

# **COAL SLURRY WASTE UNDERGROUND INJECTION ASSESSMENT**

## **Final Report: Phase II**

*for submission to*

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Office of Environmental Health Services**

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*prepared by*

**Alan Ducatman, M.D., MSc, Community Medicine and  
Project Principal Investigator  
Paul Ziemkiewicz, Ph.D, West Virginia Water Research Institute  
John Quaranta, Ph.D., P.E., Civil & Environmental Engineering  
Tamara Vandivort, M.S., West Virginia Water Research Institute  
Ben Mack, M.S., West Virginia Water Research Institute  
WEST VIRGINIA UNIVERSITY**

*and*

**Benoit VanAken, Ph.D., Civil & Environmental Engineering  
TEMPLE UNIVERSITY**

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## Foreword

This document summarizes public health concerns related to the injection of coal slurry into underground mine voids. This is Phase II of a two-part effort. The primary report data, Phase I, come from Raleigh, Boone, Kanawha, Nicholas, and Monongalia counties in West Virginia. The phase II report also seeks to identify and address data from other areas, and to be of use in consideration of potential public health implications of coal slurry injection more broadly.

In order to complete this document, several steps were necessary.

Evaluating exposure: The West Virginia University/Temple University research team started by reviewing the Senate Concurrent Resolution 15 (SCR-15) Phase I Report developed by the West Virginia Department of Environmental Protection (WVDEP) and provided by the West Virginia Department of Health and Human Resources (WVDHHR). The research team also solicited data from the U.S. Environmental Protection Agency (USEPA) Region III, U.S. Geological Survey (USGS), U.S. Department of Energy (USDOE), Pennsylvania Department of Environmental Protection, Kentucky Department of Environmental Protection, Virginia Department of Environmental Quality and other sources likely to have valid data including data submitted by researchers at one university (Wheeling Jesuit University), and historical data.

Evaluating health effects: This report focuses on public health and the evaluation is based on existing scientific data. To the degree possible, data gaps encountered by the research team were identified.

Developing recommendations: In this report, the research team outlines its conclusions regarding any potential health threat posed by the coal slurry injection sites selected for the SCR-15 Phase I environmental study, as well as other data that could be identified and acquired. This report attempts to make references regarding specific changes in water quality attributable to coal slurry injection, identifies limitations on such inferences because of substantial data gaps, and makes recommendations relating to information needed, as well as policy considerations in the current circumstances.

Soliciting community input: Two public meetings were held. These had two main purposes: (1) solicit data from stakeholders, and (2) understand stakeholder perspectives. A website was developed in order to post data that is appropriate for public review. (Any data that could violate personal health privacy is not posted.) The website also contains a place for community input, and the research team did respond to stakeholder questions as they were received.

The public was invited to attend meetings. Invitations were sent through personal invitation, when contacts were known, and by a media campaign including all print

media statewide. The public was invited to provide information/data at public meetings, via our website, via a posted e-mail address, or via post. A publicly available e-mail address was established to open lines of communication between the research team and the public.

If you have questions or comments about this report, we encourage you to:

*Write:*           Program Manager  
                  Coal Slurry Study Research Team  
                  West Virginia Water Research Institute  
                  West Virginia University  
                  PO Box 6064  
                  Morgantown, WV 26506-6064

*Or call:*         (304) 293-2867

## List of Abbreviations

AEG	Ackenheil Engineers Geologists
ALMN	Allegheny and Monongahela River Basins fish community
AMD	Acid mine drainage
ATSDR	Agency for Toxic Substances and Disease Registry
BEN	Balkan Endemic Nephropathy
BLL	Blood lead levels
BMD	Benchmark dose: An exposure level that produces some measured change in response
BTEX	Benzene, toluene, and xylene
CCA	Chromate copper arsenate
CCL	Containment Candidate List
CCR	Coarse coal refuse
CDC	Centers for Disease Control
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CI	Confidence interval
95% CI	Statistical testing provides a 95% chance that the true odds ratio (O.R.) is between the values shown
CKD	Chronic kidney disease
CNS	Central Nervous System
COMEST	Commission on Ethics of Scientific Knowledge and Technology
CSF	Cancer slope factor
CVs	Comparison values



DMR	Discharge monitoring report: A required monthly monitoring document submitted to WVDEP by an officially permitted well-injection owner. Since many coal slurry injection sites have not been officially permitted, monthly reports are often not available.
DNA	Deoxyribonucleic acid
DSWB	Downstream Wet Branch
DWEL	Drinking water exposure level
DWS	Drinking water standard
FCR	Fine coal refuse
FISH	Fluorescent in situ hybridization
GFR	Glomerular filtration rate
HA	Health advisory
HAL	Health advisory level
IARC	International Agency for Research on Cancer
IDWHA	Interim drinking water health advisory
KXRF	X-ray fluorescence of the K shell. A clinical test for detecting lead in living humans
LOAEL	Lowest observed adverse effect level. (See NOAEL)
MCL	Maximum contaminant level (primary drinking water regulation)
MCLG	Maximum concentration limit goals (secondary drinking water regulation)
MP	Monitoring Period
MRL	Minimum risk level
mRNA	Messenger RNA
MSHA	Mine Safety and Health Administration

NAMD	Neutralized alkaline mine discharge
NAS	National Academy of Sciences
NAWQA	National Water Quality Assessment Program
NHANES	National Health and Nutrition Examination Study
NIEHS	National Institute for Environmental Health Science
NOAEL	No observed adverse effect level. (See LOAEL)
NRC	National Research Council
NSDWR	U.S. EPA National Safe Drinking Water Standard
NTNCWS	Non Transient Non Community Water System
NTP	National Toxicology Program
OR	Odds ratio
OSM	Office of Surface Mining
PAH	Polycyclic aromatic hydrocarbon
PTWI	Provisional tolerable weekly uptake
RBC	Red blood cell
RCRA	Resource Conservation and Recovery Act
RDA	Recommended daily allowance
RdS	Subchronic Reference Dose
RfD	[USEPA Chronic] Reference Dose
RMEG	Reference Media Evaluation Guide
ROM	Run-of-mine
SCR-15	Senate Concurrent Resolution 15 (year 2007) mandated two reports, an environmental report to be followed by a health report. This document is the health report

SDWA	Safe Drinking Water Act
SDWR	Secondary drinking water regulations
SMCL	Secondary maximum contaminant levels
SMCRA	Surface Mining Control and Reclamation Act
SVOC	Semi Volatile Organic Compound
TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total dissolved solids
TNCWS	Transient Non-Community Water System
TPH	Total Petroleum Hydrocarbons
UIC	Underground injection control: WVDEP regulatory program, including all types of injection wells (mine waste, septic, industrial, other). Mining-waste injection is administered by the Division of Mining and Reclamation
UL	Recommended upper intake level
UNESCO	United Nations Educational, Scientific and Cultural Organization
USDHHS	United States Department of Health and Human Services
USDOE	United States Department of Energy
USDW	Underground sources of drinking water
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
USWB	Upstream Wet Branch
VOC	Volatile organic compound
WHO	World Health Organization
WJU	Wheeling Jesuit University

WVBPH	West Virginia Bureau for Public Health, the Division of the WVDHHR responsible for the Phase II report
WVDEP	West Virginia Department of Environmental Protection, responsible for the Phase I report
WVDHHR	West Virginia Department of Health and Human Resources
WVU	West Virginia University, the state land-grant university, contracted by WVBPH to perform this Phase II report
WWF	Warm water fishery

## **Executive Summary**

This document summarizes water pollution and public health knowledge and concerns related to coal slurry waste injection into underground voids such as abandoned mines. The concerns stem from the possibility that surface and underground water supplies can be negatively affected by coal slurry injection, in turn causing potential harm to drinking water for human consumption and to wildlife living in or about surface streams. The limited data available to address this concern are presented and summarized in this report. This document is the second phase of a two-part effort required by the West Virginia Legislature in February 2007 (SCR-15). The first phase was carried out by the West Virginia Department of Environmental Protection. It investigated hydrologic impacts of coal slurry injection, chiefly at four sites during a one-year period, and was issued to the public in late May 2009.

