Expanded Groundwater Monitoring for Nonpoint Source Pollution Assessment in the Kentucky River Basin: Final Report

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EXECUTIVE SUMMARY

The Groundwater Branch of the Kentucky Division of Water collected 118 groundwater samples from 37 sites in the Kentucky River Basin (Basin Management Unit 1) in support of basin-wide efforts to characterize water resources. Sites representative of ambient groundwater quality were chosen for sampling, rather than sites down gradient from known point sources of contamination. Analytical data from an additional 20 sites sampled for other programs, such as the Statewide Ambient Groundwater Monitoring Program and pesticides monitoring through an MOA with the Division of Pesticides, were also included in this report. Samples were analyzed for approximately 250 parameters, including nutrients, total and dissolved metals, pesticides, residues, major anions, and volatile organic compounds, including methyl-tert-butyl-ether (MTBE), benzene, toluene, ethylbenzene, and xylenes (BTEX). From these analytes, 30 parameters indicative of nonpoint source impacts to groundwater quality as well as naturally occurring ambient groundwater quality were selected for inclusion in this report. Results from this study are summarized in Table 1.

Several parameters are controlled primarily by underlying bedrock geology and are indicative of naturally occurring water chemistry. These include pH, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), conductivity, hardness, sulfate, chloride, fluoride, iron, manganese, lead, arsenic, barium and mercury. In some areas, oil and gas drilling or production may elevate some parameters such as chlorides, sulfate, or barium, but no sites in this study appear to be impacted by oil and gas operations. Acid mine drainage is known to reduce pH in surface water, but groundwater in BMU 1 shows no widespread impacts, although groundwater quality may be influenced locally. Nutrients (nitrate-N, nitrite, ammonia-N, orthophosphate-P and total phosphorus) are difficult to interpret because they are both naturally occurring and anthropogenic. However, the data suggest that natural levels may be elevated through agricultural and waste-disposal practices. Pesticides and volatile organic compounds do not

Table 1. Nonpoint Source Impacts to Groundwater in BMU 1

	PARAMETER	NO NPS INFLUENCE ON GROUNDWATER QUALITY	POSSIBLE NPS INFLUENCE ON GROUNDWATER QUALITY	DEFINITE NPS INFLUENCE ON GROUNDWATER QUALITY
Bulk Water Quality Parameters	Conductivity	•		
	Hardness (Ca/Mg)	•		
	pH	•		
Anions	Chloride	•		
	Fluoride	•		
	Sulfate	•		
Metals	Arsenic	•		
	Barium	•		
	Iron	•		
	Lead		•	
	Manganese	•		
	Mercury	•		
Nutrients	Ammonia-N		•	
	Nitrate-N		•	
	Nitrite-N	•		
	Orthophosphate-P		•	
	Total phosphorous		•	
Pesticides	Alachlor			•
	Atrazine (incl. desethyl)			•
	Cyanazine	•		
	Metolachlor			•
	Simazine			•
Residues	Total Dissolved Solids		•	
	Total Suspended Solids		•	
Volatile Organic Compounds	Benzene			•
	Ethylbenzene	•		
	Toluene			•
	Xylenes			•
	MTBE			•

occur naturally in groundwater and therefore these parameters are indicative of either point or nonpoint sources of contamination. The pesticides atrazine (including a degradation by-product, atrazine desethyl), metolachlor, alachlor and simazine were detected in groundwater in BMU 1. Volatile organic compounds detected were benzene, toluene, xylenes and MTBE, but only in a limited number of sites.

INTRODUCTION and BACKGROUND

The Kentucky Division of Water has adopted an integrated approach to the management of water resources. The approach, known as the Kentucky Watershed Framework, is " . . . a means for coordinating and integrating the programs, tools, and resources of stakeholders to better protect, maintain, and restore the ecological composition, structure, and function of watersheds and to support the sustainable uses of watersheds for the people of the Commonwealth" (KDOW, 2002a). Under this system, the watersheds of the state are sub-divided into five Basin Management Units (BMU). As part of the data gathering and assessment efforts of the watershed approach, the Division of Water-Groundwater Branch assessed nonpoint source pollution impacts to groundwater within the Kentucky River Basin (BMU 1).

Prior to 1995, ambient groundwater quality data throughout the state was inadequate to assess groundwater quality on a regional, basin-wide or statewide scale. In order to correct this situation, the Division of Water initiated statewide ambient groundwater monitoring in 1995 to begin the long-term, systematic evaluation of groundwater quality throughout the state. In 1998, legislation established the Kentucky Interagency Groundwater Monitoring Network, which formalized groundwater assessment efforts. Oversight for this network is through the Interagency Technical Advisory Committee on Groundwater, which includes the Division of Water.

The Division of Water regularly collects ambient groundwater samples throughout the state. To date, the Division has collected more than 3000 samples from approximately 400 sites. The information from these samples is used for several purposes, including: 1) assessment and characterization of local and regional baseline groundwater quality, 2) documentation of spatial and temporal variations in groundwater quality 3) support of public water systems, especially through source water characterization and wellhead protection, 4) development of Total Maximum Daily Loads (TMDL) for surface water in areas where groundwater directly influences this resource, 5) support of the state's pesticide management plan, 6) development of groundwater quality standards and aquifer classification, and 7) to evaluate nonpoint source conditions. The Division of Water forwards analytical data to the Kentucky Geological Survey (KGS) Ground-Water Data Repository where it is available to the public. Data requests can be made via their website (http://kgs.edu/KGS/home.htm), by phone at (859) 257-5500, or by mail at 228 Mining and Minerals Resources Building, University of Kentucky, Lexington, KY 40506-0107.

Project Description

This project provides additional groundwater quality data in areas lacking adequate information. The objective of this project was to sample 30 groundwater sites in BMU 1 on a quarterly basis for one year, beginning in 1997. However, because drought affected some low-flow springs, alternate sites had to be selected and therefore additional sites were included to meet this grant commitment. In addition, data from other sites sampled for various ambient monitoring projects from 1995 through June 2003 are also included in this report. The Groundwater Branch selected wells and springs to provide geographical representation of the diverse physiographic and hydrogeologic characteristics, and dominant land uses in BMU 1 (Figs. 1 & 2, map pocket). Samples were analyzed for numerous parameters including nutrients, pesticides, total/dissolved metals, residues, major anions, and volatile organic compounds, as shown in Table 1. Data were compared to various existing standards and to data from unimpacted ("pristine") reference springs (Table 2), to determine possible nonpoint source pollution impacts or other water quality problems, as well as to identify outstanding resources.

Table 2. Parameters and Standards for Comparison

Parameter	*Standard*	*Source/Discussion **
Bulk parameters		
Conductivity	800 µmho	No MCL, SMCL, or HAL; this roughly corresponds to 500 mg/L TDS, which is the SMCL
Hardness (Ca/Mg)	0-17 mg/L = soft 17-120 mg/L = moderate > 120 mg/L = hard	No MCL, SCML, or HAL; scale modified from USDA
pH	6.5 to 8.5 pH units	SMCL
Anions		
Chloride	250 mg/L	SMCL
Fluoride	4 mg/L	MCL
Sulfate	250 mg/L	SMCL
Metals		
Arsenic	.010 mg/L	MCL
Barium	2 mg/L	MCL
Iron	.3 mg/L	SMCL
Lead	0.015 mg/L	AL/TT
Manganese	.05 mg/L	SMCL
Mercury	.002 mg/L	MCL
Nutrients		
Ammonia-N	.110 mg/L	DEP
Nitrate-N	10 mg/L	MCL
Nitrite-N	1 mg/L	MCL
Orthophosphate-P	.04 mg/L	No MCL, SMCL, or HAL; Texas surface water standard
Total phosphorous	.1 mg/L	No MCL, SMCL, or HAL; level recommended by USGS NAWQA Program
Pesticides		
Alachlor	.002 mg/L	MCL
Atrazine	.003 mg/L	MCL
Cyanazine	.001 mg/L	HAL
Metolachlor	.1 mg/L	HAL
Simazine	.004 mg/L	MCL
Residues		
Total Dissolved Solids	500 mg/L	SMCL
Total Suspended Solids	35 mg/L	No MCL, SMCL, or HAL; KPDES permit requirement for sewage treatment plants
Volatile Organic Compounds		
Benzene	.005 mg/L	MCL
Ethylbenzene	.7 mg/L	MCL
Toluene	1 mg/L	MCL
Xylenes	10 mg/L	MCL
MTBE	.050 mg/L	DEP

* Abbreviations:

MCL = Maximum Contaminant Level
SMCL = Secondary Maximum Contaminant Level
HAL = Health Advisory Level
KPDES = Kentucky Pollutant Discharge Elimination System
NAWQA = National Water-Quality Assessment Program (USGS)
DEP = Kentucky Department for Environment Protection risk-based number
USDA = United States Department of Agriculture
AL/TT= Action Level/Treatment Technique (lead and copper are regulated by a Treatment Technique that requires systems to control the corrosiveness of their water—if more than 10% of samples exceed the Action Level, water systems must take additional action)

Previous Investigations

Groundwater in the Kentucky River Basin is discussed in Carey and others (1994). Because water quality data were limited at that time, only a few parameters could be included in their discussion. These were nitrate-N, nitrite-N, chloride, barium, ammonia-N, sulfate, conductivity, alachlor, and triazine herbicides. In their review of the analytical data available at that time, Carey and others (1994) found no atrazine results exceeding the drinking water Maximum Contaminant Level. Faust and others (1980) compiled groundwater quality data on some parameters for the entire state, but did not analyze or summarize the data. The United States Geological Survey (USGS) has prepared Hydrologic Atlases (HAs) and 7.5 minute Geological Quadrangle maps (GQs) for the entire state, and the Kentucky Geological Survey (1969,2002) has indexed these publications. Geochemical data in the Hydrologic Atlases is limited, and generally includes only common metals and major anions.

Several investigators have mapped karst groundwater basins within BMU 1, and Currens and others (1998, 2002) have compiled the results. Currens (1979) also compiled a bibliography of karst publications for the state.

Carey and Stickney (2001) have prepared county groundwater resource reports, including general descriptions of groundwater quality. Ray and others (1994), discussed further below, have interpreted inherent groundwater sensitivity to contamination for the entire state. Carey and others (1993) examined data from 4,859 groundwater samples collected throughout the state for ammonia-N, nitrate-N, nitrite-N, chloride, sulfate, conductivity, alachlor and triazine. For three important nonpoint source parameters, they found: 1) 4.6% of the samples for nitrate-N exceeded the Maximum Contaminant Level (MCL) of 10.0 mg/L, 2) 0.9% exceeded the MCL of 0.002 mg/L for alachlor, and 3) 0.3% exceeded the atrazine MCL of 0.003 mg/L. (Note that this study measured *total* triazines and did not differentiate between various triazine herbicides, including atrazine, simazine and cyanazine. Additionally, the MCL for atrazine was applied, perhaps inappropriately, to total triazines.)

Conrad and others (1999) described the occurrence of nitrate-N and fluoride in the state and Fisher (2002) described the occurrence of arsenic. In their study of nitrate-N, Conrad and others (1999) found that MCL exceedances decreased with well depth, and that for fluoride less 1% of 2,363 analyses exceeded the MCL of 2.0 mg/L. Fisher (2002) concluded that "arsenic in Kentucky generally does not exceed the MCL and there are no widespread occurrences of high arsenic concentrations."

Several researchers, including Dinger (1991), Wunsch (1991) and Minns (1993) have studied groundwater in portions of eastern Kentucky. These studies, and others, include limited water quality data but found that groundwater in eastern Kentucky is generally hard, and that naturally occurring water quality problems include iron, manganese, barium, sodium chloride and sulfate. Wunsch (1991) found that 20% of 130 wells completed in Pennsylvanian-age aquifers in eastern Kentucky exceeded drinking water standards for barium.

PHYSIOGRAPHIC AND HYDROGEOLOGIC SETTING

Kentucky River Basin

The Kentucky River Basin Management Unit is illustrated in Figure 1 (map pocket). The Kentucky River drains an area of approximately 7,000 square miles and includes all or parts of 42 counties (Carey, and others, 1994.) The Kentucky River rises in the far southeastern part of the state and flows generally north to its confluence with the Ohio River at Carrollton. The main stem of the Kentucky River is formed by the confluence of the North, South and Middle Forks near Beattyville in Lee County. Approximately 16,000 miles of rivers and streams occur in the basin. Major tributaries of the Kentucky River include the Red Bird River, the Red River, the Dix River, Elkhorn Creek, and Eagle Creek. The river flows through several physiographic provinces, as shown in Figure 1, including the Eastern Kentucky Coal Field, the Mississippian Plateau, the Knobs, and the Inner and Outer Bluegrass regions. Most of the basin, however, lies within the Eastern Coal Field and Bluegrass provinces.

Total population within the basin is approximately 710,000 people. The population varies from about 225,000 in the most populous county, Fayette, to about 5,000 in Owsley County, the least populated county. Land use (Figure 1, map pocket) within the basin consists of 58% forest cover, 37% agriculture, 3.6% urban, 1.2% mining, with water and wetlands comprising 0.1%. Potential contaminants related to land use are shown in Table 3.

Table 3. Land Use and Potential Nonpoint Source Contaminants

Land Use	% BMU 1	Potential Contaminants
Agriculture, including row crop production, livestock grazing, fuel/pesticide storage	37	Pesticides, nutrients (esp. nitrate-N), salts/chloride, volatile organics, bacteria
Urban	3.6	Pesticides, volatile organics, chlorides
Forested, including mining, logging, silviculture	59.2	Metals, pesticides, nutrients, sediment, pH

Groundwater provides domestic water for private supplies, especially in the Eastern Coal Field (Carey and others, 1994) and for some public water systems, including Georgetown (Royal Spring) in Scott County. Carey and others (1994) further state that groundwater ". . . flowing into stream channels sustains flow in the stream during droughts" and this is especially important for several public water systems in BMU 1 that draw water from the Kentucky River, including Lexington and Frankfort.

Groundwater Sensitivity

Based upon variations in geology, topography, and hydrologic flow regime, groundwater in Kentucky's various physiographic regions has varying sensitivity to contamination from activities conducted on the surface and is discussed in detail by Ray and others (1994). Groundwater sensitivity to potential impacts is based upon three primary hydrologic components: recharge, flow velocity and dispersion. In general, the quicker the recharge, the faster the flow and the more extensive the dispersion, then the greater the sensitivity. According to the scale developed by Ray and others (1994), sensitivity ranges from low (1) to high (5). Groundwater sensitivity in BMU 1 generally rates high ("5") in the Inner Bluegrass karst terrane to moderate ("3") in the Eastern Coal Field.

Physiographic Provinces

Physiographic provinces are differentiated based on geology and hydrogeology and therefore the physiographic map is used as a base map to present analytical data on each parameter. Four physiographic provinces occur in BMU 1: the Eastern Coal Field, the Mississippian Plateau, the Knobs, and the Bluegrass (Outer and Inner). The Ohio River Alluvium is not a true physiographic region, but because it is an important aquifer in Kentucky, it is included in the discussion below. Because each province differs in physiography and subsurface flow regime, sensitivity to contamination from nonpoint source pollution also differs. The information below is summarized from Noger (1988), McDowell (2001), and Ray and others (1994).

Pennsylvanian-age clastic sedimentary rocks, generally flat-lying sandstone, siltstone, shale and clay, with significant coal beds characterize the **Eastern Coal Field**, also known as the Cumberland Plateau. Erosion of this plateau has produced steeply incised, narrow valleys, with narrow ridges. Groundwater flow is primarily through shallow stress-relief fractures, rather than through primary porosity and permeability. Well yields are usually sufficient for domestic water supplies and range from one to several gallons per minute (gpm) when larger fractures are encountered. High-yield municipal or industrial supply wells are rare. Springs tend to have low flows and are usually perched on impermeable shales; large-flow, base level springs are uncommon. The Eastern Coal Field exhibits the lowest hydrogeologic sensitivity in the state and is rated as a "1."

The **Mississippian Plateau**, also known as the Pennyroyal or Pennyrile, is characterized by flat-lying Mississippian-age carbonate rocks, primarily limestone with some dolostone. Well-developed karst topography occurs in this province, with an abundance of sinkholes, caves and sinking streams. Groundwater flow is primarily through solutionally-enlarged conduits, fractures and along bedding planes. In general, yields from wells varies widely according to the size of any enlarged water-filled conduits encountered by the well-bore and can range from less than one gpm to more than one hundred gpm. Springs developed on these thick and generally pure carbonate sedimentary rocks tend to have higher flows than other areas within the watershed, with base flow discharges ranging up to several cubic feet per second (cfs). The Mississippian Plateau is very sensitive to contamination from surface activities and rates a "5."

The **Knobs** physiographic region consists of conical hills forming a horseshoe belt almost surrounding the Bluegrass on the east, south and west. This narrow belt of hills is approximately 10 to 15 miles wide and consists of generally flat-lying sedimentary rocks of Ordovician through Mississippian age. These hills are the eroded remnants of the Pottsville Escarpment in the Licking River watershed and Muldraughs Hill in the Salt River basin. In the Knobs, resistant Mississippian-age limestone or sandstone overlies more easily eroded shale and siltstone. Knobs are generally circular in plan view and are characterized by ". . . symmetrical concave-upward slopes. . .[that]. . . steepen upward into cliffs on knobs with resistant caprocks. Knobs that have lost their protective caps have rounded crests." (McDowell, 2001). Groundwater flow in this region is primarily through stress relief fractures. Groundwater in this province is less vulnerable to surface contamination (Ray and others, 1994) and generally rates a sensitivity of "2." Springs in this province tend to be gravity springs, perched on stratigraphic contacts, with low and commonly intermittent flows.

The **Outer Bluegrass** is underlain generally thin-bedded, flat-lying middle and upper Ordovician and Silurian-age limestones, dolostones and shale. Because the limestone is thin and interbedded with insoluble shale, karst development is minor and local groundwater resources are limited. Groundwater flow is through poorly developed, non-integrated karst conduits and stress relief fractures. In general, Ray and others (1994) found that sensitivity in this region is low to moderate, usually rating a "2" or "3". Springs are typically low-flow (0.1 cfs or lower) and often seasonal.

The **Inner Bluegrass** is underlain predominantly by Ordovician-age limestone and shale. In general, relief is low and the area is characterized by gently rolling hills with shallow sinkholes and thick soils. Although some karst topography, such as sinkholes, caves and sinking streams, occurs in this province, most terrain is moderately dissected by surface streams. As in the Mississippian Plateau, groundwater yield is highly variable and for wells, depends on the number and size of water-filled fractures and conduits that are intersected by the well bore. Most wells yield one or more gallons per minute, which is sufficient for domestic supplies; however, large municipal or industrial wells and springs are rare. An exception to this is Royal Spring in Scott County, which supplies water to about 18,000 people in Georgetown. Ray and others (1994) assigned high to extreme sensitivity for the Inner Bluegrass region, rating it as "4" and "5."

The **Ohio River Alluvium** is comprised of unconsolidated sand, gravel, silt and clay deposits adjacent to the Ohio River. These deposits consist of Pleistocene age glacial-outwash sediments and modern alluvial sediments. Coarse sand and gravel beds in these deposits supply large volumes of water to industrial, municipal and domestic wells. Large-diameter conventional wells commonly produce yields of 2000 gpm and radial collector wells can produce even greater amounts of water. Because groundwater can travel quickly through these coarser sediments, Ray and others (1994) rated sensitivity as high, or "4." The Ohio River Alluvium only occurs in a small area at the northern boundary of BMU 1, where the Kentucky River discharges into the Ohio River. Therefore, only one site in this aquifer was included in this study.

In addition, some alluvium deposits thick enough to serve as viable aquifers are also present along the larger rivers in this BMU, especially on lower reaches. However, these alluvial aquifers are generally thinner and finer-grained than the Ohio River Alluvium but are also highly sensitive to contamination. Note that although alluvial areas do not show up at the scale used for the maps in this report, these aquifers are nevertheless important along the Ohio River as well as along some other major drainages, particularly in their lower reaches.

Aquifer characteristics for BMU 1 are summarized in Table 4.

Table 4. Simplified Aquifer Characteristics in BMU 1

Geologic Age of Aquifer	Predominant Rock Type	Predominant Sub-Surface Flow/Speed	Characteristic of Physiographic Province
Pennsylvanian	Sandstone, siltstone, shale, coal	Fracture / Moderate	Eastern Coal Field
Mississippian	Limestone, dolostone	Well-developed Conduits / High	Mississippian Plateau
Silurian, Devonian	Limestone, shale	Fractures, Conduits / Moderate-High	Knobs
Ordovician	Limestone, shale	Fractures, Conduits / Moderate-High	Bluegrass (Inner and Outer)
Quaternary	Unconsolidated Sand, silt, gravel	Granular / Moderate	Ohio River Alluvium; alluvium adjacent to larger rivers in the above provinces

MATERIALS and METHODS

Introduction

Parameters that are most indicative of nonpoint source pollution, as well as those parameters necessary to characterize naturally occurring groundwater chemistry and the values against which the raw data were compared, are shown in Table 2. Basic water quality chemistry can be determined from common, naturally occurring major anions, metals, residues, conductivity and pH. Parameters that are not naturally occurring may be the most conclusive indicators of nonpoint source pollution; these include pesticides and volatile organic compounds. Reference conditions used for comparison are derived from a variety of sources and are discussed below.

Sample results from this study were compared to a variety of existing standards, referred to as "reference values" in this report. The highest use of groundwater is drinking water; therefore, water quality for many parameters was compared to the standards established by the United States Environmental Protection Agency (US EPA, 2000) for treated drinking water supplied to the public. The US EPA defines three types of drinking water standards: Maximum Contaminant Levels, Secondary Drinking Water Regulations and Health Advisories:

Maximum Contaminant Level (MCL) is defined (US EPA, 2000) as "the highest level of a contaminant that is allowed in drinking water." MCLs are legally enforceable limits applied to "finished" public drinking water based on various risk levels, ability to treat and other cost considerations. MCL standards are health-based and are derived from calculations based on adult lifetime exposure, with drinking water as the only pathway of concern. These standards are also based upon other considerations, including the efficacy and cost of treatment.

Secondary Drinking Water Regulations (SDWR) are defined by the US EPA (2000) as "non-enforceable Federal guidelines regarding cosmetic effects (such as tooth or skin discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water." In common usage, this is often referred to as **S**econdary **M**aximum **C**ontaminant **L**evel (**SMCL**) and this usage has been adopted for this report.

Health Advisory (HA) is defined (US EPA, 2000) as "an estimate of acceptable drinking water levels for a chemical substance based on health effects information; a Health Advisory is not a legally enforceable Federal standard, but serves as technical guidance to assist Federal, state and local officials." Again, reflecting common usage, this term has been modified slightly and is referred to in this document as the **H**ealth **A**dvisory **L**evel (**HAL**).

Treatment Technique (TT) (U. S. EPA, 2000) is "A required process intended to reduce the level of a contaminant in drinking water." Public water systems are required to control the corrosiveness of their water, and if more than 10% of tap water samples exceed the **Action Level (AL)**, then water systems must take additional action.

Many parameters discussed in this report have no MCL, SMCL, HAL or AL/TT. These parameters were compared to a variety of existing standards. These include proposed, but not adopted, Department for Environmental Protection (DEP) standards for **m**ethyl ***t**ert*-**b**utyl **e**ther (**MTBE**) and ammonia-N; the Kentucky Pollutant Discharge Elimination System (KPDES) standard for total suspended solids discharged to surface waters; and the USGS-recommended surface water standard for total phosphorous.

Although comparing raw groundwater with established drinking water quality standards is useful, another important tool is to compare data with water quality from sites that apparently have had minimal impact from anthropogenic activities. Adopting the language used for similar surface water areas, these sites are informally called "reference springs" or "reference reach springs." At this time, our understanding of such sites is limited, but under investigation.

Reference reach springs that represent the least impacted groundwater in the state are nevertheless considered important for comparison, and this concept is being evaluated in more detail. These sites drain forested areas unimpacted by routine surface land uses, such as recent logging, agricultural, industrial, or residential use. References springs (Table 5) include Cameron Spring in Lewis County (BMU 2), Fred Mullin Spring in Rockcastle County (BMU 3), and Nada Spring in Powell County (BMU 1).

Although some parameters, such as pesticides, can only come from anthropogenic sources, others, such as metals, inorganics and many organic compounds, can be both naturally occurring and from anthropogenic sources. Therefore, reviewing land-use in conjunction with geochemical data, as well as comparing data with that from reference reach springs, can help differentiate between anthropogenic and natural sources.

Statistical and Graphical Methods

Project data were evaluated with summaries and descriptive statistics presented in tables (summaries and descriptive statistics), inferential statistics correlating parameters versus land use, graduated-size maps and box and whisker plots. **Summaries** show number of samples and sites, number of detections, percent of detections above the standards, etc. **Descriptive statistics** present minimum and maximum values, median and mode. **Graduated size maps** show analytical results as symbols that increase in size as values increase. These maps show the median value for each site; however, sites of interest, such as those sites with some values exceeding the standards, are “flagged” and further details are provided on the map or discussed in the text. According to Hall (2002), a **box and whisker plot**, or simply "boxplot," is “ . . .a graphical representation of dispersions and extreme scores. Represented in this graphic are minimum, maximum and quartile scores in the form of a box with 'whiskers.' The box includes the range of scores falling into the middle 50% of the distribution (**I**nter **Q**uartile **R**ange [IQR] = 75^{th} percentile - 25^{th} percentile) and the whiskers are lines extended to the minimum and

Table 5. Reference Springs Analytical Data Summary

NPS REFERENCE SITES: SUMMARY STATISTICS						
	START DATE	END DATE	NUMBER OF SAMPLES	MEDIAN (mg/L)	MIN (mg/L)	MAX (mg/L)
Conductivity	04/27/95	10/04/00	48	111.25	46.0	448.0
Hardness	07/14/95	12/03/01	28	52.3015	14.039	140.29
pH	04/27/95	10/04/00	44	7.31	6.01	8.12
Chloride	04/27/95	03/07/00	19	1.9	0.6	16.7
Fluoride	04/27/95	03/07/00	33	0.05	< 0.023	0.253
Sulfate	04/27/95	03/07/00	36	7.425	< 5.0	69.4
Arsenic	06/03/98	12/03/01	34	0.002	< 0.002	0.0045
Barium	06/03/98	12/03/01	34	0.0305	0.0040	0.073
Iron	07/14/95	12/03/01	34	0.056	< 0.001	0.337
Lead	06/03/98	12/03/01	34	< 0.002	< 0.001	< 0.002
Manganese	06/03/98	12/03/01	34	0.0035	< 0.001	0.208
Mercury	06/03/98	12/03/01	34	0.00005	< 0.00005	< 0.00005
Ammonia-N	04/27/95	10/04/00	42	0.02	< 0.02	0.11
Nitrate-N	04/27/95	03/07/00	36	0.1805	< 0.01	0.888
Nitrite-N	04/27/95	03/07/00	21	0.005	< 0.002	0.006
Orthophosphate-P	04/27/95	10/04/00	43	0.011	< 0.003	0.069
Total Phosphorus	04/27/95	03/07/00	19	0.019	< 0.005	0.019
Alachlor	04/27/95	12/03/01	55	0.00004	< 0.00002	< 0.00006
Atrazine	04/27/95	12/03/01	55	0.00004	< 0.00004	< 0.0003
Cyanazine	05/03/95	12/03/01	48	0.00004	< 0.00004	< 0.0001
Metolachlor	04/27/95	12/03/01	55	0.00004	< 0.00004	< 0.0002
Simazine	04/27/95	12/03/01	52	0.00004	< 0.00004	< 0.0003
TDS	04/27/95	10/04/00	48	63.0	< 10.0	266.0
TSS	04/27/95	10/04/00	48	3.0	< 1.0	13.0
Benzene	04/12/00	12/03/01	20	< 0.0005	< 0.0005	< 0.0005
Ethylbenzene	04/12/00	12/03/01	20	< 0.0005	< 0.0005	< 0.0005
Toluene	04/12/00	12/03/01	20	< 0.0005	< 0.0005	< 0.0005
Xylenes	04/12/00	12/03/01	20	< 0.0005	< 0.0005	< 0.0005
MTBE	04/12/00	12/03/01	20	< 0.001	< 0.001	< 0.001

maximum scores in the distribution or to the mathematically defined (+/- 1.5* **IQR**) upper and lower fences."

Analyte samples for which there was no detection, based on analyte-specific testing methods and test-specific detection limits, are referred to as "censored observations" in the boxplots. A conservative approach was taken regarding these censored observations by plotting these data at their detection limit. The boxplot provides a pictorial representation of the data, showing the distribution of the data set. The censored data have values between zero and the detection limit and since the detection limit is typically low, the clustering of uncensored observations at this detection limit does not provide an unrealistic interpretation of the overall data set.

In order to simplify the boxplots and summary tables, data for sites in the Knobs and Outer Bluegrass Physiographic Provinces are included in the Bluegrass category. The graduated size maps are overlain on a physiographic map that differentiates these provinces, so variations in the results, if any, between these similar terranes can be noted.

Site Selection

The Groundwater Branch selected sites in order to provide representative geographical distribution throughout the basins. Monitoring sites are representative of various land uses, each with characteristic nonpoint source threats, as well as varying aquifer types of differing inherent groundwater sensitivity. United States Geological Survey 7.5 minute topographic quadrangle maps, and other maps and data were used to facilitate site selection, including hydrologic atlases, the Division for Environmental Protection's (DEP) groundwater database and field reconnaissance.

In general, previously sampled 7.5 minute quadrangles were omitted from this study. Public water supplies (PWS) using groundwater were given preference over private supplies and unused sources. Some easily accessed springs (commonly called "roadside" springs) that are used locally for drinking water were selected for this study and are noted as "unregulated public access springs". Little information is available regarding the number of people using such springs; however, observations by DOW personnel indicate that some of these springs are used by a significant number of people. Springs were given preference over wells because generally, the drainage area of a spring can be more easily determined and because of the shallow and quick-flow systems typical of springs, are usually more susceptible than wells to nonpoint source pollution.

Because this study was designed to assess ambient groundwater conditions, those areas with known point source discharges were eliminated from consideration. For example, sites affected by leaking underground storage tanks or landfills were not sampled as part of this study. Finally, other important considerations included accessibility of the site and permission to access the site.

A unique eight-digit number identifies wells and springs maintained in the DEP's database. If a well or spring selected for this study had not been assigned a number, a well inspection or spring inventory form was completed and the well or spring was numbered. The inspection or inventory notes details of the site, including owner's name and address, location, well construction or spring development data, yield and topographic map location. The data are then entered into DEP's electronic database and forwarded to the Ground Water Data Repository at the Kentucky Geological Survey. Site locations are plotted on 7.5-minute topographic quadrangle maps maintained by the Groundwater Branch, and the forms are scanned and stored in a database as an indexed electronic image.

The 57 sites included in this study, and the frequency they were sampled, are listed in Appendix C. The study area consists of about 7,000 square miles, or an average of one sampling site per 123 square miles. Although this data is inadequate to fully characterize the groundwater geochemistry of the area, this data greatly expands the knowledge that was previously available, especially before 1995.

Sample Collection Methods

Consistent with the Division of Water's other ambient groundwater monitoring efforts, samples of fresh, untreated groundwater were collected at each spring or well and analyzed for major anions; nutrients; volatile organic compounds; total organic carbon; pesticides, including the most commonly used herbicides, insecticides and fungicides; and dissolved and total recoverable metals. The analytical methods, containers, volumes collected, preservation and sample transport are consistent with the Division of Water's Kentucky Ambient/Watershed Water Quality Monitoring Standard Operating Procedure Manual, prepared by the Water Quality Branch (2002c). Parameters to be measured, volume required for analysis, container type and preservative are shown on the attached Chain-of-Custody Form (Appendix D).

Major anions are used to establish background groundwater chemistry and also to measure impacts from nonpoint source pollutants such as abandoned mine lands and abandoned hydrocarbon production operations by measuring pH, alkalinity, chloride, sulfate and fluoride. Nutrients and total organic carbon are used to measure impacts from agricultural operations (ammonia-N, nitrate-N, nitrite-N, total phosphorous and orthophosphate-P) and/or improper sewage disposal (nitrate-N, ammonia-N). Where sewage was suspected as a nonpoint source pollutant, unbleached cotton fabric swatches were used to detect optical brighteners, the whitening agents used in laundry products and commonly found in sewage (Quinlan, 1986). Pesticides are measured to determine both rural agriculture and urban domestic- and commercial-use impacts on groundwater. Metals are useful to establish rock-groundwater chemistry, local and regional background levels and to determine nonpoint source impacts from active or abandoned coal mining operations. Volatile organic compounds determine impacts from urban run-off, oil and gas production, or other point and nonpoint source impacts to groundwater.

Sampling for pathogens was not conducted because of logistical considerations. Sampling at numerous sites occurred over a one- or two-day period, commonly in remote regions. Because of the short holding time for bacteria (6 hours for fecal coliform, 24 hours for total coliform) we were unable to collect bacteria samples efficiently or regularly and still comply with the required holding times.

All samples collected to meet grant commitments were analyzed by the Division of Environmental Services (DES) laboratory according to appropriate US EPA methods. Additional data included in this study are from samples analyzed by DES for other groundwater projects, as well as data from the Kentucky Geological Survey laboratory. Appropriate US EPA analytical methods were employed for all data used in this report.

RESULTS and DISCUSSION

Introduction

General water quality information, including definitions and sources, were compiled from Hem (1985), USGS (2002a), Driscoll (1986) and Fisher and Davidson (2003). Potential impacts to human health were compiled from the United States Environmental Protection Agency (US EPA, 2002a) and the Agency for Toxic Substances and Disease Registry (ATSDR, 2001).

Parameters were divided into seven categories: bulk parameters, which includes conductivity, hardness and pH), anions, metals, pesticides, residues, volatile organic compounds and nutrients.

Because only four samples were collected at one site in the Ohio River Alluvium, conclusions regarding the chemistry and potential impacts of nonpoint source pollution in this province, which comprises only a small fraction of BMU 1, are tentative at best. More comprehensive and detailed information on groundwater chemistry in the Ohio River Alluvium can be found in Webb and others (2003).

Bulk Parameters (Conductivity, Hardness and pH)

Summaries and descriptive statistics for the bulk parameters included in this study are shown in Tables 6 and 7.

Conductivity, also known as specific conductance, is a measurement of the ability of water to conduct electrical current (Hem, 1985) and is reported in microsiemens (µS/cm). Since a microsiemen is the reciprocal of an **ohm**, the spelling of that latter unit has been reversed as an equivalent unit used to report conductivity. Hence, the term for a microsiemen reported in these units is "µ**mho**." Some laboratories report this as "uU/cm". Therefore, 800 mS/cm = 800 µmho = 800 uU/cm. There is no MCL or other regulatory standard for conductivity; however, 800 µmho corresponds roughly to the 500 mg/L SMCL for Total Dissolved Solids, or TDS. Because conductivity increases as the amount of dissolved ions increases, it may be used as a general indicator of water pollution. However, caution should be exercised in the interpretation of conductivity results, as naturally occurring ions dissolved in water will result in elevated measurements. These ions include chloride, sulfate, iron, carbonate, calcium and others.

Conductivity values found in this study are comparable to those found by Carey and others (1993), who examined 4,859 groundwater analyses throughout the state, and found an average value of 495 µmho, compared to a median value of 551 µmho for the 530 samples included in this nonpoint source study (Tables 6 & 7). Maximum values were found at three sites in the Eastern Coal Field: the Mountain Heritage well in Letcher County (about 6000 µmho), Rousseau School well in Breathitt County (about 3000 µmho) and Dad’s Spring in Perry County, which ranged from about 1600 to 2100 µmho). Median values (Figures 3 & 4) were the highest in the Eastern Coal Field and Ohio River Alluvium, and lowest in the Mississippian Plateau and Bluegrass. The boxplot of conductivity and land use (Figure 5) shows the greatest variability in forested areas, suggesting that this is the result of natural variation. Greater conductivity in the first two is probably the result of longer residence time of groundwater in these provinces, which promotes greater dissolution of the host rock and thus higher conductivity. Because conductivity measures a variety of ions, most of which are naturally occurring, this parameter alone is not an indicator of nonpoint source pollution. Absent any direct evidence to the contrary, the range of values found in this study most likely reflects ambient conditions.

Table 6. Bulk Parameters Summary

BMU1: BULK PARAMETERS SUMMARY		Conductivity[5]	Hardness[1 2 6]	pH[3 4 7]
NUMBER OF SAMPLES	TOTAL:	530	393	507
BY REGION:	BLUEGRASS (INNER & OUTER):	340	246	330
	EASTERN COAL FIELD:	112	104	99
	MISSISSIPPIAN PLATEAU:	74	39	74
	OHIO RIVER ALLUVIUM:	4	4	4
NUMBER OF SITES	TOTAL:	57	52	57
BY REGION:	BLUEGRASS (INNER & OUTER):	33	31	33
	EASTERN COAL FIELD:	19	17	19
	MISSISSIPPIAN PLATEAU:	4	3	4
	OHIO RIVER ALLUVIUM:	1	1	1
[1]Sites with at least one hardness measurement in these categories:		SOFT < 17	MODERATE 17 - 120	HARD > 120
Hardness sites	TOTAL:	4	11	45
	BLUEGRASS (INNER & OUTER):	0	2	31
	EASTERN COAL FIELD:	3	8	10
	MISSISSIPPIAN PLATEAU:	1	1	3
	OHIO RIVER ALLUVIUM:	0	0	1
[2]Hardness calculated (as equivalent $CaCO_3$ in mg/L) as Hardness = 2.5(mg/L Ca) + 4.1(mg/L)Mg		SOFT < 17	MODERATE 17 - 120	HARD > 120
Hardness samples	TOTAL:	10	46	337
	BLUEGRASS (INNER & OUTER):	0	5	241
	EASTERN COAL FIELD:	6	26	72
	MISSISSIPPIAN PLATEAU:	4	15	20
	OHIO RIVER ALLUVIUM:	0	0	4
[3]Sites with at least one pH measurement in these categories:		< 6.5	6.5 - 8.5	> 8.5
pH sites	TOTAL:	5	56	2
	BLUEGRASS (INNER & OUTER):	1	33	1
	EASTERN COAL FIELD:	3	18	1
	MISSISSIPPIAN PLATEAU:	1	4	0
	OHIO RIVER ALLUVIUM:	0	1	0
[4]pH Samples in each of these categories:		< 6.5	6.5 - 8.5	> 8.5
pH samples	TOTAL:	18	487	2
	BLUEGRASS (INNER & OUTER):	1	328	1
	EASTERN COAL FIELD:	14	84	2
	MISSISSIPPIAN PLATEAU:	3	71	0
	OHIO RIVER ALLUVIUM:	0	4	0

[5]Only 530 conductivity values out of 565 samples:
35 analyses: conductivity not included in lab analyses 1997 - 1999.

[6]Only 393 metals values out of 565 samples:
172 analyses: lab samples prior to October 1997 reported metals as dissolved, not total.
Hardness calculated from calcium and magnesium (52 out of 57 sites).

[7]Only 507 pH values out of 565 samples:
58 analyses: pH not included in lab analyses 1998 - 1999.

Table 7. Bulk Parameters Descriptive Statistics

BMU1: BULK PARAMETERS DESCRIPTIVE STATISTICS						
	Conductivity (mmho)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**5980**	**551.5**	**40**	**514**
BLUEGRASS (INNER & OUTER):	04/25/95	06/11/03	1444	552.5	219	456
EASTERN COAL FIELD:	05/02/95	05/28/03	5980	794	40	55
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	704	463.5	40	514
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	830	821	802	-
	Hardness (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**02/10/98**	**06/11/03**	**1582.1**	**255.26**	**6.3397**	**331.95**
BLUEGRASS (INNER & OUTER):	02/10/98	06/11/03	585.26	261.9425	109.696	-
EASTERN COAL FIELD:	03/11/98	05/28/03	1582.1	234.005	6.3397	-
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	351.36	140.29	14.039	-
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	414.36	408.375	385.38	-
	pH (pH units)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**8.65**	**7.49**	**3.83**	**7.83**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	8.65	7.52	6.47	7.83
EASTERN COAL FIELD:	05/02/95	05/28/03	8.51	7.27	3.83	7.27
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	8.2	7.52	6.01	7.64
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	7.78	7.48	7.28	-

The term “hardness” was first used to describe water that was hard to lather. Water is made hard primarily from dissolved calcium and magnesium. Hardness measures the ability of water to produce soap lather, or suds and is reported as equivalent $CaCO_3$ in mg/L derived from: (2.5 x mg/L Ca) + (4.1 x mg/L Mg). Hardness typically causes scaling on water pipes, boilers and in cooking pans, causing problems in the laundry, kitchen and bath. Water with excessive hardness may taste chalky, salty, or metallic, depending on the relative concentrations of various dissolved compounds. On the other hand, very soft water often has a flat, unpleasant taste. Most consumers, therefore, prefer to drink water of moderate hardness.

