# Summary and Evaluation of Groundwater Quality in Watersheds of the Kentucky River, Salt River, Licking River, Big Sandy River, Little Sandy River, and Tygarts Creek

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# **EXECUTIVE SUMMARY**

The Kentucky Geological Survey, University of Kentucky, and the Kentucky Division of Water, Kentucky Environmental and Public Protection Cabinet are evaluating groundwater quality throughout the Commonwealth to determine regional conditions, assess impacts of nonpoint-source pollutants, establish a basis for detecting changes, and provide essential information for environmental protection and resource management.

These evaluations are being conducted in stages. Under the Kentucky Watershed Management Framework, Kentucky's 12 major river basins and tributaries of the Ohio River were grouped into 5 Basin Management Units (BMUs). A previous report summarized and evaluated groundwater quality in BMU 3 (watersheds of the Upper Cumberland River, Lower Cumberland River, Tennessee River, the Jackson Purchase Region, and adjacent Ohio River tributaries) and BMU 4 (watersheds of the Green River and Tradewater River, and adjacent Ohio River tributaries). That report is available on the KGS Web site: <a href="http://www.uky.edu/KGS/water/research/bwquality.htm">http://www.uky.edu/KGS/water/research/bwquality.htm</a>. This report summarizes results of analyses of groundwater samples from wells and springs in Kentucky BMU 1 (Kentucky River watershed and adjacent Ohio River tributaries), BMU 2 (Salt River and Licking River watersheds and adjacent Ohio River tributaries), and BMU 5 (Big Sandy River, Little Sandy River, and Tygarts Creek watersheds, and adjacent Ohio River tributaries).

Analytical results for selected water properties, major and minor inorganic ions, metals, nutrients, pesticides, and volatile organic chemicals were 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 data from 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. The Kentucky Division of Water provided water-quality standards. Summary statistics such as the number of measurements reported, the number of sites sampled, quartile concentration values, and the number of sites at which water-quality standards were met or exceeded are used to summarize the data. Maps show sampled locations and sites where water-quality standards were met or exceeded. Cumulative data plots are used to show concentration distributions in each BMU. Boxand-whisker diagrams are used to compare values between physiographic regions, major watersheds, wells and springs, and total versus dissolved metal concentrations. Plots of concentrations versus well depth are used to compare groundwater quality in shallow, intermediate, and deep flow systems.

Table E1 summarizes the findings. Water-quality properties, inorganic anions, and metals are primarily controlled by natural factors such as bedrock lithology. Some exceptionally high values of conductance, hardness, chloride, and sulfate may be affected by nearby oil and gas production, leaking waste disposal systems, or other anthropogenic factors, and some exceptionally low pH values may indicate influence from acid mine drainage. Nitrate concentrations show a strong contribution from agricultural and waste-disposal practices, whereas orthophosphate and total phosphorus concentrations are determined by the chemical composition of limestone bedrock. Synthetic organic chemicals such as pesticides and volatile organic compounds do not occur naturally in groundwater. The presence of volatile organic compounds in groundwater is generally associated with anthropogenic impacts, although some volatile organic compounds do occur naturally. Although these chemicals rarely exceed water-quality criteria in the project area, the detection of these manmade chemicals in springs and shallow wells indicates there has been some degradation of groundwater quality. Monitoring of these synthetic, potentially health-threatening chemicals should continue, and efforts to protect the groundwater resource from them should be a priority for the Commonwealth of Kentucky.

Table E1. Summary of evidence for nonpoint-source impacts on groundwater quality in Basin Management Units 1, 2, and 5.

|            | Parameter                                | No strong evidence for | Evidence for minimal | Evidence for definite |
|------------|--|------------------------|----------------------|-----------------------|
|            | 1 44 44 44 44 44 44 44 44 44 44 44 44 44 | widespread             | nonpoint-            | nonpoint-             |
|            |  | nonpoint-              | source impact        | source                |
|            |  | source                 | •                    | impact                |
|            |  | impact                 |                      | -                     |
|            | Conductance                              | X                      |                      |                       |
| Water      | Hardness                                 | X                      |                      |                       |
| Properties | pН                                       | X                      |                      |                       |
|            | Total dissolved solids                   | X                      |                      |                       |
|            | Total suspended solids                   | X                      |                      |                       |
| Inorganic  | Chloride                                 | X                      |                      |                       |
| Ions       | Sulfate                                  | X                      |                      |                       |
|            | Fluoride                                 | X                      |                      |                       |
|            | Arsenic                                  | X                      |                      |                       |
| Metals     | Barium                                   | X                      |                      |                       |
|            | Iron                                     | X                      |                      |                       |
|            | Manganese                                | X                      |                      |                       |
|            | Mercury                                  | X                      |                      |                       |
|            | Ammonia nitrogen                         |                        | X                    |                       |
| Nutrients  | Nitrate nitrogen                         |                        |                      | X                     |
|            | Nitrite nitrogen                         |                        | X                    |                       |
|            | Orthophosphate                           | X                      |                      |                       |
|            | Total phosphorus                         | X                      |                      |                       |
|            | 2,4-D                                    |                        | X                    |                       |
| Pesticides | Alachlor                                 |                        | X                    |                       |
|            | Atrazine                                 |                        | X                    |                       |
|            | Cyanazine                                |                        | X                    |                       |
|            | Metolachlor                              |                        | X                    |                       |
|            | Simazine                                 |                        | X                    |                       |
|            | Benzene                                  |                        | X                    |                       |
| Volatile   | Ethylbenzene                             |                        | X                    |                       |
| Organic    | Toluene                                  |                        | X                    |                       |
| Compounds  | Xylenes                                  |                        | X                    |                       |
|            | MTBE                                     |                        | X                    |                       |

# 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 and evaluate groundwater quality in the northeastern portion of Kentucky (watersheds of the Kentucky River, Salt River, Licking River, Big Sandy River, Little Sandy River, and Tygarts Creek, and Ohio River tributaries adjacent to those watersheds). A similar report on groundwater quality in the southwestern portion of Kentucky was previously completed (Fisher and others, 2004).

#### Goals

The major goals of this report are to identify representative, regional values for a select group of groundwater-quality parameters and to determine whether nonpoint source (NPS) chemicals have entered the groundwater system. The results of this evaluation provide a basis for identifying natural and anomalous concentrations of dissolved chemicals, identify areas where NPS chemicals have entered the groundwater system and implementation of best management practices (BMPs) are needed, provide information for Kentucky Division of Water (DOW) Watershed Assessment Reports, provide groundwater-quality data to the DOW Groundwater Protection program, help the DOW Wellhead Protection program prioritize 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 DOW 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 it expensive or impractical to replace groundwater with surface-

water supplies in rural areas, and because some cities along the Ohio River are turning to groundwater from alluvial deposits for urban water supplies. It has been estimated that approximately 400,000 Kentuckians will still depend on private, domestic water supplies in the year 2020 (Kentucky Geological Survey, 1999).

Both natural and anthropogenic processes affect groundwater quality. The major 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**

There are numerous reports in or near the study area that describe the hydrology, groundwater resources and general water quality of the study area. However, few address the issue of nonpoint source contamination. In the 1960's and early 1970's the U. S. Geological Survey (USGS) published reconnaissance studies of the geology, groundwater supplies, and general groundwater quality in Kentucky. These reports include a Hydrologic Atlas series, which was made in conjunction with the Kentucky Geological Survey, with each atlas covering from two to ten counties across the state (except in the Jackson Purchase area, which had coverage for each 1:24,000 quadrangle). Each atlas includes three sheets showing geology, lithology and availability of groundwater. The atlases have been 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. Older but more comprehensive groundwater resource reports related to this study area include: Bluegrass

Region (Hendrickson and Krieger, 1964; Faust, 1977), Eastern Coal Field (Price and others, 1962), and the Mississippian Plateau Region, herein referred to as the Eastern and Western Pennyroyal Regions (Brown and Lambert, 1963). These reports considered major and minor inorganic ions and nitrate; 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 Groundwater Resource Development Commission (<a href="http://kgsweb.uky.edu/download/wrs/GWTASK1.PDF">http://kgsweb.uky.edu/download/wrs/GWTASK1.PDF</a>). Carey and others (1993) surveyed selected groundwater-quality parameters, including nutrients and pesticides, in private groundwater supplies.

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

DOW interpreted the results of expanded groundwater monitoring in BMU 2 as a contract report (Webb and others, 2003). The data used in that report are included in the larger data sets used here.

# PROJECT AREA

The DOW Watershed Management Framework grouped Kentucky's major river basins into five Basin Management Units (BMUs; Figure 1). The current project area includes the watersheds of BMU 1 (Kentucky River), BMU 2 (Salt and Licking Rivers) and BMU 5 (Big Sandy, Little Sandy and Tygarts Rivers) and adjacent tributaries of the Ohio River.

The project area includes five of Kentucky's physiographic regions: Eastern Kentucky Coal Field, Knobs, Eastern Pennyroyal, Outer Bluegrass, and Inner Bluegrass (Figure 1). Each region is distinguished by unique bedrock type, topography, and soil types (McDowell, 1986; Newell, 1986). This framework is important to understanding groundwater quality because it has a controlling effect on the natural occurrences of major and minor inorganic solutes and metals. It also strongly

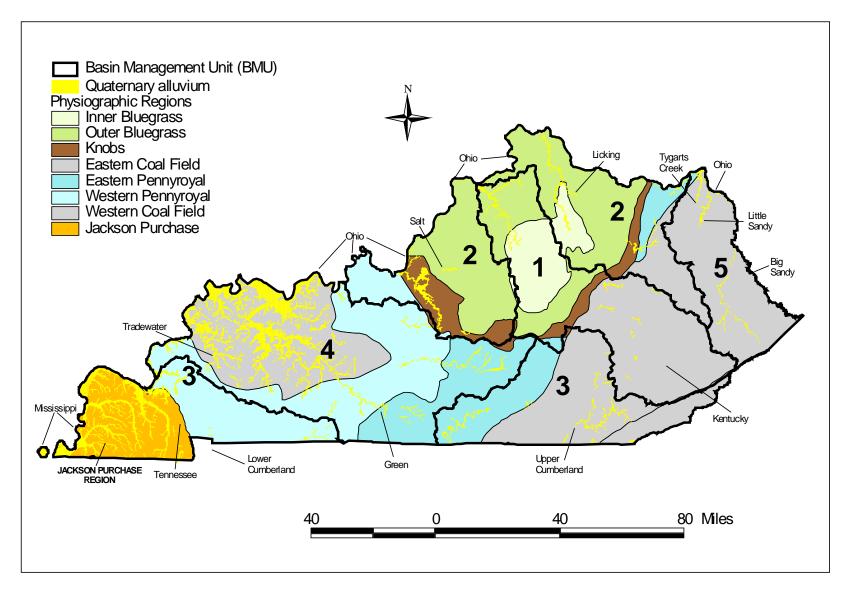


Figure 1. Map showing major river watersheds, physiographic regions, and Basin Management Units.

influences land use, urban and commercial development, and the potential use of nutrients, pesticides, and volatile organic compounds.

The Eastern Kentucky Coal Field 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).

The Eastern Pennyroyal Region consists mainly of thick, horizontally bedded limestone with minor, thin shales. The pennyroyal surface is characterized by karst features such as sinkholes and springs, connected by underground solution channels and caves. Soils are composed of insoluble residue that remains as the carbonate rocks weather.

The Knobs region is a narrow belt separating the Eastern Pennyroyal Region from the Outer Bluegrass Region. It is characterized by conical, flat-topped hills composed mostly of shale and siltstone, topped by more resistant cap rock. Soils are thin except where the lower slopes of knobs merge with alluvium in valley bottoms.

The Inner and Outer Bluegrass Regions are gently rolling to relatively flat lowlands, underlain with interbedded limestones and shales. The regions display well-developed karst features such as sinkholes, springs, underground streams, and caves. Soils in the Inner Bluegrass are generally thick and phosphatic, whereas soils in the Outer Bluegrass range from thick and rich over limestones to thin and clayey over shales (Newell, 1986).

## **Basin Management Unit 1**

Basin Management Unit 1 (Kentucky River watershed) includes the Inner and Outer Bluegrass, Knobs, Eastern Pennyroyal, and Eastern Kentucky Coal Field Regions, and covers an area of about 6,975 square miles (Figure 1). The Kentucky River originates in the mountains of the Eastern Kentucky Coal Field and flows northwest through the Knobs and the Outer and Inner Bluegrass Regions to join the Ohio River near Carrollton in Carroll County. The total length of

the river in the basin is approximately 405 miles. The main stem of the Kentucky River extends approximately 255 miles through 14 locks and dams.

Land uses and NPS chemical threats to groundwater quality in BMU 1 include oil and gas production; active and abandoned coal mines; leaking sewage disposal systems; straight pipes (household sewage dumped directly into streams or rivers), deforested areas in the Eastern Kentucky Coal Field; and farm land, urban centers, and confined animal feeding operations (Kentucky Division of Water, 2000). Groundwater is particularly vulnerable to nonpoint-source contamination in the karst regions of the Bluegrass because of the well-developed network of sink holes, caves, and springs.

BMU 1 includes all or parts of the following 47 counties: Anderson, Bell, Boone, Bourbon, Boyle, Breathitt, Carroll, Casey, Clark, Clay, Estill, Fayette, Floyd, Franklin, Gallatin, Garrard, Grant, Harlan, Harrison, Henry, Jackson, Jessamine, Kenton, Knott, Knox, Laurel, Lee, Leslie, Letcher, Lincoln, Madison, Magoffin, Menifee, Mercer, Montgomery, Morgan, Owen, Owsley, Perry, Pike, Powell, Rockcastle, Scott, Shelby, Trimble, Wolfe, and Woodford.

# **Basin Management Unit 2**

Basin Management Unit 2 consists of the Licking River and Salt River watersheds and adjacent Ohio River tributaries. The Licking River has headwaters in the mountains of Magoffin County in the Eastern Kentucky Coal Field and flows northwest toward the Ohio River. The Licking River flows through the Eastern Pennyroyal and Knobs Regions into the Outer and Inner Bluegrass Regions and enters the Ohio River between Newport and Covington. The Licking River Basin drains approximately 3,710 square miles, and provides a source of drinking water for nearly 80 percent of the population in the basin.

Although the Salt River Basin is west of the Kentucky River Basin, it is also included in BMU 2. This basin drains approximately 4,155 square miles. The Salt River itself is nearly 150 miles long and flows northwest, emptying into the Ohio River near West Point in northern Hardin County in the Fort Knox Military Reservation.

Land uses and NPS threats in BMU 2 are varied. Agricultural land accounts for approximately 57 percent of the region; forest land accounts for approximately 30 percent, and residential and

urban land account for the remainder (Kentucky Division of Water, 2001). The major NPS threats are fertilizers, pesticides, animal wastes, mine drainage, runoff from mine spoil, leaking septic systems, and urban stormwater runoff.

BMU 2 includes all or parts of the following 54 counties: Anderson, Bath, Boone, Bourbon, Boyle Bracken, Breathitt, Breckinridge, Bullitt, Campbell, Carroll, Carter, Casey, Clark, Elliott, Fayette, Fleming, Floyd, Gallatin, Grant, Green, Greenup, Hardin, Harrison, Henry, Jefferson, Johnson, Kenton, Knott, Larue, Lewis, Lincoln, Magoffin, Marion, Mason, Meade, Menifee, Mercer, Montgomery, Morgan, Nelson, Nicholas, Oldham, Pendleton, Powell, Robertson, Rowan, Scott, Shelby, Spencer, Taylor, Trimble, Washington and Wolfe.

# **Basin Management Unit 5**

Basin Management Unit 5 includes watersheds of the Big Sandy and Little Sandy Rivers, and Tygarts Creek. This basin covers approximately 4,610 square miles in the Eastern Kentucky Coal Field. The Big Sandy River forms the northeastern state boundary between Kentucky and West Virginia, and flows northwest to Boyd County where it joins the Ohio River near Cattletsburg. 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 east 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 in BMU 5 include oil and gas production, active and abandoned coal mines, leaking sewage disposal systems, deforested areas in the Eastern Kentucky Coal Field, and confined animal feeding operations (DOW, 2000). The major NPS threats are mine drainage, runoff from mine spoil, leaking septic systems, straight pipes, fertilizers, pesticides and animal wastes.

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 (USGS) has assigned Hydrologic Unit Codes (HUCs) to watersheds to identify regions, subregions, accounting units, and cataloging units (USGS, 1988). The HUC designations of watersheds in BMUs 1, 2 and 5 are listed in Tables 1 and 2.

Table 1. Watershed names and 6-digit HUC designations for Basin Management Units 1, 2 and 5.

| 6-digit HUC | HUC 6 Name  |   |
|-------------|---|---|
| 051002      | Kentucky River                                    | 1 |
| 050902      | Areas along the Ohio River                        | 2 |
| 051001      | Licking River                                     | 2 |
| 051401      | Salt River, Rolling Fork River, and Ohio River    | 2 |
| 050702      | Big Sandy River                                   | 5 |
| 050901      | Tygarts Creek, Little Sandy River, and Ohio River | 5 |

Table 2. Watershed names and 8-digit HUC designations for Basin Management Units 1, 2 and 5.

| 8-Digit HUC | -Digit HUC 8 Name                                  |   |
|-------------|--|---|
| 05100201    | North Fork Kentucky River                          | 1 |
| 05100202    | Middle Fork Kentucky River                         | 1 |
| 05100203    | South Fork Kentucky River                          | 1 |
| 05100204    | Kentucky River - Red River                         | 1 |
| 05100205    | Lower Kentucky River                               | 1 |
| 05090201    | Ohio River - Kinniconick Creek                     | 2 |
| 05090203    | Ohio River - Gunpowder Creek                       | 2 |
| 05100101    | Licking River                                      | 2 |
| 05100102    | South Fork Licking River                           | 2 |
| 05140101    | Ohio River - Little Kentucky River - Harrods Creek | 2 |
| 05140102    | Salt River   | 2 |
| 05140103    | Rolling Fork River                                 | 2 |
| 05140104    | Ohio River - Sinking Creek                         | 2 |
| 05070201    | Big Sandy River                                    | 5 |
| 05070202    | Upper Levisa Fork                                  | 5 |
| 05070203    | Levisa Fork  | 5 |
| 05070204    | Blaine Creek                                       | 5 |
| 05090103    | Tygarts Creek - Ohio River                         | 5 |
| 05090104    | Little Sandy River                                 | 5 |

# **Groundwater Sensitivity Regions**

The vulnerability of groundwater to NPS contamination varies geographically across Kentucky, and vertically at any given location, in response to both natural and anthropogenic 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 anthropogenic factors such as the type of land use, nature and amount of chemicals applied to agricultural and urban landscapes, waste-water 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, DOW 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 three factors: the potential ease and speed of vertical infiltration, the maximum potential flow velocity, and the potential for dilution by dispersion after a chemical enters the aquifer.

Groundwater sensitivity to NPS contamination generally decreases with depth as a result of the same factors: infiltration is slower and more tortuous, allowing for degradation and dilution of the chemicals, flow velocities in deep groundwater systems are slower, allowing for additional degradation and dilution of nonpoint source chemicals, and dispersion and dilution are greater because deep groundwater systems contain water from large recharge areas.

Within the study area, the sensitivity of shallow groundwater to NPS contamination can best be summarized by physiographic region (Ray and others, 1994). The uppermost groundwater system is moderately sensitive in the Knobs and the Eastern Coal Field, but highly to extremely sensitive in the Eastern Pennyroyal, Inner and Outer Bluegrass Regions.

Local groundwater sensitivity may be very different from these regional assessments, but local conditions cannot be assessed in this regional summary of groundwater quality. Well depth is an approximate indicator of whether a shallow, intermediate, or deep groundwater system is being sampled. However, two factors limit the usefulness of well depth as an indicator of groundwater system. 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. Secondly, 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**

Records for groundwater analyses were extracted from the Kentucky Groundwater Data Repository. The intent was to extract and summarize analyses of samples that are representative of regional groundwater quality, and to avoid reports from wells or springs that were known or suspected of being contaminated by local conditions. For this reason, samples collected for the Resource Conservation and Recovery Act (RCRA), Solid Waste, or Underground Storage Tank regulatory programs were excluded. Even so, some of the anomalous values that were included in the resulting data sets may represent local or point-source contamination because there was no basis in the data reports for excluding those results. Determining whether these results are naturally occurring extreme values, inaccurate data entries, or are the result of pollutants would require reviewing the original sample collection reports or visiting the site. Those activities are beyond the scope of this project.

Analytical results from wells deeper than 1000 ft were excluded because such deep wells are not generally used for domestic water supplies. However, it is possible that some deep samples are included in the data sets used here if well depths are not recorded.

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 either determine the suitability of the water for various uses, provide geochemical signatures that characterize the regional groundwater flow system, have recognized or suspected impacts on human health, or record the impacts of NPS contaminants on groundwater. The parameters selected are:

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 phosphorus

Pesticides: alachlor, atrazine, cyanazine, metolachlor, simazine

Volatile organic compounds: benzene, ethylbenzene, toluene, xylenes, MTBE

Both dissolved concentrations (measured on a sample that had been filtered to remove suspended particulate material) and total concentrations (measured on an unfiltered sample) were retrieved from the database for metals.

Many of the analytes of interest have been reported under a variety of names, and not all analytical results are identified by unique CAS numbers (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<sub>4</sub>-P)", "phosphate", "phosphate-total", "phosphate-ortho", "phosphorus", "phosphorus-ortho", "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 Basin Management Unit number, 6-digit HUC number, major watershed name, and physiographic region designation so that the data could be grouped into these categories. GIS coverages of 6-digit HUCs and physiographic regions were obtained from the KGS Web site (http://www.uky.edu/KGS/gis/intro.html).

# 2. Delete records that do not provide useful information.

The US Environmental Protection Agency (EPA) has established maximum contaminant levels (MCLs) 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 analytical data for this report and so were eliminated from the data sets.

# 3. Count the number of analytical results and sampled sites for each constituent.

Many wells and springs were sampled more than once, so there may be more than one

reported concentration for an analyte at a particular site. The number of individual 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 there are some extremely high values. 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 efficiently describe the data. Nonparametric statistical measures such as quartile values and interquartile range provide a better description of the data population (e.g. 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 which 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 which 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 (IQR: range of values between the first and third quartile values, also equal to the central fifty 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 RCRA investigations (EPA, 1992). The goals of this report are to summarize ambient groundwater quality and to locate regions affected or threatened by NPS 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 the quartile determinations.

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# 5. Determine the number of sites at which measurements exceeded water-quality standards.

Because there may have been many samples 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 DOW (Table 3).

# 6. Map sampled sites and use various symbols to represent concentration ranges and to show where MCL or other critical values were exceeded.

Maps show sample site locations, site distributions, concentration ranges, and areas where concentrations exceed MCLs or other critical values. Maps also reveal whether analyte values are randomly distributed or are 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 hundreds of feet of each other may not be resolved as separate locations. Therefore, the maps are useful for illustrating the general location of sites where various criteria are met or exceeded but they do 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 to compare analytical results between watersheds, physiographic regions, or other groupings.

Summary tables list the number of measurements and sites, quartile values, and the number of sites where concentrations exceed MCLs or other standard values for each Basin Management Unit.

Table 3. Parameters and water-quality standards used for data summaries.

|                | Parameter              | Standard (mg/L unless otherwise   | Source   |
|----------------|------------------------|---|--|
|                |                        | noted)  |  |
| Water          | Conductance            | 10,000 microsiemens   | No MCL or SMCL,<br>approximately<br>corresponds to brackish<br>water |
| Properties     | Hardness (calcium      | Soft: 0 to 17   |  |
|                | and magnesium)         | Slightly Hard: 18 to 60<br>Moderately Hard: 61 to 120<br>Hard: 121 to 180<br>Very Hard: > 180 | U.S. Geological Survey   |
|                | рH                     | 6.5 to 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  |
|                | Arsenic                | 0.010   | MCL  |
| Metals         | 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-        | 0.04  | Texas surface-water  |
|                | phosphorus             | 0.1   | standard   |
|                | Total phosphorus       | 0.1   | NAWQA  |
|                | 2,4-D                  | 0.07  | MCL  |
|                | Alachlor               | 0.002   | MCL  |
| Pesticides     | Atrazine               | 0.003   | MCL  |
| Pesticiaes     | Cyanazine              | 0.001   | HAL  |
|                | Metolachlor            | 0.1   | HAL  |
|                | Simazine               | 0.004   | MCL  |
| T7 7           | Benzene                | 0.005   | MCL  |
| Volatile       | Ethylbenzene           | 0.7   | MCL  |
| Organic        | Toluene                | 1.0   | MCL  |
| Compounds      | Xylenes                | 10  | MCL  |
| MCL M :        | 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 result in eutrophication.

HAL: Health Advisory Level. Higher concentrations may impact 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.

Normal probability plots (cumulative data plots: Figure 2) show the distribution of values as a percent of the total number of analytical results. They provide an easy way to identify outlier values. The cumulative data plots in this report exclude the highest and lowest 0.1 percent of the values so that extremely high or low values do not compress the display of the majority of the data. Therefore, probability plots may not show the absolute maximum and minimum values. Each plot also includes a straight line which shows the locus of points along which the data would fall if the measurements were normally distributed.

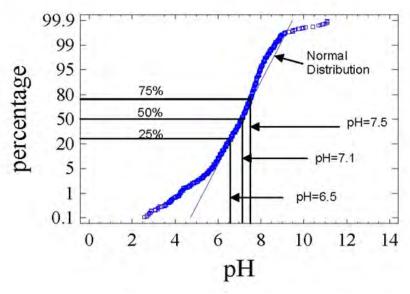


Figure 2. Cumulative data plot for all pH measurements reported in Kentucky groundwater.

Box and whisker diagrams (Figure 3) show the median value and interquartile range (IQR), and illustrate how clustered or scattered analytical results are. The box extends from the first quartile value to the third quartile value, thereby including the central 50 percent of the data. Either 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 which are more than 3.0 times the interquartile range above the third quartile value or below the first quartile value are shown as 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.

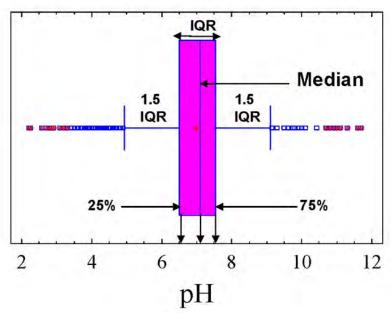


Figure 3. Box and whisker plot for all pH measurements reported in Kentucky groundwater.

The general approach for each analyte is:

- 1. Define the analyte, summarize common natural sources, uses, and potential contaminant sources, list relevant water-quality criteria, and describe how excessive amounts impact water use and human health.
- 2. Summarize analytical reports from BMUs 1, 2, and 5 by constructing summary data tables and cumulative data plots.
- 3. Show sample site distribution and sites where water-quality standards are met or exceeded by mapping sample sites and concentration ranges.
- 4. Summarize data for each physiographic region and major watershed by constructing box and whisker plots.
- 5. Compare data by site type (well versus spring) and sample type (total versus dissolved) by constructing box and whisker plots.
- 6. Evaluate the impact on shallow (< 200 ft), intermediate (200 to 500 ft), and deep (> 500 ft) groundwater systems by plotting concentrations versus well depth.
- 7. Summarize probable causes of observed concentrations and distribution of values.

### RESULTS

# **Water Properties**

# pН

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.

There are no health-based drinking-water standards for pH. However, very high or very low pH values can lead to high dissolved concentrations of some metals for which there are drinking water standards and associated health effects. 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 (EPA) has established a Secondary standard Maximum Contaminant Level (SMCL) for pH of 6.5 to 8.5.

The data repository contained 4388 pH values from 828 sites in the study area (Table 4). The pH data are generally similar in BMUs 1, 2, and 5. The median values in each Basin Management

Unit are within 0.5 pH unit of each other, and the interquartile ranges are similar. Minimum pH values are also similar, but the maximum values are quite different.

