Inorganic Anions

Chloride. Chloride (Cl) is present in most natural groundwater in low to moderate amounts. It is a highly conservative anion, meaning once in solution it is not involved in oxidation/reduction reactions, does not form complexes with other major ions or precipitate out as low-solubility minerals, and is not readily sorbed onto the aquifer matrix. In Kentucky groundwater, the main sources of chloride are interstitial fluids in shales and brackish groundwater that is commonly encountered at depth in the coal fields and the Pennyroyal Region (Hopkins, 1966; Wunsch, 1993). Nonpoint sources include contamination from oil or gas wells, road salt, confined animal feeding operations, and defective septic waste-disposal systems.

There are no health-related standards for chloride. The EPA has set a secondary maximum contaminant level of 250 mg/L for chloride because water containing more than this amount has an unpleasant taste that makes it unsuitable for domestic use.

Chloride concentrations from wells as deep as 4,200 ft have been reported. As with the conductance data discussed previously, chloride results from wells deeper than 730 ft were excluded from this data summary because they are not part of the groundwater system that could be used by citizens or municipalities for water supplies. The resulting data set is summarized in Table 10. Although chloride concentrations as high as 130,000 mg/L occur in the project area, more than 96 percent of the samples in BMU 3 contain less than 250 mg/L chloride. Seventy-five percent of the reported values are less than 12 mg/L.

Table 10. Summary of chloride values (mg/L).

Measurements	7,542
Maximum	130,000
75th percentile	11.6
Median	5.8
25th percentile	3.0
Minimum	0.0
Interquartile range	3.0–11.6
Sites	3,513
SMCL	250
Sites > 250	133

There is a sharp break in the distribution of chloride values at about 250 mg/L (Fig. 32). Chloride concentrations less than about 250 mg/L follow a normal distribution.

Chloride concentrations were reported for a very large number of sites distributed throughout the area

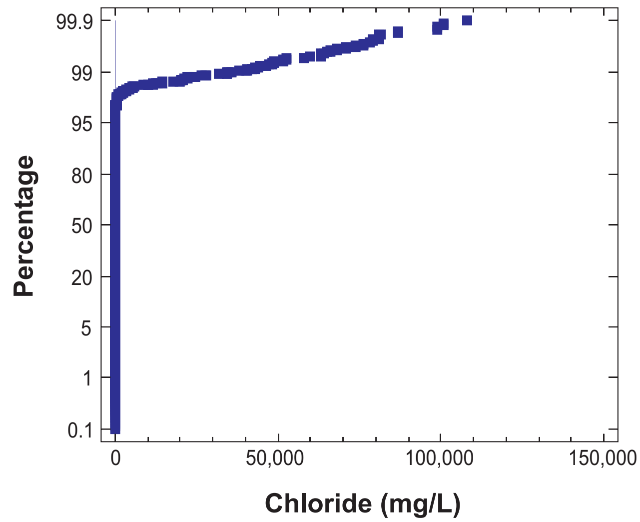

Figure 32. Cumulative plot of chloride values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

(Fig. 33). Sites having chloride concentrations greater than 250 mg/L are most common in the southwestern part of the Eastern Pennyroyal and Eastern Kentucky Coal Field Regions of the Upper Cumberland watershed.

Chloride concentrations greater than 10,000 mg/L are common only in the Eastern Kentucky Coal Field and Eastern Pennyroyal Regions of the Upper Cumberland River watershed (Figs. 34–35). Chloride concentrations in other physiographic regions and major watersheds are generally low.

Groundwater from wells is more likely to have very high chloride concentrations than groundwater from springs (Fig. 36). The highest chloride concentrations are found in wells that are less than 200 ft deep (Fig. 37). At well depths greater than about 250 ft, chloride concentrations are generally less than 100 mg/L.

In summary, more than 96 percent of the reported chloride concentrations are less than 250 mg/L throughout the project area. Sites that produce groundwater that exceeds this level are found primarily in the Eastern Pennyroyal and Eastern Kentucky Coal Field Regions of the Upper Cumberland River watershed. High chlorinity is more common in water from wells than from springs, and more common in wells less than about 250 ft deep than in deeper wells. Chloride values exceeding 100,000 mg/L have been reported from wells that are less than 730 ft deep and from wells for which depth was not reported. These samples may be from sites that are contaminated from leaking oil or gas wells or by other nonpoint sources; further investigations are needed to determine the source of the chlorinity at each site.

