

Metals

Arsenic. Arsenic (As) is a naturally occurring element found in low concentrations in rocks, soils, water, plants, and animals (Nriagu, 1994a, b). In Kentucky, arsenic is commonly found in iron sulfide 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; 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 combustion 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 (U.S. Environmental Protection Agency, 1998). The EPA set the MCL for arsenic in drinking water at 0.050 mg/L in 1974. In 2001 the EPA announced that this MCL will be lowered to 0.010 mg/L. Water-supply systems must meet the new MCL beginning in January 2006.

Both total and dissolved arsenic analyses were performed with a variety of methods and detection limits. Approximately 70 percent of the records are reported as less than a detection limit, with detection limits ranging from 0.052 to 0.001 mg/L. Because the new MCL is 0.010 mg/L, measurements reported only as below a detection limit, in which the detection limit was 0.010 or greater, provide no useful information. Therefore, these values are not included in the following discussion. Removing those values leaves a total of 1,477 measured arsenic concentrations at 308 sites (Table 13). Sixty-six percent of the values were reported as less than a detection limit. Forty-five of 308 sites have

Table 13. Summary of arsenic values (mg/L).

Measurements	1,086
Maximum	0.219
75th percentile	< 0.002
Median	< 0.002
25th percentile	< 0.002
Minimum	0.001
Interquartile range	na
Sites	188
MCL	0.010
Sites > 0.010	28

< means analytical result reported as less than the stated value

total arsenic concentrations greater than 0.010 mg/L, but only seven sites have dissolved arsenic concentrations greater than 0.010 mg/L. More than 90 percent of reported values are less than 0.010 mg/L (Fig. 50).

Sites where arsenic was measured are fairly evenly distributed throughout the project area, with clusters of sites in the northern Tennessee and Ohio River watersheds (Fig. 51).

Arsenic concentrations exceed 0.010 mg/L in all physiographic regions except the Western Pennyroyal (Fig. 52) and all major watersheds except the Lower Cumberland (Fig. 53).

Total arsenic concentrations range to higher values than dissolved arsenic concentrations, although there is considerable overlap of the values (Fig. 54). Dissolved arsenic concentrations measure a filtered sample; total arsenic concentrations measure an unfiltered sample. Well purging can stir up sediment, and arsenic that is adsorbed onto the sediment would be analyzed as part of the total sample. Arsenic associated with suspended solids would be less mobile than

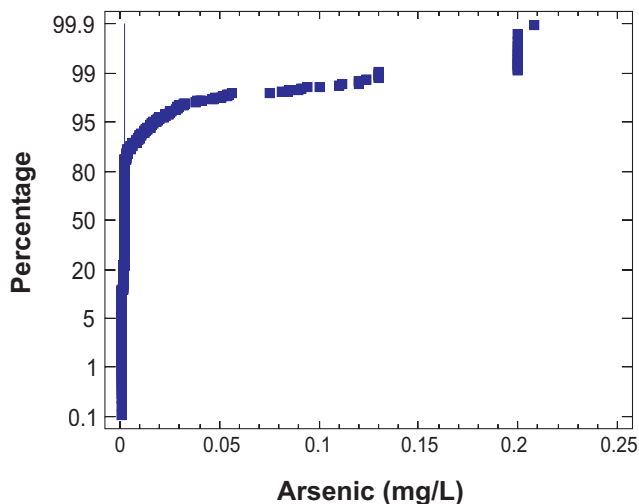


Figure 50. Cumulative plot of arsenic values. Higher values were excluded to show values in the range of the MCL.

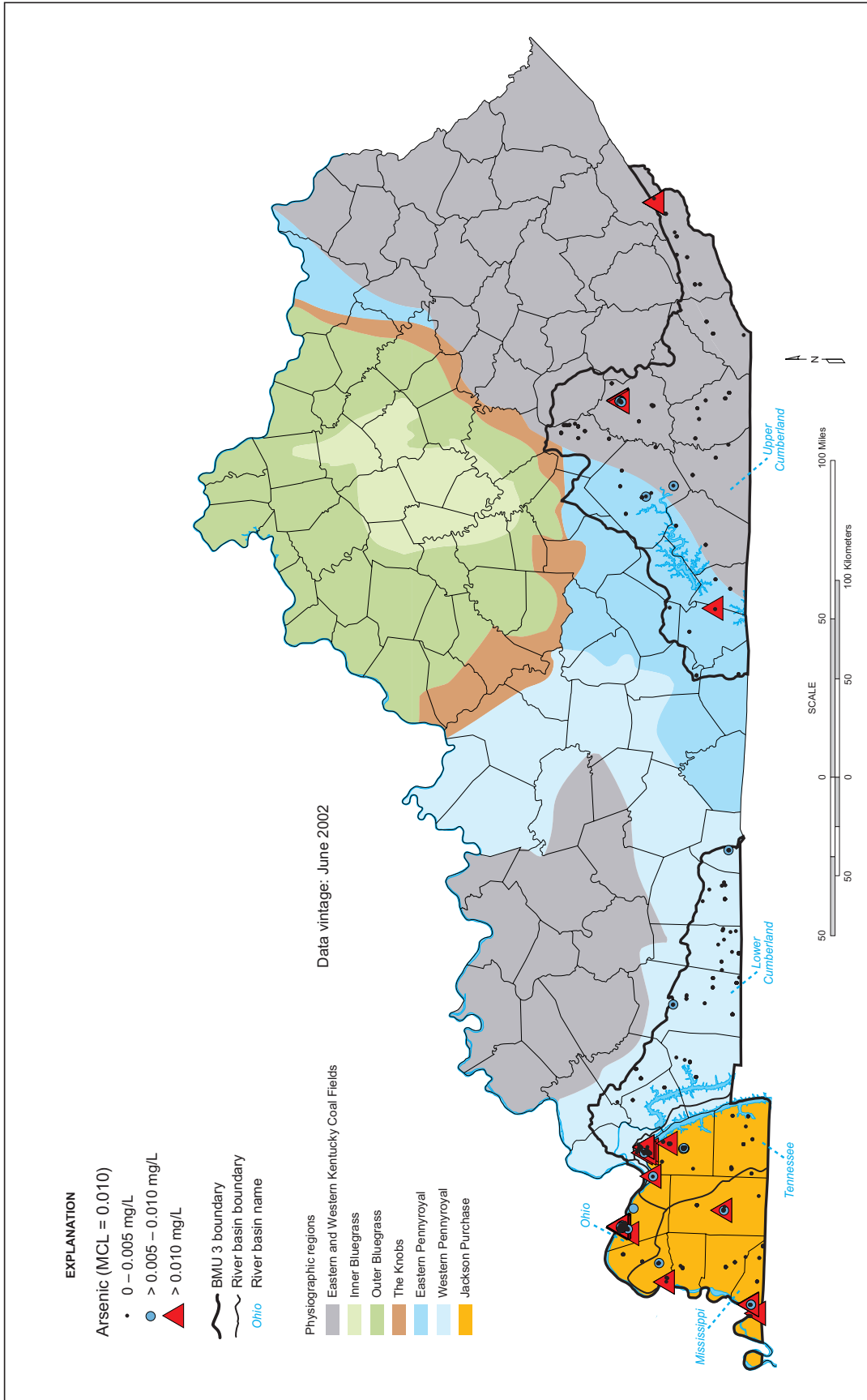


Figure 51. Sample sites and ranges of arsenic values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

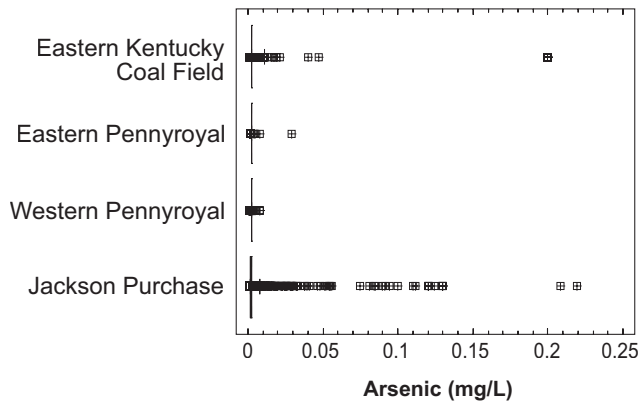


Figure 52. Summary of arsenic values grouped by physiographic region.

