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 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 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 U.S. 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 were required to meet the new MCL beginning January 2006.

Sites identified as monitoring wells by the Kentucky Division of Water's well-identification number 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 provided no useful information and were not included in the following discussion. Removing these measurements left a total of 290 reported arsenic concentrations at 106 sites (Table 14). Eighty-six percent of the values were reported as less than analytical detection. Only 10 values from five sites exceeded the MCL (Fig.43).

Table 14. Summary of arsenic concentrations (mg/L). MCL=0.01 mg/L.

Number of values	290
Maximum	0.038
75th percentile	< 0.002
Median	< 0.002
25th percentile	< 0.002
Minimum	< 0.0005
Interquartile range	na
Number of sites	106
Number of sites > 0.01 mg/L	5

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

Sites where arsenic was measured were spread throughout the project area (Fig. 44). Sites where groundwater exceeded the MCL for arsenic were not concentrated in any particular part of BMU 5.

The median arsenic value and interquartile range were nearly the same for both watersheds (Fig. 45); however, the range of concentrations in the Little Sandy–Tygarts Creek watershed was larger.

Total (unfiltered sample) and dissolved (filtered sample) arsenic concentrations had about the same distribution of values (Fig. 46), indicating that significant amounts of arsenic were not adsorbed on suspended material in the project area.

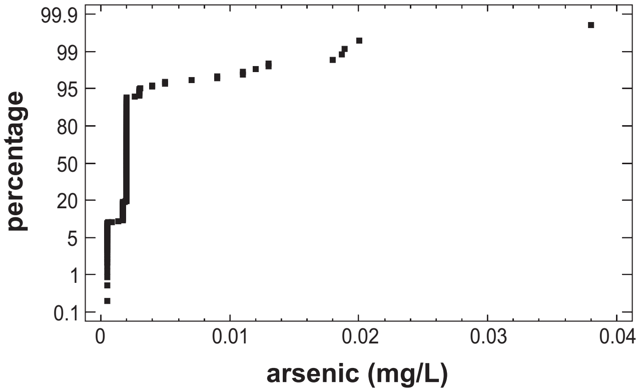

Figure 43. Cumulative plot of arsenic concentrations. MCL=0.01 mg/L.

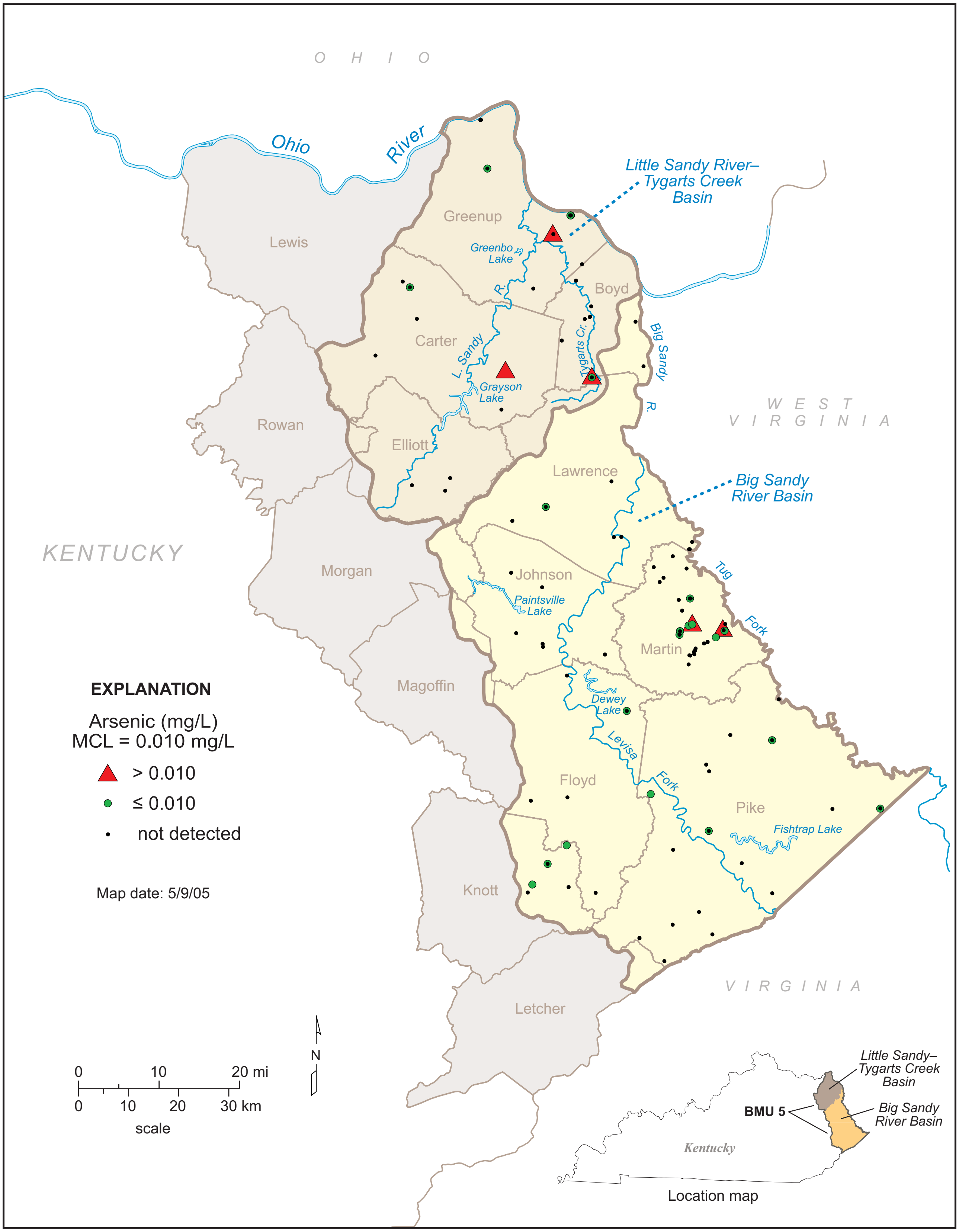

Figure 44. Locations of sampled sites and ranges of arsenic values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

