2008

Groundwater Quality in Watersheds of the Big Sandy River, Little Sandy River, and Tygarts Creek (Kentucky Basin Management Unit 5)

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Repository Citation

Fisher, R. Stephen; Davidson, Bart; and Goodmann, Peter T., "Groundwater Quality in Watersheds of the Big Sandy River, Little Sandy River, and Tygarts Creek (Kentucky Basin Management Unit 5)" (2008). *Kentucky Geological Survey Report of Investigations*. 21.
https://uknowledge.uky.edu/kgs_ri/21

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Report of Investigations 19 https://doi.org/10.13023/kgs.ri19.12 Series XII, 2008

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Technical Level

ISSN 0075-5591

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Groundwater Quality in Watersheds of the Big Sandy River, Little Sandy River, and Tygarts Creek (Kentucky Basin Management Unit 5)

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Abstract

The Kentucky Geological Survey and the Kentucky Division of Water are evaluating groundwater quality throughout the commonwealth to determine regional conditions, assess impacts of nonpoint-source contaminants, provide a baseline for tracking changes, and provide essential information for environmental-protection and resource-management decisions. These evaluations include summarizing existing regional groundwater-quality data and reporting the results of expanded, focused groundwater collection programs in specific areas. This report summarizes groundwater sampling and analysis in Kentucky basin management unit 5 (watersheds of the Big Sandy River, Little Sandy River, and Tygarts Creek in eastern Kentucky).

Thirty wells and springs were sampled quarterly between the fall of 2002 and the summer of 2003. Temperature, pH, and conductance were measured at the sample site, and concentrations of a selected group of major and minor inorganic ions, metals, nutrients, pesticides, and volatile organic chemicals were measured at the Kentucky Division of Environmental Services laboratory. The new analytical data were combined with groundwater-quality records retrieved from the Kentucky Groundwater Data Repository. This repository is maintained by the Kentucky Geological Survey and contains reports received from the Division of Water's Ambient Groundwater Monitoring Program as well as results of investigations by the U.S. Geological Survey, U.S. Environmental Protection Agency, U.S. Department of Energy, Kentucky Geological Survey, Kentucky Division of Pesticide Regulation, and other agencies. Statistical measures such as the number of measured concentrations reported, the number of sites sampled, quartile values (maximum 75th percentile, median, 25th percentile, and minimum), and the number of sites at which water-quality standards were exceeded were used to summarize the data, and probability plots were used to illustrate the distribution of reported concentrations. Maps were used to show well and spring locations and sites where water-quality standards were met or exceeded. Box-and-whisker diagrams were used to compare values between major watersheds, water from wells versus water from springs, and total versus dissolved metal concentrations. Plots of concentrations versus well depth were used to compare groundwater quality in shallow, intermediate, and deep groundwater flow systems.

Table A1 summarizes the findings. Water properties, inorganic anions, and metals are primarily controlled by natural factors such as bedrock lithology. Some exceptionally high values of conductance, chloride, and sulfate may be affected by nearby oil and gas production, leaking waste-disposal systems, or other human factors, and some exceptionally low pH values may in-

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dicate acid mine drainage. Ammonia and nitrate concentrations indicate a probable contribution from nutrient applications and waste-disposal practices. Synthetic organic chemicals such as pesticides and refined volatile organic compounds do not occur naturally. Although these chemicals rarely exceed water-quality criteria in the project area, their detection indicates there has been some degradation of groundwater quality. The occurrence of these synthetic chemicals should continue to be monitored, and renewed efforts are needed to protect the groundwater resource.

Table A1. Summary of nonpoint-source effects on groundwater quality in basin management unit 5.

	Parameter	No Strong Evidence for Nonpoint-Source Impact on Groundwater Quality	Some Evidence for Nonpoint-Source Impact on Groundwater Quality	Clear Evidence for Nonpoint-Source Impact on Groundwater Quality
Water Properties	Conductance	X		
	Hardness	X		
	pH	X		
	Total dissolved solids	X		
	Total suspended solids	X		
Inorganic Ions	Chloride	X		
	Sulfate	X		
	Fluoride	X		
Metals	Arsenic	X		
	Barium	X		
	Iron	X		
	Manganese	X		
	Mercury	X		
Nutrients	Ammonia-nitrogen		X	
	Nitrate-nitrogen			X
	Nitrite-nitrogen	X		
	Orthophosphate	X		
	Total phosphorus	X		
Pesticides	2,4-D		X	
	Alachlor		X	
	Atrazine		X	
	Cyanazine	X		
	Metolachlor		X	
	Simazine		X	
Volatile Organic Compounds	Benzene		X	
	Ethylbenzene		X	
	Toluene		X	
	Xylenes		X	
	MTBE[1]		X	

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[1] Methyl tertiary-butyl ether

Introduction

Purpose

Evaluating groundwater quality is essential for determining its suitability for various uses and the sources of dissolved chemicals, and because regional groundwater quality provides a sensitive indicator of the general condition of the natural environment. In this report we summarize groundwater quality in the northeastern part of Kentucky (Kentucky basin management unit 5, consisting of watersheds of the Big Sandy River, Little Sandy River, and Tygarts Creek).

Goals

The goals of this project were to summarize the concentrations of a select group of groundwater-quality parameters in the project area, and to evaluate whether nonpoint-source chemicals have entered the groundwater system. This was accomplished by selecting approximately 30 wells and springs that had not been previously sampled, collecting a groundwater sample from each site quarterly over a 12-month period, and having the samples analyzed by the Kentucky Division of Environmental Services laboratory. Those analytical results were combined with other data obtained from the Kentucky Groundwater Data Repository and compared to criteria selected by the Division of Water. The results provide a basis for identifying natural and anomalous concentrations of dissolved chemicals as well as areas where nonpoint-source chemicals have entered the groundwater system and where the implementation of best management practices is needed. The results also supply information for the Division of Water's watershed assessment reports, add groundwater-quality data to the Division's Groundwater Protection Program, help the Division's Wellhead Protection Program set priorities for protection areas and activities, and provide critical information for long-term protection and management of water resources.

Background

Evaluating groundwater quality is particularly important in Kentucky because groundwater use is extensive and will continue to be so. The 1990 census data and recent Division of Water estimates indicate that approximately 60 percent of public water-supply companies use groundwater as a sole or contributing water source, more than 25 percent of the population uses groundwater for domestic purposes, and more than 226 million gallons of groundwater are consumed daily by individuals, municipalities, utilities, businesses, and farms. Groundwater will continue to be important to Kentuckians because economic and logistical factors make replacing groundwater with surface-water supplies in rural areas expensive or impractical, and because some cities along the Ohio River are turning to groundwater from alluvial deposits for urban water supplies. An estimated 400,000 Kentuckians will still depend on private, domestic water supplies in the year 2020 (Kentucky Geological Survey, 1999).

Both natural and man-made processes affect groundwater quality. Natural processes that contribute cations, anions, metals, nutrients, and sediment to groundwater are dissolution of atmospheric gases as rain falls through the atmosphere, dissolution of soil particles and physical transport of chemicals and sediment as rainfall flows across the land surface, dissolution of soil gases and reactions with inorganic and organic material in the soil zone above the water table, and reactions with gases, minerals, and organic material beneath the water table.

Groundwater quality is also affected by human activities that contribute synthetic organic chemicals such as pesticides, fertilizers, and volatile organic compounds as well as cations, anions, metals, nutrients, and sediment to the water system. Nearly all activities that threaten surface waters and aquatic ecosystems also endanger groundwater systems. Agriculture, confined animal-feeding operations, forestry, mining, oil and gas production, waste disposal, and stormwater runoff can deliver pesticides, fertilizers, nutrients, metals, and hydrocarbons to groundwater.

Previous Investigations

Several earlier reports describe the hydrology, groundwater resources, and general water quality of the study area. None address the issue of nonpoint-source contamination, however. In the 1960's and early 1970's, the U.S. Geological Survey published reconnaissance studies of the geology, groundwater supplies, and general groundwater quality in Kentucky. These reports include a Hydrologic Atlas series, which was developed in conjunction with the Kentucky Geological Survey. Each atlas covers from two to 10 counties across the state, except in the Jackson Purchase Region, which had an atlas for each 7.5-minute quadrangle. Each atlas includes three sheets showing geology, lithology, and groundwater availability. The atlases have been digitally scanned and are currently available online (www.uky.edu/KGS/water/library/USGSHA.html). The Kentucky Geological Survey developed a series of county groundwater-resource reports based on the USGS Hydrologic Atlases. These reports (www.uky.edu/KGS/water/library/webintro.html) contain from 16 to 31 pages per county of information on geology, hydrogeologic characteristics of aquifers, available water supplies, and availability of groundwater for public consumption. Price and others (1962) published a comprehensive groundwater resource report for the Eastern Kentucky Coal Field. This report covered only major and minor inorganic ions and nitrate, however; other nutrients, metals, and synthetic organic chemicals were not considered. Sprinkle and others (1983) summarized general groundwater quality throughout Kentucky. The Kentucky Geological Survey (1999) summarized groundwater supply and general groundwater quality throughout the state for the Water Resource Development Commission (kgsweb.uky.edu/download/wrs/GWTASK1.PDF). Carey and others (1993) surveyed selected groundwater-quality parameters, including nutrients and pesticides, in private groundwater supplies.

Two other sources of analytical data contributed significantly to the database used here. Faust and others (1980) summarized the results of cooperative groundwater investigations involving KGS and other State, Federal, and local agencies. The National Uranium Resource Evaluation was a large source of analyses of groundwater, surface water, and stream sediments (Smith, 2001). Data from both these reports are stored in the Kentucky Groundwater Data Repository and were used in this report.

Project Area

The Division of Water's Watershed Management Framework grouped Kentucky's river basins into five basin management units (BMU's; Fig. 1). The current project area is BMU 5 (Big Sandy River, Little Sandy River, and Tygarts Creek, and adjacent tributaries of the Ohio River).

With the exception of the extreme northern tip of BMU 5, the project area is in the Eastern Kentucky Coal Field physiographic region (Fig. 1). This region is characterized by deeply incised sandstone, shale, and coal strata that are essentially horizontal throughout most of the area, but are steeply inclined to nearly vertical along the Pine Mountain Overthrust Fault in southeastern Kentucky. Steep hillsides separate narrow, flat river valleys from sharp, sinuous mountain crests. Valley slopes are typically fractured and covered by rock fragments and weathered material; soils are generally thin except in river valleys (Newell, 1986).

Basin Management Unit 5

Basin management unit 5 includes watersheds of the Big Sandy River, Little Sandy River, and Tygarts Creek (Fig. 2). This area covers approximately 4,610 mi^2. The Big Sandy River forms the northeastern boundary between Kentucky and West Virginia, and flows northwest to Boyd County, where it joins the Ohio River near Catlettsburg. The Little Sandy River flows northeast in the northern half of BMU 5, and joins the Ohio River near the town of Greenup in Greenup County. Tygarts Creek is west of and roughly parallel to the Little Sandy River, and flows into the Ohio River in northern Greenup County.

Land uses and nonpoint-source chemical threats to groundwater quality include oil and gas production, leaking sewage disposal systems, and runoff from active and abandoned coal mines, deforested areas, and confined animal-feeding operations (Kentucky Division of Water, 2000).

BMU 5 includes all or parts of the following 15 counties: Boyd, Carter, Elliott, Floyd, Greenup, Johnson, Knott, Lawrence, Letcher, Lewis, Magoffin, Martin, Morgan, Pike, and Rowan.

Hydrologic Unit Codes

The U.S. Geological Survey has assigned hydrologic unit codes to watersheds to identify regions, subregions, accounting units, and cataloging units (U.S. Geological Survey, 1976). The HUC designations of watersheds in BMU 5 are listed in Tables 1 and 2.

Groundwater Sensitivity Regions

The vulnerability of groundwater to nonpoint-source contamination varies geographically across Kentucky, and vertically at any given location, in response to both natural and human factors.

Among the most important natural controls on the transport of pollutants to the groundwater system are physiography (principally the topography, relief, land slope, and presence or absence of sinkholes or caves), soil type and thickness, bedrock type, bedrock structure (principally the bedrock porosity and permeability and the presence or absence of faults, fractures, or solution conduits), and depth to groundwater. Overprinted on the natural environment are human factors such as the type of land use, the type and amount of chemicals applied to agricultural and urban landscapes, wastewater and sewage-disposal practices, and the effects of resource extraction (principally oil and gas production and coal mining).

Recognizing the need to develop a flexible program for groundwater protection, the Division of Water developed a method for rating and delineating regions of different groundwater sensitivity (Ray and O'dell, 1993) and published a map showing the various groundwater sensitivity regions throughout the commonwealth (Ray and others, 1994). Ray and O'dell (1993) concluded that the natural factors controlling the potential for contamination of the shallowest aquifer can be assessed from the potential ease and speed

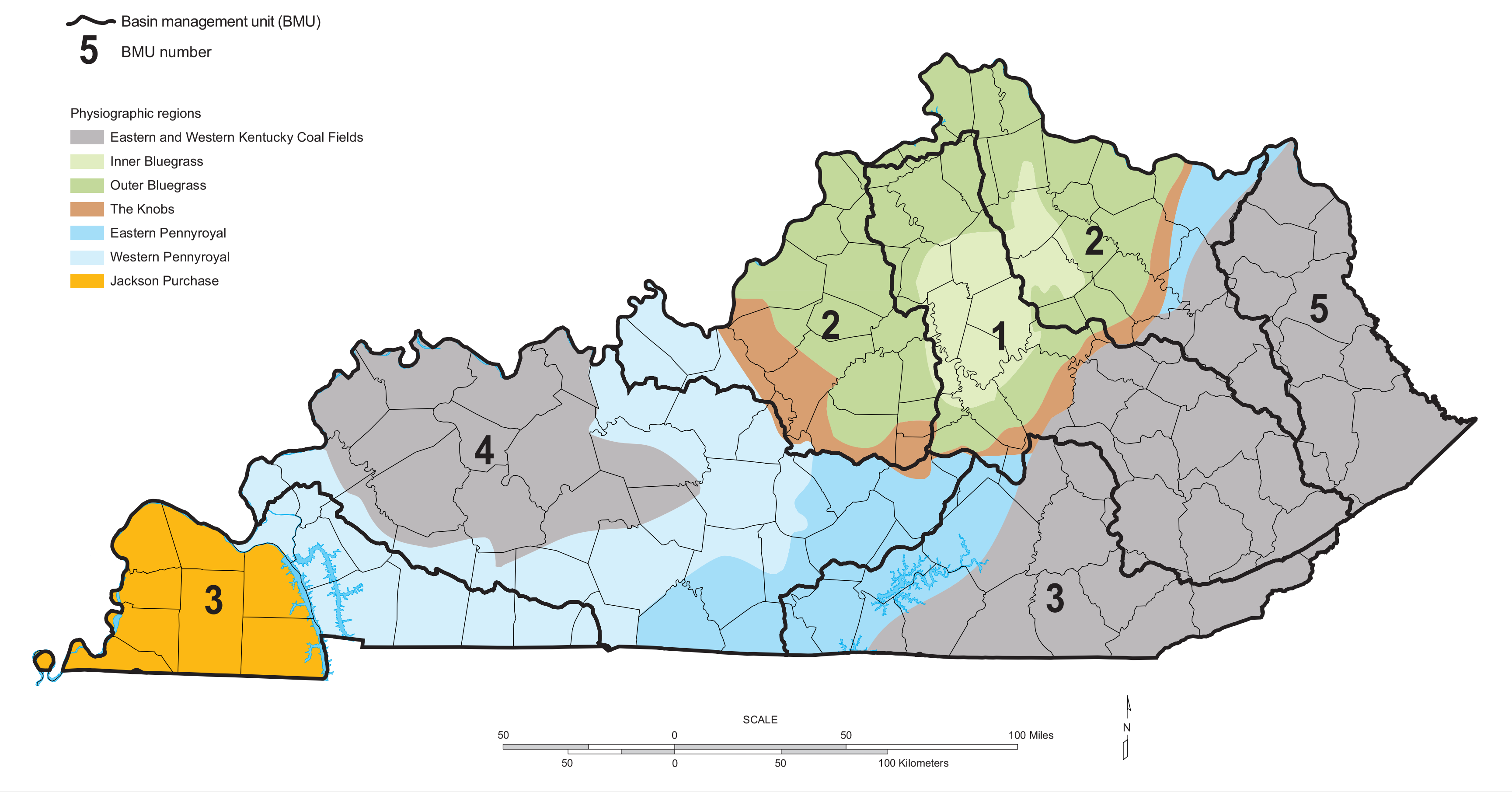

Figure 1. Major watersheds, physiographic regions, and basin management units in Kentucky.

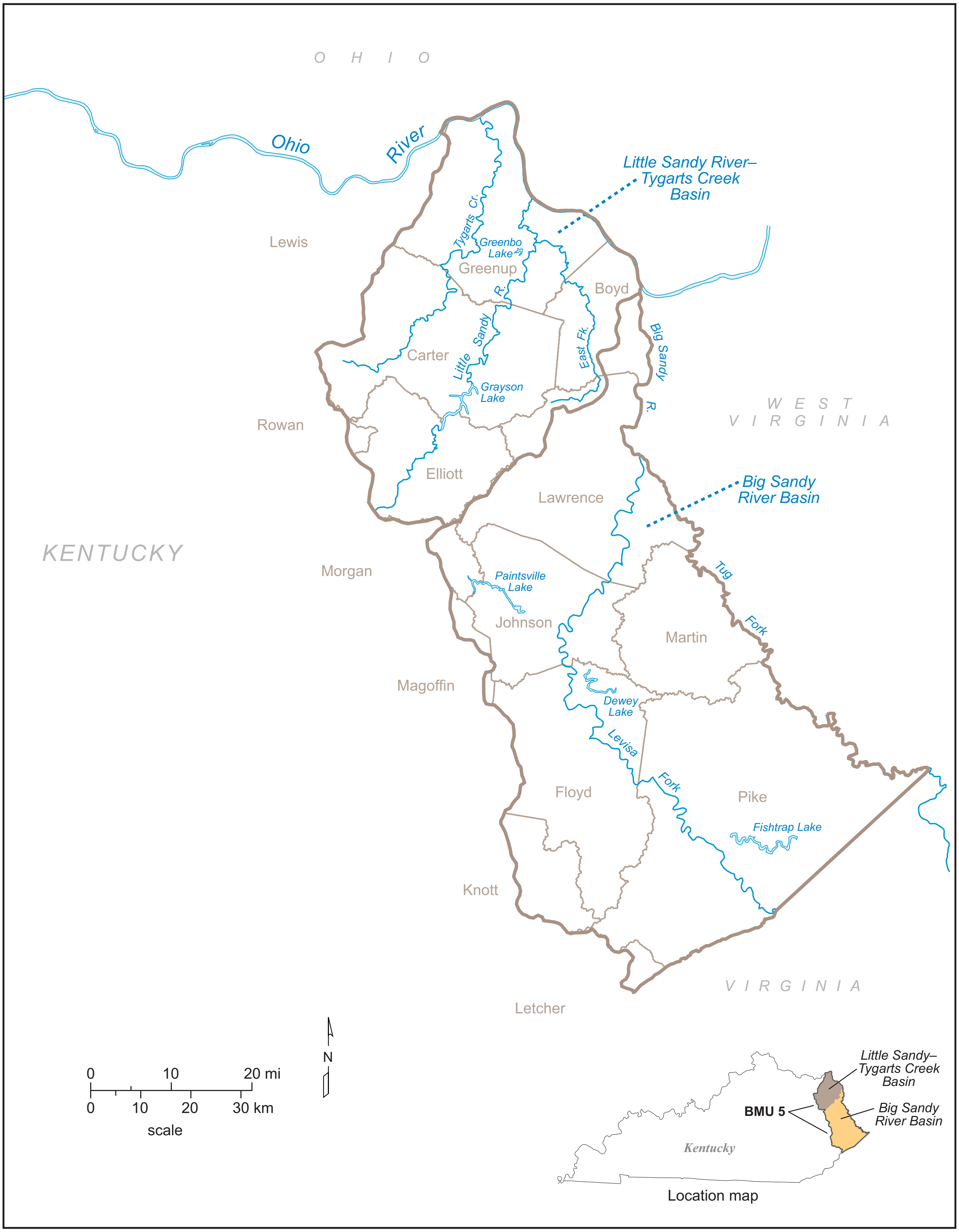

Figure 2. Major watersheds and counties in basin management unit 5.

Table 1. Watershed names and six-digit HUC designations for basin management unit 5.

Six-Digit HUC	HUC 6 Name	Area (mi²)
050702	Big Sandy River	2,290
050901	Tygarts Creek, Little Sandy River, Ohio River	2,320

Table 2. Watershed names and eight-digit HUC designations for basin management unit 5.

Eight-Digit HUC	HUC 8 Name	Area (mi²)
05070201	Big Sandy River	478
05070202	Upper Levisa Fork	359
05070203	Levisa Fork	1,116
05070204	Big Sandy River, Blaine Creek	337
05090103	Ohio River, Tygarts Creek	438
05090104	Little Sandy River	726

of vertical infiltration, the maximum potential flow velocity, and the potential for dilution by dispersion within the subsurface.

Ray and others (1994) concluded that the uppermost groundwater system is moderately sensitive to contamination in the Eastern Kentucky Coal Field, relative to the rest of the state. Groundwater sensitivity to nonpoint-source contamination generally decreases with depth because infiltration is slower and more tortuous, allowing for degradation and dilution of the chemicals; flow velocities are also slower, allowing for additional degradation of chemicals. And dispersion and dilution are greater because deep groundwater systems contain water from large recharge areas.

Local groundwater sensitivity may be very different from these regional assessments, but local conditions cannot be assessed in this regional summary. Well depth is an approximate indicator of whether a shallow, intermediate, or deep groundwater system is being sampled. Two factors limit the usefulness of well depth as an indicator of groundwater system, however. First, many wells have no depth recorded, are uncased throughout much of their length and thus collect water from various depths, or are drilled deeper than needed to serve as a water-storage system. Second, a shallow well may actually tap a deep groundwater flow system if the well is located near the discharge region of the groundwater flow system.

Methods

Site Selection

The groundwater sampling program is intended to represent the various physiographic, geologic, land-use, and demographic settings in the river basins. Resource limitations preclude drilling new wells; therefore, candidate sites were selected from existing wells and springs. The site selection process followed three steps.

1. Each 7.5-minute quadrangle in BMU 5 was assigned a number, and 30 numbers were drawn at random. To be eligible for selection, the center of each quadrangle had to fall within BMU 5. Quadrangles in which groundwater monitoring was currently being performed were not considered. If there were no suitable wells or springs in the selected quadrangle, an adjacent quadrangle was selected.
2. Within each selected quadrangle, potential sample sites were ranked according to type, use, condition, and accessibility. Large springs were preferred over wells because such springs collect water from large basin areas and are more sensitive to nonpoint-source pollution. Public wells or nonregulated public springs used for domestic purposes were chosen over private wells or wells used for livestock or irrigation. Springs protected from surface runoff and properly constructed wells were preferred to avoid sample contamination. Readily accessible springs and wells were selected over sites in remote locations or sites with limited access.
3. Final site selections were made only after field inspection to ensure that seasonal monitoring was feasible and after obtaining permission from owners. Sample sites are listed in Table 3.

Sample Collection

Samples were collected in the fall, winter, spring, and summer from November 2002 through September 2003. Conductance, temperature, and pH were measured at each site and recorded in a field log book.

Table 3. Sites used for monitoring.

Quadrangle	County	AKGWA[1]	Latitude	Longitude	Well Depth (ft)
Adams	Lawrence	0001-0545	38.068889	–82.665556	180
Argillite	Greenup	0003-2501	38.419862	–82.840755	100
Belfry	Pike	0003-2502	37.601577	–82.317562	80–100
Blaine	Lawrence	0004-6810	38.027778	–82.820000	105
Boltsfork	Boyd	0003-2503	38.258743	–82.710555	90–100
Burnaugh	Boyd	0003-2504	38.277265	–82.592570	170
Dorton	Pike	0003-2505	37.308668	–82.541591	50–60
Grahn	Carter	9000-2567	38.368571	–83.107085	spring
Grayson	Carter	0003-2506	38.272225	–82.906884	80
Inez	Martin	0005-0406	37.794139	–82.522083	90
Isonville	Elliott	0004-3781	38.070021	–83.121917	265
Jamboree	Pike	0003-2507 & 0001-8874	37.476373	–82.185014	102
Jenkins East	Pike	0003-2508	37.208845	–82569746	59
Kite	Knott	0003-2509	37.344662	–82.781904	35
Lancer	Floyd	0003-2510	37.659130	–82.644453	60
Martin	Floyd	0003-2511	37.505902	–82.781273	> 100
Mazie	Lawrence	0003-8804	38.003611	–82.896389	435(?)
Meta	Pike	0003-2512	37.612601	–82.411734	60
Millard	Pike	0003-2513	37.440980	–82.464534	35
Milo	Martin	0003-2514	37.935280	–82.533764	108
Offutt	Johnson	0001-2311	37.761111	–82.691389	75
Oil Springs	Johnson	0000-5743	37.801944	–82.891389	115
Olive Hill	Carter	9000-2570	38.303746	–83.202611	spring
Paintsville	Johnson	0003-2515	37.776712	–82.831102	103
Portsmouth	Greenup	0003-2516	38.636771	–82.941586	65
Redbush	Johnson	0003-2517	37.910626	–82.900877	160–180
Sitka	Lawrence	0003-2518	37.883641	–82.831211	120–125
Wayland	Knott	9000-2573	37.386964	–82.828231	mine
Wesleyville	Carter	0003-2521	38.435811	–83.138423	40
Willard	Carter	0003-2520	38.203626	–82.917586	98

Meters and electrodes were calibrated using standard buffer solutions and cleaned after each use according to manufacturers' specifications.

Samples for measurement of chemical constituents were collected and preserved as necessary for laboratory analysis. All materials that contacted the sample were either new, disposable equipment, or were decontaminated prior to and after each use. Sample containers were labeled with the site name and well or spring identification number, collection date and time, analysis requested, preservation method, and collector's initials.

Bacteria were not sampled for logistical reasons. Sample collection trips visited six to 12 sites over a 1- to 2-day period, commonly in remote regions. The short holding time for bacteria (6 hours for fecal coliform, 24 hours for total coliform) prohibited collecting aliquots for bacterial analysis and delivering them to a laboratory within the holding time, while maintaining sampling efficiency for all other parameters.

Duplicate samples were collected for at least 10 percent of all samples in order to check reproducibility and provide QA/QC control. One duplicate sample was submitted with each batch of samples. Field blanks of deionized water were collected, filtered, and preserved in the same manner as a sample and submitted once per quarter.

Sample containers, preservation methods, and holding-time requirements are outlined in the Kentucky Division of Water's "Standard Operating Procedures for Nonpoint Source Surface Water Quality Monitoring Projects," prepared by the Water Quality Branch. Sampling personnel completed a chain-of-custody record developed in conjunction with the Kentucky Division of Environmental Services laboratory for each sample. Specific sample-collection methods are documented in the project QA/QC plan, which was approved by the Division of Water before sampling began. The approved QA/QC plan is attached as Appendix A.

Sample Analysis

All samples were delivered to the Kentucky Division of Environmental Services laboratory for analysis. Major and minor inorganic solutes, dissolved and total metals, nutrients, pesticides, and volatile organic chemicals were determined according to EPA-approved laboratory procedures. The analytical results were entered into the Kentucky Department for Environmental Protection's Consolidated Groundwater Database and copied to the Kentucky Groundwater Data Repository at the Kentucky Geological Survey.

Data Analysis and Evaluation

Analytical results from both the current sampling program and from earlier investigations were combined for this report. Previous results of groundwater analyses were extracted from the Kentucky Groundwater Data Repository. The intent was to extract and summarize analyses of samples that were representative of regional groundwater quality, and to avoid reports from wells or springs that were known to be contaminated by local conditions. For this reason, samples collected for the Resource Conservation and Recovery Act, Solid Waste, or Underground Storage Tank regulatory programs were excluded. Even so, some of the values that were included in the resulting data sets may represent local or point-source contamination because there was nothing in the data reports to identify these samples as part of a regulatory program. Determining whether anomalous results are naturally occurring extreme values, inaccurate data entries, or the result of point-source pollution would require collecting and analyzing new samples from the site, which is beyond the scope of this project.

Analytical results from wells deeper than 1,000 ft were excluded because such deep wells are not generally used for domestic water supplies.

The following steps were taken to summarize and evaluate the analytical data.

1. **Query the repository database for reports of analyses.** Analytical reports were selected for groundwater-quality parameters that have recognized impacts on human health, determine the suitability of the water for domestic use, provide geochemical signatures that characterize the regional groundwater system, or record the impacts of nonpoint-source contaminants on groundwater. The parameters selected were:

   Water properties: pH, total dissolved solids, conductance, hardness, total suspended solids

   Inorganic anions: chloride, fluoride, sulfate

   Metals: arsenic, barium, iron, manganese, mercury

   Nutrients: ammonia, nitrate, nitrite, orthophosphate, total phosphate

   Pesticides: 2,4-D, alachlor, atrazine, cyanazine, metolachlor, simazine

   Volatile organic compounds: benzene, ethylbenzene, toluene, MTBE (methyl tertiary-butyl ether).

   Some of the analytes of interest have been reported under a variety of names, and not all analytical results are identified by unique CAS (Chemical Abstract Service registry) numbers, so queries were written to return all variations of the analyte name. For example, phosphorus measurements are reported as "orthophosphate," "orthophosphate-P (PO_4-P)," "phosphate," "phosphate-total," "phosphate-ortho," "phosphorus," "phosphorus-ortho," "phosphorus-total," "phosphorus-total by ICP," and "phosphorus-total dissolved." The results were inspected to ensure that each data set contained the appropriate chemical species. All reported analytical units were converted to milligrams per liter.

   Each sample site was assigned a six-digit HUC number and major watershed name so that the data could be grouped into these categories. GIS coverages of six-digit HUC's and watershed names were obtained from the KGS Web site (www.uky.edu/KGS/gis/intro.html).
2. **Delete records that do not provide useful information.** The U.S. Environmental Protection Agency has established maximum contaminant levels for many chemicals that present health risks. Some analytical results in the groundwater data repository were reported only as less than a detection limit, where the detection limit was greater than the MCL. These records do not provide useful data for this report and so were eliminated from the data sets.
3. **Count the number of analytical results and sample sites for each constituent.** Most wells and springs were sampled more than once, so several concentrations may have been reported for an analyte at a single site. The number of sites was determined by counting unique location identification numbers associated with the analytical records.
4. **Determine quartile values.** Water-quality data are generally positively skewed; that is, concentrations are not symmetrically distributed about a mean value and some values are extremely high. The combined effect of a non-normal distribution and extreme outlier values is that parametric statistical

measures such as mean and standard deviation do not adequately describe the data. Nonparametric statistical measures such as quartile values and interquartile range provide a better description of the data population (see, for example, Helsel and Hirsch, 1992).

The quartile values used in this report are:

zero quartile value: the minimum value; all other values are greater

first quartile value: the value that is greater than 25 percent of all values

second quartile value: the median value; greater than 50 percent of all values

third quartile value: the value that is greater than 75 percent of all values

fourth quartile value: the maximum value.

Maximum concentrations may be anomalous, but the median value and the interquartile range (range of values between the first and third quartile values, also equal to the central 50 percent of the data) provide an efficient summary of the data.

Many analytical results are “censored” data, reported as less than a detection limit rather than as an accurately measured concentration. The preferred treatment of censored data depends on the purpose of the analysis. For example, EPA has established guidelines for treating censored data in Resource Conservation and Recovery Act investigations (U.S. Environmental Protection Agency, 1992). The goals of this report are to summarize regional groundwater quality and to locate areas affected or threatened by nonpoint-source contamination. Therefore, censored data were treated as if the analyte concentration was equal to the detection limit, but the censored data were ranked below actual measurements at that value when quartile values were determined. For example, a value reported as less than a detection limit of 0.0004 mg/L was ranked below a measured value of 0.0004 mg/L and above a measured value of 0.0003 mg/L for quartile determination.

5. **Determine the number of sites at which measurements exceeded water-quality standards.** Because many samples may have been analyzed from a particular well or spring over time, the number of sites at which parameters exceed critical values is a better indicator of regional groundwater quality than the number of measurements that exceed those values. Water-quality standards were provided by the Division of Water (Table 4).
6. **Map site locations and show concentration ranges.** Maps show sample-site locations, site distribution, concentration ranges, and areas where concentrations exceeded MCL’s or other critical values. Maps also reveal whether analyte values were randomly distributed or were related to watersheds, physiography, or land use. Maps were generated using ArcView GIS 3.1. At the scale used in this report and depending on symbol size and shape, sites within a few thousand feet of each other may not be resolved as separate locations. Therefore, the maps show the locations of sites where various criteria are met or exceeded, but may not provide an accurate count of those sites. All maps are projected on NAD 83.
7. **Use summary tables, probability plots, and box-and-whisker diagrams to summarize the data and compare results between watersheds or other groupings.** Summary tables list the number of measurements and sites, quartile values, and the number of sites where concentrations exceeded critical values. Probability plots (cumulative data plots; Fig. 3) show values sorted from smallest to largest plotted versus percentage of the total number of analytical results. They provide an easy way to read percentile values, to identify extreme (outlier) values, and to answer questions such as: what is the probability that a new sample in this region will exceed a particular value? The cumulative data plots in this report exclude the highest 0.1 percent of the values so that extremely high values do not compress the display of the majority of the data. Therefore, probability plots may not show the absolute maximum value.

   Box-and-whisker diagrams (Fig. 4) show the median value and interquartile range, and illustrate how clustered or scattered the data are. The box extends from the first quartile value to the third quartile value, including the central 50 percent of the data. A center line or notches within the box show the median value. Whiskers extend from each edge of the box a distance of 1.5 times the interquartile range. Values that are more than 1.5 times the interquartile range are shown as squares; values that are more than 3.0 times the interquartile range above the third quartile value or below the first quartile value are shown as

Table 4. Parameters and water-quality standards used for data summaries.

