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 (NO_3^-) under oxidizing conditions or the cation ammonium (NH_4^+) under reducing conditions. Nitrite (NO_2^-) and ammonia (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 such as aerated groundwater (Hem, 1985). For this reason, high concentrations of these species in shallow groundwater are indicators of likely contamination by sewage or other forms of organic waste. These reduced forms of nitrogen may also occur in a deep, reducing groundwater system.

Runoff from fertilizer use, leachate from septic tanks, and sewage are major sources of nitrogen species. Nitrate is commonly used in fertilizer. High nitrate concentrations generally indicate contamination by fertilizer or by either human or animal organic 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 reacts 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 purposes. Analyses for geochemical investigations traditionally report concentrations as weight per volume of the measured ions (mg/L of NO_3^-, NO_2^-, NH_3, or NH_4^+). Analyses for environmental purposes, however, generally report the concentrations as equivalent amounts of nitrogen (nitrate-nitrogen, nitrite-nitrogen, ammonia-nitrogen, or ammonium-nitrogen). 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 as nitrate) and 1.0 mg/L for nitrite-nitrogen (equivalent to 3.2 mg/L as nitrite). Higher concentrations can lead to methemoglobinemia (blue baby syndrome) in infants, in which 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 7,085 nitrate-nitrogen measurements from 1,518 sites (Table 18). The maximum value (99 mg/L) far exceeds the MCL of 10 mg/L. The third quartile and median values are below the MCL of 10 mg/L. About 6 percent of the sites in BMU 3 yielded water with nitrate-nitrogen greater than 10 mg/L.

Table 18. Summary of nitrate-nitrogen values (mg/L of N).

Measurements	7,085
Maximum	99
75th percentile	5.31
Median	4.38
25th percentile	1.11
Minimum	0.00
Interquartile range	1.11–6.31
Sites	1,518
MCL	10.0
Sites > 10.0	90

The data distribution for measurements from BMU 3 (Fig. 85) has two inflection points, which suggests the presence of two different populations of values. This probably reflects the diverse physiographic regions and resulting land uses (mining, forestry, and agriculture) in BMU 3. More than 95 percent of the reported measurements are less than 10 mg/L.

Nitrate has been measured at many sites throughout BMU 3 (Fig. 86). The highly agricultural Jackson Purchase Region is the most densely sampled and contains the greatest number of sites where nitrate concentrations exceed 10 mg/L. The mostly agricultural Eastern and Western Pennyroyal Regions have also been well sampled and have many sites where nitrate concentrations exceed the MCL. Few sites in the Eastern Kentucky Coal Field exceed 10 mg/L.

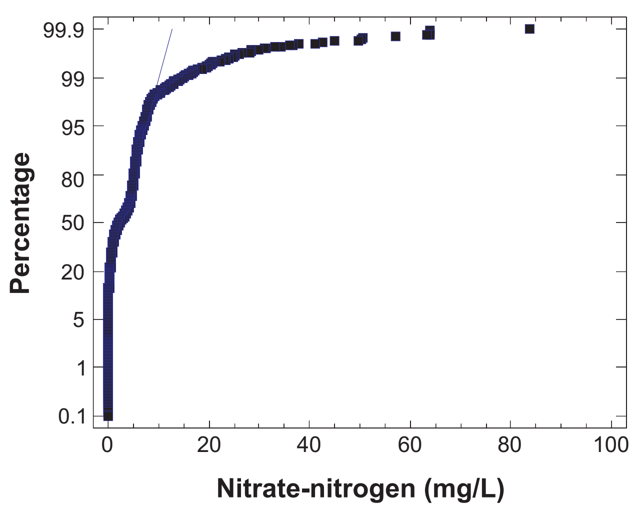

Figure 85. Cumulative plot of nitrate-nitrogen concentrations. Values greater than 90 mg/L have been omitted to show detail in the lower concentration ranges.

Grouping nitrate concentrations by physiographic region (Fig. 87) and major watershed (Fig. 88) shows that concentrations exceeding the MCL occur in all watersheds and regions. Although the Jackson Purchase Region has the greatest number of sites where nitrate-nitrogen exceeds 10 mg/L (Fig. 87) the highest reported nitrate concentrations are found in the Western Pennyroyal Region (Fig. 87), Lower Cumberland River watershed (Fig. 88). Furthermore, the middle 50 percent of reported values from the Western Pennyroyal Region, Lower Cumberland River watershed, are higher than the central 50 percent of values from any other region or watershed.

Water wells yielded the highest nitrate concentrations (Fig. 89). The central 50 percent of reported values are higher in water from springs than from wells, however. The highest nitrate concentrations are found in wells shallower than about 150 ft (Fig. 90).

In summary, approximately 6 percent of all sites produced groundwater with nitrate-nitrogen concentrations that exceed the MCL. Based on the distribution of such sites, it is highly likely these are in areas where agricultural chemicals are used, where there are animal holding facilities, or sewage is not properly disposed of. Nearly 54 percent of the sites have produced groundwater with more than 5.0 mg/L nitrate-nitrogen. Many, if not all, of these are probably affected by nonpoint-source sources of nitrate. Wells less than 150 ft deep are more likely to produce high-nitrate groundwater than deeper wells or springs.

A statewide summary of nitrate data (Conrad and others, 1999a) is available and can be viewed on the Kentucky Geological Survey Web site (www.uky.edu/KGS/water/gnet/gnet.htm).