This Phase II report builds upon the data provided by the Phase I report, and also sought additional data from all sources of information that could be identified in a formal and wide-ranging literature search, by direct contacts with federal and state agencies, by public meetings and statewide newspaper/newsletter contacts with the West Virginia public requesting data and contacts with national investigators known to be interested in this problem. At the end of that process, much but not all of the available data presented in our Phase II report is from the Phase I report, with a significant addition from Wheeling Jesuit University researchers.

The primary goal of the Phase II report is to identify known or suspected human public health consequences of coal slurry injection. A secondary goal is the analysis of the toxicity of identifiable components of coal slurry. A subsidiary but important goal in the circumstance is the identification of data gaps which may place limits on conclusions. Because we found that the current state of the national and international literature is dominated by the Phase I report and by an unpublished effort from researchers at Wheeling Jesuit University, we think it is important to both commend the importance of these landmark efforts and to make recommendations which will permit future improvement in the knowledge base and confidence in the safety of slurry disposal efforts.

The process for development of analyses of what is known about water contamination from coal slurry injection and known, probable, or potential effects upon human health involves a comparison of the known toxicity of coal slurry components “downstream” (either riverine or underground) water contamination, compared to known or suspected human toxicities from the peer-reviewed literature. There are innumerable considerations in this process, and no effort can be complete. For example, the current state of science measures inorganic compounds and elements better than organics, and provides a much richer data base on their health consequences. This is one of many immutable “data gaps” that we identified in this investigation. The absence of sufficient data implies a need to learn; it does not necessarily imply the absence or

presence of a problem or a means to do assessments in the absence of data. Because coal slurry waste is in contact with groundwater, we have considered primarily the oral route of exposure. This does not rule out dermal or even inhalation exposures; we believe those to be far less consequential in most circumstances.

In this Phase II report, we present the following conclusions.

1. Coal slurry injection can have both positive and negative effects on mine-pool water quality and leaching of toxic components. Some aspects of alkaline mine-pool water improve when slurry is injected. (Less is known about injection into acid pools.)
2. No public health problem, attributable only to coal slurry, can be documented from available data.
3. Literature review reveals theoretical and historic reasons, including examples cited in federal documents, to believe that coal slurry injection does not always work as intended. Injected slurry does not always remain trapped below gradient. It can be a potential source of contamination of groundwater, surface water, and water supplies.
4. The current regulatory framework incompletely describes the actual practice of coal slurry injection. In addition, current requirements do not address real time

monitoring, so opportunities for early detection of quality assurance problems are not assured. The requirement that injection “will not cause, result in, or contribute to a violation of water quality standards or effluent limitations” is most meaningful in the context of a quality assurance program, which would include active monitoring.

5. We have stated that “No public health problem [is] attributable only to coal slurry from available data.” However, the important limitations of the statement stem from the sparse quantity of available data, as well as the clear temporal limitations of available data.
  
6. These conclusions were based primarily on data collected at four slurry injection sites: Southern Minerals, Loadout, Panther and Power Mountain. The data represent single sampling events that prevented statistical testing to determine confidence intervals about the data points. However, the study was replicated across four sites and the consistency of the results suggests that they may be representative of slurry injection in southern West Virginia underground mines. In addition, our findings fundamentally agree with a similar study by Smith and Rauch (1987).
  
7. To ensure that coal slurry injection worked as intended would require more consistent instrumentation of both intended receptacles and potentially impacted



sites, including local wells and surface waters. A slurry-monitoring program should characterize the receiving mine area, including interconnections with other mines. It should include regular and repeated sampling with respect to chemistry, volume, and the proportion of liquid to solid fractions. Injection chemistry and flooded-area chemistry should also be characterized.

In order to better ensure against groundwater contamination, sufficient site characterization, modeling, before-and-after measurements, and ongoing instrumentation are needed to understand the environmental impact of a practice which deliberately puts coal slurry in a difficult-to-monitor environment.

8. Based on both available data and models, numerous chemicals to be reviewed are identified. The identification of chemicals to be reviewed does not mean that a health hazard has been detected in the past or present with certainty, it means that health hazards, past, present, and future, are plausible in this setting. The chemical of most health concern, from data available, is arsenic, based on low safety thresholds. However, no examples of arsenic or other concentrations above the current drinking water standards were unequivocally attributable to coal slurry injection. Chemicals to be reviewed will vary by site and can be predicted based on slurry measurements, mine-pool characteristics, and mass-balance models.

9. These recommendations are also potentially applicable to the easier-to-monitor, but also potentially problematic, environment of coal slurry impoundments. Use of data developed by ongoing monitoring can compare the effectiveness of practice alternatives.
  
10. Based on the mass of contaminants present in the liquid fraction of the slurry and their estimated dilution by infiltrating groundwater, there was good agreement between the predicted occurrence of water quality standard exceedences and observations. This strongly suggests that the liquid fraction more than the solid fraction of contaminants determines eventual water quality related to slurry injection.

## **Introduction**

### **Historical and Legislative Background of the Phase II Report**

Coal slurry injection is the practice of disposal of liquid or semi-liquid coal preparation wastes into underground voids, chiefly by drilling well entrances into abandoned underground coal mine deep spaces. There is a second usage of the term “coal slurry.” Finely ground, finished coal can be mixed with water and pumped over substantial distances to a coal-fired power generation station. This type of slurry is a commercial product, and would not normally be considered for purposes of injection into abandoned mines. Throughout this report, the term “coal slurry” will refer to the waste products of coal cleaning, and not to coal slurry used for power generation. Coal slurry contains suspended solid fine coal waste (<1.0 mm). Slurry injection began in 1958 or earlier and is most common in West Virginia’s southern, low-sulfur coal field.

The West Virginia Legislature adopted Senate Concurrent Resolution 15 (SCR-15) in February 2007, requiring a two-phase study of the environmental health impacts of coal slurry injection. Phase I investigated the hydrologic impacts of coal slurry practices and was performed by the West Virginia Department of Environmental Protection (WVDEP). It became publicly available the week of May 26, 2009. This document is the Phase II report, performed by faculty and staff at three colleges within West Virginia University (WVU) and one college at Temple University, under a contract with the West Virginia Bureau for Public Health (WVBPH). It addresses the human health effects of coal slurry injection. Appendices A and B contain all tables and figures

associated with this report, respectively. Appendix C features the names and credentials of principal contributors to this report.

### **Specific Tasks of the Legislative Resolution**

SCR-15 required six tasks:

#### ***Phase I Tasks (covered in report developed by WVDEP)***

1. An analysis of the chemical composition of coal slurry.
2. A hydrogeologic study of the migration of coal slurry into surface or groundwater.

#### ***Phase II Tasks (covered in this report)***

3. An analysis of the known or predicted effects of coal slurry and its constituent contaminants on human health.
4. A study of the effects of coal slurry and its constituent contaminants on public health.

