | 267 | 0.517 | 41.4 | <1 | 1.23 | 251 | | | |
| 12/28/05 | | Pace | 3.90 | 215 | 322 | 0.668 | 75.6 | 8.5 | 27.8 | 5,790 | | | |
| 04/04/06 | No | Pace | 4.40 | * | 178 | | 125 | 7.4 | <1 | 1,470 | | | |
| 06/15/06 | | Pace | 4.30 | 60.3 | 198 | 0.305 | <20 | 15.8 | <1 | 3,870 | | | |
| 09/13/06 | No | Pace | 4.10 | 69.3 | 300 | 0.231 | 130 | 29.8 | <20 | 1,390 | | | |
| 01/08/07 | No | Pace | 4.20 | 54.5 | 177 | 0.308 | 29.6 | 10.4 | <20 | 3,410 | | | |
| 09/27/07 | No | Pace | 3.80 | 87.9 | 222 | 0.396 | 79.6 | 98.5 | <1 | 491 | | | |

## WATER-SUPPLY AND MONITORING WELL CHARACTERISTICS

There are three water-supply wells (WW 1, 2, and 5) and eight monitoring wells (MW 1 through 8) within the alcohol facility area. Water-supply well WW 3 is a domestic well immediately adjacent to the east side of the facility area and WW 4 is a domestic well that is about a mile east of the facility. Water samples have been collected periodically from these wells in addition to those within the facility area. Table 3 lists the location and available construction information for the wells. The screened intervals of all of the wells in the facility area extend to or near the bottom of the well within the saturated thickness of the High Plains aquifer at the location. The screened intervals of the monitoring wells are 30 ft in comparison with 10 to 40 ft for the water-supply wells within the facility. The top of the screened intervals of water-supply well WW 2 and all of the monitoring wells except WW 8 are currently above the aquifer water level.

## CHEMICAL DATA FOR WATER-SUPPLY AND MONITORING WELL SAMPLES

The samples from the water-supply and monitoring wells have been analyzed for selected chemical properties, a few major and minor inorganic constituents, and many minor and trace metals. Tables 4 and 5 list only that data for field and laboratory pH, the concentrations of the major inorganic constituents sodium, chloride, and sulfate, the minor inorganic constituent nitrate, and the metals aluminum, arsenic, iron, and manganese. One sodium, one sulfate, and four chloride values in samples from MW 1, 2, and 5 appear to be anomalous based on comparison of concentrations and ratios (such as sodium/chloride) with other samples, and are not listed in Table 5. For example, the sodium and chloride values reported for the most recent sample (9/26/07) from MW 5 are 275 and 141 mg/L, respectively, which appear to have been reversed in terms of expected concentrations relative to the other sample data for this well.

### Characterization of Sample Representativeness

The most representative chemical data for interpretation of the geochemical controls on the concentrations of inorganic constituents and metals are for the dissolved concentrations of these substances. Analysis of samples in which significant amounts of suspended sediment exist and for which the analytical methods include acidification of the sample would be expected to give results with higher concentrations of selected constituents, especially metals, than had been in true solution in the water before sampling. Careful filtration of samples in the field followed by preservation are standard approaches for achieving samples suitable for measurement of dissolved metals representative of in-situ water chemistry. Low-flow pumping, as long as it produces ground water representative of the formation outside of the well screen, reduces the amount of suspended sediment in a sample and speeds field filtration because the filter units do not become clogged with large amounts of sediment.

Water-supply wells are usually pumped frequently enough that nearly all loose aquifer sediment has been removed from the gravel packs prior to sampling. Monitoring wells, especially if not developed extensively, can yield substantial amounts of particulates during sampling until their development removes loose sediment within the screen and casing and fine

Table 3. Construction information for water-supply and monitoring wells within the Leoti alcohol facility or associated with the study. The letter representations for the section quarters in the location designation are A = NE, B = NW, C = SW, D = SE. The quarters start from the largest immediately after the section number and decrease in size to the right. Water-supply wells WW 3, 4, and 5 are also named the Green, Coronado, and King wells, respectively.

| Well number | Location | Water use | Depth, ft | Screened interval, ft | Casing diameter, inches |
|---|---|---|---|---|---|
| WW 1 | 18S-36W-17CCC | Domestic | 172 | 152-162 | 16 |
| WW 2 | 18S-36W-17CCC | Industrial | 165 | 121-161 | 16 |
| WW 3 | 18S-36W-17DCC | Domestic | 165 | 145-165 | 5 |
| WW 4 | 18S-36W-16DCB | Domestic | 170 | Estd. 20 | 5 |
| WW 5 | 18S-36W-17CCC | Domestic | NA | NA | 5 |
| MW 1 | 18S-36W-17CBC | Monitoring | 150.1 | 118.3-148.3 | 4 |
| MW 2 | 18S-36W-17CCA | Monitoring | 159.8 | 127.2-157.2 | 4 |
| MW 3 | 18S-36W-17CDB | Monitoring | 154.1 | 121.5-151.5 | 4 |
| MW 4 | 18S-36W-17CDA | Monitoring | 160.9 | 129.2-159.2 | 4 |
| MW 5 | 18S-36W-17CCA | Monitoring | 152.0 | 120.9-150.9 | 4 |
| MW 6 | 18S-36W-17CDC | Monitoring | 169 | 138.3-168.3 | 4 |
| MW 7 | 18S-36W-17CDD | Monitoring | 173 | 133-163 | 4 |
| MW 8 | 18S-36W-17CDA | Monitoring | 165 | 145-165 | 4 |

sediment in the gravel pack close to the well screen. Various water collection and preservation approaches were used during the sampling of the wells associated with the alcohol facility. The sample collection methods for the monitoring wells included pumping, with the later samples collected using a low-flow pump dedicated to each well. Particulates associated with water pumped from wells in the High Plains aquifer are expected to be mainly clay and silt derived from the sediments of the aquifer, which are primarily unconsolidated clay, silt, sand, and gravel. The clays are aluminosilicates and the silt is largely quartz (silica), although iron and aluminum oxides can also coat silt or sand (Zachara et al., 1995). Thus, water analyses for metals that involve addition of acid for sample preservation before the analytical procedure should have higher aluminum concentration if suspended particulates were present in the sample because the acid could leach some aluminum from the clay and aluminum oxide coatings. Filtration through a membrane filter in the field before acidification should have removed essentially all of the clay and silt, thus resulting in a very low aluminum concentration in the analysis. Dissolved aluminum in ground water at a near neutral pH would be expected to be non-detectable at the detection limits reported for the sample analyses.

Table 4. Chemical data for ground-water samples collected from the water-supply wells at the Leoti alcohol facility. Explanations for selected column headings are given in the caption for Table 1.

| WW no. | Date | Filtered | Lab | pH lab | Na mg/L | Cl mg/L | Na/Cl ratio | $SO_4$ mg/L | $NO_3$-N mg/L | Al µg/L | As µg/L | Fe µg/L | Mn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 03/29/02 | | Pace | | 39.0 | 84.0 | 0.464 | | 1.90 | <75 | 15.2 | 6,960 | 633 |
| 1 | 06/26/02 | No | Pace | | 39.3 | | | | | <75 | <10 | 4,500 | 566 |
| 1 | 06/26/02 | Yes | Pace | | | | | | | <75 | <10 | 1,330 | 552 |
| 1 | 09/17/02 | | Pace | | 41.4 | | | | | <75 | <10 | 847 | 475 |
| 1 | 01/07/03 | No | Pace | | 46.1 | 89.5 | 0.515 | | <1 | <75 | <20 | 1,330 | 658 |
| 1 | 04/07/03 | Yes | Pace | | 49.4 | 96.1 | 0.514 | | <1 | <75 | <10 | 747 | 753 |
| 1 | 07/17/03 | Yes | Pace | | 49.9 | 98.6 | 0.506 | | <1 | <75 | <10 | 236 | 886 |
| 1 | 10/01/03 | No | Pace | | 54.0 | 93.2 | 0.579 | | <1 | <75 | <10 | 1,420 | 1,180 |
| 1 | 12/18/03 | Yes | Pace | | 49.2 | 96.5 | 0.510 | | <1 | <75 | <10 | 1,160 | 1,140 |
| 1 | 03/18/04 | Yes | Pace | | 47.9 | 108 | 0.444 | | <1 | <75 | <10 | 1,830 | 1,240 |
| 1 | 10/20/04 | Yes | Pace | 6.78 | 44.7 | 102 | 0.438 | 55.6 | <1 | <75 | <20 | 3,880 | 1,590 |
| 1 | 03/18/05 | Yes | Pace | 6.84 | 46.7 | 93.2 | 0.501 | 67.7 | 1.54 | <75 | <20 | 4,230 | 1,520 |
| 1 | 09/12/05 | Yes | Pace | 7.23 | 43.7 | 87.1 | 0.502 | 72.7 | 1.53 | <75 | 9.36 | 4,520 | 1,590 |
| 1 | 10/19/05 | Yes | Pace | 7.00 | 42.2 | 97.4 | 0.433 | 52.7 | <1 | <75 | 8.98 | 4,280 | 1,490 |
| 1 | 04/05/06 | No | Pace | 6.90 | 51.3 | 75.7 | 0.678 | 43.1 | 1.50 | <75 | 6.28 | 3,940 | 1,630 |
| 1 | 09/13/06 | No | Pace | 6.80 | 40.2 | 77.4 | 0.519 | 54.6 | 2.1 | <75 | 7.01 | 4,010 | 1,360 |
| 1 | 04/04/07 | Yes | Pace | 6.90 | 35.6 | 75.2 | 0.473 | 62.4 | 3.9 | <75 | 4.7 | 159 | 1,150 |
| 1 | 09/27/07 | Yes | Pace | 6.90 | 44.6 | 107 | 0.417 | 20.9 | <1 | <75 | 10.8 | 6,130 | 1,820 |
| | | | | | | | | | | | | | |
| 2 | 03/29/02 | | Pace | | 40.1 | 88.1 | 0.455 | | 4.26 | <75 | <5 | 8,590 | 928 |
| 2 | 06/26/02 | No | Pace | | | | | | | <75 | 11.4 | 17,600 | 1,110 |
| 2 | 06/26/02 | Yes | Pace | | | | | | | <75 | <10 | 13,800 | 1,130 |
| 2 | 09/17/02 | | Pace | | | | | | | <75 | 17.8 | 15,400 | 1,210 |
| 2 | 01/07/03 | No | Pace | | 47.2 | 83.0 | 0.569 | | 4.59 | <75 | <20 | 12,100 | 1,160 |
| 2 | 04/07/03 | Yes | Pace | | 47.9 | 81.2 | 0.590 | | 6.48 | <75 | <10 | 13,500 | 1,220 |
| 2 | 07/17/03 | Yes | Pace | | 43.5 | 88.2 | 0.493 | | 4.83 | <75 | 19.0 | 15,100 | 1,250 |
| 2 | 10/01/03 | No | Pace | | 42.9 | 85.9 | 0.499 | | 4.15 | <75 | 14.8 | 13,400 | 1,290 |
| 2 | 12/18/03 | Yes | Pace | | 42.1 | 84.4 | 0.499 | | 3.44 | <75 | <10 | 16,500 | 1,350 |
| 2 | 03/18/04 | Yes | Pace | | 40.0 | 96.7 | 0.414 | | 2.84 | <75 | 13.4 | 16,500 | 1,200 |
| 2 | 10/20/04 | Yes | Pace | 6.84 | 39.0 | 95.8 | 0.407 | 68.1 | 2.99 | <75 | <10 | 19,000 | 1,450 |

Table 4. Chemical data for ground-water samples collected from the water-supply wells at the Leoti alcohol facility (continued).

| WW no. | Date | Filtered | Lab | pH lab | Na mg/L | Cl mg/L | Na/Cl ratio | $SO_4$ mg/L | $NO_3$-N mg/L | Al µg/L | As µg/L | Fe µg/L | Mn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 03/18/05 | Yes | Pace | 6.91 | 38.9 | 93.5 | 0.416 | 78.9 | 4.13 | <75 | <20 | 13,200 | 1,020 |
| 2 | 09/12/05 | Yes | Pace | 7.00 | 37.2 | 77.9 | 0.478 | 72.5 | 4.86 | <75 | 19.8 | 15,600 | 1,180 |
| 2 | 10/19/05 | Yes | Pace | 8.10 | 38.0 | 85.6 | 0.444 | 71.3 | 4.90 | <75 | 17.6 | 15,500 | 1,090 |
| 2 | 04/06/06 | No | Pace | 7.00 | 42.9 | 78.3 | 0.548 | 64.1 | 4.30 | <75 | 18.8 | 15,300 | 1,190 |
| 2 | 09/13/06 | No | Pace | 6.80 | 40.0 | 80.4 | 0.498 | 75.4 | 4.20 | 110 | 24.1 | 21,400 | 1,150 |
| 2 | 04/04/07 | No | Pace | 6.90 | 43.7 | 90.4 | 0.483 | 66.6 | 4.40 | <75 | 19.9 | 14,800 | 1,020 |
| 2 | 09/27/07 | No | Pace | 6.90 | 40.0 | 91.2 | 0.439 | 62.2 | 1.90 | <75 | 13.7 | 8,250 | 1,200 |
| | | | | | | | | | | | | | |
| 3 | 03/29/02 | | Pace | | 24.9 | 56.2 | 0.443 | | 7.70 | <75 | <5 | 151 | <7 |
| 3 | 06/26/02 | No | Pace | | 25.9 | | | | | <75 | <10 | 139 | <5 |
| 3 | 06/26/02 | Yes | Pace | | | | | | | <75 | <10 | 301 | <5 |
| 3 | 09/17/02 | | Pace | | 26.2 | | | | | <75 | <10 | <50 | <5 |
| 3 | 01/07/03 | No | Pace | | 26.9 | 51.9 | 0.518 | | 8.97 | <75 | <20 | <50 | <5 |
| 3 | 04/07/03 | Yes | Pace | | 28.0 | 58.6 | 0.478 | | 6.48 | <75 | <20 | <50 | <5 |
| 3 | 07/17/03 | Yes | Pace | | 25.8 | 56.9 | 0.453 | | 8.34 | <75 | <10 | <50 | <5 |
| 3 | 10/01/03 | No | Pace | | 28.3 | 57.4 | 0.493 | | 7.28 | <75 | <10 | <50 | <5 |
| 3 | 12/18/03 | Yes | Pace | | 27.8 | 55.2 | 0.504 | | 6.71 | <75 | <10 | <50 | <5 |
| 3 | 03/18/04 | Yes | Pace | | 27.5 | 63.0 | 0.437 | | 6.90 | <75 | <10 | <50 | <5 |
| 3 | 10/20/04 | Yes | Pace | 7.22 | 29.2 | 65.5 | 0.446 | 72.0 | 4.38 | <75 | <30 | <50 | 5.3 |
| 3 | 03/18/05 | Yes | Pace | 7.12 | 30.2 | 64.0 | 0.472 | 69.7 | 4.92 | <75 | <30 | <50 | <5 |
| 3 | 09/12/05 | Yes | Pace | 7.11 | 30.1 | 62.2 | 0.484 | 60.5 | 5.23 | <75 | <5 | <50 | 25.8 |
| 3 | 10/19/05 | Yes | Pace | 7.20 | 30.4 | 92.1 | 0.330 | 63.4 | 5.70 | <75 | <5 | <50 | 19.2 |
| 3 | 04/05/06 | No | Pace | 7.00 | 34.0 | 63.7 | 0.534 | 55.3 | 4.00 | <75 | <5 | <50 | 6.3 |
| 3 | 04/05/06 | No | Cont. | | | | | | | | <10 | | |
| 3 | 09/13/06 | No | Pace | 6.90 | 33.8 | 68.7 | 0.492 | 68.9 | 5.00 | <75 | <5 | <50 | 69.5 |
| 3 | 04/04/07 | Yes | Pace | 7.00 | 34.4 | 72.6 | 0.474 | 63.9 | 4.70 | <75 | <5 | 52.3 | 9.6 |
| 3 | 09/27/07 | Yes | Pace | 7.00 | 31.9 | 73.1 | 0.436 | 69.1 | 6.40 | <75 | <5 | <50 | 42.3 |
| | | | | | | | | | | | | | |
| 4 | 03/29/02 | | Pace | | 29.2 | 48.2 | 0.606 | | 12.2 | <75 | <5 | 93.5 | 9.7 |
| 4 | 06/26/02 | No | Pace | | 29.9 | | | | | <75 | <10 | 669 | 10.1 |
| 4 | 06/26/02 | Yes | Pace | | | | | | | <75 | <10 | 59.9 | 9.3 |

Table 4. Chemical data for ground-water samples collected from the water-supply wells at the Leoti alcohol facility (continued).

| WW no. | Date | Filtered | Lab | pH lab | Na mg/L | Cl mg/L | Na/Cl ratio | $SO_4$ mg/L | $NO_3$-N mg/L | Al µg/L | As µg/L | Fe µg/L | Mn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | 09/17/02 |  | Pace |  | 30.0 |  |  |  |  | <75 | <10 | <50 | <5 |
| 4 | 01/07/03 | Yes | Pace |  | 29.4 | 50.8 | 0.579 |  | 12.9 | <75 | <20 | 75.3 | 9.8 |
| 4 | 04/07/03 | Yes | Pace |  | 29.7 | 49.7 | 0.598 |  | 9.5 | <75 | <10 | <50 | 8.6 |
| 4 | 07/17/03 | Yes | Pace |  | 28.0 | 47.4 | 0.591 |  | 11.7 | <75 | <10 | <50 | <5 |
| 4 | 10/01/03 | No | Pace |  | 28.7 | 39.2 | 0.732 |  | 11.8 | <75 | <10 | <50 | <5 |
| 4 | 12/18/03 | Yes | Pace |  | 27.5 | 38.3 | 0.718 |  | 13.1 | <75 | <10 | <50 | <5 |
| 4 | 03/18/04 | Yes | Pace |  | 29.2 | 50.1 | 0.583 |  | 48.9 | <75 | <10 | <50 | 8.2 |
| 4 | 10/20/04 | Yes | Pace | 7.36 | 30.6 | 47.1 | 0.650 | 101 | 64.0 | <75 | <20 | <50 | 20.0 |
| 4 | 03/18/05 | Yes | Pace | 7.43 | 34.2 | 45.8 | 0.747 | 148 | 91.7 | <75 | <30 | <50 | 24.8 |
| 4 | 09/12/05 | Yes | Pace | 7.43 | 31.5 | 44.1 | 0.714 | 108 | 71.5 | <75 | <5 | 304 | 20.3 |
| 4 | 10/19/05 | Yes | Pace | 7.40 | 32.9 | 49.5 | 0.665 | 101 | 77.4 | <75 | <5 | 310 | 16.1 |
| 4 | 04/05/06 | No | Pace | 7.40 | 33.8 | 51.4 | 0.658 | 117 | 31.3 | 81 | 4.98 | 1,990 | 15.0 |
| 4 | 09/13/06 | No | Pace | 7.30 | 31.9 | 60.0 | 0.532 | 84.5 | 56.7 | <75 | 10.5 | 6,940 | 32.9 |
| 4 | 04/04/07 | Yes | Pace | 7.20 | 28.4 | 52.7 | 0.539 | 113 | 26.5 | <75 | 8.70 | 117 | 23.9 |
| 4 | 09/27/07 | Yes | Pace | 7.60 | 31.5 | 51.4 | 0.613 | 128 | 19.3 | <75 | <5 | 82.9 | <5 |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 5 | 09/12/05 | Yes | Pace | 7.30 | 54.1 | NT |  | 31.0 | 5.5 | <75 | <10 | 156 | 20.2 |
| 5 | 04/05/06 | No | Pace | 7.30 | 56.7 | 96.6 | 0.587 | 84.3 | 4.7 | <75 | <5 | 150 | 20.8 |
| 5 | 09/13/06 | No | Pace | 7.30 | 55.1 | 90.1 | 0.612 | 85.5 | 1.7 | <75 | <5 | 786 | 47.1 |
| 5 | 04/04/07 | Yes | Pace | 7.40 | 55.8 | 104 | 0.537 | 94.5 | 6.7 | <75 | <5 | 393 | 11.0 |
| 5 | 09/27/07 | Yes | Pace | 7.30 | 57.6 | 100 | 0.576 | 88.7 | 7.0 | <75 | <5 | 593 | 17.0 |