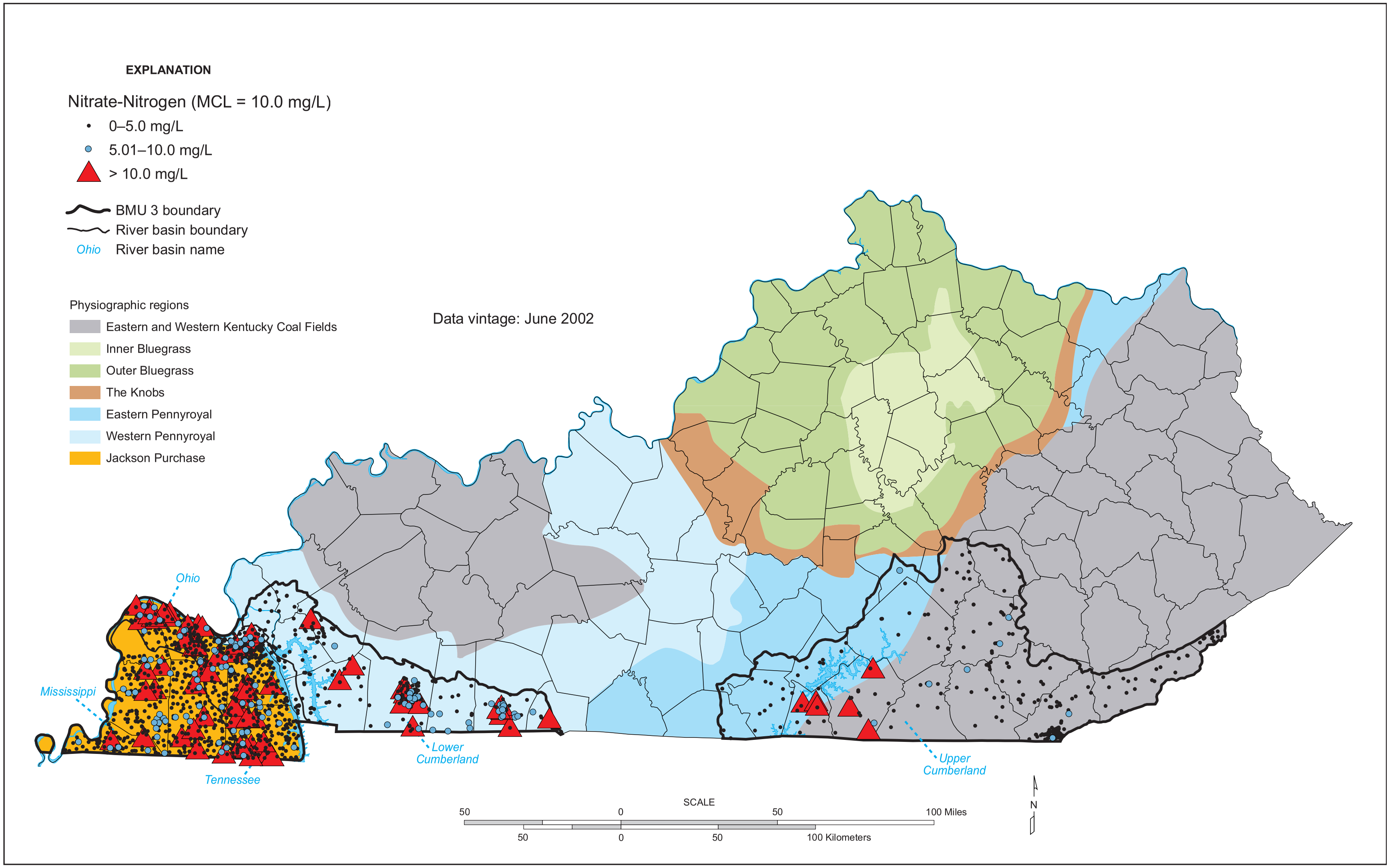

Figure 86. Sample sites and nitrate-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

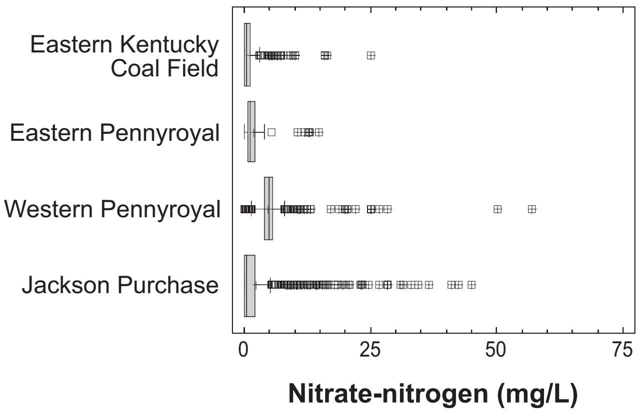

Figure 87. Summary of nitrate-nitrogen values grouped by major watershed. Values greater than 60 mg/L were omitted to show detail in the lower concentration ranges.

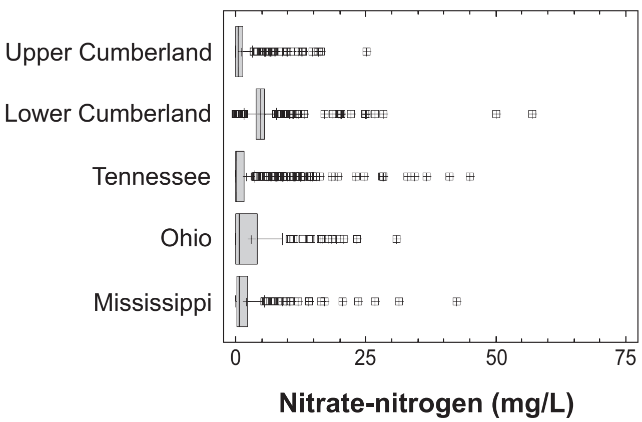

Figure 88. Summary of nitrate-nitrogen data grouped by physiographic region. Values greater than 60 mg/L were omitted to show detail in the lower concentration ranges.

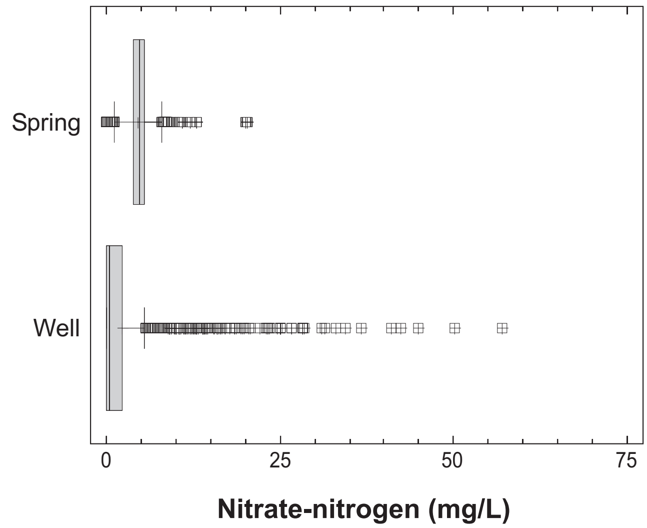

Figure 89. Comparison of nitrate-nitrogen concentrations from wells and springs. Values greater than 60 mg/L have been omitted to show detail in the lower concentration ranges.

