

## Nutrients

The nutrients nitrogen and phosphorus occur naturally and also may be introduced to groundwater systems from urban and agricultural fertilizer applications, livestock or human wastes, and fossil-fuel combustion. High nutrient levels in groundwater generally indicate contamination from fertilizer, sewage systems, or confined feedlot operations. Excessive nutrients can lead to algal blooms and eutrophication in surface-water systems, and excessive nitrate or nitrite in drinking water can pose health hazards.

**Nitrogen Species.** Nitrogen in water occurs predominantly as either the anion nitrate ( $\text{NO}_3^-$ ) under oxidizing conditions or the cation ammonium ( $\text{NH}_4^+$ ) under reducing conditions. Nitrite ( $\text{NO}_2^-$ ) and ammonia ( $\text{NH}_3$ ) are thermodynamically less stable forms of aqueous nitrogen that may be present under reducing conditions. Because it is positively charged, ammonium is readily adsorbed on soil and mineral particles, thus limiting its mobility, whereas the negatively charged nitrate and nitrite anions are highly mobile. Nitrite, ammonium, and ammonia are unstable in oxidizing environments (Hem, 1985). For this reason, high concentrations of these species in shallow, aerated groundwater are indicators of likely contamination by sewage or other forms of organic waste. Nitrite, ammonium, and ammonia may also occur in deep, old, reducing groundwater systems.

Runoff from fertilizer use, leachate from septic tanks, and sewage are major sources of nitrogen species. Nitrate is commonly used as fertilizer; high nitrate concentrations generally indicate contamination by fertilizer or by human or animal waste. Caves in karst terrain that are home to large bat colonies may accumulate large amounts of guano that contribute nitrogen to local groundwater. Nitrite concentrations in groundwater are generally low because nitrite oxidizes quickly to nitrate in oxidizing environments and to nitrogen gas in reducing environments (Fetter, 1993).

Nitrate, nitrite, ammonia, and ammonium concentrations are reported differently for different pur-

poses. Analyses for geochemical investigations traditionally report concentrations as weight per volume of the measured ions (mg/L of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_3$ , or  $\text{NH}_4^+$ ). Analyses for environmental purposes generally report the concentrations as equivalent amounts of nitrogen (nitrate-nitrogen, nitrite-nitrogen, ammonia-nitrogen, or ammonium-nitrogen), however. Consequently, nitrogen data must be examined closely to determine how they were recorded, and concentration units must be standardized before data summaries and evaluations can be made.

The EPA has established a drinking-water MCL of 10 mg/L for nitrate-nitrogen (equivalent to 44.3 mg/L nitrate) and 1.0 mg/L for nitrite-nitrogen (equivalent to 3.2 mg/L nitrite) because higher concentrations can lead to methemoglobinemia (blue baby syndrome) in infants, where the oxygen-carrying ability of the child's blood is severely reduced. Lifetime exposure to nitrite-nitrogen concentrations greater than 1 mg/L also can produce diuresis, increased starchy deposits, and hemorrhaging of the spleen. No human health-based concentration limits have been established for ammonia or ammonium. Ammonia concentrations of 1 to 10 mg/L can be toxic to aquatic life, however.

*Nitrate-Nitrogen.* The data repository contained 2,547 nitrate-nitrogen measurements at 741 sites. Nitrate-nitrogen concentrations exceeded the MCL of 10 mg/L at 45 sites (Table 18).

Cumulative data plots are similar for BMU 1 and BMU 2 (Figs. 106–107), with many values greater than 10 mg/L, whereas only four values greater than 10 mg/L were reported from BMU 5 (Fig. 108).

The map of sampled sites and ranges of nitrate-nitrogen concentrations (Fig. 109) show a sparse site distribution in the Outer Bluegrass, Knobs, and Eastern and Western Pennyroyal Regions, and a dense site distribution in the Inner Bluegrass and Eastern Kentucky Coal Field Regions in BMU 2 and BMU 5. Most sites where nitrate-nitrogen concentrations exceed 10 mg/L are found in the Inner and Outer Bluegrass Regions of BMU 1 and BMU 2.

**Table 18.** Summary of nitrate-nitrogen values (mg/L). MCL: 10 mg/L.

|                     | <b>BMU 1</b> | <b>BMU 2</b> | <b>BMU 5</b> |
|---------------------|--------------|--------------|--------------|
| Values              | 935          | 1,069        | 543          |
| Maximum             | 84.8         | 108          | 16.0         |
| 75th percentile     | 2.897        | 3.29         | 0.5          |
| Median              | 0.79         | 0.65         | 0.07         |
| 25th percentile     | 0.1          | 0.09         | 0.02         |
| Minimum             | 0.0          | 0.0          | 0.0          |
| Interquartile range | 2.77         | 3.2          | 0.48         |
| Sites               | 176          | 294          | 271          |
| Sites > 10.0 mg/L   | 20           | 22           | 3            |

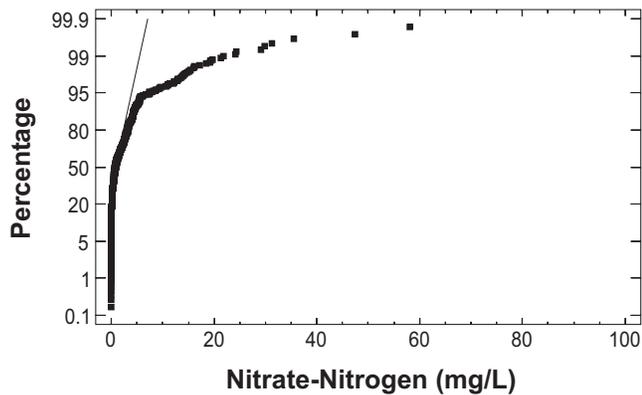


Figure 106. Cumulative plot of nitrate-nitrogen values from BMU 1.

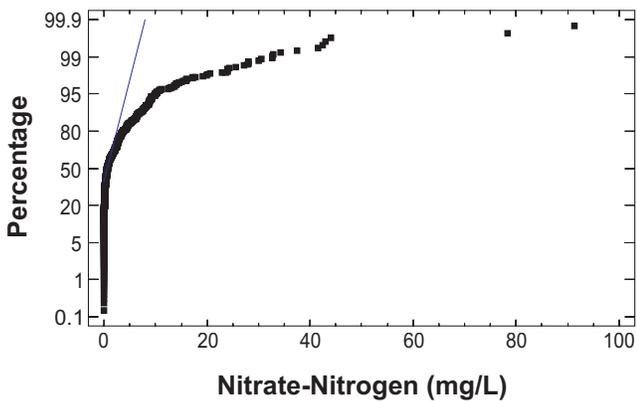


Figure 107. Cumulative plot of nitrate-nitrogen values from BMU 2.

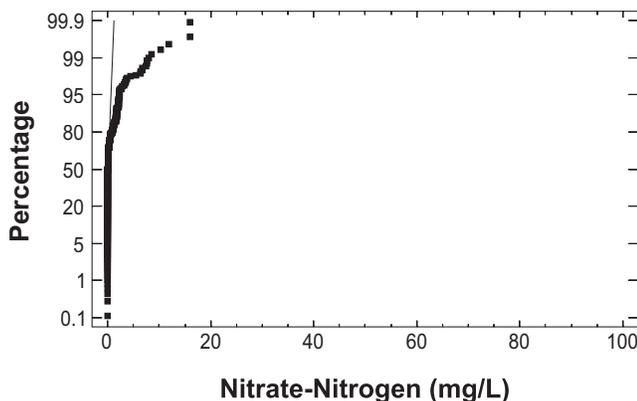


Figure 108. Cumulative plot of nitrate-nitrogen values from BMU 5.

Groundwater having nitrate-nitrogen concentrations greater than 10 mg/L is most common in the Inner and Outer Bluegrass Regions of the Kentucky, Salt, and Licking River watersheds (Figs. 109–110), and relatively rare in watersheds of the Big Sandy and Little Sandy Rivers and Tygarts Creek (Fig. 111).

Groundwater from wells and springs has about the same range of nitrate-nitrogen concentrations (Fig. 112), whereas total (unfiltered samples) nitrate-nitrogen concentrations are generally higher than dissolved (filtered samples) concentrations (Fig. 113).

The highest nitrate-nitrogen concentrations are found in shallow wells; concentrations greater than 5 mg/L are rare in groundwater from wells deeper than about 150 ft (Fig. 114).

In summary, more than 99 percent of all nitrate-nitrogen measurements in BMU 5 and more than 95 percent of all measurements in BMU 1 and BMU 2 are less than the MCL of 10 mg/L. Values as high as 108 mg/L have been recorded, however, and sites where nitrate-nitrogen concentrations exceed the recommended health-based limit occur in all basin management units. High nitrate-nitrogen concentrations are most likely in the carbonate Inner and Outer Bluegrass Regions in water from both springs and shallow wells. These results suggest that nonpoint-source nutrients are contributing nitrate to the groundwater system. A statewide summary of nitrate data (Conrad and others, 1999b) can be viewed on the KGS Web site ([kgsweb.uky.edu/olops/pub/kgs/ic60\\_11.pdf](http://kgsweb.uky.edu/olops/pub/kgs/ic60_11.pdf)).