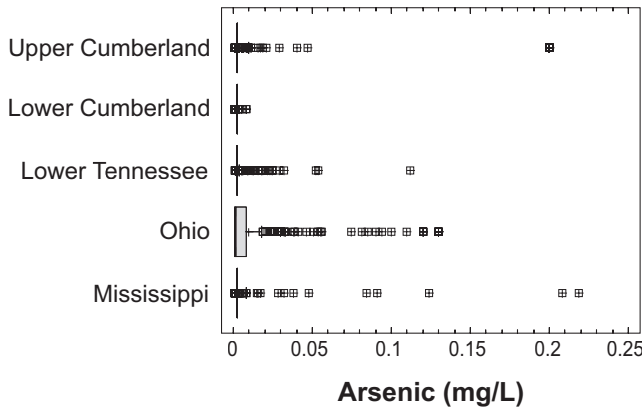


Figure 53. Summary of arsenic values grouped by major watershed.

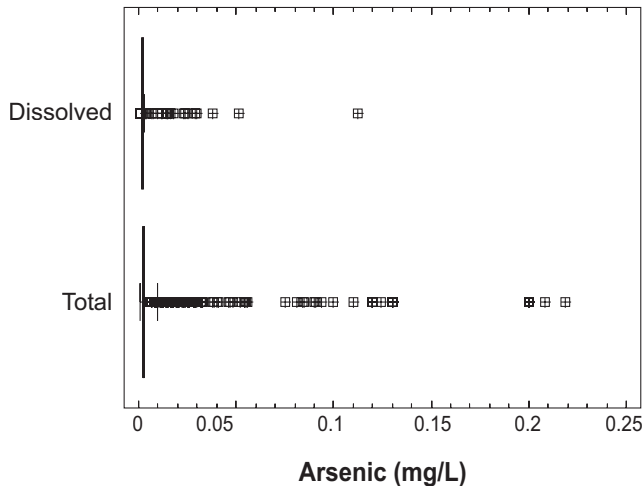


Figure 54. Comparison of total and dissolved arsenic values.

arsenic in true solution in the groundwater. Therefore, if an individual site showed a high total arsenic concentration but low dissolved arsenic concentration,

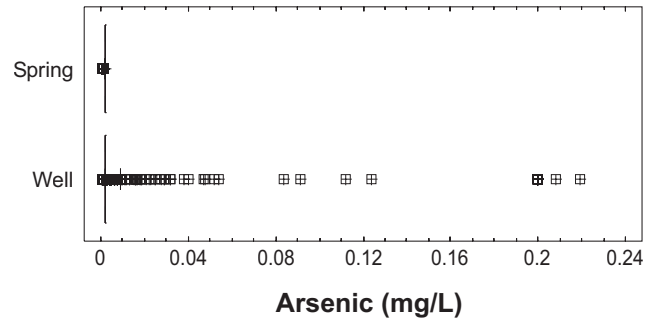


Figure 55. Comparison of arsenic values from wells and springs.

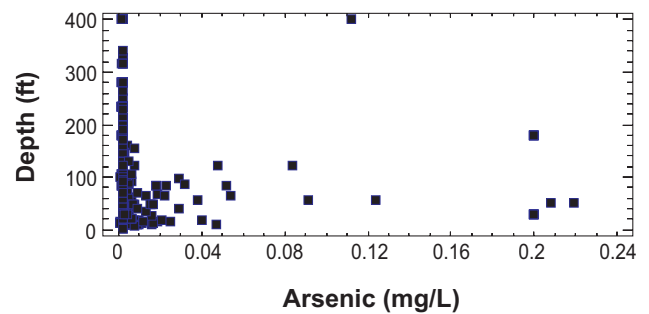


Figure 56. Arsenic concentrations versus well depth.

the arsenic is probably not mobile in a porous-media groundwater system. Dissolved arsenic (or other metals) is probably in true aqueous solution and therefore mobile in the groundwater system, however.

Samples from wells have more instances of high arsenic values than samples from springs (Fig. 55), and relatively shallow wells (30 to 80 ft deep) generally have the highest arsenic concentrations (Fig. 56).

In summary, most wells and springs in the project area produce water with arsenic levels well below the 0.010 mg/L MCL. Sites where arsenic concentrations exceed the MCL are most common in the Jackson Purchase Region. Arsenic concentrations are generally higher in unfiltered water samples than in filtered samples, suggesting an association between arsenic and suspended particulate material. High arsenic concentrations are more likely to be found in wells than in springs, and more likely to be found in the shallow groundwater system (wells less than 100 ft deep) than in deeper flow systems. Local changes in oxidation/reduction state caused by pumping or metal-reducing bacteria may lead to higher arsenic concentrations near a wellbore than in the regional groundwater system. A statewide summary of arsenic data (Fisher, 2002a) is available and can be viewed on the Kentucky Geological Survey Web site (www.uky.edu/KGS/water/gnet/gnet.htm).

Barium. Barium (Ba) is an alkaline earth element that occurs naturally as the mineral barite (BaSO_4). Barite is a common mineral 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 MCL for barium is 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.

Barium concentrations in groundwater from BMU 3 are generally well below levels of concern. The data repository contained 1,712 barium measurements from 389 sites, with no values greater than the MCL of 2.0 mg/L (Table 14). More than 99 percent of the measurements are less than 0.5 mg/L (Fig. 57).

Table 14. Summary of barium values (mg/L).

Measurements	1,712
Maximum	1.200
75th percentile	0.057
Median	0.038
25th percentile	0.019
Minimum	< 0.0007
Interquartile range	0.019–0.057
Sites	389
MCL	2.0
Sites > 2.0	0

< means analytical result reported as less than the stated value

Sites are uniformly distributed throughout the project area, except for a large cluster in the northern Tennessee River watershed and a smaller cluster in the Ohio River watershed (Fig. 58). Barium concentrations greater than 1.0 mg/L are found in the Eastern Kentucky Coal Field of the Upper Cumberland River watershed and the Jackson Purchase Region (Ohio, Tennessee, and Mississippi River watersheds) (Figs. 58–60).

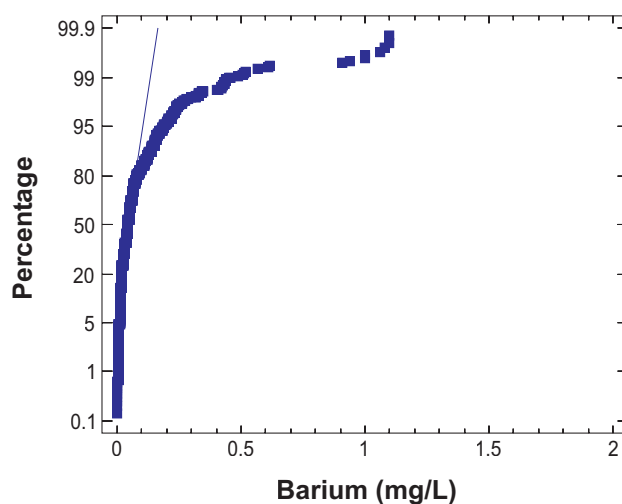


Figure 57. Cumulative plot of barium values in BMU 3. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

Barium concentrations greater than 0.5 mg/L are found only in unfiltered samples (total barium), not in filtered samples (dissolved barium), indicating that barium is associated with suspended particulate material (Fig. 61). Similarly, barium concentrations greater than 0.5 mg/L are found only in samples from wells, not from springs (Fig. 62). Higher barium concentrations are reported from wells less than 100 ft deep than from deeper wells that sample slower groundwater flow systems (Fig. 63).