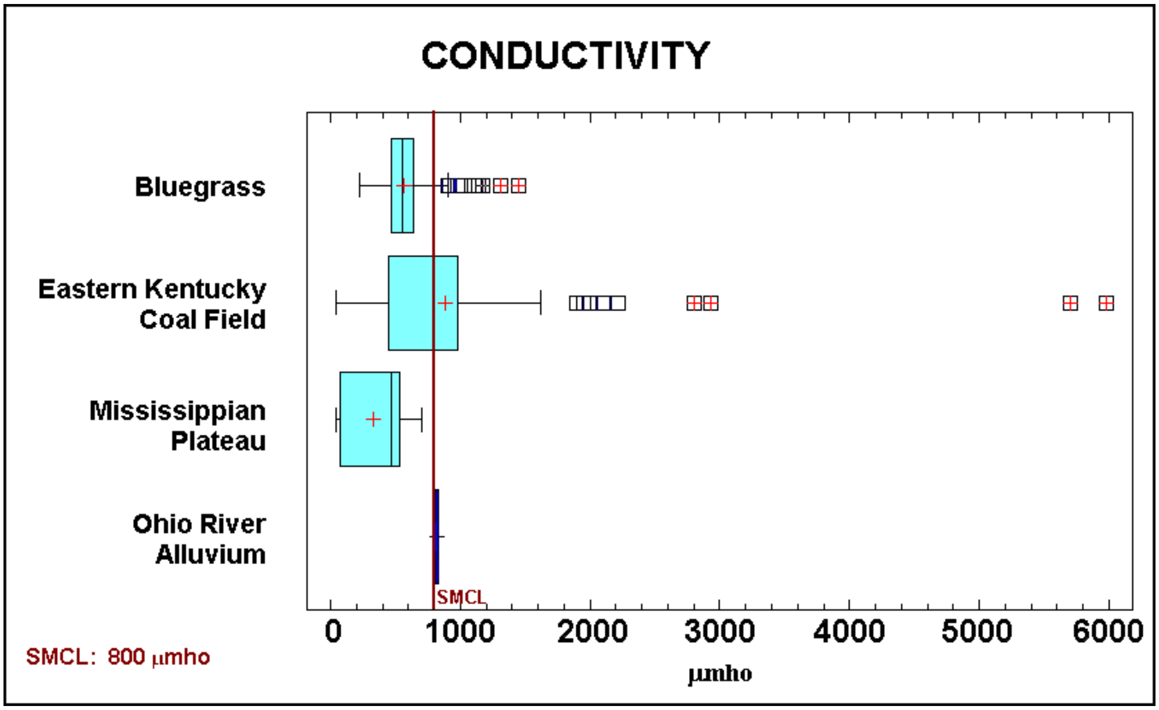

Figure 3. Boxplot of Conductivity and Physiographic Regions

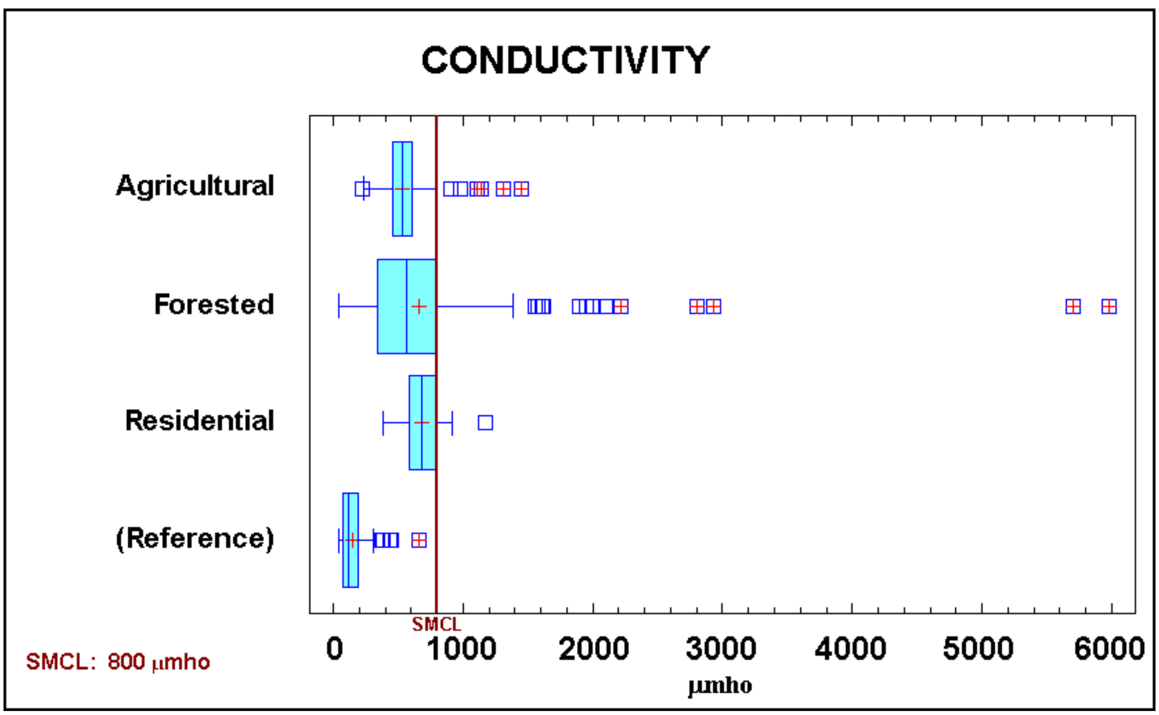

Figure 4. Boxplot of Conductivity and Land Use

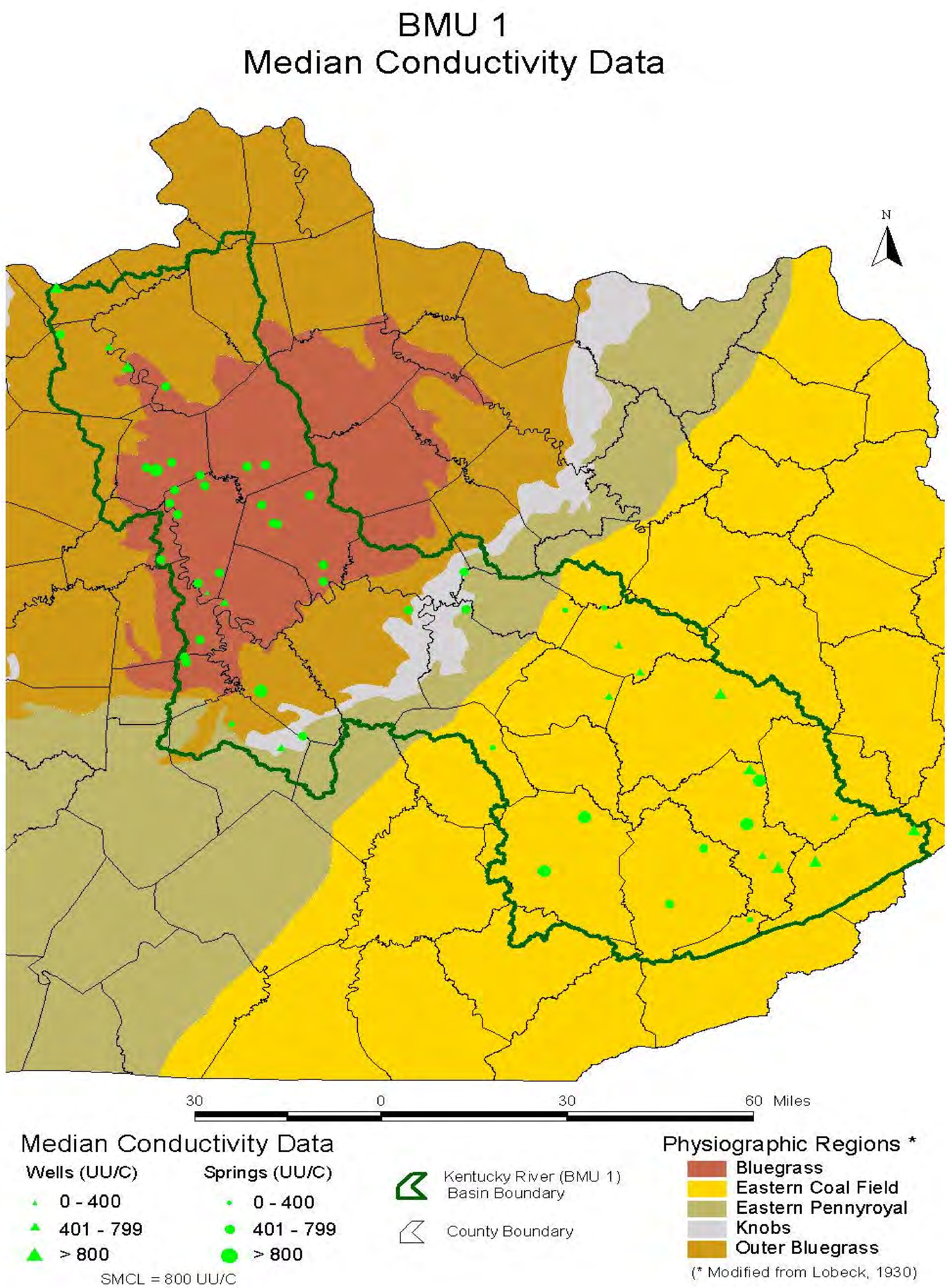

Figure 5. Conductivity Map

No regulatory standards exist for hardness. The Water Quality Association (2002) hardness scale has been modified for this report, where soft water is defined as less than 17 mg/L of calcium/magnesium, water from 17.1 to 120 mg/L is moderate and more than 120 mg/L is hard.

For 393 hardness samples included in this study, median values ranged from 140 mg/L in the Mississippian Plateau to 408 mg/L in the Ohio River Alluvium (Tables 6 & 7). The Eastern Coal Field and Bluegrass median values were 234 mg/L and 262 mg/L respectively. The majority of the samples (337) were rated as “hard”, with only 46 in the moderate and 10 in the soft categories. Distribution of hardness in BMU 1 is shown in Figure 8. The boxplot of hardness compared to land use (Figure 7) shows that median values are about 200-300 mg/L for agriculture, forest and residential areas. The physiographic province with the greatest variability is the Eastern Coal Field (Figure 6).

Hardness is not usually considered a nonpoint source pollutant, and this study supports the conclusion that variations are from naturally occurring differences in the amount of calcium and magnesium. However, because hardness is a fundamental water quality, especially for potable and industrial use, this parameter should continue to be monitored.

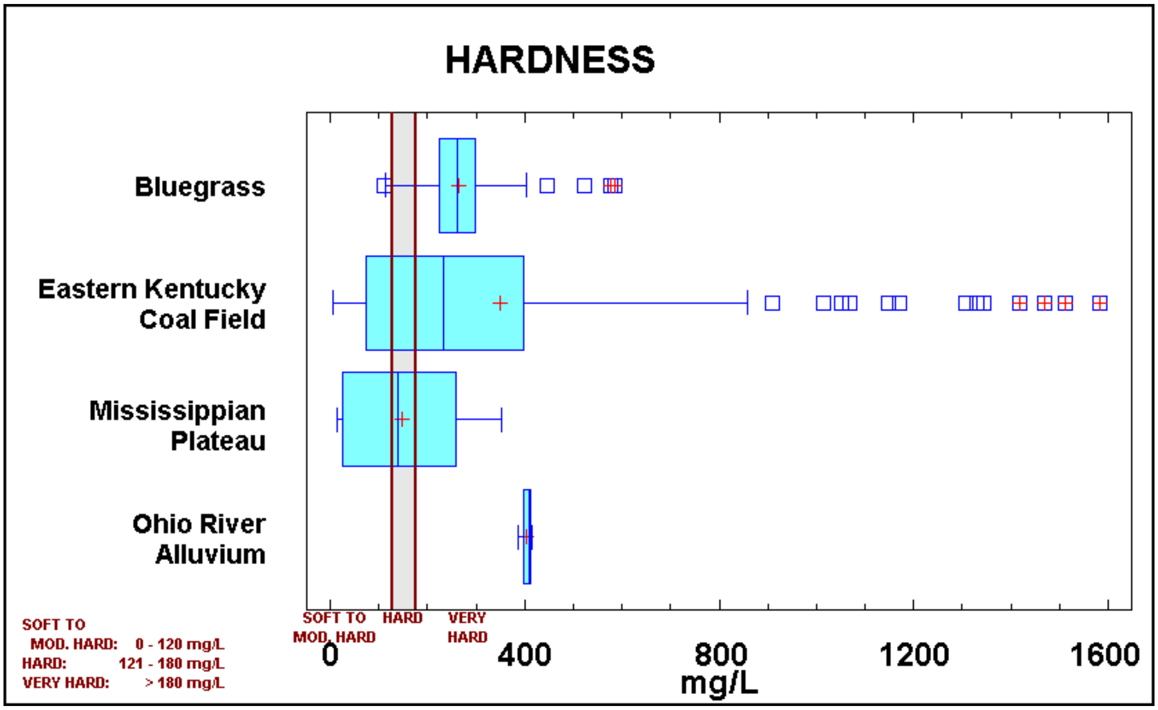

Figure 6. Boxplot of Hardness and Physiographic Regions

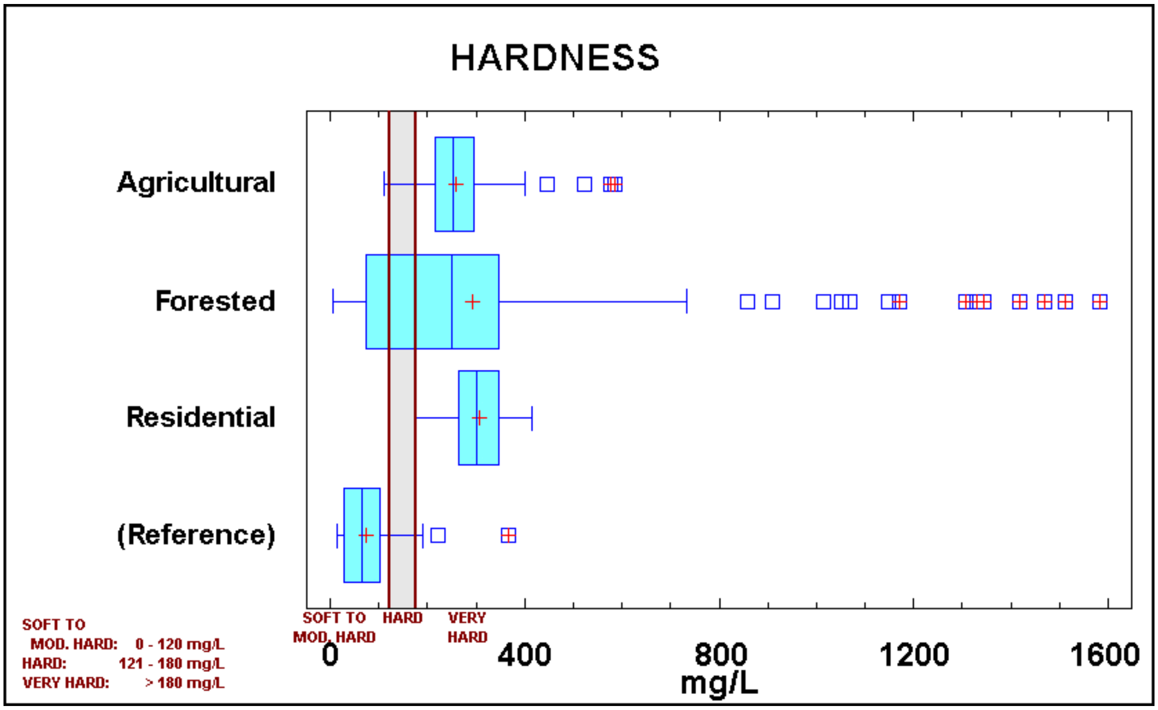

Figure 7. Boxplot of Hardness and Land Use

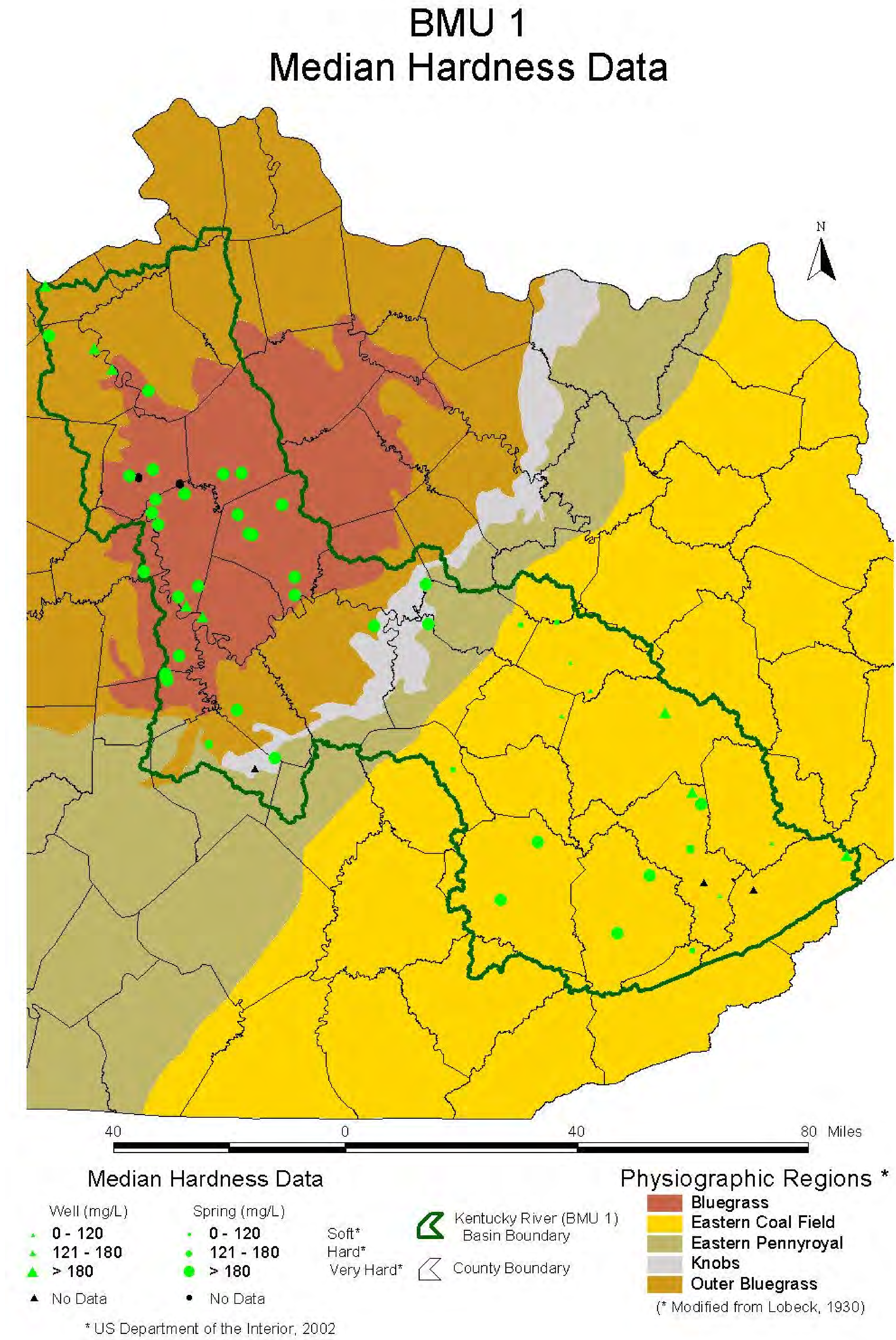

Figure 8. Hardness Map

pH is the negative log of the concentration of the hydronium ion and is essentially a measure of the relative acidity or alkalinity of water. The units of pH are dimensionless, “Standard Units” or “SU”, and the scale measures from 0 to 14. In this system, 7 represents neutral pH and values less than 7 are more acidic; values greater than 7 are more alkaline. The relative acidity/alkalinity of water is important in regard to water quality because this affects several qualities: the corrosiveness of the water, the ability to dissolve contaminants such as heavy metals, the taste of the water for human consumption and in general the overall usefulness of water for various industrial functions.

The pH range of normal aquatic systems is between 6.5 and 8.0. Low pH levels can indicate nonpoint source impacts from coal mining or other mineral extraction processes. High pH values for groundwater may indicate nonpoint source impacts to groundwater from brine intrusion from current or former oil and gas exploration and development activities. Concerning potability, pH is an aesthetic standard, with an SMCL range of 6.5 to 8.5 pH units.

For 507 samples included in this study, pH ranged from 3.83 to 8.65 (Tables 6 & 7). Median values for the physiographic provinces occur within a narrow range: 7.52 for the Bluegrass, 7.27 in the Eastern Coal Field, 7.52 in the Mississippian Plateau, and 7.48 in the Ohio River Alluvium, but outliers are relatively common (Figure 9). Land use has little effect on pH (Figure 10), but forested areas had the greatest variability. Map distribution of pH is shown in Figure 11.

Variation in pH is dependent upon several factors; however, the data collected for this study indicate that the wide range of values is probably the result of rock/water chemistry and not from any apparent sources of nonpoint source pollution. Because pH is a fundamental measure of water quality, sampling for this parameter should continue as an integral part of future programs.

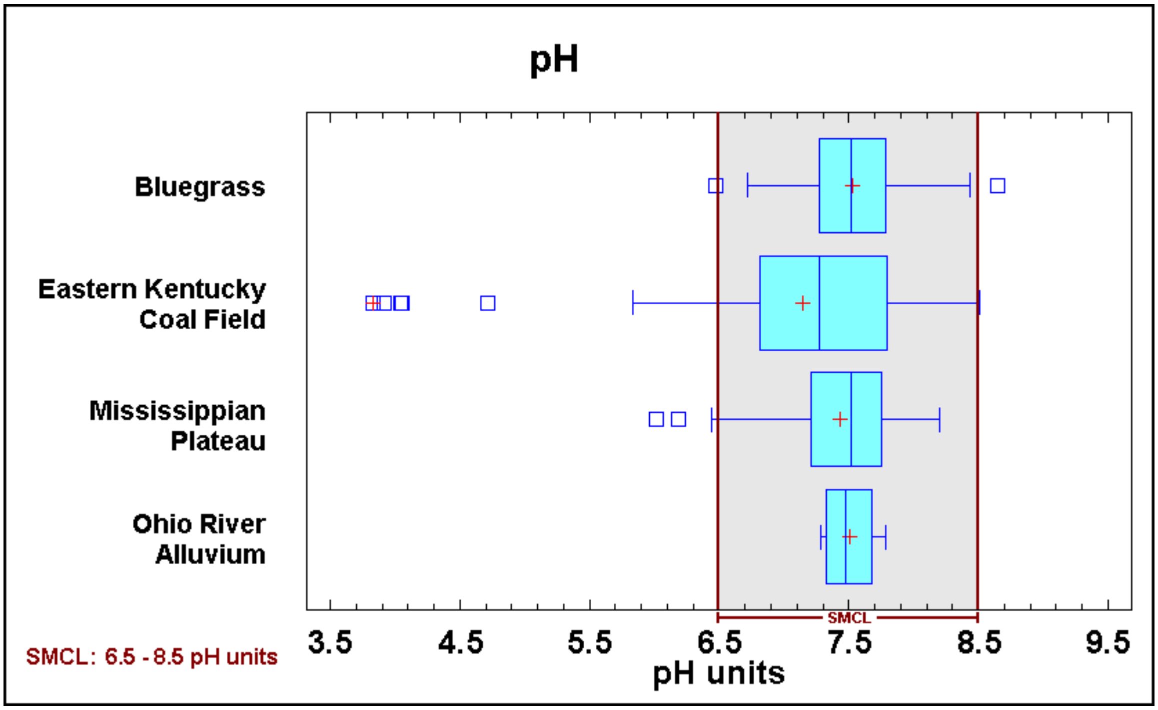

Figure 9. Boxplot of pH and Physiographic Regions

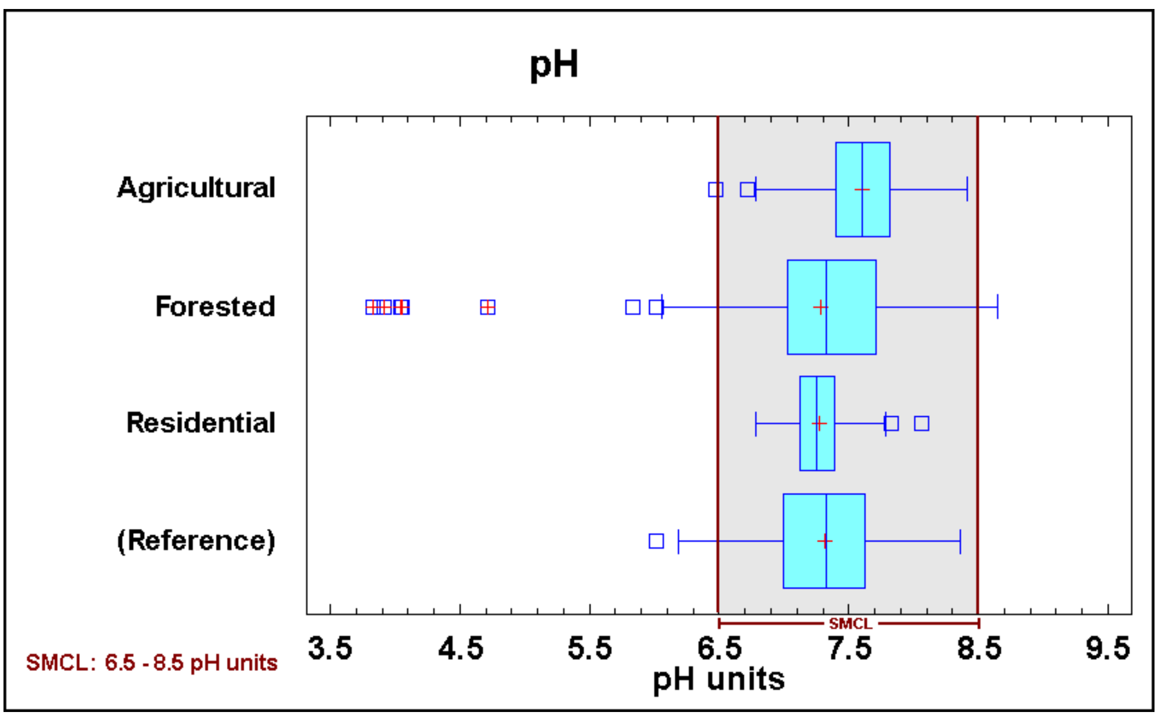

Figure 10. Boxplot of pH and Land Use

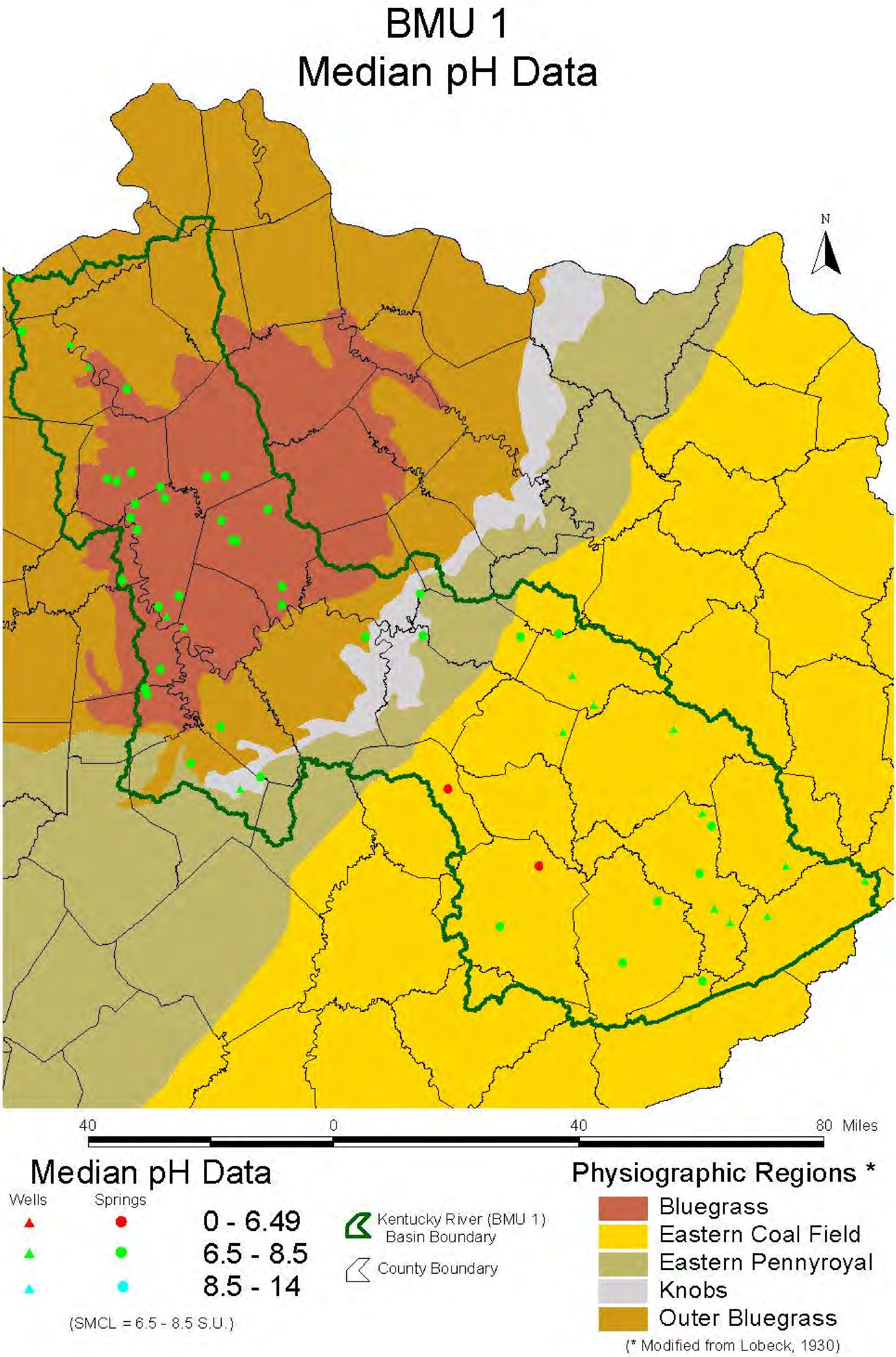

Figure 11. pH Map

Anions (Chloride, Fluoride, Sulfate)

Summary and descriptive statistics for anions in this report are shown in Tables 8 & 9.

Table 8. Anions Summary

BMU1: ANIONS SUMMARY[1]		CHLORIDE	FLUORIDE	SULFATE
NUMBER OF SAMPLES	TOTAL:	559	559	559
BY REGION:	BLUEGRASS (INNER & OUTER):	348	348	348
	EASTERN COAL FIELD:	133	133	133
	MISSISSIPPIAN PLATEAU:	74	74	74
	OHIO RIVER ALLUVIUM:	4	4	4
NUMBER OF DETECTIONS	TOTAL:	552	556	548
	% DETECTS (vs SAMPLES):	98.7%	99.5%	98.0%
BY REGION:	BLUEGRASS (INNER & OUTER):	348	346	347
	EASTERN COAL FIELD:	126	132	124
	MISSISSIPPIAN PLATEAU:	74	74	73
	OHIO RIVER ALLUVIUM:	4	4	4
NUMBER OF DETECTIONS ABOVE STANDARD	TOTAL:	5	3	50
	% DETECTIONS > STANDARD (of SAMPLES w/DETECTIONS):	0.9%	0.5%	9.1%
	% SAMPLES > STANDARD (of TOTAL SAMPLES):	0.9%	0.5%	8.9%
BY REGION:	BLUEGRASS (INNER & OUTER):	0	0	2
	EASTERN COAL FIELD:	5	3	48
	MISSISSIPPIAN PLATEAU:	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0
NUMBER OF SITES	TOTAL:	57	57	57
BY REGION:	BLUEGRASS (INNER & OUTER):	33	33	33
	EASTERN COAL FIELD:	19	19	19
	MISSISSIPPIAN PLATEAU:	4	4	4
	OHIO RIVER ALLUVIUM:	1	1	1
NUMBER OF SITES WITH DETECTIONS	TOTAL:	57	57	56
	% SITES W/DETECTIONS:	100.0%	100.0%	98.2%
BY REGION:	BLUEGRASS (INNER & OUTER):	33	33	33
	EASTERN COAL FIELD:	19	19	18
	MISSISSIPPIAN PLATEAU:	4	4	4
	OHIO RIVER ALLUVIUM:	1	1	1
NUMBER OF SITES WITH DETECTIONS ABOVE STANDARD	TOTAL:	2	1	7
	%SITES w/DETECTIONS>STANDARD (of SITES w/DETECTIONS):	3.5%	1.8%	12.5%
	%SITES w/DETECTIONS>STANDARD (of TOTAL SITES):	3.5%	1.8%	12.3%
BY REGION:	BLUEGRASS (INNER & OUTER):	0	0	2
	EASTERN COAL FIELD:	2	1	5
	MISSISSIPPIAN PLATEAU:	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0
	MCL (mg/L)	Secondary (mg/L)		Other
CHLORIDE	-	250		-
FLUORIDE	4	-		-
SULFATE	-	250		-

[1]Only 559 anion values out of 565 samples:
6 analyses: lab analyses did not include IC Anion Scan method.

Table 9. Anions Descriptive Statistics

BMU1: ANIONS DESCRIPTIVE STATISTICS						
	CHLORIDE (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**1770**	**13.2**	**0.584**	**< 1.0000**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	189	16.9	1.16	13.7
EASTERN COAL FIELD:	05/02/95	05/28/03	1770	4.82	0.584	< 1.0000
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	33.2	3.5	1.1	1.1
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	32.8	29.15	27.2	-
	FLUORIDE (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**17.5**	**0.196**	**< 0.008**	**0.21**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	1.3	0.21	0.01	0.21
EASTERN COAL FIELD:	05/02/95	05/28/03	17.5	0.17	< 0.008	0.05
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	0.22	0.09	0.01	0.06
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	0.149	0.141	0.114	-
	SULFATE (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**4280**	**43.6**	**0.216**	**< 5.0000**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	4280	38.65	1.39	34.9
EASTERN COAL FIELD:	05/02/95	05/28/03	1583	181	0.216	< 5.0000
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	108	59.15	< 5.0000	7.7
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	66	59.2	56	-

Chloride (Cl) is naturally occurring in most rocks and soils and is the primary constituent that makes water "salty”. Chloride also occurs in sewage, industrial brines and in urban runoff from the application of road salt. Brine water, or "connate water", occurs in the pore spaces and fractures of rocks and is sometimes found at shallow depths, especially in eastern Kentucky. Typically, however, water gradually becomes saltier as the depth increases. Over-pumping of fresh water in some wells can induce chloride-rich brines, which occur at depth to move, or "up well,” toward the discharge point. This phenomenon is known as "salt water intrusion.” As nonpoint source pollutants, chlorides are also associated with crude oil and are commonly produced as a by-product when oil is pumped to the surface. For disposal, these brines are typically re-injected into very deep and already briny, formations. Further, chloride-rich brines can contaminate freshwater aquifers through improperly cased or abandoned oil production wells.

Chloride was found in 552 of 559 samples (98.7%), but median values were low, 13.1 mg/L (Tables 8 & 9). Most chloride values clustered in a narrow range (Figures 12 and 13). Variations in chloride occurrence in BMU 1 appear to be the result of underlying geology, rather than nonpoint sources. Maximum values in this study were found in two wells in the Eastern Coal Field (Figure 14): Mountain Heritage in Letcher County (1770 mg/L) and four samples around 800 mg/L were found at Rousseau School in Breathitt County. Chlorides are known to occur at shallow depths in eastern Kentucky, and although oil wells and associated brine could affect groundwater in this province, none were noted in the immediate vicinity of these two sites.

No apparent impacts on groundwater quality from chloride from nonpoint sources were indicated in this study. Median values are low, reflecting normal groundwater quality variation. Fluoride (Fl) commonly occurs in trace quantities in many soils and rocks, including coal. Fluorite (CaF_2) is the primary fluorine mineral. Fluoride in the form of hydrogen fluoride enters the environment through atmospheric deposition from coal-fired power plants and from some manufacturing processes, especially aluminum smelting. Because small amounts of fluoride (1 ppm) in water help prevent tooth decay, public water systems often add this to their water. Some researchers claim this practice is potentially harmful and therefore the efficacy of drinking water fluoridation is a widely debated issue. The MCL for fluoride is 4 mg/L. Exposure to excessive amounts of fluoride can result in dental and skeletal fluorosis. Dental fluorosis is characterized by brittle, mottled and discolored tooth enamel and skeleton fluorosis causes a wide range of muscle and bone problems, including osteoporosis.

Conrad and others (1999a) compiled and analyzed statewide fluoride data. They reviewed 4,848 records from 2,630 sites and found only 24 analyses from 16 sites that exceeded the MCL.

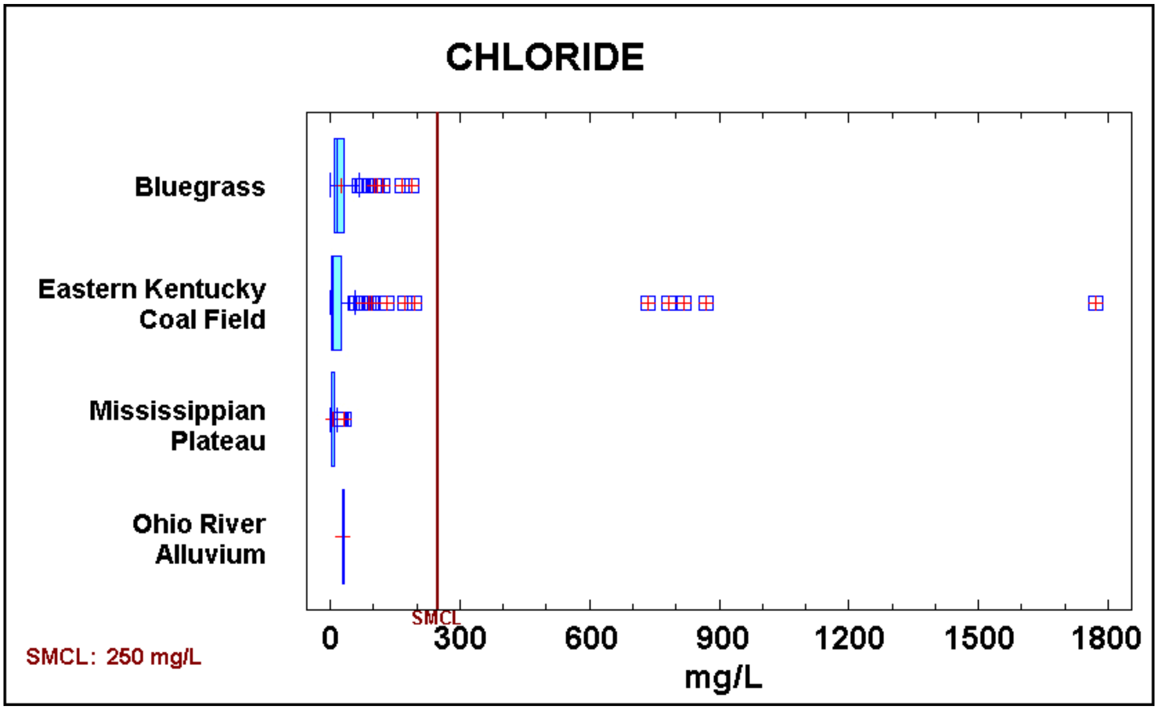

Figure 12. Boxplot of Chloride and Physiographic Regions

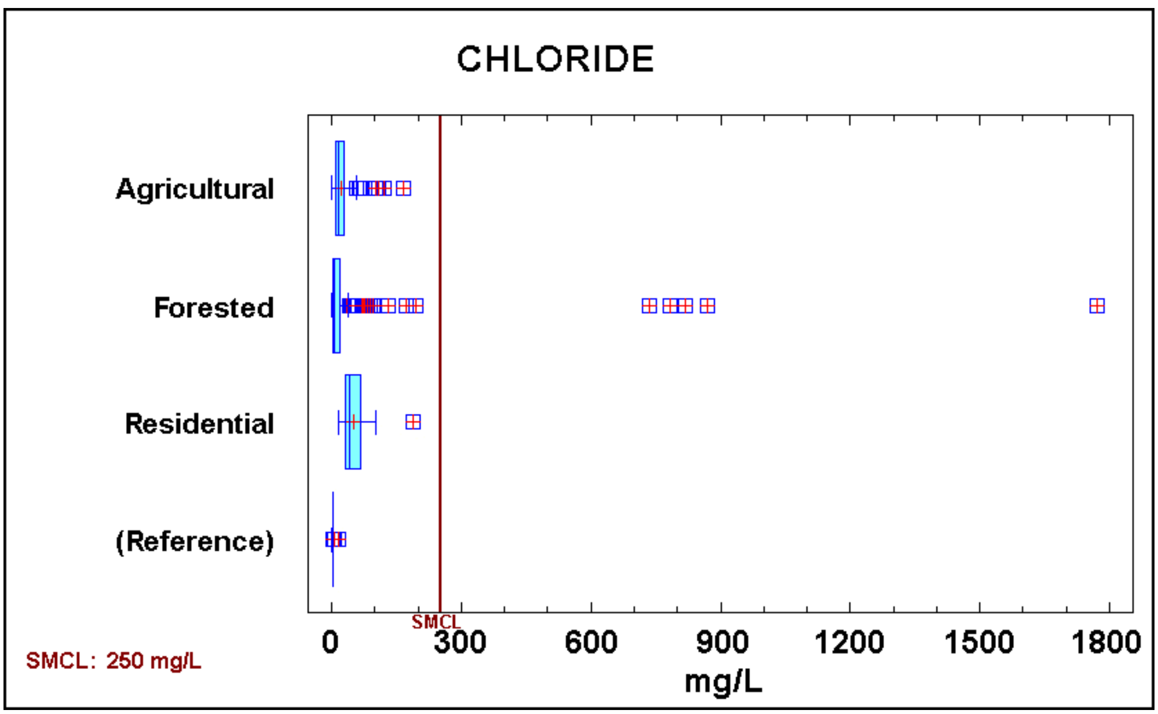

Figure 13. Boxplot of Chloride and Land Use

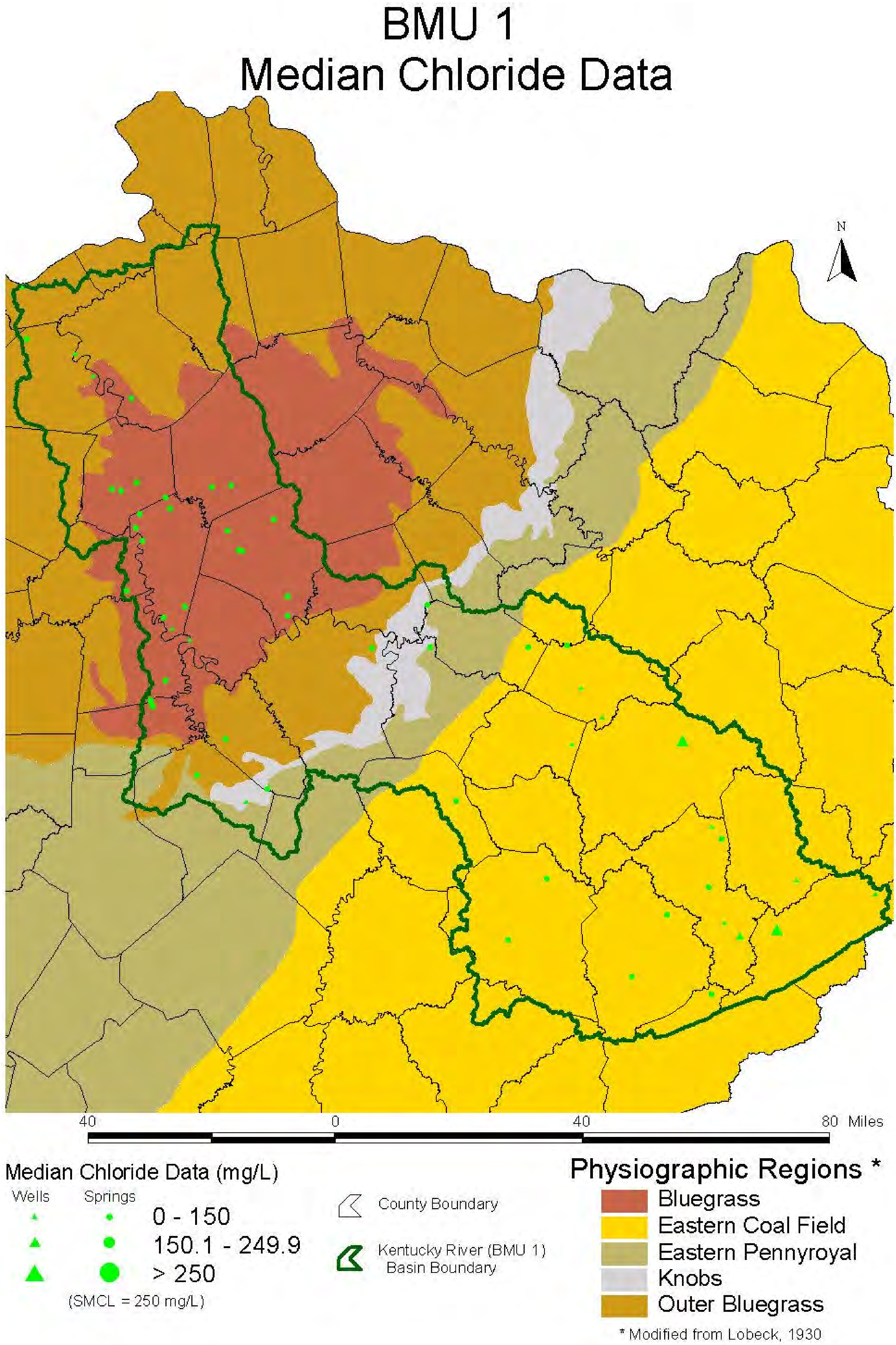

Figure 14. Chloride Map

As shown in Tables 8 & 9, fluoride was detected in 99.5% of the samples analyzed in this study (556/559), but was only found above MCL in four samples from two sites. These were Russell Cave Spring in Fayette County (64.8 mg/L) and the Viper Elementary School well in Perry County, where the highest value found was 17.5 mg/L. The one exceedance at Russell Cave is unexplained. However, the high values at Viper are the result of the removal of the raw water sampling tap and the installation of an in-line fluorinator that may have caused backflow into the well and also precluded the collection of a raw water sample. (Samples collected from the raw water tap before its removal measured less than 1.0 mg/L.)