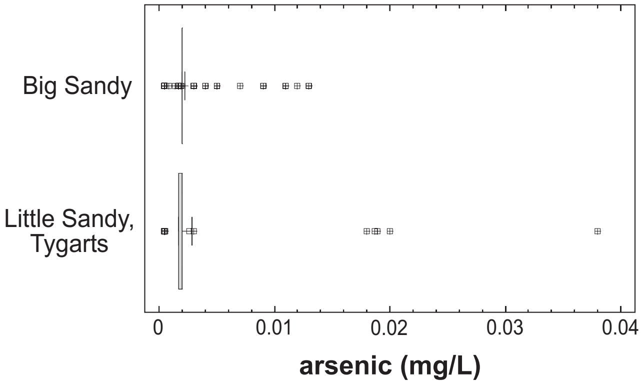

Figure 45. Summary of arsenic concentrations grouped by watershed. MCL=0.01 mg/L.

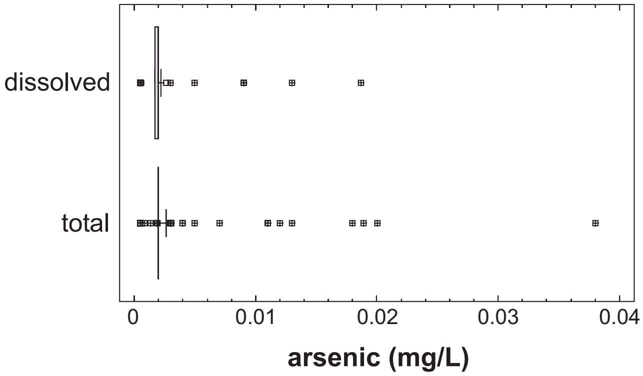

Figure 46. Comparison of total and dissolved arsenic concentrations. MCL=0.01 mg/L.

Only nine of the 290 measurements were from springs; therefore, no valid comparison of concentrations in springs and wells could be made.

The highest arsenic concentrations were found in wells less than about 100 ft deep (Fig. 47).

In summary, arsenic was below analytical detection limits in groundwater at most sites in BMU 5. Of the measurements that were above analytical detection, arsenic exceeded the MCL at only five of 106 sites. Nonpoint-source contamination with respect to arsenic in groundwater therefore 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/kgs/ic05_12.pdf).

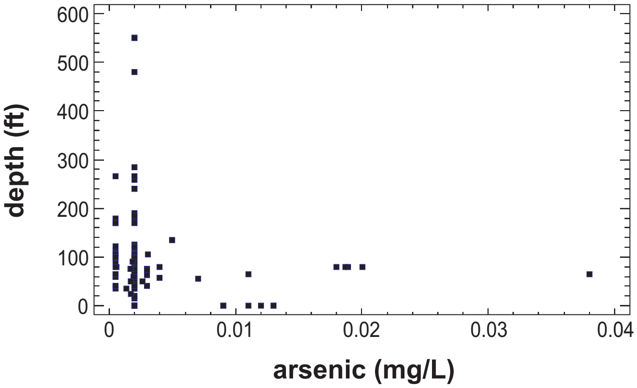

Figure 47. Arsenic concentrations versus well depth. MCL=0.01 mg/L.

Barium. Barium (Ba) is an alkaline earth element that occurs naturally as the mineral barite ($BaSO_4$), 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 waste 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 distress and muscular weakness, whereas long-term exposure can cause high blood pressure.

The data repository contained 430 barium measurements from 167 sites in BMU 5 (Table 15). Only eight of 167 sites yielded groundwater that had more than 2 mg/L of barium. Although the maximum value was quite high, only 4 percent of all measurements exceeded 2.0 mg/L (Fig. 48).

Table 15. Summary of barium concentrations (mg/L). MCL=2.0 mg/L.

Number of values	430
Maximum	100.0
75th percentile	0.59
Median	0.16
25th percentile	0.04
Minimum	0.00
Interquartile range	0.55
Number of sites	167
Number of sites > 2.0 mg/L	8

Sampled sites were evenly distributed throughout BMU 5 (Fig. 49). Most of the sites where barium exceeded 2 mg/L were found in the Big Sandy watershed, however.

Barium concentrations from the Big Sandy watershed had a higher median value, a larger interquartile range, and more values that exceeded 2 mg/L than concentrations from the Little Sandy–Tygarts Creek watershed (Fig. 50).

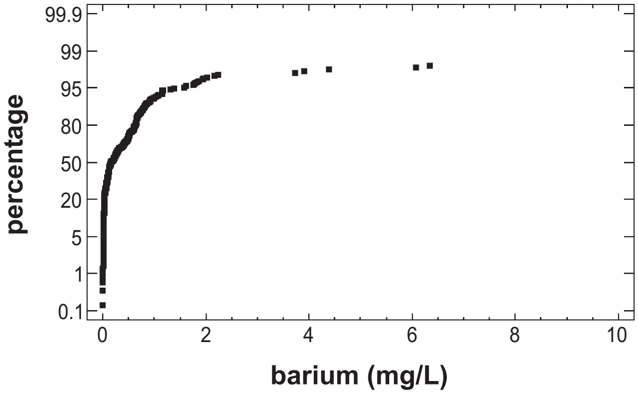

Figure 48. Cumulative plot of barium concentrations. Nine values greater than 10 mg/L were excluded to better show the majority of the values. MCL=2 mg/L.

