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 waste, 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. Nitrite, ammonium, and ammonia may also occur in deep, old, reducing groundwater systems.

Runoff from fertilizer use, leachate from septic tanks, and sewage are common 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 that are home to large bat colonies may accumulate large amounts of guano that contributes nitrogen to local groundwater. Nitrite concentrations in groundwater are generally low because nitrite converts quickly to nitrate in oxidizing environments and to nitrogen gas in reducing environments (Fetter, 1993).

Table 19. Summary of nitrate-nitrogen concentrations (mg/L). MCL=10 mg/L.

Number of values	543
Maximum	271
75th percentile	16.0
Median	0.5
25th percentile	0.07
Minimum	0.02
Interquartile range	0.0
Number of sites	0.48
Number of sites > 10 mg/L	2

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 (milligrams per liter 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, reported 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 of nitrate) and 1.0 mg/L for nitrite-nitrogen (equivalent to 3.2 mg/L of 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 urine output), increased starchy deposits, and hemorrhaging of the spleen. No human health-based concentration limits have been established for ammonia or ammonium, but ammonia concentrations of 1 to 10 mg/L can be toxic to aquatic life.

Nitrate-Nitrogen. The data repository contained 543 nitrate-nitrogen measurements at 271 sites in BMU 5 (Table 19). The maximum concentration reported was 16 mg/L. Nitrate-nitrogen concentrations exceeded the MCL of 10 mg/L at only two sites.

Only four values exceeded the MCL of 10 mg/L (Fig. 66). The cumulative data plot shows two inflection points, suggesting that there may have been two different sources of nitrate.

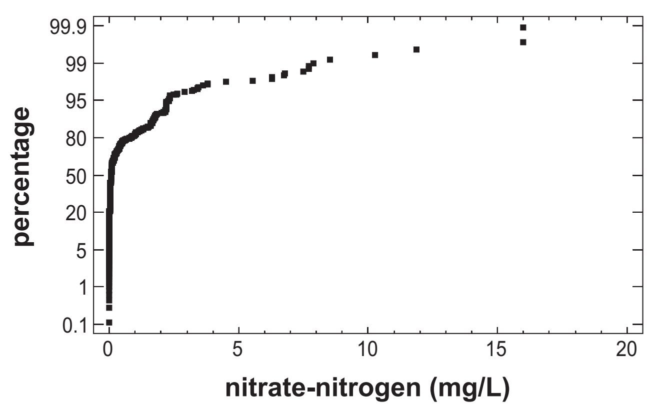

Figure 66. Cumulative plot of nitrate-nitrogen concentrations. MCL=10 mg/L.

Sampled sites were concentrated in Johnson County and along the Ohio–West Virginia border in the Big Sandy River watershed (Fig. 67). The remainder of BMU 5 was sparsely sampled.

Both the median value and the interquartile range of values were much smaller in the Big Sandy watershed than in the Little Sandy–Tygarts Creek watershed (Fig. 68). This may partly reflect the difference in number of reported values in each region: 415 of the 543 reported values were from sites in the Big Sandy watershed.

Nitrate-nitrogen concentrations from springs had a higher median value and larger interquartile range than concentrations from wells (Fig. 69). The highest concentrations were found in water from wells.

Total nitrate-nitrogen concentrations had about the same median value as dissolved nitrate-nitrogen concentrations, but the interquartile range of values was larger for total concentrations (Fig. 70).

The highest nitrate-nitrogen concentrations were found in shallow wells; concentrations greater than 5 mg/L were rare in water from wells deeper than about 100 ft (Fig. 71).

In summary, more than 99 percent of all nitrate-nitrogen measurements in BMU 5 were less than the MCL of 10 mg/L. Nitrate-nitrogen concentrations greater than 5 mg/L were most likely to be found in unfiltered samples from shallow wells. These results suggest that nonpoint-source nutrients are not contributing to the groundwater system in BMU 5 to the extent that nitrate will become a threat to human health. A statewide summary of nitrate data is available (Conrad and others, 1999b) and can be viewed on the KGS Web site (kgsweb.uky.edu/olops/pub/kgs/ic60_11.pdf).