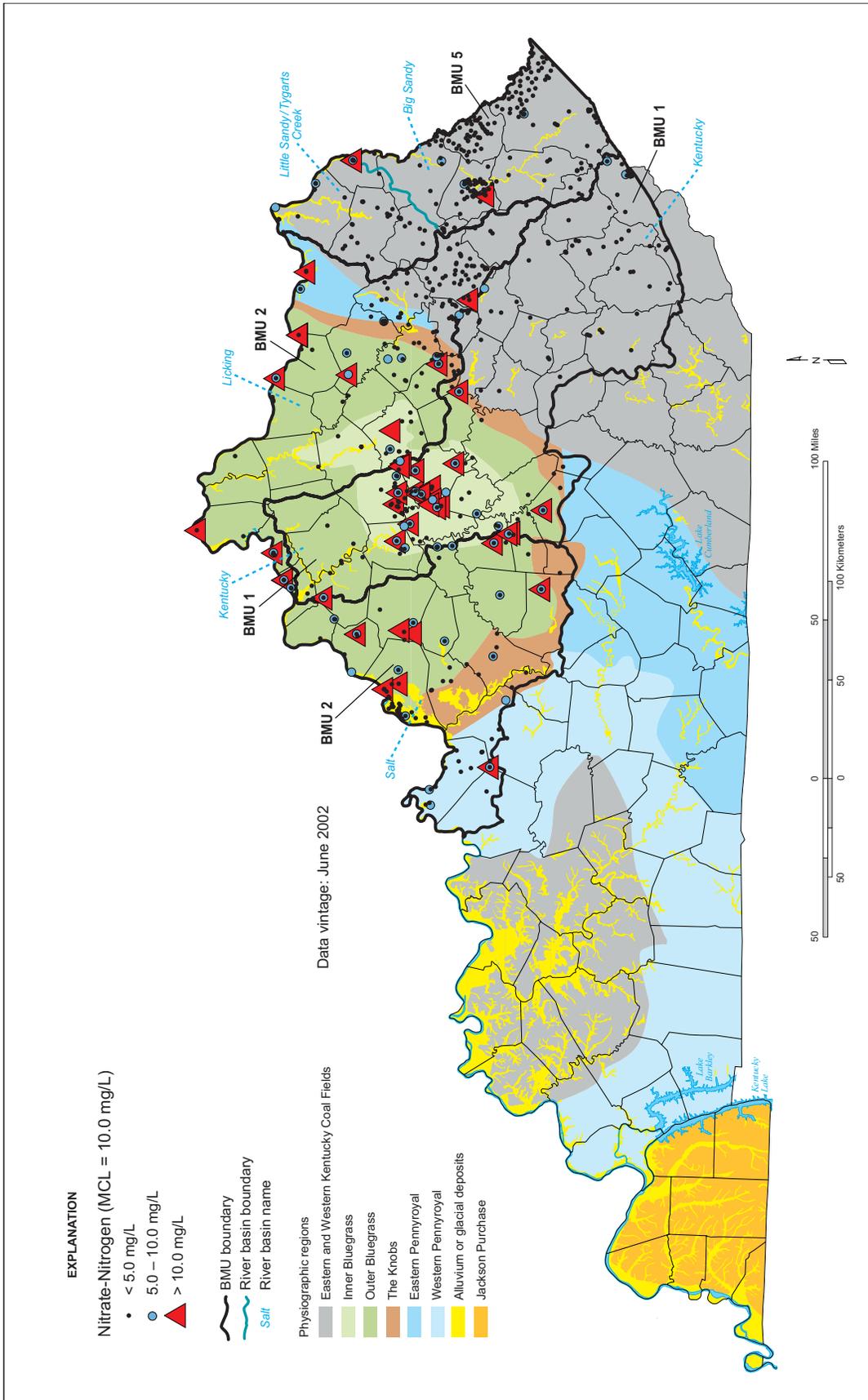


Figure 109. Locations of sampled sites and ranges of nitrate-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

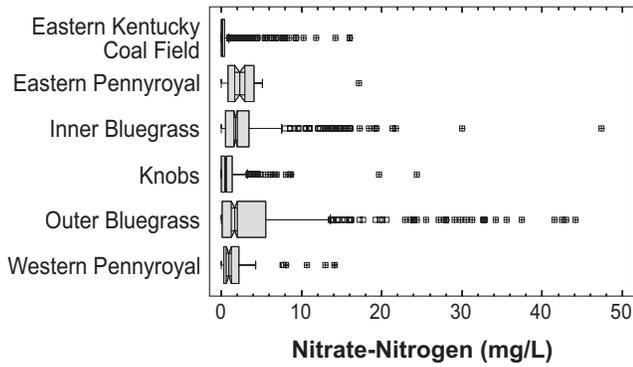


Figure 110. Summary of nitrate-nitrogen values grouped by physiographic region. Higher values were excluded for clarity.

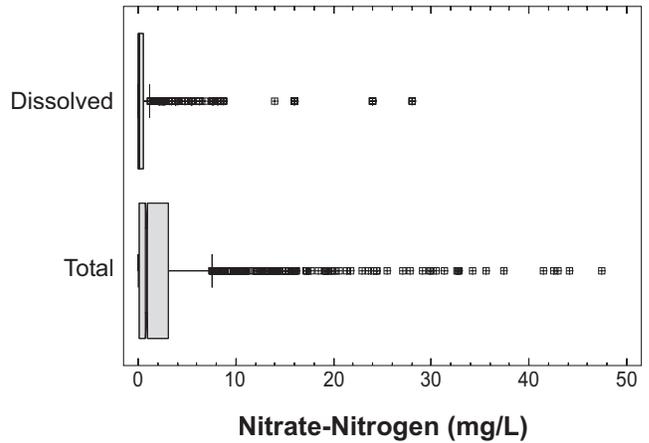


Figure 113. Comparison of total and dissolved nitrate-nitrogen values. Higher values were excluded for clarity.

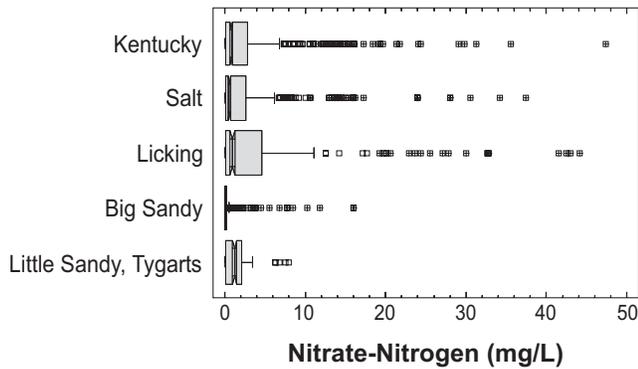


Figure 111. Summary of nitrate-nitrogen values grouped by major watershed. Higher values were excluded for clarity.

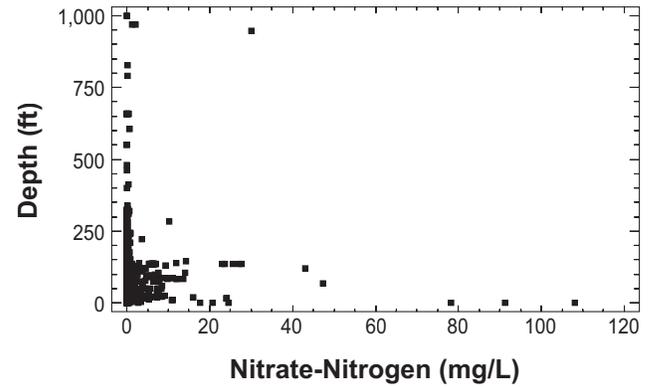


Figure 114. Plot of nitrate-nitrogen values versus well depth.

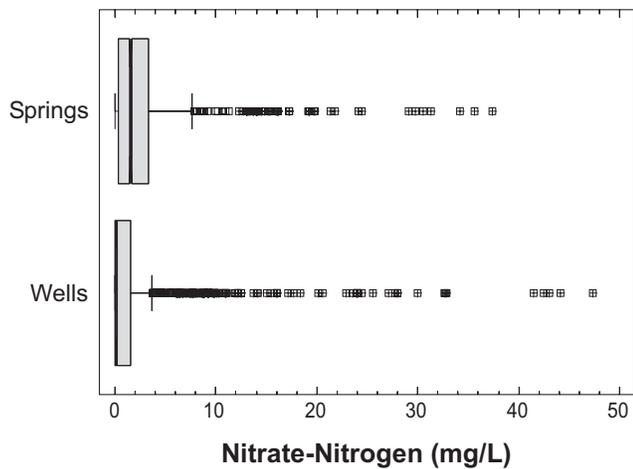


Figure 112. Comparison of nitrate-nitrogen values from wells and springs. Higher values were excluded for clarity.

