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# **SAMPLING AND ANALYSIS PLAN**

**Prenter Road Hydrologic Evaluation  
Boone County, West Virginia**

**Triad Project No. 04-10-0323**

**Submitted to:**

**West Virginia Department of Environmental Protection  
Division of Mining and Reclamation  
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Charleston, West Virginia 25304**

**Prepared by:**



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**April 2011**

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April 14, 2011

Nick Schaer  
West Virginia Department of Environmental Protection  
Division of Mining and Reclamation  
601 57th Street, S.E.  
Charleston, West Virginia 25304

**Subject:        Sampling and Analysis Plan**  
Prenter Road Hydrologic Evaluation  
Boone County, West Virginia  
Triad Project No. 04-10-0323

Dear Mr. Schaer:

Enclosed is our proposed **Sampling and Analysis Plan (SAP)** for the subject project. This **SAP** has been prepared to comply with requirements of our Scope of Work and Fee Estimate – Revised, dated September 10, 2010. We look forward to your favorable review and approval.

If you have any questions or need additional information, please feel free to contact us.

Sincerely,  
TRIAD ENGINEERING, INC.

Matthew C. Wright, LRS  
Project Geologist

John M. Meeks, PG, LRS  
Project Manager

encl

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## ACRONYM GLOSSARY

AOPC	Area of Potential Concern
Bgs	Below Ground Surface
CCV	Continuing Calibration Verification
COC	Certificate of Completion
CoC	Chain-of-Custody
COPC	Contaminant of Potential Concern
DL	Detection Limit
DOT	Department of Transportation
DQO	Data Quality Objective
FOM	Field Operations Manager
FSP	Field Sampling Plan
GPS	Global Positioning System
HAZWOPER	Hazardous Waste Operation and Emergency Response
HCl	Hydrochloric Acid
HNO <sub>3</sub>	Nitric Acid
IATA	International Air Transportation Association
ICV	Initial Calibration Verification
IDL	Instrument Detection Limit
IDW	Investigative-Derived Waste
IS	Internal Standard
LCS	Laboratory Control Sample
LOQ	Limit of Quantitation
LRS	Licensed Remediation Specialist
MB	Method Blank
MD	Matrix Duplicate
MDL	Method Detection Limit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
OER	Office of Environmental Remediation
OSHA	Occupational Safety and Health Administration
PM	Project Manager
PPE	Personnel Protective Equipment
PQL	Practical Quantitation Limit
QA	Quality Assurance
QAO	Quality Assurance Officer
QAPP	Quality Assurance Project Plan
QC	Quality Control
RBC	Risk-Based Concentration
RL	Reporting Limit
RPD	Relative Percent Difference
RSD	Relative Standard Difference
SAP	Sampling and Analysis Plan
SQL	Sample Quantitation Limit
SW-846	<i>Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3<sup>rd</sup> Edition</i>
Method TO-15	Determination of VOCs in Air Collected In Specially-Prepared Canisters and analyzed by GC/MS
TRIAD	TRIAD ENGINEERING, INC.

USEPA

United States Environmental Protection Agency  
**ACRONYM GLOSSARY-continued**

USGS

United States Geological Survey

VOC

Volatile Organic Compound

VRP

West Virginia Voluntary Remediation Program

VRRP

Voluntary Remediation and Redevelopment Act

WVDEP

West Virginia Department of Environmental Protection

46CSR12

West Virginia Groundwater Quality Standards

## 1.0 PROJECT DESCRIPTION

### 1.1 Introduction

Triad Engineering, Inc. (Triad) has prepared this ***Sampling and Analysis Plan (SAP)*** to guide the collection and analysis of groundwater and surface water samples from domestic wells, public water supplies, streams, and mine-related discharge. Data developed from the analysis of water samples collected in accordance with criteria established in this SAP will be used in the evaluation of groundwater and surface water quality in the Laurel Creek watershed.

This SAP sets forth all field and laboratory methods used to collect samples and analyze water quality, and also establishes field and laboratory quality control procedures employed to ensure that the data is reliable and defensible. The SAP includes information such as sample locations, analytical parameters, standard procedures for sample collection, sample container and preservative requirements, equipment decontamination procedures, documentation requirements, and the number and types of field and laboratory quality control samples.

Sample locations and analytical parameters were designed to detect possible evidence of hydrologic impacts caused, either directly or indirectly, by commercial and industrial land use. This includes coal mining, coal preparation, coal preparation waste disposal, gas drilling and production, and the many commercial activities that are required to support these efforts (e.g., equipment repair and maintenance, metal plating, painting, etc.).

### 1.2 Site Description

The Site includes the drainage area (watershed) of Laurel Creek and its tributaries, including Hopkins Fork, Cold Fork, Little Laurel Creek and Sandlick Creek. The area of interest begins where Laurel Creek joins Big Coal River near Seth, WV, and extends upstream (southward), including the community of Prenter, situated at the junction of Jarrells Creek and Hopkins Fork. The study area is situated within the Williams Mountain, WV and Sylvester, WV, 7.5 minute USGS topographic quadrangles. The location of the Site is depicted on **Figure 1, *Site Location Map***.

### **1.3 Physiography and Geology**

The Site is located within the Appalachian Low Plateau physiographic province, which is characterized by nearly horizontal to gently folded sedimentary bedrock of Pennsylvanian age. The Site is immediately underlain by bedrock of the Kanawha Formation, which is the uppermost formation of the Pottsville Group. The Kanawha Formation ranges up to 1000 feet thick in the vicinity of the Site and is defined as rock units extending downward from the top of the Homewood sandstone to the top of the Upper Nuttall sandstone. The Kanawha Formation is dominated by sandstone (approximately 50%) with lesser amounts siltstone, shale and coal. A number of mineable coals occur in the Kanawha Formation in the vicinity of the Site, including the Coalburg, Powellton, Peerless, No. 2 Gas, and Eagle seams.

Due to the high percentage of sandstone occurring within Kanawha Formation, residual soils that weather from these strata are generally sandy and contain a large percentage of sandstone fragments. Where shale and siltstone are exposed, soils are typically more fine-grained and cohesive, but still tend to contain a large percentage of rock fragments. Along stream valleys, soils are alluvial and colluvial, and typically consist of a fining-upward sequence ranging from boulders and cobbles at the base to silty and clayey sand at the surface. Structurally, bedrock in the area dips at approximately 100 feet per mile (2%), toward the axis of the Coalburg syncline, which crosses the study area from southwest to northeast.

### **1.4 Hydrogeology**

Bedrock within this portion of the Appalachian Low Plateau is fractured as a result of stress relief, where overlying and adjacent rock has been removed through weathering and erosion. Removal of this overburden material causes the underlying rock to expand upward and outward, resulting in horizontal fractures parallel to bedding planes and vertical fractures oriented parallel to valley walls. This fracture system significantly influences the presence and movement of groundwater within bedrock, causing relatively shallow groundwater to move parallel to topography (downward along hillsides and along stream valleys). The underground mining of coal influences deeper groundwater movement, where fracturing above mined seams tends to dewater overlying water-bearing units due to mining-related subsidence that occurs after mining ceases.



## 1.5 Land-Uses

Primary land use in the area is unmanaged forest, followed by surface and underground coal mining, and coal processing and handling. Areas along the primary stream valleys of Laurel Creek, Hopkins Fork, and Sandlick Creek have been developed for residential and commercial use. In general, residential and retail/commercial land uses are confined to the base of major stream valleys. Smaller, yet widespread areas, are used in the production and gathering of natural gas.

## 1.6 Surface Water Hydrology

The Laurel Creek watershed comprises a drainage area of approximately 35,000 acres. For purposes of our evaluation, we have subdivided the larger watershed into eight separate subareas. These subareas have been designated as follows:

- Laurel Creek (A)
- Sandlick Creek
- Hopkins Fork (A)
- Laurel Creek (B)
- Lavinia Fork
- Hopkins Fork (B)
- Prenter
- Hopkins Fork (C)

Each of the subareas is depicted on **Figure 2, Overall Watershed Map**. Our sampling effort, data presentation, and report will be organized in accordance with these designations.

## 2.0 FIELD SAMPLING PLAN (FSP)

### 2.1 Project Organization

The Project Manager (PM) for this project is John M. Meeks, PG, LRS. Decisions regarding project scope, sampling locations, collection equipment, or other project related issues will be made by the PM in consultation with WVDEP representatives.

The Quality Assurance Officer (QAO) for the project is Lydia M. Work, LRS. The level of Quality Assurance (QA), QA procedures, and overall **Quality Assurance Project Plan (QAPP)** development is the responsibility of the QAO. All decisions regarding the **QAPP** and related issues should be made by the QAO.