Table 4. Summary of pH measurements (Standard units). SMCL: 6.5 to 8.5

|                             | BMU 1 | BMU 2 | BMU 5 |
|-----------------------------|-------|-------|-------|
| Number of values            | 2005  | 778   | 1605  |
| Maximum                     | 11.6  | 8.6   | 10.4  |
| 75 <sup>th</sup> percentile | 7.5   | 7.7   | 7.4   |
| Median                      | 7.1   | 7.4   | 6.9   |
| 25 <sup>th</sup> percentile | 6.5   | 7.2   | 6.4   |
| Minimum                     | 2.3   | 2.8   | 2.6   |
| IQR                         | 1.0   | 0.5   | 1.0   |
| Number of sites             | 288   | 278   | 262   |
| Number of Sites < 6.5       | 112   | 35    | 87    |
| Number of sites $> 8.5$     | 8     | 2     | 2     |

Cumulative data plots (Figures 4, 5, and 6) show some differences between Basin Management Units. BMU 1 has many values less than 6.5 and greater than 8.5 (Figure 4), whereas samples from BMU 2 and BMU 5 show many values less than 6.5 but very few values greater than 8.5 (Figure 5 and 6). The pH values from BMU 2 are more tightly clustered about the median than values from the other Basin Management Units (Figure 5).

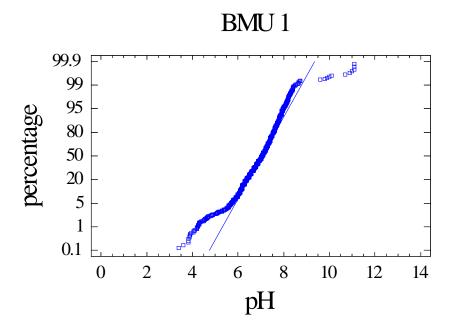


Figure 4. Cumulative plot of pH values from BMU 1. SMCL: 6.5 to 8.5

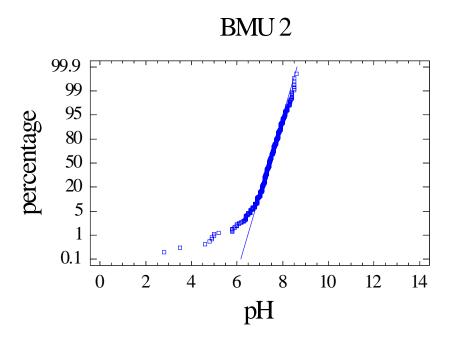


Figure 5. Cumulative plot of pH values from BMU 2. SMCL: 6.5 to 8.5

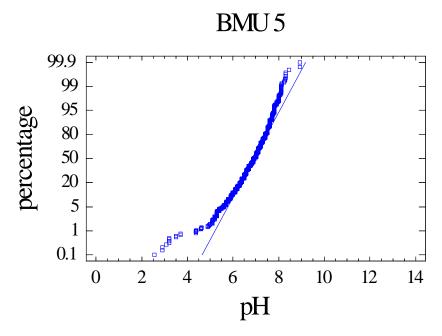


Figure 6. Cumulative plot of pH values from BMU 5. SMCL: 6.5 to 8.5

There is a very uneven distribution of sampled sites through the project area (Figure 7). The Eastern Kentucky Coal Field and Western Pennyroyal are more densely sampled than the other regions. This sample site distribution in part reflects differences in groundwater use throughout

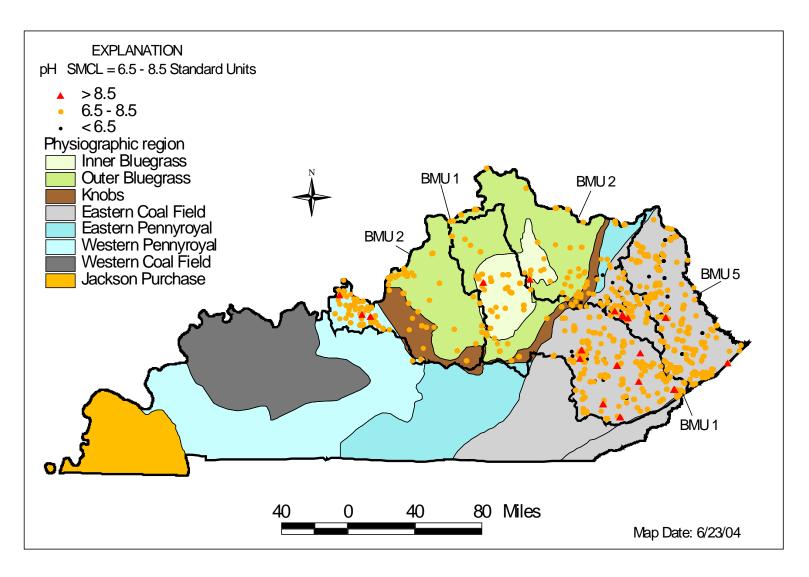


Figure 7. Map showing sampled sites and ranges of pH measurements. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

the area. The map also shows that pH values vary considerably in the coal field but are more uniform in the carbonate settings of the Inner Bluegrass, Outer Bluegrass, and Western Pennyroyal Regions. Values less than 6.5 are restricted to the Eastern Kentucky Coal Field and Knobs regions; pH values greater than 8.5 are rare outside the Eastern Kentucky Coal Field.

Grouping pH values by physiographic region (Figure 8) shows the variability within the Eastern Kentucky Coal Field relative to the other regions. Samples from the Eastern Coal Field produce the highest and lowest pH values reported and the greatest range of pH values. Also, the interquartile range of values is greater for groundwater from the Eastern Coal Field than for water from other regions. This pattern is probably the result of the lithologic heterogeneity in the coal fields, whereas bedrock type in the other regions is less variable. The lithologically similar Inner and Outer Bluegrass and Eastern and Western Pennyroyal Regions have similar interquartile ranges.

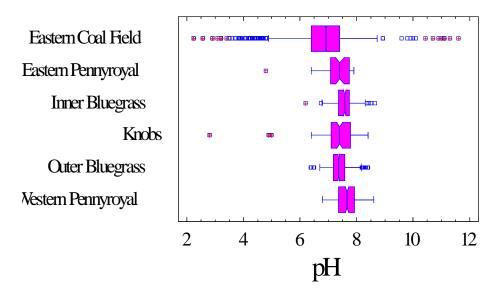


Figure 8. Summary of pH values grouped by physiographic region. SMCL: 6.5 to 8.5

Grouping pH values by major watershed (Figure 9) shows the greatest variability in the Kentucky River watershed which drains the Eastern Kentucky Coal Field, Knobs, and Inner and Outer Bluegrass Regions.

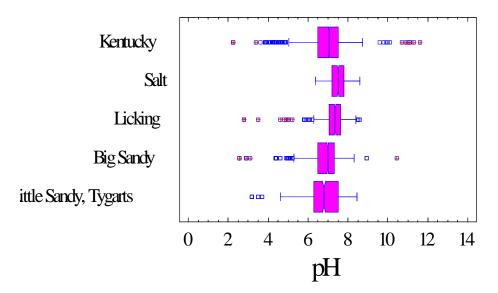


Figure 9. Summary of pH values grouped by major watershed. SMCL = 6.5 to 8.5.

Groundwater from wells generally has somewhat lower and more variable pH values than groundwater from springs (Figure 10). Wells also show more pH values greater than 8.5 than springs, probably because wells are more common in the lithologically heterogeneous Eastern Coal Field whereas springs are more common in the carbonate Bluegrass and Pennyroyal Regions.

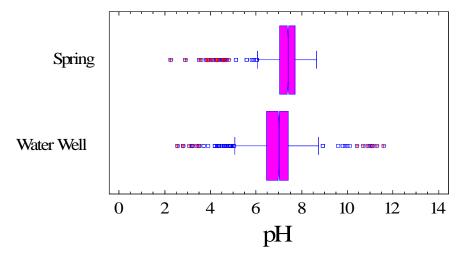


Figure 10. Comparison of pH values from wells and springs. SMCL = 6.5 to 8.5.

Shallow wells show a greater range of pH values than deeper wells (Figure 11), suggesting that groundwater in intermediate and deep flow systems has equilibrated with bedrock whereas shallower groundwater systems have not.

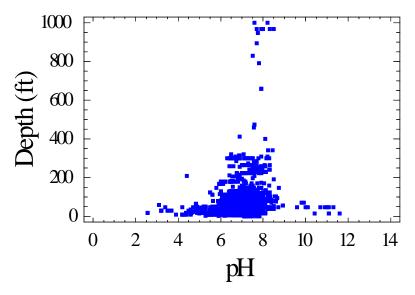


Figure 11. Plot of pH values versus well depth. SMCL = 6.5 to 8.5.

Summary: Sample site distribution for pH is not uniform throughout the project area. The Eastern Kentucky Coal Field and Western Pennyroyal regions are relatively well sampled, whereas large parts of the Inner and Outer Bluegrass have not been sampled. Groundwater pH values and ranges of values are more closely related to physiographic region and underlying bedrock lithology than to Basin Management Unit or watershed. Groundwater in the predominantly carbonate regions is nearly neutral and pH values show relatively little scatter. In the Eastern Kentucky Coal Field where bedrock lithology is more heterogeneous, most groundwater is near neutral to slightly acidic, but there is a much wider range of values. In general, pH values reflect bedrock geology rather than NPS effects. The pH of springs and shallow wells is much more variable than the pH observed in intermediate and deep wells. The decrease in variability of pH with sample depth shows that groundwater in intermediate and deep flow systems has equilibrated with bedrock to a greater extent than groundwater in springs and shallow wells.

A statewide summary of pH data is available (Fisher, 2002b) and can be viewed on the KGS Web site (http://www.uky.edu/KGS/water/gnet/gnet.htm).

#### **Total Dissolved Solids**

Total dissolved solids (TDS) is the sum of all dissolved chemicals in water, expressed as mg/L. TDS can be calculated by adding all the solute concentrations from a full chemical analysis, or measured as the weight of the residue remaining after a volume of water has been evaporated to dryness. TDS typically increases with sample depth or the distance that groundwater has traveled from recharge area to sample site.

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

Potable water: up to 500 mg/L TDS

Slightly saline water: adequate for drinking and irrigation: 500 to 1,000 mg/L TDS Medium saline water: potable only in cases of need, may be used for some crops and aquiculture: 1,000 to 2,500 mg/L TDS

 $\underline{Saline\ water}\hbox{: adequate for aquiculture and industrial use: 2,500 to 5,000\ mg/L\ TDS}$ 

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

Brine: TDS greater than 35,000 mg/L

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

The KGS data repository contained 1185 reports of total dissolved solids at 230 sites in the project area (Table 5). Nearly all samples and sites yielded potable water; the 75<sup>th</sup> percentile value for each Basin Management Unit is less than 500 mg/L. Only 59 of 230 sites (26 percent) yielded groundwater with more than 500 mg/L total dissolved solids.

Table 5. Summary of total dissolved solids measurements (mg/L). SMCL = 500 mg/L.

|                             | BMU 1  | BMU 2  | BMU 5 |
|-----------------------------|--------|--------|-------|
| Number of values            | 599    | 441    | 145   |
| Maximum                     | 60,364 | 18,000 | 2880  |
| 75 <sup>th</sup> percentile | 406    | 442    | 414   |
| Median                      | 320    | 358    | 298   |
| 25 <sup>th</sup> percentile | 254    | 234    | 222   |
| Minimum                     | 0      | 10     | 60    |
| IQR                         | 152    | 208    | 192   |
| Number of sites             | 82     | 86     | 62    |
| Number of sites > 500 mg/L  | 24     | 16     | 19    |

Cumulative data plots (Figure 12, 13, and 14) show some differences between the Basin Management Units. A break in slope at about 100 mg/L suggests two different populations of data in BMU 1 (Figure 12). More than 95 percent of the values from BMU 2 follow a normal distribution, whereas values from BMU 5 show a distribution typical of a positively skewed data set.

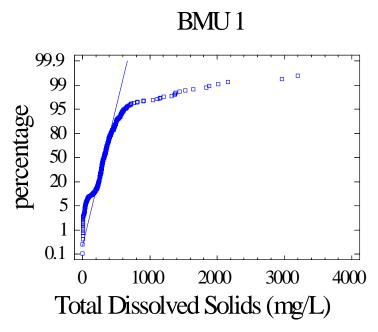


Figure 12. Cumulative plot of total dissolved solids values from BMU 1. Two values greater than 4000 mg/L were omitted for clarity. SMCL = 500 mg/L

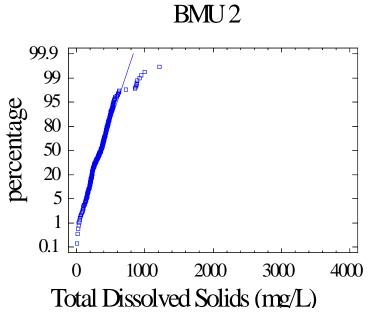


Figure 13. Cumulative plot of total dissolved solids values from BMU 2. One value greater than 4000 mg/L was omitted for clarity. SMCL = 500 mg/L

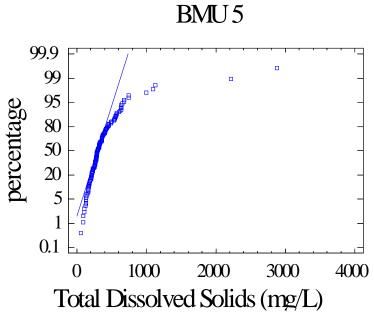


Figure 14. Cumulative plot of total dissolved solids values from BMU 5. No values exceeded 4000 mg/L. SMCL = 500 mg/L

The distribution of sampled sites is densest in the Eastern Coal Field and Inner Bluegrass, and least dense in the Outer Bluegrass (Figure 15), a consequence of variations in groundwater use in the project area.

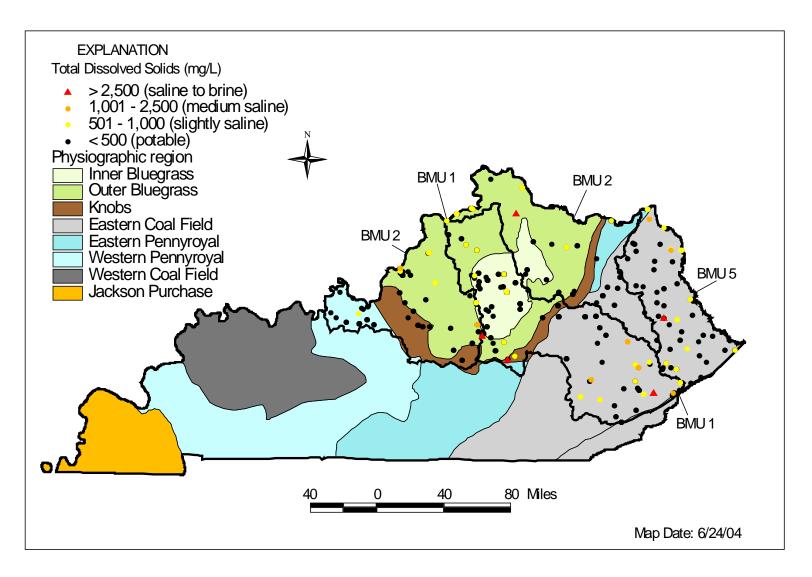


Figure 15. Map showing sampled sites and ranges of total dissolved solids values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Groundwater from the Eastern Coal Field has the highest TDS values, the greatest number of values greater than 1000 mg/L, and the largest spread in the central 50 percent of the data (Figure 16). Samples from the Eastern and Western Pennyroyal and the Inner Bluegrass regions have the smallest spread in the central 50 percent of the reported values.

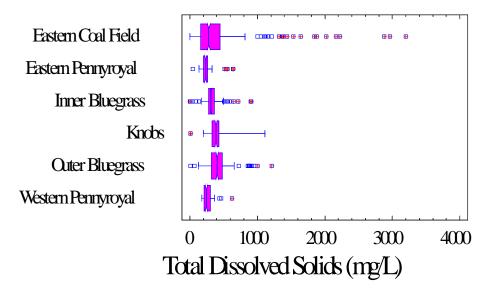


Figure 16. Summary plot of total dissolved solids values grouped by physiographic region. SMCL = 500 mg/L.

Grouping total dissolved solids values by major watershed (Figure 17) shows that all watersheds have about the same range and magnitude of values for the central 50 percent of the data. However, there are many more values greater than 1000 mg/L reported from the Kentucky River watershed than from any other major river basin.

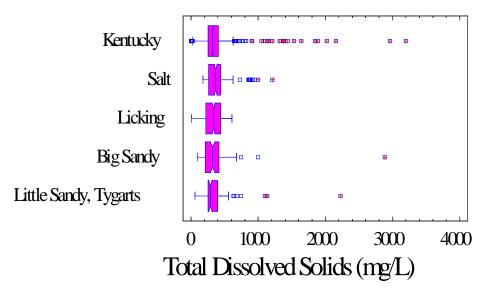


Figure 17. Summary plot of total dissolved solids values grouped by major watershed. SMCL = 500 mg/L.

Groundwater from wells has a somewhat higher median value of total dissolved solids than groundwater from springs (Figure 18), although the ranges are quite similar.

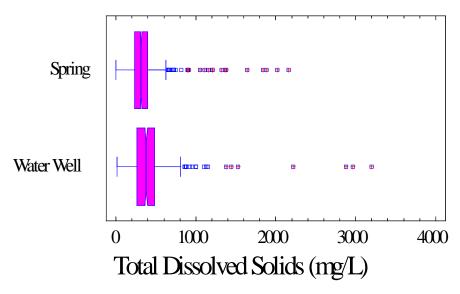


Figure 18. Comparison of total dissolved solids values for wells and springs. SMCL = 500 mg/L.

With the exception of a few high TDS reports from shallow wells, there is no systematic trend of total dissolved solids with well depth (Figure 19).

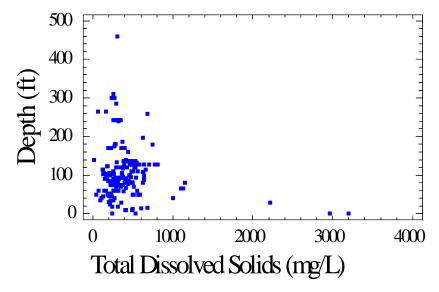


Figure 19. Plot of total dissolved solids values versus well depth. SMCL = 500 mg/L.

Summary: More than 75 percent of the groundwater sampled in the project area is potable in terms of TDS, although there are exceptions in each Basin Management Unit, physiographic region, and major watershed. Saline to brackish groundwater is most likely to be encountered in the Eastern Kentucky Coal Field. Total dissolved solids values are generally similar within each Basin Management Unit and each major river watershed. However, systematic differences exist in the data for each physiographic region. This relation indicates that total dissolved solids values are controlled more by the bedrock geologic differences between physiographic regions than by the geographic differences between Basin Management Units or major watersheds. There is no clear evidence that nonpoint-source chemicals are 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).

Conductance or conductivity is reported in micromhos per centimeter at 25 °C, or the numerically equivalent microsiemens per centimeter in the International System of Units (Hem, 1985). Because conductance does not directly indicate water quality, there are no health or water-use standards based on this parameter.

The data repository contained 10,874 conductance measurements from sites 4628 sites in the project area (Table 6). This large number of measurements is the result of the extensive field sampling program associated with the NURE project (Smith, 2001). Values range from zero to 205,000 microsiemens per centimeter. Groundwater from BMU 2 has higher 75<sup>th</sup> percentile, median, and 25<sup>th</sup> percentile conductance values and a larger interquartile range than groundwater from the rest of the project area.

Table 6. Summary of conductance measurements (microsiemens/cm).

|                             | BMU 1   | BMU 2   | BMU 5   |
|-----------------------------|---------|---------|---------|
| Number of values            | 3601    | 5119    | 2154    |
| Maximum                     | 142,000 | 172,000 | 205,000 |
| 75 <sup>th</sup> percentile | 530     | 1480    | 580     |
| Median                      | 350     | 710     | 325     |
| 25 <sup>th</sup> percentile | 195     | 450     | 195     |
| Minimum                     | 0       | 0       | 0       |
| IQR                         | 335     | 1030    | 385     |
| Number of sites             | 1753    | 1827    | 1048    |

The data distributions for the lowest 95 percent of the measured values are similar for the three Basin Management Units (Figure 20, 21, and 22). Few groundwater samples from BMU 2 have conductance values greater than 50,000 microsiemens, whereas such values are more common in BMU 1 and BMU 5. The data distribution for BMU 2 (Figure 21) has a distinct break in slope at about 20,000 microsiemens/cm, which suggests that two different populations are included in the data set.

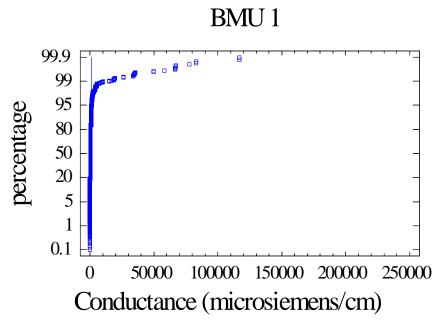


Figure 20. Cumulative plot of conductance values from BMU 1. The highest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

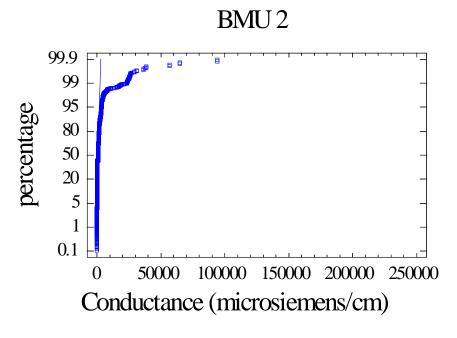


Figure 21. Cumulative plot of conductance values from BMU 2. The highest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

# BMU 5 99.9 99 95 percentage 80 50 20 5 1 0.1 50000 100000 150000 200000 0 Conductance (microsiemens/cm)

Figure 22. Cumulative plot of conductance values from BMU 5. The highest 0.1 percent of values are omitted so that the central 99.8 percent of the data can be presented more clearly.

There are many more sampled sites in the southern half of the project area, below approximately 38° North latitude, than in the northern half (Figure 23) because sampling for the NURE program did not extend north of this line. Sites where conductance exceeded 10,000 microsiemens/cm are more common in the Eastern Kentucky Coal Field than in the other regions.

The median conductance value and interquartile range of values is higher for measurements from sites in the Knobs region than in any other region (Figure 24). However, this is because 10 sites in the Knobs region have yielded high-conductance groundwater on 48 sampling occasions; the number of high conductance values is large, but the number of sites producing that water is small. Samples from the Eastern Coal Field have the lowest median value, whereas samples from the Inner Bluegrass and Western Pennyroyal regions have the smallest interquartile range. Nearly all of the conductance values are less than 4000 microsiemens/cm.

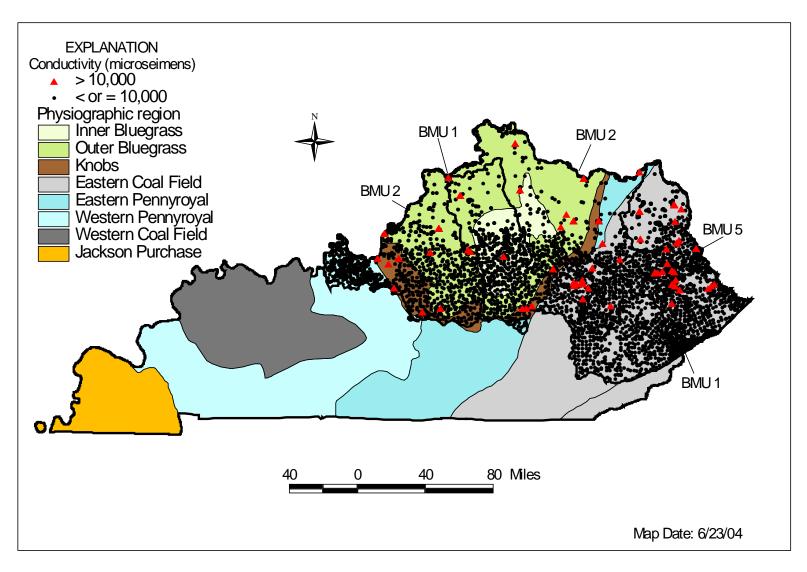


Figure 23. Map showing sampled sites and ranges of conductivity values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

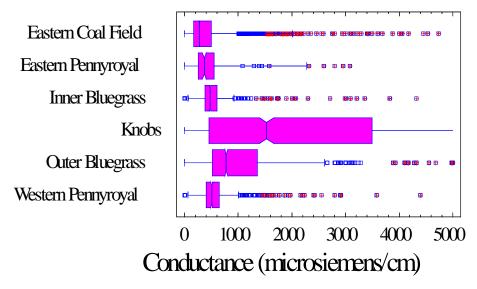


Figure 24. Summary of conductance data (microsiemens/cm) grouped physiographic region. Higher values have been omitted to better show the majority of the data.

Grouping the measurements by major river basin (Figure 25) shows the Licking River watershed to have the highest median, interquartile range, and 75<sup>th</sup> percentile values. However, nearly all of the conductance values in the project area are less than 4000 microsiemens/cm.

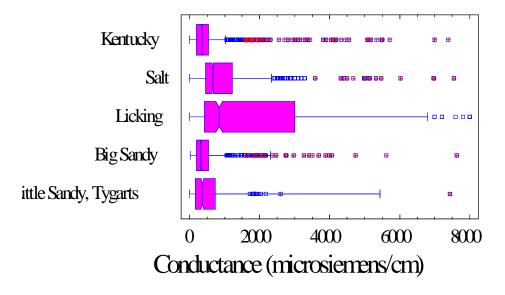


Figure 25. Summary of conductance data (microsiemens/cm) grouped by major river watershed. Higher values have been omitted to better show the majority of the data.

Groundwater from wells has higher median value and interquartile range than groundwater from springs (Figure 26), as well as many more reported values greater than 4000 microsiemens/cm.

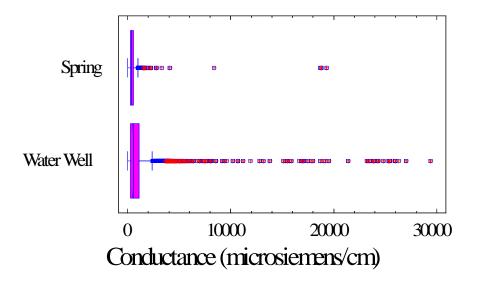


Figure 26. Comparison of conductance measurements (microsiemens/cm) from springs and wells. Higher values have been omitted to better show the majority of the data.

The vast majority of the conductance values from wells are less than 10,000 microsiemens/cm, and there is a general trend towards lower values with increasing well depth (Figure 27). However, there is considerable scatter in the data.

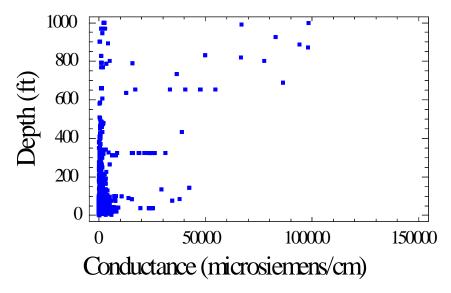


Figure 27. Plot of conductance values versus well depth.

Summary: Conductance is an indirect indicator of groundwater quality, related to salinity or total dissolved solids but not a direct measure of either. There are no health-based standards or aesthetic effects associated with high conductance values. Conductance values are as high as 205,000 microsiemens/cm in the project area. However, there is little systematic regional variation. More than 97 percent of the reported values are less than 5,000 microsiemens/cm and more than 98 percent of the reported values are less than 10,000 microsiemens/cm. The highest conductance values reported in the project area are from wells deeper than 600 ft. There are no clear indications 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.

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:

Hardness (mg/L) calcium carbonate equivalent = 2.5 Ca (mg/L) + 4.1 Mg (mg/L). (1)

Table 7 shows a frequently used classification of hardness in water supplies (U.S. Geological Survey web site: http://water.usgs.owq/explanation.html).