*Nitrite-Nitrogen.* The data repository contained 1,965 measurements of nitrite-nitrogen from 339 sites. The median value in each BMU is well below the EPA MCL of 1.0 mg/L; however, nitrite-nitrogen concentrations exceed 1.0 mg/L at four sites in the project area (Table 19).

The distribution of measured values is similar in each basin management unit, with more than 99 percent of the values being well below 1.0 mg/L (Figs. 115–117).

The distribution of sampled sites is not uniform throughout the project area (Fig. 118); the densest sampling is along the eastern border of BMU 5 and along the Ohio River in the Salt River watershed of BMU

2. Sites where nitrite-nitrogen exceeds the MCL of 1.0 mg/L occur in the Eastern Kentucky Coal Field of BMU 1 and the Western Pennyroyal and Outer Bluegrass Regions of BMU 2 (Figs. 118–120).

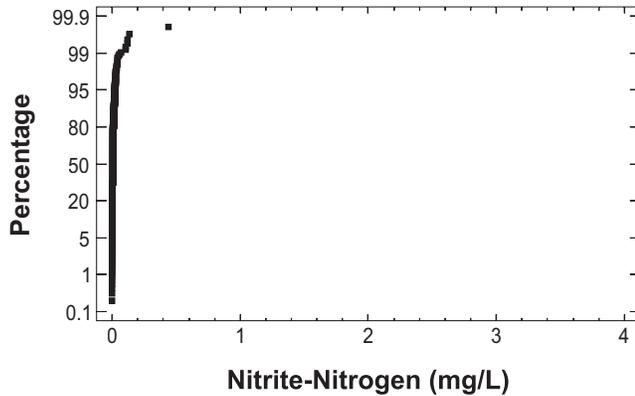


Figure 115. Cumulative plot of nitrite-nitrogen values from BMU 1.

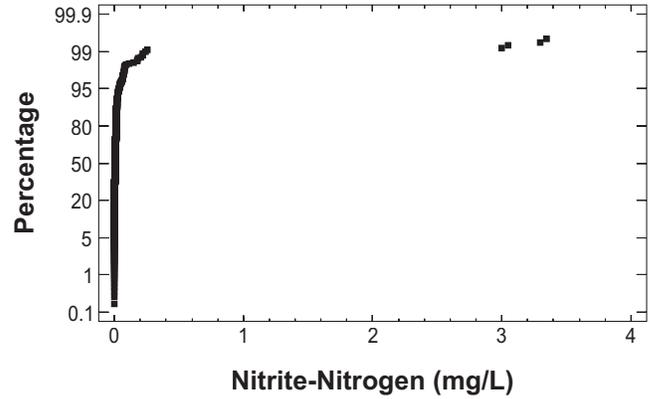


Figure 116. Cumulative plot of nitrite-nitrogen values from BMU 2.

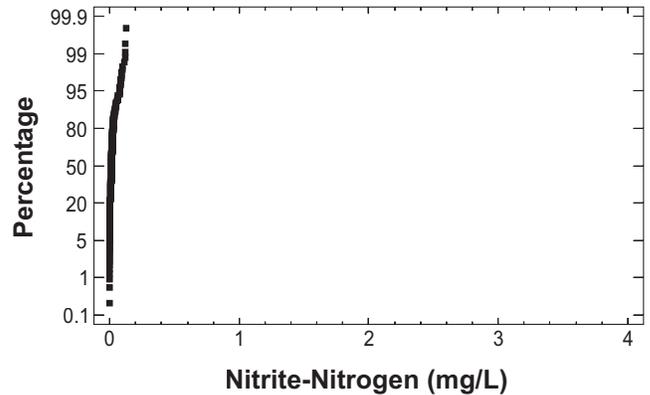


Figure 117. Cumulative plot of nitrite-nitrogen values from BMU 5.

**Table 19.** Summary of nitrite-nitrogen values (mg/L). MCL: 1.0 mg/L.

|                     | BMU 1 | BMU 2   | BMU 5 |
|---------------------|-------|---------|-------|
| Values              | 777   | 908     | 280   |
| Maximum             | 1.5   | 13.4    | 0.13  |
| 75th percentile     | 0.008 | 0.01    | 0.023 |
| Median              | 0.005 | < 0.006 | 0.01  |
| 25th percentile     | 0.002 | 0.002   | 0.004 |
| Minimum             | 0.0   | 0.0     | 0.0   |
| Interquartile range | 0.006 | 0.008   | 0.019 |
| Sites               | 85    | 145     | 109   |
| Sites > 1.0 mg/L    | 1     | 3       | 0     |

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



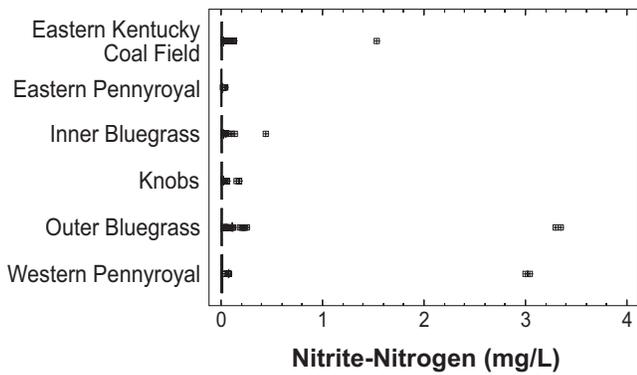


Figure 119. Summary of nitrite-nitrogen values grouped by physiographic region. Higher values were excluded for clarity.

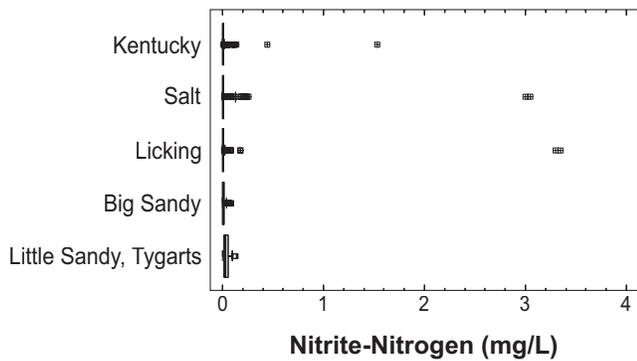


Figure 120. Summary of nitrite-nitrogen values grouped by major watershed. Higher values were excluded for clarity.

Nitrite-nitrogen concentrations that exceeded the MCL of 1.0 mg/L were reported from wells rather than from springs (Fig. 121).

Both dissolved (filtered samples) and total (unfiltered samples) groundwater can contain nitrite-nitrogen concentrations greater than the MCL of 1.0 mg/L (Fig. 122).

Nitrite-nitrogen concentrations high enough to present health concerns are found in wells less than 100 ft deep (Fig. 123).

In summary, nitrite-nitrogen concentrations that exceed the health-based limit of 1.0 mg/L are rare in the project area. Four sites produced such groundwater; three of those were in karst limestone terrain. These occurrences probably mark sites where nonpoint-source nitrate has been partially reduced in the groundwater environment.

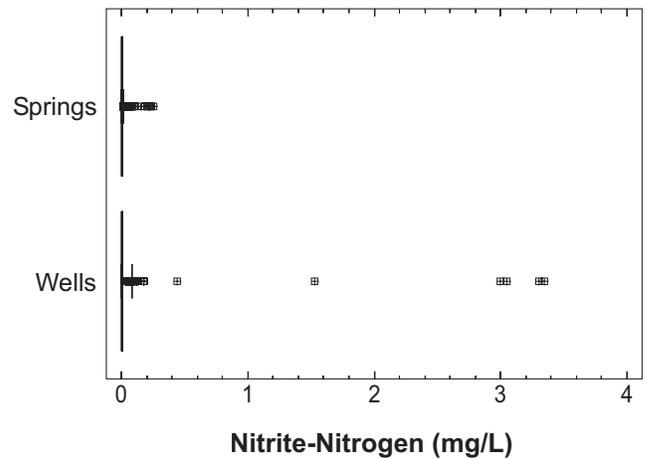


Figure 121. Comparison of nitrite-nitrogen values from wells and springs. Higher values were excluded for clarity.

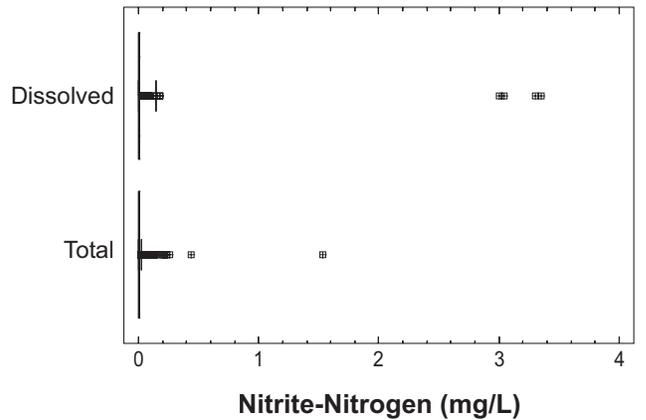


Figure 122. Comparison of total and dissolved nitrite-nitrogen values. Higher values were excluded for clarity.