Wells between approximately 50 and 100 ft deep have higher barium concentrations than deeper wells (Fig. 63).

In summary, barium concentrations in BMU 3 groundwater are generally well below the health-based MCL established by the EPA. Barium concentrations do not appear to be affected by nonpoint-source factors, but are more likely the result of natural hydrogeologic processes. The highest barium concentrations are found in unfiltered groundwater samples from wells that are between 50 and 100 ft deep.

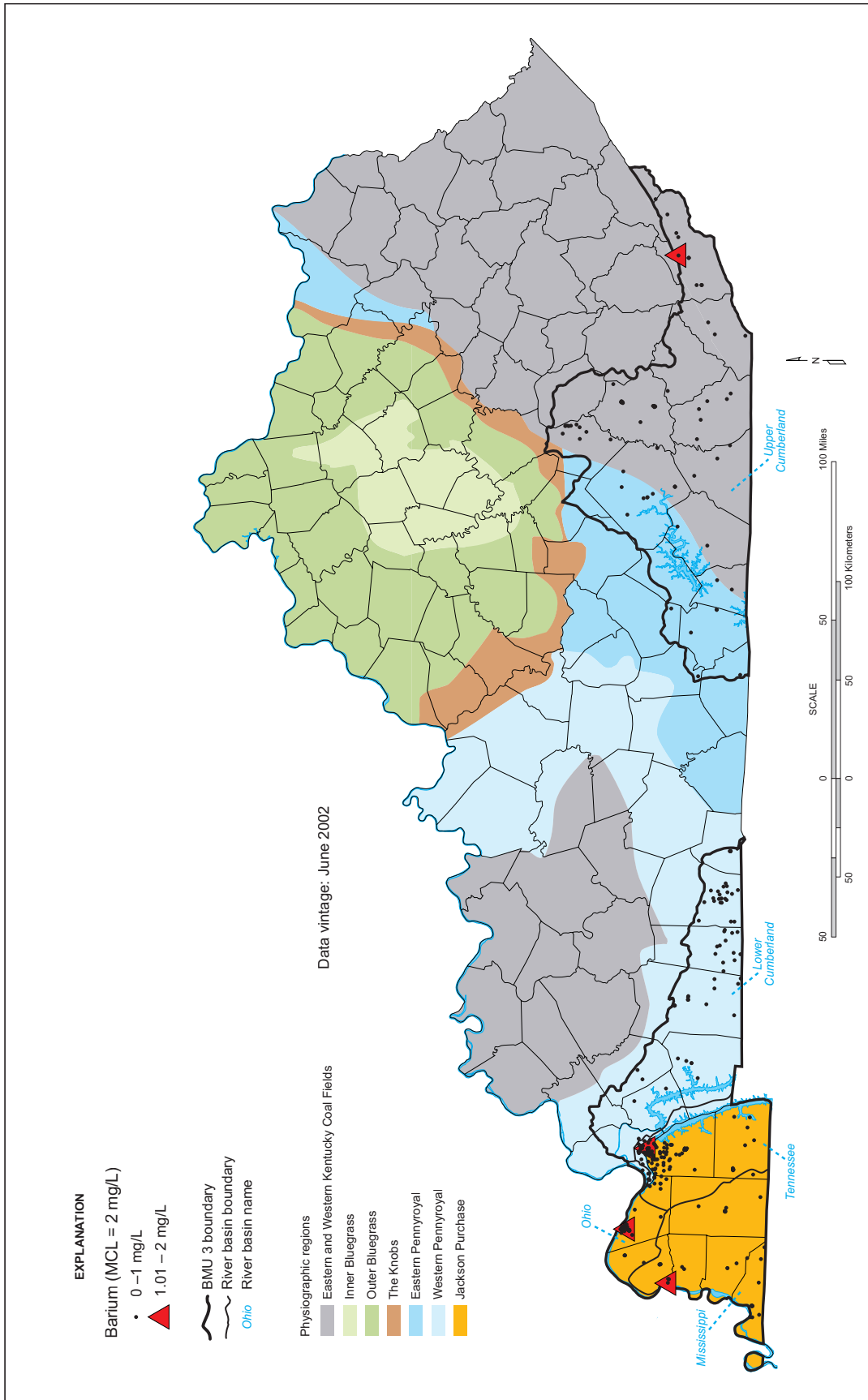


Figure 58. Sample sites and ranges of barium values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

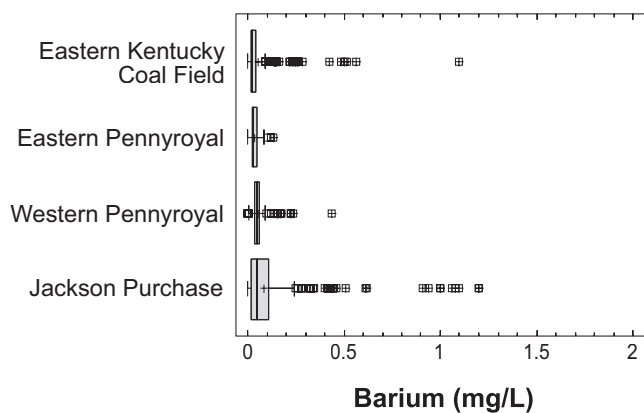


Figure 59. Summary of barium values grouped by physiographic region.

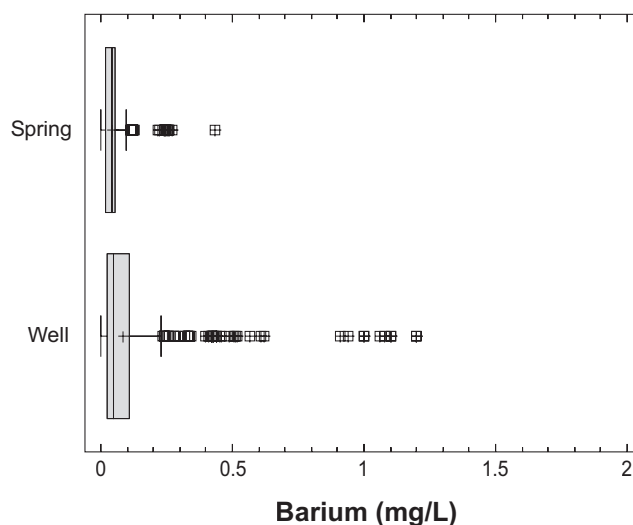


Figure 62. Comparison of barium values from wells and springs.

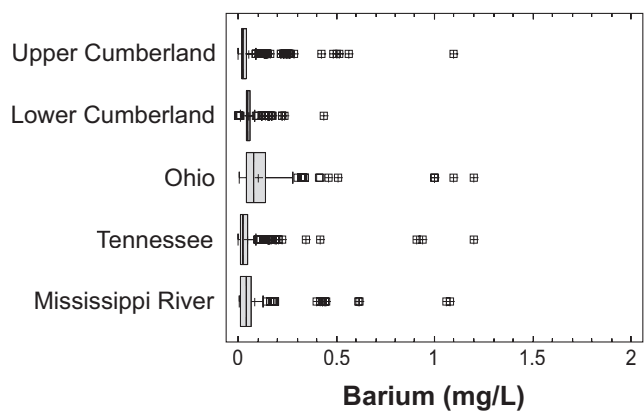


Figure 60. Summary of barium values grouped by major watershed.

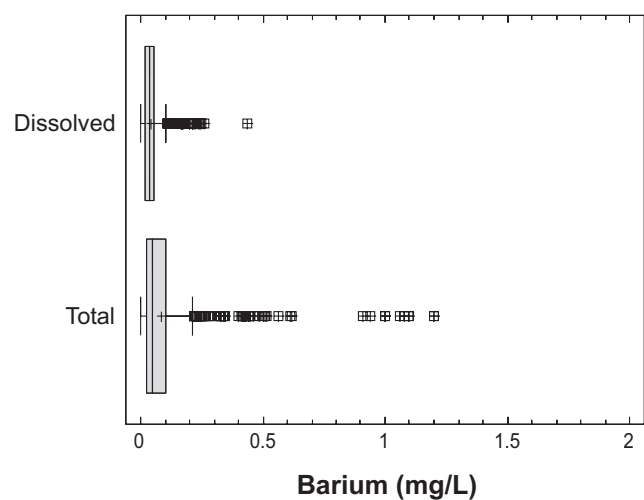


Figure 61. Comparison of total and dissolved barium values. Values greater than 1.5 mg/L were omitted to better show the majority of reported analytical results.