Table 5. Chemical data for ground-water samples collected from the monitoring wells at the Leoti alcohol facility. Explanations for selected column headings are given in the caption for Table 1. Cells with an asterisk indicate that the original values appear to be erroneous and are not listed.

| MW no. | Date | Sample location | Filtered | Lab | pH field | pH lab | Na mg/L | Cl mg/L | Na/Cl ratio | $SO_4$ mg/L | $NO_3$-N mg/L | Al µg/L | As µg/L | Fe µg/L | Mn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 01/15/02 | | | Pace | | | 50 | 131 | 0.382 | | 6.95 | 115 | <5 | 125 | 122 |
| 1 | 03/29/02 | | | Pace | | | 51.1 | 112 | 0.456 | | 6.62 | <75 | <5 | 140 | 98.3 |
| 1 | 06/26/02 | | No | Pace | | | 56.2 | | | | | 18,500 | <5 | 16,800 | 373 |
| 1 | 06/26/02 | | Yes | Pace | | | | | | | | <75 | <5 | 330 | 121 |
| 1 | 09/17/02 | | No | Pace | | | 51.7 | | | | | 4,220 | <10 | 3,860 | 133 |
| 1 | 09/17/02 | | Yes | Pace | | | 51.9 | | | | | <75 | <10 | 134 | 64 |
| 1 | 01/07/03 | | Yes | Pace | | | 51.9 | 103 | 0.504 | | 8.33 | 2,510 | <20 | 3,080 | 310 |
| 1 | 04/07/03 | | Yes | Pace | | | 55.2 | 91.0 | 0.607 | | 5.22 | 354 | <20 | 603 | 168 |
| 1 | 07/17/03 | | Yes | Pace | | | 53.2 | 106 | 0.502 | | 9.20 | 1,000 | 10.6 | 2,060 | 373 |
| 1 | 10/01/03 | | No | Pace | | | 55.2 | 106 | 0.521 | | 8.22 | 282 | <10 | 294 | 135 |
| 1 | 10/01/03 | | Yes | Pace | | | 55.9 | | | | | <75 | <10 | 59.7 | 134 |
| 1 | 12/18/03 | | Yes | Pace | | | 45.8 | 81.8 | 0.560 | | 6.74 | <75 | <10 | 111 | 538 |
| 1 | 03/18/04 | | Yes | Pace | | | 40.0 | 105 | 0.381 | | 6.49 | <75 | <20 | 185 | 195 |
| 1 | 10/20/04 | | Yes | Pace | | 7.01 | 48.8 | 102 | 0.478 | 129 | 4.73 | <75 | <20 | <50 | 126 |
| 1 | 03/18/05 | | Yes | Pace | | 7.07 | 49.8 | 86.9 | 0.573 | 121 | 5.82 | <75 | <20 | <50 | 103 |
| 1 | 09/12/05 | | Yes | Pace | | 7.12 | 47.6 | 93.7 | 0.508 | 123 | 5.90 | <75 | <5 | 238 | 244 |
| 1 | 10/19/05 | Top | Yes | Pace | | 7.50 | 43.9 | * | | * | <1 | <75 | <5 | <50 | 292 |
| 1 | 10/19/05 | Bottom | Yes | Pace | | 7.10 | 50.1 | 98.0 | 0.511 | 131 | 6.90 | 158 | <5 | 231 | 278 |
| 1 | 04/05/06 | Middle | No | Pace | 6.94 | 7.10 | 54.1 | 90.6 | 0.597 | 113 | 7.60 | <75 | <5 | <50 | <5 |
| 1 | 09/13/06 | Middle | No | Pace | | 7.10 | 49.1 | 86.1 | 0.570 | 121 | 7.40 | <75 | <5 | <50 | 19.3 |
| 1 | 04/04/07 | | Yes | Pace | 7.30 | 7.20 | 50.4 | 94.1 | 0.536 | 116 | 7.20 | <75 | <5 | 60.4 | 12.6 |
| 1 | 09/27/07 | | Yes | Pace | 6.79 | 7.00 | 47.8 | 95.8 | 0.499 | 113 | 5.90 | <75 | <5 | 138 | 10.3 |

Table 5. Chemical data for ground-water samples collected from the monitoring wells at the Leoti alcohol facility (continued).

| MW no. | Date | Sample location | Filtered | Lab | pH field | pH lab | Na mg/L | Cl mg/L | Na/Cl ratio | $SO_4$ mg/L | $NO_3$-N mg/L | Al µg/L | As µg/L | Fe µg/L | Mn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 01/15/02 | | | Pace | | | 121 | 257 | 0.471 | | <1 | 2,850 | 62.4 | 41,400 | 353 |
| 2 | 03/29/02 | | | Pace | | | 170 | 311 | 0.547 | | <1 | <75 | 144 | 93,300 | 1,900 |
| 2 | 06/26/02 | | No | Pace | | | 145 | | | | | 9,960 | 79 | 65,200 | 757 |
| 2 | 06/26/02 | | Yes | Pace | | | | | | | | <75 | 77.7 | 57,400 | 542 |
| 2 | 09/17/02 | | No | Pace | | | 140 | | | | | 4,210 | 113 | 49,000 | 461 |
| 2 | 09/17/02 | | Yes | Pace | | | 138 | | | | | <75 | 82.6 | 30,700 | 359 |
| 2 | 01/07/03 | | Yes | Pace | | | 147 | 300 | 0.490 | | <1 | <75 | 40.2 | 30,700 | 213 |
| 2 | 04/07/03 | | Yes | Pace | | | 127 | 292 | 0.435 | | <1 | <75 | 69.8 | 346 | 199 |
| 2 | 07/17/03 | | Yes | Pace | | | 145 | 312 | 0.465 | | <1 | <75 | 132 | 25,900 | 200 |
| 2 | 10/01/03 | | No | Pace | | | 153 | 271 | 0.565 | | <1 | 450 | 104 | 15,900 | 271 |
| 2 | 10/01/03 | | Yes | Pace | | | 152 | | | | | <75 | 120 | 28,300 | 234 |
| 2 | 12/18/03 | | Yes | Pace | | | 133 | * | | | <1 | <75 | 109 | 24,400 | 405 |
| 2 | 03/18/04 | | Yes | Pace | | | 127 | 330 | 0.385 | | <1 | <75 | 116 | 25,400 | 222 |
| 2 | 10/20/04 | | Yes | Pace | | 6.99 | 128 | 352 | 0.364 | <1 | <1 | <75 | 119 | 13,600 | 136 |
| 2 | 03/18/05 | | Yes | Pace | | 6.99 | 149 | 309 | 0.482 | <1 | <1 | <75 | 92.7 | 11,300 | 99.4 |
| 2 | 09/12/05 | | No | Pace | | 7.02 | 136 | 351 | 0.387 | 1.25 | <1 | <75 | 57.1 | 172 | 128 |
| 2 | 10/19/05 | Top | Yes | Pace | | 6.90 | 152 | * | | <1 | <1 | <75 | 111 | 234 | 275 |
| 2 | 10/19/05 | Bottom | Yes | Pace | | 6.90 | 153 | 493 | 0.310 | <1 | <1 | <75 | 198 | 210,000 | 311 |
| 2 | 04/04/06 | Middle | No | Pace | 6.80 | 6.90 | 195 | 433 | 0.450 | <1 | <1 | <75 | 166 | 16,900 | 324 |
| 2 | 09/13/06 | Middle | No | Pace | 7.20 | 6.80 | 186 | 439 | 0.424 | <1 | 8 | <75 | 216 | 21,500 | 243 |
| 2 | 04/04/07 | | Yes | Pace | 7.10 | 7.20 | 191 | 481 | 0.397 | 1.5 | <1 | <75 | 81.0 | 18,200 | 470 |
| 2 | 09/27/07 | | Yes | Pace | 6.68 | 7.00 | 190 | 573 | 0.332 | 2.1 | <1 | <75 | 25.6 | 19,600 | 539 |
| | | | | | | | | | | | | | | | |

Table 5. Chemical data for ground-water samples collected from the monitoring wells at the Leoti alcohol facility (continued).

| MW no. | Date | Sample location | Filtered | Lab | pH field | pH lab | Na mg/L | Cl mg/L | Na/Cl ratio | SO$_4$ mg/L | NO$_3$-N mg/L | Al µg/L | As µg/L | Fe µg/L | Mn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 | 01/15/02 | | | Pace | | | 143 | 341 | 0.419 | | <1 | 3,870 | 220 | 53,500 | 1,770 |
| 3 | 03/29/02 | | | Pace | | | 131 | 267 | 0.491 | | <1 | <75 | 201 | 39,700 | 944 |
| 3 | 06/26/02 | | No | Pace | | | 146 | | | | | 7,200 | 238 | 46,300 | 1,350 |
| 3 | 06/26/02 | | Yes | Pace | | | | | | | | <75 | 243 | 41,400 | 1,240 |
| 3 | 09/17/02 | | No | Pace | | | 134 | | | | | 6,500 | 245 | 33,500 | 1,140 |
| 3 | 09/17/02 | | Yes | Pace | | | 133 | | | | | <75 | 161 | 15,400 | 948 |
| 3 | 01/07/03 | | Yes | Pace | | | 126 | 343.0 | 0.367 | | <1 | <75 | 182 | 23,900 | 885 |
| 3 | 04/07/03 | | Yes | Pace | | | 124 | 298.0 | 0.416 | | <1 | <75 | 207 | 23,500 | 828 |
| 3 | 07/17/03 | | Yes | Pace | | | 123 | 332.0 | 0.370 | | <1 | <75 | 209 | 20,700 | 737 |
| 3 | 10/01/03 | | No | Pace | | | 131 | 295 | 0.444 | | <1 | 251 | 132 | 17,200 | 732 |
| 3 | 10/01/03 | | Yes | Pace | | | 120 | | | | | <75 | 182 | 20,500 | 631 |
| 3 | 12/18/03 | | Yes | Pace | | | 112 | 346 | 0.324 | | <1 | <75 | 159 | 19,700 | 685 |
| 3 | 03/18/04 | | Yes | Pace | | | 109 | 338 | 0.322 | | <1 | <75 | 145 | 22,600 | 926 |
| 3 | 10/20/04 | | Yes | Pace | | 7.00 | 109 | 279 | 0.391 | <1 | <1 | <75 | 121 | 19,000 | 924 |
| 3 | 03/18/05 | | Yes | Pace | | 6.91 | 125 | 233 | 0.536 | <1 | <1 | <75 | 135 | 24,800 | 1,020 |
| 3 | 09/12/05 | | No | Pace | | 6.86 | 76.6 | 143 | 0.536 | <1 | <1 | <75 | 45.7 | 1,160 | 444 |
| 3 | 10/19/05 | Top | Yes | Pace | | 6.90 | 66.6 | 90.8 | 0.733 | 75 | 2.2 | <75 | 18.2 | <50 | 305 |
| 3 | 10/19/05 | Bottom | Yes | Pace | | 6.80 | 99.4 | 238 | 0.418 | <1 | <1 | 98 | 158 | 20,500 | 956 |
| 3 | 04/05/06 | Middle | No | Pace | 6.62 | 6.80 | 111 | 187 | 0.594 | <1 | <1 | <75 | 145 | 26,700 | 706 |
| 3 | 04/05/06 | | | Cont. | | | | | | | | | 105 | | |
| 3 | 09/13/06 | Middle | No | Pace | 7.30 | 6.80 | 94.8 | 219 | 0.433 | <1 | <1 | <75 | 183 | 23,300 | 832 |
| 3 | 04/04/07 | | Yes | Pace | 7.10 | 7.30 | 102 | 214 | 0.478 | 1.5 | <0.1 | <75 | 57.3 | 17,100 | 815 |
| 3 | 09/27/07 | | Yes | Pace | 6.69 | 7.10 | 91.2 | 186 | 0.490 | 1.8 | <1 | <75 | 43.9 | 15,900 | 833 |
| | | | | | | | | | | | | | | | |
| 4 | 10/01/03 | | No | Pace | | | 48.3 | 48.4 | 0.998 | | | 4,420 | <10 | 5,000 | 252 |
| 4 | 10/01/03 | | Yes | Pace | | | 46.7 | | | | | 131 | <10 | 167 | 167 |
| 4 | 12/18/03 | | Yes | Pace | | | 156 | | | | | <75 | <10 | 69.5 | 7.3 |

Table 5. Chemical data for ground-water samples collected from the monitoring wells at the Leoti alcohol facility (continued).

| MW no. | Date | Sample location | Filtered | Lab | pH field | pH lab | Na mg/L | Cl mg/L | Na/Cl ratio | SO$_4$ mg/L | NO$_3$-N mg/L | Al µg/L | As µg/L | Fe µg/L | Mn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | 03/18/04 | | Yes | Pace | | | 102 | 94.2 | 1.083 | | 5.84 | 281 | <10 | 300 | 85.9 |
| 4 | 10/20/04 | | Yes | Pace | | 7.09 | 119 | 119 | 1.000 | 90.5 | 13.0 | <75 | <10 | 151 | 60.3 |
| 4 | 03/18/05 | | Yes | Pace | | 6.98 | 78.0 | 91.8 | 0.850 | 96.0 | 6.30 | <75 | <20 | 189 | 158 |
| 4 | 09/12/05 | | No | Pace | | 7.35 | 75.3 | 102 | 0.738 | 132 | 13.2 | <75 | <5 | ND | 94.5 |
| 4 | 10/19/05 | Top | Yes | Pace | | 7.20 | 49.6 | 92.5 | 0.536 | 78.9 | 2.00 | <75 | <5 | 127 | 323 |
| 4 | 10/19/05 | Bottom | Yes | Pace | | 7.10 | 49.6 | 93.2 | 0.532 | 64.3 | 1.30 | <75 | 5.96 | 230 | 327 |
| 4 | 04/04/06 | Middle | No | Pace | 6.72 | 6.80 | 46.6 | 80.5 | 0.579 | 57.9 | <1 | 210 | <5 | 242 | 325 |
| 4 | 09/13/06 | Middle | No | Pace | 7.40 | 6.80 | 45.1 | 100 | 0.451 | 55.9 | <1 | 95 | <5 | 525 | 330 |
| 4 | 04/04/07 | | Yes | Pace | 7.10 | 8.20 | 47.6 | 96.7 | 0.492 | 58.5 | <0.1 | <75 | 5.4 | 592 | 255 |
| 4 | 09/27/07 | | Yes | Pace | 6.91 | 8.40 | 44.2 | 87.3 | 0.506 | 54.9 | <1 | 172 | 5.8 | 864 | 250 |
| | | | | | | | | | | | | | | | |
| 5 | 09/30/03 | | | Cont. | | | 96.6 | 130 | 0.743 | | | | 89 | | |
| 5 | 10/01/03 | | No | Pace | | | 96.5 | 131 | 0.737 | | | 8,730 | 88.3 | 11,500 | 1,380 |
| 5 | 10/01/03 | | Yes | Pace | | | 90.8 | | | | | <75 | 72.6 | 2,310 | 1,210 |
| 5 | 12/18/03 | | Yes | Pace | | | 87.6 | | | | | <75 | 55.5 | 22,000 | 3,770 |
| 5 | 03/18/04 | | Yes | Pace | | | 94.3 | 172 | 0.548 | | <1 | <75 | 92.6 | 70,300 | 4,340 |
| 5 | 03/18/04 | | | Cont. | | | 103 | 170 | 0.606 | | | <75 | 110 | | 3,940 |
| 5 | 10/20/04 | | Yes | Pace | | 6.73 | 86.8 | 189 | 0.459 | <1 | <1 | <75 | 64.5 | 62,300 | 1,710 |
| 5 | 03/18/05 | | Yes | Pace | | 6.93 | 108 | 209 | 0.517 | <1 | <1 | <75 | 29.4 | 46,500 | 819 |
| 5 | 09/12/05 | | No | Pace | | 6.80 | 89.9 | 189 | 0.476 | <1 | <1 | <75 | 50.6 | 23,300 | 553 |
| 5 | 10/19/05 | Top | Yes | Pace | | 6.60 | 112 | 262 | 0.427 | <1 | <1 | <75 | 86.3 | 134,000 | 511 |
| 5 | 10/19/05 | Bottom | Yes | Pace | | 7.80 | 120 | 242 | 0.496 | 1.6 | <1 | <75 | 157 | 44,600 | 566 |
| 5 | 04/05/06 | Middle | No | Pace | 6.59 | 6.80 | 128 | 211 | 0.607 | <1 | <1 | 338 | 93.7 | 39,800 | 426 |
| 5 | 04/05/06 | | | Cont. | | | | | | | | | 164 | | |
| 5 | 09/13/06 | Middle | No | Pace | 6.59 | 6.80 | 115 | 291 | 0.395 | <1 | <1 | 172 | 123 | 34,600 | 318 |
| 5 | 04/04/07 | | Yes | Pace | 7.00 | 7.00 | 166 | 249 | 0.667 | 1.4 | <0.1 | <75 | 56.7 | 21,500 | 1,430 |
| 5 | 09/27/07 | | Yes | Pace | 6.63 | 6.90 | * | * | | 84.9 | <1 | 293 | 47.8 | 19,900 | 1,390 |
| | | | | | | | | | | | | | | | |
| 6 | 10/01/03 | | No | Pace | | | 87.1 | 113 | 0.771 | | | 746 | <10 | 3,170 | 1,000 |
| 6 | 10/01/03 | | Yes | Pace | | | 91.1 | | | | | <75 | <10 | 2,810 | 995 |
| 6 | 12/18/03 | | Yes | Pace | | | 123 | | | | | <75 | 10.6 | 42,900 | 5,840 |