The Field Operations Manager (FOM) for the project is Matthew C. Wright, LRS. Implementation of the **FSP** and the **QAPP** at the Site is the responsibility of the FOM. Field level decisions not affecting project quality will be made by the FOM. Real time assessment of the **QAPP** and recommendations for revisions will be made by the FOM to the QAO.

### 2.2 Special Training Requirements and Certification

All on-site field sampling personnel will possess experience in the collection, preservation and management of environmental samples. The FOM will have more than five years experience in the overseeing and managing environmental sampling plans.

### 2.3 Sampling Rationale

The field sampling program described in the **FSP** is designed to characterize groundwater and surface water quality within the Laurel Creek watershed. Data from this effort will be used to evaluate potential sources of water quality impact. Analytical parameters and procedures were selected to provide reliable laboratory data for use in this evaluation. Quantitative human health and ecological risk assessment calculations from the data are not planned.

### 2.4 Sample Locations and Analytical Parameters

Preliminary domestic well sample locations are summarized in **Table 1** and shown on **Figure 3** through **Figure 10, Proposed Sample Locations**. These locations may be adjusted by the FOM and PM at the time of sampling if indicated by Site conditions. Also,

additional samples may be collected if requested by residents and if deemed appropriate by the FOM and PM at the time of sampling.

Preliminary surface water sample locations are summarized in **Table 2** and shown on **Figure 2, Overall Watershed Map**. In general, surface water samples will be obtained from the main tributaries to the Laurel Creek watershed.

Preliminary mine-related discharge sample locations are summarized in **Table 3**. Precise locations are not known and therefore, are not shown on **Figure 3** through **Figure 10, Proposed Sample Locations**. However, mine-related discharge samples will be obtained from various potential sources of water-quality degradation within the watershed.

Water samples from all sources will be analyzed for several suites of parameters. Because groundwater is used extensively for domestic consumption, samples will be analyzed for metals referenced in USEPA primary drinking water standards, total and fecal Coliform, and all secondary drinking water standards. Because potential impacts from mining must be evaluated, samples will be analyzed for typical indicators of acid mine drainage (AMD) such as acidity/alkalinity, iron, manganese, aluminum and sulfate. Because potential impacts from historical industrial activities will also be evaluated, samples will be analyzed for volatile organic compounds (VOC) like petroleum and solvents. And finally, because it will be necessary to classify the various types of water encountered across the study area using Piper ternary plots and Stiff diagrams, samples will be analyzed for the major anions and cations such as calcium, magnesium, sodium, potassium, chloride, carbonate and bicarbonate.

## **2.5 Sampling Procedures**

Minimum sample volumes, container types, preservatives, and holding times for field samples are summarized in **Table 5, Field Sample Container Requirements**. These same specifications for QC samples are summarized in **Table 6, Field and Matrix QC Samples**.

### **2.5.1 Groundwater (Domestic Wells)**

During site characterization activities, Triad will collect groundwater samples from domestic wells at approximately 30 locations in the study area. At this time, we anticipate samples will be collected from the following locations:

Laurel Creek (A)

A total of 3 groundwater samples will be collected from domestic wells located in the Laurel Creek (A) subarea.

Sandlick Creek

A total of 6 groundwater samples will be collected from domestic wells located in the Sandlick Creek subarea.

Hopkins Fork (A)

A total of 4 groundwater samples will be collected from domestic wells located in the Hopkins Fork (A) subarea.

Laurel Creek (B)

A total of 3 groundwater samples will be collected from domestic wells located in the Laurel Creek (B) subarea.

Lavinia Fork

A total of 3 groundwater sample will be collected from domestic wells located in the Lavinia Fork subarea.

Hopkins Fork (B)

A total of 3 groundwater samples will be collected from domestic wells located in the Hopkins Fork (B) subarea.

Hopkins Fork (C)

A total of 3 groundwater samples will be collected from domestic wells located in the Hopkins Fork (C) subarea.

Prenter

A total of 3 groundwater samples will be collected from domestic wells located in the Prenter subarea.

Groundwater sampling procedures are provided in **Appendix 1, Domestic Supply Well Collection Procedure, Appendix 2, Dissolved Metals Collection Procedure**

and **Appendix 3, *Aqueous VOC Sample Collection Procedure.***

### **2.5.2 Surface water**

During site characterization activities, Triad will collect approximately 7 surface water samples from the following preliminary locations:

- Jarrells Creek above its junction with Hopkins Fork.
- Hopkins Fork above its junction with Jarrells Creek.
- Lavinia Fork above its junction with Hopkins Fork.
- Laurel Creek above its junction with Hopkins Fork.
- Sandlick Creek above all inhabited dwellings.
- Three Forks Creek above its junction with Sandlick Creek.
- Sandlick Creek above its junction with Laurel Creek.

Surface water sampling procedures are provided in **Appendix 4, *Shallow Surface Water Sample Collection Procedures.***

### **2.5.3 Mine-related Discharge**

During site characterization activities, Triad will collect approximately 6 water samples from mine-related discharge sites at the following preliminary locations:

- Untreated surface mine discharge (acidic) from the 5-block seam.
- Untreated surface mine discharge (non-acidic) from other seams.
- Longwall mine discharge (headwaters Laurel Creek).
- Old Omar UIC disposal mine discharge.
- Lots Fork slurry impoundment decant water.
- Decant water from currently-permitted UIC operation.

Mine-related discharge samples will be collected in accordance with procedures provided in **Appendix 4, *Shallow Surface Water Sample Collection Procedures.***

## **2.6 Paperwork Requirements**

### **2.6.1 Sample labeling**

After samples have been collected, they will be placed into certified pre-cleaned containers supplied by the laboratory. Each sample container will have a sample label generated by the sampling personnel. Each sample container label will have, at a minimum, the following information:

- Sample identification.
- Analysis requested.

### **2.6.2 Sample packaging and shipping**

After the sample labels have been placed on each sample container, the outside of each container will then be wiped clean. If necessary, a strip of clear tape will be applied on the label to ensure the ink does not smear. Each sample will then be packaged and shipped in the following manner:

- Check lid/cap to ensure proper closure to eliminate leaks.
- Check to ensure label is intact and legible.
- Place the labeled sample container in a clear plastic bag and zip bag.
- Ensure the soil and groundwater samples are cool (4-6 degrees Centigrade) before being enclosed in bubble wrap and placed in the shipping container. The soil gas samples will be kept out of direct sunlight, and will NOT be chilled.
- Place the sample in a clean waterproof shipping container (i.e. a cooler).
- Place a temperature blank (40 ml vial filled with water) in the container with the samples.
- Place double-bagged ice on top of the soil and groundwater samples and the temperature blank.
- Pack the shipping container with noncombustible packing material such as bubble wrap.
- Enclose a copy of the chain-of-custody in a clear plastic bag and tape to the underside of the shipping container lid.
- Tape the cooler shut using strapping tape over the hinges.
- Place custody seals that have been signed and dated across the top and sides of the cooler so that they will be broken at the signature section of the

seal when the shipping container is opened.

- Place clear tape over the custody seals to prevent accidental damage during shipment.
- Place return address label clearly on the outside of the shipping container.
- If more than one shipping container is being sent to a laboratory, mark shipping containers as 1 of 2, 2 of 2, etc.
- If a laboratory courier or sample drop-off at the laboratory by TRIAD personnel is not possible, ship by overnight delivery through a commercial carrier, in accordance with Department of Transportation (DOT) and International Air Transport Association (IATA) regulations.
- Fill out an air bill for the laboratory so as to be received the next calendar day. Address the recipient as “sample custodian.”

### **2.6.3 Custody seals**

Each sample shipping container will be sealed with strapping tape and with at least two custody seals. The custody seals will be placed so that they will be broken at the signature section of the seal when the shipping chest is opened. Each custody seal shall include the following information:

- Date of sample shipment (release of custody).
- Signature of FOM or authorized representative releasing custody.

### **2.6.4 Chain-of-custody (CoC)**

CoC forms will be generated at the end of the work shift for the samples procured during that shift. The CoC form sent to the laboratory shall include the following information:

- Release Signature of FOM or authorized representative.
- Date and time relinquished.
- Project number.
- Sample numbers or identifications.
- Sample matrix.
- Type of sample (grab or composite).
- Analyses requested/turnaround time.
- Preservative information.
- Date and time of sample collection.

- Designation of laboratory QC samples.
- Date shipped/method of shipment/airbill number/laboratory address.

Each chain-of-custody form will be distributed as follows:

- The original laboratory copy will be placed into a zip-lock® type bag, which will then be placed into the shipping container to accompany the sample containers to the laboratory.
- One copy to the Triad, PM.