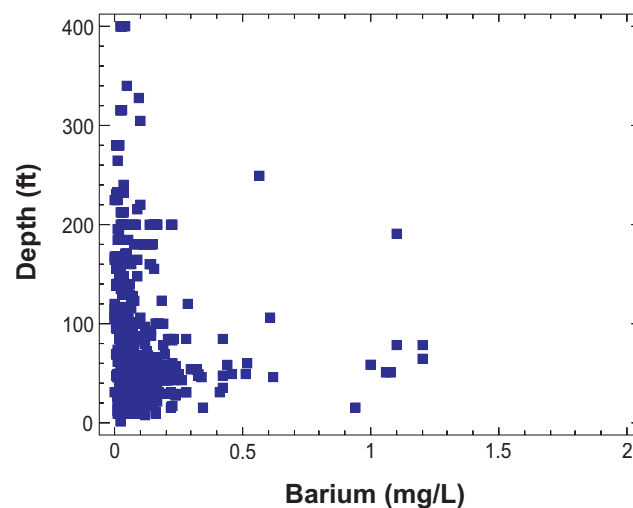


Figure 63. Barium values versus well depth.

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 oxyhydroxides (rust), or as poorly crystalline to amorphous material. Under reduced conditions, however, ferrous iron is stable and will remain dissolved in groundwater. There is no EPA primary drinking-water standard for iron in water supplies. There is a secondary standard of 0.3 mg/L, however, because higher iron concentrations will produce objectionable odor, taste, color, staining, corrosion, and scaling.

The data repository contained 8,809 iron measurements from 2,148 sites (Table 15). Values range from 1,040 to 0.0 mg/L, with a median value of 0.34 mg/L. Iron concentrations were greater than 0.3 mg/L at 1,213 sites in BMU 3.

Table 15. Summary of iron values (mg/L).

Measurements	8,809
Maximum	1,040
75th percentile	1.81
Median	0.34
25th percentile	0.08
Minimum	0.00
Interquartile range	0.08–1.81
Sites	2,148
SMCL	0.3
Sites > 0.3	1,213

Approximately 95 percent of the measured values are less than 10 mg/L; however, there are many higher values (Fig. 64).

Sample sites are densely distributed throughout the project area, particularly in the eastern part of the Eastern Kentucky Coal Field and the Jackson Purchase Region (Fig. 65). Sites where iron exceeds 0.3 mg/L are common throughout BMU 3.

The Western Pennyroyal Region (Fig. 66) and the Lower Cumberland River watershed (Fig. 67) are the only areas in BMU 3 where all iron concentrations are less than 100 mg/L.

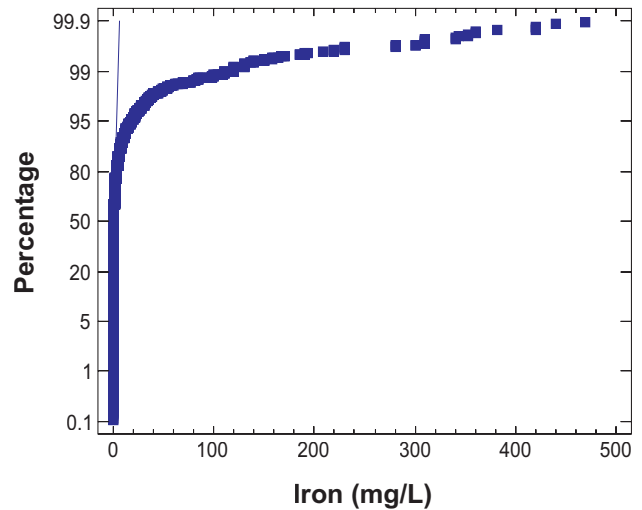


Figure 64. Cumulative plot of iron values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

The highest reported iron concentrations are from unfiltered samples (total iron) (Fig. 68) and from samples collected from wells rather than from springs (Fig. 69).

The highest iron concentrations are found in wells shallower than about 200 ft (Fig. 70).

In summary, approximately half the wells and springs in the project area produce groundwater with less than 0.3 mg/L iron. Many wells and springs produce water with much higher iron concentrations, however. Total iron concentrations are typically higher than dissolved iron concentrations, indicating that suspended particulate material also contributes iron to the analysis. Wells produce groundwater with higher iron concentrations than springs. This reflects the expected trend of oxidation conditions. Water in springs is generally more highly oxidized, and therefore iron would precipitate out, whereas water from wells is more likely to be reduced, and therefore iron will remain in solution. Groundwater users should test each well or spring before using the water for domestic purposes to avoid the problems of taste and staining associated with high iron in groundwater. There is no evidence that nonpoint-source contamination significantly contributes to iron concentrations in the project area.

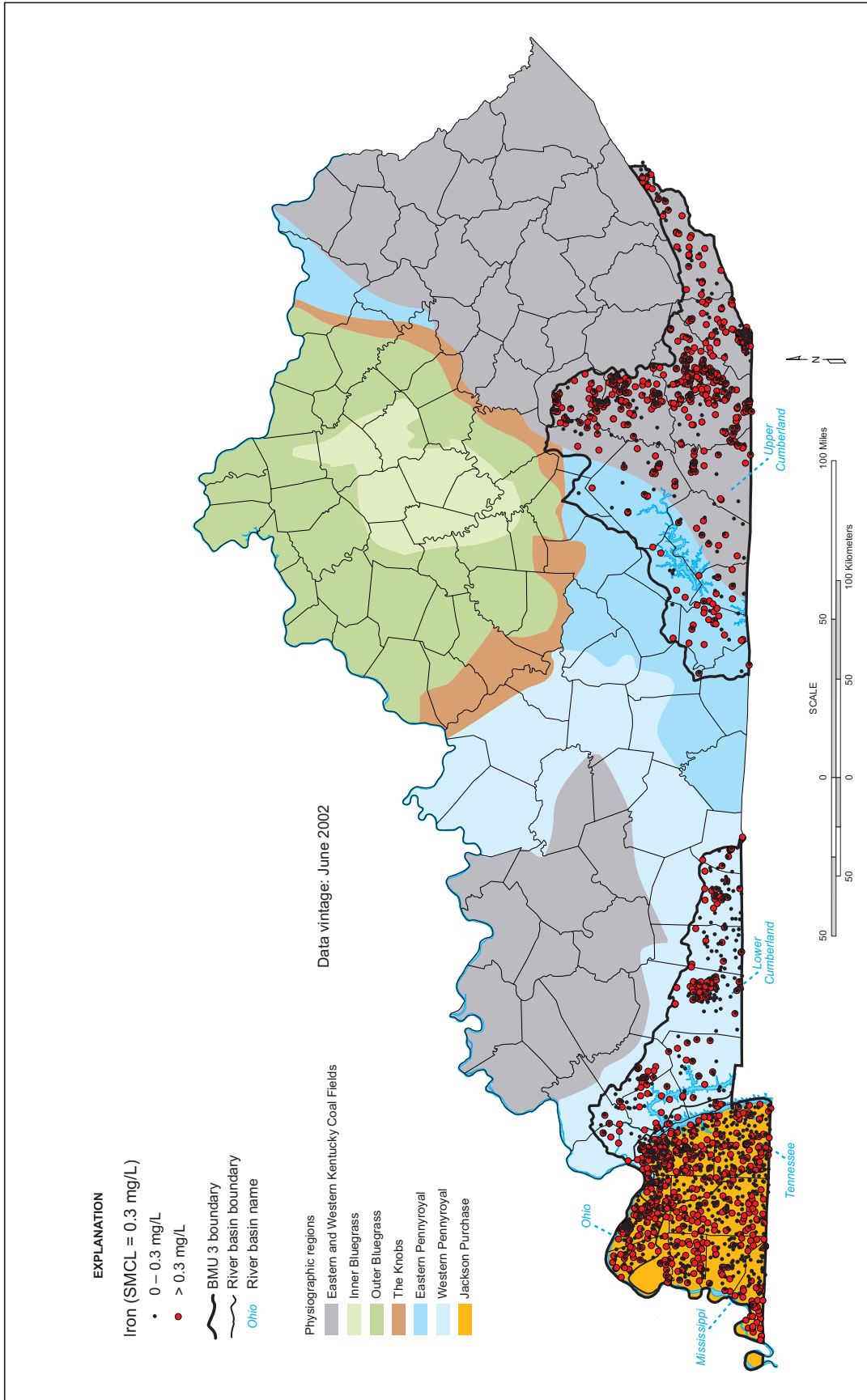


Figure 65. Sample sites and ranges of iron concentrations.