Table 5. Chemical data for ground-water samples collected from the monitoring wells at the Leoti alcohol facility (continued).

| MW no. | Date | Sample location | Filtered | Lab | pH field | pH lab | Na mg/L | Cl mg/L | Na/Cl ratio | $SO_4$ mg/L | $NO_3$-N mg/L | Al µg/L | As µg/L | Fe µg/L | Mn µg/L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 03/18/04 | | Yes | Pace | | | 135 | 309 | 0.437 | | <1 | <75 | 32.2 | 92,600 | 6,260 |
| 6 | 10/20/04 | | Yes | Pace | | 6.98 | 115 | 298 | 0.386 | <1 | 2.13 | 189 | 24.4 | 30,800 | 1,130 |
| 6 | 03/18/05 | | Yes | Pace | | 7.04 | 127 | 312 | 0.407 | <1 | <1 | <75 | 12.1 | 19,200 | 413 |
| 6 | 09/12/05 | | Yes | Pace | | 6.73 | 147 | 386 | 0.381 | <10 | <1 | <75 | 148 | 87,400 | 1,720 |
| 6 | 10/19/05 | Top | Yes | Pace | | 6.80 | 120 | 335 | 0.358 | <1 | <1 | <75 | 56.9 | 78,800 | 624 |
| 6 | 10/19/05 | Bottom | Yes | Pace | | 6.80 | 122 | 292 | 0.418 | 12.9 | <1 | <75 | 120 | 111,000 | 683 |
| 6 | 04/05/06 | Middle | No | Pace | 6.66 | 6.80 | 175 | 337 | 0.519 | 2.1 | <1 | 184 | 125 | 57,200 | 1,030 |
| 6 | 09/13/06 | Middle | No | Pace | 7.40 | 6.80 | 165 | 336 | 0.491 | 2 | <1 | <75 | 189 | 61,400 | 1,250 |
| 6 | 04/04/07 | | Yes | Pace | 7.20 | 7.50 | 178 | 372 | 0.478 | 1.6 | <0.1 | <75 | 79.1 | 29,300 | 428 |
| 6 | 09/27/07 | | Yes | Pace | 6.70 | 7.30 | 168 | 346 | 0.486 | 3.4 | <1 | 83 | 86.4 | 22,200 | 336 |
| | | | | | | | | | | | | | | | |
| 7 | 09/12/05 | | No | Pace | | 7.59 | 69 | 297 | 0.232 | 35.9 | 8.77 | <75 | <5 | <50 | <5 |
| 7 | 10/19/05 | Top | Yes | Pace | | 7.30 | 28 | 77.8 | 0.360 | 34.5 | 4.80 | <75 | <5 | 60.3 | 342 |
| 7 | 10/19/05 | Bottom | Yes | Pace | | 8.00 | 49 | 109 | 0.452 | 24.2 | 3.40 | <75 | 6.13 | 3,420 | 1,030 |
| 7 | 04/05/06 | Middle | No | Pace | 6.73 | 6.90 | 50 | 103 | 0.488 | 20.0 | <1 | <75 | 14.3 | 9,750 | 704 |
| 7 | 09/13/06 | Middle | No | Pace | 7.80 | 6.70 | 84 | 194 | 0.431 | <1 | <1 | <75 | 31.6 | 24,700 | 935 |
| 7 | 04/04/07 | | Yes | Pace | 7.10 | 7.40 | 81.3 | 191 | 0.426 | 2.4 | <0.1 | <75 | 17.4 | 18,400 | 820 |
| 7 | 09/27/07 | | Yes | Pace | 6.77 | 7.40 | 78.7 | 182 | 0.432 | <1 | <1 | <75 | 27.1 | 21,300 | 841 |
| | | | | | | | | | | | | | | | |
| 8 | 09/12/05 | | Yes | Pace | | 6.60 | 127 | 236 | 0.538 | <5 | <1 | <75 | 87.2 | 72,600 | 4,280 |
| 8 | 10/19/05 | Top | Yes | Pace | | 6.70 | 121 | 275 | 0.440 | 2.3 | <1 | <75 | 43.8 | 33,600 | 2,460 |
| 8 | 10/19/05 | Bottom | Yes | Pace | | 6.70 | 119 | 268 | 0.444 | 2.5 | <1 | <75 | 84.9 | 114,000 | 2,600 |
| 8 | 04/05/06 | Middle | No | Pace | 6.63 | 6.90 | 136 | 229 | 0.594 | 1.9 | <1 | <75 | 173 | 76,500 | 2,210 |
| 8 | 04/05/06 | | | Cont. | | | | | | | | | 188 | | |
| 8 | 09/13/06 | Middle | No | Pace | 7.80 | 6.60 | 120 | 217 | 0.553 | <1 | <1 | <75 | 153 | 62,700 | 2,300 |
| 8 | 04/04/07 | Middle | (No) total | Pace | | | | | | | | <75 | 161 | 20,900 | 645 |
| 8 | 04/04/07 | Middle | Yes | Pace | 7.60 | 7.30 | 133 | 242 | 0.550 | <1 | <0.1 | <75 | 91.6 | 59,200 | 2,010 |
| 8 | 09/27/07 | Middle | Yes | Pace | 6.78 | 7.70 | 127 | 197 | 0.645 | <1 | <1 | <75 | 112 | 31,600 | 1,110 |

All except two of the analyses of samples from the water-supply wells (Table 4) had aluminum concentrations less than the laboratory detection limit of 75 μg/L, whether unfiltered or filtered. The two with detectable amounts (110 μg/L for WW 2 and 81 μg/L for WW 4) contained concentrations not far above the detection limit for aluminum and both of these samples were unfiltered. These values and others of less than the detection limit for unfiltered samples indicate that very little sediment was produced during pumping of the water-supply wells. However, the sample (9/13/06) from WW 2 with 110 μg/L aluminum contained the highest arsenic and iron concentrations of any of the samples from this well, and the sample (4/5/06) from WW 4 with 81 μg/L aluminum had a substantially greater iron concentration than all except one other sample (9/13/06) from this well. The sample (9/13/06) with the highest iron content from WW 4 was unfiltered and also contained the highest arsenic concentration of any of the samples from this well. The very high iron content in filtered samples from WW 1 and 2 would be present as dissolved iron. Unfiltered samples with particulates could potentially include some solid ferric oxyhydroxides that contain small amounts of arsenic. This could explain the higher arsenic contents for the 4/5/06 sample from WW 2 and the 9/13/06 sample from WW 4.

In contrast to the samples from the water-supply wells, large amounts of aluminum were measured in some of the earlier water samples from MW 1 through 3 (up to 18,500 μg/L or 18.5 mg/L). No information on whether the water was filtered or unfiltered was indicated on the original data sheets for samples up to March 29, 2002. The high aluminum content suggests that these samples were not filtered. After this date, samples that were filtered tended to contain substantially lower aluminum content than those that were unfiltered. With time, whether filtered or unfiltered, the aluminum concentration generally decreased. This suggests that both continued development of the well by pumping removed fine sediment and the low-flow sampling method used later drew in less sediment. The first samples for MW 4 through MW 6 in which aluminum content was determined were unfiltered; the aluminum concentration was substantial for each of these well samples but not generally as great as in the early samples from MW 1 through 3. Wells MW 7 and 8 are the newest monitoring wells; none of the samples from these wells contained detectable aluminum, indicating that, for the filtered samples, the filtration effectively removed fine sediment, and, for the unfiltered samples, the well development successfully removed fine sediment and/or that the low-flow sampling method used did not draw in fine sediment. All except eight of the samples collected from all of the monitoring wells on and after October 1, 2003, and which were filtered and analyzed by Pace Analytical Services, contained an aluminum content less than the detection limit (<75 μg/L). The aluminum concentration range for the sample exceptions was 83-293 μg/L. Two of the exceptions were samples collected from the bottom of MW 1 and 3 on October 19, 2005. The other six exceptions were for samples collected in 2003, 2004, and 2007 for wells MW 4 through 6.

Arsenic, iron, and manganese concentrations tended to be greater for samples with very high aluminum content from the monitoring wells than for samples with less than 1,000 μg/L reported aluminum. A level of 350 μg/L aluminum content was selected as the level below which there appeared to be no noticeable effect on arsenic, iron, and manganese concentrations for the monitoring well waters. The following discussion for these three metals in the monitoring well samples is based on both filtered and unfiltered samples containing less than this aluminum value. The discussion for these three metals in the water-supply well samples excludes the two samples with detectable aluminum and also the unfiltered sample from MW 4 collected on 9/13/06.

Sodium, chloride, sulfate, and nitrate concentrations in samples from the water-supply and monitoring wells do not appear to be correlated with aluminum content. Thus, values for these four constituents in all samples listed in Tables 4 and 5 could be used in interpretation of water quality for this study.

Characterization of Water Quality

*pH and major and minor inorganic constituents*

The pH values for the ground waters from all the water-supply and monitoring wells have been near neutral. The averages of the laboratory pH measurements ranged from 6.92 to 7.39 units for the water-well samples and from 6.93 to 7.33 units for the monitoring well samples. The pH values measured in the field for the monitoring wells averaged slightly lower (6.70-7.20 units) than for those measured in the laboratory, as expected because ground waters usually slowly lose dissolved carbon dioxide with time, causing an increase in pH. Variations in the pH values for each well are probably related more to measurement error than to actual pH.

Chloride concentration has been lower in the ground waters from the water-supply wells than from the monitoring wells. The lowest chloride concentration has generally occurred in well WW 4 (range of 38-60 mg/L), which is within the range for the area ground waters listed in Table 1. The chloride concentration ranges for the other water-supply wells have been, in increasing order, 55-92 mg/L for WW 3, 81-97 mg/L for WW 2, 75-108 mg/L for WW 1, and 90-104 mg/L for WW 5. The chloride content of water samples has varied substantially for some of the monitoring wells. Monitoring well MW 2 had the highest chloride level (range of 257-573). The usual chloride concentration for the other monitoring wells generally increases in the following order (ranges listed after well number): MW 4 (48-119 mg/L), MW 1 (82-131 mg/L), MW 7 (78-297 mg/L), MW 5 (130-262), MW 8 (197-275 mg/L), MW 3 (91-346 mg/L), and MW 6 (113-386 mg/L).

The sulfate concentration range for all the ground waters associated with the facility has been smaller than that for chloride content. The ranges for sulfate content in nearly all of the samples from the water-supply wells associated with the facility (Table 4) have been about the same as for ground waters in the surrounding area (Table 1). The general increasing order for sulfate concentrations in the water-supply well samples are WW 1 (43-73 mg/L), WW 3 (55-70 mg/L), WW 2 (64-79 mg/L), WW 5 (31-95 mg/L), and WW 4 (84-148 mg/L). Sulfate concentration in samples from the monitoring wells (Table 5) has ranged from very low values (<1 mg/L) to about twice that of the highest content for the area ground waters (Table 1). The sulfate concentration has been highest in monitoring wells MW 1 (113-131 mg/L) and MW 4 (55-132 mg/L). Except for occasional samples with values within the range of MW 4, the sulfate content has usually been low in waters from five of the other monitoring wells: MW 2 (<1-2.1 mg/L), MW 3 (<1-1.8, except for one sample with 75 mg/L), MW 5 (<1-1.6, except for one sample with 85 mg/L), MW 6 (<1-13 mg/L), and MW 8 (<1-2.5 mg/L). The sulfate concentration has decreased in monitoring well MW 7 from 36 mg/L on 9/12/05 to <1 on 9/27/07. The low sulfate contents are indicative of chemical reduction of sulfate to sulfide.

Nitrate-nitrogen concentrations in samples from water-supply wells WW 2 (1.9-6.5 mg/L), WW 3 (4.0-9.0 mg/L), and WW 5 (1.7-7.0 mg/L) have been below the MCL of 10 mg/L and generally within the range for the ground waters from the High Plains aquifer in the surrounding area (1.4-6.9 mg/L, Table 1). The nitrate content for WW 1 has been lower (<1-3.9 mg/L) than for the other water-supply wells, whereas it has been greater and has nearly always exceeded the MCL for drinking water for samples from WW 4 (9.5-92 mg/L). The nitrate-nitrogen concentration has exceeded the MCL of 10 mg/L in only two samples from one of the monitoring wells during 2002-2007 (13 mg/L for the 10/20/04 and 9/12/05 samples from MW 4). MW 1 has consistently had the greatest nitrate content of any of the monitoring well waters (nitrate-nitrogen range of 2.1-9.2 mg/L, except for the sample collected from the top of the water column on 10/19/05 that had <1 mg/L). The nitrate-nitrogen content in samples from both MW 4 and MW 7 started out in the general range of that for MW 1 but then decreased to <1 mg/L. The nitrate content in all or nearly all of the samples from the other monitoring wells has been <1 mg/L. Just as the low sulfate contents are indicative of sulfate reduction, the very low and undetectable nitrate levels indicate chemical reduction of nitrate to ammonia.

### *Dissolved metals*

The earlier section on characterization of sample representativeness describes which sample records are discussed in this section. In general, the metals concentrations in the filtered and unfiltered samples with low or undetectable aluminum values are considered to represent mainly dissolved contents.

Arsenic concentration has been below the detection limit in all samples from water-supply wells WW 3 and WW 5. Although the detection limit has varied from <5 to <20 µg/L for the analyses, the detection limit has been <5 for the 2006 and 2007 samples analyzed by Pace laboratory. Dissolved arsenic content in WW 1 and WW 4 has either been below the detection limit or below the MCL of 10 µg/L, except for the first (15.2 µg/L) and last (10.8 µg/L) samples from WW 1. Dissolved arsenic has ranged from 11.4 to about 20 µg/L in water from WW 2.

Dissolved arsenic has been detectable in at least some samples from all of the monitoring wells except WW 1. The measurable arsenic values listed in Table 5 for MW 1 are all considered to be primarily associated with particulate matter and not dissolved concentrations. Arsenic content has been less than the MCL in all samples from MW 4 (<5 to 6 µg/L). Dissolved arsenic concentration in MW 6 and 7 was <10 µg/L in the first two or three samples from each well but then increased to well over the MCL of 10 µg/L. The content of dissolved arsenic from MW 2, 3, 5, and 8 has substantially exceeded 10 µg/L in all samples. Dissolved arsenic values have exceeded 100 µg/L in many samples from MW 2 and 3, and in a few samples from MW 5, 6, and 8.

Dissolved iron contents in the filtered water samples from water-supply wells WW 3 through WW 5 have all been <600 µg/L, whereas they have exceeded 1,000 µg/L in WW 1 and 10,000 µg/L in WW 2. Dissolved manganese concentrations have been <70 µg/L in all samples from WW 3 through 5, and have usually exceeded 1,000 µg/L in WW 1 and 2. The recommended or secondary standards for iron and manganese in drinking water are 0.3 mg/L (300 µg/L) and 0.05 mg/L (50 µg/L), respectively. Iron and manganese concentrations in the monitoring well waters have been lowest in MW 1 and 4; all samples with aluminum content <300 µg/L have had iron values <900 µg/L and manganese <600 µg/L, with most iron and manganese values <300 µg/L. Dissolved iron content has been very high in nearly all samples from MW 2, 3, 5, 6, 7, and 8, with values usually >10,000 µg/L. Occasional samples have had relatively low dissolved iron, such as those collected from the top of the water column in MW 2, 3, and 7 on 10/19/05; iron contents in these monitoring wells were all <300 µg/L. Manganese concentrations in samples from MW 2, 3, and 7 have nearly always been <1,000 µg/L, whereas they have usually been in the range 500-4,000 µg/L for MW 5, 6, and 8.

## GEOCHEMICAL FACTORS CONTROLLING GROUND-WATER CHEMISTRY

### Association of Arsenic with pH and Inorganic Constituents

Although the pH of the influent wastewater is acidic, the dissolved arsenic of the ground water has no significant statistical correlation to the pH of the ground water. Figure 1 displays dissolved arsenic content of the monitoring well samples versus the pH measured in the field, which is more representative of the ground-water pH than the laboratory values.

Dissolved arsenic content is positively correlated (highly statistically significant) with chloride concentration in the ground waters from within and immediately adjacent to (which includes well WW 3) the facility area (Figure 2). All ground waters with <120 mg/L chloride contained dissolved arsenic levels < 20 µg/L. There is a large scatter of points in Figure 2 for samples with chloride content >140 mg/L but, in general, samples with >100 µg/L dissolved arsenic tend to have chloride concentrations >200 mg/L. The arsenic and chloride correlation points to seepage of the wastewater influent as a contributing factor in causing the high arsenic concentrations in the ground water.