#### ***Tasks Pertinent to Phase I and Phase II***

5. An environmental assessment of the effects on surface water (Phase I) and on aquatic systems (Phase II).
6. Any other considerations that the WVDEP and the WVBPH deem to be important. As part of their mission, WVU researchers requested and received contractual responsibility to seek and evaluate any reliable data about drinking water exposures, and their human health consequences, beyond the data available in the Phase I report. The WVBPH concurred, and that additional task is a report element. This includes review of data not in the Phase I report.

### ***Specific Phase II Contract Tasks***

Specific contract tasks articulated in the Phase II agreement between WVU and WVBPH include the following:

1. Review the Phase I report (received May 29, 2009)
2. Gather additional public health data from peer-review (and potentially non-peer-review) sources.
3. Create a website ([www.coalslurry.net](http://www.coalslurry.net)) for the purpose of receiving and hosting public health data.
4. Invite federal, state, and local agencies, national foundations, and others to provide any human health effects data sources deemed important by the holder.
5. Make a news story available (hosted at [www.coalslurry.net](http://www.coalslurry.net)) to the central Appalachian media concerning the effort, also inviting others to contribute to the effort.
6. Visit state/federal agencies and foundations (up to three) as needed for input into report creation.
7. Consult with federal leaders for the purpose of selecting independent report reviewers. Appoint three to six independent report reviewers to critique the draft report before submission.
8. Create and present the draft and final report, including elements in the Center for Disease Control-Agency for Toxic Substances and Disease Registry (CDC-ATSDR) Public Health Assessment Manual format.

This list is not meant to be complete, as there are milestones and procedures in the contract. The list is intended to represent the most critical steps and intended outcome of a public product.

### **Regulatory Framework of the Permitting Process in West Virginia**

The current regulatory framework in West Virginia classifies coal slurry injection wells as Class V. In this regulation, a Class V well is generally described by two conditions:

1. Class V wells inject nonhazardous fluid.
2. Class V wells inject into strata that do contain underground sources of potable water.

Coal slurry injections are intended to inject potentially hazardous fluids into underground spaces that are not intended to be in contact with potable water, but which have sometimes been in contact with potable water. Thus, the regulatory conditions do not precisely describe the coal slurry injection operating conditions as they pertain to drinking water. Mine pool water is also a potential source of drinking water, even when not currently used.

From a human health and aquatic environmental perspective, the public health outcome may be similar to the intent, so long as injection slurry does not degrade potable groundwater or surface water, and assuming that the mine pool water is not used in whole or part for replenishment of drinking water. Should contact with sources of potable water be sufficient to cause drinking water or surface water degradation, however, the Class V regulatory intent becomes a consideration. From a public health

perspective, the intended outcome of the current framework appears to be that surface water and potable water will meet regulatory standards.

1. The operator can inject into an underground mine only in the event that injection “will not cause, result in, or contribute to a violation of water quality standards or effluent limitations.”

A second pertinent requirement is not specific to slurry injections, but may still be applicable in the event that the first requirement is not met.

2. The injection operator must replace the water supply used (by an owner) for “domestic, agricultural, industrial, or other legitimate use from an underground or surface source where such supply has been affected by contamination, diminution, or interruption proximately caused, unless waived by said owner.”

This requirement describes a remedy for when a goal of regulation (prevention of contamination above potable water standards) is not met. The presence of a remedy suggests an understanding that the goal will not necessarily always be met; the remedy pertains to an existing economic entity, and is most useful in the event of some economic and technical means to achieve rapid remediation. The remediation requirement does not specifically address the time scales of potentially persistent sources of water degradation. Also, the prevention requirement is not accompanied by defined requirements for ongoing quality assurance (measurements) which might detect failure to achieve the goal at the earliest opportunity.

A Sludge Safety Citizens’ Report (2005) questions whether slurry injection practice currently conforms to West Virginia regulation. Regulatory frameworks serve as

the background to risk assessments. The purpose of the risk assessment process is to provide data which may inform future regulatory processes.

### **Scope of the Slurry Injection Process in West Virginia**

The estimated annual burden of slurry created annually in the United States is 70 to 90 million tons annually (NAS, 2002). In West Virginia, it is unknown how many tons are created annually. The Phase I report cited *Coal Age* magazine (2008) to suggest that about 15 percent of this burden is disposed of within underground mine works. In March 2009, there were 13 West Virginia sites depicted as active and approved for slurry injection (their activity may not have been uniform at the time of publication, however), 18 additional sites that were active after 1999 but not currently, and over 60 historic sites. The Phase I study methods limited site selection to approved, active sites. As the Phase I report makes clear, there are likely to be other sites; the Phase I report lists the known sites (Figure 3.3-1: UIC slurry sites, from Phase I: Environmental Investigation).

Appendix IIC of the Phase I report lists 237 chemicals accepted by West Virginia for underground injection; other injectates are illegal. However, coal slurry has tens of thousands of individual organic chemicals and there is no external monitoring system to ensure that only the legal substances are injected.

### **Summary Statement of Study Limitations, Including Data Gaps**

The following introductory sections concern data gaps identified for purposes of this report, and summarized here. We are concerned that a discussion of data gaps could be interpreted as criticism of existing reports. That interpretation would be a



misunderstanding. The purpose of research is often to characterize existing and needed data. For coal slurry injection practices and outcomes, existing data gaps include (but need not be limited to):

- Absence of a good tracer for slurry inputs (identified as an issue in the Phase I report).
- Limited number of sites monitored, and local uniqueness of geography.
- Lack of data regarding well depth, casing, and age.
- Constrained time period of sampling, and limited periodic (not continuous) measures.
- Absence of pre-post slurry measurements at monitored sites.
- Inability to distinguish among different types of coal mining inputs to water quality from post hoc measurements.

While these data gaps pertain particularly to coal slurry injection in the context of this report, they are not unique to coal slurry injection. Similar data considerations may pertain to coal slurry impoundment practices and mine runoff more generally, or even to other nonmining disturbances to water quality.

It is important for readers to understand conclusions in the context of what we know, including data gaps which become targets for future knowledge. More detailed descriptions of these data gaps follow.

### **Coal Slurry Monitoring**

The Phase I report emphasizes the technical difficulty of using post hoc measurements for the purpose of assessing intermittent problems in potable (or

surface) water near slurry injection sites. A tracer substance was sought, but no satisfactory tracer was identified. The absence of a suitable tracer limits the ability to track injected slurry and to detect problems or reliably confirm the absence of problems. Research into the use of iron has been suggested as a tracer, but it is not clear how well this works, especially in alkaline slurry environments. And, the presence of numerous metals in natural overburden implies that linking a finding to mining is problematic (Wigginton, et al., 2007). Sulfur isotope analysis has also been suggested to distinguish sulfur originating in biogenic pyrite e.g. coal versus sulfur originating in hydrothermal or elemental sulfur deposits (Bates, et al., 2002). However, the method would not distinguish sulfur that originated from coal from power plant emissions or oxidation of pyrite in coal, coal spoil or slurry. Since these sources account for the bulk of sulfate in the study area, it is unclear if the method could be applied to the problem of discriminating the sources of sulfate in the central Appalachian coalfield. The inability to find a tracer is fully consistent with the current literature concerning slurry contents; it is not a unique attribute of any report. The following limitations stem from the absence of a unique trace substance: (1) It is not known where best to monitor post hoc in more detail. (2) It is not clear when or how long to monitor post hoc. (3) More than one and perhaps many potential contaminants are candidates for monitoring, increasing the difficulty and cost. (4) The effects of previous or present mining operations, in general, are not easily distinguished from the effects of current or past coal slurry mine injections if extensive pre-post operation data are not obtained.