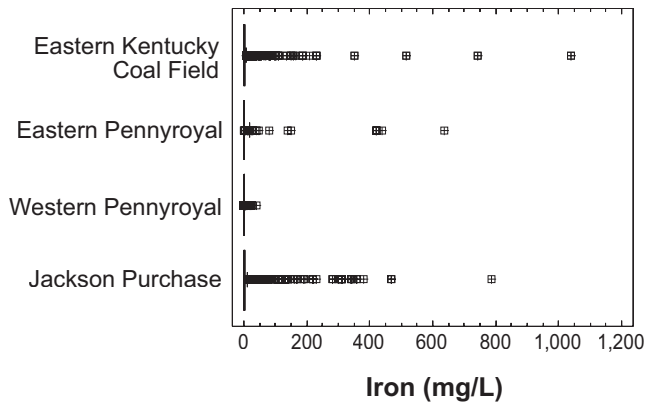


Figure 66. Comparison of iron values grouped by physiographic region. Values greater than 1,200 mg/L are omitted to better show the majority of the values.

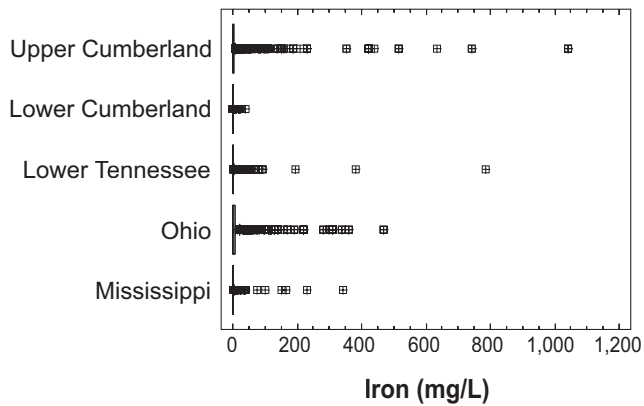


Figure 67. Comparison of iron values grouped by major watershed. Values greater than 1,200 mg/L are omitted to better show the majority of the values.

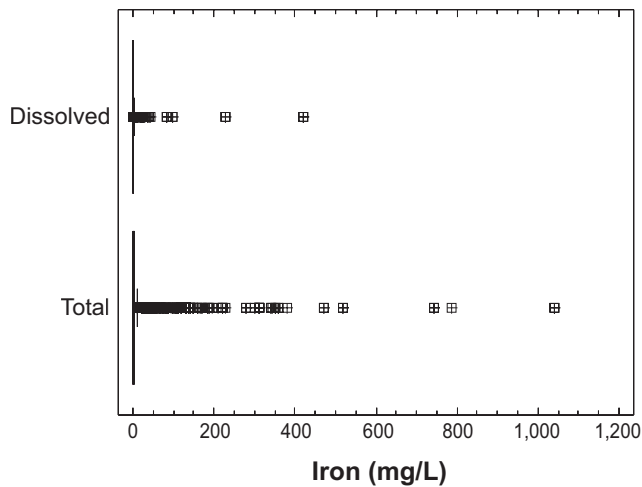


Figure 68. Comparison of total and dissolved iron values. Values greater than 1,200 mg/L are omitted to better show the majority of the values.

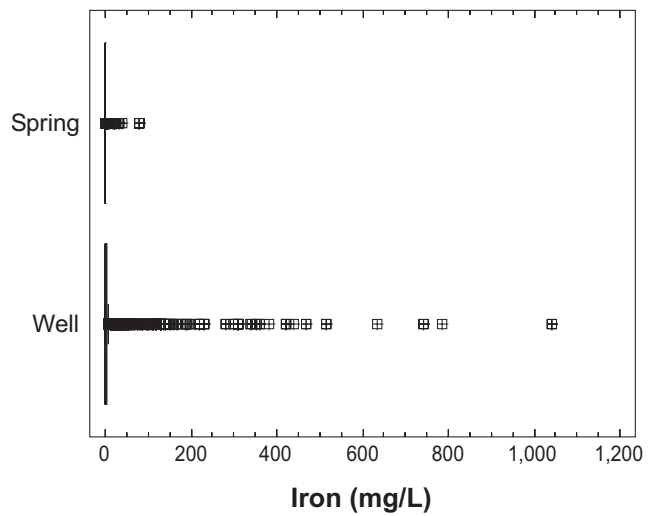


Figure 69. Comparison of iron values from wells and springs. Values greater than 1,200 mg/L are omitted to better show the majority of the values.

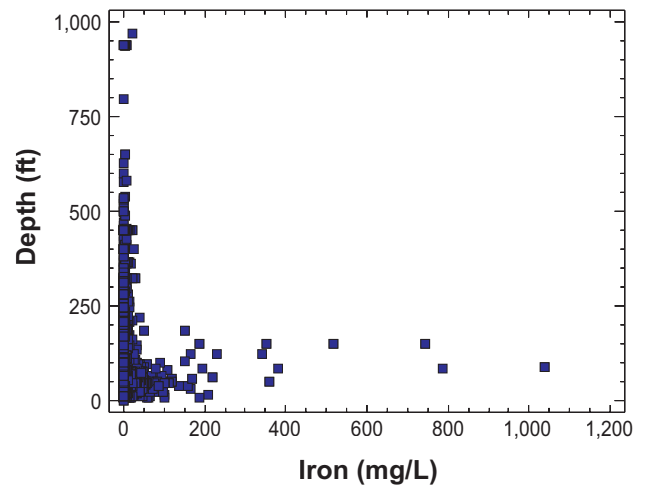


Figure 70. Iron values versus well depth. Values greater than 1,200 mg/L are omitted to better show the majority of the values.

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

There is no MCL for manganese in water supplies. The secondary standard is 0.05 mg/L; higher concentrations produce objectionable odor, taste, color, corrosion, and staining.

The data repository contained 6,469 manganese measurements at 2,013 sites. Values range from 0.0 to 114 mg/L (Table 16). Manganese concentrations exceeded 0.05 mg/L at approximately 56 percent of the sites (Table 16). Approximately 40 percent of reported manganese concentrations are less than 0.05 mg/L and approximately 80 percent are less than 1.0 mg/L (Fig. 71).

Table 16. Summary of manganese values (mg/L).

Measurements	6,469
Maximum	114
75th percentile	0.32
Median	0.076
25th percentile	0.011
Minimum	0.00
Interquartile range	0.011–9,329
Sites	2,013
SMCL	0.05
Sites > 0.05	1,138

Distribution of sample sites in BMU 3 is dense (Fig. 72). More sites where manganese exceeds 0.05 mg/L are located in the Eastern Kentucky Coal Field and northern part of the Eastern Pennyroyal than in the other physiographic regions (Fig. 72).

The highest reported manganese values are from sites in the Eastern Kentucky Coal Field and Western Pennyroyal (Fig. 73). Only two analyses were reported from The Knobs Region. Figure 74 compares manganese values by major watershed.