### **2.6.5 Communicating shipping information**

The following information will be communicated to the Laboratory PM for all shipping container shipments:

- Project identification.
- Number and matrices (water, soils, etc.) of samples shipped.
- Type of analysis required.
- Turnaround time.
- Overnight carrier (FedEx or UPS).
- Shipment date.
- Information on completions, changes, delays, continuations, etc.
- Suspected contaminants associated with the samples or site if applicable.

### **2.6.6 Field Documentation**

The FOM will be responsible for maintaining a log book and sample sheets that document field activities. Criteria for the documentation include:

- Bound log book.
- Indelible ink used for entries.
- Entries should be factual, detailed, and objective.
- Date and time of all entries.

The FOM will document on a daily basis in the log book on-site personnel, visitors, and activities. Information to be recorded either in the field log book or sample sheets will include as applicable:

- Date and time of entry.
- Purpose of sampling.



- Name, address, and affiliation of personnel performing sampling.
- Name and address of the responsible party, if known.
- Type of sample, e.g.: surface soil, groundwater, etc.
- Description of sample containers.
- Description of samples.
- Chemical components and concentrations, if known.
- Number and size of samples taken
- Analysis requested.
- Description and location of the sampling point.
- Date and time of sample collection.
- Difficulties experienced in obtaining sample if applicable.
- Visual references, such as maps or photographs of the sampling site.  
Include the film roll number, the frame number, and a written description of the picture for photographs.
- Field observation, such as weather conditions during sampling periods.
- Whether chain-of-custody forms have been filled out for the samples; chain-of-custody form numbers.
- Global Positioning System (GPS) related information (latitude and longitude) for the site and each sampling location.
- Laboratory name, address, and date shipped.

## 2.7 Analytical Procedures

The samples will be analyzed for the parameters identified in **Table 2, Sampling and Analysis Summary – Domestic Wells**, **Table 3, Sampling and Analysis Summary - Surface Water**, and **Table 4, Sampling and Analysis Summary - Mine-Related Discharge**. The samples will be analyzed according to the most current method requirements specified in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3<sup>rd</sup> Edition* (SW-846). Sample container and laboratory holding times is summarized in **Table 5, Field Sample Container Requirements**.

## 2.8 Quality Control Requirements

Field and sample matrix quality control will be performed as detailed in the *QAPP*, presented as section 3.0 of this report. Field QC samples will be collected during the work to assess sampling precision as summarized in **Table 6, Field and Matrix QC Samples**.

## **2.9 Decontamination**

In general, unused, disposable field sampling equipment shall be utilized during sample collection to prevent or reduce the potential for cross-contamination. Any non-disposable field sampling equipment shall be decontaminated between samples as per the following nine-step procedure:

1. Initially remove physical contamination by any or all of the following abrasive cleaning methods: washing, brushing, and air/water blasting.
2. Wash equipment with a non-phosphate detergent.
3. Rinse with potable water.
4. Rinse with distilled/deionized water.
5. If the sample will be analyzed for metals, rinse with 10% nitric acid.
6. Rinse with distilled/deionized water.
7. If the sample will be analyzed for organics, rinse with pesticide grade hexane.
8. Keep equipment covered from dust or other particulate matter after decontamination.
9. Air-dry equipment completely before use.

Solvent rinse is required only when organic analysis is applicable to the sample being collected. Acid rinse is required only if metals are to be analyzed. If a particular contaminant fraction is not to be analyzed, the nine-step decontamination procedure listed above may be modified for site specificity.

## **2.10 Assessment and Oversight**

### **2.10.1 Assessment of field sampling and response actions**

The FOM will constantly assess and evaluate the QA system and QC practices during the course of the project. If at any time it becomes apparent that these are not adequate to ensure collection of data of the quality required, the FOM may discontinue the project until sufficient revisions can be made. These revisions may be made in the field at the direction of the FOM, and noted by the FOM in the field log book, or may be recommended to the PM or LRS for implementation. The Triad PM and/or LRS will review any such revisions with the WVDEP, OER PM.

### **2.10.2 Reports to management**

If, in the opinion of the FOM, sufficient adjustment cannot be made to QC practices

in the field, the FOM will report these findings to the TRIAD PM and/or LRS, and discontinue data collection under the current QA system. The Triad PM and LRS, in consultation with the FOM and WVDEP, OER PM, will revise the QA system as necessary to ensure that data of adequate quality are obtained.

### 3.0 QUALITY ASSURANCE PROJECT PLAN (QAPP)

#### 3.1 Introduction

The objectives of the site characterization investigations are to determine the nature and extent of COCs at the Site, obtain validated laboratory data for human health and ecological risk assessment purposes, and to complete characterization of the Site so that a Certificate of Completion (COC) can be obtained for the Site under the West Virginia VRP.

#### 3.2 Data Quality Objectives (DQOs)

Data collected during the field sampling activities will be of a quality such that it can be screened and compared to the following *de minimis* environmental standards and criteria:

- *WV De Minimis Levels, Table 60-3B* (Revised July 2008), industrial soil, groundwater, and migration to groundwater risk-based concentrations (RBCs).
- WV Groundwater Quality Standards (46CSR12).

In accordance with the requirements of the VRRRA, field samples will be analyzed by a WVDEP certified laboratory using promulgated USEPA methodology such as those listed in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3<sup>rd</sup> Edition* (SW-846). These methodologies specify Quality Assurance and Quality Control (QA/QC) procedures that are to be implemented by the approved laboratory performing the analyses. The methods also provide guidelines regarding detection capabilities and limits of sample quantification. If for any reason the sample quantitation limit cannot meet the *de minimis* standard, either due to technological limitations of the method or sample matrix interference, the sample method detection limit will be reported.

Due to the data collected during the field sampling activities being screened and compared to the *de minimis* environmental standards and criteria, each individual solid sample result, quantitation limit, and detection limit must be corrected for percent moisture content.

Triad has selected Test America; a WVDEP certified environmental laboratory located Nashville, Tennessee to perform the soil and groundwater sample analyses. Triad has selected Integrated Analytical Laboratory, located in New Jersey to perform the soil gas sample analyses.

A minimum of 10 percent of the laboratory analytical data will be validated by Triad against the guidelines of the analytical methods performed and the *National Functional Guidelines for Organic Data Review* (USEPA, February 1994) and the *Guidance on Environmental Data Verification and Data Validation* (USEPA, November 2002) as required under the VRP.

### **3.3 Quality Assurance Level Determination**

The content and level of detail required in projects vary according to the intended use of the data. The type and quality of environmental data necessary for their intended use is as defined in the West Virginia *VRRA* legislative rule, as well as the USEPA guidance documents identified above in Section 3.2.

### **3.4 Data Acquisition**

#### **3.4.1 Sampling Rationale**

Sampling procedures and locations are discussed in Sections 2.3, 2.4, and 2.5 of the *Field Sampling Plan*.

#### **3.4.2 Data Validation Process**

The data validation review will be performed on a minimum of 10 percent of the data generated. The review will be conducted against the guidance provided in the *National Functional Guidelines for Organic Data Review* (USEPA, February 1994) and the *Guidance on Environmental Data Verification and Data Validation* (USEPA, November 2002). Data validation consists of an analyte and sample specific process to determine the analytical quality of a specific data set as compared to the applicable analytical procedures and methods. The laboratory analytical data will be examined to determine the usability of the analytical results and compliance relative to the method requirements specified in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3<sup>rd</sup> Edition* (SW-846), and the data quality considerations specified in the *Laboratory Quality Manual*. Under no circumstances should the laboratory deviate from SW-846 recommended procedure and quality control unless given written permission by the Quality Assurance Officer (QAO).

### 3.4.3 Laboratory Quality Control Requirements

#### 3.4.3.1 Detection Limit (DL)

A DL is a measure of the capability of an analytical method to distinguish samples that do not contain a specific analyte from samples that contain low concentrations of the analyte; the lowest concentration or amount of the target analyte that can be determined to be different from zero by a single measurement at a stated level of probability. DLs are analyte, instrument, and matrix specific and may be laboratory dependent. Some of the more commonly used definitions are described below.

***Instrument Detection Limit (IDL)*** - The lowest concentration or mass an instrument can detect above background instrument noise under ideal conditions. IDLs are typically applied to the analysis of metals. Sample preparation is not considered in the determination of an IDL.

***Method Detection Limit (MDL)*** - A statistically derived estimate of the lowest concentration or mass detectable under method conditions at the concentration evaluated. A series of standards at an estimated limit of detection is analyzed multiple times (usually seven), a standard deviation of these seven replicate analyses is determined and the standard deviation is multiplied by the Student's t-distribution statistic at 6 degrees of freedom. See section 3.7.2.4. of this QAPP. Sample preparation is considered in the determination of an MDL.

