# **Expanded Groundwater Monitoring**

# **For Nonpoint Source Pollution Assessment**

# In the Elkhorn Creek Sub-basin of the Big Sandy and Tygarts

# **Creek River Basins:**

# **Final Report**

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## **EXECUTIVE SUMMARY**

In order to conduct a more adequate assessment of groundwater resources in the Elkhorn Creek sub-basin of the Big Sandy and Tygarts Creek River basins, Kentucky Watershed Basin Management Unit Number 5 (BMU 5), the former Groundwater Branch of the Kentucky Division of Water (KDOW) collected 121 raw-water samples at 31 wells and springs in BMU 5. Sites selected represented ambient groundwater conditions and the various hydrogeologic flow regimes found in the basin. The sites were also selected to be as close as possible to surface water sampling stations located within the basin. Samples were analyzed for pesticides, herbicides, total and dissolved metals, nutrients, major inorganic ions, residues and volatile organic compounds, including trichloroethylene (TCE), benzene, toluene, ethylbenzene, xylenes and methyl-tert-butyl ether (MTBE). Additionally, data from 22 surface water sites collected in part to another nonpoint source study within the basin were also analyzed for this project.

Ambient groundwater quality in BMU 5 appears to be generally good with land-use being 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 ammonia and sulfate.

An evaluation of constituents that do not naturally occur, such as, volatile organic compounds or pesticides/herbicides were conducted to determine potential impacts to groundwater. In BMU 5 there were only two detections of a herbicide and these were Alachlor and Atrazine. These herbicide detections were in the same well and were present in concentrations slightly above the maximum detection limit. Therefore, volatile and semi-volatile contamination does not appear to be a factor in the study area.

Most properly constructed wells tested negative for bacteria with hand dug wells and wells with maintenance problems having elevated bacteria. The groundwater proved to be generally of higher quality than the surface water in Elkhorn Creek for most parameters of concern. Based on the data, groundwater flow to Elkhorn Creek appears to be a positive moderating factor in the condition of the surface water.

## **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 Section assessed nonpoint source pollution impacts to groundwater within the Big Sandy and Tygarts Creek river basins (BMU 5).

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 (ITAC) on Groundwater, which includes the Division of Water. Both the ambient groundwater monitoring program and the ITAC were developed in response to needs outlined in the Kentucky Groundwater Protection Strategy, 1984.

The Division of Water regularly collects ambient groundwater samples throughout the state. As of September 30, 2013, the division has collected 6,072 samples from approximately 1,581 sites (Blanset, 2013). 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 since groundwater connects directly to 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 public. to the Data requests can be made via their website (http://kgs.edu/KGS/home.htm), by phone at (859) 257-5500, or by mail at 228 Mining and Minerals Resources Building, University of Kentucky, Lexington, KY 40506-0107.

#### **Project Description**

This project provides additional groundwater quality data in areas lacking adequate information. The objective of this project was to sample 30 groundwater sites in BMU 5 on a quarterly basis for one year, beginning in May 2007. In addition, data from one additional site, a cave spring on Cumberland Mountain, was sampled one time at the request of the landowner. For comparison, the Groundwater Branch selected wells and springs located as close as possible to surface water monitoring sites previously sampled as part of an Elkhorn Creek NPS. 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 unimpacted ("pristine") reference springs (Table 2) to determine possible nonpoint source pollution impacts or other water quality problems, as well as to identify outstanding resources. Statistical analyses were performed comparing groundwater to surface water in the Elkhorn Creek sub-basin.

#### **Previous Investigations**

Comprehensive discussions of groundwater quality within the Big Sandy and Tygarts Creek 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 (HAs) and 7.5 minute Geological Quadrangle maps (GQs) for the entire state. The Kentucky Geological Survey (1969 and 2002) has indexed these publications. Geochemical data in the HAs are limited and generally includes only common metals and major inorganic ions.

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. 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-nitrogen 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-nitrogen and fluoride in the state and Fisher (2002) described the occurrence of arsenic. In their study of nitrate-nitrogen, 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 and several researchers, including Kipp and Dinger (1991) and Minns (1993) have studied groundwater in eastern Kentucky. These studies, and others, have found that groundwater in eastern Kentucky is generally hard and that naturally occurring water quality problems commonly include iron, manganese, sodium chloride and sulfate.

O.E. Meinzer in his 1923 publication "Outline of Ground-Water Hydrology with Definitions", USGS Water-Supply Paper 494, specifically discussed atmospheric, surface and subsurface waters due to the systems being completely intertwined. Unfortunately today most of the work on groundwater and surface water systems has been done independently, which in the opinion of the authors is over simplified and presents an incomplete and inaccurate analogy.

## PHYSIOGRAPHIC and HYDROGEOLOGIC SETTING

BMU 5 covers more than 9,000 square miles and includes the Big Sandy and Tygarts Creek river basins. This study has concentrated most of its focus on the impaired Elkhorn Creek basin in Pike and part of Letcher Counties. Figure 1 illustrates the location of BMU 5 and the 30 groundwater sites included in this study and 22 surface water sampling sites near by.

## **Big Sandy River Basin**

The Big Sandy River flows along the eastern border of the Commonwealth of Kentucky and West Virginia. The Big Sandy river basin extends as far west as Morgan County and as far east in West Virginia as McDowell County and as far south in Virginia as Wise County. The river flows north and empties into the Ohio River.

Elkhorn Creek begins in the eastern part of Letcher County and flows northeast into Pike County along the Kentucky and Virginia border, where it meets the Russell Fork. This watershed drains the rugged terrain of Pine Mountain (locally referred to as Cumberland Mountain), a monocline thrust fault of Pennsylvanian and Mississippian aged formations. This hydrologic unit is located in the eastern most portion of the eastern coalfield region. The Elkhorn Creek sub-basin encompasses an area about 53 square miles (Division of Water, 2011). This study collected domestic well and spring samples mostly along Elkhorn Creek and it tributaries from Jenkins to Elkhorn City. Sites were selected to be as close as possible to surface water sites so groundwater/surface water comparison could be made. The National Hydrography Dataset (NHD) basin delineation was discovered to be incorrect during the project. Shelby Gap as mapped is shown as a connection of Elkhorn Creek and Shelby Creek. Members of the Geographic Information System and Data Analysis Section (GDA) noticed the flow arrows on NHD for the headwaters of Shelby Creek, pointed in two different directions after most of the sampling was completed. Members of the Groundwater Section looked at the Shelby Gap maps also and it was determined field verification would be needed.

GDA personnel agreed to assist on a two day sampling trip so field verification could be made. Shelby Gap was determined to be a paleo-flow route that had previously been connected to Elkhorn Creek but has since been abandoned. The large contour interval used in the vicinity of Pine Mountain rendered topographic map determination impossible.

GDA's NHD Data Steward submitted changes to the NHD and the changes were accepted. They have now been incorporated into the NHD and the HUC 10 basin delineation is shown on Figure 3. A result of the new determination has been that additional sampling points are now located in the Shelby Creek basin as result of this remapping of the basin. None of the Shelby Creek sites were used for the statistical surface/groundwater analysis.

It is interesting to note that high resolution LIDAR data has recently became available for the area with a vertical accuracy of NSSDA  $RMSE_z = 15$  cm (Kentucky 2011). Overlaying the NHD over the new LIDAR data made spotting the problem easy. Future incidents like this will

be able to be solved using this new LIDAR data and corrections can be made using the LIDAR data alone.

#### **Groundwater Sensitivity**

Kentucky's various physiographic regions have varying sensitivity to contamination from activities conducted on the surface based upon variations in geology, topography and hydrologic regimes. 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 one finds, the quicker the recharge, the faster the flow and the more extensive the dispersion, the greater the sensitivity. Figure 3 illustrates generalized interpretation of groundwater sensitivity in BMU 5. Ray and others (1994) discuss this topic in detail. In BMU 5 groundwater sensitivity ranges from high in the well-developed karst on Pine Mountain to moderate in the Eastern Coal Field.



Figure 1, Elkhorn Creek sub-basin, Physiographic Regions and Study Sampling Sites.



Figure 2, Groundwater and Surface Water Sampling Locations (before NHD problem was rectified).



Figure 3, Watershed after Corrections to the NHD were made



Figure 4, Study Area shown on Groundwater Sensitivity Map for Kentucky.

## **Physiographic Provinces**

Physiographic provinces (Figure 2) are differentiated on the basis of geology and hydrology and therefore the physiographic map is used as a base map to present analytical data on each parameter. Elkhorn Creek Sub-Basin is entirely in the Eastern Coal Field physiographic province. The information below is summarized from Noger (1988), McDowell (2001) and Ray and others (1994).

Generally, flat-lying Pennsylvanian-age clastic sedimentary rocks, sandstone, siltstone, shale and clay, with significant coal beds characterize the Eastern Coal Field, also known as the Cumberland Plateau. Erosion of this plateau has produced steeply incised, narrow valleys, with narrow ridges. Maximum local topographic relief within this portion of the study area is about 3,149 ft amsl on a peak 2.25 miles southwest of Ashcamp, (Carey, 2004). Groundwater flow is primarily through shallow stress-relief fractures, rather than through primary porosity and permeability. Well yields are usually sufficient for domestic water supplies and range from one to several gallons per minute (gpm) when larger fractures are encountered. High-yield municipal or industrial supply wells are rare. Springs tend to have low flows and are usually perched on impermeable shales. Large-flow, base-level springs are rare. The Eastern Coal Field exhibits the median hydrogeologic sensitivity in the state and is rated as a "3."

#### Land Use

Land use is an important consideration regarding potential impacts to groundwater quality (Figure 4). Approximately 0.8 % of the surface area in BMU 5 is urban, 0.4 % is agricultural (row crop or pasture), 2.8% barren and 96 % is forest (Pierce, 2013). In order to simplify the

map, forest types are combined, lakes and reservoirs are combined and agriculture, pasture and grasslands are also combined. Coal mining has been very active during the last six years in BMU 5, according to the Kentucky Coal Association and Kentucky Geological Survey (2011). Pike and Letcher Counties are two primary coal-producing counties and coal mining began in the basin in the early 1900's with the Elkhorn Coal seam being a favorite coal. Table 1 illustrates potential nonpoint source impacts to groundwater from varying land use.

Land Use	% of BMU 5 Study Area	Potential Contaminants
Agriculture, including row crop production, livestock grazing, 0.4 fuel/pesticide storage		Pesticides, nutrients (esp. nitrate-n), salts/chloride, volatile organics, bacteria
Urban/Developed	0.8	Pesticides, volatile organics, chlorides
Forested, including logging, silviculture	96	Metals, pesticides, nutrients, sediment, pH
Barren Land/Mining	2.8	Metals, sediment, pH

Table 1, Land Use and Potential Nonpoint Source Contaminants, (Pierce, 2012)

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 Big Sandy River and utilize the alluvial aquifer, as shown in Figure 4. Public water systems that use groundwater service 226,757 people in BMU 5 and they are shown in Table 2.



Figure 5, Land Use in the BMU-5 Study Area

Public Water System	County	Population Served
South Shore Water Works, Inc.	Greenup	6,189
Greenup Water Department	Greenup	11,535
Worthington Municipal Department	Greenup	2,064
Russell Water Works	Greenup	7,425
Ashland Water Works	Boyd	44,402
Olive Hill Municipal Water Works	Carter	7,752
Grayson Utility Commission	Carter	12,275
Rattlesnake Ridge Water District	Elliott	11,720
Sandy Hook Water District	Elliott	3,564
Louisa Water Department	Lawrence	7,511
Martin County Water District	Martin	10,395
Paintsville Municipal Water Works	Johnson	19,587
Prestonsburg City Utilities	Floyd	21,512
Southern Water and Sewer District	Floyd	22,480
Francis Water Company	Floyd	965
Pikeville Water Department	Pike	11,589
Knott Co. Water and Sewer District	Knott	324
Wheelwright Utilities Commission	Floyd	1,040
Mountain Water District	Pike	20,092
Elkhorn City Water Department	Pike	1,366
Jenkins Water System	Letcher	2,970
Total Users		226,757

Table 2, Public Water Systems in BMU 5, (U.S. EPA, 2011)

## **Groundwater Use**

purposes. Additionally, groundwater recharge provides water to maintain base flow to surface water streams Groundwater is an important resource in BMU 5, providing private and public drinking water, as well as water for industrial and agricultural after runoff from precipitation events. 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 insignificant. Principal aquifers within the Big Sandy and Tygarts Creek river basins are shown in Table 3.

Geologic Age of Aquifer	Predominant Rock Type	Predominant Sub- Surface Flow	Characteristic of Physiographic Province
Pennsylvanian	Sandstone, siltstone, shale, coal	Fracture	Eastern Coal Field
Mississippian	Limestone, dolostone	Well-developed Conduits and fractures	Mississippian along Pine/Cumberland Mountain
Quaternary	Unconsolidated Sand, silt, gravel	Granular	Big Sandy River Alluvium

Table 3, Simplified Aquifer Characteristics in BMU 5

## **MATERIALS and METHODS**

#### Introduction

Parameters which 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 4. 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 and volatile organic compounds. A referenced stream reach in the study area, Little Pigeon Creek, was used as comparison for the surface water data. Reference values used for comparison of groundwater are from a variety of sources and there is no consensus regarding the appropriateness of comparing ambient

Parameter	Standard	Source/Discussion *
Hydroparameters		
Conductivity	800 µmho	No MCL, SMCL, or HAL; this roughly corresponds to 500 mg/L TDS, which is the SMCL
Hardness	0-17 mg/L = soft	No MCL, SCML, or HAL; scale modified from USDA
(Ca/Mg)	17-120 mg/L = moderate	
	> 120 mg/L = hard	
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	0.110 mg/L	DEP
Nitrate-n	10 mg/L	MCL
Nitrite-n	1 mg/L	MCL
Orthophosphate	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	5	
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 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 4, Parameters and Standards for Comparison (USEPA, 2009)

groundwater quality 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, 2012) 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, 2012) 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 Secondary Maximum Contaminant Level (SMCL) and this usage has been adopted for this report.

