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

By

James S. Webb
Jolene M. Blanset
Robert J. Blair

Groundwater Branch
Kentucky Division of Water
14 Reilly Road
Frankfort, KY 40601

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS 6
EXECUTIVE SUMMARY 7
INTRODUCTION and BACKGROUND 9
Project Description 10
Previous Investigations 12
PHYSIOGRAPHIC AND HYDROGEOLOGIC SETTING 14
Kentucky River Basin 14
Groundwater Sensitivity 15
Physiographic Provinces 15
MATERIALS and METHODS 19
Introduction 19
Statistical and Graphical Methods 21
Site Selection 23
Sample Collection Methods 24
RESULTS and DISCUSSION 27
Introduction 27
Bulk Parameters (Conductivity, Hardness and pH) 27
Anions (Chloride, Fluoride, Sulfate) 39
Metals (Arsenic, Barium, Iron, Lead, Manganese and Mercury) 47
Pesticides (Atrazine, Metolachlor, Simazine, Alachlor and Cyanazine) 66
Residues (Total Dissolved Solids (TDS) and Total Suspended Solids (TSS)) 77
Nutrients (Nitrate-N, Nitrite-N, Ammonia-N, Orthophosphate-P, Total Phosphorus) 84
Volatile Organic Compounds (Benzene, Toluene, Ethylbenzene, Xylenes, MTBE) 101
SUMMARY and CONCLUSIONS 108
LITERATURE CITED 111
APPENDIX A. Financial & Administrative Closeout 115
APPENDIX B. Quality Assurance / Quality Control for Water Monitoring 116
APPENDIX C. Groundwater Sites Monitored in BMU 1 124

LIST OF TABLES

Table 1. Nonpoint Source Impacts to Groundwater in BMU 1 8
Table 2. Parameters and Standards for Comparison 11
Table 3. Land Use and Potential Nonpoint Source Contaminants 14
Table 4. Simplified Aquifer Characteristics in BMU 1 18
Table 5. Reference Springs Analytical Data Summary 22
Table 6. Bulk Parameters Summary 29
Table 7. Bulk Parameters Descriptive Statistics 30
Table 8. Anions Summary 39
Table 9. Anions Descriptive Statistics 40
Table 10. Metals Summary 50
Table 11. Metals Descriptive Statistics 51
Table 12. Pesticides Summary 69
Table 13. Pesticides Descriptive Statistics 70
Table 14. Pesticide Method Detection Limits 70
Table 15. Residues Summary 78
Table 16. Residues Descriptive Statistics 79
Table 17. Nutrients Summary 85
Table 18. Nutrients Descriptive Statistics 86
Table 19. Volatile Organic Compounds Summary 102
Table 20. Volatile Organic Compounds Descriptive Statistics 103

LIST OF FIGURES

Figure 1. Sites and Land Use in BMU ..... (map pocket)
Figure 2. Sites and Physiographic Regions in BMU 1 ..... (map pocket)
Figure 3. Boxplot of Conductivity and Physiographic Regions 31
Figure 4. Boxplot of Conductivity and Land Use 31
Figure 5. Conductivity Map 32
Figure 6. Boxplot of Hardness and Physiographic Regions 34
Figure 7. Boxplot of Hardness and Land Use 34
Figure 8. Hardness Map 35
Figure 9. Boxplot of pH and Physiographic Regions 37
Figure 10. Boxplot of pH and Land Use 37
Figure 11. pH Map 38
Figure 12. Boxplot of Chloride and Physiographic Regions 42
Figure 13. Boxplot of Chloride and Land Use 42
Figure 14. Chloride Map 43
Figure 15. Boxplot of Fluoride and Physiographic Regions 45
Figure 16. Boxplot of Fluoride and Land Use 45
Figure 17. Fluoride Map 46
Figure 18. Boxplot of Sulfate and Physiographic Regions 48
Figure 19. Boxplot of Sulfate and Land Use 48
Figure 20. Sulfate Map 49
Figure 21. Boxplot of Arsenic and Physiographic Regions 54
Figure 22. Boxplot of Arsenic and Land Use 54
Figure 23. Arsenic Map 55
Figure 24. Boxplot of Barium and Physiographic Regions 57
Figure 25. Boxplot of Barium and Land Use 57