	Parameter	Standard (mg/L unless otherwise noted)	Source
Water Properties	Conductance	10,000 µS	No MCL or SMCL; approximately corresponds to brackish water
	Hardness (calcium and magnesium)	Soft: 0–17 Slightly hard: 18–60 Moderately hard: 61–120 Hard: 121–180 Very hard: > 180	U.S. Geological Survey
	pH	6.5–8.5 pH units	SMCL
	Total dissolved solids	500	SMCL
	Total suspended solids	35	KPDES
Inorganic Ions	Chloride	250	SMCL
	Sulfate	250	SMCL
	Fluoride	4.0	MCL
Metals	Arsenic	0.010	MCL
	Barium	2.0	MCL
	Iron	0.3	SMCL
	Manganese	0.05	SMCL
	Mercury	0.002	MCL
Nutrients	Ammonia-nitrogen	0.110	DEP
	Nitrate-nitrogen	10.0	MCL
	Nitrite-nitrogen	1.0	MCL
	Orthophosphate-phosphorus	0.04	Texas surface-water standard
	Total phosphorus	0.1	NAWQA
Pesticides	2,4-D	0.07	MCL
	Alachlor	0.002	MCL
	Atrazine	0.003	MCL
	Cyanazine	0.001	HAL
	Metolachlor	0.1	HAL
	Simazine	0.004	MCL
Volatile Organic Compounds	Benzene	0.005	MCL
	Ethylbenzene	0.7	MCL
	Toluene	1.0	MCL
	Xylenes	10	MCL
	MTBE	0.050	DEP

MCL: Maximum contaminant level (U.S. Environmental Protection Agency). Concentrations higher than the MCL may present health risks.
SMCL: Secondary maximum contaminant level (U.S. Environmental Protection Agency). Concentrations greater than the SMCL may degrade the sight, smell, or taste of water.
NAWQA: National Water-Quality Assessment Program (U.S. Geological Survey). Higher concentrations may promote algal growth and eutrophication.
HAL: Health advisory level. Higher concentrations may have an impact on human health.
KPDES: Kentucky Pollution Discharge Elimination System. Standard set for water-treatment facilities.
DEP: Kentucky Department for Environmental Protection risk-based concentration. Higher concentrations may present health risks.

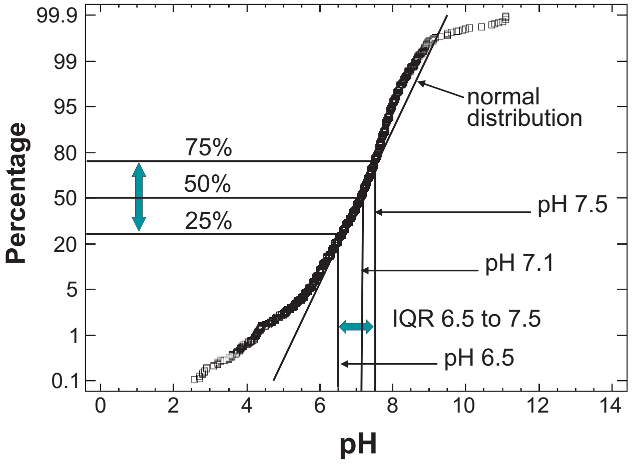

Figure 3. Example of a cumulative data plot, showing all pH values reported in Kentucky groundwater.

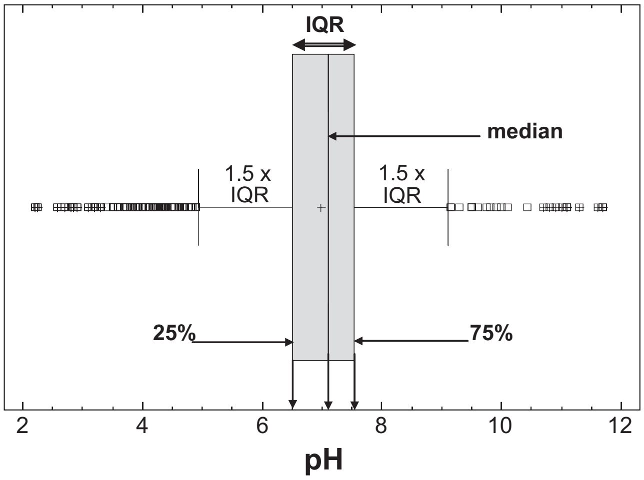

Figure 4. Example of a box-and-whisker plot showing all pH measurements reported in Kentucky groundwater.

squares with plus signs through them. The presence of far-outside points indicates suspect values or a highly skewed distribution. Probability plots and box-and-whisker plots were generated using Statgraphics Plus for Windows v. 4.1.

The approach for each analyte was:

1. Define the analyte; summarize natural sources, uses, and potential contaminant sources; list relevant water-quality criteria; and describe how excessive amounts affect water use and human health.
2. Summarize analytical results by constructing summary data tables and cumulative data plots.
3. Show sample-site distribution and sites where water-quality standards were met or exceeded on maps.
4. Summarize data for each watershed by constructing box-and-whisker plots.
5. Compare data by site type (wells versus springs) and sample type (total versus dissolved metals) by constructing box-and-whisker plots.

6. Evaluate the impact on shallow (less than 200 ft), intermediate (200 to 500 ft), and deep (greater than 500 ft) groundwater systems by plotting concentrations versus well depth.
7. Summarize probable causes of observed concentrations and distribution of values.

Results

Water Properties

pH. The parameter pH (negative base-10 logarithm of hydrogen ion activity in moles per liter) is one of the most fundamental water-quality parameters. It is easily measured, indicates whether water will be corrosive or will precipitate scale, determines the solubility and mobility of many dissolved constituents, and provides a good indication of the types of minerals groundwater has reacted with as it flows from recharge to sample site. For these reasons it is one of the most important parameters that describe groundwater quality.

The pH of neutral (neither acidic nor basic) water varies with temperature. For example, the neutral pH of pure water at 25°C (77°F) is 7.0. The neutral pH of pure water at 30°C (86°F) and 0°C (32°F) is 6.9 and 7.5, respectively (Hem, 1985). Solutes, including dissolved gases, also affect pH. Rain that has equilibrated with atmospheric carbon dioxide has a pH value of about 5.6 (Hem, 1985). Streams and lakes in humid regions such as Kentucky typically have pH values between 6.5 and 8. Soil water in contact with decaying organic material can have values as low as 4, and the pH of water that has reacted with iron sulfide minerals in coal or shale can be even lower. In the absence of coal and associated iron sulfide minerals, the pH of groundwater typically ranges from about 6.0 to 8.5, depending on the type of soil and rock contacted. Reactions between groundwater and sandstones result in pH values between about 6.5 and 7.5, whereas groundwater flowing through carbonate strata can have values as high as 8.4 (Hem, 1985).

There are no health-based drinking-water standards for pH. High or low pH values can lead to high dissolved concentrations of some metals for which there are drinking-water standards and associated health effects, however. Water with pH higher than 8.5 or lower than 6.5 can produce staining, etching, or scaling. Therefore, the U.S. Environmental Protection Agency has established a secondary maximum contaminant level for pH of 6.5 to 8.5.

The data repository contained 1,605 measurements from 262 sites (Table 5). Values from 89 sites did not meet SMCL criteria.

Table 5. Summary of pH values (standard units). SMCL=6.5 to 8.5.

Number of values	1,605
Maximum	10.4
75th percentile	7.4
Median	6.9
25th percentile	6.4
Minimum	2.6
Interquartile range	1.0
Number of sites	262
Number of sites < 6.5	87
Number of sites > 8.5	2

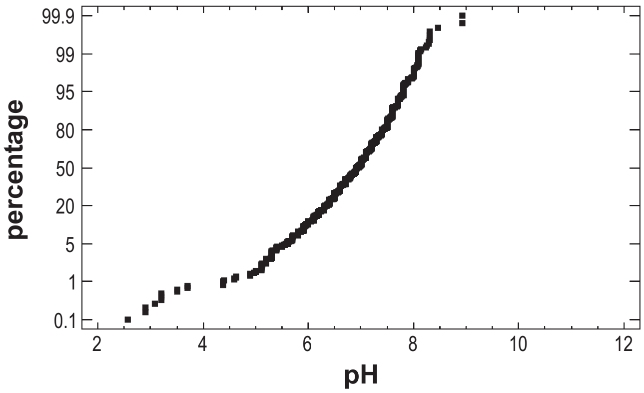

Figure 5. Cumulative plot of pH values. SMCL=6.5 to 8.5.

The cumulative data plot (Fig. 5) shows that more than 20 percent of the values were less than 6.5, but only two values were greater than 8.5.

Sampled sites were distributed fairly evenly through the project area (Fig. 6). Sites where pH values were less than 6.5 or greater than 8.5 were distributed throughout the area.

There was little difference in median values or interquartile ranges between the Big Sandy watershed and the Little Sandy River–Tygarts Creek watershed (Fig. 7). The highest pH values occurred in the Big Sandy watershed, whereas values less than 6.5 occurred in both watersheds.

There was little difference in median value or interquartile range of values between water from wells and springs; however, water from wells had a larger total range of values and more low pH values than water from springs (Fig. 8).

Shallow wells showed a greater range of pH values than deeper wells (Fig. 9). This is expected if the deeper groundwaters have equilibrated with bedrock, therefore restricting the range of pH values, whereas shallower groundwater systems have not.

In summary, within the project area, pH values ranged from 2.6 to 10.4. More than 75 percent of the values fell within the recommended range of 6.5 to 8.5.

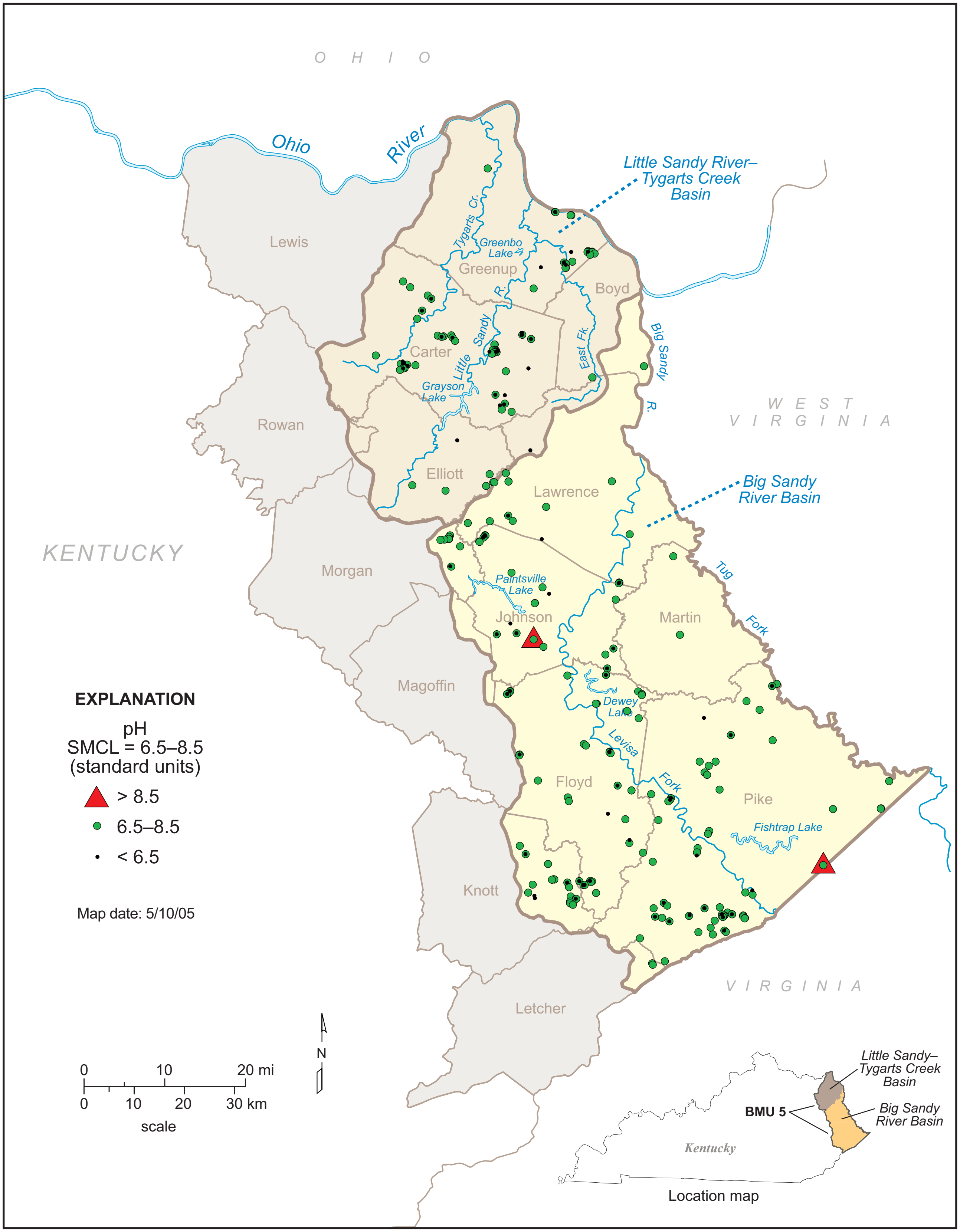

Figure 6. Locations of sampled sites and ranges of pH values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Sites that did not meet this criterion were distributed throughout the region and not concentrated in either watershed. Well water had a greater range of pH val-

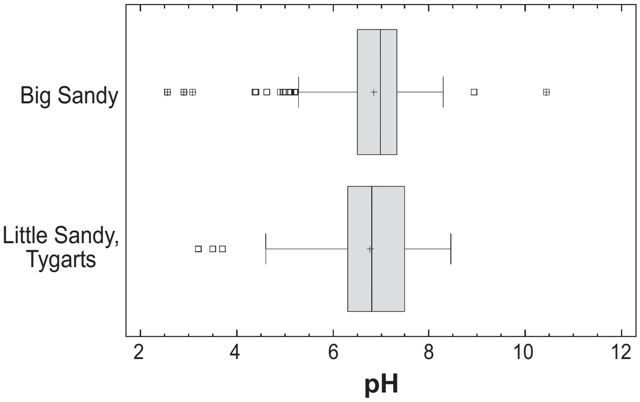

Figure 7. Summary of pH values grouped by watershed. SMCL=6.5 to 8.5.

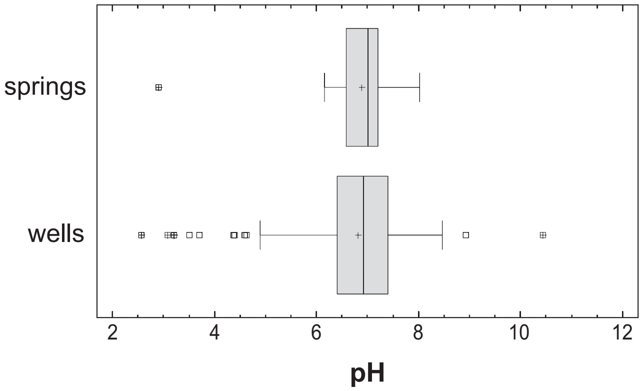

Figure 8. Comparison of pH values from wells and springs. SMCL = 6.5 to 8.5.

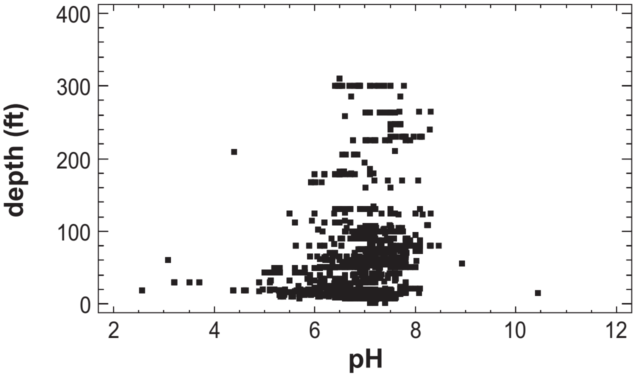

Figure 9. Well depth versus pH values. SMCL=6.5 to 8.5.

ues than water from springs; water from shallow wells showed a greater range of pH values than water from deeper wells. Some pH values less than 5.0 were very likely the result of acid mine drainage. There was no strong evidence that nonpoint-source chemicals have significantly affected pH in groundwater. A statewide summary of pH data is available (Fisher, 2002b) and can be viewed on the KGS Web site (kgsweb.uky.edu/olops/pub/kgs/ic06_12.pdf).

Total Dissolved Solids. Total dissolved solids is the sum of all dissolved chemicals in water, expressed as milligrams per liter. TDS can be measured as the weight of the residue remaining after a volume of water has been evaporated to dryness or calculated by adding all the solute concentrations from a full chemical analysis.

TDS values are a general indicator of the suitability of groundwater for various uses. One widely used classification for TDS values is the following (Mazor, 1991, p. 94–95):

Potable water: up to 500 mg/L

Slightly saline water: adequate for drinking and irrigation: 500–1,000 mg/L

Moderately saline water: potable only in cases of need; may be used for some crops and aquiculture: 1,000–2,500 mg/L

Saline water: adequate for aquiculture and industrial use: 2,500–5,000 mg/L

Brackish water: 5,000–35,000 mg/L (the salinity of seawater)

Brine: greater than 35,000 mg/L.

The EPA has set a secondary drinking-water standard of 500 mg/L for total dissolved solids. Water having TDS values greater than 500 mg/L typically has an unpleasant taste and may stain objects or precipitate scale.

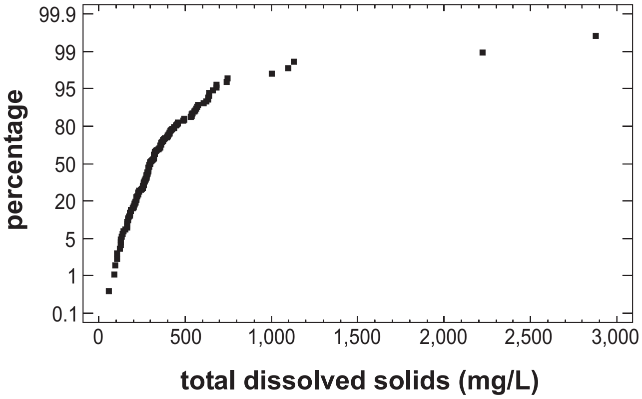

Figure 10. Cumulative plot of total dissolved solids values. SMCL=500 mg/L.

The data repository contained 145 reports of total dissolved solids from 62 sites in the project area (Table 6). The 75th percentile value was less than 500 mg/L. Only 19 of 62 sites yielded groundwater with more than 500 mg/L total dissolved solids.

More than 80 percent of all reported values were potable water (total dissolved solids less than 500 mg/L; Fig. 10).

Sites from which total dissolved solids values were reported were distributed throughout the project area, as were sites where water contained more than 500 mg/L of dissolved solids (Fig. 11).

There was little difference in median value or interquartile range of total suspended solids values between the Big Sandy and Little Sandy–Tygarts Creek watersheds (Fig. 12).

Groundwater from wells had a slightly higher median value of total dissolved solids than groundwater from springs (Fig. 13), and a slightly larger interquartile range of values.

Table 6. Summary of total dissolved solids values (mg/L). SMCL=500 mg/L.

Number of values	145
Maximum	2,880
75th percentile	414
Median	298
25th percentile	222
Minimum	60
Interquartile range	192
Number of sites	62
Number of sites > 500 mg/L	19

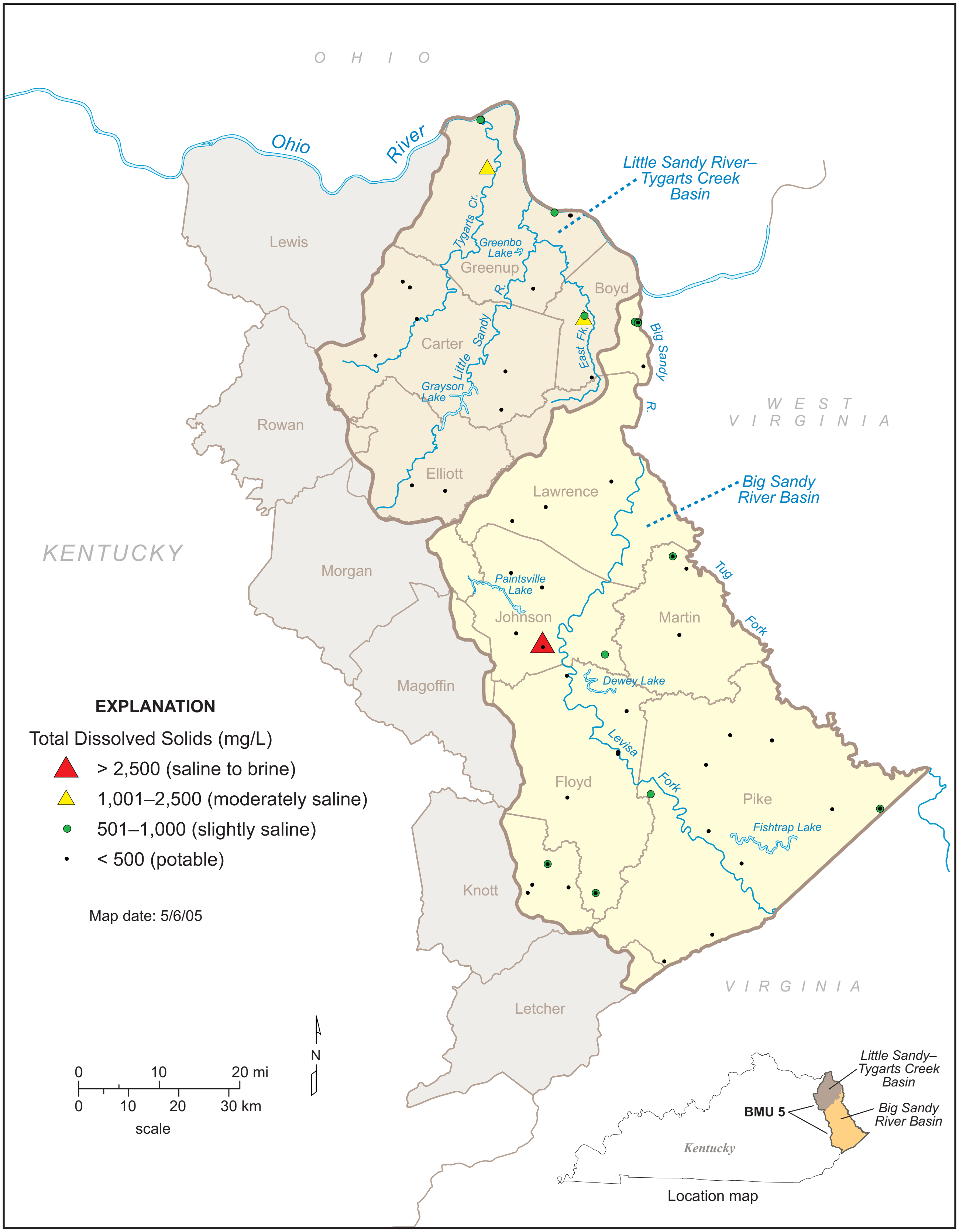

Figure 11. Locations of sampled sites and ranges of total dissolved solids values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

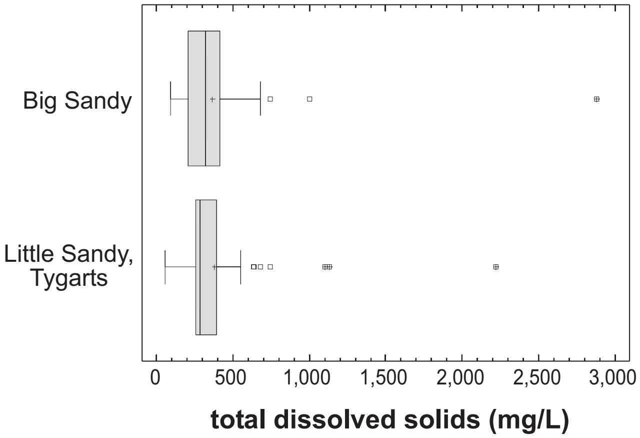

Figure 12. Summary of total dissolved solids values grouped by watershed. SMCL=500 mg/L. Higher values were excluded to better show the majority of the values.

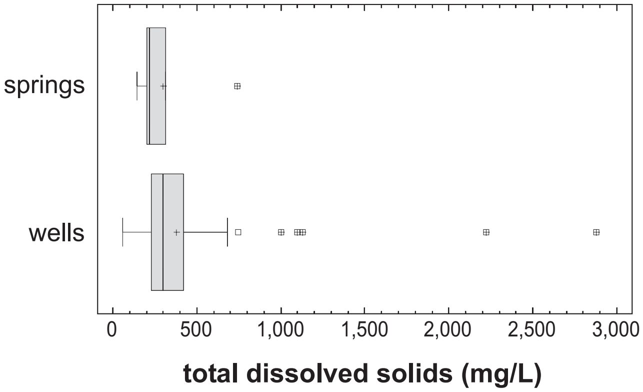

Figure 13. Comparison of total dissolved solids values from wells and springs. SMCL=500 mg/L.

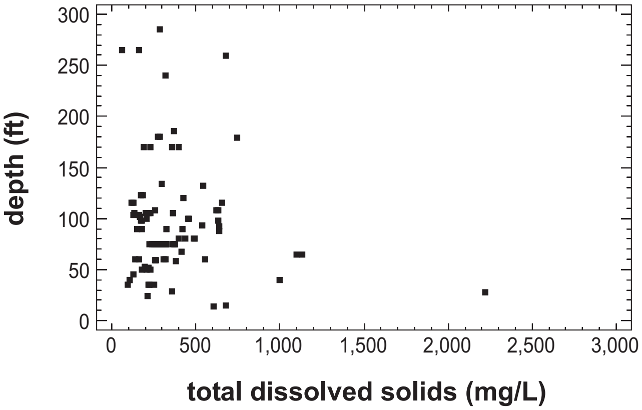

Figure 14. Total dissolved solids values versus well depth. SMCL=500 mg/L.

With the exception of a few high TDS reports from wells less than 75 ft deep, there was no systematic trend of total dissolved solids with well depth (Fig. 14).

In summary, approximately 70 percent of the sites in the project area yielded potable groundwater (total dissolved solids less than 500 mg/L). Sites where total dissolved solids values exceeded 500 mg/L were scattered throughout the area and not concentrated in either watershed. There was no evidence that nonpoint-source chemicals were strongly influencing regional trends in total dissolved solids values.

Specific Electrical Conductance. Specific electrical conductance, also referred to as conductivity, is a measure of the ease with which water conducts an electrical current. It is an indirect measure of water quality and is proportional to total dissolved solids concentrations. Specific electrical conductance is a quick and simple measurement to make in the field and provides a relative comparison of water quality if the samples being compared have nearly the same temperature and predominant cations and anions (for example, sodium and chloride, or calcium and bicarbonate).

Table 7. Summary of conductance values (µS/cm).

Number of values	2,154
Maximum	205,000
75th percentile	580
Median	325
25th percentile	195
Minimum	0
Interquartile range	385
Number of sites	1,048

Conductance is reported in micromhos per centimeter at 25°C, or the numerically equivalent microSiemens per centimeter (µS/cm) in the International System of Units (Hem, 1985). There are no health or water-use standards based on conductance because it does not directly indicate water quality.

The data repository contained 2,154 conductance measurements from 1,048 sites in the project area (Table 7). This large number of measurements was the result of the extensive field sampling program associated with the National Uranium Resource Evaluation project (Smith, 2001). Values ranged from 0 to 205,000 µS/cm.

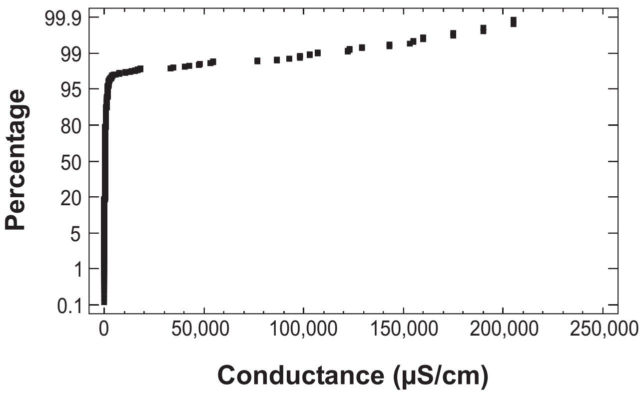

Figure 15. Cumulative plot of conductance values.

The data distribution showed a sharp break in slope at a value of about 500 µS/cm (Fig. 15), which suggests that two different populations were included in the data set. More than 95 percent of the reported values were less than 500 µS/cm.

Sample-site density is less in the northern part of the project area (Fig. 16) because sampling for the National Uranium Resource Evaluation program did not extend there. Conductance values greater than 10,000 µS/cm occurred predominantly in the central part of the Big Sandy watershed.

The Big Sandy River and Little Sandy River–Tygarts Creek watersheds produced groundwater with similar median values and interquartile ranges (Fig. 17). The total range of conductance values was also similar between the two watersheds.

The median conductance value, as well as the interquartile range of values, was similar for water from wells and from springs (Fig. 18). Water from wells showed the highest conductance values as well as the largest total range of values, however.

Most conductance values from wells were less than 5,000 µS/cm (Fig. 19). There was a sharp increase in conductance values in water deeper than 600 ft, however. This depth closely matches the depth of the freshwater–saline water interface mapped by Hopkins (1966) in the same area.

In summary, conductance is an indirect indicator of groundwater quality, related to salinity or total dis-

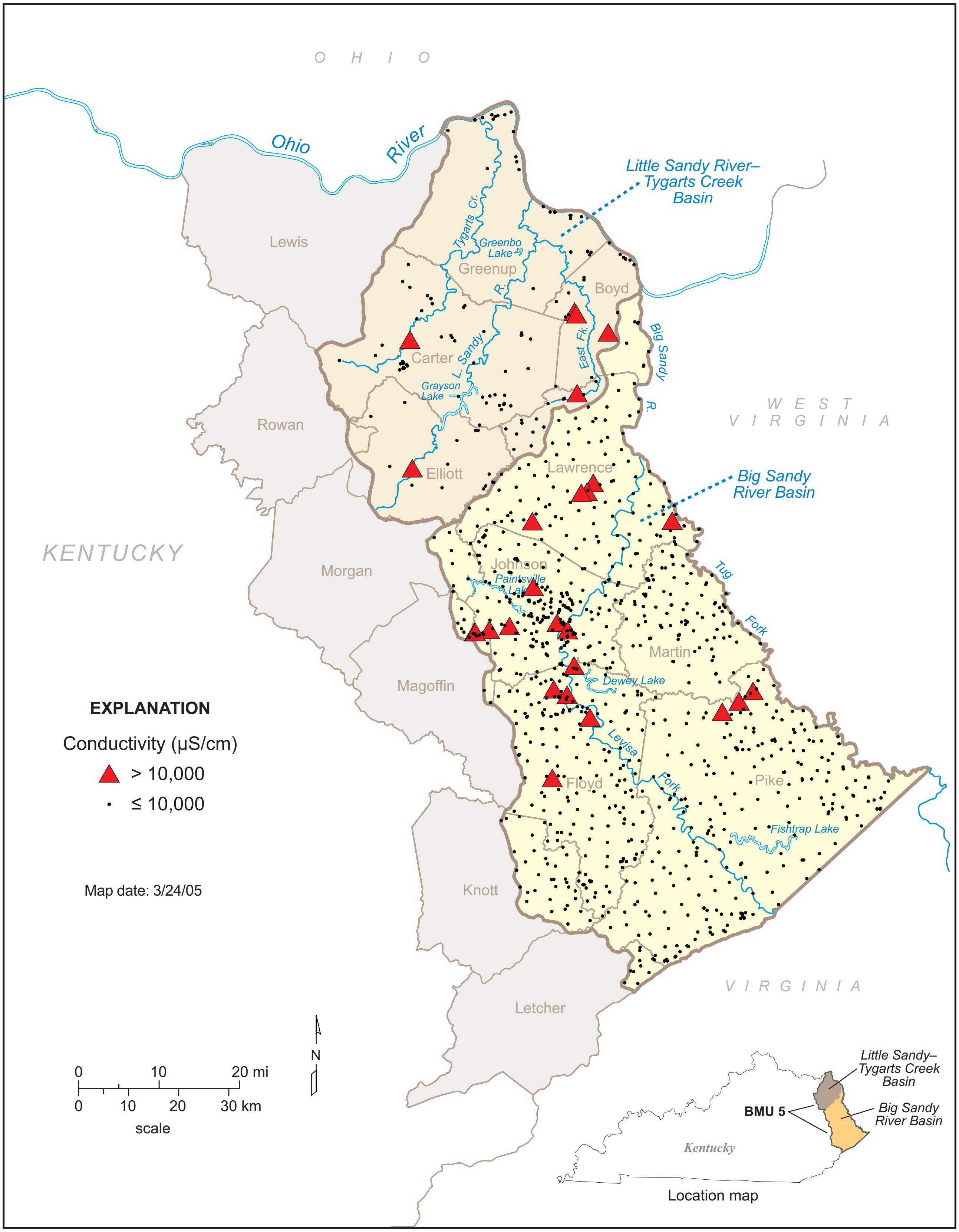

Figure 16. Locations of sampled sites and ranges of conductance values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

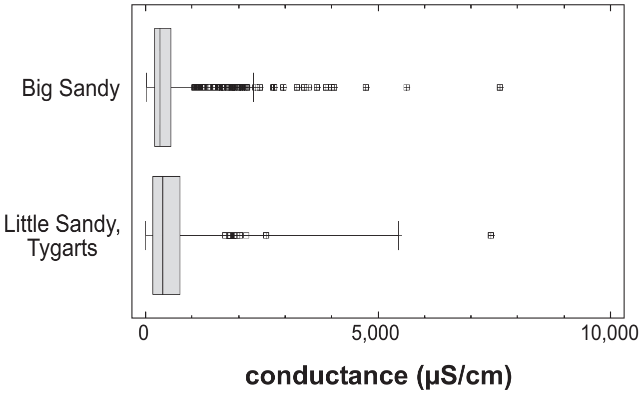

Figure 17. Summary of conductance values grouped by watershed. Higher values were excluded to better show the majority of the values.

