Expanded Groundwater Monitoring

For Nonpoint Source Pollution Assessment

In the Green and Tradewater River Basins:

Final Report

By

Phillip W. O'dell

Jolene M. Blanset

Robert J. Blair

James S. Webb

Kentucky Division of Water

Groundwater Branch

14 Reilly Road

Frankfort, KY

Grant Number: C9994861-00
Workplan Number: N/A (Re-obligated Funds)
NPS Project Number: 00-09
MOA or Grant Agreement Number: N/A
Project Period: 12/00-06/02

October 17, 2006 Version

Funding for this project as provided in part by a grant from the U. S. Environmental Protection Agency (U.S.EPA) as authorized by the Clean Water Act Amendments of 1987, §319(h) Nonpoint Source Implementation Grant #(C9994861-00). The contents of this document do not necessarily reflect the views and policies of the U.S.EPA or KDOW nor does the mention of trade names or commercial products constitute endorsement. This document was printed on recycled paper.”

All springs and wells used in this study are on private property. Do not visit any of these sites unless you have talked to the landowner and been granted permission for access.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

Page

ACKNOWLEDGEMENTS

The authors thank the following: the laboratory at the Division for Environmental Services, that performed the chemical analyses on the samples; members of the Groundwater Branch, many of whom assisted with various aspects of this project, including design and field work, especially Peter Goodmann, branch manager and David Leo, former supervisor of the Technical Services Section; and Joseph Devers, formerly with the Division of Water's Paducah Regional Field Office, who assisted with field work; and last but not least, the well and spring owners that allowed us access to collect samples for the study.

EXECUTIVE SUMMARY

In order to conduct a more adequate assessment of groundwater resources in the Green and Tradewater River basins, Kentucky Watershed Basin Management Unit Number 4 (BMU 4), the Groundwater Branch of the Kentucky Division of Water (KDOW) collected 120 raw-water samples at 30 wells and springs in BMU 4. Sites selected represented ambient groundwater conditions and the various hydrogeologic flow regimes found in the basin. Samples were analyzed for pesticides (including the most commonly used herbicides), total and dissolved metals, nutrients, major inorganic ions, residues and volatile organic compounds, including trichloroethylene (TCE), toluene, and methyl-tert-butyl ether (MTBE).

Ambient groundwater quality in BMU 4 is generally good, with land-use the primary determining factor. At some sites, naturally occurring constituents, including iron and manganese, impair groundwater quality. Additional naturally occurring constituents that may also impact groundwater include nitrate-nitrogen, ammonia, total phosphorus and ortho-phosphate. Because these nutrients occur both naturally and through anthropogenic activity, the impact of human contribution to naturally occurring groundwater chemistry is difficult to assess.

Constituents not naturally occurring that have impacted groundwater in BMU 4 are several common agricultural herbicides, including atrazine and metolachlor and volatile organic compounds, including MTBE. In BMU 4, the occurrence of herbicides is the result of nonpoint source pollution. The occurrence of volatile organic compounds occurs via point source releases or from nonpoint sources such as urban storm-water runoff.

INTRODUCTION and BACKGROUND

The Kentucky Division of Water (DOW) 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 (BMUs). 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 Green and Tradewater River basins (BMU 4).

Before 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 4,285 samples from approximately 594 sites. The information from these samples is used for a variety of 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 (TMDLs) 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 address compliance and nonpoint source issues. 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.

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 4 on a quarterly basis for one year, beginning in September 2001. The Groundwater Branch recently collaborated with the KGS on a comprehensive analysis of all available data for this BMU (Fisher, Davidson, and Goodman, 2004). Rather than duplicating their work, this report focuses only on the data collected to meet this nonpoint source grant commitment. The Groundwater Branch selected wells and springs to provide good geographical representation of the diverse physiographic and hydrogeologic characteristics and dominant land uses in BMU 4. Samples were analyzed for numerous parameters including nutrients, pesticides, total/dissolved metals, residues, major inorganic ions and volatile organic compounds, as shown in Table 1. Data were compared to various existing standards and to data from un-impacted ("pristine") reference springs (Table 2) to determine possible nonpoint source pollution impacts or other water quality problems, as well as to identify outstanding resources.

Previous Investigations

Comprehensive discussions of groundwater quality within the Green and Tradewater River basins were not found in the literature. Faust and others (1980) compiled groundwater quality data on a limited number of parameters for the entire state, but did not analyze or summarize the data. The United States Geological Survey has prepared Hydrologic Atlases (HA-26, HA-27, HA-28, HA-28, HA-29, HA-30, HA-31, HA-32, HA-33, HA-34, HA-35, HA-72, HA-74, HA-91, HA-96, HA-110, and HA-129) and 7.5 minute Geological Quadrangle maps (GQs) for the entire basin.

The Kentucky Geological Survey (1969, 2002) has prepared indexes for the both the Geolologic Quadrangle maps and the Hydrologic Atlas series. Geochemical data in the HAs is limited and generally includes only common metals and major inorganic ions. However, the atlases usually provide information that is somewhat more detailed for areas including the Ohio River alluvium. In general, groundwater found in the Ohio River alluvium is hard and may contain high amounts of iron, especially from areas adjacent to valley walls.

Several investigators have mapped karst groundwater basins within BMU 4 and Currens and others (1998, 2002) have compiled the results. Carey and Stickney (2001) have prepared county groundwater resource reports, including general descriptions of groundwater quality. Ray and others (1994) have interpreted groundwater sensitivity to contamination for the entire state.

Brown's (1966), *"Hydrology of the Cavernous Limestones of the Mammoth Cave Area, Kentucky"* describes conceptually how groundwater flows in the Mammoth Cave area. It also illustrates how nonpoint source pollution can enter the groundwater easily in this highly developed karst area.

Carey and others (1993) examined data from 4,859 samples collected throughout the state for ammonia, nitrate-nitrogen, nitrite-nitrogen, 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, this study applied, perhaps inappropriately, the MCL for atrazine for the entire triazine group.)

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 than 1% of 2,363 analyses exceeded the MCL of 2.0 mg/L. Fisher (2002) concludes that "arsenic in Kentucky groundwater generally does not exceed the MCL and there are no widespread occurrences of high arsenic concentrations."

Currens (1979) compiled a bibliography of karst publications for the state. This report includes a large number of publications that describe historical research and water quality in the Mississippian plateau karst area of BMU-4. Although dated, this publication provides direction in locating karst information in the basin.

Currens, Ray, and others (1998, 1998, 1998, 2000, 2003, Drafts) have compiled a Karst Atlas Series of Maps which show mapped karst ground-water basins in various 30 X 60 minute quadrangles. The quadrangles covering portions of the Green and Tradewater Basins include: Harrodsburg, Bowling Green, Campbellsburg, Beaver Dam, Hopkinsville (draft) and Tell City (draft). These maps include known dye traces, interpreted basin boundaries and inferred limits to karst development. They also include references to the original published and unpublished dye tracing data. These are dynamic maps which are updated as more information becomes available.

Kentucky Division of Water, (2001), *"Green and Tradewater Basins: Status Report"*; compiles all known environmental quality data for the Green and Tradewater basins and summarizes it using GIS maps and discussions. The publication also indicates known problems and data needs to better understand the basin.

Fisher and others, (2004) prepared the *"Summary and evaluation of groundwater quality in the Upper Cumberland, Lower Cumberland, Green, Tradewater, Tennessee, and Mississippi River Basins"*, The study evaluates all known water quality data from the BMU-3 and BMU-4 basins and statistically analyzes the data. The raw data from this study was included in the data used by Fisher for his evaluation.

Leist, (1986), compiled "*An evaluation of water-quality data from hydrologic accounting unit 051100, Green River Basin, Kentucky"* which compared the Green River quality before it entered the Western Kentucky Coal Field to stations in the coal field. The levels of chloride, sulfate, iron and dissolved solids increased downstream. The increase of these water quality parameters was

Table 1. 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
Inorganics		
Chloride	250 mg/L	SMCL
Fluoride	4 mg/L	MCL
Sulfate	250 mg/L	SMCL
Metals		
Arsenic	0.010 mg/L	MCL
Barium	2 mg/L	MCL
Iron	0.3 mg/L	SMCL
Manganese	0.05 mg/L	SMCL
Mercury	0.002 mg/L	MCL
Nutrients		
Ammonia-N	0.110 mg/L	DEP
Nitrate-N	10 mg/L	MCL
Nitrite-N	1 mg/L	MCL
Orthophosphate-P	0.04 mg/L	No MCL, SMCL, or HAL; Texas surface water standard
Total phosphorous	0.1 mg/L	No MCL, SMCL, or HAL; level recommended by USGS NAWQA Program
Pesticides		
Alachlor	0.002 mg/L	MCL
Atrazine	0.003 mg/L (0.00067 mg/L)	MCL (DEP)
Cyanazine	0.001 mg/L	HAL
Metolachlor	0.1 mg/L	HAL
Simazine	0.004 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	0.005 mg/L	MCL
Ethylbenzene	0.7 mg/L	MCL
Toluene	1 mg/L	MCL
Xylenes	10 mg/L	MCL
MTBE	0.050 mg/L	DEP

* Abbreviations:

MCL = Maximum Contaminant Level
SMCL = Secondary Maximum Contaminant Level (Secondary Drinking Water Regulation (SDWR))
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

Table 2. Reference Springs Analytical Data Summary (Cameron Spring/Lewis County; Nada Spring/Powell County; F. Mullin Spring/Rockcastle County), mg/L.

NPS REFERENCE SITES SUMMARY STATISTICS						
	START DATE	END DATE	NUMBER OF SAMPLES	MEDIAN	MIN	MAX
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
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

attributed to the impacts of specific land uses by both coal mining and oil production.

Krieger, (1960), and Krieger and Hendrickson’s, 1960, describes the “*Effects of Greensburg oilfield brines on the streams, wells, and springs of the upper Green River Basin, Kentucky*”. Past practices of dumping oil field brines on the ground, in sinking streams and to surface streams caused significant degradation of the water resources of the area. This is one of several publications which describe the effects.

Davis and others, (1974) discuss the "*Hydrology and geology of deep sandstone aquifers of Pennsylvanian age in part of the Western Coal Field region"*. This publication describes these unique aquifers that yield fresh water from depths that one would generally find saline water elsewhere in the state. The Nortonville well included in this study is producing from one of these deep sandstone aquifers (600-foot aquifer (Vienna datum)).

Reynolds (2001) compiled the *"Strategic Monitoring Plan for the Green and Tradewater River basins"*. The document describes all the agencies and groups that are working together to collect various types of water data in the basin. It covers surface water, groundwater, air quality and biological resources.

PHYSIOGRAPHIC and HYDROGEOLOGIC SETTING

BMU 4 covers more than 11,541 square miles (454 square miles in Tennessee) and includes the Green and Tradewater River basins, as well as several other direct minor Ohio River tributaries (MORT). For the purposes of this report, the terms "Tradewater River Basin" or "Green River Basin" will also include those adjacent areas that drain directly to the Ohio River. These minor Ohio River tributaries in this study also include an area of the Jackson Purchase that is also included in Four Rivers Basin management unit.   Figure 1 illustrates the location of BMU 4 and the sites included in this study. The study area includes all of Allen, Barren, Butler, Daviess, Edmonson, Grayson, Green, Hancock, Hart, Henderson, Hopkins, Mclean, Muhlenberg, Ohio, Taylor, Union, Warren, and Webster counties and portions of Adair, Breckinridge, Caldwell, Casey, Christian, Crittenden, Hardin, Larue, Lincoln, Livingston, Logan, Metcalf, Monroe, Simpson and Todd counties.

Tradewater River Basin

The Tradewater River rises in northern Christian County within the Western Coal Field physiographic region. The river flows northwesterly for approximately 110 miles to its confluence with the Ohio River at the Union and Crittenden county line and has a drainage basin of 1,000 square miles, approximately 2.5% of the state (ORSANCO, 2002). From south to north, the Tradewater River and its tributaries flow through the following physiographic regions (Figure 1): the Mississippian Plateau and the Western Coal Field. In addition, the area drains portions of the Ohio River Alluvium. Although the alluvium along the Ohio River is not technically a true physiographic province, it is nevertheless an important aquifer within this region and is discussed separately. Groundwater flow in the Tradewater River basin varies according to the local geology. After initial runoff of precipitation, groundwater provides base flow to surface water streams, thereby sustaining stream flow during periods without rain.

Principal tributaries are the Donaldson Creek, Piney Creek, Clear Creek, and Crab Orchard Creek. An additional 461 square miles of area draining directly to the Ohio River is included in BMU 4. Some of these more important watersheds include Highland Pond Creek, Crooked Creek and Hurricane Creek. The largest impoundments in the Tradewater Basin are Lake Besher, Maury Lake, Moffit Lake, Lake Pennyrile and Lake Peewee.

Green River Basin

The Green River rises in Casey County and flows generally northwesterly to its confluence with the Ohio River north of the city of Henderson in Henderson County. The Green River is approximately 370 miles long and drains 9,230 square miles (ORSANCO, 2002), or about 22.8% of the state. The Green River watershed drains portions of two major physiographic provinces, including the Mississippian Plateau and Western Coal Field. In the Green River portion of BMU 4, the Ohio River Alluvium is also an important aquifer.

Groundwater flow in the Green River basin varies according to local geology. As in the Tradewater River basin, after initial runoff of precipitation, groundwater provides base flow to surface water streams, thereby sustaining stream flow during periods without rain.

Principal tributaries are the Barren River, Nolin River, Rough River and the Pond River. The largest impoundments in BMU 4 are Green River Lake, Barren River Lake, Nolin Lake, Lake Malone, and Rough River Lake, which are operated by the Army Corps of Engineers. Tributaries discharging directly

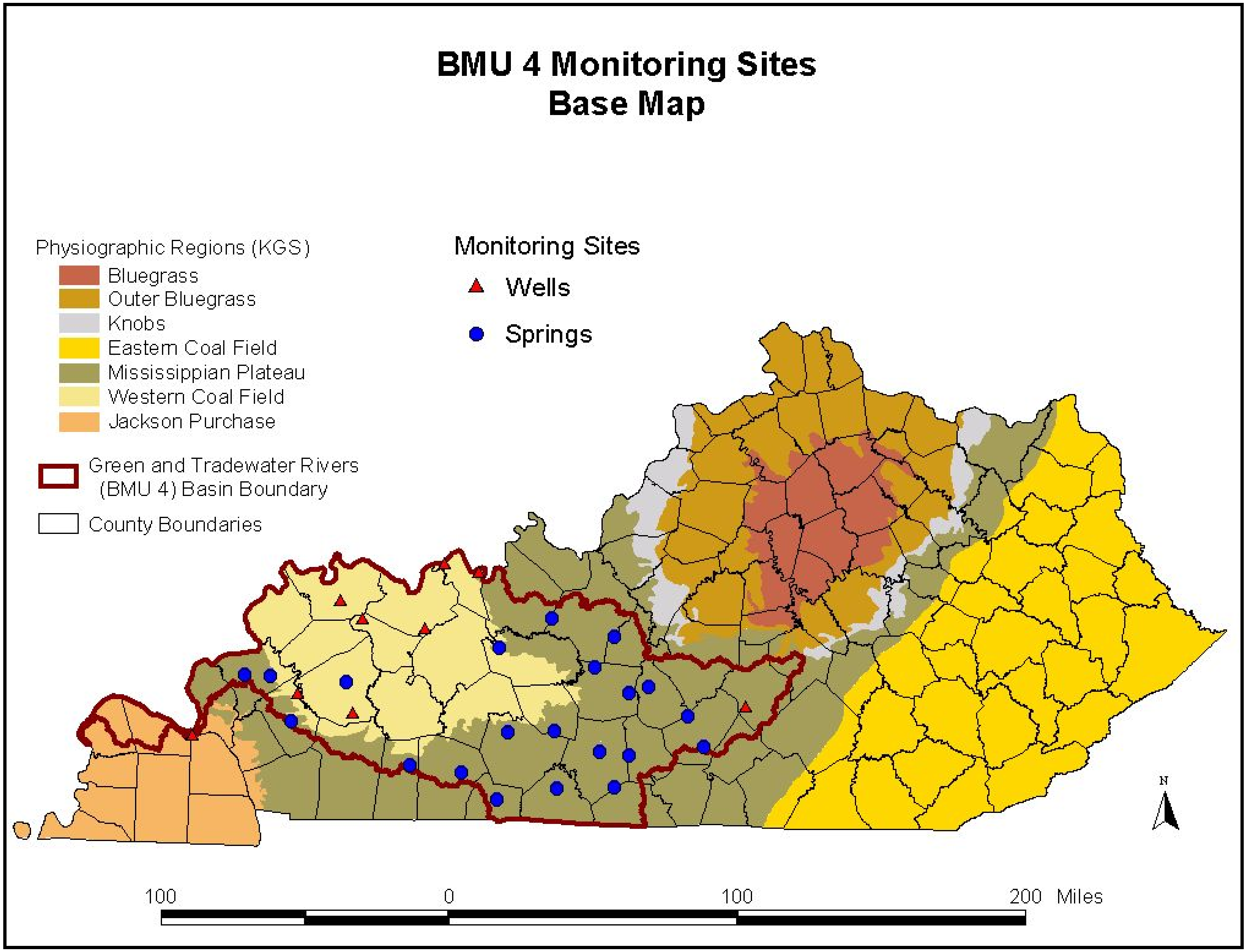

Figure 1. Basin Boundaries, Physiography and Groundwater Sample Sites

to the Ohio River drain an additional 872 square miles adjacent to the Green River Basin proper. Larger Ohio River tributaries in this area include Clover, Blackford and Pup creeks.

Groundwater Sensitivity

Based upon variations in geology, topography and hydrologic regime, groundwater underlying Kentucky's various physiographic regions has varying sensitivity to contamination from activities conducted on the surface. Groundwater sensitivity to potential impacts is based upon three primary hydrologic components: recharge, flow velocity and dispersion. Sensitivity ranges from low (1) to high (5). In general, quicker recharge, faster flow and more extensive dispersion, lead to greater sensitivity. Figure 3 illustrates generalized interpretation of groundwater sensitivity in BMU 4. Ray and others (1994) discuss this topic in detail. In BMU 4, groundwater sensitivity ranges from high in the well-developed karst of the Mississippian Plateau to low in the Western Coal Field region.

Physiographic Provinces

Physiographic provinces (Figure 1) are differentiated on the basis of geology and hydrology (Figure 2) and therefore the physiographic map is used as a base map to present analytical data on each parameter. Most of the land area in BMU 4 occurs in three physiographic provinces: the Western Coal Field, the Mississippian Plateau, the Ohio River Alluvium with a small portion of the Jackson Purchase and the Knobs. 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). Generally, the **Western Kentucky Coal Field** is characterized by flat-lying Pennsylvanian-age clastic sedimentary rocks, sandstone, siltstone, shale and clay, with significant coal beds. Erosion has produced a hilly upland of low to moderately high relief dissected by streams occupying wide, poorly drained, and often swampy valleys. Maximum local topographic relief within this portion of the study area is about 400 ft. 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

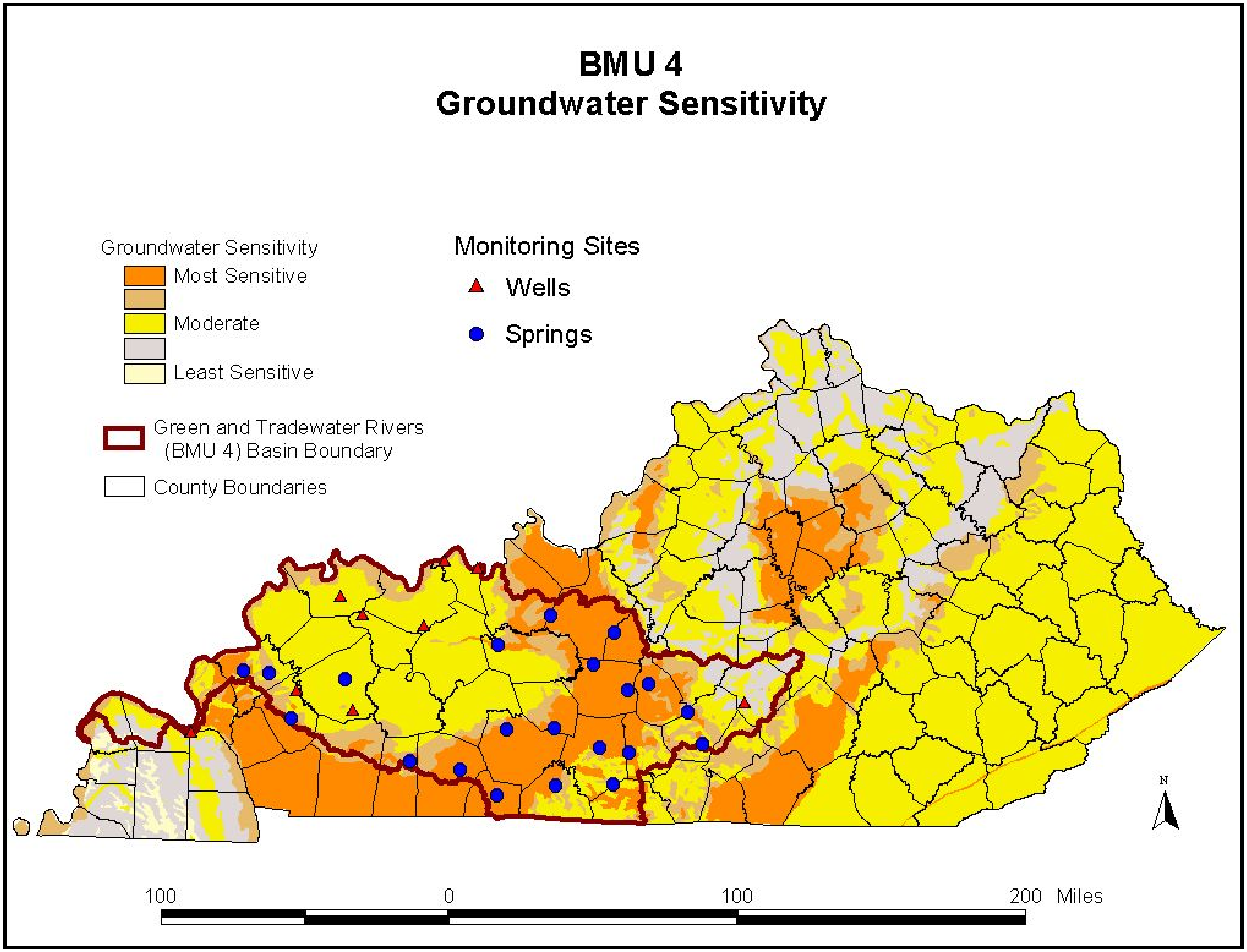

Figure 2. **Monitoring Sites Overlain on Groundwater Sensitivity Map for Kentucky (after Ray and others, 1994)**

Period	Epoch	Formation/Lithology		Stratigraphic Position of Well Production Zones and Spring Discharge Points
		Alluvium		R Lewisport Well-PWS
Quaternary	Holocene	Lacusterine & Fluvial Deposits		R Willamette Ind. Well-PWS
				R Ledbetter Well-PWS
	Pleistocene	Fluvial Deposits Sand Loess		
Tertiary(?)	Pliocene(?)	Gravel, Sand & Silt		
Cretaceous	Upper	McNairy Fm. (Ss/Sh)		
				EBrowning Sp.
Pennsylvanian	Upper	Lisman Fm. (Ss/Sh)		R Martin Well-domestic
				R McCarthy Well-domestic
		Carbondale Fm. (Ss/Sh)		R Ezell Well-domestic
	Middle	Tradewater Fm. (Ss/Sh/Ls)		R Adams Well-domestic
	Lower	Caseyville Fm. (600' aquifer)(Ss)		R Nortonville Well-PWS
Mississippian	Chester	Buffalo Wallow	Grove Church Sh	
			Kindaid Ls	
			Degonia Ss	EPickens Sp.
			Clore Ls	
			Palestine Ss	
			Menard Ls	
			Waltersburg Ss	
			Vienna Ls (datum-600' aquifer)	
		Tar Springs Ss		
		Glen Dean Ls		
		Hardinsburg Ss		
		Golconda Fm.	Haney Ls	ESpillman Sp.
				EDancehall Sp.
			Big Clifty Ss	
			Beach Creek Ls	
		Girkin Fm.	Cypress Ss	
			Paint Creek Ls	DMossy Sp. (Intermittent)
			Bethel Ls	
			Renault Ls	EPumpkin Center Sp.
	Meramec	Ste. Genevieve Ls	Levias Ls	EGreencastle Bluehole
				ERoundstone Sp.
			Rosiclare SS	EMahurin Sp.*
				EHead of Drakes Creek Sp.
			Fredonia Ls	ECrittenden Sp.*
				EBelcher Karst Window
		St. Louis Ls		EHeady Big Sp.
				EWalker Sp.
				E300 Sp.
		Salem & Warsaw Ls		EHead of Beaver Creek Sp.
				EGlasgow Town Sp.
	Osage	Borden Fm.	Fort Payne Fm	R Davis Well-domestic
				EWelch Cave Sp.
				ENorth Ford Cave Sp.
				EBledsoe Cave Sp.
			Fort Payne Ls (reef facies)	ECedar Bluff Sp.

Key

* Stratigraphic position complicated by faulting.

E Spring

DSpring (Intermittent)

R Water Well

← Unconformity (geologic units missing due to erosion or non-deposition)

Ls	Limestone
Ss	Sandstone
Sh	Shale
Sp.	Spring
Fm.	Formation

Dashed lines and (?) indicate the exact break between two units is undetermined or is reported differently by different authors.

Compiled from:

Davis, et al, 1974
Trace and Kehn, 1968
Kehn, 1964
Palmer, 1968
Palmer, 1966
Johnson and Smith, 1972
Amos and Wolfe, 1966
Moore, 1966
Fairer, 1973
Trace and Farmer, 1971
Gildersleeve, 1966
Trace, 1962
Sable and Dever, 1990

Figure 3. Diagram of Geologic Units in Green and Tradewater Basins

(gpm) when larger fractures are encountered. High-yield municipal or industrial supply wells occur in some locations. Springs tend to have low flows and are usually perched on impermeable shales. Large-flow, base-level springs are rare. The lowest sensitivity rating in the study area (2.5) was assigned to the lacusterine deposits in the Western Coal Field.

The **Jackson Purchase** exhibits the lowest hydrogeologic sensitivity in the state and some of this area is rated as a "1." The surficial geology consists of sediments deposited from Cretaceous through Eocene times when the northern portion of the Mississippian embayment covered the area (Davis, 1973). The sediments are underlain by Paleozoic rocks ranging from Mississippian age to Ordovician age. The sediments range from a few feet thick in the northeast and eastern portion of the area to over 1300 feet thick in the southwestern portion of the area. Wells capable of producing water in sufficient quantities for domestic use can be developed anywhere in the **Jackson Purchase**. Wells suitable for producing water in quantities needed by industry and public water supplies can be sited in most but not the entire Purchase region. The water is generally soft and slightly acidic. In some places iron and manganese can be present in quantities that require treatment before it can be used for domestic purposes.

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, but fracture flow and flow along bedding planes also occurs and can be locally important. In general, yields from wells vary widely according to the size of any enlarged water-filled conduits encountered by the well-bore and can range from less than one gallon per minute to more than one hundred. Springs developed on these thick and generally pure carbonate sedimentary rocks tend to have larger flows than other areas within the watershed, with base flow discharges up to several cubic feet per second (cfs). The Mississippian Plateau is very sensitive to contamination from surface activities and rates a "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 gallons per minute 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."

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 nevertheless 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.

Land Use

Land use is an important consideration regarding potential impacts to groundwater quality (Figure 4). Approximately 1.9% of the surface area in BMU 4 is urban, 47% is agricultural (row crop or pasture) and 49% is forest. In order to simplify the map, forest usage is combined with the area (2.17%) covered by wetlands, lakes and reservoirs and reclaimed strip mines. Approximately one-third of all the coal mined (27, 224, 316 tons in 2002) in the state has come from counties which are all or part in BMU 4, according to the Kentucky Department of Mines and Minerals (2002). The five primary coal-producing counties in BMU 4 are Webster, Union, Muhlenberg, Hopkins, and Henderson Counties. Surface and underground mines are active in this area according to the Kentucky Department of Mines and Minerals (2002). Table 3 illustrates potential nonpoint source impacts to groundwater from varying land use.

Groundwater Use

Groundwater is an important resource in BMU 4, providing private and public drinking water, as well as water for industrial and agricultural purposes. Additionally, groundwater recharge provides water to maintain base flow to surface water streams after runoff from precipitation events. In BMU 4, groundwater is widely used for industrial purposes, as well as for both publicly supplied and private drinking water. Permitted industrial users and larger public water supply systems are concentrated along the Ohio River and utilize the alluvial aquifer, as shown in Table 4. Public water systems, serving 200,750 people that use groundwater as their primary source in BMU 4 are shown in Table 4.

Table 3. Land Use and Potential Nonpoint Source Contaminants

Land Use	**% in BMU 4**	**Potential Contaminants**
Agriculture, including row crop production, livestock grazing, fuel/pesticide storage	47	Pesticides, nutrients (esp. nitrate-n), salts/chloride, volatile organics, bacteria
Urban	1.9	Pesticides, volatile organics, chlorides
Forested, including mining, logging, silviculture	49	Metals, pesticides, nutrients, sediment, pH

Groundwater usage from wells or springs was calculated from County Water Plan data for Counties which are entirely in the study area. Based on these data, more than 39,310 people in the Green and Tradewater Basins use self supplied groundwater as a source of drinking water (KWRIS, 1999). No figures are available for the agricultural use of groundwater, which does not require a permit. This use includes irrigation, livestock watering and general farm use. Although no figures are available, field observations indicate that such use is significant. Principal aquifers within the Green and Tradewater River basins are shown in Table 5.

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 1. Basic water quality chemistry can be determined from common, naturally occurring major inorganic ions, metals, residues, conductivity and pH. Parameters that are not naturally occurring are the best indicators of nonpoint source pollution and include pesticides

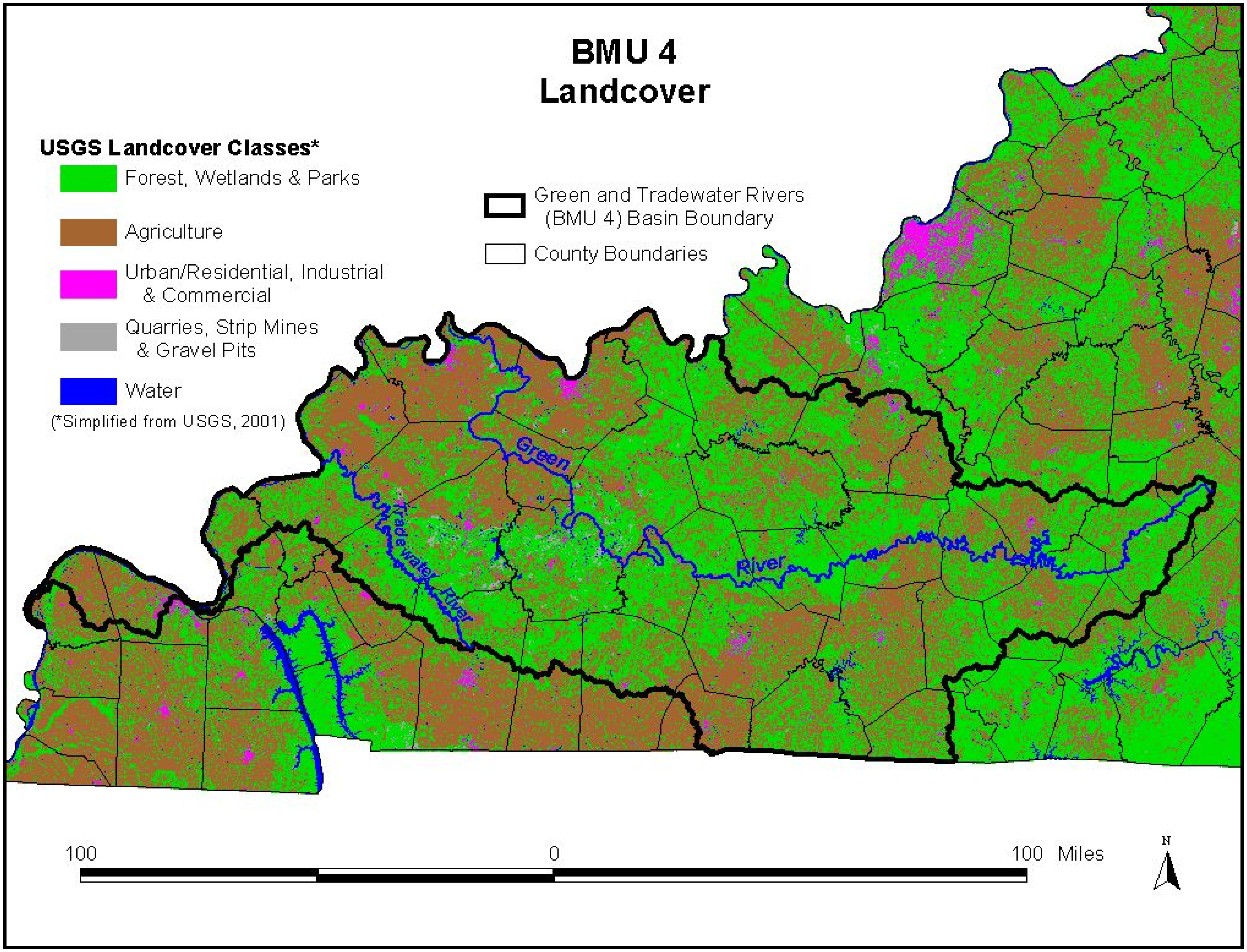

Figure 4. Land Use Map for BMU 4

Table 4. Public Water Systems in BMU 4 With Groundwater Source (KDOW, 2002b)

System	County	Source	Population Served
DIAMOND CAVERNS	BARREN	WELL	330
CLOVERPORT WATER/SEWER SYS	BRECKINRIDGE	WELLS	1930
WILDWOOD ESTATES	BRECKINRIDGE	WELL	69
OWENSBORO MUNICIPAL UTILITIES	DAVIESS	WELL FIELD	57758
KY DIAMOND CAVERNS:CEDAR HILL	EDMONSON	WELL	330
PINE KNOB DINER	GRAYSON	WELL	24
COMMONWEALTH ALUMINUM	HANCOCK	WELLS	1200
HAWESVILLE WATER WORKS	HANCOCK	WELLS	3088
LEWISPORT MUNICIPAL WATER WKS	HANCOCK	WELLS	3102
WILLAMETTE IND BLEACHED PULP	HANCOCK	WELL 0002-9717	1888
WILLAMETTE IND. CORRUGATED MED	HANCOCK	WELL 0002-9718	188
DIR ENGINEERING & HOUSING	HARDIN	WELL FIELD & MCCRACKEN SPRING	42400
ELIZABETHTOWN WATER DEPT	HARDIN	WELL FIELD, OLD CITY SP., & GAITHERS SP,(AKA Dyers Sp.)	24594
HARDIN CO WD #1	HARDIN	PIRTLE SP., HEAD OF ROUGH SP. & WELLS	29700
MEADOW VIEW WATER SYSTEM	HARDIN	WELL	85
WEST POINT WATER DEPARTMENT	HARDIN	WELLS	1200
GREEN RIVER VALLEY WATER DIST	HART	RIO SPRING	19368
ELLIS PARK RACE COURSE	HENDERSON	WELL	1500
TROCADERO PLAZA	HENDERSON	WELL	25
NORTONVILLE WATER WORKS	HOPKINS	WELL	2900
WHITE PLAINS WATER SYSTEM	HOPKINS	WELL	1594
BEAVER DAM MUN WATER/SEWER SYS	OHIO	WELLS	3061
CHERRY GROVE GOLF COURSE	TODD	WELL	30
WEBSTER CO WATER DISTRICT	WEBSTER	WELLS	4386
TOTAL			200750

Table 5. Simplified Aquifer Characteristics in BMU 4

Geologic Age of Aquifer	Predominant Rock Type	Predominant Sub-Surface Flow	Characteristic of Physiographic Province
Pennsylvanian	Sandstone, siltstone, shale, coal	Fracture	Western Coal Field
Mississippian	Limestone, dolostone	Well-developed Conduits	Mississippian Plateau
Cretaceous	Unconsolidated Sand, silt, gravel	Granular	Jackson Purchase
Tertiary	Unconsolidated Sand, silt, gravel	Granular	Jackson Purchase
Quaternary	Unconsolidated Sand, silt, gravel	Granular	Ohio River Alluvium & Jackson Purchase

and volatile organic compounds. Reference values used for comparison are from a variety of sources and there is no consensus regarding the appropriateness of comparing ambient groundwater with these standards. Therefore, the derivation of these standards and the applicability of them to groundwater are discussed below.

Sample results from this study were compared to a variety of existing standards, referred to as "reference values" in this report. Many of the parameters have limits established by the United States Environmental Protection Agency (U.S.EPA, 2000) for treated drinking water supplied to the public. The U.S.EPA defines three types of drinking water standards: Maximum Contaminant Levels, Secondary Drinking Water Regulations and Health Advisories:

Maximum Contaminant Level (MCL) is defined (U.S.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 life-time 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 U.S.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 (U.S.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**).

Many parameters discussed in this report have no MCL, SMCL, or HAL. 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**), atrazine and ammonia; 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 established water quality standards provide a valid window through which to view the data, perhaps the most important tool is to compare data with water quality from sites known to have minimal impact from anthropogenic activities. 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 man-made sources. Therefore, reviewing land-use in conjunction with geochemical data, as well as comparing data with that from previously sampled sites, can help differentiate between anthropogenic and natural sources.

Statistical and Graphical Methods

Project data were evaluated with summary statistics, summary tables, box and whisker plots and graduated-size maps. Summary statistics list simple statistics, including minimum and maximum values, median and mode. Summary tables list number of samples, numbers of detections and the number of detections above the particular standard of comparison for that parameter, such as MCL. Graduated size maps show analytical results as symbols that increase in size as values increase. These maps show the highest value for each site.

The primary use of a boxplot is to visually divide the data using quartiles that divide the dataset into fourths. Once constructed, the boxplot will graphically depict the central tendency, or where the data cluster (a "typical value"), and the dispersion, or scatter, of the data values in the set. The dataset, after being put into rank order, is divided into fourths. The values at these divisions are depicted on the boxplot: the minimum, or Q_0; the maximum, Q_4; the median, $Q_{2,}$ (the midpoint which divides the dataset into halves); the first quartile, Q_1, (the midpoint of the lower half of the dataset); and the third quartile, Q_3, (the midpoint of the upper half of the dataset). The difference between Q_3 and Q_1 is called the Inner-Quartile Range (IQR). The IQR comprises 50% of the dataset and is represented by the box of the boxplot. The horizontal lines extending below Q_1 and above Q_3 are whiskers with fences as endpoints.