Barium concentrations in total (unfiltered) samples had nearly the same median value and interquartile range as concentrations from dissolved (filtered) samples, indicating that barium is not associated with suspended material (Fig. 51).

The data set contained only 13 barium concentrations from four springs; all the other values were from wells. No samples from springs had a barium concentration above the MCL. Because there were so few analyses from springs, no comparison with concentrations from wells was made.

The highest barium concentrations were found in wells less than 100 ft deep (Fig. 52). All values that exceeded the MCL were from wells less than 100 ft deep.

In summary, only eight of 167 sites yielded groundwater that contained more than 2 mg/L of barium. All these sites were shallow wells, but there was no preferred geographic distribution of such wells. These data show that barium in groundwater sometimes exceeded established health limits in BMU 5. Naturally occurring barite is the probable source of the high barium concentrations. There was no evidence that barium concentrations were affected by nonpoint-source chemicals.

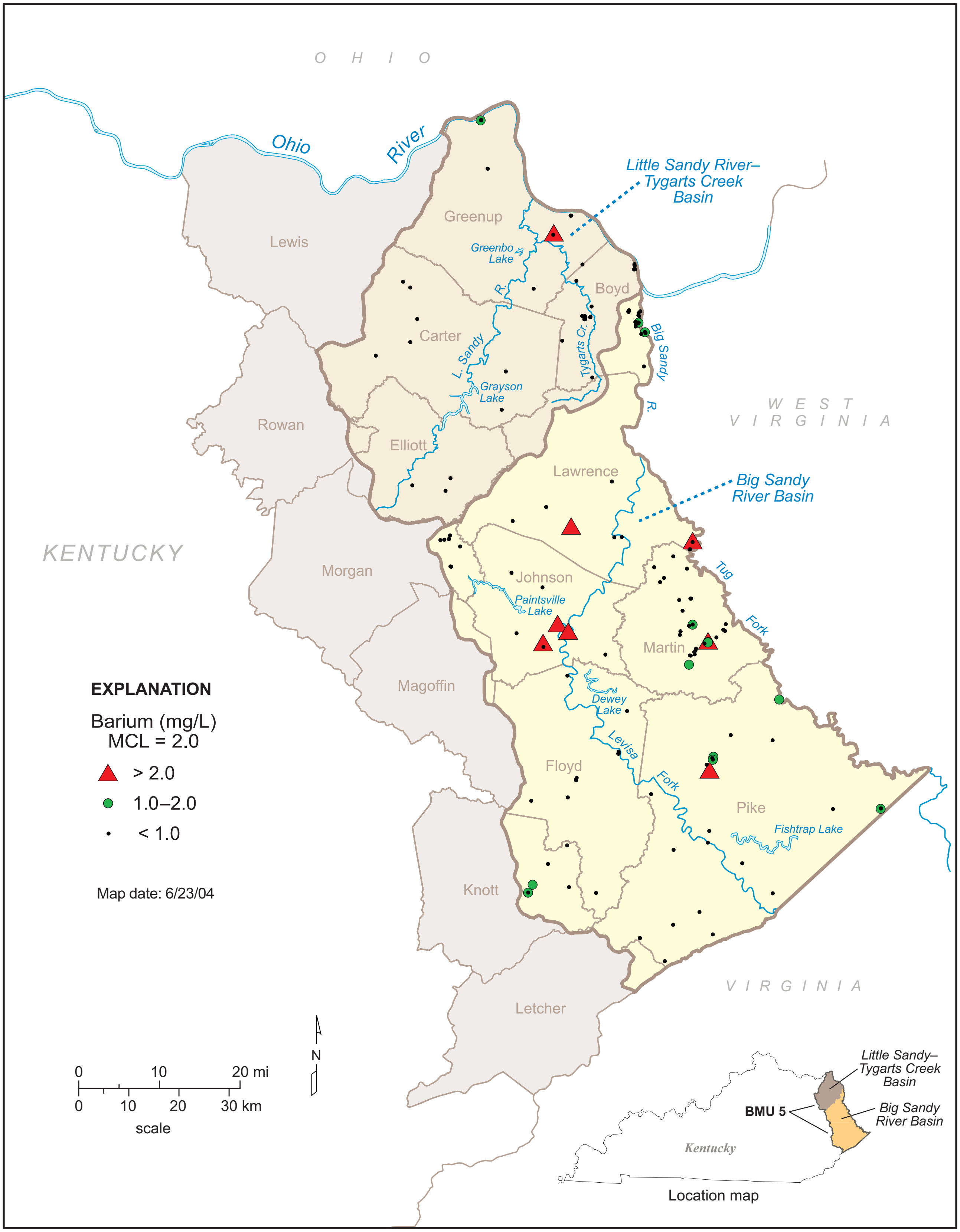

Figure 49. Locations of sampled sites and ranges of barium values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

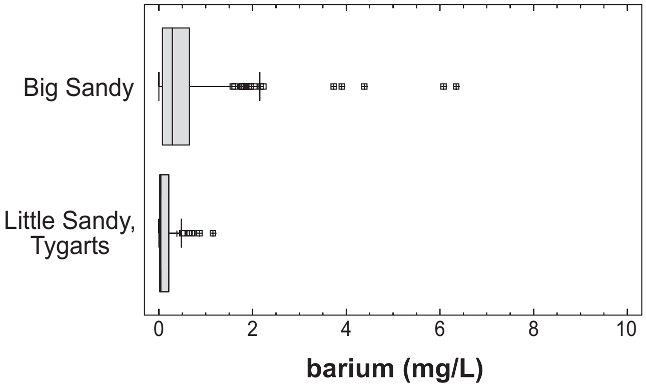

Figure 50. Summary of barium concentrations grouped by watershed. Higher values were excluded to better show the majority of the values. MCL=2 mg/L.