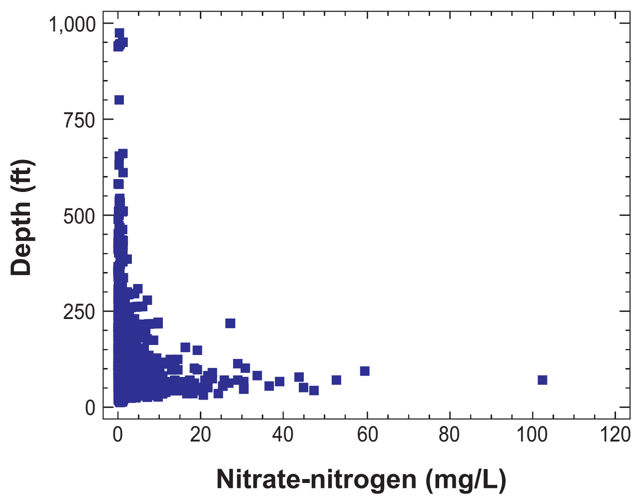

Figure 90. Nitrate concentrations versus well depth.

Nitrite-Nitrogen. The data repository contained 753 measurements of nitrite-nitrogen from 116 sites (Table 19). No reported concentrations exceeded the EPA health-based MCL of 1.0 mg/L, and only four values were greater than 0.10 mg/L.

Few sites have been sampled for nitrite-nitrogen (Fig. 91). Because of the sparse data and the absence of any reported concentration that exceeded the MCL, no further analyses were performed.

In summary, no sites in the project area produced groundwater with nitrite-nitrogen concentrations over the MCL. In light of the many high nitrate-nitrogen concentrations reported, the absence of high nitrite-nitrogen values is most likely the result of the thermodynamic instability of nitrite, rather than absence of nitrogen inputs.

Table 19. Summary of nitrite-nitrogen values (mg/L of N).

Measurements	753
Maximum	0.274
75th percentile	0.009
Median	0.005
25th percentile	0.002
Minimum	0.00
Interquartile range	0.002–0.009
Sites	116
MCL	1.0
Sites > 1.0	0

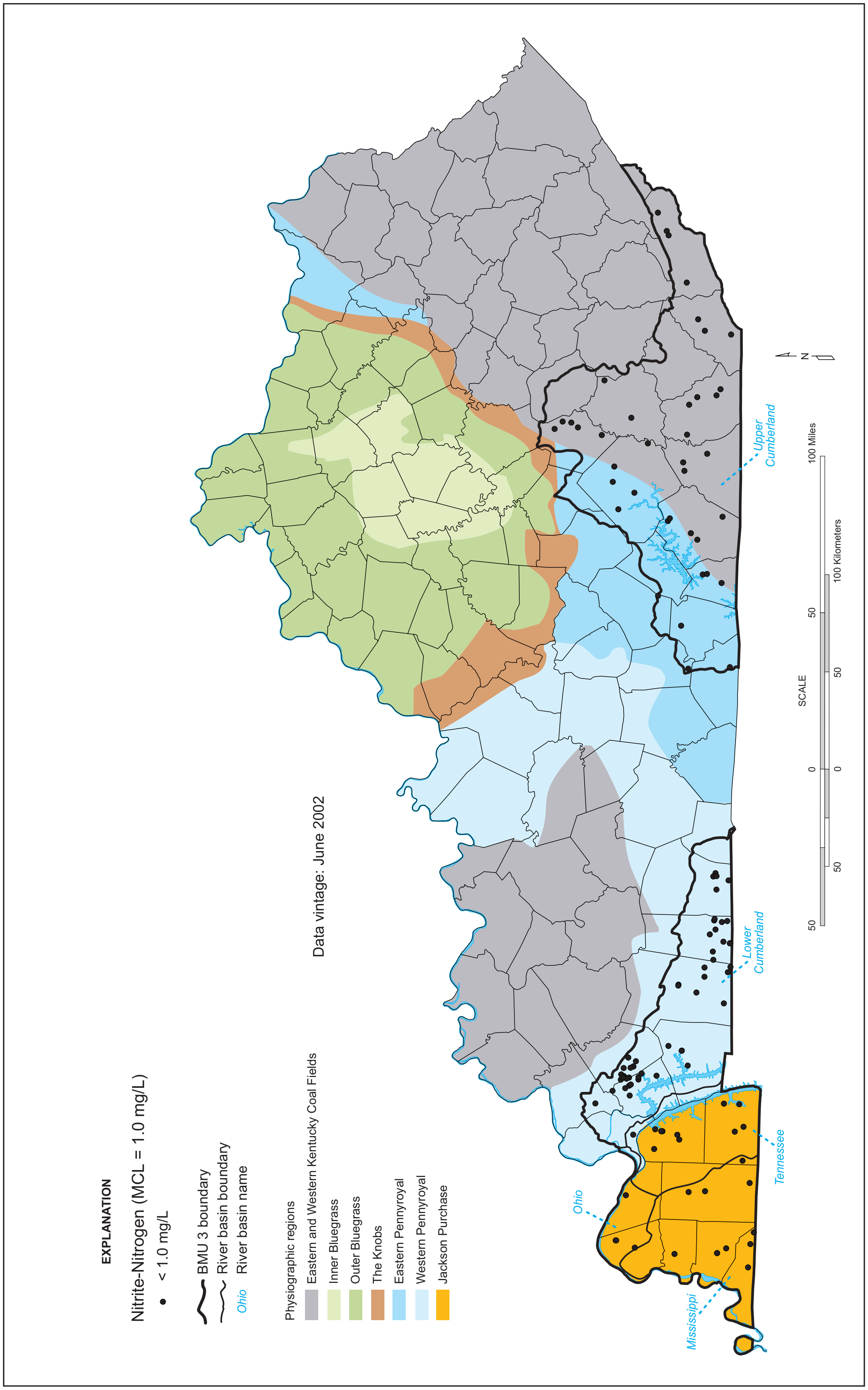

Figure 91. Sites where nitrite-nitrogen has been measured.

Ammonia-Nitrogen. The data repository contained 932 ammonia-nitrogen measurements from 146 sites in BMU 3 (Table 20). Although there are no EPA health-based standards for ammonia-nitrogen, the Kentucky Department for Environmental Protection has recommended a risk-based upper limit of 0.110 mg/L. Values exceeding 0.110 mg/L were observed at 17 sites in BMU 3. The highest value (14.7 mg/L) was reported from a well in the Jackson Purchase Region.

Table 20. Summary of ammonia-nitrogen values (mg/L as N).

Measurements	932
Maximum	14.7
75th percentile	< 0.050
Median	< 0.020
25th percentile	< 0.020
Minimum	0.000
Interquartile range	na
Sites	146
DEP	0.110
Sites > 0.110	17

< means analytical result reported as less than the stated value
DEP: Kentucky Department for Environmental Protection risk-based concentration

More than 94 percent of the reported ammonia-nitrogen concentrations are less than 0.11 mg/L (Fig. 92).