***Practical Quantitation Limit (PQL)*** - A measure of the lowest limit of detection under the conditions of a particular method. The PQL is often determined by multiplying the MDL by a factor between three and 10.

***Reporting Limit (RL), Limit of Quantitation (LOQ), or Sample Quantitation Limit (SQL)*** - For a target analyte, the RL, LOQ, or SQL (these acronyms are synonymous) is instrument dependent and based on the lowest concentration point of the instrument's current calibration curve. It is also sample specific, as percent moisture, dilution factor, and sample preparation variables are to be included in the calculation of the final RL, LOQ, or SQL.

For this project, each compound of interest will be reported at its appropriate MDL and RL, LOQ, or SQL.

Where technologically feasible, the MDLs must meet the *de minimis* environmental standards and criteria listed in section 3.2 of this QAPP. If the MDLs are not technologically feasible by the laboratory, the laboratory must communicate this prior to sample receipt and reporting.

#### **3.4.3.2 Instrument Calibrations**

A calibration is a comparison of a measurement standard, instrument, or item with a standard or instrument of higher accuracy to detect and quantify inaccuracies and to report or eliminate those inaccuracies by adjustments. Laboratory instrument calibrations typically consist of two types: initial calibration verification (ICV) and continuing calibration verification (CCV).

***Initial Calibration Verification (ICV)*** – ICV procedures establish the calibration range of the instrument and determine instrument response over that range. Typically, a minimum of three to five analyte concentrations are used to establish instrument response over a concentration range. The instrument response over that range is commonly expressed as a correlation coefficient or response factor. Any detected compound whose response is below the calibration range of the instrument must be considered quantitatively estimated, qualified with a “J,” and reported as such to the data user.

***Dilution*** - Any detected compound whose response is above the calibration range of the instrument must be considered quantitatively estimated and reanalyzed at an appropriate dilution to achieve a response within the calibration range of the instrument. If a dilution is not possible, the result is to be reported and qualified with an “E.” If multiple dilutions result in multiple compounds of interest falling within the calibration range of the instrument, all dilutions will be reported by the laboratory to the user of the data.

***Continuing Calibration Verification (CCV)*** - A CCV usually includes measurement of one or more calibration standards. The response is compared

to the initial measured instrument response. Continuing calibration is performed at least once per operating shift for laboratory analyses. Where required, the CCV standard must be a separate source (i.e. a different vendor, or if same vendor, a different lot number) from the ICV standard.

Instrument calibration procedures, both ICV and CCV, are to be analyzed according to the requirements of the USEPA approved methodologies performed. Any deviations from the above must be documented and reported to the user of the data.

#### **3.4.3.3 Laboratory Control Samples**

Laboratory control samples (LCS) are used to evaluate the accuracy of the laboratory's procedures. A LCS, or blank spike, is prepared and analyzed every one per 20 samples of the same media within the same preparation or analytical batch. Any LCS that does not meet the laboratory established recovery criteria must be prepared and analyzed again, along with any associated samples until acceptable recovery is achieved. Procedures for the preparation and analysis of the LCS are according to the requirements of the USEPA approved methods and must be the same as the samples to which the LCS is compared. Any deviations from the above must be documented by the laboratory and reported to the data user.

#### **3.4.3.4 Method Blank**

Method blank (MB) samples are used to evaluate the presence and/or effect of laboratory contamination. A MB must be analyzed every one per 20 samples of the same media within the same preparation or analytical batch. A method blank is prepared to represent the sample matrix as closely as possible and analyzed exactly like the samples for which it is associated. Any method blank that demonstrates contamination (i.e. any positive response of compounds of interest) must be prepared and analyzed again, along with any associated samples that demonstrated the same compounds of interest detected. The only acceptable deviation from this is if the compound sample concentration is greater than ten times the concentration detected in the method blank. Procedures for the MB are analyzed according to the requirements of the



USEPA approved methods performed. Any deviations from the above must be documented and reported by the laboratory to the data user, with impacted results qualified with a “B.”

#### **3.4.3.5 Internal Standard**

An internal standard (IS) is a standard unlikely to be found in environmental samples but has similar properties to the compounds of interest. The IS is added to the sample in a known amount and carried through the entire determination procedure as a reference for calibrating and controlling the precision and bias of the applied analytical method. Any sample for which an IS did not meet the USEPA approved method established recovery and retention time criteria, must be analyzed again. If the IS failure is duplicated, matrix interference is assumed and both results are to be reported by the laboratory to the data user.

#### **3.4.3.6 Surrogate Standard**

A surrogate standard of known concentration is added to environmental samples for quality control purposes. A surrogate standard is unlikely to be found in environmental samples but has similar properties to the compounds of interest. Surrogate standards are intended to monitor recovery differences, problems during the extraction phase of the analysis, and for any potential matrix interferences. Any sample that a surrogate standard did not meet the laboratory established recovery criteria must be prepared and analyzed again. If the surrogate standard failure is duplicated, matrix interference is assumed and both results are to be reported by the laboratory to the data user.

#### **3.4.4 Matrix Quality Control Samples**

Matrix spike (MS) and matrix spike duplicate (MSD) samples, performed by the laboratory, are used to evaluate the accuracy and precision of the sample matrix for the organic analyses. A MS, MSD that did not meet the laboratory established accuracy or precision criteria is indicative of possible matrix interference. Only matrix quality control samples selected from media specific to this project are to be reported. Procedures for the MS, MSD are performed according to the same requirements of the USEPA approved methods.

### 3.4.5 Technical Holding Times

A sample's technical holding time is the period of time a sample may be stored prior to its required preparation and analysis by the laboratory. While exceeding the holding time does not necessarily negate the usability of the analytical results, it causes the qualifying of any data as not meeting the specified acceptance criteria. If the technical holding time of any sample is exceeded it is to be reported by the laboratory to the data user immediately. A summary of the technical holding times is presented in **Table 6, Field Sample Container Requirements**.

### 3.4.6 Sample Preservation

A sample's preservation requirements are media and analysis specific. Preservation is required at sample collection in order to preserve the contaminants in their original state prior to analysis by the laboratory. The laboratory is required to maintain the preservation of the samples once they are in the custody of the laboratory. If the sample is found to be outside the preservation required, it is to be reported by the laboratory to the data user immediately. A summary of the preservation requirements is presented in **Table 6, Field Sample Container Requirements**.

## 3.5 Field Quality Control Samples

### 3.5.1 Blanks

A blank is a sample subjected to the usual analytical or measurement process to establish a zero baseline or background value. It is sometimes used to adjust or correct routine analytical results. It is a sample that is intended to contain none of the analytes or compounds of interest. A blank can be used to detect contamination during sample collection, handling, or shipment. There are many types of blanks, each with a specific purpose including:

**Equipment Blank** - Monitor for potential contamination from decontamination procedures (refer to section 2.10) of field equipment or from other sources of equipment contamination like oil or other lubricants. To be collected in the field following standard decontamination procedures; one per 20 samples of the same media, analytical request, and equipment used. For example, if 21 soil samples are to be collected using stainless steel scoops for VOCs and PAHs, one would collect a total of two equipment blanks for

both VOCs and PAHs following decontamination of the scoop by pouring deionized water over the equipment into the appropriate container(s).

***Trip Blank*** - A clean sample of a matrix that is taken to the sampling site and transported to the laboratory for analysis without having been exposed to sampling procedures; typically submitted for aqueous VOC analysis only. One trip blank is required with each sample shipment.

***Temperature Blank*** - An aqueous sample, typically submitted as water in a 40-ml VOC vial, is transported to the laboratory for temperature verification of the samples. One temperature blank is required with each sample shipment container.

### **3.5.2 Duplicate Samples**

Duplicate samples are two samples taken from and representative of the same population and carried through all steps of the sampling and analytical procedures in an identical manner. Duplicate samples are used to assess variance of the total method, including sampling and analysis. There are several different types of duplicate samples that provide information on the precision of specific types of environmental data operations:

***Field Duplicates*** - Independent samples that are collected as close as possible to the same point in time and space. They are two separate samples taken from the same source, stored in separate containers and analyzed independently. These types of duplicates are useful in characterizing the precision of the sampling process.

***Split Samples*** - Two or more representative portions taken from one sample in the field or in the laboratory and analyzed by different analysts or laboratories. Split samples are quality control (QC) samples that are used to assess analytical variability and comparability.

## **3.6 Assessments and Oversight**

### **3.6.1 Performance and System Audits**

#### **3.6.1.1 Technical Performance Audits**

Qualified Triad personnel will perform technical performance monitoring on an ongoing basis during the project, as field data are generated, reduced, and analyzed. These monitoring activities serve as a performance audit and are essentially ongoing due to the length of the project schedule. All numerical analyses such as manual calculations, mapping, and computer modeling, are documented and will be the subject of performance audits in the form of quality control review, numerical analysis, and peer review.