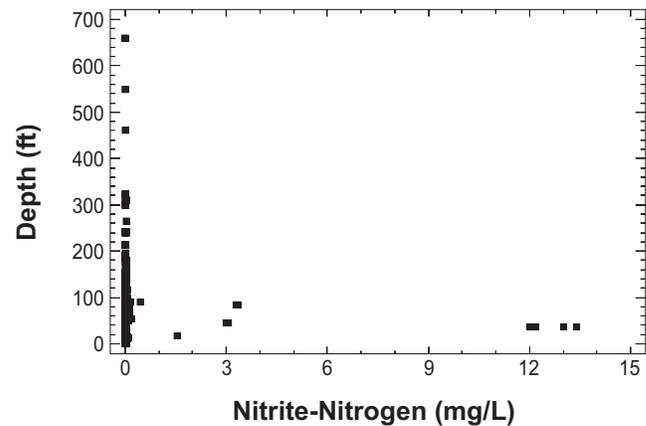


Figure 123. Plot of nitrite-nitrogen values versus well depth.

*Ammonia-Nitrogen.* The data repository contained 1,675 ammonia-nitrogen measurements from 213 sites in the project area (Table 20). The median concentration in each BMU was below analytical detection. Although there are no EPA health-based standards for ammonia-nitrogen, the Kentucky Division of Water has recommended a risk-based upper limit of 0.110 mg/L. Values greater than 0.11 mg/L are uncommon in the project area, but were observed at 81 of the 213 sites (Table 20).

Cumulative data plots show differences between the basin management units. In BMU 1, approximately 95 percent of the reported values are less than 0.11 mg/L (Fig. 124), whereas that number falls to about 90 percent in BMU 2 (Fig. 125) and to about 65 percent in BMU 5 (Fig. 126).

The map of sampled sites and ranges of concentrations (Fig. 127) shows denser sampling in the Eastern Kentucky Coal Field and more sites that exceed 0.11 mg/L ammonia-nitrogen in the Eastern Kentucky Coal Field than in other regions. Site density is lowest in the Outer Bluegrass Region.

The median and 75th percentile ammonia-nitrogen concentrations are below 0.11 mg/L in all physiographic regions (Fig. 128). Most concentrations higher than 0.11 mg/L are found in the Eastern Kentucky Coal Field and the Outer Bluegrass Region.

Groundwater from the Big Sandy River watershed has the highest median and 75th percentile ammonia-nitrogen concentrations, as well as the largest interquartile range (Fig. 129). The interquartile range

**Table 20.** Summary of ammonia-nitrogen values (mg/L). DOW recommendation: 0.11 mg/L.

|                   | <b>BMU 1</b> | <b>BMU 2</b> | <b>BMU 5</b> |
|-------------------|--------------|--------------|--------------|
| Values            | 849          | 659          | 167          |
| Maximum           | 22.5         | 20.55        | 13.15        |
| 75th percentile   | < 0.05       | < 0.05       | 0.387        |
| Median            | < 0.02       | < 0.02       | < 0.05       |
| 25th percentile   | < 0.02       | < 0.02       | < 0.02       |
| Minimum           | 0.0          | 0.0          | 0.016        |
| Sites             | 76           | 89           | 48           |
| Sites > 0.11 mg/L | 26           | 19           | 36           |

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

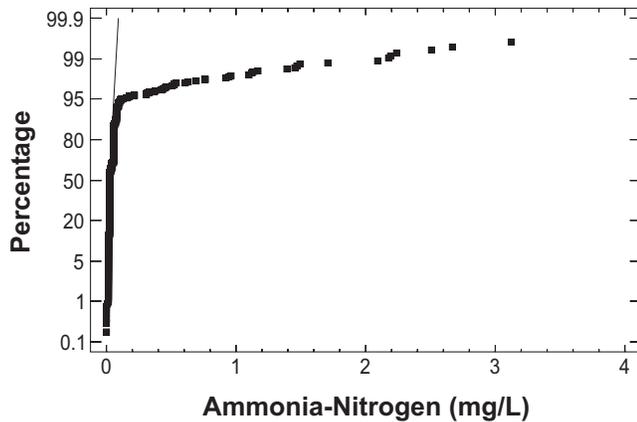


Figure 124. Cumulative plot of ammonia-nitrogen values from BMU 1. Extreme values were omitted to better show the majority of the data.

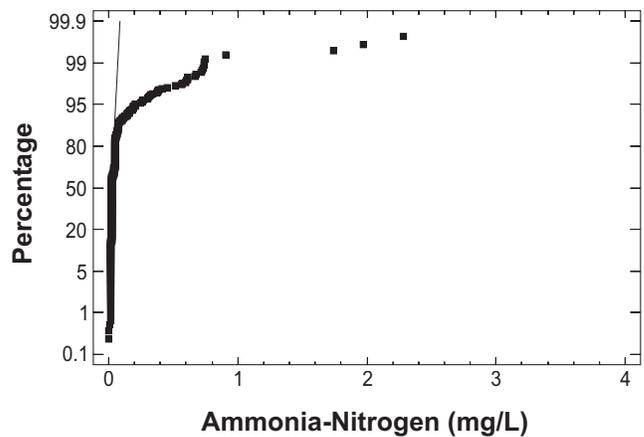


Figure 125. Cumulative plot of ammonia-nitrogen values from BMU 2. Extreme values were omitted to better show the majority of the data.

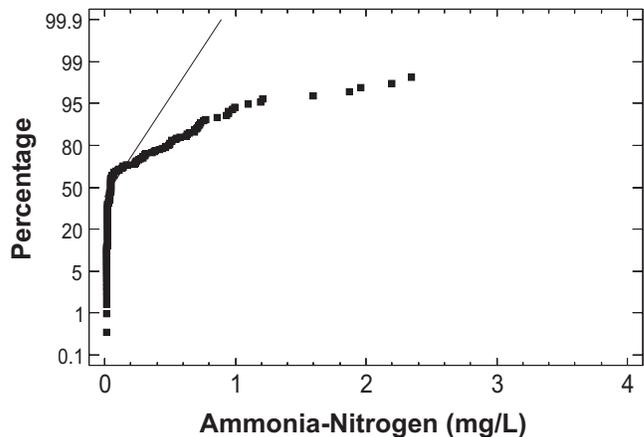


Figure 126. Cumulative plot of ammonia-nitrogen values from BMU 5. Extreme values were omitted to better show the majority of the data.

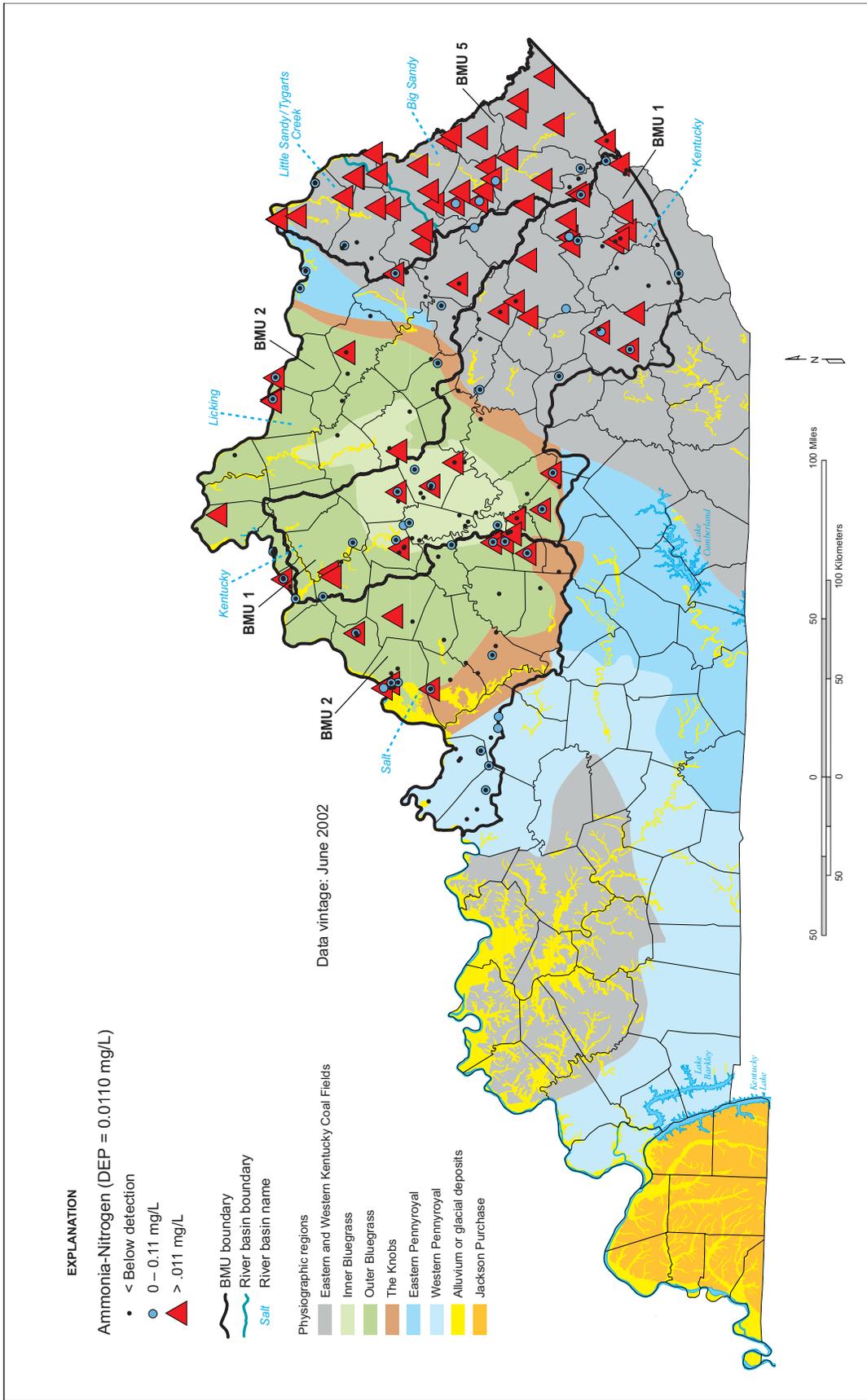


Figure 127. Locations of sampled sites and ranges of ammonia-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