High values shown in Figures 15 and 16 for forests and the Eastern Coal Field reflect the unexplained occurrence at Russell Cave Spring and the explained occurrence at Viper. Median values of fluoride ranged from 0.09 mg/L in the Mississippian Plateau to 0.141 in the Ohio River Alluvium, and are illustrated in Figure 17. This study suggests that fluoride is naturally-occurring in Kentucky's groundwater at low levels and no evidence was found that this parameter results from nonpoint source pollution.

Sulfate (SO_4) typically dissolves into groundwater from gypsum (hydrous calcium sulfate) and anhydrite (calcium sulfate), from the oxidation of several iron sulfides, such as pyrite (FeS) and from other sulfur compounds. In BMU 1 sulfate is common and naturally occurring, and therefore it is not a good indicator of nonpoint source pollution. Sulfate has an SMCL of 250 mg/L and amounts greater than this impart distasteful odor and taste to the water and commonly have a laxative effect.

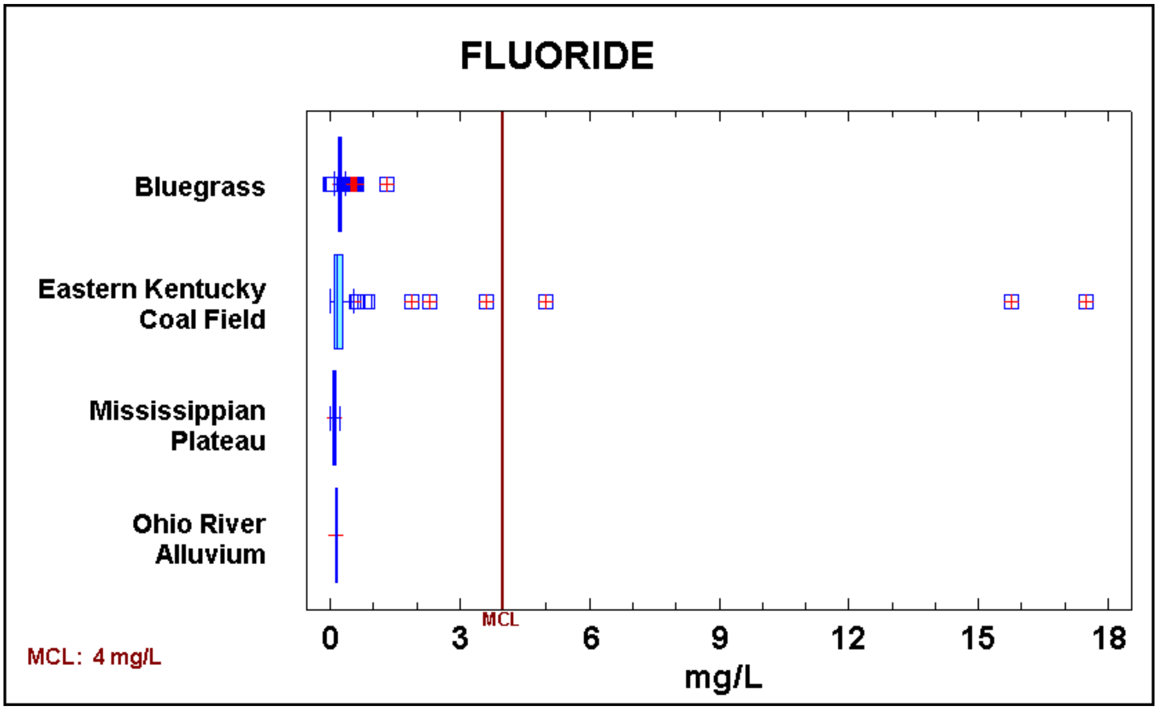

Figure 15. Boxplot of Fluoride and Physiographic Regions

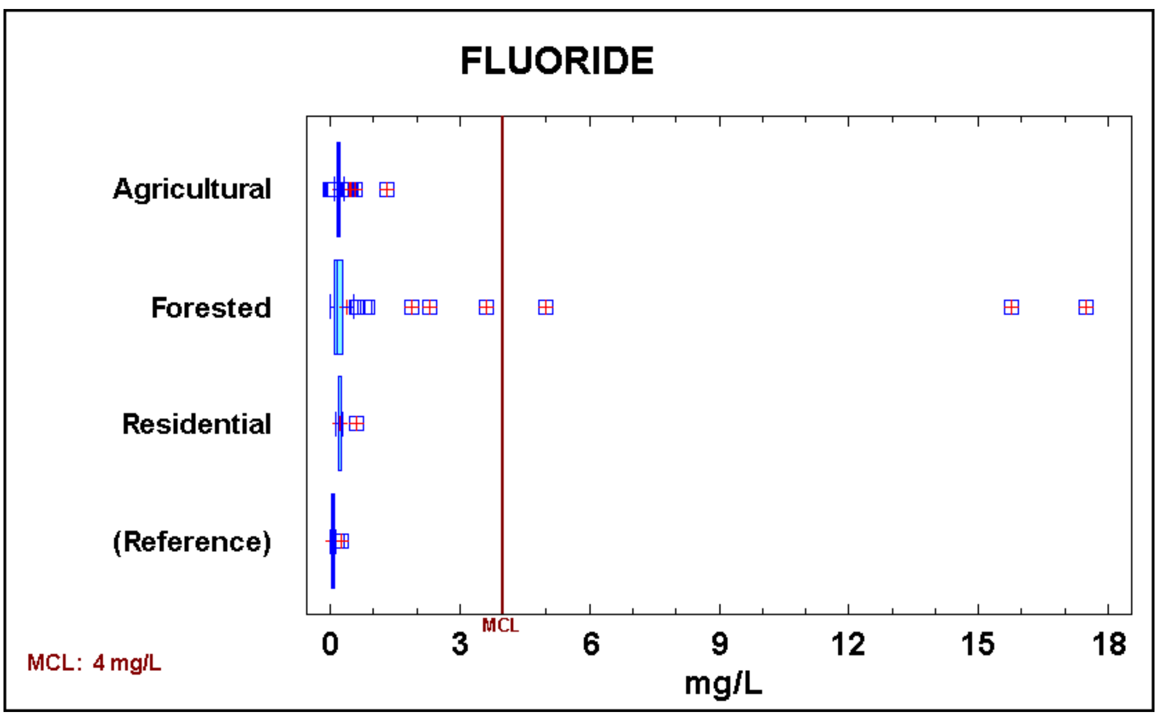

Figure 16. Boxplot of Fluoride and Land Use

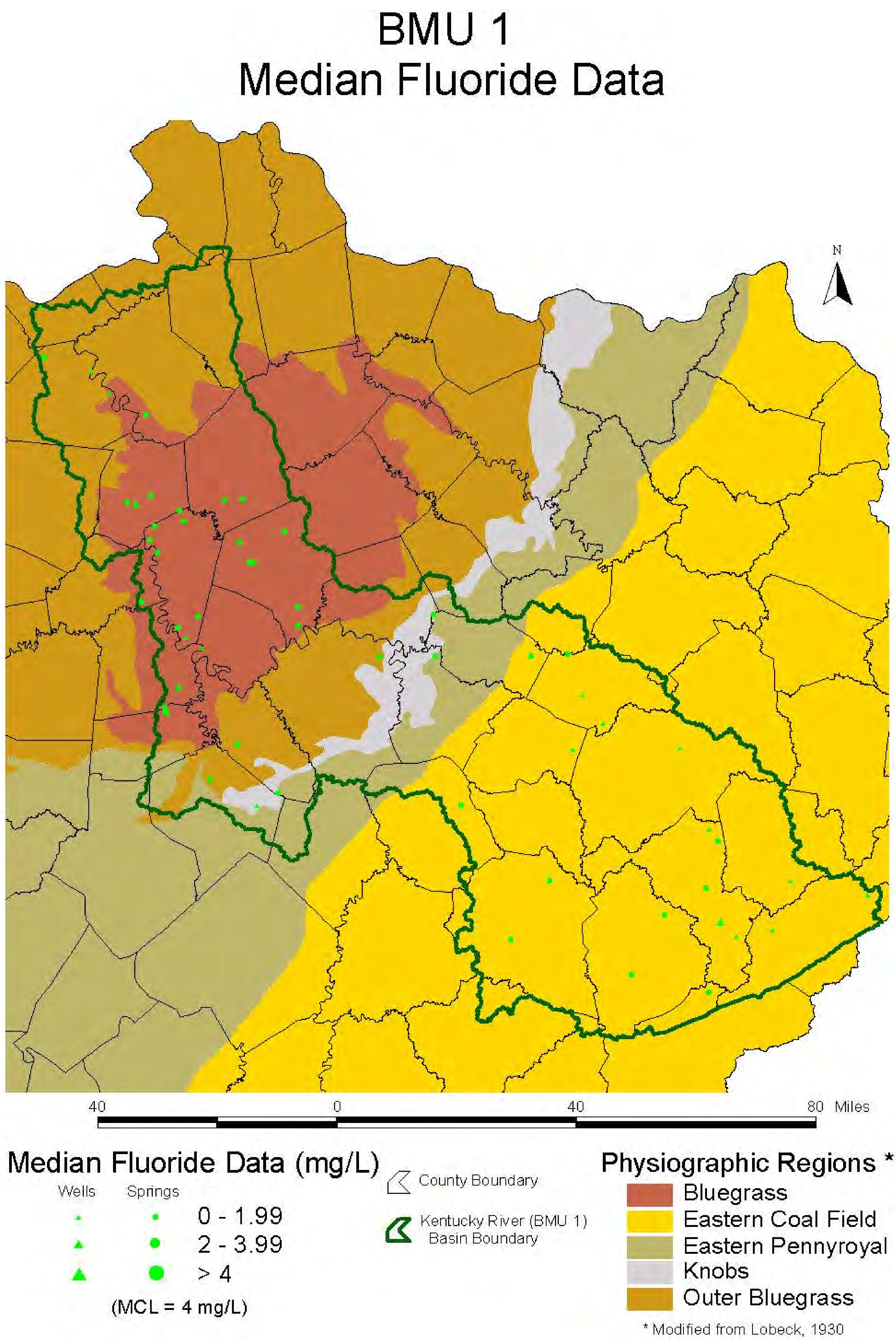

Figure 17. Fluoride Map

Sulfate was analyzed in 559 samples (Table 8) and was detected in 548 (98%). The Eastern Coal Field had the highest median value of 181 mg/L, and the Bluegrass the lowest, 38.65 mg/L (Table 9). The Mississippian Plateau and the Ohio River Alluvium had almost identical medians of 59.15 mg/L and 59.2 mg/L respectively. Boxplots (Figures 18 and 19) show that most sulfate values occur within narrow ranges whether plotted against physiographic provinces or land use, but outliers are common in the Bluegrass and the Eastern Coal Field and in agricultural and forested areas. Two springs in the Bluegrass, McCall's and Russell Cave, had single occurrences of anomalously high sulfate, which are unexplained, and two sites in the Eastern Coal Field, Dad's and Aunt Soph's springs had consistently high sulfate, which is known to occur naturally at high levels in this physiographic province. Distribution of sulfate in BMU 1 is shown in Figure 20.

The occurrence of sulfate in BMU 1 is believed to be naturally occurring and is not a nonpoint source contaminant of concern.

Metals (Arsenic, Barium, Iron, Lead, Manganese and Mercury)

For this report, groundwater data were reviewed for arsenic, barium, iron, lead, manganese and mercury. Barium, iron, and manganese were the most common metals found; lead and arsenic were much less common; and mercury was only detected in one sample. Summaries and descriptive statistics of the six metals included in this study are shown in Tables 10 and 11.

These metals were chosen because they are important contributors to ambient groundwater quality and can be introduced as pollutants from nonpoint source activities. They are common to trace constituents of soils (Logan and Miller, 2002) and sedimentary rocks, including limestone, dolostone, coal and black shales (Dever, 2000; USGS, 2002b; Tuttle and others, 2001). In water, low pH values and higher dissolved oxygen content increase the dissolution of metals. Common

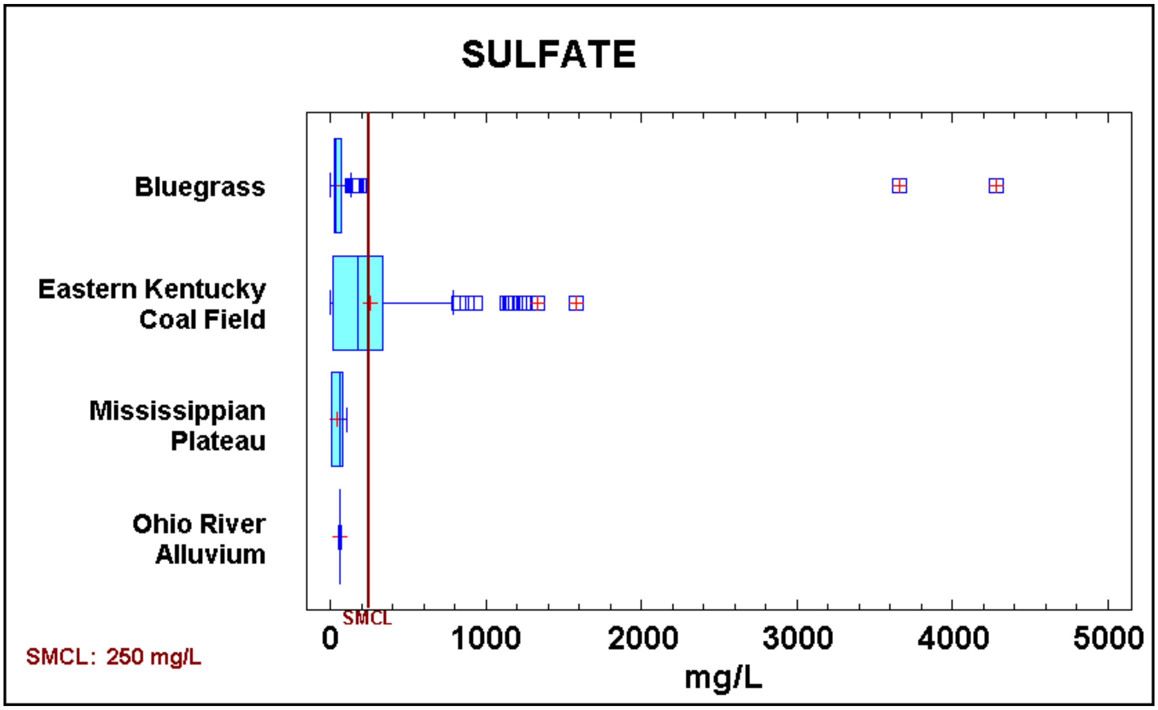

Figure 18. Boxplot of Sulfate and Physiographic Regions

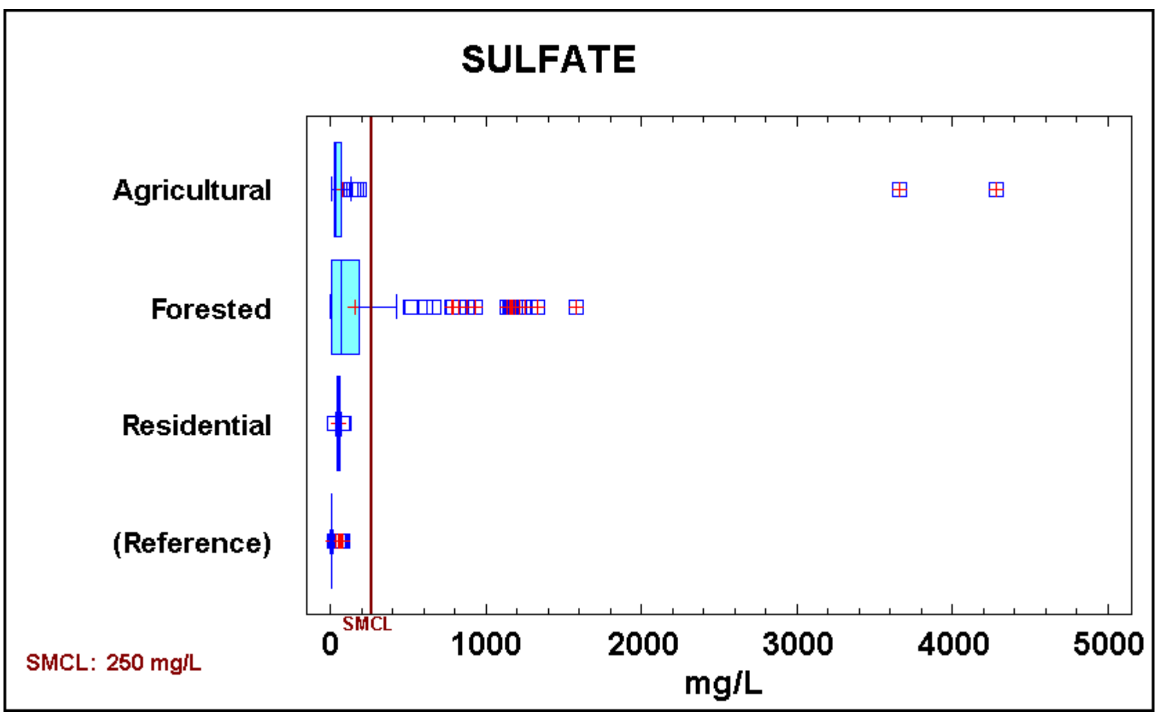

Figure 19. Boxplot of Sulfate and Land Use

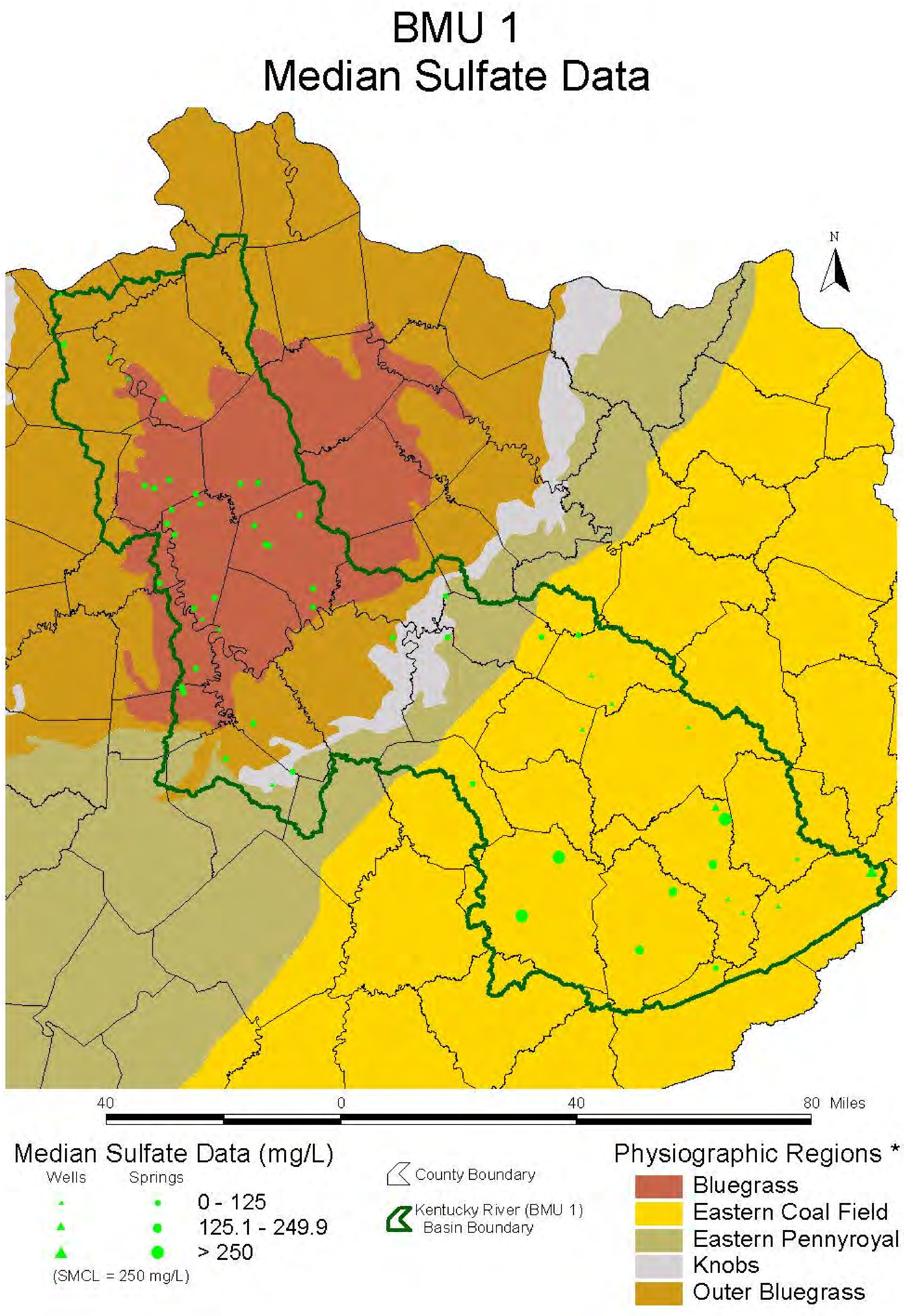

Figure 20. Sulfate Map

Table 10. Metals Summary

BMU1: METALS SUMMARY[3]

		ARSENIC	BARIUM	IRON[1]	LEAD [2]	MANGANESE [1]	MERCURY[4]
NUMBER OF SAMPLES	TOTAL:	395	393	393	395	393	392
BY REGION:	BLUEGRASS (INNER & OUTER):	248	246	246	248	246	245
	EASTERN COAL FIELD:	104	104	104	104	104	104
	MISSISSIPPIAN PLATEAU:	39	39	39	39	39	39
	OHIO RIVER ALLUVIUM:	4	4	4	4	4	4
NUMBER OF DETECTIONS	TOTAL:	15	388	379	41	355	1
	% DETECTS (vs SAMPLES):	3.8%	98.7%	96.4%	10.4%	90.3%	0.3%
BY REGION:	BLUEGRASS (INNER & OUTER):	9	241	240	21	232	1
	EASTERN COAL FIELD:	5	104	98	17	91	0
	MISSISSIPPIAN PLATEAU:	1	39	37	0	28	0
	OHIO RIVER ALLUVIUM:	0	4	4	3	4	0
NUMBER OF DETECTIONS ABOVE STANDARD	TOTAL:	5	4	100	3	91	0
	% DETECTIONS > STANDARD (of SAMPLES w/DETECTIONS):	33.3%	1.0%	26.4%	7.3%	25.6%	0.0%
	% SAMPLES > STANDARD (of TOTAL SAMPLES):	1.3%	1.0%	25.4%	0.8%	23.2%	0.0%
BY REGION:	BLUEGRASS (INNER & OUTER):	5	0	60	2	65	0
	EASTERN COAL FIELD:	0	4	32	0	22	0
	MISSISSIPPIAN PLATEAU:	0	0	4	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	4	1	4	0
NUMBER OF SITES[3]	TOTAL:	52	52	52	52	52	51
BY REGION:	BLUEGRASS (INNER & OUTER):	31	31	31	31	31	30
	EASTERN COAL FIELD:	17	17	17	17	17	17
	MISSISSIPPIAN PLATEAU:	3	3	3	3	3	3
	OHIO RIVER ALLUVIUM:	1	1	1	1	1	1
NUMBER OF SITES WITH DETECTIONS	TOTAL:	8	51	52	20	51	1
	% SITES W/DETECTIONS:	15.4%	98.1%	100.0%	38.5%	98.1%	2.0%
BY REGION:	BLUEGRASS (INNER & OUTER):	4	30	31	13	30	1
	EASTERN COAL FIELD:	3	17	17	6	17	0
	MISSISSIPPIAN PLATEAU:	1	3	3	0	3	0
	OHIO RIVER ALLUVIUM:	0	1	1	1	1	0
NUMBER OF SITES WITH DETECTIONS ABOVE STANDARD	TOTAL:	1	1	32	3	24	0
	%SITES w/DETECTIONS>STANDARD (of SITES w/DETECTIONS):	12.5%	2.0%	61.5%	15.0%	47.1%	0.0%
	%SITES w/DETECTIONS>STANDARD (of TOTAL SITES):	1.9%	1.9%	61.5%	5.8%	46.2%	0.0%
BY REGION:	BLUEGRASS (INNER & OUTER):	1	0	18	2	16	0
	EASTERN COAL FIELD:	0	1	10	0	7	0
	MISSISSIPPIAN PLATEAU:	0	0	3	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	1	1	1	0

	MCL (mg/L)	Secondary (mg/L)	Other
ARSENIC	0.010	-	-
BARIUM	2.000	-	-
IRON	-	0.300	-
LEAD	-	-	0.015
MANGANESE	-	0.050	-
MERCURY	0.002	-	-

[1]SDWR used in absence of MCL

[2]Lead and copper are regulated by a Treatment Technique that requires systems to control the corrosiveness of their water. If more than 10% of tap water samples exceed the action level, water systems must take additional steps. (EPA website)

[3]Only 393 metals values out of 565 samples:
172 analyses: lab samples prior to October 1997 reported metals as dissolved, not total (52 out of 57 sites). Since EPA uses total, not dissolved, for MCL standards, dissolved results were not considered in this study.

[4]Only 395 arsenic & lead values of 565 samples:
2 analyses: metal analyses in 1997 included only arsenic, lead, selenium and thallium.

[5]Only 392 mercury values out of 565 samples:
1 analysis: one-time sample event for Hack Well processed through different lab - mercury not included.

Table 11. Metals Descriptive Statistics

BMU1: METALS DESCRIPTIVE STATISTICS						
	ARSENIC (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**11/05/97**	**06/11/03**	**0.076**	**< 0.002**	**< 0.0005**	**< 0.002**
BLUEGRASS (INNER & OUTER):	11/05/97	06/11/03	0.076	< 0.002	< 0.0005	< 0.002
EASTERN COAL FIELD:	03/11/98	05/28/03	0.008	< 0.002	< 0.001	< 0.002
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	< 0.002	< 0.002	< 0.001	< 0.002
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.002	< 0.002	< 0.002	< 0.002
	BARIUM (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**02/10/98**	**06/11/03**	**2.95**	**0.029**	**< 0.001**	**0.016**
BLUEGRASS (INNER & OUTER):	02/10/98	06/11/03	0.328	0.026	< 0.001	0.023
EASTERN COAL FIELD:	03/11/98	05/28/03	2.95	0.03225	0.008	0.031
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	0.063	0.03	0.019	0.038
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	0.116	0.108	0.1	0.108
	IRON (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**02/10/98**	**06/11/03**	**20.8**	**0.112**	**< 0.001**	**< 0.007**
BLUEGRASS (INNER & OUTER):	02/10/98	06/11/03	12.2	0.1205	< 0.001	< 0.007
EASTERN COAL FIELD:	03/11/98	05/28/03	20.8	0.127	< 0.001	< 0.007
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	0.75	0.056	< 0.005	0.02
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	1.16	0.663	0.56	-
	LEAD (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**11/05/97**	**06/11/03**	**0.042**	**< 0.002**	**< 0.001**	**< 0.002**
BLUEGRASS (INNER & OUTER):	11/05/97	06/11/03	0.042	< 0.002	< 0.001	< 0.002
EASTERN COAL FIELD:	03/11/98	05/28/03	0.013	< 0.002	< 0.001	< 0.002
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	< 0.002	< 0.002	< 0.001	< 0.002
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	0.017	0.0035	< 0.002	-
	MANGANESE (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**02/10/98**	**06/11/03**	**1.38**	**0.015**	**< 0.001**	**< 0.001**
BLUEGRASS (INNER & OUTER):	02/10/98	06/11/03	1.01	0.018	< 0.001	< 0.001
EASTERN COAL FIELD:	03/11/98	05/28/03	1.38	0.015	< 0.001	< 0.005
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	0.035	0.003	< 0.001	< 0.001
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	0.143	0.133	0.128	-
	MERCURY (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**02/10/98**	**06/11/03**	**0.000065**	**< 0.00005**	**< 0.00005**	**< 0.00005**
BLUEGRASS (INNER & OUTER):	02/10/98	06/11/03	0.000065	< 0.00005	< 0.00005	< 0.00005
EASTERN COAL FIELD:	03/11/98	05/28/03	< 0.00005	< 0.00005	< 0.00005	< 0.00005
MISSISSIPPIAN PLATEAU:	06/03/98	06/11/03	< 0.00005	< 0.00005	< 0.00005	< 0.00005
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.00005	< 0.00005	< 0.00005	< 0.00005

anthropogenic nonpoint sources of metals include mining, urban run-off, industrial operations, land farming of sewage and other waste and emissions from coal-fired power plants. The provenance of high concentrations of metals in groundwater is sometimes difficult to interpret and may indicate point sources, nonpoint sources, or natural sources. Comparison with reference reach springs (Table 5), as well as reviewing relevant literature, can prove useful.

A complete suite of total and dissolved metals was analyzed for each sample collected. Because MCLs are based upon total metal analysis, the results presented below are for total, rather than dissolved, concentrations. Although several other metals, such as silver, vanadium and gold were analyzed, detections of these were exceedingly rare and invariably at very low concentrations. Consequently, these results are not presented here.

Arsenic (As) is found as a trace element in coal, shale, limestone, and dolostone (USGS, 2002b; Dever, 2000). Arsenic-containing minerals, occurring as veins or disseminated in sedimentary rocks or soils derived from them, include arsenopyrite (FeAsS), pyrite and marcasite (different crystalline forms of FeS2), and sphalerite (ZnFeS). The most prevalent use of arsenic is as a wood preservative, but other anthropogenic sources include atmospheric deposition from coal-fired power plants and metal-smelting/manufacturing processes. Historical and current agricultural use of arsenic-containing pesticides is very limited, according to Collins (Kentucky Division of Pesticides, personal communication May, 2004) with only about 250 pounds of arsenic sold in 2002 (Division of Pesticides, 2002). Another historic use of arsenic included embalming fluid, especially from about 1860 until its use was banned in 1910 (Fetter, 1992).

Arsenic occurs in organic and inorganic forms and generally the latter are more harmful to human health, where arsenic exposure has been linked to bladder and other cancers (USGS, 2000). Arsenic has an MCL of 0.010 mg/L, which was lowered by the US EPA from 0.05 mg/L in 2001. Public water utilities will be required to meet the new standard by January 2006.

Blanset and Goodmann (2002) reviewed the occurrence of arsenic in Kentucky's groundwater. In their study of 1,249 ambient groundwater samples from 240 sites, they found 10 sites with one or more samples exceeding the MCL. They suggested that the " . . . most prominent source of arsenic in Kentucky's aquifers results from the oxidation of arsenopyrite, incorporated in iron hydroxides." Welch and others (1999) reached a similar conclusion in their review of national data and the USGS (2002a) states that the majority of arsenic in groundwater is the " . . . result of minerals dissolving from weathered rocks and soils." In his review, which included historical data of varying quality, Fisher (2002) found that for ambient groundwater about 95% of 4,402 analyses from 930 sites were less than the MCL.

For this study, arsenic was analyzed for 395 samples (Table 10) and was detected in 15 (3.8%), and the median value was 0.002 mg/L (Table 11). One site, the Glenwood Hall well in Owen County, exceeded the MCL in five samples. This well produces from alluvium adjacent to the Kentucky River, and therefore its chemistry is not typical of the carbonate aquifers underlying the Bluegrass. Arsenic, and other metals, in this well may be related to the erosion upstream on the Kentucky River of mineralized veins containing arsenic and the deposition of these metal-rich sediments in the alluvium, combined with reduced conditions in the aquifer or at the borehole.

Boxplots of arsenic compared to physiographic provinces and land use are shown in Figures 21 and 22, and map distribution in Figure 23. Arsenic has a narrow range of occurrence at low values, but outliers are common. Most of the high outliers in the forest and Bluegrass are the result of detections at the Glenwood Hall well.

In summary, the occurrence of arsenic in BMU 1 groundwater is from natural processes and this metal is not a nonpoint source pollutant of concern at this time.

Barium (Ba) occurs most commonly as the mineral barite ($BaSO_4$) but also as witherite ($BaCO_3$). Barium occurs in the shales and coals of the Eastern Coal Field where Wunsch (1991) determined that sulphur-reducing bacteria in Eastern Coal Field aquifers affects the chemical equilibrium of groundwater ". . . thus allowing for greater concentrations of barium to exist in solution." Barium is also found as mineralized veins within the limestones and shales of the Inner Bluegrass of central Kentucky. Barium is used in a variety of products including drilling mud, glass and paint. The MCL for barium is 2.0 mg/L and exposure to high levels of barium has been associated with cardiovascular problems such as high blood pressure.