There are relatively few sampled sites in BMU 3. Sites where ammonia-nitrogen concentrations exceed 0.11 mg/L occur in all physiographic regions and all major watersheds (Fig. 93).

The highest reported concentration was from a site in the Jackson Purchase Region; however, the largest number of high concentrations were found in the Western Pennyroyal Region (Fig. 94).

With one exception, reported ammonia-nitrogen concentrations were generally lowest in the Tennessee

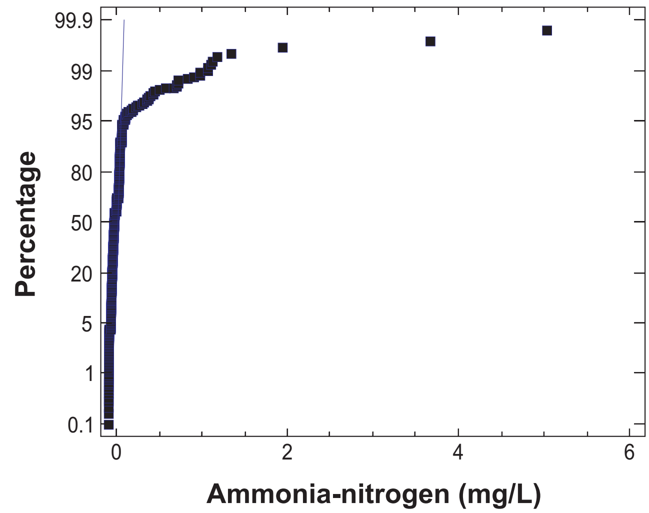

Figure 92. Cumulative plot of ammonia-nitrogen values from BMU 3. The highest value (14.7 mg/L) was omitted to better show the majority of the data.

and Mississippi River watersheds. The highest values are in the Lower Cumberland watershed (Fig. 95).

All analyzed samples were unfiltered (total concentrations), so no comparison of total versus dissolved ammonia-nitrogen can be made. High ammonia-nitrogen values are more commonly found in wells than in springs (Fig. 96) and are more common in shallow wells than in intermediate or deep wells (Fig. 97).

In summary, approximately 11 percent of the sampled wells and springs produced groundwater with more than 0.110 mg/L ammonia-nitrogen. There was no preferred location of such sites, however. The source of ammonia-nitrogen in these groundwaters cannot be established definitely without additional information. Nonpoint-source contributions from agriculture, confined animal feeding operations, or septic systems are certainly possible, however.

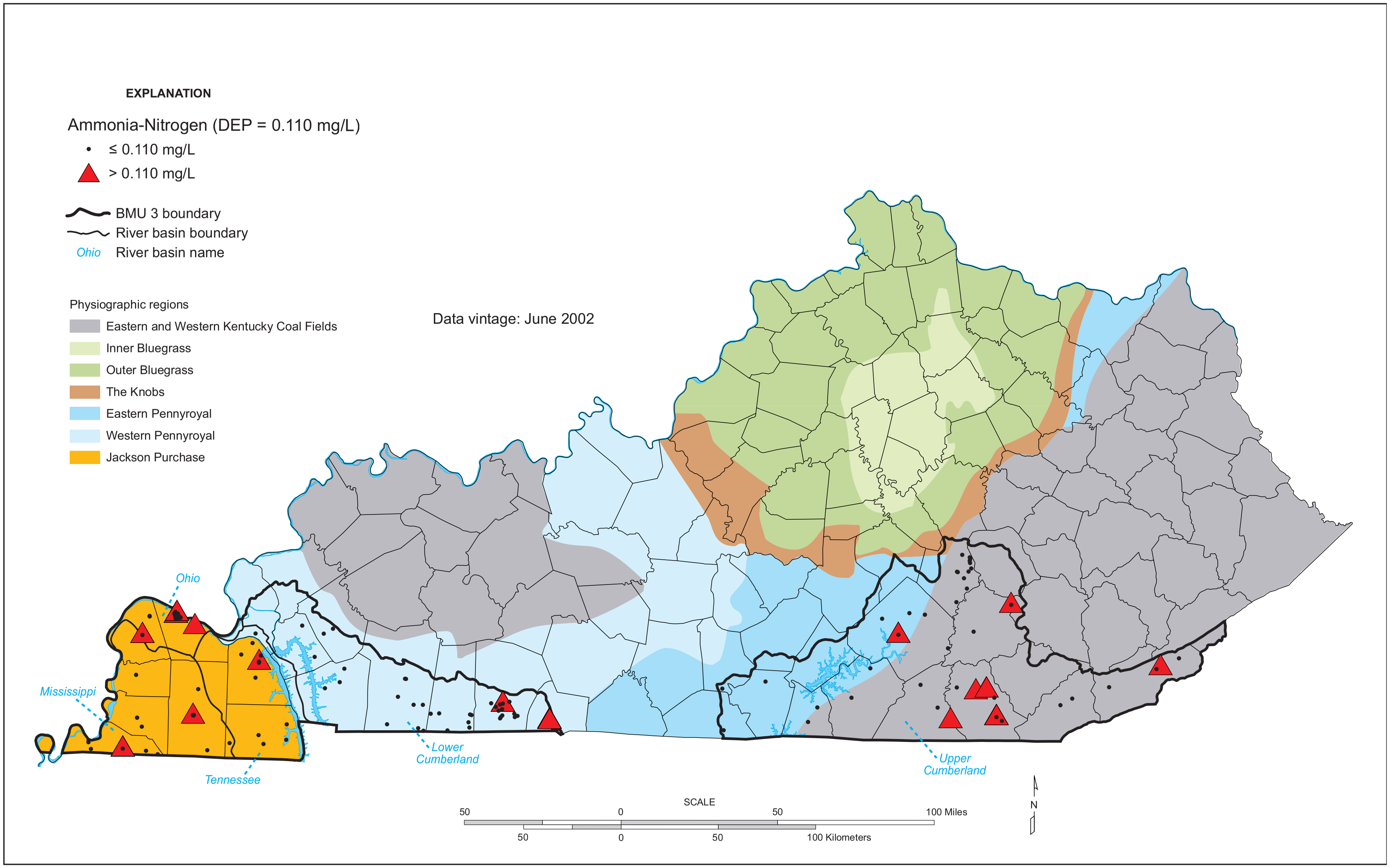

Figure 93. Sample sites and ammonia-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

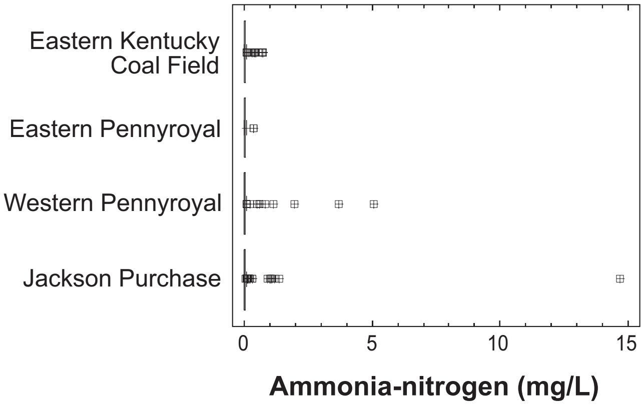

Figure 94. Ammonia-nitrogen data grouped by physiographic region.