	DESCRIPTIVE	STATISTICS		arameters	<mark>s (but Bulk</mark> a	nd Field)					
PARAMETER	START DATE	END DATE	n	MIN	MEDIAN	MAX	MODE				
INORGANICS		•									
Chloride (mg/L)	10/27/1994	07/10/2012	105	0.600	1.9500	16.700	1.50				
Fluoride (mg/L)	04/27/1995	07/10/2012	99	< 0.008	0.0452	0.253	< 0.03				
Sulfate (mg/L)	10/27/1994	07/10/2012	105	1.190	6.4600	69.400	< 5.00				
METALS											
Arsenic (mg/L)	06/03/1998	07/10/2012	121	< 0.00020	< 0.00050	0.00500	< 0.00200				
Barium (mg/L)	06/03/1998	07/10/2012	121	0.00400	0.02050	0.07600	0.02000				
Cadmium (mg/L)	06/03/1998	07/10/2012	121	< 0.00020	< 0.00040	0.00100	< 0.00040				
Chromium (mg/L)	06/03/1998	07/10/2012	121	< 0.00020	< 0.00050	0.00500	< 0.00100				
Copper (mg/L) Iron (mg/L)	06/03/1998	07/10/2012	121	< 0.00050	< 0.00100	0.00494	< 0.00050				
Lead (mg/L)	07/14/1995 06/03/1998	07/10/2012 07/10/2012	122 121	< 0.00100 < 0.00020	< 0.05000 < 0.00100	2.30000	< 0.01000				
Manganese (mg/L)	06/03/1998	07/10/2012	121	< 0.00020	0.00223	0.23200	< 0.00020				
Manganese (mg/L)	06/03/1998	07/10/2012	121	< 0.00002	< 0.000223	0.00005	< 0.00005				
Selenium (mg/L)	06/03/1998	07/10/2012	121	< 0.00050	< 0.00080	< 0.00200	< 0.00200				
NUTRIENTO											
NUTRIENTS Ammonia-N (NH <sub>3</sub> -N) (mg/L)	04/27/1995	07/10/2012	135	< 0.010	< 0.025	0.110	< 0.025				
Ammonia-N (NH₃-N) (mg/L) Nitrate-N (NO₃-N) (mg/L)	04/27/1995	07/10/2012	135	< 0.010	< 0.025 0.270	1.540	< 0.025				
Nitrite-N (NO <sub>2</sub> -N) (mg/L)	04/27/1995	07/10/2012	141	< 0.004	< 0.010	< 0.030	< 0.030				
Orthophosphate-P (PO₄-P) (mg/L)	04/27/1995	07/10/2012	141	< 0.003	0.017	0.103	< 0.025				
Phosphorus, Total (mg/L)	10/27/1994	07/10/2012	86	< 0.005	0.012	0.103	< 0.020				
PATHOGENS		T	1	I							
E. coli	NA	NA	NA	NA	NA	NA	NA				
PESTICIDES											
Acetochlor (mg/L)	05/20/1997	07/10/2012	126	< 0.00002	< 0.00004	< 0.000052	< 0.00004				
Alachlor (mg/L)	04/27/1995	07/10/2012	142	< 0.00002	< 0.00004	< 0.00006	< 0.00004				
Atrazine, Total (mg/L)	04/27/1995	07/10/2012	142	< 0.00002	< 0.00004	0.00030	< 0.00004				
Cyanazine (mg/L)	04/27/1995	07/10/2012	136	< 0.00002	< 0.00004	< 0.00010	< 0.00004				
Metolachlor (mg/L)	04/27/1995	07/10/2012	142	< 0.00002	< 0.00004	< 0.00020	< 0.00004				
Simazine (mg/L)	04/27/1995	07/10/2012	136	< 0.00002	< 0.00004	< 0.00030	< 0.00004				
RESIDUES											
RESIDUES Total Dissolved Solids (mg/L)	10/27/1994	07/10/2012	105	< 10	78	470	-				
	10/27/1994 10/27/1994	07/10/2012 07/10/2012	105 104	< 10 < 1	78 < 2	470 62	-				
Total Dissolved Solids (mg/L) Total Suspended Solids (mg/L)	10/27/1994						-				
Total Dissolved Solids (mg/L) Total Suspended Solids (mg/L) SEMI-VOLATILE ORGANIC COMPOUND	10/27/1994 S	07/10/2012	104	< 1	<2	62	- < 1.5				
Total Dissolved Solids (mg/L) Total Suspended Solids (mg/L) SEMI-VOLATILE ORGANIC COMPOUND Anthracene (mg/L)	10/27/1994 0S 07/08/2003	07/10/2012	104 66	< 0.00002	< 0.0000421	62 < 0.0000556	- < 1.5 < 0.00005				
Total Dissolved Solids (mg/L) Total Suspended Solids (mg/L) SEMI-VOLATILE ORGANIC COMPOUND Anthracene (mg/L) Benz(a)anthracene (mg/L)	10/27/1994 <b>VS</b> 07/08/2003 07/08/2003	07/10/2012 07/10/2012 07/10/2012	104 66 66	< 1 < 0.00002 < 0.00002	< 2 < 0.0000421 < 0.0000421	62 < 0.0000556 < 0.0000556	- < 1.5 < 0.00005 < 0.00005				
Total Dissolved Solids (mg/L) Total Suspended Solids (mg/L) SEMI-VOLATILE ORGANIC COMPOUNE Anthracene (mg/L) Benz(a)anthracene (mg/L) Benzo(a)pyrene (mg/L)	10/27/1994 05 07/08/2003 07/08/2003 07/08/2003	07/10/2012 07/10/2012 07/10/2012 07/10/2012	104 66 66 66	< 0.00002 < 0.00002 < 0.00002	< 2 < 0.0000421 < 0.0000421 < 0.0000421	62 < 0.0000556 < 0.0000556 < 0.0000556	< 0.00005 < 0.00005 < 0.00005 < 0.00005				
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Total Dissolved Solids (mg/L)         Total Suspended Solids (mg/L)         SEMI-VOLATILE ORGANIC COMPOUND         Anthracene (mg/L)         Benz(a)anthracene (mg/L)         Benzo(a)pyrene (mg/L)         Fluorene (mg/L)         Naphthalene (mg/L)         VOLATILE ORGANIC COMPOUNDS         Benzene (mg/L)         Chlorobenzene (mg/L)         Dichloromethane (mg/L)	10/27/1994 05 07/08/2003 07/08/2003 07/08/2003 07/08/2003 04/12/2000 04/12/2000 04/12/2000 04/12/2000	07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012	104 66 66 66 102 102 102 102	< 0.00002 < 0.00002 < 0.00002 < 0.00002 < 0.00025 < 0.00025 < 0.00025 < 0.00025	< 2 < 0.0000421 < 0.0000421 < 0.0000421 < 0.0000421 < 0.0002500 < 0.0002500 < 0.0002500 < 0.0002500 < 0.0002500	62 < 0.0000556 < 0.0000556 < 0.0001000 < 0.0005000 < 0.000500 < 0.000500 < 0.000500	<ul> <li>&lt; 1.5</li> <li>&lt; 0.00005</li> <li>&lt; 0.00005</li> <li>&lt; 0.00005</li> <li>&lt; 0.00025</li> <li>&lt; 0.00025</li> <li>&lt; 0.00025</li> <li>&lt; 0.00025</li> <li>&lt; 0.00025</li> <li>&lt; 0.00025</li> <li>&lt; 0.00050</li> </ul>				
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Total Dissolved Solids (mg/L)         Total Suspended Solids (mg/L)         SEMI-VOLATILE ORGANIC COMPOUND         Anthracene (mg/L)         Benz(a)anthracene (mg/L)         Benzo(a)pyrene (mg/L)         Fluorene (mg/L)         Naphthalene (mg/L)         VOLATILE ORGANIC COMPOUNDS         Benzene (mg/L)         Chlorobenzene (mg/L)         Dichloromethane (mg/L)	10/27/1994 05 07/08/2003 07/08/2003 07/08/2003 07/08/2003 04/12/2000 04/12/2000 04/12/2000 04/12/2000	07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012	104 66 66 66 102 102 102 102	< 0.00002 < 0.00002 < 0.00002 < 0.00002 < 0.00025 < 0.00025 < 0.00025 < 0.00025	< 2 < 0.0000421 < 0.0000421 < 0.0000421 < 0.0000421 < 0.0002500 < 0.0002500 < 0.0002500 < 0.0002500 < 0.0002500	62 < 0.0000556 < 0.0000556 < 0.0001000 < 0.0005000 < 0.000500 < 0.000500 < 0.000500	- < 0.00005 < 0.00005 < 0.00005 < 0.00005 < 0.00025 < 0.00025 < 0.00025 < 0.00025 < 0.00025 < 0.00025 < 0.00025 < 0.00050				
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Total Dissolved Solids (mg/L)         Total Suspended Solids (mg/L)         SEMI-VOLATILE ORGANIC COMPOUND         Anthracene (mg/L)         Benzo(a)anthracene (mg/L)         Fluorene (mg/L)         Fluorene (mg/L)         Naphthalene (mg/L)         VOLATILE ORGANIC COMPOUNDS         Benzene (mg/L)         Chlorobenzene (mg/L)         Dichloromethane (mg/L)         Ethylbenzene (mg/L)         MTBE (mg/L)         Tetrachloroethane (1,1,1,2-) (mg/L)	10/27/1994 05 07/08/2003 07/08/2003 07/08/2003 07/08/2003 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000	07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012	104 66 66 66 102 102 102 102 102 102 102 102	< 0.00002 < 0.00002 < 0.00002 < 0.00002 < 0.00025 < 0.00025 < 0.00025 < 0.00025 < 0.00025 < 0.00025 < 0.00025 < 0.00025	< 2 < 0.0000421 < 0.0000421 < 0.0000421 < 0.0002500 < 0.0002500 < 0.0002500 < 0.0002500 < 0.0005000 < 0.0005000 < 0.0005000 < 0.0005000 < 0.0002500	62 < 0.0000556 < 0.0000556 < 0.0000506 < 0.000500 < 0.000500 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050	<ul> <li></li></ul>				
Total Dissolved Solids (mg/L)         Total Suspended Solids (mg/L)         SEMI-VOLATILE ORGANIC COMPOUND         Anthracene (mg/L)         Benzo(a)pyrene (mg/L)         Fluorene (mg/L)         Naphthalene (mg/L)         VOLATILE ORGANIC COMPOUNDS         Benzene (mg/L)         Dichlorobenzene (mg/L)         Dichloromethane (mg/L)         Ethylbenzene (mg/L)         MTBE (mg/L)         Tetrachloroethane (1,1,1,2-) (mg/L)         Tetrachloroethene (mg/L)	10/27/1994 05 07/08/2003 07/08/2003 07/08/2003 07/08/2003 07/08/2003 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000	07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012	104 66 66 66 102 102 102 102 102 102 102 102	< 0.00002 < 0.00002 < 0.00002 < 0.00002 < 0.00025 < 0.00025	< 2 < 0.0000421 < 0.0000421 < 0.0000421 < 0.0002500 < 0.0002500	62 < 0.0000556 < 0.0000556 < 0.0001000 < 0.000500 < 0.000500 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050	< 0.00005 < 0.00005 < 0.00005 < 0.00005 < 0.00025 < 0.00025 < 0.00025 < 0.00025 < 0.00050 < 0.00025 < 0.00050 < 0.00025 < 0.00025 < 0.00025 < 0.00025				
Total Dissolved Solids (mg/L)         Total Suspended Solids (mg/L)         SEMI-VOLATILE ORGANIC COMPOUNE         Anthracene (mg/L)         Benz(a)anthracene (mg/L)         Benzo(a)pyrene (mg/L)         Fluorene (mg/L)         Naphthalene (mg/L)         VOLATILE ORGANIC COMPOUNDS         Benzene (mg/L)         Chlorobenzene (mg/L)         Dichloromethane (mg/L)         Ethylbenzene (mg/L)         Tetrachloroethane (1,1,1,2-) (mg/L)         Totuene (mg/L)         Toiluene (mg/L)         Trichloroethane (1,1,1-) (mg/L)         Trichloroethene (mg/L)	10/27/1994 05 07/08/2003 07/08/2003 07/08/2003 07/08/2003 07/08/2003 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000	07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012	104 66 66 66 102 102 102 102 102 102 102 102 102 102	< 0.0002 < 0.0002 < 0.0002 < 0.0002 < 0.0002 < 0.00025 < 0.00025	< 2 < 0.0000421 < 0.0000421 < 0.0000421 < 0.00002500 < 0.0002500 < 0.0002500	62 < 0.0000556 < 0.0000556 < 0.0000500 < 0.000500 < 0.000500 < 0.00050 < 0.00050	<ul> <li>-</li> <li>&lt; 0.00005</li> <li>&lt; 0.00005</li> <li>&lt; 0.00025</li> <li>&lt; 0.00025</li> <li>&lt; 0.00025</li> <li>&lt; 0.00025</li> <li>&lt; 0.00050</li> <li>&lt; 0.00025</li> <li>&lt; 0.00025</li></ul>				
Total Dissolved Solids (mg/L)         Total Suspended Solids (mg/L)         SEMI-VOLATILE ORGANIC COMPOUNE         Anthracene (mg/L)         Benzo(a)apyrene (mg/L)         Fluorene (mg/L)         Naphthalene (mg/L)         VOLATILE ORGANIC COMPOUNDS         Benzene (mg/L)         VOLATILE ORGANIC COMPOUNDS         Benzene (mg/L)         Chlorobenzene (mg/L)         Dichloromethane (mg/L)         Ethylbenzene (mg/L)         Tetrachloroethane (1,1,1,2-) (mg/L)         Tetrachloroethane (mg/L)         Toluene (mg/L)         Trichloroethane (1,1,1-) (mg/L)	10/27/1994 05 07/08/2003 07/08/2003 07/08/2003 07/08/2003 07/08/2003 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000 04/12/2000	07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012 07/10/2012	104 66 66 66 102 102 102 102 102 102 102 102 102 102	< 0.00002 < 0.00002 < 0.00002 < 0.00002 < 0.00025 < 0.00025	< 2 < 0.0000421 < 0.0000421 < 0.0000421 < 0.0002500 < 0.0002500	62 < 0.0000556 < 0.0000556 < 0.0001000 < 0.000500 < 0.000500 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050 < 0.00050	<ul> <li>&lt; 0.00005</li> <li>&lt; 0.00005</li> <li>&lt; 0.00005</li> <li>&lt; 0.00005</li> <li>&lt; 0.00005</li> <li>&lt; 0.00025</li> </ul>				

Table 5, Reference Springs Analytical Data Summary in mg/L.

Health Advisory (HA) is defined (U.S.EPA, 2012) 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 Health Advisory Level (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 methyl *tert*-butyl ether (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. Adopting the language used for similar surface water areas, these sites are informally called "reference springs" or "reference reach springs." Unfortunately, such sites are rare and may not truly exist, given that atmospheric deposition from automobiles, power plants and other sources is ubiquitous throughout the Commonwealth. Reference reach springs that represent the least impacted groundwater in the state are nevertheless considered important for comparison. These sites drain forested areas unimpacted by routine surface land uses, such as recent logging, agricultural, industrial, or residential use. References springs include Cameron Spring in Lewis County (located in BMU

5) and two springs outside of this study area: Fred Mullin Spring in Rockcastle County and Nada Spring in Powell County.

Background wells in BMU 5 are virtually non-existent, given that wells are typically installed adjacent to homes, farm areas, or businesses and therefore inherently reflect anthropogenic influences. In addition, wells in BMU 5 usually produce from shallow, unconfined aquifers. Wells completely cased through shallower aquifers and that produce from deep, confined aquifers protected from surface influences could be considered for reference purposes. However, these wells are rare in BMU 5 due to the presence of salt water at relatively shallow depths (Price, 1962).

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 reference reach springs, can help differentiate between anthropogenic and natural sources.

#### **Statistical and Graphical Methods**

Project data were evaluated with summary statistics and summary tables. Summary statistics list simple statistics, including minimum and maximum values along with median and mode values. 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. Some comparisons were made using Box and Whisker plots to show similarities and differences between surface and groundwater samples.

#### **Site Selection**

The Groundwater Section selected sites as close to established surface water sampling sites as possible. Under this approach, a door to door canvas of the area led to the wells that were used. The distribution of sites selected using this method therefore provided biased monitoring sites representative of various land uses, each with characteristic nonpoint source threats, as well as varying aquifer types of differing inherent groundwater sensitivity near known surface water data sites. Public water supplies using groundwater were given preference over private supplies and the study only used domestic source springs and wells that were being used at the time of the original sampling. Wells used on a daily basis was chosen to guarantee that fresh groundwater samples were obtained so that groundwater/surface water interaction could be examined.

Because this study was designed to assess ambient groundwater conditions, those areas near 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 groundwater 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 databases and forwarded to the Ground Water Data Repository at the Kentucky Geological Survey. Site locations are plotted on the Departmental GIS layers maintained by GDA, and the forms are scanned and stored in a database as an indexed electronic image. No personal well or spring owner information is included in this document to help protect the study volunteers from solicitation by commercial businesses.

Sites selected specifically for this nonpoint source study, as well as other sites monitored for other programs included in the data analysis, are listed in Appendix B on the Chain of Custody reports. Quarterly geochemical data were collected and analyzed from 30 groundwater sites and 20 surface water sites for this project. A one time sample was also collected from a spring on Pine Mountain that is used as a water source for a cabin that is used for family retreats and group outings during hunting season. The entire study area consists of approximately 53 square miles.

Statistical comparison was completed on the 24 groundwater sites and 20 surface water sites that are all entirely in the Elkhorn Creek watershed. The statistical comparison was used to contrast the surface water and groundwater in the study basin. This is the first time that the Watershed Management Branch has used statistical analysis to compare both the surface and groundwater within a watershed basin. Since surface water and groundwater are considered conjunctive systems, a proper evaluation of a watershed needs to include the whole hydrologic system to get an accurate analysis of how the hydrology and hydrogeology geochemically interact.

#### **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 <u>Kentucky Ambient Watershed</u> <u>Water Quality Monitoring Standard Operating Procedure Manual</u>, prepared by the Water Quality Branch (2002c). Parameters to be measured, volume required for analysis, container type and preservative are shown on the attached <u>Chain-of-Custody Form (Appendix B)</u>.