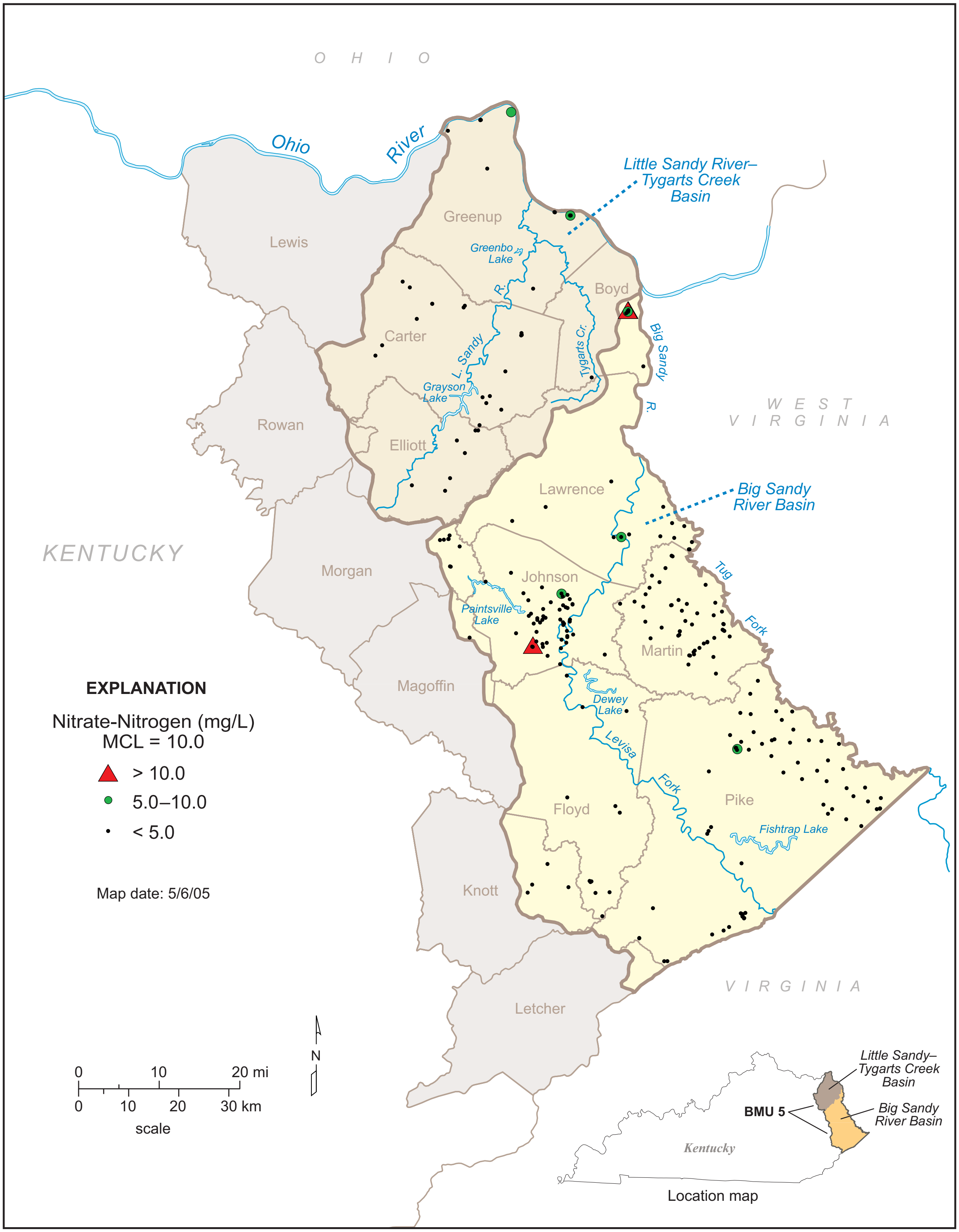

Figure 67. Locations of sampled sites and ranges of nitrate-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

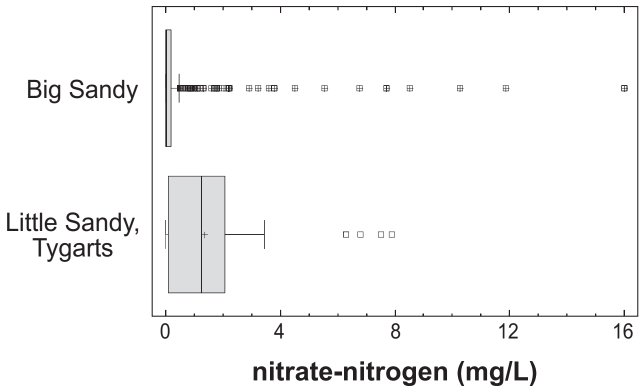

Figure 68. Summary of nitrate-nitrogen concentrations grouped by watershed. MCL=10 mg/L.

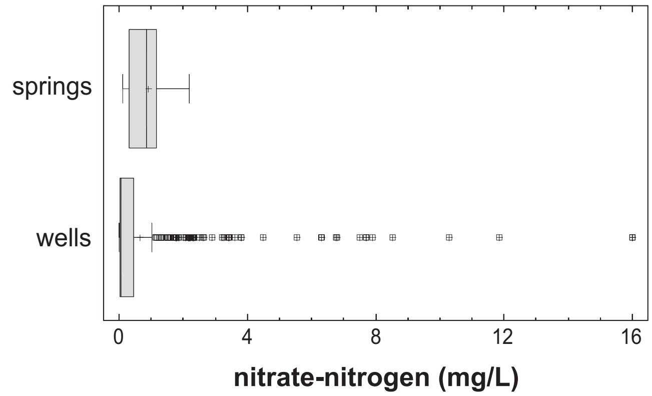

Figure 69. Comparison of nitrate-nitrogen concentrations from wells and springs. MCL=10 mg/L.

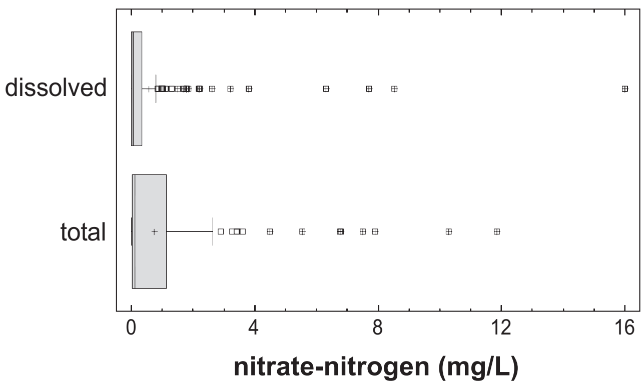

Figure 70. Comparison of total and dissolved nitrate-nitrogen concentrations. MCL=10 mg/L.

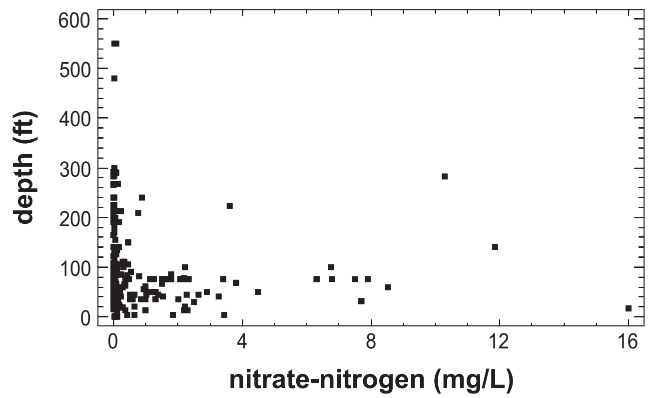

Figure 71. Nitrate-nitrogen concentrations versus well depth. MCL=10 mg/L.

Nitrite-Nitrogen. The data repository contained 280 measurements of nitrite-nitrogen from 109 sites (Table 20). No concentration exceeded the MCL of 1 mg/L; the maximum value reported was 0.13 mg/L.

More than 95 percent of the values were less than 0.1 mg/L (Fig. 72); more than half of the values were less than 0.02 mg/L.

Nearly two-thirds of the sampled sites were within the Big Sandy watershed, near the border between Kentucky and West Virginia (Fig. 73). The remainder of BMU 5 was very sparsely sampled.

Nitrite-nitrogen concentrations reported from the Big Sandy watershed had a lower median value and smaller interquartile range than values from the Little Sandy–Tygarts Creek watershed (Fig. 74). This difference is probably caused by the different number of values in each group: 207 of the 280 reported concentrations were from sites in the Big Sandy watershed.

Nitrite-nitrogen concentrations from wells and springs had nearly the same median value and interquartile range (Fig. 75).

Total (unfiltered groundwater) nitrite-nitrogen concentrations had a large median value and larger interquartile range of values than dissolved (filtered groundwater) concentrations, suggesting that some of the nutrients were associated with suspended particulate material (Fig. 76).

The highest nitrite-nitrogen concentrations were found in wells less than 100 ft deep (Fig. 77).