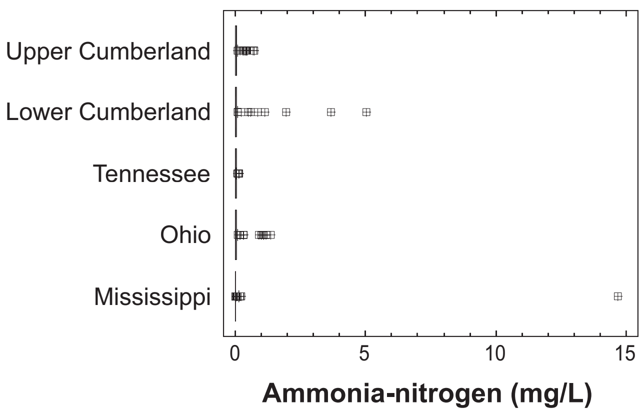

Figure 95. Ammonia-nitrogen data grouped by major watershed.

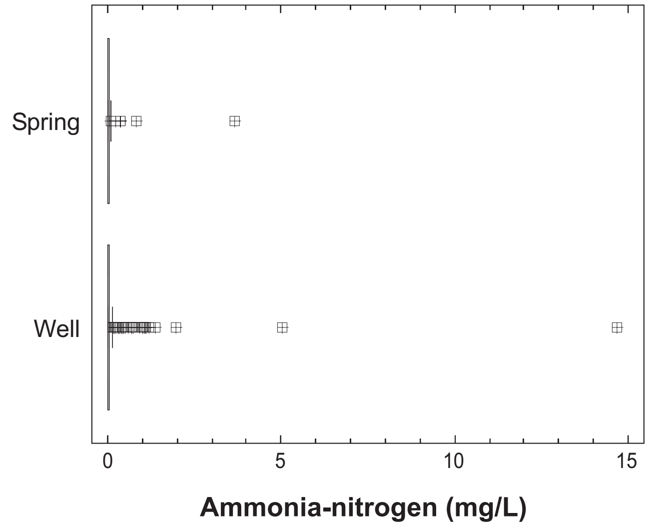

Figure 96. Comparison of ammonia-nitrogen concentrations grouped by site type.

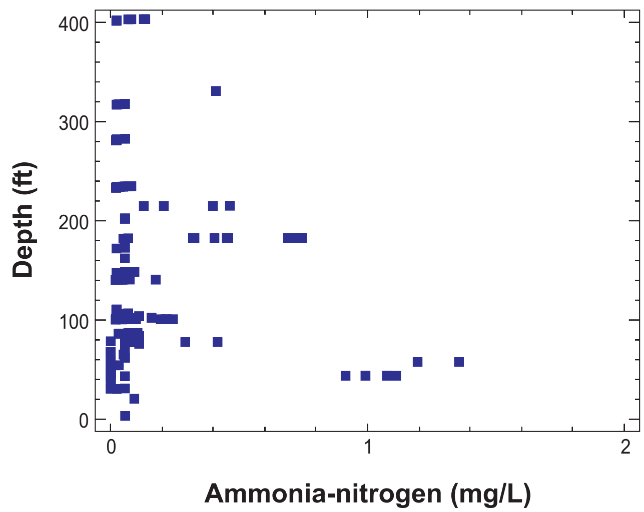

Figure 97. Ammonia-nitrogen concentrations versus well depth.

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

Phosphorus is commonly 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 PO_4^{-3}) as $H_2PO_4^{-1}$ or 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 reported as total orthophosphate and total phosphorus is usually because of particulate organic phosphorus.

There are no health-based water-quality standards for orthophosphate; however, the Kentucky Division of Water recommends that orthophosphate concentrations be less than 0.04 mg/L PO_4-P based on the Texas surface-water standard.

Orthophosphate. The data repository contained 170 orthophosphate measurements from 67 sites in BMU 3 (Table 21). Of those 170 measurements, 153 were reported as below a detection limit, and 123 were reported as less than 0.059 mg/L. Whether these 123 values exceeded the recommended water-quality standard cannot be determined. Only 13 measurements at 10 sites are known to exceed the water-quality standard in BMU 3.

Most measured orthophosphate follows a normal distribution curve (Fig. 98).

Figure 99 shows a fairly uniform but sparse distribution of sample sites. Sites where measured orthophosphate-P concentrations exceed 0.04 mg/L occur in the Upper Cumberland River watershed (Eastern Kentucky Coal Field Region), the Lower Cumberland River watershed (Western Pennyroyal Region), and the Ohio River watershed (Jackson Purchase Region).

Table 21. Summary of orthophosphate-P values (mg/L).

Measurements	170
Maximum	0.495
75th percentile	< 0.059
Median	< 0.059
25th percentile	< 0.059
Minimum	< 0.019
Interquartile range	na
Sites	67
DOW	0.04
Sites > 0.04	10

< means analytical result reported as less than the stated value
DOW: Kentucky Division of Water recommended value

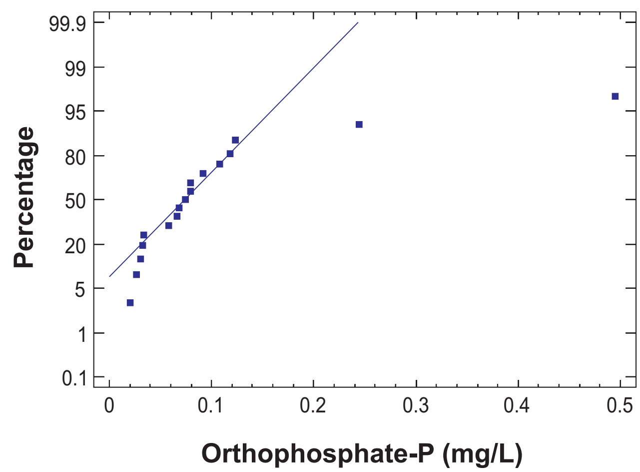

Figure 98. Cumulative plot of orthophosphate values in BMU 3. Values reported as less than a detection limit are excluded.