## **Phase I Sites and Time Frames Selected for Study**

Six sites were studied for the Phase I report, including four which were studied in depth. (Table 1 outlines the characteristics of these sites.) The actual number of coal slurry injection sites in West Virginia is unknown. An estimate is over 60 historic sites. Among known sites, a minority have gone through a formal permitting process. The Phase I study addresses four permitted sites with a hydrologic assessment and it addresses an additional two permitted sites for slurry constituents only. The sites selected for study were all formally permitted during or after the year 2000, and were intended to be representative of different regions and different kinds of conditions.

It is a statement of fact, rather than a criticism of any party, that the Phase I report could not address the following topics: non-permitted sites; geographies distinct from those chosen; longer time frames and temporal variations; pre- to post-injection measures. Furthermore, the topics of site or time frame limitations are not unique to this risk assessment and are not intended as a criticism of what is achievable in limited time frames with limited funding. Data limitations are addressed in risk assessment practice for reader comprehension. How well the selected sites represent other permitted or non-permitted sites, or the injection sites in different geographies, or any site at a different point in time, is unknown. As the primary legislative intent of the two-phased report may be a forward-looking evaluation of risk for future permitted sites, it is plausible (from a policy perspective) that the comparison with 13 active, permitted sites (at the time of the study) should be emphasized, and past practices at nonpermitted sites considered less important. An opposite perspective could be that the effects of non-permitted sites

deserve consideration as a matter of policy concerning adequacy of regulation and enforcement.

The Phase I study was unable to address data following injection into an acid mine pool (pools analyzed in the Phase I study were alkaline), or any site using a high-sulfur coal. It did not address sites outside West Virginia, nor the full range of different kinds of hydrologic conditions within the state. Study authors correctly acknowledged that downstream pollution sources, to the degree they existed, could have come from multiple sources. Importantly, pre-post injection measures do not and could not exist in the time frame of the Phase I report. A planning inference that could be made at the onset of the Phase I study is that water quality change potentially due to slurry injection specifically will be difficult or impossible to detect post hoc. The Phase I report did not sample streams for macroinvertebrates for this reason.

Inferences can be made from external data. In general, even fewer data points are available from other sources. A potential exception, water-quality concerns voiced by neighbors of one site, came from a site not addressed by measurements in the Phase I report. However, some measures pertaining to these concerns are independently available from work done at Wheeling Jesuit University. These additional measures are valuable for the further consideration of chemicals to be reviewed, and are discussed in this report. Thus, to the degree it relies on the Phase I report, the Phase II report concerning impacts upon benthic communities and human health is constrained by Phase I uncertainties about whether surface waters and drinking waters are actually affected. The additional data obtained from other sources such as Wheeling

Jesuit University measurements have expected limitations as well, and did allow the research team to expand its consideration of chemicals to be reviewed.

Although one watershed area studied in the Phase I report, Wilderness Fork, associated with Loadout LLC, experienced a slurry “artesian event” in 2005, no discernible traces of this event could be detected by the time sampling was completed. This “black water” event is considered to have been substantial, but no flow rate or duration data exist. The interpretation of this incongruity can range from an absence of measurable impact to the inadequacy of the currently available data, suggesting a clear need to sample more frequently, over longer time periods, in more places. The Phase I report leaves open the possibility that the 2005 “artesian event” could have been the source of an earlier possible contamination of an artesian well. However, the actual finding is that the Phase I report of that well does not reveal any residual slurry effects of the event at the time of sampling. Temporal limitations of the measurements relating to this event indicate the need for before-and-after as well as more frequent sampling. In the Phase I report, all sampling was done, by design, in a discrete time period (about one year), and no sampling site was continuously monitored. The Phase I part is constrained by the time period and the periodicity of sampling. This is not a criticism; it merely describes the extent of the effort requested and designed.

### **Impact of Seasonality on Phase I Measures**

Multiple times of sampling are important for understanding pollutants in surface water, groundwater, and ultimately in potable water. Flows vary by season and affect the entry of pollutants into receiving waters as well as the concentrations. Volatile

organic compounds have a high vapor pressure. They are more likely to stabilize in cold water, and more likely to be detected in cold water samples. Some volatile organics, such as acetone, carbon disulfide, and benzene, have also been detected in some systems when stream flow increased. This may demonstrate a “flush-off” effect of heavy rains and snow melts, particularly when surfaces are relatively impervious due to freezing. These are some of many time-variable conditions which can affect the presence and detection of pollutants. These limitations are not unique to any study, but, they are important in constrained time periods.

The Phase I report was designed to be accomplished in a single year. A single year of sampling has potential limitations concerning the variability of weather, pollutant inputs, and pollutant migration into receiving waters.

### **Impact of Public Health Measurement Procedures on Available Data**

Monitoring of potable water measures and current drinking water standards addresses a finite number of elements, chemicals, and indicators. These are national standards, not historically driven by consideration of all measurements that would be pertinent to contamination from coal slurry. In the appendices of this report, readers can compare primary and secondary water quality standards to data which has been provided by researchers independent of the Phase I report. (The Phase I report was not designed to measure pollutants in regional drinking water. This is not a criticism; it is a description of project scope.) Some but not all of the range of chemicals (especially many organic substances) which are potentially significant pollutants in coal slurry,

which might migrate into potable water following injection, are routinely and intermittently monitored in municipal potable water systems and rarely in private wells.

### **Confounding Impact of Historic Coal Activity**

Surface waters and groundwater have been degraded by numerous mining activities throughout Appalachia for more than a century. (Table 2 provides historic estimates of trace elements in coal and coal refuse.) A logical problem faced by the Phase I report was the inability to distinguish water degradation due to coal slurry injection from simultaneous or pre-existing environmental footprints of all aspects of mining activity. Acid mine drainage (AMD) is the best known such impact.

Pyrite, or “fool’s gold,” occurs naturally in coal and in coal overburden. It is the major source of AMD. Combined with oxygen and water, pyrite gives rise to ferrous iron, sulfate, and acidity. A secondary outcome of the AMD then brings other constituents of coal and overburden into acidified water solution. Examples include aluminum, arsenic, barium, cadmium, cobalt, copper, manganese, selenium, silver, strontium, and zinc. However, this general statement has many exceptions, and metals (or their absence) provide inferential rather than perfect data as a proxy of mining activity. The length of time that pollutants stay in solution and travel from the mining activity is highly variable. Sulfate itself tends to stay in contaminated mine drainage because it is highly soluble. Non-AMD is alkaline (by definition). However, non-AMD can also have elevated sulfate and can also carry heavy metals with it. Sulfate concentrations are typically highest in regions with the greatest historic mining activity, but what is typical has many exceptions. When water is degraded from mining activity, there is no universally

accepted method to assign relative contributions to different places and specific areas by mining practices. This report will attempt to make best available inferences using available methods.

In a study of water quality of the Monongahela and Allegheny River basins, the presence of historic coal mining activity influenced the diversity of fish species (Anderson et al., 2000). Similar findings have been found for invertebrate species in the Kanawha-New River basin (Anderson et al., 2000). Mining activities are understood as able to affect groundwater quality after mining and reclamation have ceased. Sulfate, iron, manganese, and dissolved solids are more likely to exceed USEPA potable-water SMCL standards in mined, and even in coal-bearing areas, compared to non-coal geologic areas in the absence of mining activity (Anderson et al., 2000).

