## Metals

**Arsenic.** Arsenic (As) is a naturally occurring element found in low concentrations in rocks, soils, water, plants, and animals (Nriagu, 1994a, b; U.S. EPA, 1998). In Kentucky, arsenic is commonly found in pyrite or arsenopyrite minerals associated with coal deposits and black shales. Arsenic is released when iron sulfides oxidize during weathering. Once released, arsenic is readily sorbed onto iron oxides and iron oxyhydroxides. This sorption can limit dissolved arsenic concentrations in groundwater, but can produce high arsenic concentrations in unfiltered groundwater samples that contain suspended particulate material (total arsenic concentrations).

Arsenic is used as a wood preservative and in paints, dyes, metals, drugs, soaps, semiconductors, animal feed additives, and herbicides. From 1860 through 1910, arsenic was heavily used in embalming fluids. It was banned in 1910 because it interfered with investigations into suspected poisoning deaths; but old graveyards may still be a source of arsenic in groundwater (Fetter, 1993). Waste-disposal sites and landfills may be sources of arsenic contamination because of the materials disposed of there, and coal burning can release arsenic to the atmosphere. Hydrocarbons from leaking underground storage tanks can dissolve iron oxide minerals in soils, thus releasing naturally occurring arsenic to the environment (Welch and others, 2000). Metal-reducing bacteria, as well as changes in oxidation conditions as a result of pumping, also can affect arsenic concentrations in the vicinity of a well.

Long-term exposure to arsenic in drinking water has been linked to health problems such as cancer of the skin, bladder, lungs, kidneys, nasal passages, liver, and prostate. Arsenic has also been linked to damage of the cardiovascular, pulmonary, immunological, neurological, and endocrine systems. Because of these health effects, the Environmental Protection Agency set the maximum contaminant level for arsenic in drinking water at 50 ppb (or 0.05 mg/L) in 1974. In 2001, the EPA announced that this MCL would be lowered to 10 ppb (0.01 mg/L). Water-supply systems had to meet the new MCL beginning January 1, 2006.

Sites identified as monitoring wells by the Kentucky Division of Water's well-identification numbering system were excluded from the data set used here because, although not explicitly identified as part of an underground storage tank investigation, these wells may have been installed to check for leaking hydrocarbon storage tanks. Because hydrocarbons can dissolve iron oxides from soils, arsenic results from these sites may not represent regional background conditions.

Because the new MCL is 0.01 mg/L, measurements that had a detection limit greater than 0.01 mg/L provide no useful information. Therefore, such values are not included in the following discussion. Removing these measurements leaves 1,858 reported arsenic concentrations at 308 sites (Table 13).

Table 13. Summary of arsenic values (mg/L). MCL: 0.010 mg/L.			
	BMU 1	BMU 2	BMU 5
Values	869	697	290
Maximum	0.076	0.265	0.038
75th percentile	< 0.002	< 0.002	< 0.002
Median	< 0.002	< 0.002	< 0.002
25th percentile	< 0.002	< 0.002	< 0.002
Minimum	< 0.0005	< 0.0005	< 0.0005
Interquartile range	N/A	N/A	N/A
Sites	92	110	106
Sites > 0.010 mg/L	1	3	5

< means analytical result reported as less than the stated analytical detection limit

The maximum value in each basin management unit exceeds the MCL. Nine of 308 sites produced groundwater that had an arsenic concentration greater than 0.01 mg/L, and 94 percent of the values are reported as less than analytical detection.

Cumulative plots of values (Figs. 69–71) are similar for the three basin management units. More than 95 percent of the arsenic concentrations are less than 0.01 mg/L.

There are relatively few sites in the Outer Bluegrass Region where arsenic was measured, compared to the Inner Bluegrass, Eastern Kentucky Coal Field, and Western Pennyroyal Regions (Fig. 72). Sites where arsenic exceeds the MCL of 0.01 mg/L are not concentrated in any region or major watershed.