Figure 26. Barium Map 58
Figure 27. Boxplot of Iron and Physiographic Regions 60
Figure 28. Boxplot of Iron and Land Use 60
Figure 29. Iron Map 61
Figure 30. Boxplot of Manganese and Physiographic Regions 63
Figure 31. Boxplot of Manganese and Land Use 63
Figure 32. Manganese Map 64
Figure 33. Boxplot of Lead and Physiographic Regions 67
Figure 34. Boxplot of Lead and Land Use 67
Figure 35. Lead Map 68
Figure 36. Atrazine Map 72
Figure 37. Metolachlor Map 74
Figure 38. Simazine Map 75
Figure 39. Alachlor Map 76
Figure 40. Boxplot of TDS and Land Use 79
Figure 41. Boxplot of TDS and Physiographic Regions 80
Figure 42. TDS Map 81
Figure 43. Boxplot of TSS and Physiographic Regions 82
Figure 44. Boxplot of TSS and Land Use 82
Figure 45. TSS Map 83
Figure 46. Boxplot of Nitrate-N and Physiographic Regions 87
Figure 47. Boxplot of Nitrate-N and Land Use 87
Figure 48. Nitrate-N Map 88
Figure 49. Boxplot of Nitrite-N and Physiographic Regions 91
Figure 50. Boxplot of Nitrite-N and Land Use 92
Figure 51. Nitrite-N Map 93
Figure 52. Boxplot of Ammonia-N and Physiographic Regions 94
Figure 53. Boxplot of Ammonia-N and Land Use 95
Figure 54. Ammonia-N Map 96
Figure 55. Boxplot of Orthophosphate-P and Land Use 97
Figure 56. Orthophosphate-P Map 98
Figure 57. Total Phosphorus Map 100
Figure 58. BTEX Map 105
Figure 59. MTBE Map 107

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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] = 75th percentile - 25th 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.