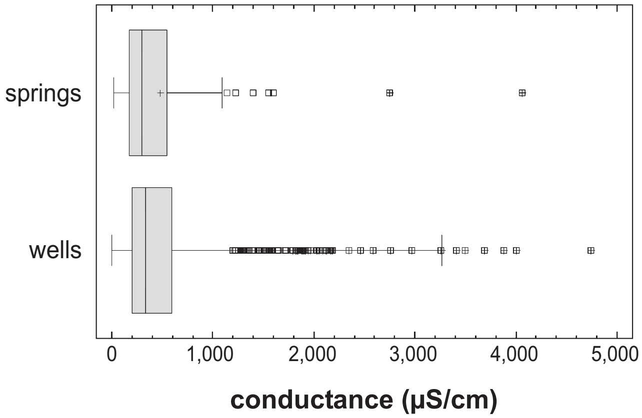

Figure 18. Comparison of conductance values from wells and springs. Higher values were excluded to better show the majority of the values.

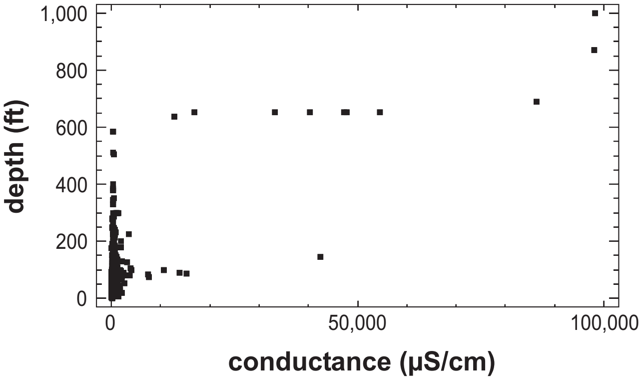

Figure 19. Conductance values versus well depth.

solved solids, but not a direct measure of either. There are no health-based standards or aesthetic effects directly associated with high conductance values. Conductance values were as high as 205,000 µS/cm in the project area. There is no systematic regional variation, however. More than 95 percent of the reported values were less than 5,000 µS/cm, and more than 98 percent of the reported values were less than 10,000 µS/cm. The highest conductance values reported in the project area were from wells deeper than 600 ft, where wells probably produce sodium chloride water. There was no strong indication of nonpoint-source effects on conductance values in the project area.

Hardness. Hardness describes the capacity of water to precipitate an insoluble residue when soap is used, and to form a scale on containers when water evaporates. Hard water reduces the ability of soap and detergents to clean clothes; leaves a sticky film on skin, clothes, and hair; and deposits scale in water heaters, boilers, and industrial equipment.

Table 8. Hardness classification of water supplies.

Hardness Category	Concentration (mg/L)
Soft	0–17
Slightly hard	18–60
Moderately hard	61–120
Hard	121–180
Very hard	> 180

Because calcium and magnesium are largely responsible for the behavior of soap in water, hardness is usually defined as the concentrations of calcium and magnesium expressed as an equivalent amount of calcium carbonate:

Table 9. Summary of hardness values.

Number of values	274
Number of sites	137
Sites with soft water (0–17 mg/L)	3
Sites with slightly hard water (18–60 mg/L)	23
Sites with moderately hard water (61–120 mg/L)	43
Sites with hard water (121–180 mg/L)	25
Sites with very hard water (> 180 mg/L)	43

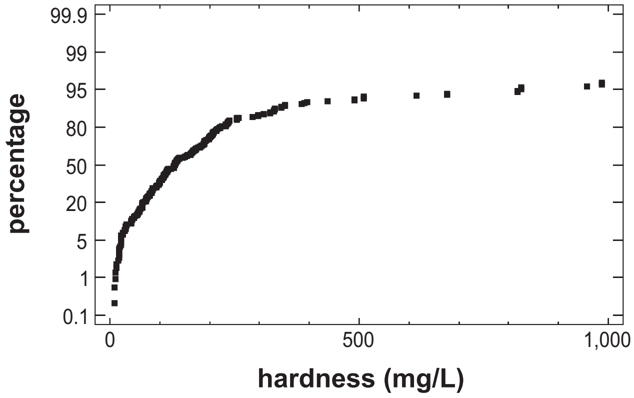

Figure 20. Cumulative plot of hardness values. Six values greater than 1,000 mg/L were excluded to better show the majority of the values.

$$\text{Hardness (mg/L calcium carbonate equivalent)}=2.5\ \text{Ca (mg/L)} + 4.1\ \text{Mg (mg/L)}.$$

Table 8 is a frequently used classification of hardness in water supplies (U.S. Geological Survey, 2006).

Calcium and magnesium concentrations for individual samples were combined according to the above equation to produce a total of 274 groundwater hardness values at 137 sites in the project area (Table 9). Soft to moderately hard water was found at 69 of 137 sites.

Approximately 50 percent of the reported values represent soft to moderately hard water (hardness less than 120 mg/L; Fig. 20).

The distribution of sampled sites was extremely uneven, most sites being in the southern part of BMU 5 (Fig. 21). Sites producing hard to very hard water were distributed throughout the Big Sandy watershed, and concentrated along the northeastern border in the Little Sandy–Tygarts Creek watershed.

Hardness values in the Big Sandy watershed had a lower median value and smaller interquartile range than values in the Little Sandy River and Tygarts Creek watersheds (Fig. 22).

All sampled sites were wells, so no comparison with groundwater from springs was possible. The hardest water was reported from wells deeper than 600 ft; three values from wells deeper than 600 ft exceeded 15,000 mg/L. Water ranging from soft (less than 17 mg/L) to very hard (greater than 180 mg/L) was found in wells between 0 and 200 ft deep (Fig. 23).

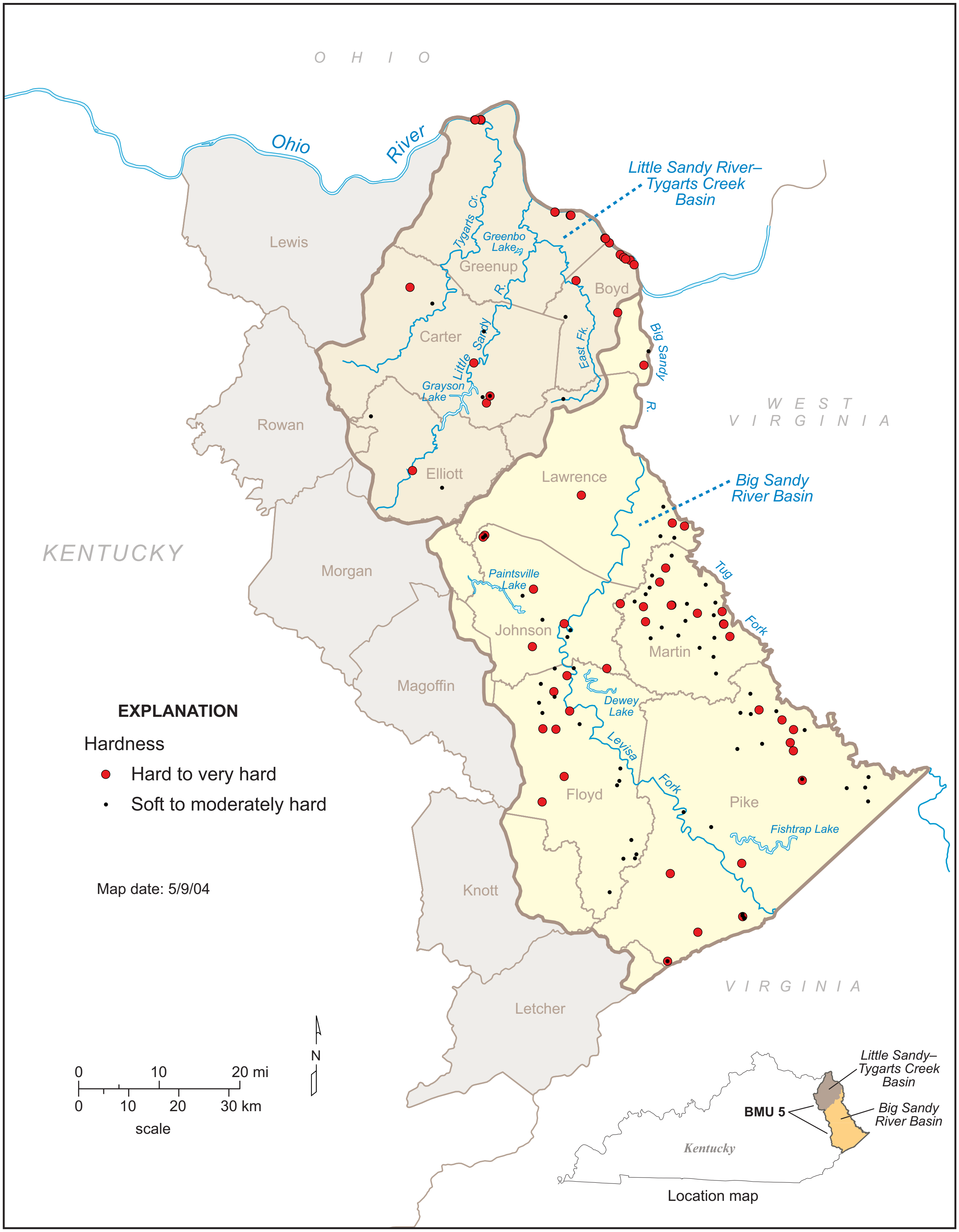

Figure 21. Locations of sampled sites and ranges of hardness values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

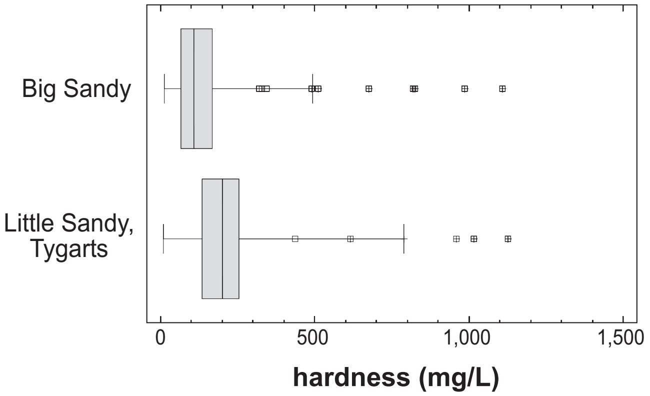

Figure 22. Summary of hardness values grouped by watershed. Higher values were excluded to better show the majority of the values.

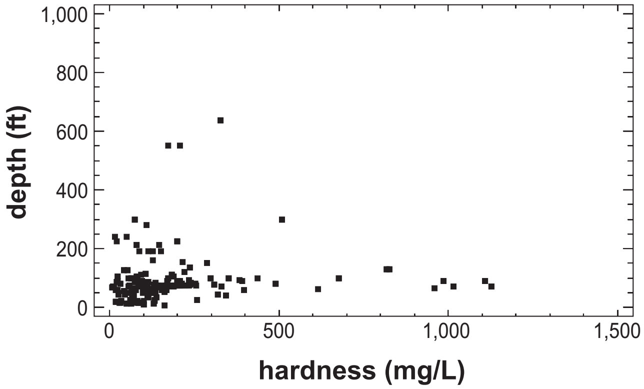

Figure 23. Hardness values versus well depth. Three values greater than 1,500 mg/L were excluded to better show the majority of the values.

In summary, approximately half the sampled sites produced soft to moderately hard water. A concentration of sites produced hard to very hard water along the northeastern border of the project area along the Ohio River, which resulted in the Little Sandy–Tygarts Creek watershed having a higher median hardness value than the Big Sandy watershed. Soft to very hard water was found in wells from a few tens of feet deep to 200 ft deep. Because hardness results from a combination of calcium and magnesium concentrations, no nonpoint-source impact was evident from the available data.

Total Suspended Solids. Particulate material is reported as total suspended solids. Total suspended solids values are typically higher in groundwater samples from karst springs, where turbulent water flow can transport fine material such as clays and particulate organic material, from uncased wells where the water has been vigorously stirred during purging prior to sample collection, or from wells that intercept a fracture or karst conduit with turbulent flow. TSS measurements also include any precipitate that formed in the sample bottle after collection.

There are no health or cosmetic standards for total suspended solids in water. Some metals and pesticides are preferentially sorbed onto suspended material, however, so water high in suspended solids may also contain significant amounts of metals, which may have health or safety implications. Also, high amounts of suspended material can clog plumbing systems and stain clothing and water containers. The Kentucky Pollution Discharge Elimination System recommends that TSS levels be less than 35 mg/L.

Table 10. Summary of total suspended solids values (mg/L). KPDES recommendation=< 35 mg/L.

Number of values	185
Maximum	125
75th percentile	5
Median	3
25th percentile	1
Minimum	< 1
Interquartile range	4
Number of sites	82
Number of sites > 35 mg/L	3

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

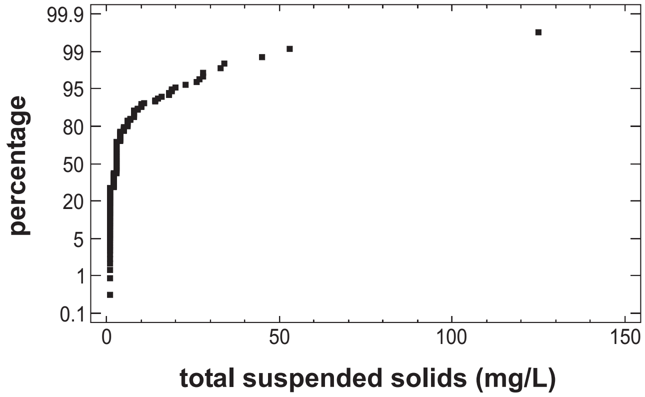

Figure 24. Cumulative plot of total suspended solids values. KPDES recommendation=< 35 mg/L.

The data repository contained 185 reports of total suspended solids from 82 sites (Table 10). Only three sites produced water that had more than 35 mg/L of suspended solids (Table 10, Fig. 24).

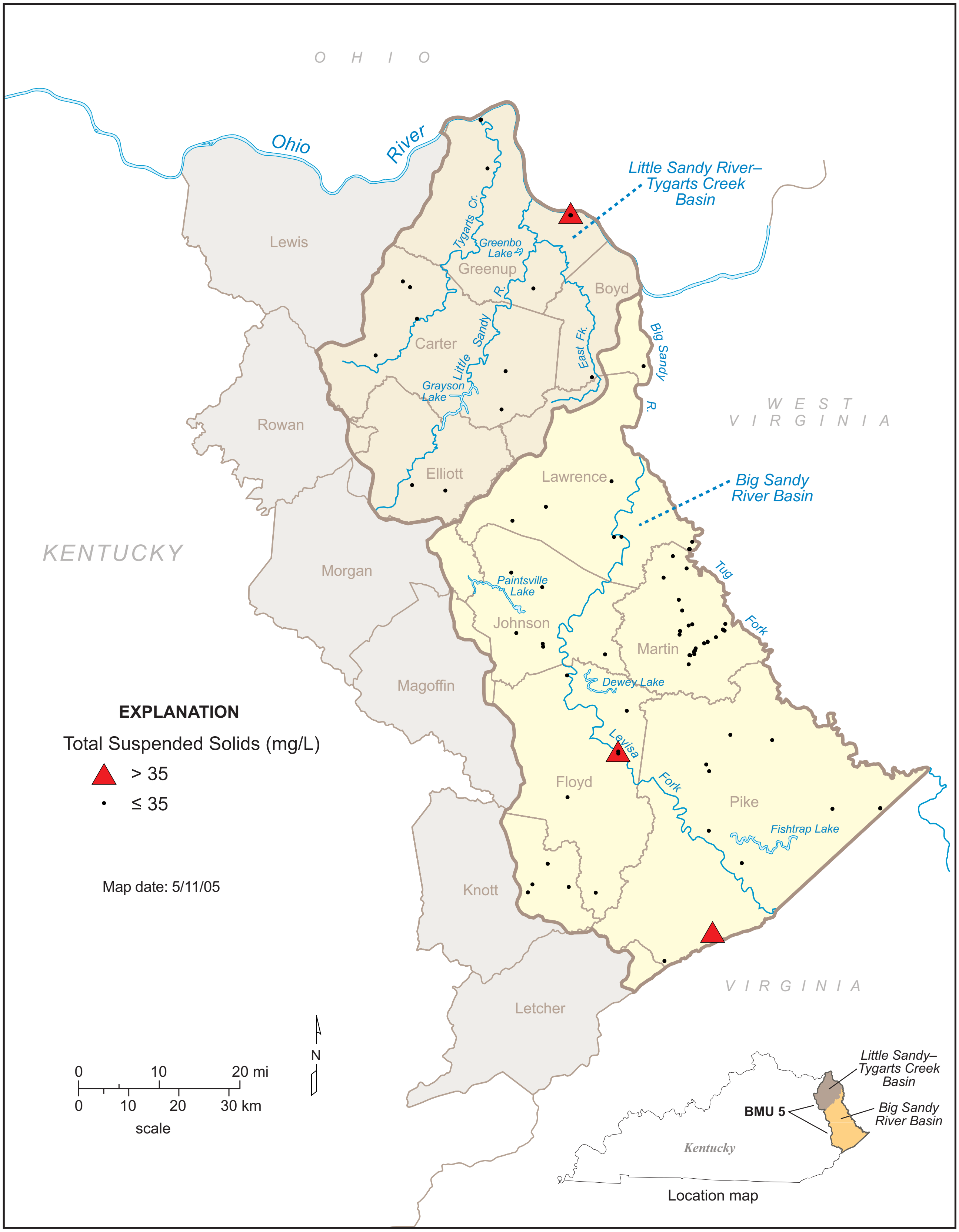

Figure 25. Locations of sampled sites and ranges of total suspended solids values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

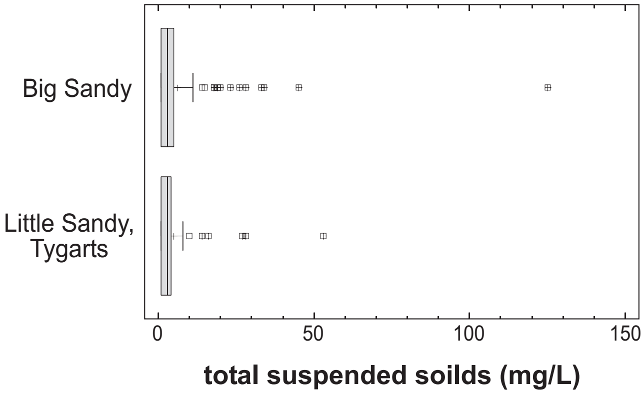

Figure 26. Summary of total suspended solids values grouped by watershed. KPDES recommendation=< 35 mg/L.

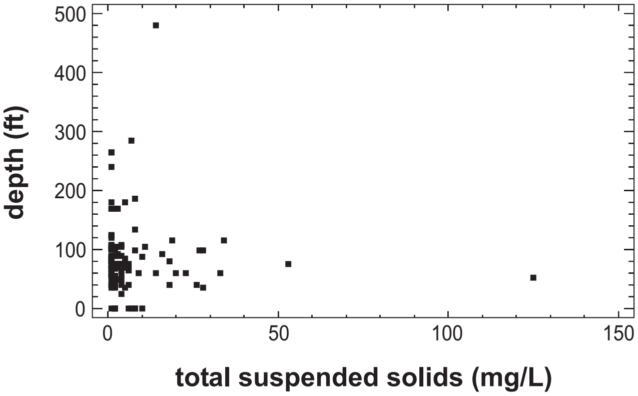

Figure 27. Total suspended solids values versus well depth. KPDES recommendation=< 35 mg/L.

Total suspended solids values were reported from relatively few sites in BMU 5 (Fig. 25). Only three sites produced water with more than 35 mg/L of total suspended solids.

The median value and range of values for total suspended solids was about the same in the two watersheds (Fig. 26).

Only four of the 82 sites were springs, so no valid comparison could be made between springs and wells.

The highest total suspended solids values occurred in shallow wells (Fig. 27).

In summary, total suspended solids refers to the amount of particulate material in a water sample. Values will be very low unless there is either turbulent flow to keep particles in suspension or dissolved solutes precipitate in the sample collection bottle. Large amounts of suspended solids can clog filters and stain clothing, but there are no health effects associated with particulate material. Total suspended solids values in BMU 5 groundwater were generally low, and there was no significant difference between the two watersheds. There was no evidence that nonpoint-source contamination has added particulate material to groundwater in the project area.

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.

Table 11. Summary of chloride concentrations (mg/L). SMCL=250 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 mg/L	69

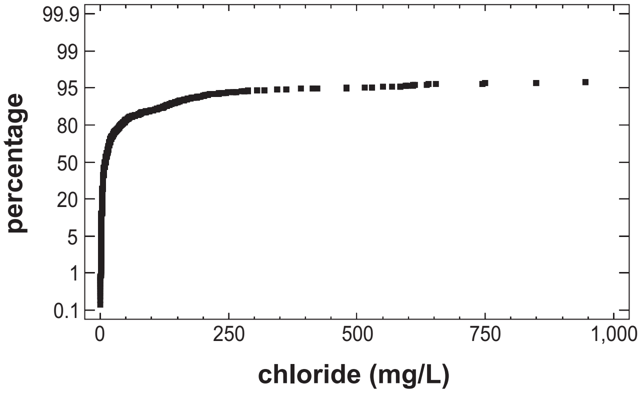

Figure 28. Cumulative plot of chloride concentrations. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.

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).

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.

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 con-

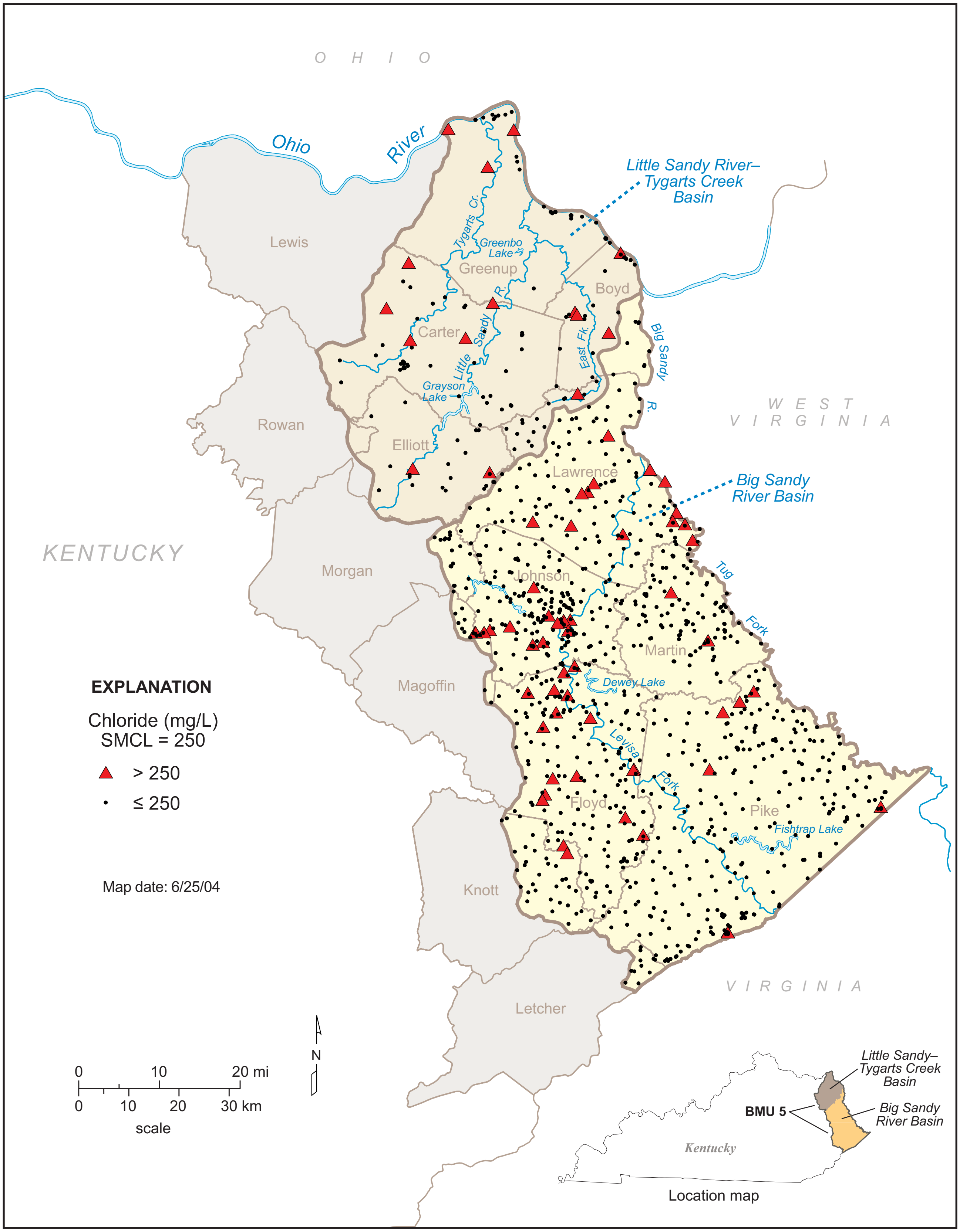

Figure 29. Locations of sampled sites and ranges of chloride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

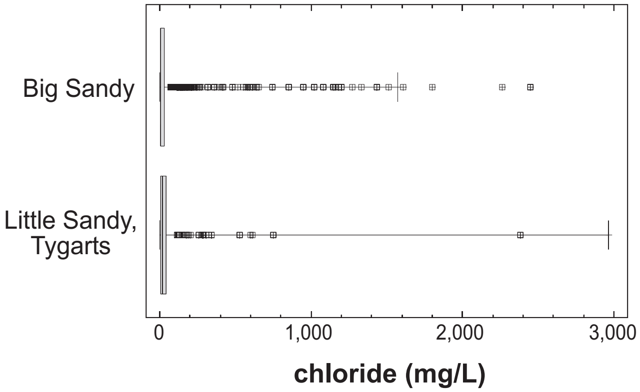

Figure 30. Summary of chloride concentrations grouped by watersheds. SMCL=250 mg/L. Higher values were excluded to better show the majority of the values.

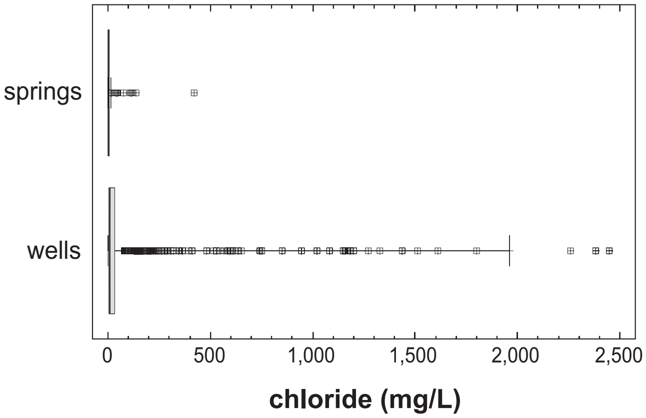

Figure 31. Summary of chloride concentrations from wells and springs. SMCL=250 mg/L. Higher values were excluded to better show the majority of the values.

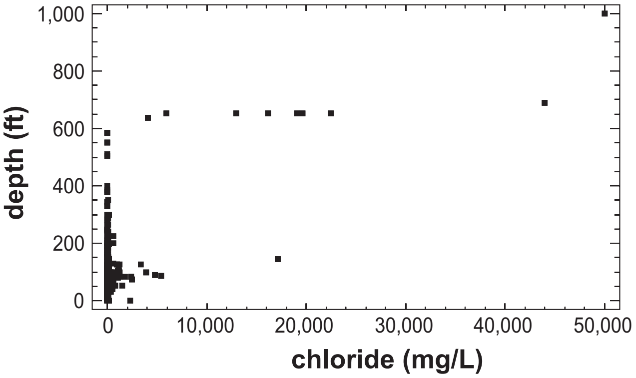

Figure 32. Chloride concentrations versus well depth. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.

ductance 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.

Table 12. Summary of sulfate concentrations (mg/L). SMCL=250 mg/L.

Number of values	3,146
Maximum	2,749
75th percentile	66.7
Median	26.8
25th percentile	7
Minimum	0
Interquartile range	59.7
Number of sites	752
Number of sites > 250 mg/L	76

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.

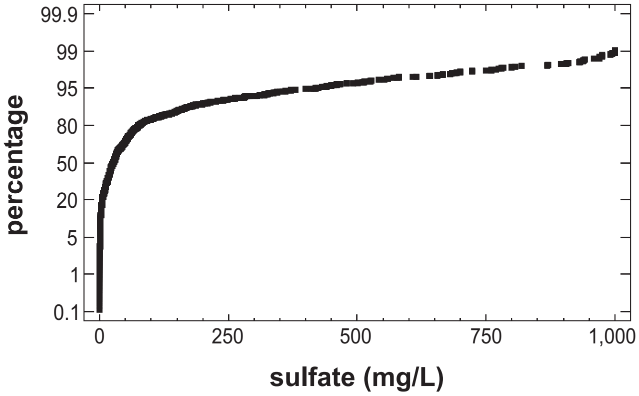

Figure 33. Cumulative plot of sulfate concentrations. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.

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.

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 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

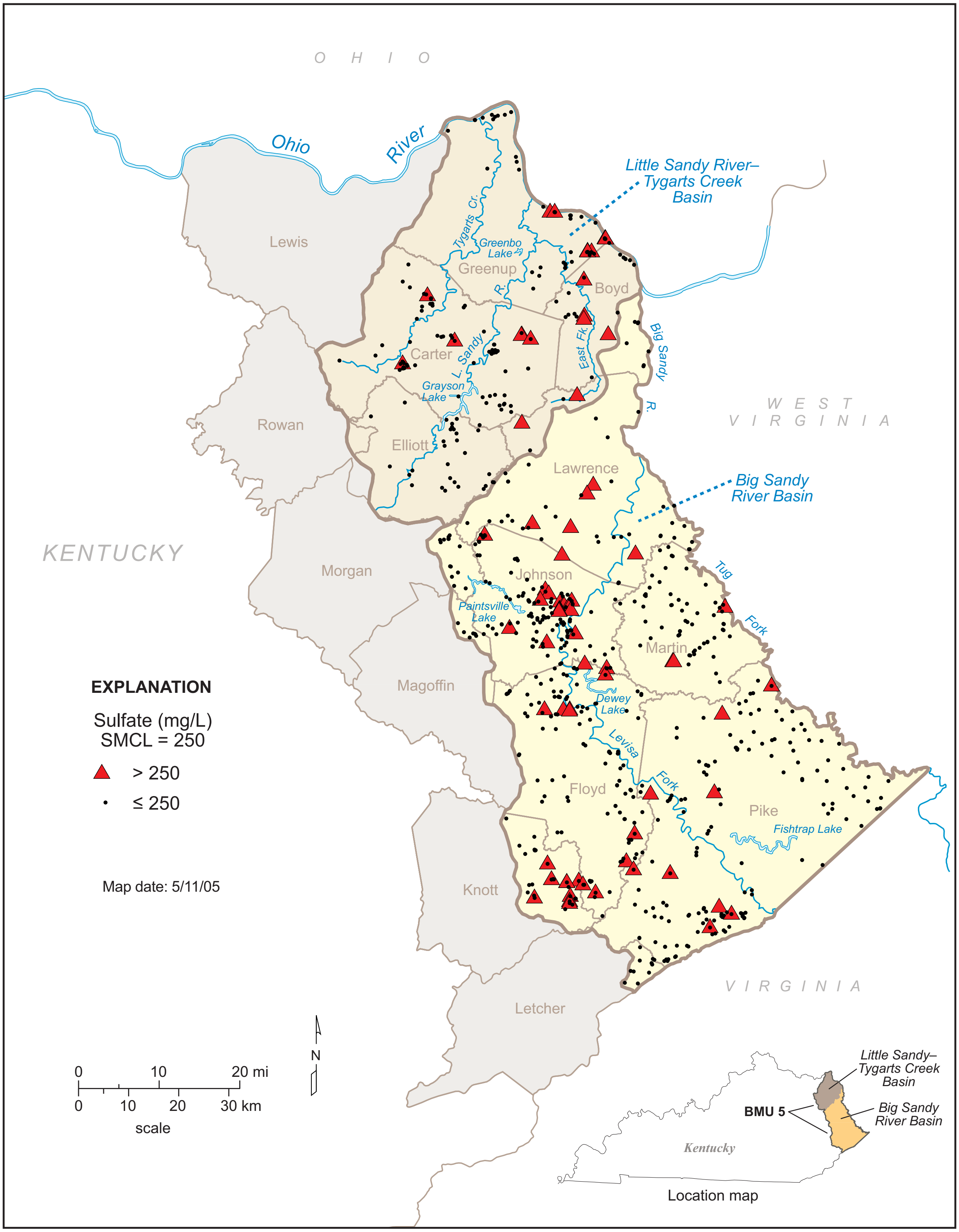

Figure 34. Locations of sampled sites and ranges of sulfate values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

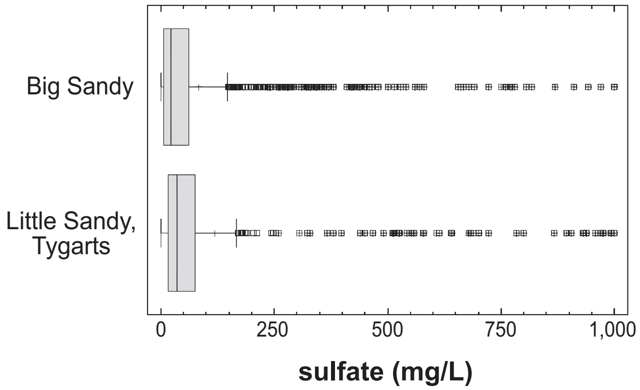

Figure 35. Summary of sulfate concentrations grouped by watershed. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.

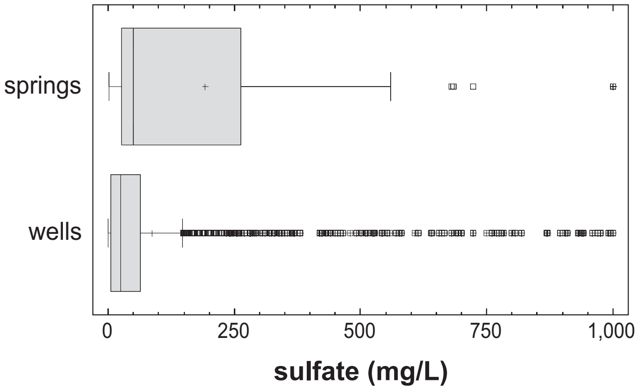

Figure 36. Summary of sulfate concentrations from wells and springs. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.