Table 7. Hardness classification of water supplies.

| <b>Hardness Category</b> | Concentration (mg/L) |
|--------------------------|----------------------|
| Soft                     | 0 to 17              |
| Slightly Hard            | 18 to 60             |
| Moderately Hard          | 61 to 120            |
| Hard                     | 121 to 180           |
| Very Hard                | more than 180        |

Calcium and magnesium concentrations for individual samples were combined according to equation (1) to produce a total of 1550 groundwater hardness values at 436 sites in the project area. Because most sites were sampled and analyzed more than once, the calculated hardness

values for individual samples at a site were averaged to give the number of sites meeting various water-quality criteria (Table 8). Hard to very hard water is predominant in each Basin Management Unit. Soft to moderately hard water is uncommon, except in BMU 5 where 69 of 137 sites produce such water.

Table 8. Summary of the number of sites in various hardness categories.

|                                  | BMU 1 | BMU 2 | BMU 5 |
|----------------------------------|-------|-------|-------|
| Number of values                 | 339   | 937   | 274   |
| Number of sites                  | 100   | 199   | 137   |
| Sites with soft water            | 2     | 1     | 3     |
| Sites with slightly hard water   | 13    | 4     | 23    |
| Sites with moderately hard water | 10    | 8     | 43    |
| Sites with hard water            | 13    | 6     | 25    |
| Sites with very hard water       | 62    | 180   | 43    |

Cumulative data plots (Figures 28, 29, and 30) show that hardness values greater than 10,000 mg/L are present in each BMU. However, more than 95 percent of the values are less than 1000 mg/L. Basin Management Unit 5 has the hardest water and the greatest number of values that exceed 10,000 mg/L

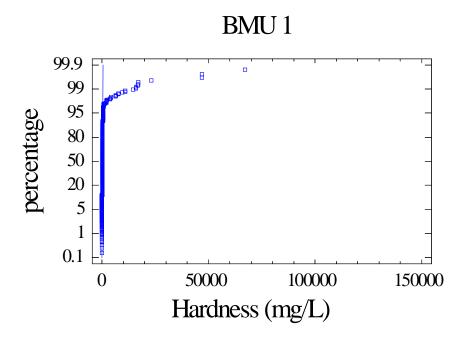


Figure 28. Cumulative plot of hardness values in BMU1.

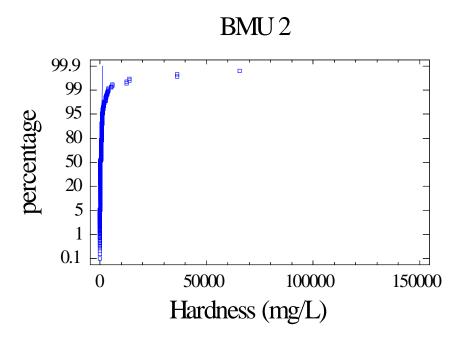


Figure 29. Cumulative plot of hardness values in BMU 2.

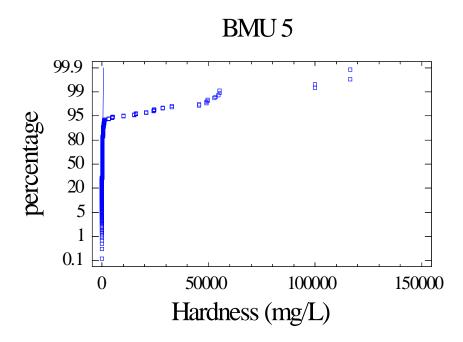


Figure 30. Cumulative plot of hardness values in BMU 5.

The distribution of sampled sites is extremely uneven throughout the project area (Figure 31). In the Licking River watershed, the northeastern half of Basin Management Unit 2, 72 sites are located mostly in the Ohio River alluvium and the Inner Bluegrass Region; very few sites in the

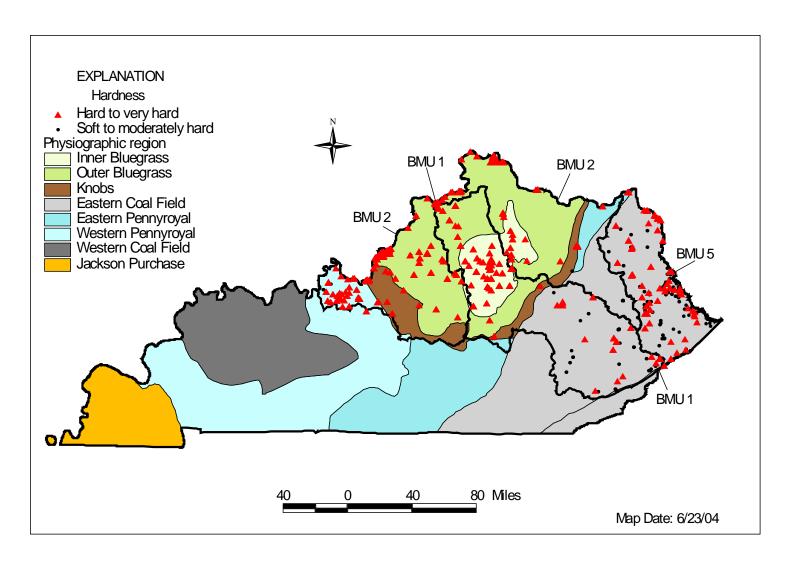


Figure 31. Map showing sampled sites and ranges of hardness values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

interior of the watershed have been sampled. The eastern part of the Eastern Coal Field Region, and the northern parts of the Salt and Kentucky River watersheds are also more densely sampled than the other parts of the project area. Hard to very hard water is found throughout, but soft to moderately hard water is rare outside of the Eastern Coal Field.

The Outer Bluegrass Region has the highest median hardness value and the largest interquartile range (Figure 32). The Eastern Coal Field has the lowest (softest) median value, whereas the Inner Bluegrass Region has the smallest interquartile range.

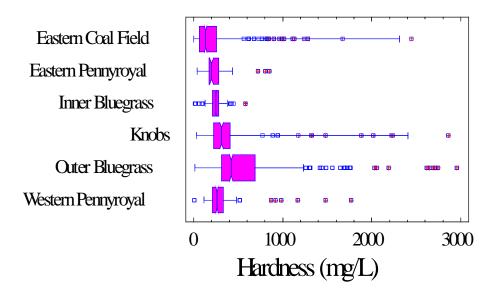


Figure 32. Summary plot of hardness values for groundwater grouped by physiographic region. Higher values have been omitted to better show the majority of the data.

Grouping the hardness values by major watershed (Figure 33) shows that samples from the Salt River basin have the highest median value and largest interquartile range, whereas samples from the Kentucky River watershed have the smallest interquartile range (least variability within the central 50 percent of the data). Groundwater from the Big Sandy River watershed has the lowest median value.

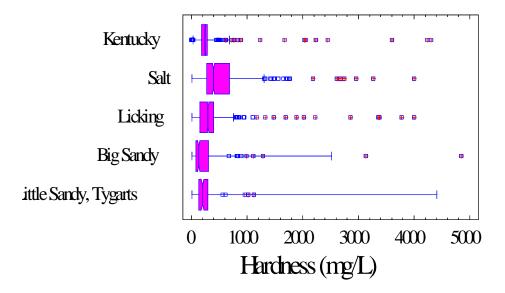


Figure 33. Summary plot of hardness values for groundwater grouped by watershed. Higher values have been omitted to better show the majority of the data.

Groundwater from wells has higher median hardness, larger spread of the central 50 percent of values, and more very high hardness values than water from springs (Figure 34).

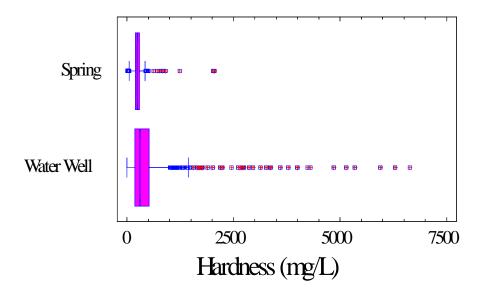


Figure 34. Comparison of hardness values from wells and springs. Higher values have been omitted to better show the majority of the data.

The hardest water is reported from wells deeper than 600 ft (Figure 35). However, the trend of the majority of reported values is to decrease with well depth.

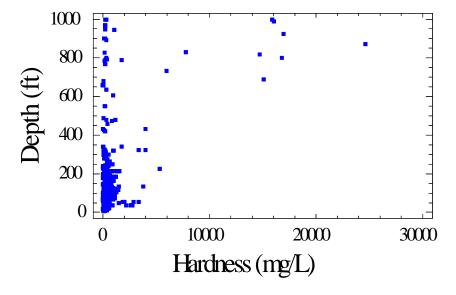


Figure 35.Plot of hardness values versus well depth.

Summary: The distribution of sites at which water hardness could be calculated is very uneven throughout the project area. However, water hardness is strongly related to bedrock geology and so can be predicted in areas where no sampled sites already exist. Groundwater in the Inner Bluegrass and Western Pennyroyal Regions, which are underlain by limestone strata, are typically hard to very hard. Groundwater in the lithologically heterogeneous Eastern Coal Field has highly variable hardness. Hard to very hard water occurs at more than 75 percent of the sites in the project area. Although groundwater is typically hard to very hard throughout the project area, few sites have hardness values greater than 1000 mg/L. For such sites, water softeners can remove much of the calcium and magnesium that causes hardness problems. No significant effect of nonpoint-source chemicals is indicated because water hardness values correspond closely with bedrock geology.

## **Total Suspended Solids**

Particulate material is reported as total suspended solids (TSS). 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 that

have been vigorously stirred during purging prior to sample collection, or from wells that intercept a fracture or karst conduit where turbulent flow may occur. 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. However, some metals and pesticides are preferentially sorbed onto or included in the matrix of suspended material, so water high in total suspended solids may also contain important 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 (KPDES) recommends that TSS levels be less than 35 mg/L.

The project area contains 1223 reports of total suspended solids from 245 sites (Table 9). Maximum values in each Basin Management Unit are quite high. However, only 40 total suspended solids values from 28 sites exceed 35 mg/L.

Table 9. Summary of total suspended solids measurements (mg/L). KPDES: < 35 mg/L.

|                                     | BMU 1 | BMU 2 | BMU 5 |
|-------------------------------------|-------|-------|-------|
| Number of values                    | 599   | 439   | 185   |
| Maximum                             | 1520  | 680   | 125   |
| 75 <sup>th</sup> percentile         | 6     | 5     | 5     |
| Median                              | 3     | 3     | 3     |
| 25 <sup>th</sup> percentile         | 3     | 3     | 1     |
| Minimum                             | 0     | <1    | <1    |
| IQR                                 | 3     | 2     | 4     |
| Number of sites                     | 81    | 82    | 82    |
| Number of sites $> 35 \text{ mg/L}$ | 15    | 10    | 3     |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

Cumulative data distribution curves for the three Basin Management Units are very similar (Figure 36, 37, and 38).

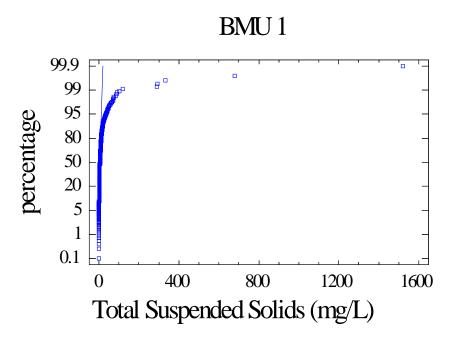


Figure 36. Cumulative plot of total suspended solids values from BMU 1. KPDES: < 35 mg/L.

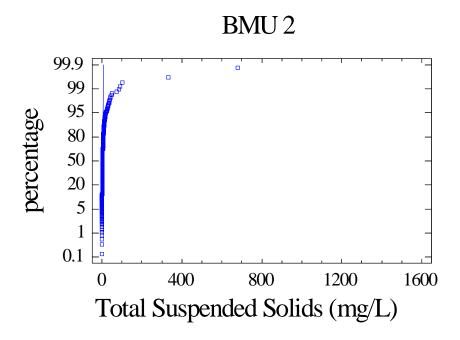


Figure 37. Cumulative plot of total suspended solids values from BMU 2. KPDES: < 35 mg/L.

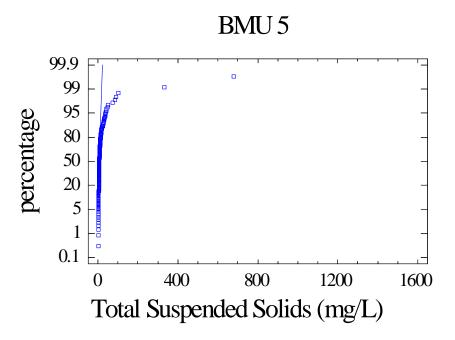


Figure 38. Cumulative plot of total suspended solids values from BMU 5. KPDES: < 35 mg/L.

Site distribution is sparse and uneven throughout the project area (Figure 39). This is probably because total suspended solids are not considered a critical parameter in determining groundwater quality.

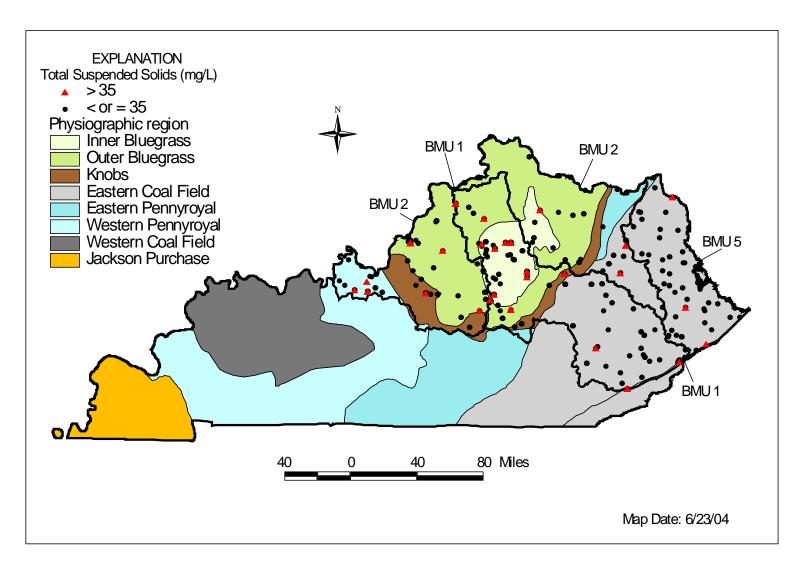


Figure 39. Map showing sampled sites and ranges of total suspended solids values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

In no physiographic region (Figure 40) or major watershed (Figure 41) does the 75<sup>th</sup> percentile of values exceed 10 mg/L. The largest interquartile range is found in the Western Pennyroyal Region, Salt River watershed.

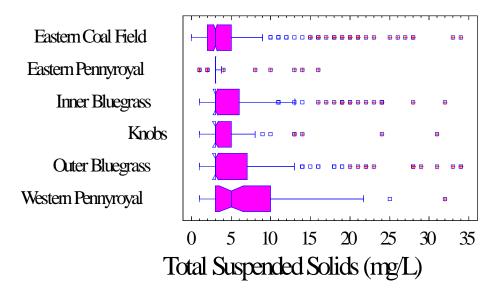


Figure 40. Summary plot of total suspended solids values for groundwater grouped by physiographic region. Higher values have been omitted to better show the majority of the data. KPDES: <35~mg/L.

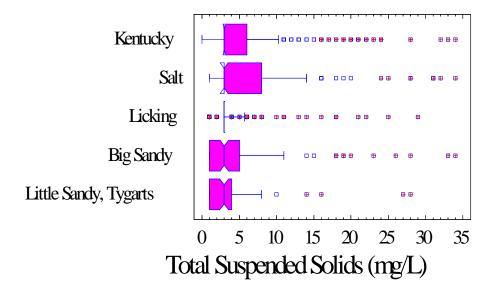


Figure 41. Summary plot of total suspended solids values for groundwater grouped by major watershed. Higher values have been omitted to better show the majority of the data. KPDES: < 35 mg/L.

Groundwater from springs is more likely to produce turbid water than groundwater from wells (Figure 42). Of the 28 sites that produce water having more than 35 mg/L total suspended solids, 24 are springs and only four are wells. Shallow wells are more likely to produce turbid water than deeper wells (Figure 43).

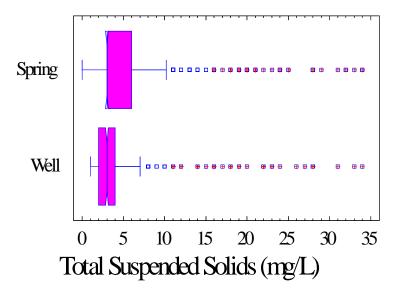


Figure 42. Comparison of total suspended solids values from wells and springs. KPDES:  $< 35 \ \text{mg/L}$ .

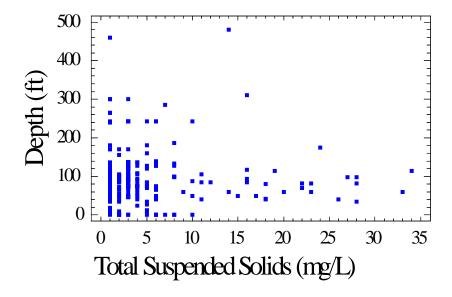


Figure 43. Plot of total suspended solids values versus well depth. KPDES: < 35 mg/L.

Summary: Total suspended solids values generally do not present problems for groundwater use in the project area. Only 40 of 1223 measurements from 28 of 245 sites exceed the DOW-recommended value of 35 mg/L. Twenty-four of the 28 sites at which this value is exceeded are springs, where turbulent flow and transport of suspended solids is expected. There is no evidence of a nonpoint-source contribution to groundwater at the sampled sites.

## **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). NPS sources include 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. The EPA has set a secondary maximum contaminant level (SMCL) of 250 mg/L for chloride because water containing more than this amount has an unpleasant taste that makes it unsuitable for domestic use.

The data repository contained 10,029 chloride measurements from 4665 sites in the project area (Table 10). The maximum value in each Basin Management Unit exceeds 100,000 mg/L. However, such high values are exceptional; 75 percent of the measured values are less than 45 mg/L and 50 percent are less than 17 mg/L.

Table 10. Summary of chloride measurements (mg/L). SMCL = 250 mg/L

|                                | BMU 1   | BMU 2   | BMU 5   |
|--------------------------------|---------|---------|---------|
| Nr. Values                     | 3327    | 4878    | 1824    |
| Maximum                        | 121,000 | 141,000 | 184,880 |
| 75 <sup>th</sup> percentile    | 19      | 44      | 31.2    |
| Median                         | 7.4     | 17      | 9.8     |
| 25 <sup>th</sup> percentile    | 3.7     | 6.4     | 3.9     |
| Minimum                        | 0       | 0       | 0       |
| IQR                            | 15.3    | 37.6    | 27.3    |
| Nr. Sites                      | 1742    | 1825    | 1098    |
| Nr. Sites $> 250 \text{ mg/L}$ | 74      | 119     | 69      |

Data distributions for the three Basin Management Units have a similar shape (Figures 44, 45, and 46) with a sharp break in slope at a chloride value less than 250 mg/L.

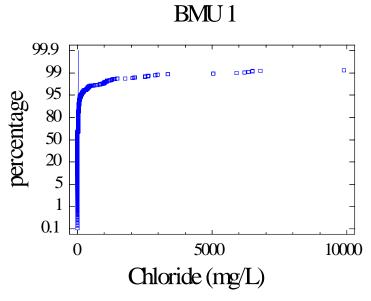


Figure 44. Cumulative plot of chloride values in BMU 1. Higher values were excluded for clarity.  $SMCL = 250 \ mg/L.$ 

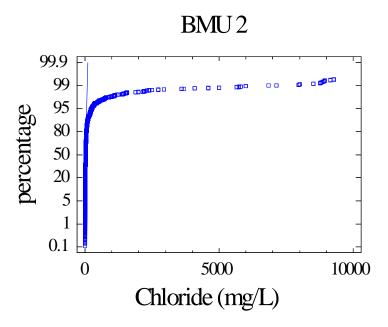


Figure 45. Cumulative plot of chloride values in BMU 2. Higher values were excluded for clarity. SMCL = 250 mg/L.

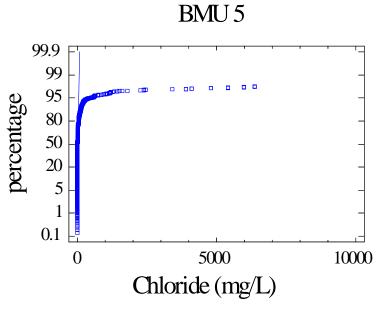


Figure 46. Cumulative plot of chloride values in BMU 5. Higher values were excluded for clarity. SMCL = 250 mg/L.

Sample site density is much greater in the southern half of the study area than in the northern half (Figure 47), because sampling for the NURE project did not extend into the northern part of the state. The percent of sites where chloride exceeds 250 mg/L is approximately the same in each Basin Management Unit and shows no relation to river basin or physiographic region.

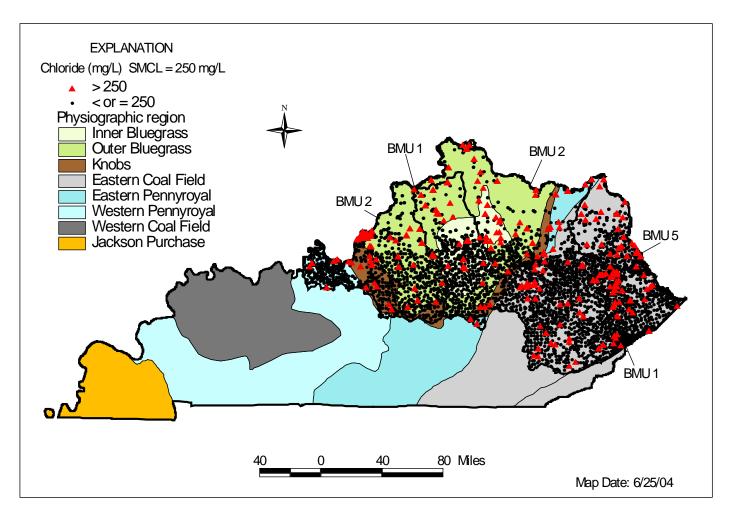


Figure 47. Map showing sampled sites and ranges of chloride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

The median and 75<sup>th</sup> percentile chloride values are well below 250 mg/L in every physiographic region (Figure 48) and major watershed (Figure 49).

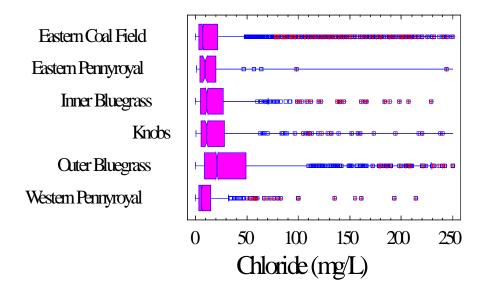


Figure 48. Summary of chloride values grouped by physiographic region. SMCL = 250 mg/L. Higher values were excluded for clarity.

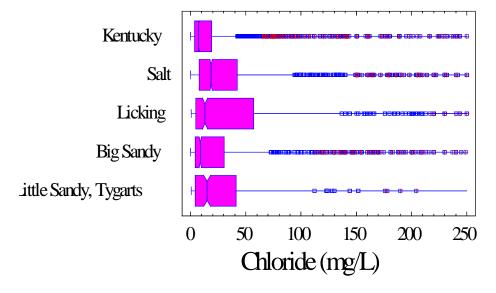


Figure 49. Summary of chloride values grouped by major watersheds. SMCL = 250 mg/L. Higher values were excluded for clarity.

Samples from wells have a higher median value, 75<sup>th</sup> percentile value, and larger interquartile range of chloride concentrations than samples from springs (Figure 50).

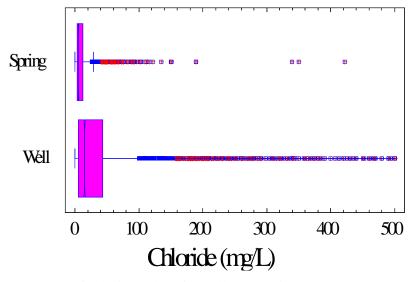


Figure 50. Summary of chloride values for wells and springs. SMCL = 250 mg/L. Higher values were excluded for clarity.

Chloride concentrations are greatest in wells shallower than about 250 ft, with a general trend to lower concentrations at depths of about 500 ft (Figure 51). Some deeper samples have concentrations that exceed 250 mg/L.

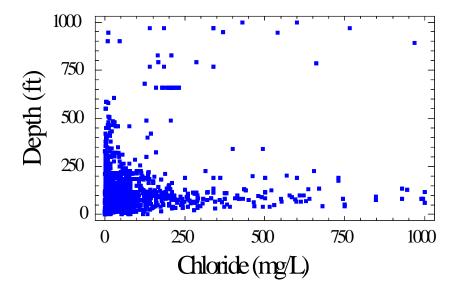


Figure 51. Plot of chloride concentrations versus well depth. Higher values were excluded for clarity. SMCL = 250 mg/L.

Summary: Chloride concentrations in excess of 100,000 mg/L are found throughout the project area but are uncommon and do not appear to be controlled by Basin Management Unit, physiographic region, or major watershed. Higher chloride concentrations are found in wells than in springs, and shallow wells (less than 200 ft) are more likely to have high chloride concentrations than deep wells. The occurrence of high chloride values in shallow wells might suggest an impact from nonpoint sources, possibly road salt applied in the winter. However, that cannot be clearly demonstrated with the available information.

## **Sulfate**

Sulfate (SO<sub>4</sub>) is a major anion in most groundwaters. The most common natural sources of sulfate in the project area are oxidation of iron sulfide minerals in coal or shale, and dissolution of the calcium-sulfate minerals gypsum or anhydrite in carbonate strata.

There is no primary drinking water standard for sulfate. The EPA has set a secondary standard (SMCL) of 250 mg/L because water containing more than 250 mg/L sulfate has an unpleasant taste that makes it unsuitable for domestic use. Water having sulfate concentrations greater than about 500 mg/L is a mild laxative.

There are 11,607 sulfate measurements reported from 2611 sites in the project area (Table 11). The highest values for maximum, 75<sup>th</sup> percentile, median, and 25<sup>th</sup> percentile are found in BMU 2, which also contains the largest number of sites that exceed 250 mg/L (Table 11).

Table 11. Summary of sulfate measurements (mg/L). SMCL = 250 mg/L

|                             | BMU 1 | BMU 2 | BMU 5 |
|-----------------------------|-------|-------|-------|
| Nr. Values                  | 4078  | 4383  | 3146  |
| Maximum                     | 1740  | 3200  | 2749  |
| 75 <sup>th</sup> percentile | 63    | 211   | 66.7  |
| Median                      | 27    | 66    | 26.8  |
| 25 <sup>th</sup> percentile | 12    | 28.7  | 7     |
| Minimum                     | 0     | 0     | 0     |
| IQR                         | 51    | 182.3 | 59.7  |
| Nr. Sites                   | 738   | 1121  | 752   |
| Nr. Sites > 250 mg/L        | 70    | 149   | 76    |

Distributions of sulfate values are generally similar in each Basin Management Unit (Figures 52, 53, 54). Most values in each BMU are less than 250 mg/L; however, groundwater from BMU 2 has more sulfate values greater than 250 mg/L than water from BMU 1 or BMU 5.

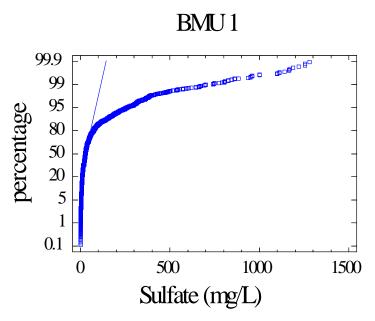


Figure 52. Cumulative plot of sulfate values in BMU 1. Higher values were excluded for clarity. SMCL = 250 mg/L.