The highest reported manganese concentrations are total analyses (unfiltered sample) (Fig. 75).

Groundwater with the highest manganese concentrations comes from wells rather than from springs (Fig. 76).

Shallow wells yield the highest reported manganese concentrations (Fig. 77). With two exceptions,

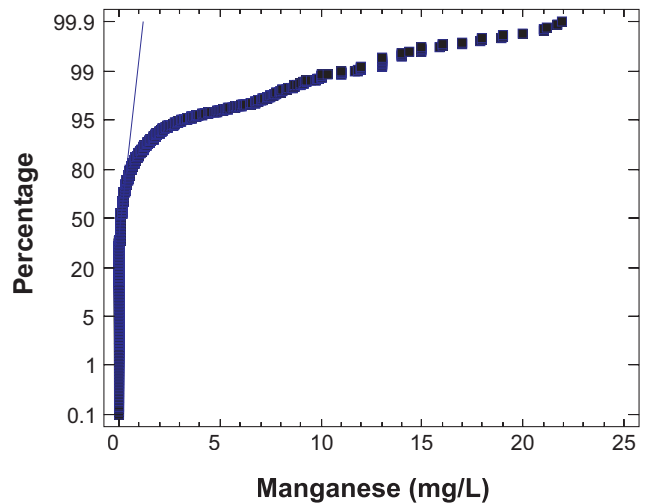


Figure 71. Cumulative plot of manganese values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

manganese concentrations are near zero in samples from wells deeper than 200 ft.

In summary, manganese concentrations above the SMCL occur in all major watersheds, and all physiographic regions. Manganese and iron are geochemically similar and behave similarly in the environment. Comparison of the map showing sites where manganese exceeds 0.05 mg/L (Fig. 72) with the map of high iron concentrations (Fig. 65) shows the similar pattern. Like iron, manganese is readily sorbed onto suspended material and is less soluble under oxidizing conditions than in reducing environments. This geochemical property is illustrated by the observation that total (unfiltered sample) manganese concentrations are higher than dissolved (filtered sample) concentrations (Fig. 75), and that high manganese concentrations are less common in groundwater from springs than in well water (Fig. 76). Very high manganese concentrations (greater than 5 mg/L) are much more common in shallow wells than in groundwater from deeper wells. The geochemical similarity between manganese and iron is demonstrated in the similarity of their concentrations in groundwater. Both commonly occur at concentrations that affect groundwater taste and can produce staining of containers and clothing. There is no evidence to suggest that nonpoint-source contamination significantly contributes to manganese concentrations in the project area.

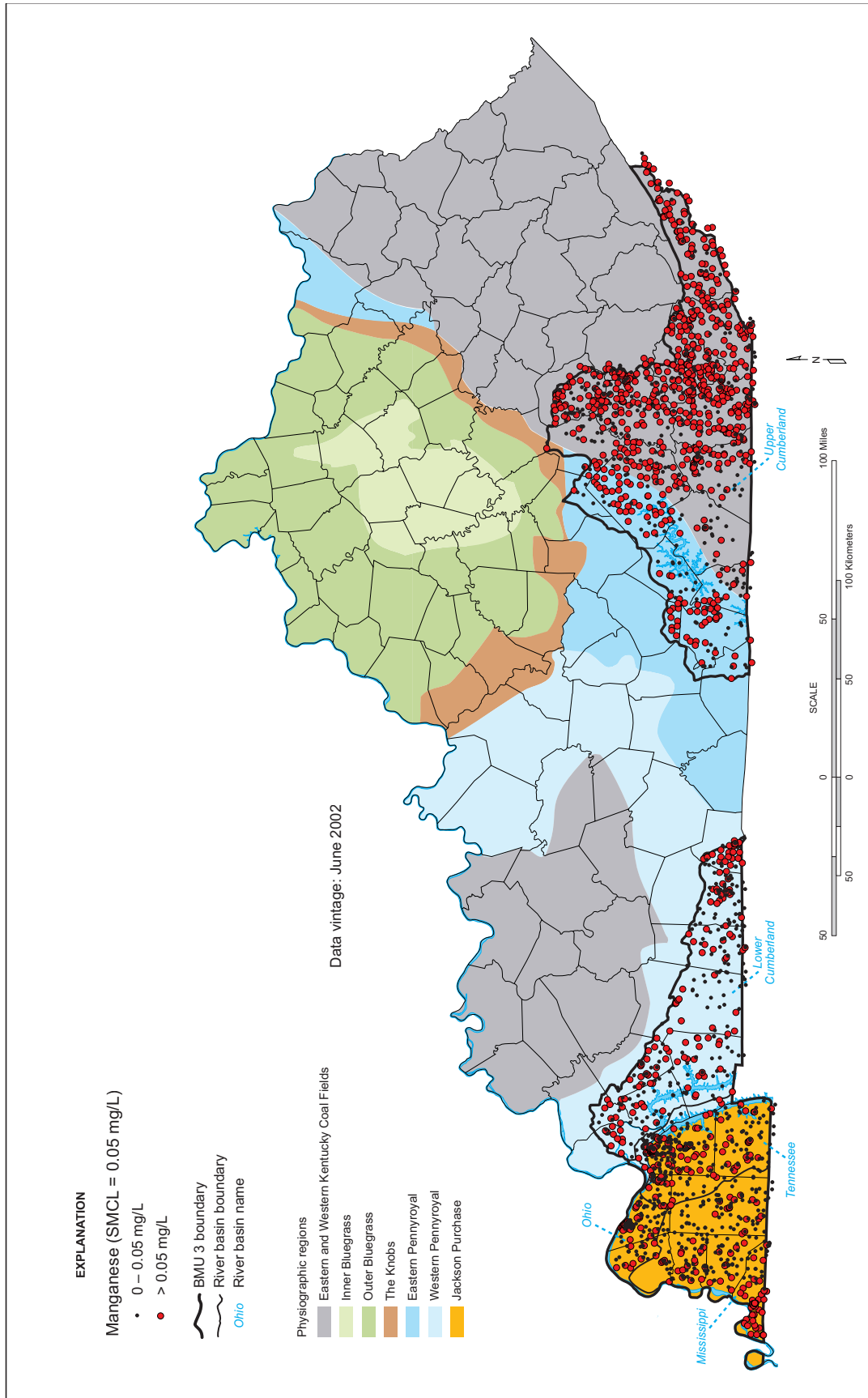


Figure 72. Sample sites and ranges of manganese concentrations.

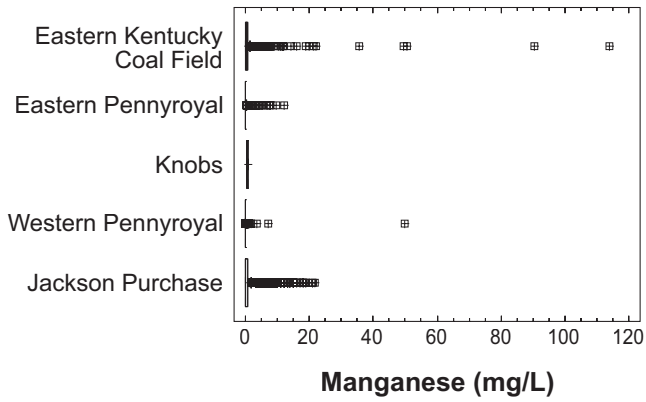


Figure 73. Comparison of manganese values grouped by physiographic region.

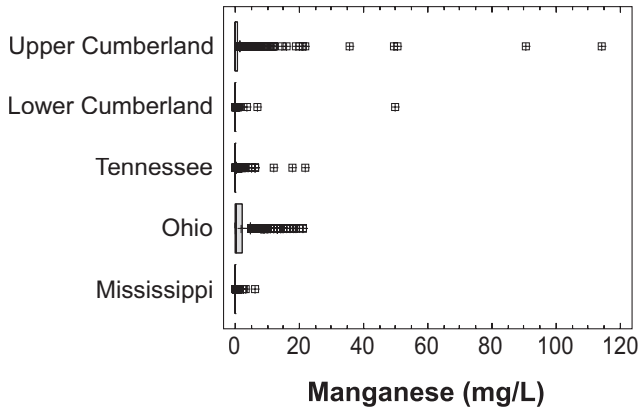


Figure 74. Comparison of manganese values grouped by major watershed.