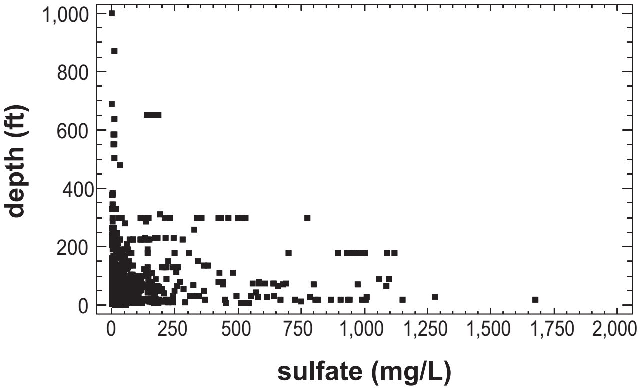

Figure 37. Sulfate concentrations versus well depth. Higher values were excluded to better show the majority of the values. SMCL=250 mg/L.

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.

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.

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

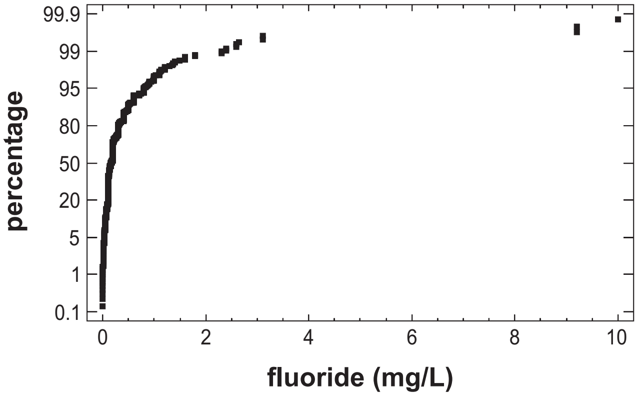

Figure 38. Cumulative plot of fluoride concentrations. MCL = 4.0 mg/L.

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).

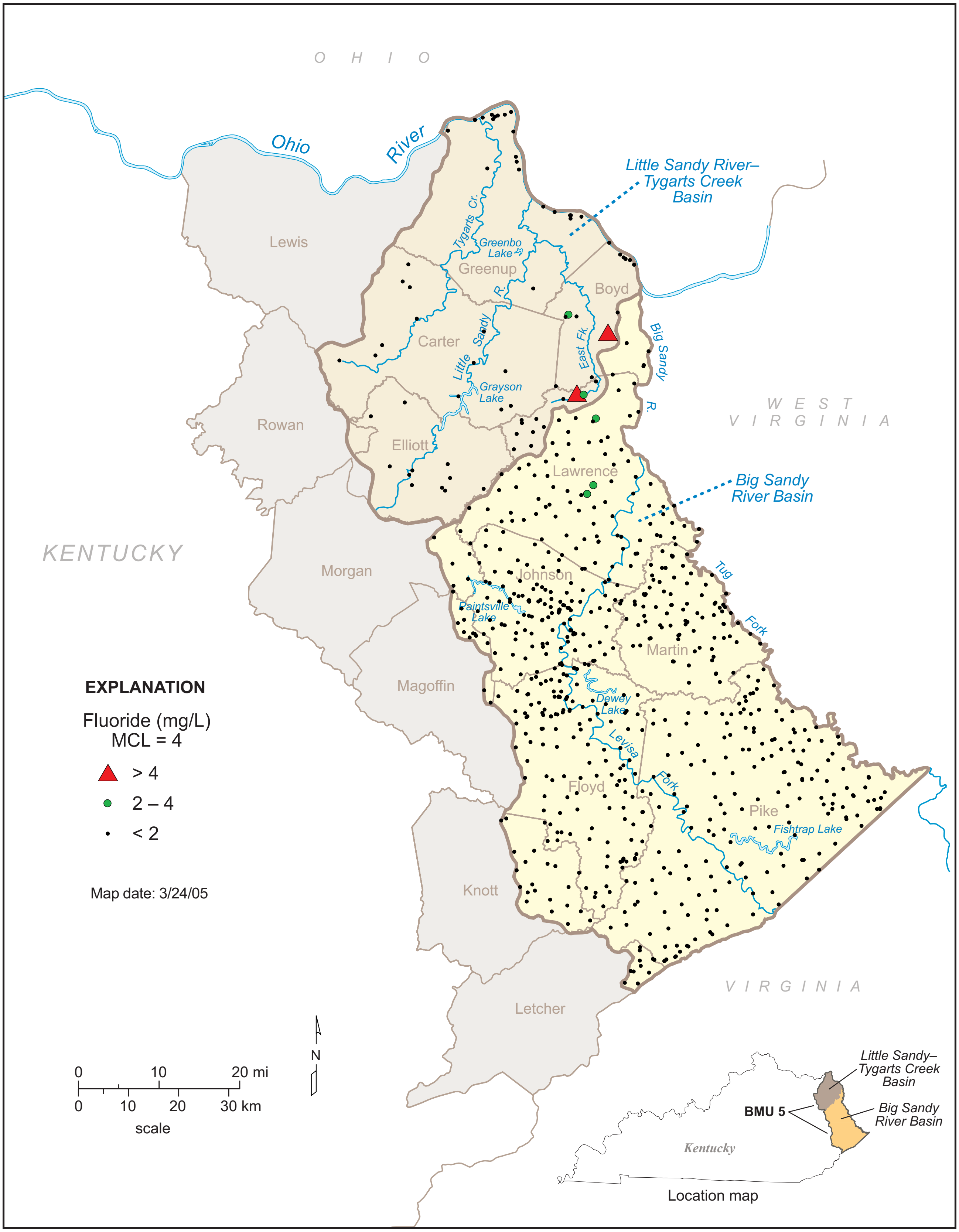

Figure 39. Locations of sampled sites and ranges of fluoride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

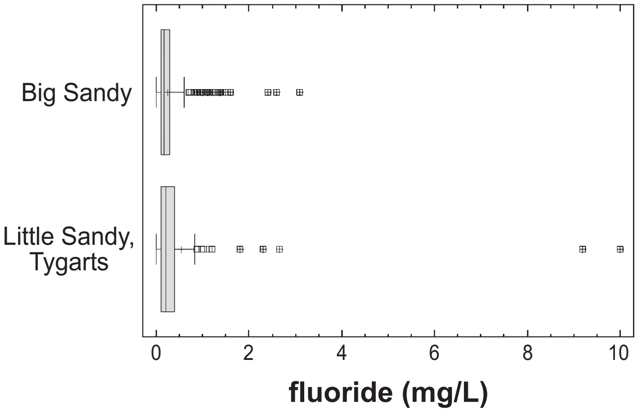

Figure 40. Summary of fluoride concentrations grouped by watershed. MCL=4.0 mg/L.

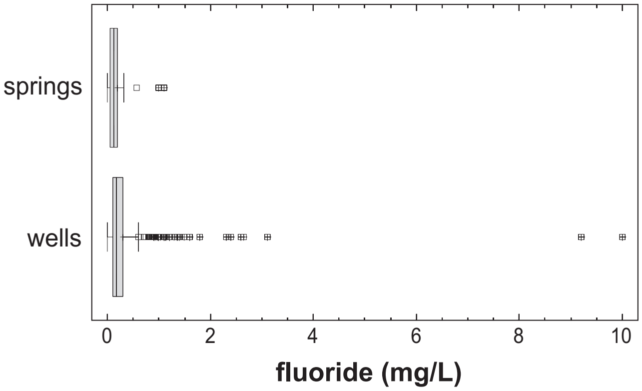

Figure 41. Summary of fluoride concentrations from wells and springs. MCL=4.0 mg/L.

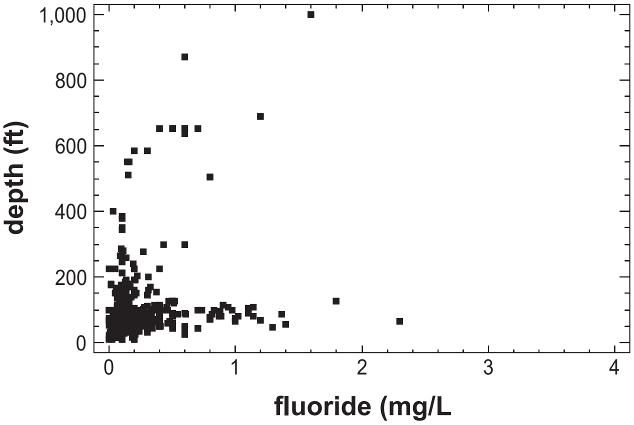

Figure 42. Fluoride concentrations versus well depth. Higher values were excluded to better show the majority of the values. MCL=4.0 mg/L.

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).

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).

Metals

Arsenic. Arsenic (As) is a naturally occurring element found in low concentrations in rocks, soils, water, plants, and animals (Nriagu, 1994a, b). In Kentucky, arsenic is commonly found in pyrite or arsenopyrite minerals associated with coal deposits and black shales. Arsenic is released when iron sulfides oxidize during weathering. Once released, arsenic is readily sorbed onto iron oxides and iron oxyhydroxides. This sorption can limit dissolved arsenic concentrations in groundwater, but produce high arsenic concentrations in unfiltered groundwater samples that contain suspended particulate material (total arsenic concentrations).

Arsenic is used as a wood preservative and in paints, dyes, metals, drugs, soaps, semiconductors, animal feed additives, and herbicides. From 1860 through 1910, arsenic was heavily used in embalming fluids. It was banned in 1910 because it interfered with investigations into suspected poisoning deaths, but old graveyards may still be a source of arsenic in groundwater (Fetter, 1993). Waste-disposal sites and landfills may be sources of arsenic contamination because of the materials disposed of there, and coal burning can release arsenic to the atmosphere. Hydrocarbons from leaking underground storage tanks can dissolve iron oxide minerals in soils, thus releasing naturally occurring arsenic to the environment (Welch and others, 2000). Metal-reducing bacteria, as well as changes in oxidation conditions as a result of pumping, also can affect arsenic concentrations in the vicinity of a well.

Long-term exposure to arsenic in drinking water has been linked to health problems such as cancer of the skin, bladder, lungs, kidneys, nasal passages, liver, and prostate. Arsenic has also been linked to damage of the cardiovascular, pulmonary, immunological, neurological, and endocrine systems. Because of these health effects, the U.S. Environmental Protection Agency set the maximum contaminant level for arsenic in drinking water at 50 ppb (or 0.05 mg/L) in 1974. In 2001, the EPA announced that this MCL would be lowered to 10 ppb (0.01 mg/L). Water-supply systems were required to meet the new MCL beginning January 2006.

Table 14. Summary of arsenic concentrations (mg/L). MCL=0.01 mg/L.

Number of values	290
Maximum	0.038
75th percentile	< 0.002
Median	< 0.002
25th percentile	< 0.002
Minimum	< 0.0005
Interquartile range	na
Number of sites	106
Number of sites > 0.01 mg/L	5

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

Sites identified as monitoring wells by the Kentucky Division of Water's well-identification number system were excluded from the data set used here because, although not explicitly identified as part of an underground storage tank investigation, these wells may have been installed to check for leaking hydrocarbon storage tanks. Because hydrocarbons can dissolve iron oxides from soils, arsenic results from these sites may not represent regional background conditions.

Because the new MCL is 0.01 mg/L, measurements that had a detection limit greater than 0.01 mg/L provided no useful information and were not included in the following discussion. Removing these

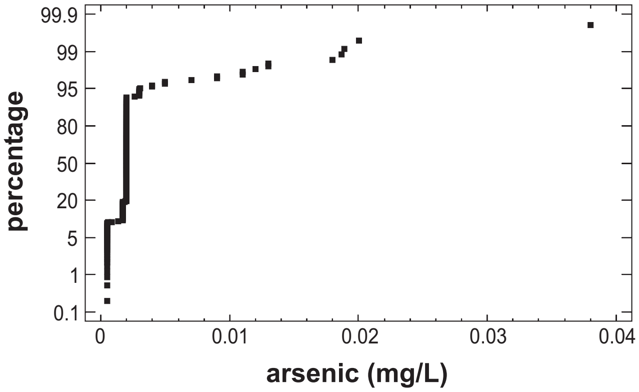

Figure 43. Cumulative plot of arsenic concentrations. MCL=0.01 mg/L.

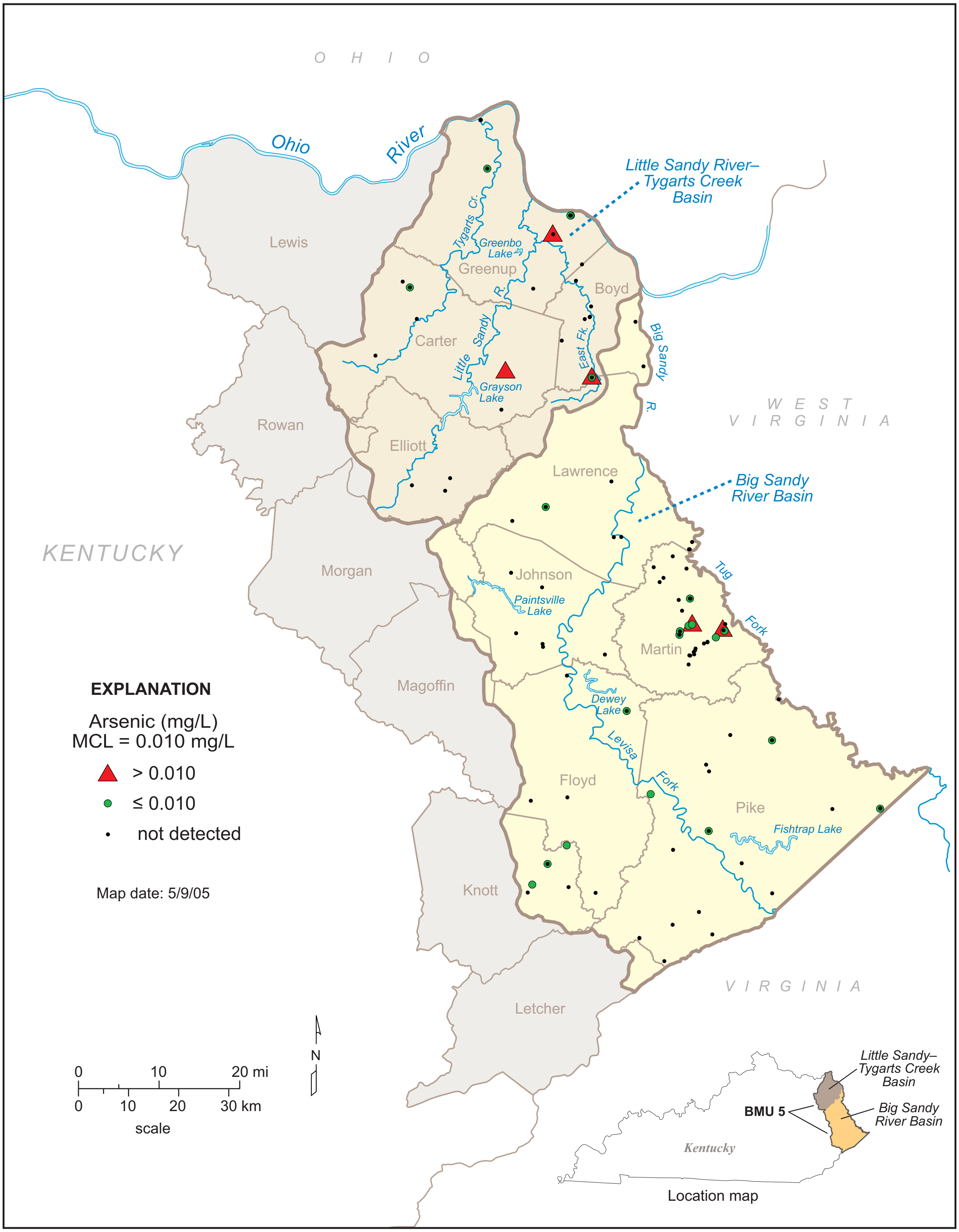

Figure 44. Locations of sampled sites and ranges of arsenic values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

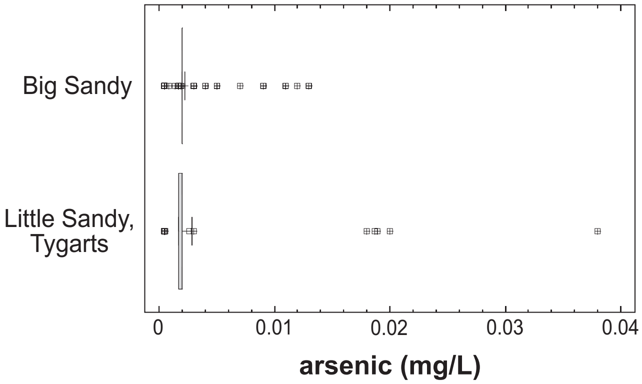

Figure 45. Summary of arsenic concentrations grouped by watershed. MCL=0.01 mg/L.

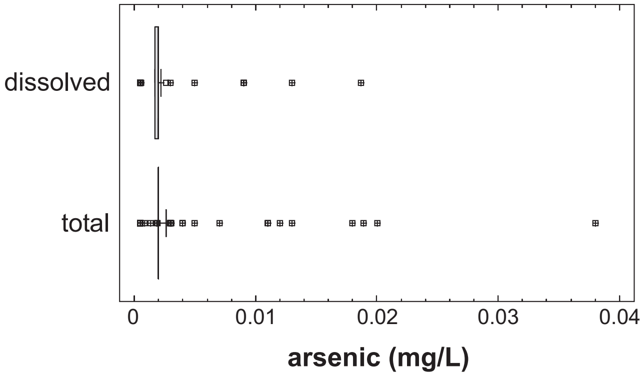

Figure 46. Comparison of total and dissolved arsenic concentrations. MCL=0.01 mg/L.

measurements left a total of 290 reported arsenic concentrations at 106 sites (Table 14). Eighty-six percent of the values were reported as less than analytical detection. Only 10 values from five sites exceeded the MCL (Fig.43).

Sites where arsenic was measured were spread throughout the project area (Fig. 44). Sites where groundwater exceeded the MCL for arsenic were not concentrated in any particular part of BMU 5.

The median arsenic value and interquartile range were nearly the same for both watersheds (Fig. 45); however, the range of concentrations in the Little Sandy–Tygarts Creek watershed was larger.

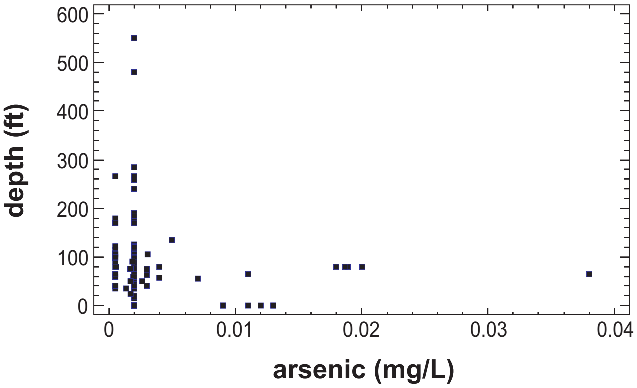

Figure 47. Arsenic concentrations versus well depth. MCL=0.01 mg/L.

Total (unfiltered sample) and dissolved (filtered sample) arsenic concentrations had about the same distribution of values (Fig. 46), indicating that significant amounts of arsenic were not adsorbed on suspended material in the project area.

Only nine of the 290 measurements were from springs; therefore, no valid comparison of concentrations in springs and wells could be made.

The highest arsenic concentrations were found in wells less than about 100 ft deep (Fig. 47).

In summary, arsenic was below analytical detection limits in groundwater at most sites in BMU 5. Of the measurements that were above analytical detection, arsenic exceeded the MCL at only five of 106 sites. Nonpoint-source contamination with respect to arsenic in groundwater therefore does not seem to be occurring in the project area. A statewide summary of arsenic data (Fisher, 2002a) can be viewed on the KGS Web site (kgsweb.uky.edu/olops/pub/kgs/ic05_12.pdf).

Table 15. Summary of barium concentrations (mg/L). MCL=2.0 mg/L.

Number of values	430
Maximum	100.0
75th percentile	0.59
Median	0.16
25th percentile	0.04
Minimum	0.00
Interquartile range	0.55
Number of sites	167
Number of sites > 2.0 mg/L	8

Barium. Barium (Ba) is an alkaline earth element that occurs naturally as the mineral barite ($BaSO_4$), which is common in both sandstone and carbonate strata. Barium is used in electronic components, metal alloys, bleaches, dyes, fireworks, ceramics, and glass, and as an additive to drilling fluids used in oil and gas wells. Barium may be released to soil and water from the discharge of drilling waste or from leaking landfills where barium-containing materials were discarded.

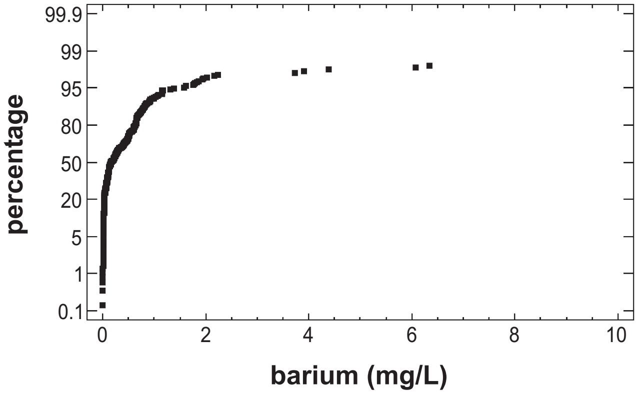

Figure 48. Cumulative plot of barium concentrations. Nine values greater than 10 mg/L were excluded to better show the majority of the values. MCL=2 mg/L.

The EPA has set the MCL for barium at 2 mg/L. Short-term exposure to higher barium concentrations can cause gastrointestinal distress and muscular weakness, whereas long-term exposure can cause high blood pressure.

The data repository contained 430 barium measurements from 167 sites in BMU 5 (Table 15). Only eight of 167 sites yielded groundwater that had more than 2 mg/L of barium. Although the maximum value was quite high, only 4 percent of all measurements exceeded 2.0 mg/L (Fig. 48).

Sampled sites were evenly distributed throughout BMU 5 (Fig. 49). Most of the sites where barium exceeded 2 mg/L were found in the Big Sandy watershed, however.

Barium concentrations from the Big Sandy watershed had a higher median value, a larger interquartile range, and more values that exceeded 2 mg/L than concentrations from the Little Sandy–Tygarts Creek watershed (Fig. 50).

Barium concentrations in total (unfiltered) samples had nearly the same median value and interquartile range as concentrations from dissolved (filtered) samples, indicating that barium is not associated with suspended material (Fig. 51).

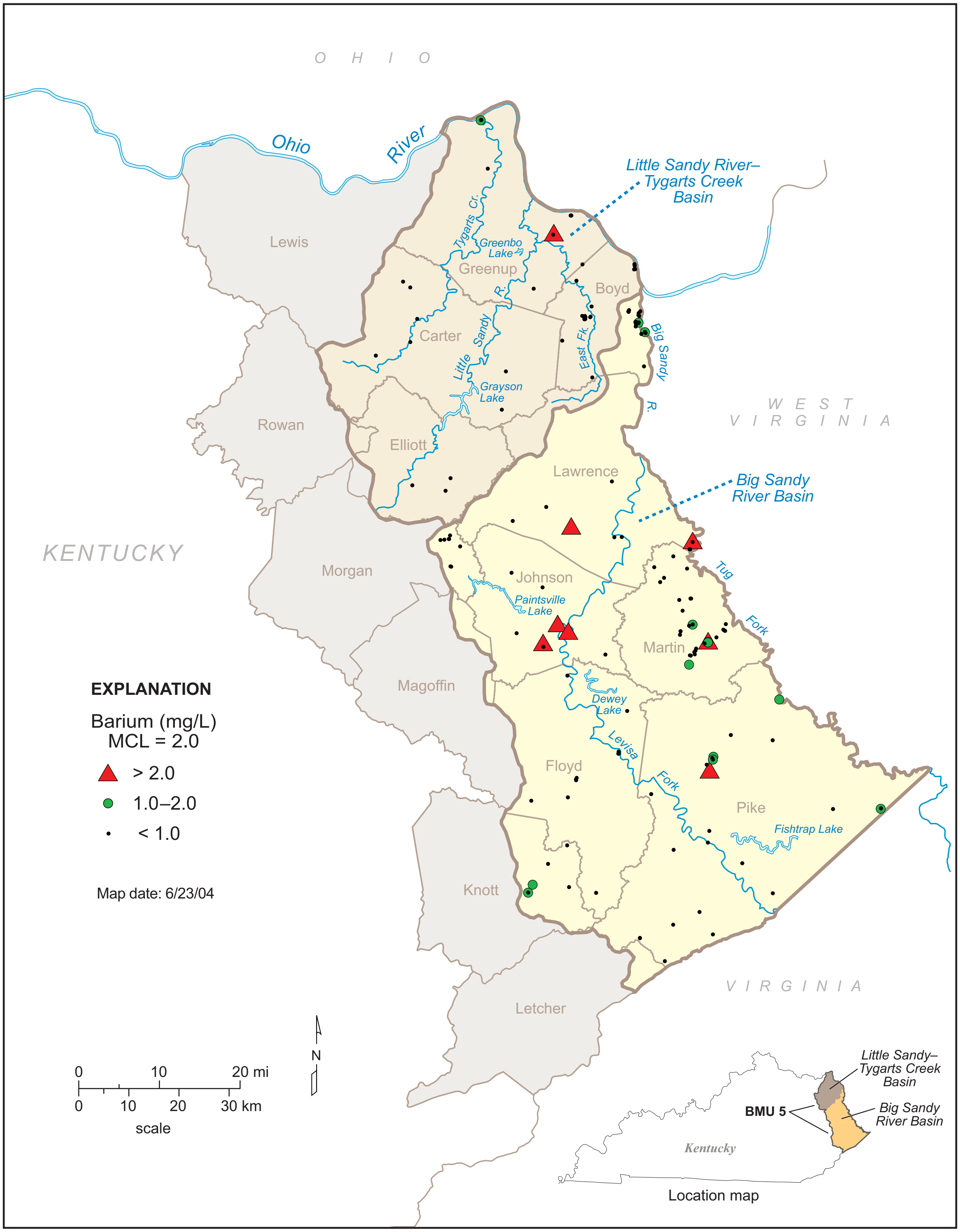

Figure 49. Locations of sampled sites and ranges of barium values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

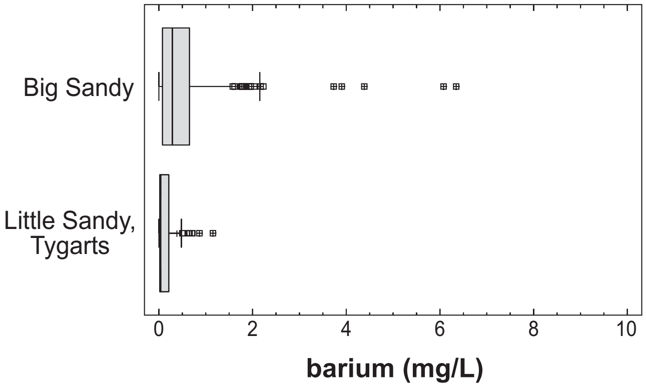

Figure 50. Summary of barium concentrations grouped by watershed. Higher values were excluded to better show the majority of the values. MCL=2 mg/L.

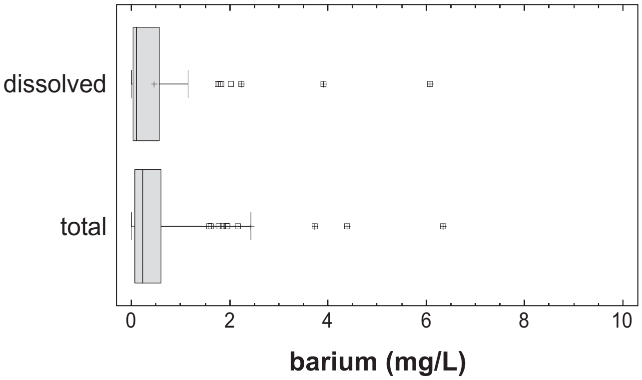

Figure 51. Comparison of total and dissolved barium concentrations. Nine values of total barium were excluded to better show the majority of the values. MCL=2 mg/L.

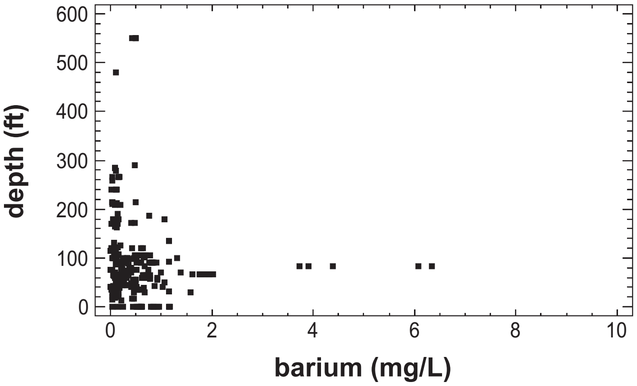

Figure 52. Barium concentrations versus well depth. Nine higher values were excluded to better show the majority of the values. MCL=2 mg/L.

The data set contained only 13 barium concentrations from four springs; all the other values were from wells. No samples from springs had a barium concentration above the MCL. Because there were so few analyses from springs, no comparison with concentrations from wells was made.

The highest barium concentrations were found in wells less than 100 ft deep (Fig. 52). All values that exceeded the MCL were from wells less than 100 ft deep.

In summary, only eight of 167 sites yielded groundwater that contained more than 2 mg/L of barium. All these sites were shallow wells, but there was no preferred geographic distribution of such wells. These data show that barium in groundwater sometimes exceeded established health limits in BMU 5. Naturally occurring barite is the probable source of the high barium concentrations. There was no evidence that barium concentrations were affected by nonpoint-source chemicals.

Table 16. Summary of mercury concentrations (mg/L). MCL=0.002 mg/L.

Number of values	235
Maximum	0.00095
75th percentile	< 0.00005
Median	< 0.00005
25th percentile	< 0.00005
Minimum	< 0.00005
Interquartile range	na
Number of sites	109
Number of sites > 0.002 mg/L	0

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

Mercury. Mercury (Hg) is a liquid metal found in natural deposits as ores containing other elements. Forest fires, coal combustion products, disposal of mercury-containing products such as electric lights and switches, computers, and blood-pressure gauges contribute mercury to the environment. Electrical products such as dry-cell batteries, fluorescent lightbulbs, switches, and other control equipment account for 50 percent of mercury used. Combustion of fossil fuels, metal smelters, cement manufacture, municipal landfills, sewage, and metal-refining operations are significant sources of mercury in the environment. When mercury from such sources is acted on by bacteria, some of it is converted to methylmercury, a much more toxic form of mercury. At high doses, mercury is a strong neurotoxin that causes destruction of the nerve's myelin coating in the brain, spinal cord, or optic nerves; delayed nerve conduction;

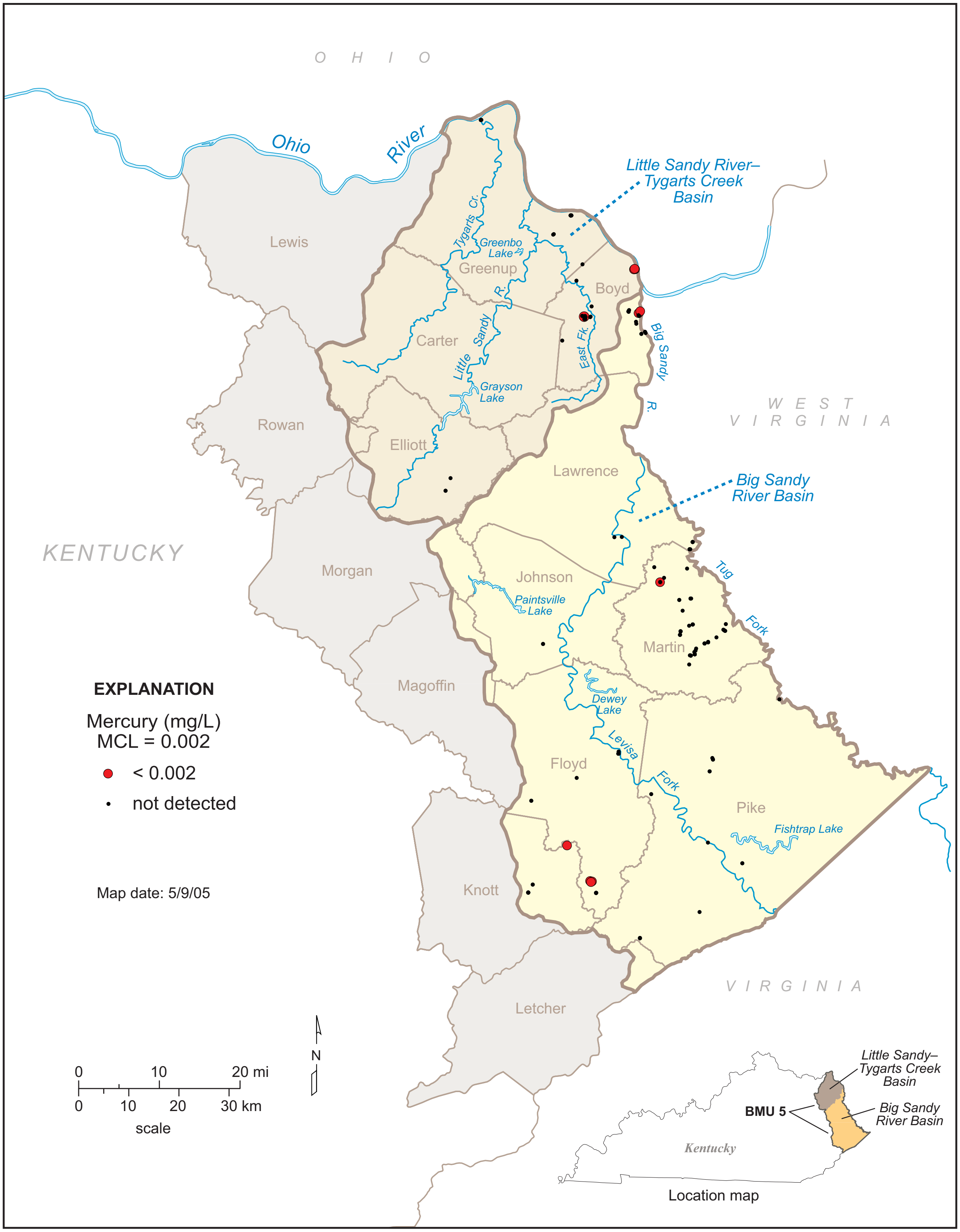

Figure 53. Locations of sampled sites and ranges of mercury values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

and kidney damage. Because of its toxicity, the EPA has set an MCL for mercury of 0.002 mg/L.