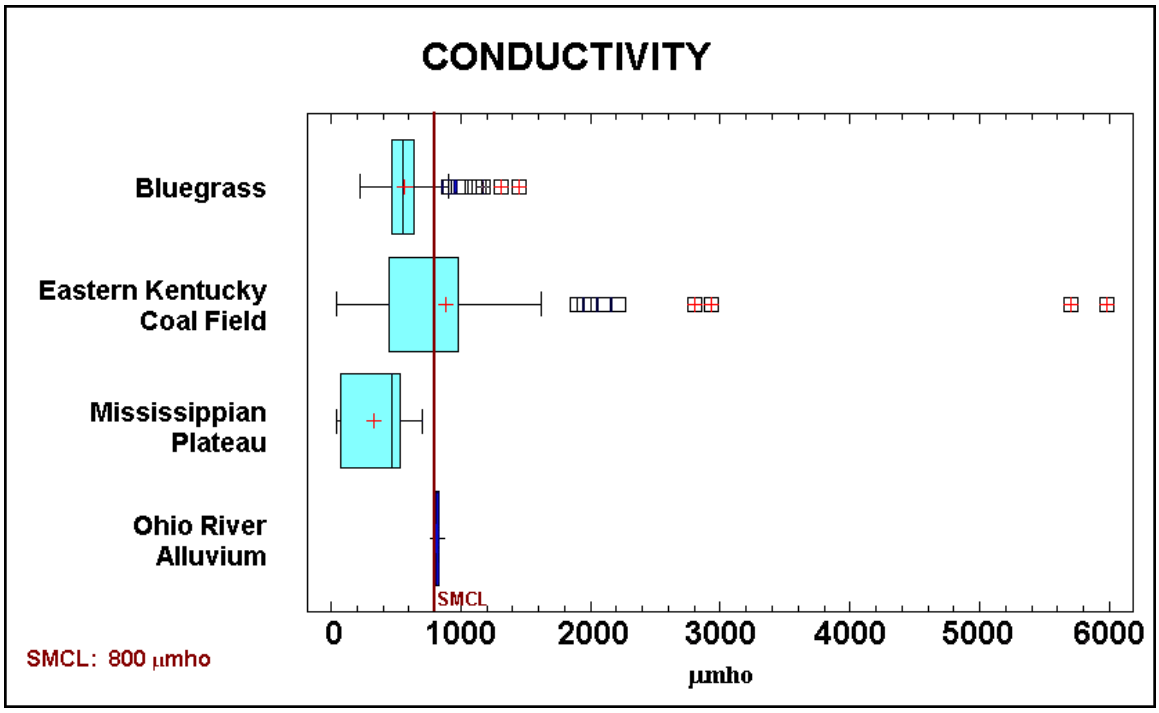

Figure 3. Boxplot of Conductivity and Physiographic Regions

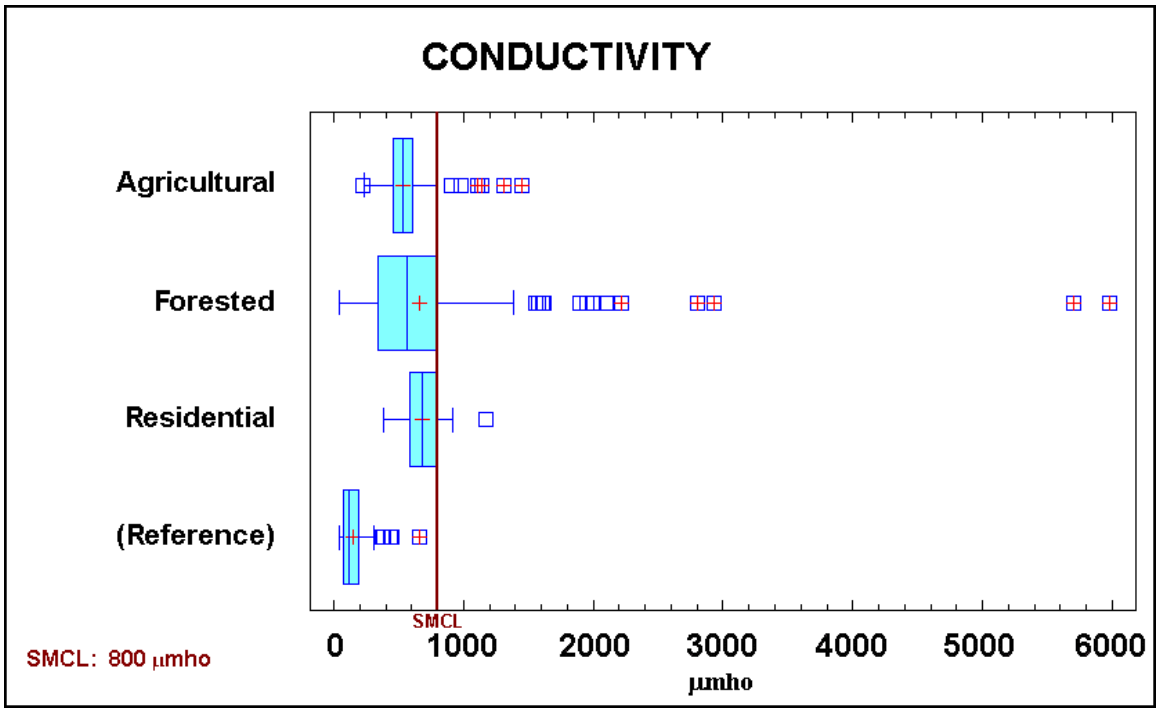