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, nitrate-n, nitrite-n, total Kjeldhal nitrogen, total phosphorous and orthophosphate) and/or improper sewage disposal (nitrates, ammonia). Pesticides are measured to determine both rural agriculture and urban domestic and commercial-use impacts on groundwater. Metals are useful to establish rock-groundwater chemistry, local and regional background levels and to determine potential 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 potential point and nonpoint source impacts to groundwater.

Samples for pathogens were only collected at each groundwater site once. Sampling at the sites occurred over two 2-day periods. Because of the short holding time for bacteria (6 hours for E-coli and 24 hours for total coliform), mobile bacteria lab equipment was used so the required holding times could be met by processing and initiating incubation in the field.

The Water Quality Branch study collected surface water samples for pathogens 10 times at each site (Pierce, 2013). Sampling occurred from May to October in 2007 and 2008. Because of the short holding time for bacteria (6 hours for E-coli) McCoy and McCoy Laboratory in Pikeville, arranged to met Division personnel near the collection sites to transport the samples to the lab for processing. Although these data are inadequate to fully characterize the groundwater/surface water geochemistry of the area, it greatly expands the information that was previously available.

All chemical samples collected to meet grant commitments were analyzed by the Environmental Services Branch laboratory (ESBL) according to appropriate U.S.EPA methods. Additional data included in this study are from samples analyzed by ESBL for other groundwater projects, as well as, data from the Watershed Management Branch's mobile lab. 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: hydroparameters (which includes conductivity, hardness and pH), inorganic ions, metals, pesticides, residues, volatile organic compounds and nutrients. The Bulk and Field Parameters summary data are shown in Tables 5 and 6. Sample location summary data are in Tables 7 and 8. A copy of the Chain of Custody form used on the project can be found in Appendix B. Tables 9 through 13 are also used to quantify water quality data.

BMU5 Round 2: SAMPLE SUMMARY - Bulk and Field Parameters (Groundwater)										ater)
			Total	<= 1/2 Std	> 1/2 Std <= Std	Exceed Std	Total	<= 1/2 Std	> 1/2 Std <= Std	Exceed Std
Parameter	Standard	Туре	Number of Samples			Number of Sites				
Conductivity (mmho)	800	SDWR	120	47	64	9	30	15	19	3
Field Conductivity (mmho)	800	SDWR	115	45	61	9	30	16	19	3
Field Temperature (°C)	25	-	115	24	91	0	30	17	30	0
					-		-			
			Total	< 6.5	6.5 - 8.5	> 8.5	Total	< 6.5	6.5 - 8.5	> 8.5
Parameter	Standard	Туре		Number	of Samples		Number of Sites			
pH (SU)	6.5 - 8.5	SDWR	120	14	102	4	30	5	26	1
Field pH (SU)	6.5 - 8.5	SDWR	115	16	98	1	30	6	28	1
				F	[				Г	
			Total	Soft < 17	Moderate 17 - 120	Hard > 120	Total	Soft < 17	Moderate 17 - 120	Hard > 120
Parameter	Standard	Туре		Number	of Samples			Num	ber of Sites	
Total Hardness <sup>1 2</sup> (mg/L)	-	-	120	12	63	45	30	3	20	14
<sup>1</sup> Total Hardness calculated (as equivalent CaCO3 (mg/L)) as Total Hardness = 2.5(mg/L Ca) + 4.1(mg/L Mg) <sup>2</sup> 0 - 17 mg/L = soft, 17 - 120 mg/L = moderate, > 120 mg/L = hard (scale modified from USDA)										
-			-	•	-					

Table 6, Bulk and Field Parameters Data for Groundwater

BMU5 Round 2: DESCRIPTIVE STATISTICS - Bulk and Field Parameters									
PARAMETER	START DATE	END DATE	n	MIN	MEDIAN	МАХ	MODE		
Conductivity (mmho)	05/07/07	04/08/08	120	13.9	435.5	2160	406		
Conductivity, Field (mmho)	05/07/07	04/08/08	115	21	457.5	1796	397		
Hardness, Total (mg/L)	05/07/07	04/08/08	120	0.25419	100.586	615.72	162.88		
pH (SU)	05/07/07	04/08/08	120	5.9	7.345	8.88	7.4		
pH, Field (SU)	05/07/07	04/08/08	115	5.71	7.09	8.56	7.18		
Temperature, Field (°C)	05/07/07	04/08/08	115	6.3	14.8	22	14.3		

Table 7, Bulk and Field Parameters Statistics Data for Groundwater

BMU5 Round 2: SAMPLE SUMMARY - Bulk and Field Parameters (Surface Water)												
			Total	<= 1/2 Std	> 1/2 Std <= Std	Exceed Std	Total	<= 1/2 Std	> 1/2 Std <= Std	Excee d Std		
Parameter	Standard	Туре	Number of Samples				Number of Sites					
Field Conductivity (mmho)	800	SDWR	226	13	41	172	21	3	13	18		
Field Temperature (°C)	25	-	226	88	137	1	21	15	20	1		
			Total	< 6.5	6.5 - 8.5	> 8.5	Total	< 6.5	6.5 - 8.5	> 8.5		
Parameter	Standard	Туре	Number of Samples					Number of Sites				
Field pH (SU)	6.5 - 8.5	SDWR	226	0	224	2	21	0	20	2		
						[						
			Total	Soft < 17	Moderate 17 - 120	Hard > 120	Total	Soft < 17	Moderate 17 - 120	Hard > 120		
Parameter	Standard	Туре	Number of Samples			Number of Sites						
Total Hardness <sup>1 2</sup> (mg/L)	-	-	149	0	7	142	15	0	1	14		
<sup>1</sup> Total Hardness calculated (as <sup>2</sup> 0 - 17 mg/L = soft, 17 - 120 m	•	,				(mg/L Mg)						

Table 8, Bulk and Field Parameters Data for Surface Water

BMU5 Round 2: Descriptive Statistics - Bulk and Field Parameters (Surface Water)									
PARAMETER	START DATE	END DATE	n	MAX	MEDIAN	MIN	MODE		
Conductivity, Field (mmho)	06/04/07	03/04/08	226	2062	1067	121	1130		
Hardness, Total (mg/L)	06/04/07	03/04/08	149	1610	397	57.6	448		
pH, Field (SU)	06/04/07	03/04/08	226	9.0	8.0	7.2	8.1		
Temperature, Field (°C)	06/04/07	03/04/08	226	28	17.8	2.8	9.5		

Table 9, Bulk and Field Parameters Sample Summary for Surface Water

	Total	Non- Detect	<= <sup>1</sup> / <sub>2</sub> Std	> <sup>1</sup> / <sub>2</sub> Std <= Std	Exceed Std	Total	Non- Detect	<= <sup>1</sup> / <sub>2</sub> Std	> <sup>1</sup> / <sub>2</sub> Std <= Std	Exceed Std
Parameter				Samples	olu			lumber o		otu
INORGANICS		1101		Jumpies						
Chloride (mg/L)	120	7	108	1	4	30	4	29	1	1
Fluoride (mg/L)	120	14	106	0	0	30	7	29	0	0
Sulfate (mg/L)	120	14	100	3	3	30	5	23	2	1
METALS	120	10	101	5	5	50	5	21		
Arsenic (mg/L)	120	89	29	2	0	30	25	12	2	0
Barium (mg/L)	120	1	109	10	0	30	25	30	4	0
Cadmium (mg/L)	120	119	109	0	0	30	30	30 1	0	0
Chromium (mg/L)	120	108	12	0	0	30	29	7	0	0
Copper <sup>1</sup> (mg/L)	120	37	83	0	0	30	29	28	0	0
Iron (mg/L)	120	5		17	80	30	20 4	20	8	24
Lead <sup>1</sup> (mg/L)	120		44	2	00 1	30	4 25	8 19	2	24
Manganese (mg/L)	120	73	 29		83	30	25	19		24
		2		6					2	
Mercury (mg/L)	120	115	5	0	0	30	29	2	0	0
Selenium (mg/L)	120	104	16	0	U	30	29	13	U	0
NUTRIENTS				_	L			_		
Ammonia-N (NH₃-N) (mg/L)	120	20	6	5	89	30	8	5	4	23
Nitrate-N (NO <sub>3</sub> -N) (mg/L)	120	79	39	2	0	30	25	18	2	0
Nitrite-N (NO2-N) (mg/L)	120	104	16	0	0	30	30	16	0	0
Orthophosphate-P <sup>2</sup> (PO <sub>4</sub> -P) (mg/L)	120	89	20	9	2	30	28	13	4	1
Phosphorus, Total <sup>3</sup> (mg/L)	120	10	76	24	10	30	5	24	9	4
PATHOGENS										
E. coli	20	0	0	0	6 <sup>2</sup>	20	0	0	0	6 <sup>2</sup>
PESTICIDES	-		-			-				
Acetochlor (mg/L)	120	120	0	0	0	30	30	0	0	0
			1	0	0			1	0	0
Alachlor (mg/L)	120	119			-	30	30			-
Atrazine, Total (mg/L)	120	119	1	0	0	30	30	1	0	0
Cyanazine (mg/L)	120	120	0	0	0	30	30	0	0	0
Metolachlor (mg/L)	120	120	0	0	0	30	30	0	0	0
Simazine (mg/L)	120	120	0	0	0	30	30	0	0	0
RESIDUES										
Total Dissolved Solids (mg/L)	120	0	52	63	5	30	0	27	30	4
Total Suspended Solids <sup>₄</sup> (mg/L)	120	28	75	15	2	30	16	27	7	2
SEMI-VOLATILE ORGANIC COMPOU	NDS									
Anthracene (mg/L)	120	120	0	0	0	30	30	0	0	0
Benz(a)anthracene (mg/L)	120	119	0	0	1	30	30	0	0	1
Benzo(a)pyrene (mg/L)	120	118	2	0	0	30	30	2	0	0
Fluorene (mg/L)	120	120	0	0	0	30	30	0	0	0
Naphthalene (mg/L)	120	120	0	0	0	30	30	0	0	0
				-				-		
VOLATILE ORGANIC COMPOUNDS				-	-			-	-	
Benzene (mg/L)	120	120	0	0	0	30	30	0	0	0
Chlorobenzene (mg/L)	120	119	1	0	0	30	30	1	0	0
Dichloromethane (mg/L)	120	120	0	0	0	30	30	0	0	0
Ethylbenzene (mg/L)	120	120	0	0	0	30	30	0	0	0
MTBE (mg/L)	120	119	1	0	0	30	30	1	0	0
Tetrachloroethane (1,1,1,2-) (mg/L)	120	120	0	0	0	30	30	0	0	0
Tetrachloroethene (mg/L)	120	120	0	0	0	30	30	0	0	0
Toluene (mg/L)	120	120	0	0	0	30	30	0	0	0
Trichloroethane (1,1,1-) (mg/L)	120	120	0	0	0	30	30	0	0	0
Trichloroethene (mg/L)	120	120	0	0	0	30	30	0	0	0
Vinyl Chloride	120	120	0	0	0	30	30	0	0	0
Xylenes, Total (mg/L)	120	120	0	0	0	30	30	0	0	0
Lead and copper are regulated by a Tre	atment Tec	hnique that r	equires svs	tems to contro	I the corrosive	ness of the	ir water. If m	ore than 10	% of tap water	
samples exceed the action level, water s										

<sup>3</sup> Total Phosphorus is not currently regulated, but EPA water quality criteria state that phosphates should not exceed 0.100 mg/L in streams or flowing waters not discharging into lakes or reservoirs to control algal growth.

<sup>4</sup> TSS: Currently no water quality standard for TSS; some KPDES permits use 35 mg/L monthly average

Table 10, Groundwater Sample Results Summary
BMU5 Rou	nd 2: DESCR	<b>IPTIVE ST</b>	ATIS	STICS (Gr	oundwa	ter)	
PARAMETER	START DATE	END DATE	n	MIN	MEDIAN	МАХ	MODE
<b>BULK &amp; FIELD PARAMETERS</b>							
Conductivity (µmho)	05/07/2007	04/08/2008	120	13.9	435.5	2160	406
Conductivity, Field (µmho)	05/07/2007	04/08/2008	115	21	457.5	1796	397
Hardness, Total (mg/L)	05/07/2007	04/08/2008	120	0.25419	100.586	615.72	162.88
pH (SU)	05/07/2007	04/08/2008	120	5.9	7.345	8.88	7.4
pH, Field (SU)	05/07/2007	04/08/2008	115	5.71	7.09	8.56	7.18
Temperature, Field (°C)	05/07/2007	04/08/2008	115	6.3	14.8	22	14.3
INORGANICS							
Chloride (mg/L)	05/07/2007	04/08/2008	120	< 0.3	24.05	549	< 1
Fluoride (mg/L)	05/07/2007	04/08/2008	120	< 0.01	0.13	0.596	< 0.025
Sulfate (mg/L)	05/07/2007	04/08/2008	120	< 0.3	11.35	316	< 0.5
METALS							
Arsenic (mg/L)	05/07/2007	04/08/2008	120	< 0.0002	< 0.0002	0.00508	< 0.0002
Barium (mg/L)	05/07/2007	04/08/2008	120	< 0.0005	0.5205	1.24	-
Cadmium (mg/L)	05/07/2007	04/08/2008	120	< 0.0004	< 0.0004	0.00145	< 0.0004
Chromium (mg/L)	05/07/2007	04/08/2008	120	< 0.0002	< 0.0002	0.00438	< 0.0002
Copper (mg/L)	05/07/2007	04/08/2008	120	< 0.0005	0.00229	0.182	< 0.001
Iron (mg/L)	05/07/2007	04/08/2008	120	< 0.01	0.874	23.8	< 0.02
Lead (mg/L)	05/07/2007	04/08/2008	120	< 0.0002	< 0.0005	0.0878	< 0.0002
Manganese (mg/L)	05/07/2007	04/08/2008	120	< 0.001	0.104	6.32	-
Mercury (mg/L)	05/07/2007	04/08/2008	120	< 0.00005	< 0.00005	0.00065	< 0.00005
Selenium (mg/L)	05/07/2007	04/08/2008	120	< 0.0005	< 0.0005	0.00882	< 0.0005
NUTRIENTS							
Ammonia-N (NH₃-N) (mg/L)	05/07/2007	04/08/2008	120	< 0.025	0.38	1.28	< 0.025
Nitrate-N (NO <sub>3</sub> -N) (mg/L)	05/07/2007	04/08/2008	120	< 0.01	< 0.01	9.63	< 0.01
Nitrite-N (NO <sub>2</sub> -N) (mg/L)	05/07/2007	04/08/2008	120	< 0.01	< 0.01	< 1	< 0.01
Orthophosphate-P (PO₄-P) (mg/L)	05/07/2007	04/08/2008	120	< 0.015	< 0.025	< 2.5	< 0.025
Phosphorus, Total (mg/L)	05/07/2007	04/08/2008	120	< 0.01	0.1025	0.606	< 0.01
PATHOGENS							
E. coli							
RESIDUES							
Total Dissolved Solids (mg/L)	05/07/2007	04/08/2008	120	78	263	1100	216
Total Suspended Solids (mg/L)	05/07/2007	04/08/2008	120	< 1.5	3	46.5	< 1.5