In contrast to its relationship with chloride content, dissolved arsenic is negatively correlated with sulfate concentration in the facility ground waters (Figure 3). The relationship is best fitted by a power function, for which the coefficient of determination is high, indicating a highly statistically significant significance. All samples with sulfate concentration >20 mg/L have an arsenic content <20 µg/L, whereas nearly all samples with sulfate <20 mg/L have arsenic levels >20 µg/L. The sample from MW 6 with a sulfate content of 12.9 mg/L appears anomalous on Figure 3. However, the sample was collected from the bottom of the well suggesting that the sulfate content could be greater there than higher up in the saturated zone. Dissolved arsenic is also inversely related to nitrate concentration, with a power function best fitting the data (Figure 4). The relationship is highly statistically significant, although the coefficient of determination is not as high as for the arsenic and sulfate correlation. Except for the data for the sample collected from MW 2 on 9/13/06, for which the nitrate value appears anomalous, all ground waters with nitrate-nitrogen >3 mg/L contain an arsenic level <20 µg/L, and all samples with arsenic concentration >30 µg/L have a nitrate-nitrogen content <1 mg/L (although not all samples with <1 mg/L nitrate contain >30 mg/L arsenic). Nitrate and sulfate

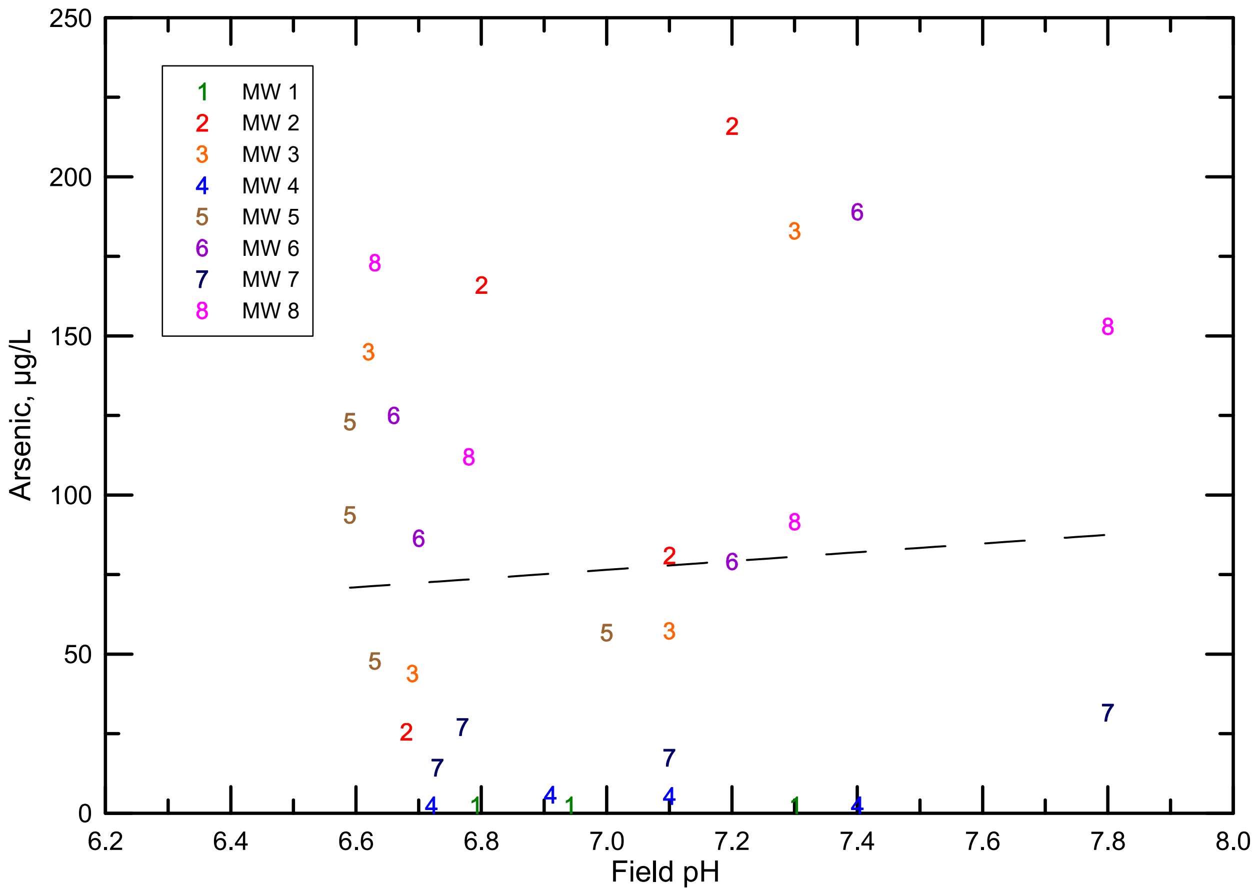

Figure 1. Dissolved arsenic concentration versus field pH of water samples from monitoring wells at the alcohol facility. The dashed line is the regression between the two variables but the correlation coefficient is not statistically significant. The line simply indicates that there is no apparent relation between the arsenic concentration and pH of the ground water.

concentrations are positively related (Figure 5) and the statistical significance of the correlation is high.

Dissolved arsenic concentration is positively correlated (highly statistically significant) with dissolved iron content in the facility ground waters (Figure 6). However, the arsenic level can vary substantially without an appreciable change in iron content for some well waters (for example, MW 3). Arsenic is not significantly correlated with manganese concentration in the facility ground waters (Figure 7). However, all water samples with a manganese level >2,000 µg/L contain an arsenic content of >30 µg/L. Dissolved manganese concentration is positively related to iron content (Figure 8) and the correlation is highly statistically significant. Dissolved iron is inversely related to sulfate (Figure 9) and nitrate (Figure 10), and the coefficients of determination for both correlations are highly statistically significant.

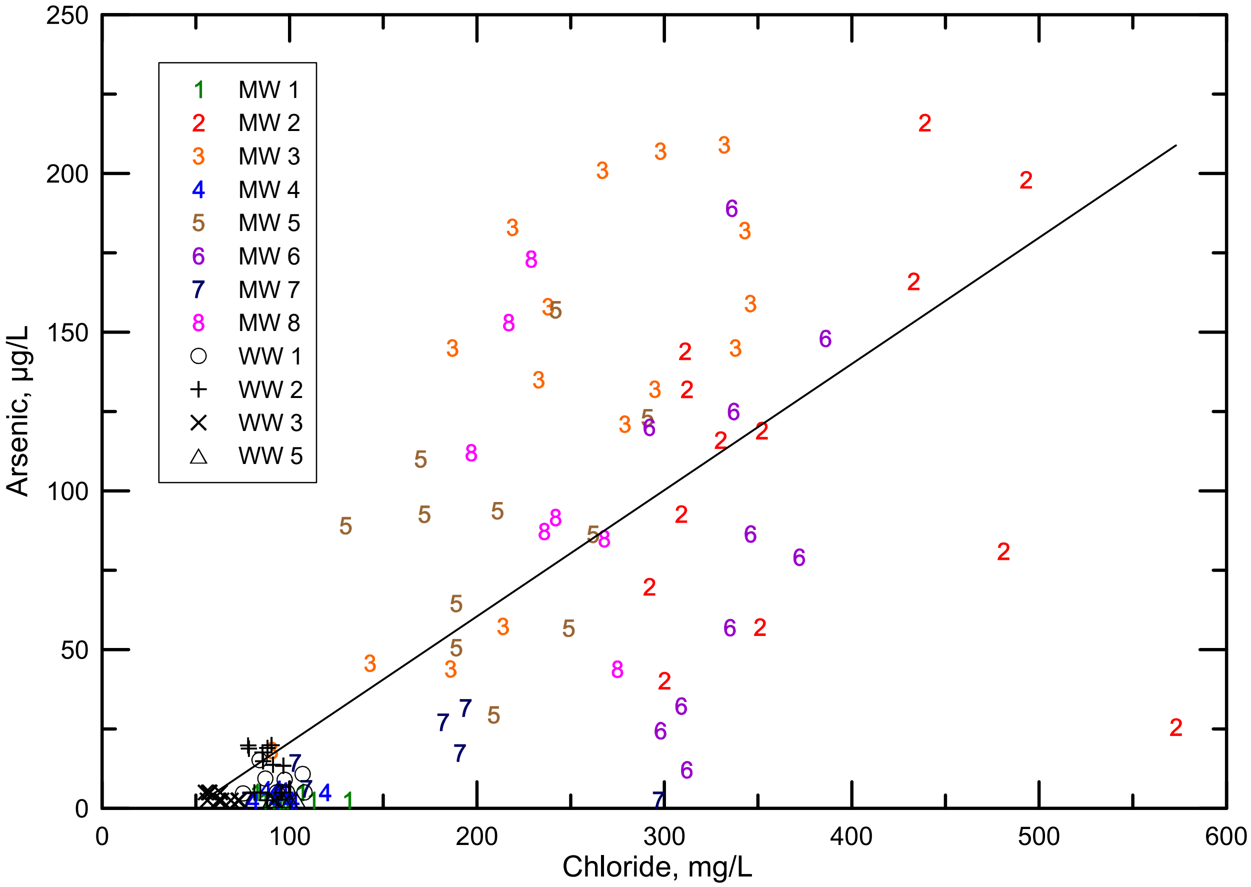

Figure 2. Dissolved arsenic versus chloride concentration of water samples from monitoring and water-supply wells at and nearby the alcohol facility. The regression line is shown for the highly statistically significant correlation between dissolved arsenic and chloride.

## Geochemical Processes Controlling Arsenic Concentration

The arsenic content of the influent wastewater (Table 2) at the facility has not been great enough to be the source of the high arsenic concentration in the ground water. Therefore, the source appears to be derived from the soil and/or the subsurface sediment associated with the High Plains aquifer. Although the pH of the wastewater influent is acidic (Table 2), the buffering capacity of the ground water and/or soil and sediment is large enough to neutralize wastewater seeping into the subsurface. As indicated above, there is no correlation between the arsenic concentration and pH of the ground water. Thus, leaching of arsenic from the soil or sediment by the acidic wastewater does not appear to be the predominant mechanism releasing arsenic to the ground water at levels exceeding the MCL. However, the acidic pH of the wastewater infiltrating through the unsaturated zone before neutralization could possibly have initially contributed to the leaching of arsenic from the sediment.

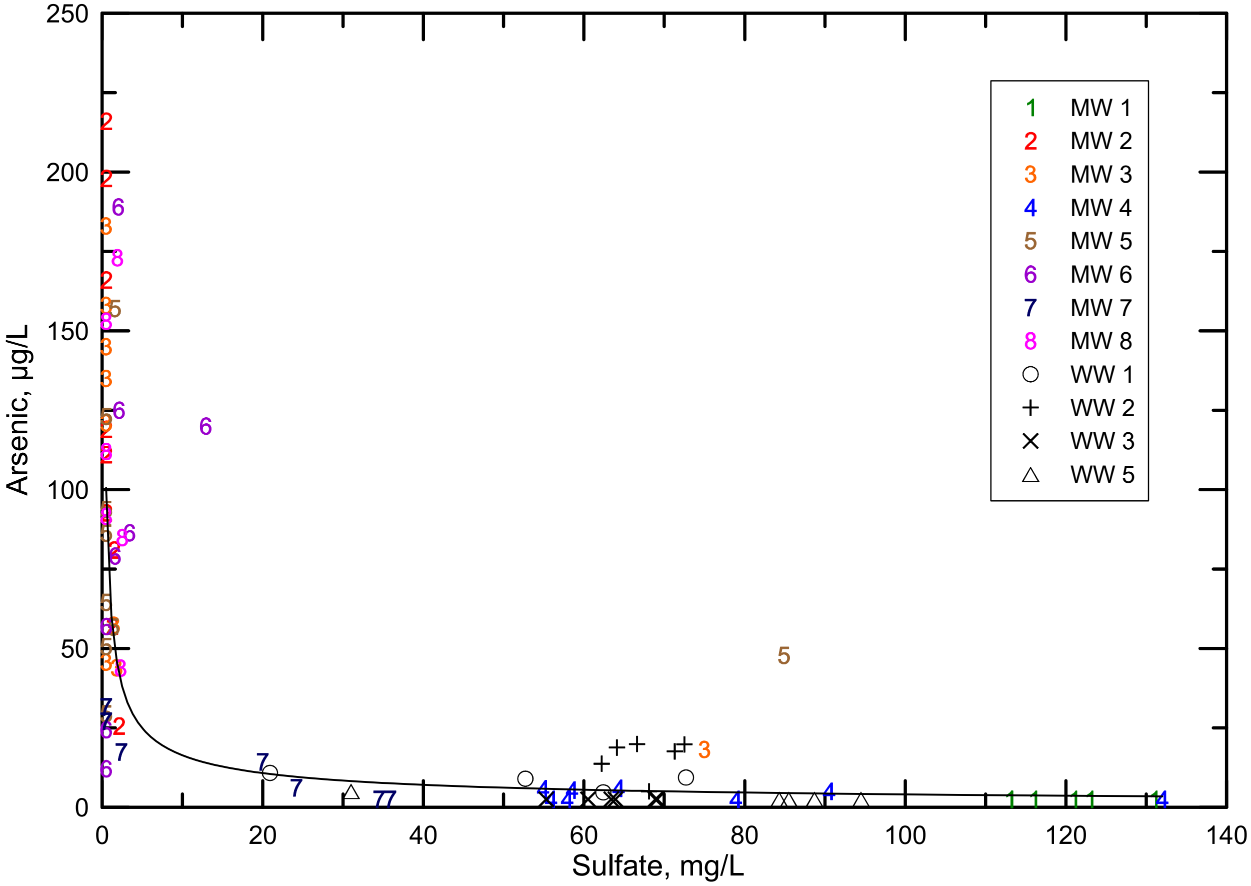

Figure 3. Dissolved arsenic versus sulfate concentration of water samples from monitoring and water-supply wells at and nearby the alcohol facility. The curve is the best-fit power function for the data, which has a coefficient of determination that is highly statistically significant.

The correlation between chloride and arsenic concentration (Figure 2) points to a connection between the wastewater and the high arsenic contents in the ground water. The inverse relationship between both the sulfate and nitrate concentrations with arsenic level in the water samples indicates that a mechanism involving chemical reduction of the ground water is controlling the dissolved arsenic. The source of the dissolved arsenic in the ground water is interpreted as primarily release from the reduction and dissolution of ferric oxyhydroxide precipitate on sediment particles within the saturated zone, as indicated by the high correlation between dissolved arsenic and iron contents of the water samples. Although some dissolved arsenic in the water could also be potentially derived from manganic oxyhydroxides, the statistically insignificant correlation of arsenic and manganese suggests that this is not a primary source.

The wastewater is expected to contain a high dissolved organic carbon content because it is derived from the grain processed to generate the alcohol. For example, Pimetel and Patzek (2005) state that the wastewater from alcohol generation has a biological oxygen demand (BOD)

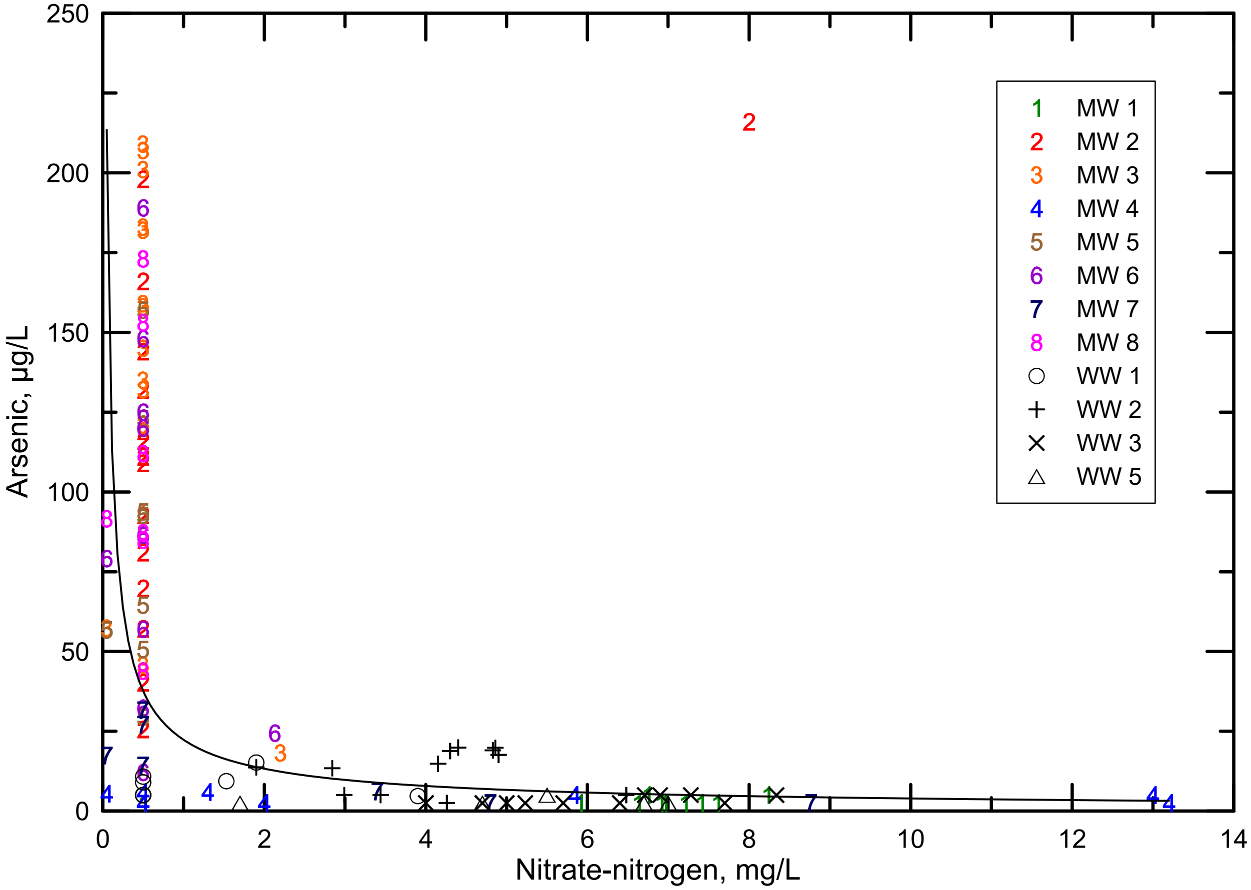

Figure 4. Dissolved arsenic versus nitrate concentration of water samples from monitoring and water-supply wells at and nearby the alcohol facility. The curve is the best-fit power function for the data, which has a coefficient of determination that is highly statistically significant.

of 18,000–37,000 mg/l depending on the type of plant (based on data from Kuby et al. [1984]). The high BOD of the wastewater seeping from under the surface ponds at the facility would have consumed oxygen in the gas within the underlying soil and dissolved in the ground water. When most of the dissolved oxygen in the ground water was consumed by the in-situ degradation of the dissolved organic matter in the wastewater mixed in the ground water, the water would have become chemically reducing. When the dissolved oxygen became low, further biochemical oxidation of the dissolved organic matter derived its oxygen from other sources, including the oxygen in sulfate ($SO_4$) and nitrate ($NO_3$) dissolved in the ground water. This is supported by the inverse relationship between the dissolved arsenic content and both sulfate and nitrate in the ground water, as well as by the positive correlation between nitrate and sulfate.