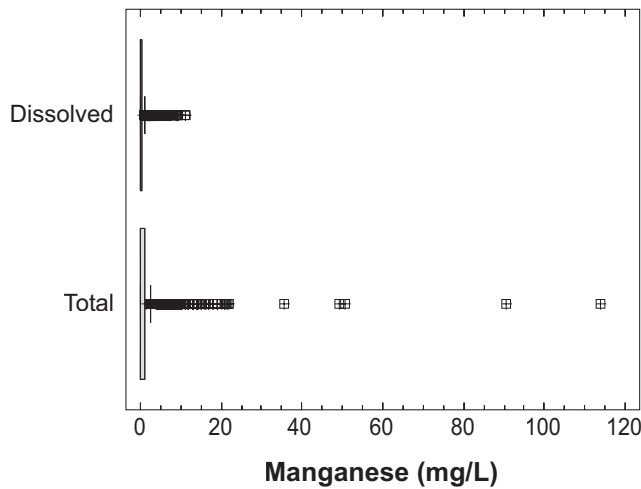


Figure 75. Comparison of total and dissolved manganese values.

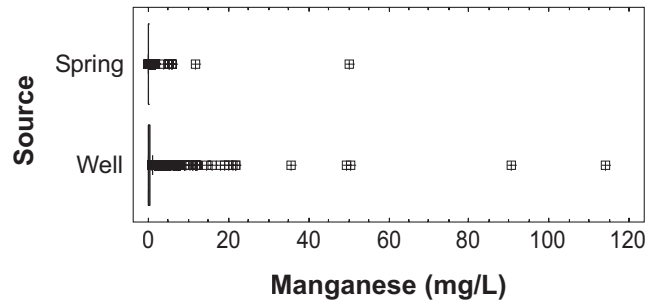


Figure 76. Summary of manganese concentrations grouped by site type.

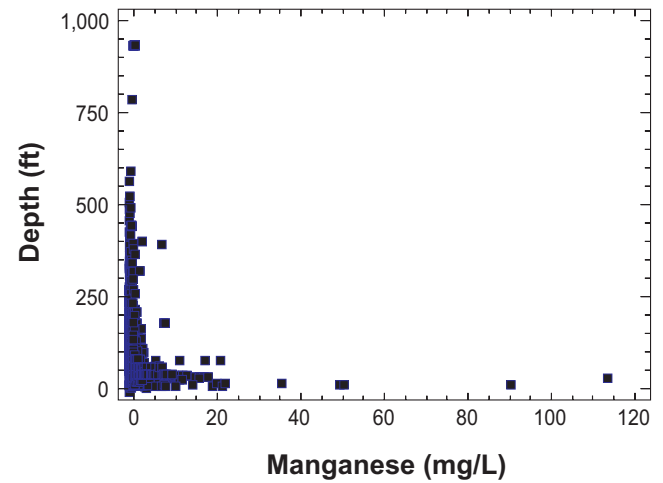


Figure 77. Manganese values versus well depth.

Mercury. Mercury (Hg) is a liquid metal found in natural deposits that also contain other elements. Forest fires, coal combustion products, disposal of mercury-containing products such as electric lights and switches, computers, thermometers, and blood-pressure gages contribute mercury to the environment. Electrical products such as dry-cell batteries, fluorescent light bulbs, 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 methyl mercury, a much more toxic form of mercury.

Because of its toxicity, the EPA has set an MCL value for mercury at 0.002 mg/L. At high doses mercury is a strong neurotoxin that causes demyelination², delayed nerve conduction, and kidney damage.

The groundwater data repository contained 1,001 mercury analyses from 269 sites from the project area (Table 17). Approximately 87 percent of the analyses were reported as less than an analytical detection limit. Only four sites yielded groundwater with mercury concentrations greater than 0.002 mg/L. The median value was less than a detection limit of 0.00005 mg/L (Table 17). More than 95 percent of the reported values are less than 0.002 mg/L (Fig. 78).

Table 17. Summary of mercury values (mg/L).

Measurements	1,001
Maximum	0.01750
75th percentile	< 0.00005
Median	< 0.00005
25th percentile	< 0.00005
Minimum	< 0.00005
Interquartile range	na
Sites	269
MCL	0.002
Sites > 0.002	4

< means analytical result reported as less than the stated value

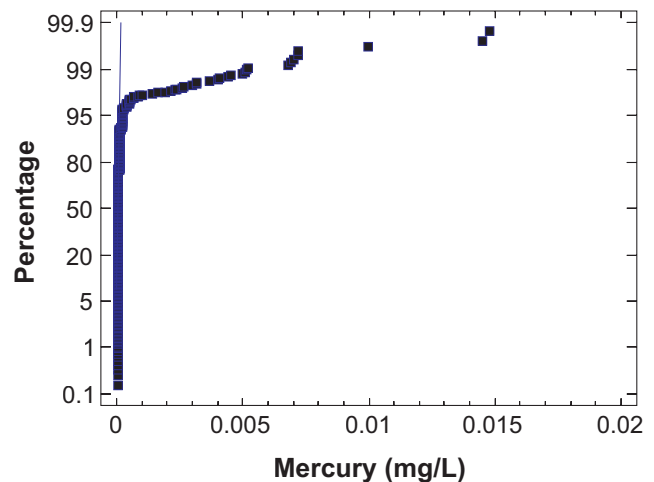


Figure 78. Cumulative plot of mercury values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

Sites where mercury was measured are uniformly distributed throughout the project area, with one cluster of sites in the northern Tennessee River watershed (Fig. 79). Mercury concentrations exceed the MCL in the Tennessee River watershed of the Jackson Purchase Region (Figs. 79–81).

The highest mercury concentrations are found in unfiltered samples (total mercury) rather than filtered samples (dissolved mercury) (Fig. 82). No dissolved mercury concentrations greater than 0.001 mg/L were reported.

Wells produce groundwater with higher mercury concentrations than springs (Fig. 83). Shallow wells produce higher mercury concentrations than intermediate or deep wells (Fig. 84).

In summary, mercury is rarely present in detectable amounts in groundwater from wells or springs in the project area. There is no evidence of nonpoint-source impacts on mercury concentrations in Kentucky groundwater in the project area. Mercury concentrations greater than 0.001 mg/L occur only in total samples and probably represent mercury associated with suspended sediment rather than in true solution.

² Destruction or loss of material that acts as a sheath around nerves.