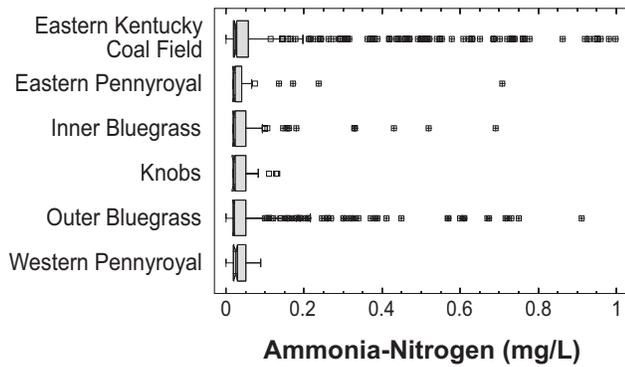


Figure 128. Summary of ammonia-nitrogen values grouped by physiographic region. Higher values were excluded for clarity.

of values is similar for samples from all other watersheds.

The median and 75th percentile concentration values for dissolved ammonia-nitrogen are significantly greater than that of total ammonia-nitrogen (Fig. 130), although the highest concentrations are found in total (unfiltered) samples.

High ammonia-nitrogen concentrations are more likely to be found in groundwater from wells than from springs (Fig. 131), and more likely to be found in shallow wells than in wells deeper than about 100 ft (Fig. 132).

In summary, ammonia-nitrogen concentrations in groundwater are generally below the criteria set by DOW (0.11 mg/L) throughout the project area. The highest concentrations occur in the Eastern Kentucky Coal Field and Outer Bluegrass Region, and particularly in the Big Sandy River watershed of the Eastern Kentucky Coal Field. The most likely sources of ammonia-nitrogen there are naturally occurring nitrogen in both coal and leaf litter. The available data do not indicate that nonpoint-source ammonia-nitrogen contributes significantly to groundwater supplies.

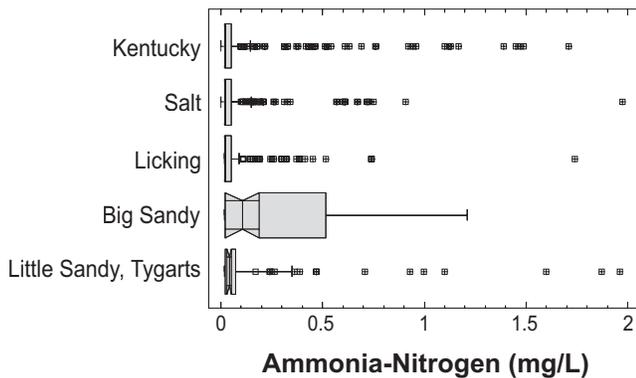


Figure 129. Summary of ammonia-nitrogen values grouped by major watershed. Higher values were excluded for clarity.

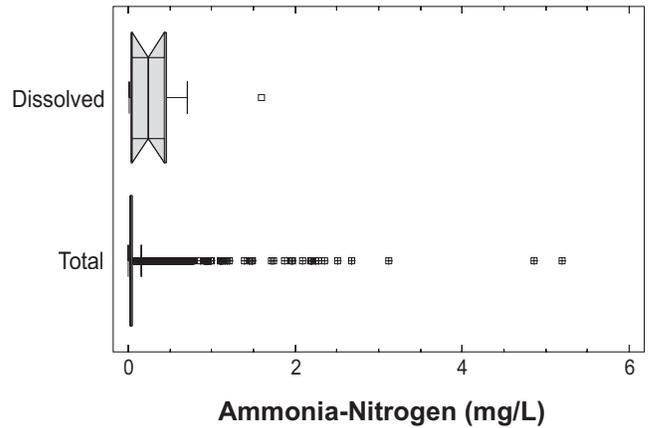


Figure 130. Comparison of total and dissolved ammonia-nitrogen values. Higher values were excluded for clarity.

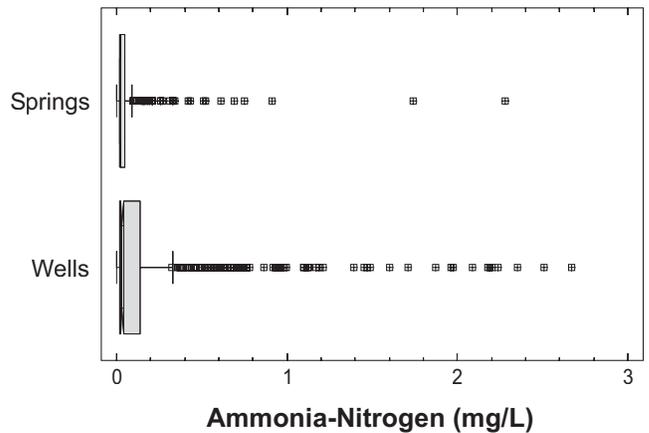


Figure 131. Comparison of ammonia-nitrogen values from wells and springs. Higher values were excluded for clarity.

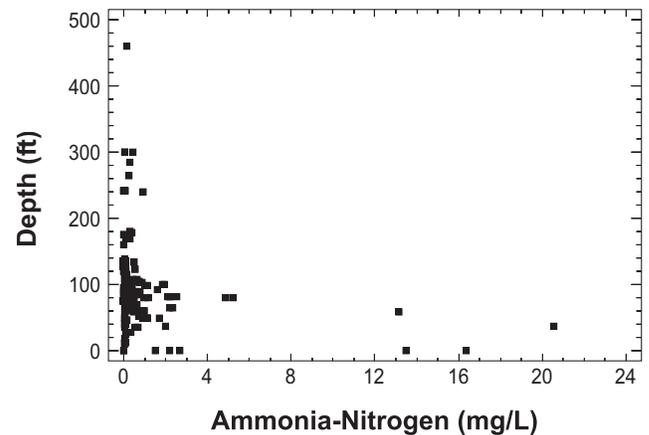


Figure 132. Plot of ammonia-nitrogen values versus well depth.

**Phosphorus Species.** Phosphorus is a common element in the earth's crust, and also is an important constituent of the carbonate rocks that make up Kentucky's karst regions. Most inorganic phosphorus compounds and minerals have low solubility, which limits phosphorus concentrations in natural waters. Phosphorus species are readily adsorbed onto soil particles and organic material, which limits their mobility in nature.

Phosphorus is an important nutrient and commonly is the limiting nutrient in aquatic ecosystems. The most important man-made sources of phosphorus are phosphate fertilizers, sewage, and animal waste. Prior to the 1960's, phosphate was added to detergents, but this practice was ended because of the eutrophication that resulted when sewage disposal facilities released the water to streams and lakes.

Orthophosphate (complexes containing  $\text{PO}_4$  as  $\text{H}_2\text{PO}_4^{-1}$  or  $\text{HPO}_4^{-2}$ ) is the most common form of phosphorus in most natural waters (Hem, 1985). The specific form of orthophosphate is pH-dependent, but normal sample collection and analysis procedures report all phosphate determined on a filtered sample as total orthophosphate. Phosphorus can also occur as organic particulate material. Reports of total or total extractable phosphorus that result from analysis of unfiltered water samples generally include both dissolved orthophosphate and particulate phosphorus. In groundwater samples, the difference between phosphorus re-

ported as total orthophosphate and total phosphorus is usually because of particulate organic phosphorus.

There are no health-based water-quality standards for phosphorus species in water. The Kentucky Division of Water recommends that orthophosphate concentrations be less than 0.04 mg/L  $\text{PO}_4\text{-P}$  based on the Texas surface-water standard, and that total phosphorus be less than 0.1 mg/L, based on results from the U.S. Geological Survey's National Water-Quality Assessment program.