The low oxidation potential generated by the biochemical conversion of the dissolved organic matter would have solubilized ferric and manganic oxyhydroxides, releasing oxygen for the BOD reaction and reducing the ferric iron and manganese IV to become dissolved ferrous iron and manganese II, respectively, in the ground water. This is supported by the statistically

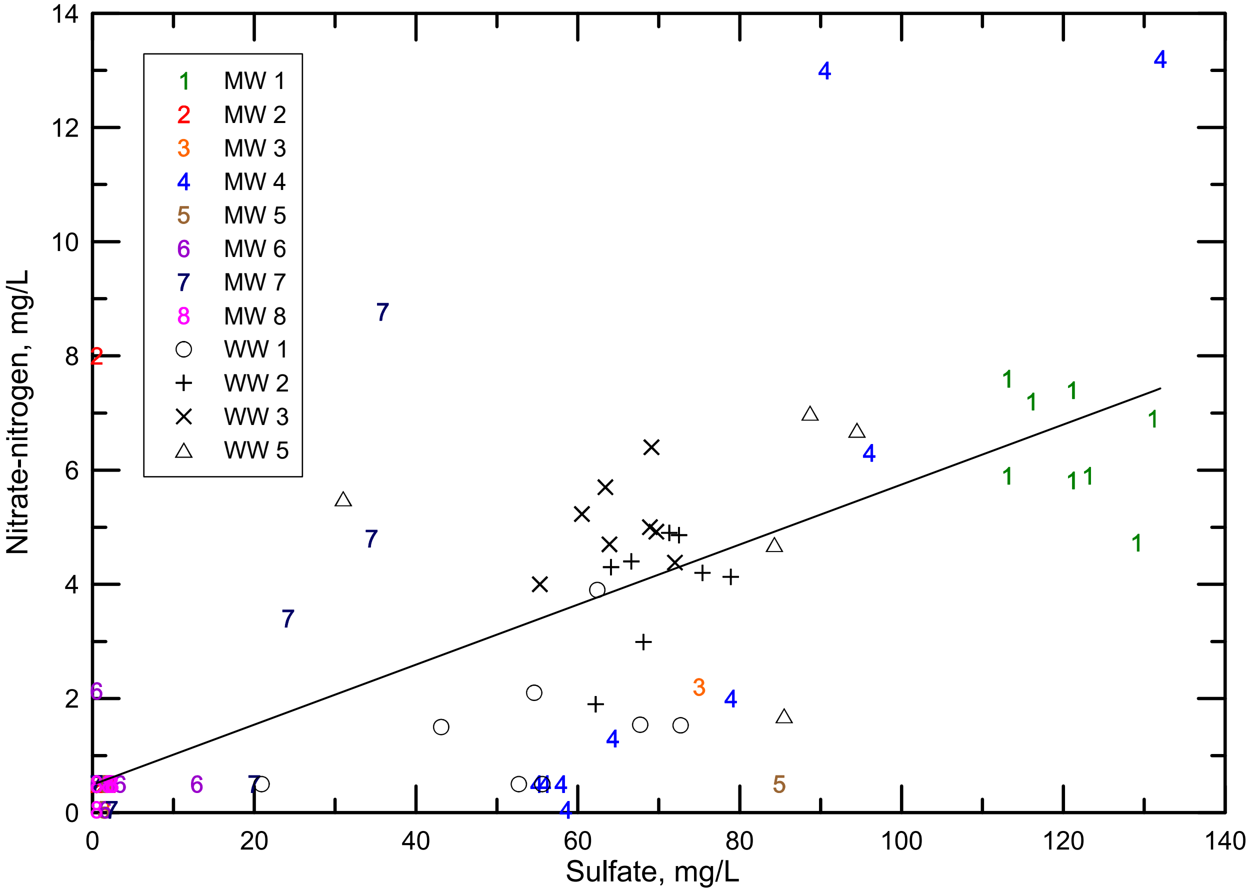

Figure 5. Dissolved nitrate versus sulfate concentration of water samples from monitoring and water-supply wells at and nearby the alcohol facility. The regression line is shown for the highly statistically significant correlation between dissolved nitrate and sulfate.

significant, positive correlation of dissolved manganese and iron concentrations and inverse relationship of dissolved iron and manganese with sulfate and nitrate concentrations of the ground-water samples. Roden and Zachara (1996) found that microbial reduction of iron oxides in sediment could remove a substantial fraction of the extractable iron. Arsenic could have also been released by this mechanism from the subsurface sediment in the unsaturated zone underlying the wastewater ponds when the organic degradation had decreased the oxidation potential great enough in the infiltrating water. As indicated above, the acidic pH of the wastewater could have contributed to the dissolution of iron and manganese oxyhydroxide coatings and the release of arsenic until the acidity was neutralized.

Most of the arsenic release probably occurred in the saturated zone once the ground water became chemically reduced in the path of the wastewater contamination plume. Comparison of data for samples collected from the top of the water column in the monitoring wells on 10/19/05 to data for other samples, including those indicated as from the middle of the water column, supports this mechanism. The chemical data indicate that the path of the wastewater

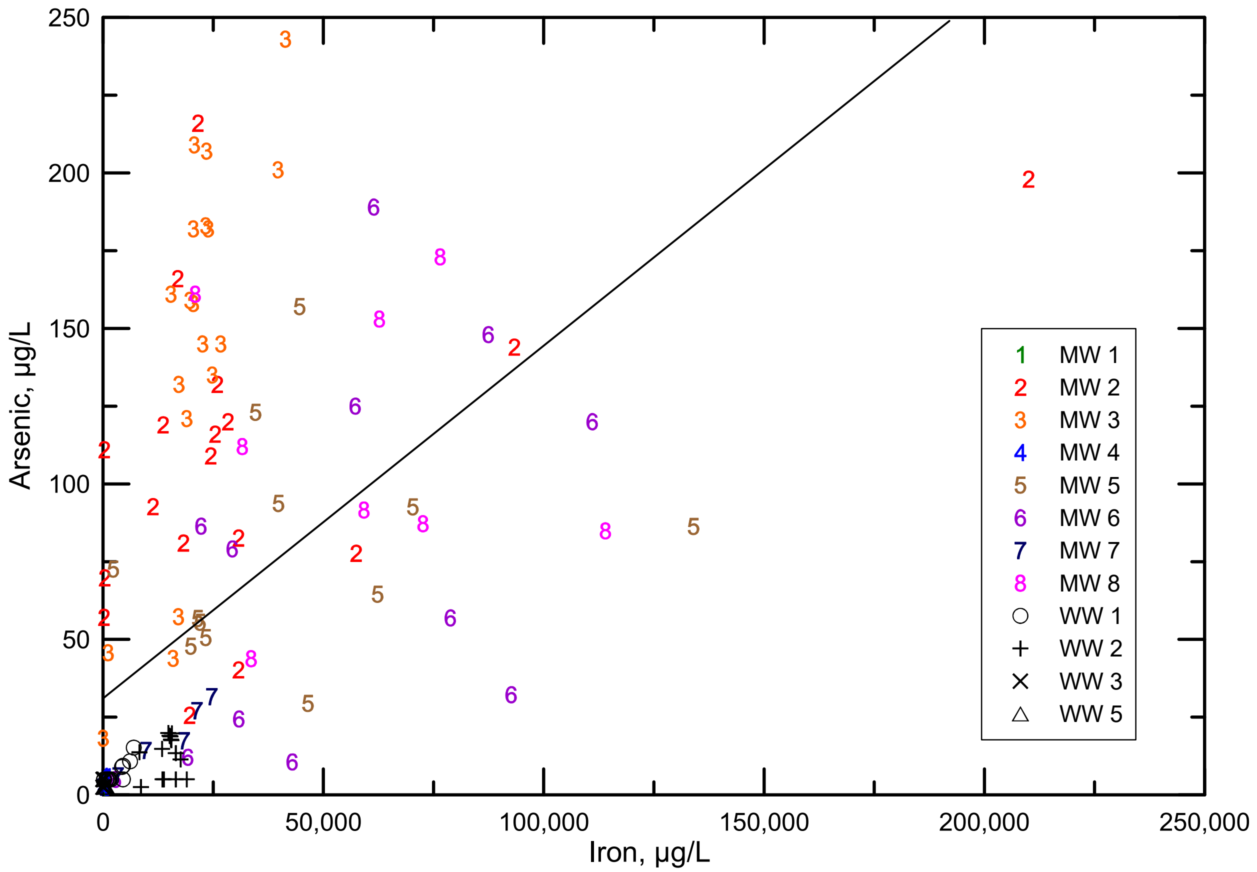

Figure 6. Dissolved arsenic versus iron concentration of water samples from monitoring and water-supply wells at and nearby the alcohol facility. The regression line is shown for the highly statistically significant correlation between dissolved arsenic and iron.

contamination plume is towards the east-southeast because MW 7 and 8 show chemical impact of the wastewater but MW 4 shows little effect. The dissolved arsenic and iron contents of the sample from the top of the water column at MW 5 are both high, as are the values for the lower part of the water column, suggesting that the proximity of this well to the ponds could have resulted in a reducing environment that extends through the unsaturated zone to the water table at this location. The arsenic concentration is smaller and the iron content is much lower in the top of the water column than the bottom samples on 10/19/05 from MW 2 and 3, the next closest monitoring wells to the ponds. Dissolved arsenic and iron contents are also smaller in the top of the water column than the bottom for the 10/19/05 samples from MW 6 through 8.

The process of arsenic release by desorption from and dissolution of iron oxyhydroxides under strongly reducing conditions is one of the main causes of high arsenic concentrations in ground water as described in a review of arsenic behavior in natural waters by Smedley and Kinniburgh (2002). Bose and Sharma (2002) and Harvey et al. (2002) reported that this mechanism is the most probable for generating the widespread arsenic contamination of ground water in Bangladesh and the West Bengal state of India.

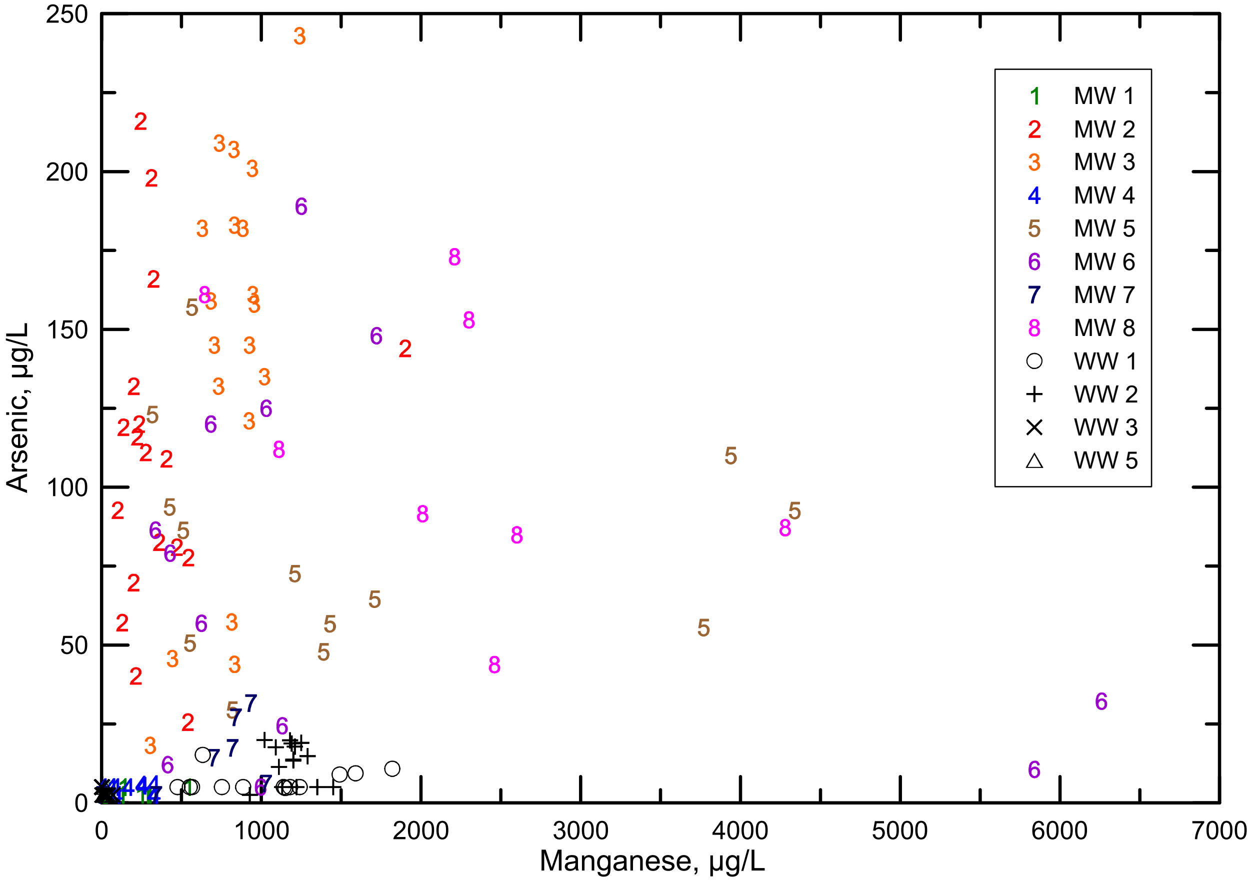

Figure 7. Dissolved arsenic versus manganese concentration of water samples from monitoring and water-supply wells at and nearby the alcohol facility. The correlation between the two variables is not statistically significant.

Another mechanism reported as explaining high arsenic content in ground water is the release of arsenic sorbed to sediments by competitive exchange with phosphate ions (mainly present as $H_2PO_4^-$ and $H_2PO_4^{2-}$ at neutral pH) that migrate into aquifers from fertilizers applied to surface soil as well as from decaying organic matter (Acharyya et al., 1999, 2000). Goh et al. (2005) found that significant amounts of arsenic can be mobilized from a fine soil fraction by exchange with dissolved phosphate. In addition to dissolved organics and nitrogen species, wastewater from the alcohol facility is expected to contain dissolved phosphorous, either associated with the organic matter or as phosphate. For example, Bing-you et al. (1998) indicate that phosphorous is one of the components of wastewater generated in alcohol production. Phosphate in the wastewater seeping from the surface ponds or generated during the biochemical breakdown of phosphorus-containing organics in the wastewater during migration in the subsurface could potentially add to the arsenic content of the ground water by ion exchange on mineral surfaces. No phosphate concentration data were available for either the wastewater or ground-water samples to test the viability of this additional process for arsenic release to the ground water.

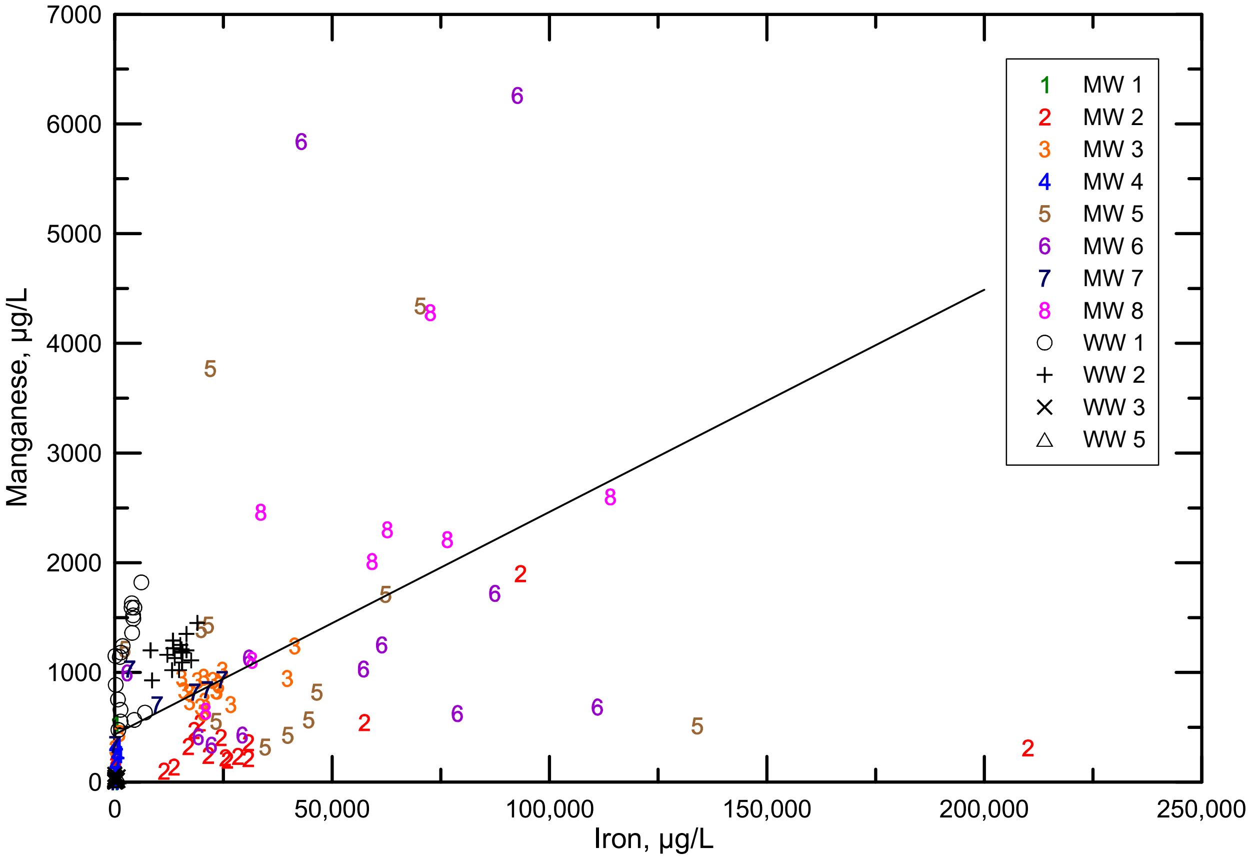

Figure 8. Dissolved manganese versus iron concentration of water samples from monitoring and water-supply wells at and nearby the alcohol facility. The regression line is shown for the highly statistically significant correlation between dissolved manganese and iron.

## Arsenic Source

The associations among the chemical data suggest that association with ferric oxyhydroxides is the most probable location of the arsenic that was released to the ground water underlying the alcohol production facility. Smedley and Kinniburgh (2002) state that iron oxides are probably the most important adsorbants of arsenic in sandy aquifers. Sracek et al. (2004) report that in oxidizing environments, adsorption on ferric oxyhydroxides is the principal attenuation mechanism of arsenic migration. Ferric oxyhydroxides can exist as coatings on other sediment particles such as clays and silt, or as discrete precipitate particles. Smedley and Kinniburgh (2002) indicate that aluminum and manganese oxides can also bind arsenic and the edges of clays can adsorb arsenic due to their oxide-like character.