Table 11, Groundwater Descriptive Statistics Summary

BMU5 Round 2: SAMPLE SUMMARY (Surface Water Samples)												
			Total	Non- Detect ( <mdl⁵)< th=""><th>&lt;= <sup>1</sup>/<sub>2</sub> Std</th><th>&gt; <sup>1</sup>/<sub>2</sub> Std &lt;= Std</th><th>Exceed Std</th><th>Total</th><th>Non- Detect</th><th>&lt;= <sup>1</sup>/<sub>2</sub> Std</th><th>&gt; <sup>1</sup>/<sub>2</sub> Std &lt;= Std</th><th>Exceed Std</th></mdl⁵)<>	<= <sup>1</sup> / <sub>2</sub> Std	> <sup>1</sup> / <sub>2</sub> Std <= Std	Exceed Std	Total	Non- Detect	<= <sup>1</sup> / <sub>2</sub> Std	> <sup>1</sup> / <sub>2</sub> Std <= Std	Exceed Std
Parameter	Standard	Туре		Nun	nber of S	amples			N	umber of	Sites	
INORGANICS												
Chloride (mg/L)	250	SDWR	149	0	149	0	0	15	0	15	0	0
Fluoride (mg/L)	4	MCL	149	1	148	0	0	15	1	15	0	0
Sulfate (mg/L)	250	SDWR	149	0	8	36	105	15	0	2	13	13
METALS											<u> </u>	
Arsenic (mg/L)	0.01	MCL	149	24	123	2	0	15	13	15	2	0
Barium (mg/L)	2	MCL	149	0	149	0	0	15	0	15	0	0
Cadmium (mg/L)	0.005	MCL	149	149	0	0	0	15	15	0	0	0
Chromium (mg/L)	0.1	MCL	149	53	96	0	0	15	15	15	0	0
Copper <sup>1</sup> (mg/L)	1	SDWR	149	0	149	0	0	15	0	15	0	0
Iron (mg/L)	0.3	SDWR	149	3	65	42	39	15	1	14	13	15
Lead <sup>1</sup> (mg/L)	0.015	TT	149	96	48	3	2	15	15	15	3	2
Manganese (mg/L)	0.05	SDWR	149	0	71	28	50	15	0	12	11	15
Mercury (mg/L)	0.002	MCL	149	139	10	0	0	15	15	8	0	0
Selenium (mg/L)	0.05	MCL	149	11	138	0	0	15	4	15	0	0
NUTRIENTS											-	
Ammonia-N (NH <sub>3</sub> -N) (mg/L)	0.11	DEP	155	131	19	3	2	20	20	12	3	2
Nitrate-N (NO <sub>3</sub> -N) (mg/L)	10	MCL	149	2	147	0	0	15	2	15	0	0
Nitrite-N (NO <sub>2</sub> -N) (mg/L)	1	MCL	149	132	17	0	0	15	15	15	0	0
Orthophosphate-P <sup>2</sup> (PO <sub>4</sub> -P) (mg/L) Phosphorus, Total <sup>3</sup>	0.04	Texas	149	148	1	0	0	15	15	1	0	0
(mg/L)	0.1	USGS	155	16	105	15	19	20	14	15	9	11
PATHOGENS												
E. coli	240	CFU/ 100mL	15	7	1	4	15					
RESIDUES				-						-	n	1
Total Dissolved Solids (mg/L)	500	SDWR	152	0	32	83	37	18	0	14	17	15
Total Suspended Solids⁴ (mg/L)	35	KPDES	155	12	106	6	31	20	10	20	6	15

<sup>1</sup> Lead and copper are regulated by a Treatment Technique that requires systems to control the corrosiveness of their water. If more than 10% of tap water samples exceed the action level, water systems must take additional steps (EPA website).

<sup>2</sup> Orthophosphate is not currently regulated, but Texas has a surface water quality standard of 0.04 mg/L.

<sup>3</sup> Total Phosphorus is not currently regulated, but EPA water quality criteria state that phosphates should not exceed 0.100 mg/L in streams or flowing waters not discharging into lakes or reservoirs to control algal growth.

<sup>4</sup> TSS: Currently no water quality standard for TSS; some KPDES permits use 35 mg/L monthly average

 $^{\rm 5}$  MDL is the Minimum Detection Limit for the method based on the dilution factor.

Table 12, Surface Water Data Results Summary

BMU5 Round 2:	DESCRIP		TISTIC urface			ers (but Bulk a	nd Field)
PARAMETER	START DATE	END DATE	n	МАХ	MEDIAN	MIN	MODE
INORGANICS							
Chloride (mg/L)	06/04/2007	03/04/2008	149	65.5	21.1	1.91	20.6
Fluoride (mg/L)	06/04/2007	03/04/2008	149	0.32	0.173	0.0412	0.179
Sulfate (mg/L)	06/04/2007	03/04/2008	149	1040	322	10.3	349
METALS							
Arsenic (mg/L)	06/04/2007	03/04/2008	149	< 0.5	0.000518	0.000209	< 0.5
Barium (mg/L)	06/04/2007	03/04/2008	149	0.15	0.0631	0.0304	0.0437
Cadmium (mg/L)	06/04/2007	03/04/2008	149	< 0.8	< 0.8	< 0.8	< 0.8
Chromium (mg/L)	06/04/2007	03/04/2008	149	< 1	0.00115	0.000202	< 0.5
Copper (mg/L)	06/04/2007	03/04/2008	149	0.0298	0.00155	0.000506	0.00138
Iron (mg/L)	06/04/2007	03/04/2008	149	8.78	0.16	0.0055	< 0.02
Lead (mg/L)	06/04/2007	03/04/2008	149	< 0.5	< 0.5	0.000201	< 0.5
Manganese (mg/L)	06/04/2007	03/04/2008	149	2.21	0.026	0.00287	0.0196
Mercury (mg/L)	06/04/2007	03/04/2008	149	< 0.5	< 0.5	0.00002	< 0.5
Selenium (mg/L)	06/04/2007	03/04/2008	149	< 1	0.00161	0.000526	< 1
NUTRIENTS							
	00/04/0007	00/04/0000	455	0.470	0.05	0.0055	0.05
Ammonia-N (NH₃-N) (mg/L)	06/04/2007	03/04/2008	155	0.173	< 0.05	0.0255	< 0.05
Nitrate-N (NO <sub>3</sub> -N) (mg/L)	06/04/2007	03/04/2008	149	2.56	0.411	0.0138	1.38
Nitrite-N (NO <sub>2</sub> -N) (mg/L)	06/04/2007	03/04/2008	149	0.163	< 0.02	0.0106	< 0.02
Orthophosphate-P (PO₄-P) (mg/L)	06/04/2007	03/04/2008	149	< 50	< 3	0.0295	< 0.03
Phosphorus, Total (mg/L)	06/04/2007	03/04/2008	155	0.492	0.0215	0.0104	0.02
PATHOGENS							
E. coli							
	·	·	·	·			
RESIDUES							
Total Dissolved Solids (mg/L)	06/04/2007	03/04/2008	152	1530	370	102	252
Total Suspended Solids (mg/L)	06/04/2007	03/03/2008	155	1180	6	< 1.5	< 1.5

Table 13, Surface Water Descriptive Statistics Summary

# Hydroparameters (conductivity, hardness and pH)

Specific conductance, also known as conductivity, is a measurement of the ability of water to conduct electrical current (Hem, 1985) and is reported in microsiemens ( $\mu$ S/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 " $\mu$ mho." Some laboratories report this as "uU/cm". Therefore, 800 mS/cm = 800  $\mu$ mho = 800 uU/cm. There is no MCL or other regulatory standard for conductivity; however, 800  $\mu$ mho **31** 

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.

Higher conductivity values in the study most likely result from shallow saline water zones, calcareous shales and the higher levels of metals like iron and manganese. Conductivity values found in this study are comparable to those found by Carey and others (1993). In this study of 4,859 groundwater analyses throughout the state, an average value of 495 µmho's was found, compared to a median value of 457.5 umho's for the 115 field samples included in the study. The varying geology across the area combined with mined areas with various degrees of reclamation was considered responsible for the extremes encountered in the study. The maximum groundwater field conductivity was 1796 µmhos from a 42 foot deep well, and the minimum was 21 µmho's measured at springs located on Cumberland Mountain, issuing from a very pure quartz sandstone. The maximum surface water field conductivity was 2062 µmhos (found where) and the minimum surface water conductivity reading was 121 µmhos with a sample set median of 1066.5 µmho's and a mode of 1130 µmhos. The median and mode values for surface water conductivity are around 2.5 times higher than groundwater conductivity data for the area. Surface water conductivity is most similar to the one mine spring sampled in the 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 found in this study most likely reflect ambient conditions and are not necessarily indicative of nonpoint source pollution.

### Hardness

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<sub>3</sub> in mg/L derived from: (2.5 x mg/L Ca) + (4.1 x mg/L Mg). Hardness typically causes scaling on water pipes, boilers and in cooking pans, causing problems in the laundry, kitchen and bath. Water with excessive hardness may taste chalky, salty, or metallic, depending on the relative concentrations of various dissolved compounds. On the other hand, very soft water often has a flat, unpleasant taste. Most consumers, therefore, prefer to drink water of moderate hardness.

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 median value for hardness of 100.6 mg/L for groundwater in this study indicates the study area has moderate hardness whereas the mode of 162.9 mg/L is in the hard range. The range for groundwater hardness was from a high of 615.7 mg/L to a low of 0.25 mg/L which is essentially no hardness. This reflects the abundance of calcium and magnesium, mostly derived from

carbonate rich sedimentary rocks such as shales and limestones. This is indicative of ambient conditions, rather than of nonpoint source impacts. Lowest values are in the Eastern Coal Field in which clastic sedimentary rocks, generally low in calcium and magnesium, are dominant.

The median hardness for surface water was 397.1 mg/L while the mode was 447.8 mg/L. The range for surface water hardness was from a high of 1609.8 mg/L to a low of 57.6 mg/L. The mode and the median for surface water are between 2.5 and 4 times higher than the mode and median of groundwater in the area. The hardness for surface water is similar to the one mine spring in the study.

## pН

The pH of a solution is the negative log of the concentration of the hydronium ion, and is essentially a measure of the relative acidity or alkalinity of the solution. The units of pH are dimensionless, 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. The pH of water is an aesthetic standard. Water is considered potable at a SMCL range of 6.5 to 8.5 pH units.

Almost all the groundwater pH values in this study are within the SMCL range of 6.5 to 8.5 pH units. The median field groundwater pH level was 7.09 (mode = 7.18) with a maximum pH of 8.56 and a minimum pH of 5.71. The dataset did include a few wells that extended beyond the SMCL range. Three wells showed a pH below 6.5 for all 4 quarters. One well and one spring had a single quarterly sample with a pH below 6.5. One well showed a pH slightly above 8.5 for all four quarters.

Surface water in the watershed tends to be more basic with a maximum pH of 9.0 and a minimum pH of 7.19. The median pH was 8.0 and the mode was 8.1. Elevated pH is consistent with the higher hardness and total dissolved solids.

# **Inorganic Ions (chloride, fluoride and sulfate)**

# Chloride

Chloride (Cl<sup>-</sup>) 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, 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 brine formations. Further, chloride-rich brines can contaminate freshwater aquifers through improperly cased or abandoned oil wells. Most roads parallel the surface streams so application of road salts are more of a direct threat to surface water in this area and have less potential to threaten groundwater.

The maximum value detected for chloride in groundwater was 549 mg/L and the minimum was 0.568 mg/L. The median chloride value was 24.15 mg/L and the mode was 22.3 mg/L. In general, one site exceeded the SMCL for chloride of 250 mg/L for all four quarters and a total of 5 samples had values that exceeded ½ the SMCL. In Kentucky, high chlorides sometimes occur at shallow depths. Because no specific point source of chloride occurs adjacent to the sites sampled within the study area, the variation observed is probably natural. The highest values found in this study were all in a single well and may be the result of the well being drilled too deep. High chloride values in this well may result from the intrusion of chloride-rich water from underlying aquifers, which as previously noted, can "up well" during over-pumping of shallower aquifers. Lower chloride values, well under the MCL, are distributed throughout the study area.

The chloride median and mode values for surface water are almost identical to the groundwater median and mode with the values being 21.1 mg/L and 20.6 mg/L respectfully. Maximum and minimum values are significantly different with a max of 65.5 mg/L and a min of 1.91 mg/L chloride.

# Fluoride

Fluoride (F) commonly occurs in trace quantities in many soils and rocks, including coal. Fluorite (CaF<sub>2</sub>) is the primary fluorine mineral. Fluoride in the form of hydrogen fluoride also 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 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 (>10 mg/day) 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. "It is generally stated that a dose of 10–20 mg/day (equivalent to 5–10 ppm in the water, for a person who ingests 2 L/day) for at least 10 years is necessary for the development of crippling skeletal fluorosis, but individual variation, variation in nutritional status, and the difficulty of determining water fluoride levels in such situations make it difficult to determine the critical dose" (ATSDR, 2003).

Fluoride showed a narrow range of values, max of 0.596 mg/L and a min of 0.0103 mg/L, for the data. The medians for surface and groundwater are approximately the same at 0.173 mg/L and 0.13mg/L respectfully. 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. This study found the median value was 0.13 mg/L (0.0452 mg/L for reference springs) with a maximum value of 0.596 mg/L (0.253 mg/L for

reference springs) and a minimum of 0.0103 mg/L. 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. None of the MCL violations from the Conrad study are located in the current study area. The area which showed several fluoride MCL violations in the Conrad study are north of the current study area in adjacent counties.

# Sulfate

Sulfate (SO<sub>4</sub>) 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. The maximum value detected in groundwater was 316 mg/L with a median of 11.6 mg/L and a minimum of 0.278 mg/L. Sulfate has an SMCL of 250 mg/L and amounts greater than this impart distasteful odor and taste to the water and commonly have a laxative effect. One site sampled had 3 quarters that exceeded the SMCL and one quarter that was just below the SMCL. This site was a water supply derived from a spring at a 1920's or 1930's mine adit and the average sulfate levels from this site were twice the levels of the next highest site.

Surface water had higher levels of sulfate with a maximum of 1040 mg/L, a median of 322 mg/L and a minimum of 10.3 mg/L. Sulfate appears to be significantly higher in surface water in the

watershed compared to groundwater. The mine spring was the only direct evidence of sulfate from a potential nonpoint source affecting the groundwater in this study. The spring user recently connected to public water and reported that the old mine was going to be re-mined using surface mining methods to recover the substantial amounts of coal left in the pillars. This will mean the un-reclaimed underground mine will be properly reclaimed which may improve water quality in Joe's Branch. Eliminating the air exposure to the coal seam, which is high in ammonium sulfate, and the underclay will minimize oxidation of minerals which pollute surface water. The Elkhorn coal seam tends to be high in ammonium sulfate (Jillson, 1924) with an average of 28.1 pounds of ammonium sulfate per ton. It is possible the elevated sulfate levels in Elkhorn Creek are nonpoint pollution from the many pre-law underground mines in the Elkhorn seam that are found throughout the basin.

Since sulfate naturally occurs in groundwater throughout the study area, this parameter was difficult assess in relationship to nonpoint source pollution. Although coal mining has affected groundwater in some areas of BMU 5, this study does not confirm that mining effects are wide spread. However, data in the Eastern Coal Field are limited and if more sites had been sampled adjacent to historical coal-mining areas, the results might have supported different conclusions.

#### Metals

Groundwater samples were analyzed for a suite of metalloids and metals. These parameters 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 runoff, 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, proved useful.

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 and vanadium were analyzed, detections of these were exceedingly rare and invariably detected at very low levels. Consequently, these results are not presented here.

Westerman, O'dell and Blanset (2013) examined groundwater data for sixteen metals (Al, Ag, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sr, Tl, Zn) and four metalloids (As, B, Se, Sb) by physiographic region. When compared to national median levels only Al, Fe and Mn were elevated. Although some individual wells in each of the physiographic regions had concentrations of constituents that were above their respective human health levels (i.e., MCL, Risk-based Screening Levels), regional levels were below human health-based levels for all constituents, with the possible exception of thallium for which an assessment could not be made. The health-based number for thallium is very close to the MDL used for this study, which makes assessment of this parameter impossible.

# Arsenic

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 metalsmelting/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 can also be found in some chicken feed and subsequent litter (Washington Post, 2012). Arsenic occurs in organic and nonorganic 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 required public water systems to meet the new standard by January 2006.

Arsenic was detected in 52 (approximately 43%) of the 120 samples. The detection limit for arsenic is 0.0005 mg/L. Fifty of these detections were less than half or the MCL and 2 were greater than half the MCL but did not exceed the MCL. The maximum value for groundwater was 0.00508 mg/L with a median of <0.0005 mg/L and the minimum value was 0.0002 mg/L. The values for surface water are nearly identical with a maximum of <0.5 mg/L, a median of 0.0005 mg/L and a minimum value of 0.0002 mg/L.

Fisher (2002) reviewed statewide arsenic data and found that for ambient groundwater about 95% of 4,402 analyses from 930 sites had concentrations 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. 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 5.