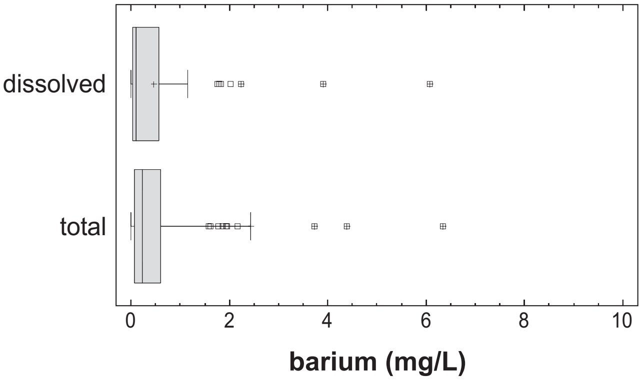

Figure 51. Comparison of total and dissolved barium concentrations. Nine values of total barium were excluded to better show the majority of the values. MCL=2 mg/L.

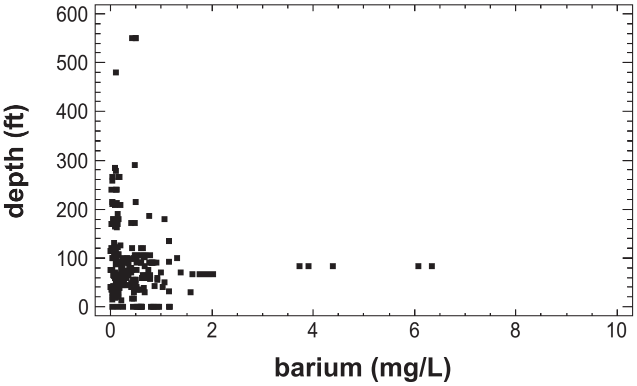

Figure 52. Barium concentrations versus well depth. Nine higher values were excluded to better show the majority of the values. MCL=2 mg/L.

Mercury. Mercury (Hg) is a liquid metal found in natural deposits as ores containing other elements. Forest fires, coal combustion products, disposal of mercury-containing 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 doses, mercury is a strong neurotoxin that causes destruction of the nerve's myelin coating in the brain, spinal cord, or optic nerves; delayed nerve conduction; and kidney damage. Because of its toxicity, the EPA has set an MCL for mercury of 0.002 mg/L.

The groundwater data repository contained 235 mercury analyses from 109 sites in BMU 5 (Table 16). No concentration exceeded the MCL of 0.002 mg/L. Only 12 sites had values above analytical detection; all of these were wells rather than springs. The highest reported value was 0.00095 mg/L, well below the MCL of 0.002 mg/L.

Table 16. Summary of mercury concentrations (mg/L). MCL=0.002 mg/L.

Number of values	235
Maximum	0.00095
75th percentile	< 0.00005
Median	< 0.00005
25th percentile	< 0.00005
Minimum	< 0.00005
Interquartile range	na
Number of sites	109
Number of sites > 0.002 mg/L	0

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

Sites sampled for mercury were clustered in Boyd County of the Little Sandy watershed and Martin County of the Big Sandy watershed (Fig. 53).

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

In summary, mercury was detected in only 12 of 109 sites in BMU 5. The maximum concentration was 0.00095 mg/L, less than half of the MCL. There was no strong evidence that mercury in groundwater was the result of widespread nonpoint-source contamination.