It is not known whether the main source of the high arsenic in the ground water at the alcohol facility is predominantly arsenic adsorbed on the surface of ferric oxyhydroxide coatings or occluded within ferric oxyhydroxide particles. In addition, if the arsenic is mainly from

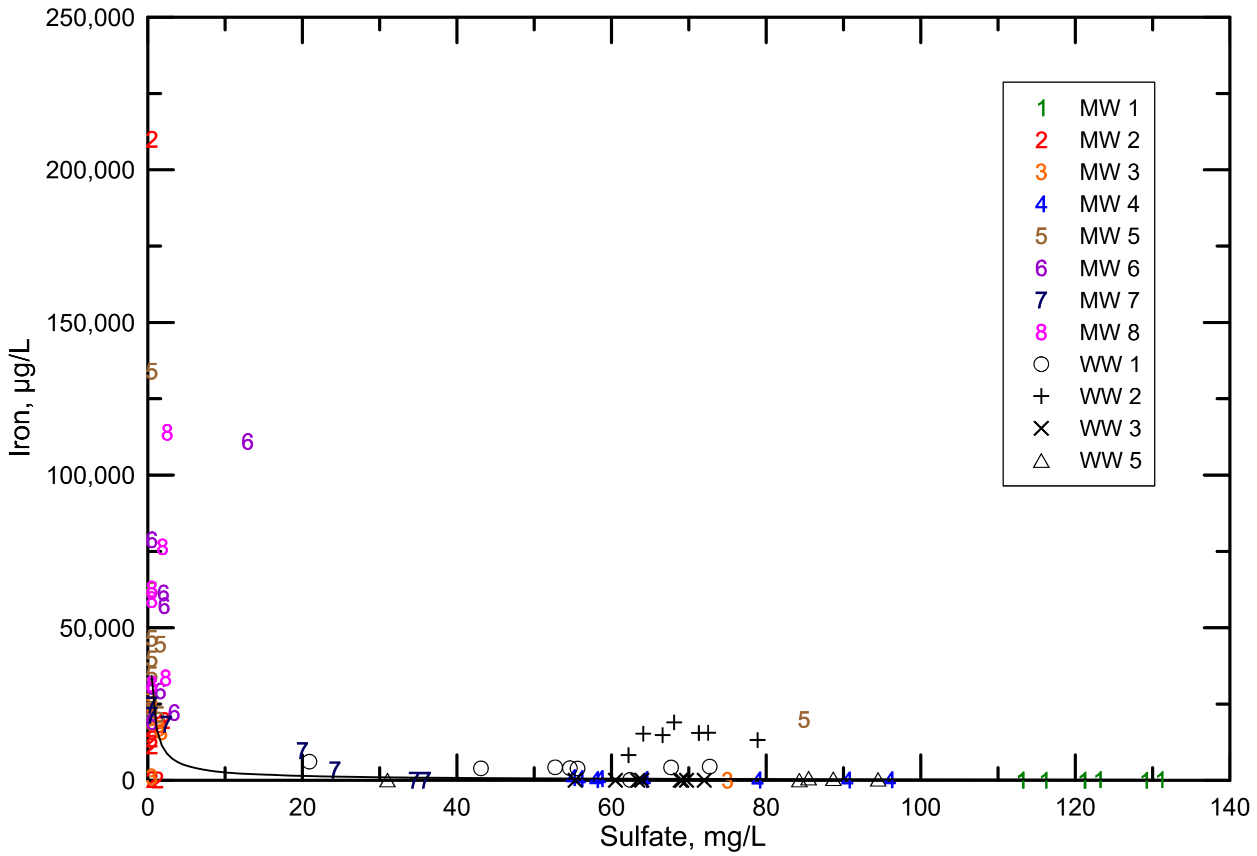

Figure 9. Dissolved iron versus sulfate concentration of water samples from monitoring and water-supply wells at and nearby the alcohol facility. The curve is the best-fit power function for the data, which has a coefficient of determination that is highly statistically significant.

coatings, it is unknown as to whether most of the arsenic is derived from oxyhydroxide coatings associated with the clays or the quartz silts and sands of the subsurface sediment.

Analyses of surface soil and subsurface sediment collected at the alcohol production site (Table 6) are useful for characterizing the arsenic source. The subsurface sediment samples were collected only to 60 ft at the locations of three of the monitoring wells. Therefore, the samples do not include the sediments within the saturated zone of the aquifer, which extended from the water level (a depth of about 137-144 ft in the fall of 2005) to the bedrock surface (157-167 ft below land surface at MW 4 through 6) in the facility area. However, patterns in the sediment data give clues as to the arsenic source.

Arsenic in the surface soil appears to be directly related to the aluminum and iron concentrations based on all the soil data in Table 6 (Figures 11 and 12). However, the substantially higher arsenic, aluminum, and iron contents of the two duplicate KDHE analyses in comparison with the lower values for the Pace analyses produce these apparent positive correlations. The procedures that KDHE used for the soil analyses recovered much more of the

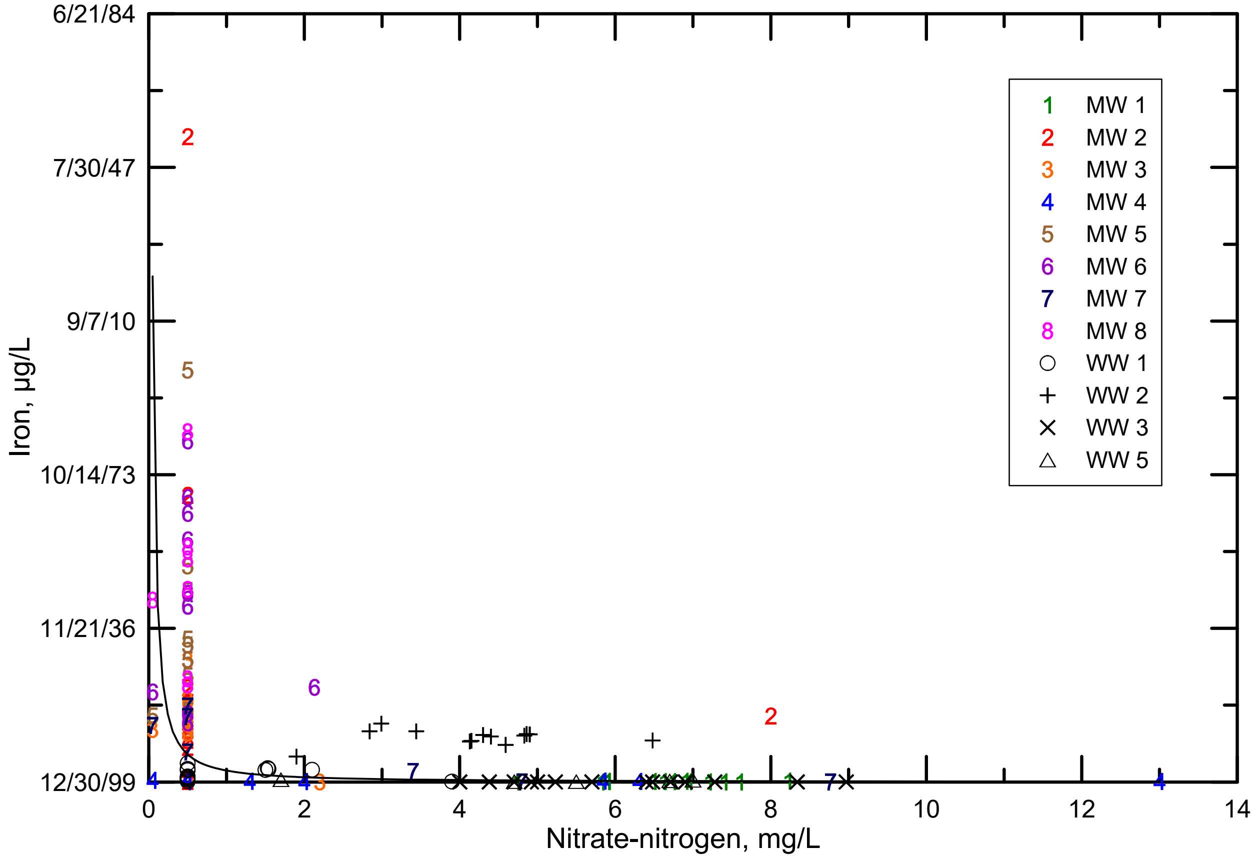

Figure 10. Dissolved iron versus nitrate concentration of water samples from monitoring and water-supply wells at and nearby the alcohol facility. The curve is the best-fit power function for the data, which has a coefficient of determination that is highly statistically significant.

total content of these metals than the Pace analytical methods. KDHE reported the concentrations as total metals and used EPA method 3051 (U.S. EPA online methods for manual SW-846) to prepare the soil samples, which includes acid digestion and microwave heating. Pace Analytical Laboratories used EPA method 3050 for metals extraction, which according to the EPA description is a very strong acid digestion that dissolves metals that could become environmentally available but is not a total digestion for most samples. Without the two KDHE analyses, the correlations of arsenic with aluminum and iron in the soil samples are not significant.

Correlation of the arsenic and aluminum concentrations of the subsurface sediment is not statistically significant, although the highest arsenic values tend to be associated with lower aluminum content and vice versa (Figure 11). Arsenic and iron concentrations in the sediment are inversely related (Figure 12); the correlation is statistically significant although the correlation coefficient is low. No statistically significant correlations occur between arsenic and manganese for the soil and the subsurface sediment (Figure 13). The general similarity of the patterns in Figures 11 and 12 is explained by the high correlation between iron and aluminum in

Table 6. Analyses of surface soil and subsurface sediment at the alcohol production site. The units mg/kg are equivalent to ppm for the solid samples.

| Sample site | Lab | Depth feet | Date | Cl mg/kg | Na mg/kg | Al mg/kg | As mg/kg | Fe mg/kg | Mn mg/kg |
|---|---|---|---|---|---|---|---|---|---|
| MW 4 | Pace | Surface | 09/17/03 | 45.5 | 74.5 | 14,300 | 1.88 | 13,000 | 297 |
| MW 4 | Pace | 9-10 | 09/17/03 | 45.0 | 293 | 10,300 | 2.50 | 10,900 | 235 |
| MW 4 | Pace | 19-20 | 09/17/03 | 81.8 | 194 | 7,410 | 10.6 | 6,170 | 85.3 |
| MW 4 | Pace | 29-30 | 09/17/03 | 3.4 | 79.3 | 4,090 | 6.67 | 3,280 | 73.1 |
| MW 4 | Pace | 39-40 | 09/17/03 | 2.0 | 98.3 | 1,620 | <1 | 4,620 | 192 |
| MW 4 | Pace | 49-50 | 09/17/03 | 7.3 | 184 | 2,180 | 13.8 | 1,500 | 246 |
| MW 4 | Pace | 59-60 | 09/17/03 | 53.9 | 259 | 17,400 | <1 | 14,600 | 133 |
| | | | | | | | | | |
| MW 5 | Pace | Surface | 09/17/03 | 65.4 | 99.5 | 13,400 | 2.83 | 13,300 | 272 |
| MW 5 | Pace | 9-10 | 09/17/03 | 54.8 | 239 | 12,000 | 3.01 | 12,700 | 255 |
| MW 5 | Pace | 19-20 | 09/17/03 | 40.4 | 245 | 7,940 | 11.7 | 6,830 | 79.5 |
| MW 5 | Pace | 29-30 | 09/17/03 | 1.6 | 74.9 | 2,380 | 4.11 | 5,650 | 140 |
| MW 5 | Pace | 39-40 | 09/17/03 | 3.0 | 65.6 | 1,190 | 1.43 | 3,860 | 39.8 |
| MW 5 | Pace | 49-50 | 09/17/03 | 9.4 | 129 | 2,210 | 14.4 | 1,700 | 117 |
| MW 5 | Pace | 59-60 | 09/17/03 | 24.0 | 98.6 | 537 | 15.9 | 407 | 151 |
| | | | | | | | | | |
| MW 6 | Pace | Surface | 09/17/03 | 49.3 | 177 | 12,900 | 4.95 | 13,400 | 256 |
| MW 6 | Pace | 9-10 | 09/17/03 | 9.9 | 338 | 10,700 | 3.46 | 11,800 | 252 |
| MW 6 | Pace | 19-20 | 09/17/03 | 60.0 | 196 | 8,550 | 9.32 | 7,430 | 72.6 |
| MW 6 | Pace | 19-20 | 09/17/03 | 51.8 | 179 | 9,380 | 5.97 | 8,500 | 123 |
| MW 6 | Pace | 29-30 | 09/17/03 | 11.9 | 89.7 | 2,900 | 9.85 | 2,010 | 22.1 |
| MW 6 | Pace | 39-40 | 09/17/03 | 12.2 | 213 | 5,110 | 3.62 | 6,110 | 114 |
| MW 6 | Pace | 49-50 | 09/17/03 | 45.0 | 115 | 2,090 | 1.01 | 4,430 | 133 |
| MW 6 | Pace | 59-60 | 09/17/03 | 6.0 | 103 | 2,310 | 15.6 | 1,900 | 71.7 |
| | | | | | | | | | |
| GS-1 | Pace | Surface | 09/18/03 | 54.5 | 114 | 12,700 | 2.30 | 12,600 | 291 |
| GS-2 | Pace | Surface | 09/18/03 | 51.7 | 73.7 | 13,600 | 2.40 | 13,200 | 309 |
| GS-3 | Pace | Surface | 09/18/03 | 52.2 | 57.7 | 11,100 | 1.65 | 10,800 | 288 |
| GS-3 | KDHE | Surface | 09/18/03 | 13 | 210 | 30,000 | 7.20 | 21,000 | 410 |
| GS-4 | Pace | Surface | 09/18/03 | 45.7 | 79.3 | 12,600 | 2.32 | 12,000 | 320 |
| GS-5 | Pace | Surface | 09/18/03 | 241 | 177 | 10,900 | 1.62 | 10,700 | 146 |
| GS-5 | KDHE | Surface | 09/18/03 | 100 | 400 | 26,000 | 6.00 | 18,000 | 220 |

the surface soil and subsurface sediment (Figure 14). Manganese is not statistically correlated with either aluminum or iron when the soil and sediment samples are considered separately, but has a statistically significant, direct correlation to both aluminum and iron when the soil and sediment samples are grouped as a whole (not shown).

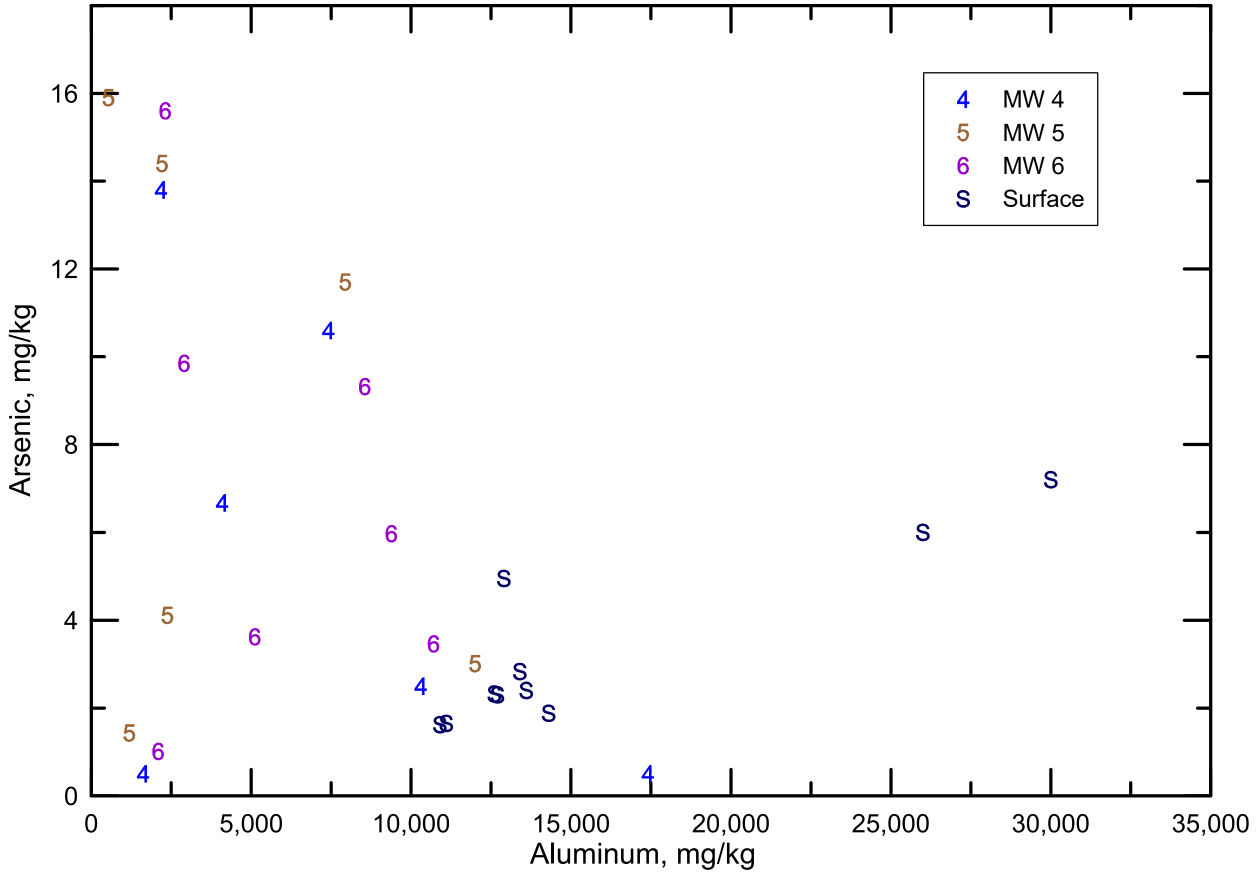

Figure 11. Arsenic versus aluminum content of surface soil and subsurface sediment from the alcohol facility. The symbol S represents surface soil samples and the numbers represent subsurface sediment collected at different depths at the locations of monitoring wells MW 4, 5, and 6. Surface soil samples were collected at the three MW locations and at five additional sites, and analyzed by Pace Analytical Laboratories. The KDHE analyzed duplicate soil samples from two of the additional five sites. The two surface soils analyzed by KDHE are represented by the two S points with the greatest aluminum and arsenic values. The correlation between the two variables is not statistically significant for the surface soils if the two KDHE duplicate analyses are not included. The correlation between the two variables is also not statistically significant for the subsurface sediments.

The range in the arsenic content of the surface soil is 1.6-7.2 mg/kg. The arsenic concentration of the subsurface sediment varies greatly with depth over a larger range (<1-15.9 mg/kg) than for the surface soil (Figure 15). These values are within typical ranges of arsenic concentrations in soils and sediments summarized by Smedley and Kinniburgh (2002). For example, they list an average arsenic content of 7.2 mg/kg for various soils based on 327 analyses, and arsenic values in alluvial sand, river bed sediments, and loess silts ranging from 1 to 18 mg/kg.