The lower fence is 1.5 times the IQR below Q_1; the upper fence extends to 1.5 times the IQR above Q_3. Any value outside this range is deemed an outlier if it is between 1.5 IQR and 3.0 IQR outside, or an extreme outlier if it is greater than 3.0 IQR outside (Blanset, 2005).

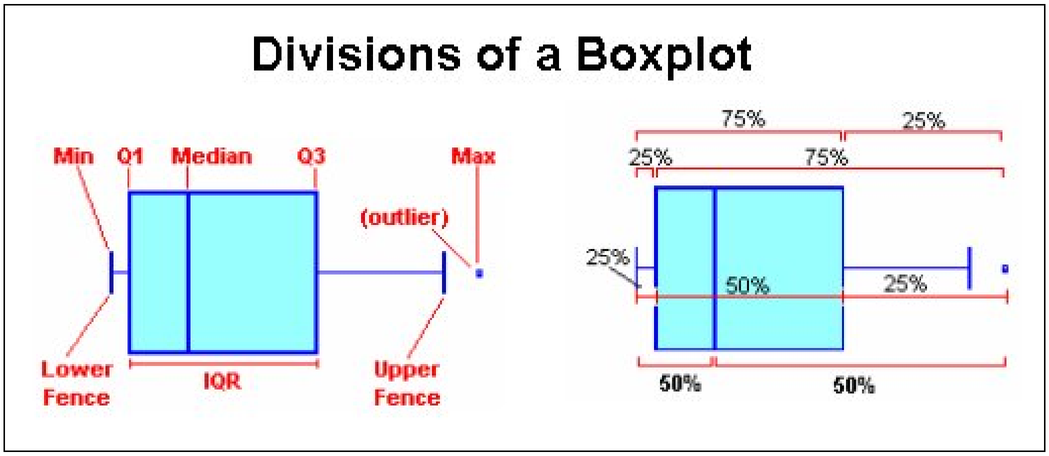

Figure 5, Boxplot Diagram

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.". A conservative approach was taken regarding these censored observations by plotting these data at their detection limit. 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.

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. Additionally, at the map scale used in this report the Ohio River Alluvium cannot be effectively illustrated. Therefore, care must be exercised in the interpretation of sites along the northern border of the study area. A good rule of thumb is that wells located on the northern edge of the area are likely in the Ohio River Alluvium, whereas springs are not.

Site Selection

The Groundwater Branch selected sites by a modified probabilistic approach in order to provide representative geographical distribution throughout the two basins. Under this approach, sites in thirty 7.5 minute quadrangles were chosen randomly for inclusion in this study. The distribution of sites selected using this method therefore provided unbiased monitoring sites representative of various land uses, each with characteristic nonpoint source threats, as well as varying aquifer types of differing inherent groundwater sensitivity. This probabilistic approach was modified because, in addition to selecting sites randomly through the use of 7.5 minute quadrangle maps, numerous other maps and data were used to facilitate site selection, including hydrologic atlases, the Division for Environmental Protection's (DEP) groundwater data base and field reconnaissance.

In general, previously sampled 7.5 minute quadrangles were omitted from this study. Public water supplies 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, they 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 identification number catalogs wells and springs maintained in the DEP's database. If a well or spring selected for this study had not been assigned an eight-digit identification number, a well inspection or spring inventory form was completed and a unique identification number was assigned. The inspection or inventory form 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.

Sites selected specifically for this nonpoint source study are listed in Table 6. Geochemical data from 30 sites were analyzed for this project. The entire study area consists of more than 11,541 square miles, or an average of one sampling site per 385 square miles. Although data are 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 inorganic ions; 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 B).

Major inorganic ions 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) and/or improper sewage disposal (nitrates, ammonia).

Table 6. List of Sample Sites for BMU 4

AKGWA	SITE NAME	PHYSIOGRAPHIC REGION	NUMBER of SAMPLES COLLECTED
0000-1575	Martin Well	Western Kentucky Coal Field	4
0000-5014	Ledbetter Well 4	Ohio River Alluvium	4
0000-9766	Ezell Well	Western Kentucky Coal Field	4
0002-9717	Willamette Well	Ohio River Alluvium	4
0003-0826	McCarty Well	Western Kentucky Coal Field	4
0003-0984	Adams Well	Western Kentucky Coal Field	4
0004-1471	Lewisport Well 2	Ohio River Alluvium	4
0004-2984	Nortonville Well 1	Western Kentucky Coal Field	4
0005-6875	Davis Well	Mississippian Plateau	4
9000-0156	Three Hundred Springs	Mississippian Plateau	4
9000-0202	Mahurin Spring	Western Kentucky Coal Field	4
9000-0226	Roundstone Spring	Mississippian Plateau	4
9000-0263	Greencastle Blue Hole (Sp.)	Mississippian Plateau	4
9000-0556	Browning Springs	Western Kentucky Coal Field	4
9000-1843	Heady Big Spring	Mississippian Plateau	4
9000-1903	Mossy Spring	Mississippian Plateau	4
9000-2231	Cedar Bluff Spring	Mississippian Plateau	4
9000-2236	Walker Spring	Mississippian Plateau	4
9000-2820	Head of Beaver Creek (Sp.)	Mississippian Plateau	4
9000-2823	Belcher Karst Window	Mississippian Plateau	4
9000-2824	Glasgow Town Spring	Mississippian Plateau	4
9000-2826	Bledsoe Cave Spring	Mississippian Plateau	4
9000-2827	North Ford Cave Spring	Mississippian Plateau	4
9000-2830	Head of Drakes Creek Sp.	Mississippian Plateau	4
9000-2835	Dancehall Spring	Mississippian Plateau	4
9000-2839	Welch Cave Spring	Mississippian Plateau	4
9000-2841	Spillman Springs	Mississippian Plateau	4
9000-2845	Pickens Spring	Mississippian Plateau	4
9000-2847	Crittenden Spring	Mississippian Plateau	4
9000-2850	Pumkin Center Spring	Mississippian Plateau	4

Pesticides are measured to determine both rural agriculture and urban domestic-use 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 sample efficiently and regularly collect bacteria samples and 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 U.S.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 U.S.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 numerous sources, primarily Hem (1985), USGS (2002a) and Driscoll (1986). Potential impacts to human health were compiled from the United States Environmental Protection Agency (U.S.EPA, 2002a) and the Agency for Toxic Substances and Disease Registry (ATSDR, 2001).

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

Bulk Parameters (conductivity, hardness and pH)

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. The term for a microsiemen reported in these units is "µmho." 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.

The boxplots for conductivity (Figures 6 and 7) show a wider variation in values for the Mississippian Plateau and the Ohio River Alluvium than for the Western Kentucky Coal Field. In the Mississippian Plateau, this is most likely the result of the natural variability of Total Dissolved Solids (TDS) in this system consisting largely of soluble carbonate bedrock. Lower values in the Western Coal Field most likely result from the prevalence of clastic sedimentary rocks, which are less soluble than more readily dissolved karst forming carbonate rock predominating in the Mississippian Plateau. Relatively high values in the Ohio River Alluvium may result from longer residence times of groundwater in these heterogeneous, unconsolidated sediments. Conductivity values found in this study are comparable to those found by Carey and others (1993). In their study of 4,859 groundwater analyses throughout the state, an average value of 495 uU/cm was found, compared to a median value of 594 uU/cm for the 120 samples included in this study. Because conductivity measures a variety of ions, most of which are naturally occurring, the interpretation of this parameter alone as an indicator of nonpoint source pollution is difficult. Absent any direct evidence to the contrary, the range of values

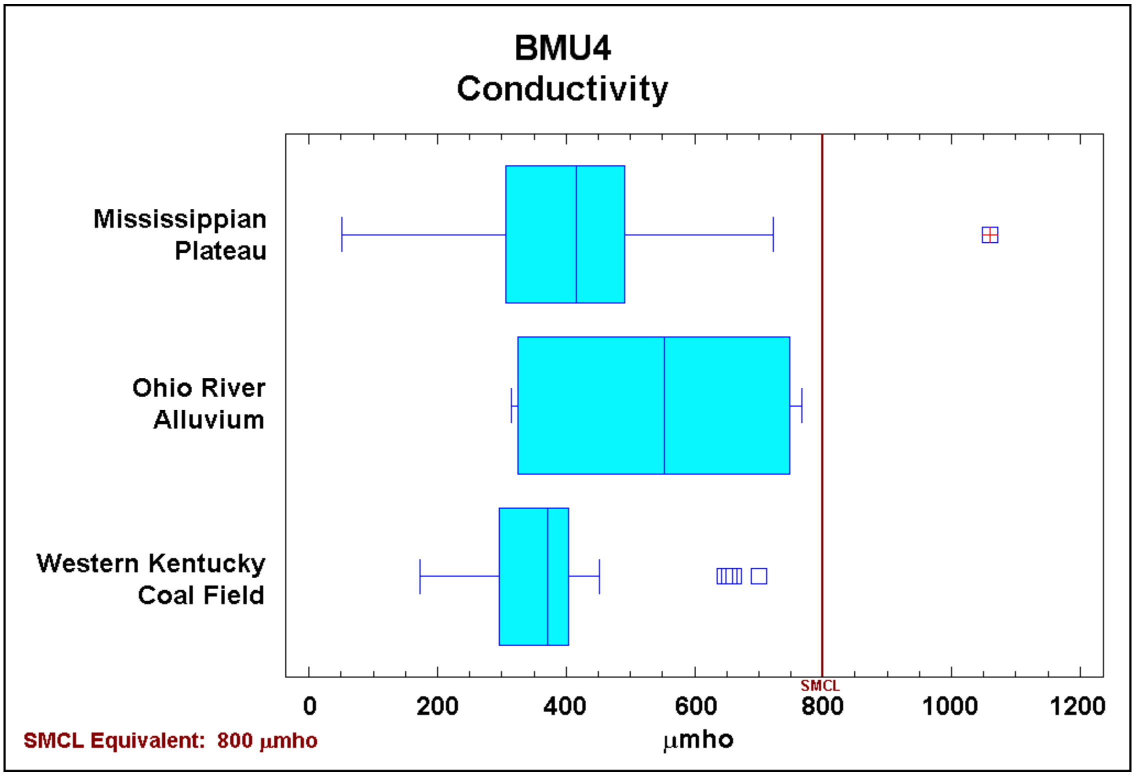

Figure 6. Boxplot for Conductivity Measurement Distributions in BMU 4

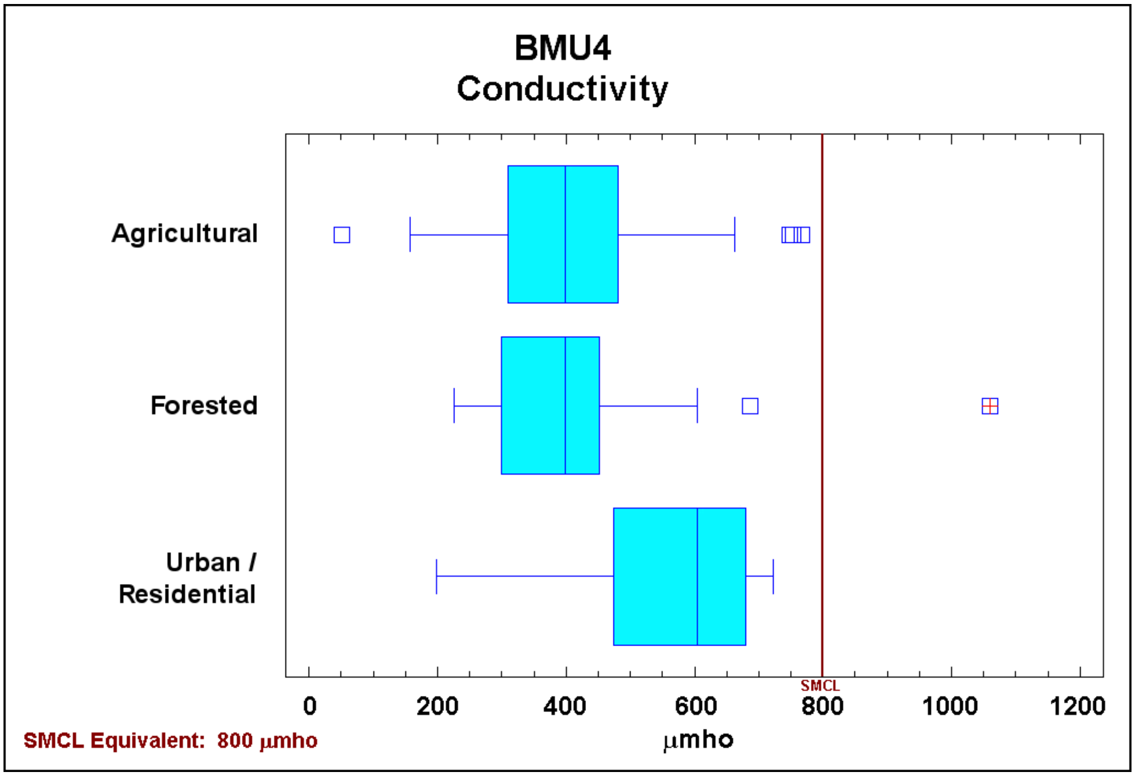

Figure 7. Boxplot for Conductivity Measurements in BMU 4 by Land Use

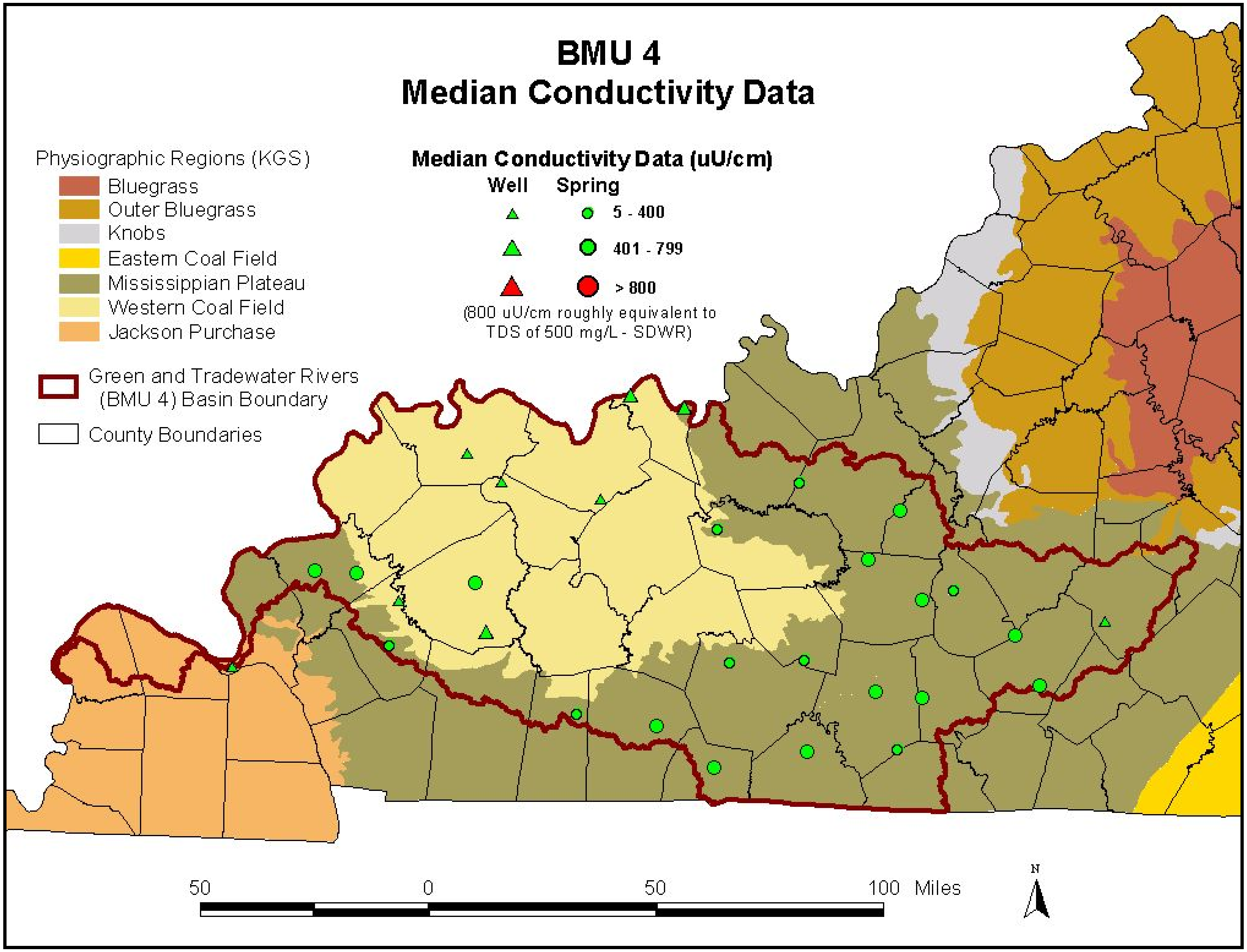

Figure 8. Map of Median Conductivity Data in BMU 4

found in this study most likely reflect ambient conditions and are not necessarily indicative of nonpoint source pollution.

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, gritty, 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.

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. The boxplots illustrating the distribution of hardness values (Figure 9 and 10) show that median values for groundwater are very hard in all physiographic provinces of BMU 4, except the Western Coal Field. This reflects the abundance of calcium and magnesium, mostly derived from carbonate sedimentary rocks, in the Mississippian Plateau and Ohio River alluvial aquifer. This is indicative of ambient conditions, rather than of nonpoint source impacts.

Hardness values are generally high in both springs and wells throughout the study area (Figure 11). Lowest values are in the Western Coal Field in which clastic sedimentary rocks, generally low in calcium and magnesium, are dominant.

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 dimension less, 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. Figures 12 and 13 illustrate that almost all pH values are within the SMCL range of 6.5 to 8.5 units. The greatest variability is in the Western Coal Field, with the outlier at approximately 10.80 pH units (from Hopkins County). The measurement is from a well that registered in the mid 7 to mid 8 pH range for the other 3 samples. The well is a deep well and based on current knowledge of the site, no obvious nonpoint source pollution exists. The other physiographic provinces show natural variability, and because there is no direct evidence of nonpoint source influences on pH in areas adjacent to the studied sites, the conclusion is that there are no probable impacts from nonpoint source pollution.

Inorganic Ions (chloride, fluoride and sulfate)

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.

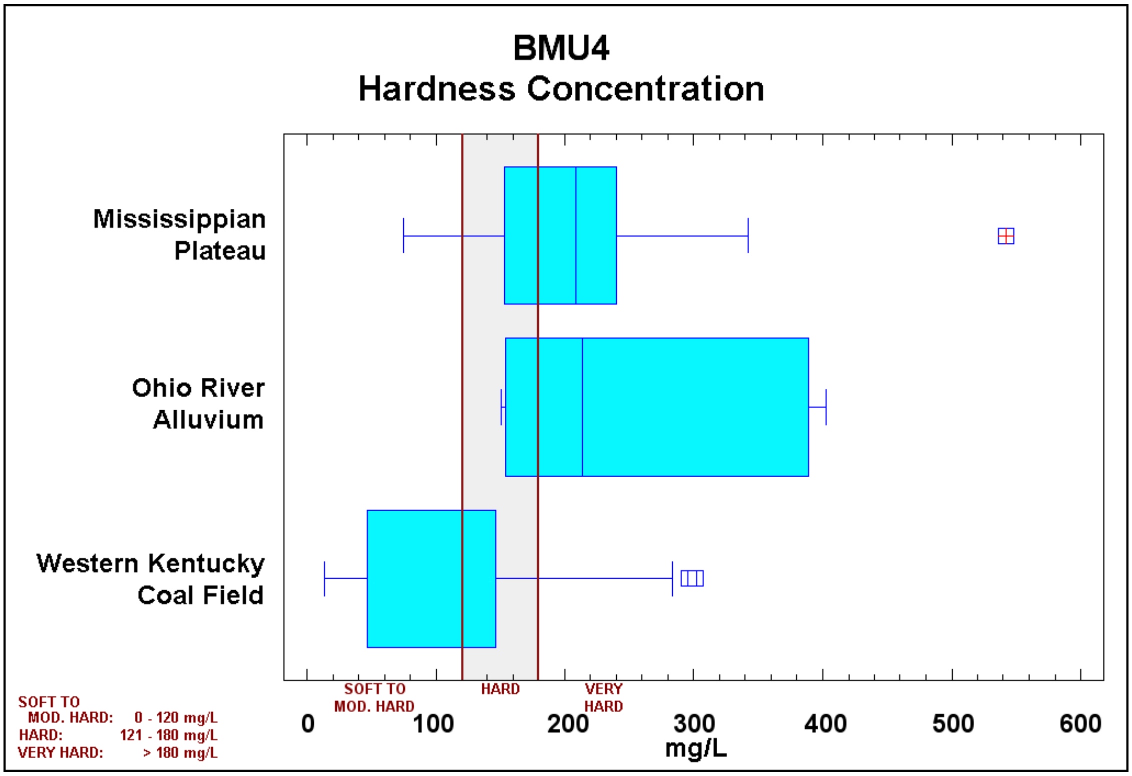

Figure 9. Boxplot for Hardness Measurement Distributions in BMU 4

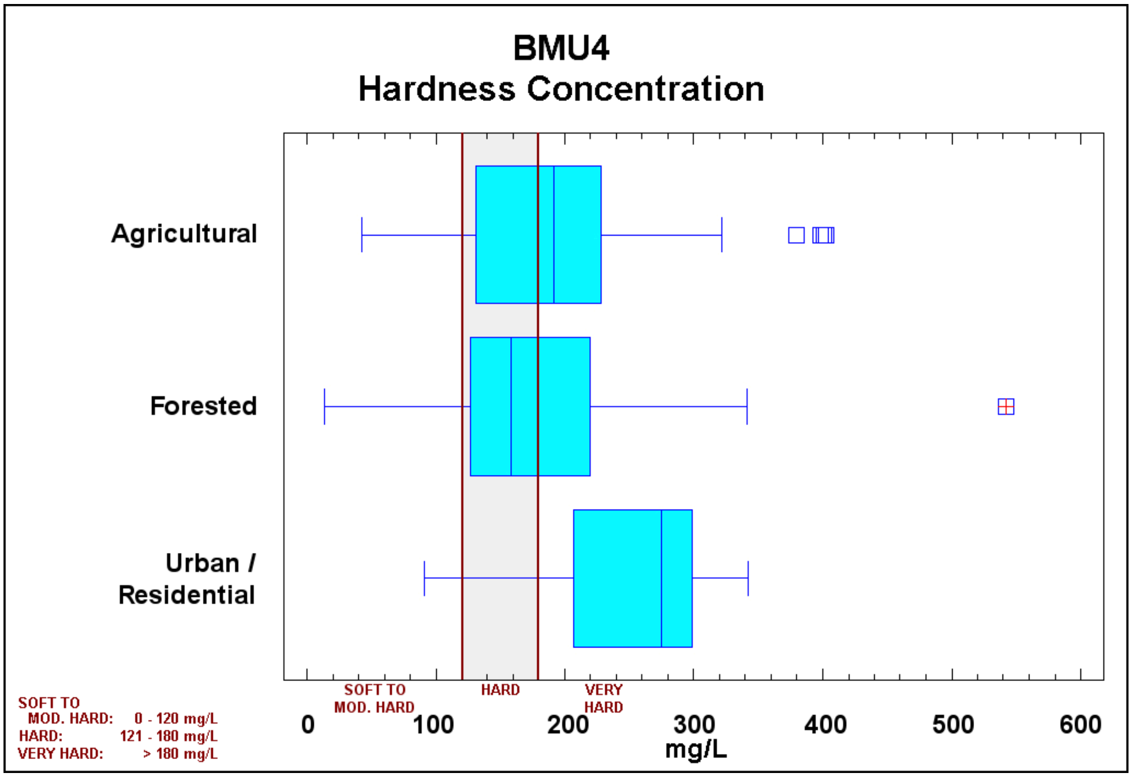

Figure 10. Boxplot for Hardness Measurements in BMU 4 by Land Use

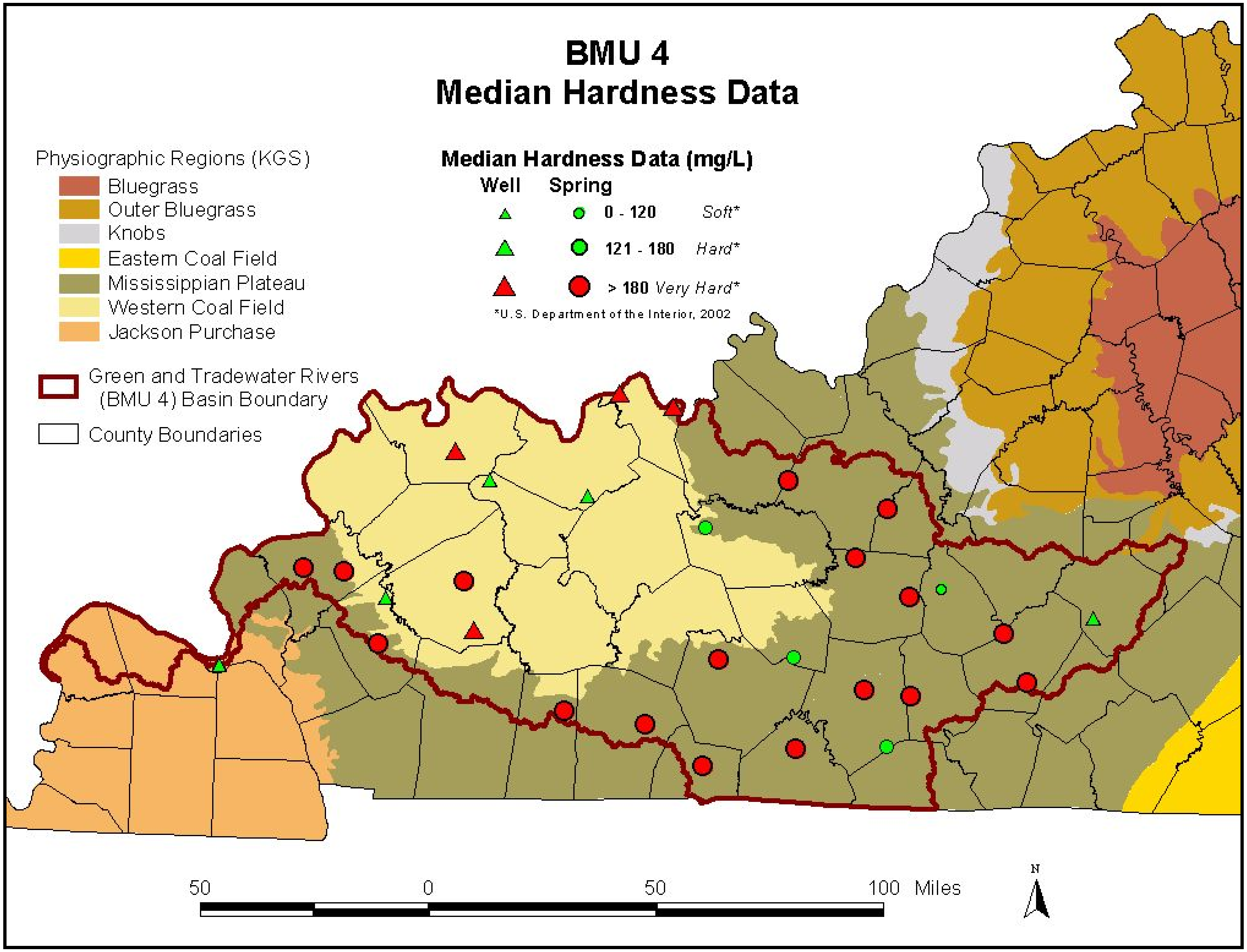

Figure 11. Map of Median hardness data in BMU 4

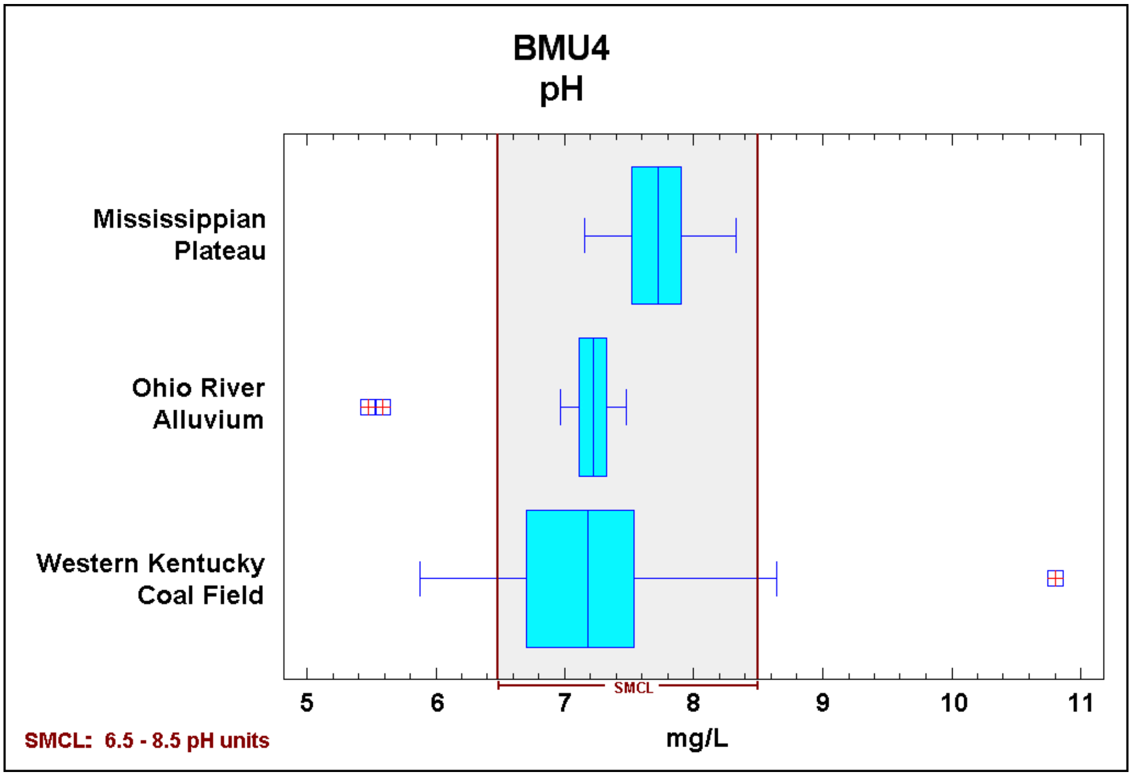

Figure 12. Boxplot for pH Measurement Distributions in BMU 4

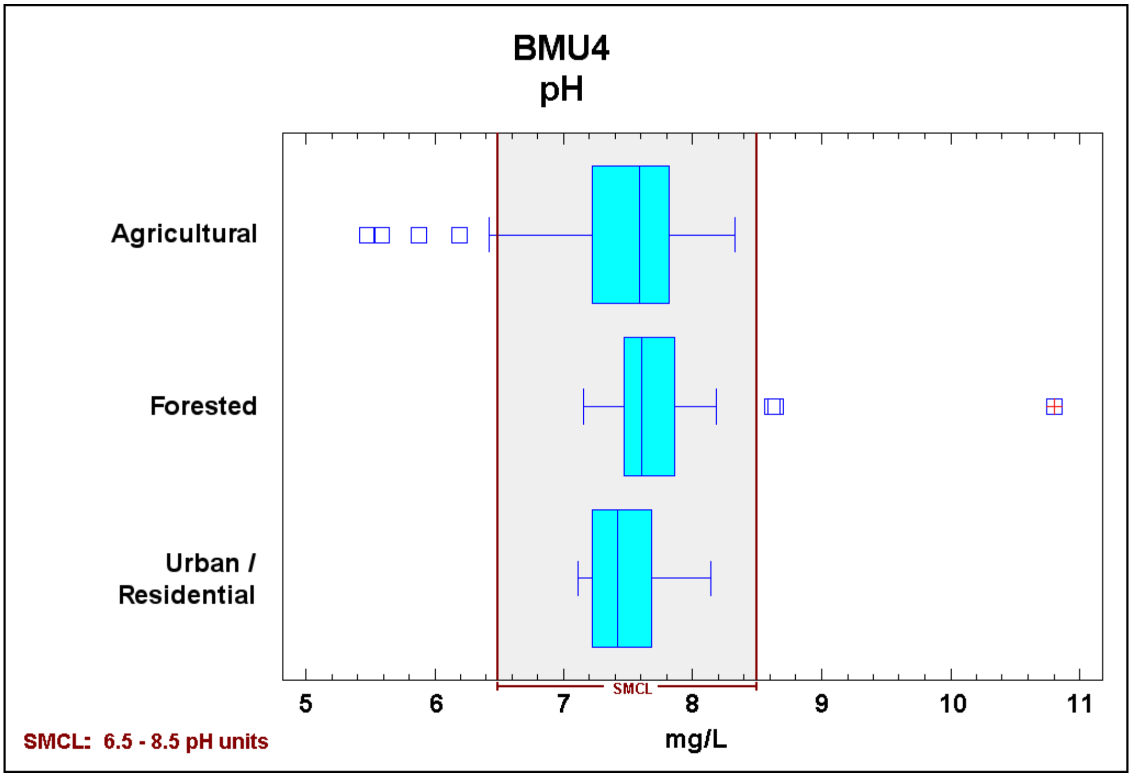

Figure 13. Boxplot for pH Measurements in BMU 4 by Land Use

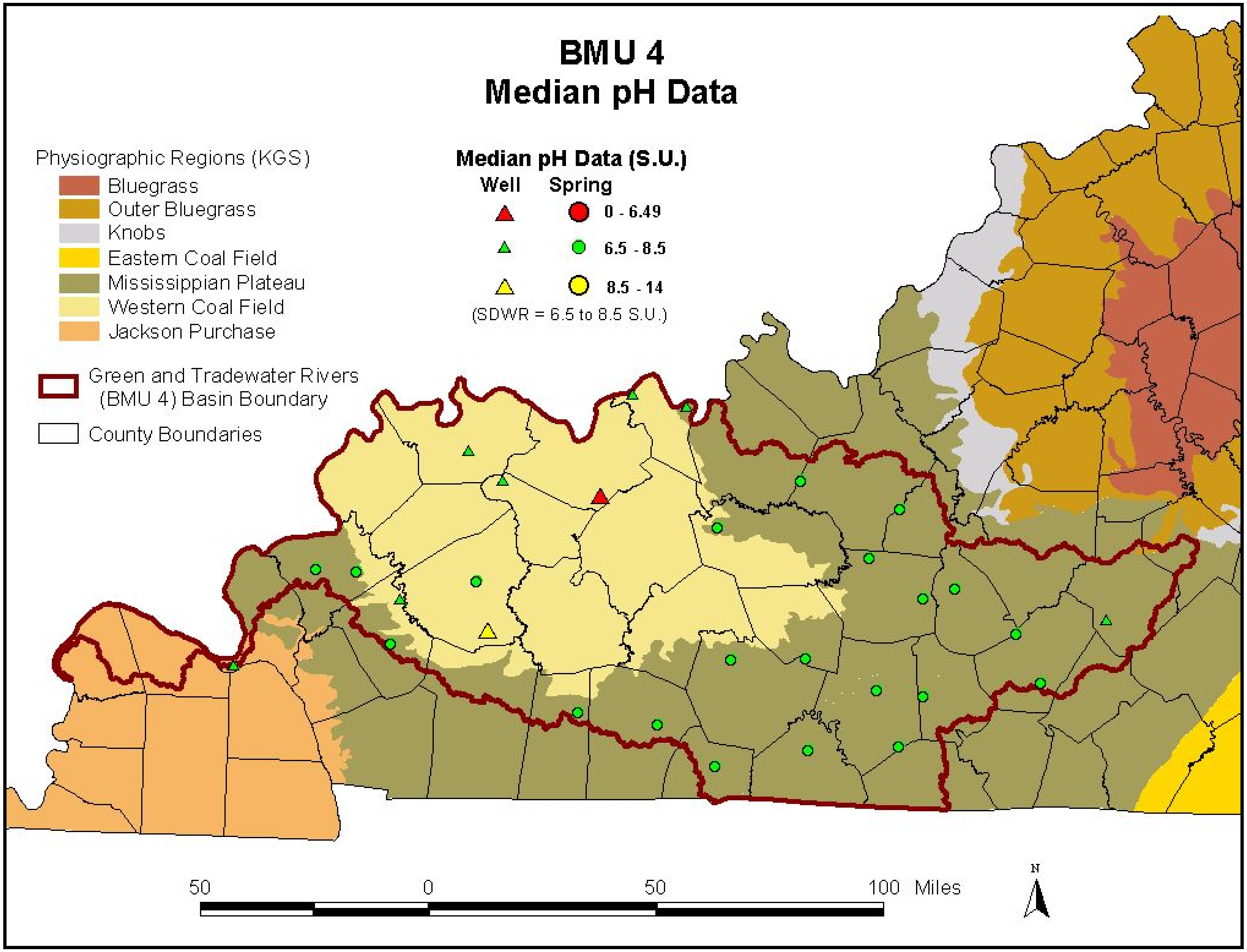

Figure 14. Map of Median pH Data for BMU 4

In general, the boxplots for chloride (Figure 15 and 16) show low chloride values in BMU 4. In Kentucky, high chlorides sometimes occur at shallow depths and because no specific point sources of chlorides occur adjacent to the sites sampled in this study, the variation observed is probably natural. The highest values found in this study were for a well in the Ohio River Alluvium and the concentration (60.9 mg/L) is still well below the SMCL of 250 mg/L (Figures 15 and 16). Lower chloride values, well under the SMCL, are distributed throughout the study area.

Fluoride (Fl) commonly occurs in trace quantities in many soils and rocks, including coal. Fluorite (CaF_2) is the primary fluorine mineral. Additionally, 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. Brittle, mottled and discolored tooth enamel characterizes dental fluorosis. Skeleton fluorosis causes a wide range of muscle and bone problems, including osteoporosis.

Figures 18 and 19 indicated that fluoride showed a narrow range of values for most of the data. Because no apparent nonpoint sources of fluoride other than possible effects from atmospheric deposition were noted, outliers may be indicative of natural variability. No sample analysis results exceeded the MCL and no specific sites are known to have been impacted by nonpoint source pollution. Since reference sites may also be impacted by possible atmospheric deposition, comparison with these sites may be invalid.

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. Sites in this study in those counties failed to confirm the values found in the 1999 study, but does not necessarily indicate an improvement in groundwater quality.