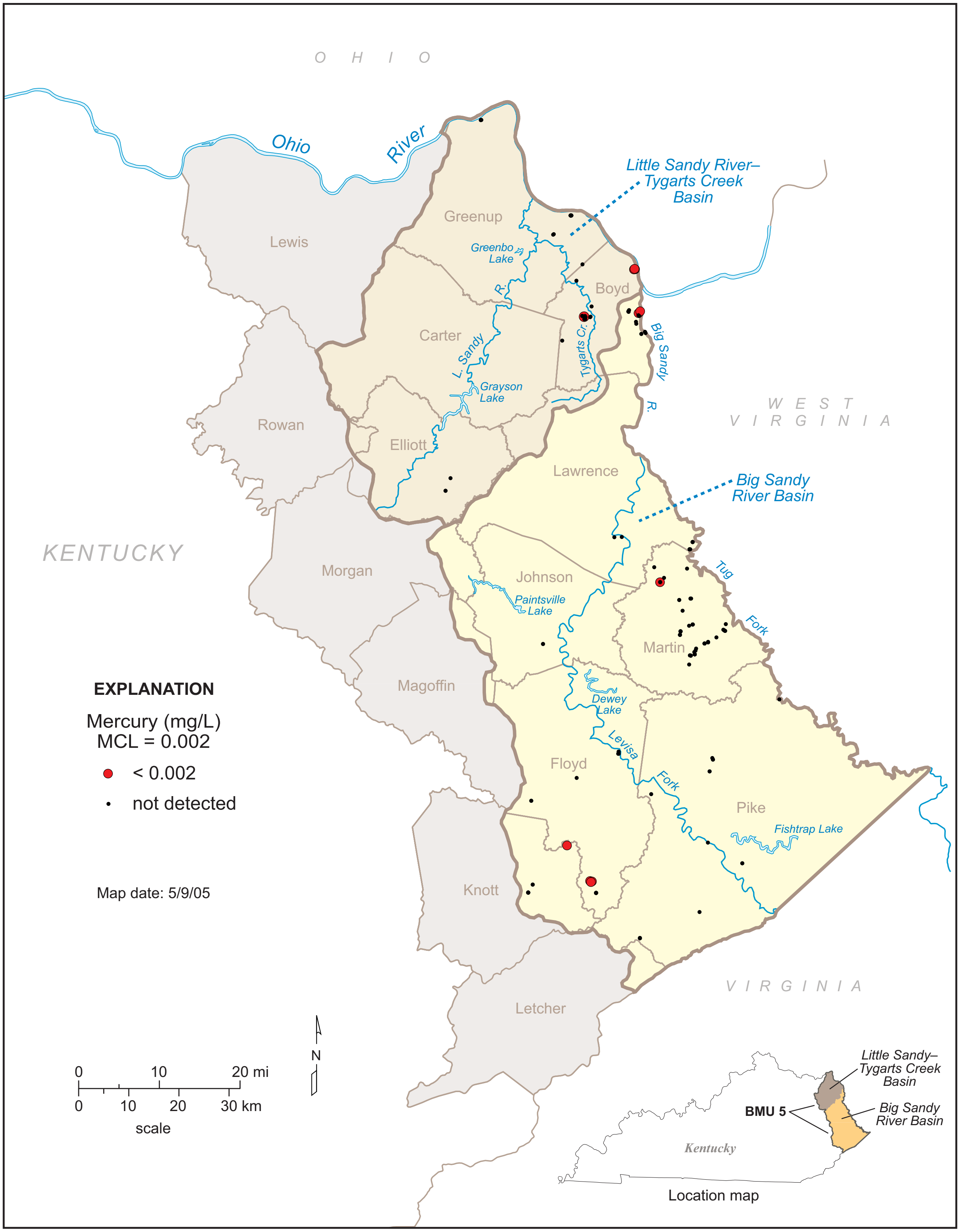

Figure 53. Locations of sampled sites and ranges of mercury values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

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 because concentrations above this level produce objectionable odor, taste, color, staining, and scaling.

The data repository contained 3,707 iron measurements from 823 sites in BMU 5 (Table 17). Iron concentrations were quite high; more than 75 percent of the sites produced groundwater that had iron concentrations above the secondary standard.

Less than half of the reported values were below the SMCL of 0.3 mg/L (Fig. 54).

Sample-site density was greater in the Big Sandy watershed, where samples were collected for the National Uranium Resource Evaluation program (Fig. 55). Values above the SMCL occurred throughout the project area.

The median value, interquartile range, and total range of iron concentrations were nearly the same for both watersheds (Fig. 56).

Total iron concentrations (unfiltered samples) had a slightly higher median value and larger interquartile range than dissolved iron concentrations (filtered samples), suggesting that some of the reported iron was associated with suspended solids (Fig. 57). The highest iron concentrations were found in unfiltered samples.

The median value and interquartile range of iron in groundwater from springs were generally similar to those for water from wells (Fig. 58). The highest values were found in water from wells, however.

High iron concentrations were found more commonly in wells less than 200 ft deep; deeper wells typically had lower iron concentrations (Fig. 59).

Table 17. Summary of iron concentrations (mg/L). SMCL=0.3 mg/L.

Number of values	3,707
Maximum	1,500
75th percentile	2.76
Median	0.60
25th percentile	0.14
Minimum	0.00
Interquartile range	2.62
Number of sites	823
Number of sites > 0.3 mg/L	641

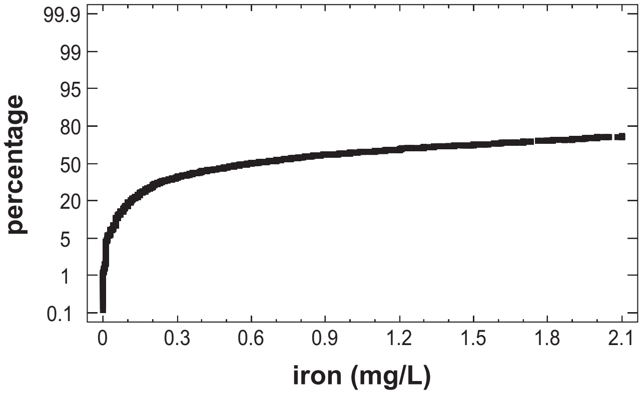

Figure 54. Cumulative plot of iron concentrations. Higher values were excluded to better show the majority of the values. SMCL=0.3 mg/L.

In summary, iron concentrations high enough to produce staining and objectionable taste were common in groundwater throughout the project area. The highest concentrations occurred in unfiltered samples, indicating that iron was present in suspended material. Water from wells had the highest iron concentrations. This suggests that spring water was more oxidized and therefore iron was removed by precipitation of iron oxide minerals in springs, whereas iron remained in solution in well water. High iron concentrations are expected in this area, and naturally occurring iron overwhelms any contribution from nonpoint sources.