The groundwater data repository contained 235 mercury analyses from 109 sites in BMU 5 (Table 16). No concentration exceeded the MCL of 0.002 mg/L. Only 12 sites had values above analytical detection; all of these were wells rather than springs. The highest reported value was 0.00095 mg/L, well below the MCL of 0.002 mg/L.

Sites sampled for mercury were clustered in Boyd County of the Little Sandy watershed and Martin County of the Big Sandy watershed (Fig. 53).

Because so few values of mercury were above analytical detection limits, no further analysis was made.

In summary, mercury was detected in only 12 of 109 sites in BMU 5. The maximum concentration was 0.00095 mg/L, less than half of the MCL. There was no strong evidence that mercury in groundwater was the result of widespread nonpoint-source contamination.

Iron. Iron (Fe) is a naturally occurring metal that is widely present in groundwater. Iron can occur in either an oxidized (ferric) or reduced (ferrous) state. At normal groundwater pH values, ferric iron is rapidly precipitated as an iron oxide, iron hydroxide, iron oxyhydroxide (rust), or poorly crystalline to amorphous material. Under reduced conditions, however, ferrous iron is stable and will remain in groundwater. There is no EPA primary drinking-water standard for iron in water supplies because there are no identified, serious health threats posed by it. There is, however, a secondary standard of 0.3 mg/L because concentrations above this level produce objectionable odor, taste, color, staining, and scaling.

The data repository contained 3,707 iron measurements from 823 sites in BMU 5 (Table 17). Iron concentrations were quite high; more than 75 percent of the sites produced groundwater that had iron concentrations above the secondary standard.

Less than half of the reported values were below the SMCL of 0.3 mg/L (Fig. 54).

Sample-site density was greater in the Big Sandy watershed, where samples were collected for the National Uranium Resource Evaluation program (Fig. 55). Values above the SMCL occurred throughout the project area.

Table 17. Summary of iron concentrations (mg/L). SMCL=0.3 mg/L.

Number of values	3,707
Maximum	1,500
75th percentile	2.76
Median	0.60
25th percentile	0.14
Minimum	0.00
Interquartile range	2.62
Number of sites	823
Number of sites > 0.3 mg/L	641

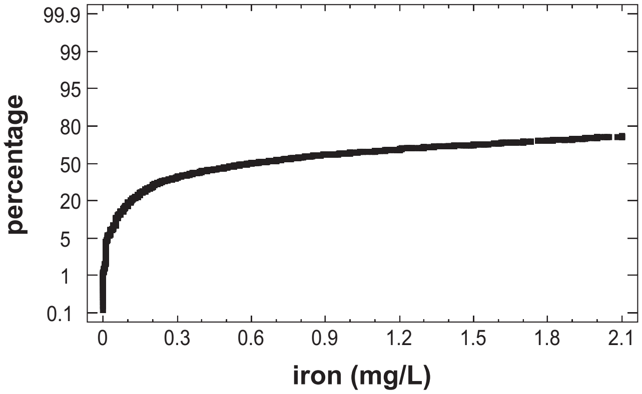

Figure 54. Cumulative plot of iron concentrations. Higher values were excluded to better show the majority of the values. SMCL=0.3 mg/L.

The median value, interquartile range, and total range of iron concentrations were nearly the same for both watersheds (Fig. 56).

Total iron concentrations (unfiltered samples) had a slightly higher median value and larger interquartile range than dissolved iron concentrations (filtered samples), suggesting that some of the reported iron was associated with suspended solids (Fig. 57).

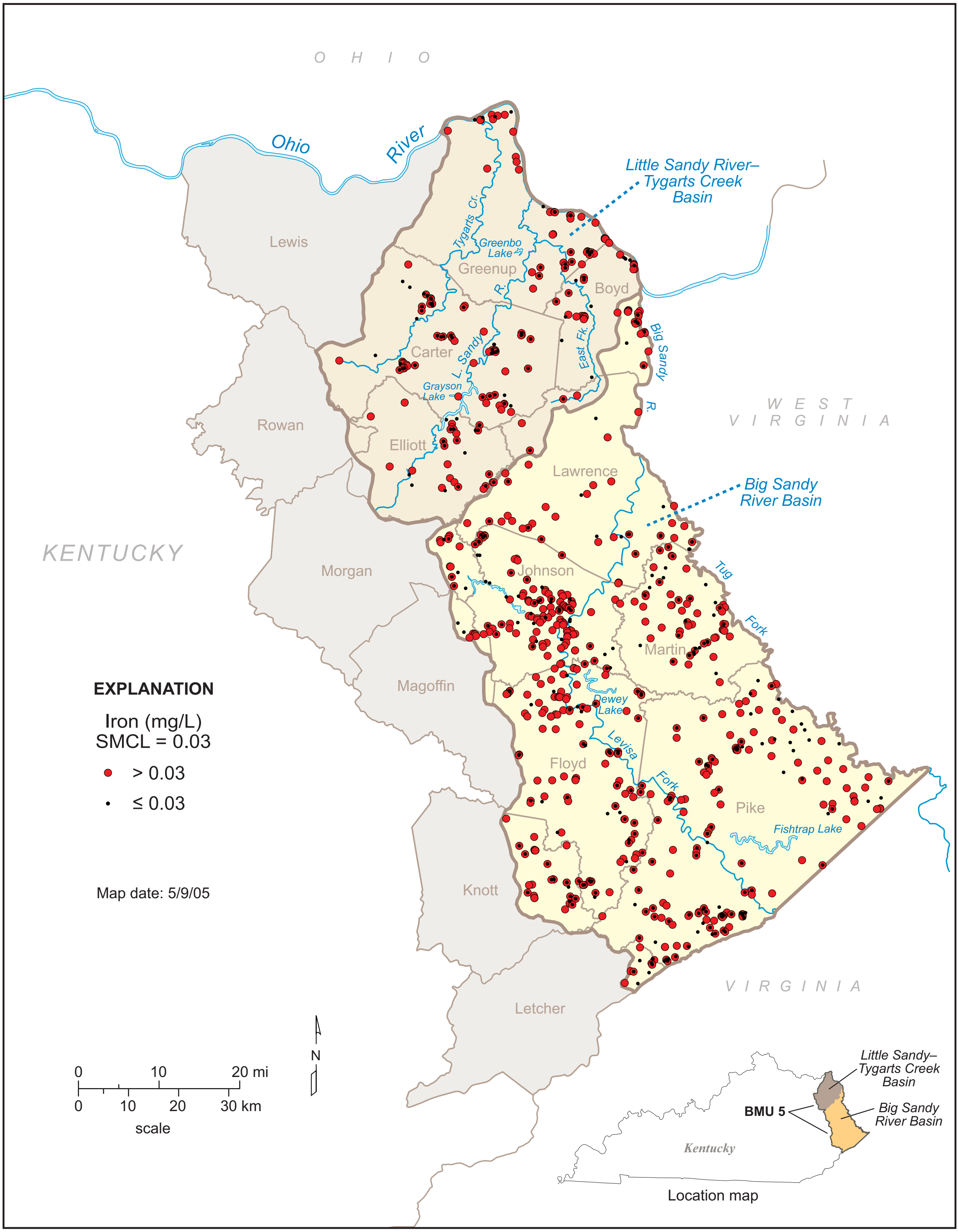

Figure 55. Locations of sampled sites and ranges of iron values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

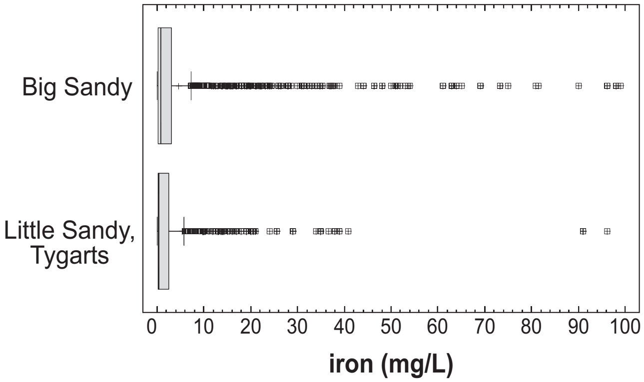

Figure 56. Summary of iron concentrations grouped by watershed. Higher values were excluded to better show the majority of the values. SMCL=0.3 mg/L.

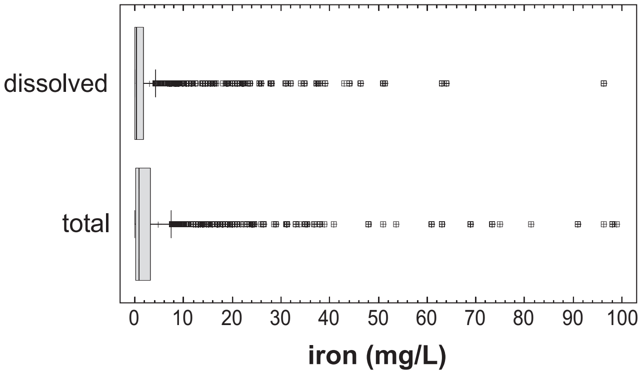

Figure 57. Comparison of total and dissolved iron concentrations. Higher values were excluded to better show the majority of the values. SMCL=0.3 mg/L.

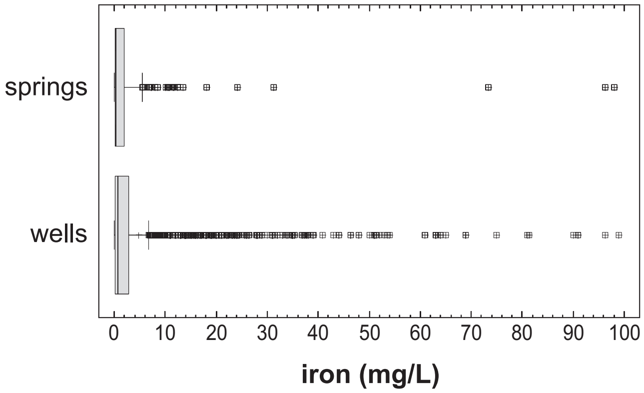

Figure 58. Comparison of iron concentrations in wells and springs. Higher values were excluded to better show the majority of the values. SMCL=0.3 mg/L.

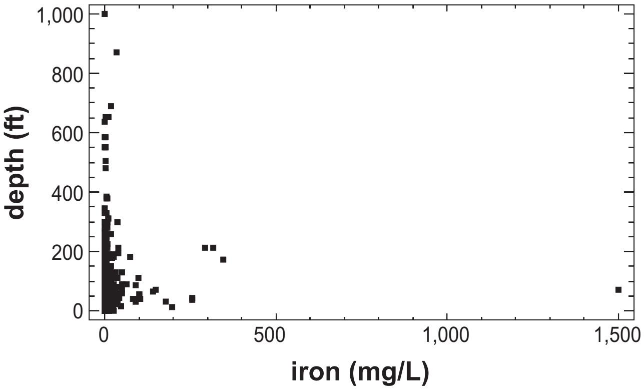

Figure 59. Iron concentrations versus well depth. SMCL=0.3 mg/L.

The highest iron concentrations were found in unfiltered samples.

The median value and interquartile range of iron in groundwater from springs were generally similar to those for water from wells (Fig. 58). The highest values were found in water from wells, however.

High iron concentrations were found more commonly in wells less than 200 ft deep; deeper wells typically had lower iron concentrations (Fig. 59).

In summary, iron concentrations high enough to produce staining and objectionable taste were common in groundwater throughout the project area. The highest concentrations occurred in unfiltered samples, indicating that iron was present in suspended material. Water from wells had the highest iron concentrations. This suggests that spring water was more oxidized and therefore iron was removed by precipitation of iron oxide minerals in springs, whereas iron remained in solution in well water. High iron concentrations are expected in this area, and naturally occurring iron overwhelms any contribution from nonpoint sources.

Manganese. Manganese (Mn) is a naturally occurring metal that is widely present in groundwater supplies. Manganese and iron are geochemically similar, so high manganese concentrations can be expected from wells and springs that produce water with high iron concentrations.

There is no EPA primary drinking-water standard for manganese in water supplies because there are no identified, serious health threats posed by it. There is, however, a secondary standard of 0.05 mg/L because higher concentrations produce objectionable odor, taste, color, corrosion, and staining.

The data repository contained 2,730 manganese concentrations from 1,731 sites in BMU 5 (Table 18). The median value was more than twice the SMCL. More than one-third of the sites produced water with more than 0.05 mg/L of manganese.

The distribution of manganese concentrations (Fig. 60) was generally similar to that of iron (Fig. 54). Less than 50 percent of the values were less than the SMCL of 0.05 mg/L.

Table 18. Summary of manganese concentrations (mg/L). SMCL=0.05 mg/L.

Number of values	2,730
Maximum	83
75th percentile	0.50
Median	0.11
25th percentile	0.03
Minimum	0.00
Interquartile range	0.47
Number of sites	1.731
Number of sites > 0.05 mg/L	642

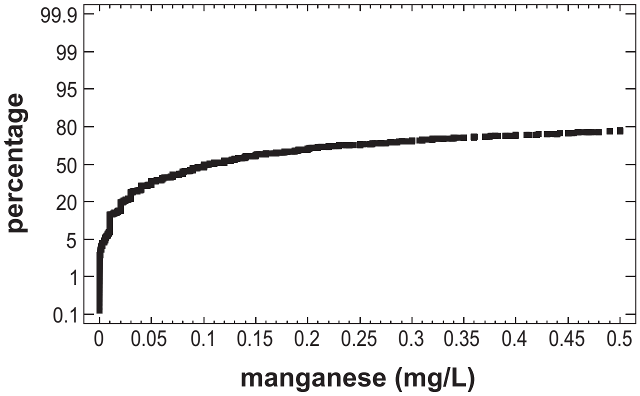

Figure 60. Cumulative plot of manganese concentrations. Higher values were excluded to better show the majority of the values. SMCL=0.05 mg/L.

Site distribution was very dense in the Big Sandy watershed (Fig. 61) because the National Uranium Resource Evaluation program sampled that area. Values that exceeded the SMCL were found throughout BMU 5.

The median manganese concentration was similar in the two watersheds (Fig. 62). The interquartile range of values was larger in the Little Sandy–Tygarts Creek watershed, however.

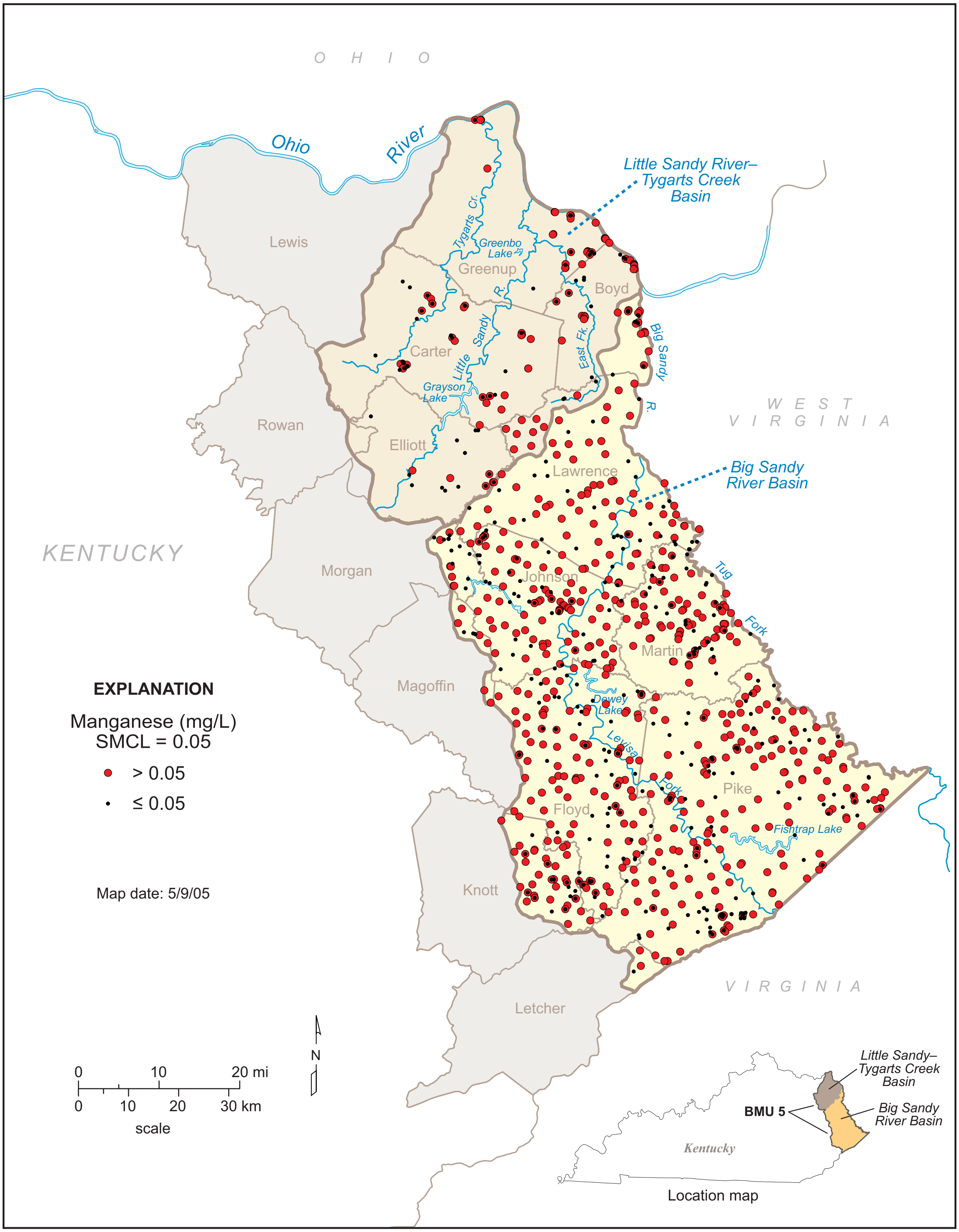

Figure 61. Locations of sampled sites and ranges of manganese values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

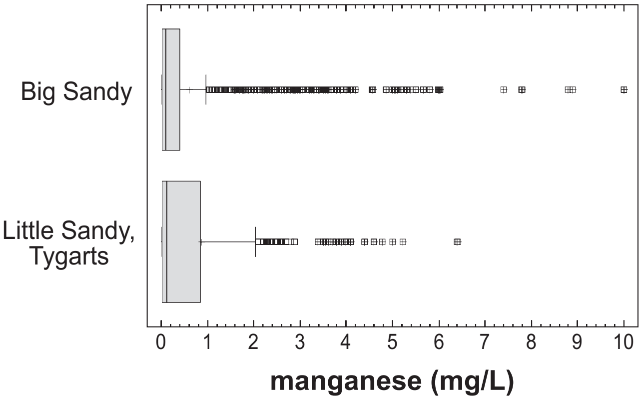

Figure 62. Summary of manganese concentrations grouped by watershed. Higher values were excluded to better show the majority of the values. SMCL=0.05 mg/L.

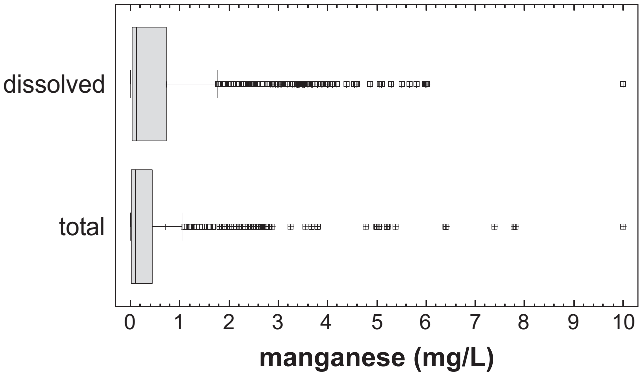

Figure 63. Comparison of total and dissolved manganese concentrations. Higher values were excluded to better show the majority of the values. SMCL=0.05 mg/L.

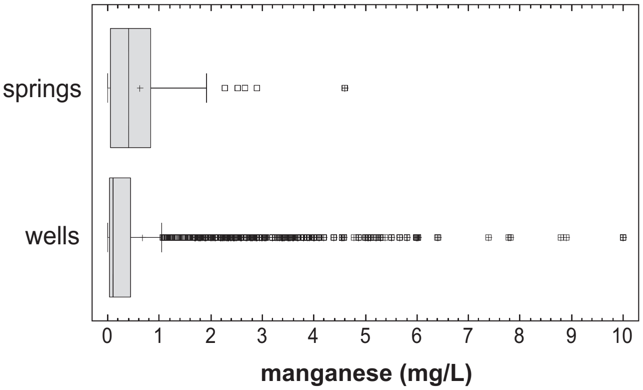

Figure 64. Comparison of manganese concentrations from wells and springs. Higher values were excluded to better show the majority of the values. SMCL=0.05 mg/L.

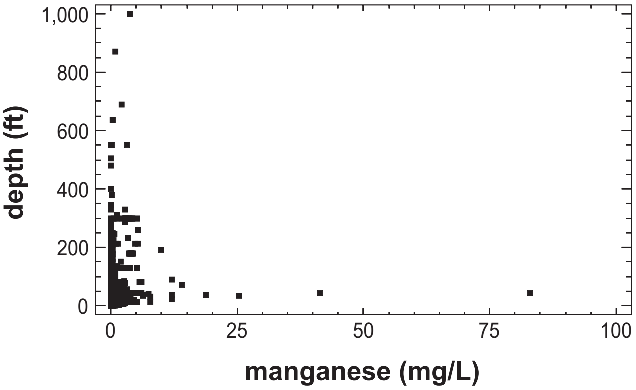

Figure 65. Manganese concentrations versus well depth. SMCL=0.05 mg/L.

Dissolved manganese concentrations had a larger interquartile range than total manganese concentrations (Fig. 63), suggesting that suspended particulate material did not contribute significant amounts of manganese to the analysis.

Groundwater from springs had a larger median value and larger interquartile range (Fig. 64). The highest manganese concentrations occurred in water from wells, however.

The highest manganese concentrations were found in wells less than 100 ft deep (Fig. 65).

In summary, the geochemical similarity between manganese and iron is demonstrated in the similarity of their concentrations in groundwater. Both commonly occurred at concentrations that affect groundwater taste and can stain containers and clothing. All features of the distribution of manganese concentrations appear primarily related to bedrock type. No evidence suggests that nonpoint-source contamination significantly contributes to manganese concentrations in the project area.

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.

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

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).

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

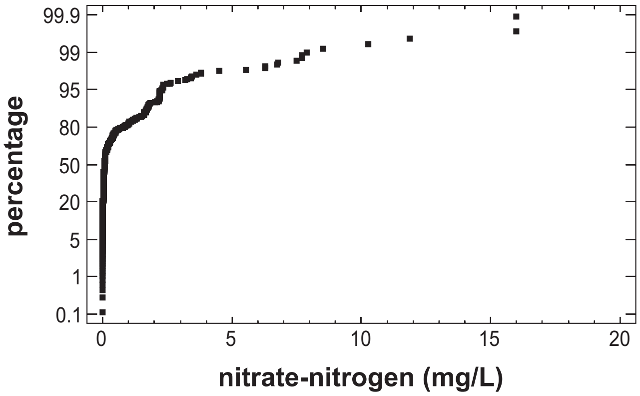

Figure 66. Cumulative plot of nitrate-nitrogen concentrations. MCL=10 mg/L.

(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.

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

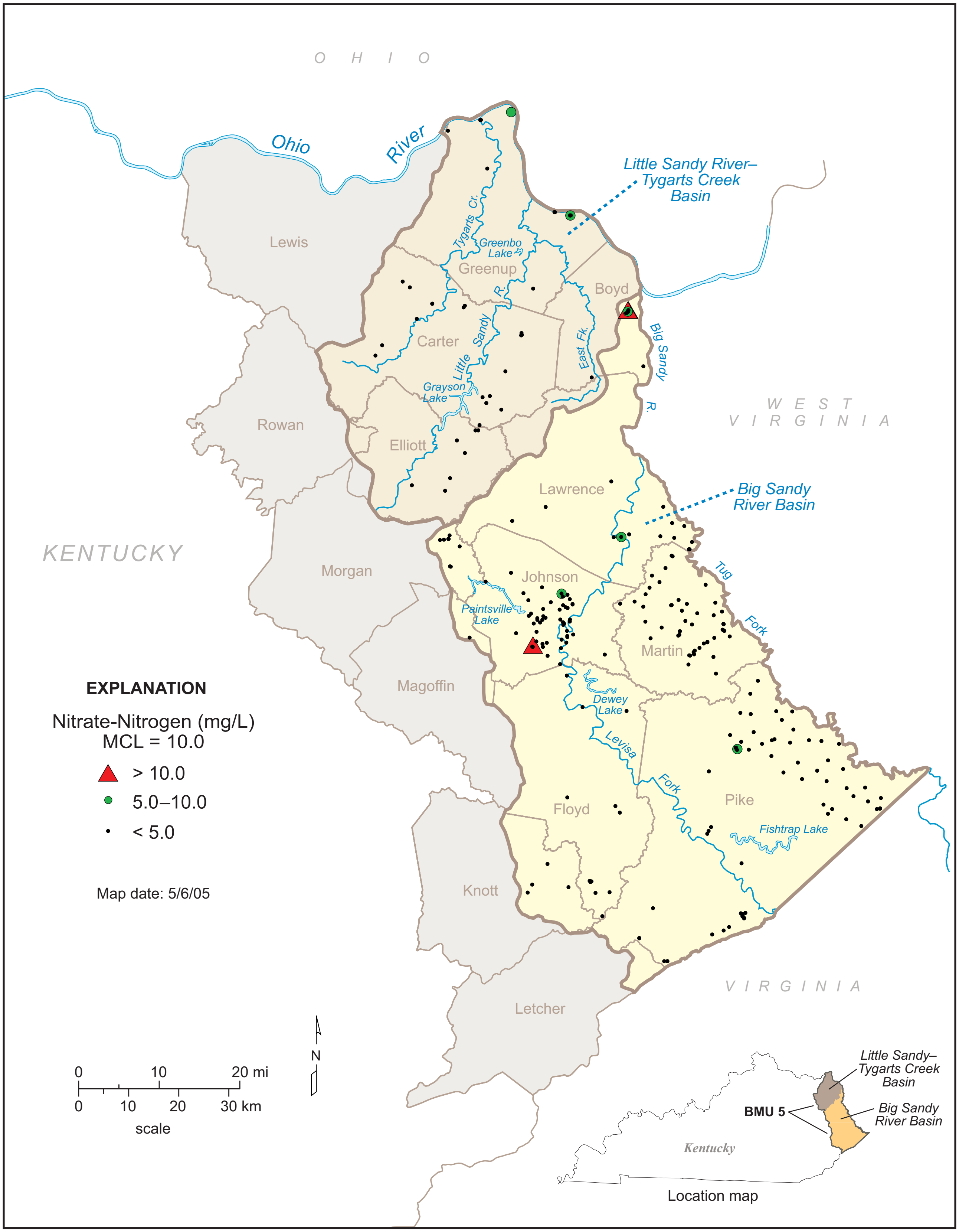

Figure 67. Locations of sampled sites and ranges of nitrate-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

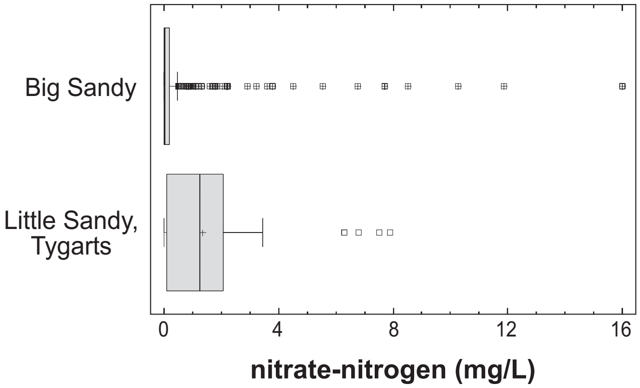

Figure 68. Summary of nitrate-nitrogen concentrations grouped by watershed. MCL=10 mg/L.

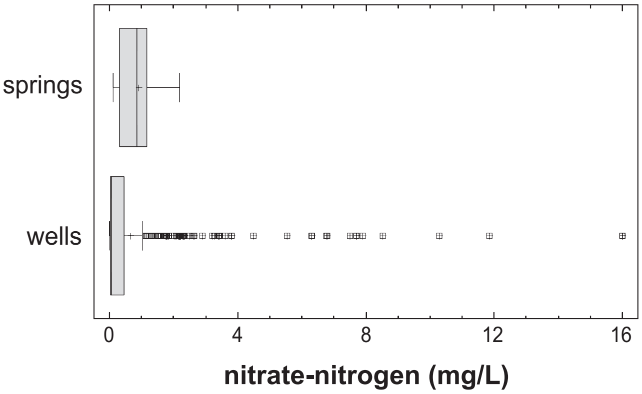

Figure 69. Comparison of nitrate-nitrogen concentrations from wells and springs. MCL=10 mg/L.

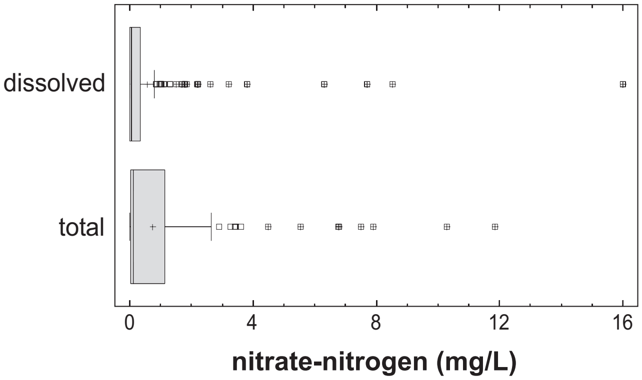

Figure 70. Comparison of total and dissolved nitrate-nitrogen concentrations. MCL=10 mg/L.

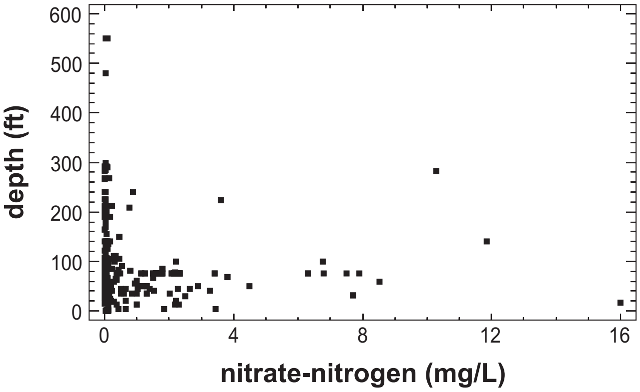

Figure 71. Nitrate-nitrogen concentrations versus well depth. MCL=10 mg/L.

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).

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

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

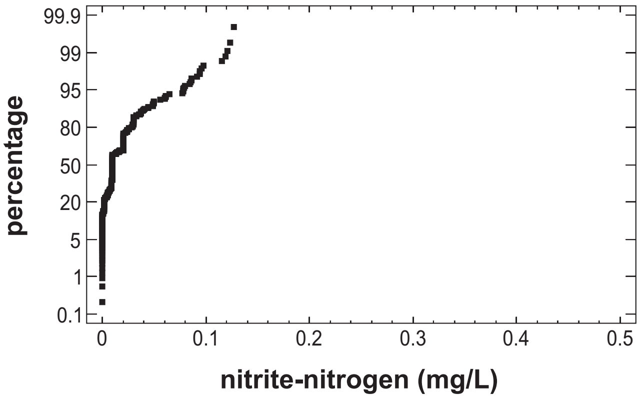

Figure 72. Cumulative plot of nitrite-nitrogen concentrations MCL=1.0 mg/L.