The highest arsenic concentrations are found in the Outer Bluegrass Region (Fig. 73) and the Kentucky River watershed (Fig. 74).



Figure 69. Cumulative plot of arsenic values from BMU 1.



Figure 70. Cumulative plot of arsenic values from BMU 2. One value of 0.265 mg/L was excluded for clarity.

Total (unfiltered sample) and dissolved (filtered sample) arsenic concentrations have the same distribution of values (Fig. 75), indicating that significant amounts of arsenic have not adsorbed on suspended material in the project area.

Arsenic concentrations from wells reach higher values than groundwater from springs (Fig. 76).

The highest arsenic concentrations in wells are found at depths of about 100 ft (Fig. 77).

In summary, arsenic is present at very low concentrations in groundwater throughout the project area. Only nine of 308 sites produced groundwater with arsenic concentrations that exceeded the MCL, and these sites are not predominantly in any one physiographic region or major river watershed. Therefore, nonpoint-source contamination with respect to arsenic in groundwater does not seem to be occurring in the project area. A statewide summary of arsenic data (Fisher, 2002a) can be viewed on the KGS Web site (kgsweb.uky.edu/olops/pub/kgs05\_12.pdf).



Figure 71. Cumulative plot of arsenic values from BMU 5.







Figure 73. Summary of arsenic values grouped by physiographic region. One value of 0.265 mg/L in the Knobs Region was excluded for clarity.



Figure 75. Comparison of total and dissolved arsenic values. One value of 0.265 mg/L total arsenic was excluded for clarity.



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Figure 74. Summary of arsenic values grouped by major watershed. One value of 0.265 mg/L in the Salt River watershed was excluded for clarity.



Figure 76. Comparison of arsenic values from wells and springs. One value of 0.265 mg/L arsenic from a well was excluded for clarity.



Figure 77. Plot of arsenic values versus well depth.

**Barium.** Barium (Ba) is an alkaline earth element that occurs naturally as the mineral barite (BaSO<sub>4</sub>), which is common in both sandstone and carbonate strata. Barium is used in electronic components, metal alloys, bleaches, dyes, fireworks, ceramics, and glass, and as an additive to drilling fluids used in oil and gas wells. Barium may be released to soil and water from the discharge of drilling wastes, or from leaking landfills where barium-containing materials were discarded.

The EPA has set the MCL for barium at 2 mg/L. Short-term exposure to higher barium concentrations can cause gastrointestinal problems and muscular weakness, whereas long-term exposure can cause high blood pressure.

The data repository contained 2,579 barium measurements from 654 sites in the project area (Table 14). Although maximum values in each basin management unit are quite high, the 75th percentile values are well below 1 mg/L throughout the region. Only 21 of 654 sites yielded groundwater that had more than 2 mg/L of barium.

Data distributions (Figs. 78–80) show the same general trend, with more than 95 percent of the values being less than 2 mg/L. Data distributions for BMU 2 (Fig. 79) and BMU 5 (Fig. 80) have a sharp break in



Figure 78. Cumulative plot of barium values from BMU 1.



Figure 79. Cumulative plot of barium values from BMU 2. Two values were excluded for clarity.



Figure 80. Cumulative plot of barium values from BMU 5. Nine values were excluded for clarity.

slope, which may indicate that two distinct populations are represented.

The distribution of sampled sites (Fig. 81) shows a greater density in the Eastern Kentucky Coal Field, Inner Bluegrass, and Western Pennyroyal Regions. Eleven of the 21 sites where barium exceeded the MCL are in the Eastern Kentucky Coal Field.

Table 14. Summary of barium values (mg/L). MCL: 2.0 mg/L.			
	BMU 1	BMU 2	BMU 5
Values	1,027	1,122	430
Maximum	8.69	79.8	100.0
75th percentile	0.43	0.07	0.59
Median	0.03	0.04	0.16
25th percentile	0.02	0.03	0.04
Minimum	0.00	0.00	0.00
Interquartile range	0.41	0.04	0.55
Sites	143	344	167
Sites > 2.0 mg/L	2	11	8





Values greater than the MCL are found primarily in the Eastern Kentucky Coal Field (Kentucky, Licking, and Big Sandy River watersheds) and the Outer Bluegrass Region (Salt River watershed) (Figs. 82–83).