#### **3.6.1.2 Laboratory System Audits**

The WVDEP commercial laboratory certification program performs external system audits of the laboratory on a pre-defined basis. The system audit may consist of review of the following:

- Laboratory quality assurance manual
- Instrumentation and/or analytical systems for the analyses of interest
- Sample preparation methodologies
- Laboratory sample handling
- Sample receiving and custody procedures
- Data reduction and reporting procedures
- Data validation procedures
- Instrument calibration procedures
- Quality control program
- Other laboratory procedures that may impact laboratory analyses

### **3.6.2 Corrective Action**

#### **3.6.2.1 Field Corrective Action**

The initial responsibility for monitoring the quality of field measurements and observation lies with the field personnel. The FOM is responsible for verifying that all QC procedures are being followed. This requires that the FOM assess

the correctness of field methods and their ability to meet the QA objectives. If a problem occurs that may jeopardize the integrity of the project or cause some specific QA objective to not be met, the field project personnel will report it to the FOM. The FOM will then report all such suspect problems to the TRIAD PM. The Triad PM documents the problem, consults with the QAO, LRS, and/or WVDEP, OER PM as applicable, develops a corrective action, and documents the results. The FOM will initiate the corrective action and identify and direct the appropriate personnel to implement the corrective action.

### **3.6.2.2 Laboratory Corrective Action**

The initial responsibility for monitoring the quality of an analytical system lies with the analyst. In this pursuit, the analyst must verify that all standard operating procedures and quality control procedures are followed and that the results of analysis of instrument calibration and quality control samples are within acceptance criteria.

If his or her assessment reveals that any of the quality control acceptance criteria were not met, he or she immediately assesses the analytical system to correct the problem. The deficiency is reported to the appropriate supervisor, who notifies the laboratory QC Officer. Specific corrective actions to exceed acceptance criteria for the laboratory quality control checks are defined in the laboratory QA program.

### **3.6.3 Reports to Management**

Reports to management encompass both routine reports and special reports, including written reports and memoranda documenting data assessment activities, results of data validations, audits, nonconformance, and corrective actions. The management hierarchy receiving some or all of the reports includes appropriate personnel from Triad such as the LRS, QAO, and PM and the WVDEP, OER PM.

## **3.7 Data Usability**

The following sections describe the processes used to generate and check data and produce reports for both field sampling and laboratory analysis data. As discussed previously in the *QAPP*, ten percent of the laboratory analytical data will be validated.

### 3.7.1 Data Reduction

Data will be reduced either manually on calculation sheets or by computer on formatted printouts. The methodology and procedures implemented by Triad to determine the accuracy of data reduction are described in this section. The following responsibilities are delegated in the data reduction process:

- Technical personnel document and review their own work and are accountable for its correctness.
- Major calculations receive both a method and an arithmetic check by an independent checker. The checker is accountable for the correctness of the checking process.
- The QAO is responsible for ensuring that data reduction is performed in a manner that produced quality data through review and approval of calculations.

Hand calculations are to be legibly recorded on calculation sheets and in logical progression with sufficient descriptions. Major calculations are checked by an engineer or scientist of professional level equal to or higher than that of the originator. After completing the check, the checker will initial and date the calculation sheet immediately below the originator. Both the originator and checker are responsible for the correctness of calculations. A calculation sheet will contain the following, at a minimum:

- Project title and brief description of the task.
- Date performed.
- Initials of person who performed the calculation.
- Basis for calculation.
- Assumptions made or inherent in the calculation.
- Complete reference for each source of input data.
- Methods used for calculations.
- Results of calculations, clearly annotated.

Computer analyses include the use of models, programs, and data management systems. For published software with existing documentation, test case runs are performed periodically to verify that the software is performing correctly. Both systematic and random-error analyses are investigated and appropriate corrective action measures are taken.

### 3.7.2 Data Validation and Verification

The process through which data is accepted or rejected is based on specific data verification and validation criteria. These criteria are discussed below for both field and laboratory data. Personnel experienced with sampling and analytical protocols and procedures will perform the data validation in accordance with the established criteria and the intended use of the data.

Field data verification and validation are used to eliminate or limit the use of field data that are not collected or documented in accordance with specified protocols outlined here or in the *FSP*. In some instances, the field data are used only for approximation purposes. In all cases, evaluations of field data are performed on two separate levels. First, all field data will be verified at the time of collection by following the QC checks outlined throughout the *FSP* and *QAPP*. Second, field data will be validated by the PM, or designee, who will review the field data documentation to identify discrepancies or unclear entries. Field data documentation will be validated against the following criteria, as appropriate:

- Sample location and adherence to the *FSP*.
- Adherence to procedures and protocols.
- Field instrumentation and calibration.
- Sample collection protocol.
- Sample volume.
- Sample preservation.
- Equipment QC samples collected and submitted.
- Field duplicate QC samples collected and submitted.
- Sample labels protocols.
- Sample documentation protocols.
- Chain-of-custody protocol.
- Sample shipment.

Under the review procedures, the following data validation criteria for the requested analyses are to be prepared by the laboratory for potential validation in an organized, legible, and tabulated manner:

- Sample paperwork, both preparatory and analysis.
- Chromatograms.
- Retention times.
- Peak integration and labels.
- Mass spectral library comparisons.
- ICV.
- CCV.
- LCS.
- Method Blank/Instrument Blank.
- MS/MSD/MD.
- Holding time.
- Surrogate recovery
- Internal standards recovery and retention time.
- Dilution factor.
- Moisture content.
- Confirmation Data.

### **3.7.3 Data Quality Assessment**

Data quality assessments are prepared to document the overall quality of data collected in terms of the established DQOs and the effectiveness of the data collected and generation processes. The data assessment parameters calculated from the results of the field measurements and laboratory analyses will be reviewed to ensure that all data used in subsequent evaluations were scientifically valid, of known and documented quality, and, where appropriate, legally defensible. In addition, the performance of the overall measurement system will be evaluated in terms of the completeness of the project plans, effectiveness of field measurement and data collection procedures, and relevance of laboratory analytical methods used to generate data as planned. Finally, the goal of the data quality assessment is to present the findings in terms of data usability.

Generally, to achieve an acceptable level of confidence in the decisions that were made from the data, the degree to which the total error in the results derived from data



collected and generated will be controlled. The methods and procedures used to implement and accomplish these QC objectives are as follows:

- Assess the quality of data values measured and generated to ensure that all were scientifically valid, of known and documented quality, and, where appropriate, legally defensible. This is accomplished by assessing actual data values generated or measured against the established DQOs for parameters such as precision, accuracy, completeness, representativeness, and comparability, and by testing generated data against acceptance criteria established for these parameters.
- Achieve an acceptable level of confidence in the decisions that were to be made from measurements and data by controlling the degree of total error permitted in the data through QC checks. Data that failed the QC checks or did not fall within the acceptance criteria established will be rejected from further use or qualified for limited use.

The major components of a data quality assessment are presented below and show the logical progression of the assessment leading to determination of data usability:

- *Data Validation Summary.* Summarizes the individual data validation reports for all sample delivery groups by analytical method. Systematic problems, data generation trends, general conditions of the data, and reasons for data qualification are presented.
- *Data Evaluation Procedures.* Describes the procedures used to further qualify data caused by such factors as dilution, reanalysis, matrix effect and duplicate analysis of samples. Examples of the decision logic are provided to illustrate the methods by which qualifiers are applied.
- *QC Sample Evaluation.* Evaluates QC samples such as field blanks, trip blanks, equipment rinsates, field replicates, and laboratory control samples to assess the quality of the field activities and laboratory procedures.
- *Assessment of Data Quality Objectives.* Assesses the quality of data measured and generated in terms of accuracy, precision, representativeness, and completeness through the examination of laboratory and field control samples in relation to objectives established.

- *Summary of Data Usability.* Summarizes the usability of data, based on the assessment of data conducted during the previous four steps. Sample results for each analytical method will be qualified as acceptable, rejected, estimated, biased high, or biased low.

#### **3.7.4 Data Reporting**

Field measurements and observations will be recorded in the field log book maintained by the FOM. Laboratory data is reported in standard formats that identify the specific sample, date, parameter, parameter value, detection limit, and various analytical parameters. Both field and laboratory data will be combined and summarized as appropriate in tables, graphs, and other formats that are appropriate to the type of data and conveyed information, to support the findings of the data collection program. In all cases, data will be clearly tabulated and presented in a consistent manner to support comparison of common sets of data. Finally, data will be presented so as to logically lead to and substantiate the conclusions and recommendations provided by the final report.