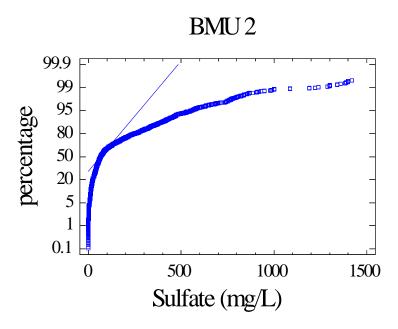


Figure 53. Cumulative plot of sulfate values in BMU 2. Higher values were excluded for clarity. SMCL = 250 mg/L.

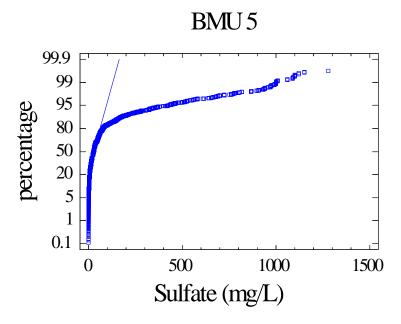


Figure 54. Cumulative plot of sulfate values in BMU 5. Higher values were excluded for clarity. SMCL = 250 mg/L.

The distribution of sampled sites varies throughout the project area (Figure 55). The Eastern Kentucky Coal Field, Inner Bluegrass, and Western Pennyroyal Regions are more densely sampled than the Outer Bluegrass Region of the Licking River watershed. Sites where sulfate values exceed 250 mg/L occur mainly in the Outer Bluegrass region of the Salt River watershed and the Eastern Coal Field region of the Kentucky River and Big Sandy River watersheds (Figure 55, 56, 57).

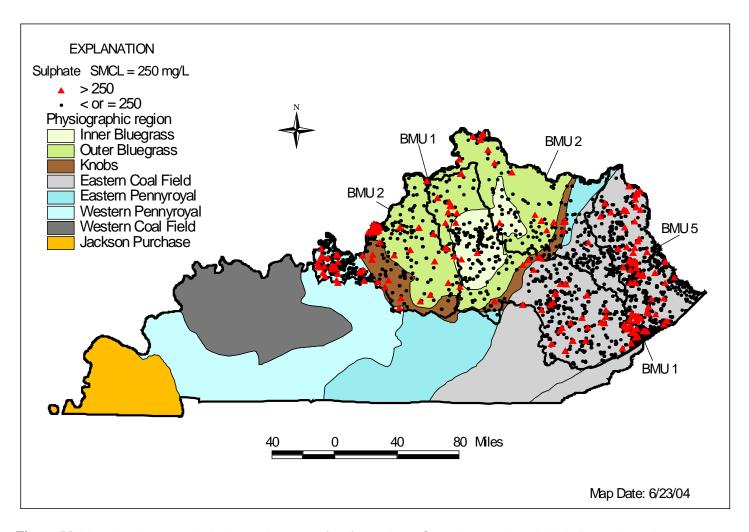


Figure 55. Map showing sampled sites and ranges of sulfate values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

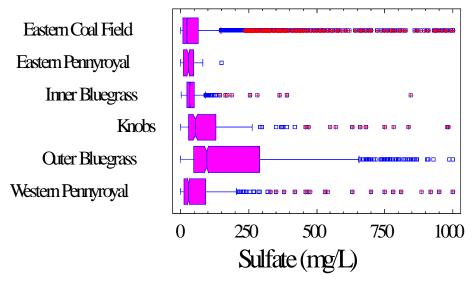


Figure 56. Summary of sulfate concentrations grouped by physiographic region. Higher values were excluded for clarity. SMCL = 250 mg/L.

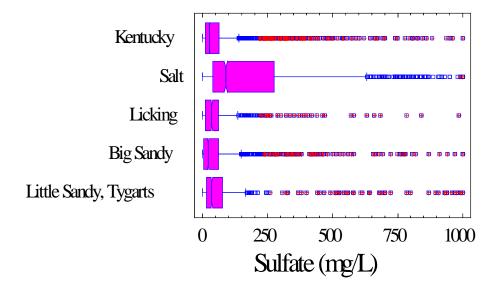


Figure 57. Summary of sulfate concentrations grouped by major watershed. Higher values were excluded for clarity. SMCL = 250 mg/L.

Groundwater samples from well and springs have nearly the same median sulfate concentration (Figure 58). However, water from wells has a higher 75<sup>th</sup> percentile value, larger interquartile range, and more values that exceed 250 mg/L than water from springs.

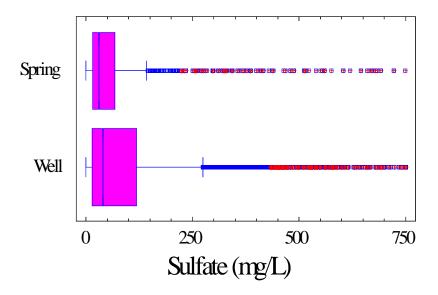


Figure 58. Summary of sulfate values for wells and springs. SMCL = 250 mg/L. Higher values were excluded for clarity.

The highest sulfate concentrations occur in shallow wells (Figure 59). Sulfate concentrations decrease with well depth.

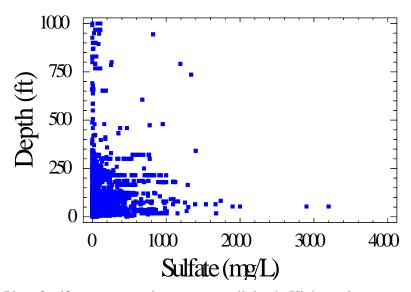


Figure 59. Plot of sulfate concentrations versus well depth. Higher values were excluded for clarity. SMCL = 250 mg/L.

Summary: Most wells and springs in the project area contain sulfate concentrations that are below the secondary standard of 250 mg/L. Higher values are found most commonly in the Eastern Kentucky Coal Field, Outer Bluegrass, and the Western Pennyroyal Regions. Wells produce high-sulfate water more commonly than springs, and shallow wells are more likely to have high sulfate concentrations than deeper wells. The distribution of sulfate values greater than 250 mg/L suggests that natural sources mask any nonpoint source effects. High sulfate concentrations are expected in the coal fields, where oxidation of iron sulfide minerals in shale and coal produces sulfate, and in carbonate strata such as the Outer Bluegrass and Western Pennyroyal, where the sulfate-bearing minerals gypsum and anhydrite are widely distributed.

# 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 major anthropogenic 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 is maintained in public water at 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 a maximum contaminant level (MCL) of 4 mg/L fluoride in public drinking water.

Fluoride in Kentucky groundwater has been measured in 6897 samples from 3498 sites (Table 12). The maximum value in each Basin Management Unit greatly exceeds 4 mg/L. However, concentrations above the MCL value are rare. The 75<sup>th</sup> percentile and median values in each Basin Management Units are less than 1.0 mg/L (Table 12).

Table 12. Summary of fluoride measurements (mg/L). MCL = 4.0 mg/L

|                             | BMU 1 | BMU 2 | BMU 5 |
|-----------------------------|-------|-------|-------|
| Nr. Values                  | 2585  | 3220  | 1092  |
| Maximum                     | 64.8  | 73.0  | 10.0  |
| 75 <sup>th</sup> percentile | 0.22  | 0.3   | 0.3   |
| Median                      | 0.13  | 0.13  | 0.164 |
| 25 <sup>th</sup> percentile | 0.08  | 0.1   | 0.1   |
| Minimum                     | 0     | 0     | 0     |
| IQR                         | 0.14  | 0.2   | 0.2   |
| Nr. Sites                   | 1355  | 1400  | 743   |
| Nr. Sites > 4.0 mg/L        | 11    | 7     | 2     |

The distribution of reported fluoride concentrations is similar in BMU 1, 2, and 5. More than 99 percent of all measured values in each Basin Management Unit are less than 4 mg/L (Figures 60, 61, 62).

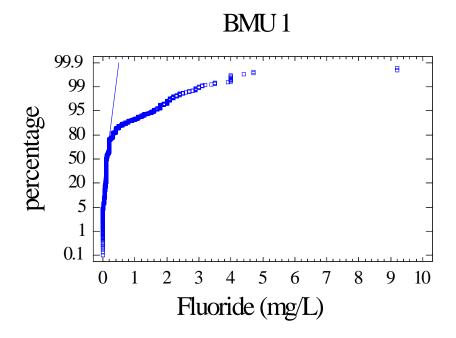


Figure 60. Cumulative plot of fluoride values in BMU 1. Higher values were excluded for clarity. MCL = 4.0 mg/L.

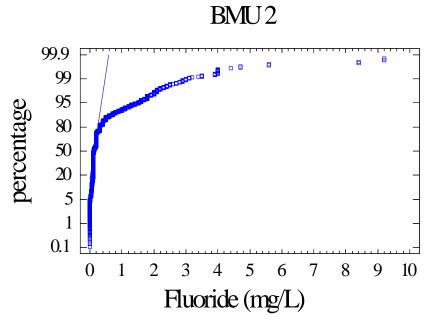


Figure 61. Cumulative plot of fluoride values in BMU 2. Higher values were excluded for clarity. MCL = 4.0 mg/L.

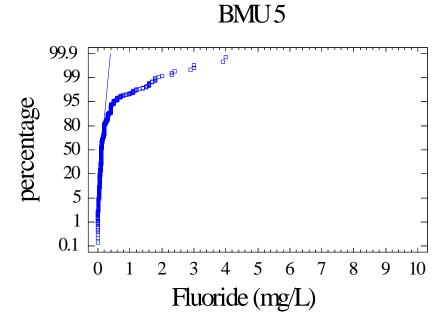


Figure 62. Cumulative plot of fluoride values in BMU 5. Higher values were excluded for clarity. MCL = 4.0 mg/L.

Sample site density is much greater in the southern half of the project area than in the northern part (Figure 63), because sampling for the NURE project did not extend into northern Kentucky. Sites where fluoride exceeds 2 mg/L or 4 mg/L do not appear to be concentrated in any particular physiographic region or watershed, but are randomly distributed throughout the region.

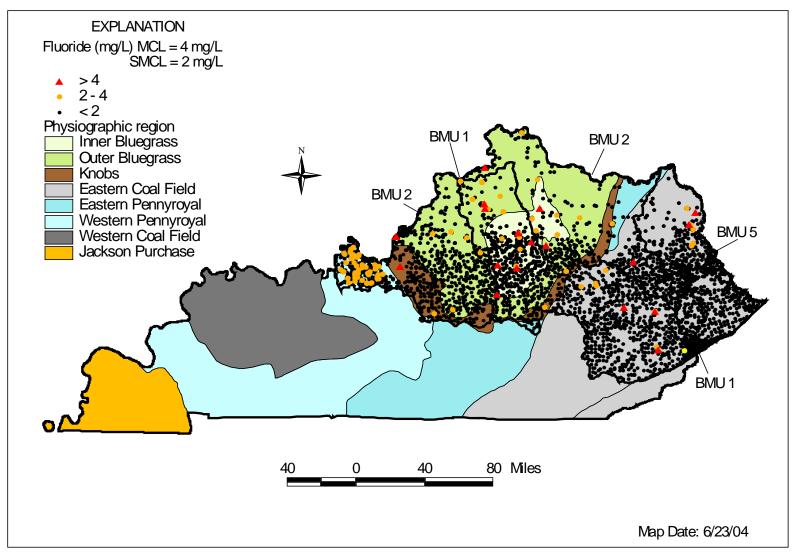


Figure 63. Map showing sampled sites and ranges of fluoride values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Groundwater samples from the Western Pennyroyal region have the largest interquartile range of values (Figure 64). The interquartile range of values from all other regions is much less than 1.0 mg/L, suggesting either stronger geochemical control on fluoride concentrations or an absence of naturally occurring fluoride in the area.

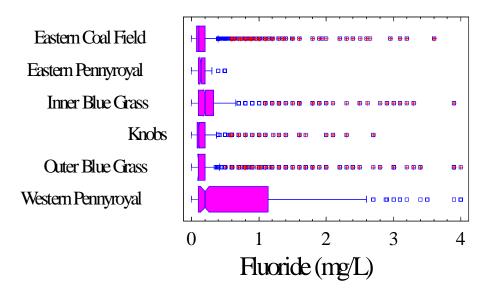


Figure 64. Summary of fluoride concentrations grouped by physiographic region. Higher values were excluded for clarity. MCL=4.0~mg/L

More than 75 percent of all fluoride values in each river basin are less than 1 mg/L (Figure 65).

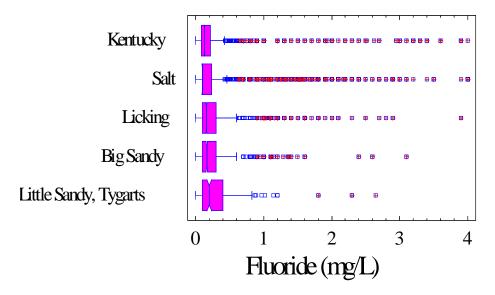


Figure 65. Summary of fluoride concentrations grouped by major watershed. Higher values were excluded for clarity. MCL=4.0 mg/L

Total and dissolved fluoride concentrations are very similar, as expected because fluoride is not associated with suspended solids (Figure 66).

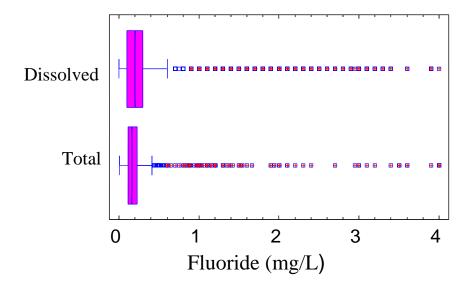


Figure 66. Comparison of total and dissolved fluoride concentrations. MCL = 4.0 mg/L. Higher values were excluded for clarity.

Groundwater samples from wells and springs have nearly the same median fluoride value and interquartile range, although higher fluoride values may be found in well water (Figure 67).

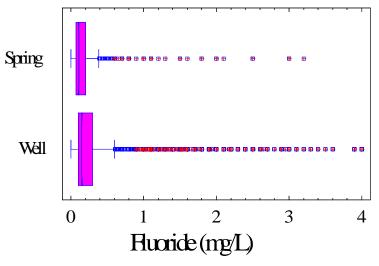


Figure 67. Summary of fluoride values for wells and springs. MCL = 4.0 mg/L. Higher values were excluded for clarity.

Fluoride concentrations show no strong trend with well depth (Figure 68).

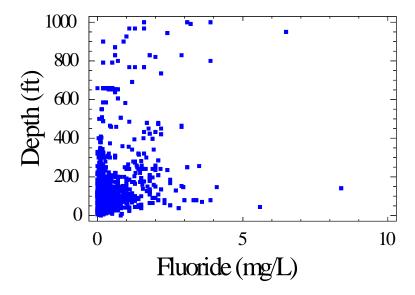


Figure 68. Plot of fluoride values versus well depth. MCL = 4.0 mg/L. Higher values were excluded for clarity.

Summary: Fluoride concentrations less than the MCL of 4.0 mg/L predominate throughout the project area. A few groundwater samples contain more than 4.0 mg/L fluoride, but they are widely scattered and show no strong correlation with physiographic region or major river watershed. The fluoride values that exceed the MCL probably result from natural variations in bedrock composition rather than the effects of nonpoint source contamination.

A statewide summary of fluoride data is available (Conrad and others, 1999) and can be viewed on the KGS Web site (http://www.uky.edu/KGS/water/gnet/gnet.htm).

#### 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 can 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 (EPA) set the maximum contaminant level (MCL) for arsenic in drinking water at 50 parts per billion (ppb, or 0.050 mg/L) in 1974. In 2001 the EPA announced that this MCL will be lowered to 10 ppb (0.010 mg/L). Water supply systems must meet the new MCL beginning January 2006.

Sites identified as monitoring wells by the Kentucky Division of Water's well identification numbering 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 provide no useful information. Therefore, such values are not included in the following discussion. Removing these leaves a total of 1858 reported arsenic concentrations at 308 sites (Table 13).

The maximum value in each Basin Management Unit exceeds the MCL. Nine of 308 sites produced groundwater that had an arsenic concentration greater than 0.01 mg/, and 94 percent of the values are reported as less than analytical detection.

Table 13. Summary of arsenic measurements (mg/L). MCL = 0.010 mg/L

|                                 | BMU 1    | BMU 2    | BMU 5    |
|---------------------------------|----------|----------|----------|
| Nr. Values                      | 869      | 697      | 290      |
| Maximum                         | 0.076    | 0.265    | 0.038    |
| 75 <sup>th</sup> percentile     | < 0.002  | < 0.002  | < 0.002  |
| Median                          | < 0.002  | < 0.002  | < 0.002  |
| 25 <sup>th</sup> percentile     | < 0.002  | < 0.002  | < 0.002  |
| Minimum                         | < 0.0005 | < 0.0005 | < 0.0005 |
| IQR                             | na       | na       | na       |
| Nr. Sites                       | 92       | 110      | 106      |
| Nr. Sites $> 0.01 \text{ mg/L}$ | 1        | 3        | 5        |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

Cumulative plots of values (Figure 69, 70, 71) are similar for the three Basin Management Units. More than 95 percent of the arsenic values are less than 0.01 mg/L.

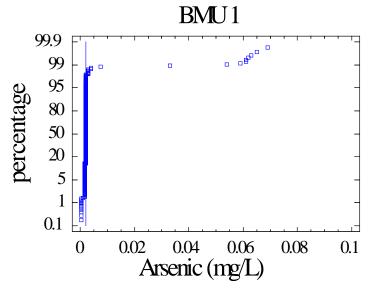


Figure 69. Cumulative plot of arsenic values in BMU 1. MCL = 0.01 mg/L.

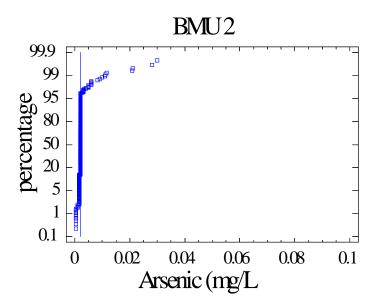


Figure 70. Cumulative plot of arsenic values in BMU 2. One value of 0.265 mg/L was excluded for clarity. MCL = 0.01 mg/L.

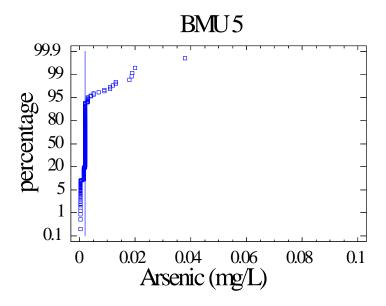


Figure 71. Cumulative plot of arsenic values in BMU 5. MCL = 0.01 mg/L.

There are relatively few sites in the Outer Bluegrass region where arsenic was measured, compared to the sites in the Inner Bluegrass, Eastern Kentucky Coal Field, and Western Pennyroyal regions (Figure 72). Sites where arsenic exceeds the MCL value of 0.01 mg/L are not concentrated in any region or major watershed.

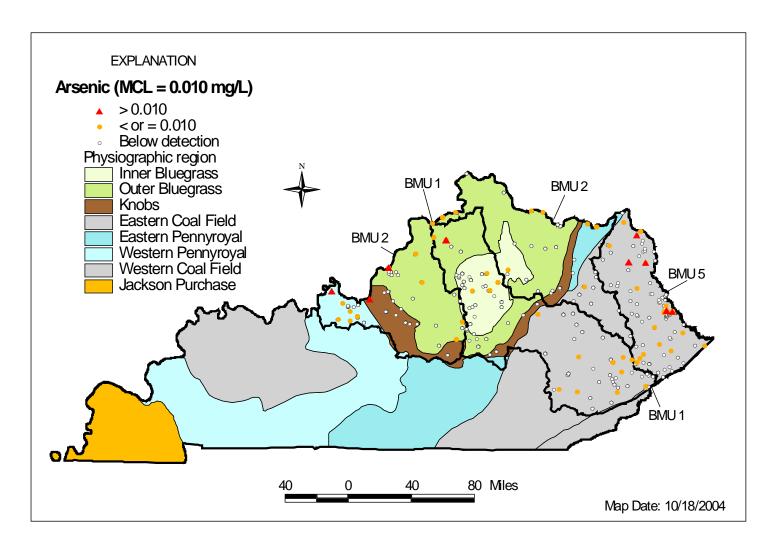


Figure 72. Map showing sampled sites and ranges of arsenic values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

The highest arsenic concentrations are found in the Outer Bluegrass Region (Figure 73) and the Kentucky River watershed (Figure 74).

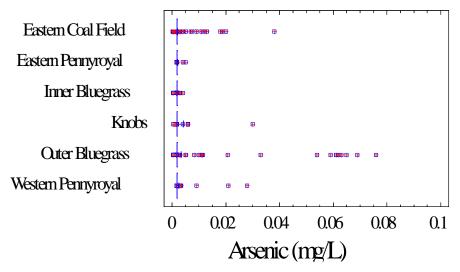


Figure 73. Summary of arsenic concentrations grouped by physiographic region. One value of 0.265 mg/L in the Knobs Region was excluded for clarity. MCL = 0.01 mg/L.

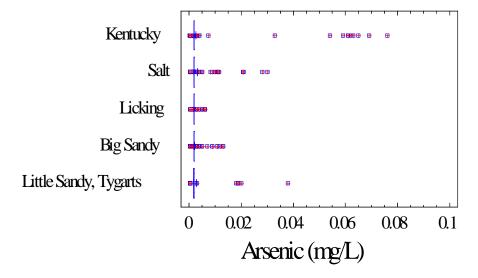


Figure 74. Summary of arsenic concentrations grouped by major watershed. One value of 0.265 mg/L in the Salt River watershed was excluded for clarity. MCL = 0.01 mg/L.

Total (unfiltered sample) and dissolved (filtered sample) arsenic concentrations have the same distribution of values (Figure 75), indicating that significant amounts of arsenic are not adsorbed on suspended material in the project area.

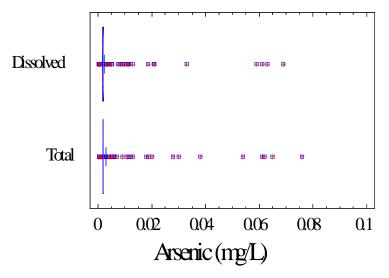


Figure 75. Comparison of total and dissolved arsenic concentrations. One value of 0.265 mg/L total arsenic was excluded for clarity.

Arsenic concentrations from wells reach higher values than groundwater from springs (Figure 76).

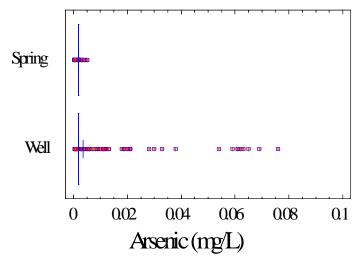


Figure 76. Comparison of arsenic values from wells and springs. One value of 0.265 mg/L arsenic from a well was excluded for clarity.

The highest arsenic concentrations in wells are found at depths of about 100 ft (Figure 77).

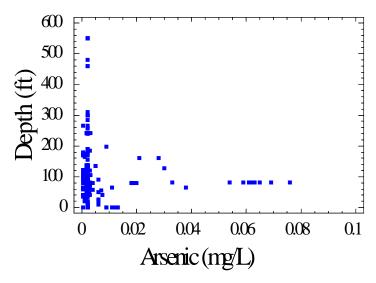


Figure 77. Plot of arsenic concentrations versus well depth. MCL = 0.1 mg/L.

Summary: Arsenic is present at very low concentrations in groundwater throughout the project area. Only 9 of 308 sites produced groundwater with arsenic concentrations that exceeded the MCL, and these sites are not predominantly in any one physiographic region or major river watershed. Therefore, nonpoint source contamination with respect to arsenic in groundwater 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 (http://www.uky.edu/KGS/water/gnet/gnet.htm).

# Barium

Barium (Ba) is an alkaline earth element that occurs naturally as the mineral barite (BaSO<sub>4</sub>), 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 wastes, or from leaking landfills where barium-containing materials were discarded.

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

The data repository contained 2579 barium measurements from 654 sites in the project area (Table 14). Although maximum values in each Basin Management Unit are quite high, the 75<sup>th</sup> percentile values are well below 1 mg/L throughout the region. Only 21 of 654 sites yielded groundwater that had more than 2 mg/L barium.

Table 14. Summary of barium measurements (mg/L). MCL = 2.0 mg/L

|                                | BMU 1 | BMU 2 | BMU 5 |
|--------------------------------|-------|-------|-------|
| Nr. Values                     | 1027  | 1122  | 430   |
| Maximum                        | 8.69  | 79.8  | 100.0 |
| 75 <sup>th</sup> percentile    | 0.43  | 0.07  | 0.59  |
| Median                         | 0.03  | 0.04  | 0.16  |
| 25 <sup>th</sup> percentile    | 0.02  | 0.03  | 0.04  |
| Minimum                        | 0.00  | 0.00  | 0.00  |
| IQR                            | 0.41  | 0.04  | 0.55  |
| Nr. Sites                      | 143   | 344   | 167   |
| Nr. Sites $> 2.0 \text{ mg/L}$ | 2     | 11    | 8     |

Data distributions (Figure 78, 79, 80) show the same general trend, with more than 95 percent of the values being less than 2 mg/L. Data distributions for BMU 2 (Figure 79) and BMU 5 (Figure 80) have a sharp break in slope, which may indicate that two distinct populations are represented.

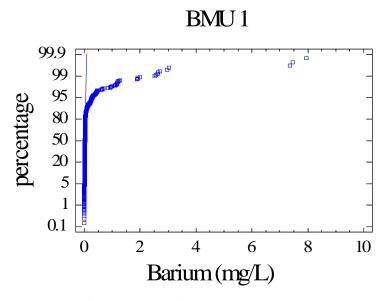


Figure 78. Cumulative plot of barium values in BMU 1. MCL = 2 mg/L.

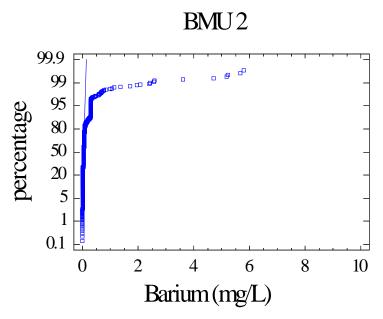


Figure 79. Cumulative plot of barium values in BMU 2. Two values were excluded for clarity. MCL = 2 mg/L.

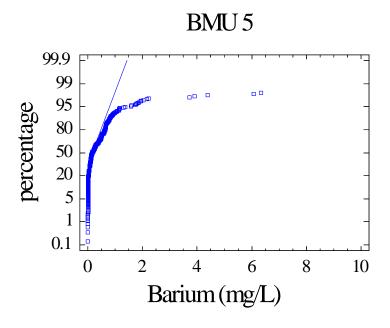


Figure 80. Cumulative plot of barium values in BMU 5. Nine values were excluded for clarity. MCL = 2 mg/L.

The distribution of sampled sites (Figure 81) shows a greater density in the Eastern Kentucky Coal Field, Inner Bluegrass, and Western Pennyroyal regions. Eleven of the 21 sites where barium exceeded the MCL are in the Eastern Kentucky Coal Field.