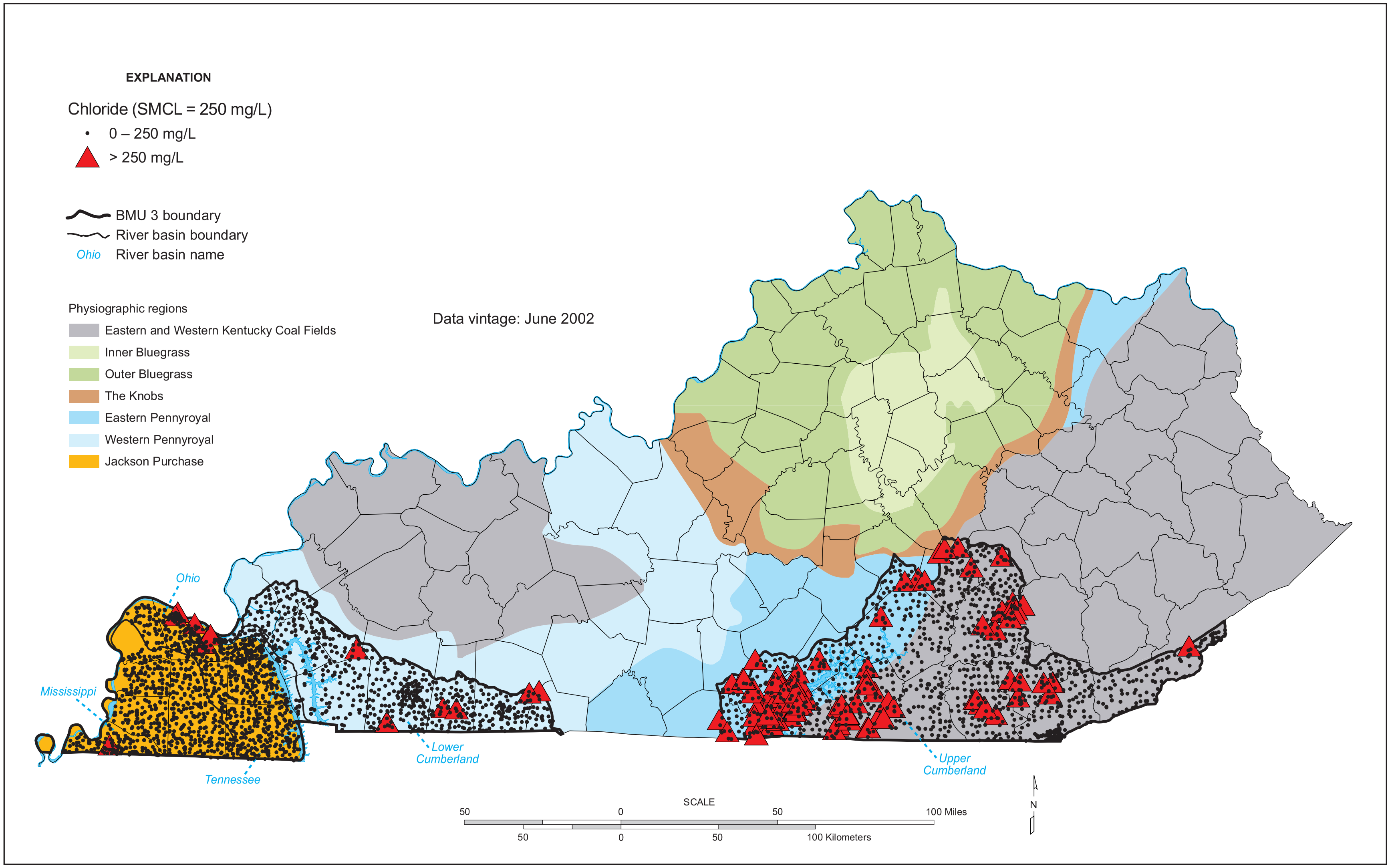

Figure 33. Sample sites and ranges of chloride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

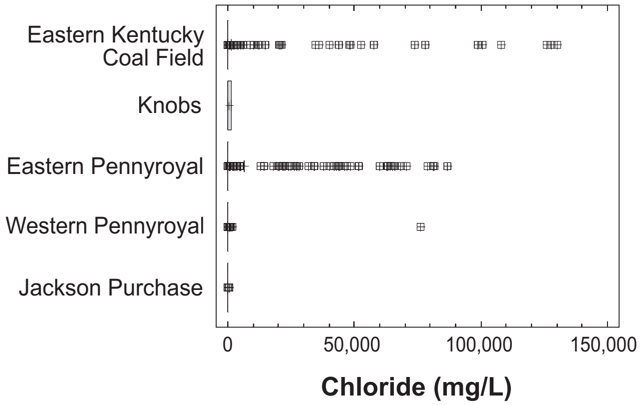

Figure 34. Summary of chloride values grouped by physiographic region.