Figure 4. Boxplot of Conductivity and Land Use

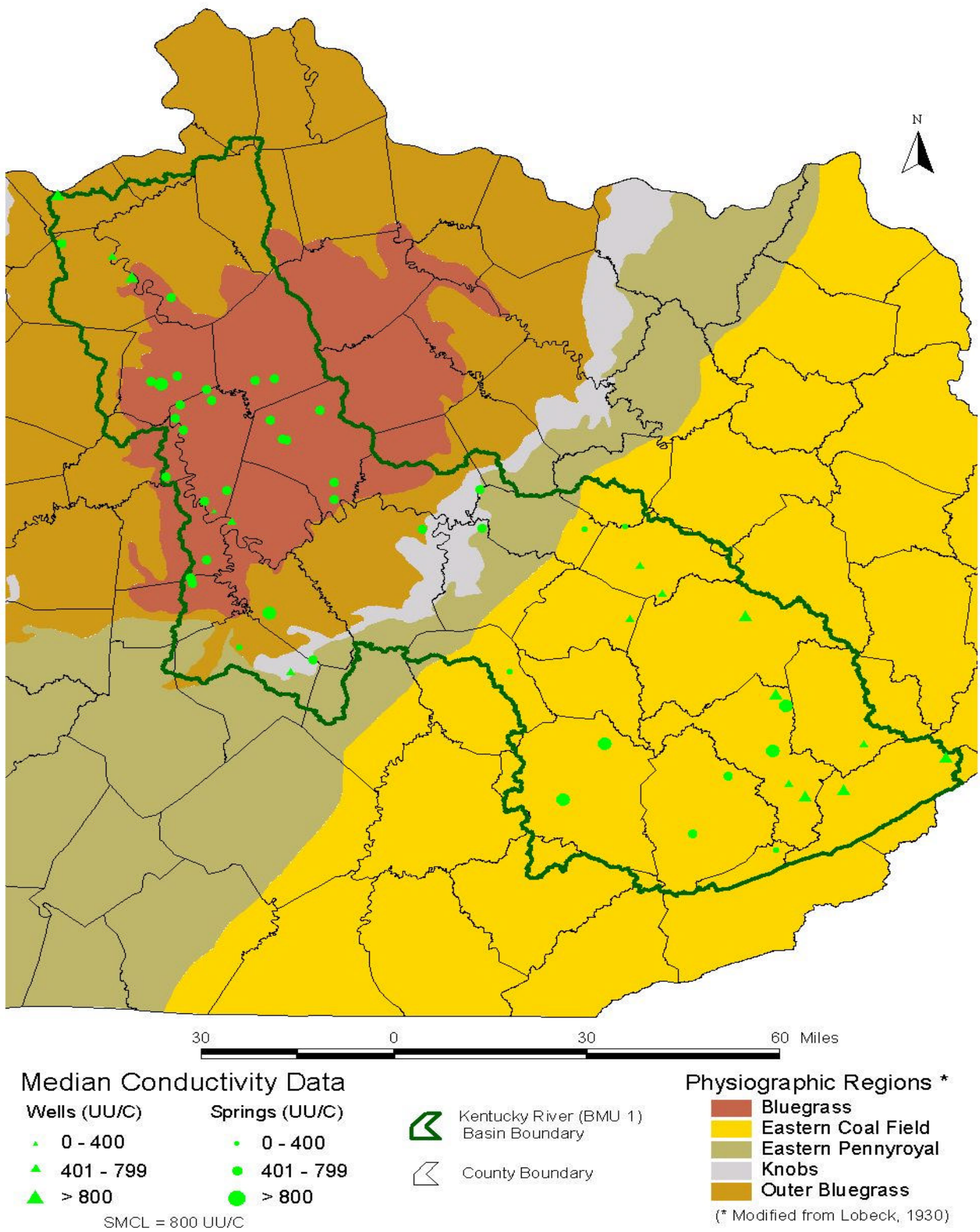

Figure 5. Conductivity Map

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.