In summary, nitrite-nitrogen concentrations were uniformly low throughout BMU 5. No site produced groundwater that had a nitrite-nitrogen concentration above the MCL; the maximum concentration was only 0.13 mg/L. These results, combined with the finding of generally low nitrate-nitrogen concentrations in groundwater, suggest that nonpoint-source applications of fertilizer or other nutrients are minimal in BMU 5, and that nitrate and nitrite occurrences are natural.

Table 20. Summary of nitrite-nitrogen concentrations (mg/L). MCL=1.0 mg/L.

Number of values	280
Maximum	0.13
75th percentile	0.023
Median	0.01
25th percentile	0.004
Minimum	0.0
Interquartile range	0.019
Number of sites	109
Number of sites > 1.0 mg/L	0

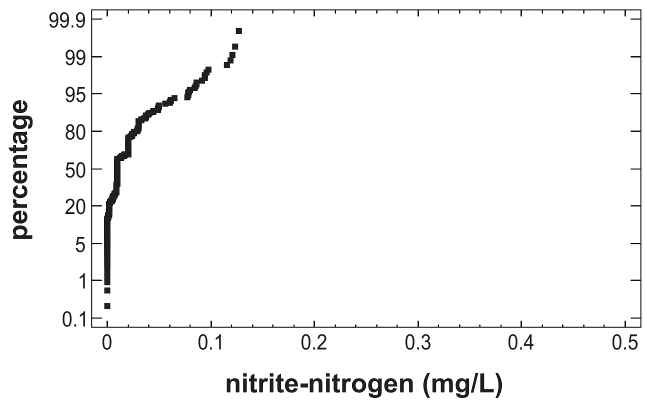

Figure 72. Cumulative plot of nitrite-nitrogen concentrations MCL=1.0 mg/L.

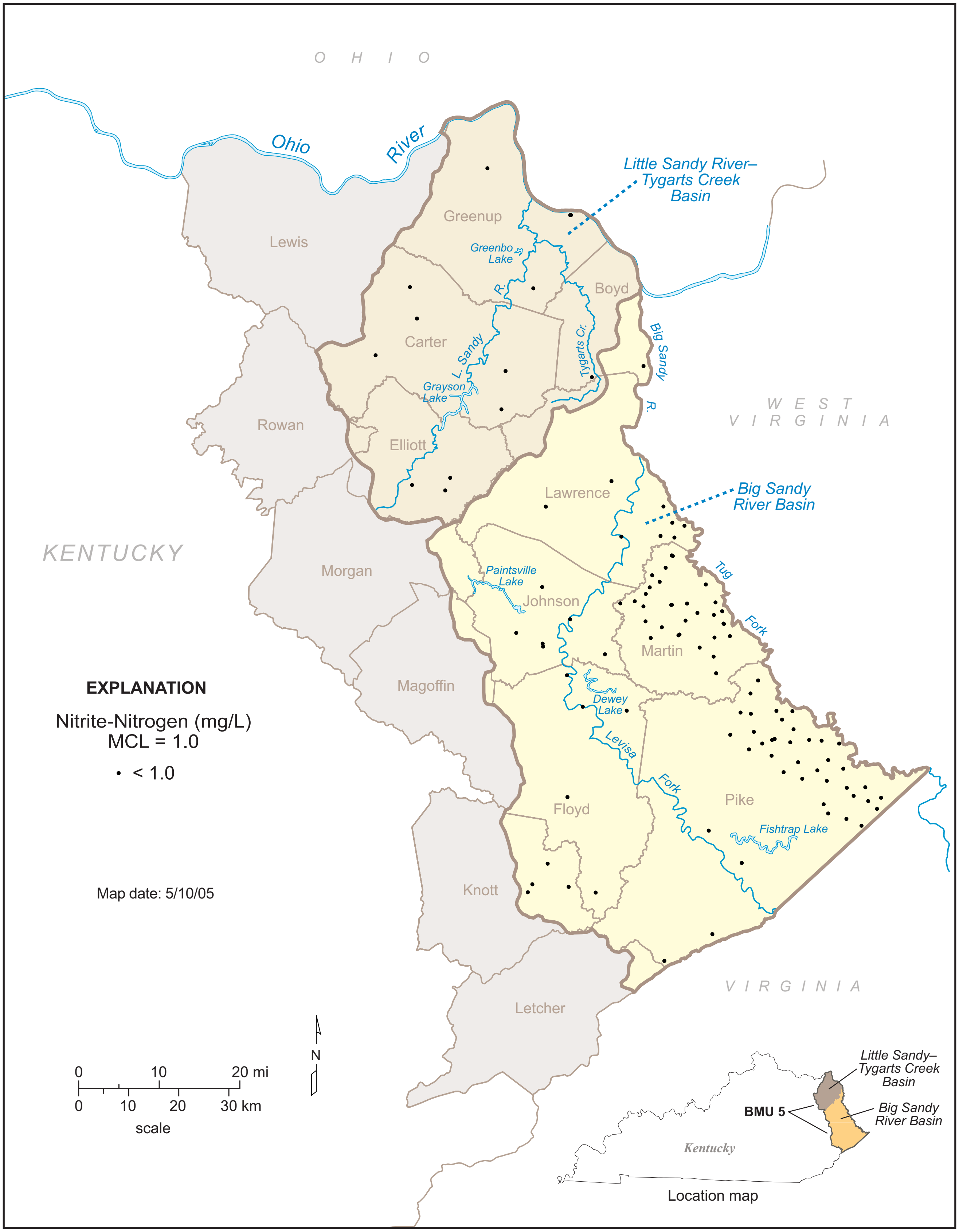

Figure 73. Locations of sampled sites and ranges of nitrite-nitrogen values.

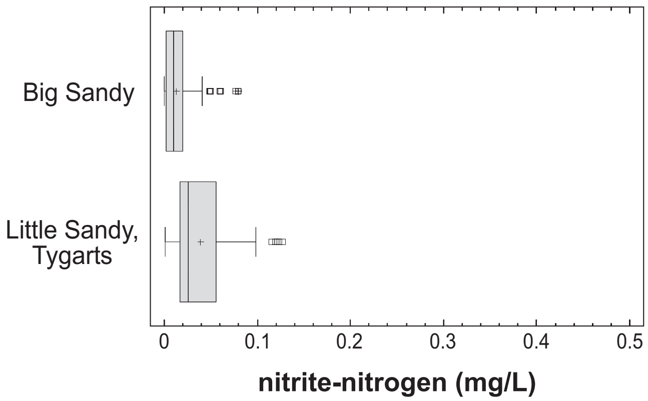

Figure 74. Summary of nitrite-nitrogen concentrations grouped by watershed. MCL=1.0 mg/L.