### **3.8 Reconciliation with Data Quality Objectives**

All data generated for the project will be assessed for accuracy, precision, completeness, representativeness, and comparability. The methods for calculating accuracy, precision, and completeness, and for evaluating representativeness and comparability are summarized in USEPA guidance documents (EPA 1990a). Generally, data that does not meet the established acceptance criteria may be probable cause for re-sampling and re-analysis. However, in some cases, data that did not meet acceptance criteria are usable with specified limitations. Data that are marked as usable with limitations are included in the project reports, but will be clearly marked as having limited usability.

#### **3.8.1 Qualitative Quality Assurance Objectives**

##### **3.8.1.1 Representativeness**

Representativeness expresses the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or an environmental condition. Representativeness is a qualitative parameter that pertains to the proper design of the sampling program.

The representativeness criterion is best satisfied by making certain that sampling locations are selected properly and a sufficient number of samples are collected.

This parameter is addressed in the project-specific work plans by collecting samples at locations specified in such work plans, and by following the procedures for sample collection/analyses that are described in the *FSP*. Additionally, analytical programs utilize procedures that are consistent with USEPA approved analytical methodology. QA/QC parameters that are utilized to aid representativeness of environmental samples are technical holding time and sample preservation. The technical holding time and sample preservation requirements, presented in **Table 6, *Field Sample Container Requirements***, are used in accordance with this *QAPP* to ensure that the environmental samples submitted to the laboratories remained representative of site conditions.

### **3.8.1.2 Comparability**

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another. This goal is achieved through the use of the standardized techniques for sample collection and analysis presented in the *FSP*. The USEPA *Methods of Chemical Analysis for Water and Waste or Test Methods for Evaluating Solid Waste (SW846)* analytical methods are updated on occasion by the USEPA to benefit from recent technological advancements in analytical chemistry and instrumentation. In most cases, the method upgrades include the incorporation of new technology that improves the sensitivity and stability of the instrumentation or allows the laboratory to increase throughput without hindering accuracy and precision. The overall goal for analytical programs conducted in accordance with this *QAPP* is to provide comparable analytical data over time through the use of approved analytical techniques that remain consistent in their general approach and continued use of the basic analytical techniques (i.e., sample extraction/ preparation, instrument calibration, QA/QC procedures, etc.). Through this use of consistent base analytical procedures and by requiring that updated procedures meet the QA/QC criteria specified in this *QAPP*, the analytical data from past, present,

and future sampling events are comparable to allow for qualitative and quantitative assessment of site conditions.

### 3.8.2 Quantitative Quality Assurance Objectives

#### 3.8.2.1 Completeness

Completeness is defined as a measure of the amount of valid data obtained from an event or investigation compared to the total data planned. Completeness of laboratory tests are expected to be 90 percent (90%) or better for investigations conducted in accordance with this *QAPP*. The reasons for any variances from 100 percent completeness will be identified and addressed, as required, in the appropriate data validation report. Completeness is calculated as follows:

$$\text{Completeness (\%)} = \frac{V}{P} \times 100$$

Where      **V = number of valid measurements**  
              **P = number of planned measurements**

#### 3.8.2.2 Precision

Precision measures the reproducibility of measurements under a given set of conditions. Specifically, it is a quantitative measure of the variability of a group of measurements compared to their average value. For investigations conducted in accordance with this *QAPP*, precision is defined as the relative percent difference (RPD) or the relative standard deviation (RSD) between duplicate sample results. The lower these values are, the more precise that data. These quantities are defined as follows:

$$\text{RPD (\%)} = 100 \times \frac{(S - D)}{(S + D)/2}$$

or:

$$\text{RSD (\%)} = \frac{100 \times 2 (S - D)}{(S + D)}$$

$$\sqrt{2} \quad (S + D)$$

where **S** = Analyte or compound concentration in a sample

**D** = Analyte or compound concentration in a duplicate sample

Or when there are more than two measurements:

$$\text{RSD (\%)} = 100 \frac{(s)}{\bar{x}}$$

where **s** = Standard deviation of replicate measurements

$\bar{x}$  = Mean of replicate measurements

The duplicate samples utilized to evaluate precision include laboratory MD, MS, MSD, and field duplicates samples. The goal is to maintain a level of analytical precision consistent with the objectives of the sampling event. To maximize precision, consistent sampling and analytical procedures are to be followed as presented in the *FSP*. Control limits for field duplicate sample analyses are 40%. Control limits for laboratory MS, MSD, and MD sample analyses are determined by the laboratory's internal QA plan.

### 3.8.2.3 Accuracy

Accuracy measures the bias in an analytical system, or the degree of agreement of a measurement with a known reference value. This measure is defined as the difference between the average of reported values and the actual value. Accuracy is expressed as the percent bias for standard reference samples. The closer this value is to zero, the more accurate the data. This quantity is defined as follows:

$$\text{Bias (\%)} = \frac{(MC - KC)}{KC} \times 100$$

**Where KC = Known analyte or compound (i.e. spike) concentration**  
**MC = Measured analyte or compound concentration**

In cases where accuracy is determined from spiked samples, such as the LCS, accuracy is expressed as the percent recovery. The closer the value is to 100, the more accurate the data. Recovery is calculated as follows:

$$\text{Recovery (\%)} = \frac{\text{MC}}{\text{SC}} \times 100$$

**Where SC = Known analyte or compound (i.e. spike) concentration**  
**MC = Measured analyte or compound concentration**

Matrix spike percent recovery is calculated as follows:

$$\text{Recovery (\%)} = \frac{\text{MC} - \text{USC}}{\text{KC}} \times 100$$

**Where SC = Known analyte or compound (i.e. spike) concentration**  
**MC = Measured analyte or compound concentration**  
**USC = Unspiked sample concentration**

For investigations conducted in accordance with this *QAPP*, accuracy is defined as the percent recovery of QA/QC samples that are spiked with a known concentration of an analyte of interest. The QA/QC samples used to evaluate analytical accuracy included instrument calibration, internal standards, ICP serial dilution analysis, laboratory control samples, MS/MSD samples, and surrogate compound recoveries. Control limits for instrument calibration, internal standards, ICP serial dilution analysis, laboratory control samples, MS/MSD samples, and surrogate compound recoveries are provided in the applicable USEPA approved methods or determined by the laboratory's internal QA plan.

### 3.8.2.4 Sensitivity

The sensitivity is defined by the method detection limits (MDLs). Unless otherwise specified in the project-specific work plan, the analytical results are reported against the laboratory MDLs.

The achievement of MDLs depends on instrument sensitivity and matrix effects. Therefore, it is important to monitor the instrument sensitivity to ensure data quality through constant checks on instrument performance. The method detection limit is defined as the minimum concentration of a substance that can be measured with 99 percent confidence that the concentration is above zero. The MDL is calculated as follows:

$$\text{MDL} = s * t_{(n-1, 1-a=0.99)}$$

**Where:**

**s = standard deviation of replicate analyses**  
 **$t_{(n-1, 1-a=0.99)}$  = student's t-value for a one-sided 99% confidence level and a standard deviation estimate with n-1 degrees of freedom**

## TABLES



Table 1. Sampling Locations - Domestic Wells  
 Laurel Creek Hydrologic Study  
 Boone County, WV

Watershed	Homeowner	Address	Latitude	Longitude	Previous Sample Source	Previous Sample ID
Sandlick Creek		1331 Sandlick Road	38.0866666	81.6450391	well	WS-1/WJ-22
		80 Baker Drive	38.0938426	81.6409133	well	WS-14
		Baker Drive	38.0936022	81.6417386	well	WS-15
		Sandlick	38 05.343	81 38.553	wellhead	WJ-23
		683 Sandlick Road	38.0907138	81.6427651	well	WL-3
		897 Three Fork Branch	38.0920860	81.6495415	well	WS-2/WL-6
Laurel Creek (A)		585 Prenter Road	38.0952503	81.6331813	well	WS-13
		1189 Prenter Road	38.0850152	81.6419823	well	WL-2
		NA	38 05.075	81 38.526	kitchen tap	WJ-21
Laurel Creek (B)		247 Hurricane Branch Road	38.0677808	81.6436298	well	WL-7/WJ-13
		Hurricane Branch	38 04.067	81 38.629	hot water heater	WJ-13
		NA	38 04.075	81 38.719	wellhead	WJ-15
		Laurel Creek Road	38.0688817	81.6463397	well	WS-16
Hopkins Fork (A)		6359 Prenter Road	38.0768818	81.6345284	well	WS-10
		1 Spalding Lane	38.0690551	81.6226278	well	WS-12
		11710 Prenter Rd.	38 03.343	81 36.605	tap water	WJ-8
		13390 Prenter Rd	38 02.727	81 37.048	well	WJ-11
Hopkins Fork (B)	<i>Three (3) locations to be selected in the field. No homeowners were previously sampled in this watershed.</i>					
Hopkins Fork (C)	<i>Three (3) locations to be selected in the field. No homeowners were previously sampled in this watershed.</i>					
Lavinia Fork	<i>Three (3) locations to be selected in the field. No homeowners were previously sampled in this watershed.</i>					
Prenter Area (Jarrells Creek)	Prenter Community Center	Prenter	38.0161446	81.6248126	well	WL-11
<i>Two (2) additional locations to be selected in the field.</i>						