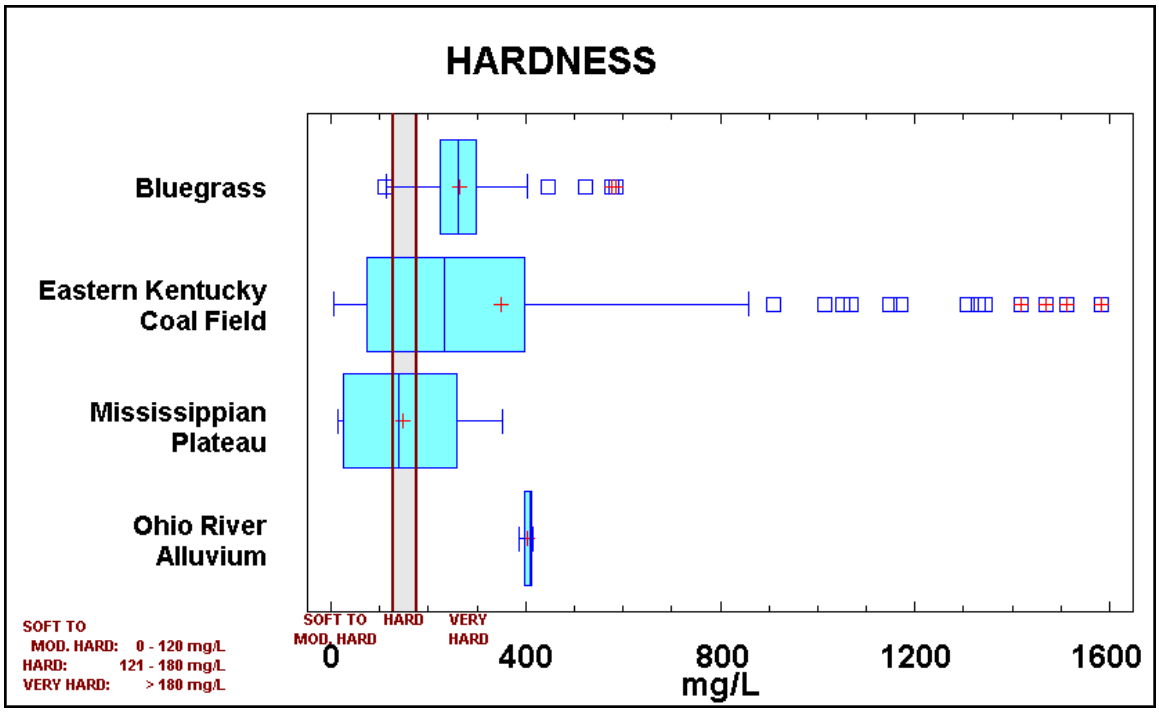

Figure 6. Boxplot of Hardness and Physiographic Regions

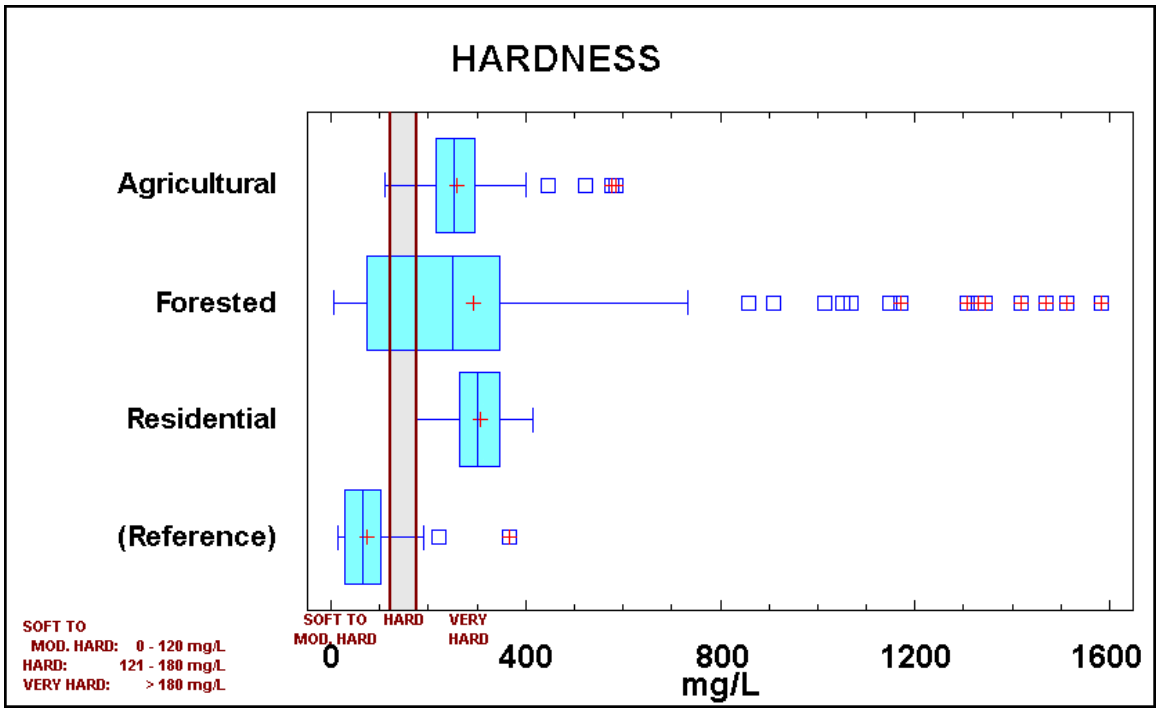