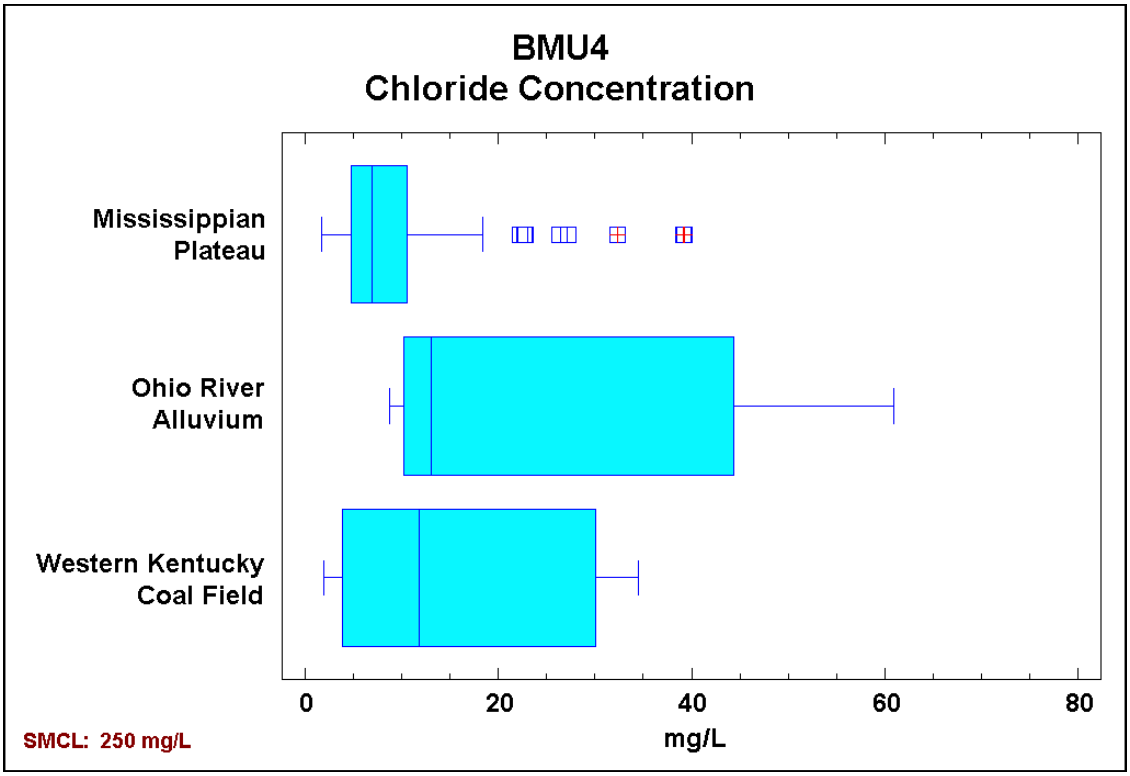

Figure 15. Boxplot for Chloride Measurement Distributions in BMU 4

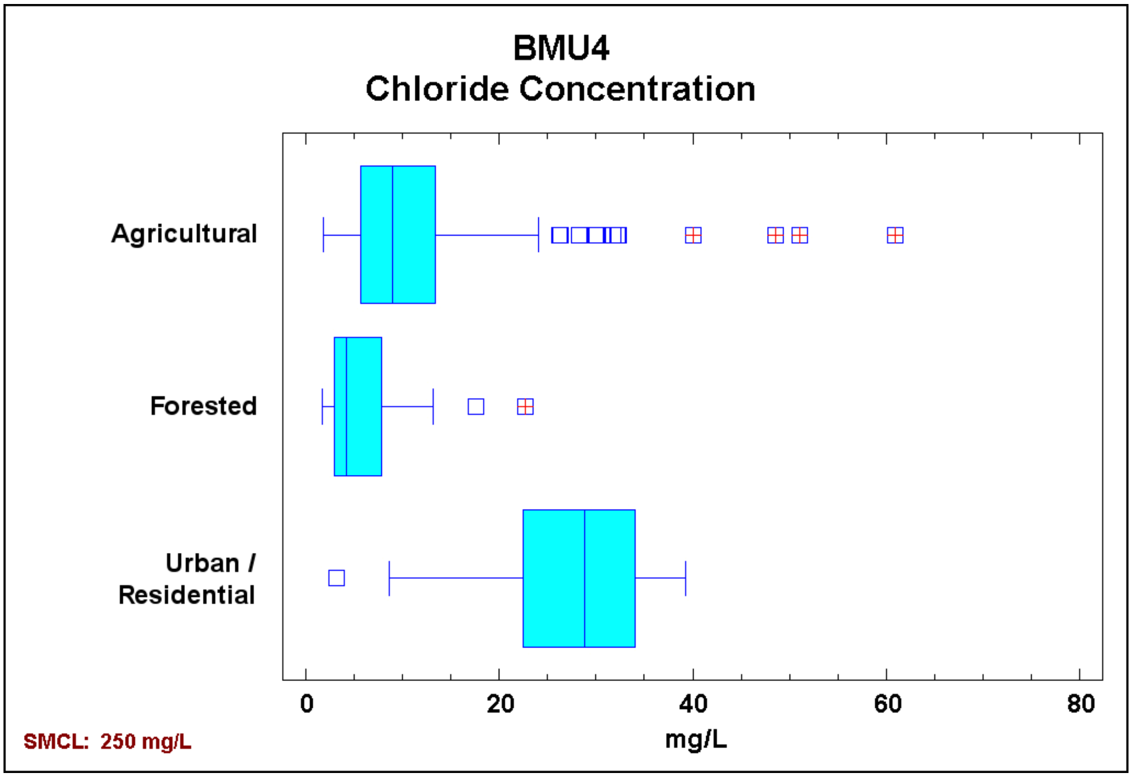

Figure 16. Boxplot for Chloride Measurements in BMU 4 by Land Use

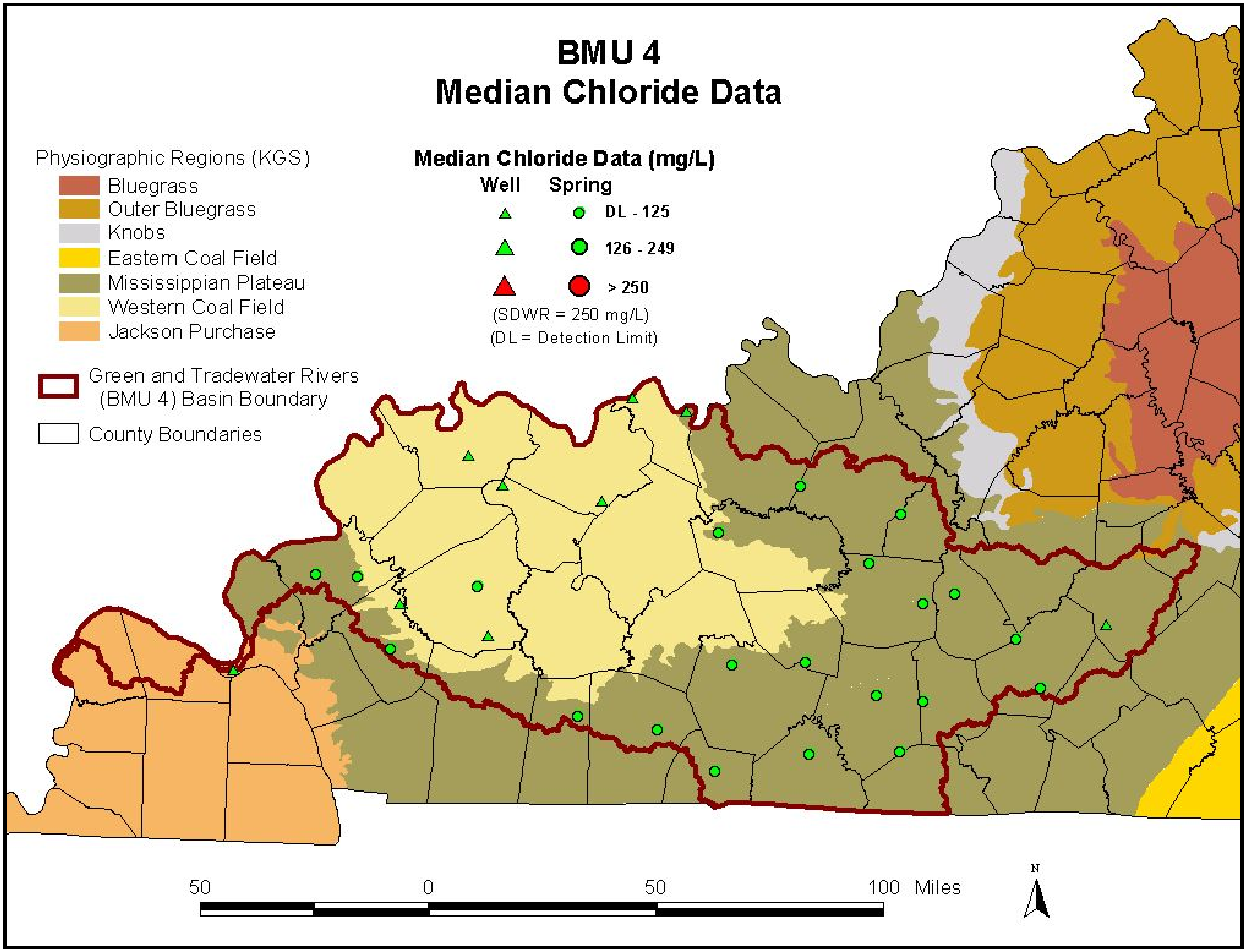

Figure 17. Map of Median Chloride Data for BMU 4

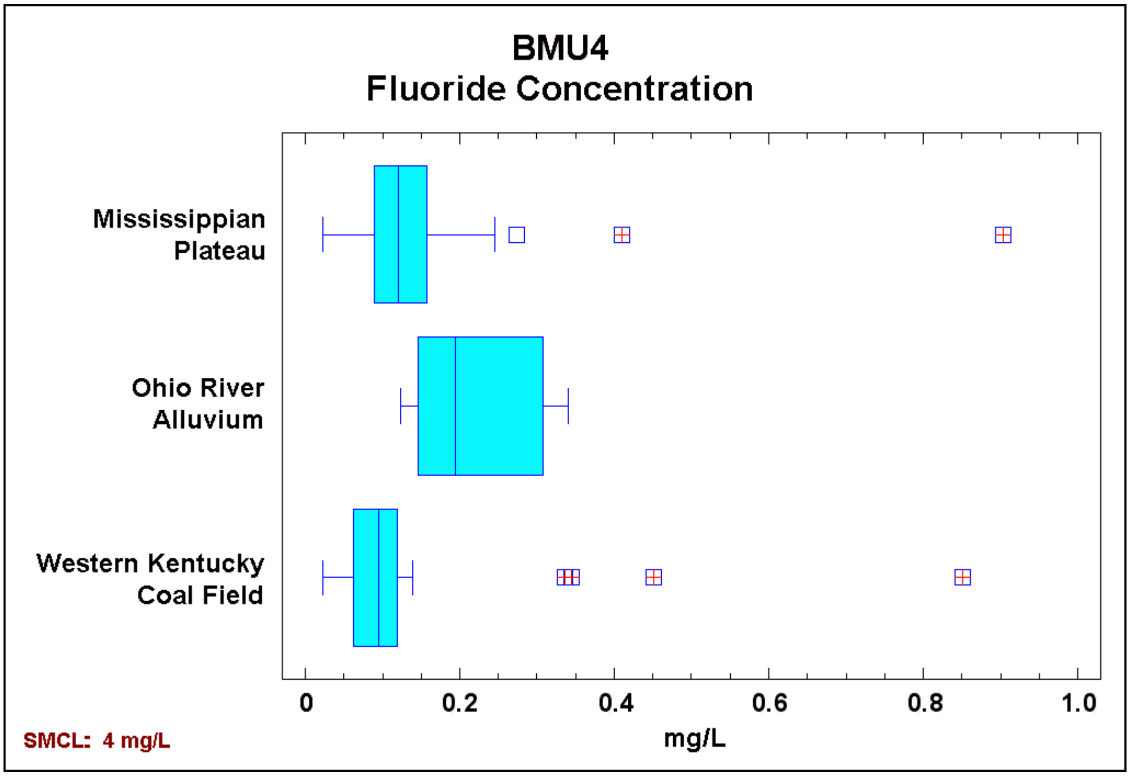

Figure 18. Boxplot for Fluoride Measurement Distributions in BMU 4

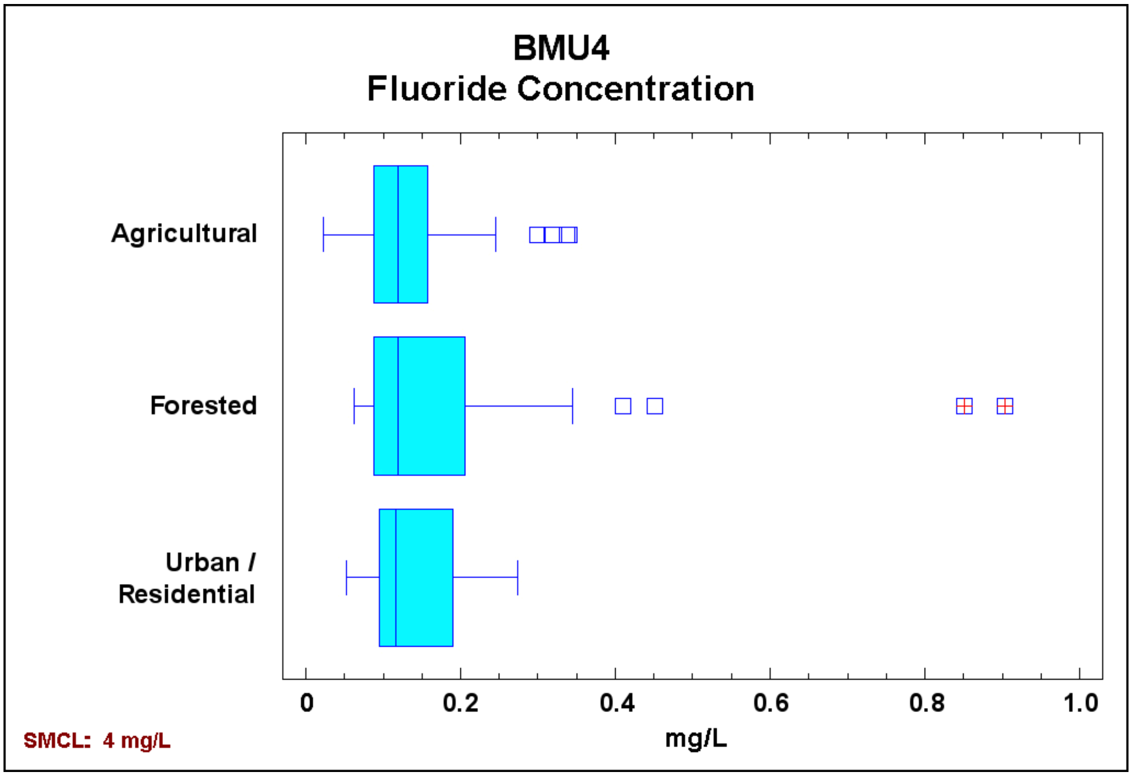

Figure 19. Boxplot for Fluoride Measurements in BMU 4 by Land Use

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 the project area, 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 undesirable odor and taste to the water and commonly have a laxative effect.
In general, Figures 21 and 22 illustrate a narrow range of sulfate values, well under the SMCL, especially in the Western Coal Field. The far outlier of approximately 303 mg/L in the Mississippian Plateau is at Crittenden Spring, shown in Figures 21 and 22. The other samples at this spring were much lower at 13.2, 32.9 and 90.3 mg/L. This may indicate a slug of nonpoint source pollution during the time the 303 mg/L sample was collected.

Because there is no direct evidence of nonpoint sources of sulfate affecting the groundwater sites in this study and because sulfate is commonly naturally occurring in groundwater throughout the study area, this parameter was not found a useful indicator of nonpoint source pollution. Although coal mining is known to affect groundwater in some areas of BMU 4, this study does not confirm that. However, data in the Western Coal Field are limited and if other sites had been sampled immediately adjacent to current or historical coal-mining areas, the results might have supported different conclusions.

Metals

For this report, data is presented for arsenic, barium, iron, manganese and mercury. These metals were chosen because they are common constituents of sedimentary rocks, especially coal and black shales (USGS, 2002b; Tuttle and others, 2001) and soils (Logan and Miller 2002). In water, lower pH values, as well as higher dissolved oxygen content, increase the dissolution of metals. Common anthropogenic nonpoint sources of problem metals include mining, urban run-off, industrial operations, land farming of sewage and other waste and emissions from coal-fired power plants. High concentrations of metals in groundwater are sometimes difficult to interpret and may indicate point or nonpoint sources of contamination, or may even be naturally occurring. Comparison with reference reach springs (Table 2), as well as reviewing relevant literature, can prove useful.

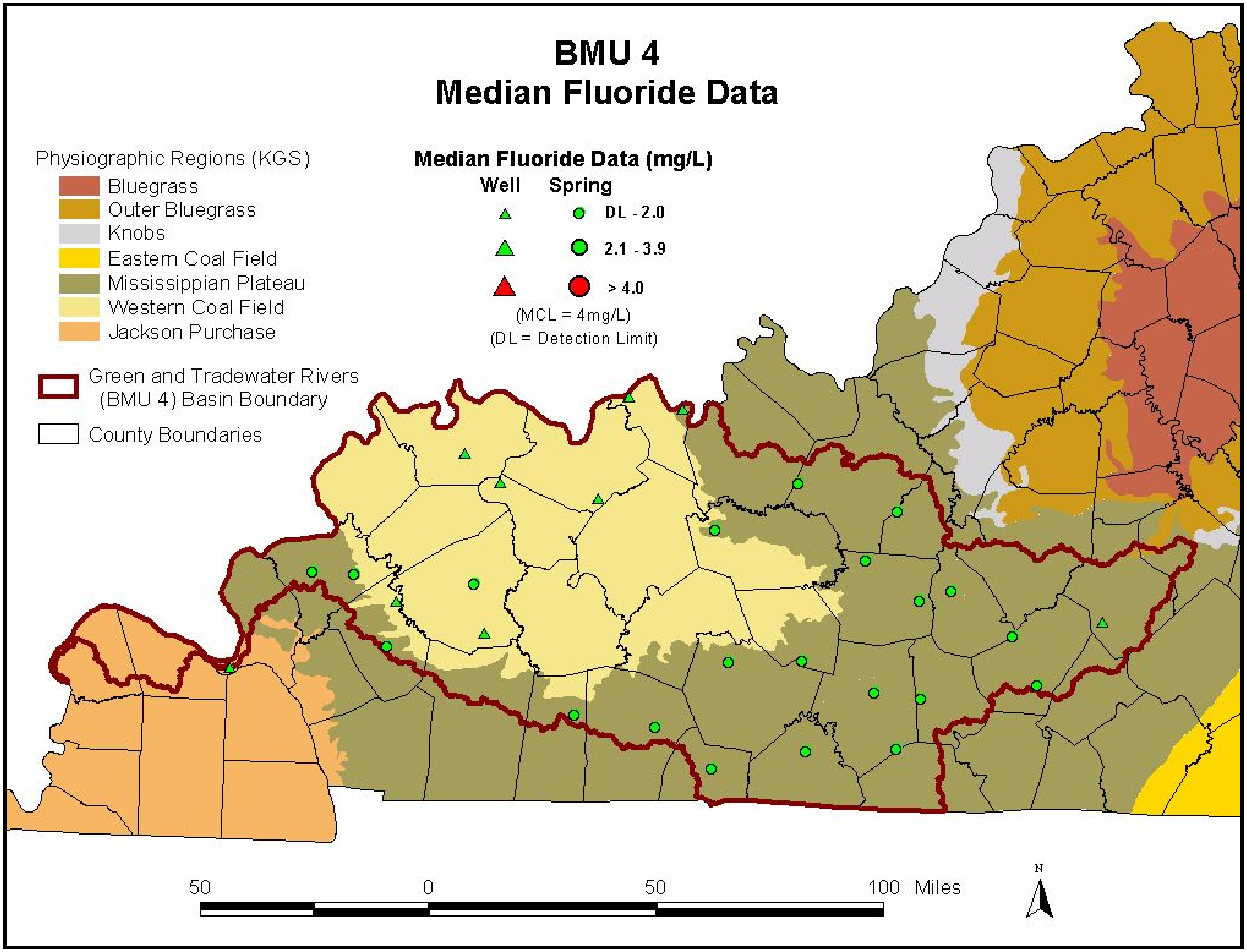

Figure 20. Map of Median Fluoride Data for BMU 4

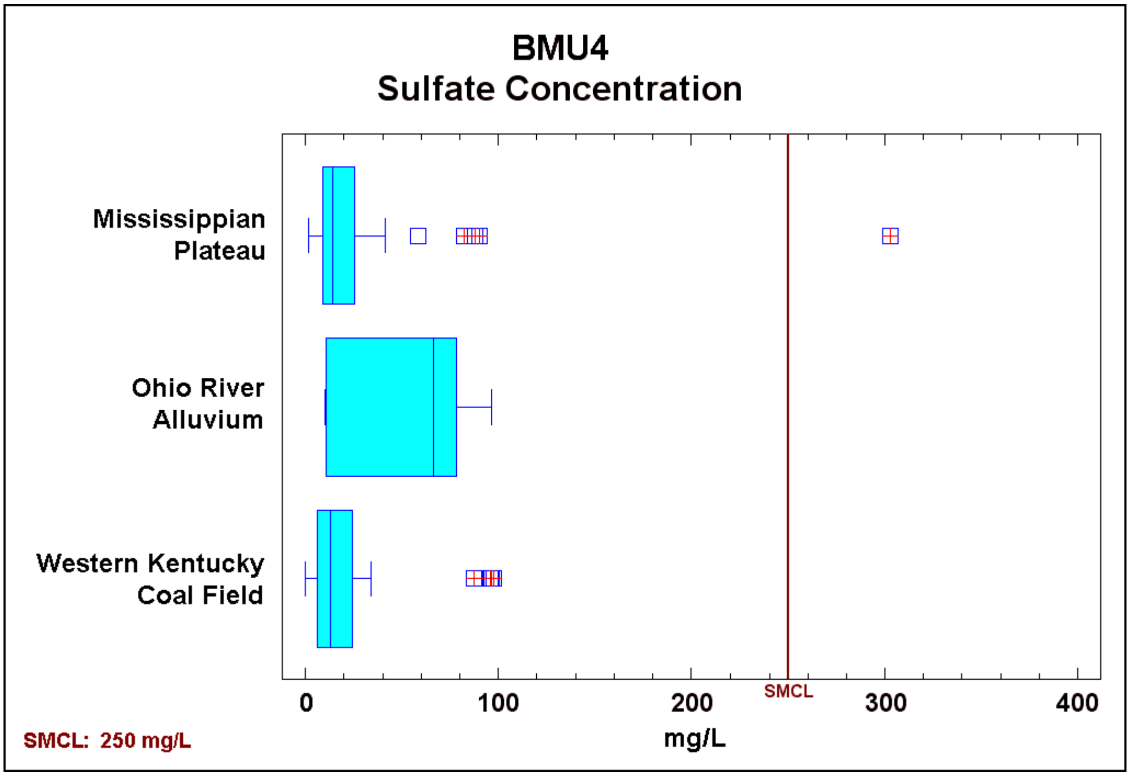

Figure 21. Boxplot for Sulfate Measurement Distributions in BMU 4

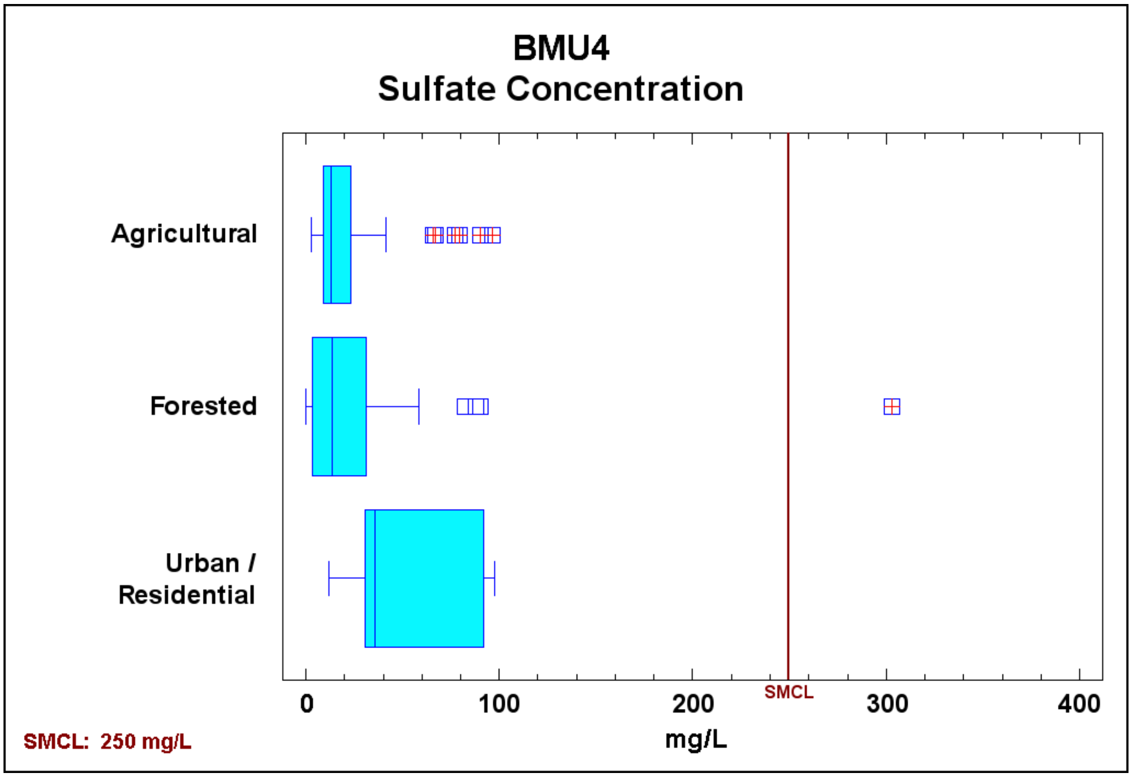

Figure 22. Boxplot for Sulfate Measurements in BMU 4 by Land Use

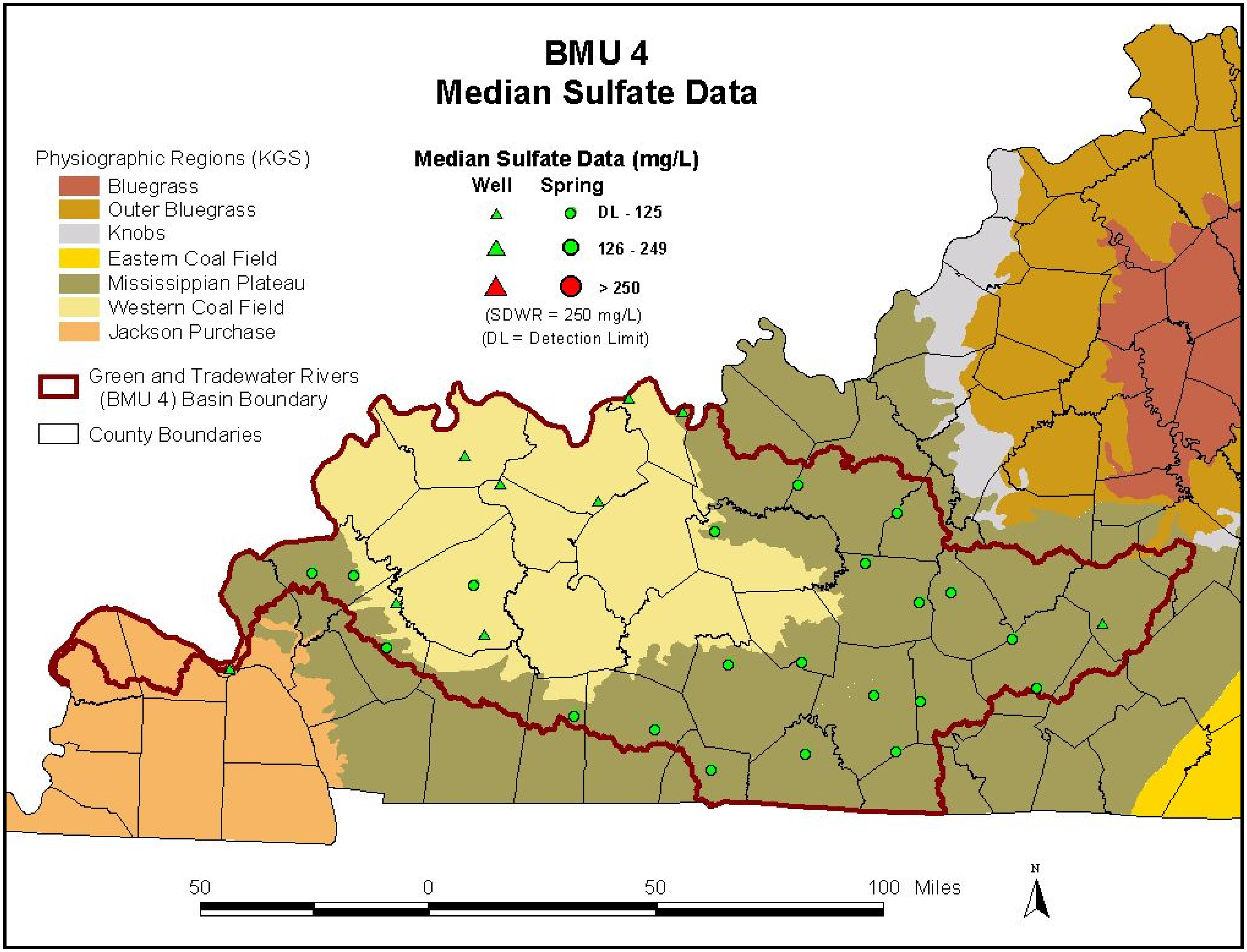

Figure 23. Map of Median Sulfate Data for BMU 4

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

Arsenic is often found as a trace element associated with coal and shale (USGS, 2002b). In addition, the USGS (2002a) notes that the majority of arsenic in groundwater is the ". . . result of minerals dissolving from weathered rocks and soils." Blanset and Goodmann (2002) note that the ". . . most prominent source of arsenic in Kentucky's aquifers results from the oxidation of arsenopyrite, incorporated in iron hydroxides."

Other sources of arsenic include deposition from coal-fired power plants and metal-smelting/manufacturing processes, historical use in pesticides (U.S.EPA, 2002a) and from 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. Arsenic exposure in humans has been linked to bladder and other cancers (USGS, 2000). Arsenic has an MCL of 0.010 mg/L. The U.S.EPA lowered this MCL from 0.05 mg/L in 2001 and will require public water systems to meet the new standard by January 2006.

Arsenic was detected in 10 (approximately 8.3%) of the 120 samples. The detection limit for arsenic is 0.002 mg/L; figures 24 and 25 indicate that most samples were not detectable at this limit. The largest concentration of arsenic was 0.006 mg/L, from a water well in the Ohio River alluvium, but this value is still well below the MCL of 0.010 mg/L. Three other samples taken at this site have concentrations of 0.005 mg/L. The other detections were one-time detections at or just above the MDL. Fisher (2002) reviewed statewide arsenic data and found that for ambient groundwater about 95% of 4,402 analyses from 930 sites were less than the MCL of 0.010 mg/L. Blanset and Goodmann (2002) reviewed total arsenic data from 1,249 ambient groundwater samples from 240 sites and found 10 sites with total arsenic exceeding the MCL of 0.010 mg/L. In their study, Blanset and Goodmann concluded that alluvial aquifers were most at-risk through the reduction of arsenic containing iron hydroxides. Our study found similar differences in the occurrence of arsenic between alluvial aquifers and other physiographic provinces, as shown in Figure 24 and 25. The low levels of arsenic found in our study, as well as the absence of any apparent sources, indicate no negative impacts through nonpoint source pollution in BMU 4.

Barium occurs most commonly as the mineral barite ($BaSO_4$). This naturally occurring mineral occurs in nodules in sedimentary rocks and as a trace element in coal. The drilling industry uses barium, and this mineral also occurs in a variety of products such as glass and paint. The MCL for barium is 2 mg/L and exposure to high levels of barium has been associated with cardiovascular problems such as high blood pressure.

Barium was found in almost all of the samples collected. However, most detections occurred within a narrow range in all physiographic provinces (Figures 27 and 28). Outliers reflect the natural variability in the study area. Barite vein deposits are common in both the Western Coal Field and the Mississippian Plateau areas. Barium drilling mud is used in some oil and gas drilling operations but the extent of its use as barite drilling fluids is unknown. Barium is not typically indicative of nonpoint source pollution and in the absence of any known nonpoint sources in the study area; barium occurrence in Kentucky represents natural groundwater quality.

Iron (Fe) is commonly found in at least trace amounts in practically all sediments and sedimentary rocks (Driscoll, 1986). Iron is also one of the most prevalent groundwater quality problems 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 may be associated with run-off from coal mining. Typically, this high iron discharge affects surface water rather than groundwater, but wells in old mine works and adjacent areas can also be affected.