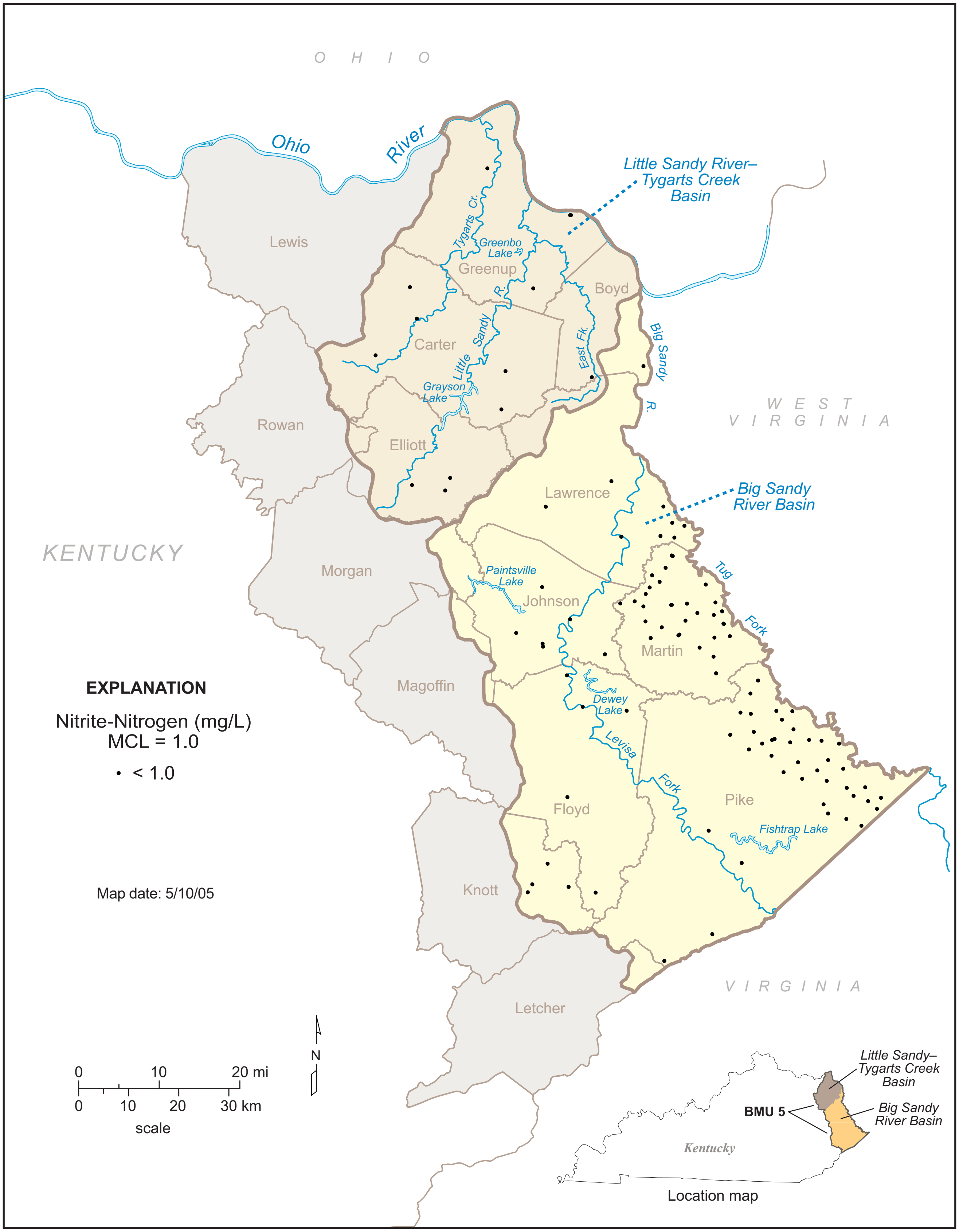

Figure 73. Locations of sampled sites and ranges of nitrite-nitrogen values.

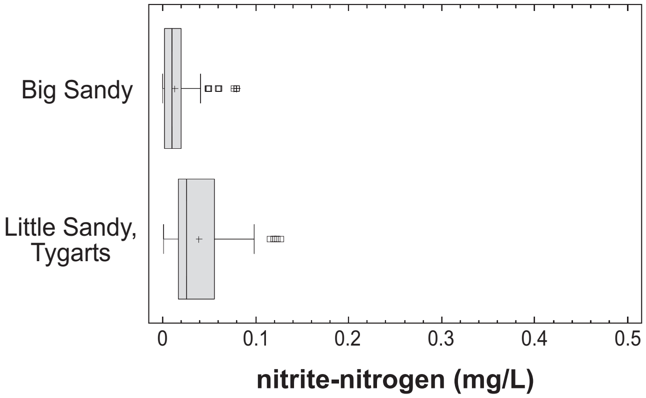

Figure 74. Summary of nitrite-nitrogen concentrations grouped by watershed. MCL=1.0 mg/L.

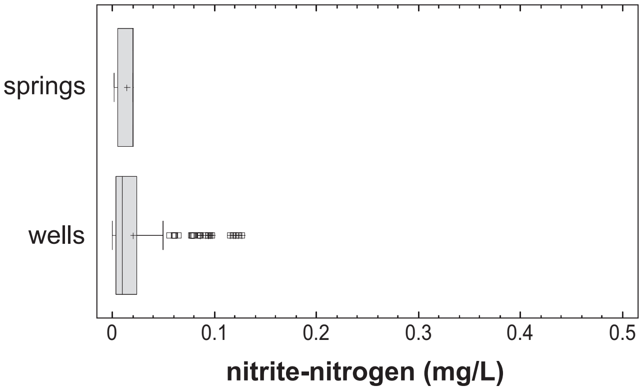

Figure 75. Comparison of nitrite-nitrogen concentrations from wells and springs. MCL=1.0 mg/L.

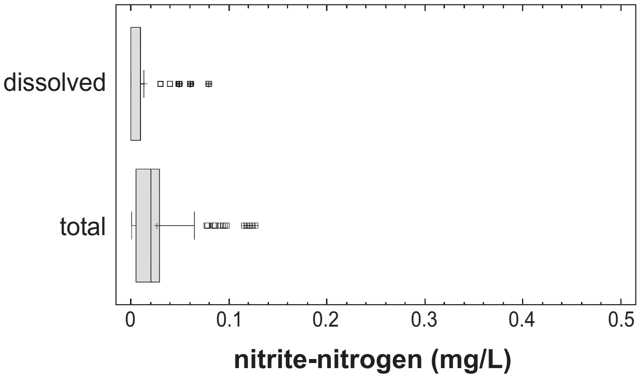

Figure 76. Comparison of total and dissolved nitrite-nitrogen concentrations. MCL=1.0 mg/L.

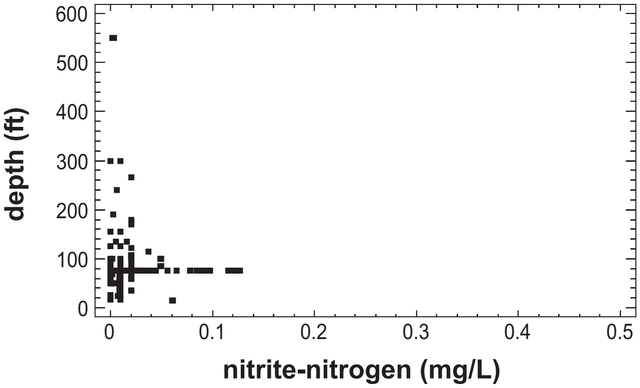

Figure 77. Nitrite-nitrogen concentrations versus well depth. MCL=1.0 mg/L.

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.

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.

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

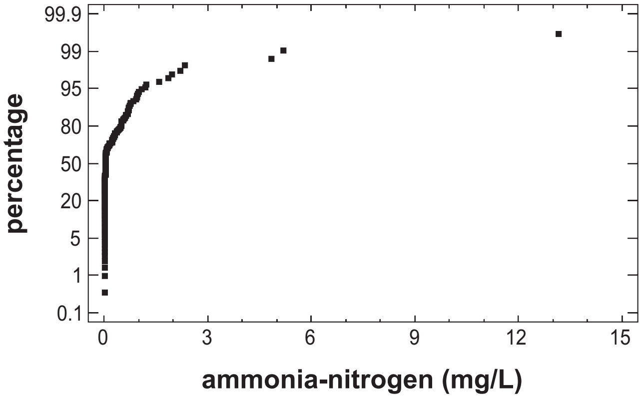

Figure 78. Cumulative plot of ammonia-nitrogen concentrations. DOW recommendation=0.11 mg/L.

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

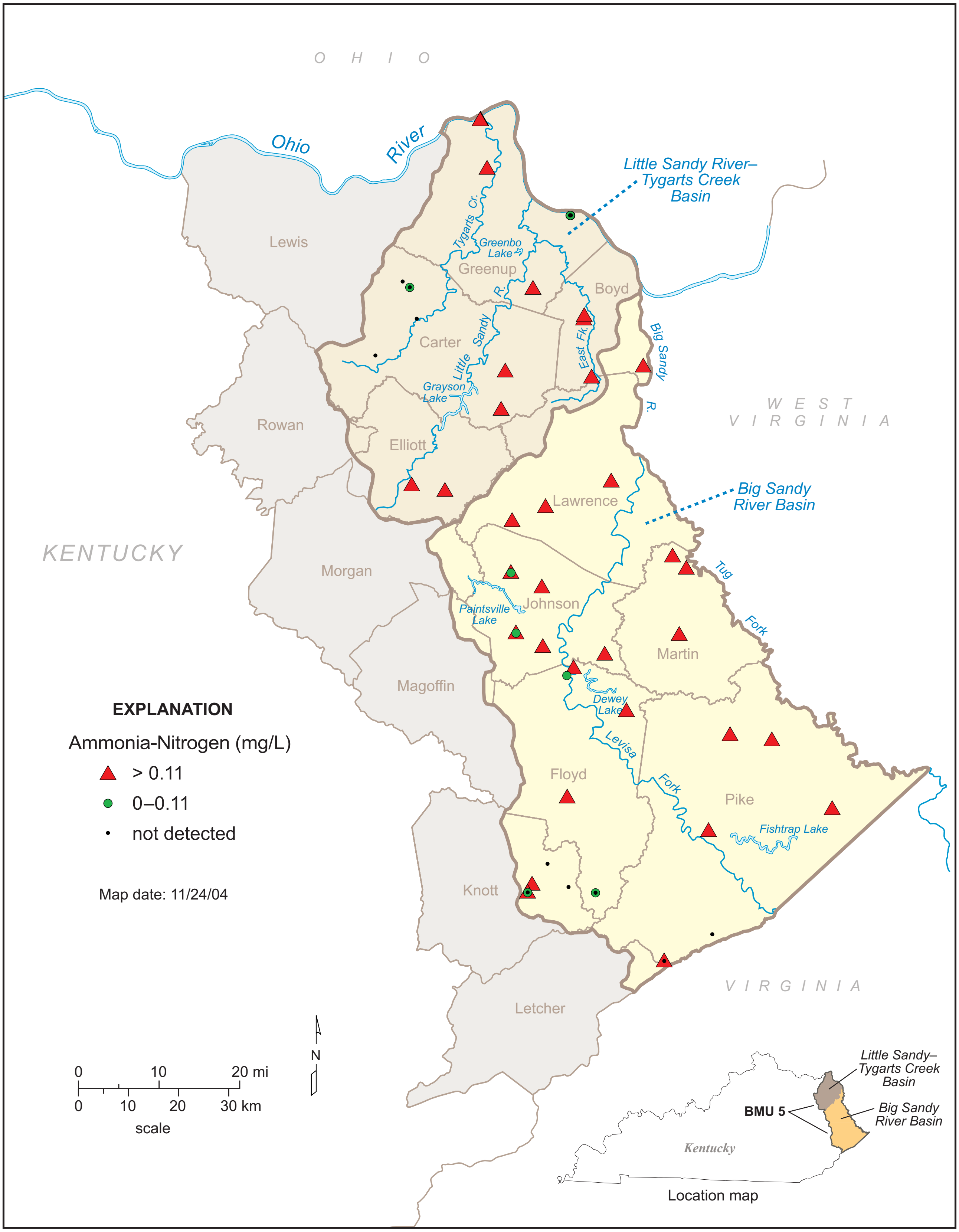

Figure 79. Locations of sampled sites and ranges of ammonia-nitrogen values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

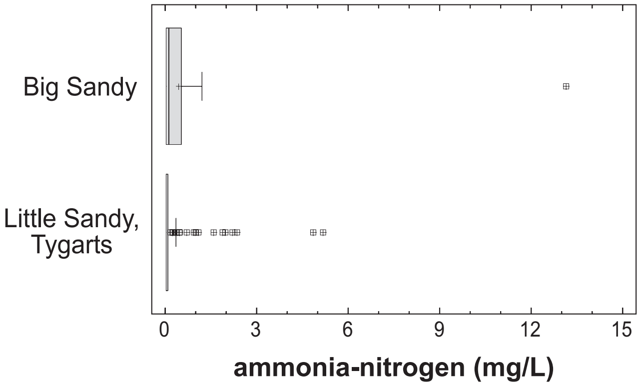

Figure 80. Summary of ammonia-nitrogen concentrations grouped by watershed. DOW recommendation=0.11 mg/L.

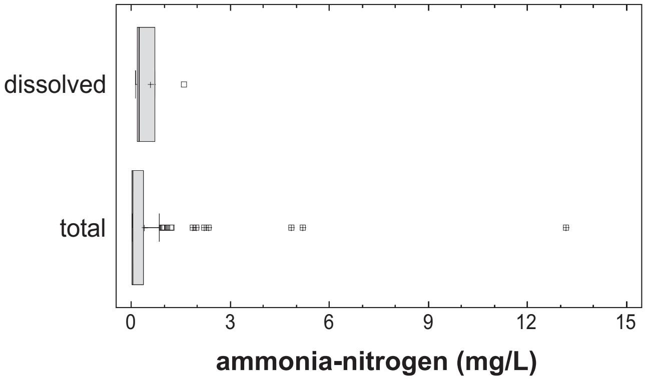

Figure 81. Comparison of total and dissolved ammonia-nitrogen concentrations. DOW recommendation=0.11 mg/L.

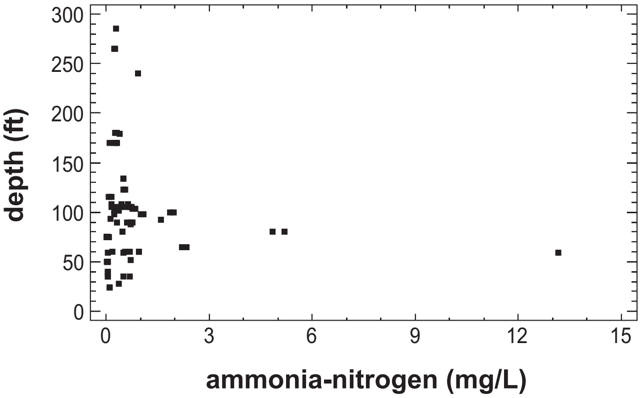

Figure 82. Ammonia-nitrogen concentrations versus well depth. DOW recommendation=0.11 mg/L.

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.

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.

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

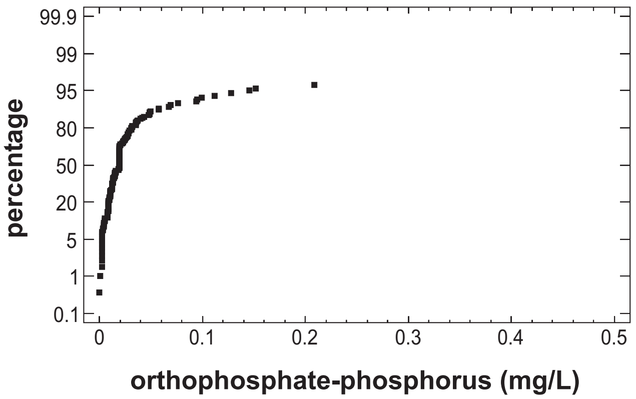

Figure 83. Cumulative plot of orthophosphate concentrations. Seven values greater than 100 mg/L were excluded to better show the majority of the values. DOW recommendation=0.04 mg/L.

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

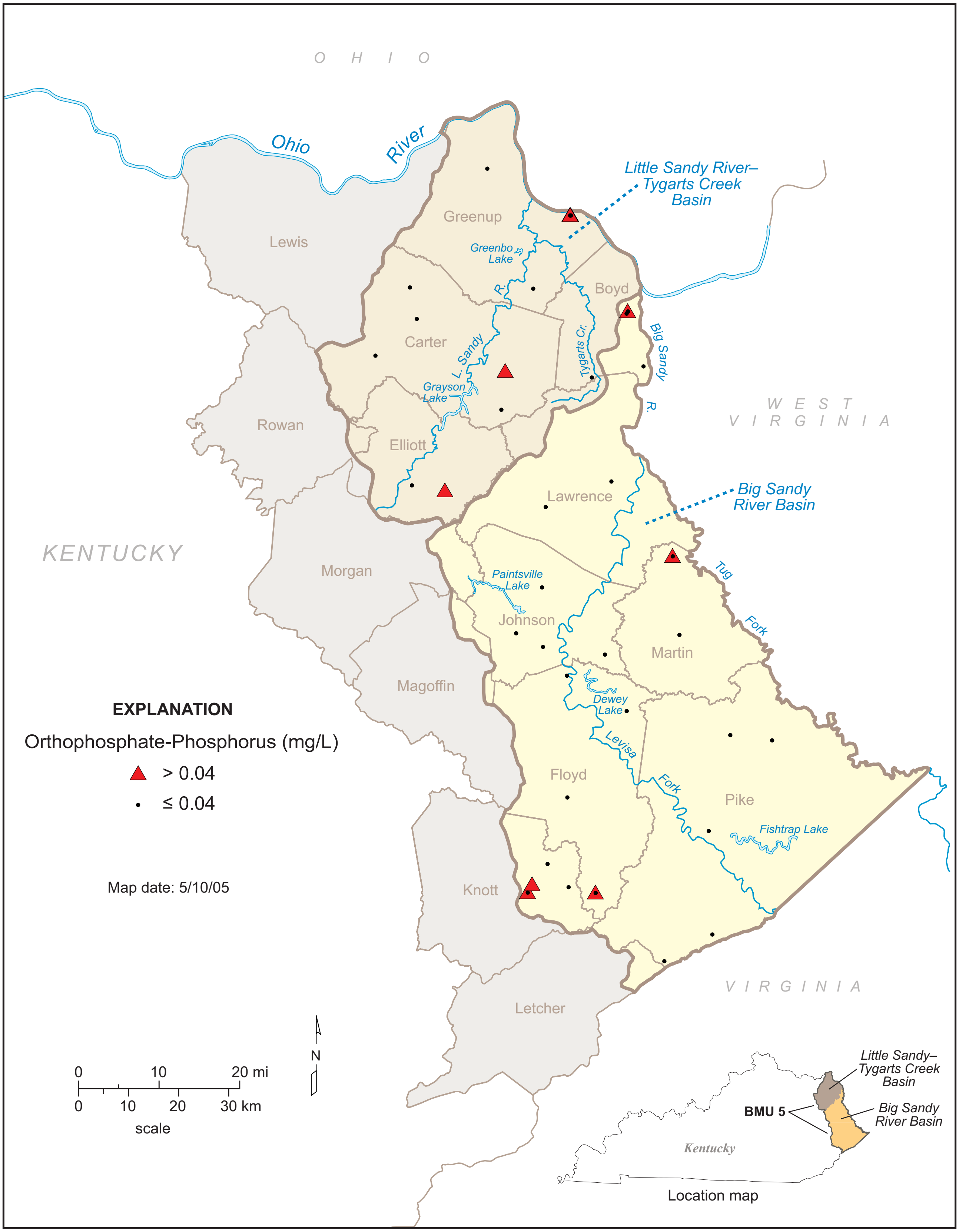

Figure 84. Locations of sampled sites and ranges of orthophosphate values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

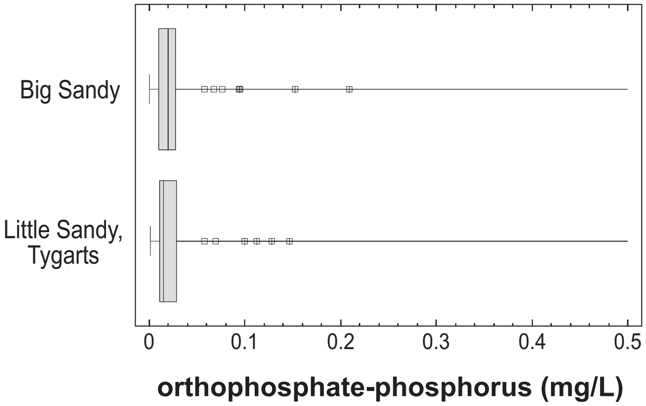

Figure 85. Summary of orthophosphate concentrations grouped by watershed. Seven values greater than 100 mg/L were excluded to better show the majority of the values. DOW recommendation=0.04 mg/L.

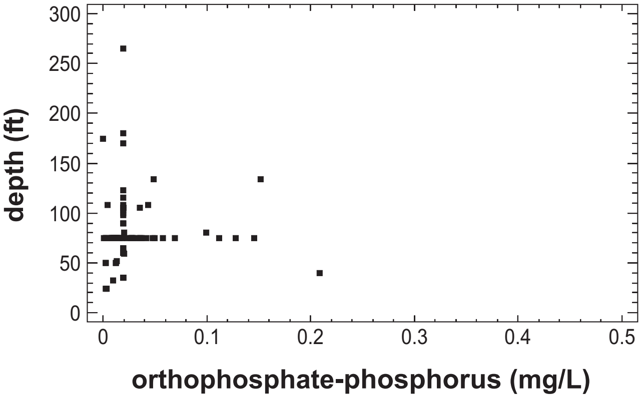

Figure 86. Orthophosphate concentrations versus well depth. Values greater than 100 mg/L were found at well depths from 75 to 250 ft. These high values were excluded to better show the majority of the values. DOW recommendation=0.04 mg/L.

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

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.

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,

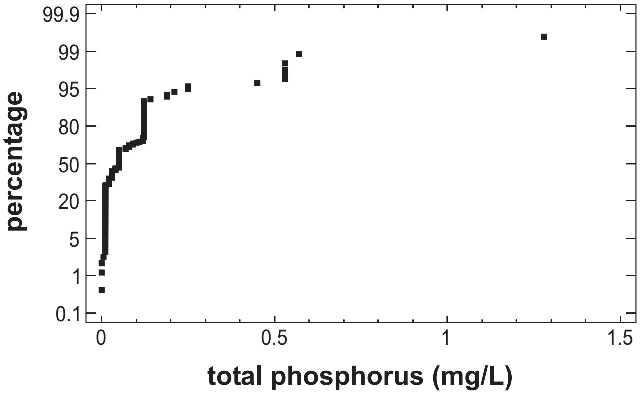

Figure 87. Cumulative plot of total phosphorus concentrations. DOW recommendation=0.1 mg/L.

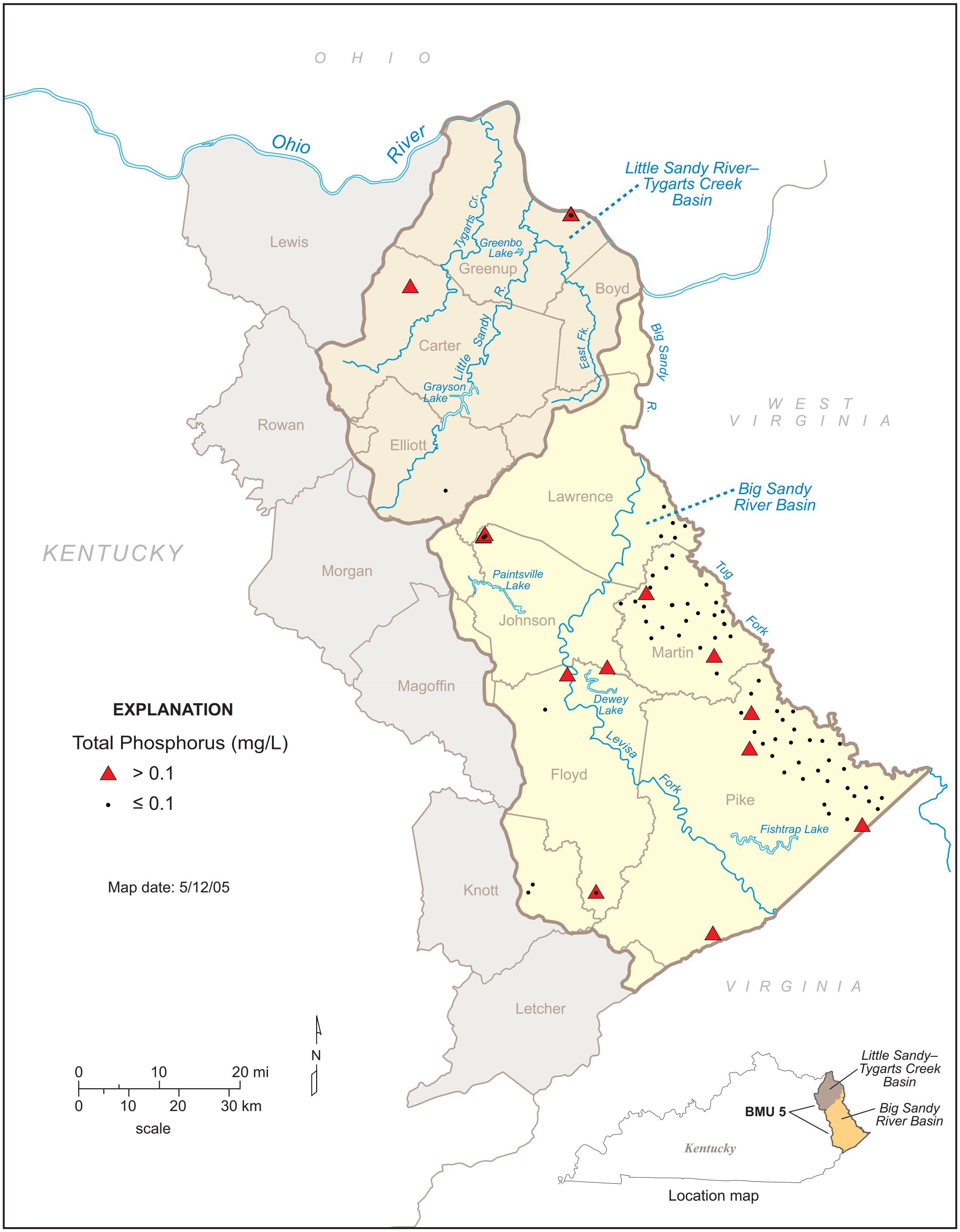

Figure 88. Locations of sampled sites and ranges of total phosphorus values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

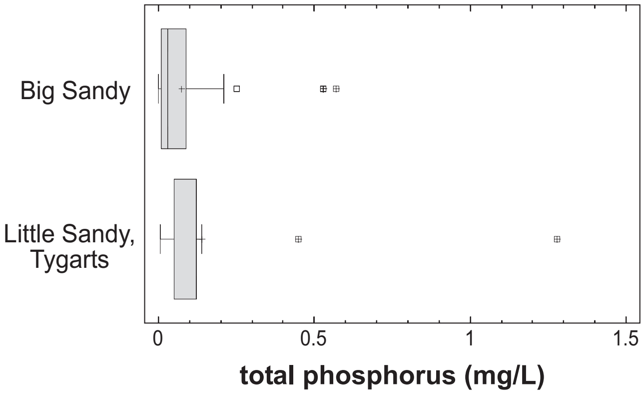

Figure 89. Summary of total phosphorus concentrations grouped by watershed. DOW recommendation=0.1 mg/L.

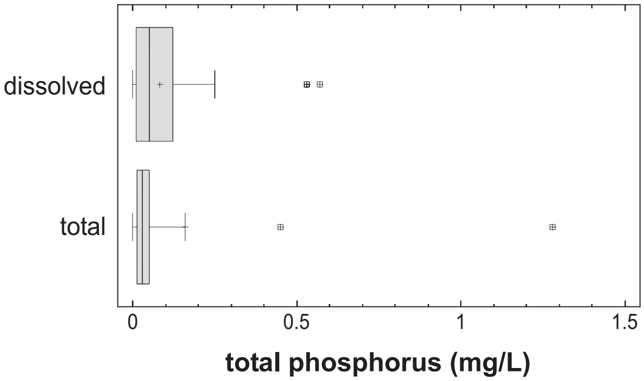

Figure 90. Comparison of total and dissolved phosphorus concentrations. DOW recommendation=0.1 mg/L.

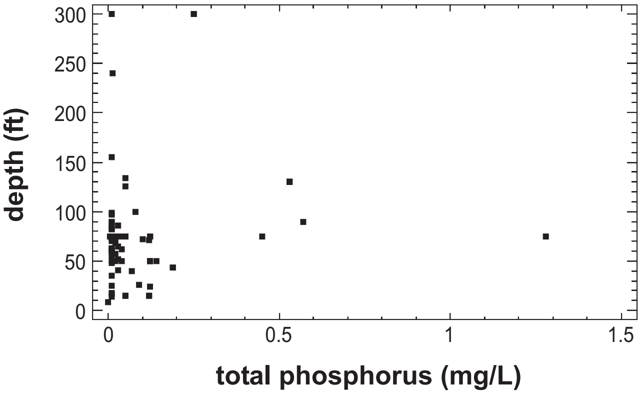

Figure 91. Total phosphorus concentrations versus well depth. DOW recommendation=0.1 mg/L.

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.

Pesticides

A large number of synthetic organic pesticides (including insecticides, herbicides, and growth regulators) have been developed and applied in agricultural and urban settings. Some, such as the organochlorine insecticide DDT, were banned decades ago but still persist in soils and sediments and could still be released to groundwater systems. Most recently developed pesticides that have been approved for use are less persistent in natural environments; however, they may still have undesirable impacts on human health and groundwater suitability for various uses.

The environmental significance of pesticides in groundwater is difficult to determine precisely for several reasons (U.S. Geological Survey, 1999): (1) standards and guidelines are available for only a small number of individual pesticide chemicals and are generally not available for the equally important degradation products, (2) new pesticides are being developed continually, (3) environmental testing does not account for pesticide mixtures or breakdown products, which may be more potent than the original active ingredients, (4) only a limited suite of health and ecological effects have been tested, (5) concentrations much higher than those used in testing may be introduced to groundwater systems when pesticides are applied after rains, and (6) some detrimental effects such as endocrine disruption and other subtle health effects have not been fully assessed. For these reasons, and because once contaminated, groundwater typically is slow to respond to changes in pesticide type and application methods, it is important to quantify the occurrence of any detectable pesticides in Kentucky groundwater.

According to the 2000 agricultural sales data, atrazine, glyphosate, metolachlor, simazine, and 2,4-D are the top five pesticides sold in Kentucky. Alachlor and cyanazine have also been used extensively in the past. Glyphosate has not been measured in groundwater samples, and so will not be discussed in this report. Toxicological information for pesticides was obtained from the Extension Toxicology Network (ace.orst.edu/info/exotoxnet/pips/) and the U.S. Environmental Protection Agency's Integrated Risk Information System (www.epa.gov/iris/).

2,4-D. The pesticide 2,4-D belongs to the chemical class of phenoxy compounds. Predominant uses are as a

Table 24. Summary of 2,4-D concentrations (mg/L). MCL=0.07 mg/L.

Number of values	114
Maximum	0.000653
75th percentile	< 0.0001
Median	< 0.0001
25th percentile	< 0.0001
Minimum	< 0.0001
Interquartile range	na
Number of sites	47
Number of where detected	11
Number of sites > 0.07 mg/L	0

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

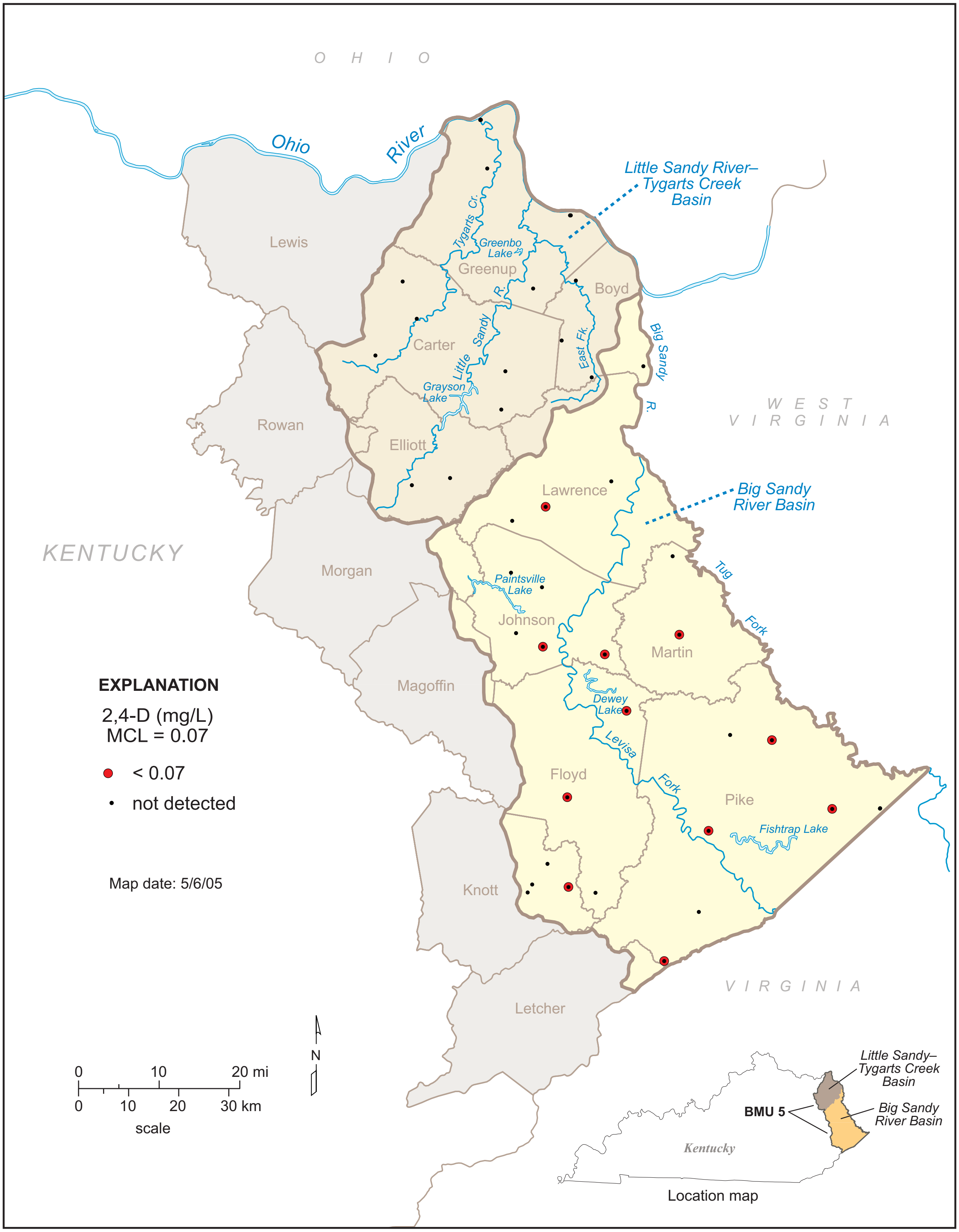

Figure 92. Locations of sampled sites and ranges of 2,4-D values.

systematic herbicide used to control broadleaf weeds in cultivated agriculture, pasture and range land, forest management, home and garden settings, and to control aquatic vegetation. It has a low persistence in soils with a half-life of less than 7 days, and is readily degraded by microorganisms in aquatic environments. The EPA has established an MCL of 0.07 mg/L for 2,4-D because the nervous system can be damaged from exposure at higher levels.

The database contained 114 analyses of 2,4-D from 47 sites in BMU 5 (Table 24). No value exceeded the MCL of 0.07 mg/L. Only 12 values from 11 sites exceeded analytical detection limits; all these sites were wells in the Big Sandy watershed.