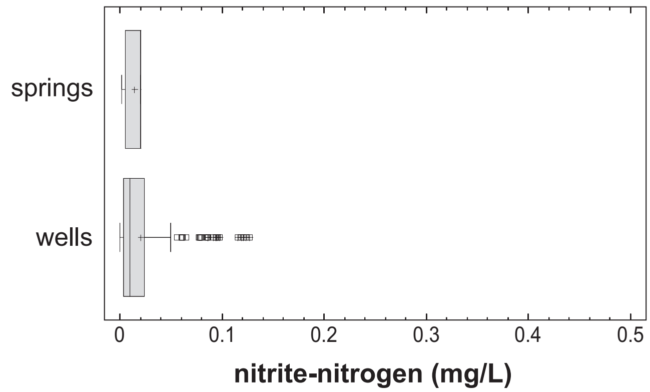

Figure 75. Comparison of nitrite-nitrogen concentrations from wells and springs. MCL=1.0 mg/L.

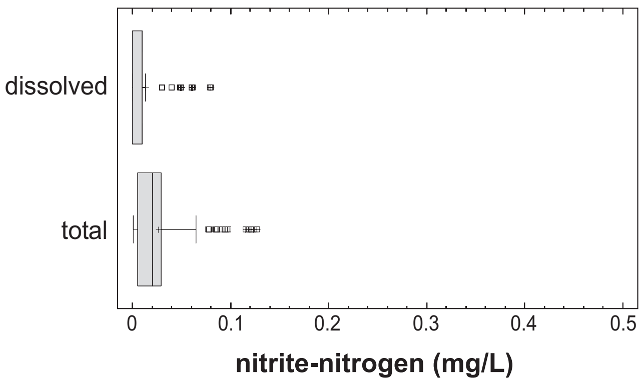

Figure 76. Comparison of total and dissolved nitrite-nitrogen concentrations. MCL=1.0 mg/L.

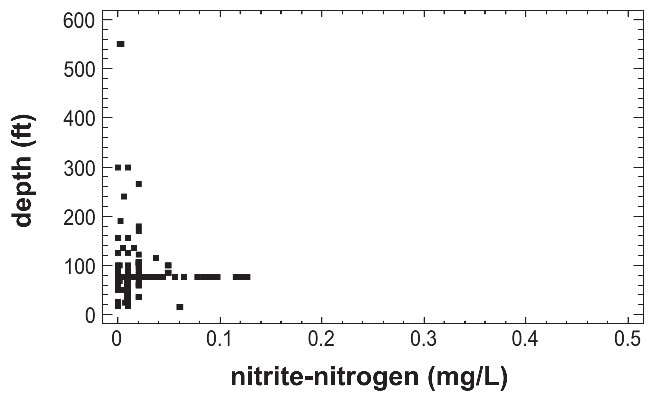

Figure 77. Nitrite-nitrogen concentrations versus well depth. MCL=1.0 mg/L.

Ammonia-Nitrogen. The data repository contained 167 ammonia-nitrogen measurements from 48 sites in BMU 5 (Table 21). There are no EPA health-based standards for ammonia-nitrogen, but the Kentucky Division of Water has recommended a risk-based upper limit of 0.11 mg/L for drinking water. Concentrations greater than 0.11 mg/L were found in water from 36 of the 48 sites in BMU 5.

All but three reported values were less than 3 mg/L (Fig. 78). About 5 percent of the values were greater than 1 mg/L, and about 35 percent of the values were greater than 0.11 mg/L.

Relatively few sites in BMU 5 were sampled for ammonia-nitrogen (Fig. 79). Sites where ammonia-nitrogen concentrations exceeded 0.11 mg/L were found throughout the project area, but were more common in the Big Sandy watershed.

Groundwater from the Big Sandy watershed had nearly the same median value as water from the Little Sandy–Tygarts Creek watershed. Groundwater from the Big Sandy watershed had a much larger interquartile range than water from the Little Sandy–Tygarts Creek watershed, however (Fig. 80).

The median value was about the same for total and dissolved ammonia-nitrogen, but the interquartile range of values was slightly greater for dissolved ammonia-nitrogen concentrations (Fig. 81). The highest concentrations were found in total (unfiltered) samples.

Springs accounted for only four sites and seven reported values. Therefore, springs and wells were not compared.

The highest ammonia-nitrogen concentrations were found in wells less than 100 ft deep (Fig. 82). Ammonia-nitrogen concentrations greater than 0.11 mg/L were found in even the deepest wells.

In summary, 75 percent of the sampled sites produced groundwater with more than 0.11 mg/L of ammonia-nitrogen. Such water was produced from wells at all depths. The available data, including the results for nitrate and nitrite in groundwater, do not indicate that nonpoint-source ammonia-nitrogen contributes significantly to groundwater supplies. The most likely sources of ammonia-nitrogen in BMU 5 are naturally occurring nitrogen in coal and leaf litter.

Table 21. Summary of ammonia-nitrogen concentrations (mg/L). DOW recommendation=0.11 mg/L.

Number of values	167
Maximum	13.15
75th percentile	0.387
Median	< 0.05
25th percentile	< 0.02
Minimum	0.016
Number of sites	48
Number of sites > 0.110 mg/L	36

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

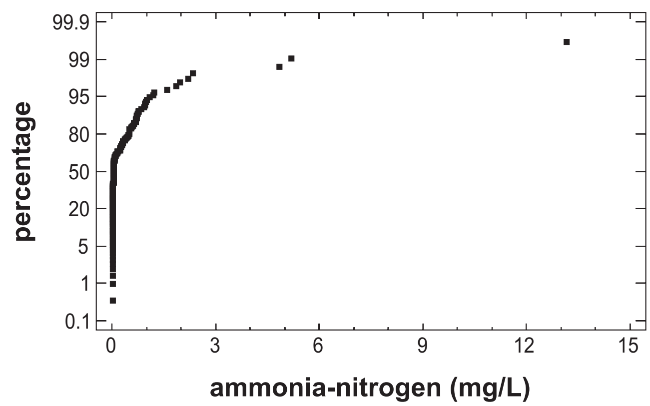

Figure 78. Cumulative plot of ammonia-nitrogen concentrations. DOW recommendation=0.11 mg/L.