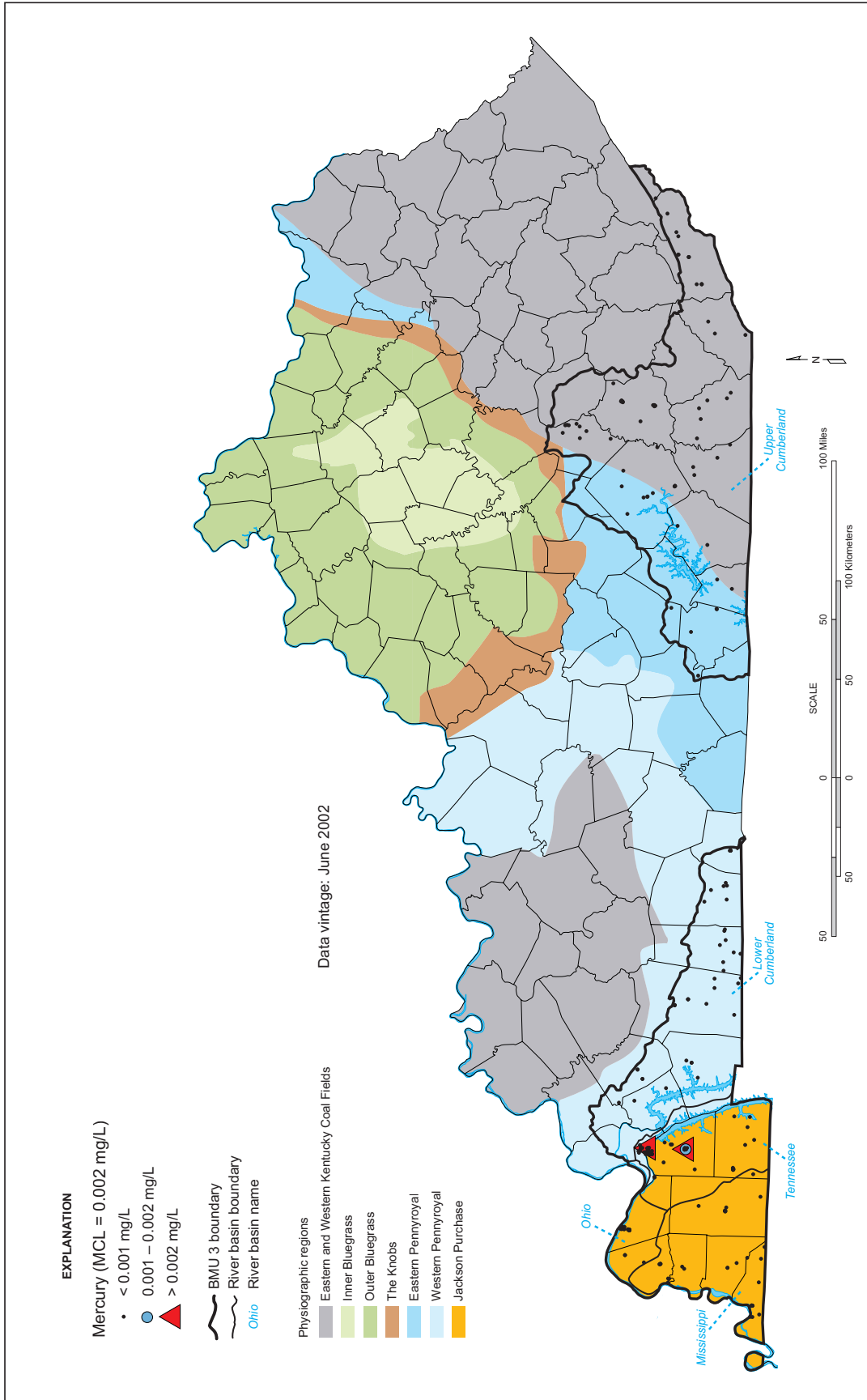


Figure 79. Sample sites and ranges of mercury values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

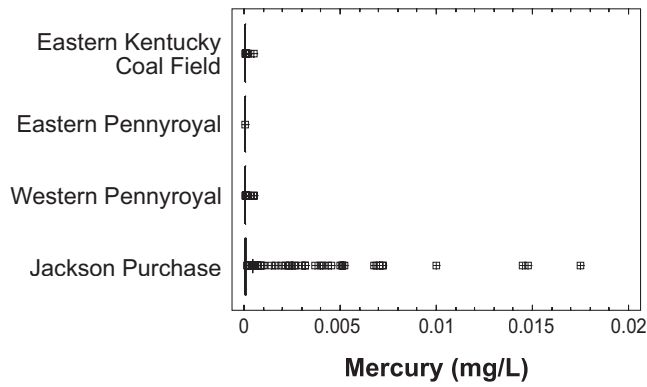


Figure 80. Comparison of mercury values grouped by physiographic region.

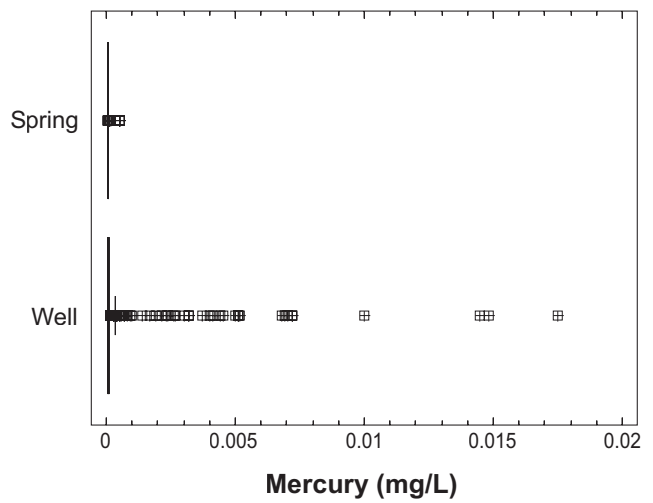


Figure 83. Comparison of mercury values in springs and wells.

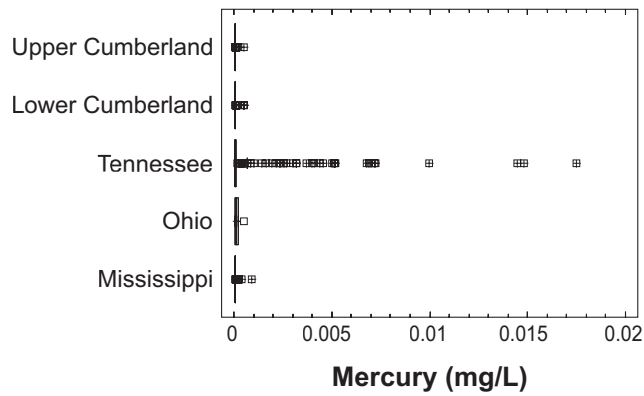


Figure 81. Comparison of mercury values grouped by major watershed.

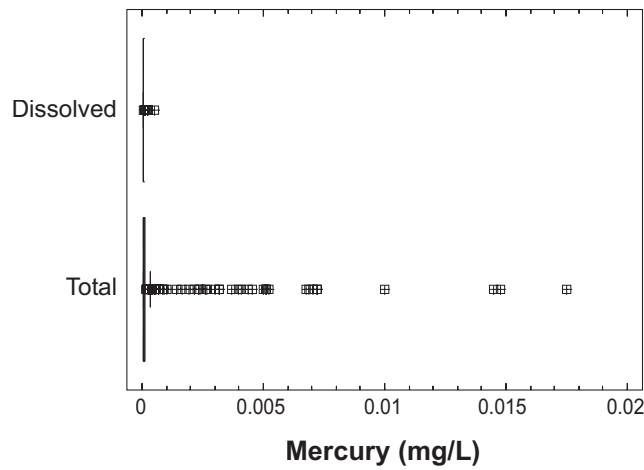


Figure 82. Comparison of dissolved and total mercury values.

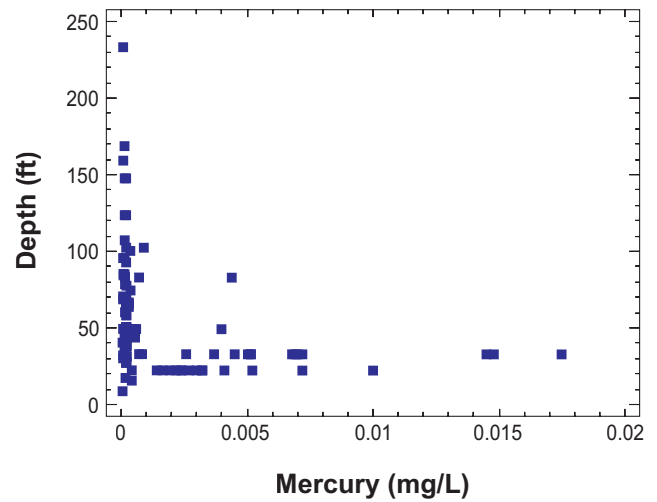


Figure 84. Mercury concentrations versus well depth. Only concentrations reported as above detection limits are shown.