Sample-site density was uniform but sparse throughout BMU 5 (Fig. 92). No detection of 2,4-D occurred at any of the sampled sites in the Little Sandy–Tygarts Creek watershed. Because no value exceeded the MCL and concentrations exceeded analytical detection limits at only 11 sites, the data were not analyzed further.

Table 25. Summary of alachlor concentrations (mg/L). MCL=0.002 mg/L.

Number of values	136
Maximum	< 0.00027
75th percentile	< 0.00004
Median	< 0.00004
25th percentile	< 0.00004
Minimum	< 0.00002
Interquartile range	na
Number of sites	49
Number of where detected	0
Number of sites > 0.002 mg/L	0

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

In summary, 2,4-D concentrations do not exceed the MCL in the project area, and are typically less than analytical detection. Detectable amounts of 2,4-D were found in 11 wells, all less than 110 ft deep and all in the Big Sandy watershed. The presence of 2,4-D at some sites in the project area indicates that 2,4-D is enter-

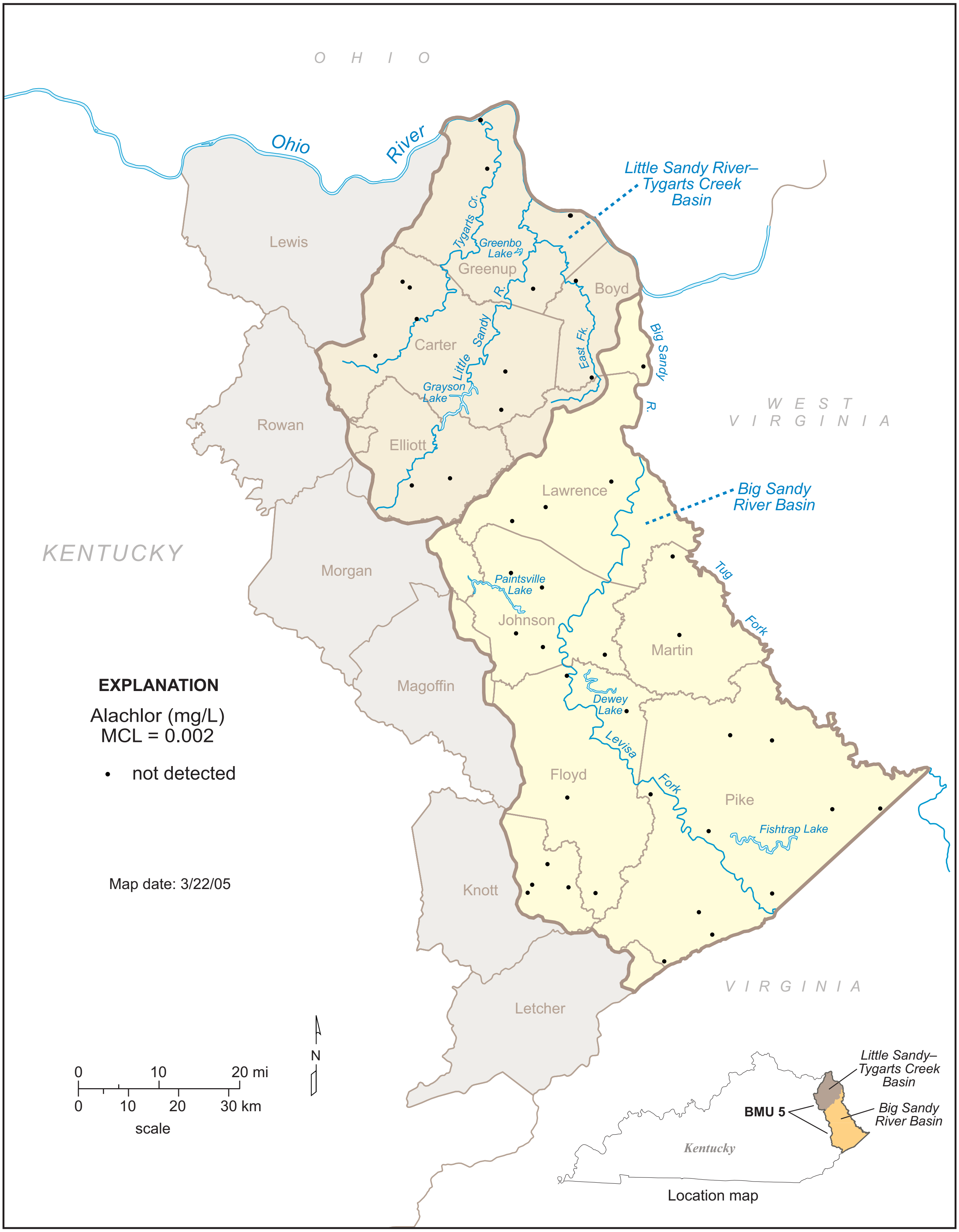

Figure 93. Locations of sampled sites and ranges of alachlor values.

ing the groundwater system, although it does not currently present a health hazard.

Alachlor. Alachlor belongs to the chemical class of analines. Predominant uses are the control of annual grasses and broadleaf weeds in field corn, soybeans, and peanuts. It has a low persistence in soils and a half-life of about 8 days. It is moderately mobile in sandy and silty soils and breaks down rapidly in natural water due to microbial activity. The breakdown is significantly slower under reducing conditions. The EPA has found alachlor to pose a risk for skin and eye irritation on short-term exposure, and to potentially cause damage to the liver, kidneys, spleen, lining of the nose and eyelids, and possibly cause cancer on long-term exposure. For these reasons, the EPA has set an MCL of 0.002 mg/L for alachlor.

The data repository contained 136 measurements of alachlor from 49 sites in BMU 5 (Table 25). No value exceeded the MCL; all results were below analytical detection limits.

Sample-site density was uniform but sparse throughout BMU 5 (Fig. 93). Because alachlor was not detected, the data were not analyzed further.

In summary, alachlor was not detected at any of the 49 sites where groundwater was sampled in BMU 5. Alachlor use is probably very limited in the project area because corn, soybeans, and peanuts are not produced in this part of Kentucky.

Table 26. Summary of atrazine concentrations (mg/L). MCL=0.003 mg/L.

Number of values	76
Maximum	0.00194
75th percentile	< 0.0003
Median	< 0.0003
25th percentile	< 0.0005
Minimum	< 0.0004
Interquartile range	na
Number of sites	14
Number of where detected	3
Number of sites > 0.003 mg/L	0

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

Atrazine. Atrazine belongs to the chemical class of triazines. Predominant uses are to control broadleaf and grassy weeds in corn, sorghum, and other crops and in conifer reforestation plantings. It is highly persistent in soils, moderately soluble in water, and not readily sorbed to sediments.

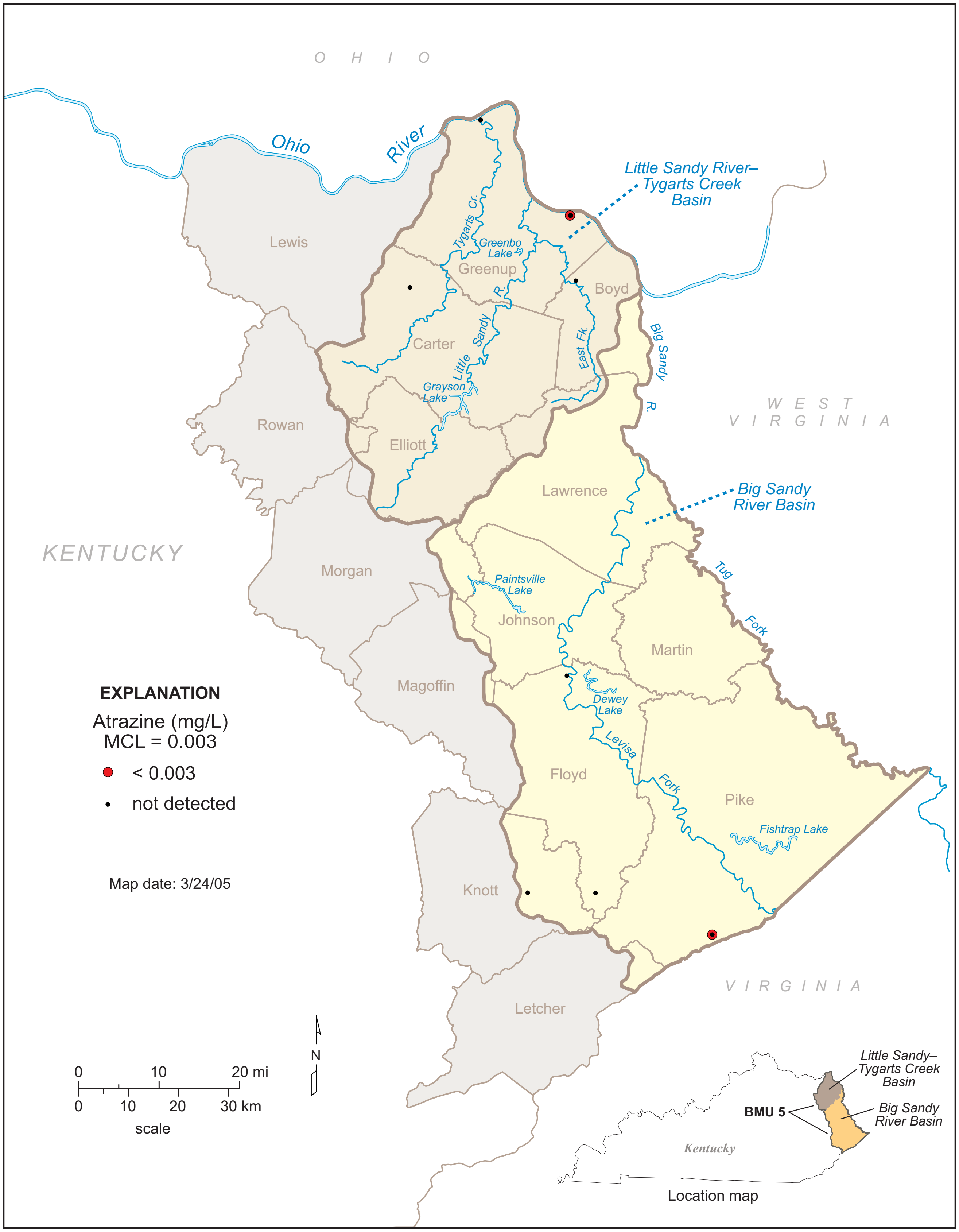

Figure 94. Locations of sampled sites and ranges of atrazine values.

The EPA has set an MCL of 0.003 mg/L for atrazine. Atrazine can cause a variety of acute health effects from acute exposures at higher levels. These effects include congestion of the heart, lungs, and kidneys; hypotension; reduction of urinary output; muscle spasms; weight loss; and adrenal degeneration. Atrazine also has the potential to cause weight loss, cardiovascular damage, retinal and some muscle degeneration, and mammary tumors from a lifetime exposure at levels above the MCL.

The data repository contained 76 reports of atrazine concentrations from only 14 sites in BMU 5 (Table 26). No reported value exceeded the MCL of 0.003 mg/L. Only five of the 76 measurements exceeded analytical detection limits, and only two wells and one spring yielded groundwater with an atrazine concentration greater than the analytical detection limit.

Sample-site density was very sparse (Fig. 94). The data were not analyzed further because only five values were above analytical detection and because there were so few sampled sites.

Table 27. Summary of cyanazine concentrations (mg/L). HAL=0.001 mg/L.

Number of values	128
Maximum	0.00126
75th percentile	< 0.00005
Median	< 0.00004
25th percentile	< 0.00004
Minimum	< 0.00004
Interquartile range	na
Number of sites	47
Number of where detected	1
Number of sites > 0.001 mg/L	1

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

In summary, only 14 sites were sampled for atrazine in BMU 5. None of the samples had an atrazine concentration above the MCL; only three sites produced water with detectable levels of atrazine. Atrazine use is probably very limited in the project area

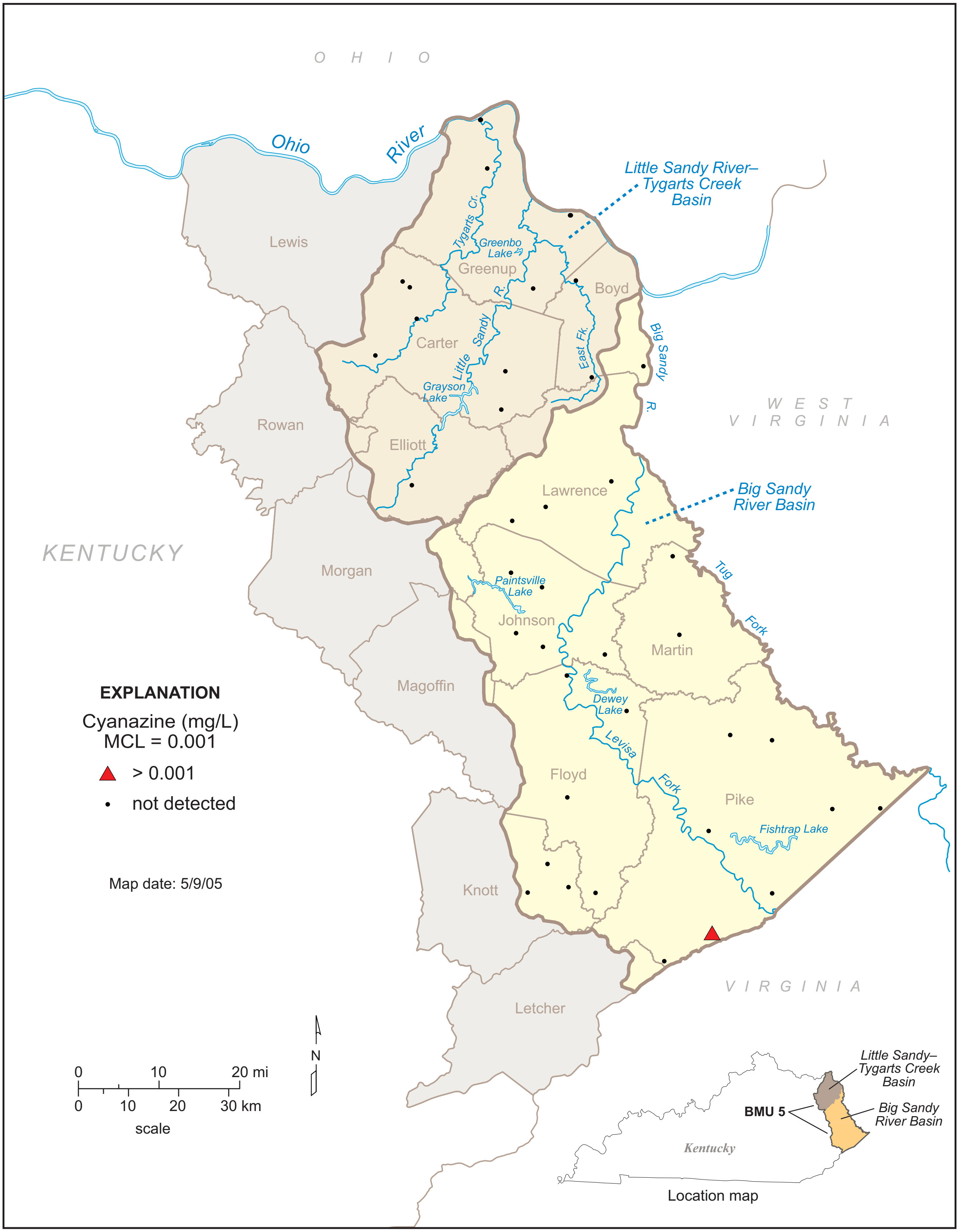

Figure 95. Locations of sampled sites and ranges of cyanazine values.

because the types of crops atrazine is used on are not grown in this part of the state. Nevertheless, the presence of any detectable atrazine in the project area indicates that some atrazine is entering the groundwater system.

Cyanazine. Cyanazine belongs to the chemical class of triazines. It is used mainly to control annual grasses and broadleaf weeds in corn. It has low to moderate persistence in soils and is rapidly degraded by microbial activity. Cyanazine has a half-life of 2 to 14 weeks, depending on soil type, and is stable in water. There is no MCL for cyanazine; however, the Division of Water has set a health advisory limit of 0.001 mg/L.

The groundwater data repository contained 128 results of cyanazine analyses from 47 sites in the project area (Table 27). Only one value exceeded analytical detection limits; this site (a spring) also exceeded the HAL. Sampled sites were widely spaced (Fig. 95).

Table 28. Summary of metolachlor concentrations (mg/L). HAL=0.1 mg/L.

Number of values	135
Maximum	0.000022
75th percentile	< 0.0002
Median	< 0.00005
25th percentile	< 0.00004
Minimum	< 0.00004
Interquartile range	na
Number of sites	48
Number of where detected	1
Number of sites > 0.1 mg/L	0

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

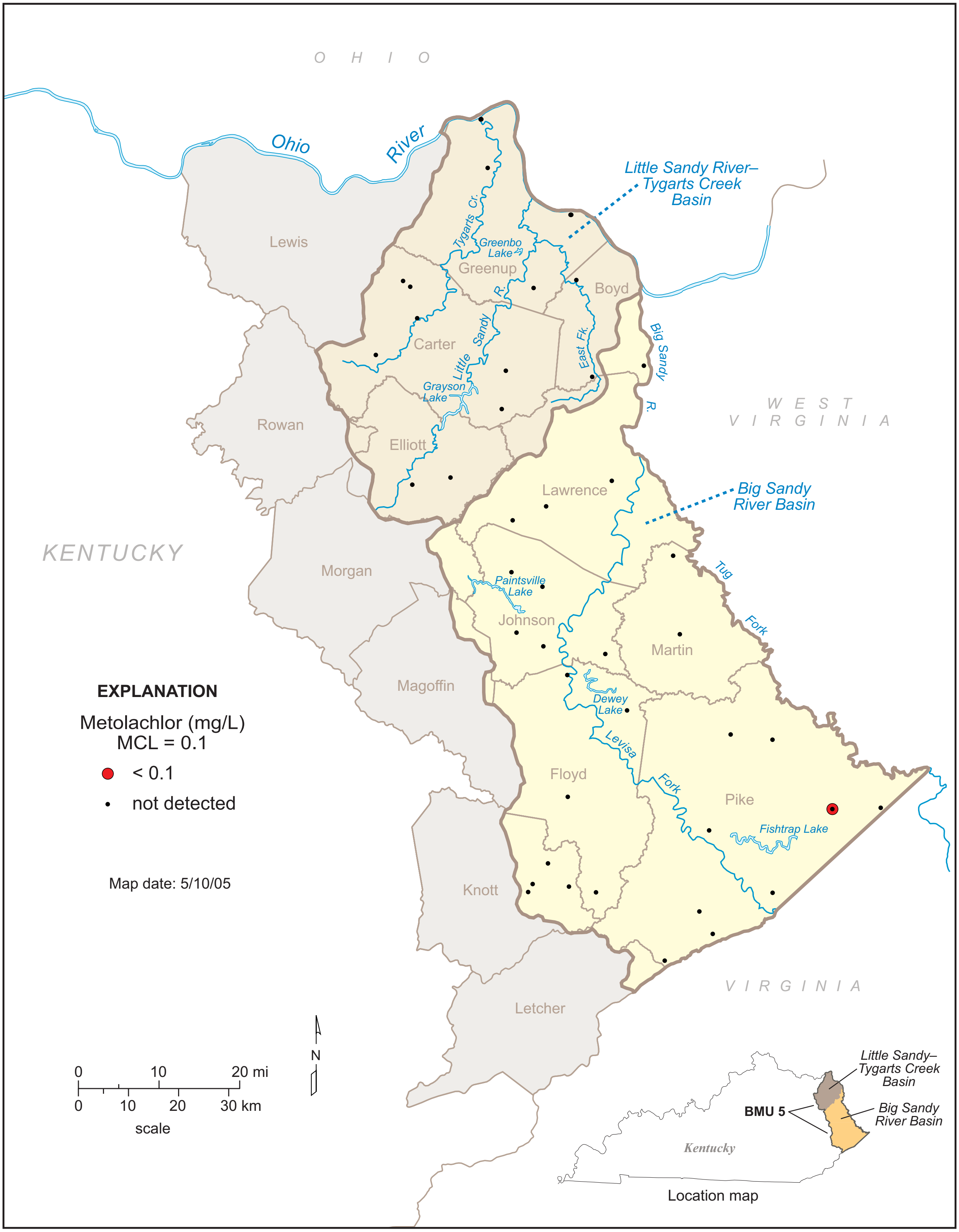

Figure 96. Locations of sampled sites and ranges of metolachlor values.

Because only one cyanazine concentration was greater than the analytical detection limit, the data were not analyzed further.

In summary, only one of 47 sites in the project area produced water with detectable cyanazine, and at that site the cyanazine concentration was greater than the HAL. Cyanazine use is probably very limited in the project area because the types of crops cyanazine is used on are not grown in this part of the state. The presence of cyanazine in the project area indicates that some pesticides are entering the groundwater system, however.

Metolachlor. Metolachlor belongs to the chemical class of amides. It is predominantly used to control broadleaf and grassy weeds in field corn, soybeans, peanuts, grain sorghum, potatoes, pod crops, cotton, safflower, stone fruits, nut trees, highway rights-of-way, and woody ornamentals. It is moderately persistent in soils with a half-life of 15 to 70 days, and is highly persistent in water. There is no MCL for metolachlor; the Division of Water has set a health advisory limit of 0.1 mg/L.

Table 29. Summary of simazine concentrations (mg/L). MCL=0.004 mg/L.

Number of values	151
Maximum	0.000689
75th percentile	< 0.0003
Median	< 0.00004
25th percentile	< 0.00004
Minimum	0.00003
Interquartile range	na
Number of sites	48
Number of where detected	2
Number of sites > 0.04 mg/L	0

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

The data repository contained 135 metolachlor concentrations from 48 sites in BMU 5 (Table 28). No values exceeded the HAL. Metolachlor was detected at only one site (Fig. 96), a shallow well in the Big Sandy watershed. Because metolachlor was detected at only one site, the data were not analyzed further.

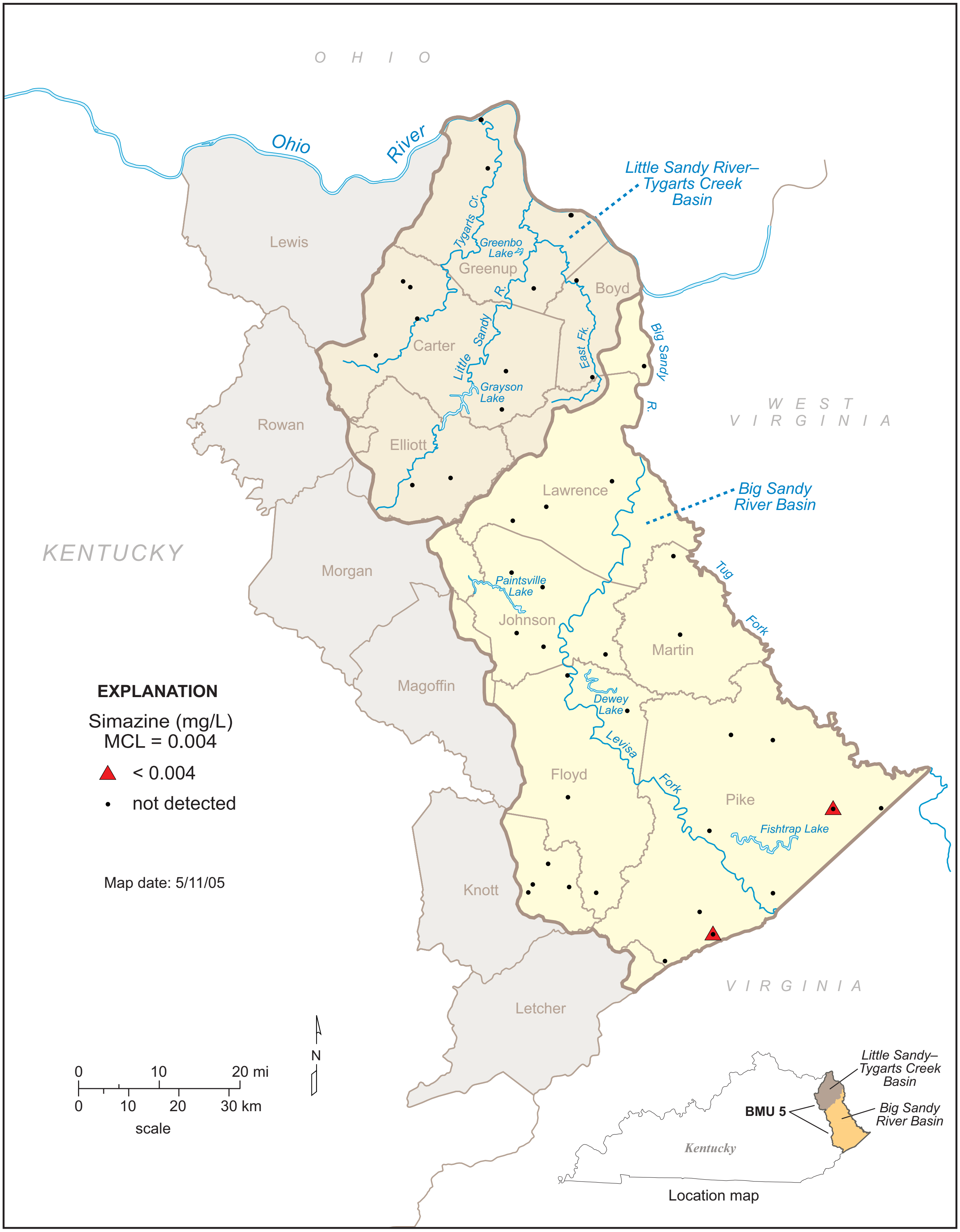

Figure 97. Locations of sampled sites and ranges of simazine values.

In summary, metolachlor is probably not used much in the project area; it was detected at only one site. The presence of detectable metolachlor in the project area indicates that some of this synthetic organic chemical has entered the groundwater system.

Simazine. Simazine belongs to the chemical class of triazines. It is predominantly used to control broadleaf weeds and annual grasses in fields where berry fruits, nuts, vegetables, and ornamental crops are grown, and on turfgrass. It is moderately persistent in soils, with a half-life of about 60 days, and is moderately persistent in water, with a half-life that depends on the amount of algae present.

The MCL for simazine is 0.004 mg/L. At levels above 0.004 mg/L, long-term exposure to simazine can cause tremors; damage to the testes, kidneys, liver, and thyroid; and gene mutations. There is some evidence that simazine may have the potential to cause cancer from a lifetime exposure at levels above the MCL.

The data repository contained 151 simazine measurements from 48 sites in the project area (Table 29). No measurement exceeded 0.004 mg/L. Only two sites, one spring and one shallow well, had simazine concentrations that exceeded analytical detection limits. The sampled sites were widely distributed throughout BMU 5 (Fig. 97). Because of the very small number of sites where simazine exceeded analytical detection limits, the data were not analyzed further.

In summary, simazine is probably not used much in the project area. It is rarely detected in groundwater. When found, it is more common in springs than in wells. The presence of detectable simazine in the project area indicates that some pesticides are entering the groundwater system.

Volatile Organic Compounds

The volatile organic compounds benzene, ethylbenzene, toluene, and total xylenes are a group of chemicals characterized by a pale to colorless appearance, sweet odor, and high volatilization. They are used as solvents and in the production of plastics, rubber, and resins. They are also components of gasoline, and are most commonly introduced to the environment through spills from leaking gasoline storage tanks, fumes and exhaust from gas-powered engines, and runoff from gasoline- or oil-contaminated surfaces such as highways and parking lots. Local groundwater contamination from these compounds can also result from improper disposal of used oil. MTBE (methyl tertiary-butyl ether) is an oxygenate additive used to promote fuel combustion and reduce carbon monoxide and ozone emissions from vehicles. Releases to the environment are most commonly the result of leaking underground storage tanks and pipelines, other spills, and, to a lesser extent, from air deposition around refineries or urban areas.

VOC occurrences are not primarily controlled by bedrock geology, physiography, or river watershed, because VOC's are synthetic. Any detected amount of these refined volatile organic chemicals indicates groundwater contamination from human activities.

Volatile organic compounds may be present in groundwater at extremely low concentrations, and measurement techniques have improved over time. As a result, some older measurements in the data repository are reported only as less than a detection limit, where the detection limit is larger than some more recently measured values. In such cases, the maximum value reported in the following tables is the maximum value actually measured, not the value of the detection limit. For example, if two VOC analyses are reported as "< 0.02 mg/L" and "0.01 mg/L," the maximum value reported here would be 0.01 mg/L.

Table 30. Summary of benzene concentrations (mg/L). MCL=0.005 mg/L.

Number of values	127
Maximum	0.003
75th percentile	< 0.0005
Median	< 0.0005
25th percentile	< 0.0005
Minimum	< 0.0005
Interquartile range	na
Number of sites	72
Number of where detected	2
Number of sites > 0.005 mg/L	0

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

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[1] Assembled Kentucky Ground Water Database

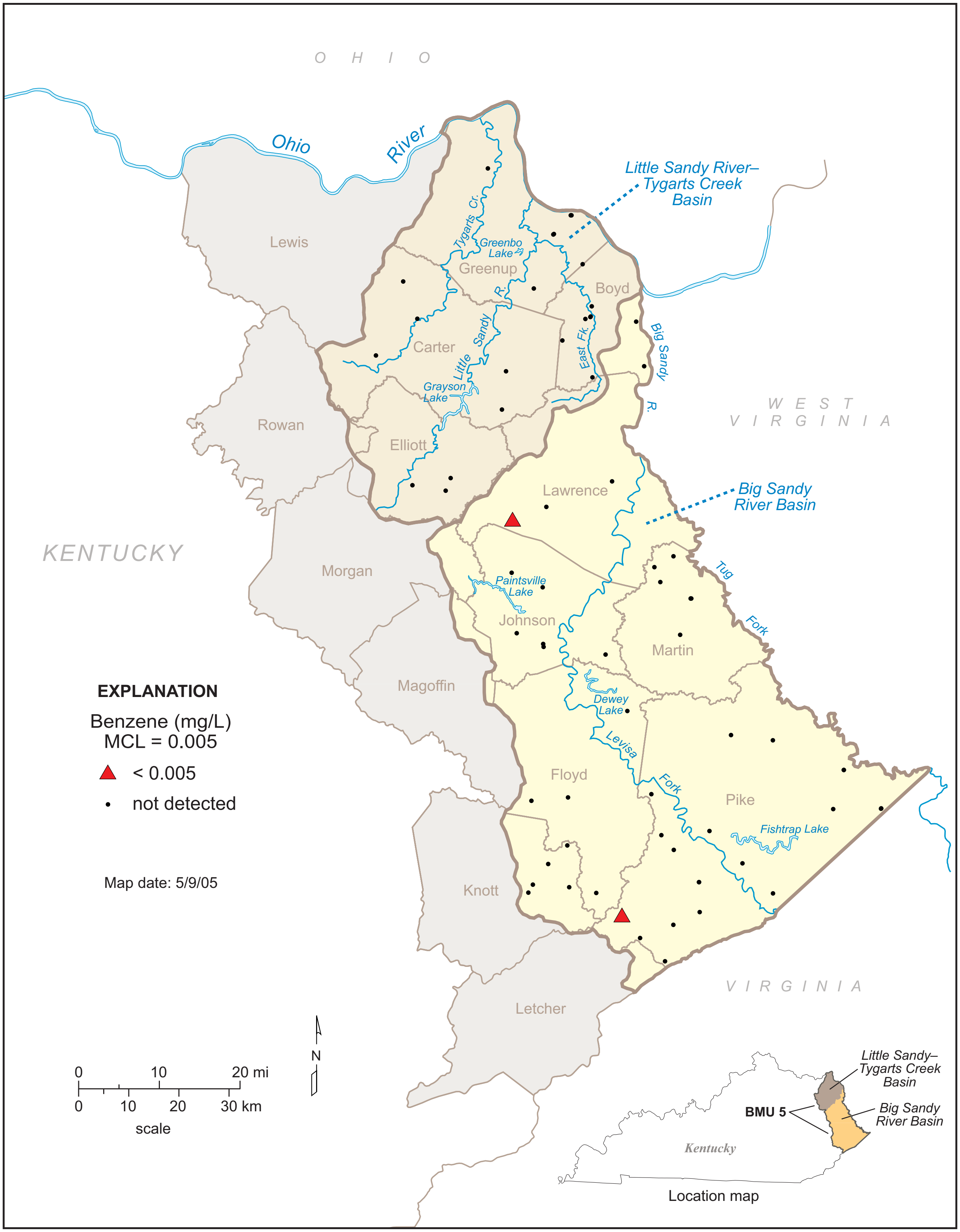

Figure 98. Locations of sampled sites and ranges of benzene values.

In addition to excluding groundwater-quality data from any sampling associated with underground storage tank investigations, all records from monitoring wells (identified by an AKGWA[1] number that begins with "8" (e.g., 80001234) were excluded from this report to ensure that locally contaminated sites are not skewing regional groundwater-quality trends. In the following discussions, summaries of potential sources and health effects of the selected pesticides were taken from the U.S. Environmental Protection Agency (2006, 2007).

Benzene. The most common sources of benzene in groundwater are leaks from underground gasoline storage tanks and landfills, and from improper disposal of oil and gasoline from domestic sources. Potential health effects include anemia, decrease in blood platelets, and increased risk of cancer. For these reasons, the EPA has established an MCL of 0.005 mg/L for benzene.

The data repository contained 127 benzene measurements from 72 sites in BMU 5 (Table 30). No sample exceeded the MCL; only two sites had groundwa-

Table 31. Summary of ethylbenzene concentrations (mg/L). MCL=0.7 mg/L.