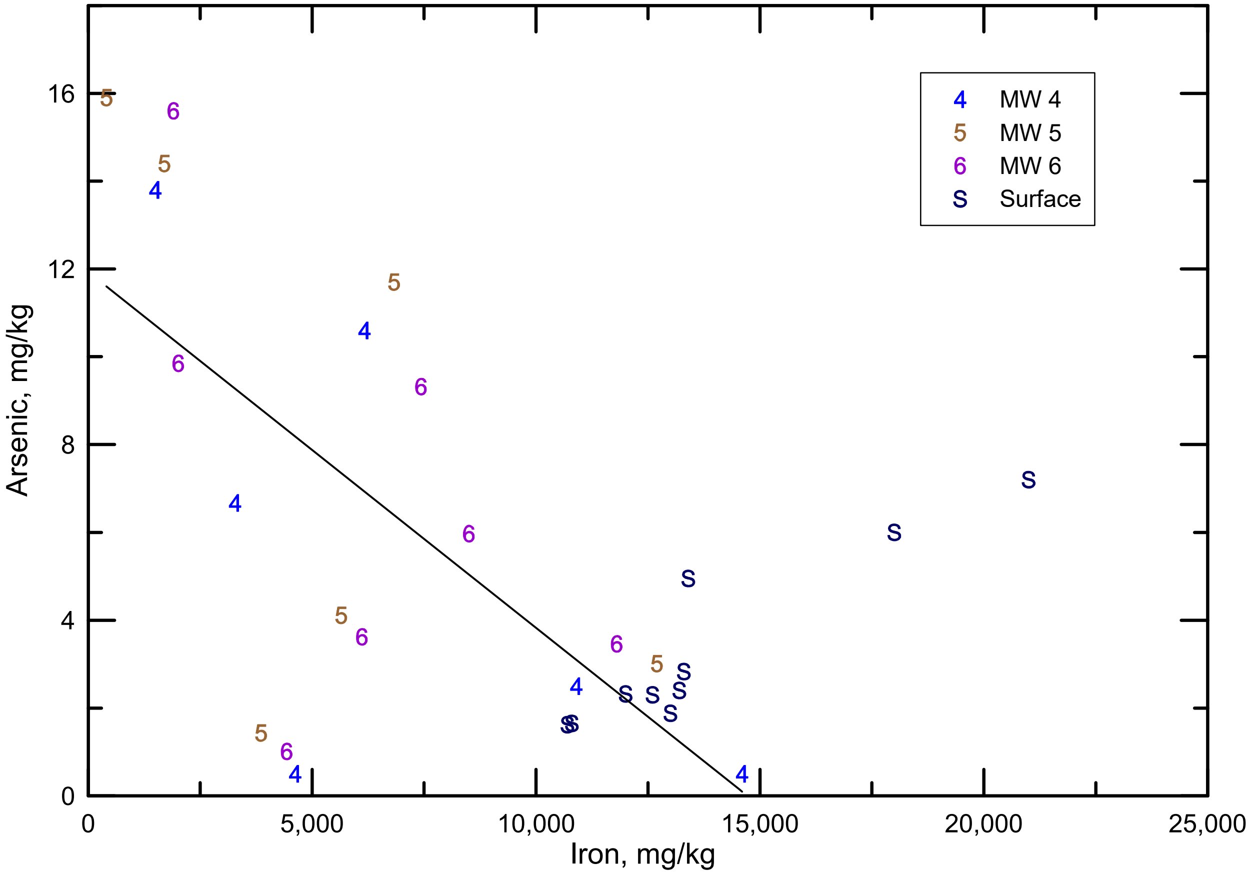

Figure 12. Arsenic versus iron content of surface soil and subsurface sediment from the alcohol facility. The symbol S represents surface soil samples and the numbers represent subsurface sediment collected at different depths at the locations of monitoring wells MW 4, 5, and 6. Surface soil samples were collected at the three MW locations and at five additional sites, and analyzed by Pace Analytical Laboratories. The KDHE analyzed duplicate soil samples from two of the additional five sites. The two surface soils analyzed by KDHE are represented by the two S points with the greatest iron and arsenic values. The correlation between the two variables is not statistically significant for the surface soils if the two KDHE duplicate analyses are not included. The regression line is shown for the highly statistically significant correlation between arsenic and iron for the subsurface sediments.

The arsenic data for the alcohol facility sediment indicate that some horizons with relatively low and high arsenic content extend across the area of MW 4 through 6 (Figure 15). The ranges in both the aluminum (10,900-30,000 mg/kg) and iron (10,700-21,000 mg/kg) contents of the surface soil are roughly the same, and the differences (19,100 mg/kg and 10,300 mg/kg for aluminum and iron, respectively) between the low and high values are approximately the same as those for the subsurface sediment (16,900 mg/kg for the aluminum range of 537-17,400 mg/kg and 14,300 mg/kg for the iron range of 407-14,600 mg/kg). If only the Pace laboratory data are considered, then the aluminum and iron contents in the surface soil samples

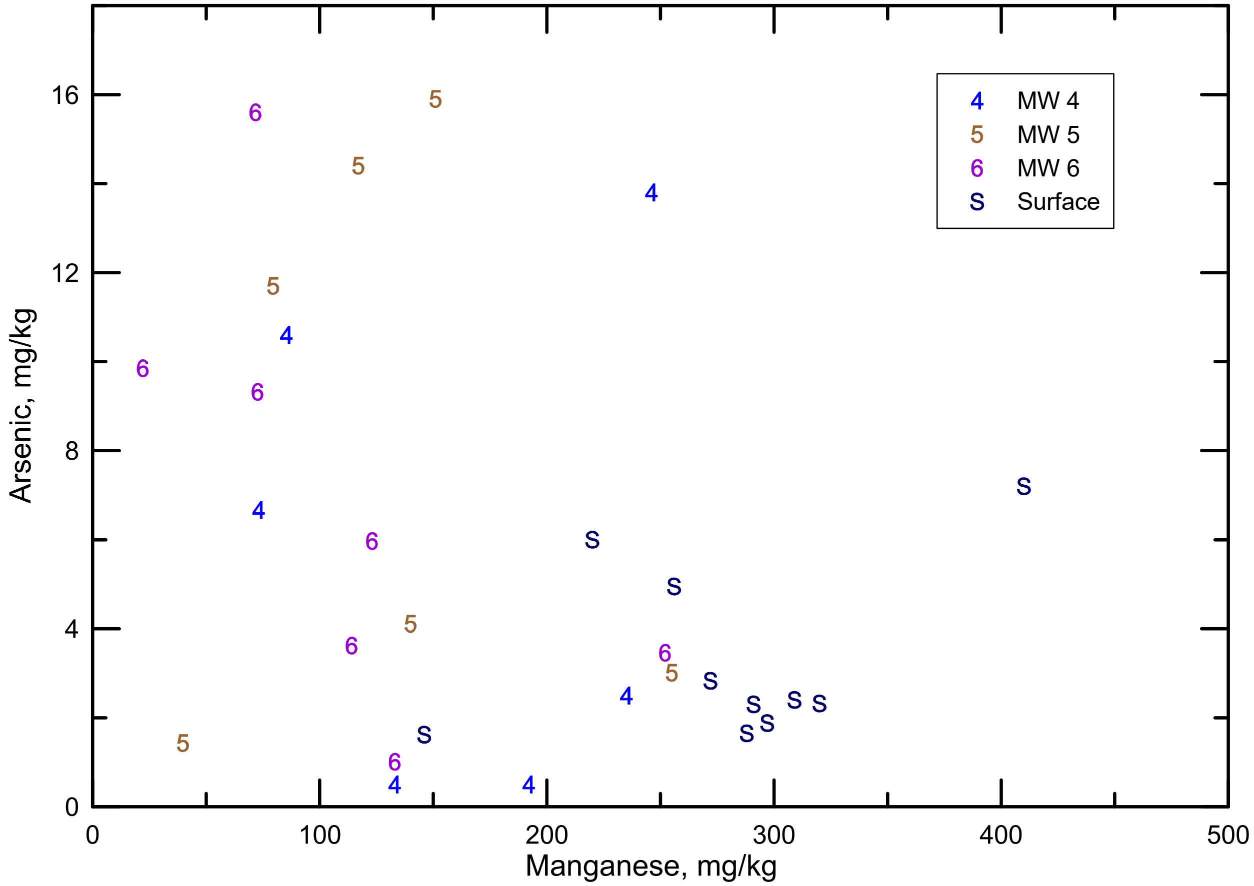

Figure 13. Arsenic versus manganese content of surface soil and subsurface sediment from the alcohol facility. The symbol S represents surface soil samples and the numbers represent subsurface sediment collected at different depths at the locations of monitoring wells MW 4, 5, and 6. Surface soil samples were collected at the three MW locations and at five additional sites, and analyzed by Pace Analytical Laboratories. The KDHE analyzed duplicate soil samples from two of the additional five sites. The correlation between the two variables is not statistically significant for either the surface soils or the subsurface sediments.

are within the upper ranges for these metals in the subsurface sediments. Both aluminum and iron concentrations generally decrease with depth at the MW 4 through 6 locations (Figures 16 and 17), except for MW 4, for which the aluminum and iron levels decrease to a depth of 49-50 ft and then increase substantially at 59-60 ft (where the arsenic content decreases appreciably).

The apparent inverse relationship of arsenic and iron concentrations in the subsurface sediment would appear at first contradictory to the high correlation of dissolved arsenic and iron in the ground-water contamination plume of the facility. However, it is the mode of occurrence of arsenic in the subsurface materials that is of greatest importance in controlling arsenic release to the sediment. Computation of the relative amount of arsenic and iron dissolved in the ground water compared to that present in the sediment assists in determining the main mode of occurrence causing the high arsenic content of the ground water.

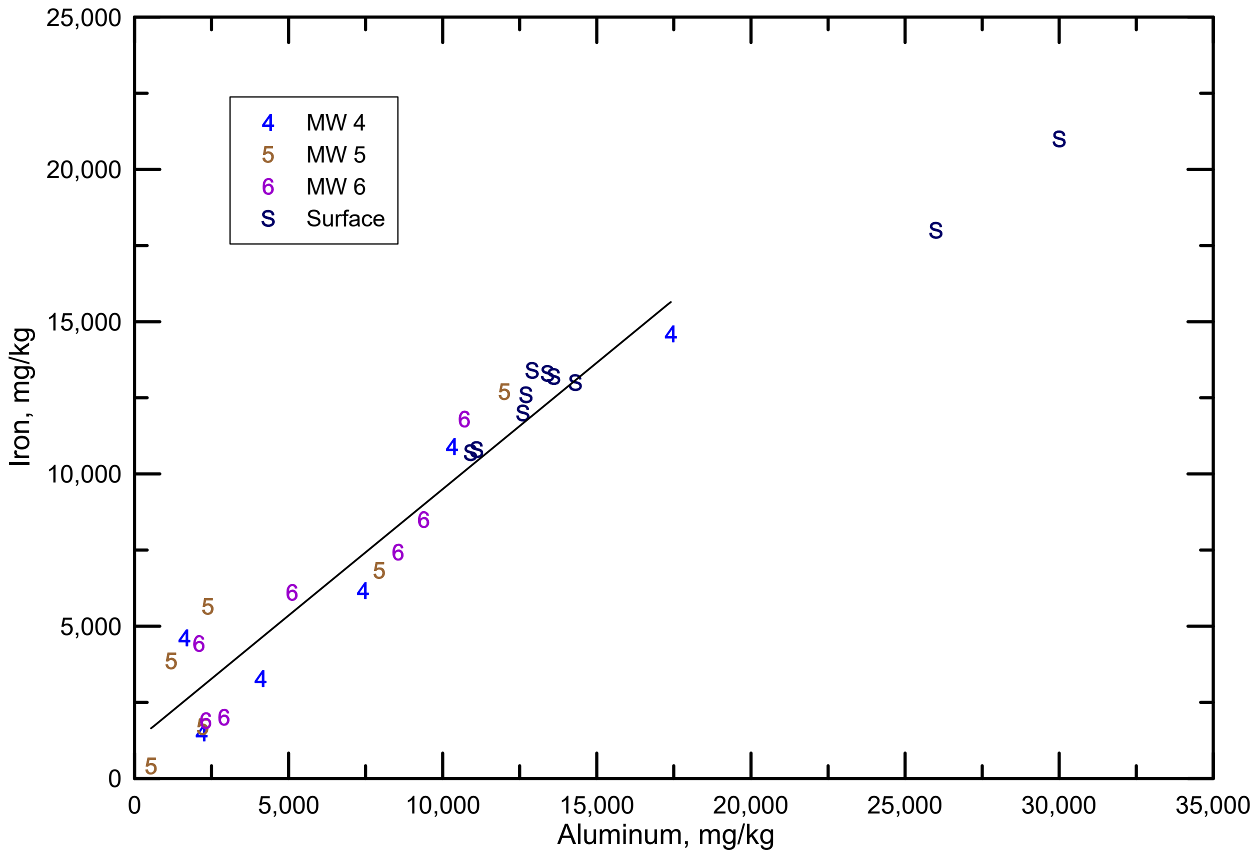

Figure 14. Iron versus aluminum content of surface soil and subsurface sediment from the alcohol facility. The symbol S represents surface soil samples and the numbers represent subsurface sediment collected at different depths at the locations of monitoring wells MW 4, 5, and 6. Surface soil samples were collected at the three MW locations and at five additional sites, and analyzed by Pace Analytical Laboratories. The KDHE analyzed duplicate soil samples from two of the additional five sites. The two surface soils analyzed by KDHE are represented by the two S points with the greatest iron and aluminum values. The regression line is shown for the highly statistically significant correlation between arsenic and iron for the subsurface sediments.

Wet, compacted clay, silt, and gravel have a bulk density of about 1,800-2,100 kg/$m^3$ (http://www.simetric.co.uk/si_materials.htm). If the porosity of the High Plains aquifer is assumed to be approximately 20%, then the weight of the water is 200 kg and the weight of the dry sediment is about 1,800 kg (2,000 minus 200 kg) in a cubic meter of aquifer. Given that a liter of water at aquifer temperatures is essentially equivalent to 1 kg, then there are approximately 200 L of water in a cubic meter of the aquifer.

The highest dissolved arsenic concentration observed in the ground-water samples, 243 µg/L, is equivalent to an arsenic content of 48.6 mg in a cubic meter of the aquifer. If the lowest value of arsenic in the subsurface sediment is assumed to be 0.5 mg/kg (half of the <1 mg/kg value measured for two sediment samples from MW 4), then the lowest arsenic content of a

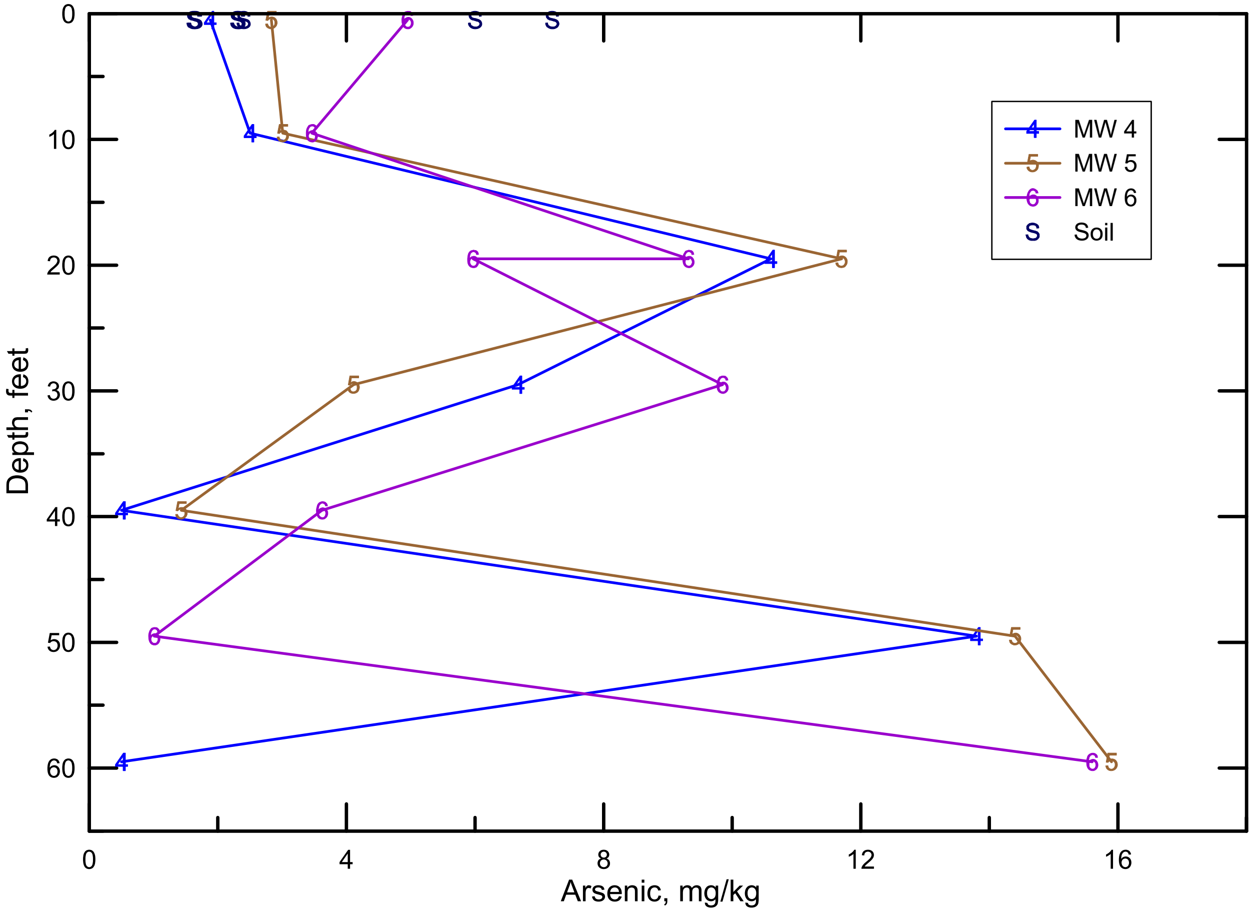

Figure 15. Variation in arsenic content of surface soil and subsurface sediment with depth at the alcohol facility. The symbol S represents surface soil samples and the numbers represent surface soil and subsurface sediment samples collected at the locations of monitoring wells MW 4, 5, and 6. The S points with the greatest arsenic values represent KDHE duplicate analyses of two of the soil samples.