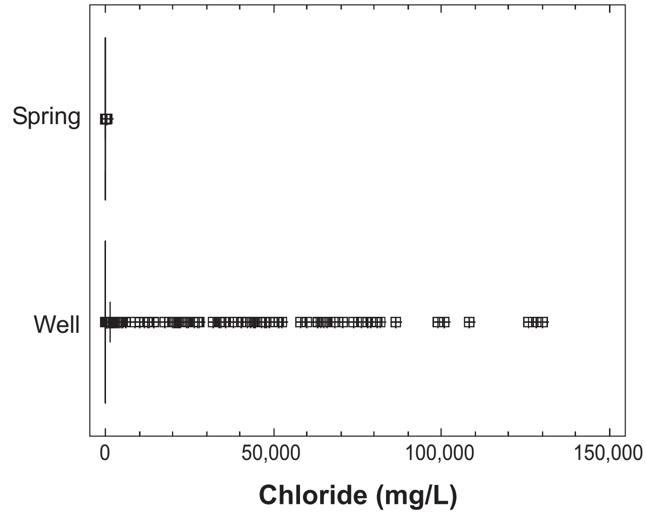

Figure 36. Comparison of chloride values from wells and springs.

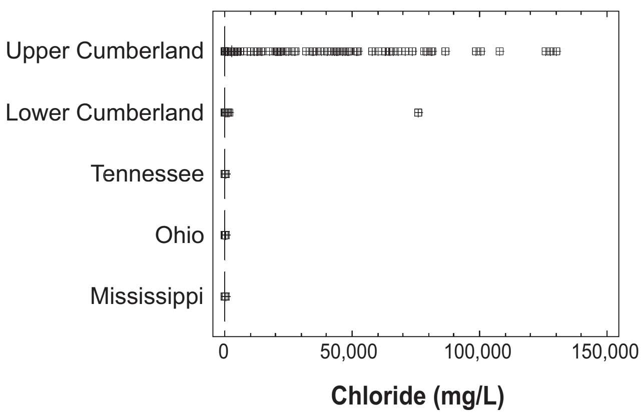

Figure 35. Summary of chloride concentrations grouped by major watersheds.

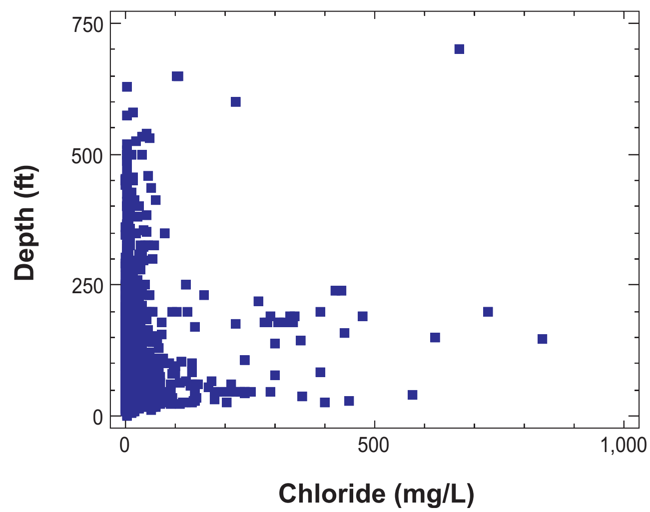

Figure 37. Chloride concentrations versus well depth. Values greater than 1,000 mg/L have been excluded to better show the majority of the results.

Sulfate. Sulfate (SO_4) is one of the major anions in most groundwater. The most significant sources of sulfate in groundwater are oxidation of iron sulfide minerals in coal or shale and dissolution of the calcium-sulfate minerals gypsum or anhydrite in carbonate strata.

There is no primary drinking-water standard for sulfate. The EPA has set a secondary standard of 250 mg/L because water containing more than 250 mg/L sulfate has an unpleasant taste that makes it unsuitable for domestic use. Water having sulfate concentrations greater than about 500 mg/L is a mild laxative.

The data set for sulfate is similar to that for conductance and chloride. Many sites that are identified as water wells have reported depths as great as 4,096 ft, and many wells do not have a depth recorded. In this data summary we excluded sulfate results from depths greater than 730 ft because the deepest groundwater sample reported by the Division of Water was 730 ft. Deeper wells are not likely to be used as groundwater supplies.

Table 11 summarizes sulfate measurements from groundwaters in BMU 3. Although the maximum value is 3,840 mg/L, 75 percent of the results are 40 mg/L or less, and more than 95 percent of the values are less than 250 mg/L (Fig. 38).

Table 11. Summary of sulfate values (mg/L).