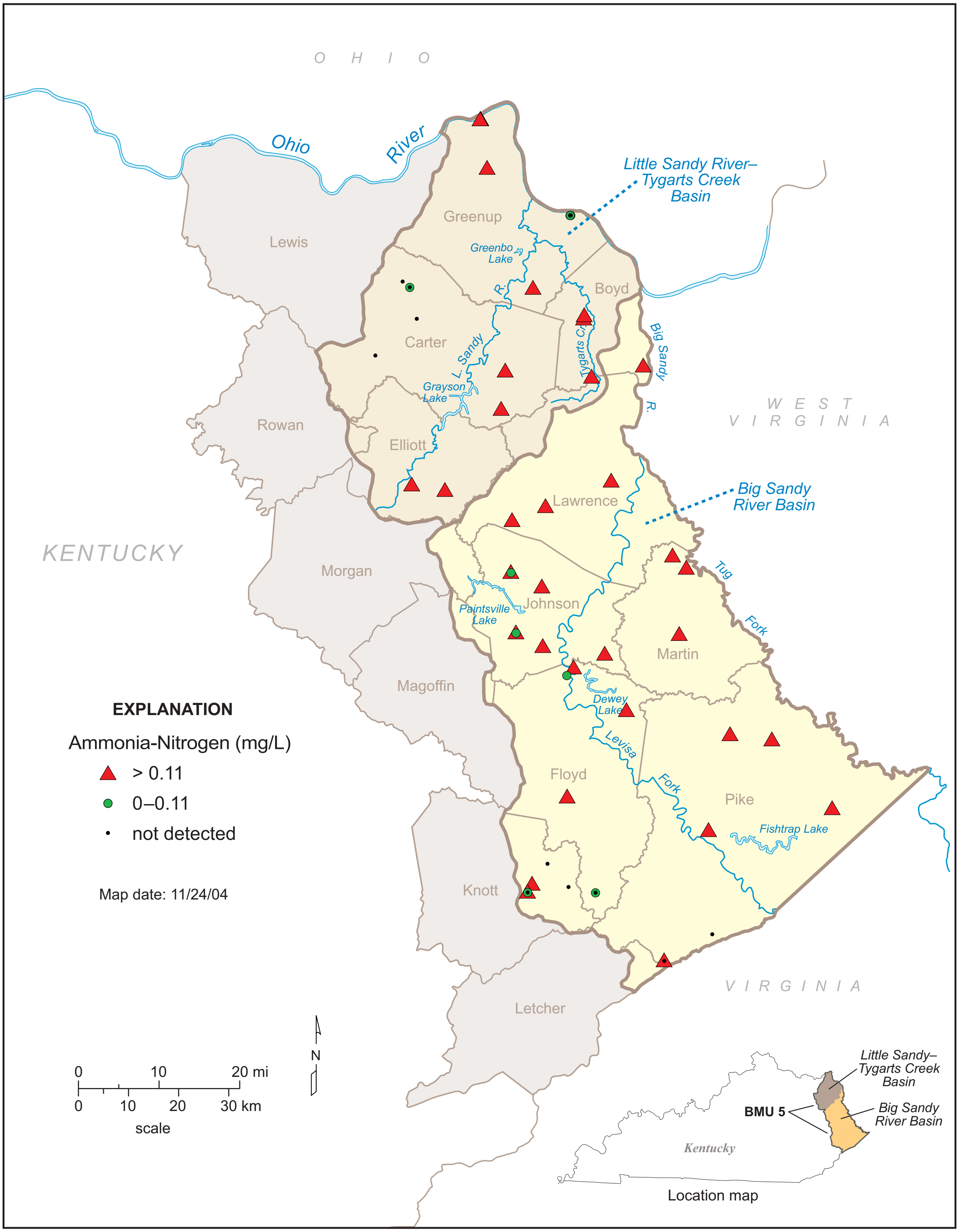

Figure 79. Locations of sampled sites and ranges of ammonia-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

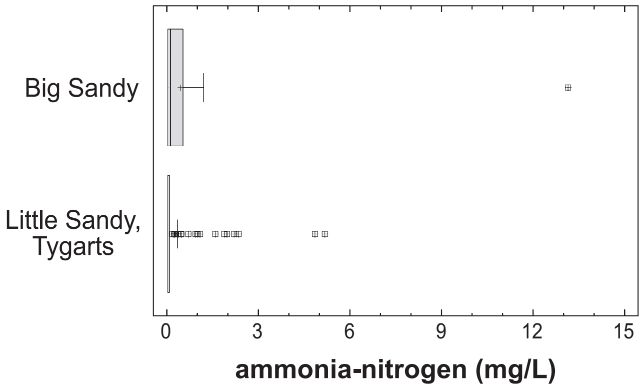

Figure 80. Summary of ammonia-nitrogen concentrations grouped by watershed. DOW recommendation=0.11 mg/L.

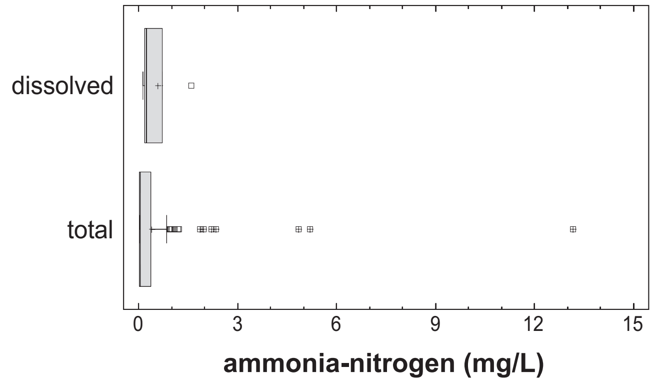

Figure 81. Comparison of total and dissolved ammonia-nitrogen concentrations. DOW recommendation=0.11 mg/L.

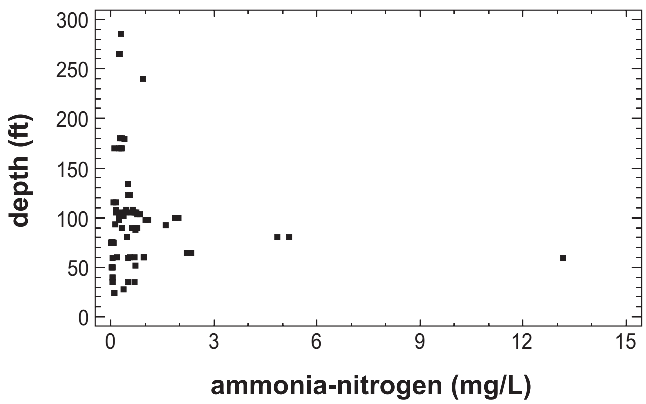

Figure 82. Ammonia-nitrogen concentrations versus well depth. DOW recommendation=0.11 mg/L.