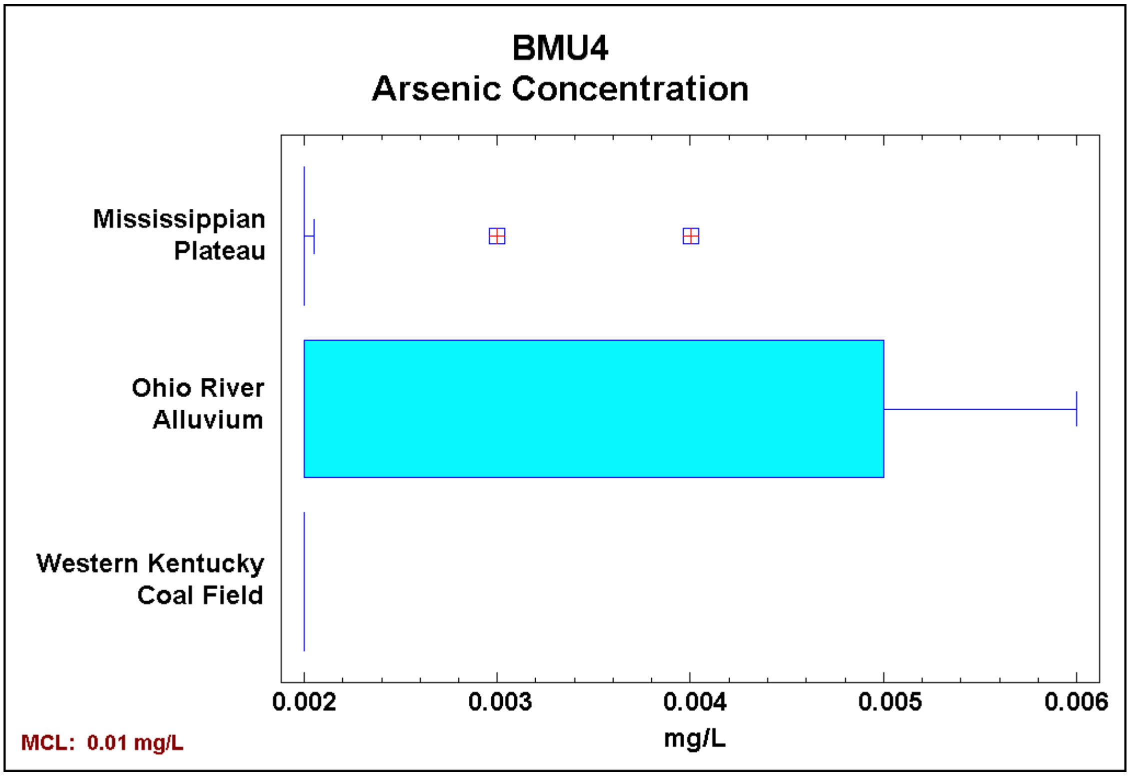

Figure 24. Boxplot for Total Arsenic Measurement Distributions in BMU 4

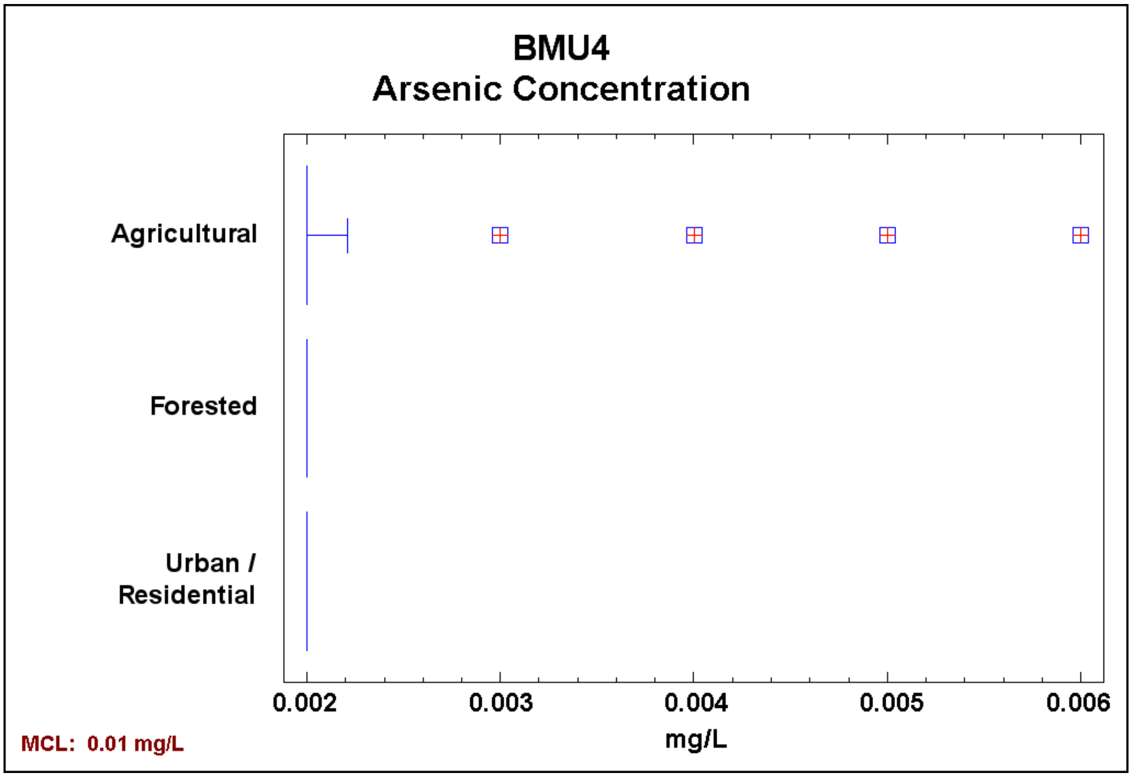

Figure 25. Boxplot for Total Arsenic Measurements in BMU 4 by Land Use

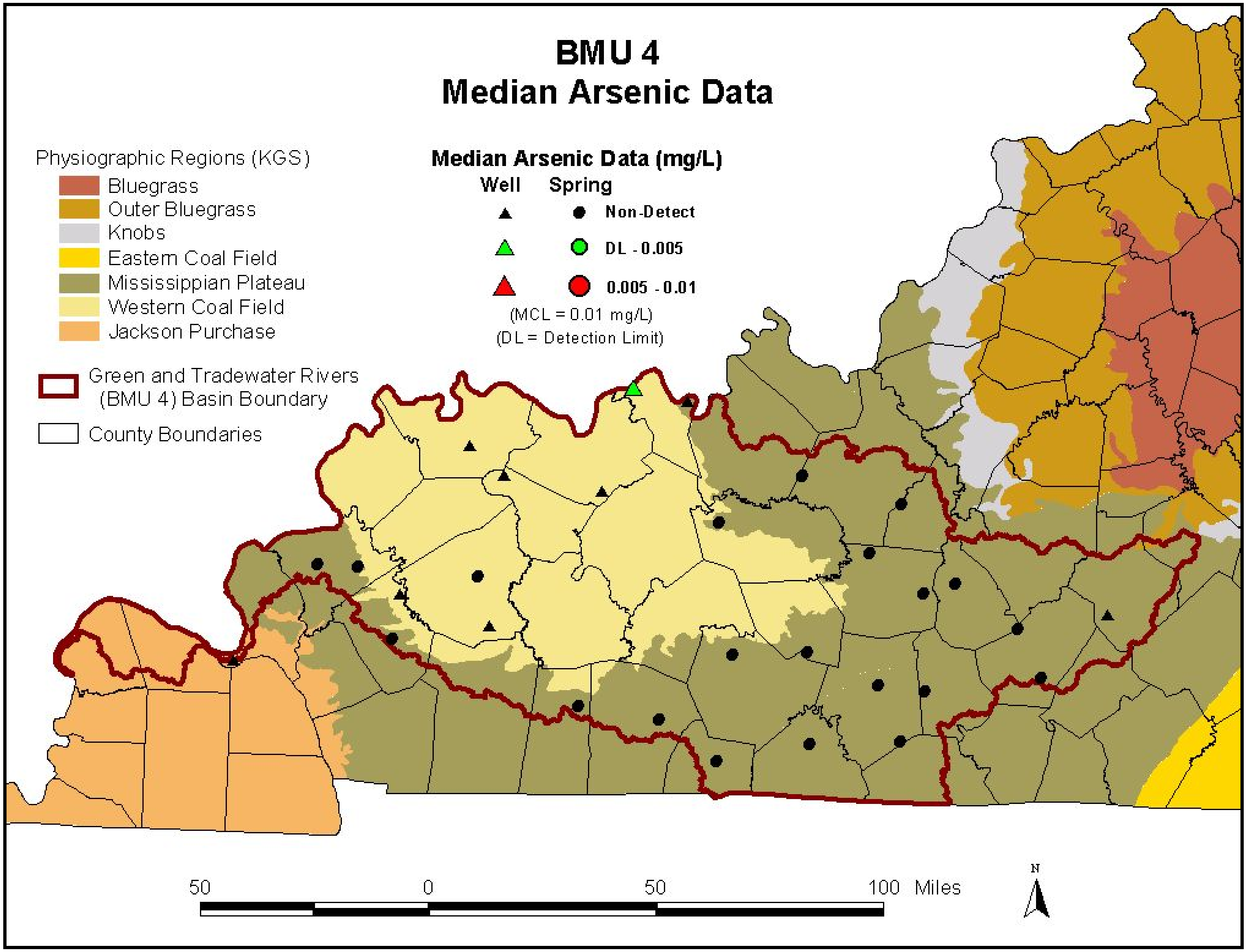

Figure 26. Map of Median Arsenic Data for BMU 4

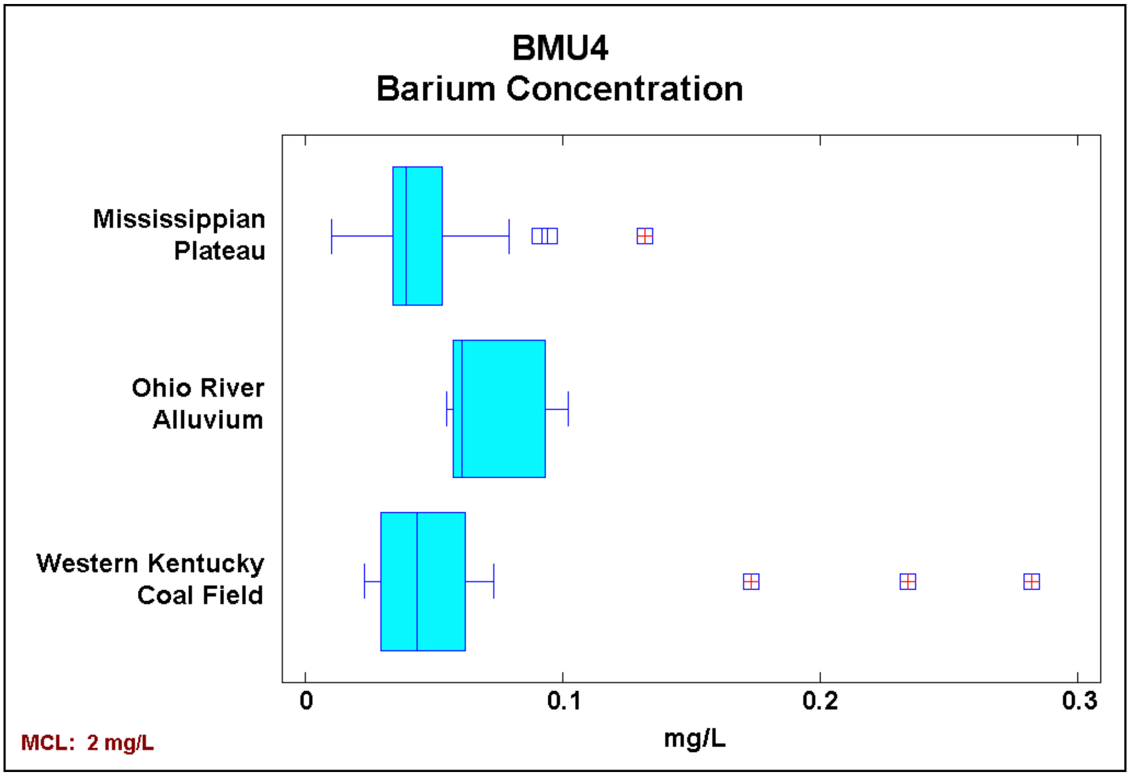

Figure 27. Boxplot for Barium Measurement Distributions in BMU 4

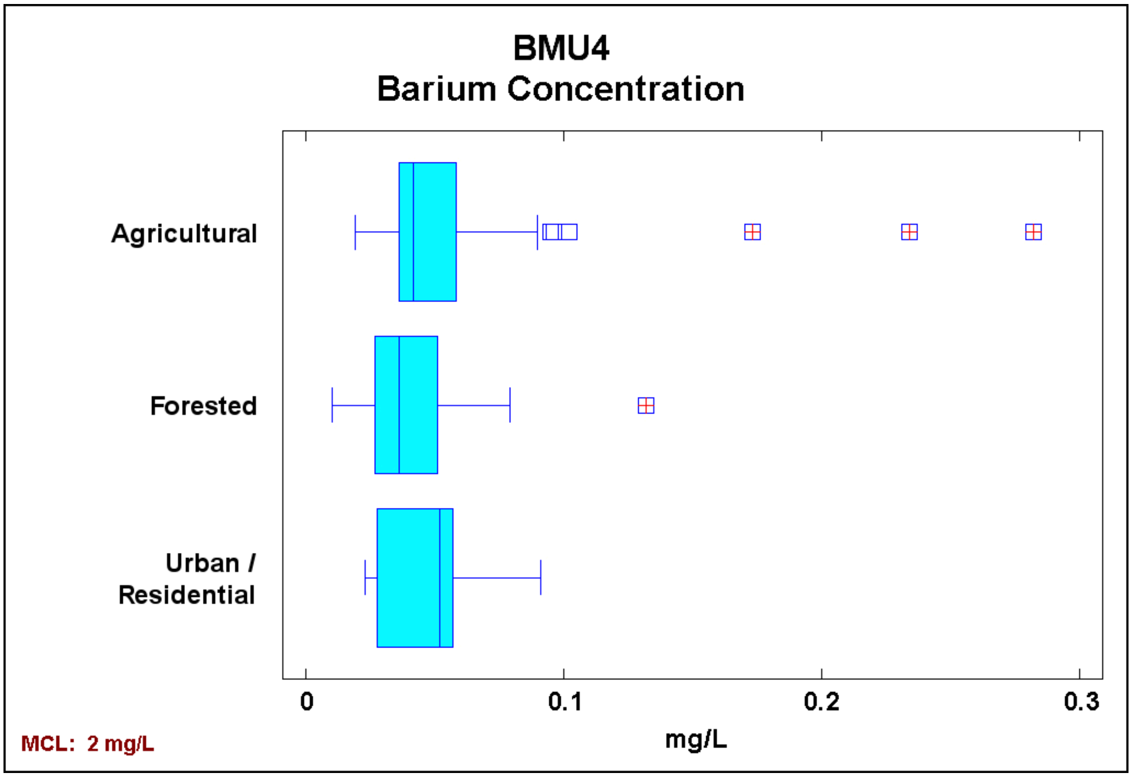

Figure 28. Boxplot for Barium Measurements in BMU 4 by Land Use

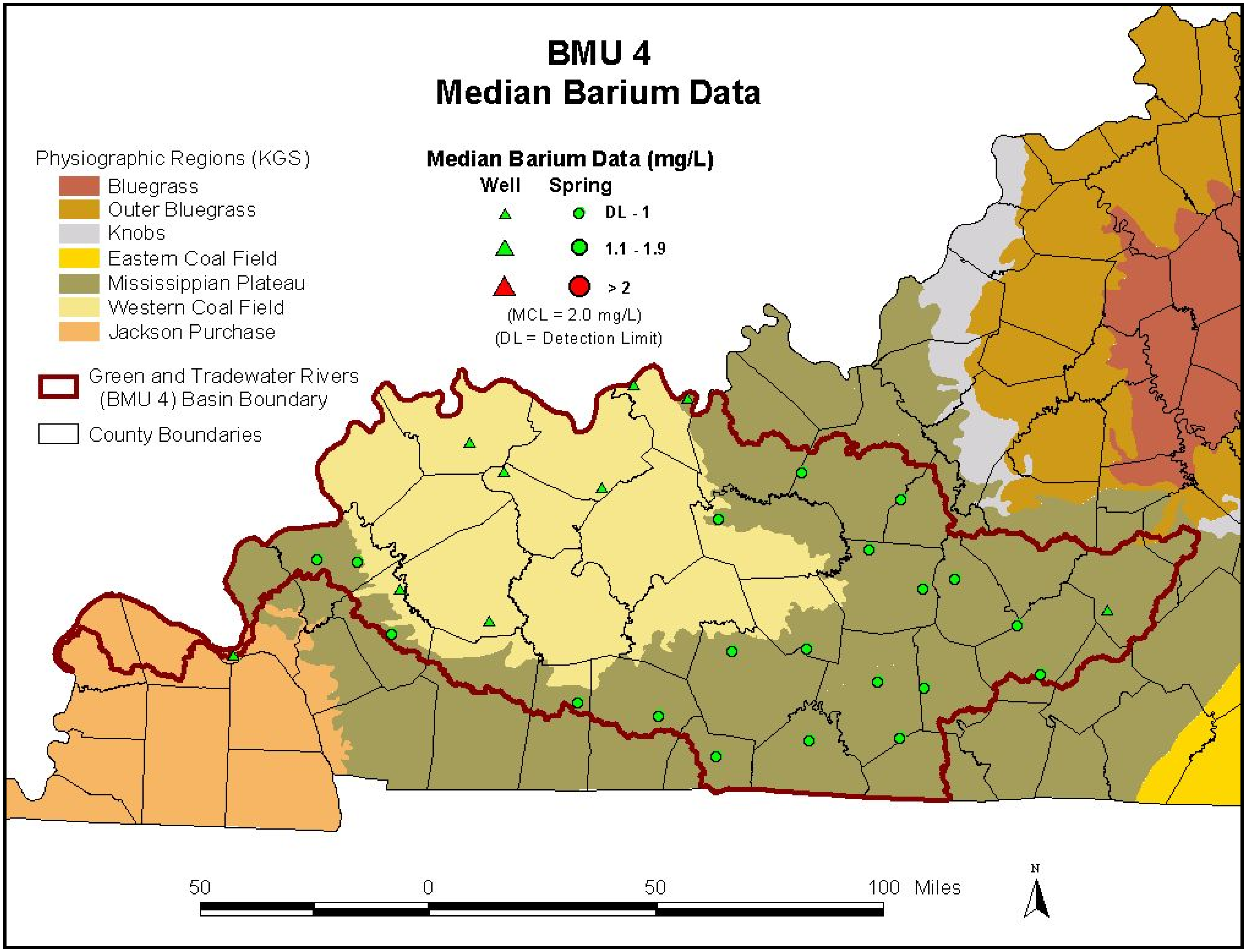

Figure 29. Map of Median Barium Data for BMU 4

Iron is a basic water quality parameter regarding 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 for most people. Iron in water is a health concern for people who have hemochromatosis, a common genetic disorder for persons with Scotch/Irish backgrounds. Iron has an SMCL of 0.3 mg/L.

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 that feed on iron can coat fixtures. Sometimes iron 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 do render the water unpalatable and are indicators of unsanitary conditions that may harbor other, more harmful, bacteria.

In this study, more than 95% of the samples had detections of iron (Figure 32), and slightly more than 39% of the detections exceeded the SMCL. Numerous outliers show the natural variability of this element. Given the absence of specific nonpoint sources of iron, Figures 30 and 31 indicate naturally occurring variations. Figure 32 illustrates the wide-spread occurrence of iron throughout all physiographic provinces.

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. It occurs in more than 91% of the samples. As shown in Figures 33 and 34, values clustered in a narrow range just below the SMCL of 0.05 mg/L, but levels above this are common. Manganese is generally not a direct indicator of nonpoint source pollution. A few samples were approximately 10 times the drinking water SMCL. Figure 35 shows the occurrence of manganese throughout the study area, with no apparent pattern of distribution among the various physiographic provinces.

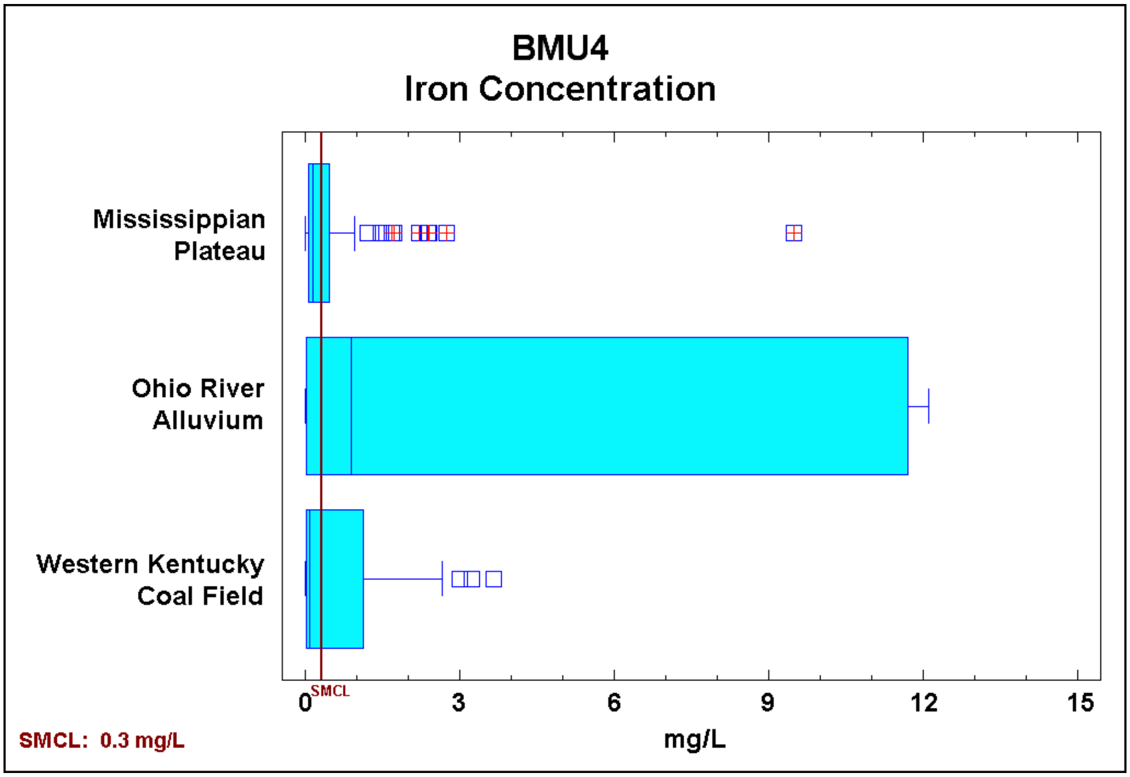

Figure 30. Boxplot for Iron Measurement Distributions in BMU 4

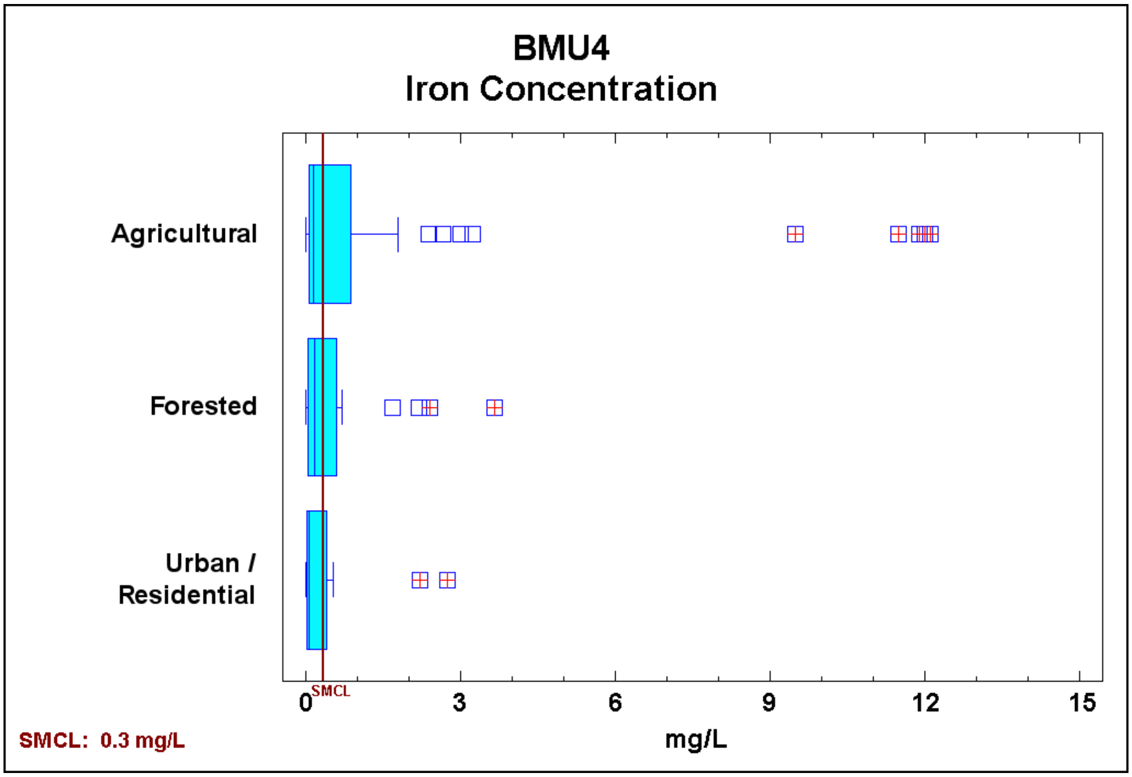

Figure 31. Boxplot for Iron Measurements in BMU 4 by Land Use

Mercury (Hg) occurs naturally in the Western 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. The MCL for mercury is 0.002 mg/L.

Mercury was not detected in any of the 120 samples. Because there were no detections of mercury, no map is presented. Mercury data indicate that this metal does not occur naturally in groundwater in the study area, nor does it occur in 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 4 does not appear to contribute to this surface water problem. Because mercury occurs 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 fully determine the potential long-term impacts of this metal on 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.

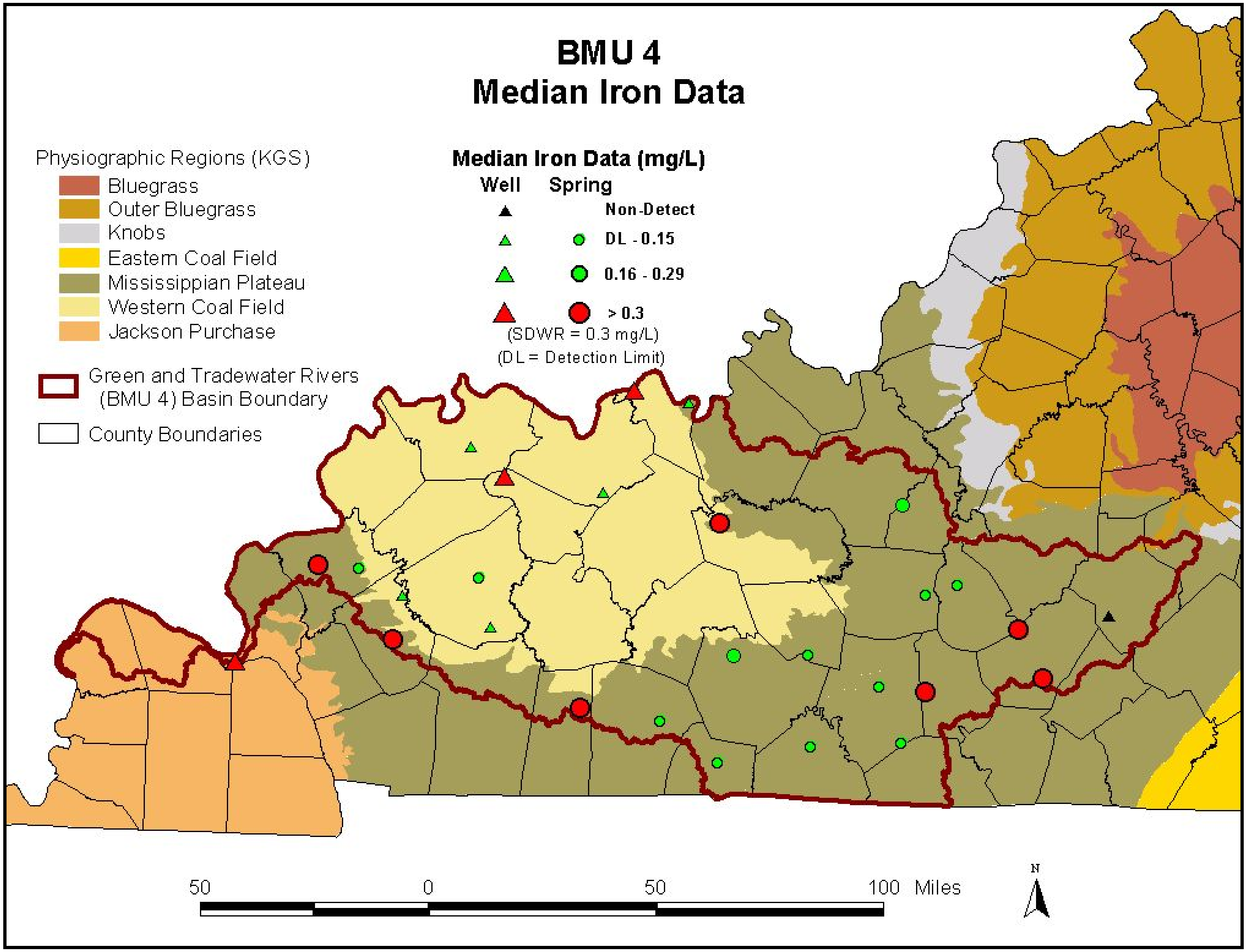

Figure 32. Map of Median Iron Data for BMU 4

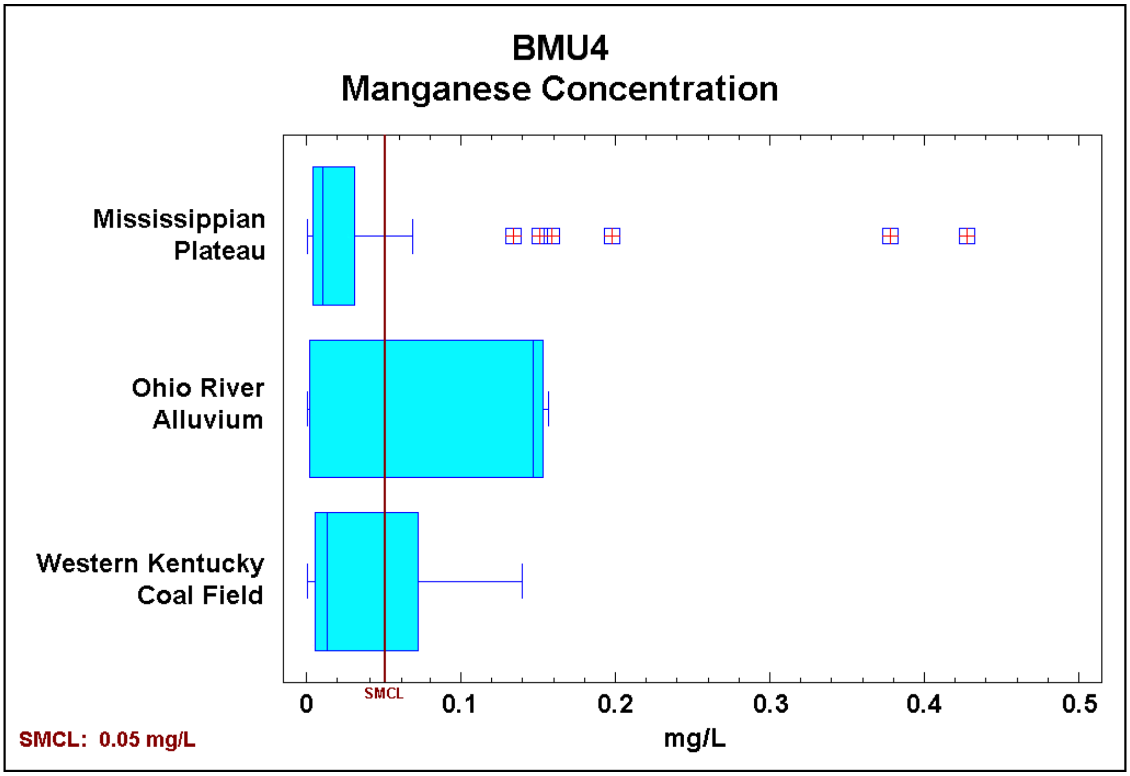

Figure 33. Boxplot for Manganese Measurement Distributions in BMU 4

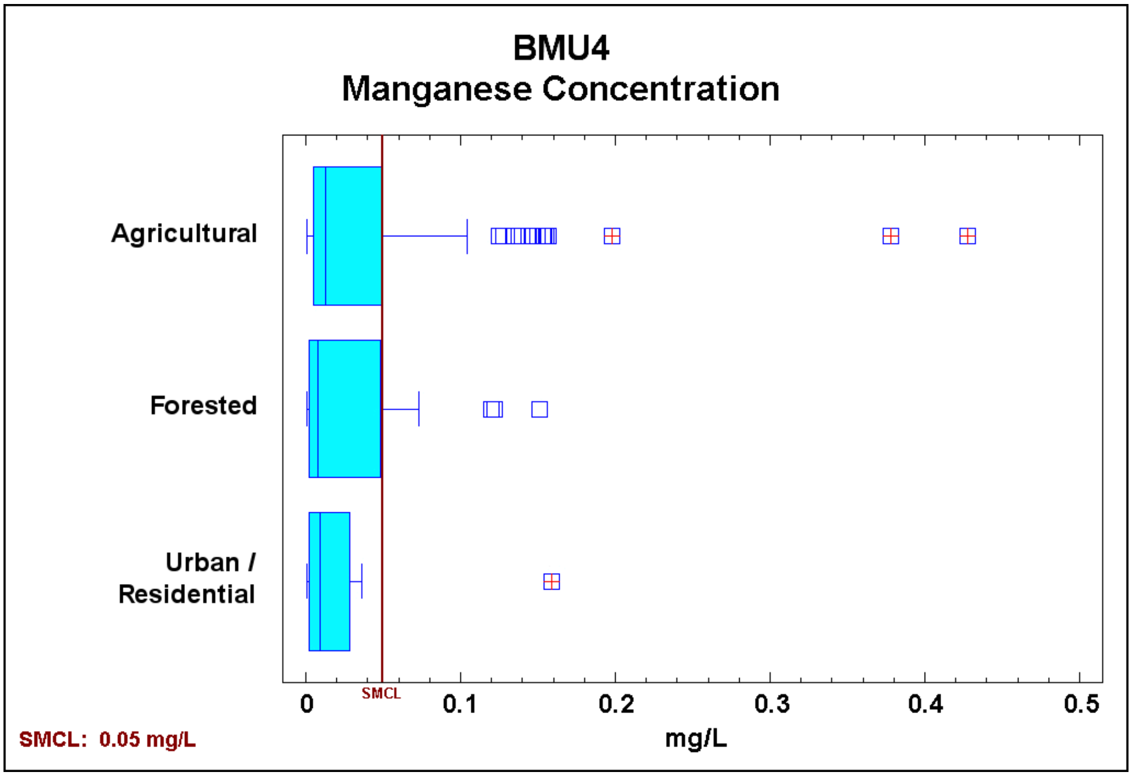

Figure 34. Boxplot for Manganese Measurements in BMU 4 by Land Use

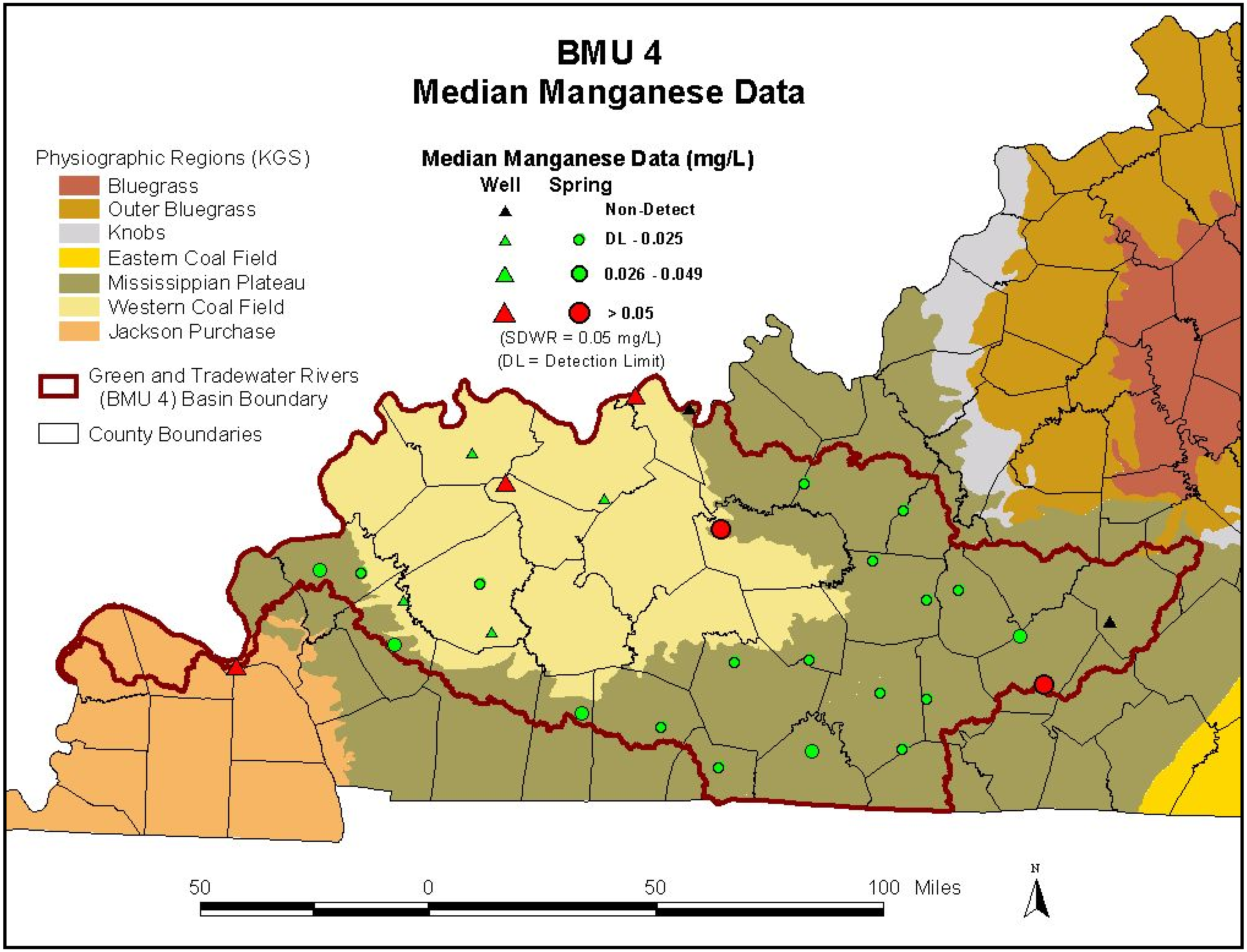

Figure 35. Map of Median Manganese Data for BMU 4

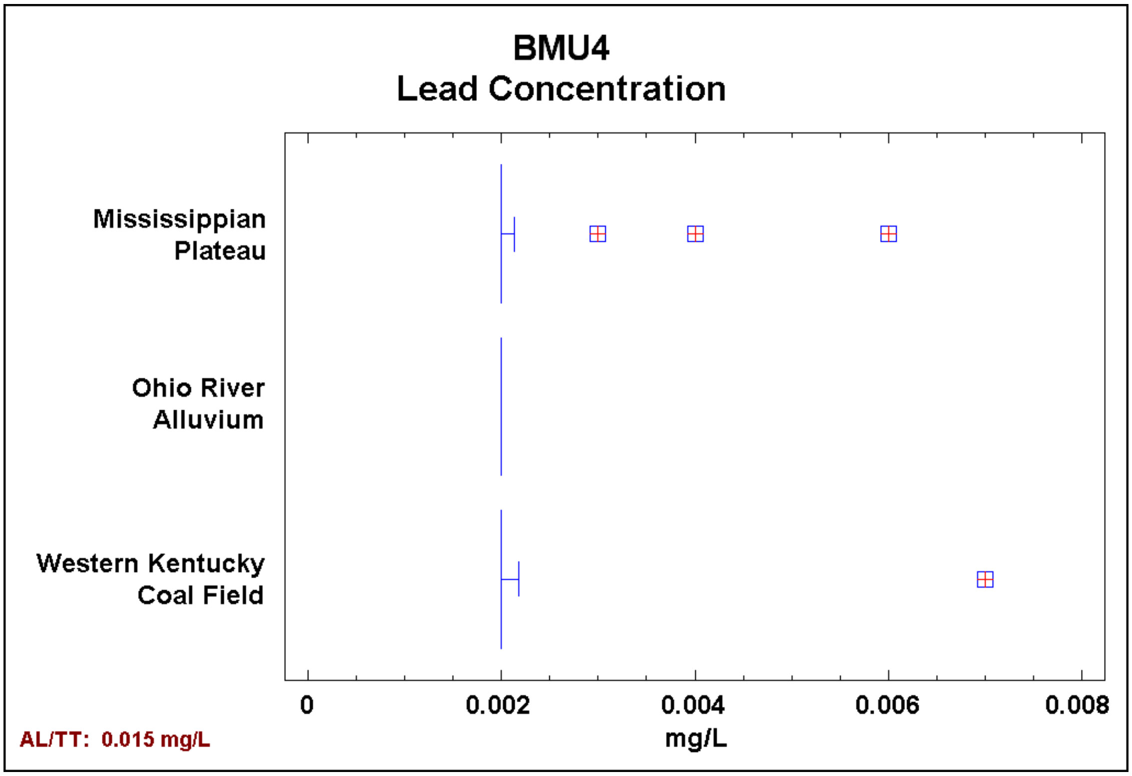

Figure 36. Boxplot for Lead Measurement Distributions in BMU 4

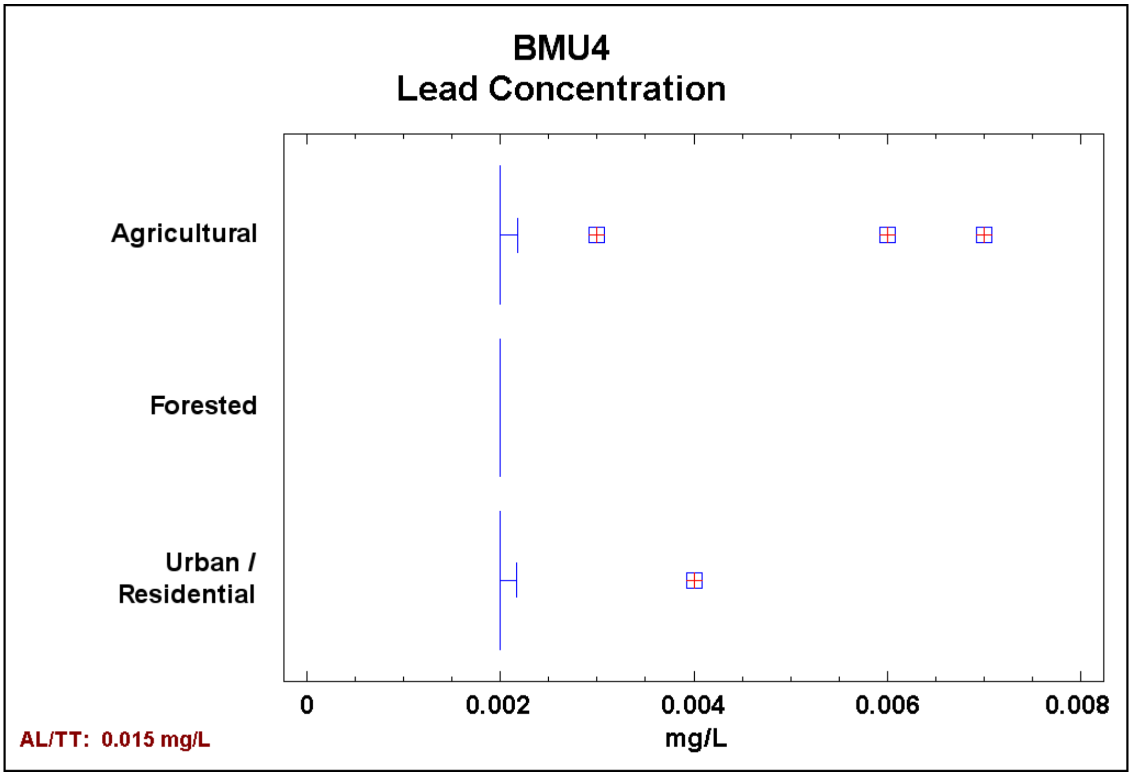

Figure 37. Boxplot for Lead Measurements in BMU 4 by Land Use

Lead was detected in 9 of 120 (7.5%) samples analyzed in this study. The median for BMU 4 was less than 0.002 mg/L and no sites exceeded one half the action level. Median values are low in all physiographic provinces and land uses (Figure 36 and 37). The boxplot of lead and land use (Figure 37) shows most values are low, but with variability in all areas. No map showing the distribution of lead detections in BMU 4 was prepared due to the very low levels and the sporadic occurrence of this element.