Number of values	127
Maximum	0.0045
75th percentile	< 0.0005
Median	< 0.0005
25th percentile	< 0.0005
Minimum	< 0.0005
Interquartile range	na
Number of sites	72
Number of where detected	2
Number of sites > 0.7 mg/L	0

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

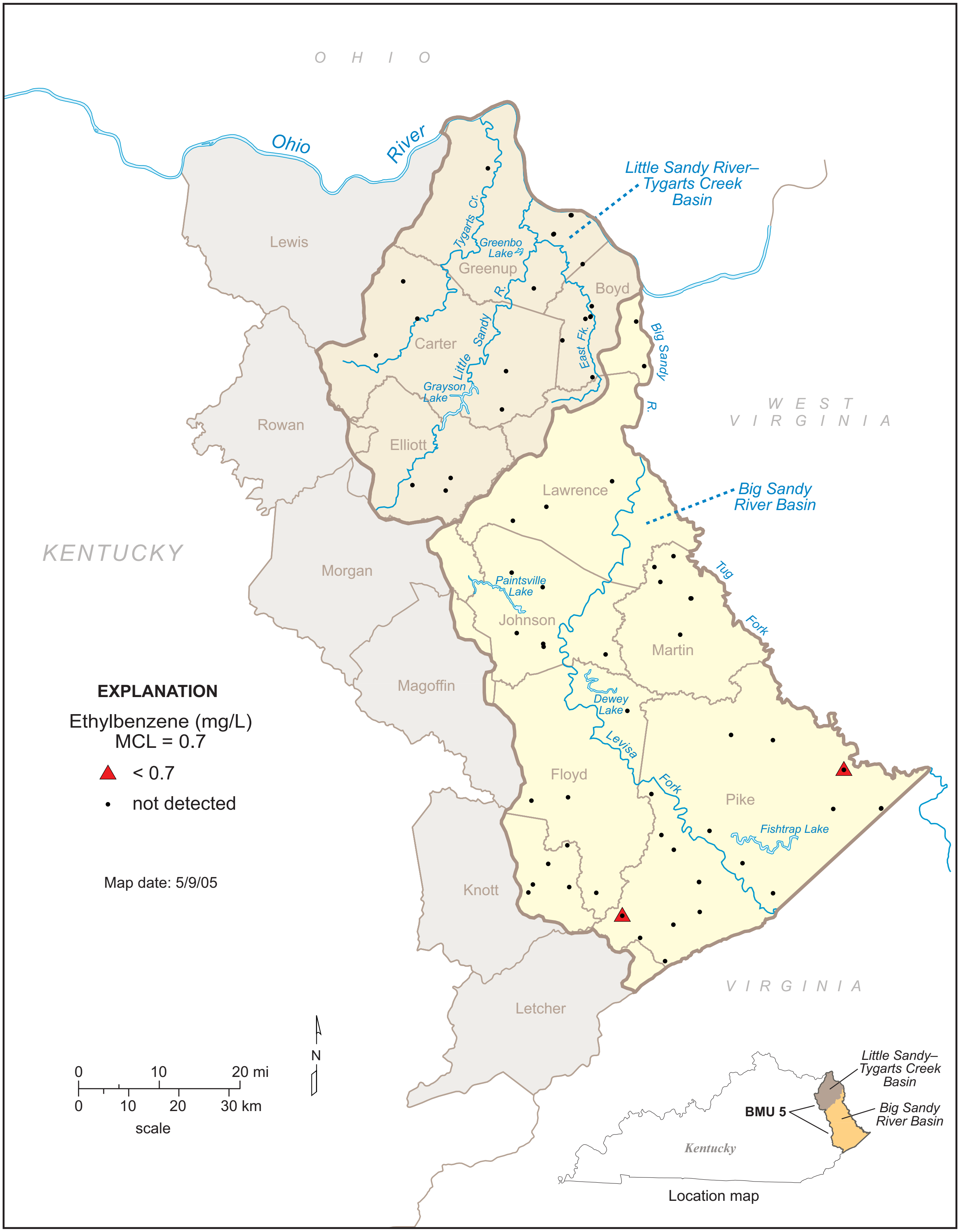

Figure 99. Locations of sampled sites and ranges of ethylbenzene values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

ter with benzene concentrations greater than the analytical detection limit.

The sampled sites were widely but evenly distributed throughout BMU 5 (Fig. 98). Both sites where benzene was detected were in the Big Sandy watershed. Because benzene was detected at only two sites, the data were not analyzed further.

In summary, occurrences of benzene in groundwater were rare and isolated in BMU 5. No widespread pattern of benzene in groundwater was found. The presence of benzene at sites that were not considered locations of point-source releases, however, indicates that the groundwater system is being affected by this volatile organic chemical.

Ethylbenzene. Common sources of ethylbenzene are discharges from petroleum refineries and leaking underground gasoline storage tanks. Because ethylbenzene can have health effects such as liver or kidney damage, the EPA has set an MCL for

Table 32. Summary of toluene concentrations (mg/L). MCL=1.0 mg/L.

Number of values	131
Maximum	0.008
75th percentile	< 0.0005
Median	< 0.0005
25th percentile	< 0.0005
Minimum	< 0.0005
Interquartile range	na
Number of sites	77
Number of where detected	9
Number of sites > 1.0 mg/L	0

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

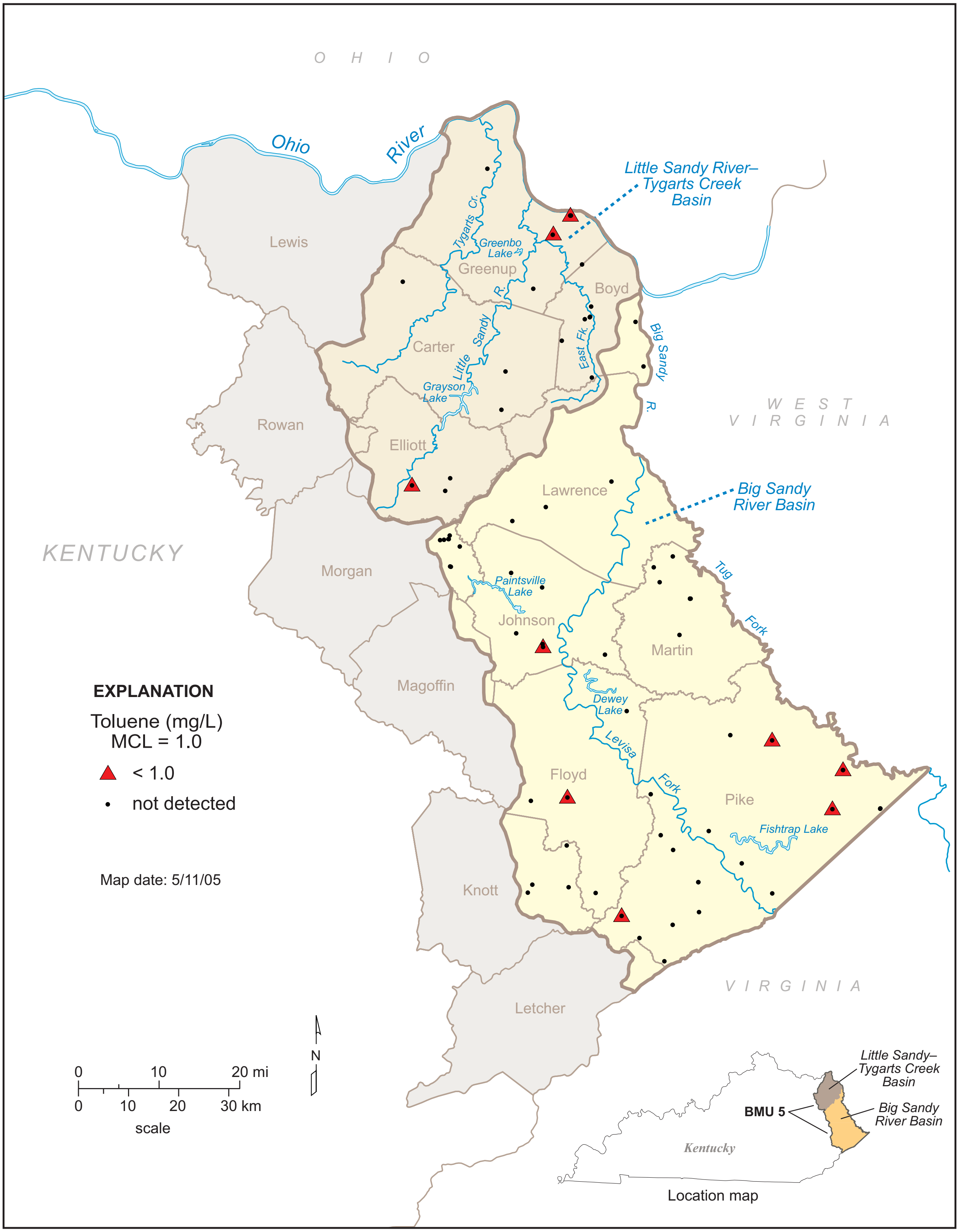

Figure 100. Locations of sampled sites and ranges of toluene values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

ethylbenzene of 0.7 mg/L.

The data repository contained 127 ethylbenzene measurements at 72 sites in the project area (Table 31). Two sites produced detectable ethylbenzene; no samples exceeded the MCL.

The sampled sites were widely but evenly distributed throughout BMU 5 (Fig. 99). Both sites where ethylbenzene was detected were in the Big Sandy watershed. Because ethylbenzene was detected at only two sites, the data were not analyzed further.

In summary, detectable levels of ethylbenzene in groundwater are isolated and rare in the project area. No widespread pattern of ethylbenzene occurrence in groundwater was found. The presence of ethylbenzene at sites that were not considered locations of point-source releases, however, indicates that the groundwater system is being affected by this volatile organic chemical.

Toluene. Common sources of toluene in groundwater are discharge from petroleum refineries and leaking underground gasoline storage tanks. The potential health effects are damage to the nervous system, kidneys, or liver. The MCL for toluene is 1.0 mg/L.

Table 33. Summary of total xylenes concentrations (mg/L). MCL=10.0 mg/L.

Number of values	115
Maximum	0.0305
75th percentile	< 0.001
Median	< 0.0005
25th percentile	< 0.0005
Minimum	< 0.0005
Interquartile range	na
Number of sites	45
Number of where detected	2
Number of sites > 10.0 mg/L	0

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

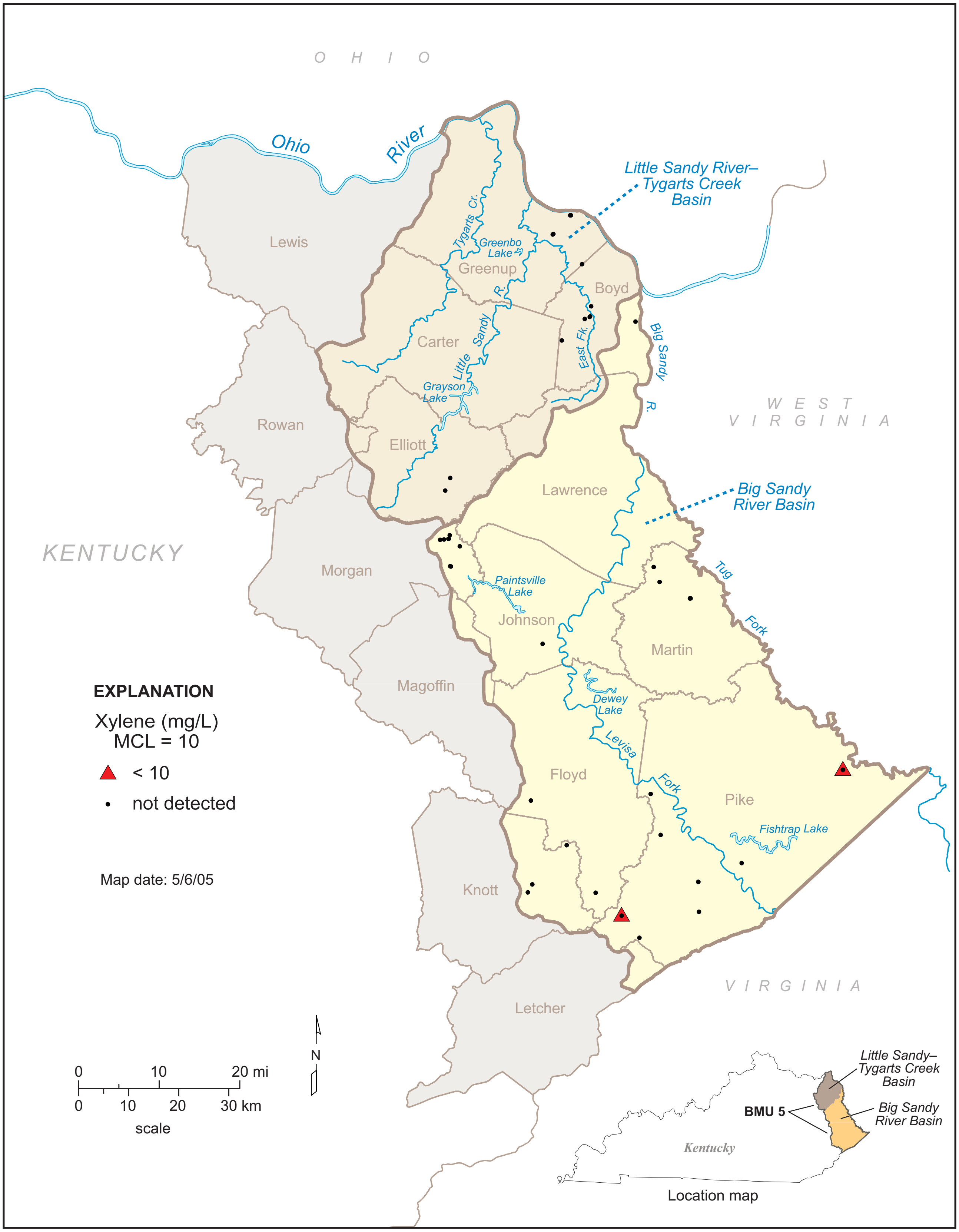

Figure 101. Locations of sampled sites and ranges of total xylenes values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

The data repository contained 131 toluene measurements at 77 sites in the project area (Table 32). No values exceeded the MCL; nine sites yielded detectable toluene.

The samples sites were widely but evenly distributed throughout BMU 5 (Fig. 100). Sites where toluene was detected were not geographically close. Because toluene was detected at only nine sites, the data were not analyzed further.

In summary, like the other volatile organic chemicals, toluene was not commonly detected in groundwater in the project area. The presence of toluene at sites that were not considered locations of point-source releases, however, indicates that the groundwater system is being affected by this volatile organic chemical.

Xylenes. Xylenes in groundwater are usually the result of discharge from petroleum refineries or chemical factories, or leaking underground gasoline storage tanks. The primary health effect is damage to the nervous system. The MCL is 10 mg/L for the sum of O-xylene, P-xylene, and M-xylene.

Table 34. Summary of MTBE concentrations (mg/L). DOW recommendation=0.05 mg/L.

Number of values	138
Maximum	0.002
75th percentile	< 0.001
Median	< 0.001
25th percentile	< 0.001
Minimum	< 0.001
Interquartile range	na
Number of sites	61
Number of where detected	3
Number of sites > 0.05 mg/L	0

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

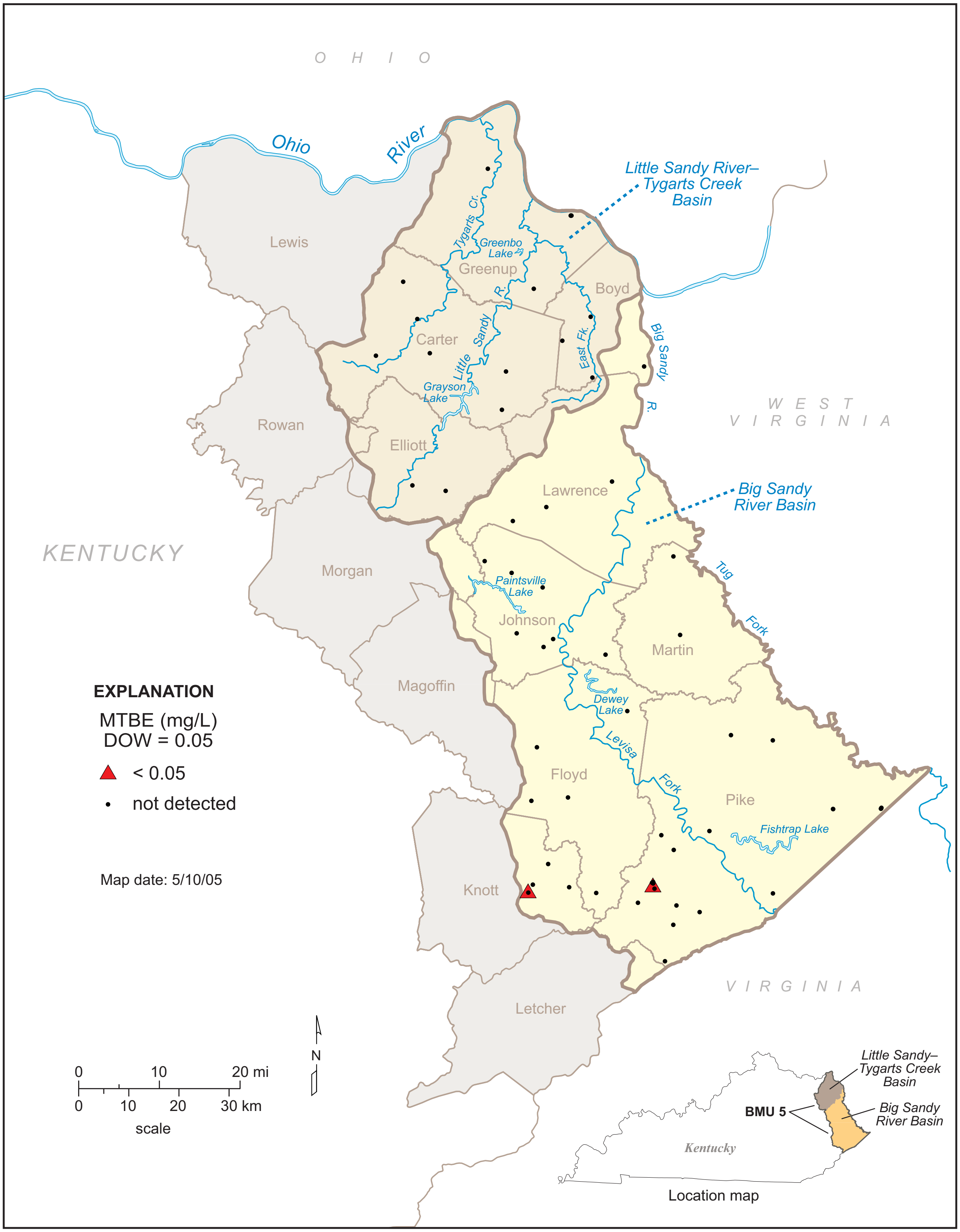

Figure 102. Locations of sampled sites and ranges of MTBE values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Xylene analyses in the data repository are reported as “1,3-xylene & 1,4-xylene,” “1,4-xylene,” “M-xylene,” “O-xylene,” “P-xylene,” “total xylene,” “xylene,” and “xylene mixed isomers.” The data repository contained 115 such measurements at 45 sites in the project area (Table 33). No samples exceeded the MCL of 10 mg/L. Two sites produced detectable xylenes.

The sampled sites were widely but evenly distributed throughout BMU 5 (Fig. 101). Both sites where xylene was detected were in the Big Sandy watershed. Because xylene was detected at only two sites, the data were not analyzed further.

In summary, xylenes were detected at two widely separated sites. None of the groundwater samples had xylene concentrations above the established MCL. Xylene has no natural sources, however, so any detection in groundwater is an indication that volatile organic chemicals are entering the groundwater system.

MTBE. MTBE (methyl tertiary-butyl ether) is a gasoline additive used to promote combustion and reduce emissions. The primary sources of MTBE in groundwater are leaks from gasoline storage tanks or gasoline spills; atmospheric fallout of exhaust gases is also a potential source. Potential health effects have not been established; however, the Division of Water has set a risk-based water-quality standard of 0.05 mg/L.

The data repository contained 138 MTBE measurements at 61 sites in BMU 5 (Table 34). No groundwater exceeded 0.05 mg/L; however, MTBE was detected at three sites in the Big Sandy watershed.

The sampled sites were widely but evenly distributed throughout BMU 5 (Fig. 102). Sites where MTBE was detected are in the far southern part of the Big Sandy watershed. Because MTBE was detected at only three sites, the data were not analyzed further.

In summary, MTBE generally does not occur at detectable levels in water from wells and springs in the project area. The presence of detectable MTBE at two sites shows that some contamination of groundwater is occurring, however.

Summary and Conclusions

The goal of this project was to summarize groundwater quality from wells and springs in basin management unit 5 (watersheds of the Big Sandy River, Little Sandy River, and Tygarts Creek in eastern Kentucky) and evaluate analyte concentrations with respect to criteria provided by the Division of Water. Thirty sites that had not been sampled previously were selected and sampled quarterly from fall 2002 through summer 2003. Results of those analyses were combined with data obtained from the Kentucky Groundwater Data Repository, which is the largest and most inclusive collection of information about groundwater in Kentucky. The water-quality data were compared to criteria provided by the Kentucky Division of Water, including maximum contaminant levels, secondary maximum contaminant levels, health advisory limits set by the U.S. Environmental Protection Agency, and other criteria established by the Division of Water.

The results show that the overall quality of Kentucky groundwater is generally good in the project area. This may be in part because of no extensive urban, industrial, or agricultural factors that could contribute nonpoint-source contamination. Coal mining, timber cutting, and oil and gas production occur in the area, and historically there has been a lack of adequate waste-disposal systems. Table 35 summarizes the findings.

Water properties (pH, total dissolved solids, total suspended solids, electrical conductance, and hardness), inorganic ions (chloride, sulfate, fluoride), and most metals (arsenic, barium, mercury, iron, and manganese) have natural sources and are largely controlled by bedrock lithology. Some exceptionally high values of conductance, chloride, and sulfate may be

Table 35. Summary of nonpoint-source effects on groundwater quality in basin management unit 5.

	Parameter	No Strong Evidence for Nonpoint-Source Impact on Groundwater Quality	Some Evidence for Nonpoint-Source Impact on Groundwater Quality	Clear Evidence for Nonpoint-Source Impact on Groundwater Quality
Water Properties	Conductance	X		
	Hardness	X		
	pH	X		
	Total dissolved solids	X		
	Total suspended solids	X		
Inorganic Ions	Chloride	X		
	Sulfate	X		
	Fluoride	X		
Metals	Arsenic	X		
	Barium	X		
	Iron	X		
	Manganese	X		
	Mercury	X		
Nutrients	Ammonia-nitrogen		X	
	Nitrate-nitrogen			X
	Nitrite-nitrogen	X		
	Orthophosphate	X		
	Total phosphorus	X		
Water Properties	2,4-D		X	
	Alachlor		X	
	Atrazine		X	
	Cyanazine	X		
	Metolachlor		X	
	Simazine		X	
Volatile Organic Compounds	Benzene		X	
	Ethylbenzene		X	
	Toluene		X	
	Xylenes		X	
	MTBE		X	

the effects of deep saline water associated with coal fields, oil and gas production, or leaking on-site waste-disposal systems, and some exceptionally low pH values may show the input of mine drainage. Some anomalously high metal concentrations may be natural or may be the result of human contamination; however, widespread nonpoint-source contamination is not suggested by these data.

Nutrient concentrations show the effects of both natural sources and nonpoint-source inputs. Nitrate-nitrogen concentrations that far exceeded natural contributions were common and probably caused by fertilizer applications. Ammonia-nitrogen concentrations were also commonly above recommended limits; however, this may have been caused by nitrogen from coal beds or leaf litter.

Pesticides and volatile organic chemicals are synthetic organic compounds that do not occur naturally. Although pesticides or volatile organic chemicals exceeded analytical detection limits at relatively few sites, the presence of any amounts of synthetic organic chemicals in groundwater indicates some contamination is occurring.

Throughout the project area, springs and shallow wells were more likely to have harmful levels of metals, nutrients, pesticides, and volatile organic chemicals than deeper wells. The potential contamination of the shallow groundwater system (springs and shallow wells) is cause for concern.

Acknowledgments

Many people contributed to this report. Jim Webb and Jo Blanset helped with data transfers. Rick Sergeant assisted with database management. Dan Carey helped with GIS issues. And Henry Francis helped resolve questions about analyte names, CAS numbers, and reporting practices. The final report was reviewed by Jim Dinger.

Funding for this project was provided in part by a grant from the U.S. Environmental Protection Agency as authorized by the Clean Water Act Amendments of 1987, Section 319(h) Nonpoint Source Implementation Grant C9994861-01.

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Appendix A: QA/QC Plan for Expanded Groundwater Monitoring for Nonpoint-Source Pollution Assessment in Basins of the Big Sandy River, Little Sandy River, and Tygarts Creek (Basin Management Unit 5)

Monitoring Program/Technical Design

Sampling Design and Strategies. Approximately 30 previously untested wells and springs in BMU 5 will be selected for sampling. These sample sites will be in addition to other stations currently sampled by the Groundwater Branch. For all selected sites, either a Kentucky Water Well Record or a Kentucky Spring Inventory Form will be placed on record with the Division of Water if one does not already exist. Site locations will be plotted on 7.5-minute topographic maps, and identified by a site name and unique identification number (AKGWA number) for incorporation into the Department for Environmental Protection's Consolidated Groundwater Database and the Kentucky Geological Survey's Kentucky Groundwater Data Repository. The precise latitude and longitude of each site will be determined by GPS measurements.

Sampling Locations. Specific sample sites will be chosen after the Division of Water's groundwater database has been reviewed for candidate sites and field inspection has confirmed that the candidate sites are suitable for monitoring.

Sampling Frequency and Duration. Quarterly monitoring of the sites will begin in October 2002 and will continue through September 2003.

Types of Data to Be Collected. Consistent with other monitoring efforts, samples will be collected at each spring or well and analyzed for some or all of the following: major inorganic ions; nutrients; total organic carbon; pesticides, including the most commonly used herbicides, insecticides, and fungicides; and dissolved and total metals. The analytical methods, containers, volumes collected, preservation, and sample transport will be consistent with the Division of Water's *Standard Operating Procedures for Nonpoint Source Surface Water Quality Monitoring Projects,* prepared by the Water Quality Branch (August 1995). Parameters to be measured, volumes required for analysis, container types, preservatives, holding times, transport conditions, and analytical methods to be used are given on the Chain-of-Custody form.

Where sewage is suspected as a nonpoint-source pollutant, unbleached cotton fabric swatches may be used to detect optical brighteners, the whitening agents used in laundry products and commonly found in sewage (Quinlan, 1987). Bacteria will not be sampled because of logistical considerations. Sampling at numerous sites occurs over a 1- or 2-day period, commonly in remote regions. Because of the short holding time for bacteria (6 hours for fecal coliform, 24 hours for total coliform), we are unable to sample efficiently and regularly collect bacteria samples and comply with the required holding times.

Chain-of-Custody Procedures

Sample containers will be labeled with the site name and well or spring identification number, sample collection date and time, analysis requested, preservation method, and collector's initials. Sampling personnel will complete a Chain-of-Custody form developed in conjunction with the DES laboratory for each sample. The DES laboratory will be responsible for following approved laboratory QA/QC procedures, conducting analyses within the designated holding times, following EPA-approved analytical techniques, and reporting analytical results to the Groundwater Branch. Parameters to be measured, volumes required for analysis, container types, preservatives, holding times, transport conditions, and analytical methods to be used are given on the accompanying Chain-of-Custody form.

Quality Control Procedures

Container and Equipment Decontamination. All sampling supplies that come in contact with the sample will be new, disposable equipment, or will be decontaminated prior to and after each use, using the following protocols. Whenever possible, sample collection is conducted using the sample container, except for dissolved metals, which are filtered on-site. Sample collection equipment such as bailers and buckets will be made of Teflon. Pesticide samples will be collected using the sample container or a stainless steel bailer or bucket, in order to avoid the problem of pesticide adsorption to the sampling device (as is considered to occur with Teflon instruments). Any reusable equipment will be decontaminated by rinsing with a 10 percent hydrochloric acid (HCl) solution, triple-rinsed with deionized water, and triple-rinsed with water from the source to be sampled prior to collecting a sample. After sampling is complete, excess sample will be disposed of, and the equipment will again be rinsed with the 10 percent HCl solution and triple-rinsed with deionized water.

New 0.45-micron filters will be used at each sampling site. Any tubing that contacts the sample will also be new. Any reusable filter apparatus will be decontaminated in the same manner as sample collection equipment. In addition, any intermediary collection vessel will be triple-rinsed with filtrate prior to use.

Equipment Calibration

Conductivity, temperature, and pH will be measured in the field at each site using portable automatic temperature compensating meters, and recorded in a field log book. Meters will be calibrated according to the manufacturer's specifications, using standard buffer solutions. Meter probes will be decontaminated according to decontamination protocols for field meters and stored according to the manufacturer's recommendations.

Sample Contamination Prevention

Water samples will be fresh groundwater collected prior to any type of water treatment. Samples not requiring field filtration will be collected directly in the sampling container. Samples requiring field filtration will be collected in a Teflon bucket decontaminated in accordance with decontamination protocols for sample collection and filtration equipment, filtered, and transferred to the appropriate container. Pesticide samples will be collected using the sample container or a stainless steel bailer or bucket, wherever necessary.

Sample containers will be obtained from approved vendors, and will be new or laboratory-decontaminated in accordance with Division of Environmental Services accepted procedures. Sample containers, preservation, and holding time requirements are outlined in the Division of Water's *Standard Operating Procedures for Nonpoint Source Surface Water Quality Monitoring Projects,* prepared by the Water Quality Branch (Kentucky Division of Water, 1995). Necessary preservatives will be added in the field; preservatives for dissolved constituents will be added after field filtration. Samples will be stored in coolers packed with ice for transport to the Division of Environmental Services laboratory.

Sample containers will be labeled with the site name and identification number, sample collection date and time, analysis requested, preservation method, and collector's initials. Sampling personnel will complete a Chain-of-Custody form for each sample. The Division of Environmental Services laboratory will be responsible for following approved laboratory QA/QC procedures, conducting analyses within the designated holding times, following EPA-approved analytical techniques, and reporting analytical results to the Groundwater Branch.

Wells will be purged until conductivity readings stabilize prior to sampling, in order to ensure that groundwater, rather than water that has been standing in the wellbore, is being sampled. Spring samples will be collected as close to the spring resurgence as possible. If inhospitable terrain prohibits spring access, a decontaminated Teflon bucket attached to a new polypropylene rope may be lowered to the spring to collect the sample. Samples for pesticide analysis will be collected using a stainless steel bucket.

Quality Control Samples

Duplicate samples may be collected periodically to verify reproducibility and provide QA/QC control. Ideally, 10 percent of the samples should be duplicated, and at least one duplicate sample submitted with each batch of samples, regardless of the number of samples in the batch. Blanks of deionized water should also be submitted at least once per quarter. Because of laboratory constraints, however, the frequency with which duplicates and blanks will be submitted will be determined based on QA/QC data from other sampling programs.

Acceptable Levels of Variance for Duplicate Results

According to Division of Environmental Services' accepted procedures, duplicate analyses will be accepted if they are within 20 percent relative standard deviation. If unacceptable results are found, samples will be analyzed again and field records will be examined to determine the cause.

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CHAIN OF CUSTODY RECORD

NATURAL RESOURCES AND ENVIRONMENTAL PROTECTION CABINET
DIVISION OF WATER - GROUNDWATER BRANCH - Big Sandy/Tygarts Creek 319 Project - Funding Source A-21

Site Identification	***Collection Date/Time***	***Field Measurements***
Location:	Date: ______	pH: ______ Conductivity: ______ μmhos
County:		
AKGWA #:	Time: ______	Temp: ______ °C Spring flow: ______

Sampler ID: ______________________

Division for Environmental Services Samples			
Analysis Requested	**Container Size, Type**	**Preservation Method**	**Parameters**
	1,000 ml plastic Cubitainer	cool to 4°C	***Bulk Parameters*** By ICP: chloride, fluoride, nitrate-N, nitrite-N, sulfate, ortho-P plus alkalinity, conductivity, pH, TSS, TDS
	1,000 ml plastic Cubitainer	H_2SO_4 cool to 4°C	***Nutrients:*** NH_3/TKN/TOC/total phosphorus
	1,000 ml plastic Boston Round	filtered HNO_3 cool to 4°C	***Dissolved Metals by ICP:*** aluminum, barium, calcium, iron, magnesium, manganese, nickel, potassium, silver, sodium, zinc
	1,000 ml plastic Boston Round	HNO_3 cool to 4°C	***Total Metals by ICP:*** aluminum, barium, calcium, iron, magnesium, manganese, nickel, potassium, silver, sodium, zinc ***By Graphite Furnace:*** arsenic, cadmium, chromium, copper, lead, selenium ***By Cold Vapor Extraction:*** mercury
	1,000 ml amber glass	cool to 4°C	***N/P Pesticides:*** organochlorine pesticides/PCBs methods 507/508
	1,000 ml amber glass	cool to 4°C	***Herbicides:*** method 515.1
	three 40 ml glass	HCl cool to 4°C	***VOCs:*** (field blank required)

COMMENTS:

Signatures:

Relinquished by: ______________________ Date: __________ Time: __________

Received by: ______________________

Relinquished by: ______________________ Date: __________ Time: __________

Received by: ______________________

Sample #: ______________________ Report #: __________

DISCARD SAMPLES UPON COMPLETION

Revised 5/14/02

CHAIN OF CUSTODY RECORD

NATURAL RESOURCES AND ENVIRONMENTAL PROTECTION CABINET
DIVISION OF WATER - GROUNDWATER BRANCH

Preparation Date/Time

Date:_______________

Time:_______________

Prepared by: ______________________

Funding Source -

☐ **A21** General Groundwater ☐ **A39** Monitoring Network

☐ **A42** Pesticides MOA ☐ Other ________________

Site Identification

FIELD BLANK FOR:

Field Sampler ID: ___________________________

Division for Environmental Services Samples

Analysis Requested	Container Size, Type	Preservation Method	Parameters
	40 ml glass	50% HCl cool to 4°C	**VOCs:**

Signatures:

Relinquished by: _____________________________ Date:_______________ Time:_______________

Received by: _____________________________

Relinquished by: _____________________________ Date:_______________ Time:_______________

Received by: _____________________________

Relinquished by: _____________________________ Date:_______________ Time:_______________

Received by: _____________________________

Sample #: ___________________________________ Report #:______________

DISCARD SAMPLES UPON COMPLETION

Revised 1/22/07