As was the case for other nutrients, higher orthophosphate concentrations are more likely to be reported from wells than from springs (Fig. 100). Because of the very small number of measured values, no relation between orthophosphate and depth is apparent (Fig. 101).

In summary, more than three-fourths of the orthophosphate-phosphorus measurements in BMU 3 were reported as less than a detection limit of 0.059 mg/L. Many of these were probably below the recommended water-quality standard of 0.04 mg/L, but the exact number cannot be determined. Only 10 sites yielded groundwater with measured orthophosphate-phosphorus concentrations that exceeded the water-quality standard. Nonpoint-source contributions of orthophosphate nutrients to groundwater cannot be evaluated in BMU 3 at this time because of the very small number of accurate measurements.

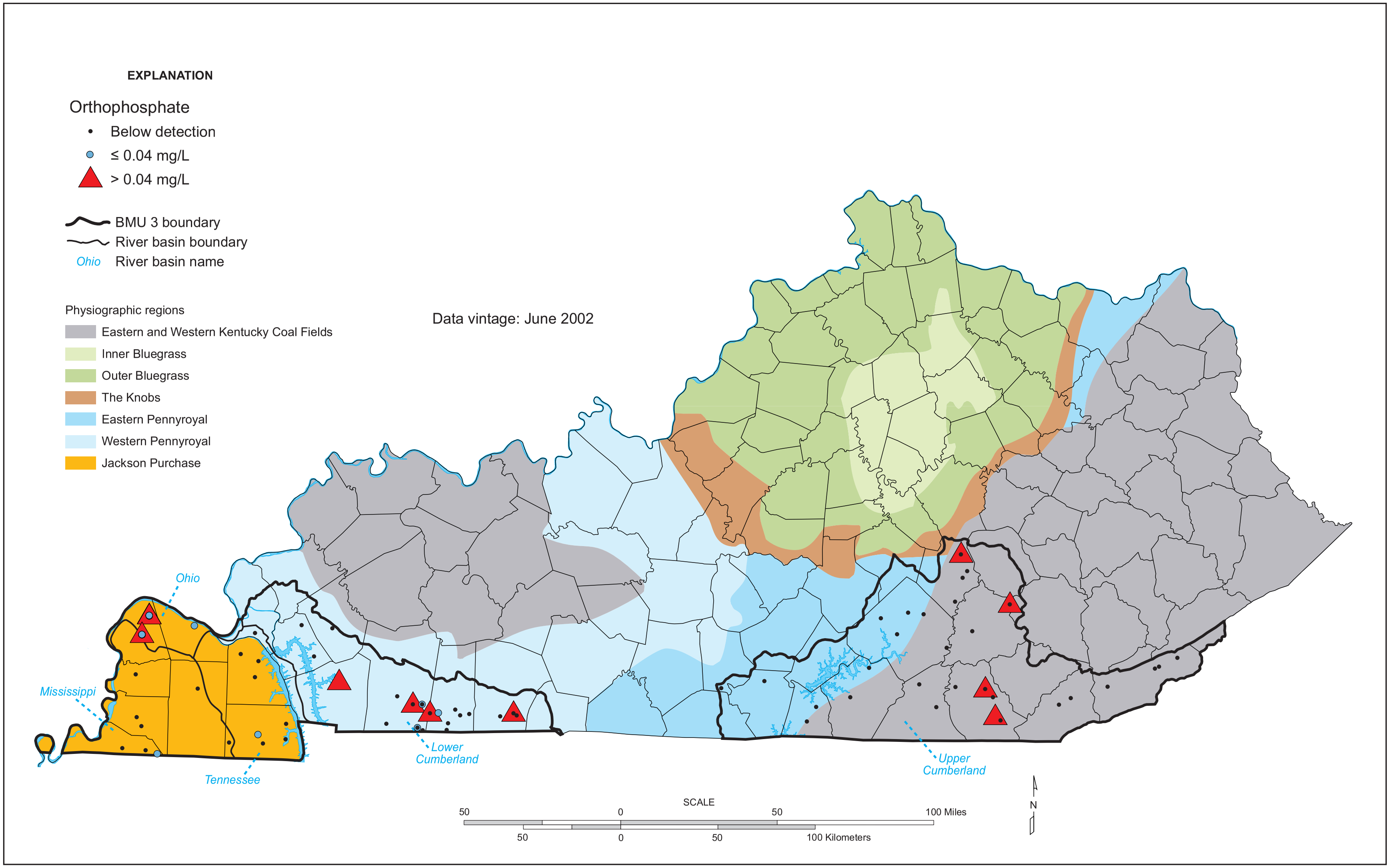

Figure 99. Sample sites and orthophosphate-P values. Superimposed symbols indicate that values recorded at different collection times fell into different ranges.

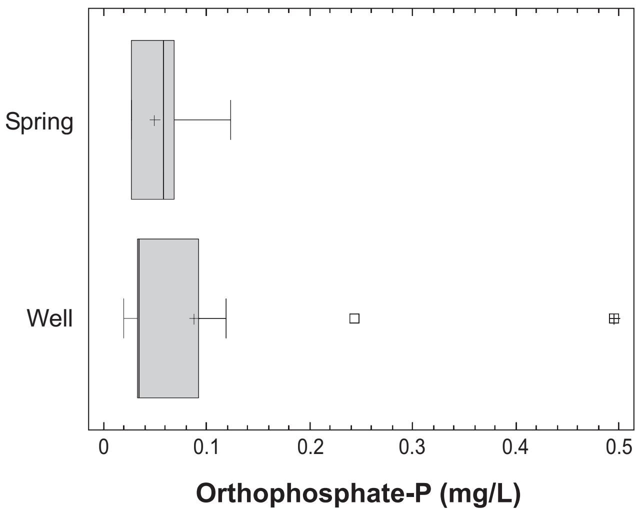

Figure 100. Comparison of orthophosphate values from springs and wells. Values below detection limits are not plotted.

