# Appendix A: QA/QC Plan for Expanded Groundwater Monitoring for Nonpoint-Source Pollution Assessment in Basins of the Big Sandy River, Little Sandy River, and Tygarts Creek (Basin Management Unit 5)

## Monitoring Program/Technical Design

**Sampling Design and Strategies.** Approximately 30 previously untested wells and springs in BMU 5 will be selected for sampling. These sample sites will be in addition to other stations currently sampled by the Groundwater Branch. For all selected sites, either a Kentucky Water Well Record or a Kentucky Spring Inventory Form will be placed on record with the Division of Water if one does not already exist. 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 Database and the Kentucky Geological Survey's Kentucky Groundwater Data Repository. The precise latitude and longitude of each site will be determined by GPS measurements.

**Sampling Locations.** Specific sample sites will be chosen after the Division of Water's groundwater database has been reviewed for candidate sites and field inspection has confirmed that the candidate sites are suitable for monitoring.

**Sampling Frequency and Duration.** Quarterly monitoring of the sites will begin in October 2002 and will continue through September 2003.

**Types of Data to Be Collected.** Consistent with other monitoring efforts, samples will be collected at each spring or well and analyzed for some or all of the following: major inorganic ions; nutrients; total organic carbon; pesticides, including the most commonly used herbicides, insecticides, and fungicides; and dissolved and total metals. The analytical methods, containers, volumes collected, preservation, and sample transport will be consistent with the Division of Water's *Standard Operating Procedures for Nonpoint Source Surface Water Quality Monitoring Projects,* prepared by the Water Quality Branch (August 1995). Parameters to be measured, volumes required for analysis, container types, preservatives, holding times, transport conditions, and analytical methods to be used are given on the Chain-of-Custody form.

Where sewage is suspected as a nonpoint-source pollutant, unbleached cotton fabric swatches may be used to detect optical brighteners, the whitening agents used in laundry products and commonly found in sewage (Quinlan, 1987). Bacteria will not be sampled because of logistical considerations. Sampling at numerous sites occurs over a 1- or 2-day period, commonly in remote regions. Because of the short holding time for bacteria (6 hours for fecal coliform, 24 hours for total coliform), we are unable to sample efficiently and regularly collect bacteria samples and comply with the required holding times.

## Chain-of-Custody Procedures

Sample containers will be labeled with the site name and well or spring identification number, sample collection date and time, analysis requested, preservation method, and collector's initials. Sampling personnel will complete a Chain-of-Custody form 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. Parameters to be measured, volumes required for analysis, container types, preservatives, holding times, transport conditions, and analytical methods to be used are given on the accompanying Chain-of-Custody form.

## Quality Control Procedures

**Container and Equipment Decontamination.** 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. Whenever possible, sample collection is conducted using the sample container, except for dissolved metals, which

are filtered on-site. Sample collection equipment such as bailers and buckets will be made of Teflon. Pesticide samples will be collected using the sample container or a stainless steel bailer or bucket, in order to avoid the problem of pesticide adsorption to the sampling device (as is considered to occur with Teflon instruments). Any reusable equipment will be decontaminated by rinsing with a 10 percent 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 percent HCl solution and triple-rinsed with deionized water.

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

## Equipment Calibration

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

## Sample Contamination Prevention

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

Sample containers will be obtained from approved vendors, and will be new or laboratory-decontaminated in accordance with Division of Environmental Services accepted procedures. Sample containers, preservation, and holding time requirements are outlined in the Division of Water's *Standard Operating Procedures for Nonpoint Source Surface Water Quality Monitoring Projects,* prepared by the Water Quality Branch (Kentucky Division of Water, 1995). Necessary preservatives will be added in the field; preservatives for dissolved constituents will be added after field filtration. Samples will be stored in coolers packed with ice for transport to the Division of Environmental Services laboratory.

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

Wells will be purged until conductivity readings stabilize prior to sampling, in order to ensure that groundwater, rather than water that has been standing in the wellbore, is being sampled. Spring samples will be collected as close to the spring resurgence as possible. If inhospitable terrain prohibits spring access, a decontaminated Teflon bucket attached to a new polypropylene rope may be lowered to the spring to collect the sample. Samples for pesticide analysis will be collected using a stainless steel bucket.