The occurrences of lead in groundwater in BMU 4 are 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

Five commonly used pesticides are included in this report: atrazine, metolachlor, cyanazine, simazine and alachlor. 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.

Atrazine was the most frequently detected pesticide, found in 32.5% of 120 samples analyzed. Metolachlor and simazine were the next most frequently detected pesticides where both were detected in about 10.8% of the samples. Cyanazine was not detected in 120 samples. Detection limits for the pesticides discussed in this report vary widely, depending on the laboratory method used, as shown in Table 7.

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, with almost two million pounds sold annually (KDA, 2002). Atrazine has an

Table 7. Pesticide Method Detection Limits

Pesticide	Method Detection Limit Used for Samples, mg/L
Atrazine	0.00004
Metolachlor	0.00004
Cyanazine	No detects at MDL of 0.00004
Simazine	0.00004
Alachlor	0.00004

MCL of 0.003 mg/L. Atrazine is a carcinogen 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).

Not surprisingly, atrazine was most often detected in agricultural areas characterized by row crop production, primarily in the Western Kentucky Coal Field and Mississippian Plateau (Figure 38). Karst springs in particular are vulnerable to pesticide contamination via surface water runoff to sinkholes, sinking streams and macroporic flow through soils. The variability of pesticide levels in karst areas, such as the Mississippian Plateau, reflects the variability of flow in quick recharge/quick discharge karst systems. The lack of the occurrence of atrazine in the Ohio River Alluvium is difficult to explain since row cropping is extensive. The thickness, organic content, and fineness of the soil particles may be the cause of this anomaly. The number of sites in the Ohio River Alluvium (3 sites) was low compared to the Western Kentucky Coal Field (7 sites), and the Mississippian Plateau (20 sites).

Figure 39 illustrates the occurrence of atrazine in BMU 4. The highest occurrence, and the only detection of any pesticide above MCL, was 0.004331 mg/L at Heady Big Spring in Larue County, which is in an area with extensive row cropping (Figures 37 and 38). Atrazine was also detected at 15 other sites besides Heady Big Spring in the Mississippian Plateau as well as at 2 sites in the Western Kentucky Coal Field. Atrazine detections were found in all land use areas.

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, approximately

800,000 pounds of metolachlor (combined metolachlor and s-metolachlor) were sold in Kentucky (KDA, 2000). Metolachlor is a possible human carcinogen and has an HAL of 0.1 mg/L.

Metolachlor occurred at very low levels in approximately 10.8 % of the samples analyzed (Figures 41 and 42). The Mississippian Plateau area showed more variation in detection levels. Eight of the thirteen detections occurred in 2 springs. Glasgow Town Spring had the highest levels and all samples contained metolachlor even though the concentrations were well below the HAL. The spring with 100% detections and the second highest concentrations was Belcher Karst Window. Glasgow Town Spring and Belcher Karst Window both contain a significant portion of urban and residential land use in their basins. Although the number of detections of this herbicide does indicate nonpoint source pollution, the low levels showed minimal impacts to groundwater quality.

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 occurred in approximately 32.5% of the samples, but never above the MCL. The highest occurrence was in the Mississippian Plateau (Big Heady Spring, Larue County) at a concentration slightly below the MCL. Simazine was detected primarily in the Mississippian Plateau with a single detection in the Western Kentucky Coal Field (Figures 44 and 45).

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 also been linked with non-cancerous effects in the liver, spleen and kidneys.

Alachlor occurred at 3 sites in this study, but never above the MCL (Figures 47 and 48). As shown in Figure 48, alachlor was found once in each of the 3 land use categories in the Mississippian Plateau. The maximum detected value was at Pumpkin Center Spring in Caldwell County at less than 4% of the MCL. Based upon its limited occurrence, alachlor has apparently had minor impacts on groundwater in this area.

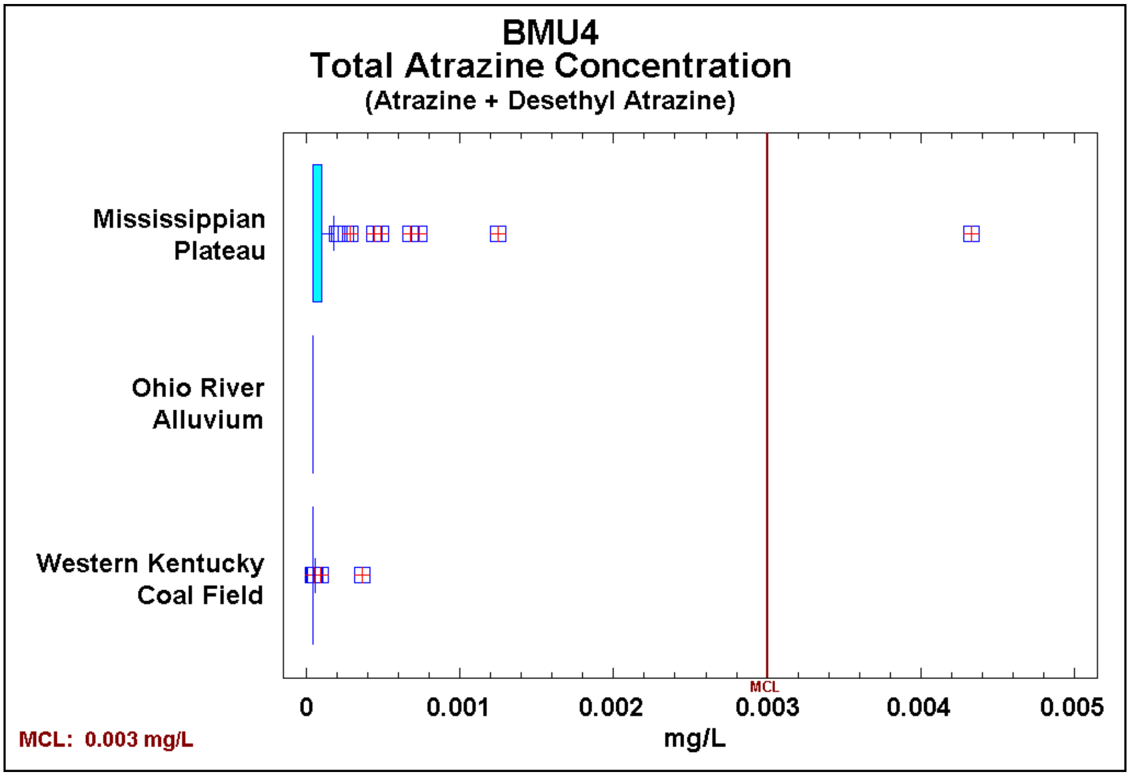

Figure 38. Boxplot for Atrazine Measurement Distributions in BMU 4

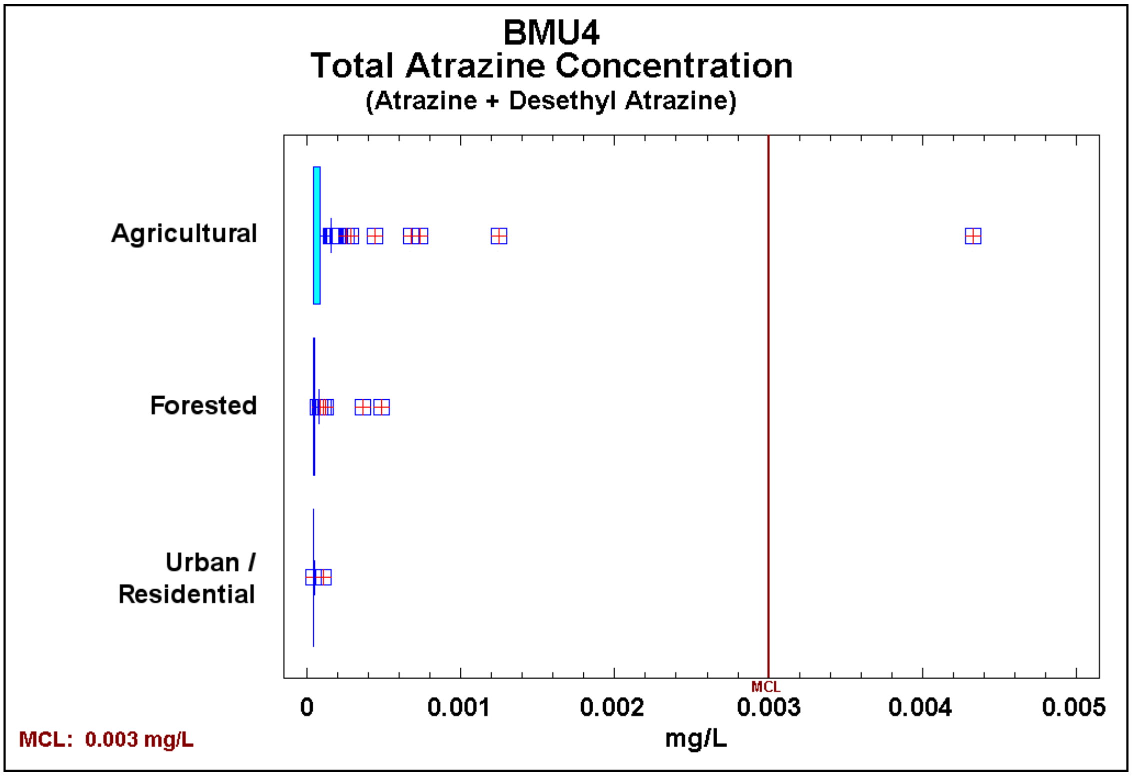

Figure 39. Boxplot for Atrazine Measurements in BMU 4 by Land Use

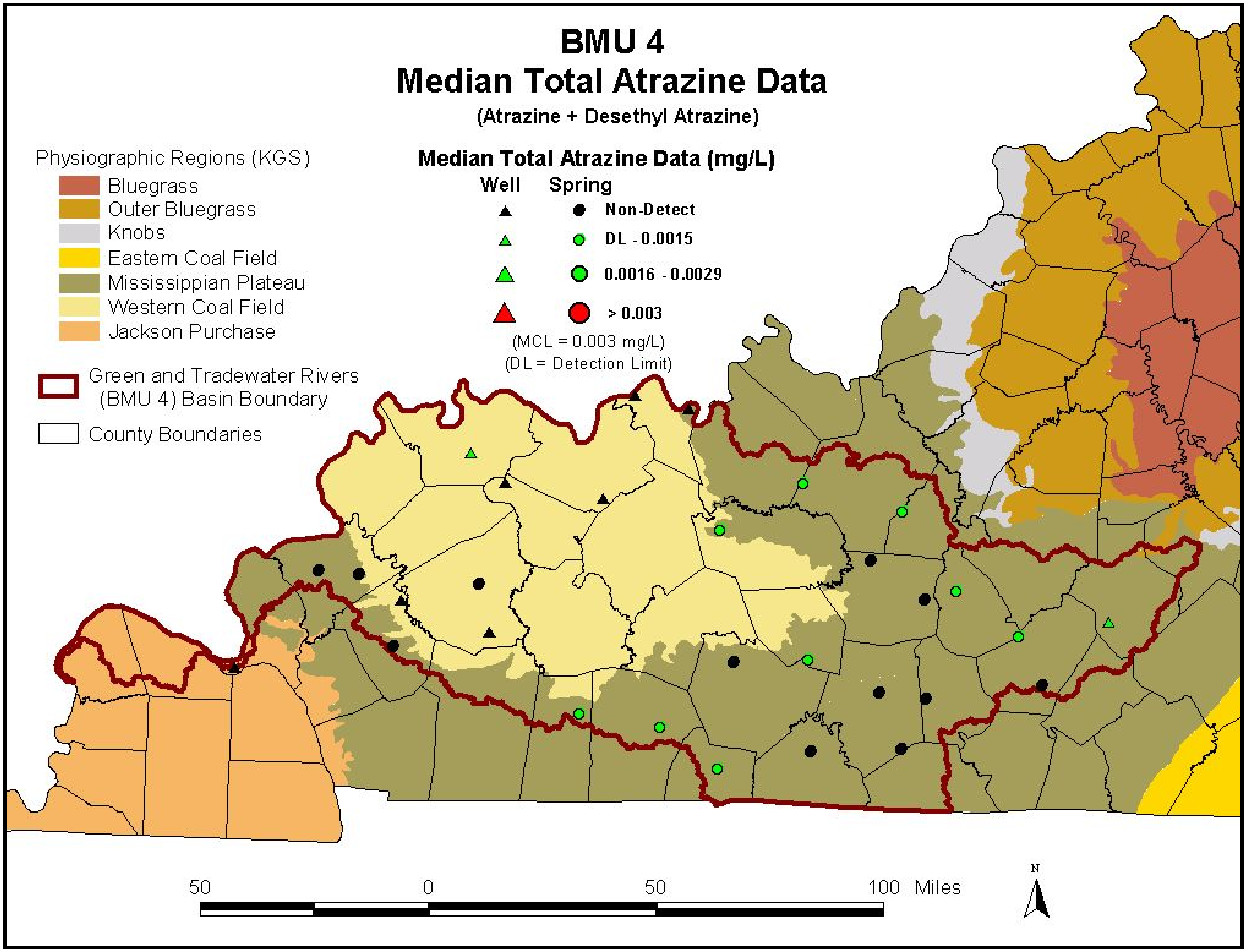

Figure 40. Map of Median Atrazine Data for BMU 4

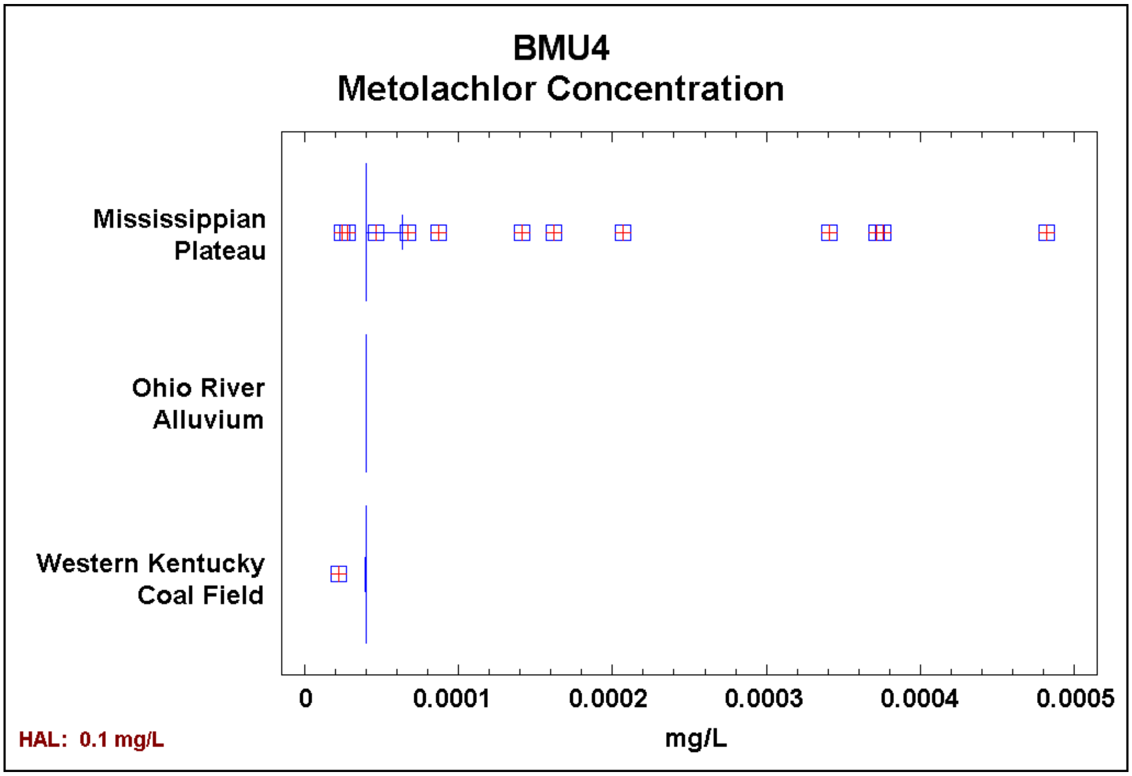

Figure 41. Boxplot for Metolachlor Measurement Distributions in BMU 4

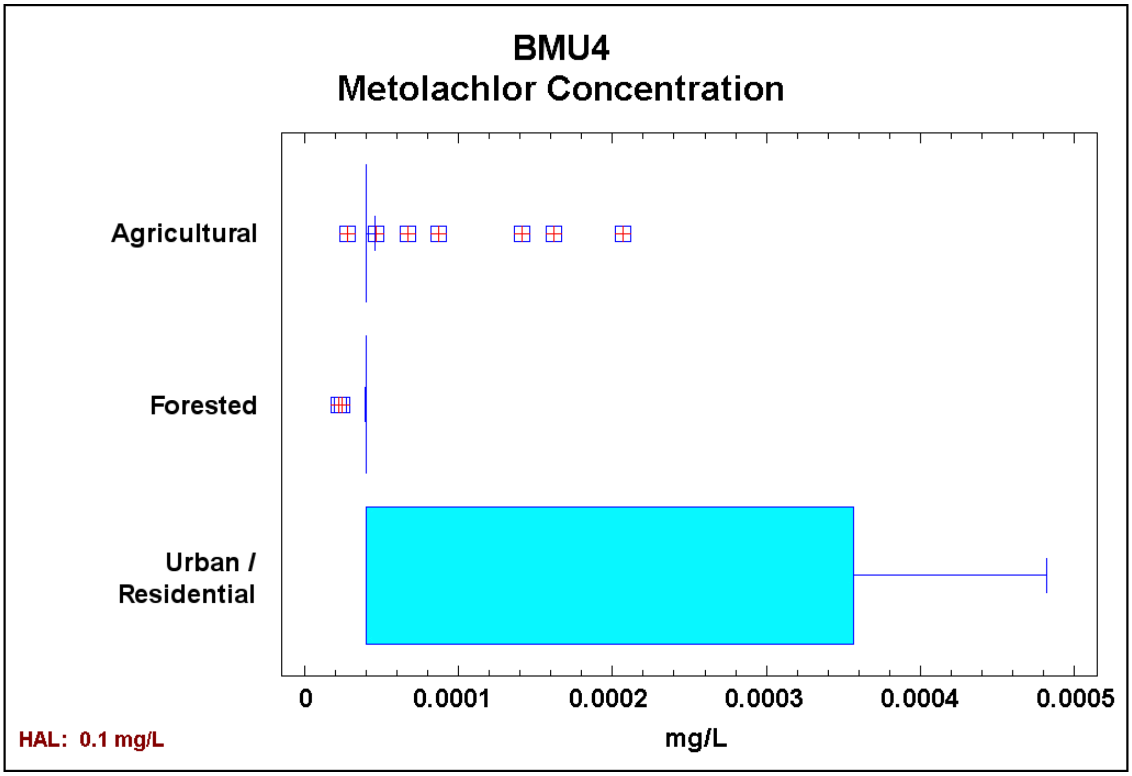

Figure 42. Boxplot for Metolachlor Measurements in BMU 4 by Land Use

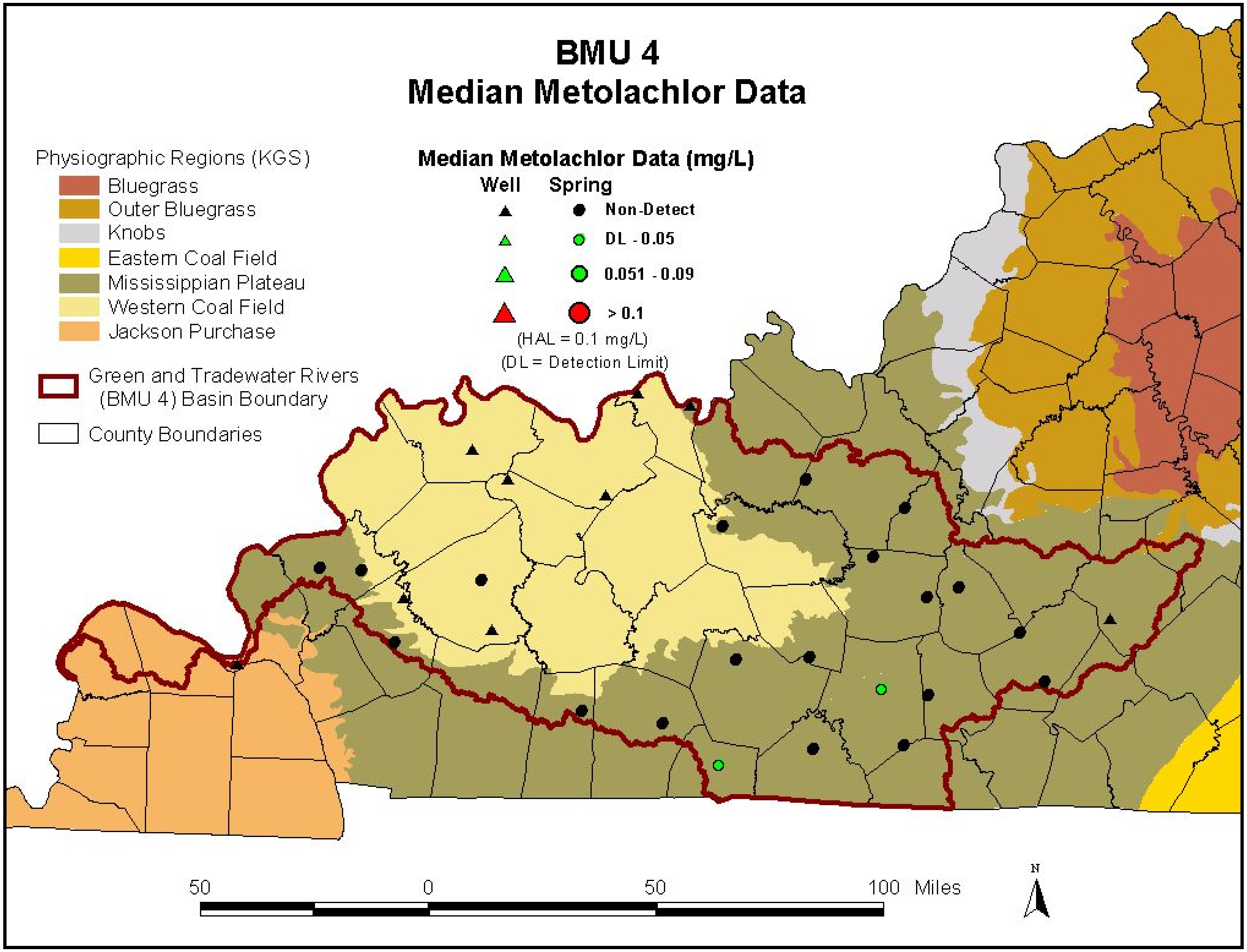

Figure 43. Map of Median Metolachlor Data for BMU 4

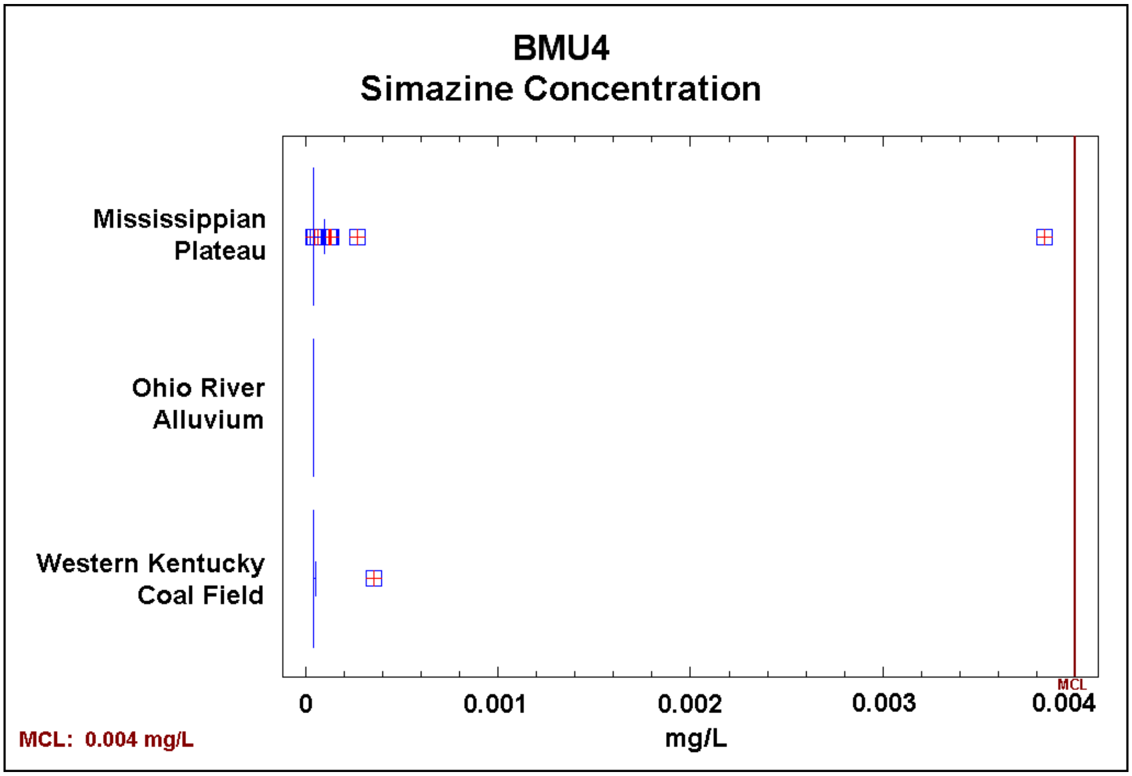

Figure 44. Boxplot for Simazine Measurement Distributions in BMU 4

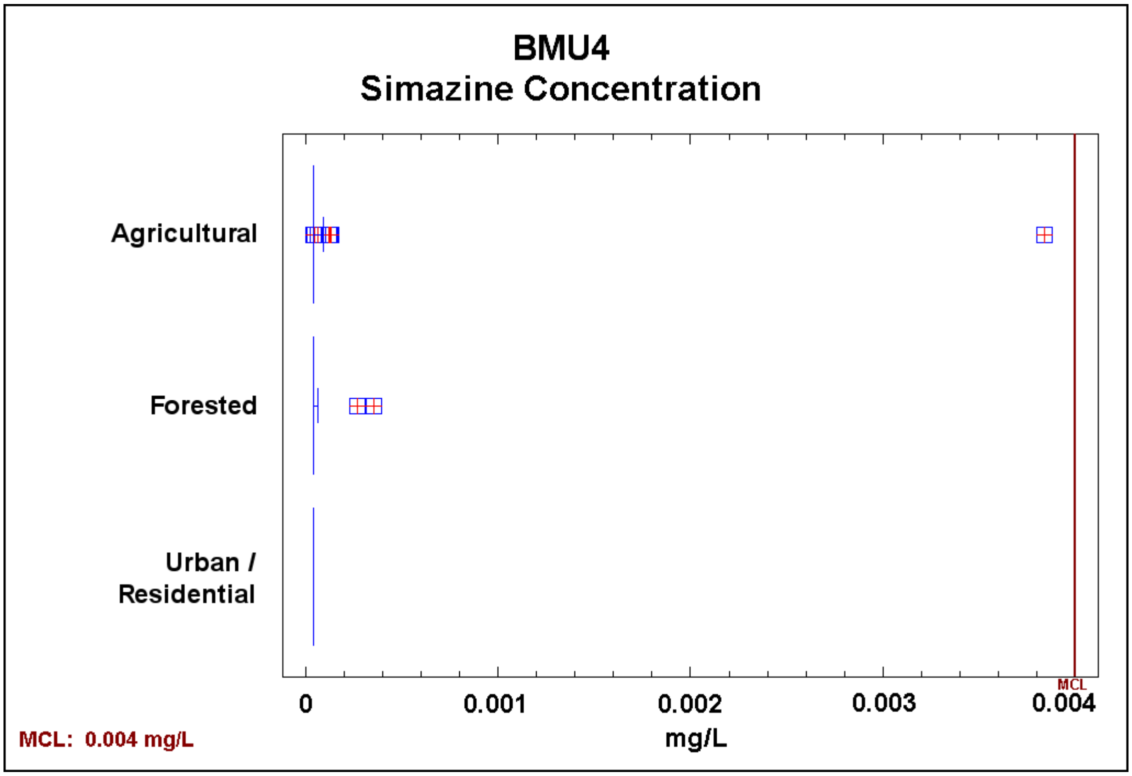

Figure 45. Boxplot for Simazine Measurement in BMU 4 by Land Use

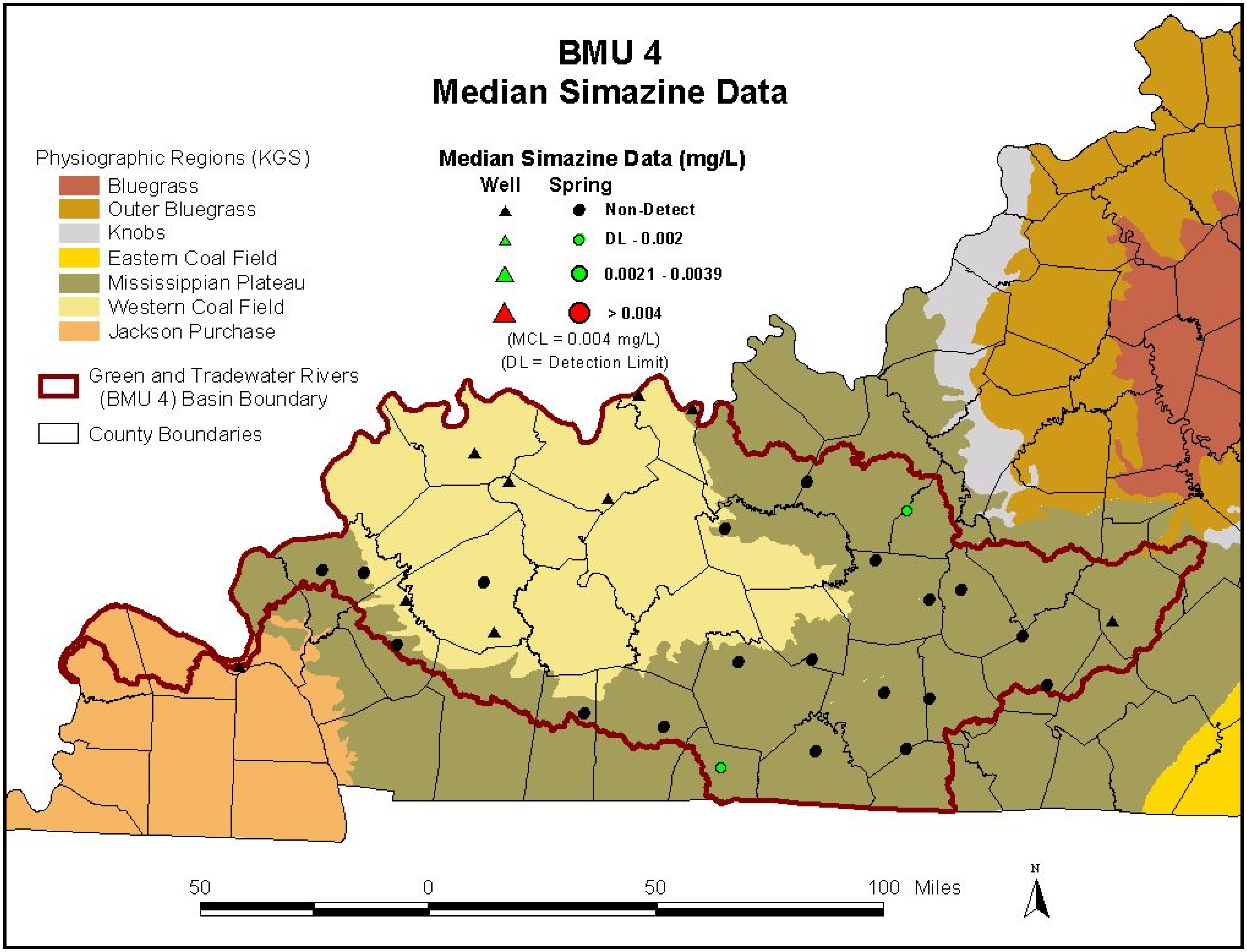

Figure 46. Map of Median Simazine Data for BMU 4

Cyanazine production ceased in December 1999 and the sale and use of this herbicide was prohibited effective September 2002. Cyanazine was not detected in the 120 samples analyzed for this study.

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

Total Dissolved Solids 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. Median values of TDS were found below the SMCL of 500 mg/L, but one outlier in the Mississippian Plateau exceeded the SMCL (Figures 50 and 51). TDS was surprisingly low in the Mississippian Plateau, especially considering that this is soluble carbonate terrane. One possible explanation is that the quick flow characteristics of this region reduce the contact time between water and rock, thereby retarding dissolution. In general, TDS is not usually an important primary indicator of nonpoint source pollution of groundwater, although this parameter can serve as a surrogate indicative of general water quality. Because no probable sources for elevated TDS were noted adjacent to sampling sites, no nonpoint source impacts could be confirmed. Figure 50 shows higher values in general in the Ohio River Alluvium. These higher values are probably natural, resulting from longer residence times, which allow for more dissolution in these areas.

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 (U.S.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,

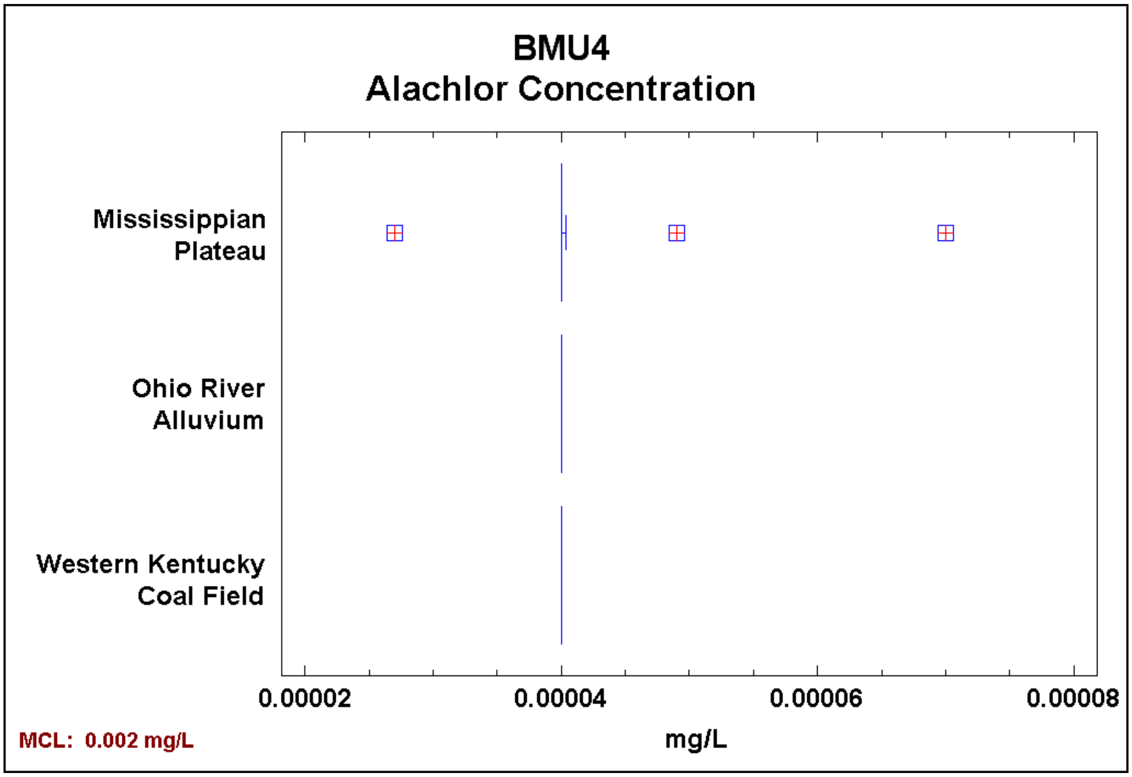

Figure 47. Boxplot for Alachlor Measurement Distributions in BMU 4

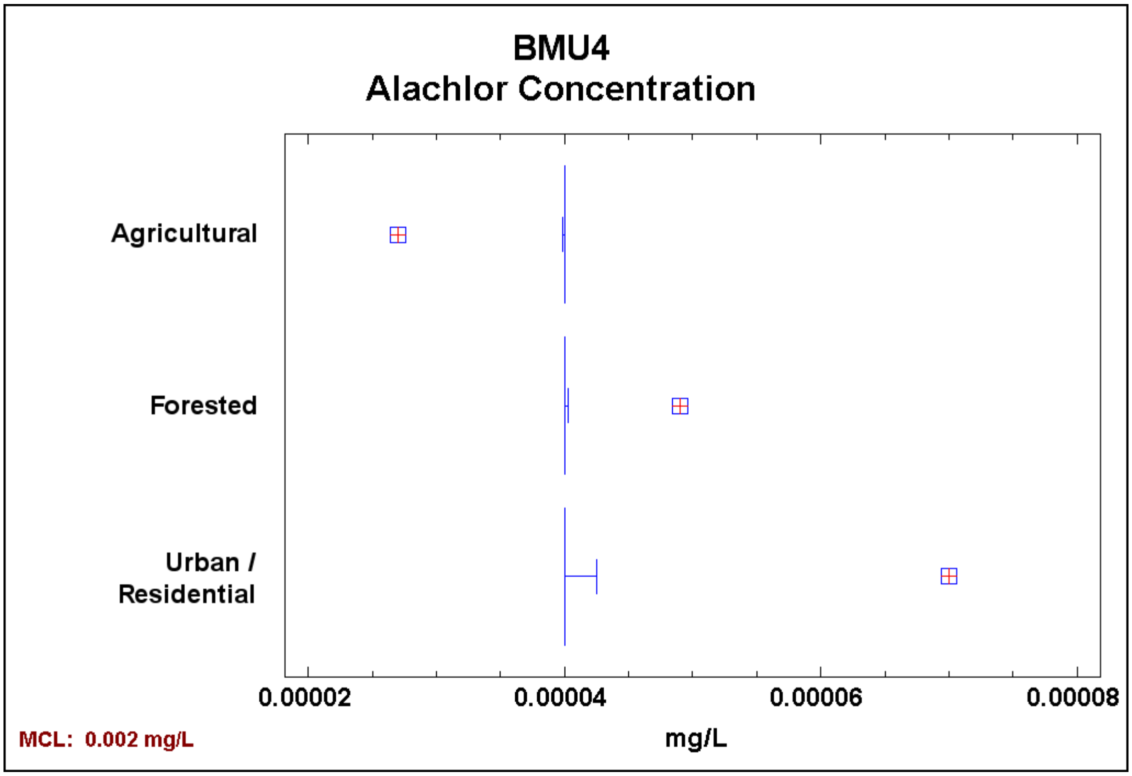

Figure 48. Boxplot for Alachlor Measurement in BMU 4 by Land Use

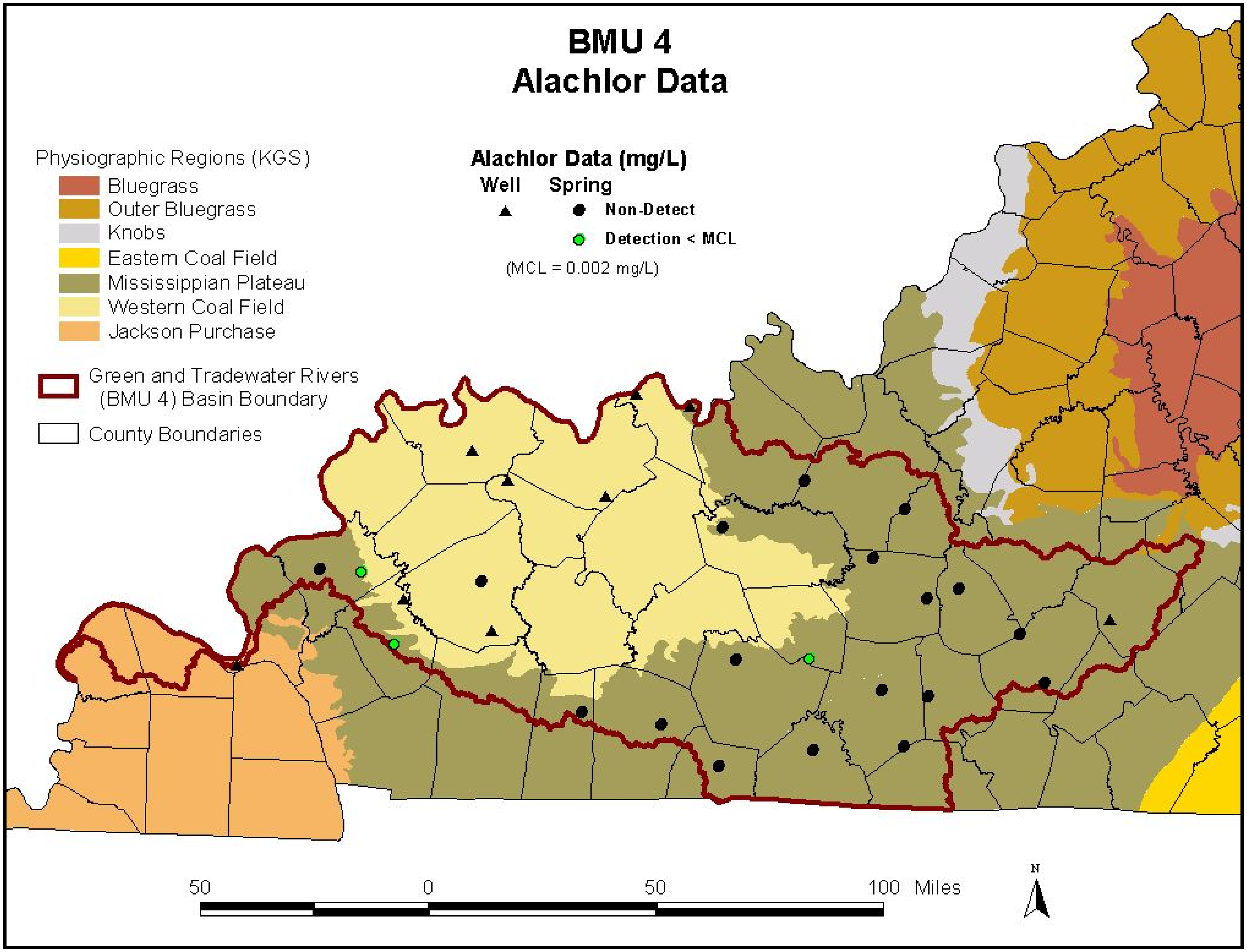

Figure 49. Map of Alachlor Data for BMU 4

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.