Figure 7. Boxplot of Hardness and Land Use

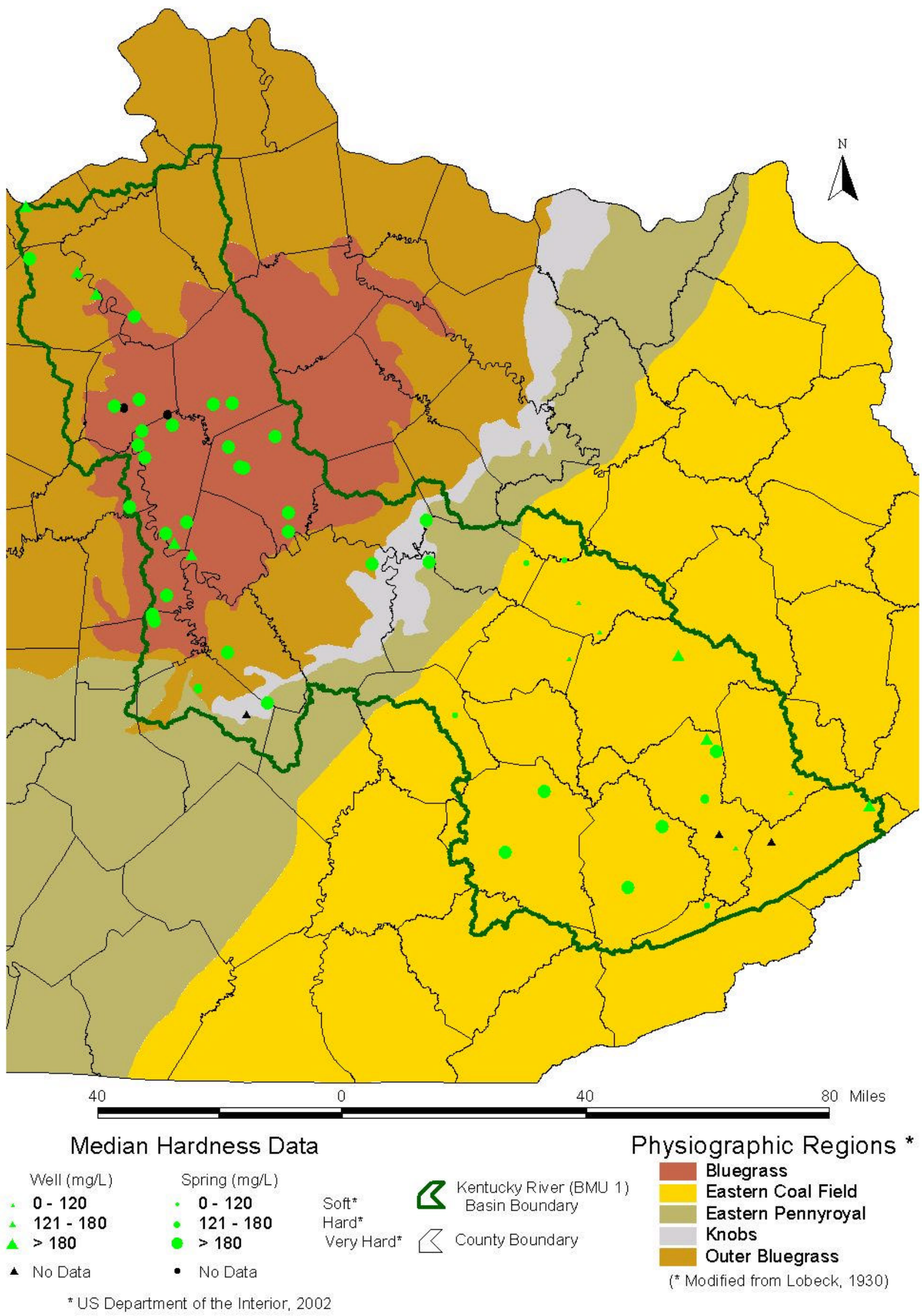

Figure 8. Hardness Map

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.