*Orthophosphate.* The data repository contained 1,722 orthophosphate measurements from 186 sites in the project area (Table 21). The maximum concentration in each basin management unit is well in excess of the 0.04 mg/L criterion. Furthermore, the 75th percentile values for each basin management unit and the median value for BMU 1 all exceed 0.04 mg/L. More than 75 percent of the sites in BMU 1 and BMU 2 have produced values greater than 0.04 mg/L.

Cumulative data plots are different for each basin management unit (Figs. 133-135). In BMU 1 (Fig. 133), more than 80 percent of the reported concentrations are less than 10 mg/L, but there are many values that are more than 500 mg/L.

The data distribution in BMU 2 (Fig. 134) shows that more than 80 percent of the reported values are less than 10 mg/L, but there are fewer extremely high values than in BMU 1.

**Table 21.** Summary of orthophosphate-P values (mg/L as P). DOW recommendation: 0.04 mg/L.

|                     | <b>BMU 1</b> | <b>BMU 2</b> | <b>BMU 5</b> |
|---------------------|--------------|--------------|--------------|
| Values              | 867          | 699          | 156          |
| Maximum             | 1,950        | 368          | 254          |
| 75th percentile     | 0.31         | 0.20         | 0.03         |
| Median              | 0.14         | 0.04         | 0.02         |
| 25th percentile     | 0.01         | 0.01         | 0.01         |
| Minimum             | 0.0          | 0.0          | 0.0          |
| Interquartile range | 0.30         | 0.19         | 0.02         |
| Sites               | 68           | 78           | 40           |
| Sites > 0.04 mg/L   | 53           | 66           | 10           |

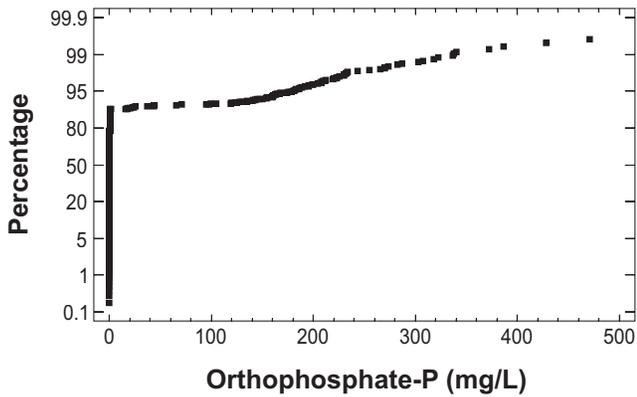


Figure 133. Cumulative plot of orthophosphate values from BMU 1. Extreme values were omitted to better show the majority of the data.

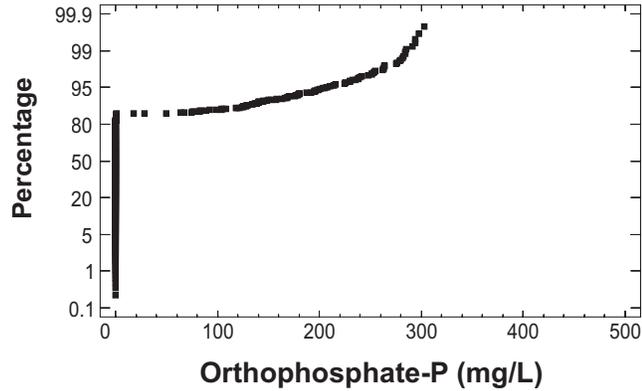


Figure 134. Cumulative plot of orthophosphate values from BMU 2. Extreme values were omitted to better show the majority of the data.

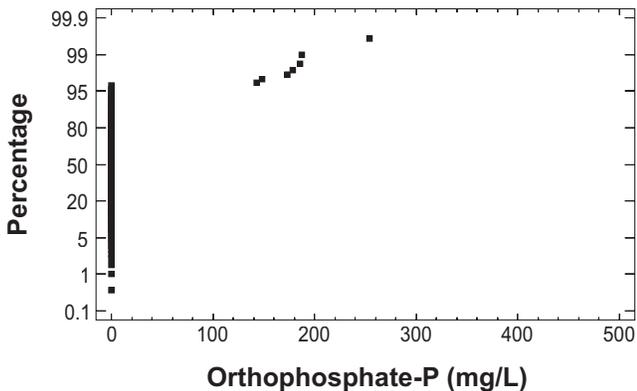


Figure 135. Cumulative plot of orthophosphate values from BMU 5. Extreme values were omitted to better show the majority of the data.

The data distribution in BMU 5 (Fig. 135) shows that more than 95 percent of the reported values are less than 10 mg/L, and there are few extremely high values.

Sampled sites are sparsely distributed throughout the project area (Fig. 136). More than half of the sites in the Inner and Outer Bluegrass and Western Pennyroyal Regions of the Kentucky, Salt, and Licking River watersheds exceed 0.4 mg/L (Figs. 137–138). Most sites in the Eastern Kentucky Coal Field in watersheds of the Big Sandy River, Little Sandy River, and Tygarts Creek produce groundwater that has orthophosphate concentrations below the recommended limit.

Springs and wells show the same range of orthophosphate concentrations (Fig. 139), and values much greater than the recommended limit are found at all well depths (Fig. 140).

In summary, orthophosphate concentrations exceeded the recommended limit of 0.04 mg/L by several orders of magnitude in the project area. Such sites are concentrated in the Inner and Outer Bluegrass and Western Pennyroyal Regions, where limestone strata are known to be enriched in phosphorus. The high orthophosphate concentrations are therefore considered to reflect the composition of bedrock rather than any significant nonpoint-source contamination.

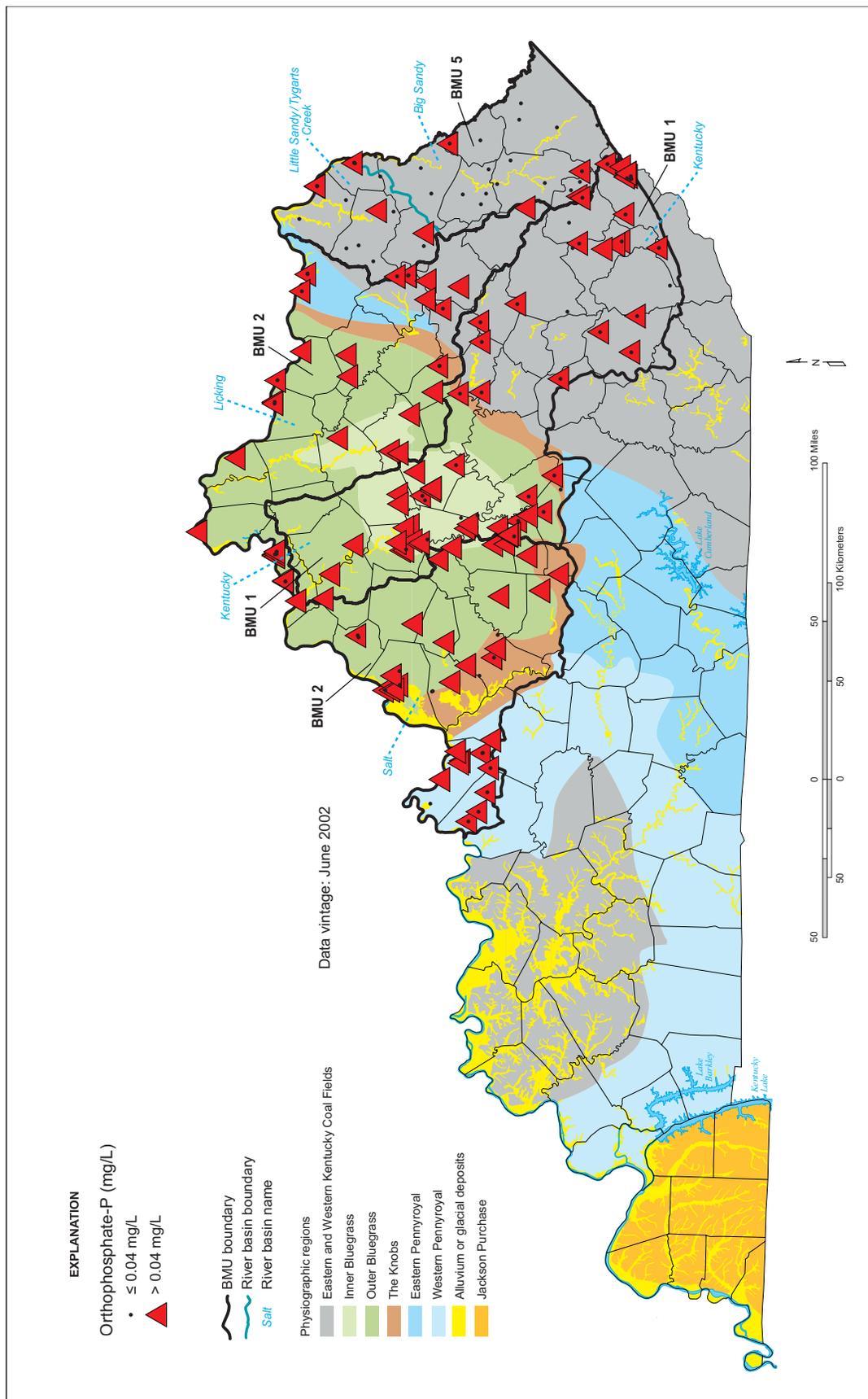


Figure 136. Locations of sampled sites and ranges of orthophosphate values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

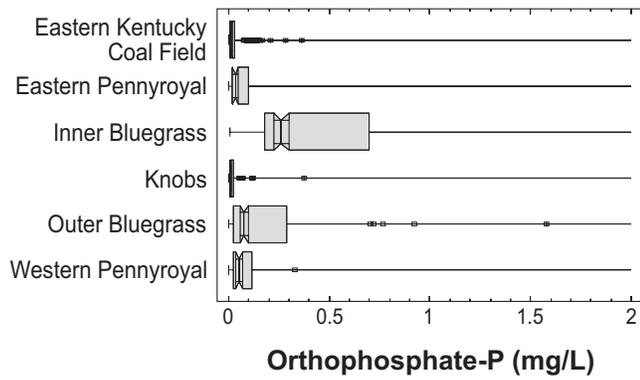


Figure 137. Summary of orthophosphate values grouped by physiographic region. Higher values were excluded for clarity.