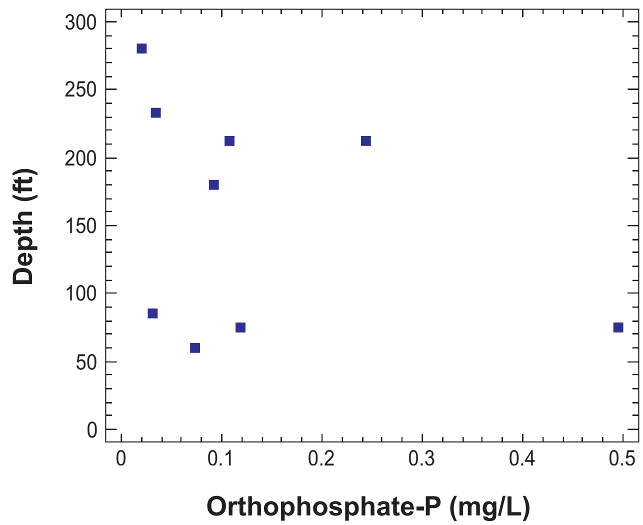

Figure 101. Orthophosphate values versus well depth. Values below detection limits are not plotted.

Total Phosphorus. The database contained 443 reports of total phosphorus at 48 sites (Table 22). The maximum reported total phosphorus measurement was 93.6 mg/L from a well in the Upper Cumberland River watershed, in the Eastern Pennyroyal Region. Because the second highest reported value was only 3.3 mg/L, the maximum value is considered anomalous and is not included in the following discussion.

Table 22. Summary of total phosphorus values (mg/L).

Measurements	443
Maximum	93.92
75th percentile	< 0.08
Median	0.024
25th percentile	0.008
Minimum	0.005
Interquartile range	na
Sites	48
DOW	0.1
Sites > 0.1	22

< means analytical result reported as less than the stated value
DOW: Kentucky Division of Water recommended value

The Division of Water has proposed a value of 0.1 mg/L as the groundwater-quality standard, based on information from the U.S. Geological Survey National Water-Quality Assessment Program. Twenty-two sites in BMU 3 yielded groundwater that exceeded 0.1 mg/L total phosphorus. Three sites accounted for a total of 44 analyses that were reported as less than a detection limit of 0.12 mg/L; that is, less than a detection limit that is greater than the value of interest (0.1 mg/L). One of these sites had also produced a sample having a total phosphorus concentration greater than 0.1 mg/L. For the other two sites, analytical results of "less than 0.12 mg/L" are the only entries in the database. Whether the actual total phosphorus concentrations at these sites were less than the recommended value of 0.1 mg/L cannot be determined.

The data distribution is not normal (Fig. 102). Approximately 95 percent of the values follow a normal distribution from 0.0 to about 0.1 mg/L, but there is also a small group of much higher values.

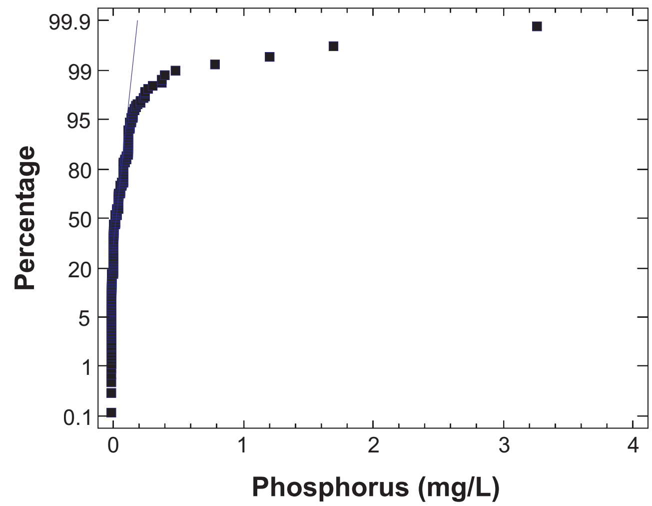

Figure 102. Cumulative plot of total phosphorus values.

Sample sites are well distributed throughout the project area (Fig. 103). Sites where total phosphorus exceeds 0.1 mg/L occur in all physiographic regions (Figs. 104–105) and all major watersheds except that of the Ohio River (Figs. 103 and 105).

High total phosphorus concentrations are more common in wells than in springs (Fig. 106), and more common in wells less than 100 ft deep than in deeper wells (Fig. 107).

In summary, total phosphorus concentrations that exceed the recommended value of 0.1 mg/L were reported throughout BMU 3. Such sites are widespread throughout the Eastern Kentucky Coal Field, areally restricted in the Western Pennyroyal Region, and isolated in the Jackson Purchase. Shallow wells are more likely to produce groundwater with total phosphorus concentrations above 0.1 mg/L than deep wells or springs. Nonpoint-source contributions of total phosphorus to groundwater are probably minor compared to natural sources in the coal fields and the carbonate Pennyroyal regions. That shallow wells are most likely to produce groundwater having high phosphorus concentrations suggests, however, that there may be a nonpoint-source contribution.