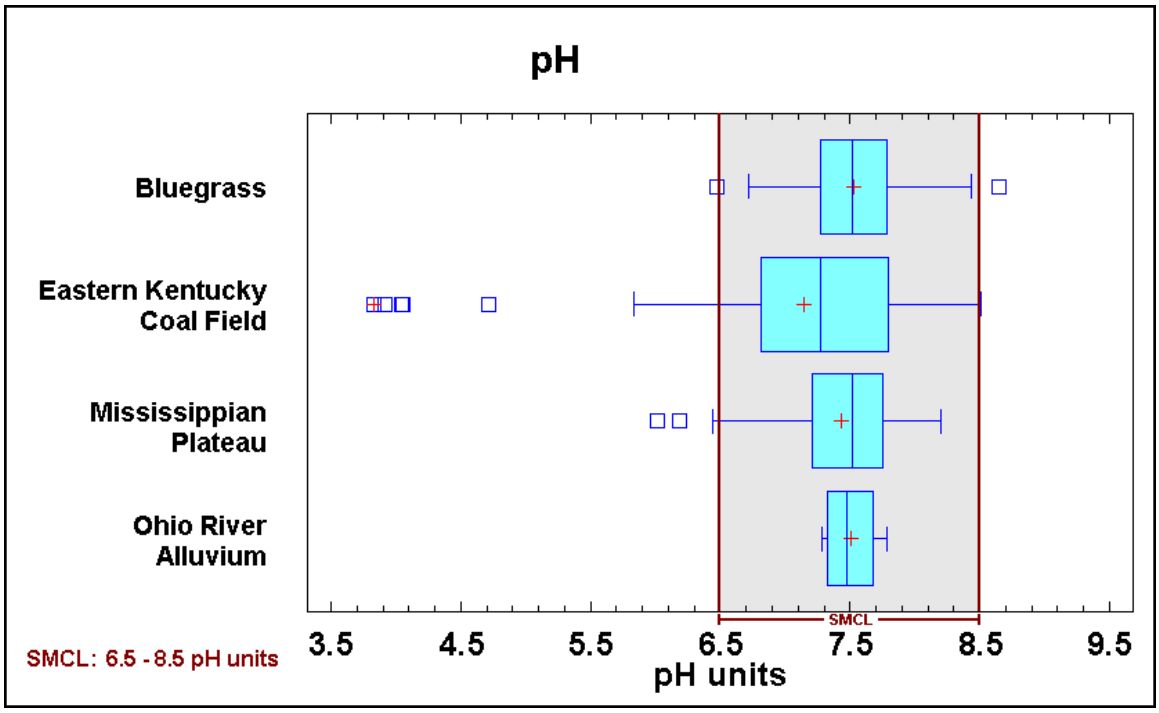

Figure 9. Boxplot of pH and Physiographic Regions

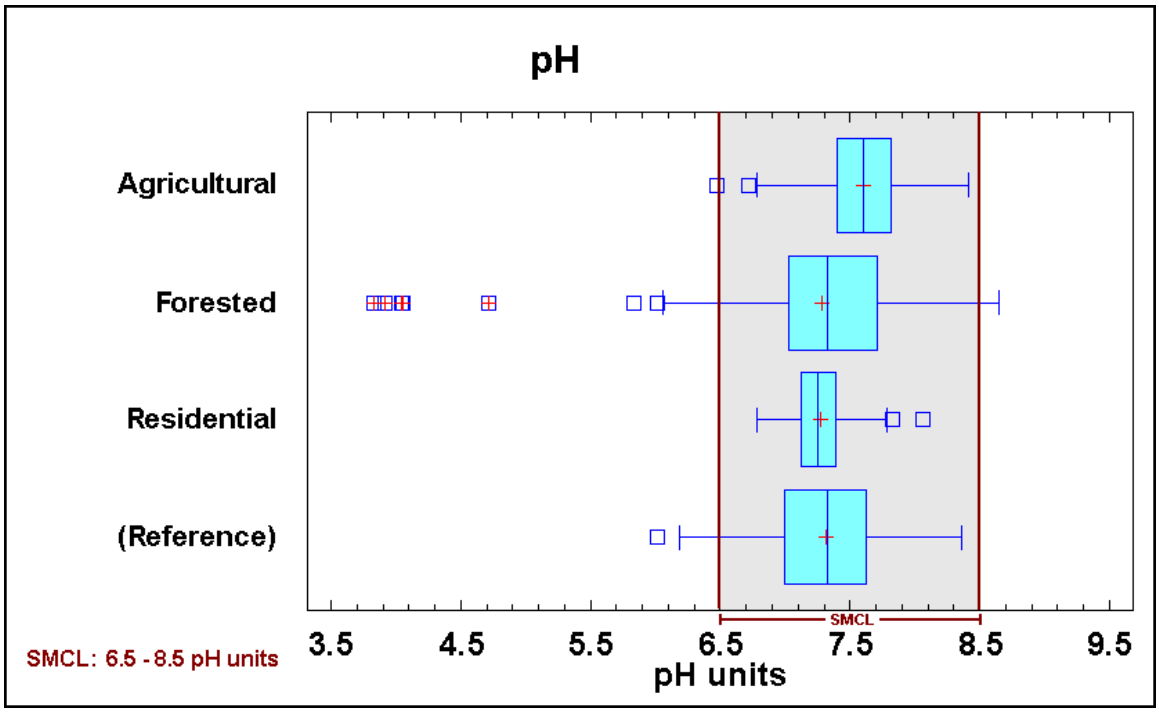