Phosphorus Species. Phosphorus is a common element in the earth's crust; it also is an important constituent of the marine sediments such as carbonate strata. Most inorganic phosphorus compounds and minerals have low solubility, which limits dissolved phosphorus concentrations in surface water and groundwater. Phosphorus species are readily adsorbed onto soil particles and organic material; thus, suspended solids in groundwater may contain important amounts of phosphorus.

Phosphorus is an important nutrient and commonly is the "limiting nutrient" in aquatic ecosystems. Plants and animals need many different nutrients in various proportions, which are naturally present in different amounts. The "limiting nutrient" is the one that is used up first. Even if other nutrients are still available, the plant or animal cannot grow because one essential nutrient is no longer available. The most important man-made sources of phosphorus are 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 as $H_2PO_4^-$ 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 may 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 due to organic particulate 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 of PO_4-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 National Water-Quality Assessment Program.

Orthophosphate. The data repository contained 156 orthophosphate measurements from 40 sites in BMU 5 (Table 22). Seven values were greater than 100 mg/L; the remainder were less than 0.5 mg/L. Ten of the 40 sites produced groundwater with more than 0.04 mg/L of orthophosphate phosphorus.

The cumulative data plot (Fig. 83) shows that more than 95 percent of the values were less than 0.2 mg/L. Eighty-two percent of the reported values were 0.04 mg/L or less.

Sampled sites were sparsely distributed throughout BMU 5 (Fig. 84). Sites where groundwater contained more than 0.04 mg/L of orthophosphate are not concentrated in any particular region.

The median value and interquartile range of concentrations were approximately equal in the two watersheds (Fig. 85).

Only six analyses from four sites were from springs, so valid comparison of concentrations in springs versus wells was not possible. Orthophosphate concentrations greater than the recommended limit were found at all well depths (Fig. 86).

In summary, relatively few wells and springs were sampled for orthophosphate in BMU 5. Of the reported values, seven were greater than 100 mg/L; these concentrations occurred in wells as deep as 250 ft. Ten of 40 sites produced groundwater that exceeded the recommended level of 0.04 mg/L. The results suggest that most orthophosphate concentrations were the result of natural processes; however, values greater than 100 mg/L were found, and these very high concentrations may reflect an input from nonpoint sources.

Table 22. Summary of orthophosphate concentrations (mg/L as P). DOW recommendation=0.04 mg/L.

Number of values	156
Maximum	254
75th percentile	0.03
Median	0.02
25th percentile	0.01
Minimum	0.0
Interquartile range	0.02
Number of sites	40
Number of sites > 0.04 mg/L	10

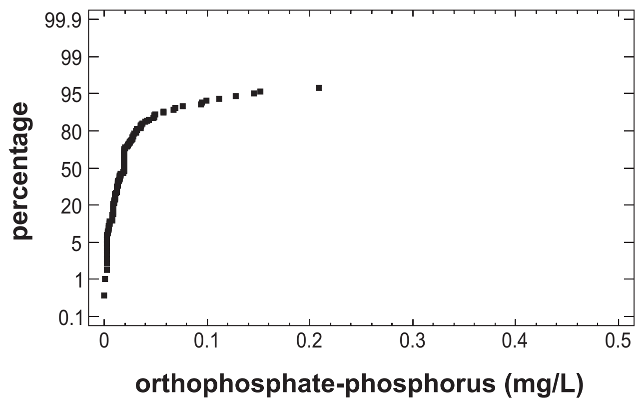

Figure 83. Cumulative plot of orthophosphate concentrations. Seven values greater than 100 mg/L were excluded to better show the majority of the values. DOW recommendation=0.04 mg/L.

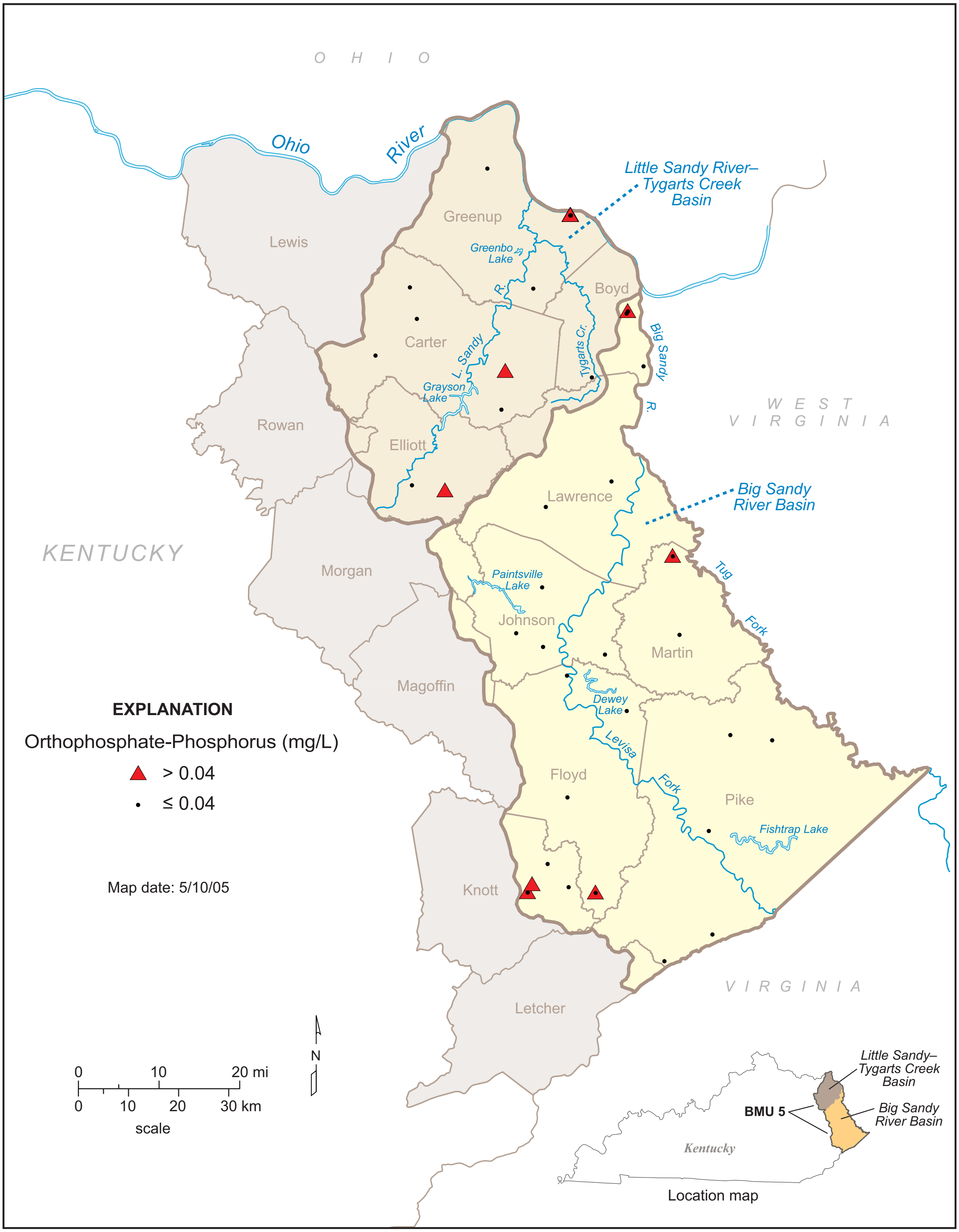

Figure 84. Locations of sampled sites and ranges of orthophosphate values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