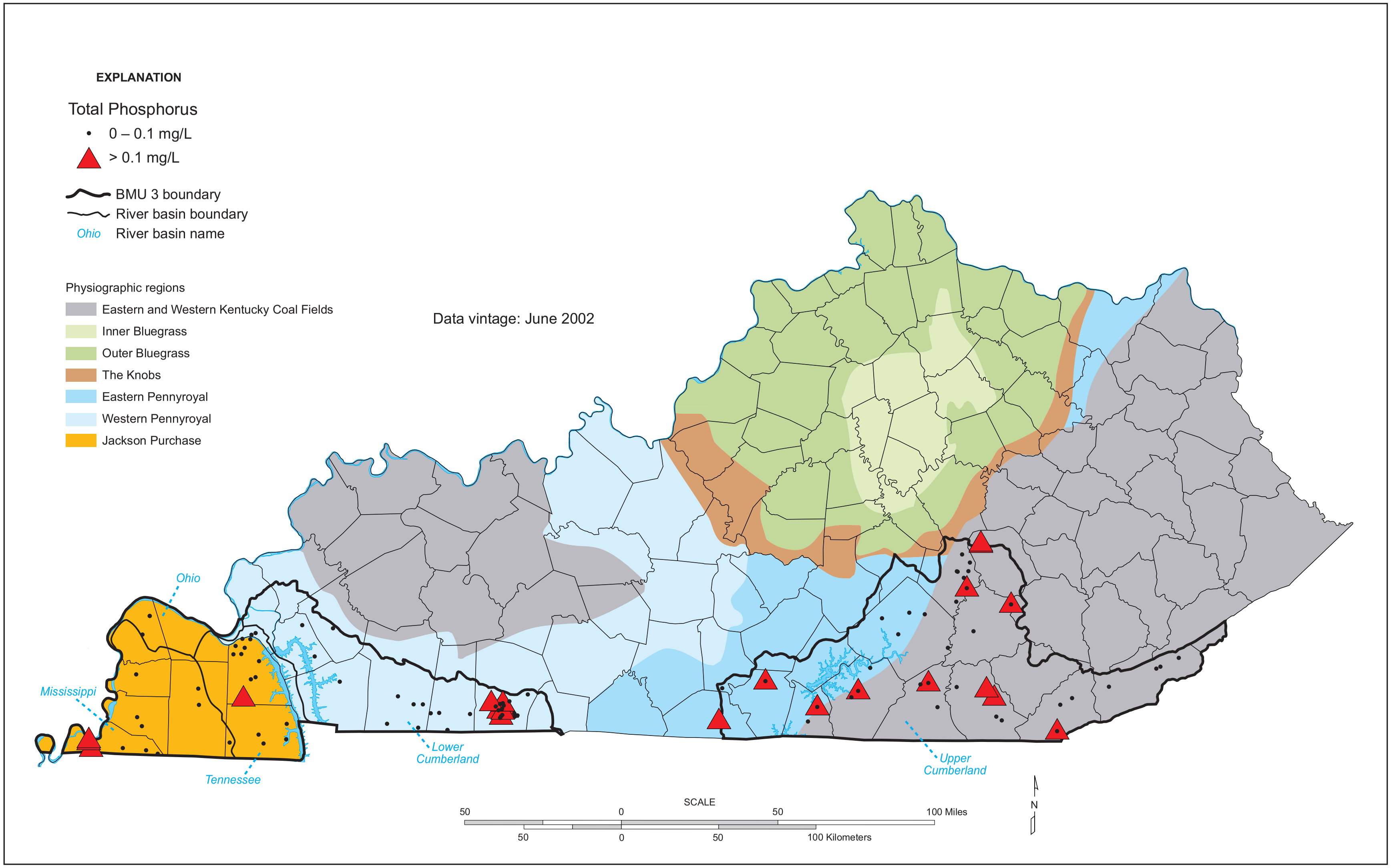

Figure 103. Sample sites and ranges of total phosphorus values. Superimposed symbols indicate that values measured at the same site but at different sampling times fell into different ranges.

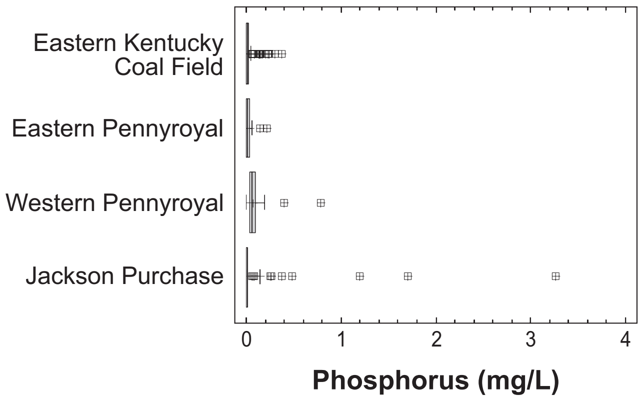

Figure 104. Summary of total phosphorus values grouped by physiographic region.

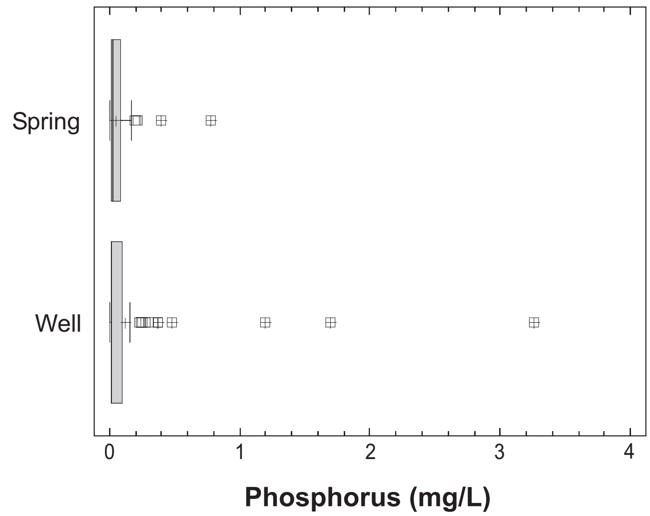

Figure 106. Comparison of total phosphorus values from wells and springs.

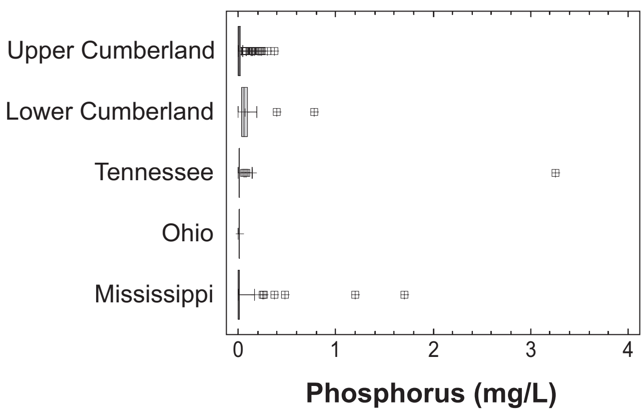

Figure 105. Total phosphorus values grouped by major watershed.

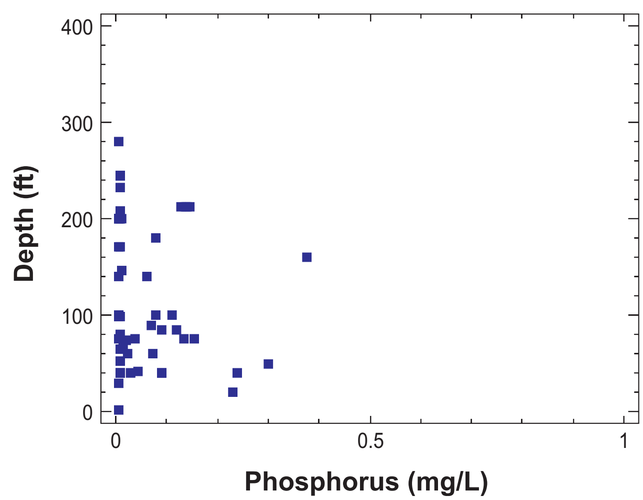

Figure 107. Total phosphorus concentrations versus well depth.