Westerman and O'dell (2012) looked at arsenic and chromium in both private wells and public water supplies statewide by region. No detections of arsenic or chromium were found above the MCL in any public water supply sample. A few isolated occurrences of arsenic above MCL were present in the private drinking water well data but no widespread trends indicating that arsenic and chromium play a role in the region's higher than normal cancer rates.

### Barium

Barium occurs most commonly as the mineral barite (BaSO<sub>4</sub>). This naturally occurring mineral occurs in nodules in sedimentary rocks and as a trace element in coal. Barite is particularly common in the Inner Bluegrass of central Kentucky. 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 detected in all of the samples collected. However, most detections were less than half the MCL (110 samples). Ten samples were more than one

half the MCL but still below the MCL. Barium is known to occur naturally and at relatively high levels, often above the MCL, in the Eastern Coal Field (Wunsch, 1991). Barite veins can be occasionally seen in road cuts, highwalls and cliff faces. However, this study did not detect barium at such levels. 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

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.

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 in most people. A portion of the population has problems eliminating excess iron from the body due to a genetic hemochromatosis or iron overload disease. It is most common in people with Scottish, Irish or northern European backgrounds. The April 1998 American Hemochromatosis Society Newsletter indicates in the USA, 1 in 8 people have the single gene

mutation and 1 in 200 have the double gene mutation. They also indicate studies in Ireland show 1 in 4 have the single gene mutation and 1 in 64 have the double gene mutation. Eastern Kentucky and the Bluegrass area both have large populations of persons with Scotch/Irish ancestry. The double gene mutation causes iron to accumulate in body organs causing symptoms such as: chronic fatigue, diabetes, early menopause, impotence, infertility, arthritis/joint replacement, heart disease, hypothyroidism, liver cirrhosis, (with or without a history of alcohol consumption), liver cancer, premature death. Detection and treatment can completely avoid all these symptoms. 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 known to be 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 99.2% of the groundwater samples and 96.97 % of the surface water samples had detections of iron (Figure 21). Eighty groundwater and 56 surface water sampling sites had detections that were above the SMCL. Numerous outliers show the natural variability of this element. Values ranging from non-detect to 23.8 mg/L for groundwater and non-detect to 8.78 for surface water indicates the naturally occurring variations in water quality. The mix of pre and post law mining in the area makes determining whether the cause of the elevated iron is

nonpoint source pollution, or naturally occurring, difficult with the limited sampling done for this study.

# Manganese

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 black and brown 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 occurred in 100% of the groundwater and surface water samples. As shown in Figure 23 eighty-three samples exceeded the health standard, 6 wells were greater than half of the SMCL but less than the SMCL. The remaining 31 samples contained detectable concentrations of manganese but were less than half the SMCL. Eighty nine of the 363 surface water samples exceed the SMCL for manganese. Manganese is generally not a direct indicator of nonpoint source pollution but it is often present in high concentrations in some coal bearing units.

# Mercury

Mercury (Hg) occurs naturally in the Eastern Coal Field as a trace element in coal (USGS, 2002b). Primary nonpoint sources of mercury pollution are via atmospheric deposition from coal-burning power plants and boilers, waste incineration and manufacturing. The MCL for mercury is 0.002 mg/L.

Mercury occurred in 5 of 121 samples. Hg was present in Well 0006-5175 in all four quarters of sampling and one of the detections slightly exceeded the MCL. Well 0006-5175 was one of the two shallow hand dug wells tested in the study and has not been used for a domestic drinking water source for quite a while. Well 0006-5029 had a single detection of Hg and 3 non-detects for the other 3 quarters. Thirty six surface water samples had detections of mercury, none exceeded the MCL.

Although the Division of Water has issued statewide fish consumption advisories for mercury, groundwater in BMU 5 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.

# Pesticides

Six commonly used pesticides are included in this report: atrazine, metolachlor, cyanazine, simazine, acetochlor 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. Other pesticides not mentioned above, were detected in concentrations right at the detection limit, but were at such a low levels it is unsure if they were accurate detections. Detection limits for the pesticides discussed in this report were fairly consistent, depending on the laboratory method used, as shown in Table 14.

Pesticide	Method Detection Limit Used for Samples, mg/L
Atrazine	0.00004 to 0.000047
Metolachlor	0.00004 to 0.000047
Cyanazine	0.00004 to 0.000047
Simazine	0.00004 to 0.000047
Alachlor	0.00004 to 0.000047

Table14, Pesticide Method Detection Limits

# Atrazine

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 commonlyused herbicides in Kentucky. In 1999, when this study began, approximately two million pounds of atrazine were sold in Kentucky (KDA, 2000). Atrazine has an 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).

Atrazine has been most often detected in agricultural areas characterized by row crop production, primarily in the Bluegrass and Mississippian Plateau. Karst springs in particular are vulnerable to pesticide contamination via surface water runoff to sinkholes, sinking streams and macropore 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 occurrence of atrazine is rare in the Eastern Coal Field where row cropping is limited. Atrazine was detected in one sample from a single quarterly sampling event.

### Metolachlor

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 used in Kentucky. Metolachlor was not detected in any of the 120 sample in this study.

# Simazine

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 and was not detected in this study.

# Alachlor

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 noncancerous effects in the liver, spleen and kidneys. A single detection from one quarterly sampling round showed alachlor present very close to the detection limit.

# Acetochlor

Acetochlor is an herbicide that is commonly used on corn. Acetochlor has been named a probable cancer-causing substance and has been shown to reproduction and development

problems in animals. Common trade names for acetochlor include Harness, Keystone, SureStart, Surpass, Volley and Warrant. Acetochlor was not detected in any samples in this study.

#### Cyanazine

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

As mentioned above, Atrazine was detected in 1 of 121 samples analyzed. Alachlor was detected in 1 of the 121 samples. Both were a single detection from the same well (AKGWA number 0001-6116) on the same sampling event and were not detected in the three other quarterly samples collected from that well. Both detections were very close to the detection limit and below any level of concern. Cyanazine, Simazine, Alachlor, Metolachlor and Acetochlor were not detected in any samples. Pesticides were not included as part of the surface water sampling parameter suite.

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

#### **Total Dissolved Solids**

Total Dissolved Solids measures the solids remaining in a water sample filtered through a 1.2  $\mu$ m (micron) filter. According to the World Health Organization (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 (Bruvoid, 1969). 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 six samples from four wells and a mine spring were outliers. The four well exceedances were a single quarter exceedance from different wells. The two quarterly exceedances from the spring (exits from a collapsed mine adit) were taken in the spring and the fall and winter quarter samples were much lower. Seventy five surface water samples exceeded the SMCL of 500 mg/L.

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. These higher values are probably natural, resulting from longer residence times, which allow for more dissolution or the upwelling and mixing of connate waters in these areas, or drainage from pre-law underground mines.

#### **Total Suspended Solids (TSS)**

Total Suspended Solids (TSS), also known as non-filterable residue, are those solids (minerals and organic material) that remain trapped on a 1.2  $\mu$ m 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, decrease **50** 

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 75% of the samples analyzed detected TSS, with about 1.6% of the detections above 35 mg/L. Most values occurred within a narrow range, but outliers were common (Figure 36). In general, TSS is not usually considered a good indicator for nonpoint source pollution in groundwater. However, in some karst systems and mine springs, turbidity and TSS vary with change in flow. Poor management practices associated with activities such as construction and mining can strip vegetation and allow the quick influx of sediment into groundwater via overland flow. Therefore, outliers in the karst on Cumberland Mountain and Eastern Kentucky Coal Field may represent nonpoint source impacts. Typically, given the nature of the activities that introduce sediments into karst groundwater, these impacts are transient. In the Eastern Coal Field wells, high 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. Wells that have growths of iron related bacteria, sulfur related bacteria, and/or slime forming bacteria can have colloidal bacteria fragments and bacteria waste particles that could account for some of the TSS in wells (Cullimore, 1996 & 2005). Thirty five of the surface water samples exceeded the 35 mg/L with 1180 mg/L being the highest detected TSS for surface water.

#### Nutrients

Nutrients included in this report are nitrate-nitrogen, nitrite-nitrogen, ammonia, orthophosphate 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 overabundance of some plant life, such as algal blooms and may also have adverse effects on animal life, because excessive oxygen consumption by plants leaves little available for animal use. In addition to comparisons with various water quality standards, nutrient data from sites in this study were compared to the two reference springs.

# Nitrate-n

Nitrate (NO<sub>3</sub>) 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<sub>3</sub>, or as the equivalent molecular nitrogen-n. Since 1 mg/L of nitrogen equals 4.5 mg/L nitrate; therefore, the drinking water MCL of 10 mg/L nitrate-n equals 45 mg/L nitrate. In this report, results are reported as "nitrate-n."

Excess nitrate consumption by infants can cause methemoglobinemia or "blue-baby" syndrome. Possible adverse adult health effects of nitrate ingestion are under study and are much debated. Nitrate is difficult to remove through ordinary water treatment, its occurrence at levels above the MCL in public water systems cause problems. Table 8 shows the values for nitrate-n varied from a low of non-detect (at <0.03 mg/L) in the Eastern Coal Field to a high of 9.63 mg/L. The median value for the study is <0.03 mg/L for groundwater and 0.411 mg/L for surface water. None of the nitrate-n groundwater or surface water detections exceeded the MCL of 10.0 mg/L. 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, a review of nitrate-n analyses from three reference springs (Table 2) shows a median value of 0.1805 mg/L for these sites. In addition, 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 value of <0.03 mg/L for nitrate-n found in this study is well below background levels and indicates minimal nonpoint source impact on groundwater in all physiographic provinces except the Eastern Coal Field. Figure 40 shows the geographical distribution of nitrate-n values in BMU 5.

# Nitrite (NO<sub>2</sub>)

Nitrite (NO<sub>2</sub>) 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 to occur at very low levels in groundwater samples. Nitrite-n was not detected above the  $\frac{1}{2}$  the MCL in any well. No surface water samples exceeded 0.163 mg/L. The median value found in this study for nitrite was 0.02 mg/L in groundwater and <0.02 mg/L for surface water.

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 was not dependent on land use. In addition, since only 16 one time detections at less than <sup>1</sup>/<sub>2</sub> the standard occurred at 16 sites, further supports the conclusion that nitrite poses no significant problem to nonpoint source groundwater pollution in this study. However, surface water nitrate-n and nitrite-n did show broad nonpoint source impacts.

# Ammonia (NH<sub>3</sub>)

Ammonia (NH<sub>3</sub>) 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 ammoniabased fertilizers. No drinking water standards exist for ammonia; however, the proposed DEP limit for groundwater is 0.110 mg/L.

Reference spring data (Table 2) shows that ammonia 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 44 and 45 seem to indicate impacts from nonpoint source pollution. In this study, ammonia occurred in almost 78% of the groundwater samples, with the range of values being 0.0281 mg/L to 1.28 mg/L for groundwater. The median value for ammonia was 0.38 mg/L. Ammonia only occurred in 4.7 % of the surface water samples with a high of 0.163 mg/L and a median of <0.02. The reason for the high ammonia in groundwater is unknown but it may relate to the naturally occurring organic material present in the coal and shales in the area. Jillson (1924) noted coals from southeastern Kentucky had a higher level of ammonium sulfate than coals from other areas with an average of 28.1 pounds per ton (max was 34.1 and min was 22.4 pounds per ton).

In personal communication, ESB Lab personnel, Eric Scott and Todd Adams on 12/19/12 informed us that ammonium sulfate disassociates into ammonia and sulfate in water producing ammonia gas. The one mine spring in the study had low ammonia suggesting the ammonia probably had degassed before the water made it to the adit. The elevated ammonia in the water wells seems to indicate natural conditions related to ammonium sulfate leaching from the rocks instead of NPS pollution.

#### **Phosphorus**

Two forms of phosphorus are discussed in this report: orthophosphate-p and total phosphorus. Orthophosphate-P (PO<sub>4</sub> -P), or simply "orthophosphate," or "ortho-p," is the final product of the dissociation of phosphoric acid, H<sub>3</sub>PO<sub>4</sub>. 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 in the Bluegrass. Neither orthophosphate nor total phosphorus has a drinking water standard. Orthophosphate data are compared to the Texas surface water quality standard of 0.04 mg/L and total phosphorus data to the surface water limit of 0.1 mg/L used by the USGS.

In natural systems relatively unimpacted from anthropogenic sources, orthophosphate occurs at very low levels. For example, reference reach springs typically were either non-detect for orthop, or had values in the range of <0.003 – 0.103 mg/L. Sensitive laboratory methods were used in this study and the MDL was 0.02 mg/L. Approximately 0.83 % of the samples were detects using this detection limit. This does not appear to indicate possible nonpoint source pollution. Total phosphorus is the sum of organic and inorganic forms of phosphorus. Total phosphorus in reference reach springs was a maximum of 0.103 mg/L and a median of 0.012 mg/L. Total phosphorus was detected in the study area with 7.5% of the samples exceeding 0.1 mg/L recommendation used by the USGS. This may be due to natural phosphate in the rocks or could be possible nonpoint source impacts from animal waste in agricultural areas and human waste and phosphatic detergents from straight pipes, as well as the application of lawn fertilizer.

# **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 **56**  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 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. These and other, physical and chemical characteristics, make clean up of contaminated groundwater is difficult. "Pump and treat" and bioremediation techniques have proven to be useful techniques.

# Benzene

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, 2012). The MCL for benzene is 0.005 mg/L. Benzene was not detected in any groundwater samples in this study.

### Toluene

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, 2012), 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 not detected in groundwater samples collected for this study.

# Ethylbenzene

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 studies groundwater samples.

### **Xylenes**

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, 2012). Xylenes were not detected in any groundwater samples from this study.

# Methyl-tertiary-butyl-ether

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 well sampled contained a trace of MTBE in one of the four quarterly samples. The amount detected was 0.00117 mg/L and the detection limit was 0.001 mg/L. No MTBE occurred in any

other sample in this study. This occurrence may be due to a minor leak, lab contamination, or possibly atmospheric deposition, but because no other volatile organic compounds were detected, any conclusions for this single detection are tentative at best.

#### Pathogens

A one time sample was collected at each well or spring to analyze for E-coli bacteria and total coliform bacteria. Ten sites were not available due to changes since the chemical sampling was performed. Three sites have connected to city water and the wells are no longer accessible. At one site the house had burnt down; one house had the phone disconnected, had the gate locked and the yard was grown up; one shallow hand dug well had been filled in, and at four additional sites the owners could not be contacted during multiple visits and phone calls. The groundwater analyses were performed by Watershed Management Branch personnel using the Branch's mobile bacteria lab using the IDEXX QuantiTray2000<sup>®</sup> most probable number (MPN) method. Surface water bacteria analyses were performed by a contract lab in Pikeville. Statistical evaluations of these data are presented in Table 15 below. Tables with the surface and groundwater data can be found in Appendix C.

A table showing the variability of the surface water data by showing Max, Min, Mode and Median for each of the surface water sites is presented in Appendix C. The groundwater wells that are currently in use and constructed to meet current standards were all free of pathogen except for 4 wells where minor detects of total coliform bacteria or total coliform and E-coli were detected. One unused well had a MPN greater than 2420 colonies per 100 mL of water (the maximum for the method with out dilutions) of total coliform bacteria, but no E-coli were

detected. Another currently used well had a MPN of one (1) both in the sample and in a duplicate taken at the site. Both the original and the duplicate were collected from a swivel faucet in a kitchen, so this low MPN may be from a contaminated faucet or it could be from the well. Another well that had a MPN of 14 for total coliform was also collected from a swivel kitchen faucet. Swivel kitchen faucets are not recommended sampling points unless nothing else is available. A MPN of 45 for total coliform and a MPN of 2 for E-coli were shown for a sample collected from a rarely used outside spigot. The 30+ year old well had never been disinfected. Disinfection of the well and plumbing system should correct this problem.