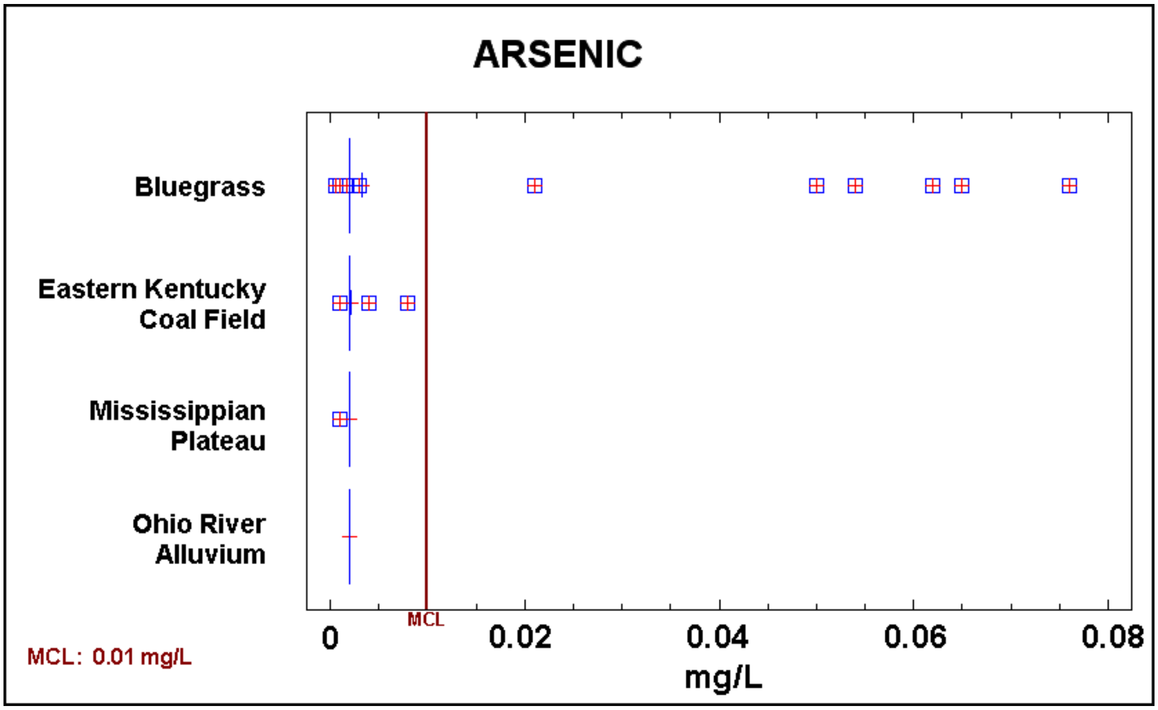

Figure 21. Boxplot of Arsenic and Physiographic Regions

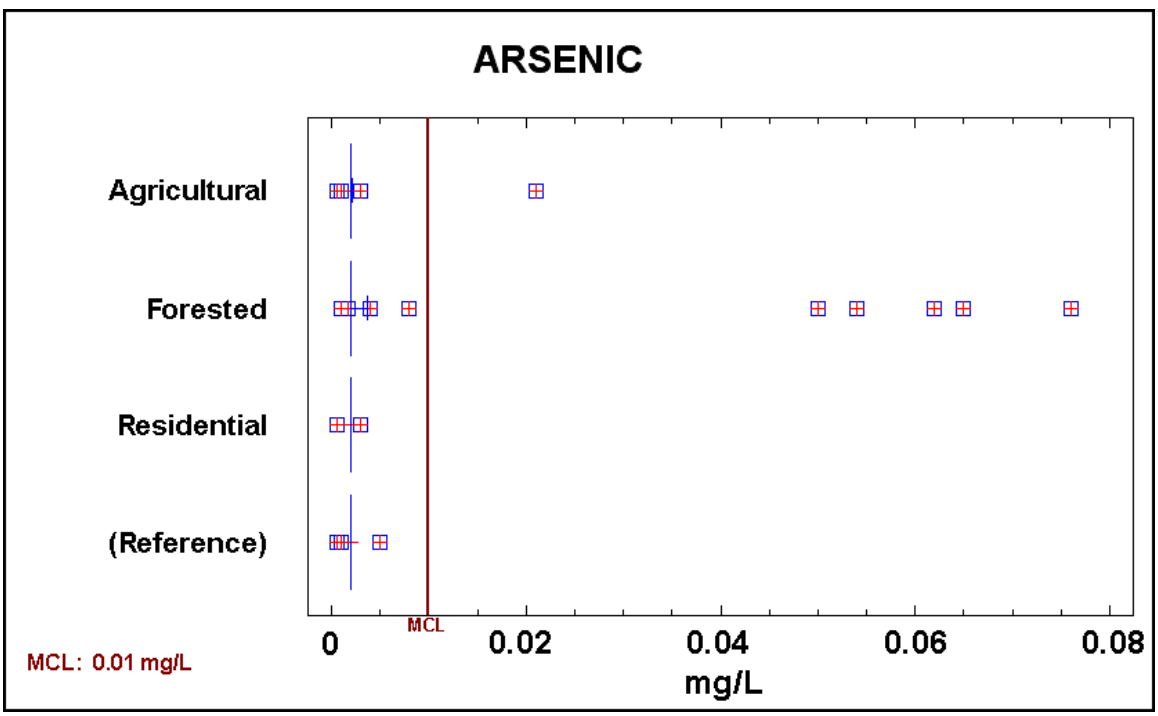

Figure 22. Boxplot of Arsenic and Land Use

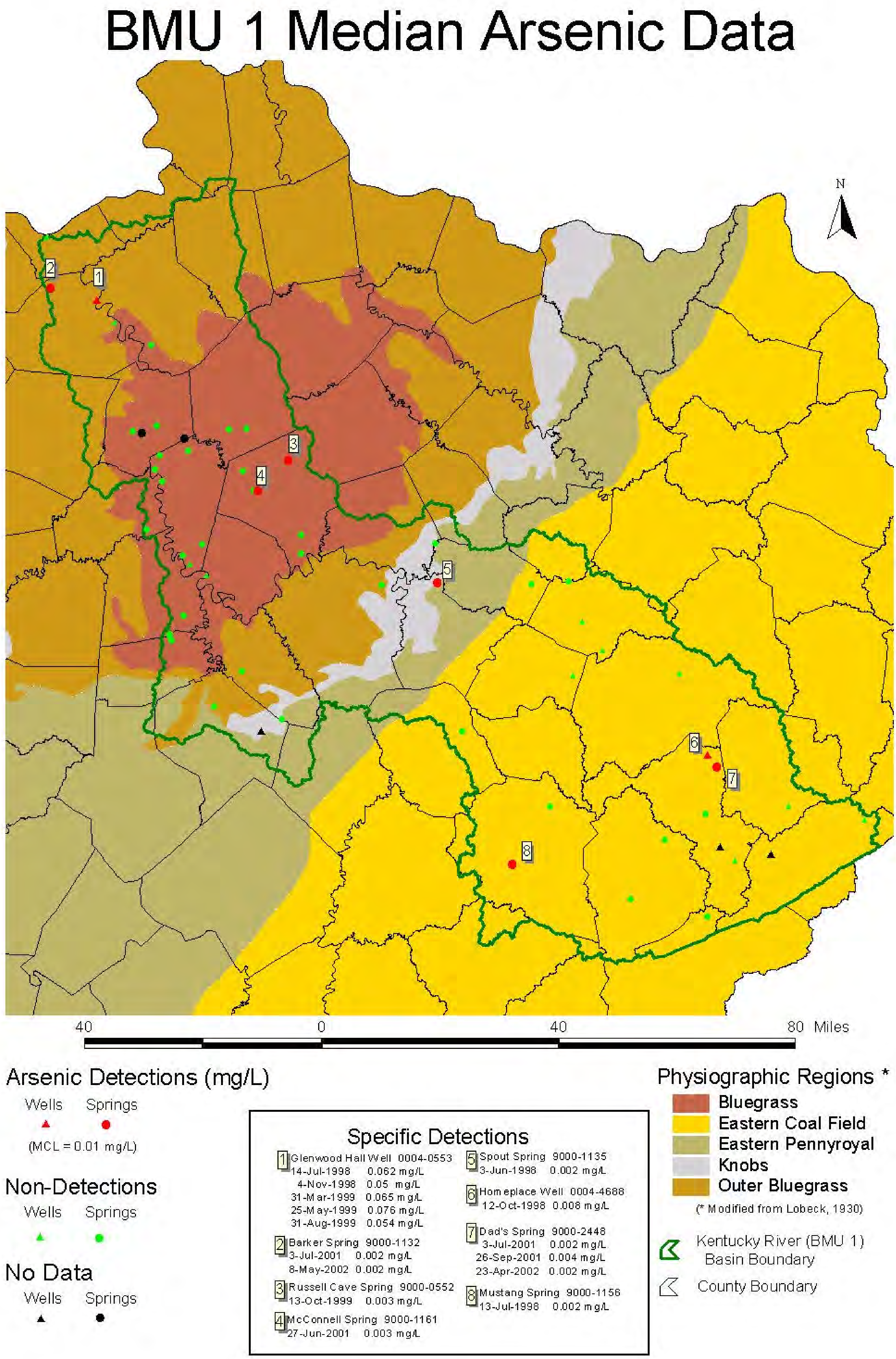

Figure 23. Arsenic Map

Barium was analyzed in 393 samples for this study and was found in 388, or 98.7% (Table 10). Plotted against physiographic provinces and land use, the majority of barium values occur within narrow ranges (Figures 24 and 25). The widest range of values occurs in the Eastern Coal Field and in forested areas. Four sites in the Eastern Coal Field (Figure 26) had the highest detections of barium, including the Rousseau well in Breathitt County, with values approaching 3.0 mg/L, and the Whiskey Store well in Perry County, which measured from about 1-2 mg/L. The Baker and Homeplace wells were also high in barium, as was the Glenwood Hall well in Owen County.

Barium distribution in BMU 1 is most likely naturally occurring and no nonpoint sources were noted that could explain the high results in the wells discussed above.

Iron (Fe) is commonly found in trace amounts (or more) in practically all sediments and sedimentary rocks (Driscoll, 1986). Iron is one of the most common groundwater quality problems encountered in wells in Kentucky. However, in almost all cases, elevated iron is naturally occurring and therefore not generally diagnostic of nonpoint source pollution. One notable exception is that high levels of iron are often associated with run-off from coal mining. Typically, this high iron discharge affects surface water rather than groundwater, but wells penetrating old mine works, or those under the direct influence of surface water, can also be affected.

Iron is a common element found in most groundwater and affects the suitability of water for drinking and industrial use. Iron helps transport oxygen in the blood and is essential for good health. Excessive iron in water used for human consumption is an aesthetic, rather than a health-based, concern. Iron has an SMCL of 0.3 mg/L. For most people, amounts greater than this cause objectionable taste and odor.

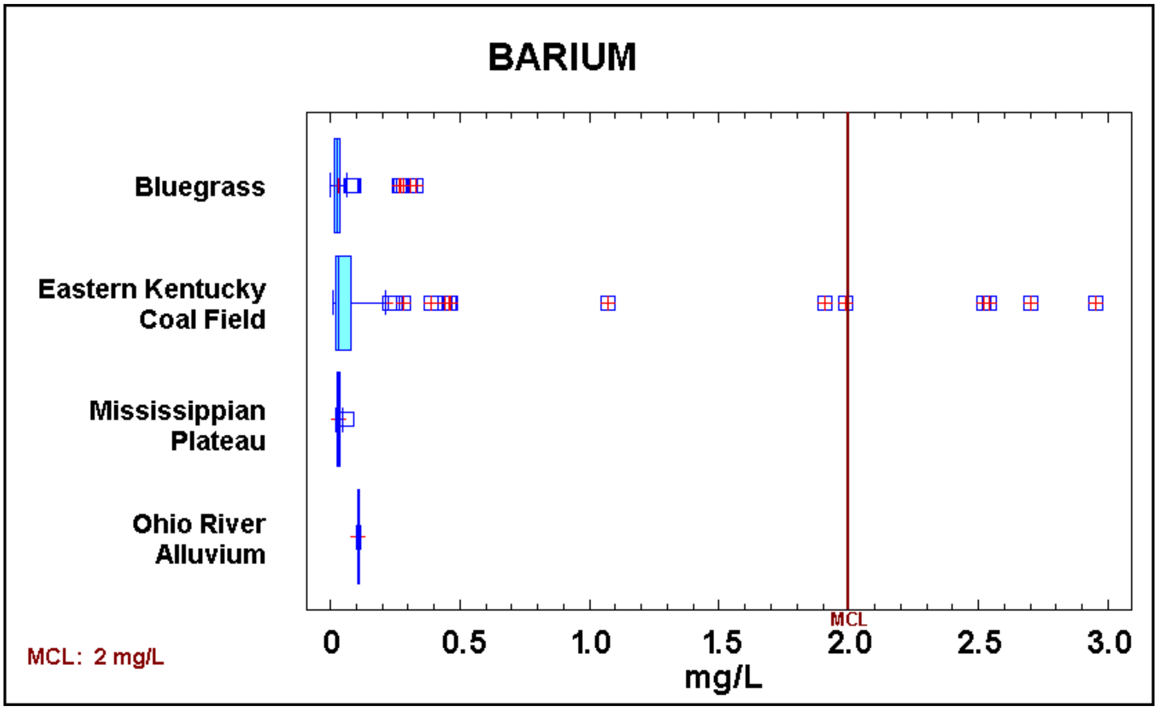

Figure 24. Boxplot of Barium and Physiographic Regions

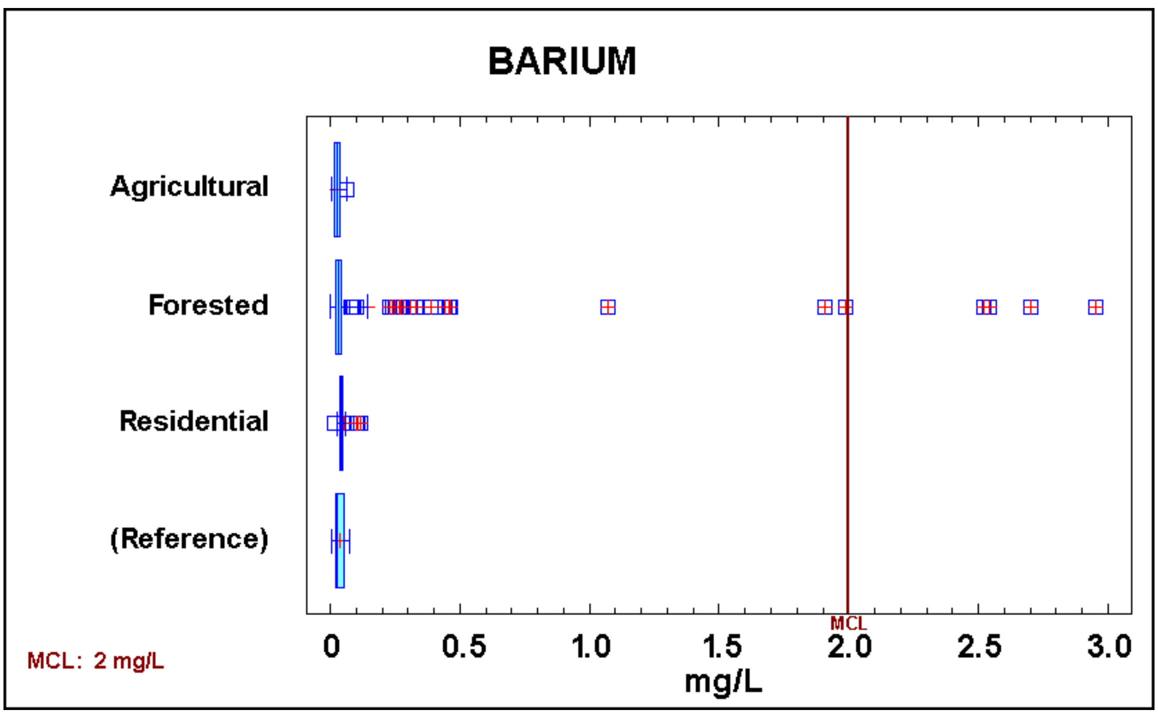

Figure 25. Boxplot of Barium and Land Use

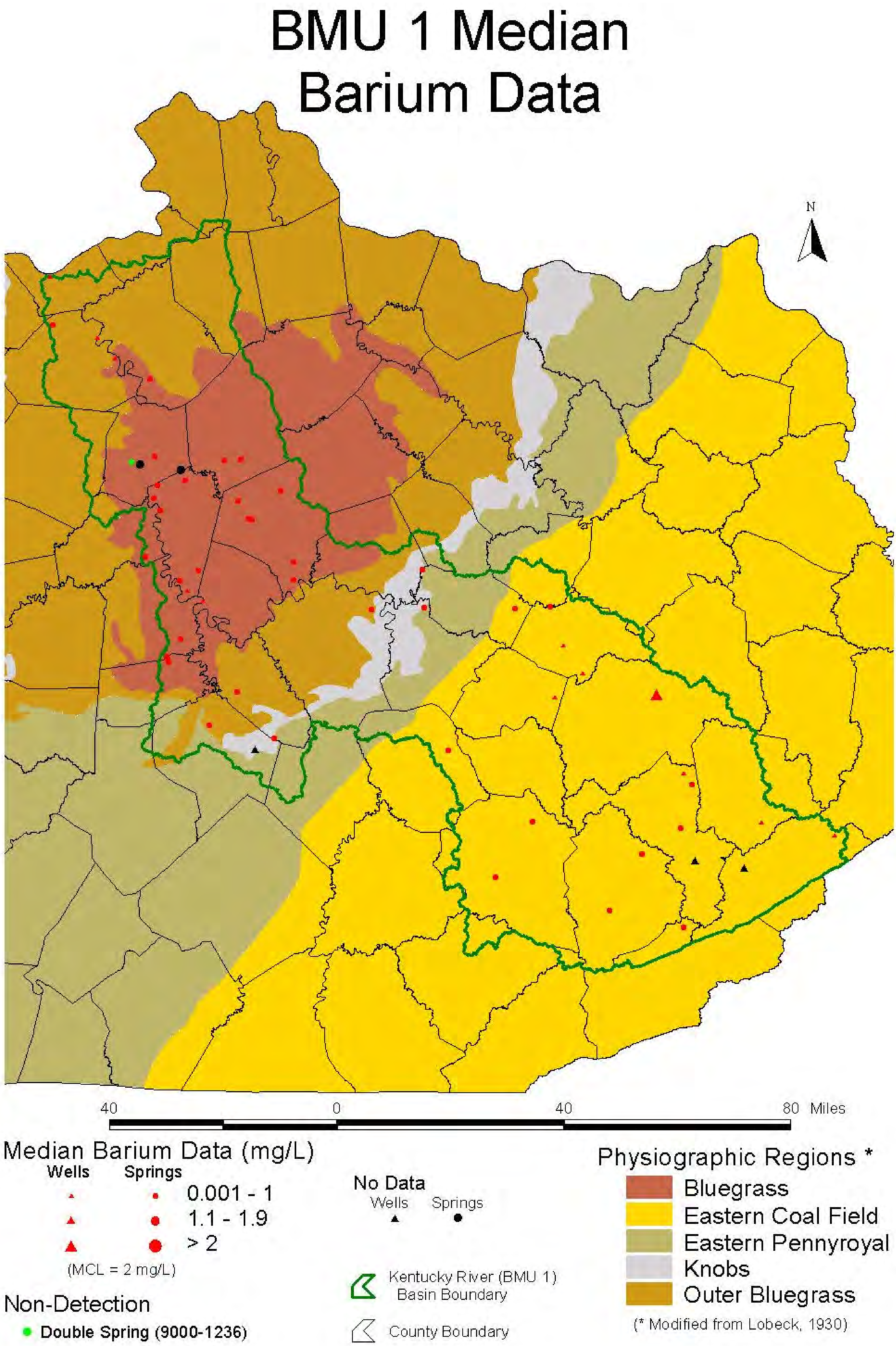

Figure 26. Barium Map

Iron causes problems when it changes from the dissolved, or *ferrous*, state to the precipitated state, or as *ferric* iron. Precipitated iron can coat or encrust well screens and casing, pipes, pumping equipment and plumbing fixtures. Additionally, various metal-reducing bacteria, or “iron bacteria”, that feed on iron can coat fixtures. These bacteria can grow to such an extent that a gelatinous mass is formed that can completely plug a well and associated equipment. Although iron bacteria are not usually a health problem, they render the water unpalatable and are indicators of unsanitary conditions that may harbor other, more harmful, bacteria.

Iron (Table 10) was measured in 393 samples and detected in 379 (96.4%). Median values (Table 11) ranged from a low of 0.056 mg/L in the Mississippian Plateau to a high of 0.663 mg/L in the Ohio River Alluvium. The Eastern Coal Field, which is well known for the high content of iron in wells, and the Bluegrass had surprisingly similar median values of 0.127 mg/L and 0.1205 mg/L respectively. Figures 27 and 28 plot the distribution of iron against physiographic provinces and land use. Median values are low, but there is a great amount of variability, especially in the Bluegrass and the Eastern Coal Field, and in agricultural and forested areas. Map distribution is shown in Figure 29. The highest iron values were found in the Rousseau and Baker wells in the Eastern Coal Field. Glenwood Hall had the highest iron content in the Bluegrass; however, as noted above, this well is completed in alluvium and does not produce from the carbonate bedrock typical of the Bluegrass.

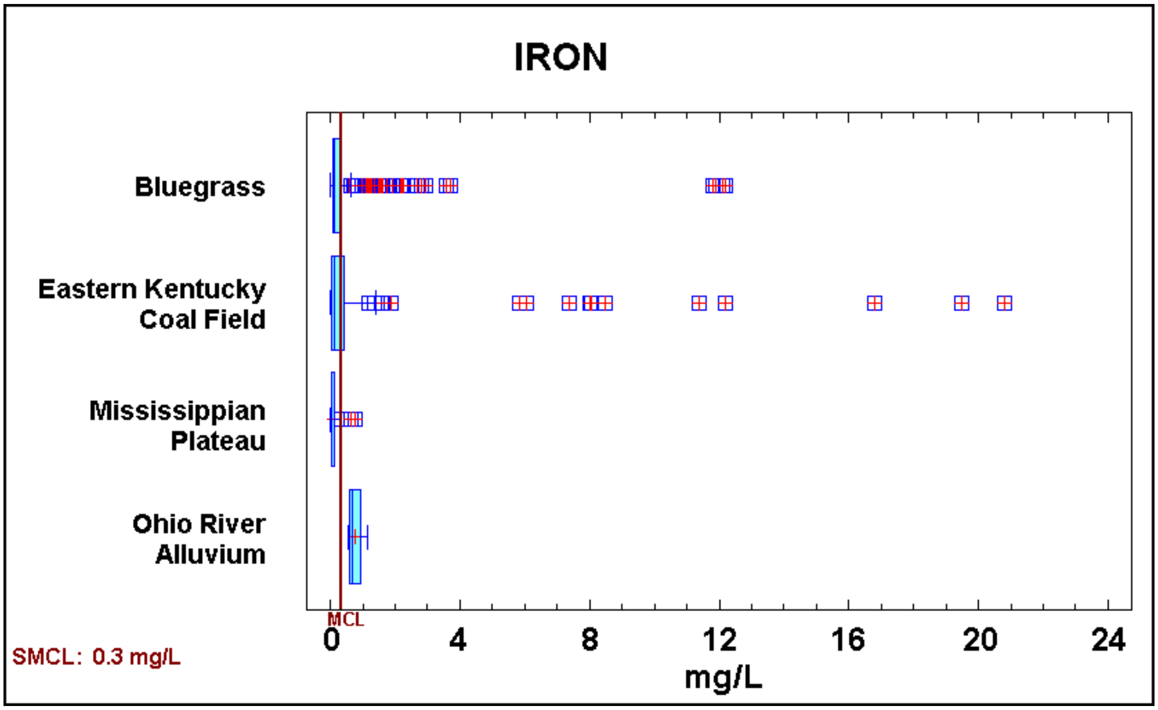

Figure 27. Boxplot of Iron and Physiographic Regions

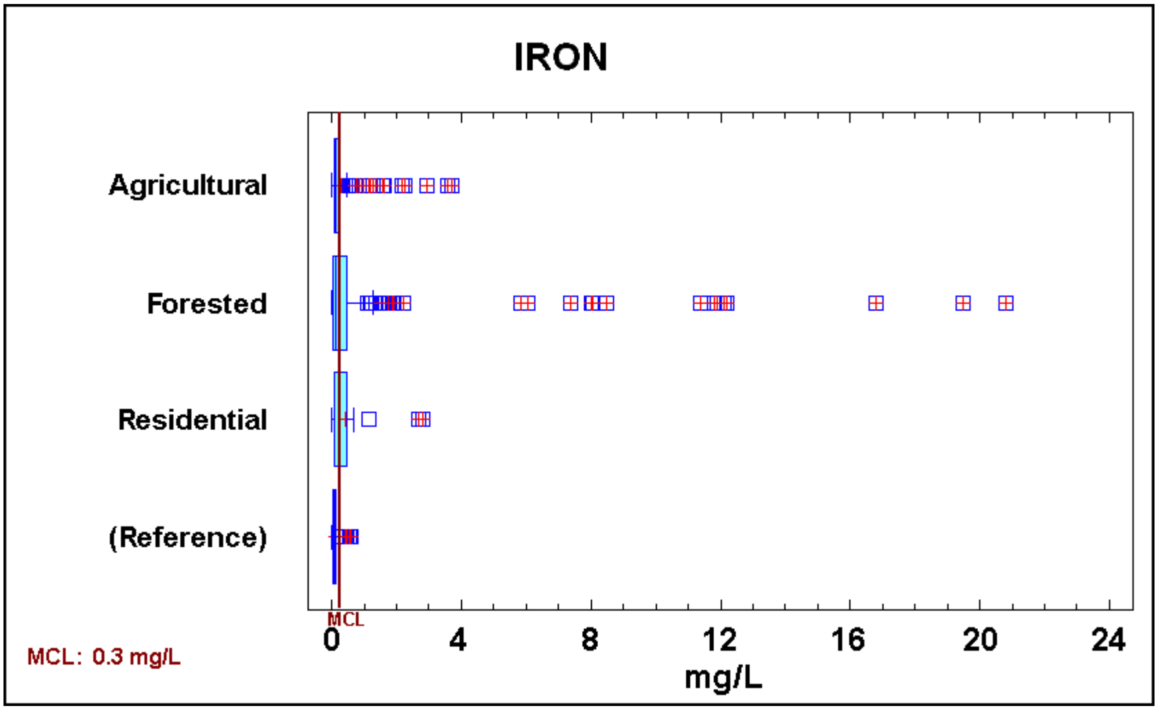

Figure 28. Boxplot of Iron and Land Use

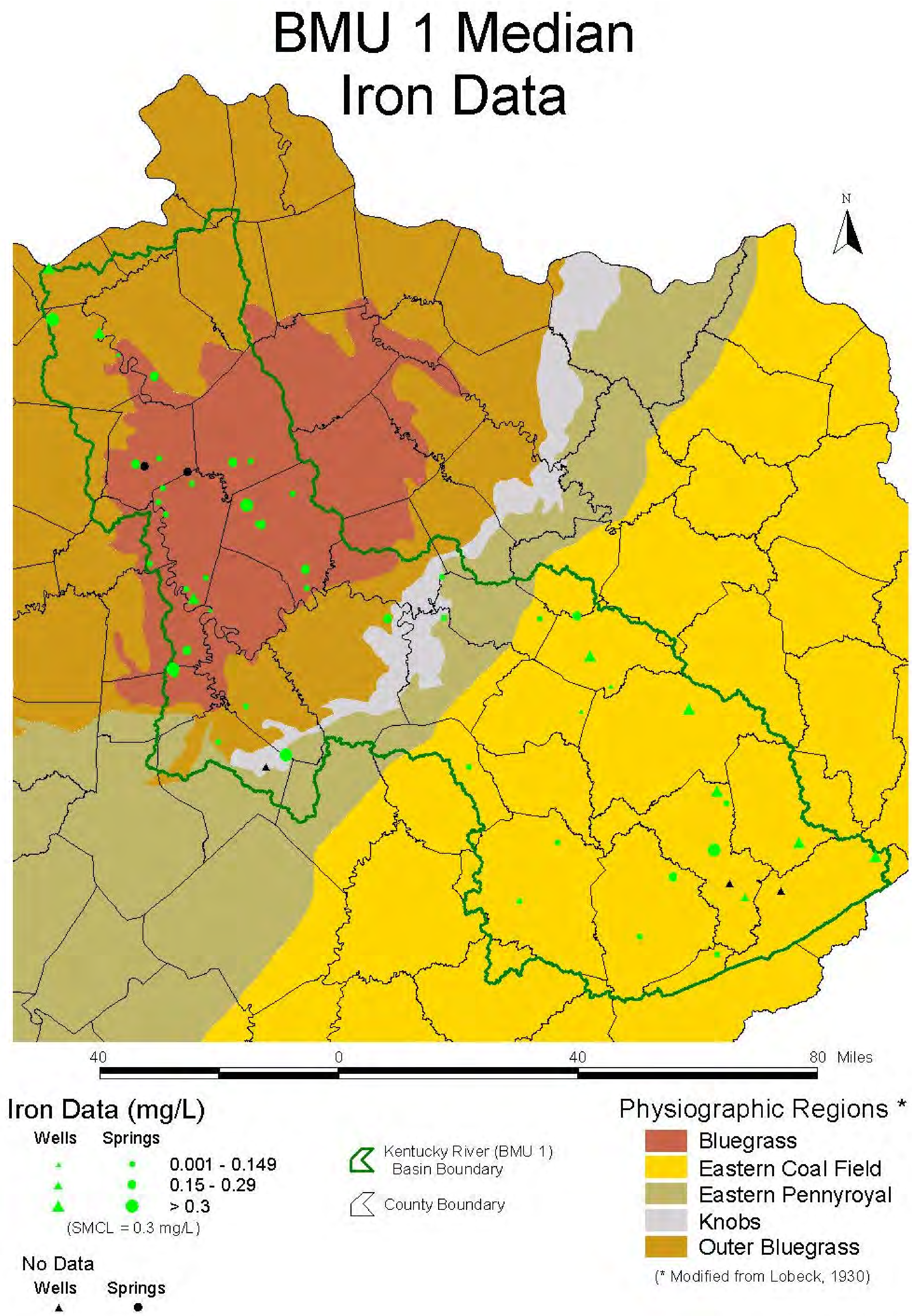

Figure 29. Iron Map

In summary, based upon the well-documented occurrence of iron in Kentucky's groundwater and the lack of any apparent nonpoint sources, iron in BMU 1 groundwater results from natural sources and is not a nonpoint source pollutant.

Manganese (Mn) is a relatively common element, but it occurs less abundantly in groundwater than does iron. Manganese is associated with discharges from coal mining and metal manufacturing. Manganese in water supplies can cause staining and encrustation of plumbing fixtures, piping and well screens, as well as discolored laundry. The SMCL for manganese is 0.05 mg/L. Manganese is a common, naturally occurring, water quality problem in Kentucky.

Manganese was detected in 355 of 393 (90.3%) of the samples included in this study and twenty-four sites had at least one detection above SMCL (Tables 10 and 11). Median values ranged from a low of 0.003 mg/L in the Mississippian Plateau to a high of 0.133 mg/L in the Ohio River Alluvium, but the highest value of 1.38 was found in the Eastern Coal Field at Aunt Soph's Spring in Clay County (Table 11). Boxplots (Figures 30 and 31) show the variability of manganese in two physiographic provinces, the Bluegrass and the Eastern Coal Field, and especially in agricultural and forested areas. Map distribution is shown in Figure 32.

Without direct evidence of any apparent nonpoint sources of this common metal, the manganese results found in this study are interpreted as the result of naturally occurring variations in water chemistry.

Mercury (Hg) occurs naturally in the Eastern Coal Field as a trace element in coal (USGS, 2002b). Primary nonpoint sources of mercury pollution are via atmospheric deposition from coal-burning power plants and boilers, waste incineration and manufacturing. Berryman and others (2004) note in their study of Mammoth Cave National Park that mercury levels in surface and groundwater are " . . . quite low (0-25 ppt) since mercury preferentially binds to sediments and organic material." Some mercury is converted to organic mercury (primarily methylmercury) in the environment and accumulates in fish. Because mercury can then

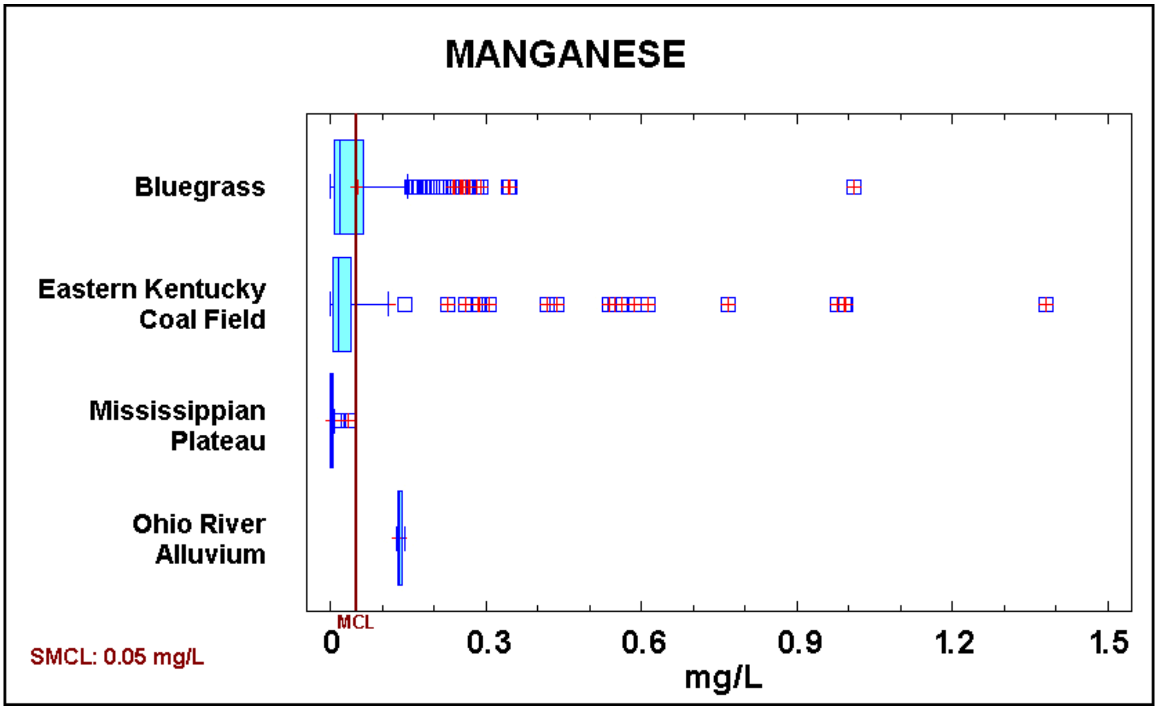

Figure 30. Boxplot of Manganese and Physiographic Regions

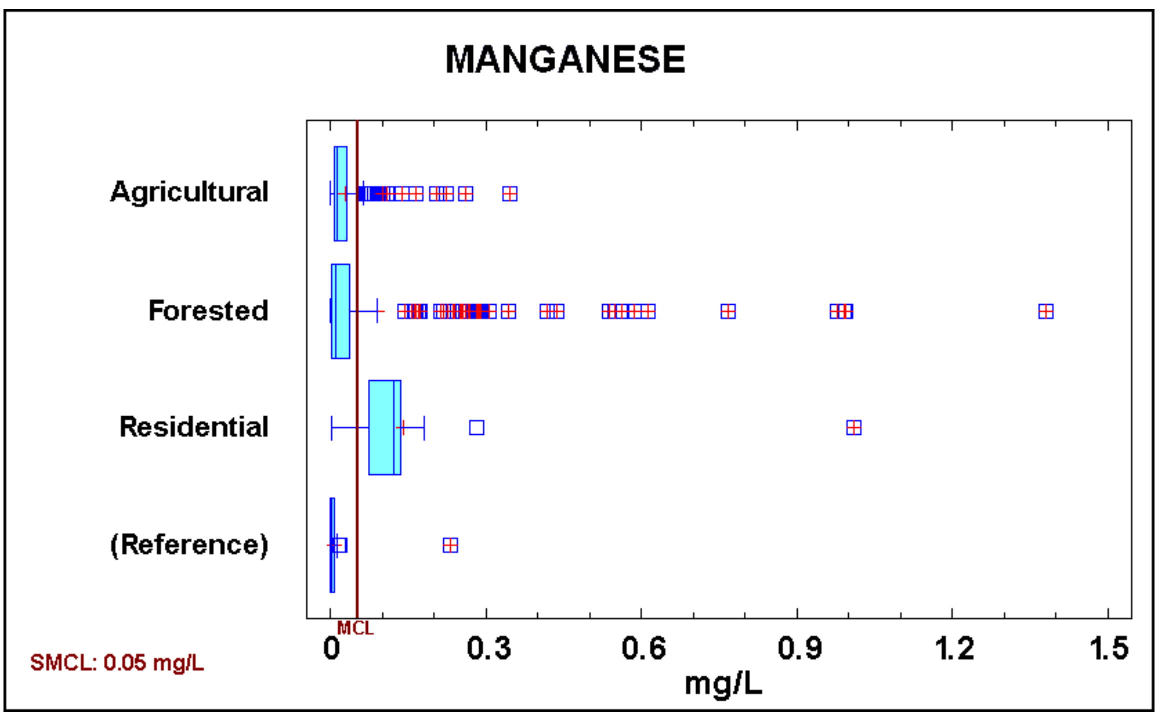

Figure 31. Boxplot of Manganese and Land Use

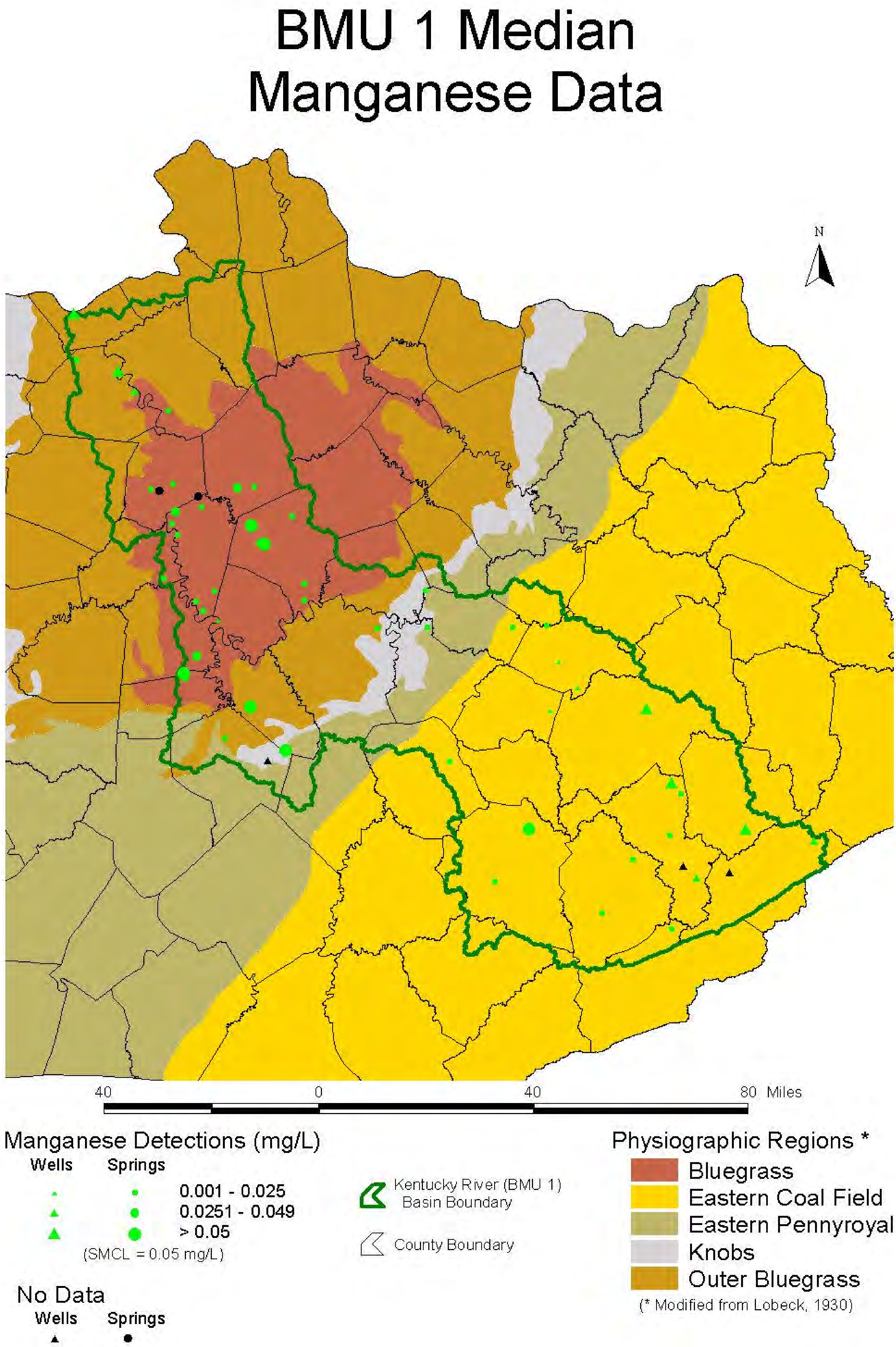

Figure 32. Manganese Map

accumulate in humans with serious effects upon the nervous system, the US EPA (2004) has issued consumer advisories to limit consumption. The MCL for mercury is 0.002 mg/L.

Mercury occurred in 1 of 392 samples, or 0.3% (Table 10). The single detection, 0.000065 mg/L, was in one of 28 samples collected at Russell Cave Spring (Fayette County) in the Inner Bluegrass Physiographic province (Table 11). No source of this anomalous detection of mercury was found.

Mercury data strongly suggest that this metal does not occur naturally in groundwater in the study area, nor does it apparently impact groundwater through air-borne deposition from coal-fired power plants or other sources. Although the Division of Water has issued statewide fish consumption advisories for mercury, groundwater in BMU 1 does not appear to contribute to this surface water problem. However, because mercury does occur as a trace element in coal and because air-borne deposition from coal-fired power plants is on going, additional sampling should include mercury to monitor potential long-term impacts to groundwater.

Lead (Pb) occurs naturally as the mineral galena (PbS), which is found as a vein mineral in central Kentucky (Anderson and Dever, 1998). Lead also occurs in carbonate sedimentary rocks (Dever, 2000) and is found as a trace element in coal (USGS, 2002b). Atmospheric deposition through coal-fired power plants, as well as the historical use of “leaded” gasoline has dispersed lead throughout the environment. Industrial uses of lead include historical use as an additive in paint, but current use is dominated by lead batteries, which accounts for about 88% of current use, with the remaining 12% used in a variety of products, including ceramics and ammunition (USGS, 2004). Lead toxicity is well documented (US EPA, 2002c), and in children can severely affect growth and intellectual development. Lead (along with copper) is regulated by “Treatment Technique” which requires public water systems to control the corrosiveness of their water. The action level for lead is 0.015 mg/L, and if more than 10% of tap water samples exceed this, then water systems are required to take additional steps.

Lead was detected in 41 of 395 (10.4%) samples analyzed in this study (Table 10). The median for BMU 1 was less than 0.002 mg/L (Table 11), but two springs in the Bluegrass and one well in the Ohio River Alluvium had detections exceeding the action level: Russell Cave Spring (Fayette County), Royal Spring (Scott County), and a well in Carrollton (Carroll County). These sites occur in locales with numerous potential sources of contamination, and the provenance of lead occurrence at these sites is unknown. Median values are low in all physiographic provinces (Figure 33), but elevated outliers are common in the Bluegrass and Eastern Coal Field. The boxplot of lead and land use (Figure 34) shows most values are low, but with variability in all areas. Distribution of lead in BMU 1 is shown in Figure 35.

The provenance of lead in groundwater in BMU 1 is difficult to interpret, but may be, at least in part, the result of nonpoint source pollution, possibly through current and historical atmospheric re-deposition from coal and gasoline. Because of its detrimental impacts, lead should continue to be monitoring and additional studies developed to more fully characterize potential impacts to groundwater.

Pesticides (Atrazine, Metolachlor, Simazine, Alachlor and Cyanazine)

Five commonly used pesticides are included in this report: atrazine (and one of its degradation by-products, atrazine desethyl), metolachlor, cyanazine, simazine and alachlor. A summary and descriptive statistics are shown in Tables 12 and 13.

Because these pesticides do not occur naturally and because their introduction into the environment from point sources such as leaking tanks is relatively limited geographically, the detection of pesticides in groundwater indicates nonpoint source pollution.