Approximately 72% of the samples analyzed detected TSS, with about 10% of the detections above 35 mg/L. Most values occurred within a narrow range, but outliers were common (Figures 53 and 54). In general, TSS is not usually considered a good indicator for nonpoint source pollution in groundwater. However, in some karst systems, turbidity and TSS vary with change in flow. Poor management practices associated with activities such as construction and agricultural tillage can strip vegetation and allow the quick influx of sediment into groundwater via overland flow. Therefore, outliers in the karst of the Mississippian Plateau may represent nonpoint source impacts. Typically, given the nature of the activities that introduce sediments into karst groundwater, these impacts are transient. The Western Kentucky Coal Field outliers may indicate some effects from land disturbance due to both surface and underground mining. In the Ohio River Alluvium however, elevated TSS values are more difficult to interpret. Outliers here may represent sloughing of unstable beds within the well bore or possibly failure of the well's annular seal. Figure 54 illustrates that high levels of TSS generally occur in karst areas where aquifers can be under the direct influence of surface water runoff.

Nutrients

Nutrients included in this report are nitrate-N, nitrite-N, ammonia-N, orthophosphate-P and total phosphorous. 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 over abundance 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.

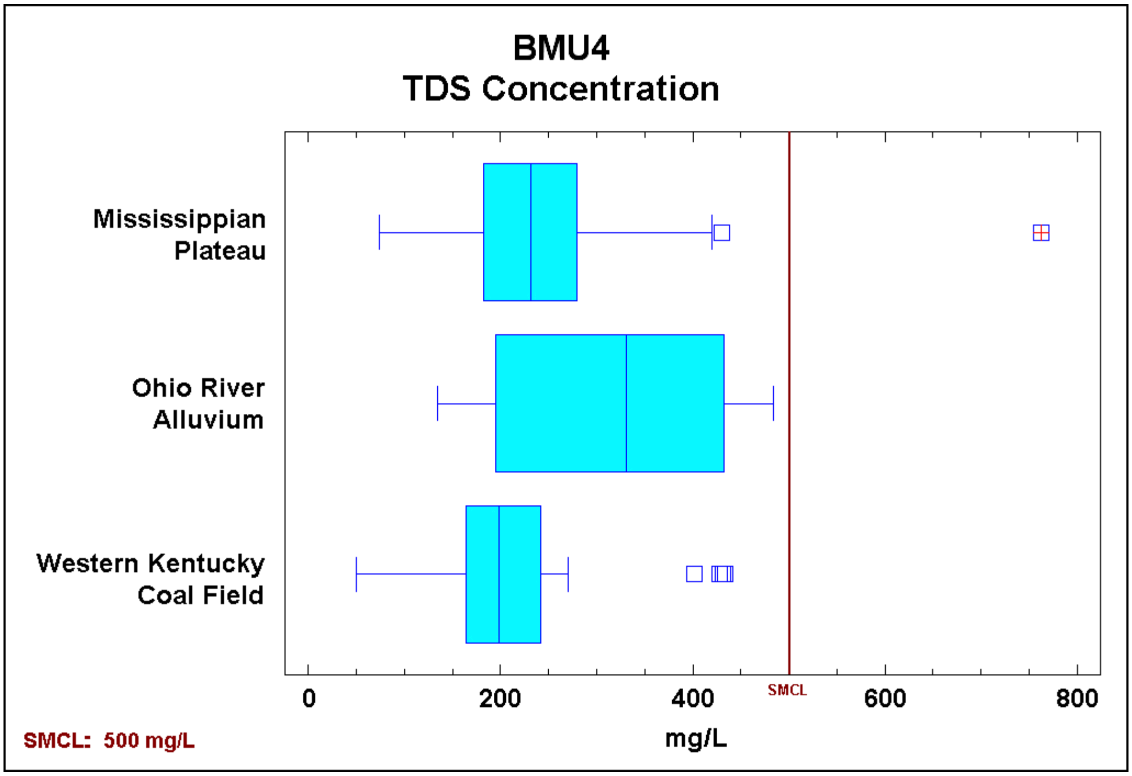

Figure 50. Boxplot for TDS Measurement Distributions in BMU 4

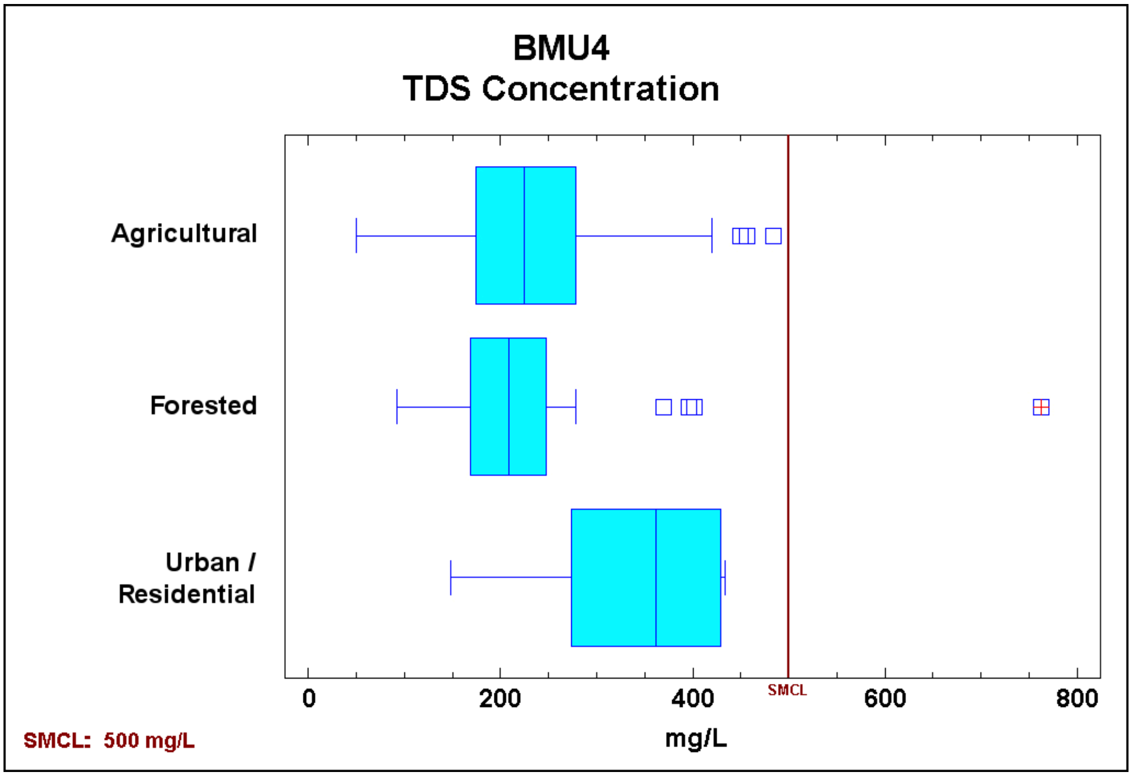

Figure 51. Boxplot for TDS Measurements in BMU 4 by Land Use

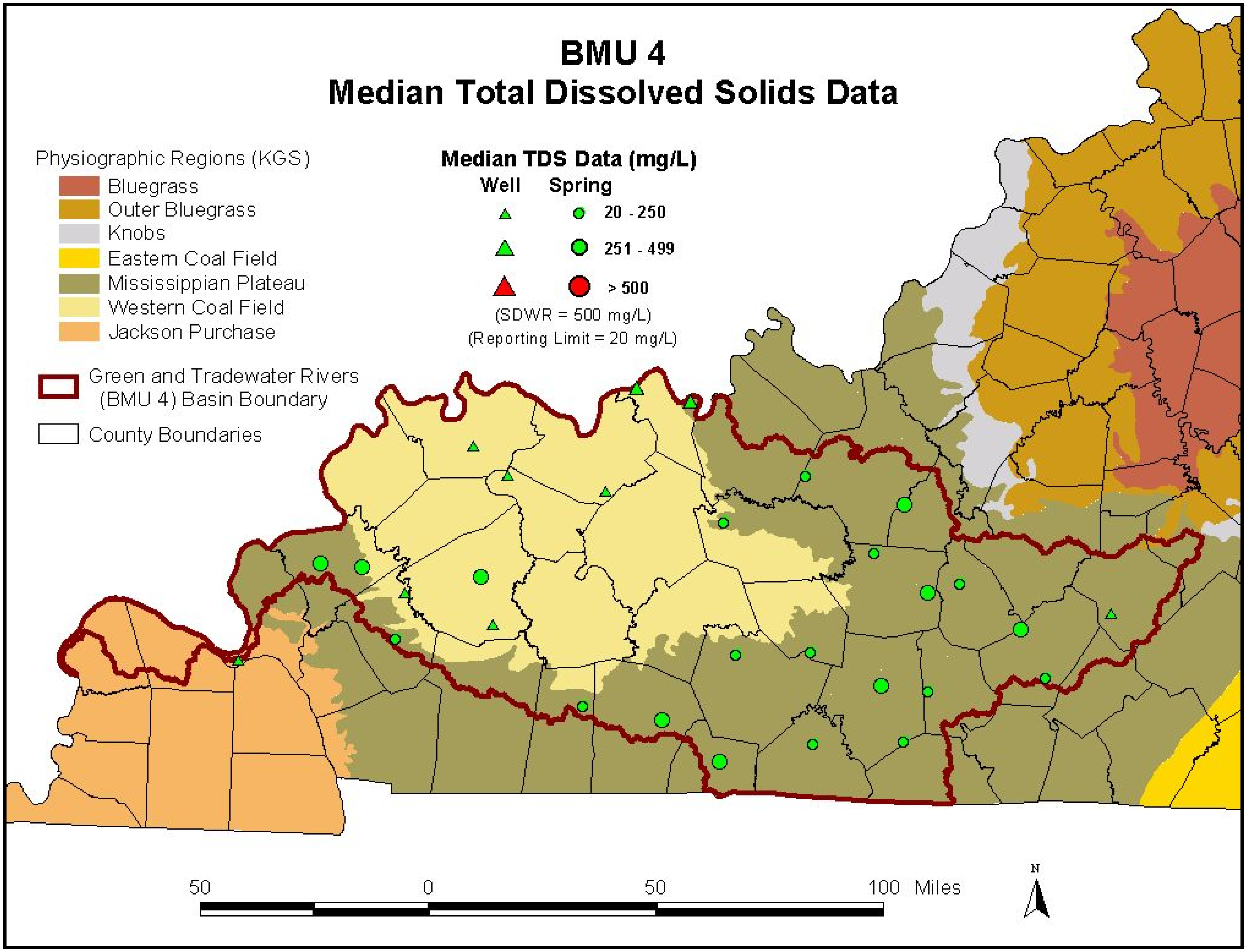

Figure 52. Map of Median Total Dissolved Solids Data for BMU 4

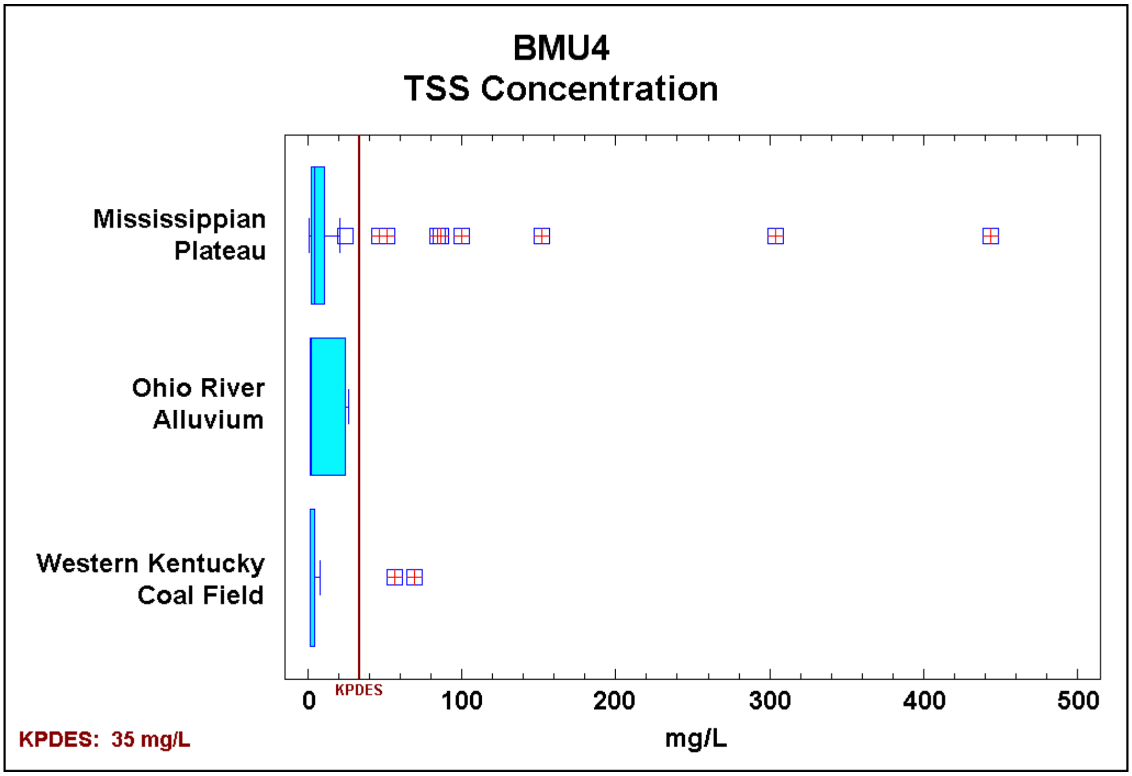

Figure 53. Boxplot for TSS Measurement Distributions in BMU 4

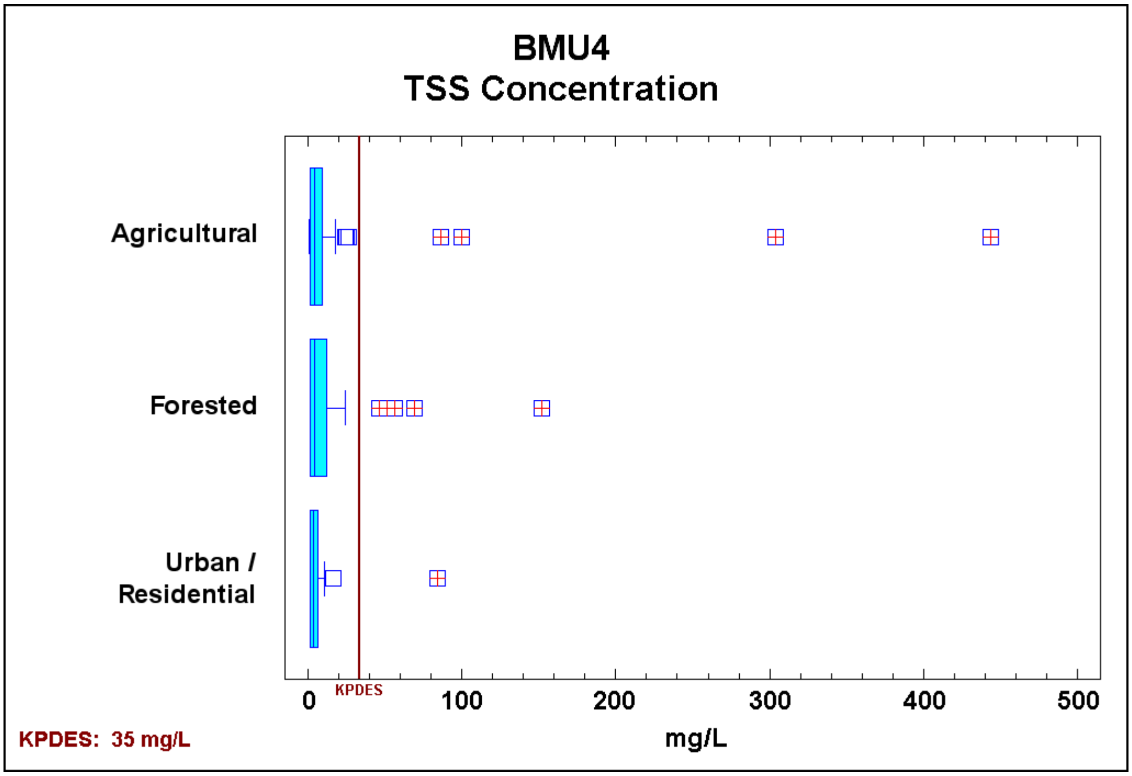

Figure 54. Boxplot for TSS Measurements in BMU 4 by Land Use

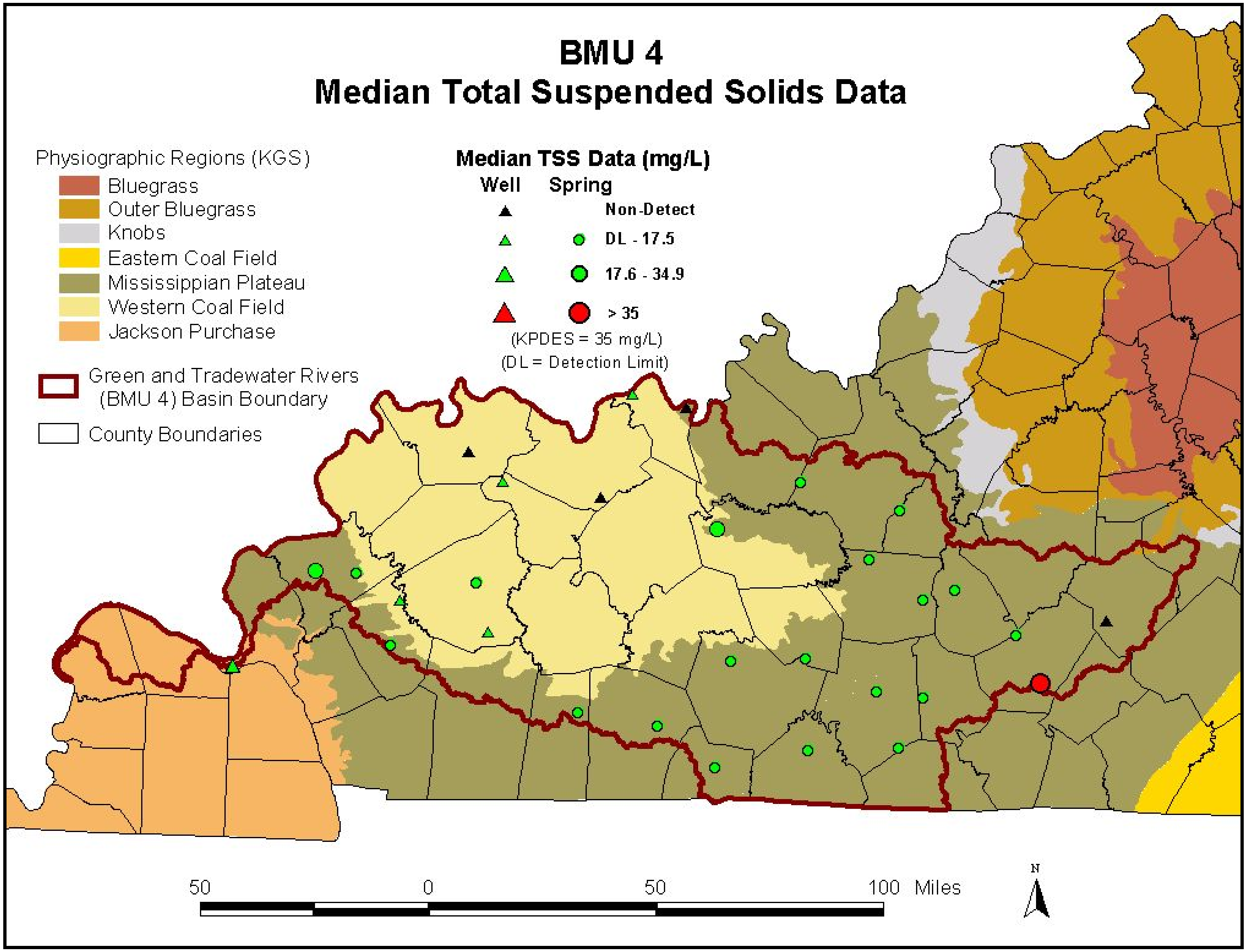

Figure 55. Map of Total Suspended Solids Data for BMU 4

Nitrate (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 is reported either as the complex ion NO_3, or as the equivalent molecular nitrogen. Since 1 mg/L of nitrogen equals 4.5 mg/L nitrate, the drinking water MCL of 10 mg/L nitrate-N equals 45 mg/L nitrate. In this report, results are reported as "nitrate-N."

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

As shown in Figure 56, median values of nitrate-N varied from non-detects in the Western Kentucky Coal Field and Ohio River Alluvium to a high of 8.89 mg/L in the Mississippian Plateau. Median values for the Western Kentucky Coal Field, Ohio River Alluvium and the Mississippian Plateau were 0.8235 mg/L, 0.4095 mg/L and 2.735 mg/L respectively. No MCL exceedances occurred in this study. Nitrate-N values found in this study were compared to the values found in other studies, as well as those from reference springs (Table 2). 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 support significantly lower levels for ambient conditions. For example, 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 groundwater. MCL exceedances occurred most frequently in shallow dug wells and declined with depth. Nearly 10% of dug wells exceeded the MCL; whereas only about 1% of wells greater than 151 feet were in exceedance and median values were only 0.6 mg/L. In conclusion, the median values for nitrate-N found in this study for the Mississippian Plateau is well above background levels and may indicate long-term nonpoint source impacts on groundwater.

Forested areas showed the lowest median and maximum values of nitrate-N for any of the three main land uses. The higher values in the Mississippian Plateau area may be the result of nearby failing septic systems, which could allow untreated waste to infiltrate into the groundwater, the lack of filtration and/or agricultural activities. High nitrate-N values in agricultural areas are expected and are the result of the application of nitrogen fertilizers combined with livestock grazing and feeding operations.

Figure 57 shows the geographical distribution of nitrate-N values in BMU 4. High values in springs in the Mississippian Plateau, were observed. The highest value found in this study (8.89 mg/L) occurred at Mossy Spring in Logan County and is probably the result of intense livestock grazing and septic systems (caffeine was also detected) in the area immediately up-gradient of the spring. Nitrate values from 3 of the 4 samples taken from Mossy Spring were in the top 6 highest values detected during this study.

Nitrite (NO_2) also occurs naturally from most of the same sources as nitrate. 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 only to occur at very low levels, all less than one half the MCL, in all the samples including the Mississippian Plateau samples, as shown in Figures 59, 60 and 61. The lowest median values found in this study were in the Ohio River Alluvium and the Western Kentucky Coal Field which had median nitrite-N values less than 0.02 mg/L. The highest median value of 0.447 mg/L occurred in the Mississippian Plateau.

In the environment, nitrite-N generally converts rapidly to nitrate through oxidation, which this study reflects. Nitrite is not a significant nonpoint source pollutant, although it may contribute to high levels of nitrate. In this study, the occurrence of nitrite-N appears to be dependent on land use, as shown in Figures 59 and 60. In addition, Figure 61 further supports the conclusion that no significant problem with nonpoint source pollution from nitrite-N was found in this study. However, when viewed together nitrate-N and nitrite-N do have broad nonpoint source impacts.

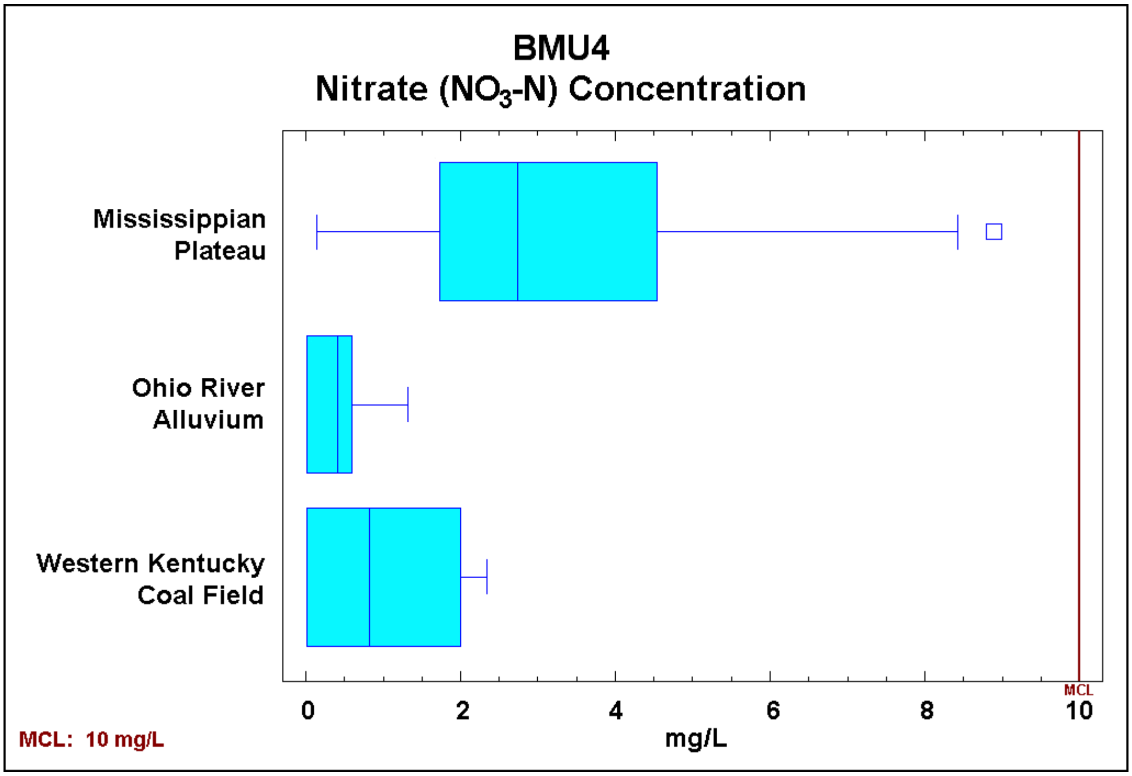

Figure 56. Boxplot for Nitrate-Nitrogen Measurement Distributions in BMU 4

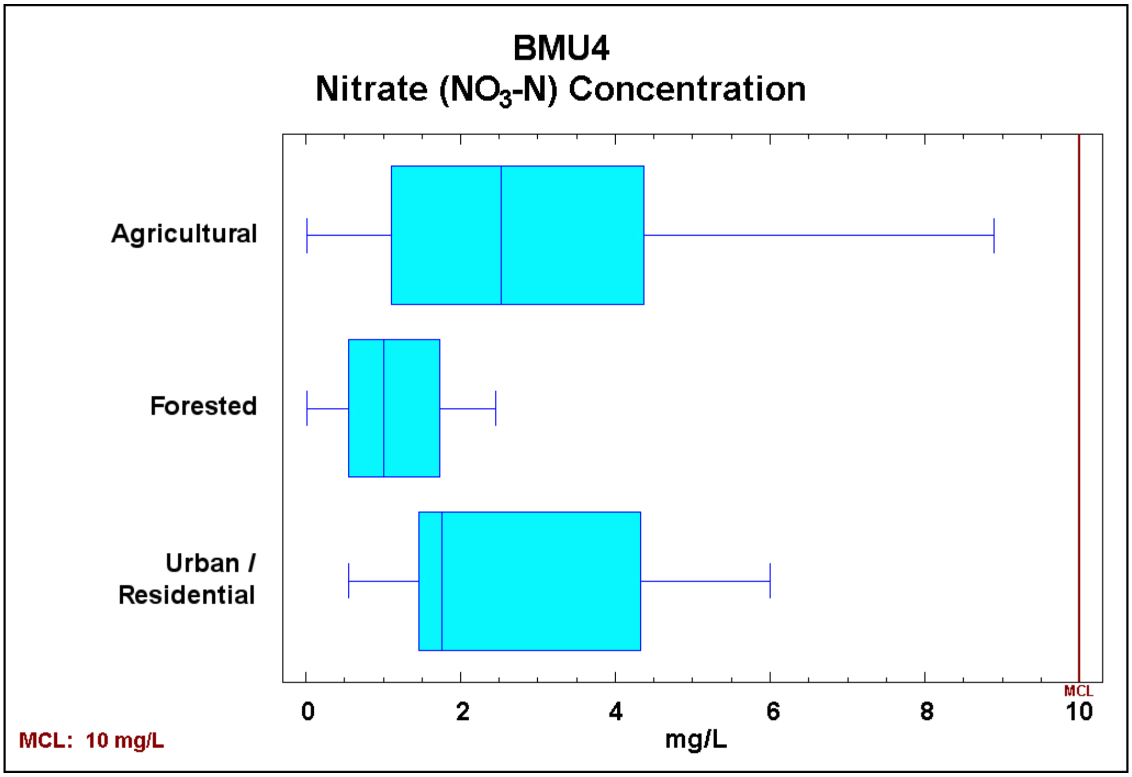

Figure 57. Boxplot for Nitrate-Nitrogen Measurements in BMU 4 by Land Use

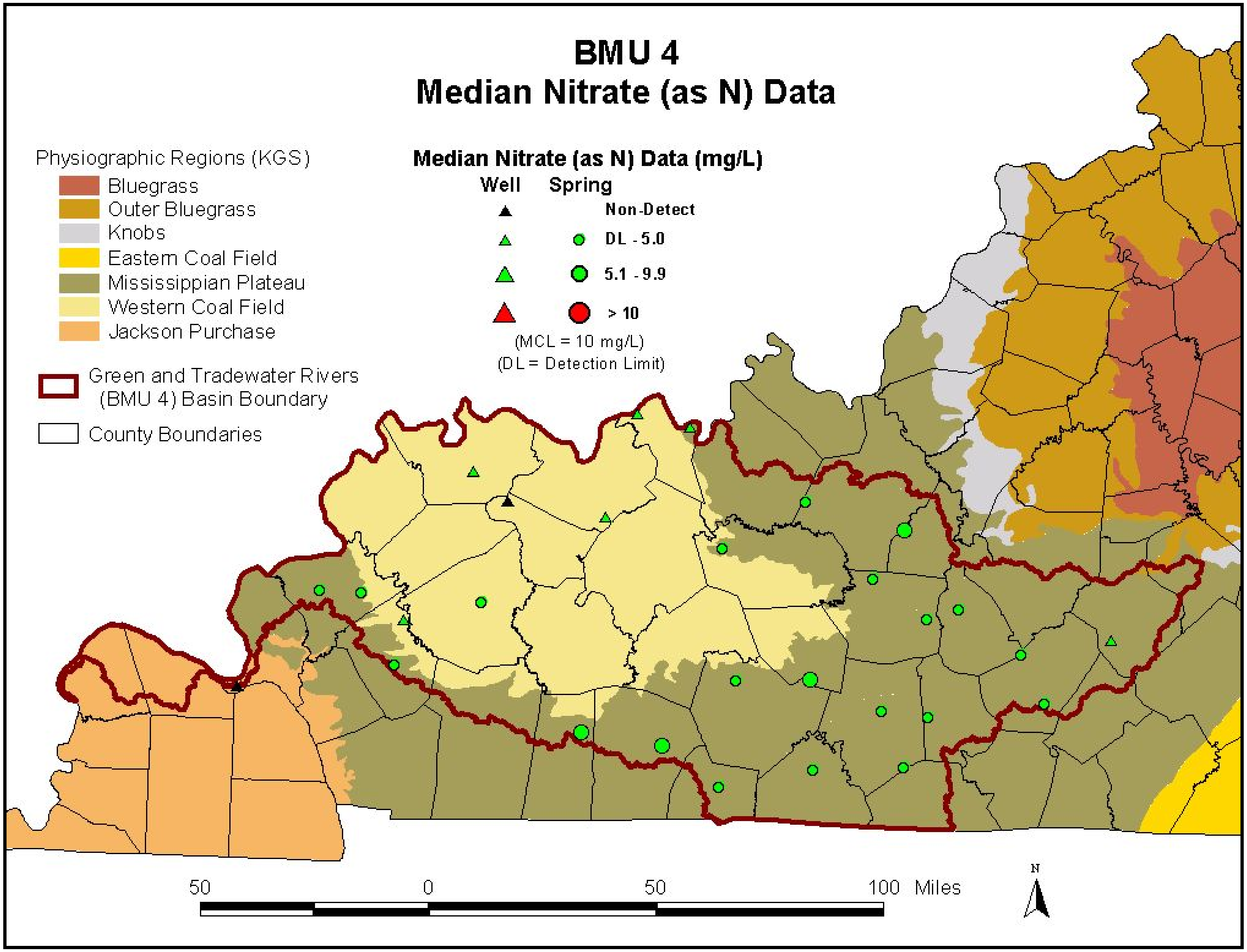

Figure 58. Map of Median Nitrate-N Data for BMU 4

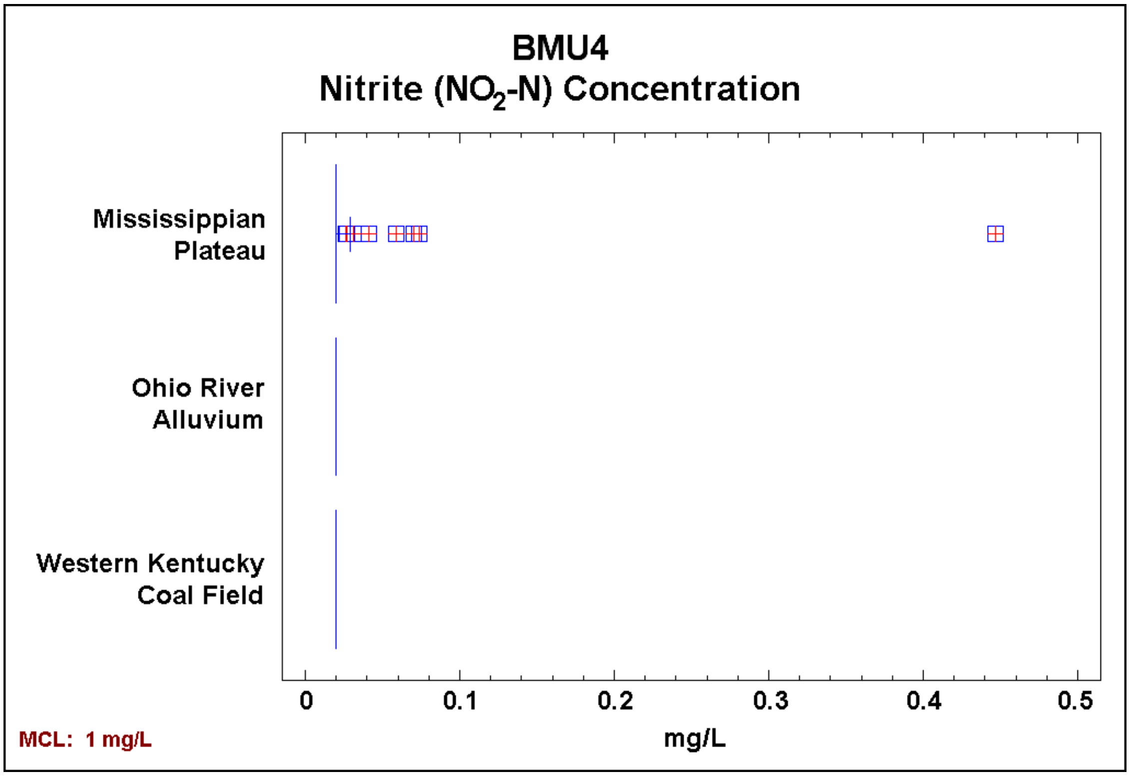

Figure 59. Boxplot for Nitrite-Nitrogen Measurement Distributions in BMU 4

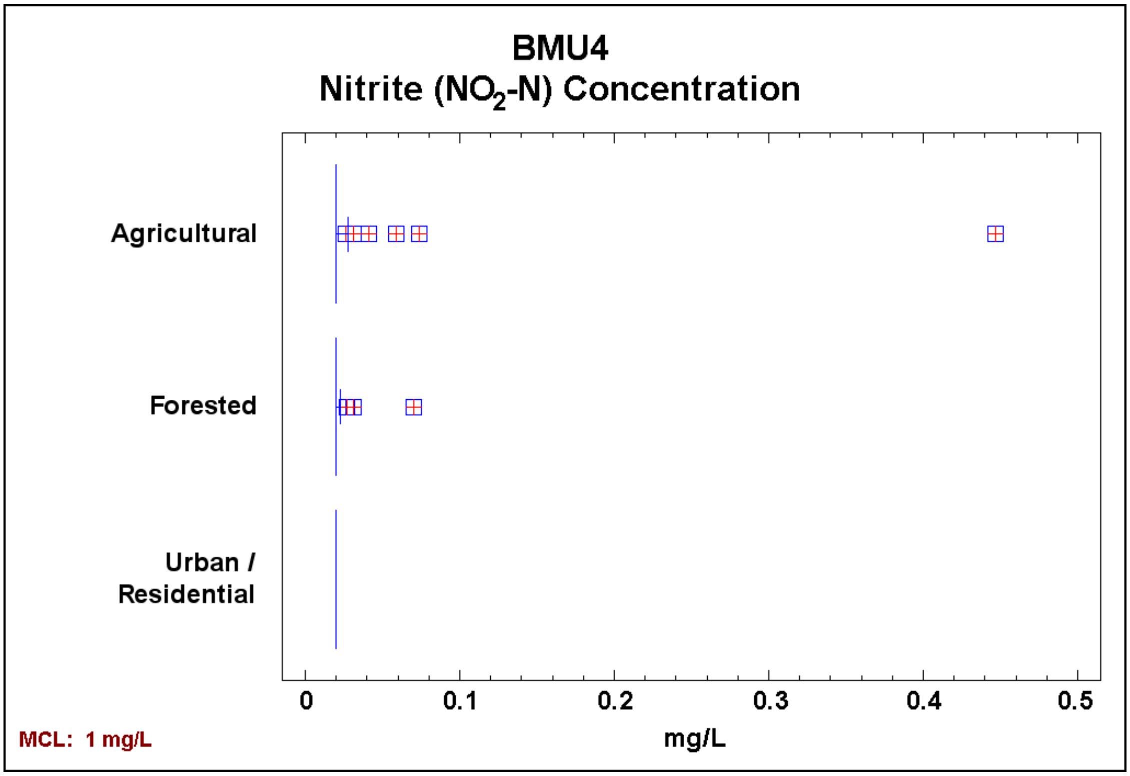

Figure 60. Boxplot for Nitrite-Nitrogen Measurements in BMU 4 by Land Use

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

Historic groundwater data around the state shows that ammonia-N values are typically very low, often below the method detection limit of 0.02 mg/L. Low values, but above this level, may indicate natural variations. However, increasing values, as shown in the outliers in Figures 62 and 63 seem to indicate impacts from nonpoint source pollution. In this study, ammonia-N occurred in almost 11.7% of the samples, with the narrowest range of values in the Mississippian Plateau and Western Coal Field (Figure 64). High levels of ammonia-N were found in Adair County at Cedar Bluff Spring, which is in a cow pasture and may explain elevated ammonia-N.