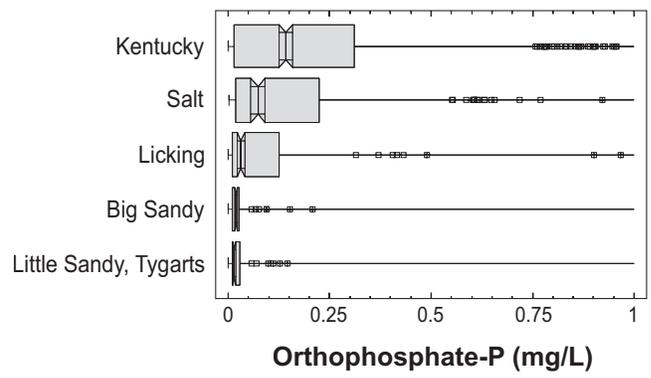


Figure 138. Summary of orthophosphate values grouped by major watershed. Higher values were excluded for clarity.

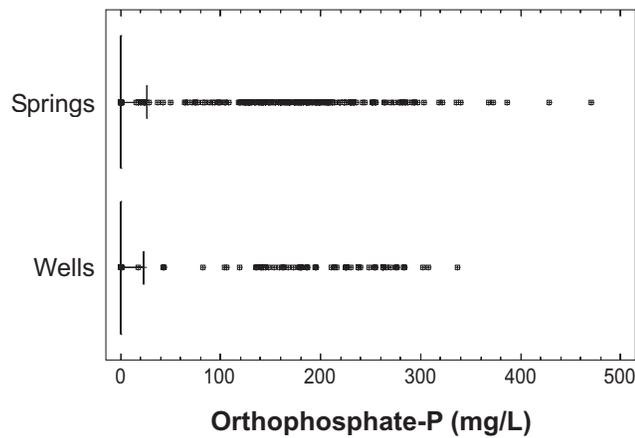


Figure 139. Comparison of orthophosphate values from wells and springs. Higher values were excluded for clarity.

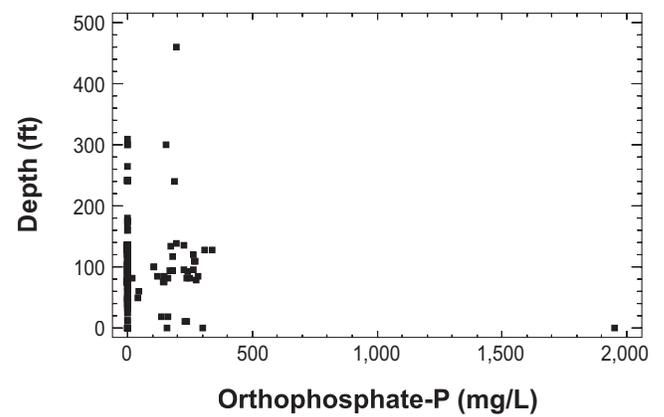


Figure 140. Plot of orthophosphate values versus well depth.

*Total Phosphorus.* The database contained 1,356 reports of total phosphorus at 301 sites (Table 22). The median concentration in BMU 1 (Kentucky River watershed) exceeded the recommended value of 0.1 mg/L, and 130 of the 301 sites have produced groundwater that exceeds the recommended concentration of total phosphorus.

The distribution of reported values from BMU 1 (Fig. 141) differs slightly from the data distribution in BMU 2 (Fig. 142) and BMU 5 (Fig. 143). Only about 50 percent of the concentrations reported from sites in BMU 1 are less than 0.1 mg/L, whereas that percentage in BMU 2 and BMU 5 is 75 percent to 80 percent. Samples from BMU 5 (Fig. 143) have the fewest values greater than 0.1 mg/L.

Site distribution is uneven throughout the project area (Fig. 144); many sites are along the Ohio River in BMU 2 and the eastern part of BMU 5. Sites where total phosphorus exceeds the recommended value occur more commonly in the Inner and Outer Bluegrass Regions (Figs. 144–146).

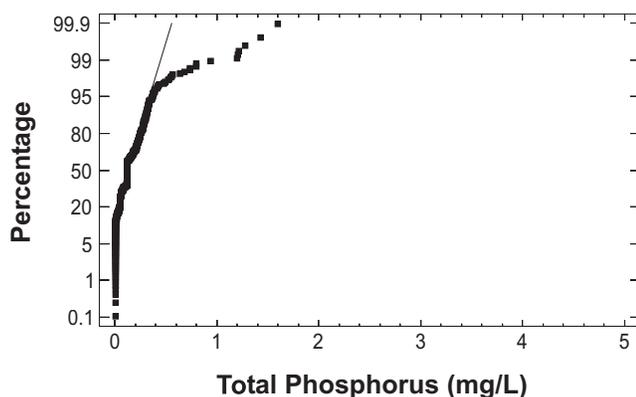


Figure 141. Cumulative plot of total phosphorus values from BMU 1. Extreme values were omitted to better show the majority of the data.

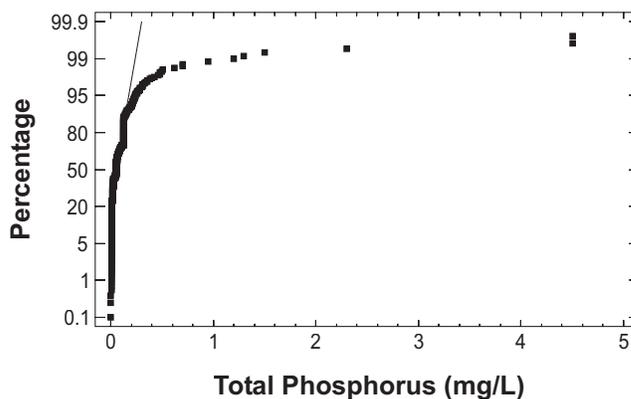


Figure 142. Cumulative plot of total phosphorus values from BMU 2. Extreme values were omitted to better show the majority of the data.

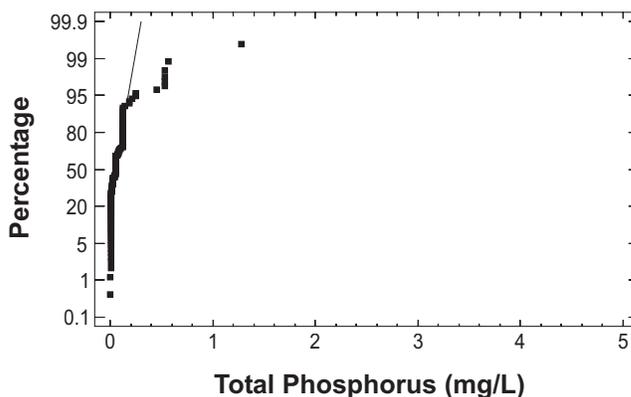


Figure 143. Cumulative plot of total phosphorus values from BMU 5. Extreme values were omitted to better show the majority of the data.