## Quality Control Samples

Duplicate samples may be collected periodically to verify reproducibility and provide QA/QC control. Ideally, 10 percent of the samples should be duplicated, and at least one duplicate sample submitted with each batch of samples, regardless of the number of samples in the batch. Blanks of deionized water should also be submitted at least once per quarter. Because of laboratory constraints, however, the frequency with which duplicates and blanks will be submitted will be determined based on QA/QC data from other sampling programs.

## Acceptable Levels of Variance for Duplicate Results

According to Division of Environmental Services' accepted procedures, duplicate analyses will be accepted if they are within 20 percent relative standard deviation. If unacceptable results are found, samples will be analyzed again and field records will be examined to determine the cause.

## 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, 138 p.

Kentucky Division of Water, 2002, Big and Little Sandy River Basin status report: Kentucky Division of Water, 18 p.

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

## CHAIN OF CUSTODY RECORD

**NATURAL RESOURCES AND ENVIRONMENTAL PROTECTION CABINET**
**DIVISION OF WATER - GROUNDWATER BRANCH - Big Sandy/Tygarts Creek 319 Project - Funding Source A-21**

| ***Site Identification*** | ***Collection Date/Time*** | ***Field Measurements*** |
|---|---|---|
| Location: | Date: _____ | pH: _____ Conductivity: _____ µmhos |
| County: | | |
| AKGWA #: | Time: _____ | Temp: _____ °C Spring flow: _____ |

Sampler ID: _____

| **Division for Environmental Services Samples** | | | |
|---|---|---|---|
| **Analysis Requested** | **Container Size, Type** | **Preservation Method** | **Parameters** |
| | 1,000 ml plastic Cubitainer | cool to 4°C | ***Bulk Parameters*** By ICP: chloride, fluoride, nitrate-N, nitrite-N, sulfate, ortho-P plus alkalinity, conductivity, pH, TSS, TDS |
| | 1,000 ml plastic Cubitainer | $H_2SO_4$ cool to 4°C | ***Nutrients:*** $NH_3$/TKN/TOC/total phosphorus |
| | 1,000 ml plastic Boston Round | filtered $HNO_3$ cool to 4°C | ***Dissolved Metals by ICP:*** aluminum, barium, calcium, iron, magnesium, manganese, nickel, potassium, silver, sodium, zinc |
| | 1,000 ml plastic Boston Round | $HNO_3$ cool to 4°C | ***Total Metals by ICP:*** aluminum, barium, calcium, iron, magnesium, manganese, nickel, potassium, silver, sodium, zinc ***By Graphite Furnace:*** arsenic, cadmium, chromium, copper, lead, selenium ***By Cold Vapor Extraction:*** mercury |
| | 1,000 ml amber glass | cool to 4°C | ***N/P Pesticides:*** organochlorine pesticides/PCBs methods 507/508 |
| | 1,000 ml amber glass | cool to 4°C | ***Herbicides:*** method 515.1 |
| | three 40 ml glass | HCl cool to 4°C | ***VOCs:*** (field blank required) |
| | | | |

**COMMENTS:**

**Signatures:**

Relinquished by: _____ Date: _____ Time: _____

Received by: _____

Relinquished by: _____ Date: _____ Time: _____

Received by: _____

Sample #: _____ Report #: _____

***DISCARD SAMPLES UPON COMPLETION***

Revised 5/14/02

**CHAIN OF CUSTODY RECORD**

**NATURAL RESOURCES AND ENVIRONMENTAL PROTECTION CABINET**
**DIVISION OF WATER - GROUNDWATER BRANCH**

**Preparation Date/Time**

Date: _____

Time: _____

**Prepared by:** _____

**Funding Source -**

☐ **A21** General Groundwater ☐ **A39** Monitoring Network

☐ **A42** Pesticides MOA ☐ Other _____

**Site Identification**

**FIELD BLANK FOR:**

Field Sampler ID: _____

| **Division for Environmental Services Samples** | | | |
|---|---|---|---|
| **Analysis Requested** | **Container Size, Type** | **Preservation Method** | **Parameters** |
| | 40 ml glass | 50% HCl<br>cool to 4°C | **VOCs:** |

**Signatures:**

Relinquished by: _____ Date: _____ Time: _____

Received by: _____

Relinquished by: _____ Date: _____ Time: _____

Received by: _____

Relinquished by: _____ Date: _____ Time: _____

Received by: _____

Sample #: _____ Report #: _____

***DISCARD SAMPLES UPON COMPLETION***

Revised 1/22/07