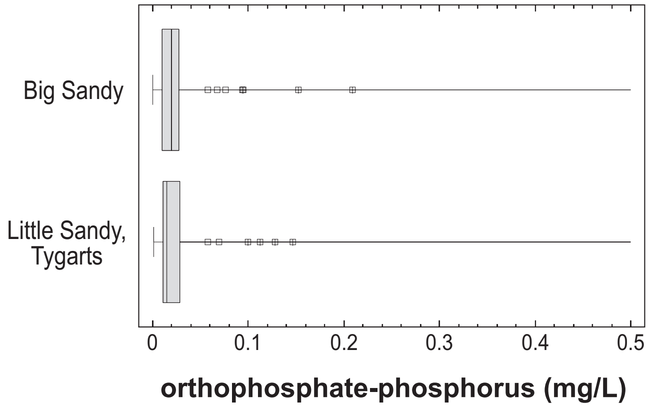

Figure 85. Summary of orthophosphate concentrations grouped by watershed. Seven values greater than 100 mg/L were excluded to better show the majority of the values. DOW recommendation=0.04 mg/L.

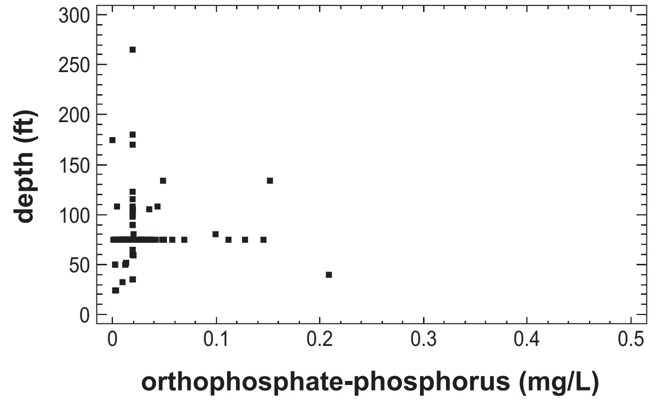

Figure 86. Orthophosphate concentrations versus well depth. Values greater than 100 mg/L were found at well depths from 75 to 250 ft. These high values were excluded to better show the majority of the values. DOW recommendation=0.04 mg/L.

Total Phosphorus. The database contained 136 reports of total phosphorus at 83 sites (Table 23). Sixteen of the 83 sites produced water with more than 0.1 mg/L of total phosphorus. Almost 95 percent of the values were less than 0.1 mg/L (Fig. 87).

The sampled sites were concentrated along the Kentucky–West Virginia border in the Big Sandy watershed (Fig. 88); very few sampled sites were in the remainder of BMU 5. Sites where groundwater exceeded 0.1 mg/L of total phosphorus were found throughout the region.

The number of sampled sites and reported values were very different for the two watersheds: 104 values were reported from the Big Sandy watershed but only 33 from the Little Sandy–Tygarts Creek watershed. Despite the different number of values in the two groups, the median values and interquartile ranges were similar (Fig. 89).

Only one value was reported from a spring, so it was not possible to compare total phosphorus concentrations between wells and springs. Phosphorus concentrations in filtered samples (dissolved phosphorus) had a similar median value but larger interquartile range than concentrations from unfiltered (total) groundwater (Fig. 90).

The highest total phosphorus concentrations occurred in wells less than 150 ft deep (Fig. 91). Despite one value of 0.24 mg/L at about 290 ft, there was a general trend toward lower concentrations as well depth increased beyond 130 ft.

In summary, most sampled sites were along the eastern border of the Big Sandy watershed. The otherwise sparse distribution of sampled sites in the project area makes it impossible to use the available reported total phosphorus concentrations to characterize all of BMU 5. Sixteen of 83 sites produced groundwater with more than the recommended 0.1 mg/L of phosphorus. Natural sources of phosphorus are present, however, and the maximum reported concentration was only 1.28 mg/L. Although contributions from fertilizer or leaking sewage-disposal systems are possible, there was no clear evidence that these nonpoint sources significantly affected phosphorus concentrations in BMU 5.

Table 23. Summary of total phosphorus concentrations (mg/L). DOW recommendation=0.1 mg/L.

Number of values	136
Maximum	1.28
75th percentile	0.12
Median	0.05
25th percentile	0.01
Minimum	0.0
Interquartile range	0.11
Number of sites	83
Number of sites > 0.10 mg/L	16

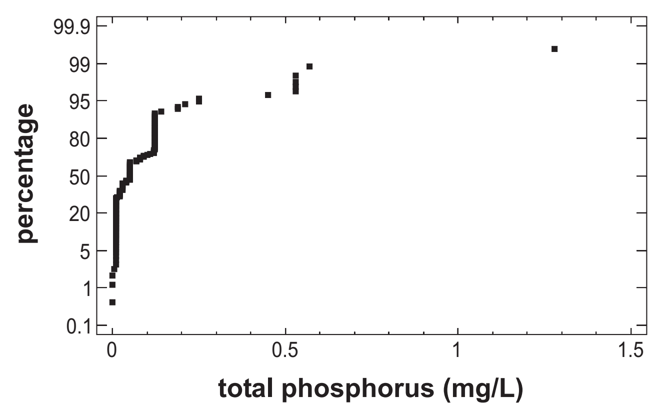

Figure 87. Cumulative plot of total phosphorus concentrations. DOW recommendation=0.1 mg/L.