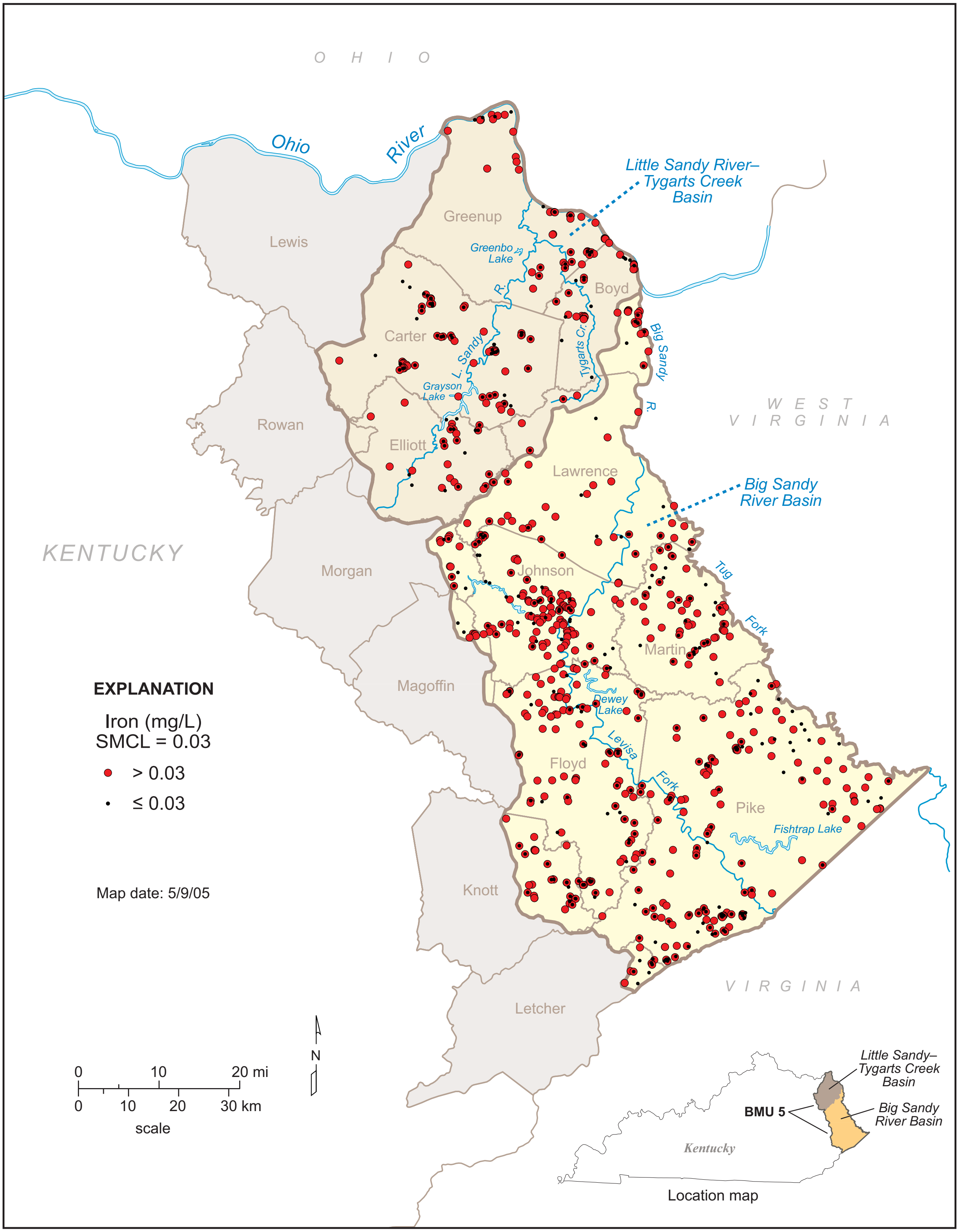

Figure 55. Locations of sampled sites and ranges of iron values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

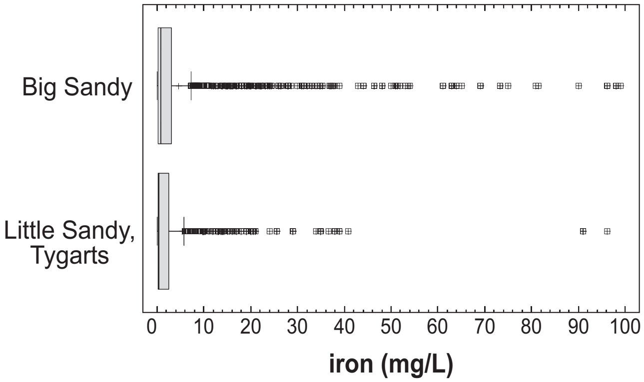

Figure 56. Summary of iron concentrations grouped by watershed. Higher values were excluded to better show the majority of the values. SMCL=0.3 mg/L.

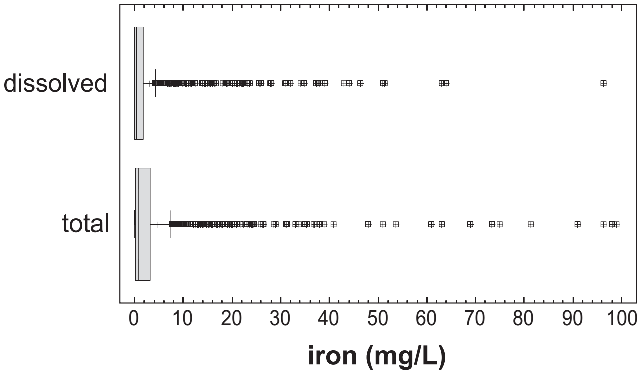

Figure 57. Comparison of total and dissolved iron concentrations. Higher values were excluded to better show the majority of the values. SMCL=0.3 mg/L.

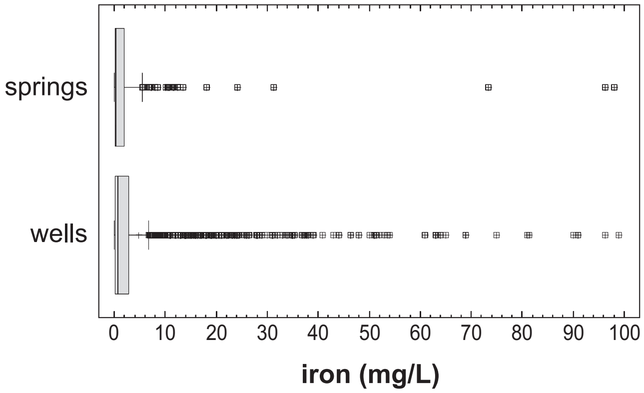

Figure 58. Comparison of iron concentrations in wells and springs. Higher values were excluded to better show the majority of the values. SMCL=0.3 mg/L.