BMU5 Rour	nd 2: PAT	HOG	ENS S	UMMA	ARY - G	roundw	ater a	nd Surf	ace V	Vater	
Groundwater			Total	<= 1/2 Std	> 1/2 Std <= Std	Exceed Std	Max	Median	Min	Mode	
Parameter	Standard	Туре		Numbe	er of Samples			Colonies p	er 100/m	L,	
E-Coli, Groundwater	<1	SDWR	20	0	0	6 <sup>2</sup>	107 <sup>1</sup>	0	0	0	
Total Coliform, Groundwater	<1	SDWR	20	0	0	8	>2420	0	0	0	
Surfac	e Water		Total	<= 1/2 Std	> 1/2 Std <= Std	Exceed Std	Max	Median	Min	Average	
Parameter	Standard	Туре		Number of Sites				Colonies per 100/mL			
E-coli, Surface Water based on Geomean at each site	Geometric Mean of 130	SDWR	15	1	4	10	875	180	60	300	
E-coli, Surface Water based on percent of samples exceeding 240 col/100 mL at each site	Shall not exceed 240 Col/100 mL in 20 % of samples	SDWR	15	0	0	15					
<sup>1</sup> The E-Coli sample with 107 Colonies / 100mL is from an unused hand dug well. Sample was collected by lowering a bottle on a string into the well. <sup>2</sup> 2 springs with treatment; 1 spring currently unused; 1 minor detect from outside hydrant-owner disinfecting the well; 1 unused hand dug well; 1 buried wellhead – disinfected twice and retested dirty both times, working with well owner to figure out the problem, possibly a bad sanitary seal or a hole corroded through the steel casing. The Groundwater Section reports total coliform bacteria because it is an indication on how well a system is sealed and maintained. A properly functioning and operating well and pump system should have 0 total coliform bacteria. Groundwater raw bacteria data can be found in Appendix C.											

Table15, Summary of Groundwater and Surface Water Pathogens Results

A used well with a buried wellhead became a side project from this study. The initial sample collected during one of the combined BMU-5 and Statewide Pathogens Study sampling trips was contaminated with a MPN of 42 E-coli and 276 total coliform bacteria, which was odd because the family took pride in the fact they disinfected the well once or twice a year. They re-**61** 

disinfected the well and the well was re-sampled during a Statewide Pathogens Study sampling trip and once again showed positive for significant total coliform and E-coli bacteria. Once again they re-disinfected the well and made some corrections to the vent. The last resample included a duplicate and both showed a MPN of 45 & 47 for E-coli and 1733 & >2420 for total coliform bacteria. The well is over 40 years old and the owner is going to dig up the wellhead to check the integrity of the sanitary seal. We have offered to run the downhole camera in the well to see if casing corrosion is the problem if the owner gets the well dug up and the pump and pipe out of the well. A copy of the combination COC and Mobile Lab sheet can be found in Appendix B.

# STATISTICAL COMPARISON of GROUNDWATER to SURFACE WATER

The purpose of this portion of the BMU5 second round study was to explore the relationship between ground water (GW) and surface water (SW) by HUC 12. An overview of the data found that only two HUC 12s had ground water and surface water for the 2007-2008 time period. These HUC 12s were Lower Elkhorn Creek (LEC) and Upper Elkhorn Creek (UEC). Data was grouped into four groups: UEC GW, UEC SW, LEC GW, LEC SW.

The parameters that were common to both surface and ground water were determined and available for this analysis. Analyses were not conducted on parameters with more than 50% of the data as non-detects in 2 or more groups.

To determine if differences between ground and surface water were significant, one-way ANOVA tests were conducted using SAS v. 9.3. Most environmental data are not normally distributed and, therefore, parametric methods are not appropriate for statistical analysis. For the log normally distributed data in this study, nonparametric methods were used. Data were ranked from smallest to largest, and the one-way ANOVA was conducted on the ranks. This method is equivalent to the Kruskal Wallis test. Some parameters were normally distributed: pH, conductivity, and temperature. These parameters were analyzed using one-way ANOVA on the result value. Boxplots were produced for all parameters. A description on how box plots are constructed can be found in Appendix D. The F-value was produced from which the p-value was determined. A p-value of less than 0.05 was considered a significant difference.

The one-way ANOVA, whether conducted on the result value or rank, tells if there are significant differences between groups, but does not indicate which groups differ. The Tukey-Kramer method was used to determine which groups differed. Box plots and summary tables were produced indicating which groups (HUC 12 and GW SW combinations) were significantly different.



<u>Bulk</u>	and	Field	Parameters

WaterSource	HUC12	N Obs	Minimum	Mean	Median	Maximum
GW	LEC	16	6.1350000	7.0368750	7.1150000	8.5000000
	UEC	6	6.5700000	6.9566667	6.9975000	7.1850000
SW	LEC	11	7.7700000	8.0200000	8.0000000	8.2000000
	UEC	5	7.5500000	7.8500000	7.9000000	8.1000000


WaterSource	HUC12	N Obs	Minimum	Mean	Median	Maximum
GW	LEC	16	12.7000000	14.6125000	14.3500000	17.5000000
	UEC	6	12.2000000	14.1583333	14.1750000	15.3500000
SW	LEC	11	9.7500000	17.4500000	18.2000000	19.4000000
	UEC	5	11.0500000	16.9500000	18.3000000	19.2500000



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.9070250	95.3147500	248.0150000
	UEC	6	96.3475000	141.7002500	537.9000000
SW	LEC	11	70.9640000	362.1200000	969.5000000
	UEC	5	253.3150000	440.5600000	627.2600000



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	204.0000000	255.0000000	343.0000000
	UEC	6	191.0000000	259.0000000	473.0000000
SW	LEC	11	242.0000000	385.0000000	716.0000000
	UEC	5	274.0000000	368.0000000	660.0000000



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	1.5000000	2.6250000	23.5000000
	UEC	6	1.5000000	4.8750000	27.0000000
SW	LEC	11	2.5000000	7.0000000	27.7500000
	UEC	5	4.0000000	5,5000000	9.5000000

Significant Differences between Bulk and Field Parameters by Water Source and HUC 12													
Wate	er Source	G	W	S	W	G	W	SW		G	W	SW	
	HUC 12	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC
			p	H*		Conductivity*			Temperature*				
GW	UEC	-		Х	X	-				-			X
GW	LEC			Х	X		-	X	Х				X
SW	UEC	X	Х	-			X	-	Х			•	
SVV	LEC	Х	Х		-	Х	Х		-	Х	Х		-
			Hard	ness			TI	DS		TSS			
GW	UEC	-			X				Х				X
Gw	LEC		-		X		-		Х		-		X
SW	UEC			-	Х			-	Х			-	X
SVV	LEC	X	Х	Х	-	Х	X	Х	-	Х	Х	Х	-

Table16, Significant Defferences between Bulk and Field Parameters by Water Source and HUC 12. \*The one-way ANOVA was used on the result value for these normally distributed parameters.

TSS

# Inorganics

Ammonia



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.0500000	0.3462500	1.2100000
	UEC	6	0.0500000	0.4040000	0.7395000
SW	LEC	11	0.0500000	0.0500000	0.0500000
	UEC	5	0.0500000	0.0500000	0.0500000



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.6140000	16.7500000	100.7500000
	UEC	6	14.2000000	29.6000000	49.5000000
SW	LEC	11	2.6300000	21.2500000	25.9000000
	UEC	5	14.3500000	29.0000000	37.0000000



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.0420000	0.1170000	0.4840000
	UEC	6	0.0846500	0.1347500	0.1620000
SW	LEC	11	0.0534000	0.1772500	0.2240000
	UEC	5	0.0906000	0.1530000	0.2530000





WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.0268500	0.0300000	0.7540000
	UEC	6	0.0300000	0.0300000	0.2145000
SW	LEC	11	0.0751500	0.3622500	0.7755000
	UEC	5	0.1700000	0.4120000	0.6340000



watersource	nuc12	IN OUS	Winninum	Meulan	Maximum
GW	LEC	16	1.0000000	15.7500000	98.3000000
	UEC	6	1.7450000	10.3250000	276.0000000
SW	LEC	11	27.2000000	328.0000000	804.0000000
	UEC	5	154.0000000	299.0000000	381.0000000

	Significant Differences between Inorganics by Water Source and HUC 12																
Wate	Water Source GW SW GW SW GW SW																
	HUC 12	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC
			Amn	nonia			Chlo	oride			Nitr	rate			Sul	fate	
GW	UEC	-	Х			-				-			Х	-			Х
GW	LEC	Х	-	Х	Х		-				-		Х		-		Х
SW	UEC		Х	-				-				-	Х			-	Х
300	LEC		Х		-				-	Х	Х	Х	-	Х	Х	Х	-

Table17, Significant Defferences between Inorganics by Water Source and HUC 12

# <u>Metals</u>



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.000402500	0.000500000	0.0025600
	UEC	6	0.000454000	0.000500000	0.000583000
SW	LEC	11	0.000361000	0.000493500	0.0032900
	UEC	5	0.000383000	0.000560000	0.0010900



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.000585000	0.2360000	1.1000000
	UEC	6	0.0296500	0.6197500	0.7415000
SW	LEC	11	0.0422000	0.0631250	0.0730000
	UEC	5	0.0444000	0.0636000	0.0674500



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.000719000	0.0014300	0.0280500
	UEC	6	0.0013800	0.0063400	0.0233000
SW	LEC	11	0.000801000	0.0014400	0.0017400
	UEC	5	0.0015450	0.0017400	0.0020900



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.0341000	0.5085000	14.3000000
	UEC	6	0.0531000	1.1805000	22.4000000
SW	LEC	11	0.0552500	0.1332500	0.1980000
	UEC	5	0.1320000	0.1910000	0.3860000



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.000331500	0.000500000	0.0034050
	UEC	6	0.000500000	0.000779500	0.0039350
SW	LEC	11	0.0071700	0.5000000	0.5000000
	UEC	5	0.0136000	0.2531700	0.5000000



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.0010900	0.0846225	0.8955000
	UEC	6	0.0051500	0.1752500	0.7475000
SW	LEC	11	0.0082000	0.0183250	0.0789500
	UEC	5	0.0313000	0.0521000	0.0842000



WaterSource	HUC12	N Obs	Minimum	Median	Maximum
GW	LEC	16	0.000815500	0.0010000	0.0010200
	UEC	6	0.0010000	0.0010000	0.0037450
SW	LEC	11	0.000879000	0.0014800	1.0000000
	UEC	5	0.0014300	0.0018200	0.0023550

	Significant Differences between Metals by Water Source and HUC 12																
Wate	Water Source GW SW GW SW GW SW																
	HUC 12	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC	UEC	LEC
			Ars	enic			Bar	ium			Cop	per			Fluc	oride	
GW	UEC	-			Х	-	Х	Х	Х	-				-			Х
GW	LEC		-			Х	-	Х	Х		-				-		
SW	UEC			-		X	X	-	X			-				- 1	X
500	LEC	Х				Х	Х	Х					-	Х		Х	-
	1		Ir	on			Le	ad			Mang	anese			Sele	nium	
GW	UEC		Х			-	Х										
GVV	LEC	X		Х	X	Х	-	Х			-		Х				
SW	UEC		Х	-			Х	-			Х	-					
500	LEC		X		-				-				-				

Indicates that GW and SW had > 50% non detect, and the GW and SW had different detection limits, making ranking and the Tukey –Kramer test inaccurate.

Table18, Significant Defferences between Metals by Water Source and HUC 12.

# 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 5 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.

Table 19 below summarizes the conclusions reached in this study. This table categorizes impacts to groundwater and surface water 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 nitrate-n, fluoride, hardness, total dissolved solids, total suspended solids, conductivity, and pH.

	PARAMETER	NO NPS INFLUENCE ON GROUNDWATER QUALITY	POSSIBLE NPS INFLUENCE ON GROUNDWATER QUALITY	DEFINITE NPS INFLUENCE ON GROUNDWATER QUALITY	NO NPS INFLUENCE ON SURFACE WATER QUALITY	POSSIBLE NPS INFLUENCE ON SURFACE WATER QUALITY	DEFINITE NPS INFLUENCE ON SURFACE WATER QUALITY	DEFINITE NPS INFLUENCE ON WATERSHED WATER QUALITY
Bulk Water	Conductivity		•			•		
Quality	Hardness (Ca/Mg)	•				•		
Parameters	PH		•			•		
	Chloride	•				•		
Inorganic lons	Fluoride	•			•			
	Sulfate		•				•	
	Arsenic	•			•			
	Barium	•			•			
Metals	Iron		•					
	Manganese		•		•			
	Mercury	•						
	Ammonia		•		•			
	Nitrate-n	•					•	
Nutrients	Nitrite-n	•					•	
	Orthophosphate	•						
	Total phosphorous	•				•		
	Alachlor	•			?			
	Atrazine	•			?			
Pesticides	Cyanazine	•			?			
	Metolachlor	•			?			
	Simazine	•			?			
Residues	Total Dissolved Solids		•			•		
Residues	Total Suspended Solids		•			•		
	Benzene	•			?			
Volatile Organic	Ethylbenzene	•			?			
Compounds	Toluene	•			?			
compounds	Xylenes	•			?			
	MTBE	•			?			

? indicates these parameters were not analyzed for surface water samples

Table 19, Nonpoint Source Impacts to Elkhorn Creek Watershed in BMU 5

A "Possible" groundwater 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 pH, sulfate, iron, manganese, conductivity 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.

A "Possible" surface water impact is a tentative category for those parameters that also 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 pH, sulfate, nitrate-n, hardness, chloride, conductivity, total suspended solids and total dissolved solids.

The water quality of the one mine spring which exits from an Elkhorn Coal seam is very similar to water quality in Elkhorn Creek. This pre-law mine is currently leased and a major coal extraction company is looking at the possibility of surface mining the remaining coal. Coal was first discovered in this area in 1750 by Dr. Walker but was not commercially mined until 1904 (Jillson, 1924) and has been a top producing area ever since. The plus or minus 7 foot thick low sulfur Elkhorn Coal seam was a popular coal to mine with 12 active mines in the Jenkins area in 1924 alone.

The underground mines of this period were drift mines that entered the seam from a natural exposure on a valley wall on the down dip portion of the seam. This allows any water that

accumulates in the mine to run out the entrance eliminating the need for pumps and protects the miners from flooding. In the primary author's opinion, it is possible that the elevated hardness, TDS, conductivity, pH, and sulfate are the result of numerous old up dip drift mines draining into tributaries of Elkhorn Creek. Significant coal reserves are left in the pillars of these old mines. Many companies are now re-mining these old works via surface mining techniques so modern reclamation requirements should help improve water quality as more of these old prelaw sites are re-mined and reclaimed.

Most of the homes along the main roads are on a public water supply today with only a few people still on wells. The highest well use is on small side roads with low population density. Lack of sufficient flat land has lead to the use of septic tanks and "straight pipes" in the area for sewage disposal instead of lateral fields. The elevated fluoride and nitrate-n in the stream are most likely related to these "straight pipes" that discharge directly to Elkhorn Creek or its tributaries. These two parameters are significantly higher in the surface water than the groundwater in the watershed. Regional sewer collection systems tied to modern sewer treatment plants would help tremendously but are cost prohibitive at this time.

The elevated TSS levels in Elkhorn Creek are the result of a variety of anthropogenic sources such as logging, failure to maintain adequate vegetative cover, the popularity of trail riding 4 wheelers and 4 wheel drive vehicles, lack of BMP's at construction sites, insufficient vegetative filter strips between roadways and the streams along with a multitude of other sediment producing activities. The most difficult one of these NPS sources to deal with is the highway runoff due to the very narrow valley bottoms and lack of separation between the roadway and the edge of the stream channel.

Surface water geochemical balance problems cannot be resolved by making a blanket assumption that the groundwater's chemical contribution to the hydrologic system will be filtered by interaction with the soil and overburden materials. All filters, whether natural or manmade have a capacity that can be exceeded over time. An example of which are macropores, which can develop over time and bypass a significant portion of the mechanical and biological filtering in the hydrologic system within a watershed.

TMDL problems that occur in surface streams during low flow conditions may be an indication of significant contaminated groundwater contribution to the hydrologic system within basin, because groundwater provides the baseflow of surface streams in low flow conditions. They may also be caused by insufficient groundwater input to dilute surface water point and non-point sources. This may be caused by overuse of the groundwater resource during dry times.

Parameters with "No" significant impacts 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.

