## Inorganic Anions

Chloride. Chloride (Cl) is present in most natural groundwater in low to moderate amounts. It is a highly conservative anion; once in solution it is not involved in oxidation/reduction reactions, does not 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 (Wunsch, 1993) and the Pennyroyal Region (Hopkins, 1966). Nonpoint sources include leaking oil or gas wells, road salt, confined animalfeeding 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.

The data repository contained 10,029 chloride measurements from 4,665 sites in the project area (Table 10). The maximum value in each basin management unit exceeds 100,000 mg/L.

Table 10. Summary of chloride values (mg/L). SMCL: 250 mg/L. BMU 1 BMU 2 BMU 5 Values 3.327 4.878 1.824 Maximum 121,000 141,000 184,880 75th percentile 19 44 31.2 Median 7.4 17 9.8 25th percentile 3.7 6.4 3.9 Minimum 0 0 0 Interguartile range 15.3 37.6 27.3 1,742 1,825 1,098 Sites Sites > 250 mg/L 74 119 69

Such high values are exceptional, however; 75 percent of the measured values are less than 45 mg/L and 50 percent are less than 17 mg/L.

Data distributions for the three basin management units have a similar shape (Figs. 44–46) with a sharp break in slope at a chloride value less than 250 mg/L.



Figure 44. Cumulative plot of chloride values from BMU 1.

Higher values were excluded for clarity.

Sample-site density is much greater in the southern half of the study area than in the northern half (Fig. 47), because sampling for the National Uranium Resource Evaluation project did not extend into the northern part of the state. The percentage of sites where chloride exceeds 250 mg/L is approximately the same in each basin management unit and shows no relation to river basin or physiographic region.



Figure 45. Cumulative plot of chloride values from BMU 2. Higher values were excluded for clarity.



Figure 46. Cumulative plot of chloride values from BMU 5. Higher values were excluded for clarity.



The median and 75th percentile chloride concentrations are well below 250 mg/L in every physiographic region (Fig. 48) and major watershed (Fig. 49).

Samples from wells have a higher median value, 75th percentile value, and larger interquartile range of chloride concentrations than samples from springs (Fig. 50).

Chloride concentrations are greatest in wells shallower than about 250 ft, with a general trend of lower concentrations at depths of about 500 ft (Fig. 51). Some deeper samples have concentrations that exceed 250 mg/L.



Figure 48. Summary of chloride values grouped by physiographic region. Higher values were excluded for clarity.



Figure 50. Summary of chloride values for wells and springs. Higher values were excluded for clarity.

In summary, chloride concentrations in excess of 100,000 mg/L are found throughout the project area, but are uncommon and do not appear to be controlled by basin management unit, physiographic region, or major watershed. Higher chloride concentrations are found in wells than in springs, and shallow wells (less than 200 ft) are more likely to have high chloride concentrations than deep wells. The occurrence of high chloride concentrations in shallow wells might suggest an impact from nonpoint sources, possibly road salt applied in the winter. That cannot be clearly demonstrated with the available information, however.



Figure 49. Summary of chloride values grouped by major watersheds. Higher values were excluded for clarity.



Figure 51. Plot of chloride values versus well depth. Higher values were excluded for clarity.

**Sulfate.** Sulfate  $(SO_4)$  is a major anion in most groundwater. The most common natural sources of sulfate in the project area 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 of 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.

There are 11,607 sulfate measurements reported from 2,611 sites in the project area (Table 11). The high-



Figure 52. Cumulative plot of sulfate values in BMU 1. Higher values were excluded for clarity.



Figure 53. Cumulative plot of sulfate values in BMU 2. Higher values were excluded for clarity.

Table 11. Summary of sulfate values (mg/L). SMCL: 250 mg/L.				
	BMU 1	BMU 2	BMU 5	
Values	4,078	4,383	3,146	
Maximum	1,740	3,200	2,749	
75th percentile	63	211	66.7	
Median	27	66	26.8	
25th percentile	12	28.7	7	
Minimum	0	0	0	
Interquartile range	51	182.3	59.7	
Sites	738	1,121	752	
Sites > 250 mg/L	70	149	76	

est values for maximum, 75th percentile, median, and 25th percentile are found in BMU 2, which also contains the largest number of sites that exceed 250 mg/L (Table 11).

Distributions of sulfate concentrations are generally similar in each basin management unit (Figs. 52– 54). Most values in each BMU are less than 250 mg/L; however, groundwater from BMU 2 has more sulfate concentrations greater than 250 mg/L than water from BMU 1 or BMU 5.

The distribution of sampled sites varies throughout the project area (Fig. 55). The Eastern Kentucky Coal Field, Inner Bluegrass, and Western Pennyroyal Regions are more densely sampled than the Outer Bluegrass Region of the Licking River watershed. Sites where sulfate concentrations exceed 250 mg/L occur mainly in the Outer Bluegrass Region of the Licking River watershed. Sites where sulfate concentrations exceed 250 mg/L occur mainly in the Outer Bluegrass Region of the Salt River watershed and the Eastern Kentucky Coal Field Region of the Kentucky River and Big Sandy River watersheds (Figs. 56–57).

Groundwater samples from wells and springs have nearly the same median sulfate concentration



Figure 54. Cumulative plot of sulfate values in BMU 5. Higher values were excluded for clarity.