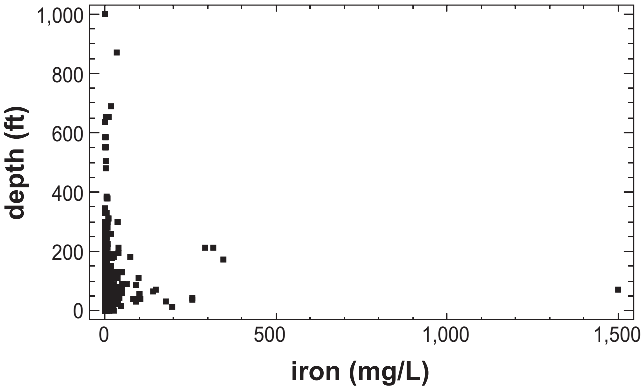

Figure 59. Iron concentrations versus well depth. SMCL=0.3 mg/L.

Manganese. Manganese (Mn) is a naturally occurring metal that is widely present in groundwater supplies. Manganese and iron are geochemically similar, 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 because higher concentrations produce objectionable odor, taste, color, corrosion, and staining.

The data repository contained 2,730 manganese concentrations from 1,731 sites in BMU 5 (Table 18). The median value was more than twice the SMCL. More than one-third of the sites produced water with more than 0.05 mg/L of manganese.

The distribution of manganese concentrations (Fig. 60) was generally similar to that of iron (Fig. 54). Less than 50 percent of the values were less than the SMCL of 0.05 mg/L.

Site distribution was very dense in the Big Sandy watershed (Fig. 61) because the National Uranium Resource Evaluation program sampled that area. Values that exceeded the SMCL were found throughout BMU 5.

The median manganese concentration was similar in the two watersheds (Fig. 62). The interquartile range of values was larger in the Little Sandy–Tygarts Creek watershed, however.

Dissolved manganese concentrations had a larger interquartile range than total manganese concentrations (Fig. 63), suggesting that suspended particulate material did not contribute significant amounts of manganese to the analysis.

Groundwater from springs had a larger median value and larger interquartile range (Fig. 64). The highest manganese concentrations occurred in water from wells, however.

The highest manganese concentrations were found in wells less than 100 ft deep (Fig. 65).

Table 18. Summary of manganese concentrations (mg/L). SMCL=0.05 mg/L.

Number of values	2,730
Maximum	83
75th percentile	0.50
Median	0.11
25th percentile	0.03
Minimum	0.00
Interquartile range	0.47
Number of sites	1.731
Number of sites > 0.05 mg/L	642

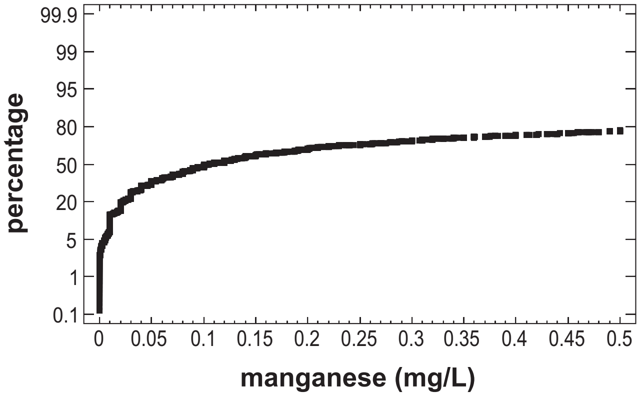

Figure 60. Cumulative plot of manganese concentrations. Higher values were excluded to better show the majority of the values. SMCL=0.05 mg/L.

In summary, the geochemical similarity between manganese and iron is demonstrated in the similarity of their concentrations in groundwater. Both commonly occurred at concentrations that affect groundwater taste and can stain containers and clothing. All features of the distribution of manganese concentrations appear primarily related to bedrock type. No evidence suggests that nonpoint-source contamination significantly contributes to manganese concentrations in the project area.