Several biases inherent in any sampling program are a concern in the design, implementation and analysis of results. The groundwater sites were chosen near surface water sample site locations that were given to groundwater section personnel so that the nexus between groundwater and surface water could be examined. The varied geology of the area with some of the wells and springs on the toe of a major monocline tends to bias the results. 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 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 unique geologic settings.

Based upon a review of groundwater data from this study in conjunction with surface water data, several areas in BMU 5 will receive additional monitoring in the next cycle of the watershed management system.

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# **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 Big Sandy and Tygarts Creek 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 \$88,000

Budget has been expended in personnel costs approximately equivalent to 1.25 person years

Groundwater Branch has managed the project, including:

- ✓ researching background data
- $\checkmark$  conducting on-site inspections to identify sampling sites
- ✓ collecting groundwater samples
- $\checkmark$  transporting samples to the laboratory
- $\checkmark$  interpreting sample results
- $\checkmark$  preparing maps and reports
- ✓ providing reports to interested parties
- Time codes used for this project were:
  - ✓ Division for Environmental Services: A-38
  - ✓ DOW original time code: NACA131
  - $\checkmark$  DOW new time code:

ORG	2DOW
PBU	BA00
FUND	1200

ACT	MOAM
FUNCTION	B007
PROJECT	NPS9602Z

Budget Summary Table

Category	BMP	Management	Public	Monitoring	Technical	Other	Total
	Implementation	-	Education		Assistance		
Personnel				\$88,000			\$88,000
Supplies							
Equip.							
Travel							
Contract							
Op. Costs							
Other							
Total				\$88,000			\$88,000

# Detailed Budget Table

Budget Categories	Section 319(h)	Non-Federal Match	Total
Personnel	\$55,000	\$33,000	\$88,000
Supplies	\$	\$	\$
Equipment	\$	\$	\$
Travel	\$	\$	\$
Contractual	\$	\$	\$
Operating Costs	\$	\$	\$
Other	\$	\$	\$
TOTAL	\$55,000	\$33,000	\$88,000

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 Project Plan

# Groundwater Impacts to Surface Water Quality in

**Portions of Basin Management Units 5** 

# Prepared by

James S. Webb

Geologist-Registered, Supervisor

Phillip W. O'dell

Groundwater Hydrologist III

Groundwater Branch

Kentucky Division of Water

**Organizations Implementing Project** 

Kentucky Division of Water

Kentucky Division of Environmental Services

**Effective Date** 

May 2006 through December 2010

**Approving Officials** 

Kentucky Division of Water QA Officer:

Kentucky Division of Water Principal Investigator:

Kentucky Division of Water Supervisor:

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### **PROJECT MANAGEMENT ELEMENTS**

### **A3-Distribution List**

Phillip W. O'dell, Division of Water, Groundwater Branch, Groundwater Hydrologist III, Principal Investigator

Peter Goodmann, Division of Water, Groundwater Branch Manager

## A4-Project/Task Organization

### **Key Personnel**

Phillip O'dell will coordinate this project in cooperation with staff of the Groundwater Branch (GWB), Kentucky Division of Water, and with staff at the Division of Environmental Services, which will conduct the laboratory analyses.

GWB staff will scout and select groundwater sources for a year of quarterly sampling. Thirty wells and/or springs will be selected for water quality monitoring. GWB 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. A private lab in Pikeville will be used for bacteriological samples.

Phillip O'dell will be the Principal Investigator and QA Officer. Address: Kentucky Division of Water, Groundwater Branch, 14 Reilly Road, Frankfort, Kentucky 40601, phone (502) 564-3410.
## Laboratory

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

## **Participating Agencies**

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

# A5-Problem Definition/Background

Previous groundwater quantity and quality studies in this area of Kentucky are limited. The stream basins that contain the groundwater sources are listed as "Impaired" and are currently being studied by the Watershed Branch personnel. The GWB has conducted very limited water quality sampling in this part of the Big Sandy Basin in the past. Because groundwater quality has a direct impact on surface water quality in dissected terrain such as this, it is important that the surface and groundwater water quality investigated be investigated together.

## A6-Project/Task Description

As part of its statewide ambient groundwater monitoring program, the Kentucky Division of Water currently conducts quarterly nonpoint source groundwater monitoring at approximately 70 sites across the state, but only four sites in the proposed project area. This project will expand that monitoring effort in portions of Basin Management Unit 5.

The goal of this project is to monitor groundwater and identify the impacts of nonpoint source pollution on these aquifers, which in turn discharge to surface waters, thus having a direct impact on water quality in those streams. 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.

#### **Study Area Description**

The study area is in the far southeastern Eastern Kentucky Coalfield region.

The Eastern Kentucky Coal Field is underlain by sequences of Pennsylvanian sandstones, shales and coal (McDowell, et al, 2001). In addition, narrow alluvial valleys characterize the inhabited areas of the study area. Approximately 70% of the land use in the area is forest (USGS, 2004) and the groundwater throughout the are generally has a moderate inherent sensitivity to contamination (Ray, and others, 1994).

#### Watershed Information

#### **Stream Names**

Elkhorn Creek and it's minor and major tributaries define the study area—this is a groundwater project.

## **Major River Basins**

The project is within Basin Management Unit 5 consists of the area around Elkhorn Creek and it's minor and major tributaries. BMU consists of the Big Sandy River and Tygrarts Creek basins .

## **USGS Hydrologic Unit Number**

Not applicable—this is a groundwater project.

## **Stream Order**

Not applicable—this is a groundwater project.

## **Counties in the Study Area**

Pike and Letcher Counties

## A7-Quality Objectives and Criteria

Groundwater quality data collected from this project will be utilized to complete the following

objectives.

- 1) Determine impacts of nonpoint source pollution on groundwater resources in selected areas of BMU 5.
- 2) Provide guidance for the nonpoint source program to focus future resources relating to nonpoint source pollution of groundwater.

- 3) Support other programs, such as the Wellhead Protection program, the Groundwater Protection Plan program and the Agriculture Water Quality Authority.
- 4) Provide additional data useful for the long-term management of the resource.

#### A8-Special Training/Certification

This section is not applicable because no special training or certification will be required to complete this project in its entirety.

#### **A9-Documents and Records**

All chains-of-custody and lab reports will be maintained in the Groundwater Branch for the required document retention period for the grant. At the end of the required period, documents will be archived by the Groundwater Branch Data Management and Support Section and stored in electronic format in the Kentucky Department for Environmental Protection's Consolidated Groundwater Database and the Kentucky Geological Survey's Groundwater Data Repository.

#### DATA GENERATION AND ACQUISITION ELEMENTS

#### **B1-Sampling Process Design**

#### **Monitoring Approaches**

Monitoring will begin in May 2008 and each site will be sampled quarterly for a year. Specific sample sites will be selected by Division of Water personnel in areas near the Watershed Branches surface water sampling locations. Duplicate samples will be collected randomly from sites 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 and Spring Inventory Forms 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. A Global Positioning System location will also be taken at each location.

#### **Monitoring Station Location Strategy**

Monitoring station locations will be wells and springs that have been identified by field reconnaissance and that have a Watershed Branch surface water sample site near by.

#### **Sample Frequency and Duration**

Water quality sampling will be conducted at thirty wells and springs. These sites will be sampled quarterly for one year beginning in early 2008.

#### Sample Parameters Containerization, Preservation, and Handling

Consistent with other monitoring efforts, samples will be collected at each spring and analyzed for the following: major inorganic ions; nutrients; caffeine; pesticides, including the most commonly used herbicides, insecticides, and fungicides; dissolved and total metals; volatile organic compounds; and total coliform and fecal coliform bacteria. The analytical methods, containers, volumes collected, preservation, and sample transport will be consistent with the Division of Water's <u>Standard Operating Procedures for Nonpoint Source Surface Water Quality</u> <u>Monitoring Projects</u> (1995) and <u>Groundwater Branch Safe Sampling Procedures</u> (2003). 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 <u>Chain-of-Custody Form.</u>

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 (USEPA, 2006). Nutrients (ammonia, nitrate, nitrite, TKN, and orthophosphate) are used to measure impacts from agricultural operations and/or improper sewage disposal (DOW, 2006). Caffeine will be analyzed to better determine the impact of improper sewage disposal on groundwater. Pesticides are measured to determine both rural agriculture and urban domestic- and commercial-use impacts on groundwater (DOW, 2006). Metals are used to establish the rock-groundwater chemistry and establish local and regional backgrounds levels. Volatile organic compounds are a useful indicator of anthropogenic impacts.

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

Bacteria will be sampled by Groundwater Branch, Kentucky Division of Water personnel. Because of logistic considerations, a contract lab in Pikeville will be used to analyze water well and spring samples for total coliform and fecal coliform. Delivery to the nearby contract laboratory will ensure that bacteria samples are analyzed within the required holding times (6 hours for fecal coliform, 24 hours for total coliform). Bacteria will be sampled once during the period of May through October.

#### **B2-Sampling Methods**

Samples will be collected following established Division of Water protocol (1995, 2003).

Whenever possible, sample collection is conducted using the sample container, except for dissolved metals, which is filtered on site from a new 1000 ml container, which is then disposed of after use. At each site, water from the container will be pumped using a peristaltic pump through new (unused) tubing and a new 0.45-micron filter into the sample container.

#### **B3-Sample Handling and Custody**

Sample containers will be labeled with the site name and well 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 <u>Chain-of-Custody Form</u> is attached (See Appendix).

#### **B4-Analytical Methods**

All analytical methods with the exception of field parameters (pH, temperature, conductivity, and estimated discharge and turbidity) will be performed by the Division of Environmental Services laboratory according to the appropriate EPA method. Field parameters will be determined according to the field meters manufacturer's instructions.

#### **B5-Quality Control**

#### **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 is filtered on site from a clean container. Sample collection equipment such as bailers and buckets will be made of Teflon. Pesticide samples will be collected using the sample container. 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 water.

#### **Field Meters**

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

#### **Equipment Calibration**

Field meters will be calibrated in accordance with the manufacturer's instructions.

### 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 (dissolved metals) will be collected in a 1000 ml container, then filtered, and transferred to the appropriate container.

Sample containers will be obtained from approved vendors, and will be new or laboratorydecontaminated 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</u> <u>Monitoring Projects (1995)</u>, and <u>Groundwater Branch Safe Sampling Procedures</u> (2003). 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 in Frankfort.

#### **Duplicates and Blanks**

In order to check reproducibility and provide QA/QC control, one duplicate sample will be

submitted with each batch of samples, regardless of the number of samples in the batch. One blank of deionized water (volatile trip blank) will be submitted for each sampling day. Deionized water used for the volatile trip blanks will be obtained from the Division of Environmental Services. Any significant deviations from duplicate samples will be flagged by Division of Environmental Services and those sites will be resampled or an explanation of the reason for the deviation will be given.

## **Field Measurements**

Conductivity, temperature, and pH will be measured in the field at each site using portable automatic temperature compensating meters, and recorded on the Chain of Custody form. 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. Estimated spring discharge and turbidity will also be recorded on the Chain of Custody form.

#### **B6-Instrument/Equipment Testing, Inspection, and Maintenance**

Division of Environmental Services laboratory personnel will carry out and follow in-house guidelines to ensure that all analytical equipment used is tested and working properly.

#### **B7-Instrument/Equipment Calibration and Frequency**

Division of Environmental Services laboratory personnel will carry out and follow in house guidelines to ensure that all analytical equipment is calibrated to maintain performance within specified limits.

#### **B8-Inspection/Acceptance of Supplies and Consumables**

GWB personnel will be responsible for selecting and ordering all consumable supplies (sample bottles, tubing, filters, etc). Sample containers will be obtained from approved vendors, and will be new or laboratory-decontaminated in accordance with Division of Environmental Services accepted procedures. Deionized water used for blanks and rinsing sampling equipment will be obtained from the Division of Water.

#### **B9-Non-direct Measurements**

Non-direct measurements include a review of any relevant literature that may exist and a review of water quality databases at the Kentucky Geological Survey and the Division of Water. Approximately ten years of water quality data collected quarterly at two sites within the proposed study area are known; other data may also exist.

#### **B10-Data Management**

In the field, sample containers will be labeled with the site name and well identification number, sample collection date and time, analysis requested, preservation method, and collector's initials. In the office, sampling personnel will complete a Chain-of-Custody Record, developed in conjunction with the DES

laboratory, for each sample. In the laboratory, 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. Groundwater Branch and Kentucky Geological Survey personnel will enter the data into the Department for Environmental Protection's Consolidated Groundwater Data Base and the Kentucky Groundwater Data Repository, respectively.

See the Appendix for the Chain of Custody (COC) form.

## ASSESSMENT AND OVERSIGHT ELEMENTS

#### **C1-Assessments and Response Actions**

The Nonpoint Source Section, and/or a Division of Water Quality Assurance Officer (QAO) may review all field and laboratory activities as requested. Any problems identified will be corrected based on recommendations by the QAO.

#### **C2-Reports to Management**

The principal investigator, with assistance from other GWB personnel, will prepare a final report describing all methods and findings of the project. The final report will satisfy final report requirements for the grant.

#### DATA VALIDATION AND USABILITY ELEMENTS

#### **D1-Data Review, Verification, and Validation**

GWB personnel will review all data for completeness and accuracy. Decisions to reject or qualify data

will be made by GWB hydrogeologists with assistance, if necessary, from laboratory and data management personnel.

# **D2-Verification and Validation Methods**

Groundwater Branch hydrogeologists will investigate any unusual data.

# **D3-Reconciliation with User Requirements**

As soon as possible, data will be reviewed by the GWB and if problems are found, the appropriate corrective action will be taken.

#### **REFERENCES CITED**

- 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.
- Kentucky Division of Water, 2003, Groundwater Branch Safe Sampling Procedures, Kentucky Natural Resources and Environmental Protection Cabinet, Frankfort, KY, 23 p.
- McDowell, R. C. (ed.), 2001, The Geology of Kentucky, USGS Professional Paper 1151 H, on-line version 1.0, cited May 2004, <u>http://pubs.usgs.gov/prof/p1151h</u>
- 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
- United States Geological Survey, 2004, GIS land cover data, cited April 2006, http://landcover.usgs.gov/

#### CHAIN OF CUSTODY RECORD ENVIRONMENTAL AND PUBLIC PROTECITON CABINET DIVISION OF WATER - GROUNDWATER BRANCH - NPS BMU-5 Second Round

Site Identification	Collection Date/Time	Field Measurements
Location:	Date:	pH: Conductivity: µmhos
County:	Time:	Torres 00 Oracion flows
AKGWA #:		Temp: °C Spring flow:

Sampler ID:

Division for Envi	ronmental Services Samples		
Analysis Requested	Container Size, Type	Preservation Method	Parameters
	1000 ml Plastic Cubitainer	Cool to 4°C	Bulk Parameters Chloride, Conductivity, Fluoride, Nitrate-N, Nitrite-N, pH, Sulfate, TSS, TDS, Ortho-P
	1000 ml Plastic Cubitainer	H₂SO₄ Cool to 4°C	Nutrients NH₃ / TKN / TOC/Total Phosphorous
	1000 ml Plastic Boston Round	Filtered HNO₃ Cool to 4°C	Dissolved Metals by ICP Plus: Arsenic, Lead, Mercury, Selenium
	1000 ml Plastic Boston Round	HNO₃ Cool to 4°C	Total Metals by ICP plus Arsenic, Lead, Mercury, Selenium
	1000 ml Amber Glass	Cool to 4°C	NP Pesticides Pesticides/PCBs Methods 507/508
	1000 ml Amber Glass	5ml HCl Cool to 4°C	Herbicides/Caffeine
	250 ml HDPE Wide Mouth	Cool to 4°C NO HEAD SPACE	Alkalinity
	Three 40ml Amber Glass	50% HCI Cool to 4°C	VOCs (Trip Blank Required)
	125ml Amber Glass Two - 1000 ml	Cool to 4º C 5ml HCl	Glyphosate Duplicate
	Amber Glass	Cool to 4°C	(only collect if requested)
Signatures: Relinquished by:	Date:	Tim	1 <b>6</b> .
Received by:			
Relinquished by:	Date:	Tim	ne:
Relinquished by:	Date:	Tim	ie:
Received by:			
Sample #: DISCARD SAMPI Comments:	Report #: LES UPON COMPLETION		
	(Expiration Date)		
	(Expiration Date)		
	(Expiration Date)		