cubic meter of dry aquifer sediment is about 900 mg. Thus, the highest dissolved arsenic concentration measured is only around 5% of the lowest arsenic content of the subsurface sediment. The more typical, high arsenic values for the dissolved content in the ground water are about 200 mg/L and the common arsenic contents for the aquifer sediment are in the range 2-12 mg/kg. This would give a mass of arsenic dissolved in the ground water in a cubic meter of aquifer (40 mg) that would be in the range 0.2-1% of the arsenic content of the dry sediment (3,600-21,600 mg). The average dissolved arsenic concentration of the water samples from MW 2, 3, and 5 through 8 is equivalent to about 0.2% of the average arsenic content of the subsurface sediment based on the data in Tables 5 and 6. Therefore, the amount of arsenic leached from the subsurface sediment to the contaminated ground water is a very small fraction of that in the sediment. This fraction would be even smaller assuming that there are zones in the sediment in the saturated zone in the facility area that contain arsenic content similar to the high concentration zone at 49-50 ft for the wells WW 4 and 5 locations and at 59-60 ft for the wells

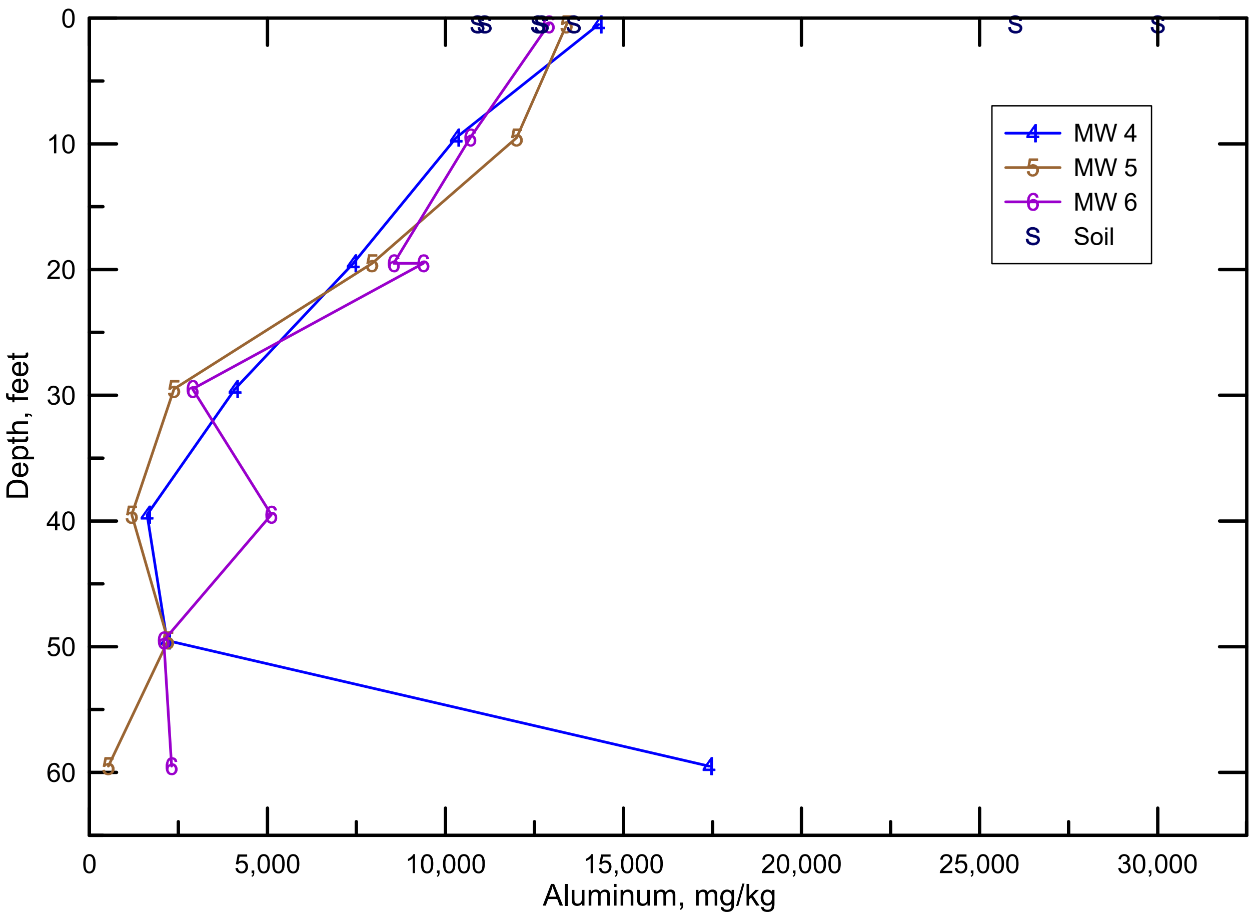

Figure 16. Variation in aluminum content of surface soil and subsurface sediment with depth at the alcohol facility. The symbol S represents surface soil samples and the numbers represent surface soil and subsurface sediment samples collected at the locations of monitoring wells MW 4, 5, and 6. The S points with the greatest aluminum values represent KDHE duplicate analyses of two of the soil samples.

WW 5 and 6 sites. If the source of reducing water continued to enter and flow through the aquifer, more arsenic would be removed from the sediment. However, even for a few aquifer volumes the amount of arsenic leached to the ground water would still probably sum to less than one percent of the arsenic in the sediment.

The amount of the high dissolved iron observed in the ground water in the contamination plume at the facility is similarly a very small component of the iron in the subsurface sediment. For example, a few of the ground water samples contained a dissolved iron concentration as high as over 100,000 µg/L (0.1 g/L). A dissolved iron level of 0.1 g/L is equivalent to 20 g iron in a cubic meter of aquifer. The iron concentration of the subsurface sediment, based on Table 6 data, is usually in the range 2,000-13,000 mg/kg, which is equivalent to a total iron content in the aquifer sediment of 3,600-23,400 g/m$^3$. Therefore, the amount of iron leached from the sediment

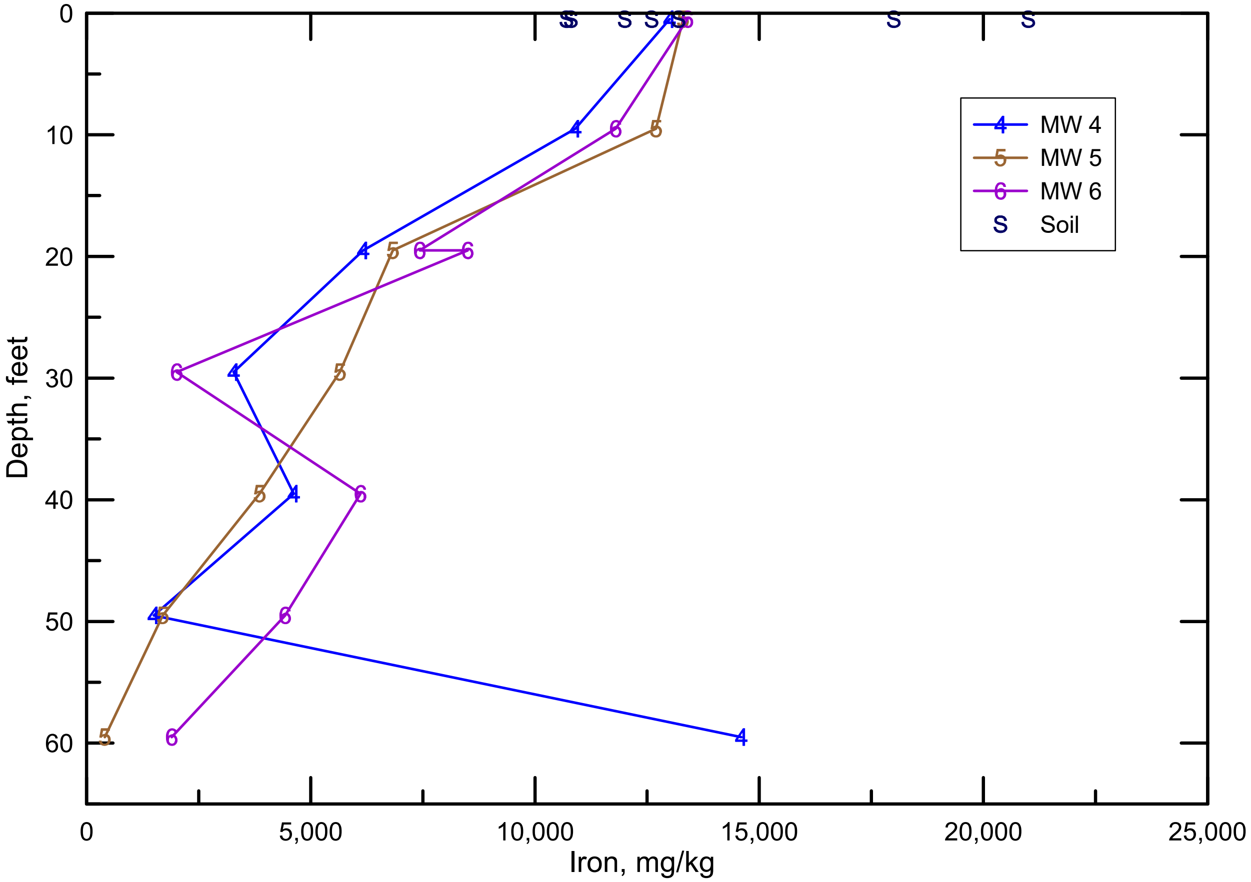

Figure 17. Variation in iron content of surface soil and subsurface sediment with depth at the alcohol facility. The symbol S represents surface soil samples and the numbers represent surface soil and subsurface sediment samples collected at the locations of monitoring wells MW 4, 5, and 6. The S points with the greatest iron values represent KDHE duplicate analyses of two of the soil samples.

to the ground water in the contaminant plume could be in the range of from <0.1% to about 0.6% of the iron in the sediment.

The relatively small mass of arsenic and iron leached from the sediment to the ground water means that arsenic desorbed from the surface of and dissolved from a thin layer of ferric oxyhydroxide in the subsurface sediment should be sufficient to explain the concentrations observed in the water samples. Iron-oxide coatings and particles occur in both soils and sediments. For example, sand-textured Quaternary and Pliocene fluvial sediments in Delaware and Virginia that form aquifers contain iron-oxide coated grains (Zachara et al., 1995).

Clays can contain iron in their structure as well as having iron oxide coatings. The iron oxide content of predominantly clay horizons in Ogallala Formation sediments can be in the range of several percent (Ives and Hill, 1960). Clay-sized particulates could have a greater total amount of oxide coatings due to a larger surface area than larger sand-sized grains, and could include iron oxide particles and colloids. However, the general inverse relationship between arsenic and both iron and aluminum in the facility sediments could represent a greater amount of arsenic associated with ferric oxyhydroxide coatings on sand grains than in the layers of finer-grained, clay-sized material in the sediment.

The original source of much of the arsenic in the subsurface sediment could explain why more arsenic appears to be generally associated with sediment with lower iron and aluminum content, which would be the more sandy portions of the strata. Arsenic is a volatile element in volcanic eruptions that becomes predominantly associated and enriched in volcanic ash (Kotra et al., 1983). High arsenic ground waters have been found in aquifers composed of fluvial sediments containing volcanoclastic material (Smedley et al., 2002; Smedley and Kinniburgh, 2002, Bundschuh et al., 2004). Ash deposits are known to have occurred during the deposition of the Ogallala sediments and have altered to montmorillonite clay beds (Ives and Hill, 1960). Ash deposits in the Ogallala could have been associated with some organic matter that the ash covered or that was associated with clay deposits in which eroded ash became redeposited. The decomposition of the organic matter could have led to reducing conditions in local pore waters in the fine-grained sediments. The simultaneous alteration of the volcanic ash to montmorillonite clays could have released arsenic to this chemically reducing water. The dissolved arsenic in the water migrating from the fine-grained deposits then could have been adsorbed on the ferric oxyhydroxide coatings on the silt and sand grains in the more permeable sediments that contained an oxidizing environment.

## IMPLICATIONS FOR ARSENIC FATE AND TRANSPORT

Water containing dissolved organic compounds that seeped from the wastewater ponds of the alcohol facility to the water table would flow more readily through the coarser sand and gravels of the High Plains aquifer. Thus, the migrating ground water that developed chemically reducing conditions would preferentially be in contact with and be able to solubilize arsenic associated with iron, manganese, and aluminum oxide coatings on the sandy sediments in the aquifer. Pumping from the water-supply and monitoring wells that intercepted the plume of ground water with admixed wastewater would preferentially derive their water from these coarser sediment flow paths along which arsenic had been released.

The plume of high-arsenic ground water should continue to migrate as long as the chemically reducing environment exists along the front of the plume. This will depend on the amount of degradable, dissolved organic matter remaining in the plume front relative to the rate of essentially complete degradation of the dissolved organics. If the amount of degradable organic matter becomes very small and the rate of mixing of precipitation recharge containing dissolved oxygen is great enough to maintain a high oxidation potential at the front of the plume, then the dissolved iron and manganese will oxidize and precipitate as oxyhydroxides in the sediment. This would then allow readsorption of the arsenic on the sediments and decrease the dissolved arsenic concentration. The faster migrating parts of the ground-water plume within the preferential paths of the most permeable sediment will encounter and mix with more water with a higher oxidation potential, which will limit the amount of additional arsenic release, and then eventually allow arsenic readsorption. Recharge by oxygenated precipitation recharge into the lower permeability sediments of the aquifer will take longer to mix with the high-arsenic ground water and, thus, take longer to degrade more completely most of the remaining dissolved organic matter, raise the oxidation potential, and reprecipitate oxyhydroxides and readsorb arsenic. The main factor in the fate and transport of the existing high-arsenic ground water will be the amount of dissolved organic matter that continues to enter the subsurface below the ponds and that will maintain the low oxidation potential of the ground water.

The substantially different values for metals concentrations in the duplicate analyses by KDHE of two of the surface soil samples indicate the importance of using data for consistent sample preparation of solid samples in interpretation of metals contamination. In addition, data for dissolved metals in waters should be based on samples filtered through membrane filters in the field followed by acidification for sample preservation before analysis. The measurement of aluminum concentration in filtered samples can be a good test of how well the samples were filtered.

## IMPLICATIONS FOR REMEDIATION

The data indicate that the primary cause of the high arsenic concentration in the ground water of the alcohol facility is the creation of a chemically reducing environment from the degradation of dissolved organic matter in the infiltrating wastewater. Thus, the most effective way in which to mitigate the long-term problem is to either substantially decrease the amount of dissolved organics in this wastewater or decrease the amount of wastewater seeping from below the ponds. If part of the high dissolved arsenic is related to exchange on sediment surfaces with dissolved phosphate from the wastewater, then the phosphate concentration of the wastewater would need to be decreased. To immediately prevent further migration of the existing contamination plume, ground water would need to be pumped from the front of the plume. Alternatively, the oxidation potential of the ground water along the front of the contamination plume would need to be increased to reprecipitate ferric and manganic oxyhydroxides and allow readsorption of the dissolved arsenic during the formation of the oxyhydroxide coatings and particulates.

If the amount of wastewater seeping from below the ponds were substantially reduced such that the rate of essentially complete degradation of the dissolved organic matter reaching and within the ground water were greater than the influx of additional dissolved organics in the wastewater to the ground water, then natural in-situ remediation of the contaminated plume would eventually occur. Precipitation recharge would be expected to carry dissolved oxygen with the water passing through the unsaturated zone to allow greater degradation of organics in the sediment pore water above the water table, followed by eventual reestablishment of a high enough oxidation potential in the ground water to reprecipitate oxyhydroxides and readsorb arsenic.

Application of the wastewater on the land surface for irrigation would not be expected to create arsenic contamination in ground water below the fields as long as the application rate were not great enough to allow substantial recharge of the wastewater below the root zone of the crops. Thus, management of the application rates would be especially important in the non-growing season when crops would not actively be using the water.

If ground water with high arsenic concentration were pumped from the contamination plume and applied to the land as irrigation water, there should not be a substantial concern in terms of the arsenic. The reason is related to the mass of arsenic naturally occurring in the soil relative to that present in the contaminated ground water. The arsenic content of a volume of soil for the area can be calculated in a similar manner as that described earlier for the subsurface sediment. The bulk density of a soil is generally in the range 1,000-1,800 kg/m$^3$ (Brady, 1974). For a bulk density of 1,400 kg/m$^3$ and an arsenic concentration of 3.4 mg/kg (the average for the soil analyses in Table 6), the arsenic content of a soil in the facility area would be 4,700 mg/m$^3$. The root zone of cultivated crops is about one meter. If water pumped from the contamination plume was assumed to contain 200 µg/L arsenic and was used for irrigation, the total arsenic annually added to the soil to a meter depth would be 91 mg/m$^3$, assuming an application rate of 18 in/yr and that all of the arsenic remained above the bottom of the root zone. This added arsenic would be approximately 2% of the arsenic mass already in the soil. Ten years of irrigation with this water would only increase the total arsenic content of the soil by about 20%. The soil arsenic concentration would still be substantially below the average of 6.6 mg/kg for the two arsenic values in Table 6 determined by the KDHE. The amount of arsenic accumulated in the upper one meter of soil would be even less assuming that some of the applied irrigation water passed the root zone to deeper in the unsaturated zone where the arsenic could also be adsorbed.

## IMPLICATIONS FOR HIGH ARSENIC GROUND WATER AT OTHER LOCATIONS

The results of this study suggest that the generation of high arsenic concentrations in ground water may not be unusual in conditions where waters with large amounts of dissolved organic matter are applied at the surface in sufficient quantities to substantially increase recharge to unconsolidated aquifers in areas of low ground-water recharge. The main factor involved is the introduction of amounts of organic compounds that can be biochemically degraded to appreciably decrease the oxidation potential of the ground water and reduce and dissolve ferric oxyhydroxide coatings and particulates in the sediment. Locations where volcanic ash was deposited in High Plains and alluvial aquifer sediments probably contain permeable horizons where arsenic mobilized during the alteration of the ash was subsequently adsorbed to oxide coatings and possibly clays. These aquifer strata probably exacerbate the generation of the high arsenic ground water. Thus, ground waters in the High Plains and alluvial aquifers in western Kansas below unsealed ponds and lagoons containing wastewater with substantial organic matter may have arsenic contents higher than background.

Unconsolidated aquifers in areas of greater rainfall and ground-water recharge would also be potential locations for generation of high-arsenic ground waters below not only organic-rich wastewaters but also landfills with organic matter and spills and leaks of organics such as hydrocarbons. In eastern Kansas, such aquifers would be alluvial systems associated with major rivers.

An unknown consideration is the application of high-phosphate concentration wastewaters in quantities sufficient to substantially recharge underlying ground waters in unconsolidated aquifers. Phosphate is known to exchange for arsenic adsorbed on sediments and could therefore potentially increase arsenic contents of ground waters. Thus, application of high-phosphate waters to fields in large quantities is not only a potential issue relative to contamination of surface-water runoff but possibly to increase of arsenic content in underlying ground water.

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