Figure 10. Boxplot of pH and Land Use

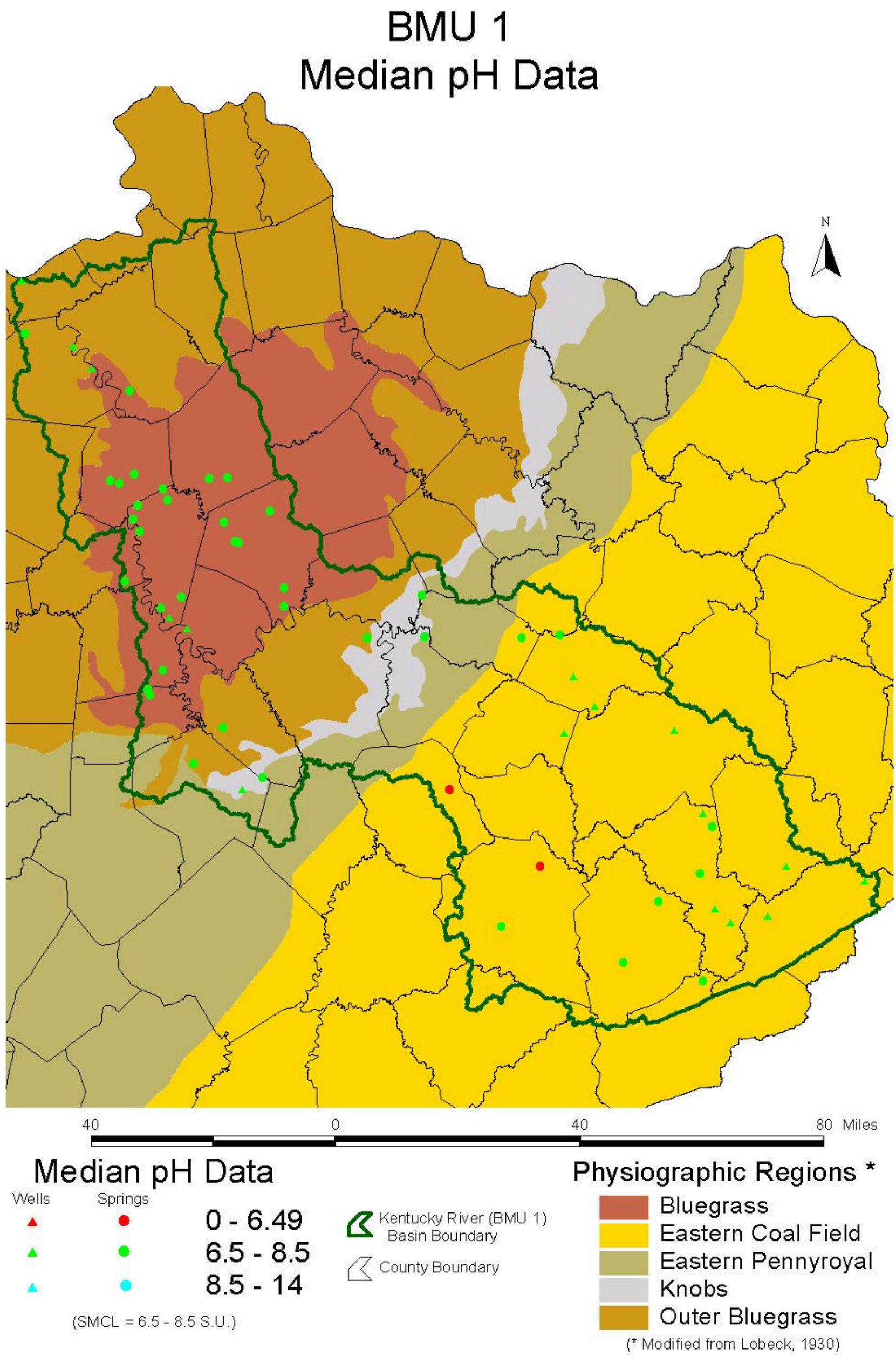

Figure 11. pH Map