Barium concentrations in total (unfiltered) samples have a larger interquartile range than concentra-



Figure 82. Summary of barium values grouped by physiographic region. Higher values were excluded for clarity.



Figure 83. Summary of barium values grouped by major watershed. Higher values were excluded for clarity.

tions from dissolved (filtered) samples, and more values greater than 2 mg/L (Fig. 84).

Barium concentrations from wells have a larger interquartile range than concentrations from springs (Fig. 85). No samples from springs had a barium concentration above the MCL.

The highest barium concentrations are found in wells that are less than 100 ft deep (Fig. 86).

In summary, 21 of 654 sites yielded groundwater that contained more than 2 mg/L barium in the project area. All these sites were shallow wells in the Eastern Kentucky Coal Field. Wunsch (1991) reported similar observations from 130 wells in the Eastern Kentucky Coal Field, and attributed the barium concentrations greater than 1.0 mg/L primarily to a mixing of deep, barium-rich brines with shallow groundwater. Naturally occurring barite is another probable source of the barium concentrations observed. Strong influence of



Figure 84. Comparison of total and dissolved barium values. Nine values of total barium were excluded for clarity.



Figure 85. Comparison of barium values from wells and springs. Nine values from wells were excluded for clarity.

man-made, nonpoint sources of barium contamination are not suggested by the observed barium concentrations.



Figure 86. Plot of barium values versus well depth.

Mercury. Mercury (Hg) is a liquid metal found in natural deposits as ores containing other elements. Forest fires, coal combustion products, disposal of mercurycontaining products such as electric lights and switches, computers, and blood pressure gauges contribute mercury to the environment. Electrical products such as dry-cell batteries, fluorescent lightbulbs, switches, and other control equipment account for 50 percent of mercury used. Combustion of fossil fuels, metal smelters, cement manufacture, municipal landfills, sewage, and metal refining operations are significant sources of mercury in the environment. When mercury from such sources is acted on by bacteria, some of it is converted to methylmercury, a much more toxic form of mercury. At high does, mercury is a strong neurotoxin that causes demyelination<sup>1</sup>, delayed nerve conduction, and kidney damage. Because of its toxicity, the EPA has set an MCL for mercury at 0.002 mg/L.

The Kentucky Groundwater Data Repository contained 1,587 mercury analyses from 430 sites from the project area (Table 15, Fig. 87). No measured mercury concentration exceeded the MCL of 0.002 mg/L.

Only 21 of the 430 sites had values above analytical detection. Most of these were in the Western Pennyroyal Region of the Salt River watershed. Four of these sites are springs and 17 are wells. Three of these values were dissolved mercury and 18 were measurements of total mercury. The highest reported value was 0.00095 mg/L, well below the MCL of 0.002 mg/L.

Because so few values of mercury were above analytical detection limits, no further analysis was performed.

In summary, mercury was detected in 21 of 430 sites in the project area. The maximum mercury concentration reported was 0.00095 mg/L, less than half of the MCL. Detections were more common in unfiltered samples, suggesting that mercury was adsorbed onto suspended material rather than in true solution. Most of the sites where mercury was detected are located in the Western Pennyroyal Region of the Salt River watershed, BMU 2. This concentration of mercury detections most likely indicates either a geologic control or the influence of atmospheric fallout.

Table 15. Summary of mercury values (mg/L). MCL: 0.002 mg/L.			
	BMU 1	BMU 2	BMU 5
Values	622	731	235
Maximum	< 0.002	< 0.002	0.00095
75th percentile	< 0.00005	<0.0001	< 0.00005
Median	< 0.00005	< 0.00005	< 0.00005
25th percentile	< 0.00005	< 0.00005	< 0.00005
Minimum	< 0.00005	< 0.00005	< 0.00005
Interquartile range	N/A	N/A	N/A
Sites	100	221	109
Sites > 0.002 mg/L	0	0	0

< means analytical result reported as less than the stated analytical detection limit

<sup>&</sup>lt;sup>1</sup>Destruction or loss of material that acts as a sheath around nerves.