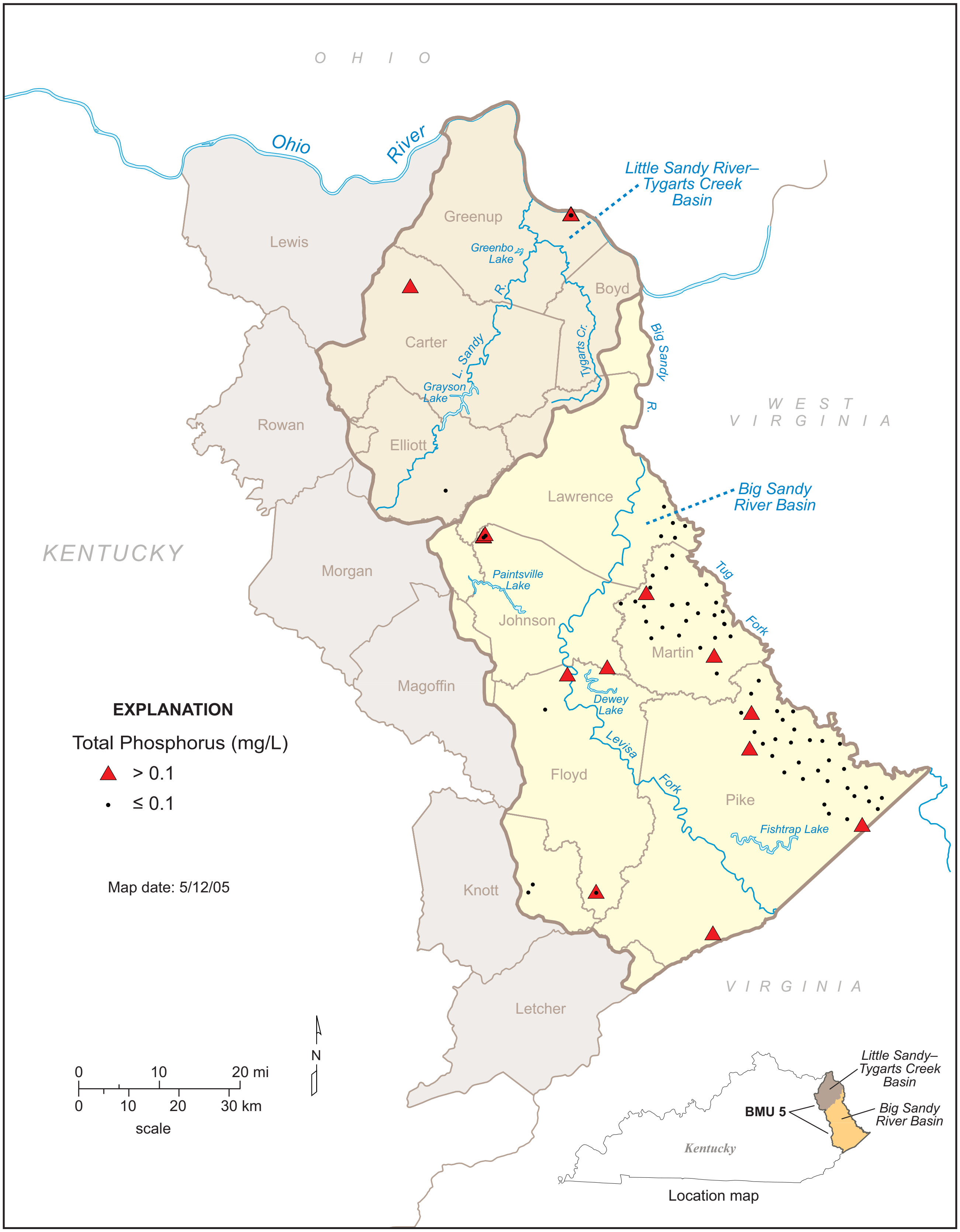

Figure 88. Locations of sampled sites and ranges of total phosphorus values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

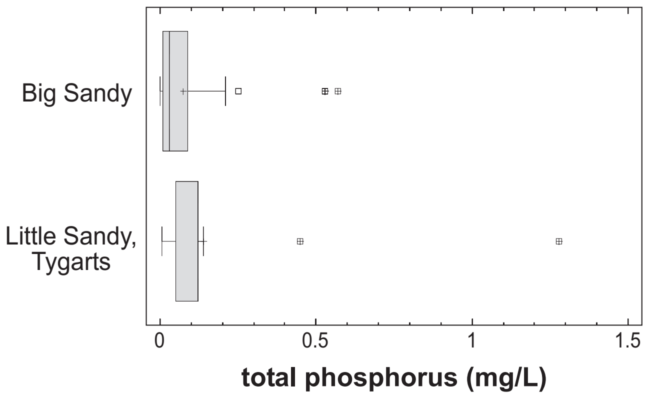

Figure 89. Summary of total phosphorus concentrations grouped by watershed. DOW recommendation=0.1 mg/L.

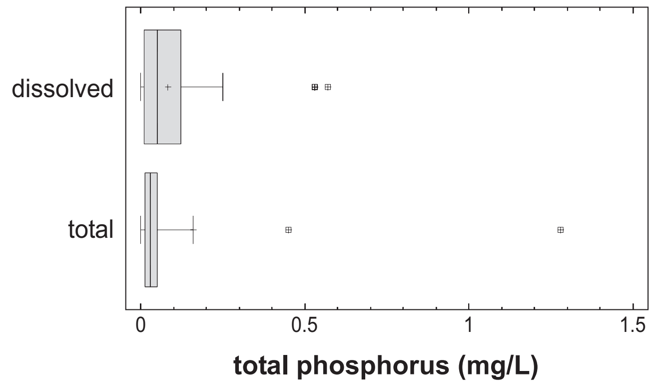

Figure 90. Comparison of total and dissolved phosphorus concentrations. DOW recommendation=0.1 mg/L.

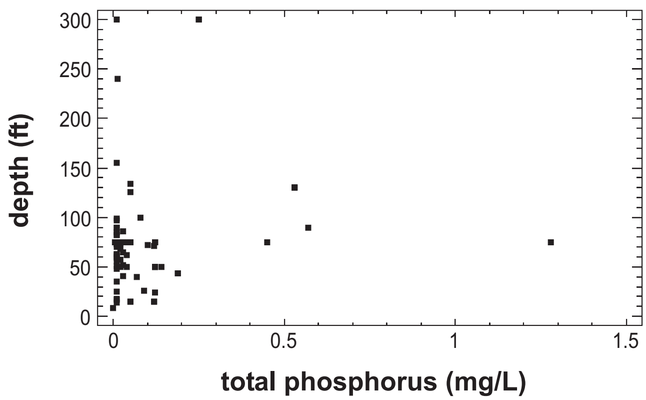

Figure 91. Total phosphorus concentrations versus well depth. DOW recommendation=0.1 mg/L.