Revised 6/18/07

Gro Watei	undwa rshed   Bra	Groundwater Section Watershed Management Branch	ш	coli and	J Total	Chain of C Coliform	Mobi Sustody Analyse	Mobile Laboratory tody (COC)/Observ alyses via Colilert (	Mobile Laboratory Chain of Custody (COC)/Observation Report E. coli and Total Coliform Analyses via Colilert Quanti-tray 2000 MPN Method	eport ray 2000 MF	N Method
Sample Collection	Sample Collection	Sample Identification/Location IDEXX Sample	IDEXX Sample	24 Hour Incubation	ubation			24 Hour F	24 Hour Positive Test		
Date	Time		Preparation Time and Color	Start Time	End Time	Temperature C	Media	# of Lg Cells	# of Sm Cells	(cfu/100 ml)	Total Coliform (cfu/100 ml)
Test Requested	D E. Coli B.	E. Coli Bacteria, 🗆 Total Coliforms Bacteria	sria								
Relinquished By:				Date		Time		Sample(s) Collected By:	By:		(
Received By:			,	Date		Time		Sample Matix:		]	
Relinquished By:				Date				County:			
Received By:			T	Date		Time	,	Project:			Division of
Relinquished By:			T	Date		Time	·	Incident # / Al #:		Ĩ	
Received By:				Date		Time					

Sheet \_\_\_\_\_ of \_\_\_\_\_

# **APPENDIX C. Monitored Site Data**

		BMU5 Roun	
AKGWA Number	Total Coliform Colonies/100 mL	Total Coliform Colonies/100 mL	Sample Site Description, Duplicate Sample Results, Notes and Comments
9000-2650	411	40	Mine spring, black pipe transports water several hundred feet down the hillside. No longer used
0001-1817	0	0	Sampled at well house spigot
0005-5381	0	0	Sampled from freeze proof hydrant on side of garage
0005-5382	276	42	Sampled from spigot by the pressure tank in the well house. Disinfected and resampled twice.
0001-6116	0	0	Sampled from spigot by the pressure tank in the well house
0005-5384	0	0	Sampled from spigot by the pressure tank in the well house
0005-5383	11	0	Sampled from swivel faucet at kitchen sink
0006-5021	0	0	Sampled from freeze proof spigot on the side of the well house
9000-2651	>2420	29	Spring, owner uses a whole house Ultraviolet Light Disinfection system. Forest Pine Mtn. recharge area
0006-5025	0	0	Sampled from kitchen sink faucet. Duplicate run, TC=0, EC=0
0006-5174	>2420	0	Not used as a potable water source, sampled from outside freeze proof faucet.
0000-5177	0	0	Sampled from freeze proof spigot on the side of the well house
0006-5171	0	0	Sampled at kitchen sink
0006-5179	0	0	Sampled at well house faucet
0006-5175	>2420	107	Hand dug well, not used, sampled with bottle on string
0000-7508	45	2	Sampled at outside hydrant on side of garage
0002-8088	0	0	Sampled from freeze proof spigot on the side of the well house
0006-5009	0	0	Sampled from spigot by the pressure tank in the well house
9000-1101	345	1	Spring, Source water for Mother Nature Spring Water Company. Forest Pine Mtn. recharge area
0006-5176	1	0	Sampled from swivel faucet at kitchen sink. Duplicate run, TC=1, EC=0
0006-5173	NS	NS	House burnt down
0006-5178	NS	NS	Shallow hand dug well was filled in
0006-5022	NS	NS	Died, new owner on public water
0006-5023	NS	NS	House appears to be abandoned, gate locked, yard over grown, neighbors have not seen anyone there.
0005-5389	NS	NS	Stopped multiple times on 2 different trips and never found anyone at home
0005-5386	NS	NS	Stopped multiple times on 2 different trips and never found anyone at home
0003-3307	NS	NS	Pump burned out, connected to public water
0000-7937	NS	NS	Pump burned out, connected to public water
0005-5390	NS	NS	Pump burned out, connected to public water

NS= Not Sampled, see description for reason.

		π		n		u .		n	Page
	DOW01032003 DOW01032006			DOW01032007		DOW01032008		032009	
Date	E. Coli	Date	E. Coli	Date	E. Coli	Date	E. Coli	Date	E. Coli
05/15/07	20	05/15/07	15000	05/15/07	420	05/15/07	2800	05/15/07	5700
06/06/07	90	06/05/07	710	06/05/07	4700	06/05/07	9000	06/05/07	82000
06/25/07	3200	06/25/07	720	06/25/07	630	06/25/07	630	06/25/07	390
07/11/07	900	07/11/07	5000	07/11/07	19000	07/11/07	1700	07/11/07	2600
08/21/07	100	•	•	08/21/07	250	08/21/07	2800	08/21/07	230
09/12/07	30	•	•	09/11/07	3200	09/11/07	1800	09/11/07	600
09/25/07	40	•	٠	09/25/07	5900	09/25/07	380	09/25/07	46000
10/09/07	20	•	•	10/08/07	40	10/08/07	40	10/08/07	160
10/23/07	10	•	•	10/23/07	270	10/23/07	110	10/22/07	160
10/30/07	<u>10</u>	10/29/07	40	10/29/07	360	10/29/07	140	10/29/07	4000
05/06/08	250	05/05/08	20	05/05/08	70	05/05/08	60	05/05/08	100
05/22/08	70	05/22/08	230	05/22/08	1400	05/22/08	90	05/22/08	190
06/04/08	230	06/04/08	310	06/04/08	3800	06/04/08	160	06/04/08	4100
06/17/08	40	06/17/08	1400	06/17/08	580	06/17/08	24000	06/17/08	200
07/08/08	220	07/08/08	680	07/08/08	600	07/08/08	490	07/08/08	1900
07/22/08	30	07/21/08	3100	07/21/08	190	07/21/08	460	07/21/08	2800
08/05/08	60	08/05/08	2200	08/05/08	520	08/04/08	370	08/05/08	260
08/20/08	70	08/19/08	280	08/19/08	100	08/19/08	240	08/19/08	100
09/10/08	50	09/09/08	890	09/09/08	5100	09/09/08	4100	09/09/08	1100
09/24/08	40	09/23/08	170	09/23/08	1000	09/23/08	110	09/23/08	50
10/08/08	3500	10/07/08	210	10/07/08	1600	10/07/08	40	10/07/08	1700

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DOW01	032010	DOW01	032011	DOW01	032012	DOW01	032013	DOW01	Page 032014
Date	E. Coli	Date	E. Coli	Date	E. Coli	Date	E. Coli	Date	E. Coli
05/15/07	270	05/15/07	210	05/15/07	130	05/15/07	140	05/15/07	20
06/05/07	380	06/05/07	430	06/06/07	1800	06/05/07	390	06/06/07	100
06/25/07	240	06/25/07	370	06/25/07	790	06/25/07	240	06/25/07	160
07/11/07	36000	07/11/07	3300	07/11/07	2000	07/11/07	1900	07/11/07	7000
08/21/07	180	08/21/07	270	•	•	•	•	08/21/07	690
09/11/07	900	09/12/07	260	•	•	09/12/07	170	09/11/07	700
09/25/07	290	09/25/07	40	•	•	09/25/07	90	09/25/07	270
10/08/07	30	10/09/07	30	•	•	10/09/07	40	10/08/07	6900
10/22/07	<u>10</u>	10/23/07	90	•	•	10/23/07	400	10/22/07	40
10/29/07	50	10/30/07	320	10/30/07	300	10/30/07	<u>10</u>	10/29/07	60
05/05/08	40	05/06/08	280	05/06/08	40	05/06/08	80	05/05/08	70
05/22/08	210	05/22/08	60	05/22/08	350	05/22/08	80	05/22/08	30
06/04/08	180	06/04/08	120	06/04/08	780	06/04/08	90	06/04/08	120
06/17/08	270	06/17/08	170	06/17/08	290	06/17/08	80	06/17/08	290
07/08/08	240	07/08/08	70	07/08/08	350	07/08/08	40	07/08/08	200
07/21/08	30	07/22/08	6500	07/22/08	410	07/22/08	10	07/21/08	60
08/04/08	520	08/05/08	150	08/05/08	1300	08/05/08	50	08/04/08	230
08/19/08	10	08/20/08	430	•	•	08/20/08	<u>10</u>	08/19/08	40
09/09/08	1200	09/10/08	140	09/10/08	680	09/10/08	170	09/09/08	810
09/23/08	30	09/24/08	70	•	•	09/24/08	30	09/23/08	170
10/07/08	20	10/08/08	290	•	•	10/08/08	360	10/07/08	40

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DOW01	032003	DOW01	032006	DOW01	032007	DOW01	032008	DOW01	Page 032009
Date	E. Coli	Date	E. Coli	Date	E. Coli	Date	E. Coli	Date	E. Col
05/15/07	100	05/15/07	710	05/15/07	420	05/15/07	140	05/15/07	310
06/05/07	600	06/06/07	750	06/05/07	580	06/06/07	680	06/05/07	760
06/26/07	700	06/26/07	350	06/26/07	360	06/26/07	340	06/26/07	800
07/11/07	1700	07/11/07	1100	07/11/07	1800	07/11/07	1800	07/11/07	3000
08/21/07	250	08/21/07	350	08/21/07	530	08/21/07	120	08/21/07	900
09/12/07	380	09/11/07	250	09/11/07	630	09/11/07	80	09/11/07	420
09/25/07	90	09/25/07	180	09/25/07	100	09/25/07	40	09/25/07	110
10/09/07	100	10/09/07	<u>10</u>	10/09/07	<u>10</u>	10/09/07	40	10/08/07	100
10/23/07	110	10/22/07	50	10/23/07	350	10/23/07	<u>10</u>	10/22/07	80
10/30/07	240	10/29/07	20	10/30/07	210	10/30/07	60	10/29/07	290
05/06/08	70	05/05/08	70	05/06/08	640	05/06/08	190	05/06/08	50
05/22/08	10	05/22/08	<u>10</u>	05/22/08	20	05/22/08	<u>10</u>	05/22/08	80
06/04/08	20	06/04/08	80	06/04/08	90	06/04/08	70	06/04/08	620
06/17/08	30	06/17/08	60	06/17/08	180	06/17/08	60	06/17/08	170
07/08/08	60	07/08/08	110	07/08/08	120	07/08/08	30	07/08/08	210
07/22/08	90	07/22/08	90	07/22/08	140	07/22/08	140	07/22/08	610
08/05/08	30	08/04/08	60	08/05/08	70	08/05/08	20	08/04/08	100
08/20/08	90	08/19/08	40	08/20/08	40	08/20/08	<u>10</u>	08/19/08	<u>10</u>
09/10/08	310	09/09/08	2200	09/10/08	150	09/10/08	80	09/09/08	120
09/24/08	10	09/23/08	20	09/24/08	10	09/24/08	10	09/23/08	1700
10/08/08	200	10/07/08	10	10/08/08	670	10/08/08	10	10/07/08	180

March 9, 2011

# Table C-1 Groundwater Sites Monitored in BMU 5

		BMU5 Round 2: Groundwater Sample Sites
AKGWA Number	Type of Source	Well or Spring Site Description, Notes and Comments
9000-2650	Mine Spring	Mine spring, Active in the 1920's or 1930's, Elkhorn Coal seam
0001-1817	Drilled Well	Sampled at well house spigot
0005-5381	Drilled Well	Sampled from freeze proof hydrant on side of garage
0005-5382	Drilled Well	Buried wellhead, multiple bad bacteria samples, owner dug up the well and replaced the sanitary seal and foot valve
0001-6116	Drilled Well	Sampled from spigot by the pressure tank in the well house
0005-5384	Drilled Well	Sampled from spigot by the pressure tank in the well house
0005-5383	Drilled Well	Sampled from swivel faucet at kitchen sink
0006-5021	Drilled Well	Sampled from freeze proof spigot on the side of the well house
9000-2651	Spring	Spring, owner uses a whole house Ultraviolet Light Disinfection system. Forest Pine Mtn. recharge area
0006-5025	Drilled Well	Sampled from kitchen sink faucet. Duplicate run, TC=0, EC=0
0006-5174	Drilled Well	Not used as a potable water source, sampled from outside freeze proof faucet.
0000-5177	Drilled Well	Sampled from freeze proof spigot on the side of the well house
0006-5171	Drilled Well	Sampled at kitchen sink
0006-5179	Drilled Well	Sampled at well house faucet
0006-5175	Hand Dug Well	Hand dug well, not used, sampled with bottle on string
0000-7508	Drilled Well	Sampled at outside hydrant on side of garage
0002-8088	Drilled Well	Sampled from freeze proof spigot on the side of the well house
0006-5009	Drilled Well	Sampled from spigot by the pressure tank in the well house
9000-1101	Spring	Sandstone Spring, Source water for Mother Nature Spring Water Co. From near the top of Pine Mtn., Forest recharge area
0006-5176	Drilled Well	Sampled from swivel faucet at kitchen sink. Duplicate run, TC=1, EC=0
0006-5173	Drilled Well	Well above ground with sanitary seal in well house, home and well house burned down before bacteria sampling
0006-5178	Drilled Well	Shallow hand dug well, no pump, peristaltic pump and tubing used for chemical samples, filled in before the bacteria sampling
0006-5022	Drilled Well	Died, new owner on public water
0006-5023	Drilled Well	Well above ground in well house
0005-5389	Drilled Well	Stopped multiple times on 2 different trips and never found anyone at home
0005-5386	Drilled Well	Stopped multiple times on 2 different trips and never found anyone at home
0003-3307	Drilled Well	Pump burned out, connected to public water
0000-7937	Drilled Well	Pump burned out, connected to public water
0005-5390	Drilled Well	Pump burned out, connected to public water

NS= Not Sampled, see description for reason.

## **APPENDIX D. Constructing a Boxplot**

Boxplots are useful to graphically depict the central location (point about which data points in a set will cluster) and the scatter or dispersion of the observations in a data set. This will better convey statistically significant information about a data set to a reader.

To construct a boxplot, first determine the quartiles Q1, Q2 (median) and Q3.

IQR:	inter-quartile range	$Q_3$ - $Q_1$ (the center 50% of the data will lie within this range)
Q3:	75 <sup>th</sup> quartile	75% of the data lies below and 25% of the data lies above this point
Q2:	(median)	50% of the data lies below and 50% of the data lies above this point
$Q_1$ :	25 <sup>th</sup> quartile	25% of the data lies below and 75% of the data lies above this point

The box is then plotted as shown below:



In this example,  $Q_3 = 9$  and  $Q_1 = 3$ , so the IQR = 6. You will note that the rectangular part of the boxplot extends for 6 units. The minimum sample point is 0 units and the maximum is 30 units, so the range of this data set is 30 units. The lines extending from the box are called "whiskers." The upper and lower boundaries for the whiskers are  $Q_3 + 1.5$  IQR and  $Q_1 - 1.5$  IQR, respectively. These boundary areas are called fences, but are not actually drawn in a boxplot. Vertical lines appear at the end of each whisker. These lines represent the smallest value within the lower fence area and the largest value within the upper fence area. Note the presence of two outliers: one at 25 units and one at 30 units. Outliers are observations more than 1.5 IQR from the quartiles, denoted by an open square. Extreme

outliers, observations that lie greater than 3.0 IQR from the quartiles, are denoted by an open square overlain by a red cross.

Outliers are significant because they represent distinct deviations from the bulk of the data points in a set. In water quality data, values are generally skewed to the right, or positively skewed, due to the presence of a few high outliers. Most of the values in this type of data set cluster at or near 0, or some laboratory-defined detection limit. An example of this type of data is shown below:



The nitrate data range from 0.02 mg/L to 12.5 mg/L. The lower and upper quartiles are 0.859 mg/L and 5.330 mg/L, respectively, resulting in an IQR of 4.471 mg/L. Note the 12.5 mg/L is an outlier, as it is greater than 6.7065 mg/L above the upper quartile (1.5 \* 4.471 = 6.7065).

Source: Brosius, 2001