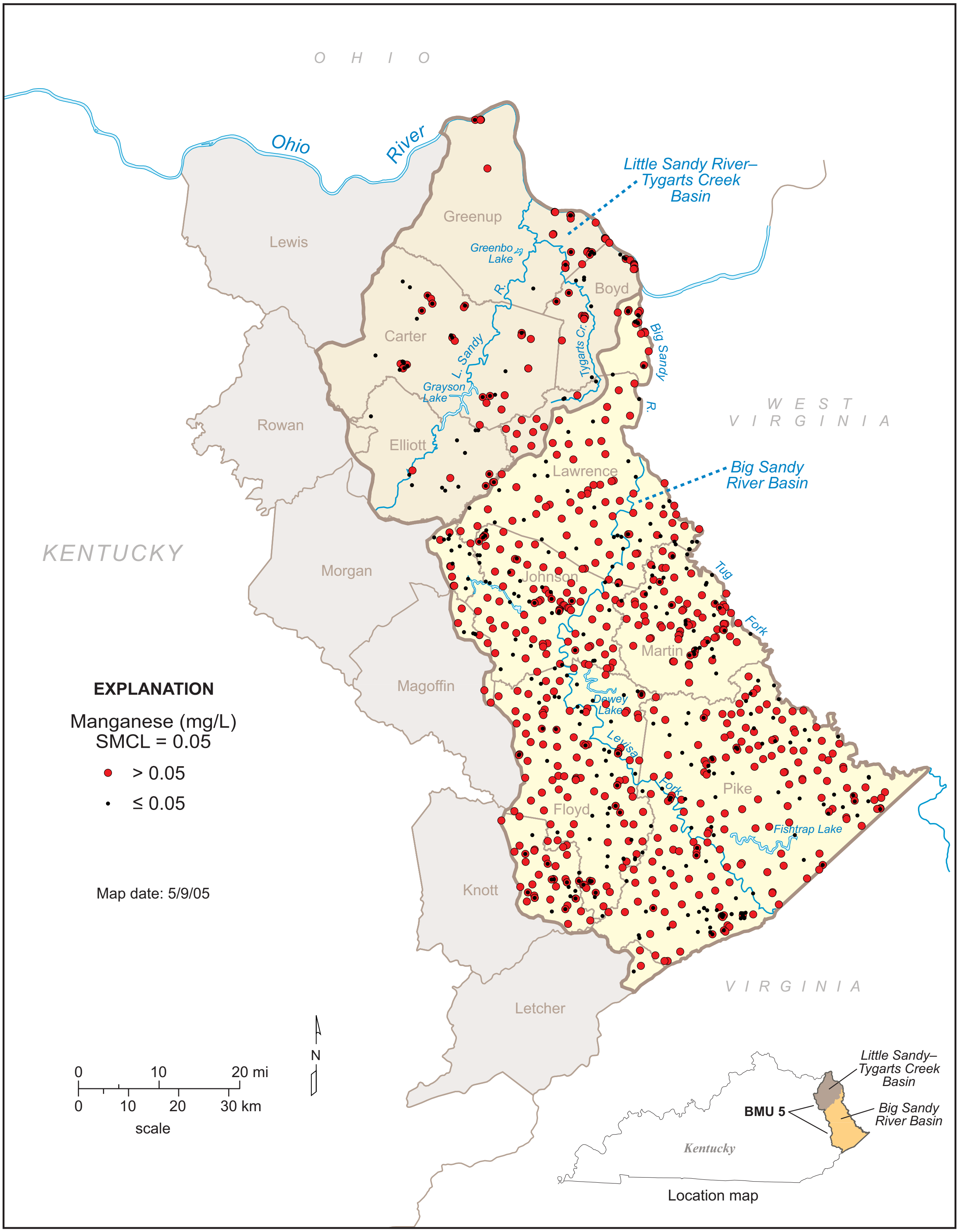

Figure 61. Locations of sampled sites and ranges of manganese values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

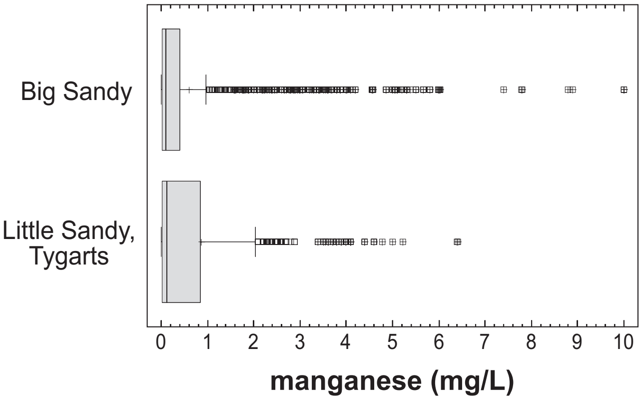

Figure 62. Summary of manganese concentrations grouped by watershed. Higher values were excluded to better show the majority of the values. SMCL=0.05 mg/L.

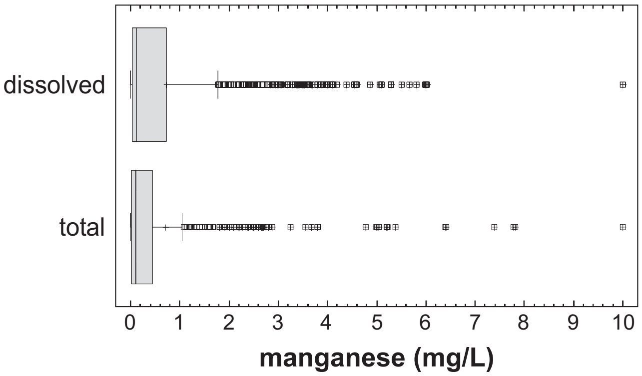

Figure 63. Comparison of total and dissolved manganese concentrations. Higher values were excluded to better show the majority of the values. SMCL=0.05 mg/L.

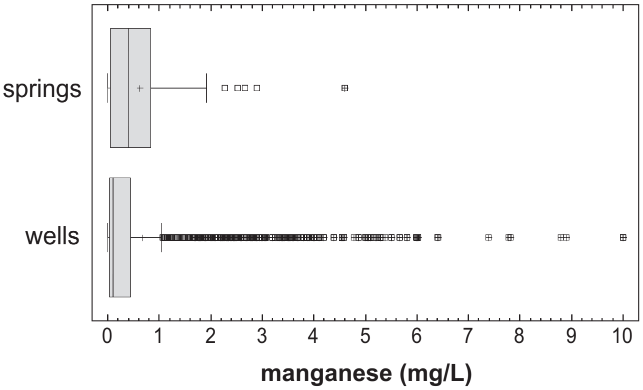

Figure 64. Comparison of manganese concentrations from wells and springs. Higher values were excluded to better show the majority of the values. SMCL=0.05 mg/L.

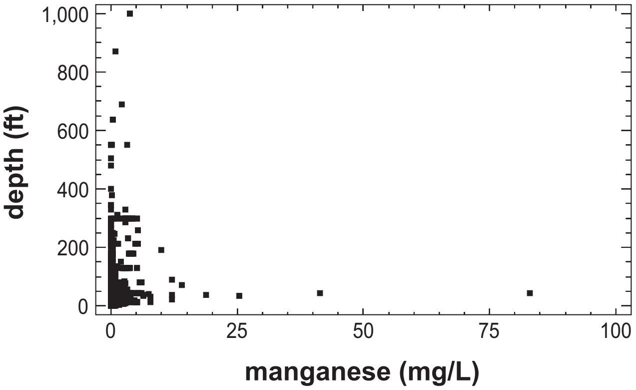

Figure 65. Manganese concentrations versus well depth. SMCL=0.05 mg/L.