Measurements	9,814
Maximum	3,840
75th percentile	40
Median	11
25th percentile	5
Minimum	0
Interquartile range	5–40
Sites	2,103
SMCL	250
Sites > 250	173

The distribution of sampled sites and sites where sulfate concentrations exceed 250 mg/L (Fig. 39) is similar to that for chloride (Fig. 33). Sites where chloride exceeds 250 mg/L are clustered in the southern part of the Upper Cumberland River watershed, the eastern part of the Lower Cumberland River watershed, and in the northern part of the Tennessee River watershed.

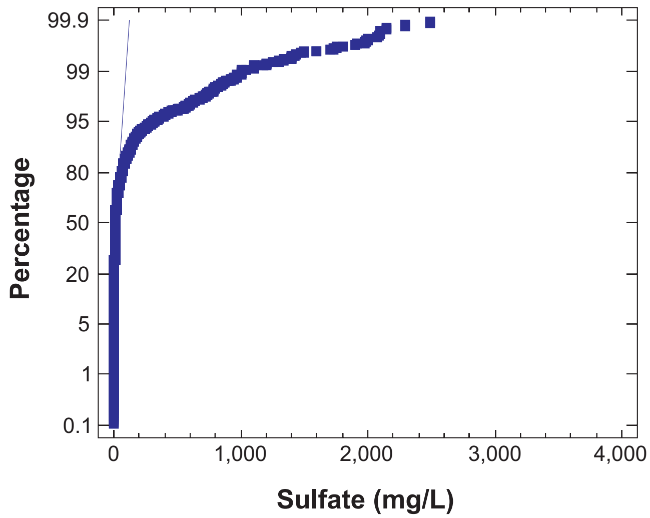

Figure 38. Cumulative plot of sulfate values. The highest and lowest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

All physiographic regions have produced groundwater with more than 1,000 mg/L sulfate (Fig. 40). No such values were found in the Mississippi River watershed in the Jackson Purchase Region, however (Fig. 41).

The highest sulfate concentrations are found in groundwater from wells, not springs (Fig. 42). This observation was also reported by Brown and Lambert (1963).

Although there is scatter in the data, sulfate concentrations generally increase from near surface to about 50 ft, then decrease with well depth (Fig. 43).

In summary, approximately 95 percent of the reported sulfate concentrations in BMU 3 are less than the SMCL of 250 mg/L. Natural oxidation of pyrite is the most probable cause of high sulfate concentrations in the Eastern Kentucky Coal Field, whereas dissolution of gypsum or anhydrite can yield high sulfate concentrations in the Eastern and Western Pennyroyal Regions. Dissolution of pyrite, gypsum, or anhydrite may produce high sulfate values in the Jackson Purchase Region.