### **The Use of Predictive Models**

Predictive models can be useful where measures are absent or insufficient. Predictive models of what will be in coal leachates are heavily influenced by volumes of water added and by pH (Heaton, 1981). Depending on the simulation method used, and the pH of the extraction, the metal content can be under- or overestimated compared to real-life conditions. (Note: The metals do not increase or go away. They will ultimately be in the coal, the leachate, or settled. However, the estimate of what will be in the leachate can vary with the method.) In general, historic predictive testing suggests that slurry could contain undesirable direct additions to drinking water for the following metals: cadmium, mercury, lead in some instances, arsenic and barium less often (Heaton, 1981). Similar considerations pertain to coal. Because industrial practices vary



greatly, predictive models have not been developed for slurry-pertinent additives such as surfactants, solvents, cations, and flocculants.

### **Slurry Disposal Methods**

Most slurry waste from coal preparation is created above ground in slurry impoundments where the slurry solids are left to settle. The discarded water in the impoundment can be recirculated within the preparation plant for some period of time. Impoundments can be consistently enlarged to receive greater volumes and to make up for the volume lost to settled solids or the impoundment water can be injected into underground voids. Impoundment water is contained, but it also migrates to some degree. Slurry impoundments are not designed to fully contain contents. To assist containment of solid particles, flocculants may be added to the process at one or more points in slurry handling to hasten settling. A single preparation plant can generate millions of cubic feet of required storage.

Slurry impoundments present several challenges to the environment and to public health. The eventual potential for catastrophic releases is small at any time, yet over time such events have occurred resulting in drownings and in the release of toxic sediments which affect soil and water flows for miles. The best known catastrophic failure released an estimated 16.6 million cubic feet of slurry water, killed 125 people, and displaced an additional 4,000 people from their Logan County, West Virginia, homes (Davies, 1973). Other breakthroughs have occurred, including a recent vertical breakthrough from a slurry impoundment into underlying coal mines in Martin County, Kentucky, followed by pollution of local tributaries and flooded surface areas. Further,

surface impoundments, when operated as intended, create an unusable terrain for years, and leave sediments behind, including settled toxins. The several problems of above-ground slurry disposal are not the point of this project, yet any discussion of the problems of slurry injection into mining voids lacks context in the absence of mention of the comparison to currently available alternatives that also carry potential risk for local water contamination, i.e., slurry impoundments.

To inject slurry into subsurface voids, preferably well below the local water table that connects to any regional drinking water supplies, may improve upon the problems associated with direct releases of impoundments. And, releasing cold water from underground sources has theoretical advantages including advantages for aquatic life over releases of warmer water from above-ground storage. However, the absence of research providing proof of principle concerning the theoretical superiority of this practice has been noted for decades (Henton, 1987; NSF, 1975; Ackman, 1982; Smith, 1987). Just as slurry injection has some theoretical advantages over surface impoundments and releases, there are theoretical problems with slurry injection that do not pertain to slurry impoundments. Underground mine walls and bulkheads could sustain blowouts or ruptures if slurry injection raises a mine pool to the point that its weight is unsustainable within the current mine structure. Water saturation may degrade mine pillars, causing subsidence. Introduction of methane-forming products could add the risk of underground fires. Subsurface soil saturation may create pathways for water and suspended or dissolved toxicants to reach the surface or to contaminate nearby aquifers, even in the absence of blowouts or visible releases.

The suitability of an abandoned mine void for purposes of slurry injection is theoretically affected by a number of conditions. In order to work well, the void areas should be large and access to them unhindered. The ability to maintain access is advantageous for both the introduction of slurry into the intended area, and for the capability to monitor the outcome. If there are roof falls, the resulting floor rubble should be permeable so that pools do not build up unevenly.

With unhindered entrance, the pool created by injections should, in theory, not require substantial treatment before it could be subsequently drained. All of these considerations, and others, are part of the intent of the permitting process.

Historic reports of contamination events from slurry injection do exist, so the potential problem to be addressed by environmental considerations leading to a valid permit is known to be practical rather than theoretical (Sludge Safety Citizens' Report, 2005) However, the specific conditions leading to problems are poorly characterized. For example, in 1984 a large-scale slurry injection (250 gallons/minute) containing arsenic, barium, cadmium, chromium, lead, selenium, and mercury, all above then-current Safe Drinking Water Act standards, was investigated by the USEPA following a citizen's complaint. The subsequent USEPA evaluation concluded that site injections could endanger water quality and human health for 300 residents who used the pool as a source for drinking water (USEPA, 1985a). In contrast to historic reports of slurry-injection contamination events, there are also some dilution improvements in alkaline mine-water-pool pH following the addition of slurry, noted in references that address this topic for alkaline receiving waters, such as ATSDR (2004).

## **Literature Review**

### **Identification of Sources Being Used for the Investigation**

Specific documentation about potential or reported health effects resulting from underground coal slurry injection is almost nonexistent. However, since coal slurry contains mostly coal-related substances, data about exposure to coal-related products and activities can be used. Also, coal mining and other mining activities share several potential health concerns with slurry injection, such as leaching of heavy metals. Health hazard data related to other mining activities was used for modeling purposes in this review. Extension of health effects reported below about coal and/or mining activities to the specific cases of underground coal slurry injection must be pursued with caution since potential leaching mechanisms and environmental and human exposure routes are likely to be different.

The present literature review focuses on health data related to the following key words and concepts:

- Exposure to coal, coal slurry, coal refuse, coal ash, coal waste, and coal processing products.
- Exposure to other substances resulting from diverse mining activities (e.g. toxic metals or breakdown products of flocculants, known to be in coal waste-processing streams).
- Exposure to hazardous substances detected in significant concentrations in coal slurry during Phase I of this investigation, or in data collected from Phase II researchers' request for public data.

Data reviewed are categorized as followed:

- Peer-reviewed published articles/proceedings obtained using search tools, such as the Web of Science, PubMed/MEDLINE, and Google Scholars. Within PubMed, the toxicology and environmental health sites including the TOXNET databases and linked resources were also accessed. For substances identified as chemicals to be reviewed, ATSDR reports and recent peer review literature from the national library of medicine were accessed.
- Public Health Assessments and Health Consultation previously conducted by ATSDR or other agencies related to the impact of coal mining/processing on community health, such as Martin County, Kentucky and Williamson, West Virginia (<http://www.atsdr.cdc.gov/HAC/PHA/index.asp>).

Reports on worker health and technical reports about processes which were unrelated to human health or water quality were excluded, unless there was a specific reason to include them in order to illustrate a point about human populations more generally. In the few instances in which workplace reports are referenced in order to illustrate a point potentially pertinent to wider populations, the authors have tried to be consistent to cite the workplace origin of the data. Reports which contained references to coal slurry and to human health, to coal slurry and water quality, or to coal slurry and policy recommendations which might reflect on public health, were included.

- Review and analysis of toxicology profiles (ATSDR) of contaminants detected in Phase I at “significant levels.”