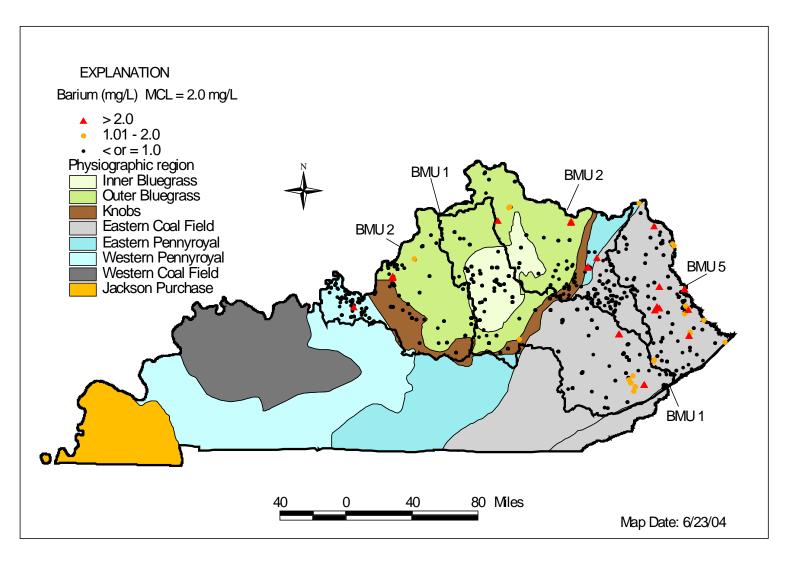


Figure 81. Map showing sampled sites and ranges of barium values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Values greater than the MCL are found primarily in the Eastern Coal Field Region (Kentucky, Licking and Big Sandy River watersheds) and the Outer Bluegrass Region (Salt River watershed (Figures 82 and 83).

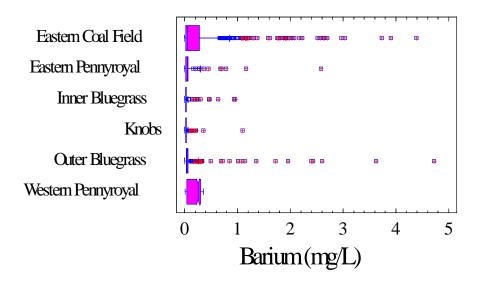


Figure 82. Summary of barium concentrations grouped by physiographic region. Higher values excluded for clarity. MCL = 2 mg/L

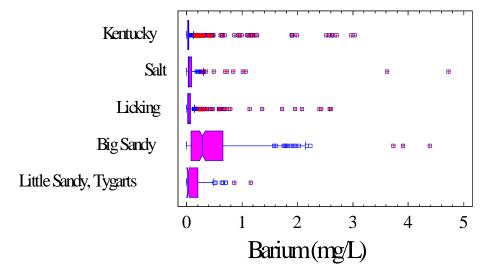


Figure 83. Summary of barium concentrations grouped by major watershed. Higher values excluded for clarity. MCL = 2 mg/L

Barium concentrations in total (unfiltered) samples have a larger interquartile range than concentrations from dissolved (filtered) samples, and more values greater than 2 mg/L (Figure 84).

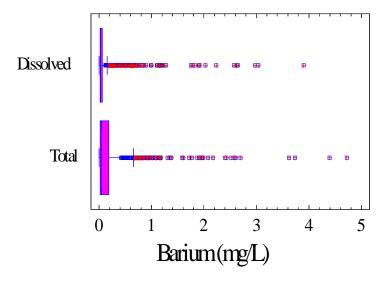


Figure 84. Comparison of total and dissolved barium values. Nine values of total barium excluded for clarity. MCL = 2 mg/L.

Barium concentrations from wells have a larger interquartile range than concentrations from springs (Figure 85). No samples from springs had a barium concentration above the MCL.

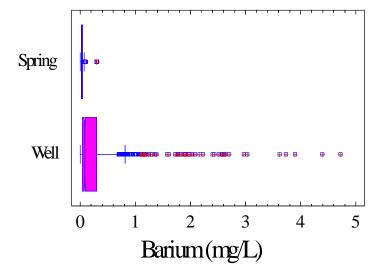


Figure 85. Comparison of barium values from wells and springs. Nine values from wells excluded for clarity. MCL = 2 mg/L.

The highest barium concentrations are found in wells that are less than 100 ft deep (Figure 86).

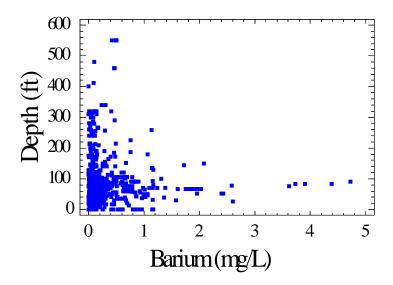


Figure 86. Plot of barium concentrations versus well depth. MCL = 2 mg/L.

Summary: Twenty-one of 654 sites yielded groundwater that contained more than 2 mg/L barium in the project area. All these sites were shallow wells in the Eastern Kentucky Coal Field. Wunsch (1991) reported similar observations from 130 wells in the Eastern Coal Field, and attributed the barium concentrations greater than 1.0 mg/L primarily to a mixing of deep, barium-rich brines with shallow groundwater. Naturally occurring barite is another probable source of the barium concentrations observed. Strong influences of anthropogenic, nonpoint sources of barium contamination are not suggested by the observed barium concentrations.

# 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 light bulbs, 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 Hg is a strong neurotoxin that causes demyelination, delayed nerve conduction, and kidney damage. Because of its toxicity, the EPA has set a MCL value for mercury at 0.002 mg/L.

The groundwater data repository contained 1587 mercury analyses from 430 sites from the project area (Table 15, Figure 87). No measured mercury concentration exceeded the MCL of 0.002 mg/L. Only 21 of the 430 sites had values were above analytical detection. Most of these were in the Western Pennyroyal Region of the Salt River watershed. Four of these sites are springs and 17 are wells. Three of these values were dissolved mercury and 18 were measurements of total mercury. The highest reported value was 0.00095 mg/L, well below the MCL value of 0.002 mg/L.

Table 15. Summary of mercury measurements (mg/L). MCL = 0.002 mg/L

|                             | BMU 1     | BMU 2     | BMU 5     |
|-----------------------------|-----------|-----------|-----------|
| Nr. Values                  | 621       | 731       | 235       |
| Maximum                     | < 0.002   | < 0.002   | 0.00095   |
| 75 <sup>th</sup> percentile | < 0.00005 | < 0.0001  | < 0.00005 |
| Median                      | < 0.00005 | < 0.00005 | < 0.00005 |
| 25 <sup>th</sup> percentile | < 0.00005 | < 0.00005 | < 0.00005 |
| Minimum                     | < 0.00005 | < 0.00005 | < 0.00005 |
| IQR                         | na        | na        | na        |
| Nr. Sites                   | 100       | 221       | 109       |
| Nr. Sites $> 0.002$ mg/L    | 0         | 0         | 0         |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

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

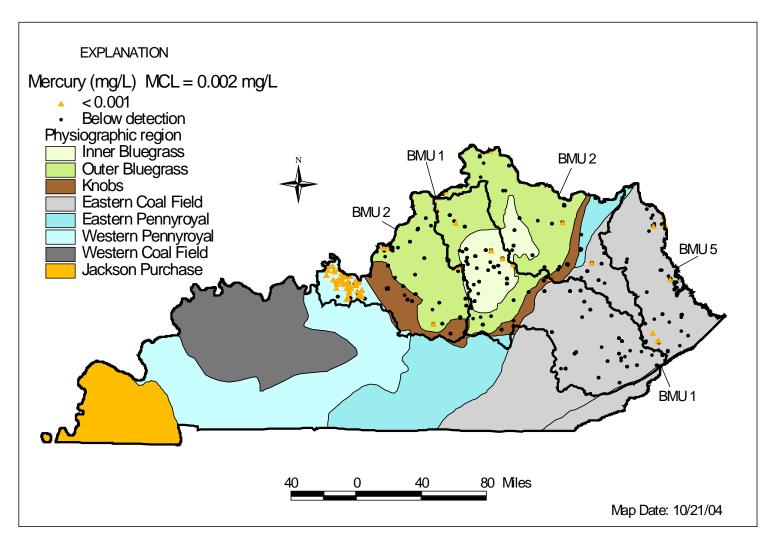


Figure 87. Map showing sampled sites and ranges of mercury values. No values exceeded the MCL. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Summary: Mercury was detected in 21 of 430 sites in the project area. The maximum mercury concentration reported was 0.00095 mg/L, less than half the MCL value. Detections were more common in unfiltered samples, suggesting that mercury was adsorbed onto suspended material rather than in true solution. Most of the sites where mercury was detected are located in the Western Pennyroyal Region of the Salt River watershed, BMU 2. This concentration of mercury detections most likely indicates either a geologic control or the influence of atmospheric fallout.

# Iron

Iron (Fe) is a naturally occurring metal that is widely present in groundwater. Iron can exists 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 oxyhydroxides (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 for iron because concentrations above this level produce objectionable odor, taste, color, staining, corrosion, and scaling.

The data repository contained 11,288 iron measurements from 2629 sites in the project area (Table 16). Iron concentrations are quite high; more than half of the sites in each Basin Management Unit produced groundwater that has iron concentrations above the secondary standard.

Table 16. Summary of iron measurements (mg/L). SMCL = 0.3 mg/L

|                                | BMU 1 | BMU 2 | BMU 5 |
|--------------------------------|-------|-------|-------|
| Nr. Values                     | 4394  | 3187  | 3707  |
| Maximum                        | 735   | 9660  | 1500  |
| 75 <sup>th</sup> percentile    | 1.0   | 1.9   | 2.76  |
| Median                         | 0.23  | 0.26  | 0.60  |
| 25 <sup>th</sup> percentile    | 0.05  | 0.04  | 0.14  |
| Minimum                        | 0.00  | 0.00  | 0.00  |
| IQR                            | 0.95  | 1.86  | 2.62  |
| Nr. Sites                      | 751   | 1055  | 823   |
| Nr. Sites $> 0.3 \text{ mg/L}$ | 523   | 599   | 641   |

The distribution of reported iron concentrations is similar in the three Basin Management Units (Figures 88, 89, 90).

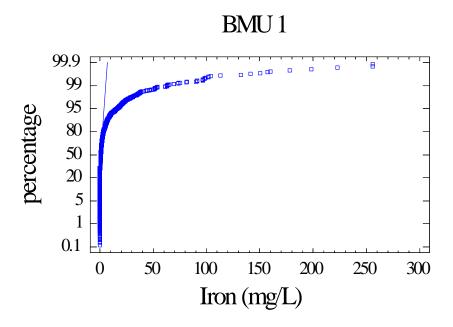


Figure 88. Cumulative plot of iron values in BMU 1. Higher values were excluded for clarity.  $SMCL=0.3\ mg/L$ .

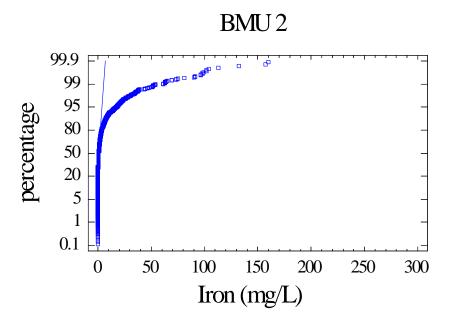


Figure 89. Cumulative plot of iron values in BMU 2. Higher values were excluded for clarity. SMCL = 0.3 mg/L.

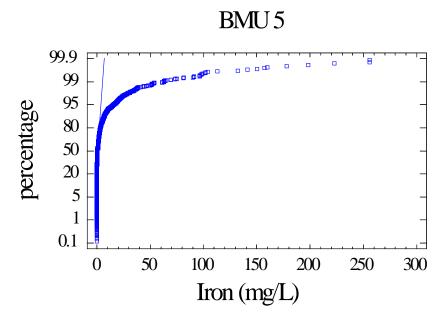


Figure 90. Cumulative plot of iron values in BMU 5. Higher values were excluded for clarity. SMCL = 0.3 mg/L.

Sample site density is greatest in the Eastern Kentucky Coal Field and lowest in the eastern part of the Outer Bluegrass region (Figure 91). Values above the SMCL are found throughout the project area and are most common in the Eastern Kentucky Coal Field, western Outer Bluegrass, and Western Pennyroyal Regions.

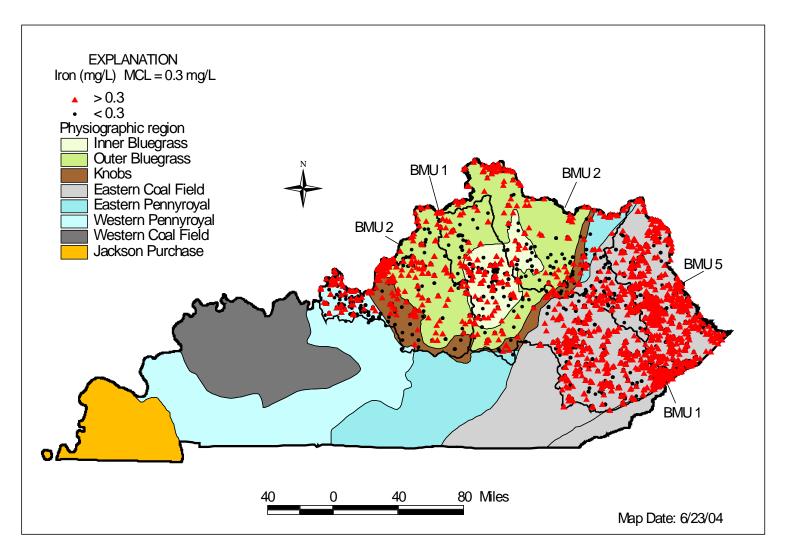


Figure 91. Map of sampled sites and ranges of iron concentrations. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Samples from the Eastern Coal Field and the Outer Bluegrass regions have the highest iron concentrations and the largest range of values, whereas sites from the Inner Bluegrass and Western Pennyroyal have the lowest concentrations and smallest range of values (Figure 92).

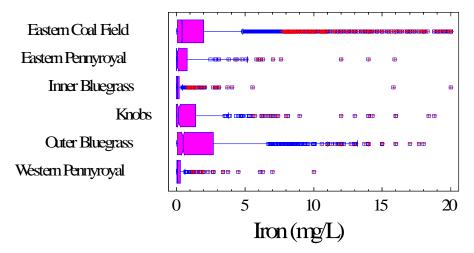


Figure 92. Summary of iron concentrations grouped by physiographic region. Higher values excluded for clarity. SMCL = 0.3 mg/L

Samples from the Licking River watershed have the lowest median value and smallest interquartile range of iron concentrations (Figure 93). Samples from the Salt River, Big Sandy River, Little Sandy River, and Tygarts Creek watersheds have high median values, a large interquartile range, and a large number of iron concentrations greater than 5 mg/L.

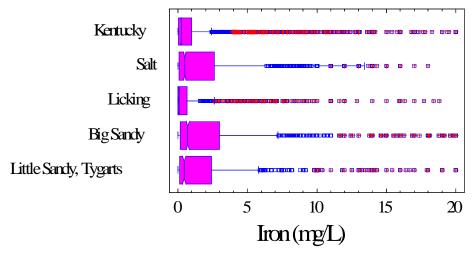


Figure 93. Summary of iron concentrations grouped by major watershed. Higher values excluded for clarity. SMCL = 0.3 mg/L

Total iron concentrations (unfiltered sample) have a higher median value and greater interquartile range than dissolved iron concentrations (filtered sample), suggesting that some of the reported iron is associated with suspended solids (Figure 94).

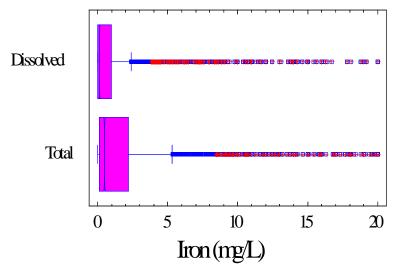


Figure 94. Comparison of total and dissolved iron values. Higher values excluded for clarity.  $SMCL = 0.3 \ mg/L$ 

Groundwater from springs is generally much lower in iron than water from wells (Figure 95.)

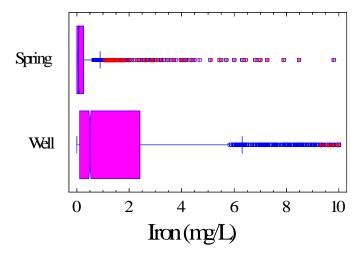


Figure 95. Comparison of iron concentrations in wells and springs. Higher values excluded for clarity.  $SMCL=0.3\ mg/L$ 

High iron concentrations are found more commonly in wells that are less than 100 ft deep; deeper wells typically have much lower iron concentrations (Figure 96).

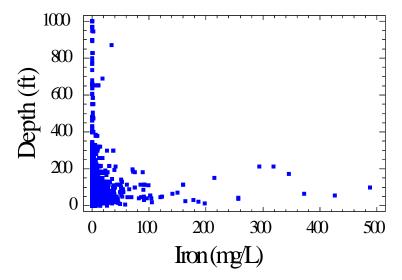


Figure 96. Plot of iron concentrations versus well depth. Higher values excluded for clarity. SMCL = 0.3 mg/L

Summary: Iron concentrations that are high enough to produce staining and objectionable taste are common in groundwater throughout the project area. High iron concentrations are especially common in the Eastern Kentucky Coal Field and western part of the Outer Bluegrass regions. Total iron concentrations are higher than dissolved concentrations, indicating that iron is also present in suspended material. Wells have higher iron concentrations than springs, probably because many springs in this area are in carbonate bedrock, which is naturally lower in iron than sandstones and shales.

# Manganese

Manganese (Mn) is a naturally occurring cation that is widely present in groundwater supplies. Manganese and iron behave similarly geochemically, 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 for manganese based on the fact that higher concentrations may produce objectionable odor, taste, color, corrosion, and staining.

The data repository contained 9079 manganese concentrations from 6005 sites in Basin Management Units 1, 2, and 5 (Table 17). Like iron, manganese concentrations are sufficiently high to require treatment before groundwater is suitable for domestic use. More than one-third of all sites produce water having more than 0.05 mg/L manganese.

Table 17. Summary of manganese measurements (mg/L). SMCL = 0.05 mg/L

|                             | BMU 1 | BMU 2 | BMU 5 |
|-----------------------------|-------|-------|-------|
| Nr. Values                  | 3788  | 2561  | 2730  |
| Maximum                     | 20.1  | 540   | 83    |
| 75 <sup>th</sup> percentile | 0.20  | 0.29  | 0.50  |
| Median                      | 0.06  | 0.04  | 0.11  |
| 25 <sup>th</sup> percentile | 0.01  | 0.01  | 0.03  |
| Minimum                     | 0.00  | 0.00  | 0.00  |
| IQR                         | 0.19  | 0.28  | 0.47  |
| Nr. Sites                   | 2458  | 1816  | 1731  |
| Nr. Sites $> 0.05$ mg/L     | 840   | 663   | 642   |

The distribution of manganese concentrations is generally similar in the three Basin Management Units (Figures 97, 98, 99), although BMU 1 has fewer very high values than BMU 2 or BMU 5.

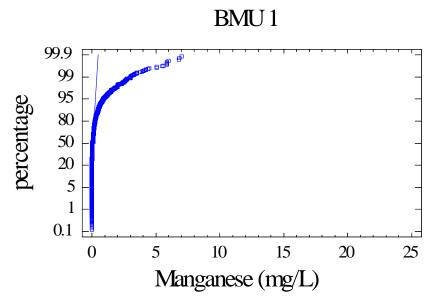


Figure 97. Cumulative plot of manganese values from BMU 1. Higher values excluded for clarity. SMCL = 0.05 mg/L.

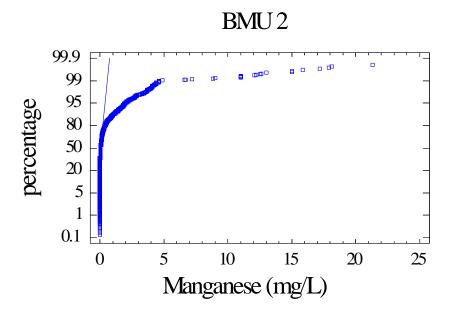


Figure 98. Cumulative plot of manganese values from BMU 2. Higher values excluded for clarity. SMCL = 0.05 mg/L.

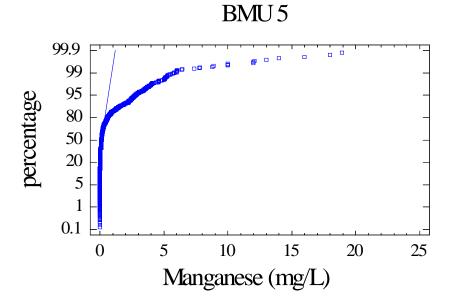


Figure 99. Cumulative plot of manganese values from BMU 5. Higher values excluded for clarity. SMCL = 0.05 mg/L.

Site distribution is very dense in the southern part of the Eastern Kentucky Coal Field and the western part of the Outer Bluegrass regions (Figure 100) because the NURE program sampled these areas. Values that exceed the SMCL are found throughout the project area.

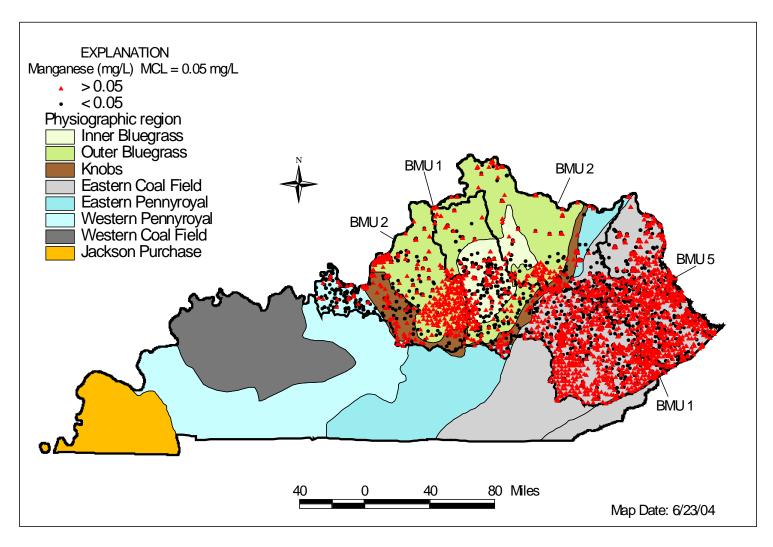


Figure 100. Map showing sampled sites and ranges of manganese concentrations. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Although manganese concentrations that exceed the SMCL are found in every region and major watershed, they are most common in the Eastern Coal Field Region (Kentucky River, Big Sandy River, Little Sandy River, and Tygarts Creek watersheds) and the Outer Bluegrass Region (Salt River watershed) (Figures 101, 102).

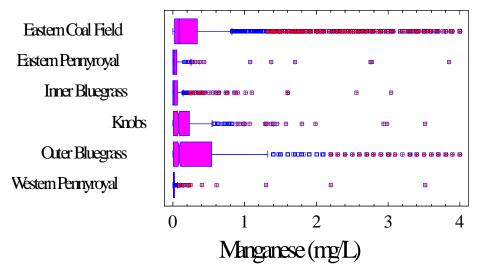


Figure 101. Summary of manganese concentrations grouped by physiographic region. Higher values excluded for clarity. SMCL = 0.05 mg/L

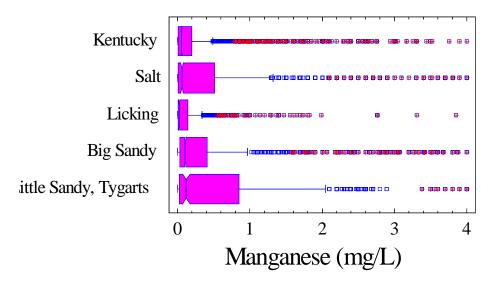


Figure 102. Summary of manganese concentrations grouped by major watershed. Higher values excluded for clarity. SMCL = 0.05 mg/L

Dissolved manganese concentrations have a higher median value and larger interquartile range than total manganese concentrations (Figure 103), suggesting that suspended particulate material does not contribute significant amounts of manganese to the analysis.

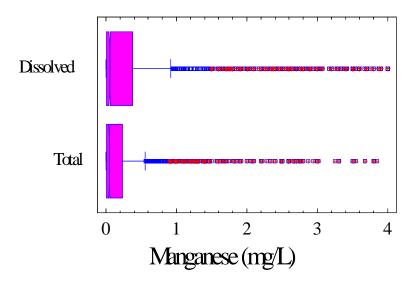


Figure 103. Comparison of total and dissolved manganese values. Higher values excluded for clarity.  $SMCL=0.05\ mg/L$ 

Groundwater from wells is generally higher in manganese than groundwater from springs (Figure 104).

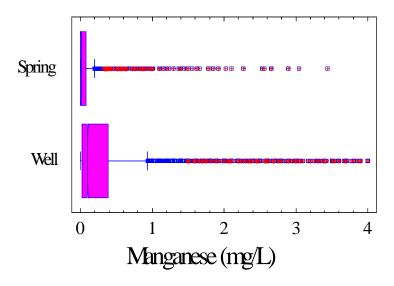


Figure 104. Comparison of manganese values from wells and springs. Higher values excluded for clarity.  $SMCL=0.05\ mg/L$ 

The highest manganese concentrations are typically found in wells less than 100 ft deep, rather than in deeper wells (Figure 105).

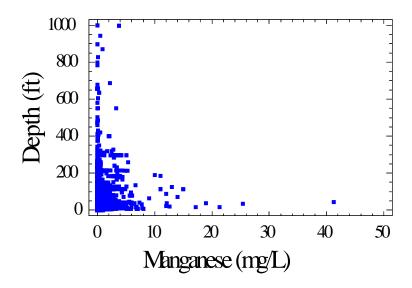


Figure 105. Plot of manganese concentrations versus well depth. SMCL = 0.05 mg/L.

Summary: The geochemical similarity between manganese and iron is demonstrated in the similarity of their concentrations in groundwater. Both commonly occur at concentrations that affect groundwater taste and can stain containers and clothing. The highest manganese concentrations are found in groundwater from the Eastern Kentucky Coal Field and the western part of the Outer Bluegrass Regions, and in shallow wells rather than deep wells or springs. All features of the distribution of manganese concentrations appear primarily related to bedrock type. There is no evidence to suggest that NPS 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 wastes, and fossil fuel combustion. High nutrient levels in groundwater generally indicate contamination from fertilizer, sewage systems, or confined feedlot operations. Excessive nutrients can lead to algal blooms and eutrophication in surface water systems, and excessive nitrate or nitrite in drinking water can pose health hazards.

## **Nitrogen Species**

Nitrogen in water occurs predominantly as either the anion nitrate (NO<sub>3</sub><sup>-</sup>) under oxidizing conditions or the cation ammonium (NH<sub>4</sub><sup>+</sup>) under reducing conditions. Nitrite (NO<sub>2</sub><sup>-</sup>) and ammonia (NH<sub>3</sub>) are thermodynamically less stable forms of aqueous nitrogen that may be present under reducing conditions. Because it is positively charged, ammonium is readily adsorbed on soil and mineral particles, thus limiting its mobility, whereas the negatively charged nitrate and nitrite anions are highly mobile. Nitrite, ammonium, and ammonia are unstable in oxidizing environments (Hem, 1985). For this reason, high concentrations of these species in shallow, aerated groundwater are indicators of likely contamination by sewage or other forms of organic waste. Nitrite, ammonium, and ammonia may also exist in deep, old, reducing groundwater systems.

Runoff from fertilizer use, leachate from septic tanks, and sewage are common sources of nitrogen species. Nitrate is commonly used as fertilizer; high nitrate concentrations generally indicate contamination by fertilizer or by human or animal organic waste. Caves in karst terrain 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 oxidizes quickly to nitrate in oxidizing environments and to nitrogen gas in reducing environments (Fetter, 1993).

Nitrate, nitrite, ammonia, and ammonium concentrations are reported differently for different purposes. Analyses for geochemical investigations traditionally report concentrations as weight per volume of the measured ions (mg/L of NO<sub>3</sub>-, NO<sub>2</sub>-, NH<sub>3</sub> or NH<sub>4</sub>+). However, analyses for environmental purposes 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 it was recorded, and concentration units must be standardized before data summaries and evaluations can be made.