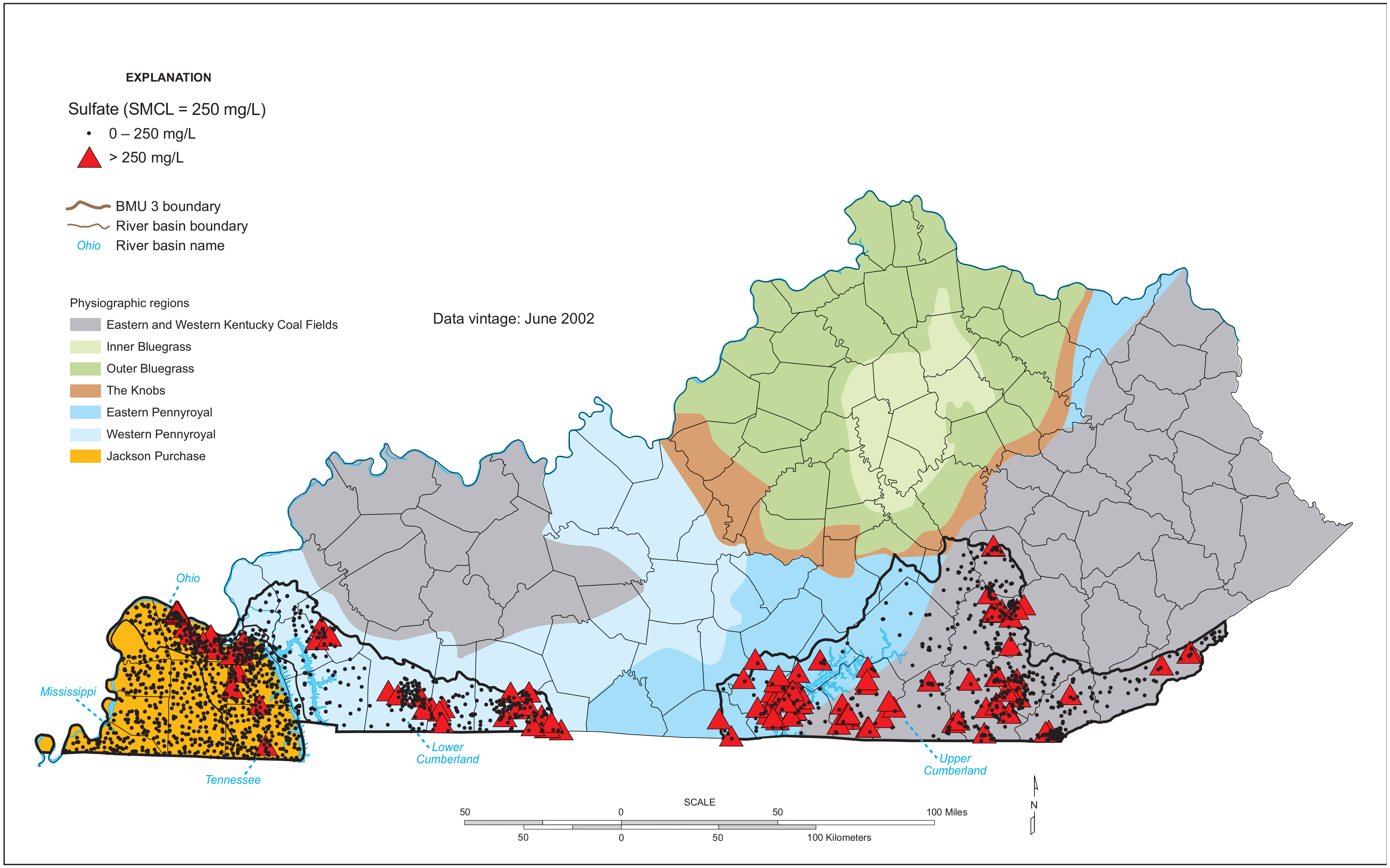

Figure 39. Sample sites and ranges of sulfate values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

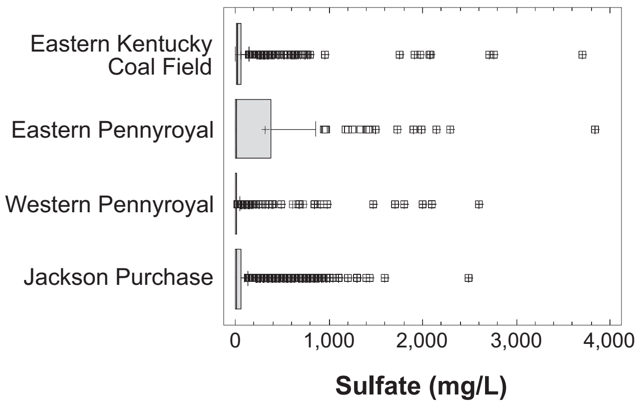

Figure 40. Summary of sulfate values grouped by physiographic region.

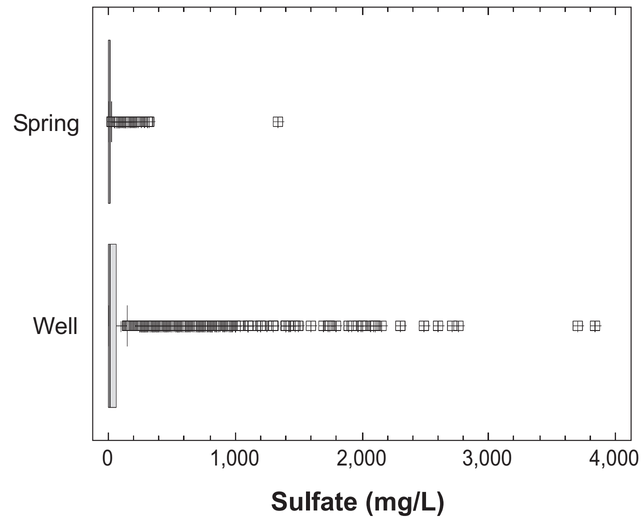

Figure 42. Comparison of sulfate values from wells and springs.

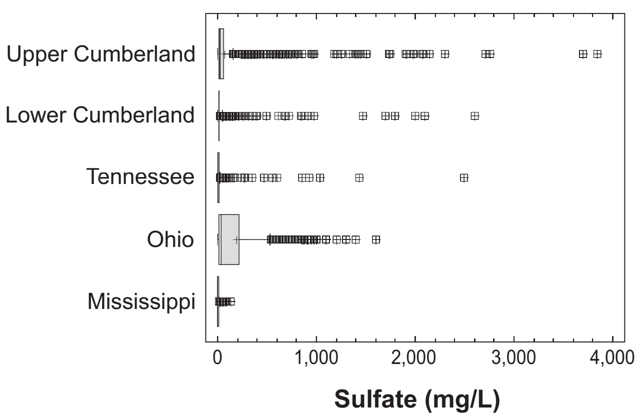

Figure 41. Summary of sulfate values grouped by major watershed.