**Table 5. Sample Container Requirements  
Laurel Creek Hydrologic Study  
Boone County, West Virginia**

<b>ENVIRONMENTAL MEDIA</b>	<b>ANALYSIS</b>	<b>EPA METHOD</b>	<b>QUANTITY/SIZE CONTAINER(S)</b>	<b>PRESERVATIVE</b>	<b>HOLDING TIME</b>
<b>Domestic Groundwater</b>	Primary SDWA Metals	6010	1 - liter plastic	HNO <sub>3</sub> to pH<2	6 months
	Secondary SDWA Parameters	6010/Various	1 - liter plastic	Cool 4° C	48 hours
			1 - liter plastic	Cool 4°C, HNO <sub>3</sub> to pH<2	6 months
	Coliform	9222	1 - 250 ml plastic	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.008%)	30 hours
	AMD Indicators	Various	1 - liter plastic	Cool 4°C	7 days
	VOC	8260B	3 - 40 ml glass	Cool 4°C, HCL to pH<2	14 days
Cations/Anions	Various	1 - liter plastic	Cool 4°C	7 days	
<b>Surface Water</b>	Primary SDWA Metals	6010	1 - liter plastic	HNO <sub>3</sub> to pH<2	6 months
	Secondary SDWA Parameters	6010/Various	1 - liter plastic	Cool 4° C	48 hours
			1 - liter plastic	Cool 4°C, HNO <sub>3</sub> to pH<2	6 months
	Coliform	9222	1 - 250 ml plastic	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.008%)	30 hours
	AMD Indicators	Various	1 - liter plastic	Cool 4°C	7 days
	VOC	8260B	3 - 40 ml glass	Cool 4°C, HCL to pH<2	14 days
Cations/Anions	Various	1 - liter plastic	Cool 4°C	7 days	
<b>Mine-Related Discharge</b>	Primary SDWA Metals	6010	1 - liter plastic	HNO <sub>3</sub> to pH<2	6 months
	Secondary SDWA Parameters	6010/Various	1 - liter plastic	Cool 4° C	48 hours
			1 - liter plastic	Cool 4°C, HNO <sub>3</sub> to pH<2	6 months
	Coliform	9222	1 - 250 ml plastic	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (0.008%)	30 hours
	AMD Indicators	Various	1 - liter plastic	Cool 4°C, HCL to pH<2	7 days
	VOC	8260B	3 - 40 ml glass	Cool 4°C, HCL to pH<2	14 days
Cations/Anions	Various	1 - liter plastic	Cool 4°C	7 days	

**Table 6. Field and Matrix QC Samples  
Laurel Creek Hydrologic Study  
Boone County, West Virginia**

QC Sample	Number of Samples						Total QC Samples Collected
	Field Samples			QC Samples			
	Domestic Wells	Surface Water	Mine Discharge	Domestic Wells	Surface Water	Mine Discharge	
<b>Field QC Samples:</b>							
<b>Field Duplicate</b>							
Primary DW	29	7	6	2	1	1	
Secondary DW	29	7	6	2	1	1	
AMD Indicators	29	7	6	2	1	1	
VOC	29	7	6	2	1	1	4
Cations/Anions							
<b>Matrix QC Samples:</b>							
<b>Matrix Spike and Matrix Spike Duplicate (MS/MSD)</b>							
Primary DW	29	7	6	2	1	1	
Secondary DW	29	7	6	2	1	1	
AMD Indicators	29	7	6	2	1	1	
VOC	29	7	6	2	1	1	4
Cations/Anions							
<b>TOTAL</b>							<b>8</b>

**Notes:**

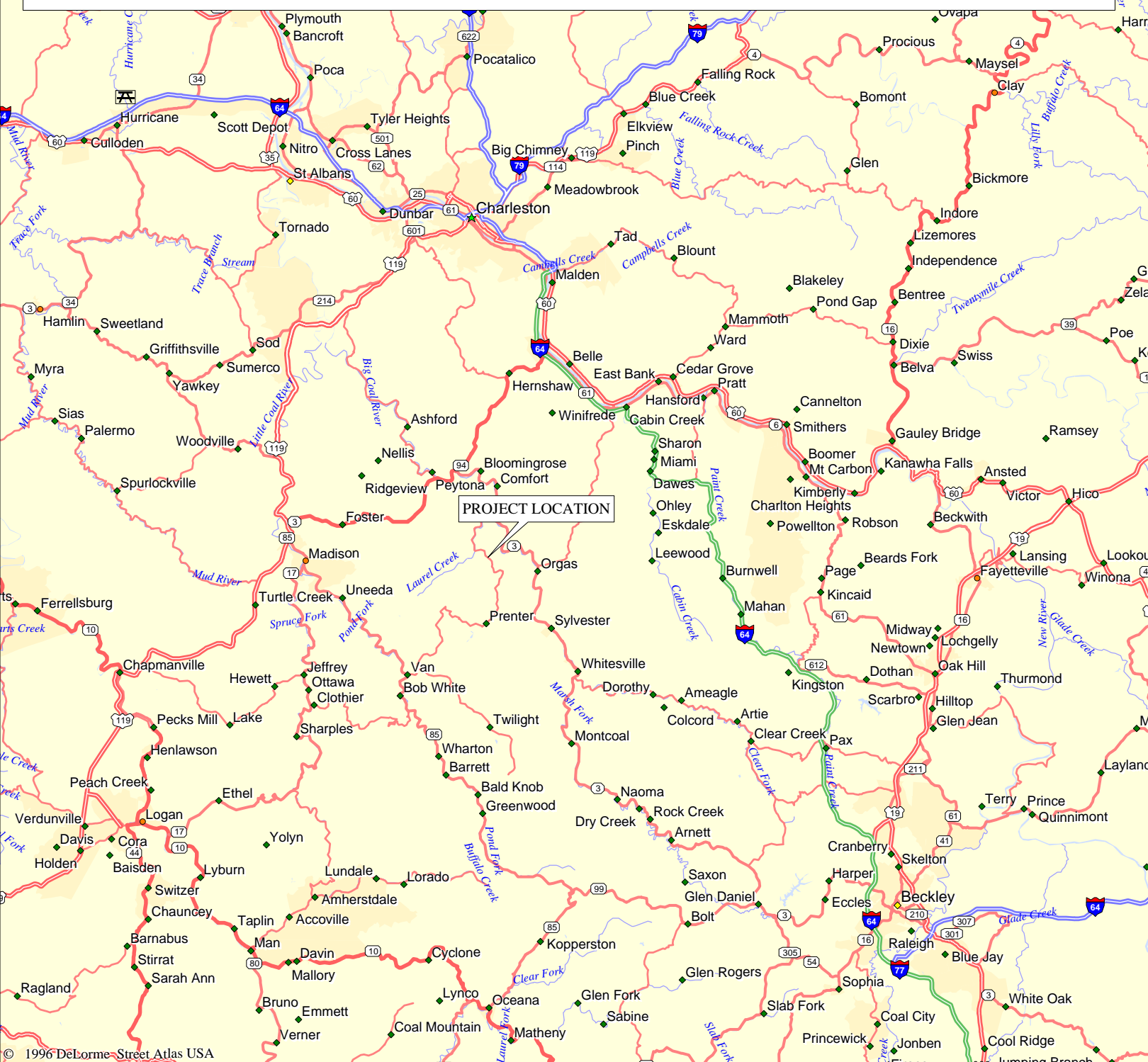
Number of QC samples to be collected based on the following:

- Matrix QC sample based on 1 QC sample per 20 field samples per environmental media.
- 1 sample container containing "clean" water will be placed in each cooler as a temperature blank.