Figure 87. Locations of sampled sites and ranges of mercury values. Superimposed symbols indicate that values recorded at different sampling times fell into differ-ent ranges.

**Iron.** Iron (Fe) is a naturally occurring metal that is widely present in groundwater. Iron can occur in either an oxidized (ferric) or reduced (ferrous) state. At normal groundwater pH values, ferric iron is rapidly precipitated as an iron oxide, iron hydroxide, iron oxyhydroxide (rust), or poorly crystalline to amorphous material. Under reduced conditions, however, ferrous iron is stable and will remain in groundwater. There is no EPA primary drinking-water standard for iron in water supplies because there are no identified serious health threats posed by it. There is, however, a secondary standard of 0.3 mg/L for iron because concentrations above this level produce objectionable odor, taste, color, staining, corrosion, and scaling.

The data repository contained 11,288 iron measurements from 2,629 sites in the project area (Table 16). Iron concentrations are quite high; more than half of the sites in each basin management unit produced groundwater that has iron concentrations above the secondary standard.

The distribution of reported iron concentrations is similar in the three basin management units (Figs. 88–90).

Sample-site density is greatest in the Eastern Kentucky Coal Field and lowest in the eastern part of the Outer Bluegrass Region (Fig. 91). Values above the



Figure 88. Cumulative plot of iron values in BMU 1. Higher values were excluded for clarity.

SMCL are found throughout the project area and are most common in the Eastern Kentucky Coal Field, western part of the Outer Bluegrass, and Western Pennyroyal Regions.

Samples from the Eastern Kentucky Coal Field and the Outer Bluegrass Regions have the highest iron concentrations and the largest range of values,



Figure 89. Cumulative plot of iron values from BMU 2. Higher values were excluded for clarity.



Figure 90. Cumulative plot of iron values from BMU 5. Higher values were excluded for clarity.

whereas sites from the Inner Bluegrass and Western Pennyroyal Regions have the lowest concentrations and smallest range of values (Fig. 92).

Samples from the Licking River watershed have the lowest median value and smallest interquartile range of iron concentrations (Fig. 93). Samples from the Salt River, Big Sandy River, Little Sandy River, and Tygarts Creek watersheds have high median values, a large interquartile range, and a large number of iron concentrations greater than 5 mg/L.

Table 16. Summary of iron values (mg/L). SMCL: 0.3 mg/L.			
	BMU 1	BMU 2	BMU 5
Values	4,394	3,187	3,707
Maximum	735	9,660	1,500
75th percentile	1.0	1.9	2.76
Median	0.23	0.26	0.60
25th percentile	0.05	0.04	0.14
Minimum	0.00	0.00	0.00
Interquartile range	0.95	1.86	2.62
Sites	751	1,055	823
Sites > 0.3 mg/L	523	599	641





Total iron concentrations (unfiltered samples) have a higher median value and greater interquar-



Figure 92. Summary of iron values grouped by physiographic region. Higher values were excluded for clarity.

tile range than dissolved iron concentrations (filtered samples), suggesting that some of the reported iron is associated with suspended solids (Fig. 94).

Groundwater from springs is generally much lower in iron than water from wells (Fig. 95).

High iron concentrations are found more commonly in wells that are less than 100 ft deep; deeper wells typically have much lower iron concentrations (Fig. 96).

In summary, iron concentrations that are high enough to produce staining and objectionable taste are common in groundwater throughout the project area. High iron concentrations are especially common in the Eastern Kentucky Coal Field and western part of the Outer Bluegrass Region. Total iron concentrations are higher than dissolved concentrations, indicating that iron is also present in suspended material. Wells have higher iron concentrations than springs, probably because many springs in this area are in carbonate bedrock, which is naturally lower in iron than sandstones and shales.