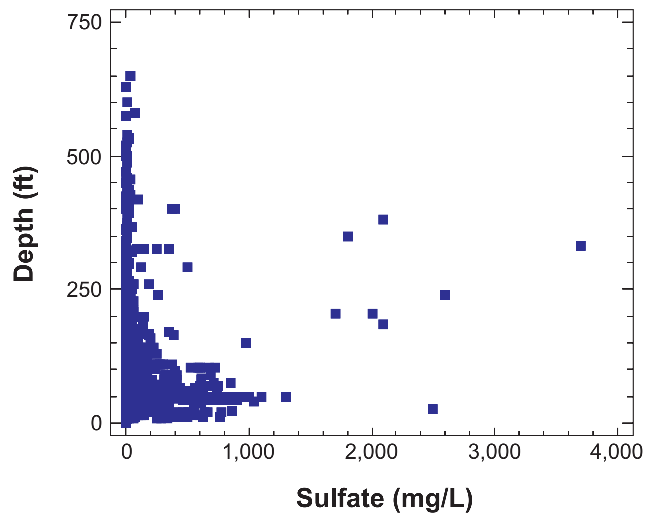

Figure 43. Sulfate values versus well depth.

Fluoride. Fluoride (F) is a minor anion, usually present in concentrations of less than 1 mg/L in groundwater. Natural sources of fluoride include the mineral fluorite (CaF_2), which is common in carbonate rocks. The major man-made sources are discharges from fertilizer and aluminum production facilities.

Fluoride is added to public water supplies in Kentucky to maintain a concentration of approximately 1 mg/L, because of its proven value in promoting healthy teeth and bones. At higher concentrations, fluoride may cause pain and weakness of the bones, and staining or mottling of teeth. The Environmental Protection Agency has established an MCL of 4 mg/L for fluoride in public drinking water.

Fluoride has been measured in 5,069 samples from 2,585 sites in BMU 3 (Table 12). The maximum value reported (78 mg/L) may be an error, although this cannot be confirmed. The second highest value is 19 mg/L. More than 99 percent of all measurements are less than 4.0 mg/L (Fig. 44).

Table 12. Summary of fluoride values (mg/L).

Measurements	5,069
Maximum	78
75th percentile	0.20
Median	0.10
25th percentile	0.10
Minimum	0.00
Interquartile range	0.10–0.20
Sites	2,585
MCL	4.0
Sites > 4.0	26

Fluoride has been measured at many wells and springs throughout BMU 3 (Fig. 45). Concentrations greater than 4 mg/L are found mainly in the Upper Cumberland and Lower Cumberland River watersheds, and are rare in the Tennessee and Mississippi River watersheds (Fig. 45).

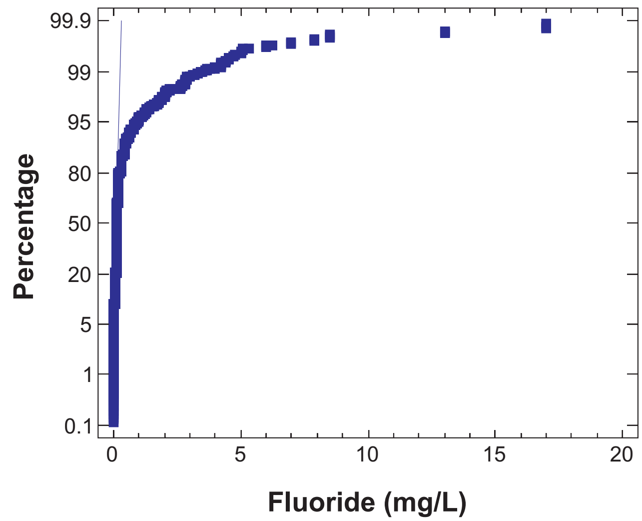

Figure 44. Cumulative plot of fluoride values. One value of 78 mg/L has been omitted so that the remaining data can be viewed more clearly.

Fluoride concentrations greater than 5 mg/L are found in the Eastern Kentucky Coal Field and Eastern Pennyroyal Regions of the Upper Cumberland River watershed and the Western Pennyroyal Region of the Lower Cumberland River watershed (Figs. 46–47).

More fluoride concentrations greater than 4 mg/L are reported in groundwater from wells than from springs (Fig. 48). The majority of the fluoride data show a general increase with well depth to about 100 ft, followed by a decrease with further depth (Fig. 49).