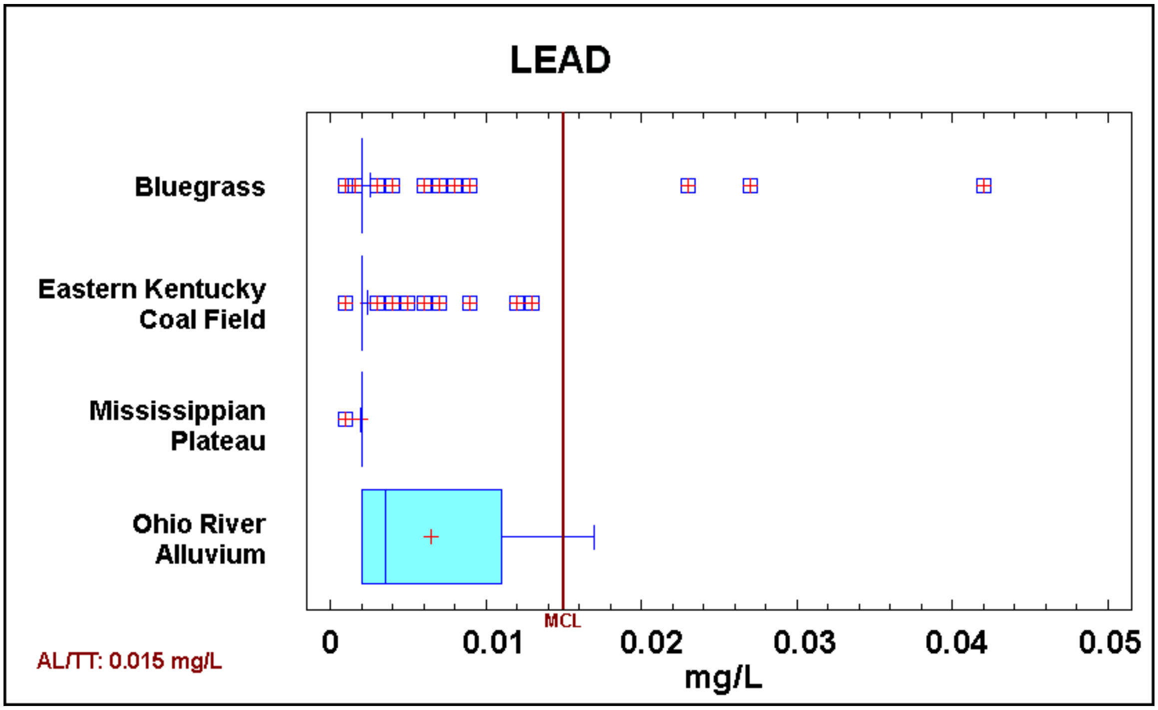

Figure 33. Boxplot of Lead and Physiographic Regions

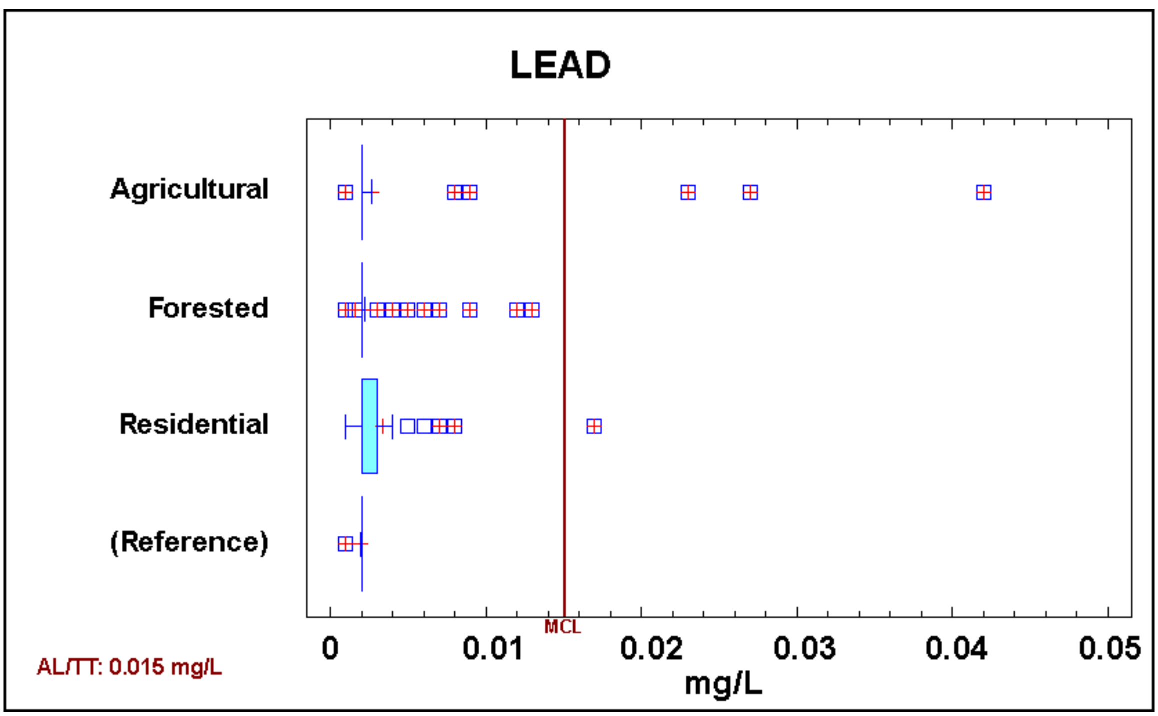

Figure 34. Boxplot of Lead and Land Use

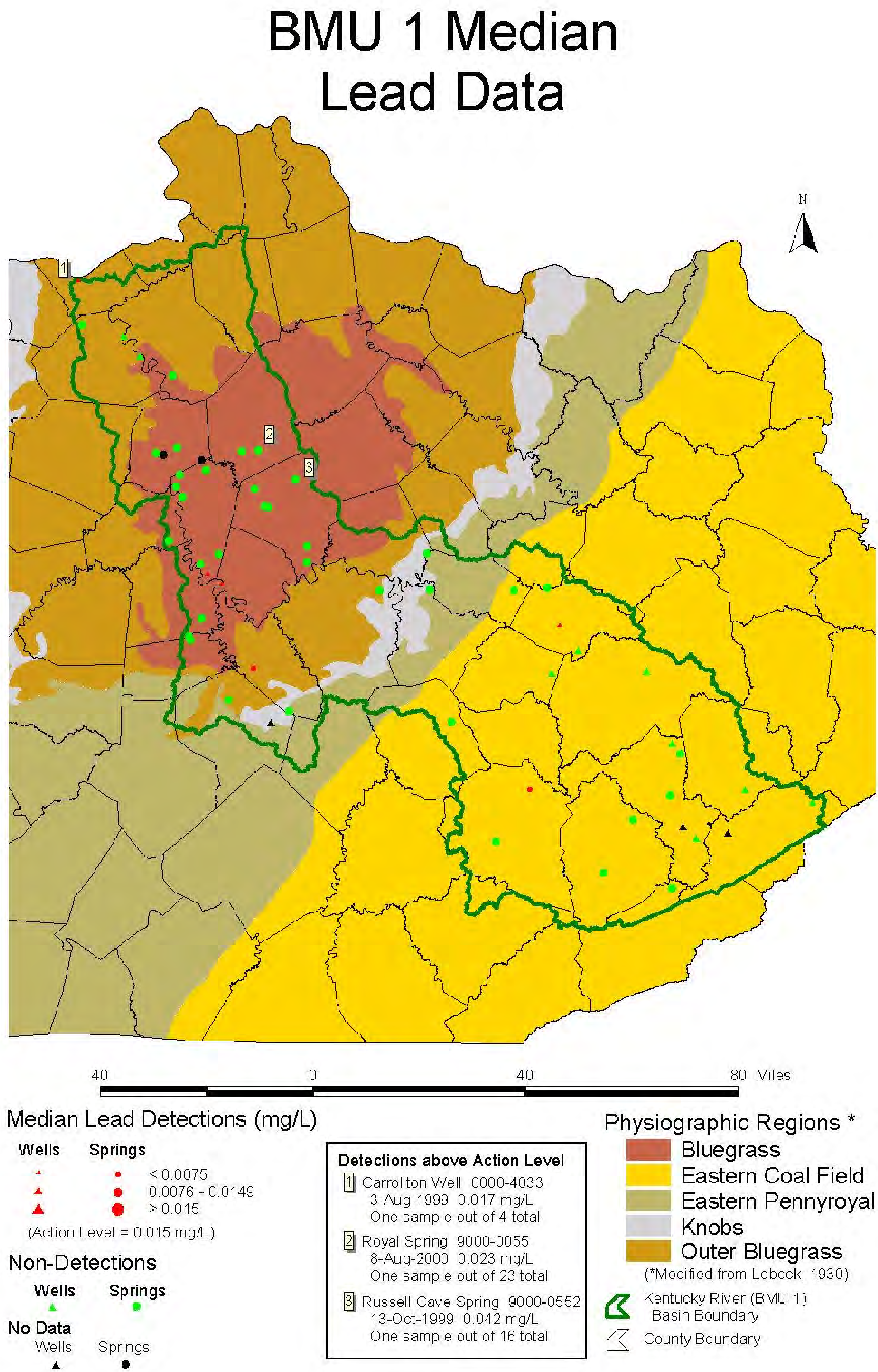

Figure 35. Lead Map

Table 12. Pesticides Summary

BMU1: PESTICIDES SUMMARY

		ALACHOR	ATRAZINE	CYANAZINE[1 2 3]	METOLACHLOR[1]	SIMAZINE[2 4]
NUMBER OF SAMPLES	TOTAL:	563	563	522	563	526
BY REGION:	BLUEGRASS (INNER & OUTER):	350	350	322	350	325
	EASTERN COAL FIELD:	135	135	130	135	130
	MISSISSIPPIAN PLATEAU:	74	74	66	74	67
	OHIO RIVER ALLUVIUM:	4	4	4	4	4
NUMBER OF DETECTIONS	TOTAL:	2	94	0	16	16
	% DETECTS (vs SAMPLES):	0.4%	16.7%	0.0%	2.8%	3.0%
BY REGION:	BLUEGRASS (INNER & OUTER):	2	91	0	15	15
	EASTERN COAL FIELD:	0	0	0	1	1
	MISSISSIPPIAN PLATEAU:	0	3	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0	0	0
NUMBER OF DETECTIONS ABOVE STANDARD	TOTAL:	0	0	0	0	0
	% DETECTIONS > STANDARD (of SAMPLES w/DETECTIONS):	0.0%	0.0%	0.0%	0.0%	0.0%
	% SAMPLES > STANDARD (of TOTAL SAMPLES):	0.0%	0.0%	0.0%	0.0%	0.0%
BY REGION:	BLUEGRASS (INNER & OUTER):	0	0	0	0	0
	EASTERN COAL FIELD:	0	0	0	0	0
	MISSISSIPPIAN PLATEAU:	0	0	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0	0	0
NUMBER OF SITES[3]	TOTAL:	57	57	56	57	56
BY REGION:	BLUEGRASS (INNER & OUTER):	33	33	32	33	32
	EASTERN COAL FIELD:	19	19	19	19	19
	MISSISSIPPIAN PLATEAU:	4	4	4	4	4
	OHIO RIVER ALLUVIUM:	1	1	1	1	1
NUMBER OF SITES WITH DETECTIONS	TOTAL:	2	14	0	5	7
	% SITES W/DETECTIONS:	3.5%	24.6%	0.0%	8.8%	12.5%
BY REGION:	BLUEGRASS (INNER & OUTER):	2	13	0	4	6
	EASTERN COAL FIELD:	0	0	0	1	1
	MISSISSIPPIAN PLATEAU:	0	1	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0	0	0
NUMBER OF SITES WITH DETECTIONS ABOVE STANDARD	TOTAL:	0	0	0	0	0
	%SITES w/DETECTIONS>STANDARD (of SITES w/DETECTIONS):	0.0%	0.0%	0.0%	0.0%	0.0%
	%SITES w/DETECTIONS>STANDARD (of TOTAL SITES):	0.0%	0.0%	0.0%	0.0%	0.0%
BY REGION:	BLUEGRASS (INNER & OUTER):	0	0	0	0	0
	EASTERN COAL FIELD:	0	0	0	0	0
	MISSISSIPPIAN PLATEAU:	0	0	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0	0	0

	MCL (mg/L)	HAL (mg/L)	Other
ALACHLOR	0.002	-	-
ATRAZINE	0.003	-	-
CYANAZINE	-	0.001	-
METOLACHLOR	-	0.100	-
SIMAZINE	0.004	-	-

[1] HAL used in absence of MCL

[2] 9000-1103 Shane's Spring - no analyses for cyanazine or

[3] Only 522 cyanazine values out of 565 samples:
4 analyses: samples prior to May 97 not analyzed for cyanazine,
34 analyses: KGS samples Aug 1996 - Apr 1997 analyzed for "triazines" - no separate results for cyanazine,
4 analyses: no N/P Pesticides included in lab analyses,
1 analysis: lab analysis for metals only.

[4] Only 526 simazine values out of 565 samples:
34 analyses: KGS samples Aug 1996 - Apr 1997 analyzed for "triazines" - no separate results for simazine,
4 analyses: no N/P Pesticides included in analyses,
1 analysis: lab analysis for metals only.

Table 13. Pesticides Descriptive Statistics

BMU1: PESTICIDES DESCRIPTIVE STATISTICS						
	ALACHLOR (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**< 0.00006**	**< 0.00004**	**< 0.00002**	**< 0.00004**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	< 0.00006	< 0.00004	< 0.00002	< 0.00004
EASTERN COAL FIELD:	05/02/95	05/28/03	< 0.00006	< 0.00004	< 0.00002	< 0.00004
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	< 0.00006	< 0.00004	< 0.00002	< 0.00004
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.00004	< 0.00004	< 0.00004	< 0.00004
	ATRAZINE (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**0.00041**	**< 0.00005**	**0.000007**	**< 0.00004**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	0.00041	< 0.00005	0.000007	< 0.00004
EASTERN COAL FIELD:	05/02/95	05/28/03	< 0.0003	< 0.00005	< 0.00004	< 0.00004
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	< 0.0003	< 0.00005	< 0.00004	< 0.00004
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.00004	< 0.00004	< 0.00004	< 0.00004
	CYANAZINE (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**< 0.0001**	**< 0.00004**	**< 0.00004**	**< 0.00004**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	< 0.0001	< 0.0004	< 0.00004	< 0.00004
EASTERN COAL FIELD:	05/02/95	05/28/03	< 0.0001	< 0.000049	< 0.00004	< 0.00004
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	< 0.0001	< 0.00005	< 0.00004	< 0.00004
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.00004	< 0.00004	< 0.00004	< 0.00004
	METOLACHLOR (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**0.00024**	**< 0.000049**	**< 0.00004**	**< 0.00004**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	0.00024	< 0.00004	< 0.00004	< 0.00004
EASTERN COAL FIELD:	05/02/95	05/28/03	< 0.0002	< 0.00005	< 0.00004	< 0.00004
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	< 0.0002	< 0.00005	< 0.00004	< 0.00004
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.00004	< 0.00004	< 0.00004	< 0.00004
	SIMAZINE (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**< 0.0003**	**< 0.00004**	**0.00001**	**< 0.00004**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	< 0.0003	< 0.00004	0.000028	< 0.00004
EASTERN COAL FIELD:	05/02/95	05/28/03	< 0.0003	< 0.000048	0.00001	< 0.00004
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	< 0.0003	< 0.00005	< 0.00004	< 0.00004
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.00004	< 0.00004	< 0.00004	< 0.00004

Table 14. Pesticide Method Detection Limits

Pesticide	Method Detection Limit Used for Samples, mg/L
Atrazine	0.0003, 0.00004, 0.00005
Metolachlor	0.00002, 0.00004, 0.00005, 0.00006, 0.00008
Cyanazine	No detects at any MDL; 0.00004 most frequent MDL
Simazine	0.0003, 0.00004, 0.00005
Alachlor	0.00002, 0.00004, 0.00005, 0.00006

Atrazine (most commonly sold under the trade name AAtrex or simply Atrazine) is used primarily for weed control for corn and soybean production and is one of the most commonly used herbicides in Kentucky. In 1999, when this study began, approximately two million pounds of atrazine were sold in Kentucky (KDA, 2000). Atrazine, with an MCL of 0.003 mg/L, is carcinogenic and exposure to excess amounts is associated with weight loss, cardiovascular damage and degeneration of muscle tissue and the retina. Atrazine has also recently been suspected to cause hermaphroditism in frogs (Hayes and others, 2002). Atrazine desethyl, a degradation by-product of atrazine, was also analyzed in this study. However, because no MCL has been established for atrazine desethyl, and because it is probably appropriate to evaluate atrazine and its chlorinated metabolites via additive analysis, only data for combined atrazine/atrazine desethyl is presented in this report. For simplicity, this is referred to as "atrazine" in this report.

Atrazine was the most detected herbicide in this study. Atrazine was analyzed in 563 samples and detected in 94, or 16.7% (Tables 12 and 13). As shown in Figure 36, atrazine occurred at 13 sites in the Bluegrass and one in the Mississippian Plateau. The median value for atrazine was less than 0.00004 mg/L, and nothing exceeded the MCL (Table 13). As expected, groundwater in agricultural areas with high row-crop production is most likely impacted by atrazine, and forests and residential areas are relatively unlikely to be affected.

Although no MCL exceedances for atrazine were found in this study, this compound does occur in groundwater from anthropogenic sources and is therefore a nonpoint source pollutant of concern. Ideally, this compound should be non-detect in groundwater. Monitoring for atrazine and its chlorinated degradation by-products should continue, as well as research into its effects upon the environment and human health.

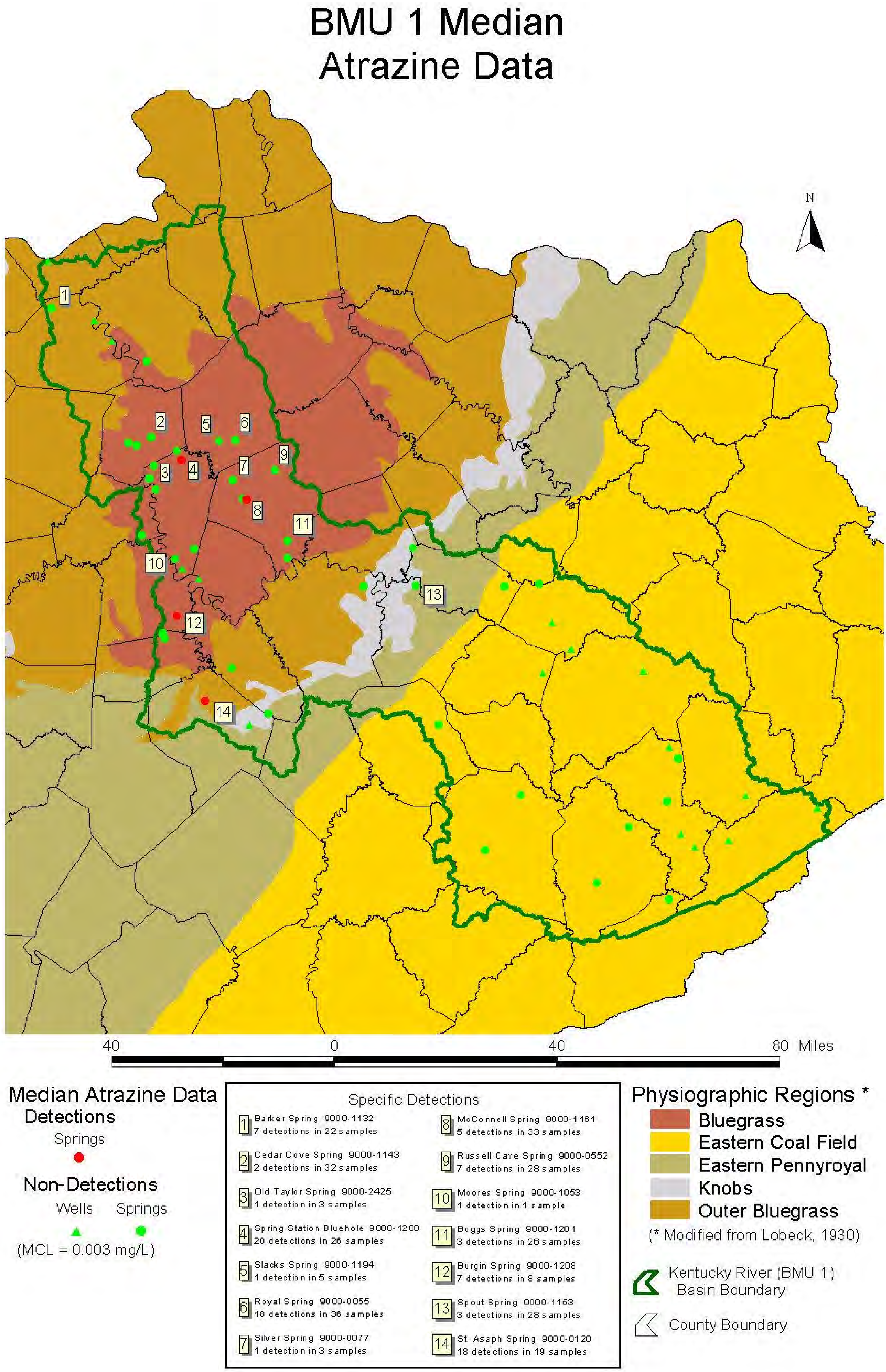

Figure 36. Atrazine Map

Metolachlor (trade names include Bicep II Magnum and Dual II Magnum) is used as a pre-emergent and pre-plant weed control for the production of corn and soybeans. In 1999 (KDA, 2000), approximately 800,000 pounds of metolachlor (combined metolachlor and s-metolachlor) were sold in the state. Metolachlor has an HAL of 0.10 mg/L, and is possibly carcinogenic in humans.

As shown in Tables 12 & 13, metolachlor was found in 2.8 % of the samples analyzed (16 of 563), and the median for BMU 1 was less than 0.000049 mg/L, but nothing exceeding the HAL was found. This herbicide occurred at four sites in the Bluegrass and one in the Mississippian Plateau (Figure 37).

Although the number of detections does indicate that metolachlor is a nonpoint source pollutant, the low levels found in this study suggests that its impacts to groundwater quality are minimal.

Simazine (trade names include Princep) is used to control annual nuisance grasses and broadleaf weeds, especially for corn and alfalfa production. In humans, simazine is carcinogenic and exposure to simazine is associated with tremors, damage to liver, testes, kidneys and thyroid and gene mutation. Simazine has an MCL of 0.004 mg/L.

Simazine was analyzed in 526 samples (Table 12), and found in 16, or 3.0%. Median values for BMU 1 were less than 0.00004 mg/L, and no MCL exceedances were noted (Table 13). Seven sites, as shown in Figure 39, had detections of simazine. As with metolachlor, simazine is a nonpoint source pollutant; however, its effects upon the environment appear to be minimal at this time.

Alachlor (trade names include Bullet and Micro-Tech) is used for corn and soybean production for pre-emergent weed control. Alachlor has an MCL of 0.002 mg/L. Alachlor has been associated with cancer in humans and has been linked with noncancerous effects in the liver, spleen and kidneys.

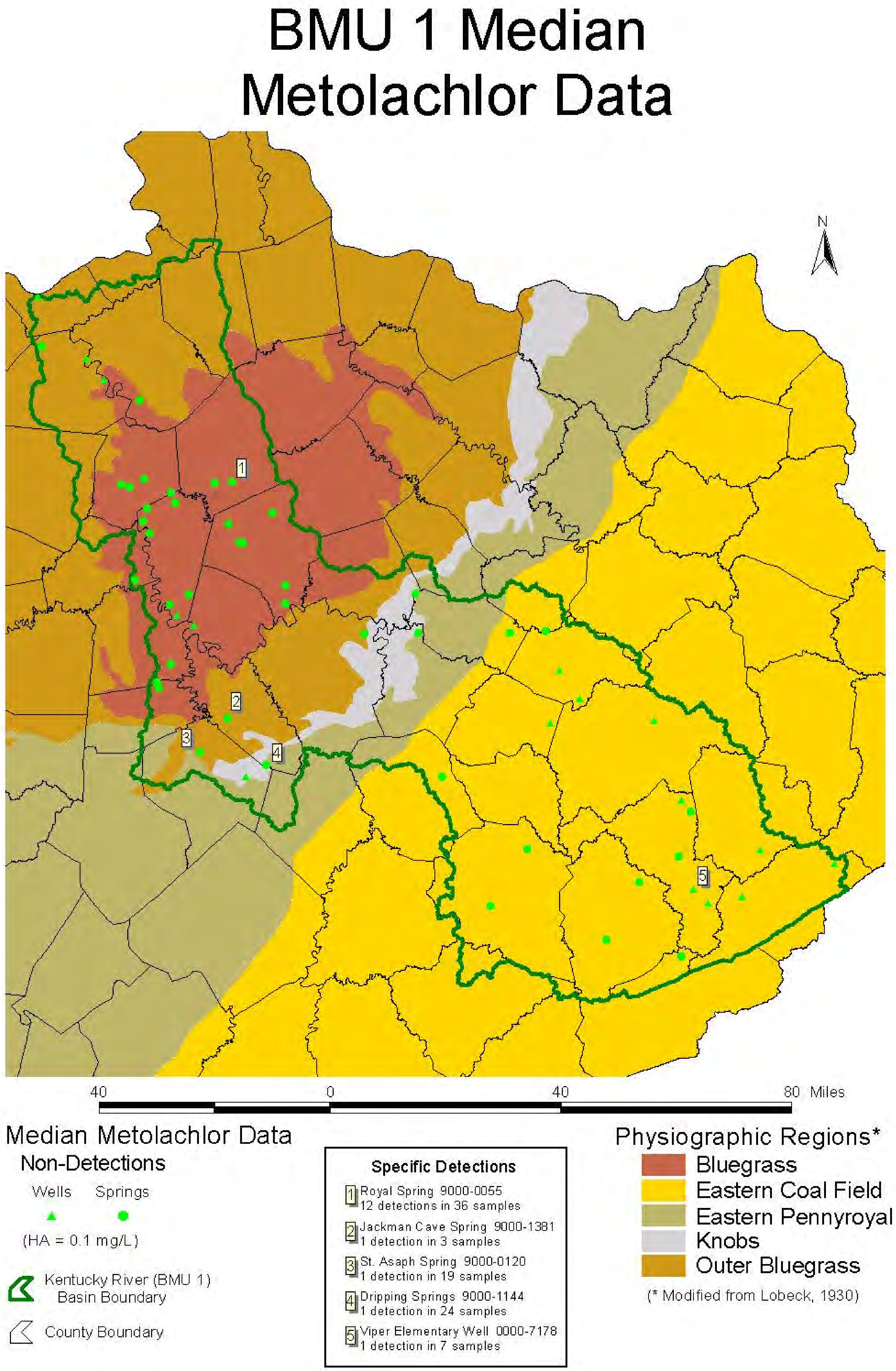

Figure 37. Metolachlor Map

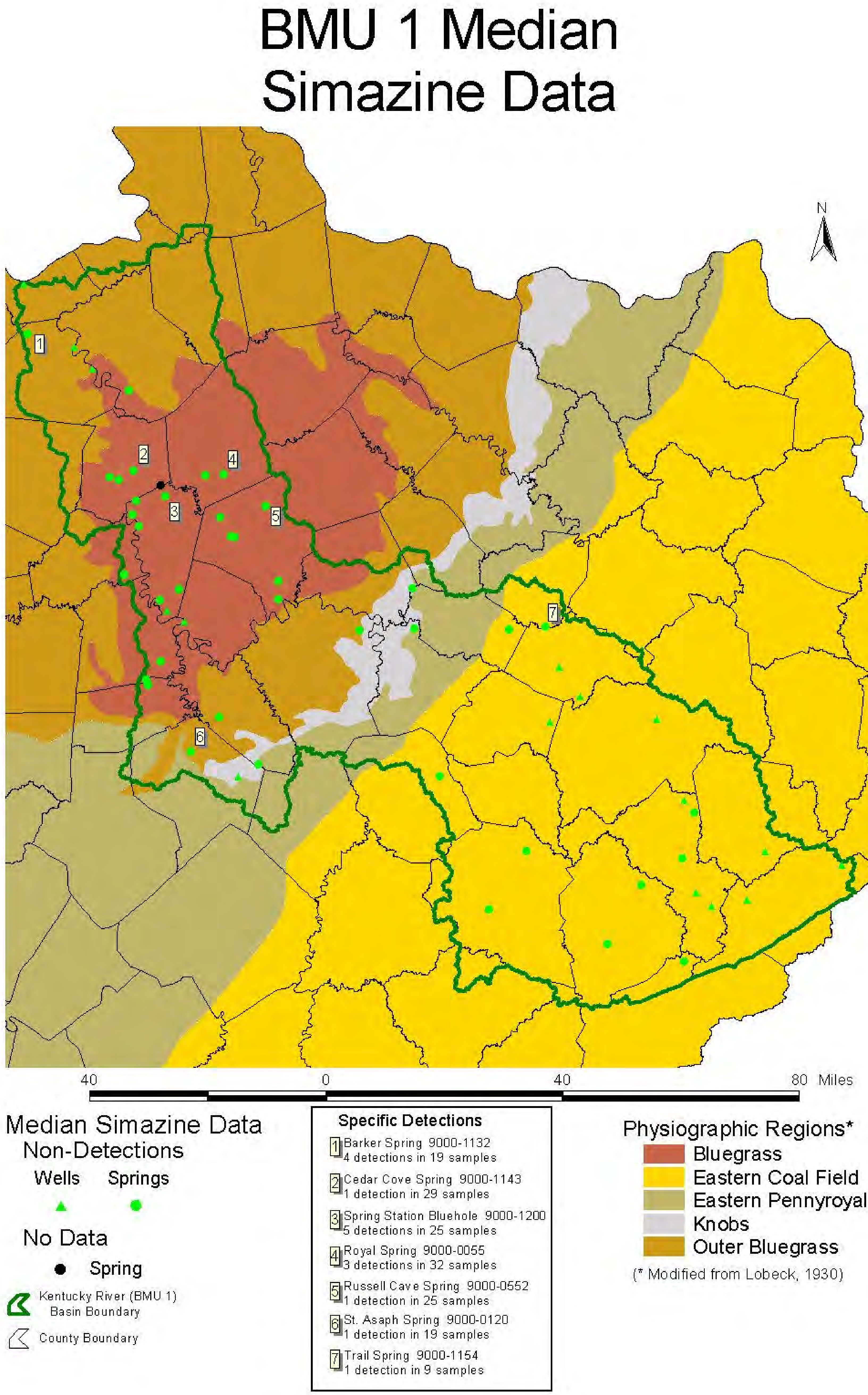

Figure 38. Simazine Map

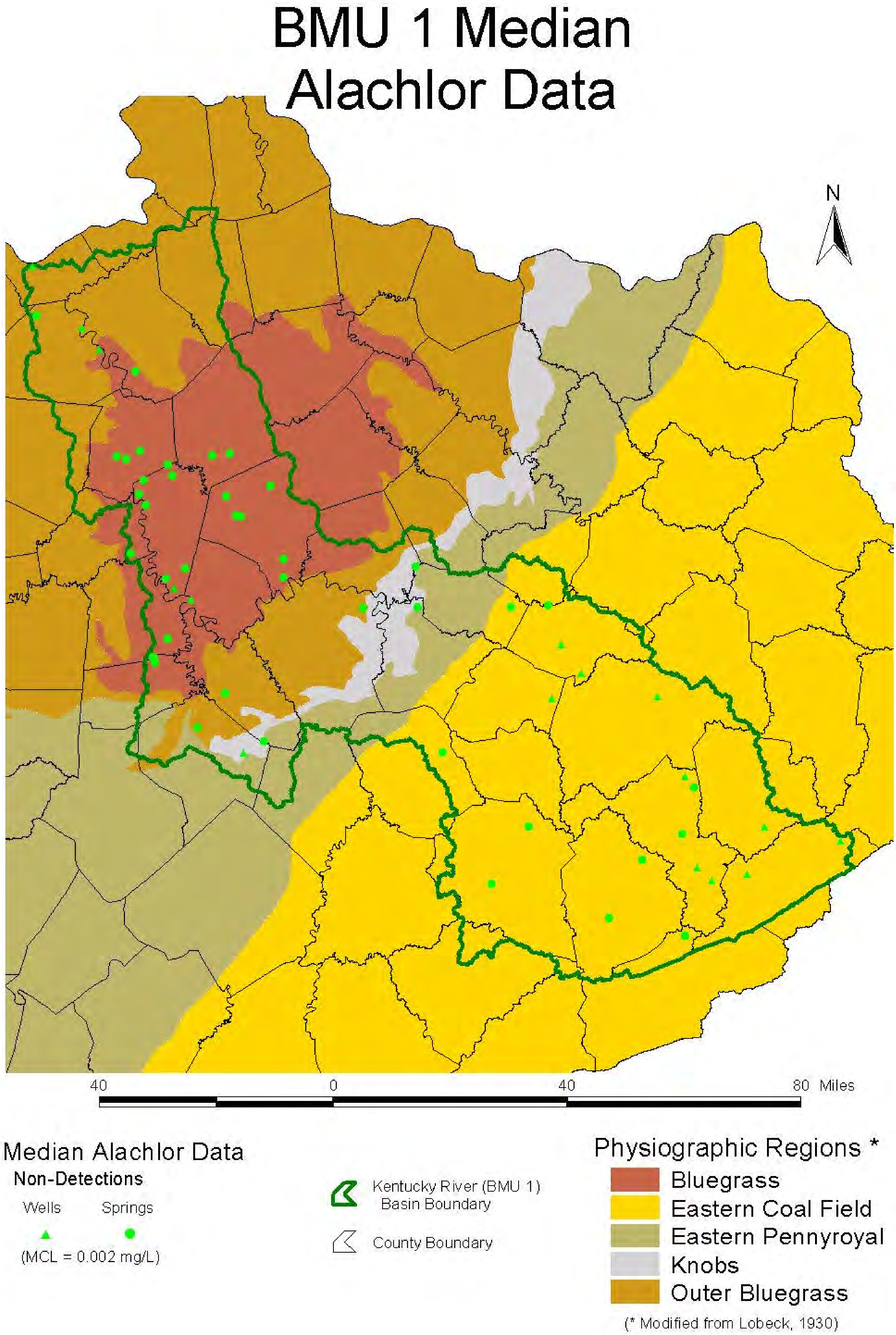

Figure 39. Alachlor Map

Alachlor was detected in only two of 563 samples, or 0.4% (Table 12). These detections occurred in the Bluegrass (Figure 39), but did not exceed MCL. Alachlor is a nonpoint source pollutant, although minor, in BMU 1, but monitoring for this compound should continue.

Cyanazine production ceased in December 1999 and the sale and use of this herbicide was prohibited effective September 2002. Cyanazine was analyzed for in 522 samples, but not detected (Table 13). These results indicate that, at least in BMU 1, cyanazine is not a nonpoint source pollutant of concern.

Residues (Total Dissolved Solids (TDS) and Total Suspended Solids (TSS))

Descriptive statistics and summaries for the residues included in this report are shown in Tables 15 and 16.

Total Dissolved Solids (TDS) measures the solids remaining in a water sample filtered through a 1.2 μm filter. According to the World Health Organization (WHO, 1996), the compounds and elements remaining after filtration are commonly calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, sulfate, silica and nitrate-N. High TDS affects the taste and odor of water and in general, levels above 300 mg/L become noticeable to consumers. As TDS increases, the water becomes increasingly unacceptable. Although the SMCL for TDS is 500 mg/L, levels above 1200 mg/L are unacceptable to most consumers. Because TDS measurements may include a variety of parameters, which can be naturally occurring, or anthropogenic, its value as an indicator of nonpoint source pollution is limited.

In this study, TDS was analyzed for 558 samples (Table 15), and found in 546, or 97.8%. A maximum value of 3200 mg/L was found in the Eastern Coal Field, where the median was 501 mg/L, which slightly exceeds the SMCL (Table 16). TDS was most variable in the Eastern Coal Field and forested areas (Figures 40 and 41). The SMCL was exceeded at 21 sites (Figure 42): ten each in the Bluegrass and Eastern Coal Field and at one site in the Ohio River Alluvium.

Table 15. Residues Summary

BMU1: RESIDUES SUMMARY		TDS[2]	TSS[1 3]
NUMBER OF SAMPLES	TOTAL:	558	560
BY REGION:	BLUEGRASS (INNER & OUTER):	347	347
	EASTERN COAL FIELD:	134	135
	MISSISSIPPIAN PLATEAU:	73	74
	OHIO RIVER ALLUVIUM:	4	4
NUMBER OF DETECTIONS	TOTAL:	546	333
	% DETECTS (vs SAMPLES):	97.8%	59.5%
BY REGION:	BLUEGRASS (INNER & OUTER):	345	221
	EASTERN COAL FIELD:	129	81
	MISSISSIPPIAN PLATEAU:	68	29
	OHIO RIVER ALLUVIUM:	4	2
NUMBER OF DETECTIONS ABOVE STANDARD	TOTAL:	86	19
	% DETECTIONS > STANDARD (of SAMPLES w/DETECTIONS):	15.8%	5.7%
	% SAMPLES > STANDARD (of TOTAL SAMPLES):	15.4%	3.4%
BY REGION:	BLUEGRASS (INNER & OUTER):	17	16
	EASTERN COAL FIELD:	67	2
	MISSISSIPPIAN PLATEAU:	0	1
	OHIO RIVER ALLUVIUM:	2	0
NUMBER OF SITES[3]	TOTAL:	57	57
BY REGION:	BLUEGRASS (INNER & OUTER):	33	33
	EASTERN COAL FIELD:	19	19
	MISSISSIPPIAN PLATEAU:	4	4
	OHIO RIVER ALLUVIUM:	1	1
NUMBER OF SITES WITH DETECTIONS	TOTAL:	57	52
	% SITES W/DETECTIONS:	100.0%	91.2%
BY REGION:	BLUEGRASS (INNER & OUTER):	33	29
	EASTERN COAL FIELD:	19	18
	MISSISSIPPIAN PLATEAU:	4	4
	OHIO RIVER ALLUVIUM:	1	1
NUMBER OF SITES WITH DETECTIONS ABOVE STANDARD	TOTAL:	21	13
	%SITES w/DETECTIONS>STANDARD (of SITES w/DETECTIONS):	36.8%	25.0%
	%SITES w/DETECTIONS>STANDARD (of TOTAL SITES):	36.8%	22.8%
BY REGION:	BLUEGRASS (INNER & OUTER):	10	10
	EASTERN COAL FIELD:	10	2
	MISSISSIPPIAN PLATEAU:	0	1
	OHIO RIVER ALLUVIUM:	1	0
	MCL (mg/L)	Secondary (mg/L)	Other
TDS	-	500	-
TSS	-	-	35

[1] Currently no water quality standard for TSS; some KPDES permits use 35 mg/L monthly avg

[2]Only 558 TDS values out of 565 samples:
3 analyses: lab analyses for only pesticides and PCBs,
1 analysis: lab analysis for metals only,
1 analysis: no analysis for TDS,
1 analysis: could not be performed for TDS or TSS since no bulk split received for sample,
1 value could not be verified (Wm Whitley well - 60,364 mg/L) - treated as missing value.

[3]Only 560 TSS values out of 565 samples:
3 analyses: lab analyses for only pesticides and PCBs,
1 analysis: lab analysis for metals only,
1 analysis: could not be performed for TDS or TSS since no bulk split received for sample.

Table 16. Residues Descriptive Statistics

BMU1: RESIDUES DESCRIPTIVE STATISTICS						
	TDS (Total Dissolved Solids) (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**3200**	**326**	**< 1**	**< 10**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	908	322	< 1	284
EASTERN COAL FIELD:	05/02/95	05/28/03	3200	501	6.34	< 10
MISSISSIPPIAN PLATEAU:	05/03/95	06/11/03	462	266	< 10	< 10
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	563	494	484	484
	TSS (Total Suspended Solids) (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**1520**	**< 3**	**< 1**	**< 3**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	1520	< 3	< 1	< 3
EASTERN COAL FIELD:	05/02/95	05/28/03	40	< 3	< 1	< 3
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	73	< 3	< 1	< 3
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	1	< 1	< 1	-

As noted above, the value of TDS as an indicator of nonpoint source pollution is limited, and the values in this study are apparently the result of naturally occurring rock/water chemistry.

