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 Regions (Hopkins, 1966). Nonpoint sources include saline water from leaking oil or gas wells, road salt, confined animal-feeding operations, and defective septic waste-disposal systems. There are no health-related standards for chloride in drinking water, but the EPA has set a secondary maximum contaminant level of 250 mg/L because water containing more than this has an unpleasant taste.

Seventy-five percent of the reported values were less than 32 mg/L and 50 percent were less than 10 mg/L. Only 69 sites produced groundwater that had more than 250 mg/L of chloride (Table 11). Approximately 95 percent of all reported values were less than 250 mg/L (Fig. 28).

Table 11.SummarySMCL=250 mg/L.	of chloride	concentrations	(mg/L).
Number of values	1,824		
Maximum	184,880		
75th percentile	31.2		
Median	9.8		
25th percentile	3.9		
Minimum	0		
Interquartile range	27.3		
Number of sites	1,098		
Number of sites > 250 i	mg/L 69		

Site density was greater in the Big Sandy watershed (Fig. 29), because sampling for the National Uranium Resource Evaluation project included this region. The distribution of sites at which chloride exceeded 250 mg/L was greatest in the western part of the Big Sandy watershed.



Figure 28. Cumulative plot of chloride concentrations. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.

The median value and interquartile range of chloride measurements was approximately the same in each watershed (Fig. 30). Both watersheds also had groundwater with very high chloride concentrations.

The highest chloride concentrations occurred in water from wells rather than water from springs (Fig. 31).

Some very high chloride concentrations occurred in wells shallower than about 150 ft, and there was a sharp trend toward higher concentrations at about 650 ft (Fig. 32). A similar pattern was observed for conductance values. We attribute the increase in both cases to the presence of saline, sodium chloride water at about 600 to 650 ft below ground surface in this region.

In summary, most chloride concentrations in the project area were well below the SMCL of 250 mg/L. Higher chloride concentrations were found in wells than in springs, the highest values in wells deeper than about 650 ft. The occurrence of high chloride concentrations in shallow wells may suggest an impact from nonpoint sources, or an upward leaking of deep, saline groundwater. Chloride concentrations greater than several thousand milligrams per liter in shallow wells may be the result of either nonpoint-source effects or upward discharge of deeper, saline groundwater.



Figure 29. Locations of sampled sites and ranges of chloride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.





Figure 30. Summary of chloride concentrations grouped by watersheds. SMCL=250 mg/L. Higher values were excluded to better show the majority of the values.

Figure 31. Summary of chloride concentrations from wells and springs. SMCL=250 mg/L. Higher values were excluded to better show the majority of the values.



Figure 32. Chloride concentrations versus well depth. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.

Sulfate. Sulfate (SO_4) is a common anion in most groundwater. The most likely natural sources of sulfate in BMU 5 are oxidation of iron sulfide minerals in coal or shale, and dissolution of the calcium sulfate minerals gypsum and anhydrite.

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 this amount has an unpleasant taste that makes it unsuitable for domestic use. Water with sulfate concentrations greater than about 500 mg/L is a mild laxative.

There were 3,146 sulfate measurements reported from 752 sites in the project area (Table 12). Approximately 10 percent of the sites produced water that had more than 250 mg/L of sulfate.

Table12.Summary oSMCL=250 mg/L.	f sulfate	concentrations	(mg/L).
Number of values	3,146	;	
Maximum	2,749	1	
75th percentile	66.7	,	
Median	26.8		
25th percentile	7	,	
Minimum	0	1	
Interquartile range	59.7	,	
Number of sites	752		
Number of sites > 250 mg	g/L 76	ì	

Nearly 90 percent of the reported values were less than 250 mg/L; 80 percent were less than 75 mg/L (Fig. 33).

The Big Sandy watershed was sampled more densely than the Little Sandy-Tygarts Creek watershed (Fig. 34) and contained most of the sites where sulfate concentrations exceeded 250 mg/L.

The median value and interquartile range of sulfate concentrations were approximately the same in the



Figure 33. Cumulative plot of sulfate concentrations. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.

two watersheds (Fig. 35); both watersheds produced water with very high sulfate concentrations.

Water from springs had a much larger interquartile range than water from wells (Fig. 36). The highest sulfate concentrations were found, however, in water from wells.

The highest sulfate concentrations occurred in shallow wells (Fig. 37). Sulfate concentrations generally decreased with well depth.

In summary, most wells and springs in the project area contained sulfate concentrations that were less than the SMCL of 250 mg/L. Both wells and springs produced groundwater with more than 250 mg/L of sulfate; shallow wells were 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 field, where oxidation of iron sulfide minerals in shale and coal produces sulfate.



Figure 34. Locations of sampled sites and ranges of sulfate values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.



Figure 35. Summary of sulfate concentrations grouped by watershed. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.

Figure 36. Summary of sulfate concentrations from wells and springs. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.



Figure 37. Sulfate concentrations versus well depth. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.

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

Because of the proven value of fluoride in maintaining healthy teeth and bones, fluoride is added to public water supplies in Kentucky. The concentration maintained in public water is 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 U.S. Environmental Protection Agency has established an MCL of 4 mg/L in public drinking water. There is also an SMCL of 2.0 mg/L because higher concentrations can cause tooth discoloration.

Fluoride in groundwater was measured in 1,092 samples from 743 sites in BMU 5 (Table 13). The maximum value was 10.0 mg/L. Concentrations above the MCL were rare, however. The 75th percentile and median values were well below 1.0 mg/L (Table 13). Only two sites produced water in which fluoride concentrations exceeded 4 mg/L.

Approximately 95 percent of the fluoride concentrations were 1 mg/L or less (Fig. 38). Only two values exceeded the MCL of 4 mg/L.

Sample-site density was much greater in the southern part of the project area (Fig. 39), because of sampling for the National Uranium Resource Evaluation project. Sites where fluoride exceeded 2 or 4 mg/L were randomly distributed throughout the region.

Samples from both watersheds had nearly the same median value and interquartile range (Fig. 40).

Samples from wells and springs had nearly the same median fluoride value and interquartile range, although higher fluoride concentrations were found in well water (Fig. 41).

Table 13.Summary of fluoride concentrations (mg/L).MCL=4.0 mg/L.

Number of values	1,092	
Maximum	10.0	
75th percentile	0.3	
Median	0.164	
25th percentile	0.1	
Minimum	0	
Interquartile range	0.2	
Number of sites	743	
Number of sites > 4.0 mg/L	2	



Figure 38. Cumulative plot of fluoride concentrations. MCL=4.0 mg/L.

Fluoride concentrations showed no strong correlation with well depth (Fig. 42).

In summary, fluoride concentrations less than the MCL of 4.0 mg/L predominated throughout the project area. Only a few groundwater samples contained more than 4.0 mg/L of fluoride, but they were widely scattered and showed no strong correlation with physiographic region or river watershed. No strong evidence of nonpoint-source contribution to fluoride in groundwater was found. A statewide summary of fluoride data is available (Conrad and others, 1999a) and can be viewed on the KGS Web site (kgsweb.uky. edu/olops/pub/kgs/ic01_12.pdf).



Figure 39. Locations of sampled sites and ranges of fluoride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.





Figure 40. Summary of fluoride concentrations grouped by watershed. MCL=4.0 mg/L.

Figure 41. Summary of fluoride concentrations from wells and springs. MCL=4.0 mg/L.



Figure 42. Fluoride concentrations versus well depth. Higher values were excluded to better show the majority of the values. MCL=4.0 mg/L.