In summary, the fluoride concentration of ambient groundwater samples in Basin Management Unit 3 is primarily controlled by bedrock lithology. Less than 1 percent of all reported analyses exceeded the EPA MCL of 4.0 mg/L. There are no obvious non-point-source contributions of fluoride to groundwater in the project area. A statewide summary of fluoride data (Conrad and others, 1999b) is available and can be viewed on the Kentucky Geological Survey Web site (www.uky.edu/KGS/water/gnet/gnet.htm).

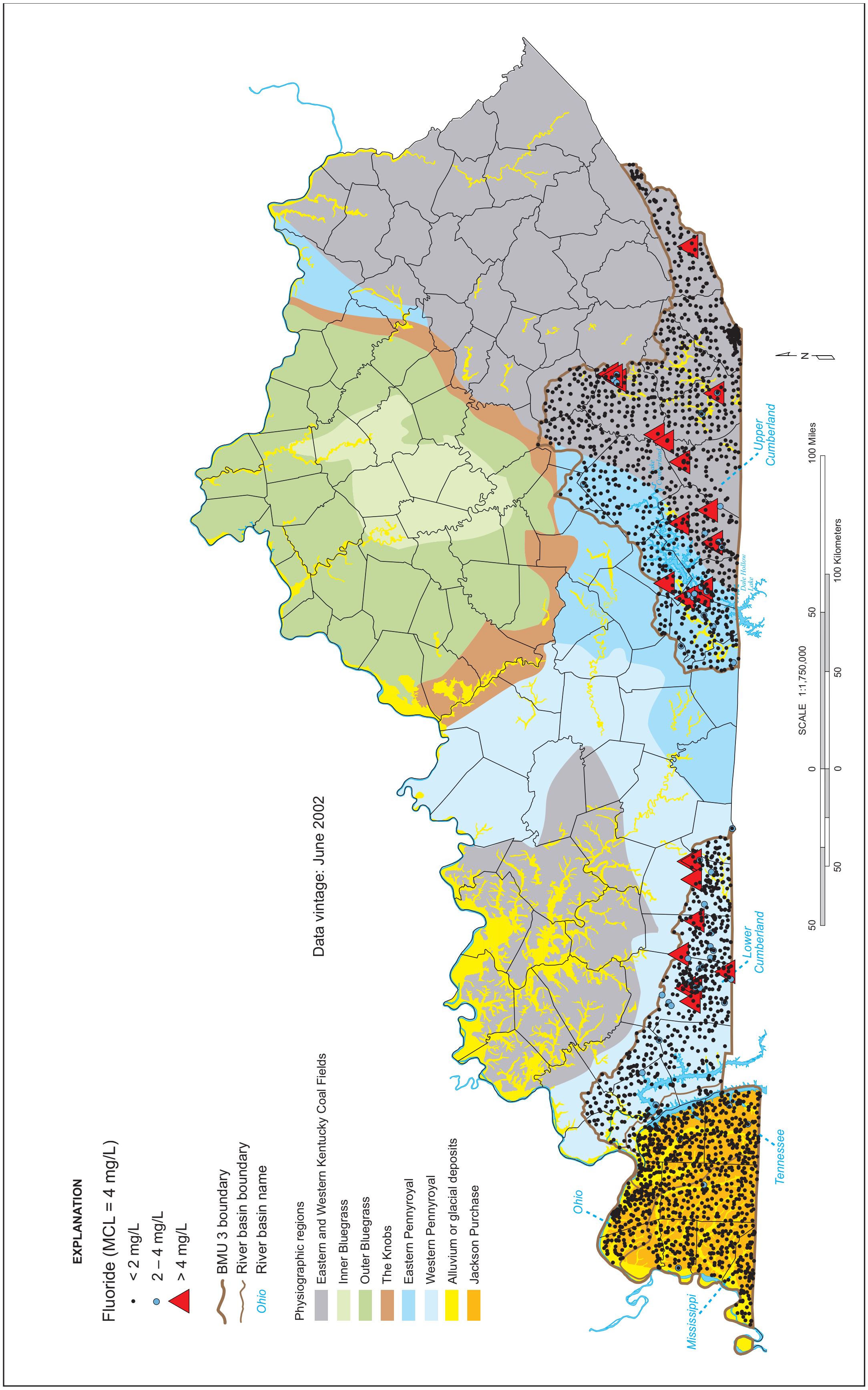

Figure 45. Sample sites and ranges of fluoride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