The EPA has established a drinking water MCL of 10 mg/L for nitrate nitrogen (equivalent to 44.3 mg/L nitrate) and 1.0 mg/L for nitrite nitrogen (equivalent to 3.2 mg/L nitrite) because higher concentrations can lead to methemoglobinemia (blue baby syndrome) in infants, where the oxygen-carrying ability of the child's blood is severely reduced. Lifetime exposure to nitrite

nitrogen concentrations greater than 1 mg/L also can produce diuresis, increased starchy deposits and hemorrhaging of the spleen. No human health based concentration limits have been established for ammonia or ammonium. However, ammonia concentrations of 1 to 10 mg/L can be toxic to aquatic life.

# **Nitrate Nitrogen**

The data repository contained 2547 nitrate nitrogen measurements at 741 sites. Nitrate nitrogen concentrations exceeded the MCL of 10 mg/L at 45 sites (Table 18).

Table 18. Summary of nitrate nitrogen measurements (mg/L). MCL = 10 mg/L

|                          | BMU 1 | BMU 2 | BMU 5 |
|--------------------------|-------|-------|-------|
| Measurements             | 935   | 1069  | 543   |
| Sites                    | 176   | 294   | 271   |
| Maximum                  | 84.8  | 108   | 16.0  |
| 3 <sup>rd</sup> quartile | 2.87  | 3.29  | 0.5   |
| Median                   | 0.79  | 0.65  | 0.07  |
| 1 <sup>st</sup> quartile | 0.1   | 0.09  | 0.02  |
| Minimum                  | 0.0   | 0.0   | 0.0   |
| Interquartile range      | 2.77  | 3.2   | 0.48  |
| Sites > 10.0             | 20    | 22    | 3     |
| Sites > 5.0              | 35    | 44    | 9     |

Cumulative data plots are similar for BMU 1 and BMU 2 (Figures 106, 107) with many values greater than 10 mg/L, whereas there are only 4 values greater than 10 mg/L reported from BMU 5 (Figure 108).

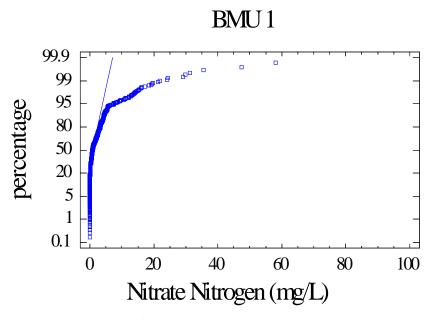


Figure 106. Cumulative plot of nitrate nitrogen values from BMU 1. MCL = 10 mg/L.

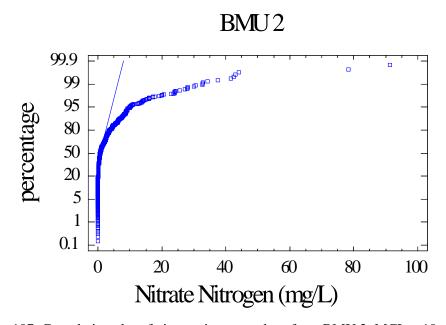


Figure 107. Cumulative plot of nitrate nitrogen values from BMU 2. MCL = 10 mg/L.

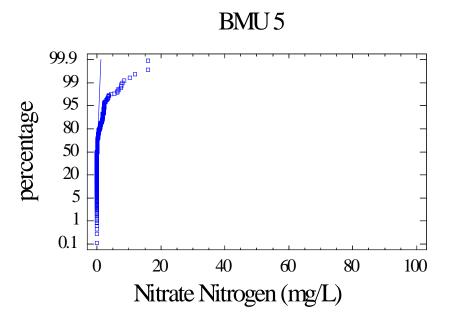


Figure 108. Cumulative plot of nitrate nitrogen values from BMU 5. MCL = 10 mg/L.

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

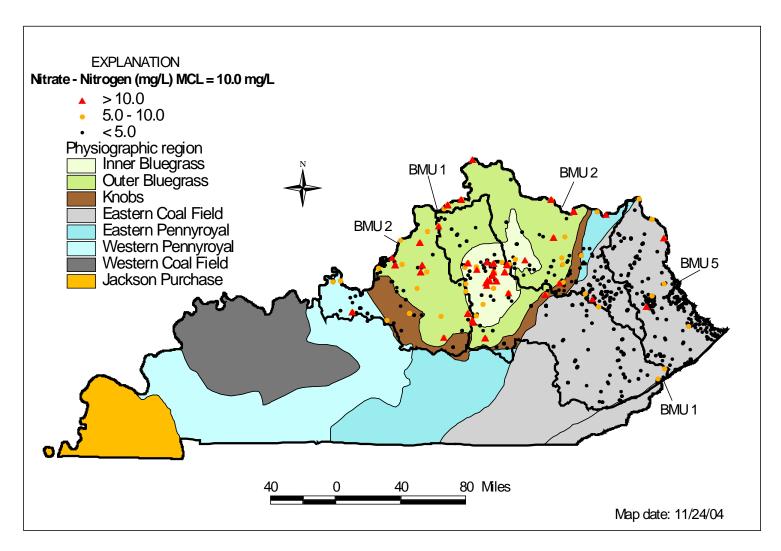


Figure 109. Map showing sampled sites and ranges of nitrate nitrogen concentrations. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

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

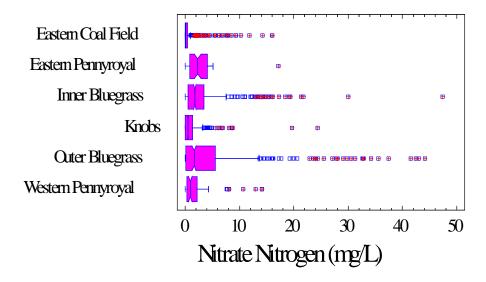


Figure 110. Summary of nitrate nitrogen concentrations grouped by physiographic region. Extreme values were excluded for clarity. MCL = 10 mg/L

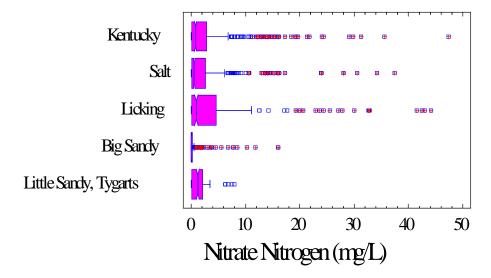


Figure 111. Summary of nitrate nitrogen concentrations grouped by major watershed. Extreme values were excluded for clarity. MCL = 10 mg/L

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

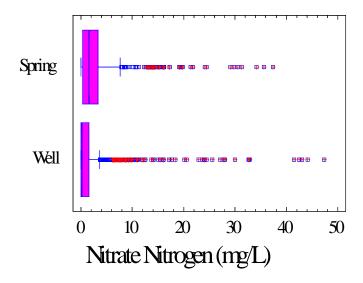


Figure 112. Comparison of nitrate nitrogen values from wells and springs. Extreme values were excluded for clarity. MCL = 10 mg/L

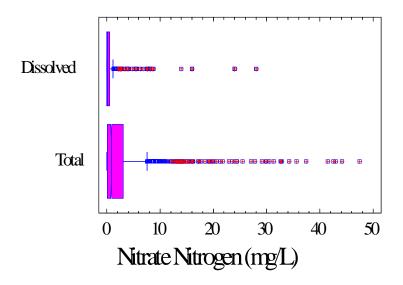


Figure 113. Comparison of total and dissolved nitrate nitrogen values. Extreme values were excluded for clarity. MCL = 10 mg/L

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

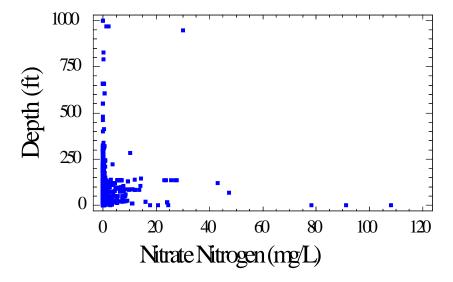


Figure 114. Plot of nitrate nitrogen concentrations versus well depth. MCL = 10 mg/L.

Summary: More than 99 percent of all nitrate nitrogen measurements in BMU 5, and more than 95 percent of all measurements in BMU 1 and BMU 2 are less than the MCL value of 10 mg/L. However, values as high as 108 mg/L have been recorded, and sites where nitrate nitrogen concentrations exceed the recommended health-based limit occur in all Basin Management Units. High nitrate nitrogen concentrations are most likely to occur in the carbonate Inner and Outer Bluegrass Regions in water from both springs and shallow wells. These results suggest that nonpoint-source nutrients are contributing nitrate to the groundwater system. A statewide summary of nitrate data is available (Conrad and others, 1999) and can be viewed on the KGS Web site (http://www.uky.edu/KGS/water/gnet/gnet.htm).

## Nitrite Nitrogen

The data repository contained 1965 measurements of nitrite nitrogen from 339 sites. The median value in each BMU is well below the EPA MCL of 1.0 mg/L; however, nitrite nitrogen values exceed 1.0 mg/L at 4 sites in the project area (Table 19).

Table 19. Summary of nitrite nitrogen measurements (mg/L). MCL = 1.0 mg/L

|                          | BMU 1 | BMU 2   | BMU 5 |
|--------------------------|-------|---------|-------|
| Measurements             | 777   | 908     | 280   |
| Sites                    | 85    | 145     | 109   |
| Maximum                  | 1.5   | 13.4    | 0.13  |
| 3 <sup>rd</sup> quartile | 0.008 | 0.01    | 0.023 |
| Median                   | 0.005 | < 0.006 | 0.01  |
| 1 <sup>st</sup> quartile | 0.002 | 0.002   | 0.004 |
| Minimum                  | 0.0   | 0.0     | 0.0   |
| Interquartile range      | 0.006 | 0.008   | 0.019 |
| Sites > 1.0              | 1     | 3       | 0     |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

The distribution of measured values is similar in each Basin Management Unit, with more than 99 percent of the values being well below 1.0 mg/L (Figures 115, 116, and 117).

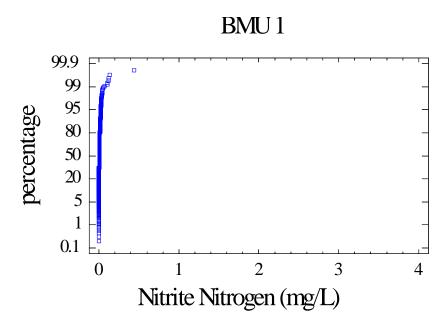


Figure 115. Cumulative plot of nitrite nitrogen values from BMU 1. MCL = 1.0 mg/L.

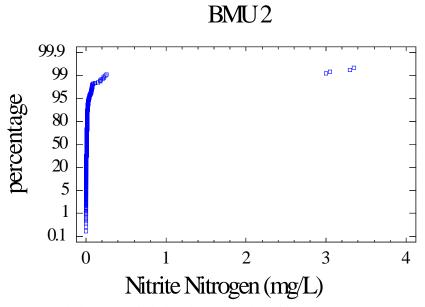


Figure 116. Cumulative plot of nitrite nitrogen values from BMU 2. MCL = 1.0 mg/L.

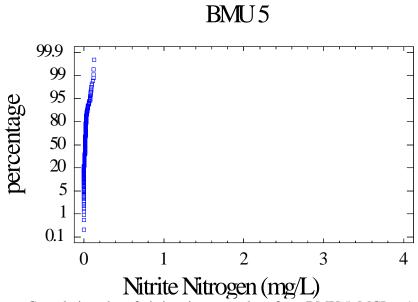


Figure 117. Cumulative plot of nitrite nitrogen values from BMU 5. MCL = 1.0 mg/L.

The distribution of sampled sites is not uniform throughout the project area (Figure 118), with the densest sampling along the eastern border of BMU 5 and along the Ohio River in the Salt River watershed of BMU 2. Sites where nitrite nitrogen exceeds the MCL of 1.0 mg/L occur in the Eastern Coal Field section of BMU 1, and the Western Pennyroyal and Outer Bluegrass sections of BMU 2 (Figures 118, 119, 120).

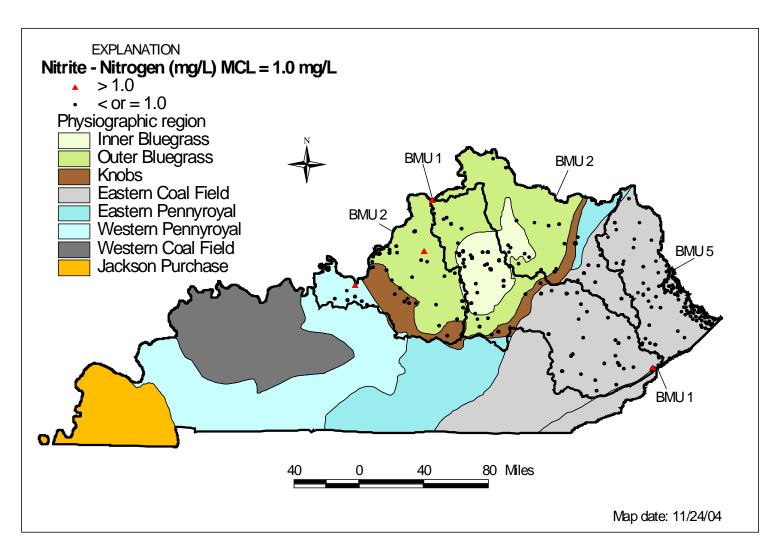


Figure 118. Map showing sampled sites and ranges of nitrite nitrogen concentrations. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

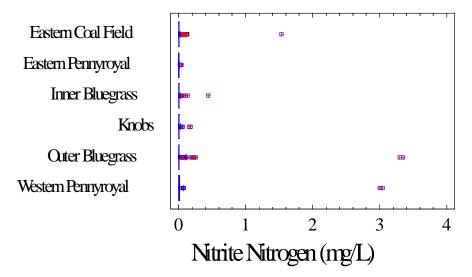


Figure 119. Summary of nitrite nitrogen concentrations grouped by physiographic region. Extreme values were excluded for clarity. MCL = 1.0 mg/L

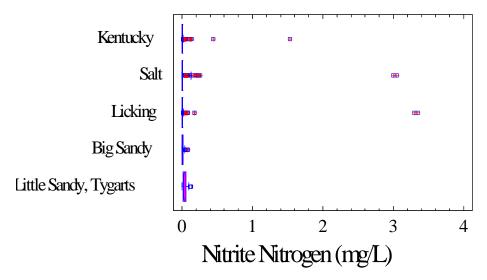


Figure 120. Summary of nitrite nitrogen concentrations grouped by major watershed. Extreme values were excluded for clarity. MCL = 1.0 mg/L

Nitrite nitrogen concentrations that exceed the MCL of 1.0 mg/L are reported from wells rather than from springs (Figure 121).

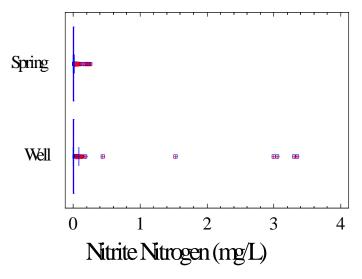


Figure 121. Comparison of nitrite nitrogen values from wells and springs. Extreme values were excluded for clarity. MCL = 1.0 mg/L

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

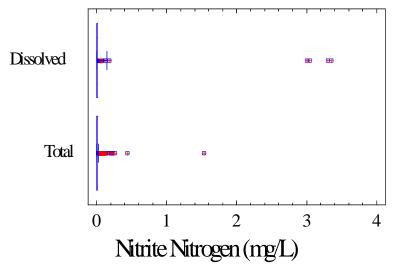


Figure 122. Comparison of total and dissolved nitrite nitrogen values. Extreme values were excluded for clarity. MCL = 1.0 mg/L

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

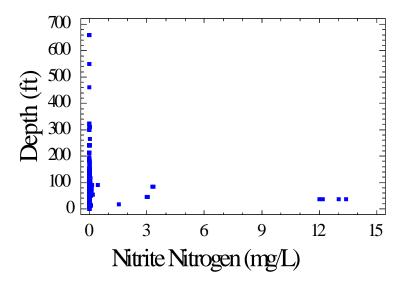


Figure 123. Plot of nitrate nitrogen concentrations versus well depth. MCL = 10 mg/L.

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

### **Ammonia Nitrogen**

The data repository contained 1675 ammonia nitrogen measurements from 213 sites in the project area (Table 20). The median concentration in each BMU was below analytical detection. Although there are no EPA health-based standards for ammonia nitrogen, the Kentucky Division of Water has recommended a risk-based upper limit of 0.110 mg/L. Values greater than 0.11 mg/L are uncommon in the project area but were observed at 81 of the 213 sites (Table 20).

| Table 20. Summary | of a | ımmonia | nitrogen | measurements. | DOW = | 0.110  mg/L |
|-------------------|------|---------|----------|---------------|-------|-------------|
|                   |      |         |          |               |       |             |

|                          | BMU 1  | BMU 2  | BMU 5  |
|--------------------------|--------|--------|--------|
| Measurements             | 849    | 659    | 167    |
| Sites                    | 76     | 89     | 48     |
| Maximum                  | 22.5   | 20.55  | 13.15  |
| 3 <sup>rd</sup> quartile | < 0.05 | < 0.05 | 0.387  |
| Median                   | < 0.02 | < 0.02 | < 0.05 |
| 1 <sup>st</sup> quartile | < 0.02 | < 0.02 | < 0.02 |
| Minimum                  | 0.0    | 0.0    | 0.016  |
| Sites > 0.110            | 26     | 19     | 36     |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

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

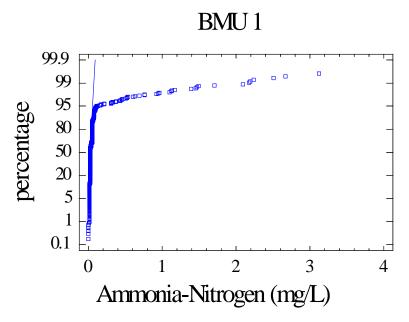


Figure 124. Cumulative plot of ammonia nitrogen values from BMU 1. Extreme values were omitted to better show the majority of the data. DOW = 0.110 mg/L

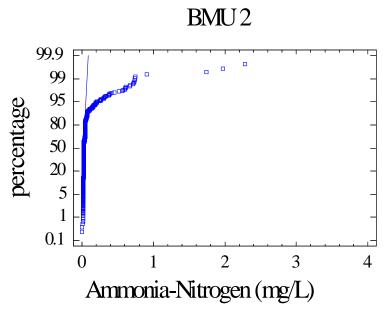


Figure 125. Cumulative plot of ammonia nitrogen values from BMU 2. Extreme values were omitted to better show the majority of the data. DOW = 0.110 mg/L

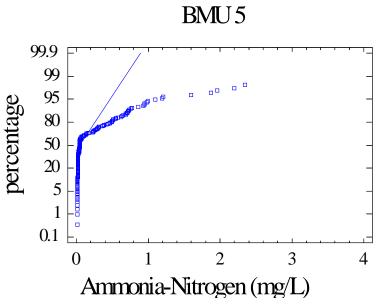


Figure 126. Cumulative plot of ammonia nitrogen values from BMU 5. Extreme values were omitted to better show the majority of the data. DOW = 0.110 mg/L

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

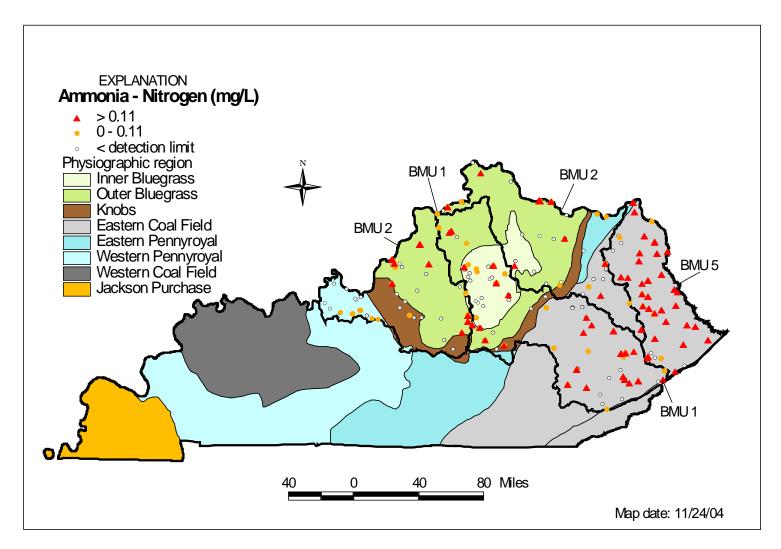


Figure 127. Map showing sampled sites and ranges of ammonia nitrogen concentrations. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

The median and 75<sup>th</sup> percentile ammonia nitrogen concentrations are below 0.11 mg/L in all physiographic regions (Figure 128). Most concentrations higher than 0.11 mg/L are found in the Eastern Coal Field and the Outer Bluegrass Regions.

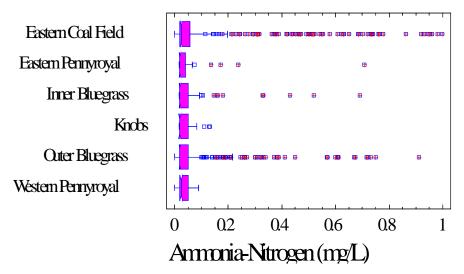


Figure 128. Summary of ammonia nitrogen concentrations grouped by physiographic region. values were excluded for clarity. DOW = 0.11 mg/L.

Groundwater from the Big Sandy River watershed has the highest median and 75<sup>th</sup> percentile ammonia nitrogen concentrations, as well as the largest interquartile range (Figure 129). The interquartile range of values is similar for samples from all other watersheds.

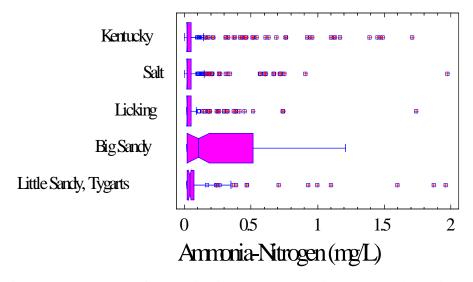


Figure 129. Summary of ammonia nitrogen concentrations grouped by major watershed. Extreme values were excluded for clarity. DOW = 0.11 mg/L.

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

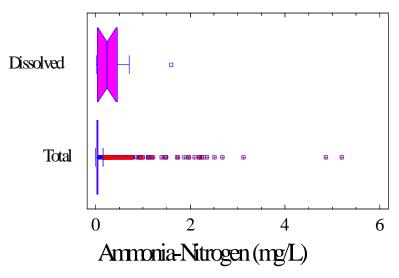


Figure 130. Comparison of ammonia nitrogen values from dissolved and total samples. Extreme values were excluded for clarity. DOW = 0.11 mg/L

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

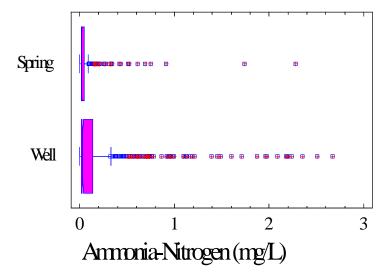


Figure 131. Comparison of ammonia nitrogen values from wells and springs. Extreme values were excluded for clarity. DOW = 0.11 mg/L

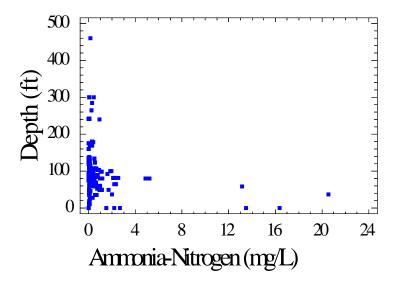


Figure 132. Plot of ammonia nitrogen concentrations versus well depth. DOW = 0.11 mg/L.

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

#### **Phosphorus Species**

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

Phosphorus is an important nutrient and commonly is the limiting nutrient in aquatic ecosystems. The most important anthropogenic sources of phosphorus are phosphate fertilizers, sewage, and animal waste. Prior to the 1960s, 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<sub>4</sub> as H<sub>2</sub>PO<sub>4</sub><sup>-</sup> or HPO<sub>4</sub><sup>-2</sup>) 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 PO<sub>4</sub>-P based on the Texas surface-water standard, and that total phosphorus be less than 0.1 mg/L, based on results from the U.S. Geological Survey National Water-Quality Assessment Program.

## Orthophosphate Phosphorus

The data repository contained 1722 orthophosphate measurements from 186 sites in the project area (Table 21). The maximum concentration in each Basin Management Unit is well in excess of the 0.04 mg/L criterion. Furthermore, the 75<sup>th</sup> percentile values for each Basin Management Unit, and the median value for BMU 1 all exceed 0.04 mg/L. More than 75 percent of the sites in BMU 1 and BMU 2 have produced values greater than 0.04 mg/L.

Table 21. Orthophosphate-P measurements (mg/L as P). DOW = 0.04

|                          | BMU 1 | BMU 2 | BMU 5 |
|--------------------------|-------|-------|-------|
| Measurements             | 867   | 699   | 156   |
| Sites                    | 68    | 78    | 40    |
| Maximum                  | 1950  | 368   | 254   |
| 3 <sup>rd</sup> quartile | 0.31  | 0.20  | 0.03  |
| Median                   | 0.14  | 0.04  | 0.02  |
| 1 <sup>st</sup> quartile | 0.01  | 0.01  | 0.01  |
| Minimum                  | 0.0   | 0.0   | 0.0   |
| Interquartile range      | 0.30  | 0.19  | 0.02  |
| Sites > 0.04             | 53    | 66    | 10    |

Cumulative data plots are different for each Basin Management Unit (Figures 133, 134, 135). In BMU 1 (Figure 133), more than 80 percent of the reported concentrations are less than 10 mg/L, but there are many values that extend to more than 500 mg/L.

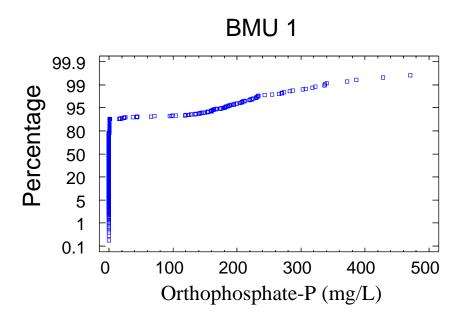


Figure 133. Cumulative plot of orthophosphate values from BMU 1. Extreme values were omitted to better show the majority of the data. DOW = 0.04 mg/L

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

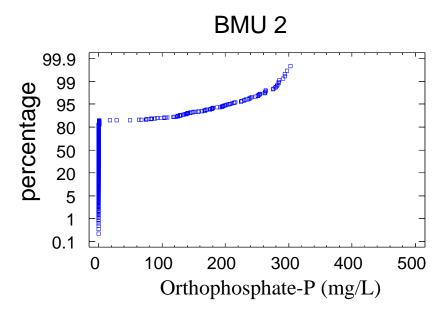


Figure 134. . Cumulative plot of orthophosphate values from BMU 2. Extreme values were omitted to better show the majority of the data. DOW = 0.04 mg/L

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

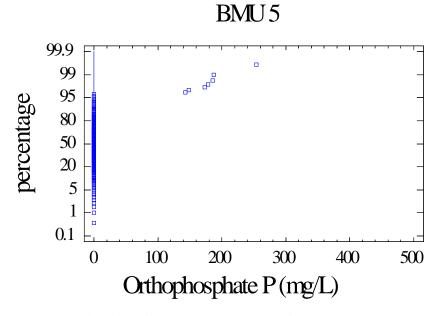


Figure 135. Cumulative plot of orthophosphate values from BMU 5. Extreme values were omitted to better show the majority of the data. DOW = 0.04 mg/L

Sampled sites are sparsely distributed throughout the project area (Figure 136). More than half of the sites in the Inner and Outer Bluegrass and Western Pennyroyal Regions of the Kentucky, Salt, and Licking River watersheds exceed 0.4 mg/L (Figures 135, 136, 137). Most sites in the Eastern Coal Field Region in watersheds of the Big Sandy River, Little Sandy River, and Tygarts Creek, produce groundwater that has orthophosphate concentrations below the recommended limit.