**Table 22.** Summary of total phosphorus values (mg/L of P). DOW recommendation: 0.1 mg/L.

|                     | BMU 1 | BMU 2 | BMU 5 |
|---------------------|-------|-------|-------|
| Values              | 596   | 624   | 136   |
| Maximum             | 1.6   | 14.0  | 1.28  |
| 75th percentile     | 0.24  | 0.12  | 0.12  |
| Median              | 0.12  | 0.05  | 0.05  |
| 25th percentile     | 0.05  | 0.01  | 0.01  |
| Minimum             | 0.0   | 0.0   | 0.0   |
| Interquartile range | 0.19  | 0.11  | 0.11  |
| Sites               | 83    | 13    | 83    |
| Sites > 0.1 mg/L    | 58    | 55    | 16    |

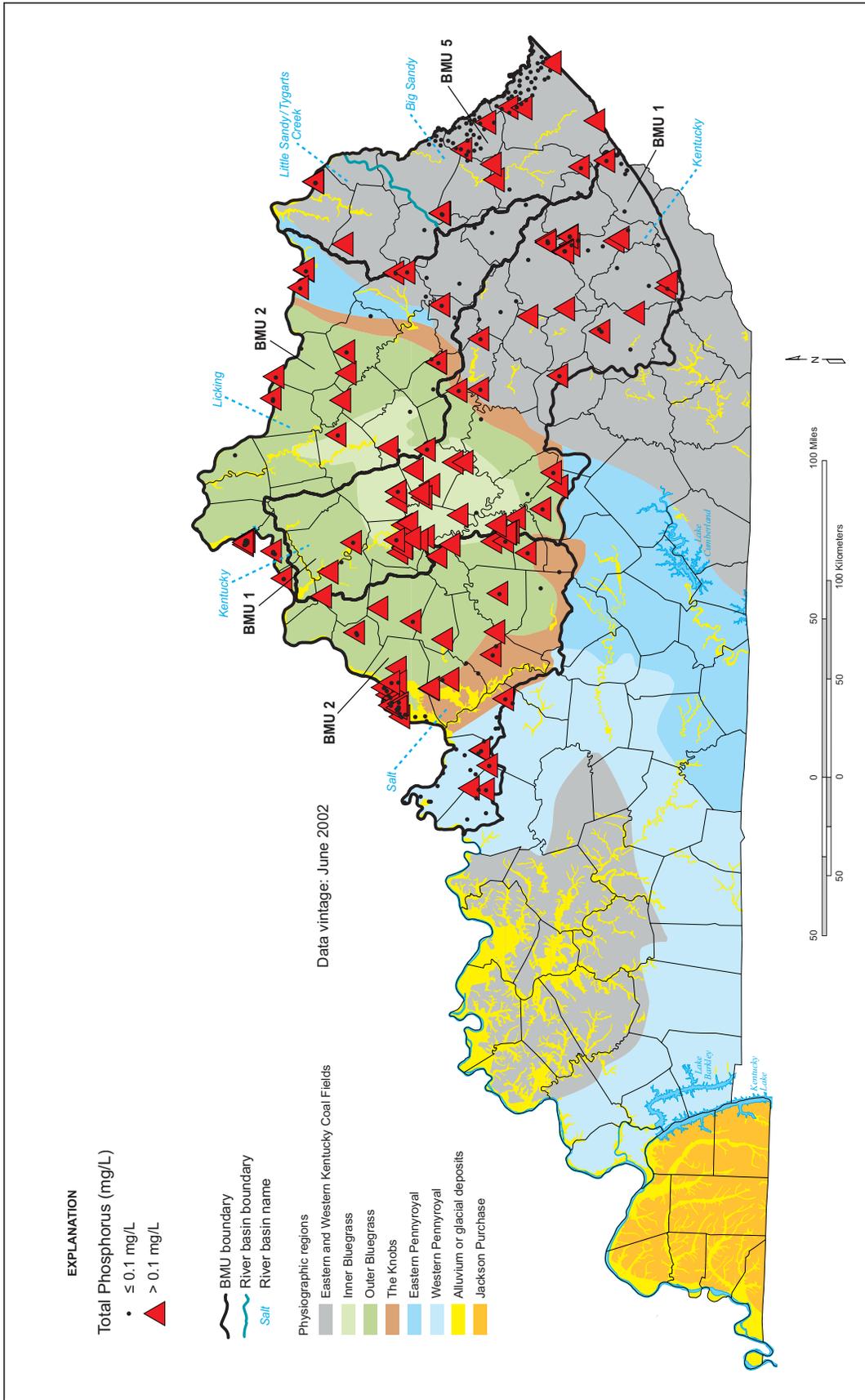


Figure 144. Locations of sampled sites and ranges of total phosphorus values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Groundwater from springs has a higher median value and larger interquartile range of values than groundwater from wells, although the total range of values is similar (Fig. 147).

Phosphorus concentrations in filtered samples (dissolved phosphorus) are generally lower than concentrations from unfiltered (total) groundwater (Fig. 148).

As was the case for orthophosphate, total phosphorus concentrations well in excess of the recommended concentrations are found in wells as deep as 300 ft. Between land surface and a depth of 300 ft, there is no significant trend in total phosphorus concentrations (Fig. 149).

In summary, like orthophosphate concentrations, total phosphorus commonly exceeds the recommended limit of 0.1 mg/L in all regions and watersheds of the project area. Also as with orthophosphate, such sites are most common in the Inner and Outer Blue-

grass Regions, where limestone bedrock is known to be enriched in phosphorus. The high phosphorus concentrations are therefore considered to reflect the composition of bedrock rather than any significant nonpoint-source contribution.

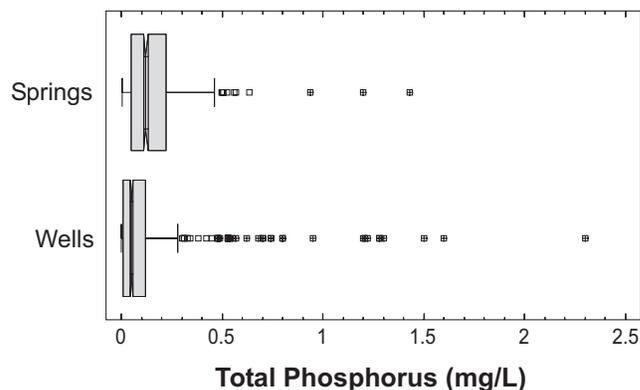


Figure 147. Comparison of total phosphorus values from wells and springs. Higher values were excluded for clarity.

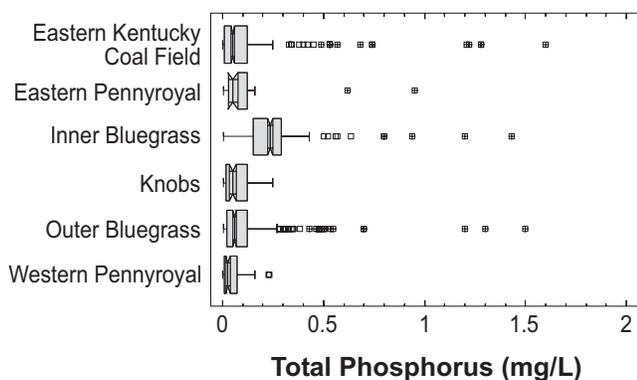


Figure 145. Summary of total phosphorus values grouped by physiographic region. Higher values were excluded for clarity.

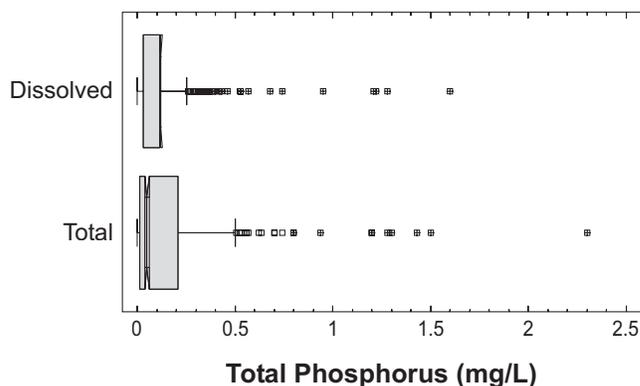


Figure 148. Comparison of total and dissolved phosphorus values. Higher values were excluded for clarity.

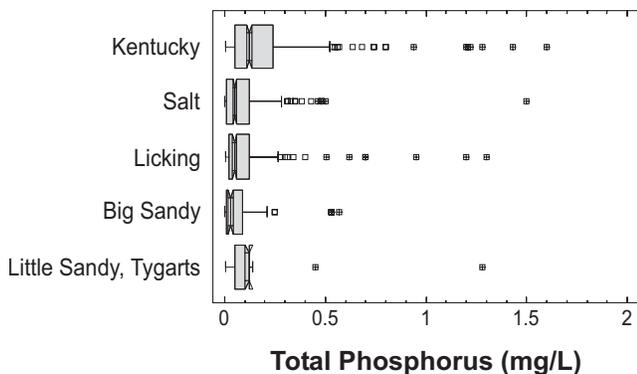


Figure 146. Summary of total phosphorus values grouped by major watershed. Higher values were excluded for clarity.

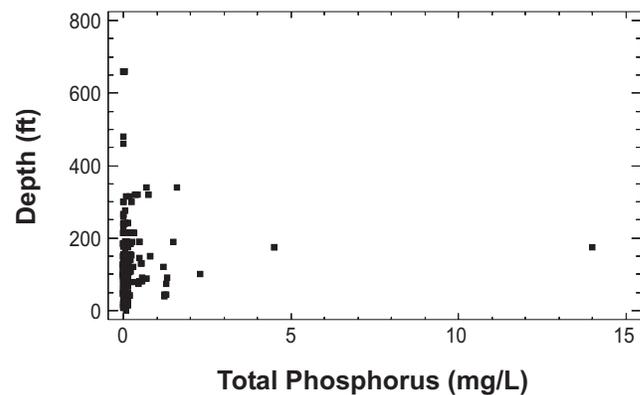


Figure 149. Plot of total phosphorus values versus well depth.