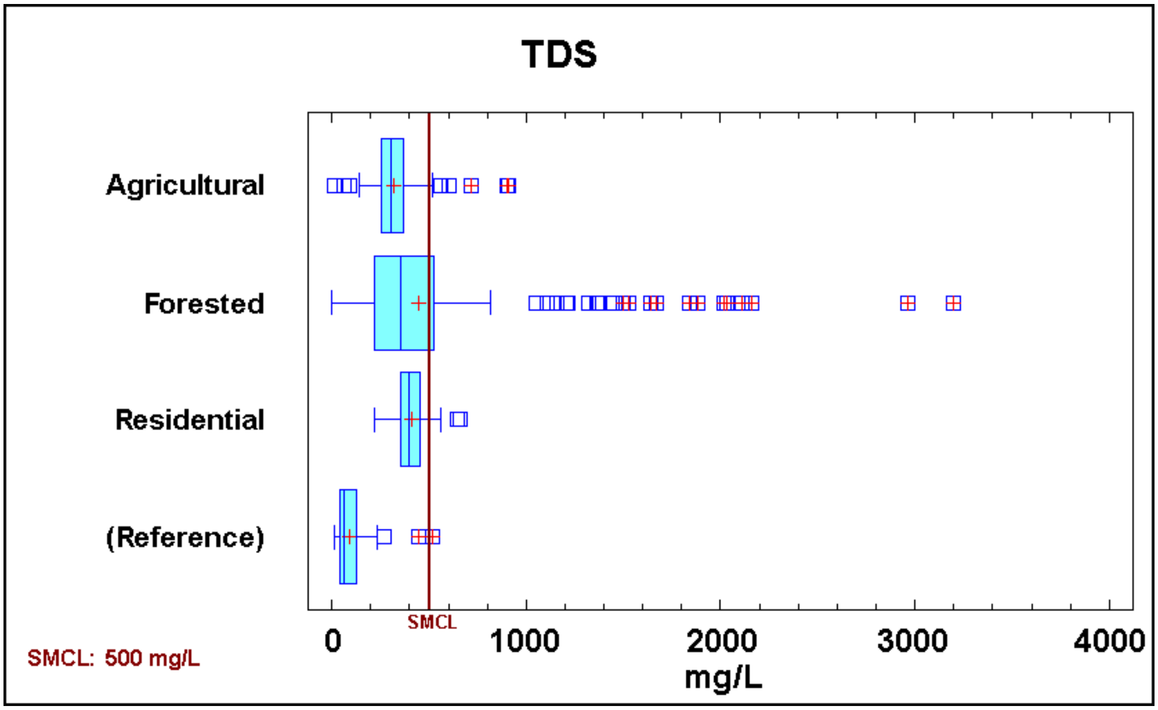

Figure 40. Boxplot of TDS and Land Use

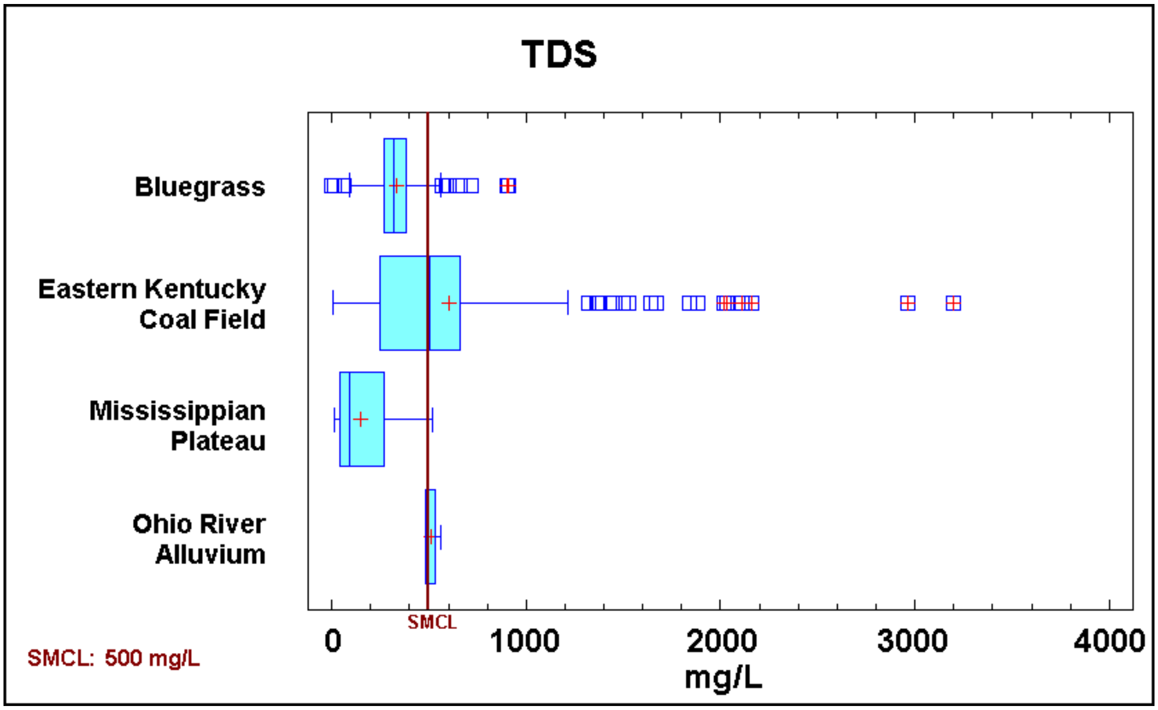

Figure 41. Boxplot of TDS and Physiographic Regions

Total Suspended Solids (TSS), also known as non-filterable residue, are those solids (minerals and organic material) that remain trapped on a 1.2 μm filter (US EPA, 1998). Suspended solids can enter groundwater through runoff from industrial, urban or agricultural areas. Elevated TSS (MMSD, 2002) can "... reduce water clarity, degrade habitats, clog fish gills, decrease photosynthetic activity and cause an increase in water temperatures." TSS has no drinking water standard. Therefore, data in this report are compared to the KPDES surface water discharge permit requirement for sewage treatment plants of 35 mg/L.

TSS was measured in 560 samples and detected in 333, or 59.5%, and the KPDES standard was exceeded in 19 samples (Tables 15 and 16). Median values for TSS in BMU 1 are low, as shown in Figures 43 and 44, but outliers occur. Map distribution of TSS in BMU 1 is shown in Figure 45. TSS is generally not considered an indicator of nonpoint source pollution. In summary, TSS occurrence in this study is most likely naturally occurring and not from nonpoint sources.

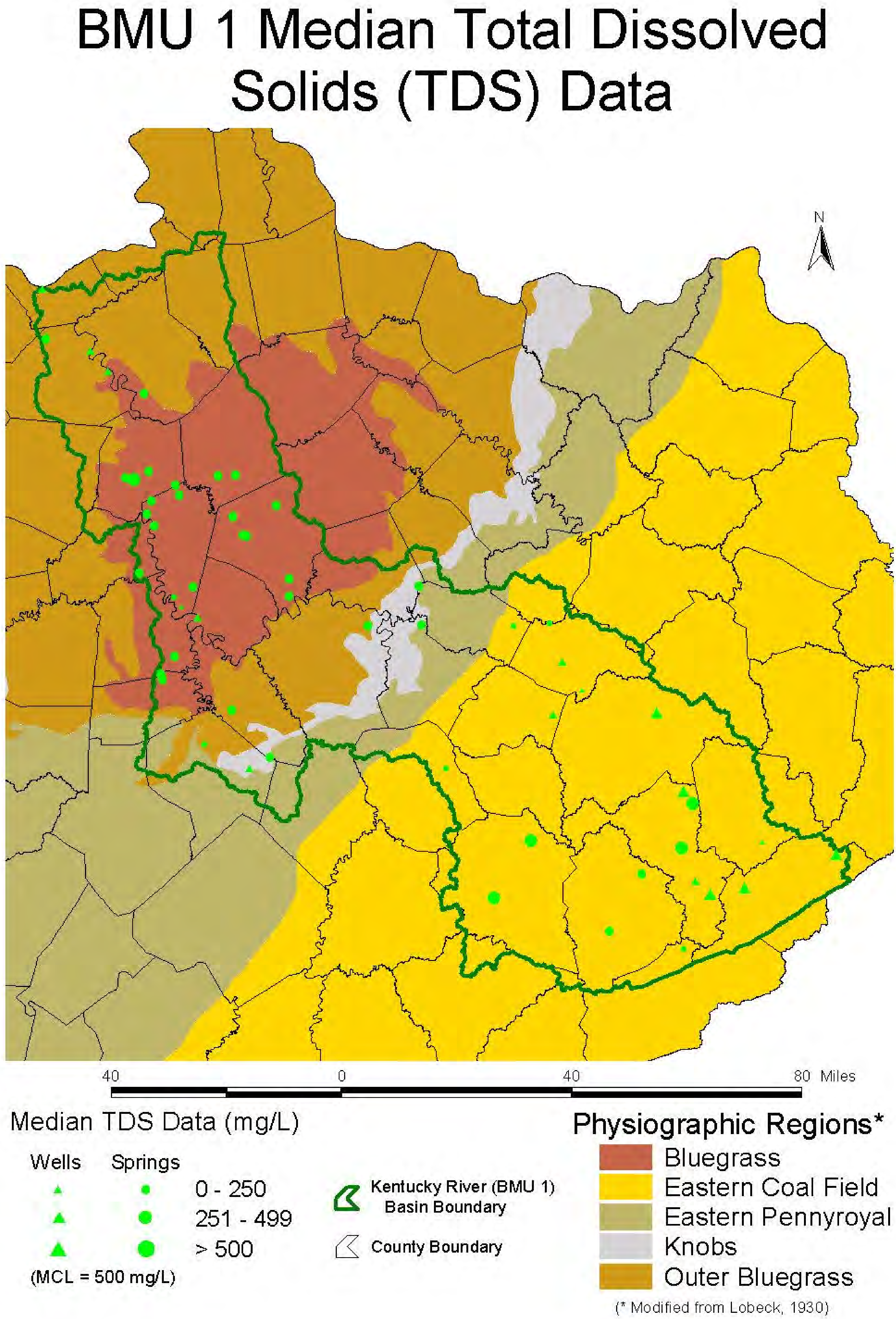

Figure 42. TDS Map

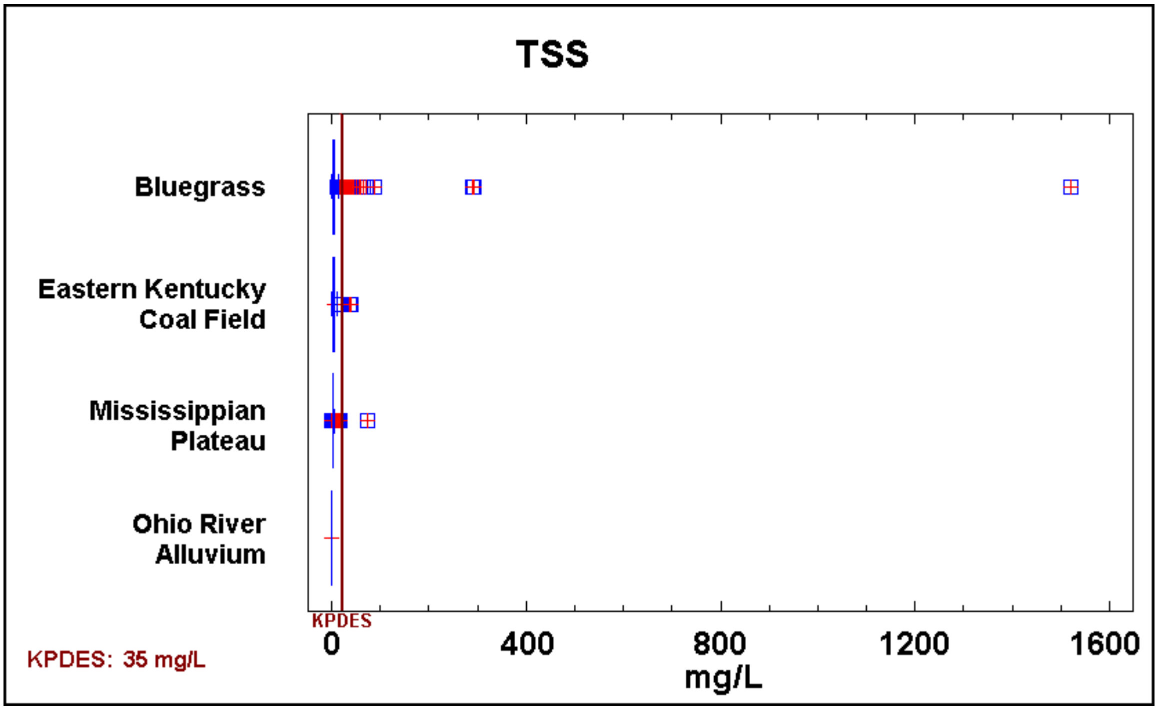

Figure 43. Boxplot of TSS and Physiographic Regions

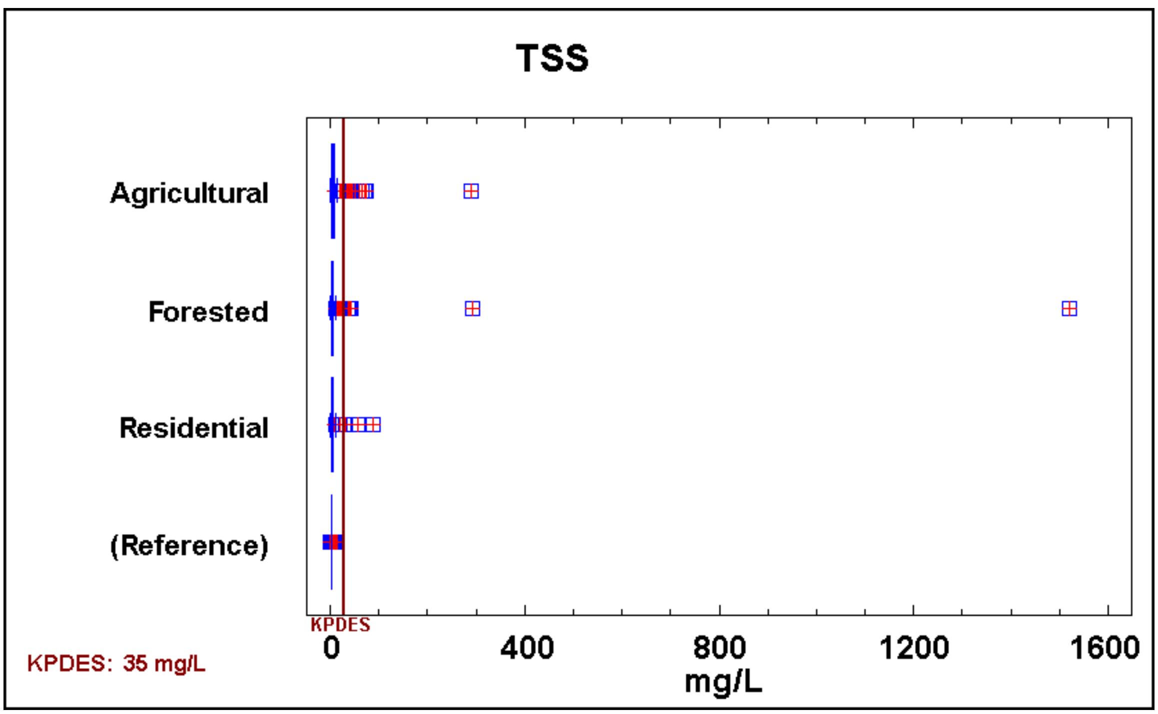

Figure 44. Boxplot of TSS and Land Use

BMU 1 Median Total Suspended Solids (TSS) Data

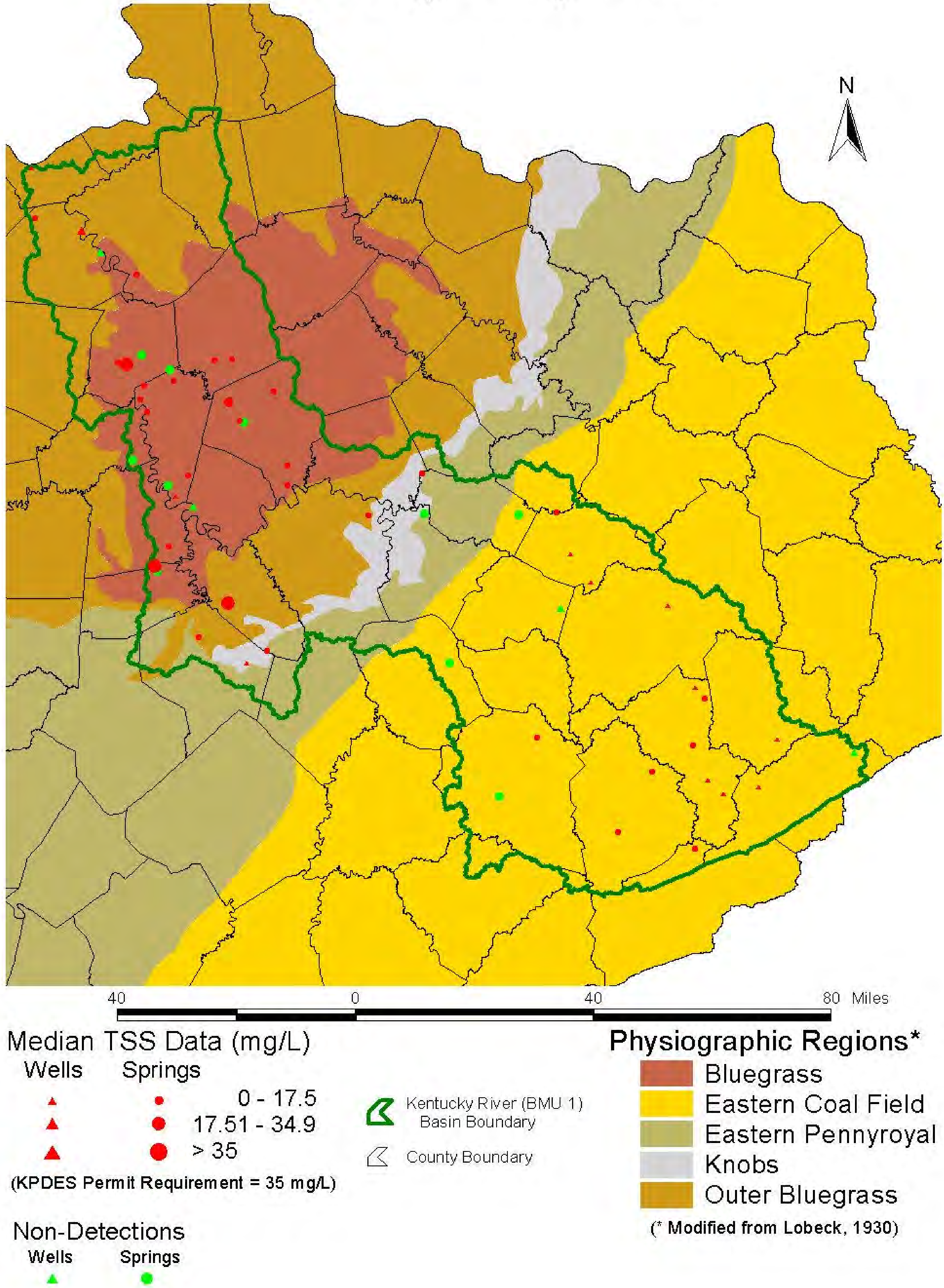

Figure 45. TSS Map

Nutrients (Nitrate-N, Nitrite-N, Ammonia-N, Orthophosphate-P, Total Phosphorus)

Nutrients included in this report are nitrate-N, nitrite-N, ammonia-N, orthophosphate-P and total phosphorous. Summaries and descriptive statistics are shown in Tables 17 and 18.

Nutrients are particularly important in surface water, where they are the main contributors to eutrophication, which is excessive nutrient enrichment of water. This enrichment can cause an overabundance of some plant life, such as algal blooms and may also have adverse effects on animal life, because excessive oxygen consumption by plants leaves little available for animal use. In addition to comparisons with various water quality standards, nutrient data from sites in this study were compared to the two reference springs.

Nitrate-N (NO_3) occurs in the environment from a variety of anthropogenic and natural sources: nitrogen-fixing plants such as alfalfa and other legumes, nitrogen fertilizers, decomposing organic debris, atmospheric deposition from combustion and human and animal waste. Nitrate-N is reported either as the complex ion NO_3, or as the equivalent molecular nitrogen-n. Since 1 mg/L of nitrogen equals 4.5 mg/L nitrate-N, the drinking water MCL of 10 mg/L nitrate-N equals 45 mg/L nitrate-N. In this report, results are reported as "nitrate-N."

In infants, excess nitrate-N consumption can cause methemoglobinemia or "blue-baby" syndrome. In adults, possible adverse health effects of nitrate-N ingestion are under study and much debated. Because nitrate-N is difficult to remove through ordinary water treatment, its occurrence at levels above the MCL in public water systems is an emerging problem, as well as a public health concern.

Table 17. Nutrients Summary

BMU1: NUTRIENTS SUMMARY		AMMONIA[3] (NH_3-N)	NITRATE[4] (NO_3-N)	NITRITE[5] (NO_2-N)	ORTHO-PHOSPHATE[1 6] (PO_4-P)	TOTAL PHOSPHORUS[2 7]
NUMBER OF SAMPLES	TOTAL:	560	559	546	549	426
BY REGION:	BLUEGRASS (INNER & OUTER):	347	348	336	338	270
	EASTERN COAL FIELD:	135	133	132	133	108
	MISSISSIPPIAN PLATEAU:	74	74	74	74	44
	OHIO RIVER ALLUVIUM:	4	4	4	4	4
NUMBER OF DETECTIONS	TOTAL:	107	512	304	417	325
	% DETECTS (vs SAMPLES):	19.1%	91.6%	55.7%	76.0%	76.3%
BY REGION:	BLUEGRASS (INNER & OUTER):	65	325	211	304	255
	EASTERN COAL FIELD:	34	114	46	57	52
	MISSISSIPPIAN PLATEAU:	6	69	47	56	14
	OHIO RIVER ALLUVIUM:	2	4	0	0	4
NUMBER OF DETECTIONS ABOVE STANDARD	TOTAL:	39	6	0	290	235
	% DETECTIONS > STANDARD (of SAMPLES w/DETECTIONS):	36.4%	1.2%	0.0%	69.5%	72.3%
	% SAMPLES > STANDARD (of TOTAL SAMPLES):	7.0%	1.1%	0.0%	52.8%	55.2%
BY REGION:	BLUEGRASS (INNER & OUTER):	13	5	0	278	229
	EASTERN COAL FIELD:	26	0	0	12	5
	MISSISSIPPIAN PLATEAU:	0	1	0	0	1
	OHIO RIVER ALLUVIUM:	0	0	0	0	0
NUMBER OF SITES	TOTAL:	57	57	57	57	52
BY REGION:	BLUEGRASS (INNER & OUTER):	33	33	33	33	30
	EASTERN COAL FIELD:	19	19	19	19	18
	MISSISSIPPIAN PLATEAU:	4	4	4	4	3
	OHIO RIVER ALLUVIUM:	1	1	1	1	1
NUMBER OF SITES WITH DETECTIONS	TOTAL:	31	55	36	51	48
	% SITES W/DETECTIONS:	54.4%	96.5%	63.2%	89.5%	92.3%
BY REGION:	BLUEGRASS (INNER & OUTER):	15	33	22	31	29
	EASTERN COAL FIELD:	13	17	10	16	15
	MISSISSIPPIAN PLATEAU:	2	4	4	4	3
	OHIO RIVER ALLUVIUM:	1	1	1	0	1
NUMBER OF SITES WITH DETECTIONS ABOVE STANDARD	TOTAL:	17	4	0	39	31
	%SITES w/DETECTIONS>STANDARD (of SITES w/DETECTIONS):	54.8%	7.3%	0.0%	76.5%	64.6%
	%SITES w/DETECTIONS>STANDARD (of TOTAL SITES):	29.8%	7.0%	0.0%	68.4%	59.6%
BY REGION:	BLUEGRASS (INNER & OUTER):	7	3	0	30	27
	EASTERN COAL FIELD:	10	0	0	9	3
	MISSISSIPPIAN PLATEAU:	0	1	0	0	1
	OHIO RIVER ALLUVIUM:	0	0	0	0	0

	MCL (mg/L)	Secondary (mg/L)	Other
AMMONIA (NH_3-N)	0.110	-	-
NITRATE (NO_3-N)	10.000	-	-
NITRITE (NO_2-N)	1.000	-	-
ORTHO-PHOSPHATE (PO_4-P)	-	-	0.040
PHOSPHORUS, TOTAL	-	-	0.100

[1]Orthophosphate is not currently regulated, but Texas has a surface water quality standard for orthophosphate-P of 0.04 mg/L.

[2]Total Phosphorus is not currently regulated, but EPA water quality criteria state that phosphates should not exceed 0.100 mg/l in streams or flowing waters not discharging into lakes or reservoirs to control algal growth.

[3]Only 560 ammonia values out of 565 samples:
3 analyses: lab analyses for only pesticides and PCBs,
1 analysis: lab analysis for metals only,
1 analysis: ammonia not included in lab analysis.

[4]Only 559 nitrate values out of 565 samples:
3 analyses: lab analyses for only pesticides and PCBs,
1 analysis: lab analysis for metals only,
2 analyses: nitrate not included in lab analyses.

[5]Only 546 nitrite values out of 565 samples:
3 analyses: lab analyses for only pesticides and PCBs,
1 analysis: lab analysis for metals only,
5 analyses: nitrite not included in lab analyses,
10 analyses: analyses cancelled due to exceeded holding time.

[6]Only 549 orthophosphate values out of 565 samples:
3 analyses: lab analyses for only pesticides and PCBs,
1 analysis: lab analysis for metals only,
2 analyses: orthophosphate not included in lab analyses,
10 analyses: analyses cancelled due to exceeded holding time.

[7]Only 426 total phosphorus values out of 565 samples:
137 analyses: lab samples prior to October 1997 reported metals as dissolved, not total (52 out of 57 sites),
2 analyses: total phosphorus not included in lab analyses.

Table 18. Nutrients Descriptive Statistics

BMU1: NUTRIENTS DESCRIPTIVE STATISTICS						
	AMMONIA-N (NH_3-N) (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**22.5**	**0.02**	**< 0.005**	**< 0.02**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	22.5	< 0.02	< 0.02	< 0.02
EASTERN COAL FIELD:	05/02/95	05/28/03	2.19	< 0.05	< 0.005	< 0.02
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	< 0.09	< 0.02	< 0.02	< 0.02
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	0.08	0.052	< 0.05	< 0.05
	NITRATE-N (NO_3-N) (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**18.28**	**1.55**	**< 0.004**	**0.02**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	18.28	3.05	< 0.004	< 0.004
EASTERN COAL FIELD:	05/02/95	05/28/03	9.33	0.18	< 0.004	< 0.007
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	10.53	0.18	< 0.004	0.02
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	2.8	2.525	2.35	-
	NITRITE-N (NO_2-N) (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**0.134**	**0.0045**	**0.0006**	**< 0.02**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	0.134	< 0.005	0.0006	< 0.02
EASTERN COAL FIELD:	05/02/95	05/28/03	0.031	< 0.005	< 0.001	< 0.02
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	< 0.02	0.002	< 0.001	< 0.001
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.02	< 0.02	< 0.02	< 0.02
	ORTHOPHOSPHATE-P (PO_4-P) (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**04/26/95**	**06/11/03**	**1.04**	**0.06**	**< 0.003**	**< 0.059**
BLUEGRASS (INNER & OUTER):	04/26/95	06/11/03	1.04	0.1805	< 0.003	< 0.059
EASTERN COAL FIELD:	05/02/95	05/28/03	0.197	< 0.019	< 0.003	< 0.059
MISSISSIPPIAN PLATEAU:	04/27/95	06/11/03	< 0.059	0.008	< 0.003	< 0.003
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.059	< 0.059	< 0.003	< 0.059
	TOTAL PHOSPHORUS (mg/L)					
	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
TOTAL:	**07/16/97**	**06/11/03**	**0.938**	**0.1405**	**< 0.005**	**< 0.05**
BLUEGRASS (INNER & OUTER):	07/16/97	06/11/03	0.938	0.23	0.022	< 0.05
EASTERN COAL FIELD:	11/17/97	05/28/03	0.14	< 0.05	< 0.005	< 0.05
MISSISSIPPIAN PLATEAU:	12/02/97	06/11/03	0.12	< 0.05	< 0.005	< 0.05
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	0.055	0.032	0.018	-

Nitrate-N was analyzed in 559 samples and found in 512, or 91.6% (Table 17). Results ranged from non-detect to 18.28 mg/L, which occurred in the Bluegrass (Table 18). In BMU 1, row crops are common in the Bluegrass and the Mississippian Plateau and the occurrence of elevated nitrate-N, especially in the former, is evident in Figure 46. The median value for BMU 1 was 1.55 mg/L, and values were elevated in agricultural and residential areas compared to reference sites and those in forested areas (Figure 47). Four sites (Figure 48) had detections above the MCL.

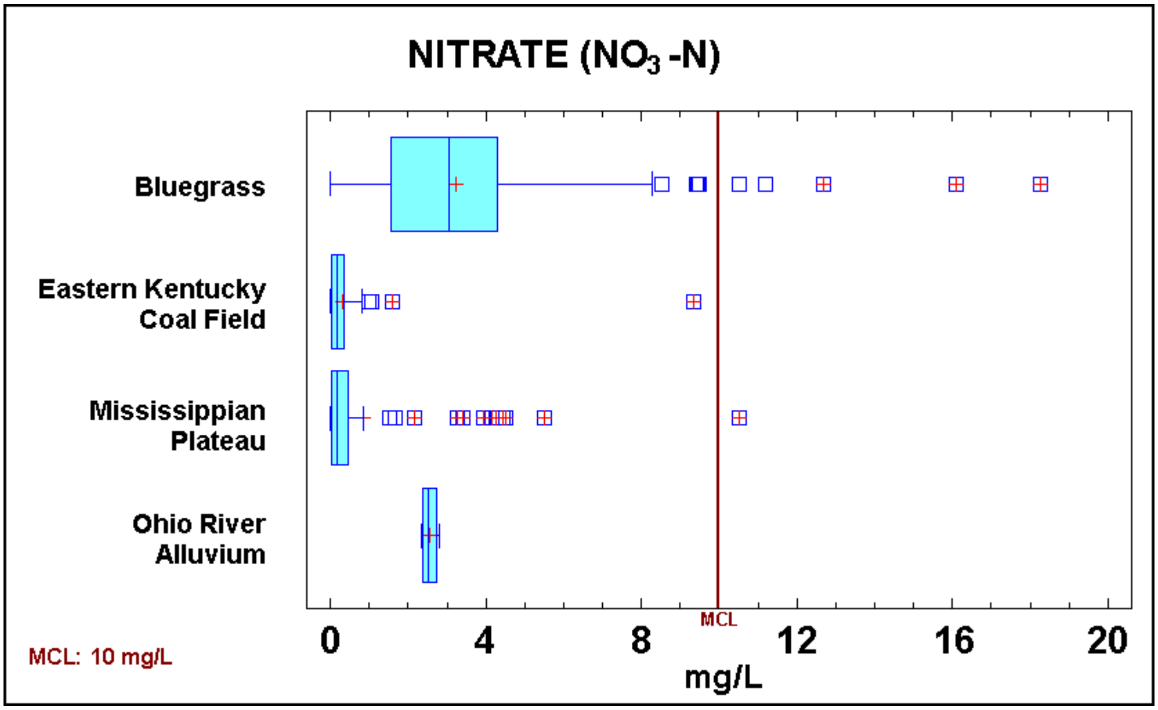

Figure 46. Boxplot of Nitrate-N and Physiographic Regions

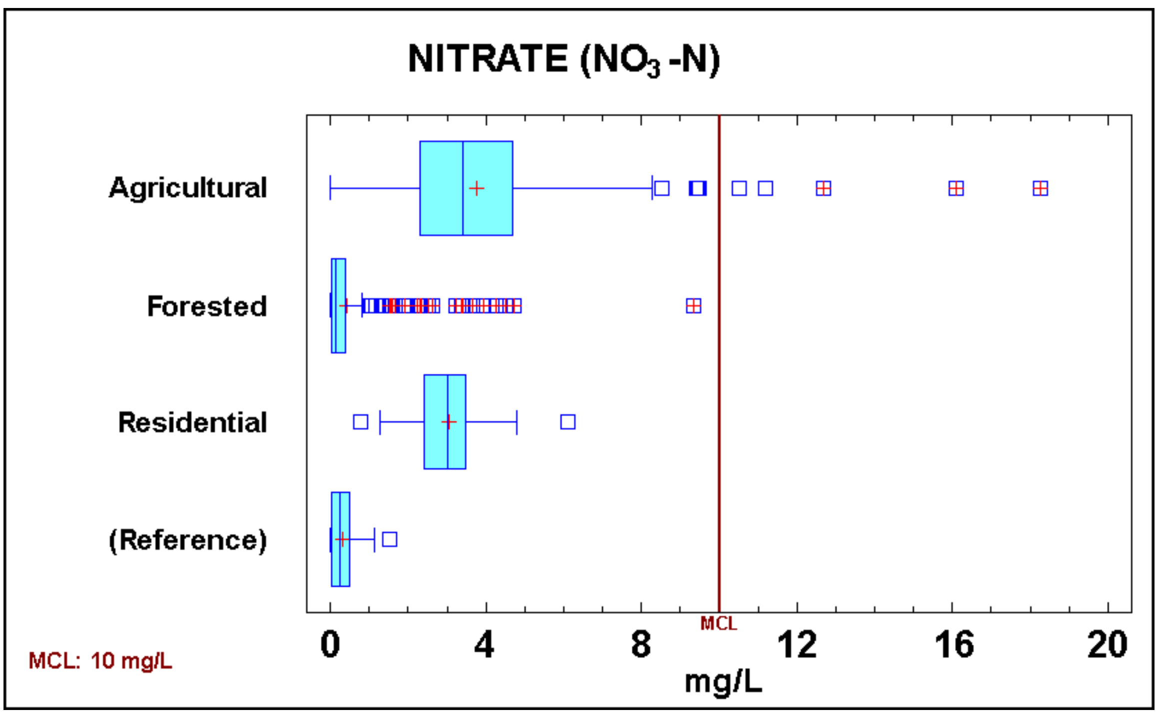

Figure 47. Boxplot of Nitrate-N and Land Use

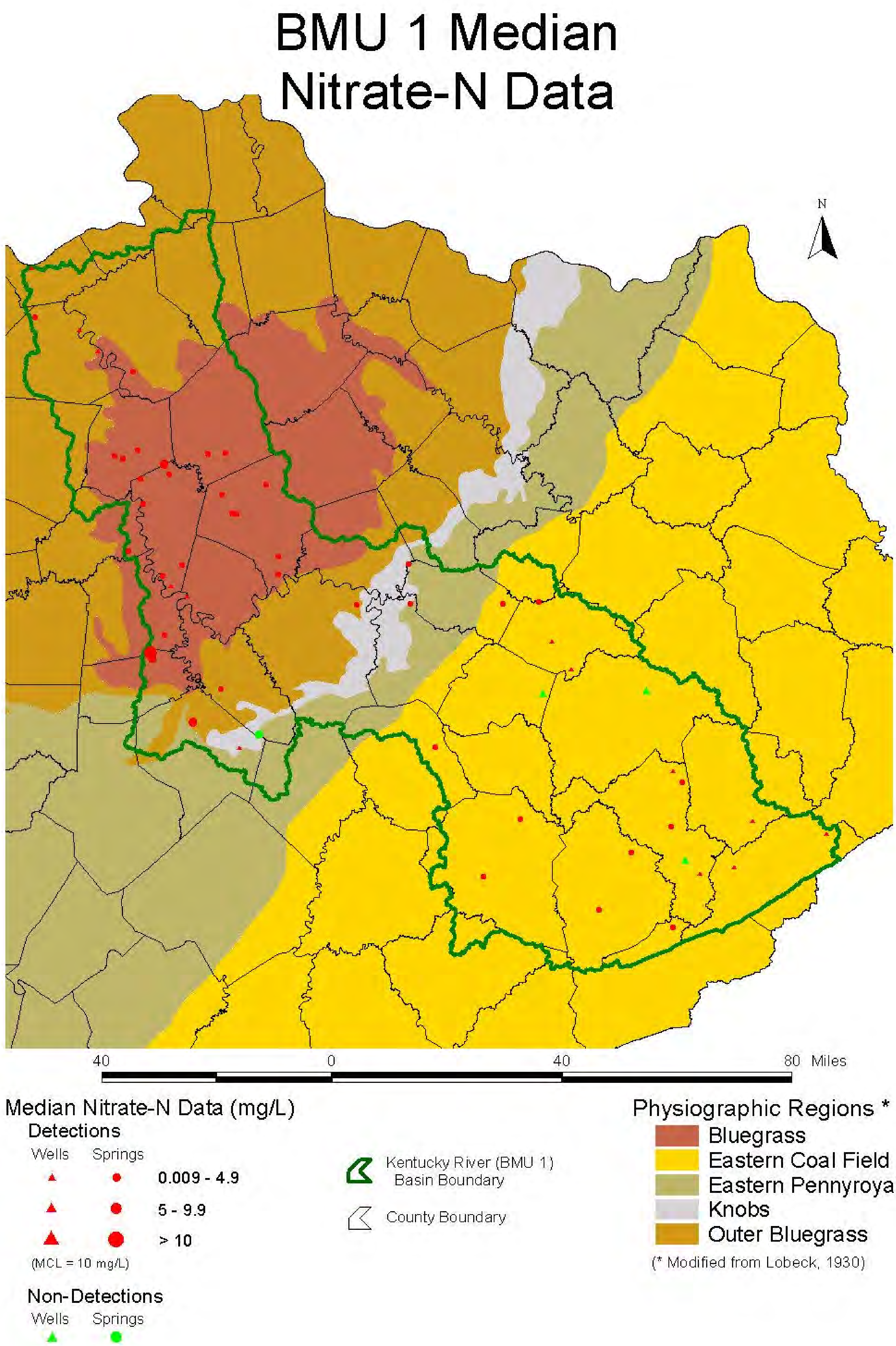

Figure 48. Nitrate-N Map

Nitrate-N values in this study were compared to the values found in other studies, as well as those from reference springs (Table 5). Based upon nitrate-N data from throughout the United States (USGS, 1984), most researchers believe that nitrate-N levels of 3.0 mg/L or lower represent background levels. However, in Kentucky some nitrate-N data suggest significantly lower levels for reference conditions. For example, a review of nitrate-N analyses from three reference springs in Kentucky (Table 5) shows a median value of 0.1805 mg/L. Carey and others (1993) found a median of 0.71 mg/L for nitrate-N in 4,859 groundwater samples collected from predominantly domestic water wells throughout the state. In their statewide study of nitrate-N, Conrad and others (1999) found that depth was a determining factor regarding the occurrence of nitrate-N in wells. Nearly 10% of shallow hand dug wells exceeded the MCL, but only about 1% of wells greater than 151 ft. were in exceedance, and median values for all wells statewide was 0.6 mg/L.

The strong positive correlation between nitrate-N concentration and percentage of agricultural land was significant (Spearman rank coefficient (r_s) = 0.78, $p < 0.0001$). Regionally, stronger positive correlations were observed in the Mississippian Plateau region ($r_s = 0.83$, $p < 0.0001$) than in the Bluegrass region ($r_s = 0.59$, $p < 0.0001$). No significant correlation was observed between nitrate-N concentration and percentage of agricultural land in the East Kentucky Coal Field or Ohio River Alluvium regions. Overall, the relationship between nitrate-N concentration and percentage of pasture land ($r_s = 0.76$, $p < 0.0001$) was stronger than that between nitrate-N concentration and percentage of row crop land use ($r_s = 0.62$, $p < 0.0001$). In the Mississippian Plateau region, correlations between nitrate-N concentration and percentage of pasture land and between nitrate-N concentration and percentage of row crop land use were equally strong ($r_s = 0.83$, $p < 0.0001$). The strong inverse relationship between nitrate-N concentration and percentage of forested land was also significant ($r_s = -0.76$, $p < 0.0001$).

These correlations do not imply that increased percentages of agricultural land cause elevated nitrate-N concentrations, rather they show that elevated nitrate-N concentrations are observed alongside increased percentages of agricultural land use. Bear in mind that 293 of 559 samples were taken at sites with less than 50% agricultural land use (90 Bluegrass, 133 East Kentucky Coal Field, 66 Mississippian Plateau, and 4 Ohio River Alluvium). Of the 266 samples taken at sites with 50% or more agricultural land use, 110 came from sites with 50% or more pasture land (102 Bluegrass, 8 Mississippian Plateau) while 156 came from sites with less than 50% pasture land (all Bluegrass).

Moderate positive correlations between nitrate-N concentration and percentage of residential land use ($r_s = 0.51$, $p < 0.0001$) and between nitrate-N concentration and percentage of commercial land use ($r_s = 0.44$, $p < 0.0001$) were also observed. Regionally, moderate positive correlations were observed in the East Kentucky Coal Field region between nitrate-N concentration and percentage of commercial land use ($r_s = 0.39$, $p < 0.0001$) and in the Mississippian Plateau region between nitrate-N concentration and percentage of residential land use ($r_s = 0.37$, $p = 0.0011$). No significant correlation was observed between nitrate-N concentration and percentage of residential or commercial land in the Bluegrass or Ohio River Alluvium regions.

Although moderate positive correlation was observed, 557 of 559 samples were taken at sites with less than 50% residential land use. Only 1 site had 50% or more residential land use; only 2 samples were taken at this site. 494 of 559 samples were taken at sites with less than 25% residential land use. Only 1 of 4 sites in the Mississippian Plateau region showed any residential land use. No sites had more than 50% commercial land use; 532 of 559 samples were taken at sites with less than 25% commercial land use. The 19 sites in the East Kentucky Coal Field region all had 10% or less commercial land use; 136 of 559 samples were taken in this region.

In conclusion, the nitrate-N medians of 3.05 mg/L for the Bluegrass and 2.525 mg/L for the Ohio River Alluvium are above statewide background levels and indicate possible nonpoint source impacts in those physiographic provinces. Elevated nitrate-N in BMU 1 may be the result of the application of nitrogen fertilizers in row crop areas, especially in the Bluegrass and the

Mississippian Plateau, and throughout the basin, other likely sources include improper management and disposal of domestic and animal waste.

Nitrite (NO_2) also occurs naturally from most of the same sources as nitrate-N. However, nitrite is an unstable ion and is usually quickly converted to nitrate in the presence of free oxygen. The MCL for nitrite-N is 1 mg/L.

Nitrite-N was found in 304 of 546 (55.7%) of the samples included in this study (Table 17). The median for BMU 1 was 0.0045 mg/L, and the maximum was 0.134 mg/L, which occurred in the Bluegrass (Table 18). Nitrite-N values occur within narrow ranges plotted against physiographic regions and land use, but some outliers do occur (Figures 49 and 50). Map distribution is shown in Figure 51.