Figure 56. Summary of sulfate values grouped by physiographic region. Higher values were excluded for clarity.

(Fig. 58). Water from wells has a higher 75th percentile value, larger interquartile range, and more values that exceed 250 mg/L than water from springs, however.

The highest sulfate concentrations occur in shallow wells (Fig. 59). Sulfate concentrations decrease with well depth.

In summary, most wells and springs in the project area contain sulfate concentrations that are below the secondary standard of 250 mg/L. Higher values are found most commonly in the Eastern Kentucky Coal Field, Outer Bluegrass, and Western Pennyroyal Regions. Wells produce high-sulfate water more com-



Figure 58. Comparison of sulfate values from wells and springs. Higher values were excluded for clarity.



Figure 57. Summary of sulfate values grouped by major watershed. Higher values were excluded for clarity.

monly than springs, and shallow wells are more likely to have high sulfate concentrations than deeper wells. The distribution of sulfate concentrations greater than 250 mg/L suggests that natural sources mask any nonpoint-source effects. High sulfate concentrations are expected in the coal fields, where oxidation of iron sulfide minerals in shale and coal produces sulfate, and in carbonate strata such as occurs in the Outer Bluegrass and Western Pennyroyal, where the sulfatebearing minerals gypsum and anhydrite are widely distributed.



Figure 59. Plot of sulfate values versus well depth. Higher values were excluded for clarity.

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

Because of the proven Si value of fluoride in maintain-

ing healthy teeth and bones, fluoride is added to public water supplies in Kentucky. The concentration in public water is maintained at approximately 1 mg/L. Although fluoride has a beneficial effect at low concentrations, at higher concentrations it may cause pain and weakness of the bones, and staining or mottling of teeth. For these reasons, the Environmental Protection Agency has established a maximum contaminant level of 4 mg/L of fluoride in public drinking water.

Fluoride in Kentucky groundwater has been measured in 6,897 samples from 3,498 sites (Table 12). The maximum value in each basin management unit greatly exceeds 4 mg/L, but concentrations above the MCL are rare. The 75th percentile and median values in each basin management unit are less than 1.0 mg/L (Table 12).

The distribution of reported fluoride concentrations is similar in BMU's 1, 2, and 5. More than 99 percent of all measured values in each basin management unit are less than 4 mg/L (Figs. 60–62).

Sample-site density is much greater in the southern half of the project area than in the northern part (Fig. 63), because sampling for the National Uranium Resource Evaluation project did not extend into north-



Figure 60. Cumulative plot of fluoride values from BMU 1. Higher values were excluded for clarity.

	BMU 1	BMU 2	BMU 5
Values	2,585	3,220	1,092
Maximum	64.8	73.0	10.0
75th percentile	0.22	0.3	0.3
Median	0.13	0.13	0.164
25th percentile	0.08	0.1	0.1
Minimum	0	0	0
Interquartile range	0.14	0.2	0.2
Sites	1,355	1,400	743
Sites > 4.0 mg/L	11	7	2



Figure 61. Cumulative plot of fluoride values from BMU 2. Higher values were excluded for clarity.



Figure 62. Cumulative plot of fluoride values from BMU 5. Higher values were excluded for clarity.

ern Kentucky. Sites where fluoride exceeds 2 mg/L or 4 mg/L do not appear to be concentrated in any particular physiographic region or watershed, but are randomly distributed throughout the region.

Groundwater samples from the Western Pennyroyal Region have the largest range of interquartile values (Fig. 64). The range of interquartile values from all other regions is much less than 1.0 mg/L, suggest-





Figure 63. Locations of sampled sites and ranges of fluoride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.



Figure 64. Summary of fluoride values grouped by physiographic region. Higher values were excluded for clarity.

ing either stronger geochemical control on fluoride concentrations or an absence of naturally occurring fluoride in the area.

More than 75 percent of all fluoride concentrations in each river basin are less than 1 mg/L (Fig. 65).

Total and dissolved fluoride concentrations are very similar, as expected, because fluoride is not associated with suspended solids (Fig. 66).



Figure 65. Summary of fluoride values grouped by major watershed. Higher values were excluded for clarity.



Figure 66. Comparison of total and dissolved fluoride values. Higher values were excluded for clarity.

Groundwater samples from wells and springs have nearly the same median fluoride value and interquartile range, although higher fluoride concentrations may be found in well water (Fig. 67).

Fluoride concentrations show no strong trend with well depth (Fig. 68).



Figure 67. Comparison of fluoride values from wells and springs. Higher values were excluded for clarity.



Figure 68. Plot of fluoride values versus well depth. Higher values were excluded for clarity.

In summary, fluoride concentrations less than the MCL of 4.0 mg/L predominate throughout the project area. A few groundwater samples contain more than 4.0 mg/L of fluoride, but they are widely scattered and show no strong correlation with physiographic region or major river watershed. The fluoride concentrations that exceed the MCL probably result from natural variations in bedrock composition rather than the effects of nonpoint-source contamination.

A statewide summary of fluoride data (Conrad and others, 1999a) can be viewed on the KGS Web site (kgsweb.uky.edu/olops/pub/kgs/ic01\_12.pdf).