## **Toxic Components of Coal, Coal Refuse, and Coal Combustion Products**

### ***Coal Slurry Composition***

According to the Mine Safety and Health Administration (MSHA), there are more than 600 impoundments throughout the Appalachian region. Mined coal has impurities and small pieces unsuitable for use (“fines”) that are removed from coal by washing with water and flocculants, starches, or lime (ATSDR, 2006). Coal slurry typically consists primarily of coal fines, containing carbon (bonded with another carbon, hydrogen, oxygen, sulfur, or nitrogen), hydrocarbons, including complex organic compounds, sulfur, silica, iron oxide, calcium oxide, sodium, and traces of metals (Landsberger et al., 1995; Hower et al., 1996). Genotoxicity and mutagenicity of coal, coal refuse, and coal ash can arise principally from two groups of compounds: polycyclic aromatic hydrocarbons (PAH’s) with a high molecular weight, and salts of heavy metals (Griest et al., 1982; Liu et al., 2000; Manerikar et al., 2008).

### ***Organic Contaminants***

In contrast to metals, which are associated with coal, most of the hydrocarbons are intermittently and variably introduced. No one of these is predicted to be consistently present downstream of coal operations. Numerous hydrocarbon contaminants are neurotoxins, some are carcinogens, and none are known to be consistently found in water downstream from coal operations. This is not because hydrocarbons are absent from slurry. It is because the specific species vary and are

unpredictable. When specific toxicants rather than total hydrocarbons are considered, benzene and toluene are sometimes featured. Shallow wells in close proximity to mining areas may have increased concentrations of benzene and toluene (USGS, 2006).

In addition, the slurry may contain traces of flocculent used to settle out the coal fines. Polyacrylamide flocculent used by coal preparation facilities also contains some hydrocarbons and traces of acrylamide (ATSDR, 2006). Acrylamide monomer is of concern because it is neurotoxic to mammals, including humans, and is also a suspected human carcinogen. Case reports substantiate the neurotoxicity, including but certainly not limited to two coal preparation workers from West Virginia (Mulloy, 1996). Acrylamide is a potential carcinogen. Population studies of acrylamide exposure have not shown a clear relationship to cancer, but evidence of exposure to acrylamide is present in the entire U.S. population (Vesper et al., 2010). Acrylamide biomonitoring is done by measuring adducts. The additional contribution of coal slurry to acrylamide adducts in exposed populations has not been characterized by biological testing. The residual monomer is generally believed to be present in very small quantities in coal slurry settings; however, continuous-monitoring data to conclusively support this prevailing view are not available.

Polyacrylamides are known to bind strongly with soil particles, which are expected to reduce its mobility and bioavailability of a contaminant. On the contrary, acrylamide does not bind to soil and is highly mobile in soil. However, acrylamide is rapidly degraded by microbes in soil (ATSDR, 2006).

Oils and alcohols are added during the coal cleaning process to agglomerate and separate the coal.

### ***Metal and Inorganic Contaminants in Coal Beds***

Presence of toxic metals in coal beds has been investigated in order to characterize the potential release of toxic metals from coal handling and combustion. Hower et al. (1997) analyzed Middle Pennsylvanian Breathitt Formation (Westphalian B) Pond Creek and Fire Clay coals from active coal mines in 22 localities (Pike and Martin Counties, Kentucky). Two metals, arsenic and lead, included in the 1990 Clean Air Act Amendments were analyzed. Findings showed levels as high as 4000 ppm arsenic (ash basis). Most of arsenic compounds (and lead) were associated with pyrite, which is largely removed by coal processing and likely to be found at even higher levels in coal slurries. High levels of arsenic and lead are found in coarse pyrite, enter into coal slurries, raising the problem of coal refuse disposal (Hower et al., 1996; Hower et al., 1997).

Although data about potentially toxic organic compounds in coal are very scarce, there have been several reports suspecting a link between coal organic compounds and human disease. For instance, Balkan endemic nephropathy (BEN) is today hypothesized to be related to long-term exposure to PAHs and other toxic organic compounds leaching from low rank coals (lignite) into drinking water sources (Tatu et al., 1998). Bunnell et al. (2006) investigated the relationship between chemicals and pathogens associated with low rank coal (lignite) and renal pelvis cancer rates in northwestern Louisiana. The authors analyzed samples from private drinking water wells in northwestern Louisiana likely to have been in contact with lignite. Water samples were analyzed for organic compounds, and nutrient and anion concentrations. Significant associations were revealed between the cancer rates and the presence in



drinking water of organic compounds, nutrients (phosphate and ammonia), and 13 chemical elements. This study suggests possible linkages between aquifers containing chemically reactive lignite deposits, hydrologic conditions favorable to leaching of toxic organic compounds, and cancer risk. Although these examples illustrate the potential toxic character of various forms of coal, there is no lignite in West Virginia and this particular case is, therefore, not an issue for human health in the state.

A recent USEPA report characterized coal refuse and determined that mining rejects have a higher concentration of mercury than normal coals (USEPA, 2008). For instance, in West Virginia and Pennsylvania, gob has 3.5-4 times more mercury than bituminous coal. Also, Pennsylvania culm and gob have about four times more chromium and three times more lead, and high levels of arsenic as compared to coal.

### ***Metals Added During Coal Processing***

Magnetite (iron) can be added during coal cleaning processes (beneficiation). Most can be recovered, some adheres to the coal product, and some is lost to waste and appears later in slurry. For practical purposes of public health considerations, magnetite is indistinguishable from the iron that may enter into slurry from the overburden or the mine drainage.

### ***Metal and Nonmetal Electrolytes in Coal Mining***

Sodium chloride and magnesium chloride can be used as electrolyte solutions to assist the flotation aspect of coal cleaning operations. The solution may then become part of the slurry. A variety of simple salts may also be present in overburden; the most notable of these are sulfates. Coal mining activities can increase the electrolyte content

of surface waters downstream. These increases can lead to variations in the electrolyte content and specific conductance of drinking water.

## **Toxicity and Environmental Impact of Coal and Coal-Related Compounds**

### ***Generality***

Coal contaminants from numerous stages of coal mining, cleaning, transport, and waste can enter waste streams. Influential health advocacy groups point out that contaminants can potentially affect all major body organ systems, leading to major causes of mortality in the U.S., such as heart disease and cancer (Lockwood et al., 2009). Although such reports generally consider exposure by inhalation of particles and gases generated by coal combustion, authors also observed that each step of coal processing, from mining to waste disposal, including coal washing can potentially impact human health. Besides other environmental and health threats, the authors pointed out that coal washing generating coal slurry can release arsenic, barium, lead, and manganese, and contaminate nearby wells and local water supplies.

### ***Environmental and Health Effects of Coal Mining Activities***

Intensive Appalachian coal mining has caused extensive surface and groundwater contamination. These are contamination problems which precede any history of coal slurry injection, and which can occur independently of coal slurry injection, yet coal slurry injection may contribute to them. Surface and underground coal mining exposes pyrite and marcasite (iron disulfides) naturally occurring in coal to weathering processes, leading to AMD. AMD results from geochemical and bacterial reactions that occur when pyrite is exposed to air and water. The reactions generate

dissolved ferrous iron that precipitates in the form of insoluble ferric hydroxide. Acidic water then also dissolves other coal and overburden metals such as, aluminum, arsenic, barium, cadmium, cobalt, copper, manganese, and zinc. These metals may enter the water table or surface water, affect wildlife, and render drinking water unfit for consumption (USGS, 2000). Mining activity can also generate neutralized or alkaline mine drainage (NAMD). NAMD is produced when the metals in the mine drainage are precipitated through a rise in the pH of the solution. Adding oxygen to the mine drainage aids in the precipitation and settling of the metal hydroxides (USEPA, 1983). NAMD often contains elevated concentrations of sulfate, iron, manganese, and other constituents. The USEPA has established Secondary Maximum Contaminant Level (SMCL) of 250 mg/L for sulfate. Besides taste and odor problems, high sulfate concentrations in water may cause diarrhea in sensitive populations. Concentrations of sulfate are, on average, five times greater in coal mine-impacted stream basins than in unmined basins. As reported in a study conducted on the Allegheny and Monongahela River Basins fish community (ALMN), a difference in fish abundance and diversity of species was observed between streams receiving mine drainage as compared to those in unmined basins (USGS, 2000). Similarly, a study conducted on aquatic invertebrates (insects, worms, crustaceans, and mollusks) showed an inverse relationship between sulfate concentrations and the diversity for three groups of sensitive insect species (mayflies, stoneflies, and caddisflies).