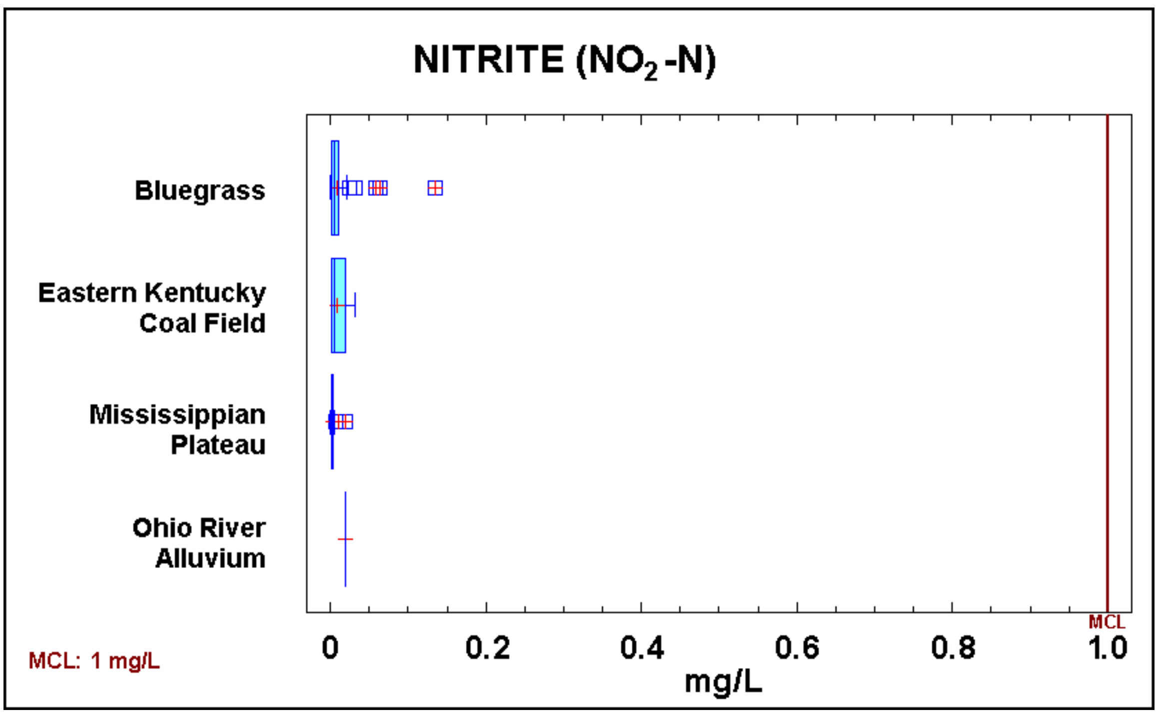

Figure 49. Boxplot of Nitrite-N and Physiographic Regions

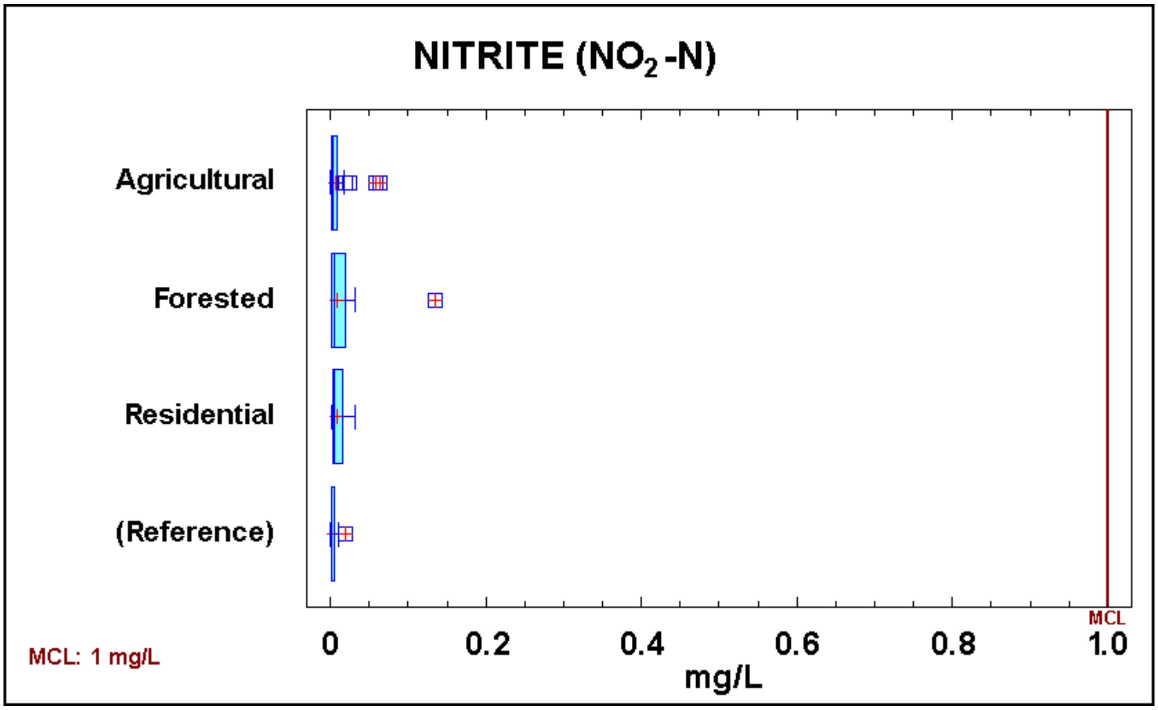

Figure 50. Boxplot of Nitrite-N and Land Use

In the environment, nitrite generally converts rapidly to nitrate through oxidation. This study supports that and nitrite-N was not found to be a significant nonpoint source pollutant in BMU 1, although it may contribute to high levels of nitrate-N.

Ammonia-N (NH_3) occurs naturally in the environment, primarily from the decay of plants and animal waste. The principal source of anthropogenic ammonia-N in groundwater is from ammonia-N based fertilizers. No drinking water standards exist for ammonia-N; however, the proposed DEP limit for groundwater is 0.110 mg/L.

In 560 samples included in this study, ammonia-N was detected in 107, or 19.1% (Table 17). The maximum value of 22.5 mg/L found in the Bluegrass and the median for BMU 1 was 0.02 mg/L (Table 18). Ammonia-N occurs in a narrow range in all physiographic provinces (Figure 52), but outliers are common in the Bluegrass and the Eastern Coal Field. In the former, this may reflect the application of ammonia-N based fertilizers on row crops; in the latter, where

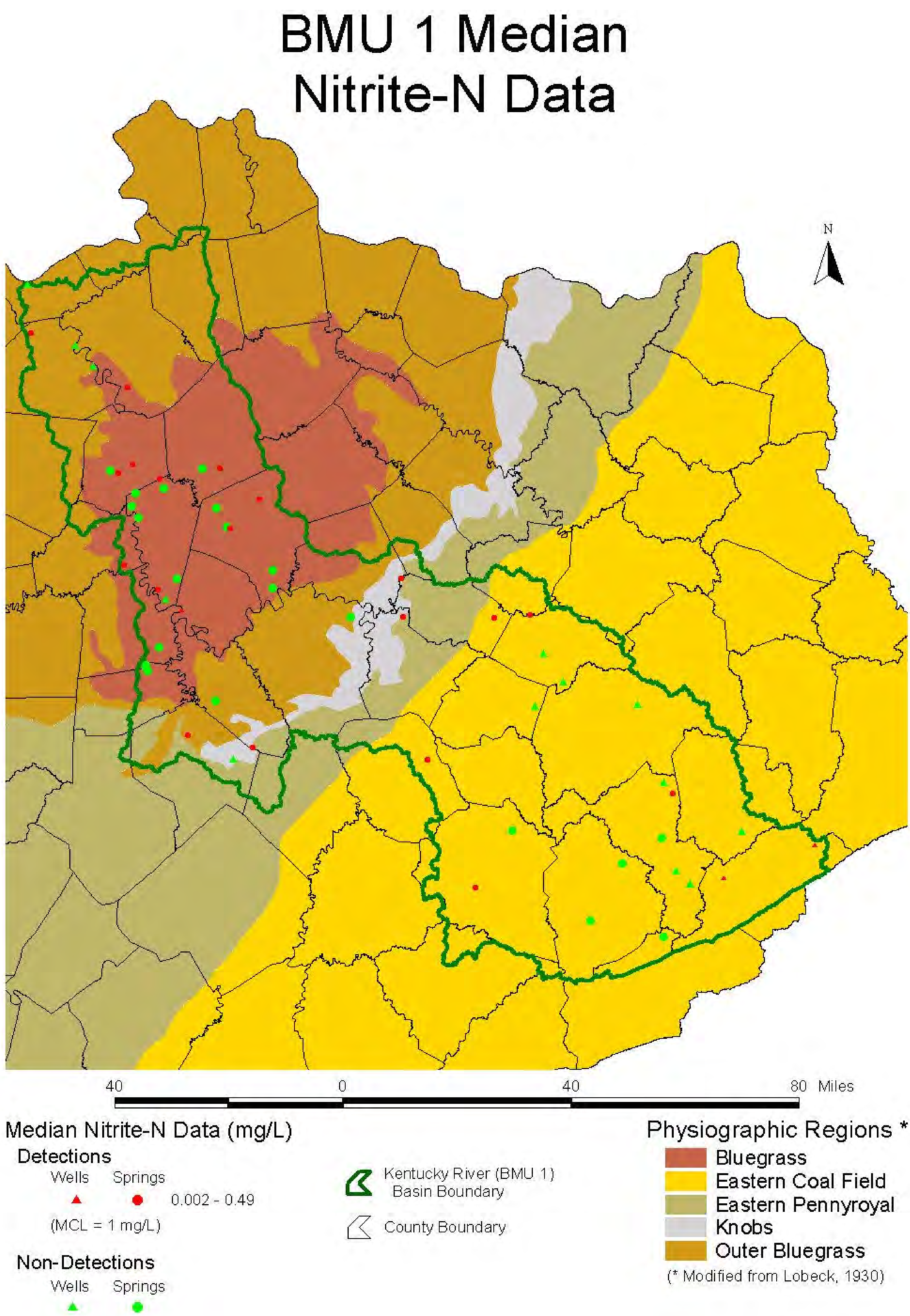

Figure 51. Nitrite-N Map

row crops are uncommon, this may be the result of the improper disposal of household septic waste. Figure 53 shows elevated values in agricultural areas, which is expected; however, an unexpected result was that elevated values were also found in forested areas. Reference springs, which drain forested areas, had a median value of 0.02 mg/L, suggesting that values above this indicate nonpoint source impacts. The source of elevated ammonia-N from groundwater in forested areas is therefore difficult to interpret. The MCL was exceeded at seven sites in the Bluegrass and ten in the Eastern Coal Field (Figure 54).

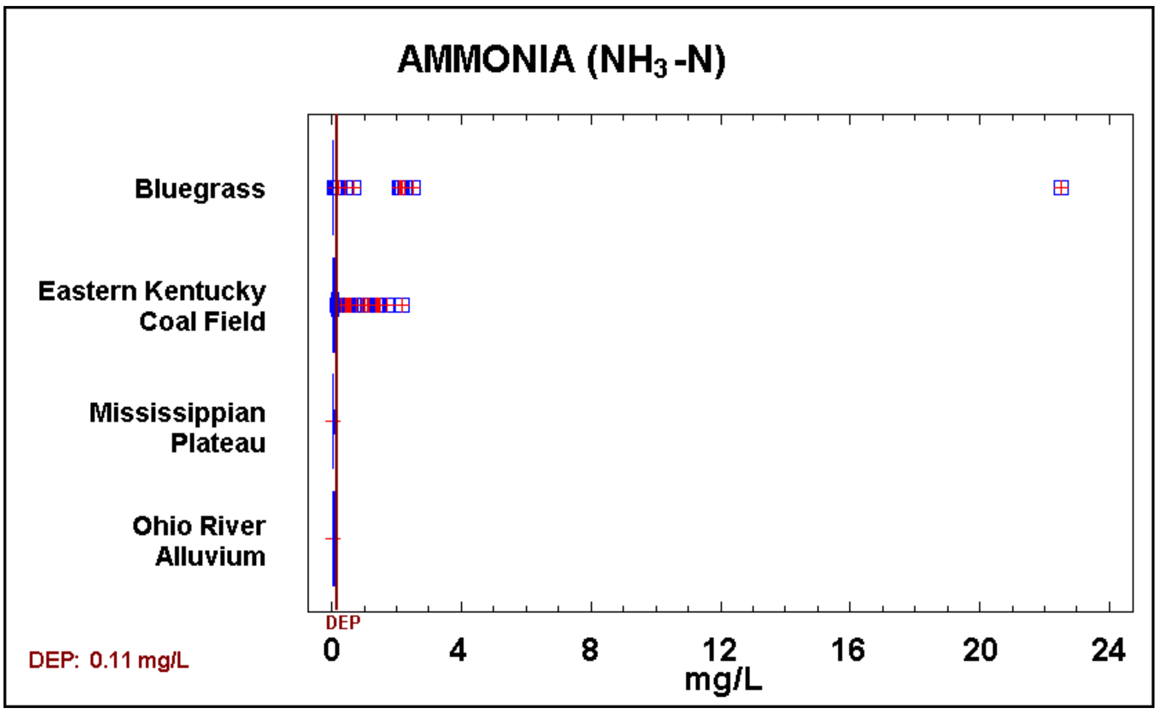

Figure 52. Boxplot of Ammonia-N and Physiographic Regions

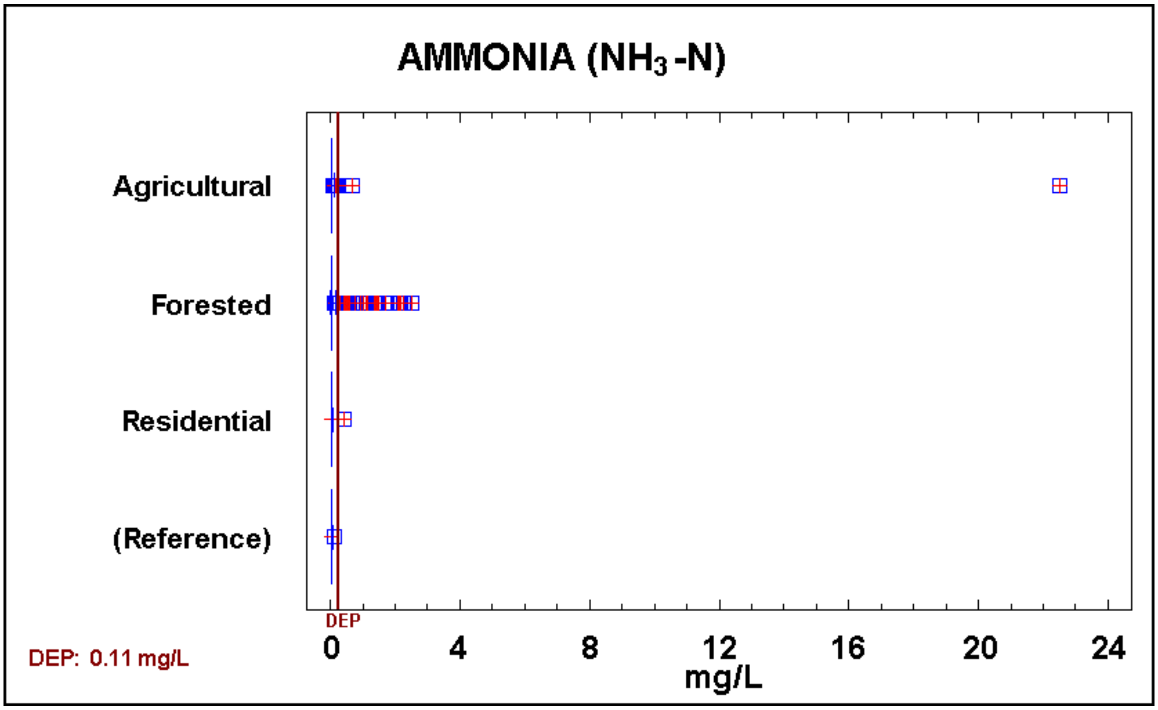

Figure 53. Boxplot of Ammonia-N and Land Use

Two forms of phosphorus are discussed in this report: orthophosphate-P and total phosphorus. Orthophosphate-P (PO_4 -P), or "ortho-p," is the final product of the dissociation of phosphoric acid, H_3PO_4. It occurs naturally in the environment most often as the result of the oxidation of organic forms of phosphorus; it is found in animal waste and in detergents. Orthophosphate-P is the most abundant form of phosphorus, usually accounting for about 90% of the available phosphorus. Phosphorus contributes to the eutrophication of surface water, particularly lakes, commonly known as "algal blooms".

The most common phosphorus mineral is apatite [$Ca_5(PO_4)_3(OH,F,Cl)$], which is found in the phosphatic limestones in the Bluegrass. Neither orthophosphate-P nor total phosphorus has a drinking water standard. Orthophosphate-P data are compared to the Texas surface water quality standard of 0.04 mg/L and total phosphorus data to the surface water limit of 0.1 mg/L recommended by the USGS.

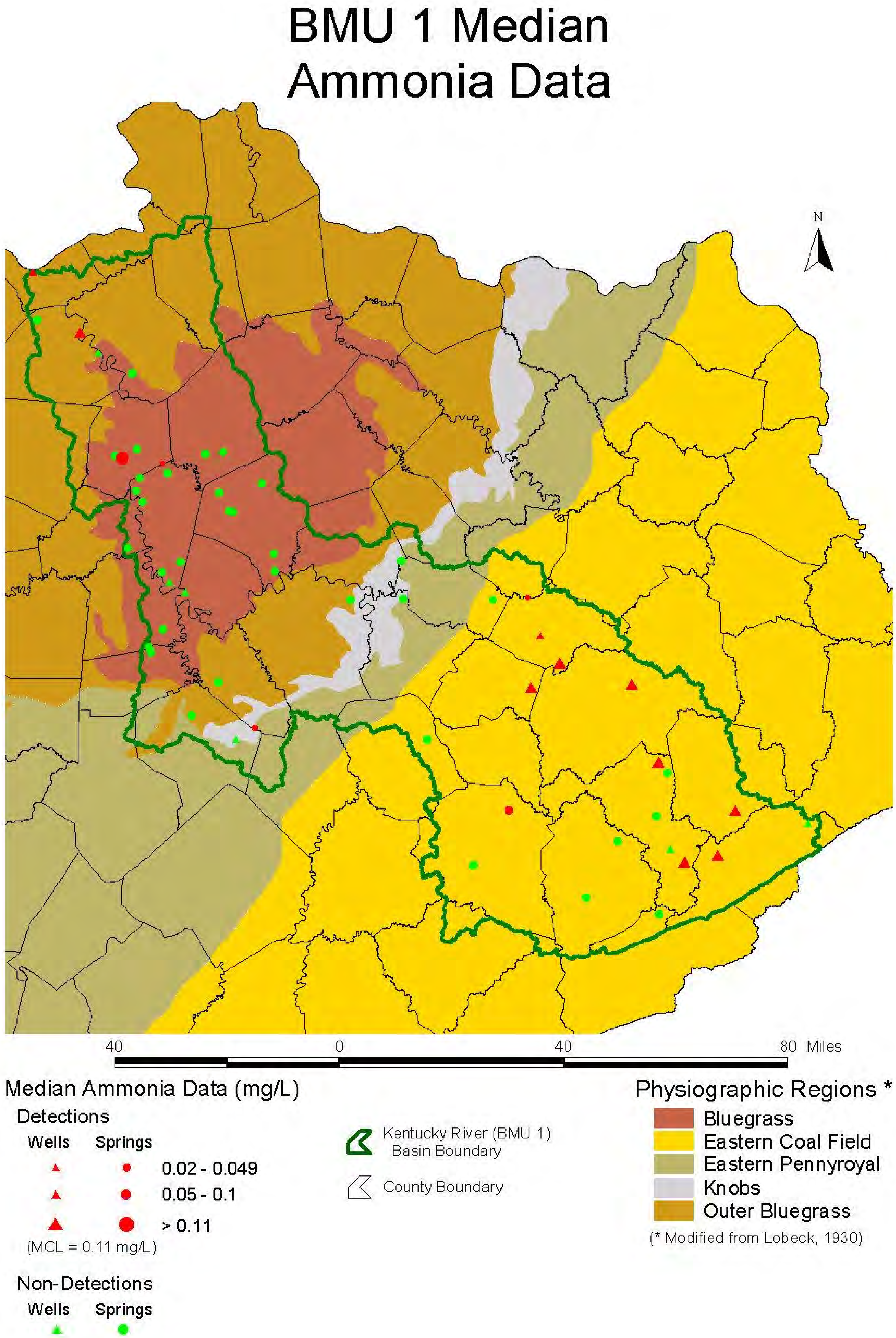

Figure 54. Ammonia-N Map

In natural systems relatively unimpacted from anthropogenic sources, orthophosphate-P occurs at very low levels. For example, reference reach springs typically were either non-detect for orthophosphate-P, or had values in the range of 0.002 – 0.004 mg/L. Although some more sensitive laboratory methods were used in this study, the most common MDL was 0.059 mg/L, which is above the surface water quality standard of 0.04 mg/L used for comparison in this study.

Orthophosphate-P was analyzed in 549 samples and found in 417, or 76.0% (Table 17). The median for BMU 1 was 0.06 mg/L. In general, the Bluegrass had the highest orthophosphate-P with a median of 0.1805 mg/L (Table 18), which may result in part from the underlying geology, but which also may reflect agricultural and residential land use (Figure 55). Nonpoint source impacts of orthophosphate-P on groundwater are difficult to interpret because this compound is both naturally occurring and can be introduced through anthropogenic activity. Map distribution of orthophosphate-P in BMU 1 is shown in Figure 56.

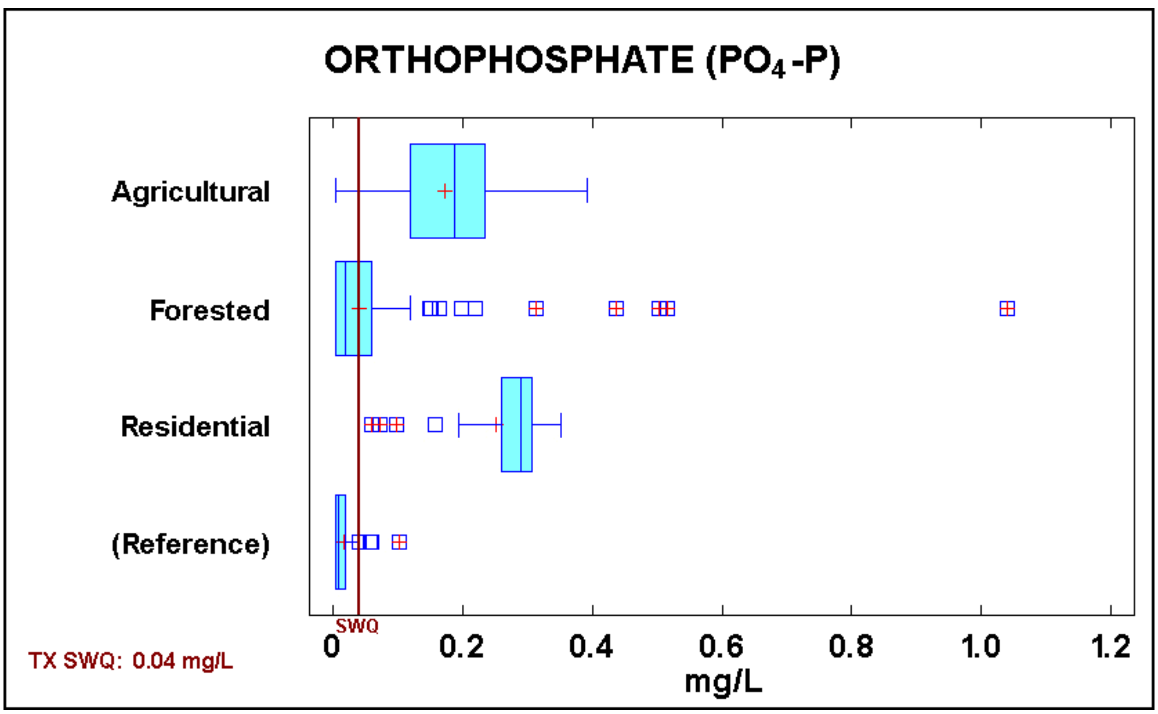

Figure 55. Boxplot of Orthophosphate-P and Land Use

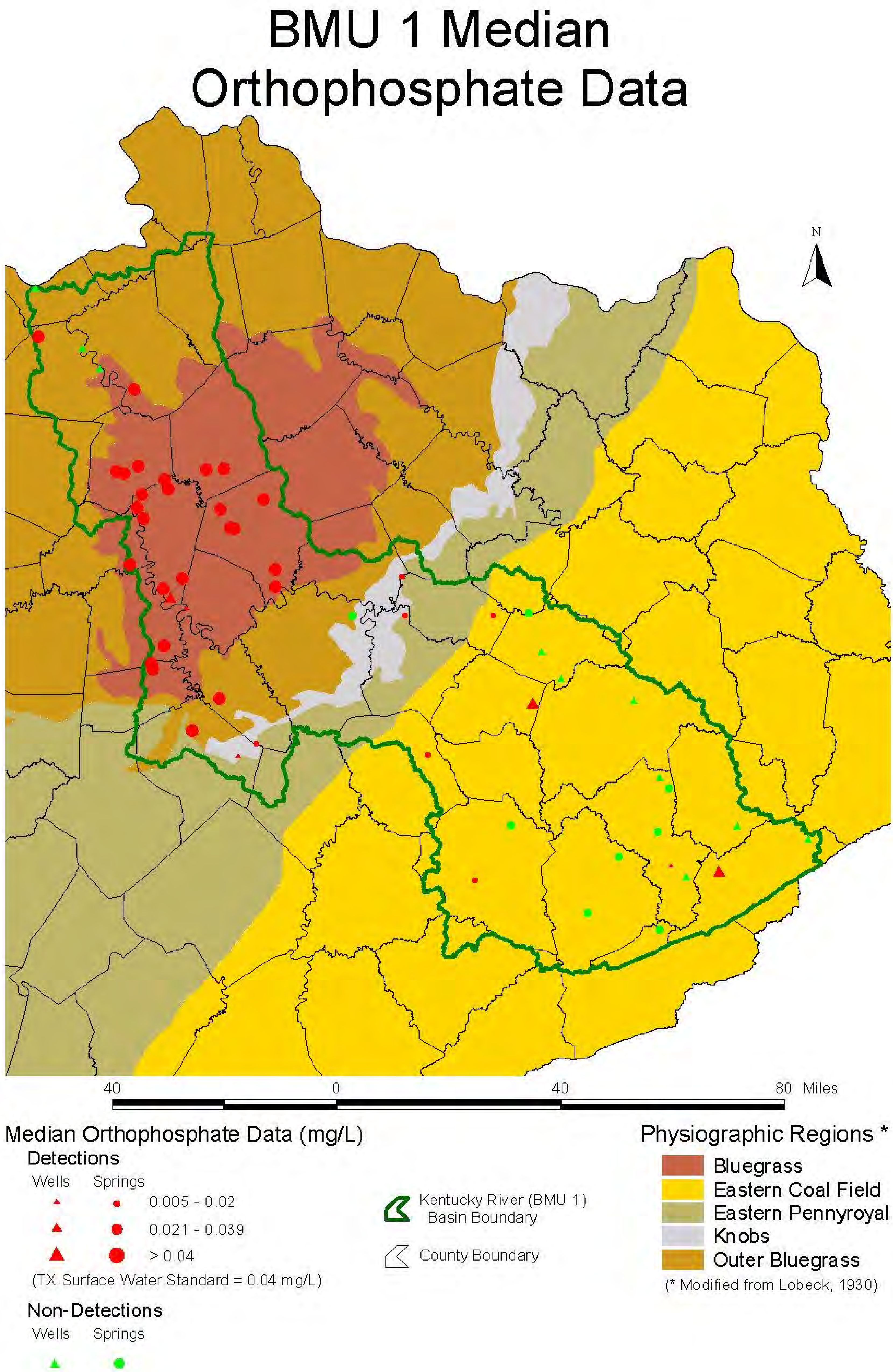

Figure 56. Orthophosphate-P Map

A moderate positive correlation between orthophosphate-P concentration and percentage of agricultural land was observed (Spearman rank coefficient (r_s) = 0.51, $p < 0.0001$). Overall, the relationship between orthophosphate-P concentration and percentage of row crop land use ($r_s = 0.57$, $p < 0.0001$) was stronger than that between orthophosphate-P concentration and percentage of pasture land ($r_s = 0.49$, $p < 0.0001$). A moderate inverse relationship between orthophosphate-P concentration and percentage of forested land was also observed ($r_s = -0.67$, $p < 0.0001$).

Moderate positive correlations were observed between orthophosphate-P concentration and percentage of residential land use ($r_s = 0.66$, $p < 0.0001$) and between orthophosphate-P concentration and percentage of commercial land use ($r_s = 0.71$, $p < 0.0001$). Regionally, correlations between both orthophosphate-P concentration and percentage of residential land use and between orthophosphate-P concentration and percentage of commercial land use were moderate ($r_s = 0.61$, $p < 0.0001$) in the Bluegrass region, but no significant correlation was observed between orthophosphate-P concentration and percentage of residential or commercial land in the East Kentucky Coal Field, Mississippian Plateau or Ohio River Alluvium regions. 351 of 565 samples were taken in the Bluegrass region; 349 were taken at sites with less than 50% residential land use. All 33 sites had less than 30% commercial land use. In summary, orthophosphate-P occurrence in groundwater in BMU 1 may be elevated from nonpoint sources.

Total phosphorus is the sum of organic and inorganic forms of phosphorus. Total phosphorus in reference reach springs was usually nondetect, using an MDL of 0.05 mg/L.

Phosphorus was analyzed in 426 samples and found in 325, or 76.3% (Table 17). Median values were less than 0.05 mg/L in the Eastern Coal Field and the Mississippian Plateau, and 0.032 mg/L in the Ohio River Alluvium (Table 18). The highest median was 0.23 mg/L in the Bluegrass and the highest value (0.938 mg/L) also occurred in that physiographic province. Map distribution of total phosphorus is shown in Figure 57. Reference springs had a median

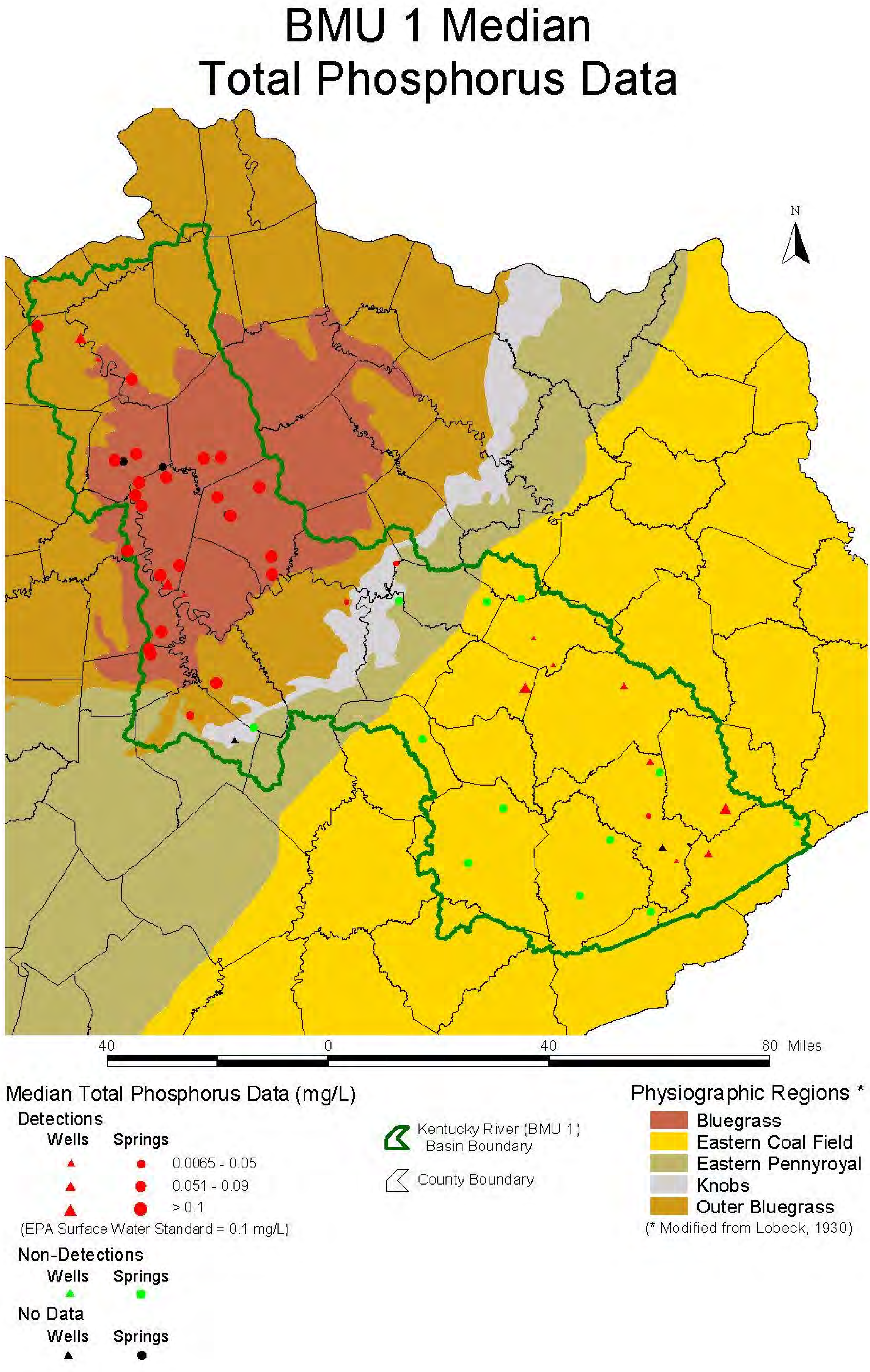

Figure 57. Total Phosphorus Map

phosphorus value of 0.019 mg/L (Table 5), suggesting that values elevated above that level may reflect nonpoint source pollution.

In summary, phosphorus may have impacted groundwater in the study area, but a definitive interpretation is difficult, given this parameter occurs naturally, especially in the phosphatic limestones of the Bluegrass.

Volatile Organic Compounds (Benzene, Toluene, Ethylbenzene, Xylenes, MTBE)

Summaries and descriptive statistics for the volatile organic compounds included in this report are shown in Tables 19 and 20.

The volatile organic compounds most often detected in groundwater are the BTEX compounds: **b**enzene, **t**oluene, **e**thylbenzene and **x**ylenes. Also of concern is **m**ethyl-**t**ertiary-**b**utyl-**e**ther, or MTBE. Because these compounds are among the most commonly found hazardous components of gasoline (Irwin and others, 1997) and because of potential acute and long-term impacts to aquatic life and human health, they are included in this report. Although BTEX compounds also occur naturally, their occurrence in groundwater is usually indicative of point source contamination, most often leaking underground storage tanks.

In urban areas, nonpoint sources of BTEX and MTBE include leaks from automobile gas tanks. Some researchers are concerned with possible air-borne deposition of BTEX and MTBE from the incomplete combustion of fossil fuels. An additional potential source is from pesticides that may contain volatile organic compounds, including BTEX, used as carriers for the active ingredient. These volatile organic compounds are important to evaluate because of various detrimental effects to human health and the environment.

BTEX and MTBE are moderately persistent in the environment, particularly groundwater, for two primary reasons. First, the water solubility of the BTEX constituents range from moderate to high; from 161 mg/L for ethylbenzene to 1730 mg/L for benzene. In

Table 19. Volatile Organic Compounds Summary

BMU1: VOCs SUMMARY[1]		BENZENE	TOLUENE	ETHYLBENZENE	XYLENE	MTBE [2]
NUMBER OF SAMPLES	TOTAL:	209	209	209	209	198
BY REGION:	BLUEGRASS (INNER & OUTER):	147	147	147	147	137
	EASTERN COAL FIELD:	37	37	37	37	37
	MISSISSIPPIAN PLATEAU:	22	22	22	22	21
	OHIO RIVER ALLUVIUM:	3	3	3	3	3
NUMBER OF DETECTIONS	TOTAL:	4	4	0	6	12
	% DETECTS (vs SAMPLES):	1.9%	1.9%	0.0%	2.9%	6.1%
BY REGION:	BLUEGRASS (INNER & OUTER):	4	4	0	6	12
	EASTERN COAL FIELD:	0	0	0	0	0
	MISSISSIPPIAN PLATEAU:	0	0	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0	0	0
NUMBER OF DETECTIONS ABOVE STANDARD	TOTAL:	0	0	0	0	1
	% DETECTIONS > STANDARD (of SAMPLES w/DETECTIONS):	0.0%	0.0%	0.0%	0.0%	8.3%
	% SAMPLES > STANDARD (of TOTAL SAMPLES):	0.0%	0.0%	0.0%	0.0%	0.5%
BY REGION:	BLUEGRASS (INNER & OUTER):	0	0	0	0	1
	EASTERN COAL FIELD:	0	0	0	0	0
	MISSISSIPPIAN PLATEAU:	0	0	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0	0	0
NUMBER OF SITES[3]	TOTAL:	34	34	34	34	31
BY REGION:	BLUEGRASS (INNER & OUTER):	20	20	20	20	17
	EASTERN COAL FIELD:	10	10	10	10	10
	MISSISSIPPIAN PLATEAU:	3	3	3	3	3
	OHIO RIVER ALLUVIUM:	1	1	1	1	1
NUMBER OF SITES WITH DETECTIONS	TOTAL:	2	2	0	1	1
	% SITES W/DETECTIONS:	5.9%	5.9%	0.0%	2.9%	3.2%
BY REGION:	BLUEGRASS (INNER & OUTER):	2	2	0	1	1
	EASTERN COAL FIELD:	0	0	0	0	0
	MISSISSIPPIAN PLATEAU:	0	0	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0	0	0
NUMBER OF SITES WITH DETECTIONS ABOVE STANDARD	TOTAL:	0	0	0	0	1
	%SITES w/DETECTIONS>STANDARD (of SITES w/DETECTIONS):	0.0%	0.0%	0.0%	0.0%	100.0%
	%SITES w/DETECTIONS>STANDARD (of TOTAL SITES):	0.0%	0.0%	0.0%	0.0%	3.2%
BY REGION:	BLUEGRASS (INNER & OUTER):	0	0	0	0	1
	EASTERN COAL FIELD:	0	0	0	0	0
	MISSISSIPPIAN PLATEAU:	0	0	0	0	0
	OHIO RIVER ALLUVIUM:	0	0	0	0	0

	MCL (mg/L)
BENZENE	0.005
TOLUENE	1.000
ETHYLBENZENE	0.700
XYLENE	10.000
MTBE	0.050

[1]VOCs were not included in all analyses:
209 out of 565 samples (at 34 out of 57 sites) show VOC values in this report.

[2]Only 198 MTBE values out of 565 samples:
366 analyses: samples prior to 1999 were not analyzed for MTBE
1 analysis: analysis by different lab did not include MTBE

Table 20. Volatile Organic Compounds Descriptive Statistics

BMU 1: VOCs DESCRIPTIVE STATISTICS	START DATE	END DATE	MAX	MEDIAN	MIN	MODE
	BENZENE (mg/L)					
TOTAL:	**10/16/96**	**06/11/03**	**0.00147**	**< 0.0005**	**0.00038**	**< 0.0005**
BLUEGRASS (INNER & OUTER):	10/16/96	06/11/03	0.00147	< 0.0005	0.00038	< 0.0005
EASTERN COAL FIELD:	04/13/99	05/28/03	< 0.0005	< 0.0005	< 0.0005	< 0.0005
MISSISSIPPIAN PLATEAU:	12/03/96	06/11/03	< 0.0005	< 0.0005	< 0.0005	< 0.0005
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.0005	< 0.0005	< 0.0005	< 0.0005
	TOLUENE (mg/L)					
TOTAL:	**10/16/96**	**06/11/03**	**0.00336**	**< 0.0005**	**0.00038**	**< 0.0005**
BLUEGRASS (INNER & OUTER):	10/16/96	06/11/03	0.00147	< 0.0005	0.00038	< 0.0005
EASTERN COAL FIELD:	04/13/99	05/28/03	< 0.0005	< 0.0005	< 0.0005	< 0.0005
MISSISSIPPIAN PLATEAU:	12/03/96	06/11/03	< 0.0005	< 0.0005	< 0.0005	< 0.0005
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.0005	< 0.0005	< 0.0005	< 0.0005
	ETHYLBENZENE (mg/L)					
TOTAL:	**10/16/96**	**06/11/03**	**< 0.0005**	**< 0.0005**	**< 0.0005**	**< 0.0005**
BLUEGRASS (INNER & OUTER):	10/16/96	06/11/03	< 0.0005	< 0.0005	< 0.0005	< 0.0005
EASTERN COAL FIELD:	04/13/99	05/28/03	< 0.0005	< 0.0005	< 0.0005	< 0.0005
MISSISSIPPIAN PLATEAU:	12/03/96	06/11/03	< 0.0005	< 0.0005	< 0.0005	< 0.0005
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.0005	< 0.0005	< 0.0005	< 0.0005
	XYLENES (mg/L)					
TOTAL:	**10/16/96**	**06/11/03**	**0.0119**	**< 0.0005**	**< 0.0005**	**< 0.0005**
BLUEGRASS (INNER & OUTER):	10/16/96	06/11/03	0.0119	< 0.0005	< 0.0005	< 0.0005
EASTERN COAL FIELD:	04/13/99	05/28/03	< 0.0005	< 0.0005	< 0.0005	< 0.0005
MISSISSIPPIAN PLATEAU:	12/03/96	06/11/03	< 0.0005	< 0.0005	< 0.0005	< 0.0005
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.0005	< 0.0005	< 0.0005	< 0.0005
	MTBE (mg/L)					
TOTAL:	**04/13/99**	**06/11/03**	**0.0501**	**< 0.001**	**0.000433**	**< 0.001**
BLUEGRASS (INNER & OUTER):	04/13/99	06/11/03	0.0501	< 0.001	0.000433	< 0.001
EASTERN COAL FIELD:	04/13/99	05/28/03	< 0.02	< 0.001	< 0.001	< 0.001
MISSISSIPPIAN PLATEAU:	04/12/00	06/11/03	< 0.001	< 0.001	< 0.001	< 0.001
OHIO RIVER ALLUVIUM:	04/21/99	03/07/00	< 0.02	< 0.02	< 0.001	< 0.02

comparison, MTBE is very soluble, with values from 43,000 mg/L to 54,300 mg/L. Because of this solubility, MTBE in contaminant plumes moves at virtually the same rate as the water itself, whereas BTEX plumes move at somewhat slower rates. Second, because these compounds (except for benzene) have relatively low vapor pressure and Henry's law constants, they tend to remain in solution, rather than being volatilized. Because of these and other, physical and chemical characteristics, clean up of contaminated groundwater is difficult.