Figure 93. Summary of iron values grouped by major watershed. Higher values were excluded for clarity.



Figure 94. Comparison of total and dissolved iron values. Higher values were excluded for clarity.



Figure 95. Comparison of iron values from wells and springs. Higher values were excluded for clarity.



Figure 96. Plot of iron values versus well depth. Higher values were excluded for clarity.

**Manganese.** Manganese (Mn) is a naturally occurring cation that is widely present in groundwater supplies. Manganese and iron behave similarly geochemically, so high manganese concentrations can be expected from wells and springs that produce water with high iron concentrations.

There is no EPA primary drinking-water standard for manganese in water supplies because there are no identified serious health threats posed by it. There is, however, a secondary standard of 0.05 mg/L for manganese, because higher concentrations produce objectionable odor, taste, color, corrosion, and staining.

The data repository contained 9,079 manganese concentrations from 6,005 sites in basin management units 1, 2, and 5 (Table 17). Like iron concentrations, manganese concentrations are high enough to require



Figure 98. Cumulative plot of manganese values from BMU 2. Higher values were excluded for clarity.

Table 17. Summary of manganese values (mg/L). SMCL: 0.05 mg/L.			
	BMU 1	BMU 2	BMU 5
Values	3,788	2,561	2,730
Maximum	20.1	540	83
75th percentile	0.20	0.29	0.50
Median	0.06	0.04	0.11
25th percentile	0.01	0.01	0.03
Minimum	0.00	0.00	0.00
Interquartile range	0.19	0.28	0.47
Sites	2,458	1,816	1,731
Sites > 0.05 mg/L	840	663	642

treatment before groundwater is suitable for domestic use. More than one-third of all sites produce water having more than 0.05 mg/L of manganese.

The distribution of manganese concentrations is generally similar in the three basin management units (Figs. 97–99), although BMU 1 has fewer very high values than BMU 2 or BMU 5.

Site distribution is very dense in the southern part of the Eastern Kentucky Coal Field and the west-



Although manganese concentrations that exceed the SMCL are found in every physiographic region and major watershed, they are most common in the Eastern Kentucky Coal Field (Kentucky

River, Big Sandy River, Little Sandy River, and Tygarts Creek watersheds) and the Outer Bluegrass Region (Salt River watershed) (Figs. 101–102).

Dissolved manganese concentrations have a higher median value and larger interquartile range than total manganese concentrations (Fig. 103), suggesting that suspended particulate material does not



Figure 97. Cumulative plot of manganese values from BMU 1. Higher values were excluded for clarity.



Figure 99. Cumulative plot of manganese values from BMU 5. Higher values were excluded for clarity.





contribute significant amounts of manganese to the analysis.

Figure 101. Summary of manganese values grouped by physiographic region. Higher values were excluded for clarity.



Figure 102. Summary of manganese values grouped by major watershed. Higher values were excluded for clarity.



Figure 103. Comparison of total and dissolved manganese values. Higher values were excluded for clarity.

Groundwater from wells is generally higher in manganese than groundwater from springs (Fig. 104).

The highest manganese concentrations are typically found in wells less than 100 ft deep, rather than in deeper wells (Fig. 105).

In summary, the geochemical similarity between manganese and iron is demonstrated in the similarity of their concentrations in groundwater. Both commonly occur at concentrations that affect taste and can stain containers and clothing. The highest manganese concentrations are found in groundwater from the Eastern Kentucky Coal Field and the western part of the Outer Bluegrass Region, and in shallow wells rather than deep wells or springs. All features of the distribution of manganese concentrations appear primarily related to bedrock type. There is no evidence to suggest that nonpoint-source contamination significantly contributes to manganese concentrations in the project area.



Figure 104. Comparison of manganese values from wells and springs. Higher values were excluded for clarity.



Figure 105. Plot of manganese values versus well depth.