A recent USGS report compared groundwater quality in mined and unmined areas in the northern and central Appalachian coal regions of Pennsylvania and West Virginia (USGS, 2006). Groundwater in the mined high-sulfur coal region (northern

Appalachian coal region) has higher concentrations of sulfate, calcium, and specific conductance as compared to the unmined high-sulfur-coal region (and to both mined and unmined areas in the low-sulfur-coal region). This phenomenon is explained by the transport of pyrite-oxidation products from the mined site and subsequent neutralization reactions by calcareous materials at the mine site or along the flow path. These mine-drainage constituents generally exceeded background concentrations only in the close vicinity of mined sites (<500 ft). Concentrations of sulfate, hardness, and TDS were higher in shallow groundwater (50-150 ft) and generally less than background concentrations in deeper groundwater. Also, concentrations of iron, manganese, and aluminum were reported higher than background concentrations in many shallow wells. The USGS report also presents data about the analysis of volatile organic compounds (VOCs) measured in mined and unmined areas in the northern Appalachian coal region (30 and 15 wells, respectively). Of the 86 compounds analyzed, seven compounds were detected in mined areas only and eight compounds were detected in unmined areas. The detected chemicals included benzene, toluene, and xylene (BTEX), halogenated alkanes and alkenes, ketones, tetrahydrofuran, and carbon disulfide. Detection frequencies of benzene and toluene were greater in mined areas than unmined areas.

### ***Environmental Contamination by Coal Slurry Impoundments***

In an attempt to assess well and drinking water contamination by the coal slurry impoundment failure in Martin County, Kentucky, in 2000, Wigginton and coworkers analyzed water samples collected from hot water tanks in the affected area (Wigginton et al., 2007). The hypothesis for this sampling strategy was that hot water tanks indicate

previous contamination from the water supply because sediment and precipitates accumulate in the tanks. (Technical constraints of this strategy include but need not be limited to the independent contributions of the tank, and its anode, valves, and fittings, as well as any biofilms and their contributions. In addition, the time course over which precipitates accumulate and flush has not been modeled. These data gaps represent potential constraints upon the interpretation of collected hot water tank precipitates data as it may reflect long term concentrations of the measured contaminants in water.) Results obtained show that samples taken from affected and reference area hot water tanks often exceeded USEPA drinking water guidelines including arsenic, cadmium, chromium, copper, iron, manganese, and lead. Barium, mercury, and selenium did not exceed USEPA limits in any samples. The report also showed strong correlations among metal concentrations for arsenic, barium, cadmium, chromium, cobalt, and iron, indicating that these metals may accumulate proportionally. Importantly, the authors did not find any clear relationship between metals in the hot water tanks and at the current water source, as sampled from the cold-water tap, which may be explained either by the high efficacy of hot water tanks to concentrate metals from source water, or by the historic presence of more metals in source water than at present, or by limitations of the sampling strategy. The authors pointed out that accumulated copper, iron, and lead may come from water system pipes and plumbing.

An unpublished study investigated the water quality of 15 wells collected within 2 air miles of the Sprouse Creek Slurry Impoundment (Stout and Papillo, 2004). The study focused on seven heavy metals regulated by USEPA primary drinking water standards and five metals regulated by secondary standards. Results indicated that primary

drinking water standards were exceeded for lead, arsenic, barium, beryllium, and selenium. Secondary drinking water standards were exceeded for iron, manganese, aluminum, and zinc. A comparison of water quality during low flow versus high flow events showed the detection of arsenic and lead at a higher frequency during high flow. Comparing well water in the Williamson area with neighboring counties of southern West Virginia and eastern Kentucky indicated that Williamson area wells had the poorest water quality in the coalfield region.

### ***Coal Combustion Residues***

Although they are not coal or coal slurry *per se*, coal combustion residues illustrate chemicals/elements that are found in coal and coal slurries (Elmogazi et al., 1988), especially the inorganic contaminants.

Intentional or accidental releases of coal combustion residues result in deleterious effects to aquatic environments (Gupta et al., 2002; Reijnders, 2005). Metals and trace elements present in combustion residues have accumulated in aquatic organisms to reach very high concentrations, sometimes much higher than concentrations detected in contaminated water (Rowe et al., 2002). Biological effects were observed in both vertebrates and invertebrates, including histopathological, behavioral, and physiological (reproductive, energetic, and endocrine) effects. Release of coal combustion products has resulted in fish kills and extirpation of sensitive species, with indirect effects on the entire ecosystem due to changes in resource abundance or quality (Rowe et al., 2002). Recovery of impacted sites can be extremely slow due to cycling of elemental contaminants, even in sites that have been exposed for

short periods of time. Many studies have focused biological effects of exposure to selenium because of associated teratogenic and reproductive toxic effects. The complex mixture of metals and trace elements characteristic of coal combustion residues suggests that a large variety of inorganic compounds enter sediments, water, and organisms, including terrestrial, semiaquatic, and avian species that live at or visit impacted aquatic sites (Rowe et al., 2002).

Brieger and coworkers (1992) reported on 48 plant species, 18 terrestrial animal species, and 7 aquatic animal species collected on a coal fly ash slurry impoundment site and a dry deposit site. These were analyzed for the presence of metals using neutron activation analysis. Based on phytotoxicity levels found in the literature, the authors concluded that, in general, plants did not accumulate toxic levels of metals; one plant exhibited high levels of cadmium and sixteen had excessive levels of selenium concentrations (>5 ppm). (The ability of plants to concentrate cadmium is a specific health concern. Because inhaled cadmium is well absorbed, tobacco plants can be a significant source of cadmium, and the presence of cadmium in crop soil is a seldom considered additional public health concern where tobacco is planted.) Yet, trace metal concentration in terrestrial animals was generally in between that of control animals and that of the fly ash itself. Zinc was concentrated in all the terrestrial animals to levels higher than in fly ash. Crickets concentrated high levels of chromium, selenium, and zinc, and all animal species studied accumulated high levels of selenium.

Selenium was also found to accumulate into aquatic organisms, such as observed in a selenium-contaminated lake (Lake Macquarie, Australia); *Marphysa sanguinea* and *Spisula trigonella* accumulated significantly more selenium when

exposed to contaminated sediment than when exposed to uncontaminated sediments. Most of the selenium in mollusk tissues was found to be associated with the protein fraction as selenomethionine (Peters et al., 1999)

Research on responses of aquatic organisms to exposure to coal combustion residues suggests that disposal methods which prevent an aquatic slurry phase may limit environmental risks (Rowe et al., 2002).