Two forms of phosphorus are discussed in this report: orthophosphate-P and total phosphorus. Orthophosphate-P (PO_4 -P), or simply "orthophosphate," 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 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 and nodules. Neither orthophosphate nor total phosphorus has a drinking water standard.   Orthophosphate data are compared to the Texas surface water quality std. of 0.04 mg/L and total phosphorus data to the surface water limit of 0.1 mg/L recommended by the USGS, Taylor 2002.

In natural systems relatively un-impacted from anthropogenic sources, orthophosphate occurs at very low levels. For example, in some areas of Kentucky with little anthropogenic sources, springs typically were either non-detect for ortho-P, or had values in the range of 0.002 – 0.004 mg/L. Although

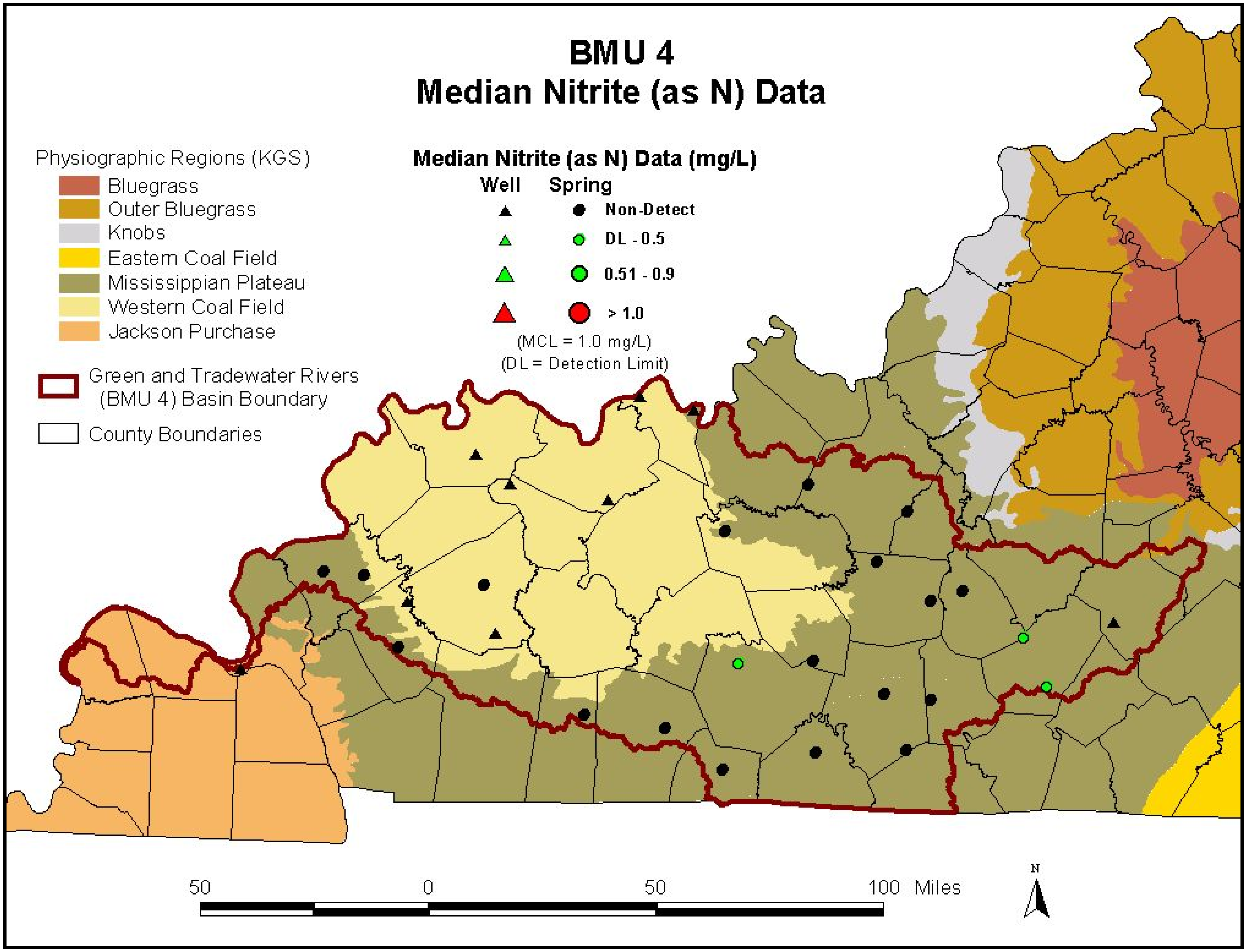

Figure 61. Map of Median Nitrite-N Data for BMU 4

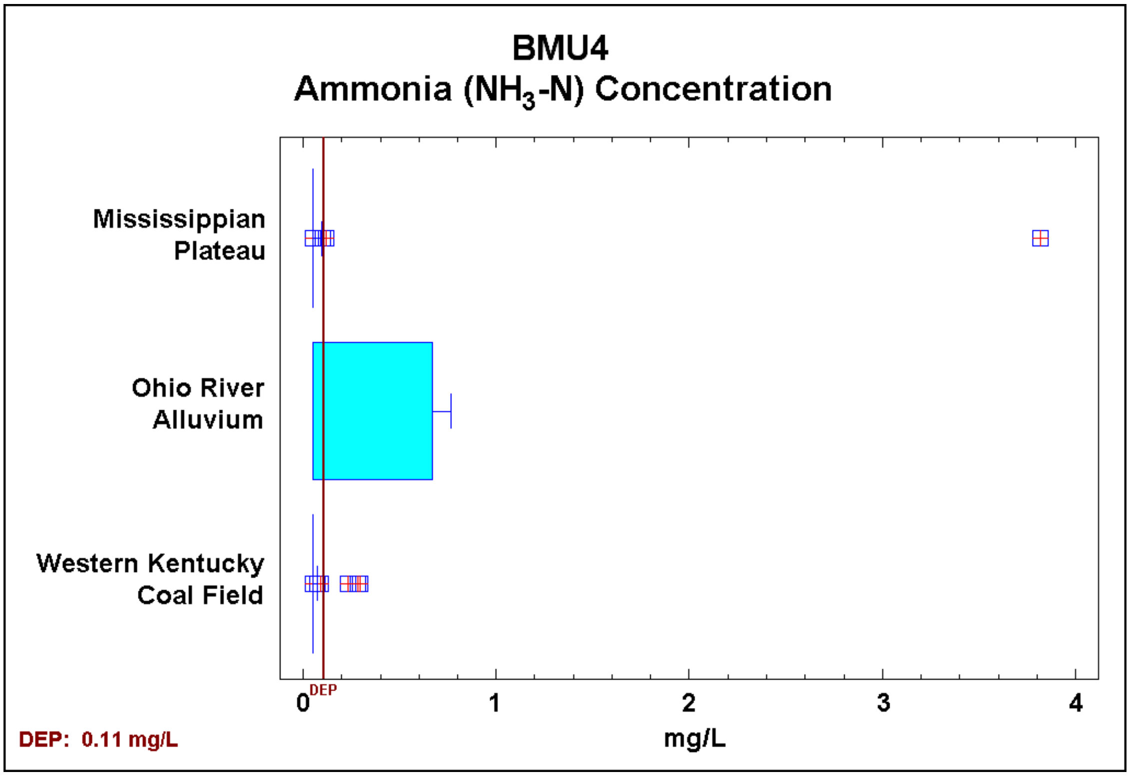

Figure 62. Boxplot for Ammonia Measurement Distributions in BMU 4

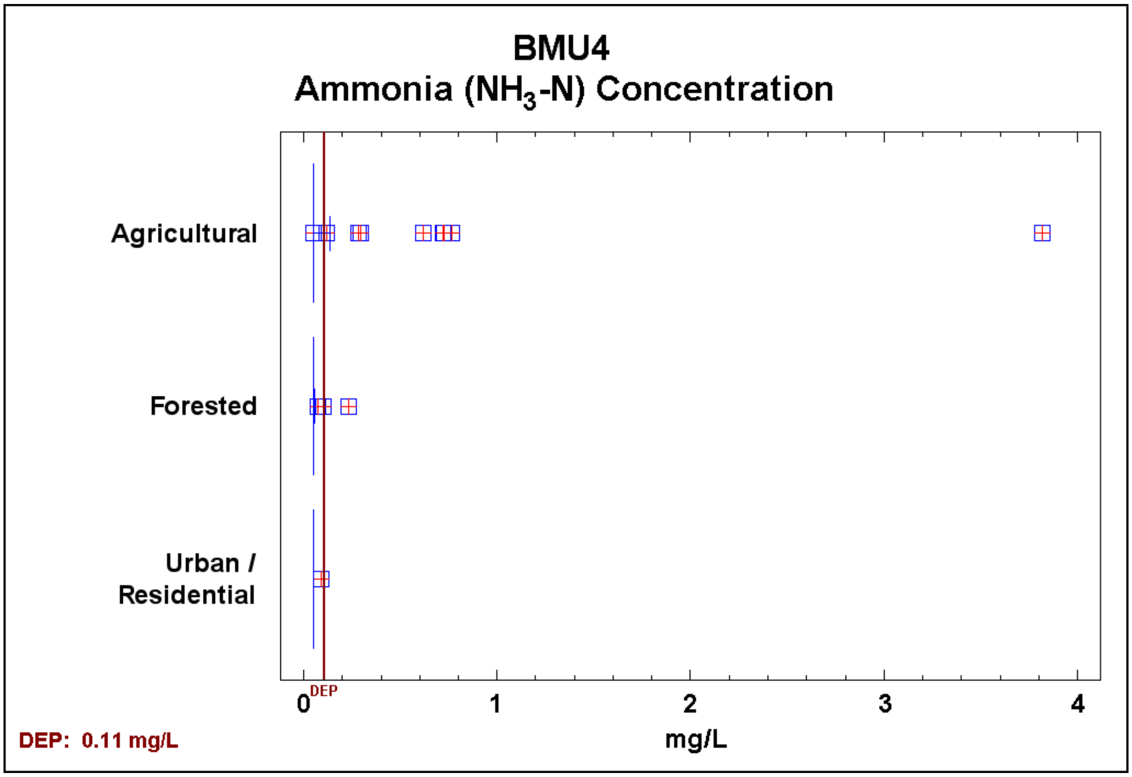

Figure 63. Boxplot for Ammonia Distribution by Land Use in BMU 4

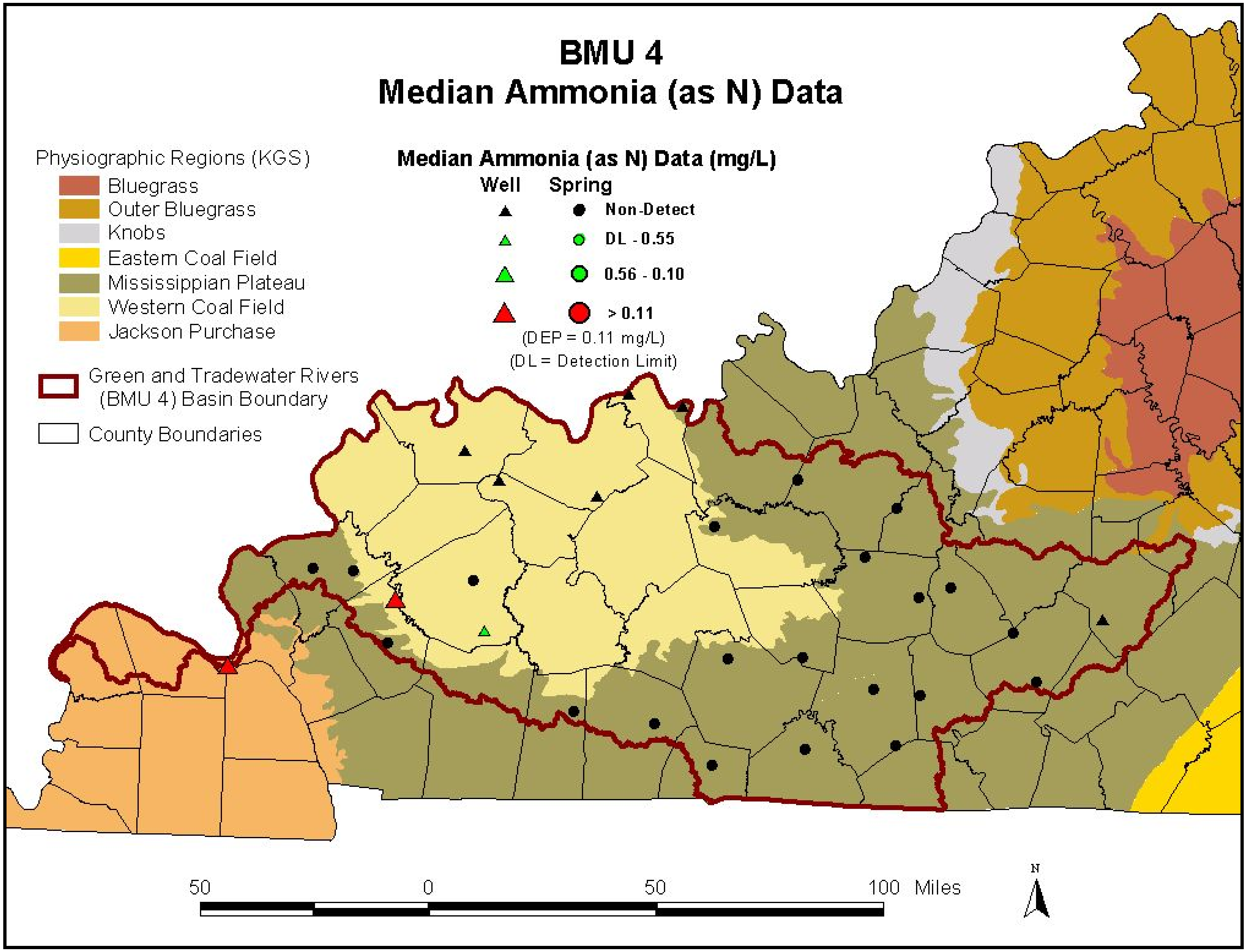

Figure 64. Map of Median Ammonia Data for BMU 4

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.

Because approximately 92.3% of the samples were non-detect using that relatively high detection limit, the narrow range of values shown in Figure 65 and 66 may not reflect the true occurrence of orthophosphate in this area. In the Mississippian Plateau, numerous high outliers of orthophosphate may be the result of naturally occurring phosphate nodules in some of the limestones and from agricultural practices, including livestock production and grazing or the application of phosphate-rich fertilizers. Therefore, this may indicate possible nonpoint source pollution. A map illustrating the distribution of orthophosphate data is presented in Figure 67, which shows that most of the higher values occur within the Mississippian Plateau.

Total phosphorus is the sum of organic and inorganic forms of phosphorus. Total phosphorus values from historic spring data has normally been non-detect, using an MCL of 0.05 mg/L. Low amounts of phosphorus within a narrow range occur in BMU 4. Therefore, in the Mississippian Plateau and Ohio River Alluvium most of the variability of this parameter is probably the result of natural variability in the system, with some possible introduction from anthropogenic sources. As expected, forested areas show the lowest median levels of total phosphorus, as shown in Figure 68 and 69. An unexpected result was the low urban/residential total phosphorus values detected in this study since one would expect phosphatic detergents from sanitary sewer leaks, as well as the application of lawn fertilizer in urban areas. Agricultural areas showed only slightly greater levels, indicating possible nonpoint source impacts from animal waste in agricultural areas and human waste and possibly septic systems. Figure 70 shows the distribution of total phosphorus in BMU 4.

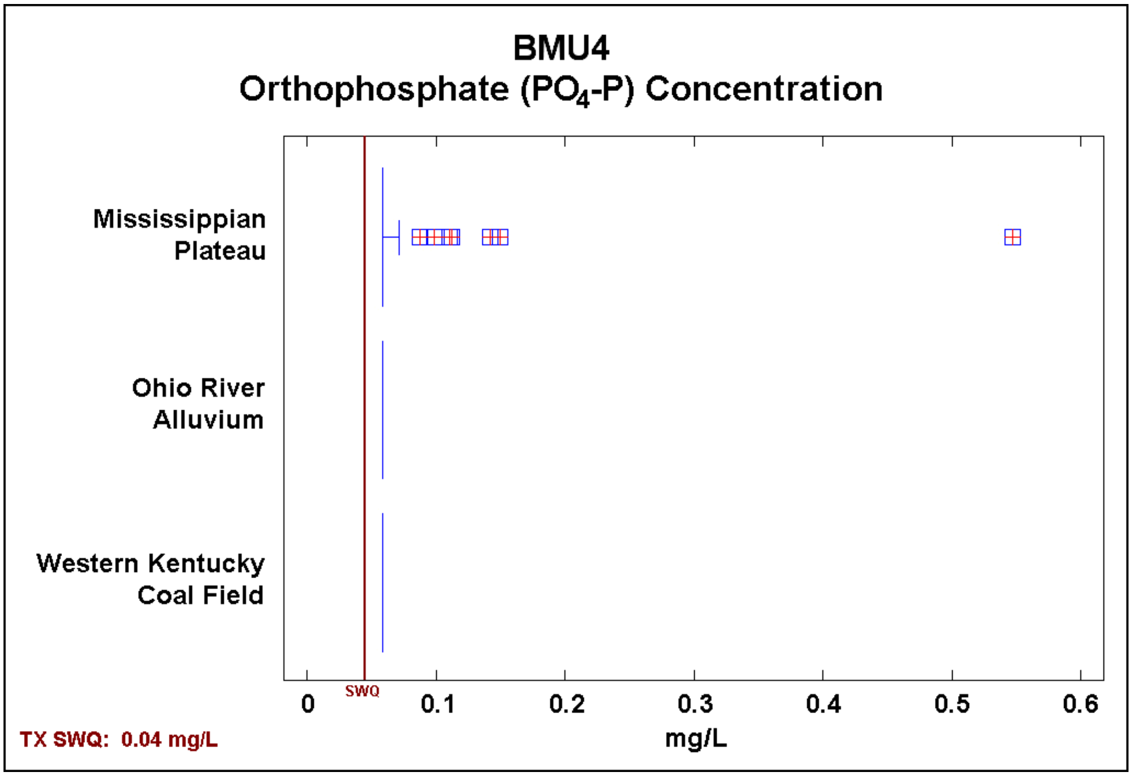

Figure 65. Boxplot for Orthophosphate Measurement Distributions in BMU 4

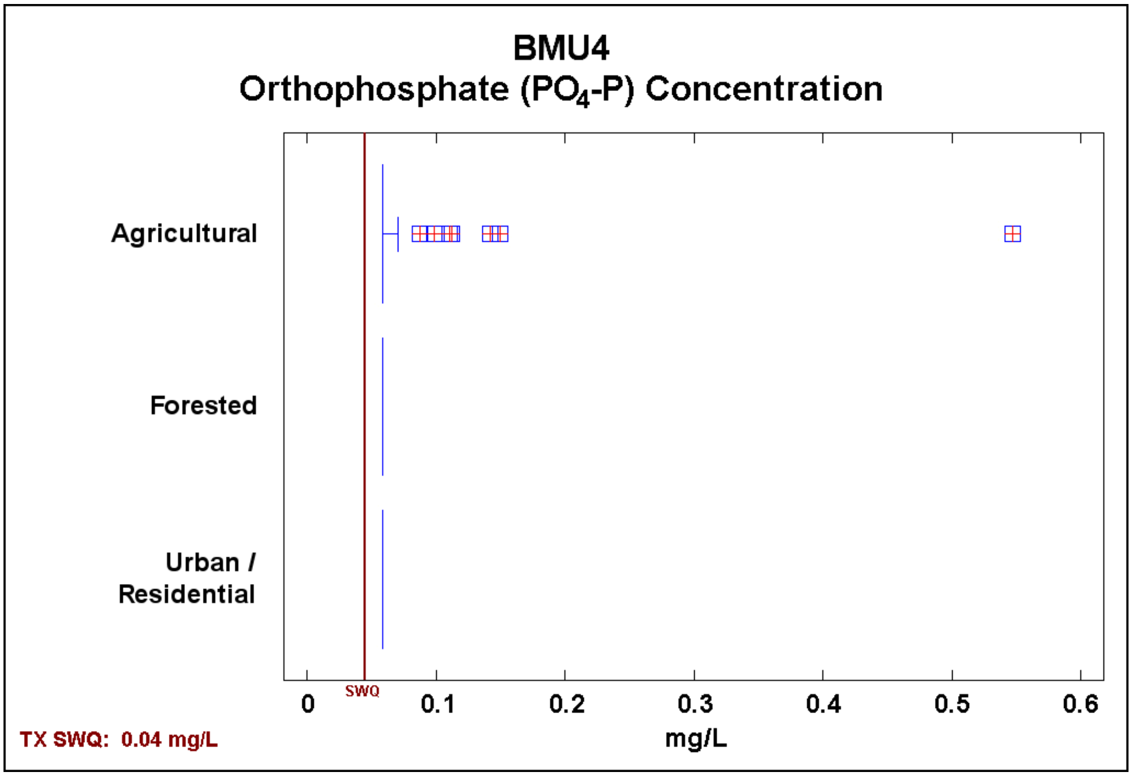

Figure 66. Boxplot for Orthophosphate Measurements in BMU 4 by Land Use

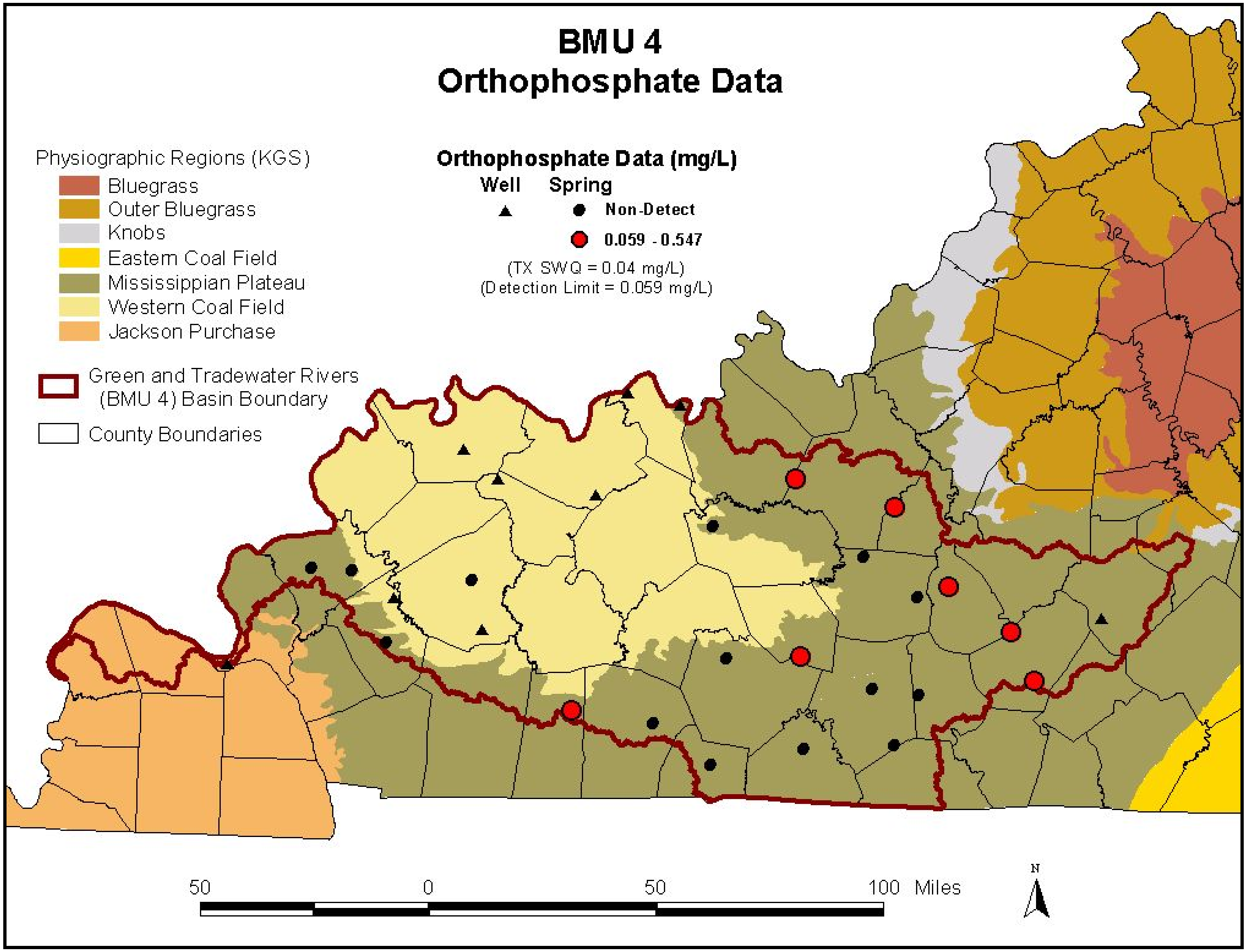

Figure 67. Map of Orthophosphate Data for BMU 4

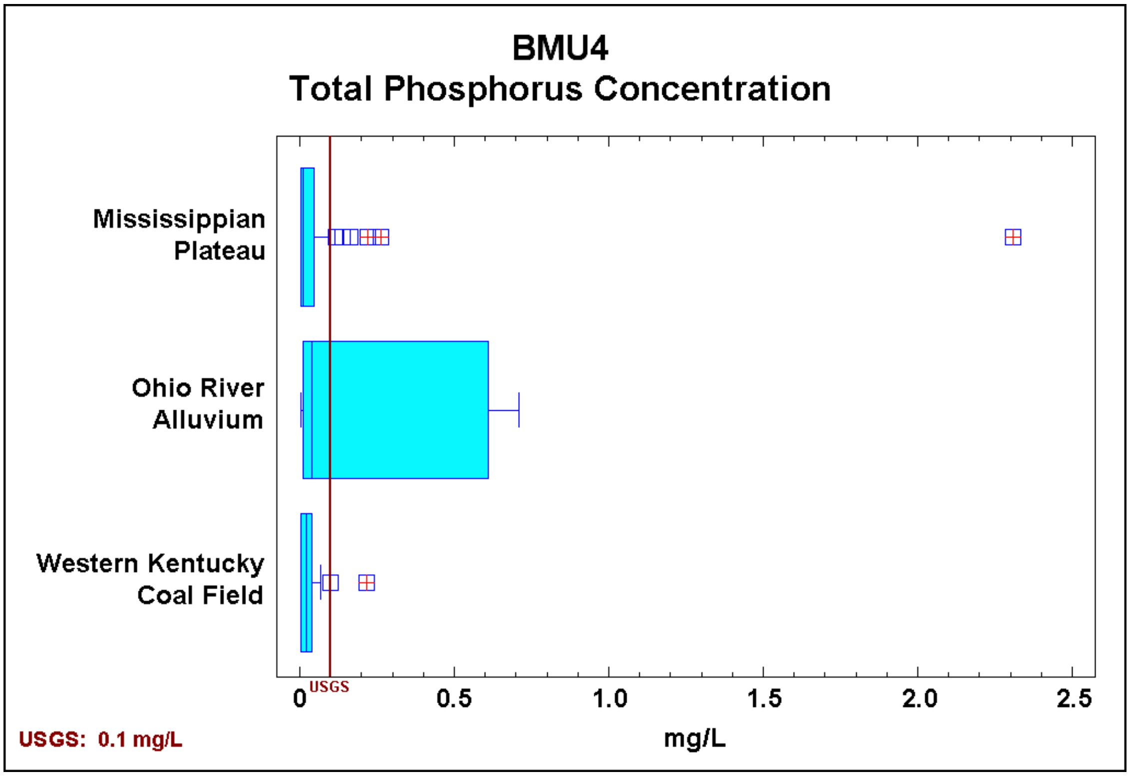

Figure 68. Boxplot for Total Phosphorus Measurement Distributions in BMU 4

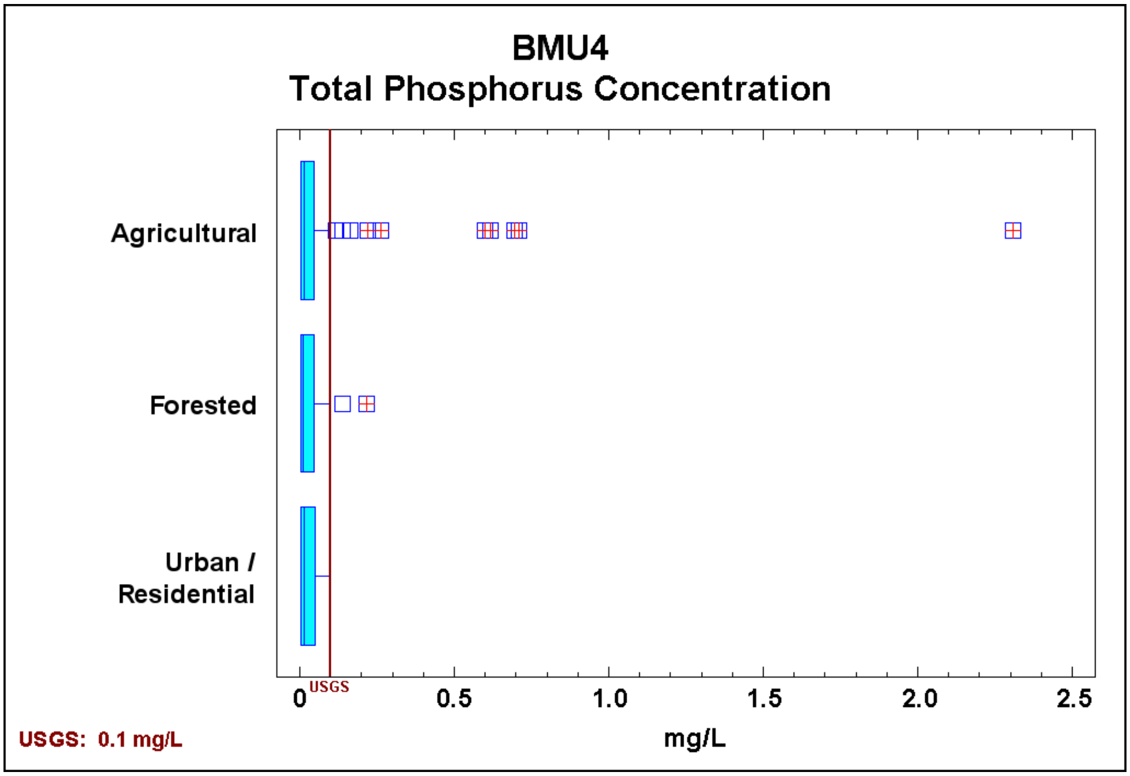

Figure 69. Boxplot of Total Phosphorus Measurements in BMU 4 by Land Use

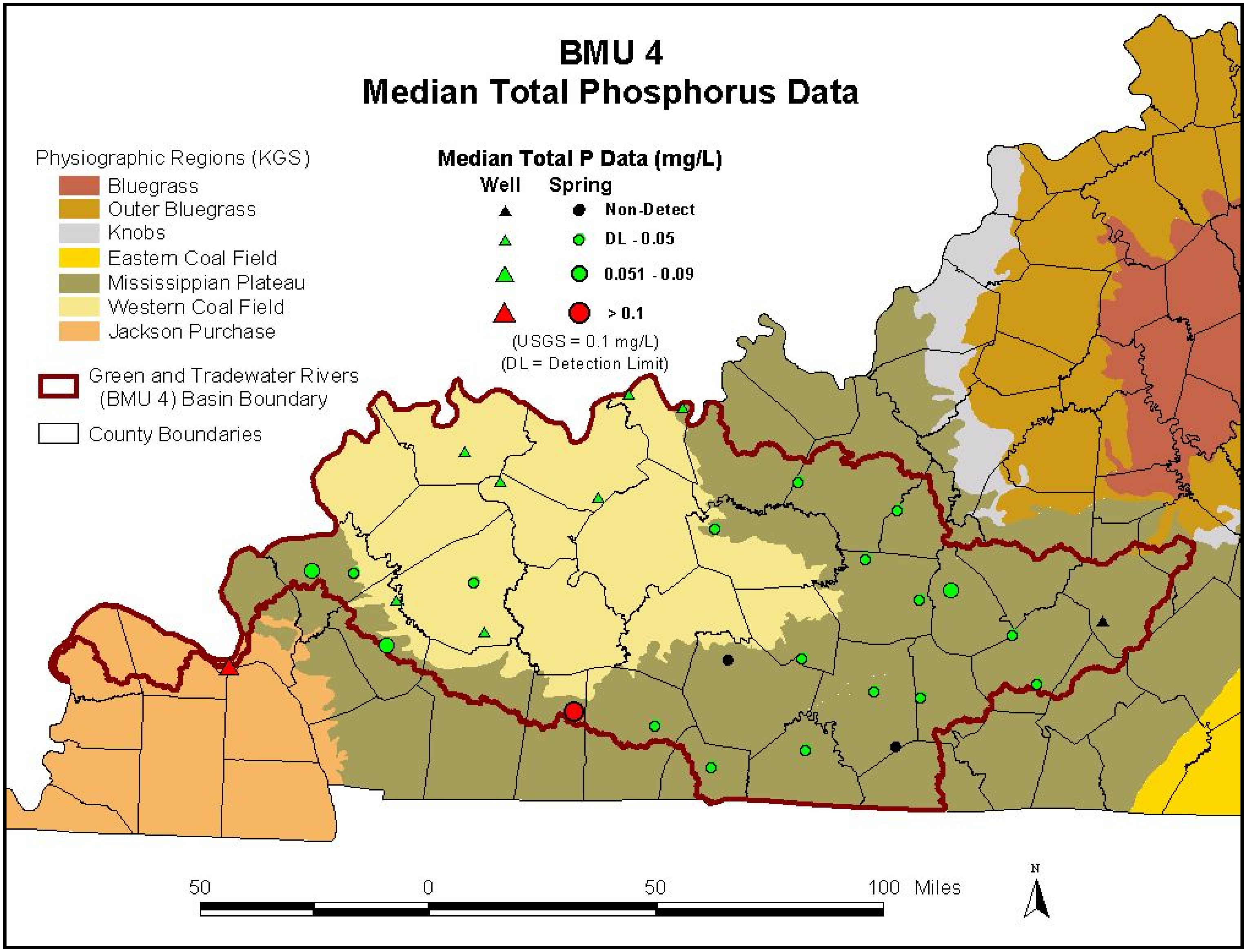

Figure 70. Map of Median Total Phosphorus Data for BMU 4

Volatile Organic Compounds

The volatile organic compounds most often detected in groundwater are the BTEX compounds: benzene, toluene, ethylbenzene and xylenes. Also of concern is methyl-tertiary-butyl-ether, 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 persistent in the environment, particularly groundwater, for two primary reasons. First, water solubility of BTEX is moderate to high, ranging from a low of 161 mg/L for ethylbenzene to 1730 mg/L for benzene. In 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. “Pump and treat” and various bioremediation techniques have proven the most useful techniques.