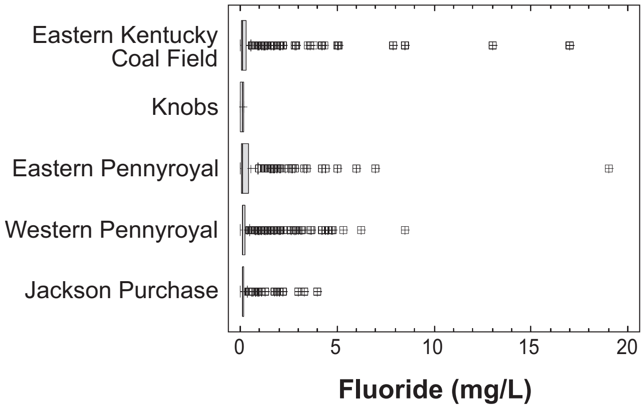

Figure 46. Summary of fluoride values grouped by physiographic region. One extreme value of 78 mg/L at a site in the Upper Cumberland watershed is probably erroneous and was omitted so that the majority of the data could be shown more clearly.

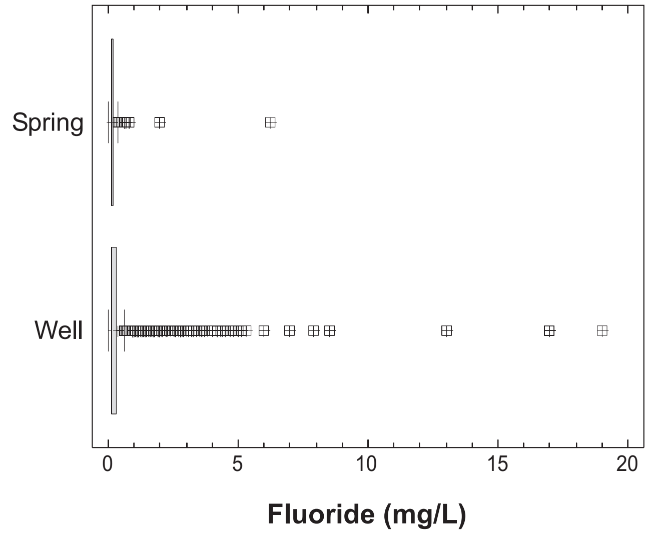

Figure 48. Comparison of fluoride values from wells and springs. One extreme value of 78 mg/L from a 62-ft-deep well is probably erroneous and was omitted so that the majority of the data could be shown more clearly.

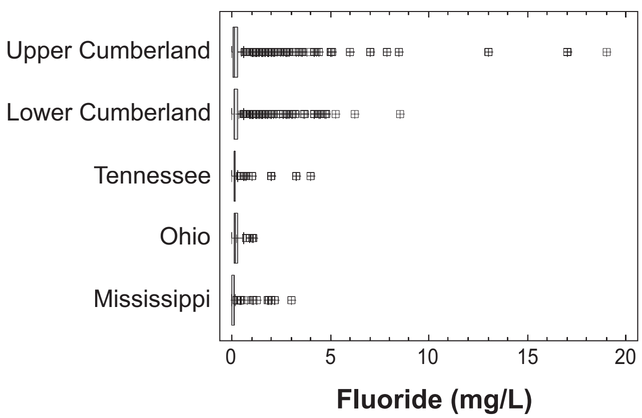

Figure 47. Summary of fluoride values grouped by major watershed. One extreme value of 78 mg/L at a site in the Eastern Kentucky Coal Field is probably erroneous and was omitted so that the majority of the data could be shown more clearly.

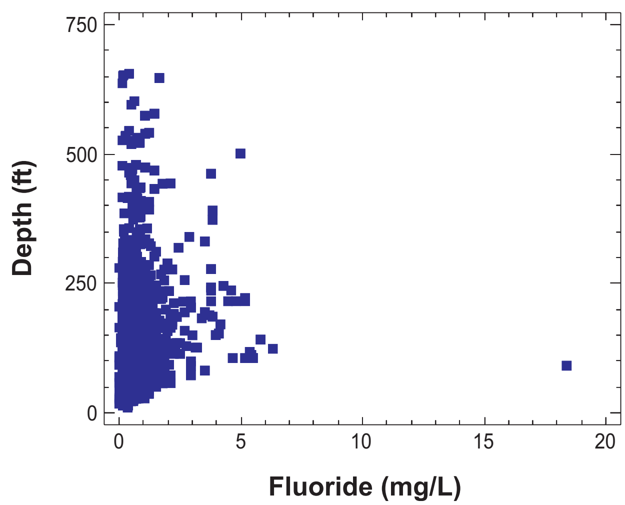

Figure 49. Fluoride values versus well depth. One extreme value of 78 mg/L from a 62-ft-deep well is probably erroneous and was omitted so that the majority of the data could be shown more clearly.