**FIGURE 1**

**Site Location Map**

# Figure 1. Project Location Map



Mag 10.00  
 Mon Apr 11 10:21 2011  
 Scale 1:500,000 (at center)

10 Miles  
 10 KM

- |  |                           |  |                   |  |                    |
|--|---------------------------|--|-------------------|--|--------------------|
|  | Major Connector           |  | State Capital     |  | Intermittent River |
|  | State Route               |  | Small Town        |  |                    |
|  | Primary State Route       |  | Large City        |  |                    |
|  | Interstate/Limited Access |  | City              |  |                    |
|  | Toll Highway              |  | Population Center |  |                    |
|  | US Highway                |  | Land              |  | Water              |
|  | Rest Area with facilities |  | River/Canal       |  |                    |
|  | County Seat               |  |                   |  |                    |



**FIGURE 2**

**Overall Watershed Map**

**FIGURE 3 Through FIGURE 10**

**Sample Location Maps**

## **APPENDIX 1**

### **Standard Operating Procedure Domestic Groundwater Supply Well Collection**

# **DOMESTIC GROUNDWATER SUPPLY WELL COLLECTION**

**TRIAD ENGINEERING, INC.**

## **STANDARD OPERATING PROCEDURE**

**Prepared April 2005**

Groundwater samples obtained from domestic supply wells will be collected using the following sampling procedure:

*Note: Drinking water standards for metals are derived from total metals analyses; therefore, filtering of public groundwater supply wells for metals analyses is not recommended.*

1. Samples will be collected from a tap source.
2. Allow the COLD WATER ONLY to run for a minimum of 60 seconds at full pressure in order to flush the lines of any stagnant water. You do not want any hot water sample as it may introduce contaminants as well as chemical or physical changes from the hot water tank. This purge water does not need to be treated as IDW.
3. Fill the appropriate containers and verify the appropriate preservative(s) has been used. Take care not to overfill and potentially dilute preservatives.
4. Seal each container, label and place on ice.

Note:

*At a minimum, groundwater temperature, pH, and specific conductivity will be measured and recorded during sampling. To minimize the potential for cross-contamination, these measurements will be made on aliquots that are not to be submitted to the laboratory for analysis.*

*Record, if known:*

- *age of well,*
- *how the well was constructed,*
- *well depth,*
- *whether the water is pre-treated (i.e. chlorinated or if bleach is historically added to the well).*
- *if solids are present in an unpreserved sample,*
- *any discoloration, and*
- *any odor.*

**APPENDIX 2**  
**Standard Operating Procedure**  
**Dissolved Metals Sample Collection**

# **DISSOLVED METALS IN GROUNDWATER COLLECTION**

**TRIAD ENGINEERING, INC.**

## **STANDARD OPERATING PROCEDURE**

**Prepared April 2005**

Groundwater samples that will be analyzed for dissolved (also known as filtered) metals will be collected by using the following groundwater filtering procedure:

1. From the collection device (i.e. bailer, low-flow cell, or direct-push tubing), immediately fill a plastic unpreserved sample container wearing disposable nitrile gloves.
2. Designate an area where the filtration process will be performed. The area must have a dust-free environment. When filtration apparatus is not in use, keep it covered to protect from airborne particles. Use either a glass or plastic filtering apparatus that has been decontaminated. Stainless steel is unacceptable since it can contaminate the samples.
3. Filtration must be initiated immediately after sample collection. Filtration must be completed before preservation to a pH of less than 2.
4. The following are recommended filter specifications:
  - A 0.45 micron pore size. Other pore size filters may be appropriate for site-specific conditions. However, deviations from the 0.45 micron pore size must be justified and documented in the field log book.
  - Certified pre-cleaned disposable polycarbonate membrane type filter. If the filter is not certified pre-cleaned, each filter and filtration apparatus must be prepared before use since they often contain trace amounts of metals. Filtrations with approximately 20 milliliter of a 25 percent nitric acid solution (three parts water and one part concentrated nitric acid) followed by three, 20 milliliter rinses of trace metal free deionized (DI) water is required to remove any trace amounts of metals. The filtered liquid is then discarded as investigative derived waste (IDW) before filtering each sample.
5. Fill the vessel of the filtering apparatus with the unpreserved sample and seal air tight.
6. Attach the filter to the filtering apparatus being careful to attach the filter in the appropriate direction of flow. The arrow on the filter denotes direction of flow.
7. Attach the filtering apparatus to the pump maintaining an air tight seal.

*If the sample is highly turbid, filter into a clean un-preserved container and retain for a second filtration repeating the filtration steps. If the sample is not highly turbid, filter directly into the appropriate container pre-preserved with nitric acid to achieve a pH less than 2.*

8. Begin pumping.
9. Collect filtered sample (i.e. the filtrate) immediately from the filter to the appropriate container (unpreserved if very turbid, preserved if not very turbid). Avoid air contact of the sample between the filter and the container to reduce particles that may be in the air getting into the filtered sample.

*Repeat steps 5 through 9 if original sample was very turbid and had been pre-filtered into an unpreserved container.*

10. Tightly cap the container.
11. Label container as “Dissolved” and place on ice.

Note:

*Record a general description of the turbidity. Groundwater with a very high concentration of solids (evidenced visually or by a slow filtration rate) should be noted in the field log book.*

*A filtering apparatus equipment blank must accompany the samples to the laboratory for analysis. The ratio is one blank for every twenty filtered samples. This is done in order to demonstrate cross-contamination of samples has not occurred during the filtration process. The blank is collected by performing steps 1 through 11 using DI water as the sample media.*

## **APPENDIX 3**

### **Standard Operating Procedure Aqueous VOC and GRO Sample Collection**



# **AQUEOUS VOC AND GRO SAMPLE COLLECTION**

**TRIAD ENGINEERING, INC.**

## **STANDARD OPERATING PROCEDURE**

**Prepared April 2005**

Aqueous samples to be analyzed for **Volatile Organic Compounds (VOC)** or **Gasoline Range Organics (GRO)** will be collected to prevent bio-degradation using the following zero head space, hydrochloric acid preservation procedure:

### **Required Containers for Each Sample Location:**

Minimum two 40 milliliter glass vials with Teflon® sealed caps. Vials must be pre-cleaned and certified free of VOCs.



**Example of typical vial for VOC and GRO sample collection.**

### **Preservation:**

1. If the vials are purchased pre-preserved with concentrated hydrochloric acid (HCl), skip these steps.
2. If the vials are not purchased pre-preserved, add two to three drops of 1:1 hydrochloric acid to each empty vial.

### **Sample Collection:**

3. To be performed immediately following sample collection.
4. Slowly fill the vials, taking care not to force out the preservative.

5. Slightly overfill each vial to form a meniscus.
6. Tightly cap each vial and invert.
7. Tap the sides of the vial to check for trapped air bubbles in the sample.
8. If air bubbles are present, place the vial in an upright position and open cap. Repeat steps 3 through 7.
9. If air bubbles are still present, discard the sample and resample, completing all steps until there are no visible air bubbles.

*Note: Some media effervesce when added to acid; if this is the case, a lack of air bubbles may be impossible. If this occurs, document in the field notes and submit to the laboratory with bubbles present. Estimate the size of the bubbles in the field notes.*

10. Label and immediately place samples on ice.

## **APPENDIX 4**

### **Standard Operating Procedure Shallow Surface Water Sample Collection**

# **SHALLOW SURFACE WATER COLLECTION**

**TRIAD ENGINEERING, INC.**

## **STANDARD OPERATING PROCEDURE**

**Prepared April 2005**

Surface water samples to be collected at near surface or in shallow waters will be collected using the following surface water sample collection procedure:

1. At a minimum, the following field measurements will be made at each surface water sampling location:
  - Temperature
  - pH
  - specific conductivity

These field measurements will be determined at the time of sample collection. To minimize the potential for cross-contamination, these measurements will be made on aliquots that are not to be submitted to the laboratory for analysis.

2. When sampling running water, the further downstream sample will be obtained first then collect the subsequent samples working upstream.

*Note: If a sediment sample is to be collected at the same location, collect the surface water sample first.*

3. Sampling will not be performed at the surface, unless sampling for a constituent that is known to be immiscible and lighter than water.
4. Use a clean unpreserved one-liter glass container to collect the surface water sample.
5. Invert the container so that the mouth is at an angle away from the stream (facing downstream).
6. Lower the container to the approximate depth.
7. Turn the container at about a 45 degree angle with the mouth of the bottle facing upstream.
8. Fill the one-liter glass container.
9. Immediately sub-sample, filling each appropriate sample container. Take care not to overfill and potentially dilute preservatives.
10. Repeat steps 5 through 9 until each sample container is full.

11. Seal each container, label, and place on ice.
12. Once the sampling is completed, dispose of one liter glass container unless used for a sample container.

Record:

- *pH, temperature, conductivity,*
- *whether sample was collected in running water,*
- *approximate depth of sample in feet or inches below surface,*
- *if solids are present in an unpreserved sample,*
- *color, and*
- *any odor.*

Note:

*An equipment blank is not needed if only clean disposable equipment was used.*