Benzene is found naturally in the environment in organic matter, including coal and petroleum and is released into the environment during combustion. Benzene is also found in products manufactured from crude oil, including gasoline, diesel and other fuels, plastics, detergents and pesticides. Benzene is also produced during the combustion of wood and vegetation. Benzene is a known carcinogen in humans and has been associated with various nervous system disorders, anemia and immune system depression (U.S.EPA, 2000). The MCL for benzene is 0.005 mg/L. Benzene was not detected in this study so no map or boxplots were prepared.

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

In this study, toluene was detected in one sample out of 120 samples so no box plot was created. The sample was taken from the Nortonville Well number 1 (0004-2984) and was well below the MCL at a concentration of 0.00442 mg/L. However, the map presented in Figure 71 shows this occurrence. This occurrence may be due to urban runoff, or possibly atmospheric deposition, but because no other volatile organic compounds were detected, any conclusions for this single estimated detection are tentative at best.

Ethylbenzene is a 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 U.S.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. Ethylbenzene was not detected in this study.

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 (U.S.EPA, 2000). Xylenes were not detected during this study.

Methyl-tertiary-butyl-ether, or MTBE, is a man-made 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 DEP standard is 0.05 mg/L. According to the U.S.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.

One sample in 105 analyses detected a trace of MTBE (0.00263 mg/L). Because MTBE was detected in only one sample, at Roundstone Spring (9000-0226), no boxplot is presented. However, the map presented in Figure 72 shows this occurrence. This occurrence may be due to an undocumented farm spill, or possibly atmospheric deposition, but because no other volatile organic compounds were detected, any conclusions for this single estimated detection are tentative at best.

CONCLUSIONS

Although limited in scope, this study adds valuable data to the existing body of knowledge regarding groundwater in the state in general and this BMU in particular. This additional information will assist efforts to understand and manage this resource. As mentioned above, differentiating between substances that are naturally-occurring and those that impact groundwater through nonpoint source pollution is sometimes difficult. For parameters that are man-made, such as pesticides and MTBE, the determination of nonpoint source pollution can be readily made; however, for parameters that also occur naturally, such as metals and nutrients, such a determination is problematic. For these parameters, data from this study of BMU 4 can be compared with data from reference reach springs and the statewide ambient network, as well as with data published by other researchers. Through these comparisons, tentative conclusions can be made.

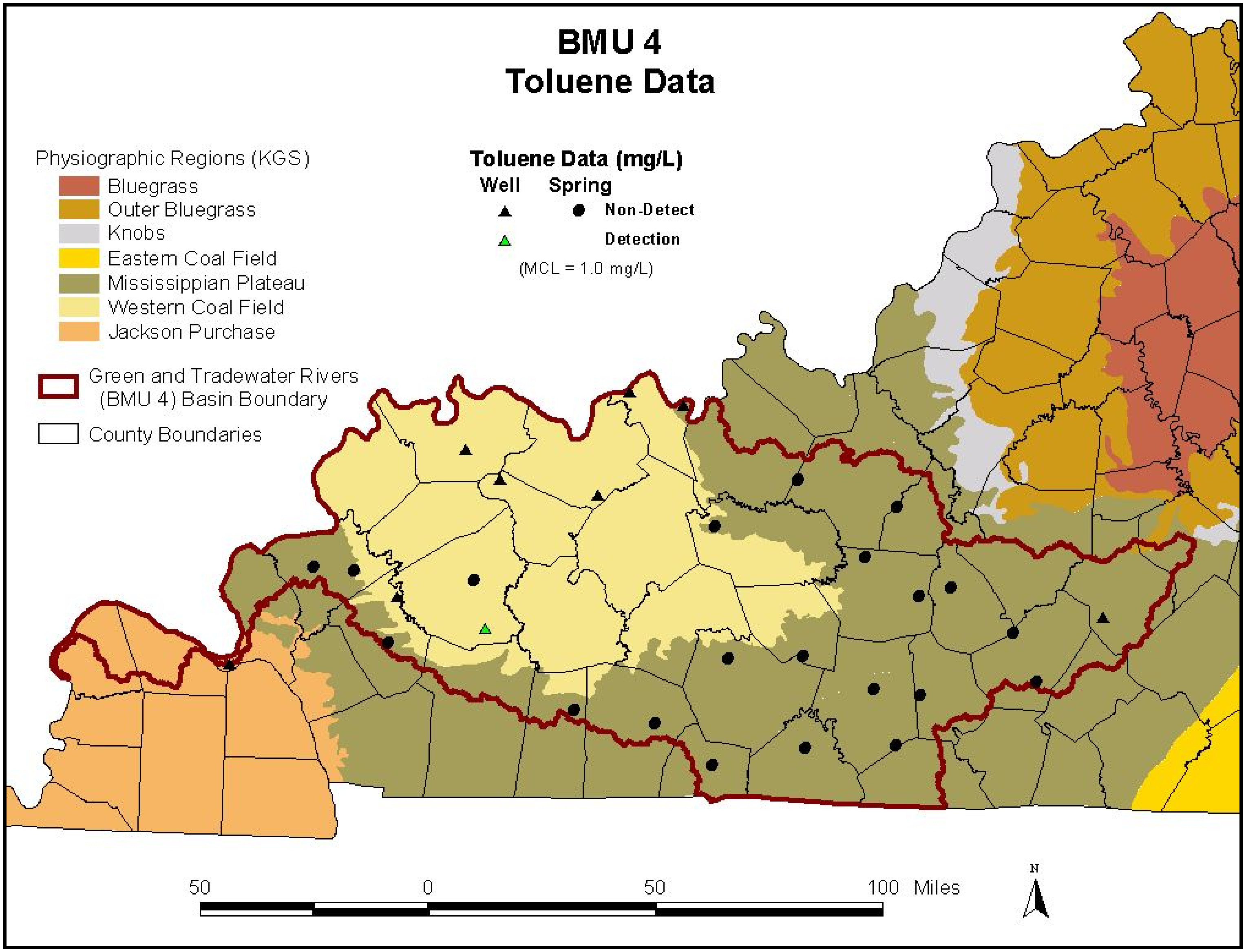

Figure 71. Map of Toluene data for BMU 4

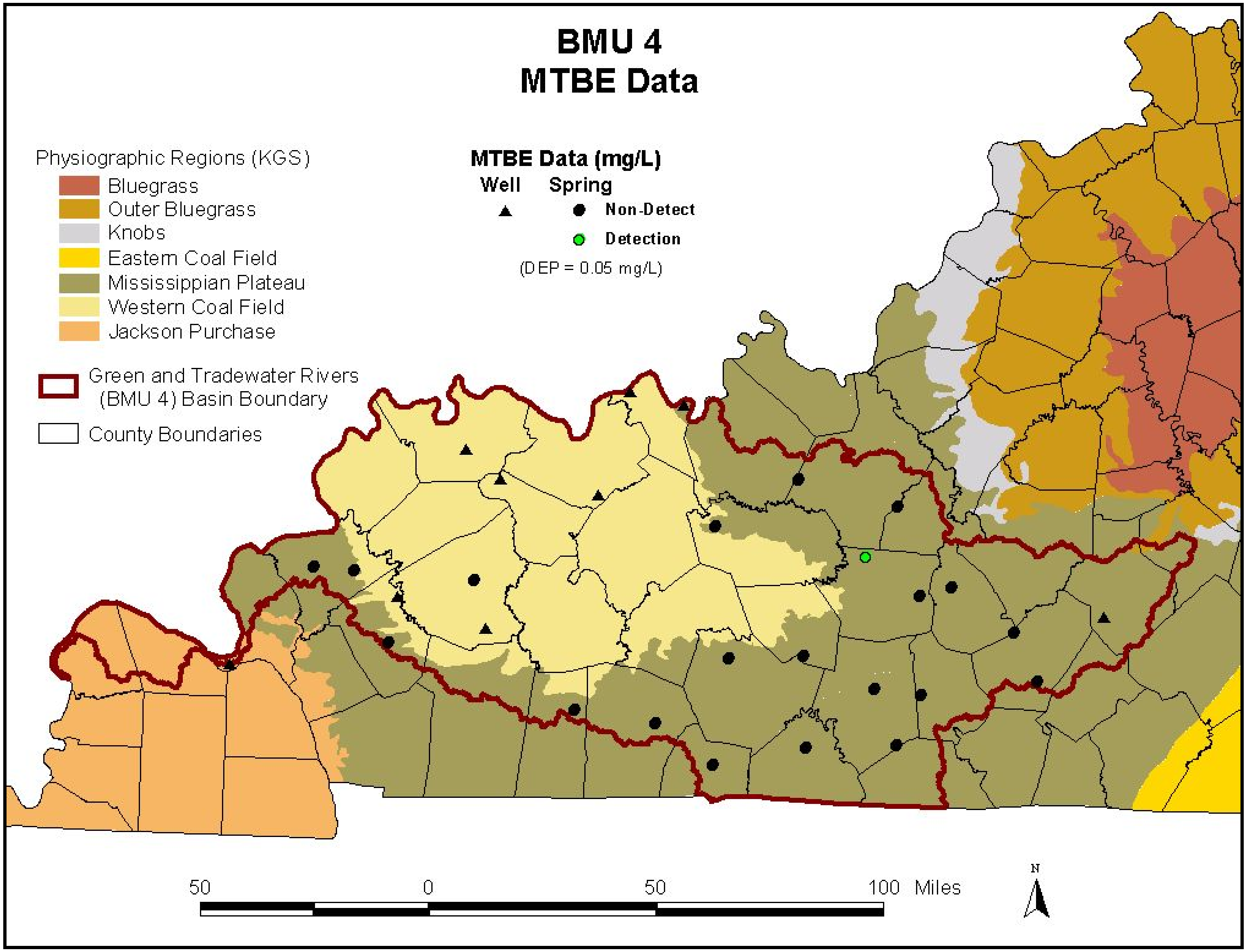

Figure 72. Map of MTBE data for BMU 4

Table 8 summarizes the conclusions reached in this study. This table categorizes impacts to groundwater from various nonpoint sources as "Definite”, "Possible”, or as not existing or simply as "No”.

A "Definite" impact is defined as an occurrence or detection of an unnatural parameter, such as a pesticide, or the detection of a compound that is both naturally occurring and anthropogenic, such as nitrate-N, which far exceeds background concentrations, as determined by comparison with reference site data or data from other groundwater studies. Whether such impacts are detrimental would require receptor studies outside the scope of this particular inquiry. Definite nonpoint source impacts to groundwater were documented for the following parameters: nitrate-N and several herbicides, including atrazine, metolachlor, alachlor and simazine.

A "Possible" impact is a tentative 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 made. Possible nonpoint source impacts to groundwater were found for several nutrients, including ammonia-N, total phosphorus and orthophosphate-P; and for total suspended solids and total dissolved solids. The latter two parameters in particular are difficult to assess because they each measure numerous elements and compounds, rather than discrete ones.

Parameters with "No" significant impacts to groundwater were: 1) either not detected; 2) were detected in a limited number of samples or at very low values, such as mercury; or 3) are thought to occur at natural levels. This study concluded that No impacts to groundwater were apparent for the following parameters: conductivity, hardness, chloride, fluoride, sulfate, arsenic, barium, iron, manganese, mercury, nitrite-n, cyanazine, BTEX and MTBE. (Note: toluene occurred at one site in one of the 4 samples collected, the source of this detection is unknown and therefore not indicative of nonpoint source pollution. The source of the single occurrence of MTBE at one site in Hart County is unexplained, as previously noted.)

Table 8. Nonpoint Source Impacts to Groundwater, BMU 4

	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	●		
Inorganic Ions	Chloride	●		
	Fluoride	●		
	Sulfate	●		
Metals	Arsenic	●		
	Barium	●		
	Iron	●		
	Manganese	●		
	Mercury	●		
Nutrients	Ammonia-N		●	
	Nitrate-N		●	
	Nitrite-N	●		
	Orthophosphate-P		●	
	Total phosphorous	●		
Pesticides	Alachlor			●
	Atrazine			●
	Cyanazine	●		
	Metolachlor			●
	Simazine			●
Residues	Total Dissolved Solids		●	
	Total Suspended Solids		●	
Volatile Organic Compounds	Benzene	●		
	Ethylbenzene	●		
	Toluene	●		
	Xylenes	●		
	MTBE	●		

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 itself. Therefore, only one site per approximately 384.7 square miles (one site per 383 miles in Kentucky) 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 a quarterly sampling schedule over one year's time. Another bias of the study was that there was only one well sampled in the Mississippian Plateau. Although these problems may preclude definitive conclusions regarding short-term changes in groundwater quality, this project and others like it, contribute vital data that add to our continued 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 continue the characterization, protection and management of this resource. In particular, continued studies should focus on increasing the density of sampling sites as well as addressing temporal water quality variations, especially in karst terrane.

Based upon a review of groundwater data from this study in conjunction with surface water data, several areas in BMU 4 will receive additional monitoring in the next cycle of the watershed management system: In the Tradewater River basin, the GWB will sample areas lacking groundwater quality data.

LITERATURE CITED

ATSDR, 2001, ToxFAQ, cited July 2002, http://www.atsdr.cdc.gov/toxfaq.html.

Blanset, J. and Goodmann, P. T., 2002, Arsenic in Kentucky's Groundwater and Public Water Supplies, Geological Society of America, Abstracts with Programs Vol. 34, No. 2, March 2002, Abstract No: 32458.

Brosius, L., 2001, STA 215, unpublished lecture notes, Richmond, Ky., Eastern Kentucky University, 2 p.

Brown, R. F., 1966, Hydrology of the Cavernous Limestones of the Mammoth Cave Area, Kentucky, USGS Water-Supply Paper 1837.

Carey, D. I. and Stickney, J. F., 2001, County Ground-Water Resources in Kentucky, Series XII, 2001, Cited December 2002, http://www.uky.edu/KGS/water/library/webintro.html

Carey, D. I., Dinger, J. S., Davidson, O. B., Sergeant, R. E., Taraba, J. L., Ilvento, T. W., Coleman, S., Boone, R. and Knoth, L. M., 1993, Quality of Private Ground-Water Supplies in Kentucky, Information Circular 44 (series 11), 155p.

Conrad, P. G., Carey, D. I., Webb, J. S., Fisher, R. S. and McCourt, M. J., 1999a, Ground-Water Quality in Kentucky: Fluoride, Information Circular 1 (series 12), 4 p.

Conrad, P. G., Carey, D. I., Webb, J. S., Dinger, J. S. and McCourt, M. J., 1999b, Ground-Water Quality in Kentucky: Nitrate-Nitrogen, Information Circular 60 (series 11), 4 p.

Currens, J. C., Paylor, R. L. and Ray, J. A., 2003, Mapped Karst Ground-Water Basins in the Harrodsburg 30 x 60 Minute Quadrangle, Map and Chart Series 58 (Series XII), scale 1:100,000.

Currens, J. C. and Ray, J. A., 1998, Mapped Karst Ground-Water Basins in the Harrodsburg 30 x 60 Minute Quadrangle, Map and Chart 16 (Series XI), scale 1:100,000.

Currens, J. C. and Ray, J. A., 1998, Mapped Karst Ground-Water Basins in the Somerset 30 x 60 Minute Quadrangle, Map and Chart 18 (Series XI), scale 1:100,000.

Currens, J. C. and Ray, J. A., 1998, Mapped Karst Ground-Water Basins in the Campbellsville 30 x 60 Minute Quadrangle, Map and Chart 17 (Series XI), scale 1:100,000.

Currens, J. C., 2001, Generalized Block Diagram of the Eastern Pennyroyal Karst, Map and Chart 17, Series XII.

Currens, J. C., 2001, Generalized Block Diagram of the Western Pennyroyal Karst, Map and Chart 16, Series XII

Currens, J. C. and McGrain, P., 1979, Bibliography of Karst Geology in Kentucky, Special Publication 1 (series 11), 59 p.

Davis, R. W., Lambert, WM., and Hansen, Jr., A. J., 1973, Subsurface Geology and Ground-Water Resources of the Jackson Purchase Region, Kentucky, USGS Water-Supply Paper 1987, 66 p.

Dever, G. R. Jr., 2000, Limestone and Dolostone Resources in Kentucky, Cited June 2004, http://uky.edu/KGS/coal/webindmn/pages/mineral/limeston.htm.

Driscoll, F. G., 1986, Groundwater and Wells, Johnson Division, St. Paul, Minn., 1089 p.

Faust, R. J., Banfield, G. R. and Willinger, G. R., 1980, A Compilation of Ground Water Quality Data for Kentucky, USGS Open File Report (OFR 80-685), 963 p.

Fetter, C. W., 1992, Contaminant Hydrogeology: New York, Macmillan, 458 p.

Fisher, R. S., 2002, Ground-Water Quality in Kentucky: Arsenic, Information Circular 5 (series 12), 4 p.

Fisher, R.S., Davidson, B., and Goodmann, P.T., 2004, Summary and evaluation of groundwater quality in the Upper Cumberland, Lower Cumberland, Green, Tradewater, Tennessee, and Mississippi River Basins", Kentucky Geological Survey publication OF_04-0004_12

Hall, B., 2002, Statistics Notes, cited June 2002, http://bobhall.tamu.edu/FiniteMath/Module8/Introduction.html.

Hayes, T. B., Collins, A., Lee, M., Mendoza, M., Noriega, A., Stuart, A. and Vonk, A., 2002, Hermaphroditic, demasculinized frogs after exposure to the herbicide atrazine at low ecologically relevant doses, Proceedings of the National Academy of Sciences, PNAS 2002 99, p. 5476-5480.

Hem, J., 1985, Water-Supply Paper 2254, USGS, 263 p., cited May 2002, http://water.usgs.gov/pubs/wsp/wsp2254/.

Irwin, R. J., Mouwerik, M. V., Stevens, L., Seese, M. D. and Basham, W., 1997, Environmental Contaminants Encyclopedia Entry for BTEX and BTEX Compounds, National Park Service, Water Resources Division, Water Operations Branch, Fort Collins, Colo., 35 p., cited December 2002: http://www.nature.nps.gov/toxic/list.html

Kentucky Department of Agriculture, 2002, 2002 Pesticide Sales Data, electronic file from Ernest Collins, KDA, Jan, 2003.

Kentucky Division of Water, 2002a, cited May 2002, http://kywatersheds.org/Kentucky.

Kentucky Division of Water, 2002b, unpublished Alphabetical Listing of Active Public Water Systems, March 26, 2002, 14 p.

Kentucky Division of Water, 2002c, Kentucky Ambient/Watershed Water Quality Monitoring Standard Operating Procedure Manual, 39 p.

Kentucky Geological Survey, 1969, Index to Hydrologic Atlases for Kentucky, 1 p.

Kentucky Geological Survey, 1993, Index to Geologic Maps for Kentucky, Misc. Map 27 (series 10), 1 p.

Kentucky Department for Environmental Protection (compiler), 2002, digital land-use and physiographic province maps, cited May 2002, http://www.nr.state.ky.us/nrepc/ois/gis/library/statedocs.

Kentucky Department of Mines and Minerals, 2002, Annual Reports 1996-2001, cited November 2002, http://www.caer.uky.edu/kdmm/homepage.htm

McDowell, R. C. (ed.), 2001, The Geology of Kentucky, USGS Professional Paper 1151 H, on-line version 1.0, cited May 2002, http://pubs.usgs.gov/prof/p1151h.

Milwaukee Metropolitan Sewerage District (MMSD), 2002, Environmental Performance Report-2002, cited December 2002, http:// www.mmsd.com/envper2001/page3.asp

Noger, M. C.(compiler), 1988, Geologic Map of Kentucky, scale 1:250,000.

Ohio River Valley Sanitation Commission (ORSANCO), 2002, cited May 2002, http://www.orsanco.org/rivinfo.

Quinlan, J. F. (ed.), 1986, Practical Karst Hydrogeology, with Emphasis on Groundwater Monitoring, National Water Well Association, Dublin, Ohio, 898 p.

Ray, J. A. and Currens, J. C., 1998, Mapped Karst Ground-Water Basins in the Beaver Dam 30 x 60 Minute Quadrangle, Map and Chart 16 (Series XI), scale 1:100,000.

Ray, J. A., and Currens, J. C., 2000, Mapped Karst Ground-Water Basins in the Bowling Green 30 x 60 Minute Quadrangle, Map and Chart 22 (Series XII), scale 1:100,000.

Ray, J. A., Moody, J., Blair, R. J , Currens, J. C., and Paylor, R., Pre-published Draft, Mapped Karst Ground-Water Basins in the Tell City 30 x 60 Minute Quadrangle, Map and Chart number pending (Series pending), scale 1:100,000.

Ray, J. A., O’dell, P. W.,Blair, R. J., and Currens, J. C., Pre-published Draft, Mapped Karst Ground-Water Basins in the Hopkinsville 30 x 60 Minute Quadrangle, Map and Chart number pending (Series pending), scale 1:100,000.

Ray, J. A., Webb, J. S. and O'dell, P. W., 1994, Groundwater Sensitivity Regions of Kentucky, Kentucky Division of Water, scale 1:500,000.

Taylor, L. C., 2002, Personal communication to James Webb concerning standards for phosphorous compounds.

Tuttle, M. L. W., Goldhaber, M. B. and Breit, G. N., 2001, Mobility of Metals from Weathered Black Shale: The Role of Green Efflorescences, (abs.) Geological Society of America, Annual Meeting, 2001, cited May 2002, http://gsa.confex.com/gsa/2001AM/finalprogram/abstract 26237.htm.

U.S.EPA, 1997, Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl-Tertiary-Butyl-Ether, Dec. 1997, EPA 822/F-97-008, cited August 2002, http://www.epa.gov/waterscience/drinking/mtbefact.pdf

U.S.EPA, 1998, Total Suspended Solids Laboratory Method 160.2, cited August 2002: http://www.epa.gov/region09/lab/sop

U.S.EPA, 2000, Drinking Water Standards and Health Advisories, cited June 2002, http://www.epa.gov/ost/drinking/standards/dwstandards.pdf.

U.S.EPA, 2002a, Drinking Water Priority Rulemaking: Arsenic, cited July 2002, http://www.epa.gov/safewater/ars/arsenic.html.

U.S.EPA, 2002b, Drinking Water and Health, cited July 2002, http://www.epa.gov/safewater.

USEPA, 2002c, Health Effects of Lead, cited June 2004, http://yosemite.epa.gov/R10/OWCM.NSF/.

United States Geological Survey, 1984, Overview of the Occurrence of Nitrate in Ground Water of the United States: USGS National Water Summary 1984; USGS Water-Supply Paper 2275, pages 93-105.

United States Geological Survey, 2002a, Groundwater quality information, cited May 2002, http://co.water.usgs.gov.

United States Geological Survey, 2002b, Coal Quality Data, cited May 2002, http://energy.er.usgs.gov/products/databases/coalqual.

United States Geological Survey, 2004, Lead Statistics and Information, cited June 2004, http://minerals.usgs.gov/minerals/pubs/commodity/lead/.

Water Quality Association, 2002, Hardness Chart, cited July 2002, http://www.wqa.org.

World Health Organization, 1996, Guidelines for drinking water quality, 2nd edition, cited August 2002, http://www.who.int/water_sanitation_health/.

Appendix A. Financial and Administrative Closeout

Workplan Outputs

The Groundwater Branch has committed to the following outputs:

- Identification of suitable groundwater monitoring sites in the Green and Tradewater River basins
- 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 these basins 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

- Total project budget is $83,333
- Budget has been expended in personnel costs approximately equivalent to 1.23 person years
- Groundwater Branch has managed the project, including:
    - ✓ researching background data
    - ✓ conducting on-site inspections to identify sampling sites
    - ✓ collecting groundwater samples
    - ✓ transporting samples to the laboratory
    - ✓ interpreting sample results
    - ✓ preparing maps and reports
    - ✓ providing reports to interested parties

- Time code used for this project was:

ORG	2DOW
PBU	BA00
FUND	1200
ACT	MOAM
FUNCTION	B284
PROJECT	NPS0002Z

Project Budget:

The total project budget is $83,333. The budget will be expended in personnel costs reflecting a total equivalent of approximately 1.23 person years. Groundwater Branch personnel will manage the project, research background data, conduct on-site inspections and groundwater sampling, transport samples, interpret sample results, prepare maps and reports, and present the summary information to stakeholders and other interested parties. The Division of Environmental Services lab personnel will conduct chemical analysis at the DES lab. A time code will be established to track personnel time spent on the project. Match for this grant will be provided by DOW and DES personnel costs, including fringe and overhead.

Budget Summary:

Budget Categories	**BMP Implementation**	**Project Management**	**Public Education**	**Monitoring**	**Technical Assistance**	**Other**	**Total**
Personnel	$	$	$	$83,333	$	$	$83,333
Supplies							
Equipment							
Travel							
Contractual							
Operating Costs							
Other							
TOTAL	**$**	**$**	**$**	**$83,333**	**$**	**$**	**$83,333**

Detailed Budget

Budget Categories	**Section 319(h)**	**Non-Federal Match**	**Total**
Personnel	$50,000	$33,333	$83,333
Supplies	$	$	$
Equipment	$	$	$
Travel	$	$	$
Contractual	$	$	$
Operating Costs	$	$	$
Other	$	$	$
TOTAL	$**50,000**	**$33,333**	**$83,333**

Funds Expended

All funds for this project were expended using personnel dollars.

Equipment Summary

No equipment was purchased for this project.

Special Grant Conditions

No special grant conditions were placed on this project by the EPA.

Appendix B. Quality Assurance / Quality Control for Water Monitoring

QA/QC Plan for Expanded Groundwater Monitoring for Nonpoint Source Pollution Assessment in Tradewater and Green River Basins (Basin Management Unit 4)

Prepared by

Peter T. Goodmann, Manager, Groundwater Branch
David P. Leo, Supervisor, Groundwater Branch
Phillip W. O'dell, Groundwater Hydrologist III, Groundwater Branch

Kentucky Division of Water

1. Title Section

A. Project Name

Expanded Groundwater Monitoring for Nonpoint Source Pollution Assessment in Tradewater and Green River Basins (Basin Management Unit 4).

B. QA/QC Plan Preparers

Peter T. Goodmann, Manager, Groundwater Branch
David P. Leo, Supervisor, Groundwater Branch
Phillip W. O’dell, Groundwater Hydrologist III, Groundwater Branch
Kentucky Division of Water
14 Reilly Road
Frankfort, Kentucky 40601
(502) 564-3410

C. Date

January 31, 2001

D. Project Description

The project is part of the Green/Tradewater River Strategic Watershed Monitoring Plan. The Kentucky Division of Water currently conducts quarterly nonpoint source groundwater monitoring at approximately 70 sites across the state. This project will expand that monitoring effort in the Tradewater and Green River Basins by increasing the number of monitoring sites and focusing additional efforts of the existing monitoring network in these watersheds. 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 Tradewater and Green River Basins. 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. Project Organization and Responsibility

A. Key Personnel

The Technical Services Section of the Groundwater Branch will coordinate this project in cooperation with Data Management Section staff of the Groundwater Branch, Kentucky Division of Water.

The Groundwater Branch, Kentucky Division of Water, will scout and select suitable sampling locations. Groundwater Branch staff will perform sampling and sample 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 Department for Environmental Protection’s Consolidated Groundwater Database and will be forwarded to the Kentucky Geological Survey's Groundwater Data Repository.

Phillip W. O’dell, P.G., will be the Project Officer, QA Officer, and Field Sampling Officer. Address: 14 Reilly Road, Frankfort, KY 40601. Phone (502)-564-3410.

B. Laboratory

Division of Environmental Services
100 Sower Boulevard
Frankfort, Kentucky 40601
(502) 564-6120

C. Participating Agencies

The Groundwater Branch, Division of Water currently conducts statewide ground water monitoring for the Ambient Groundwater Monitoring Program.

This project will cooperate with the Division of Water's Watershed Initiative, the Tradewater and Green River Basins Teams, and the Division of Water's Water Quality Branch.

3. Watershed Information

A. Stream Names

Tradewater River, the Green River and their tributaries.

B. Major River Basins

Tradewater and Green River Basins.

USGS Hydrologic Unit Number (HUC)

Tradewater River Basin:	05130205
Green River Basin:	05110001 05110002 05110003 05110004 05110005 05110006
Minor Ohio River Tributaries (MORT)	05140201 05140202 05140203 05140206 05140104

C. Stream Order

This project encompasses basins of the Tradewater and Green River.

D. Counties in the Study Area

Tradewater River Basin: Caldwell, Christian, Crittenden, Henderson, Hopkins, Livingston, Union, and Webster.

Green River Basin: Adair, Allen, Barren, Butler, Breckinridge, Casey, Christian, Daviess, Edmonson, Grayson, Green, Hancock, Hardin, Hart, Henderson, Hopkins, Larue, Lincoln, Logan, McLean, Metcalf, Monroe, Muhlenberg, Ohio, Pulaski, Russell, Simpson, Taylor, Todd, Warren, and Webster.

Minor Ohio River Tributaries (MORT): Breckinridge, Ballard, Crittenden, Daviess, Hancock, Henderson, Livingston, Marshall, McCracken, and Union.

4. Monitoring Objectives

- Determine impacts of nonpoint source pollution on groundwater resources in selected areas of basins of the Tradewater and Green Rivers.
- Provide guidance for the nonpoint source program to focus future resources relating to nonpoint source pollution of groundwater.
- Support other programs, such as the Wellhead Protection program, the Groundwater Protection Plan program and the Agriculture Water Quality Authority.
- Provide additional data useful for the long-term management of the resource.

5. Study Area Description

The Tradewater River and Green River basins occur mainly in the Western Kentucky Coal Field and the Mississippian Plateau physiographic provinces of western Kentucky. The Western Coal Field is underlain by Pennsylvanian shale, sandstone, siltstone, coal, and limestone and is characterized by gently rolling topography. The Mississippian Plateau is underlain by thick sequences of Mississippian limestone with well-developed karst topography. In addition, wide alluvial valleys characterize the lower portions of these basins. Minor portions of the project area are located within the Ohio River Alluvium. (McDowell, et al., 1988)

Late Pliocene and Pleistocene unconsolidated sand, gravel, silt, and clay characterize the Ohio River Alluvium. Groundwater flow regimes vary within the project area. Karst areas in the Mississippian Plateau are dominated by conduit flow in the subsurface. Areas of interbedded clastic sediments, as found in the Western Coal Field, are primarily fracture-flow regimes. Systems characterized by unconsolidated sediments, such as the Ohio River Alluvium, are dominated by intergranular flow (Ray, et al., 1994). All three of these flow regimes occur within the study area and will be assessed.

Approximately 70% of the land in the project area is used for agriculture. Therefore, constituents such as pesticides and nutrients, which are potential groundwater contaminants in agricultural areas, will be sampled. Other land uses within the project area include urban, abandoned mine lands, coal mining, both current and historical, oil and gas production, and silviculture. Impacts of these land uses on groundwater will be assessed. For example, constituents related to abandoned mine lands, such as heavy metals, sulfate, pH, and residues will be analyzed. Other examples include chloride pollution due to oil and gas production, and nutrient pollution from on-site sewage disposal.
The Western Kentucky Coal Field consists of relatively flat-lying, repetitive sequences of sandstone, shale, coal, and underclay, with minor amounts of limestone. These strata are highly dissected by streams, resulting in topographic relief of 100 to 500 ft. between ridge tops and valley bottoms. Most domestic wells are completed in fractured bedrock at depths less than 100 ft.

The Mississippian Plateaus (Pennyroyal) region consists primarily of limestone strata with minor shales and siltstones, fractured sandstone, and unconsolidated alluvium along major rivers. Limestone in this region is characterized by solution-enlarged sinkholes, caves, and caverns. Karst springs are the most common sources of ground water, although shallow (<150 ft.) wells in alluvium or fractured bedrock also provide water to some residents.

The Tradewater/Green River Basins, along with some areas that drain directly to the Ohio River, have been targeted as priority basins in the fourth year of the watershed initiative. For the purposes of the watershed initiative, these adjacent Minor Ohio River Tributaries (MORT) are included within the study area. This project will conduct quarterly groundwater monitoring at thirty sites within the Tradewater/Green and adjacent MORT basins.

6. Monitoring Program/Technical Design

A. Monitoring Approaches

Monitoring of approximately 30 sites will begin in April 2001. Specific sample sites will be selected after the Division of Water’s groundwater database has been reviewed for candidate sites and field inspection has confirmed that the candidate sites are suitable for monitoring. For all selected sites, either a Kentucky Water Well Record or a Kentucky Spring Inventory Form (examples attached as Appendix 1) will be placed on record with the Division of Water. 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 final site selection 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 2001 and samples will be collected quarterly through March 2002.

D. Sample Parameters, Containerization, 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; and dissolved and total metals. The analytical methods, containers, volumes collected, preservation, and sample transport will be consistent with the Division of Water's Standard Operating Procedures for Nonpoint Source Surface Water Quality Monitoring Projects, prepared by the Water Quality Branch (August, 1995) and current guidance from the Division of Environmental Services. Parameters to be measured, volume required for analysis, container type, preservative (if any), holding times (if any), and analytical methods are shown on the attached Chain-of-Custody Form.

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, TKN, and orthophosphate) and/or improper sewage disposal (nitrates, ammonia). Where sewage is suspected as a nonpoint source pollutant, unbleached cotton fabric swatches may be used to detect optical brighteners, the whitening agents used in laundry products and commonly found in sewage (Quinlan, 1987). 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.

All samples will be analyzed by the Division of Environmental Services laboratory according to the appropriate EPA 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. Additionally, any intermediary collection vessel will be triple rinsed with filtrate prior to use.

Field Meters

Field meter probes will be rinsed with deionized water prior to 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 directly into a new clean sampling container and will be transferred to the appropriate new clean sample container during the filtration process container. New disposable single use filters and tubing will be used in the filtration process. 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 <u>Standard Operating Procedures for Nonpoint Source Surface Water Quality Monitoring Projects</u>, prepared by the Water Quality Branch (August, 1995) and current guidance from the Division of Environmental Services. 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 until conductivity readings stabilize prior to sampling, in order to ensure that groundwater, rather than water that has been standing in the well bore, is being sampled. Spring samples will be collected as close to the spring resurgence as possible. If inhospitable terrain prohibits spring access, a decontaminated Teflon bucket attached to a new polypropylene rope may be lowered to the spring to collect the sample. Samples for pesticide analysis will be collected using a stainless steel bucket.

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. According to Division of Environmental Services accepted procedures, duplicate analyses will be accepted if they are within 20 % rsd. If unacceptable results are found, samples will be re-analyzed and field records will be examined to determine the cause.

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.

9. References

Kentucky Division of Water, 1995, Standard operating procedures for nonpoint source surface water quality monitoring projects: Kentucky Natural Resources and Environmental Protection Cabinet, Frankfort, KY, 138 p.

McDowell, Robert C., Grabowski, Gilbert J, Moore, Samuel L., 1988, Geologic Map of Kentucky, Sesquicentennial Edition of the Kentucky Geological Survey, by U.S. Geological Survey, Daniel Peck, Director, and in cooperation with the Kentucky Geological Survey, Donald C. Haney, State Geologist and Director. Compiled by Martin C. Noger, Kentucky Geological Survey.

Quinlan, J. F., ed., 1987, Qualitative water-tracing with dyes in karst terrains – Practical karst hydrogeology, with emphasis on groundwater monitoring, National Water Well Association 26 p.

Ray, Joseph, Webb, James, S., and O'dell, Phillip W., 1994, Groundwater Sensitivity Regions of Kentucky, Kentucky Department for Environmental Protection, Division of Water, Groundwater Branch, map.

CHAIN OF CUSTODY RECORD
NATURAL RESOURCES AND ENVIRONMENTAL PROTECTION CABINET
DIVISION OF WATER - GROUNDWATER BRANCH - NPS Green/Tradewater River Basin Project - Funding Source A-40

Site Identification

Location:

County:

AKGWA #:

Collection Date/Time

Date: _______________

Time: _______________

Field Measurements

Temp: _______________ ºC

pH: _______________

Cond: _______________ umhos

Sampler ID: ___________________________________

Division for Environmental Services Samples

Analysis Requested	**Container Size, Type**	**Preservation Method**	**Parameters**	**Analysis Requested**	**Container Size, Type**	**Preservation Method**	**Parameters**
	1000 ml Plastic	Cool to 4ºC	**Bulk Parameters** **IC Scan** (includes Chloride, Fluoride, Nitrate-N, Nitrite-N, Sulfate, Ortho-P), **Alkalinity, Conductivity, pH, TSS, TDS**		1000 ml Plastic	Filtered HNO_3 Cool to 4ºC	**Dissolved Metals by ICP** plus Arsenic, Lead, Mercury, Selenium
	1000 ml Plastic	H_2SO_4 Cool to 4ºC	**NH_3/TKN/TOC** **Total P**		1000 ml Plastic	HNO_3 Cool to 4ºC	**Total Metals by ICP** plus Arsenic, Lead, Mercury, Selenium
					1000 ml Glass	Cool to 4ºC	**N/P Pesticides** Method 507
					1000 ml Glass	Cool to 4ºC	**Pesticides/PCBs** Method 508
					1000 ml Glass	Cool to 4ºC	**Herbicides** Method 515.1

Signatures:

Relinquished by: ___________________ Date: ________ Time: ________

Received by: _______________________________________

Relinquished by: ___________________ Date: ________ Time: ________

Received by: _______________________________________

Sample #: _______________ Report #: _______________

APPENDIX C Groundwater Sites Monitored in BMU 4

Groundwater Fixed Network Sites in the Green River Management Unit	
Site	**Comments**
Auburn Spring/Logan	PWS Spring
Beaver Dam/Ohio	PWS Wells (4)
City Spring/Hardin	PWS Spring (AKA "E-town Spring or Municipal Spring")
Dyers Spring/Hardin	PWS Spring (AKA "Gaithers Spring")
Hawesville/Hancock	PWS Wells (3)
Head of Mud Spring/Logan	Spring
Island/McLean	PWS Wells (2)
Johnson Spring/Hart	Spring
Lost River Rise/Warren	Spring
Marcum Mill Spring/Metcalfe	Spring
Owensboro/Daviess	PWS Wells (4)
Pine Knob Spring/Grayson	Unregulated Public Access Spring
Pirtle Spring/Hardin	PWS Spring
Scottsville Spring/Allen	Spring
Groundwater Fixed Network Sites in the Tradewater River Management Unit	
Site	**Comments**
No Bottom Spring/Crittenden	Spring
Webster Co. Water District/Webster	PWS Well (used as back-up now)
White Plains/Hopkins	PWS Wells (4)