Benzene is found naturally in the environment in organic matter, including coal and petroleum and is released into the environment during combustion. This compound is found in products manufactured from crude oil, including gasoline, diesel and other fuels, plastics, detergents and pesticides. Benzene has an MCL of 0.005 mg/L, is a known carcinogen, and has been associated with various nervous system disorders, anemia and immune system depression (US EPA, 2000).

Toluene is a clear liquid that occurs naturally in crude oil, as well as in products made from refined crude, such as gasoline and diesel fuel. Toluene also occurs naturally in coal and is common in manufactured products including paint, paint thinner, and fingernail polish. Although toluene is not considered carcinogenic in humans (US EPA, 2000), it has been linked with several detrimental physical and neurological effects, including diminished coordination and the loss of sleep. Toluene has an MCL of 1.0 mg/L.

Ethylbenzene is another component of crude oil and is a constituent of refined petroleum products, including gasoline. In addition, this colorless liquid is used to manufacture styrene. According to the US EPA (2000), limited studies of ethylbenzene have shown no carcinogenic effects in humans; however, animal studies have shown detrimental health effects to the central nervous system. The MCL for ethylbenzene is 0.7 mg/L.

Xylenes are any one of a group of organic compounds typically found in crude oil, as well as in refined petroleum products such as gasoline. Xylenes are clear and sweet-smelling. They are used as solvents and in the manufacture of plastics, polyester and film. Xylenes have an MCL of 10 mg/L. They are not carcinogenic in humans, although data are limited. In humans, exposure to excessive amounts is associated with disorders of the central nervous system, kidneys and liver (US EPA, 2000).

BTEX compounds were analyzed for in 209 samples at 147 sites. Benzene and toluene were each detected four times, or 1.9%; xylenes were found in six samples (2.9%); and ethylbenzene was not detected (Table 20). As shown in Figure 58, benzene, toluene and xylenes

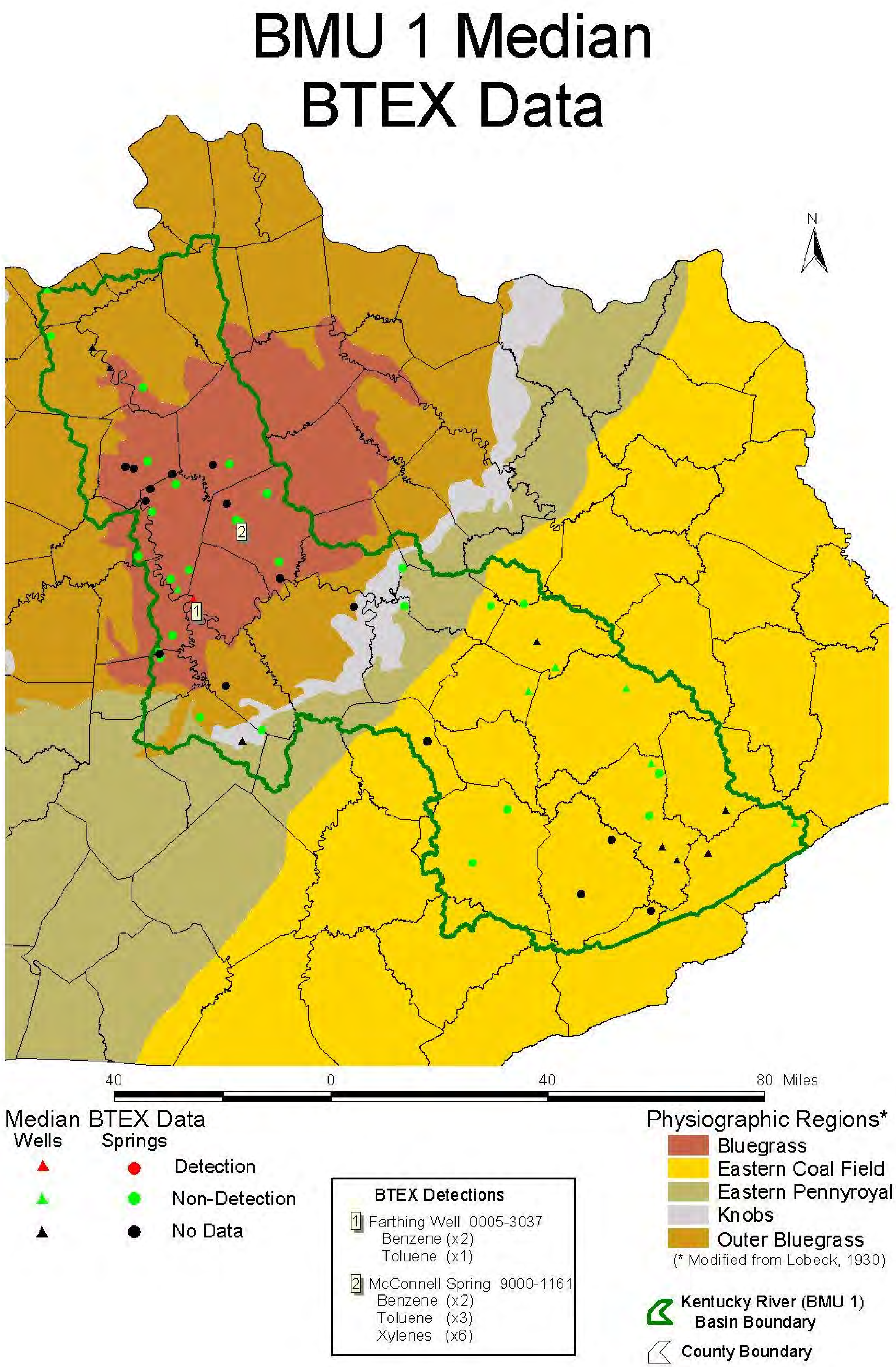

Figure 58. BTEX Map

were detected at the Farthing well and McConnell Spring. The source at the Farthing well is unknown, but the detections at McConnell Spring are probably the result of nonpoint source pollution from urban runoff.

Methyl-tertiary-butyl-ether, or MTBE, is a manufactured compound and does not occur naturally. It is used as an oxygenate added to gasoline in order to promote more complete combustion, increase octane and to reduce emissions of carbon monoxide and ozone. MTBE is very mobile in groundwater and has contaminated numerous aquifers throughout the United States. This compound has no MCL; however, the proposed risk-based DEP standard is 0.05 mg/L. According to the US EPA (1997), no studies have documented human health effects from the consumption of MTBE-contaminated water. However, animal studies have shown some carcinogenic and non-carcinogenic effects.

MTBE was analyzed in 198 samples and detected 12 times, or 6.1% (Tables 19 & 20). As shown in Figure 59, MTBE was detected four times in Royal Spring, seven times at McConnell Spring, and once at Prestons Cave Spring, which is a resurgence of McConnell. The occurrence of MTBE in BMU 1 is the result of nonpoint source pollution from urban runoff.

BTEX and MTBE are not widespread nonpoint source pollutants of concern, but they do impact groundwater in some urban springs. The occurrence of these pollutants should continue to be monitored.

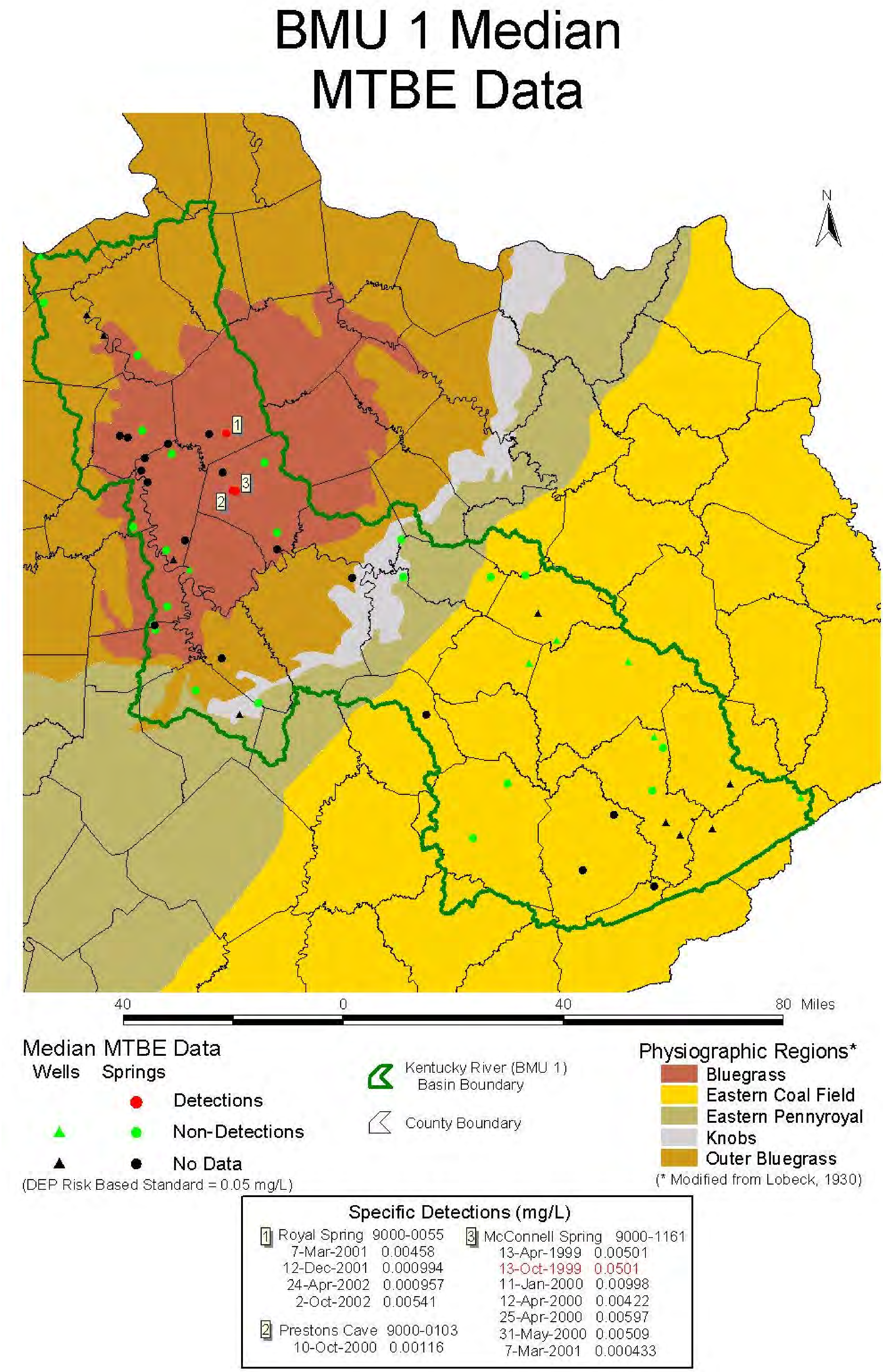

Figure 59. MTBE Map

SUMMARY and CONCLUSIONS

The purpose of this project was to collect data and evaluate ambient groundwater quality in BMU 1 and assess nonpoint source impacts to groundwater. Samples collected specifically for this grant were analyzed along with additional data collected in BMU 1 for other projects, including the Statewide Ambient Groundwater Monitoring Program and through an MOA with the Kentucky Division of Pesticides. Almost 600 analyses from 57 sites were reviewed for this report. Although limited in scope, this study adds valuable data to the existing body of groundwater knowledge for the state in general and BMU 1 in particular. The results should prove useful to environmental regulators, resource planners, researchers and private citizens.

Thirty analytes indicative of naturally occurring groundwater chemistry and potential nonpoint source impacts were review. In general, ambient groundwater quality in BMU 1 is good; however, nonpoint sources have impacted, and continue to threaten, the resource in some areas. The table below summarizes these impacts.

A “Definite” impact is defined as an occurrence or detection of an anthropogenic parameter, such as a pesticide or volatile organic compound. Whether such impacts are detrimental would require receptor studies outside the scope of this inquiry. Definite nonpoint source impacts to groundwater in BMU 1 were documented for the following parameters: atrazine (and atrazine desethyl), metolachlor, alachlor and simazine.

A “Possible” impact is a category for those parameters that occur both naturally as well as from anthropogenic sources. These impacts are difficult to assess and at this time, only tentative conclusions can be made. Possible nonpoint source impacts to groundwater were found for several nutrients (nitrate-N, ammonia-N, total phosphorus, orthophosphate-P), pH, lead, total dissolved solids and total suspended solids. The latter two parameters in particular are difficult to assess because they measure numerous elements and compounds, rather than discrete ones.

Parameters with “No” significant impacts to groundwater in BMU 1 were: 1) either not detected, 2) detected in a very limited number of samples or at very low values, such as mercury,

Table 1. Nonpoint Source Impacts to Groundwater in BMU 1

	PARAMETER	NO NPS INFLUENCE ON GROUNDWATER QUALITY	POSSIBLE NPS INFLUENCE ON GROUNDWATER QUALITY	DEFINITE NPS INFLUENCE ON GROUNDWATER QUALITY
Bulk Water Quality Parameters	Conductivity	•		
	Hardness (Ca/Mg)	•		
	pH	•		
Anions	Chloride	•		
	Fluoride	•		
	Sulfate	•		
Metals	Arsenic	•		
	Barium	•		
	Iron	•		
	Lead		•	
	Manganese	•		
	Mercury	•		
Nutrients	Ammonia-N		•	
	Nitrate-N		•	
	Nitrite-N	•		
	Orthophosphate-P		•	
	Total phosphorous		•	
Pesticides	Alachlor			•
	Atrazine (incl. desethyl)			•
	Cyanazine	•		
	Metolachlor			•
	Simazine			•
Residues	Total Dissolved Solids		•	
	Total Suspended Solids		•	
Volatile Organic Compounds	Benzene			•
	Ethylbenzene	•		
	Toluene			•
	Xylenes			•
	MTBE			•

or 3) detected at levels thought to occur naturally. This study found no impacts to groundwater for the following: conductivity, hardness, chloride, fluoride, sulfate, arsenic, barium, iron, manganese, mercury, nitrite, and cyanazine.

Several biases inherent in any sampling program are a concern in the design, implementation and analysis of results. Most importantly, personnel and funding limit both the geographical distribution of sites, as well as the sampling schedule and frequency. For this study, only one site per approximately 123 square miles could be sampled. Temporal variations, which are important in all groundwater systems, but especially in quick-flow karst systems, may not be adequately addressed through quarterly sampling for one year. Although these problems may preclude definitive conclusions regarding groundwater quality, this project and others like it, contribute vital data that add to our incremental understanding of this resource.

The authors recommend that additional groundwater studies continue, including expansion of the statewide ambient monitoring program and more focused nonpoint source projects, in order to characterize, protect and manage this resource. In particular, future studies should increase the density of sampling sites and the frequency of monitoring, especially in karst terrane.

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APPENDIX A Financial & Administrative Closeout

The Groundwater Branch has committed to the following outputs:

- Identification of suitable groundwater monitoring sites in the Kentucky River basin
- Collection of samples from 30 sites quarterly for one year and delivering these samples to the laboratory for analysis for several parameters, including major inorganic ions, nutrients, pesticides, metals, volatile organic compounds and residues
- Data analysis, including data collected within the basin for other projects
- Production of a report summarizing all relevant groundwater data for this BMU
- Delivering hard-copies of the basin report to the River Basin Teams, local conservation districts, Natural Resource Conservation Service, Agricultural Water Quality Authority, Agricultural Extension offices, and interested stakeholders
- Posting the report on the Division of Water’s internet site

Budget Summary

Budget Categories	**Section 319(h)**	**Non-Federal Match**	**Total**	**Final Expenditures**
Personnel	$30,000	$20,000	$50,000	$50,000
Supplies				
Equipment				
Travel				
Contractual				
Operating Costs				
Other				
TOTAL	**$30,000**	**$20,000**	**$50,000**	**$50,000**

There was no equipment purchased for this project and there were no special grant conditions placed on this project.

APPENDIX B Quality Assurance / Quality Control for Water Monitoring

1. <u>Title Section</u>

A. Project Name

Expanded Groundwater Monitoring for Nonpoint Source Pollution Assessment in the Kentucky River Basin

B. QA/QC Plan Preparers

James S. Webb, Geologist - Registered
David P. Leo, Geologist Supervisor - Registered

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Frankfort, Kentucky 40601

(502) 564-3410

C. Date

April, 1997

D. Project Description

The Kentucky Division of Water currently conducts quarterly nonpoint source groundwater monitoring at approximately 70 sites across the state. This project means to expand that monitoring effort in the Kentucky River Basin (Kentucky Basin Management Unit Two) by increasing the number of monitoring sites and focusing additional efforts of the existing monitoring network in this watershed. This project is intended to work in coordination with other members of the River Basin Team who are conducting surface water and biological sampling.

The goal of this project is to identify the impacts of nonpoint source pollution on the groundwater in the Kentucky River Basin. The objective of this study is to identify aquifers that have been impacted by nonpoint source pollution. Problems in these areas will be identified in order that future nonpoint source resources may be properly focused regarding nonpoint source pollution prevention and pollution abatement.

2. <u>Project Organization and Responsibility</u>

A. Key Personnel

James Webb, Geologist-Registered, Technical Services Section of the Kentucky Division of Water Groundwater Branch will coordinate this project. David P. Leo, Geologist Supervisor - Registered, Technical Services Section, and Peter T. Goodmann, Manager, Groundwater Branch, will provide additional project oversight. James Webb, and Kevin Francis, Hazard Regional Office, will perform field reconnaissance to select sites and will be responsible for sample collection and delivery. The Kentucky Department for Environmental Protection's Division of Environmental Services laboratory will be responsible for sample analysis. All data generated will be delivered to the Kentucky DEP Consolidated Groundwater Database and will be forwarded to the Kentucky Geological Survey's Groundwater Data Repository.

B. Laboratory

Division of Environmental Services
100 Sower Boulevard
Frankfort, Kentucky 40601

(502) 564-6120

C. Participating Agencies

The Groundwater Branch will coordinate with the Division of Water's Watershed Initiative, the Kentucky River Basin Team, and the Division of Water's Water Quality Branch.

3. Watershed Information

A. Stream Names

Groundwater in the Kentucky River and its tributaries is the focus of this study. Numerous groundwater monitoring sites in these areas have been identified.

B. Major River Basin

The entire Kentucky River basin is included in this study. This includes the lower and central subbasins of the main stem, as well as the North, South, and Middle Forks of the Kentucky River, and tributaries. (Note that the central subbasin of the main stem of the Kentucky River is labeled as the "Upper Kentucky River" by the USGS.)

USGS Hydrologic Unit Number

Lower Kentucky River	05100205
Upper Kentucky River	05100204
North Fork Kentucky River	05100201
South Fork Kentucky River	05100203
Middle Fork Kentucky River	05100202

C. Stream Order

This project encompasses the entire Kentucky River basin, including the North, South, and Middle Forks.

D. Counties in Which Study Area is Located

Lower Kentucky River Subbasin:

Anderson, Boone, Boyle, Carroll, Clark, Fayette, Franklin, Gallatin, Garrard, Grant, Henry, Jessamine, Lincoln, Madison, Mercer, Owen Rockcastle, Scott, Shelby, Woodford

Central (Upper) Kentucky River Subbasin:

Clark, Estill, Jackson, Lee, Madison, Menifee, Montgomery, Owsley, Powell, Wolfe

North Fork Kentucky River:

Breathitt, Knott, Lee, Letcher, Perry, Wolfe

South Fork Kentucky River:

Bell, Clay, Jackson, Knox, Lee, Leslie, Owsley

Middle Fork Kentucky River:

Breathitt, Harlan, Lee, Leslie, Perry

4. Monitoring Objectives

Determine impacts of nonpoint source pollution on groundwater resources in selected areas of the Kentucky River basin

Provide guidance for the nonpoint source program to focus future resources relating to nonpoint source pollution of groundwater.

Support other programs, such as Wellhead Protection program, Groundwater Protection Plan program, Agriculture Water Quality Authority, etc.

Provide additional data useful for the long-term management of the resource.

5. Study Area Description

The Kentucky River rises in the Eastern Kentucky Coal Field Region, which is generally underlain by Pennsylvanian shale, sandstone, coal, and siltstone. The middle reaches of the Kentucky River traverse through the Outer Bluegrass Region and the Inner Bluegrass Region, which is characterized by gently rolling topography and is underlain by Ordovician limestone with some interbedded shale and moderately developed karst hydrology. Between the Eastern Coal Field and the Bluegrass, the Kentucky River also passes through a narrow sections of the Mississippian Plateau and the Knobs Physiographic Regions.

6. Monitoring Program/Technical Design

A. Monitoring Approaches

Monitoring will begin in April 1997. Duplicate samples will be collected for at least 10% of all samples in order to check reproducibility and provide QA/QC.

Field reconnaissance will be conducted prior to groundwater sampling to assess the suitability and accessibility of each site. The appropriate Well Inspection or Spring Inventory records will be completed. Site locations will be plotted on 7.5-minute topographic maps, and identified by a site name and unique identification number (AKGWA number) for incorporation into the Department for Environmental Protection's Consolidated Groundwater Data Base and the Kentucky Geological Survey's Groundwater Data Repository.

B. Monitoring Station Location Strategy

All monitoring station locations will be in addition to other stations currently sampled in the basin. All monitoring sites will be karst groundwater basin springs or karst windows, fracture springs, contact springs or water wells.

C. Sample Frequency and Duration

Monitoring will begin in April 1997 and samples will be collected quarterly through April 1998.

D. Sample Parameters, Containers, Preservation, and Handling

Consistent with other monitoring efforts, samples will be collected at each spring or well and analyzed for some or all of the following: major inorganic ions; nutrients; total organic carbon; pesticides, including the most commonly used herbicides, insecticides, and fungicides; dissolved and total metals; and residues. The list of parameters can be found on the attached Chain-of-Custody Form. The analytical methods, containers, volumes collected, preservation, and sample transport will be consistent with the Division of Water's Standard Operating Procedures for Nonpoint Source Surface Water Quality Monitoring Projects, prepared by the Water Quality Branch (August, 2002).

Major inorganic ions are used to establish background groundwater chemistry and also used to measure impacts from nonpoint source pollutants such as abandoned mine lands and abandoned oil and gas production operations by measuring pH, alkalinity, chloride, sulfate, and fluoride. Nutrients and total organic carbon are used to measure impacts from agricultural operations (ammonia, nitrate, nitrite, total Kjeldahl nitrogen or TKN, and orthophosphate) and/or improper sewage disposal (nitrates, ammonia). Where sewage is suspected as a nonpoint source pollutant, unbleached cotton "bugs" may be used to detect optical brighteners (whitening agents used in laundry products and commonly found in sewage). Pesticides are measured to determine both rural agriculture and urban domestic- and commercial-use impacts on ground water. Metals are used to establish the rock-groundwater chemistry, establish local and regional backgrounds for metals, and determine nonpoint source impacts from abandoned coal mine operations.

Bacteria are **<u>not</u>** a proposed sampling parameter because of logistic considerations. Sampling at numerous sites occurs over a one or two-day period, commonly in remote regions. Because of the short holding time for bacteria (6 hours for fecal coliform, 24 hours for total coliform) we are unable to sample efficiently and regularly collect bacteria samples and comply with the required holding times. Where bacteria are suspected to be a nonpoint source pollutant, bacteria samples may be collected or other sampling events may be scheduled. In addition, unbleached cotton "bugs" may be used to detect optical brighteners, common in domestic sewage, originating from laundry products.

All samples will be analyzed by the Division of Environmental Services laboratory according to the appropriate EPA water method.

7. Chain-of-Custody Procedures

Sample containers will be labeled with the site name and well or spring identification number, sample collection date and time, analysis requested, preservation method, and collector's initials. Sampling personnel will complete a Chain-of-Custody Record, developed in conjunction with the DES laboratory, for each sample. The DES laboratory will be responsible for following approved laboratory QA/QC procedures, conducting analyses within the designated holding times, following EPA-approved analytical techniques, and reporting analytical results to the Groundwater Branch. A sample Chain-of-Custody Form is attached.

8. Quality Assurance/Quality Control Procedures

A. Decontamination Protocols

All sampling supplies that come in contact with the sample will be new, disposable equipment, or will be decontaminated prior to and after each use, using the following protocols.

Sample Collection and Filtration Equipment

Whenever possible, sample collection is conducted using the sample container, except for dissolved metals, which are filtered on site. Sample collection equipment, such as bailers and buckets, will consist of Teflon. Pesticide samples will be collected using the sample container or a stainless steel bailer or bucket, in order to avoid the problem of pesticide adsorption to the sampling device (as is considered to occur with Teflon instruments). Any reusable equipment will be decontaminated by rinsing with a 10% hydrochloric acid (HCL) solution, triple rinsed with deionized water, and triple rinsed with water from the source to be sampled prior to collecting a sample. After sampling is complete, excess sample will be disposed of, and the equipment will again be rinsed with the 10% HCL solution and triple rinsed with deionized water.

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

Field Meters

Field meter probes will be rinsed with deionized water before and after each use.

B. Equipment Calibration

Field meters will be calibrated in accordance with the manufacturers instructions.

C. Sample Collection and Preservation/Contamination Prevention

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

Sample containers will be obtained from approved vendors, and will be new or laboratory-decontaminated in accordance with Division of Environmental Services accepted procedures. Sample containerization, preservation, and holding time requirements are outlined in the Division of Water's Standard Operating Procedures for Nonpoint Source Surface Water Quality Monitoring Projects, prepared by the Water Quality Branch (August, 2002). Necessary preservatives will be added in the field; preservatives for dissolved constituents will be added after field filtration. Samples will be stored in coolers packed with ice for transport to the Division of Environmental Services laboratory.

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

Samples will be collected as close to the spring resurgence as possible. If inhospitable terrain prohibits spring access, a decontaminated Teflon bucket attached to a new polypropylene rope may be lowered to the spring to collect the sample. Samples for pesticide analysis will be collected using a stainless steel bucket.

Duplicates and Blanks

Duplicate samples will be collected for at least 10% of all samples in order to check reproducibility and provide QA/QC control. At least one duplicate sample will be submitted with each batch of samples, regardless of the number of samples in the batch. Blanks of deionized water will be submitted at least once per quarter. Blanks will be collected, filtered, and preserved in the same manner as a sample.

Field Measurements

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

CHAIN OF CUSTODY RECORD
NATURAL RESOURCES AND ENVIRONMENTAL PROTECTION CABINET
DIVISION OF WATER - GROUNDWATER BRANCH - Monitoring Network - Billing Code: WPC0400Z

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

Sampler ID: ___________________________

Division for Environmental Services Samples			
Analysis Requested	**Container Size, Type**	**Preservation Method**	**Parameters**
	1000 ml Plastic Cubitainer	Cool to 4°C	**Bulk Parameters** By **ICP:** Chloride, Fluoride, Nitrate-N, Nitrite-N, Sulfate, Ortho-P **plus** Alkalinity, Conductivity, pH, TSS, TDS
	1000 ml Plastic Cubitainer	H_2SO_4 Cool to 4°C	**Nutrients** NH_3 / TKN / TOC/Total Phosphorous
	1000 ml Plastic Boston Round	Filtered HNO_3 Cool to 4°C	**Dissolved Metals** Aluminum, Barium, Calcium, Iron, Magnesium, Manganese, Nickel, Potassium, Silver, Sodium, Zinc
	1000 ml Plastic Boston Round	HNO_3 Cool to 4°C	**Total Metals** By **ICP**: Aluminum, Barium, Calcium, Iron, Magnesium, Manganese, Nickel, Potassium, Silver, Sodium, Zinc By **Graphite Furnace**: Arsenic, Cadmium, Chromium, Copper, Lead, Selenium By **Cold Vapor Extraction**: Mercury
	1000 ml Amber Glass	Cool to 4°C	**N/P Pesticides** Organochlorine Pesticides/PCBs Methods 507/508
	1000 ml Amber Glass	Cool to 4°C	**Herbicides** Method 555
	Three 40 ml Glass	HCl Cool to 4°C	**VOCs** (Trip Blank Required)

COMMENTS:

Signatures:

Relinquished by: ______________________ Relinquished by: ______________________

Received by: _________________________ Received by: _________________________

Date: ______ Time: ______ Date: ______ Time: ______

Relinquished by: ______________________ Relinquished by: ______________________

Received by: _________________________ Received by: _________________________

Date: ______ Time: ______ Date: ______ Time: ______

Sample #: _______________ Report #: _______________

Revised 5/26/04

APPENDIX C Groundwater Sites Monitored in BMU 1

COUNTY	SITE NUMBER	SITE NAME	PHYSIOGRAPHIC REGION	7.5 QUADRANGLE	TYPE	LATITUDE	LONGITUDE
Carroll	00004033	Carrollton Well	Ohio River Alluvium	Carrollton	PWS Well	38.68040556	85.17739444
Perry	00007178	Viper Elem Well	E KY Coal Field	Hazard S	PWS Well	37.16194444	83.13194444
Letcher	00028100	Fleming/Neon Well	E KY Coal Field	Jenkins W	PWS Well	37.2174003	82.6854692
Wolfe	00029638	Bethany Well	E KY Coal Field	Landsaw	PWS Well	37.6498811	83.4738028
Lincoln	00039352	Wm Whitley Well	Miss Plateau	Crab Orchard	Unused Well	37.4683333	84.53
Owen	00040553	Glenwood Hall Well	Bluegrass	Worthville	PWS Well	38.52438889	85.02344444
Letcher	00044576	Mountain Heritage Well	E KY Coal Field	Blackey	PWS Well	37.14097222	82.97777778
Wolfe	00044679	Campton Double-Kwik	E KY Coal Field	Campton	PWS Well	37.72152778	83.53416667
Perry	00044688	Homeplace Well	E KY Coal Field	Noble	PWS Well	37.38805556	83.16111111
Perry	00046635	Whiskey Store Well	E KY Coal Field	Vicco	PWS Well	37.12805556	83.08583333
Knott	00046639	Baker Well	E KY Coal Field	Hindman	Private Well	37.2569442	82.9166667
Breathitt	00047174	Rousseau School Well	E KY Coal Field	Guage	PWS Well	37.5886019	83.2388969
Lee	00048656	Samples Well	E KY Coal Field	Tallega	Private Well	37.58916667	83.56694444
Henry	00048657	Cox Well	Bluegrass	Gratz	Unused Well	38.47138889	84.96666667
Mercer	00053037	Farthing Well	Bluegrass	Wilmore	Private Well	37.8508333	84.6897222
Woodford	00054122	Hack Well	Bluegrass	Keene	Private Well	37.8777567	84.7413889
Scott	90000055	Royal Spring	Bluegrass	Georgetown	PWS Spring	38.20888889	84.56166667
Fayette	90000077	Silver Spring	Bluegrass	Lexington W	Unused Spring	38.1039786	84.5746872
Fayette	90000103	Prestons Cave Spring	Bluegrass	Lexington W	Unused Spring	38.05694444	84.54194444
Lincoln	90000120	St Asaph Spring	Bluegrass	Stanford	Unused Spring	37.53138889	84.67361111
Fayette	90000552	Russell Cave Spring	Bluegrass	Centerville	Unused Spring	38.12861111	84.43444444
Boyle	90000583	Rankin Spring	Bluegrass	Danville	Private Spring	37.69361111	84.80222222
Woodford	90001053	Moores Spring	Bluegrass	Salvisa	Unreg Public Spring	37.90138889	84.76527778
Woodford	90001103	Shanes Spring	Bluegrass	Frankfort E	Unused Spring	38.1877611	84.7580167
Henry	90001132	Barker Spring	Bluegrass	Campbellsburg	Unused Spring	38.55583333	85.16666667
Jackson	90001133	Turkey Foot Spring	E KY Coal Field	Mckee	Unreg Public Spring	37.45972222	83.91111111
Powell	90001134	Nada Spring	Miss Plateau	Slade	Unreg Public Spring	37.81638889	83.68777778
Estill	90001135	Spout Spring	Miss Plateau	Clay City	Unreg Public Spring	37.82277778	83.97916667
Anderson	90001139	McCalls Spring	Bluegrass	Salvisa	Unused Spring	37.96447222	84.87388889
Franklin	90001143	Cedar Cove Spring	Bluegrass	Frankfort E	Unused Spring	38.21888889	84.84166667
Garrard	90001144	Dripping Springs	Bluegrass	Brodhead	Unreg Public Spring	37.49638889	84.46666667
Franklin	90001152	Sanchez Spring	Bluegrass	Frankfort W	Unused Spring	38.19861111	84.88805556
Menifee	90001154	Trail Spring	E KY Coal Field	Pomeroyton	Unused Spring	37.82027778	83.57361111
Clay	90001155	Aunt Sophs Spring	E KY Coal Field	Oneida	Unreg Public Spring	37.27277778	83.64777778
Clay	90001156	Mustang Spring	E KY Coal Field	Manchester	Unreg Public Spring	37.13194444	83.76805556
Woodford	90001157	Watts Ferry Spring	Bluegrass	Tyrone	Unreg Public Spring	38.11194444	84.84638889
Madison	90001159	Corren Spring	Bluegrass	Union City	Unused Spring	37.8225	84.15
Owen	90001160	Ford Spring	Bluegrass	Monterey	Unused Spring	38.41666667	84.85416667
Fayette	90001161	McConnell Spring	Bluegrass	Lexington W	Unused Spring	38.05416667	84.53
Powell	90001178	Sizemore Spring	Miss Plateau	Levee	Unused Spring	37.92194444	83.98388889
Scott	90001194	Slacks Spring	Bluegrass	Georgetown	Unused Spring	38.20638889	84.61777778
Woodford	90001200	Spring St Blue Hole	Bluegrass	Midway	Irrigation Spring	38.15722222	84.74305556
Fayette	90001201	Boggs Spring	Bluegrass	Coletown	Unused Spring	37.94611111	84.39722222
Mercer	90001208	Burgin Spring	Bluegrass	Harrodsburg	Unused Spring	37.75277778	84.76333333
Franklin	90001236	Double Springs	Bluegrass	Frankfort W	Unused Spring	38.2047219	84.9152778
Garrard	90001381	Jackman Cave Spring	Bluegrass	Lancaster	Unused Spring	37.61555556	84.58555556
Fayette	90001949	Lauras Spring	Bluegrass	Coletown	Private Spring	37.90083333	84.3975
Mercer	90002197	Gwinn Spring	Bluegrass	Danville	Livestock Spring	37.70777778	84.80777778
Boyle	90002199	Blacksmith Spring	Bluegrass	Danville	Unused Spring	37.70444444	84.80694444
Woodford	90002424	Labrador Spring	Bluegrass	Keene	Unused Spring	37.92722222	84.70333333
Woodford	90002425	Old Taylor Spring	Bluegrass	Frankfort E	Unused Spring	38.14527778	84.83305556
Woodford	90002427	Clifton Spring	Bluegrass	Tyrone	Unused Spring	38.0825	84.82583333
Leslie	90002445	Tower Mnt. Spring	E KY Coal Field	Hoskinston	Private Spring	37.04	83.40694444
Perry	90002448	Dads Spring	E KY Coal Field	Hazard N	Unused Spring	37.3574778	83.1333622
Perry	90002449	Lothair Spring	E KY Coal Field	Hazard S	Private Spring	37.24555556	83.17333333
Harlan	90002451	Hemlock Spring	E KY Coal Field	Nolansburg	Unused Spring	36.9925	83.175
Leslie	90002452	Wooton Spring	E KY Coal Field	Hyden E	Private Spring	37.18333333	83.3

Table C-1 Groundwater Sites Monitored in BMU1

SITE NUMBER	SITE NAME	SAMPLE EVENTS PER SITE	1 QTR 1995	2 QTR 1995	3 QTR 1995	4 QTR 1995	1 QTR 1996	2 QTR 1996	3 QTR 1996	4 QTR 1996	1 QTR 1997	2 QTR 1997	3 QTR 1997	4 QTR 1997	1 QTR 1998	2 QTR 1998	3 QTR 1998	4 QTR 1998	1 QTR 1999	2 QTR 1999	3 QTR 1999	4 QTR 1999	1 QTR 2000	2 QTR 2000	3 QTR 2000	4 QTR 2000	1 QTR 2001	2 QTR 2001	3 QTR 2001	4 QTR 2001	1 QTR 2002	2 QTR 2002	3 QTR 2002	4 QTR 2002	1 QTR 2003	2 QTR 2003
00004033	Carrollton Well	**4**																		1	1	1	1													
00007178	Viper Elem Well	**7**		1		1	1	1	1	1		1																								
00028100	Fleming/Neon Well	**18**		1			1	1	1			1	1	1	1	1			1	1				1	1		1				1	1		1		1
00029638	Bethany Well	**4**																1	1	1					1											
00039352	Wm Whitley Well	**5**		1	1	1	1	1																												
00040553	Glenwood Hall Well	**5**															1	1	1	1	1															
00044576	Mountain Heritage Well	**2**											1	1																						
00044679	Campton Double-Kwik	**5**											1				1	1	1	1																
00044688	Homeplace Well	**7**											1	1			1	1	1	2																
00046635	Whiskey Store Well	**3**																1	1	1																
00046639	Baker Well	**4**															1	1	1	1																
00047174	Rousseau School Well	**6**											1				1	1	1	1	1															
00048656	Samples Well	**1**																		1																
00048657	Cox Well	**4**															1	1	1	1																
00053037	Farthing Well	**2**																						1	1											
00054122	Hack Well	**1**																						1												
90000055	Royal Spring	**36**		1	1	1	1	1	1	1	1	2	1	1	1	1	1	1	1	2	1	1	1	3	1		1	1	1	1		1	2	1	1	1
90000077	Silver Spring	**3**					1												1	1																
90000103	Prestons Cave Spring	**2**											1													1										
90000120	St Asaph Spring	**19**											1	1	1		1	1		1		1	1	1	1		1	1	1	1		1	1	1	1	1
90000552	Russell Cave Spring	**28**		1	1	1	1	1		1	1	2	1	1		1			1	1		1	1	3			1	1	1	1		1	1	1	1	1
90000583	Rankin Spring	**2**																			1		1													
90001053	Moores Spring	**1**																					1													
90001103	Shanes Spring	**1**							1																											
90001132	Barker Spring	**22**		1		1	1	2		2	1	1	1	1	1	1			1								1	1	1		1	1		1	1	1
90001133	Turkey Foot Spring	**15**		1	1	1	1	1	1	1	1	1	1	1	1	1	1		1																	
90001134	Nada Spring	**33**		1	1	1	1	1	1	1	1	1	2	1	1	1		1	2	1	1	1		2	2		1	1	1	1		1	1	1	1	1
90001135	Spout Spring	**28**		1	1	1	1	1	1	1	1	1	2		1	1		1		1	1	1		1	1		1	1	1	1		1	1	1	1	1
90001139	McCalls Spring	**32**		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		2		2	1	2	1		1	1	1	1		1	1	1	1	1
90001143	Cedar Cove Spring	**32**			1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2	1	1	1	2	1		1	1	1	1		1	1	1	1	1
90001144	Dripping Springs	**24**			1	1	1	1	1	1	1	1	1	1	1				1			1	1	1			1	1	1	1		1	1	1	1	1
90001152	Sanchez Spring	**1**											1																							
90001154	Trail Spring	**9**															1	1	1	1	1	1		2	1											
90001155	Aunt Sophs Spring	**7**															1	1	1	2		1		1												
90001156	Mustang Spring	**17**															1	1	1	2		1		1	1		1		2		1	1	1	1	1	1
90001157	Watts Ferry Spring	**6**															1	1	2	1			1													
90001159	Corren Spring	**3**															1	1		1																
90001160	Ford Spring	**7**															1	1	1	1	1		1	1												
90001161	McConnell Spring	**33**		1	1	1	1	1	1	1	1	2	1	1	1	1	1	1	1	2		1	1	3			1	1	1	1		1	1	1	1	1
90001178	Sizemore Spring	**8**								1		1	1	1	1	1		1						1												
90001194	Slacks Spring	**5**															1		2	1			1													
90001200	Spring St Blue Hole	**26**								1	1	1	2	1	1	3	2		1	2	1		1	4	1			3	1							
90001201	Boggs Spring	**26**										1	2	1	1	3	2	1	1	3	1		1	4	1			3	1							
90001208	Burgin Spring	**8**											1	1	1		1	1		1			1	1												
90001236	Double Springs	**1**															1																			
90001381	Jackman Cave Spring	**3**															1	1		1																
90001949	Lauras Spring	**5**													1		1	1	1	1																
90002197	Gwinn Spring	**1**																					1													
90002199	Blacksmith Spring	**1**																					1													
90002424	Labrador Spring	**4**															1	1	1	1																
90002425	Old Taylor Spring	**3**															1	1	1																	
90002427	Clifton Spring	**4**																1	2	1																
90002445	Tower Mnt. Spring	**3**															1	1		1																
90002448	Dads Spring	**15**															1	1	1	2				1	1		1		2			1	1	1	1	1
90002449	Lothair Spring	**5**															1	1	1	1				1												
90002451	Hemlock Spring	**4**															1	1	1	1																
90002452	Wooton Spring	**4**															1	2	1																	
57	**TOTALS**	**565**	0	11	10	12	14	14	11	14	11	18	26	17	16	17	34	35	38	49	12	14	18	38	15	1	13	16	16	9	3	13	12	13	12	13

Table C-2 Number of Groundwater Samples per Site in BMU1