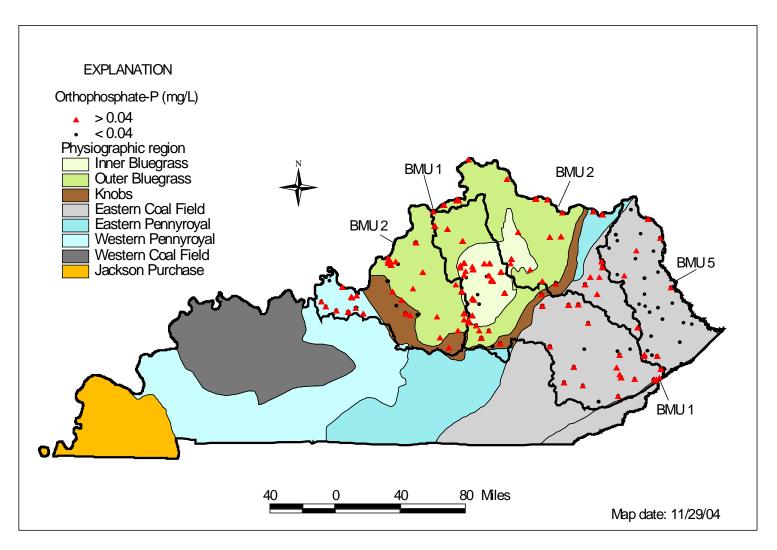


Figure 136. Map showing sampled sites and ranges of orthophosphate concentrations. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

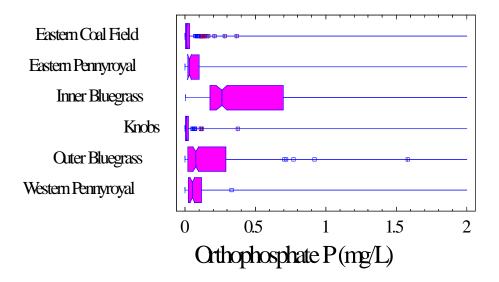


Figure 137. Summary of orthophosphate concentrations grouped by physiographic region. Extreme values were excluded for clarity. DOW = 0.04 mg/L.

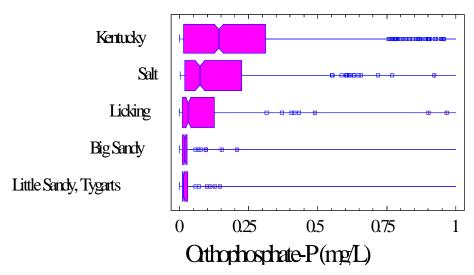


Figure 138. Summary of orthophosphate concentrations grouped by major watershed. Extreme values were excluded for clarity. DOW = 0.04 mg/L.

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

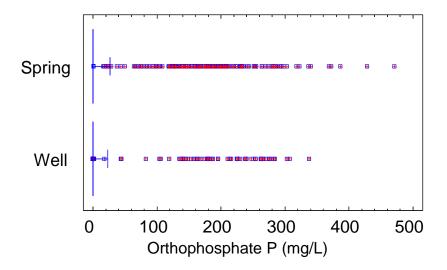


Figure 139. Comparison of orthophosphate values from wells and springs. Extreme values were excluded for clarity. DOW = 0.04 mg/L

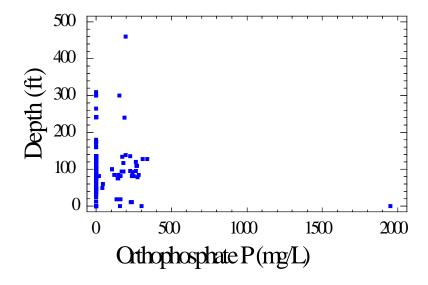


Figure 140. Plot of orthophosphate concentrations versus well depth. DOW = 0.04 mg/L.

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

### **Total Phosphorus**

The database contained 1356 reports of total phosphorus at 301 sites (Table 22). The median concentration in BMU 1 (Kentucky River watershed) exceeded the recommended value of 0.1 mg/L, and 130 of the 301 sites have produced groundwater that exceeds the recommended concentration of total phosphorus.

Table 22. Summary of total phosphorus measurements (mg/L of P). DOW = 0.1 mg/L

|                            | BMU 1 | BMU 2 | BMU 5 |
|----------------------------|-------|-------|-------|
| Measurements               | 596   | 624   | 136   |
| Sites                      | 83    | 135   | 83    |
| Maximum                    | 1.6   | 14.0  | 1.28  |
| 3 <sup>rd</sup> quartile   | 0.24  | 0.12  | 0.12  |
| Median                     | 0.12  | 0.05  | 0.05  |
| 1 <sup>st</sup> quartile   | 0.05  | 0.01  | 0.01  |
| Minimum                    | 0.0   | 0.0   | 0.0   |
| Interquartile range        | 0.19  | 0.11  | 0.11  |
| Sites with values $> 0.10$ | 58    | 55    | 16    |

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

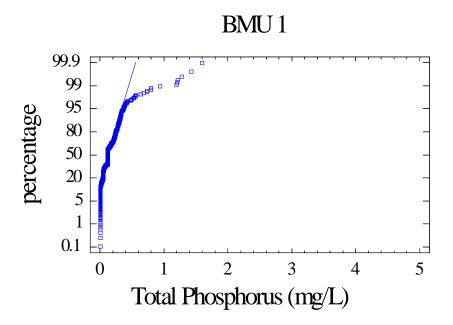


Figure 141. Cumulative plot of total phosphorus values from BMU 1. Extreme values were omitted to better show the majority of the data. DOW = 0.1 mg/L

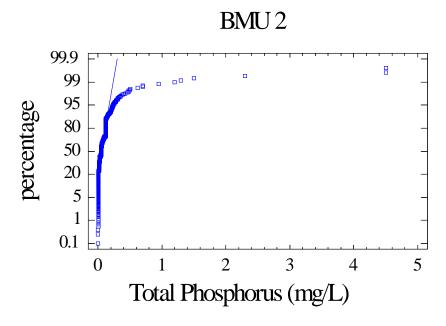


Figure 142. Cumulative plot of total phosphorus values from BMU 2. Extreme values were omitted to better show the majority of the data. DOW = 0.1 mg/L

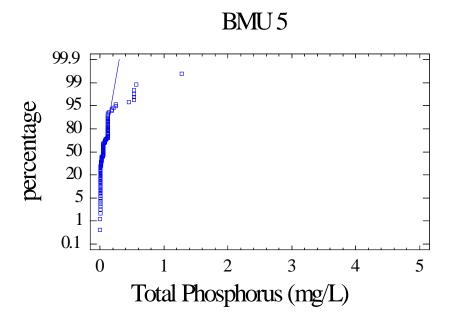


Figure 143. Cumulative plot of total phosphorus values from BMU 5. Extreme values were omitted to better show the majority of the data. DOW = 0.1 mg/L

Site distribution is uneven throughout the project area (Figure 144), with many sites along the Ohio River in BMU 2 and the eastern portion of BMU 5. Sites where total phosphorus exceeds the recommended value occur more commonly in the Inner and Outer Bluegrass Regions (Figures 143, 144, 145).

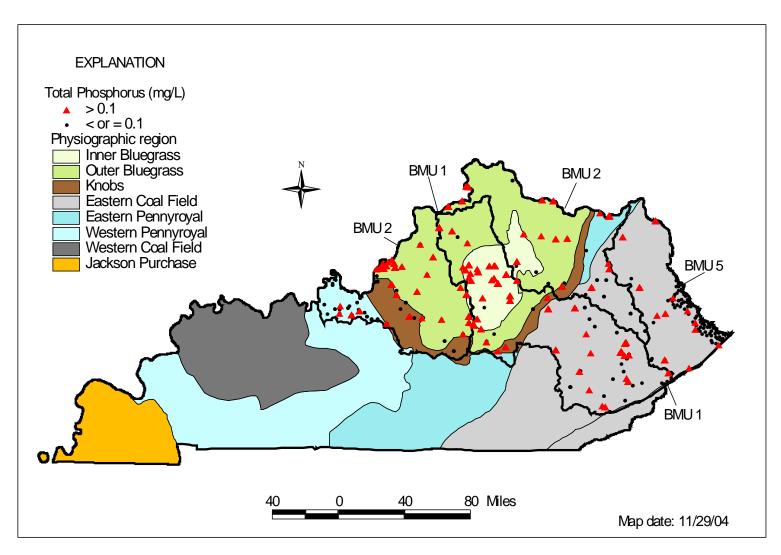


Figure 144. Map showing sampled sites and ranges of total phosphorus concentrations. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

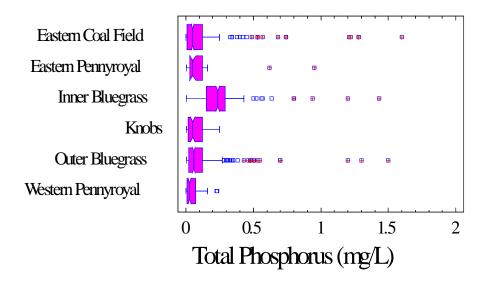


Figure 145. Summary of total phosphorus concentrations grouped by physiographic region. Extreme values were excluded for clarity. DOW = 0.1 mg/L.

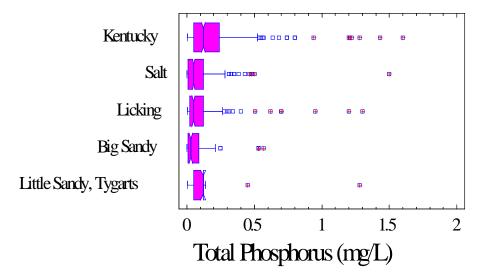


Figure 146. Summary of total phosphorus concentrations grouped by major watershed. Extreme values were excluded for clarity. DOW = 0.1 mg/L.

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

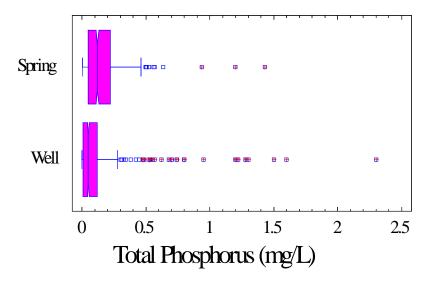


Figure 147. Comparison of total phosphorus values from wells and springs. Extreme values were excluded for clarity. DOW = 0.1 mg/L

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

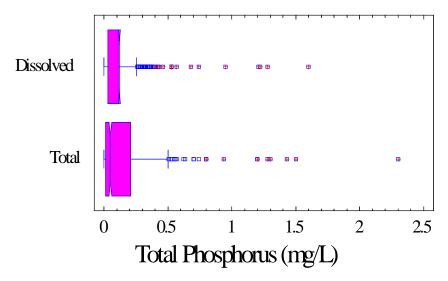


Figure 148. Comparison of phosphorus values in dissolved and total samples. Extreme values were excluded for clarity. DOW = 0.1 mg/L

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

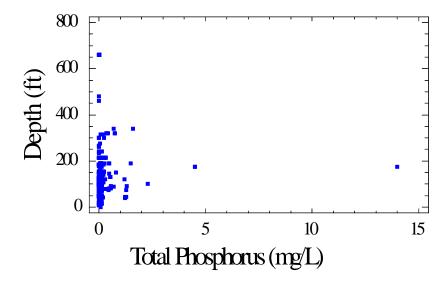


Figure 149. Plot of total phosphorus concentrations versus well depth. DOW = 0.1 mg/L.

Summary: Like orthophosphate concentrations, total phosphorus commonly exceeds the recommended limit of 0.1 mg/L in all regions and watersheds of the project area. Also like orthophosphate, such sites are most common in the Inner and Outer Bluegrass Regions where limestone bedrock is known to be enriched in phosphorus. The high phosphorus concentrations are therefore considered to reflect the composition of bedrock rather than any significant nonpoint source contribution.

#### **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 (USGS, 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 or 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 existence of any detectable pesticides in Kentucky groundwater.

According to the 2000 agriculture 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 (<a href="http://ace.orst.edu/info/extoxnet/pips/">http://ace.orst.edu/info/extoxnet/pips/</a>) and the U. S. Environmental Protection Agency Integrated Risk Information System (<a href="http://www.epa.gov/iris">http://www.epa.gov/iris</a>).

### 2,4-D

The pesticide 2,4-D belongs to the chemical class of phenoxy compounds. Predominant uses are as a systemic 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 less than 7 days, and is readily degraded by microorganisms in aquatic environments. EPA has established a 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 1054 2,4-D analyses from 232 sites in the project area (Table 23). No value exceeded the MCL of 0.07 mg/L. The maximum reported concentration was 0.0276 mg/L, found in a spring in the Outer Bluegrass Region of BMU 2. The second highest value was 0.0011 mg/L, and more than 99 percent of all reported concentrations were 0.001 mg/L or less. Only 21

percent of all measured 2,4-D concentrations exceeded analytical detection limits; 29 percent of all sites had detectable 2,4-D concentrations. Detectable concentrations of 2,4-D were found in 40 percent of the sampled wells and 22 percent of the sampled springs. There was no significant variation in 2,4-D concentrations with well depth.

Table 23. Summary of 2,4-D measurements (mg/L). MCL = 0.07 mg/L

|                          | BMU 1    | BMU 2    | BMU 5    |
|--------------------------|----------|----------|----------|
| Analyses                 | 493      | 447      | 114      |
| Sites                    | 67       | 118      | 47       |
| Maximum                  | 0.0011   | 0.0276   | < 0.0009 |
| 3 <sup>rd</sup> Quartile | < 0.0001 | < 0.0009 | < 0.0001 |
| Median                   | < 0.0001 | < 0.0001 | < 0.0001 |
| 1 <sup>st</sup> Quartile | < 0.0001 | < 0.0001 | < 0.0001 |
| Minimum                  | 0.00     | < 0.0001 | < 0.0001 |
| Sites where MCL exceeded | 0        | 0        | 0        |
| Sites where detected     | 7        | 51       | 11       |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

Sample site density was greatest in the Western Pennyroyal Region, and lowest in the Knobs and Outer Bluegrass Regions (Figure 150). Sites where 2,4-D exceeded analytical detection are found predominantly in the limestone terrain of the Western Pennyroyal and Inner Bluegrass Regions.

Because of the narrow range of values and the small number of sites where concentrations exceeded analytical detection limits, no further analysis was performed.

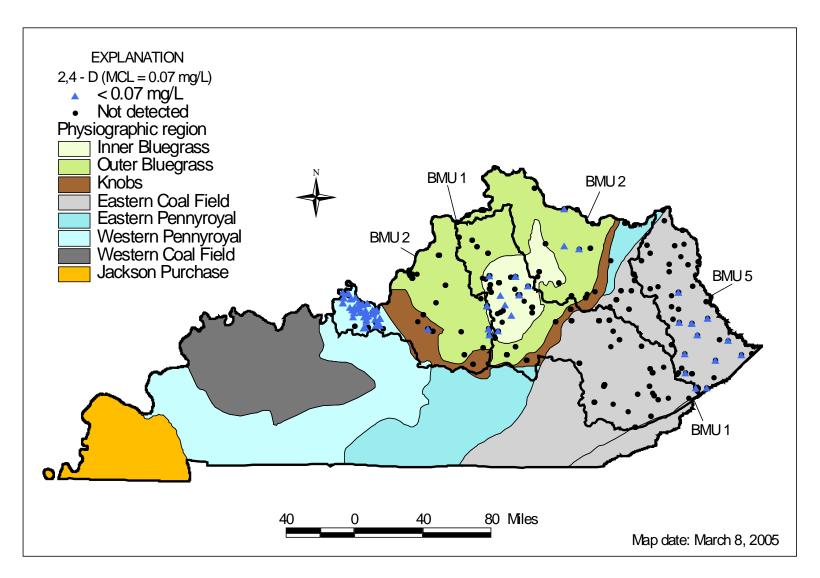


Figure 150. Map showing sampled sites and ranges of 2,4-D concentrations. No values exceeded the MCL. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Summary: Concentrations of 2,4-D do not exceed the MCL in the project area, and are typically less than 0.001 mg/L. Detectable amounts of 2,4-D are found most commonly in wells and springs in the limestone terrain of the Western Pennyroyal and Inner Bluegrass Regions. The presence of detectable 2,4-D at some sites in the project area indicates that some pesticides are entering the groundwater system.

#### **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 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. EPA has found alachlor to pose a risk for skin and eye irritation on short-term exposure, and to potentially cause damage to liver, kidney, spleen, lining of nose and eyelids, and possibly cancer on long-term exposure. For these reasons, EPA has set a MCL of 0.002 mg/L for alachlor.

The data repository contained 1130 measurements of alachlor from 196 sites in the project area (Table 24). No values exceeded the MCL. Fifteen analyses exceeded detection limits; 10 sites produced water that had detectable alachlor.

Table 24. Summary of alachlor measurements (mg/L). MCL = 0.002 mg/L

|                          | BMU 1     | BMU 2     | BMU 5     |
|--------------------------|-----------|-----------|-----------|
| Analyses                 | 574       | 420       | 136       |
| Sites                    | 70        | 77        | 49        |
| Maximum                  | 0.0004    | 0.000721  | 0.00027   |
| 3 <sup>rd</sup> Quartile | < 0.00005 | < 0.00005 | < 0.00004 |
| Median                   | < 0.00004 | < 0.00004 | < 0.00004 |
| 1 <sup>st</sup> Quartile | < 0.00004 | < 0.00004 | < 0.00004 |
| Minimum                  | < 0.00002 | < 0.00002 | < 0.00002 |
| Sites > MCL              | 0         | 0         | 0         |
| Sites where detected     | 2         | 8         | 0         |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

Sample density was greatest in the Eastern Coal Field and Inner Bluegrass Regions, lowest in the Outer Bluegrass and Western Pennyroyal Regions (Figure 151).

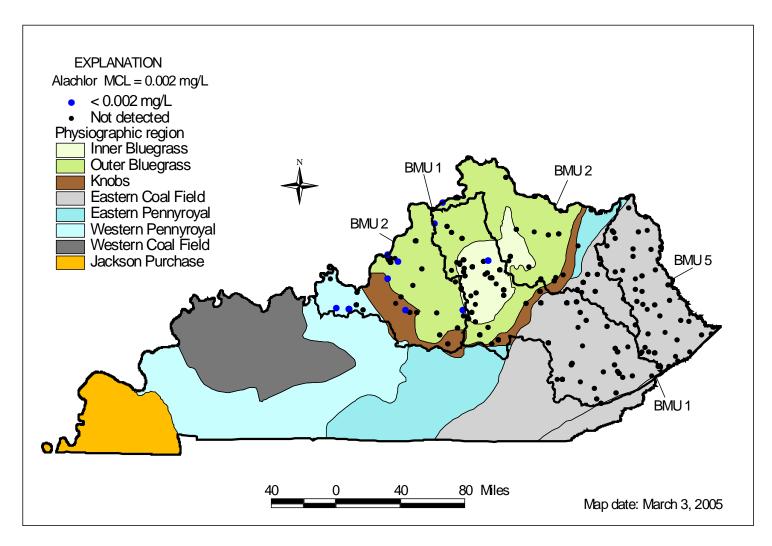


Figure 151. Map showing sampled sites and ranges of alachlor concentrations. No values exceeded the MCL. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Of the reported concentrations that exceeded analytical detection, 12 were samples from springs and 3 were samples from wells. No further analysis was performed because of the small number of detected alachlor concentrations.

Summary: Alachlor was detected at only 5 percent of the sampled sites, and none of the measured concentrations exceeded the EPA MCL of 0.002 mg/L. Alachlor use is probably very limited in the project area because corn, soybeans, and peanuts are not produced in this part of Kentucky. The presence of detectable alachlor at some sites in the project area indicates that some pesticides are entering the groundwater system.

#### **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.

The EPA has set a MCL value of 0.003 mg/L for atrazine. Atrazine can potentially cause a variety of acute health effects from acute exposures at higher levels. These effects include: congestion of heart, lungs and kidneys; hypotension; antidiuresis; muscle spasms; weight loss; 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 804 reports of atrazine concentrations from 137 sites in the project area (Table 25). Only 97 of the 804 measurements exceeded analytical detection limits, and only one site, a spring in the Western Pennyroyal Region of the Salt River watershed, yielded groundwater with an atrazine concentration greater than the MCL. Atrazine was detected at 33 of 137 sites in the project area.

Table 25. Summary of atrazine measurements (mg/L). MCL = 0.003 mg/L

|                          |           | \ |           |
|--------------------------|-----------|---|-----------|
|                          | BMU 1     | BMU 2                                   | BMU 5     |
| Analyses                 | 428       | 300                                     | 76        |
| Sites                    | 60        | 63                                      | 14        |
| Maximum                  | 0.001039  | 0.004753                                | 0.00194   |
| 3 <sup>rd</sup> Quartile | < 0.0003  | < 0.0003                                | < 0.0003  |
| Median                   | < 0.00006 | < 0.00006                               | < 0.0003  |
| 1 <sup>st</sup> Quartile | < 0.00005 | < 0.00005                               | < 0.00005 |
| Minimum                  | 0.000005  | 0.000018                                | < 0.00004 |
| Sites where MCL exceeded | 0         | 1                                       | 0         |
| Sites where detected     | 12        | 18                                      | 3         |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

Sample density is greatest in the Inner Bluegrass Region of the Kentucky River watershed (Figure 152). Twenty-seven springs and five wells produced water with detectable amounts of atrazine. Because of the narrow range of values and the small number of sites where concentrations exceeded analytical detection limits, no further analysis was performed.

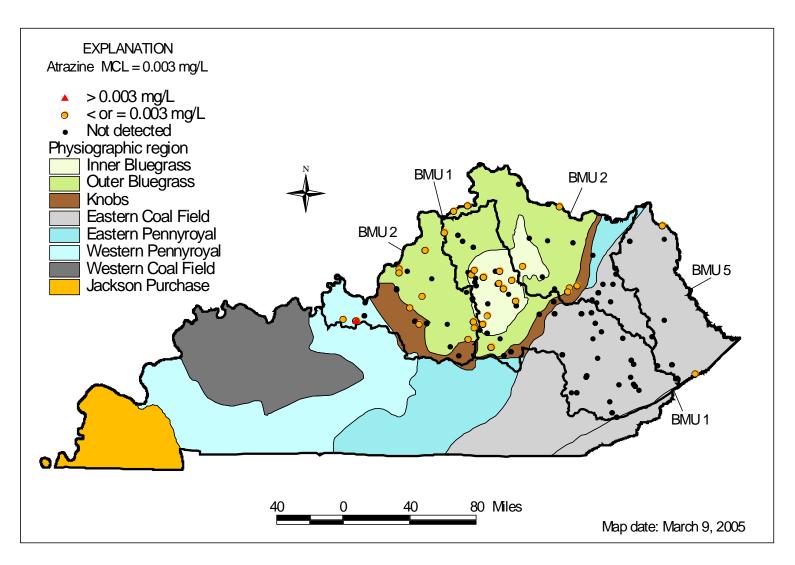


Figure 152. Map showing sampled sites and ranges of atrazine concentrations. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Summary: One site produced water that had an atrazine concentration greater than the MCL of 0.003 mg/L. Atrazine was detected at 27 springs and 5 wells in the project area, most of which were in the limestone terrain of the Inner and Outer Bluegrass and Western Pennyroyal Regions. Atrazine use is probably very limited in the project area because the types of crops atrazine is used on are not grown in this part of the state. The presence of detectable atrazine in the project area indicates that some pesticides are 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 EPA MCL for cyanazine; however DOW has set a health advisory limit (HAL) of 0.001 mg/L.

The groundwater data repository contained 776 results of cyanazine analyses from 170 sites in the project area (Table 26). Only one value exceeded analytical detection limits; this site also exceeded the HAL. Because only one cyanazine concentration was greater than analytical detection, no further analyses were performed.

Table 26. Summary of cyanazine measurements (mg/L). HAL = 0.001 mg/L

|                          | BMU 1     | BMU 2     | BMU 5     |
|--------------------------|-----------|-----------|-----------|
| Analyses                 | 492       | 374       | 128       |
| Sites                    | 68        | 74        | 47        |
| Maximum                  | < 0.001   | < 0.001   | 0.00126   |
| 3 <sup>rd</sup> Quartile | < 0.00005 | < 0.00005 | < 0.00005 |
| Median                   | < 0.00005 | < 0.00004 | < 0.00004 |
| 1 <sup>st</sup> Quartile | < 0.00004 | < 0.00004 | < 0.00004 |
| Minimum                  | < 0.00004 | < 0.00004 | < 0.00004 |
| Sites where HAL exceeded | 0         | 0         | 1         |
| Sites where detected     | 0         | 0         | 1         |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

As with the other pesticides, sample site density was greatest in the Eastern Coal Field and Inner Bluegrass Regions, and lowest in the Outer Bluegrass and Western Pennyroyal Regions (Figure 153).

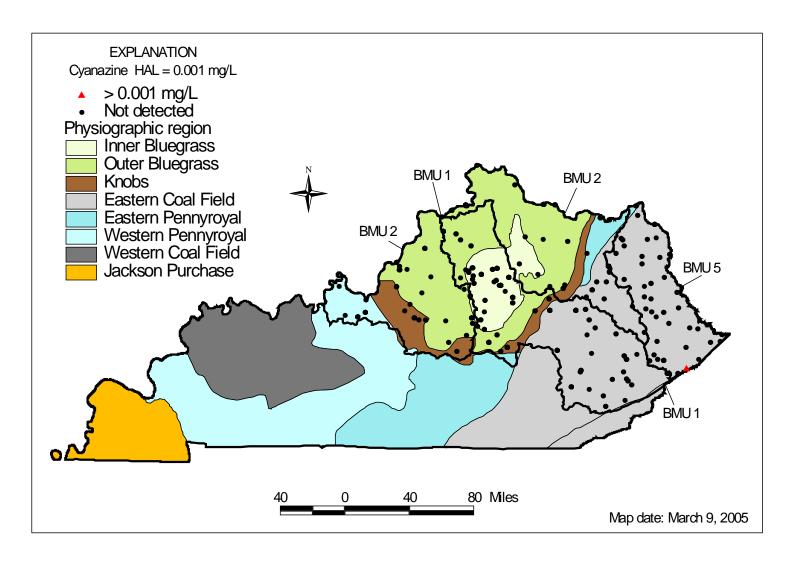


Figure 153. Map showing sampled sites and ranges of cyanazine concentrations. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Summary: Only one of 170 sites in the project area produced water that had detectable cyanazine. 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 detectable cyanazine in the project area indicates that some pesticides are entering the groundwater system.

#### 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, and nut trees, highway rights-of-way, and woody ornamentals. It is moderately persistent in soils with half-lives of 15 to 70 days, and is highly persistent in water. There is no MCL for metolachlor; DOW has set a health advisory limit (HAL) of 0.1 mg/L.

The data repository contained 1125 metolachlor concentrations from 192 sites in the project area (Table 27). No values exceeded the HAL; 64 measurements from 15 springs and 2 wells exceeded analytical detection limits.

Table 27. Summary of metolachlor measurements (mg/L). HAL = 0.1 mg/L

|                          | BMU 1     | BMU 2     | BMU 5     |
|--------------------------|-----------|-----------|-----------|
| Analyses                 | 572       | 418       | 135       |
| Sites                    | 69        | 75        | 48        |
| Maximum                  | < 0.004   | 0.000908  | < 0.0002  |
| 3 <sup>rd</sup> Quartile | < 0.00005 | < 0.00005 | < 0.00005 |
| Median                   | < 0.00005 | < 0.00004 | < 0.00004 |
| 1 <sup>st</sup> Quartile | < 0.00004 | < 0.00004 | < 0.00004 |
| Minimum                  | 0.000004  | 0.000008  | 0.000022  |
| Sites where HAL exceeded | 0         | 0         | 0         |
| Sites where detected     | 7         | 9         | 1         |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

Sample site distribution is most dense in the Eastern Coal Field and Inner Bluegrass Regions (Figure 153). Because of the very small number of sites where metolachlor exceeded analytical detection limits, no further analysis was performed.

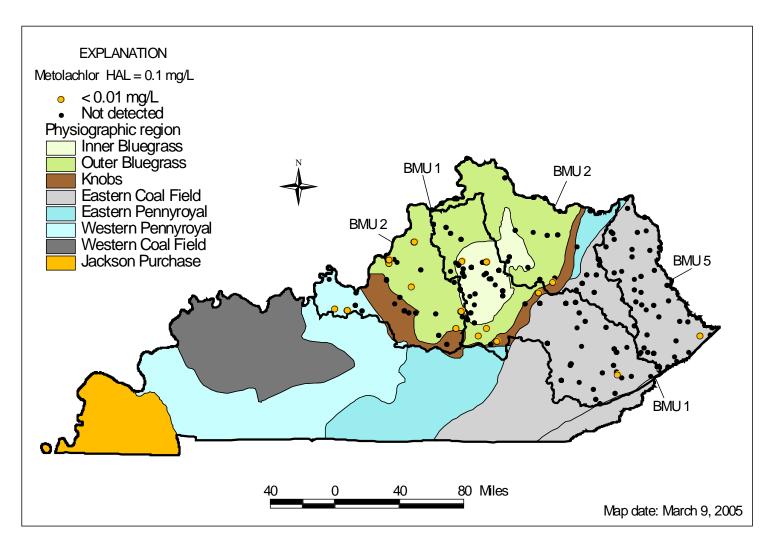


Figure 154. Map showing sampled sites and ranges of metolachlor concentrations. No values exceeded the HAL. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Summary: Metolachlor is probably not used much in the project area. It is rarely detected in groundwater, more commonly in springs than in wells. The presence of detectable metolachlor in the project area indicates that some pesticides are entering 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 turf grass. 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 EPA 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 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 1193 simazine measurements from 191 sites in the project area (Table 28). No measurement exceeded the MCL of 0.004 mg/L. Groundwater from 15 springs and one well had simazine concentrations that exceeded analytical detection limits.

Table 28. Summary of simazine measurements (mg/L). MCL = 0.004 mg/L

|                          | BMU 1     | BMU 2     | BMU 5     |
|--------------------------|-----------|-----------|-----------|
| Analyses                 | 602       | 440       | 151       |
| Sites                    | 69        | 74        | 48        |
| Maximum                  | 0.000119  | 0.002528  | 0.000689  |
| 3 <sup>rd</sup> Quartile | < 0.0003  | < 0.0003  | < 0.0003  |
| Median                   | < 0.00005 | < 0.00004 | < 0.00004 |
| 1 <sup>st</sup> Quartile | < 0.00004 | < 0.00004 | < 0.00004 |
| Minimum                  | 0.00001   | 0.000017  | 0.00003   |
| Sites where MCL exceeded | 0         | 0         | 0         |
| Sites where detected     | 7         | 7         | 2         |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

Sample site distribution is most dense in the Eastern Coal Field and Inner Bluegrass Regions (Figure 155). Because of the very small number of sites where simazine exceeded analytical detection limits, no further analysis was performed.

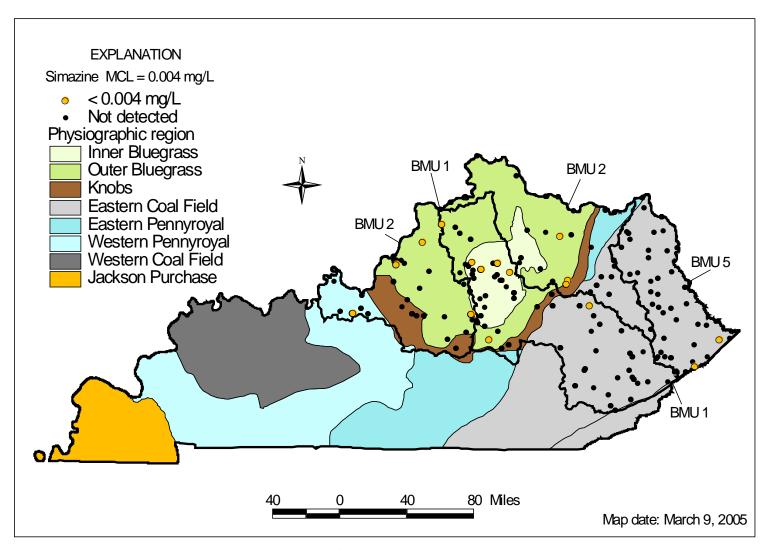


Figure 155. Map showing sampled sites and ranges of simazine concentrations. No values exceeded the MCL. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges

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 (VOCs) 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 gas storage tanks, fumes and exhaust from gas-power engines, and runoff from gas-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 tert-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.

Natural sources of these chemicals such as crude oil seeps are rare in the project area. Therefore, any detected amount of these refined volatile organic chemicals indicates groundwater contamination from human activities. Because they are synthetic chemicals, VOC occurrences are not primarily controlled by bedrock geology, physiography, or major river watershed.

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.

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 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 data trends. In the following discussions, summaries of potential sources and health effects of the selected pesticides were taken from the U.S. EPA Web pages "Current Drinking Water Standards" (<a href="http://www.epa.gov/safewater/mcl/html">http://www.epa.gov/safewater/mcl/html</a>) and "Integrated Risk Information System" (<a href="http://www.epa.gov/iris">http://www.epa.gov/iris</a>).

#### 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, EPA has established a MCL of 0.005 mg/L for benzene.

The data repository contained 619 benzene measurements at 238 sites in the project area (Table 29). Twelve sites produced groundwater with detectable benzene.

Table 29. Summary of benzene measurements (mg/L). MCL = 0.005 mg/L

|                          | BMU 1    | BMU 2    | BMU 5    |
|--------------------------|----------|----------|----------|
| Analyses                 | 254      | 238      | 127      |
| Sites                    | 78       | 88       | 72       |
| Maximum                  | 0.0103   | 3.2      | 0.003    |
| 3 <sup>rd</sup> Quartile | < 0.0005 | < 0.0005 | < 0.0005 |
| Median                   | < 0.0005 | < 0.0005 | < 0.0005 |
| 1 <sup>st</sup> Quartile | < 0.0005 | < 0.0005 | < 0.0005 |
| Minimum                  | < 0.0005 | 0.0003   | < 0.0005 |
| Sites > MCL              | 1        | 3        | 0        |
| Sites where detected     | 3        | 7        | 2        |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

Few sites in the Outer Bluegrass Region were sampled for benzene compared to the other regions (Figure 156). Three of the 4 sites where benzene exceeds the MCL are in the Outer Bluegrass Region, and 8 of the 12 sites where benzene was detected are in the limestone terrain of the Bluegrass and Pennyroyal Regions.

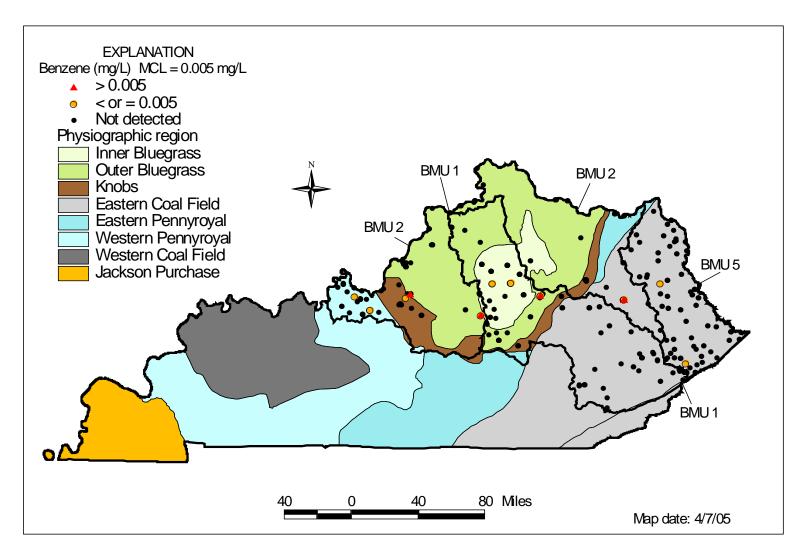


Figure 156. Map showing sampled sites and ranges of benzene concentrations. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges

Summary: Occurrences of detectable benzene in groundwater are rare and isolated in the project area. Four sites produced groundwater with benzene concentrations above the MCL, and 12 sites had detectable amounts of benzene. No widespread pattern of benzene in groundwater was found. However, the presence of detectable benzene at sites that were not considered locations of point-source releases 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 potential health effects such as liver or kidney damage, the EPA has set a MCL value for ethylbenzene of 0.7 mg/L.

The data repository contained 596 ethylbenzene measurements at 235 sites in the project area (Table 30). Six sites produced detectable ethylbenzene; no samples exceeded the MCL.

Table 30. Summary of ethylbenzene measurements (mg/L). MCL = 0.7 mg/L

|                          | BMU 1    | BMU 2    | BMU 5    |
|--------------------------|----------|----------|----------|
| Analyses                 | 245      | 224      | 127      |
| Sites                    | 78       | 85       | 72       |
| Maximum                  | 0.006    | 0.062    | 0.0045   |
| 3 <sup>rd</sup> Quartile | < 0.0005 | < 0.0005 | < 0.0005 |
| Median                   | < 0.0005 | < 0.0005 | < 0.0005 |
| 1 <sup>st</sup> Quartile | < 0.0005 | < 0.0005 | < 0.0005 |
| Minimum                  | < 0.0005 | < 0.0005 | < 0.0005 |
| Sites > MCL              | 0        | 0        | 0        |
| Sites where detected     | 2        | 2        | 2        |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

Sampled site distribution is most dense in the Eastern Coal Field Region of BMU 5, The Inner Bluegrass Region of BMU 1, and the Western Pennyroyal Region of BMU 2 (Figure 157). Four of the 6 sites where ethylbenzene was detected are in the limestone terrain of the Inner and Outer Bluegrass Regions.

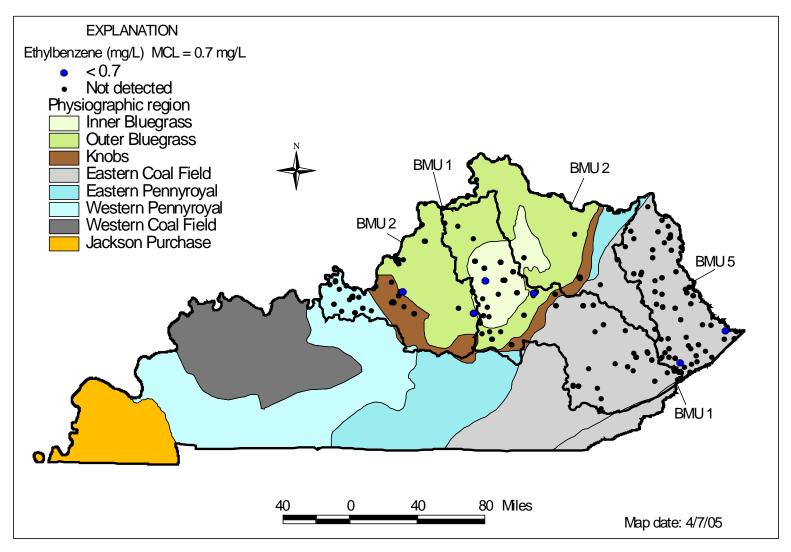


Figure 157. Map showing sampled sites and ranges of ethylbenzene concentrations. No values exceeded the MCL. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

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. However, the presence of detectable ethylbenzene at sites that were not considered locations of point-source releases 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 EPA MCL for toluene is 1.0 mg/L.

The data repository contained 417 toluene measurements at 278 sites in the project area (Table 31). One concentration in BMU 2 exceeded the MCL; 16 sites yielded detectable toluene.

Table 31. Summary of toluene measurements (mg/L). MCL = 1.0 mg/L

|                          | BMU 1    | BMU 2    | BMU 5    |
|--------------------------|----------|----------|----------|
| Analyses                 | 57       | 229      | 131      |
| Sites                    | 43       | 158      | 77       |
| Maximum                  | 0.026    | 2.6      | 0.008    |
| 3 <sup>rd</sup> Quartile | < 0.0005 | < 0.001  | < 0.0005 |
| Median                   | < 0.0005 | < 0.001  | < 0.0005 |
| 1 <sup>st</sup> Quartile | < 0.0005 | < 0.0005 | < 0.0005 |
| Minimum                  | < 0.0005 | < 0.0005 | < 0.0005 |
| Sites > MCL              | 0        | 1        | 0        |
| Sites where detected     | 2        | 5        | 9        |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

The Eastern Coal Field Region of BMU 2 and 5 has more sampled sites than the rest of the project area (Figure 158). Most sites where toluene was detected are in the Eastern Coal Field Region of BMU 5.

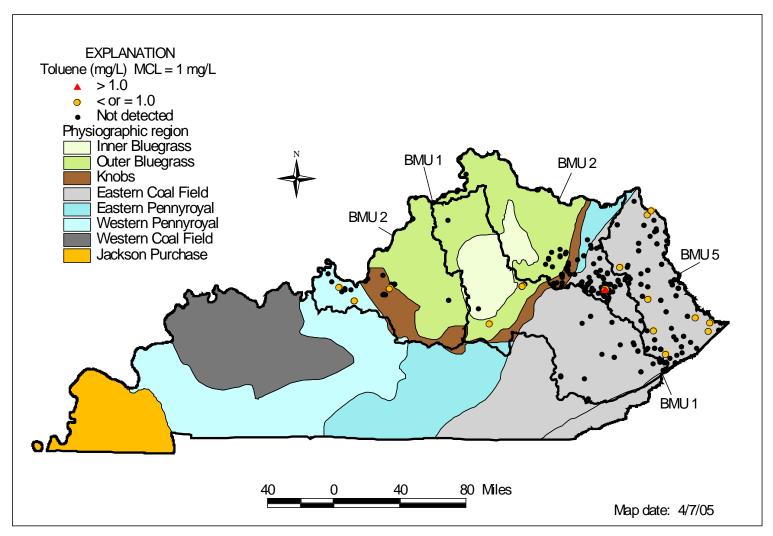


Figure 158. Map showing sampled sites and ranges of toluene concentrations. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Summary: Like the other volatile organic chemicals, toluene has rarely been detected in groundwater in the project area. However, the presence of detectable toluene at sites that were not considered locations of point-source releases indicates that the groundwater system is being affected by this volatile organic chemical.

# **Xylenes (total)**

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 EPA MCL is 10 mg/L for the sum of O-Xylene, P-Xylene, and M-Xylene.

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 contains 735 such measurements at 239 sites in the project area (Table 32). No samples exceeded the MCL of 10 mg/L. Seven of 239 sites produced detectable xylenes.

Table 32. Summary of total xylenes measurements (mg/L). MCL = 10.0 mg/L

|                          | BMU 1    | BMU 2    | BMU 5    |
|--------------------------|----------|----------|----------|
| Analyses                 | 94       | 527      | 114      |
| Sites                    | 40       | 154      | 45       |
| Maximum                  | 0.0195   | 1.3      | 0.0305   |
| 3 <sup>rd</sup> Quartile | < 0.0005 | < 0.001  | < 0.001  |
| Median                   | < 0.0005 | < 0.001  | < 0.0005 |
| 1st Quartile             | < 0.0005 | < 0.001  | < 0.0005 |
| Minimum                  | < 0.0005 | < 0.0005 | < 0.0005 |
| Sites > MCL              | 0        | 0        | 0        |
| Sites where detected     | 2        | 3        | 2        |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

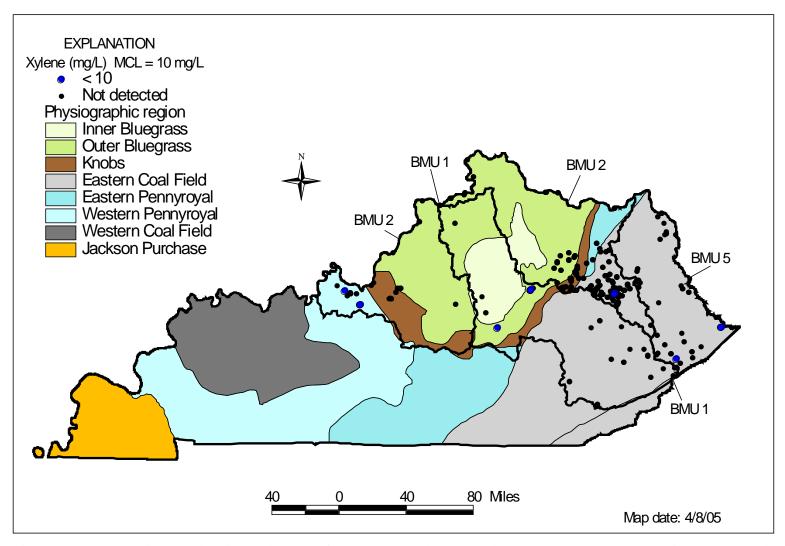


Figure 159. Map showing sampled sites and ranges of total xylenes values. No values exceeded the MCL. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges.

Summary: Few sampled sites had total xylene concentrations that were above analytical detection limits. Three sites where xylenes were detected are in the Eastern Coal Field and four are in the limestone terrain of the Outer Bluegrass and Western Pennyroyal Regions. The presence of detectable xylene at sites that were not considered locations of point-source releases indicates that the groundwater system is being affected by this volatile organic chemical.

# MTBE (methyl tert-butyl ether)

MTBE 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, DOW has set a risk-based water-quality standard of 0.050 mg/L.

The data repository contained 574 MTBE measurements at 202 sites in the project area (Table 33). Four sites exceeded 0.05 mg/L, and 19 of 202 sites produced water with detectable MTBE.

Table 33. Summary of MTBE measurements (mg/L). DOW = 0.05 mg/L

|                          | BMU 1   | BMU 2   | BMU 5   |
|--------------------------|---------|---------|---------|
| Analyses                 | 268     | 168     | 138     |
| Sites                    | 86      | 55      | 61      |
| Maximum                  | 0.0501  | 0.18    | 0.0857  |
| 3 <sup>rd</sup> Quartile | < 0.001 | < 0.001 | < 0.001 |
| Median                   | < 0.001 | < 0.001 | < 0.001 |
| 1 <sup>st</sup> Quartile | < 0.001 | < 0.001 | < 0.001 |
| Minimum                  | < 0.001 | < 0.001 | < 0.001 |
| Sites > MCL              | 1       | 2       | 1       |
| Sites where detected     | 8       | 8       | 3       |

<sup>&</sup>lt;: result reported as "less than" the stated analytical detection limit

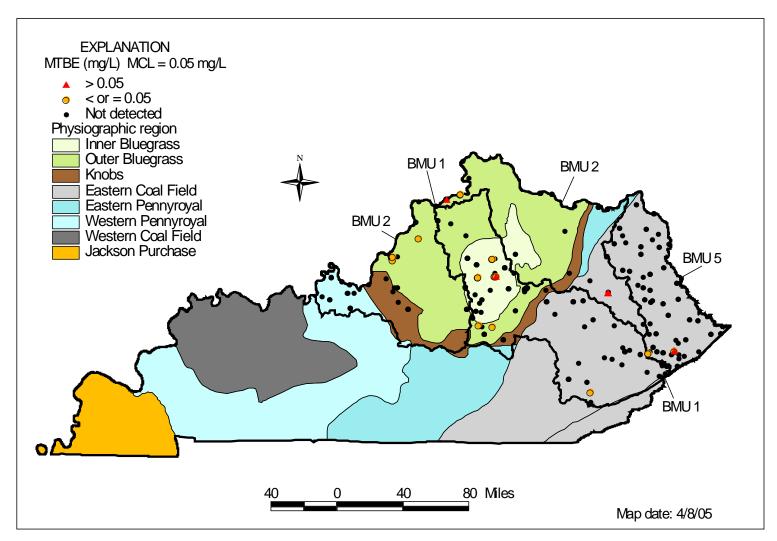


Figure 160. Map showing sampled sites and ranges of MTBE values. Superimposed symbols indicate that values recorded at different sampling times fell into different ranges

Summary: MTBE generally does not occur at detectable levels in water from wells and springs in the project area. Four of the sites where MTBE was present above analytical detection levels are in the Eastern Coal Field; the remainder are in the limestone terrain of the Inner and Outer Bluegrass Region. The presence of detectable MTBE at sites that were not considered locations of point-source releases indicates that the groundwater system is being affected by this volatile organic chemical.

## **SUMMARY AND CONCLUSIONS**

The goal of this project was to summarize and evaluate groundwater quality from Basin Management Units 1, 2, and 5 (watersheds of the Kentucky River, Salt River, Licking River, Big Sandy River, Little Sandy River, and Tygarts Creek, and adjacent tributaries of the Ohio River). Results of groundwater analyses were obtained from the Kentucky Groundwater Data Repository, which is the largest and most inclusive collection of information regarding groundwater in Kentucky. The water-quality data were compared to criteria provided by the Kentucky Division of Water; these criteria included maximum contaminant levels (MCLs), secondary maximum contaminant levels (SMCLs), and health advisory limits (HALs) set by the U. S. Environmental Protection Agency, and other criteria established by the Division of Water if no MCL, SMCL, or HAL existed.

The results show that the overall quality of Kentucky groundwater in the project area is good. However, there are many wells and springs where groundwater exceeds recommended levels for water properties, inorganic anions, metals, nutrients, pesticides, and volatile organic chemicals. In many cases the sources appear to be entirely natural, in other cases there is evidence of contamination by nonpoint source chemicals. Table 34 summarizes the findings.

Table 34. Summary of evidence for nonpoint-source impacts on groundwater quality in Basin

Management Units 1, 2, and 5.

|            | mits 1, 2, and 3.      | No strong    | Evidence for  | Evidence for |
|------------|------------------------|--------------|---------------|--------------|
|            | Parameter              | evidence for | minimal       | definite     |
|            |                        | widespread   | nonpoint-     | nonpoint-    |
|            |                        | nonpoint-    | source impact | source       |
|            |                        | source       |               | impact       |
|            | ~ .                    | impact       |               |              |
|            | Conductance            | X            |               |              |
| Water      | Hardness               | X            |               |              |
| Properties | pН                     | X            |               |              |
|            | Total dissolved solids | X            |               |              |
|            | Total suspended solids | X            |               |              |
| Inorganic  | Chloride               | X            |               |              |
| Ions       | Sulfate                | X            |               |              |
|            | Fluoride               | X            |               |              |
|            | Arsenic                | X            |               |              |
| Metals     | Barium                 | X            |               |              |
|            | Iron                   | X            |               |              |
|            | Manganese              | X            |               |              |
|            | Mercury                | X            |               |              |
|            | Ammonia nitrogen       |              | X             |              |
| Nutrients  | Nitrate nitrogen       |              |               | X            |
|            | Nitrite nitrogen       |              | X             |              |
|            | Orthophosphate         | X            |               |              |
|            | Total phosphorus       | X            |               |              |
|            | 2,4-D                  |              | X             |              |
| Pesticides | Alachlor               |              | X             |              |
|            | Atrazine               |              | X             |              |
|            | Cyanazine              |              | X             |              |
|            | Metolachlor            |              | X             |              |
|            | Simazine               |              | X             |              |
|            | Benzene                |              | X             |              |
| Volatile   | Ethylbenzene           |              | X             |              |
| Organic    | Toluene                |              | X             |              |
| Compounds  | Xylenes                |              | X             |              |
| •          | MTBE                   |              | X             |              |
| L          | -: <b>-</b>            | l            |               |              |

General water properties (pH, total dissolved solids, total suspended solids, electrical conductance, and hardness), inorganic ions (chloride, sulfate, fluoride), and metals (arsenic, barium, mercury, iron, and manganese) are largely controlled by bedrock lithology. Some exceptionally high values of conductance, hardness, chloride, and sulfate may be the effects of deep brines 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.

Nutrient concentrations show the effects of both bedrock lithology and nonpoint source inputs. Nitrate nitrogen concentrations that far exceed natural contributions are common, particularly in regions where the land is used for agriculture. Phosphorus concentrations are generally higher in the Inner and Outer Bluegrass Regions, where limestone bedrock is known to be enriched in phosphate.

Pesticides are synthetic organic chemicals that do not occur naturally. The presence of any detectable pesticide in groundwater indicates a nonpoint-source contribution from agricultural or urban applications. The relative scarcity of detectable pesticide concentrations found in this study may be misleading for two reasons. First, shallow wells in rural areas, those most susceptible to pesticide contamination, were not specific targets for sampling in the ambient groundwater quality investigations that provide much of the data for this summary. Second, it is known that pesticide levels in groundwater are highest following applications and after rainfall events.

Sampling one time or on a quarterly schedule may miss the presence of pesticides if the sampling does not closely follow field and lawn applications or significant rainfalls. High pesticide concentrations in water from a well or spring are a health hazard when the water is used regularly for domestic purposes, even though the available analyses did not show high pesticide concentrations at the time of sample collection. For these reasons, it is possible that pesticides may be a greater health threat at some times of the year than these data suggest.

Like pesticides, refined volatile organic chemicals generally do not occur naturally in groundwater and can have significant health effects at very low concentrations. The detection of volatile organic chemicals in groundwater is not natural and can only be the result of anthropogenic activities. This study excluded analyses of groundwater from wells or springs that were known to be affected by leaking underground storage tanks and other sources of volatile organic chemicals. The detection of volatile organic chemicals in springs and shallow wells that were previously thought to be free of such compounds suggests that volatile organic chemicals are entering regional groundwater systems.

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

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## Appendix A. Financial and Administrative Closeout

# **Workplan Outputs**

The following products were committed to in the Workplan for this project.

- 1. Produce an annual report for the DOW NPS Section as requested.
  - Presented a progress report at the 2002 Kentucky Nonpoint Source Conference, Lake Barkley State Resort Park, Kentucky, September 23-25, 2002.
- 2. Prepare draft copies of reports for review by the KY Division of Water Groundwater Branch and Nonpoint Source Section.
  - Submitted draft final report to the Groundwater Branch, Kentucky Division of Water May 25, 2005 for review. Received comments and revised report in July 2005.
- 3. Finalize reports for distribution to the Division of Water, other state and federal agencies, River Basin Teams, and educational institutions.

Revised report was submitted to Nonpoint Source Group, Kentucky Division of Water for review and acceptance with this transmittal.

4. Prepare and submit final project close-out report.

Close-out report is included with the draft final report enclosed.

#### **Budget Summary**

The Detailed Budget from the approved Workplan is shown in Table A-1. Columns labeled "Budget Categories", "Section 319(h) Funds", "Non-Federal Match", and "Total" were copied from the budget in the Project Workplan. Dollar amounts for the column titled "Final Expenditures" in Table A-1 were taken from University of Kentucky invoices # 06631300B (period 01/01/03 through 03/31/03) and #065056004A-FINAL (period 06/01/02 through 06/30/02) (Attached). Amounts in this column include both federal and non-federal match dollars.

No budget revisions were requested for this project.

The University of Kentucky was reimbursed \$66,164.80 for work on this project. A total of \$3,994.76 was spent but has not yet been reimbursed. A total of \$20.26 of the budgeted \$70,400 of Federal 319(h) funds remains unspent. These federal funds were not needed for completion of the project.

Table A1. Detailed Budget Summary.

# Detailed Budget

| Budget             | Section  | Non-Federal | Total     | Final        |
|--------------------|----------|-------------|-----------|--------------|
| Categories         | 319(h)   | Match       |           | Expenditures |
| Personnel          | \$59,000 | \$18,190    | \$77,190  | \$79,788.13  |
| Supplies           |          |             |           | \$0          |
| Equipment          | \$4,000  |             | \$4,000   | \$0          |
| Travel             |          |             |           | \$0          |
| Operating<br>Costs | \$1,000  |             | \$1,000   | \$260.45     |
| Other              | \$6,400  | \$28,740    | \$35,140  | \$37,261.16  |
| TOTAL              | \$70,400 | \$46,930    | \$117,330 | \$117,309.74 |
|                    | 60%      | 40%         | 100%      |              |