Genotoxicity and mutagenicity of coal, coal refuse, and coal ash arise principally from two groups of compounds: higher molecular weight PAHs and salts of heavy metals (Griest et al., 1982; Liu et al., 2000; Manerikar et al, 2008). Chakraborty and Mukherjee (2009) investigated the toxicity of leachate from ash ponds used for disposal of coal ash slurry near power stations. Elemental analyses of leachate showed predominance of sodium, silicon, potassium, calcium, magnesium, iron, manganese, zinc, and sulfur. Ames *Salmonella* mutagenicity assay revealed that the leachate was mutagenic, even though sterilization by autoclaving rendered it non-toxic, presumably because of the removal of metals by precipitation. However, based on Comet assay, the leachate was found to be directly mutagenic and induced significant ( $P < 0.05$ ) concentration-dependent increases in DNA damage in whole blood cells, lymphocytes, and *Nicotiana* plants. These results indicate that leachate from fly ash dump ponds has genotoxic character, potentially leading to adverse effects on plants, animals, and human health (Chakraborty and Mukherjee, 2009).



### ***Underground Backfilling of Coal-Related Waste***

A USEPA report was published in 1999 on Class V underground injection wells to evaluate the risk posed to underground sources of drinking water (USEPA, 1999). This study was conducted to develop background information the Agency can use to evaluate the risk that these wells pose to underground sources of drinking water (USDWs). The report reviewed here (USEPA, 1999), volume 10, covers Class V mining, sand, or other backfill wells. Although the report concerns various kinds of mine backfilling materials, it also includes coal cleaning waste and other coal-related waste. Mine backfill wells are used to inject a mixture of water and other materials, including sand, mine tailing, coal combustion ash, coal cleaning wastes, AMD treatment sludge, and/or flue gas desulfurization sludge, into mined out portions of underground mines. Mine shafts and pipelines in an underground mine, as well as more conventional drilled wells, used to place slurries and solids in underground mines are considered mine backfill. In a summary statement that applies to all kinds of mine backfills, the document reports that, even though the physical and chemical characteristics of the injected materials vary widely, data from leaching tests of backfill materials indicate that concentrations of heavy metals (e.g., antimony, arsenic, barium, beryllium, boron, cadmium, chromium, lead, mercury, molybdenum, nickel, selenium, thallium, and zinc) frequently exceed primary maximum contaminant levels (MCLs) or health advisory levels (HALs), while concentrations of aluminum, copper, iron, manganese, TDS, and sulfate, as well as the pH, frequently exceed secondary MCLs. However, the report indicates that no incidents of contamination of a drinking water supply have been identified that are directly attributable to injection into mine backfill wells. The report also

mentions that groundwater contamination is common at mining sites, making it difficult to identify the specific causes. The likelihood of groundwater contamination from backfill injection is dependent on site conditions, including mine mineralogy, site hydrogeology, backfill characteristics, and injection practices. Based on this report, approximately 5,000 documented mine backfill wells and more than 7,800 wells are estimated to exist in the U.S., with 401 known in West Virginia only (USEPA, 1999).

Constituent properties of backfill-wells material that may affect drinking-water supplies are toxicity, persistence, and mobility. Constituents frequently exceeding health-based standards in Toxicity Characteristic Leaching Procedure (TCLP) or other leachate from backfill material include antimony, arsenic, barium, beryllium, boron, cadmium, chromium, lead, mercury, molybdenum, nickel, selenium, thallium, and zinc. In addition, aluminum, copper, iron, manganese, TDS, sulfate, and pH have been frequently measured above secondary MCLs in TCLP or other leachate. The persistence of constituents that leach from mine backfill depends on complex solution-mineral equilibria that are determined by site-specific conditions such as leachate and groundwater characteristics, host rock characteristics, and oxygen availability in the mine workings and surrounding formation (USEPA, 1999). For injected backfill, mobility of metals in the mine environment is primarily dependent on their tendency to dissolve, which generally increases as pH decreases. Precipitation can also occur as a result of oxidation when reducing environment is exposed to oxygen supply, although the same phenomenon can also result in dramatic pH reduction, therefore, increasing metal solubility. Injection of backfill material often occurs at sites where low pH water is present and in contact with the backfill injection zone. At these sites, mobility of most

metals present in the backfill will be greater than if injection occurred under neutral or alkaline pH conditions. However, backfill injection under these conditions can also result in a decrease in metal mobility by reduction of water flow rates through the mine if the backfill eliminates direct air contact with pyrite or other sulfide minerals, which will greatly reduce acid generation and metal solubility and mobility (USEPA, 1999). In other words, mine backfill can improve water quality. When this occurs, the specific contribution of coal slurry is unknowable among the constituents.

### ***Injection of Coal-Cleaning Waste***

The USEPA report (USEPA, 1999) includes also a distinct section specifically dedicated to the injection of “coal-cleaning waste” that is of special relevance for our review. “Coal-cleaning waste,” the results from the wet cleaning of raw coal, is defined as extremely fine solids, including coal particles and coal associated minerals, suspended in water. The report indicates that the chemical composition of the injected material depends primarily on the characteristics of the coal, associated bedrock, and water used in the cleaning process. For instance, the injected slurry of a Colorado mine (New Elk Mine) was shown not to exceed the relevant primary or secondary MCLs or HALs for the constituents tested, with the exception of arsenic and total suspended solids. On the other hand, cleaning waste slurry and slurry leachate from an Indiana mine (Kindall mine) exceeded the primary MCLs for arsenic, cadmium, and lead, and the secondary MCLs for TDS, sulfate, and manganese.

A 1987 study assessed the injection of coal slurry wastes from coal preparation and sludge from treatment of AMD into underground coal mines in West Virginia (Smith

and Rauch, 1987) In some cases (7 mines), slurry injection was found to improve the already degraded water quality by increasing alkalinity and pH, and decreasing concentration of iron and manganese, even though sulfate concentration was shown to increase. The researchers could not determine if this pH increase was due to a chemical reaction or dilution. Only minor changes in trace element concentrations were detected that did not appear to be a concern for drinking water. Sludge injection at other sites (3 mines) appeared to increase alkalinity, pH, sulfate, and total suspended solids. Generally speaking, injection into mines with high pH water resulted in lower iron and manganese concentrations and injection into mines with low pH resulted in increase of iron concentrations, although most changes in other trace element concentrations were negligible, with the possible exception of arsenic.

## **Transport and Mobility of Coal-Associated Contaminants**

### ***General Considerations***

For many years, coal fly ash produced by thermal power plants has been hydraulically placed openly in impoundments in the form of wet slurry. There is evidence that leaching of trace toxic metals from these impoundments has occurred that contaminate both surface and groundwater. Wasay (1992) investigated leaching of chromium (III), chromium (VI), mercury (II), and arsenic from fly ash at various pH levels through monitoring wells surrounding a dumping site and designed for studying these metals in groundwater. It was estimated that at pH 7.0, about 40% of these toxic elements were leachable and susceptible to contaminate groundwater.

A report from Krishnan et al. (1992) studied leachability of the toxic elements, cadmium, arsenic, mercury, and selenium from various solid wastes, including coal fly ash. The results concluded that cadmium displayed the greatest leachability in all waste types (up to 76%). Leachability and bioavailability of metal in ashes appeared to be mainly determined by the volatility of the element.

Based on the history of selenium pollution in a lake (Lake Macquarie, Australia), the authors observed major selenium contamination in the last 30 years, due to a fly ash dam associated with nearby electric power generation plants (Peters et al., 1999). Changing redox condition in lake sediments resulted in a release of selenium under oxidizing conditions and immobilization under reducing conditions. The sediment-bound selenium was associated with organic/sulfide fraction under reducing conditions, and, as the redox potential increased, it moved into more exchangeable iron/manganese oxyhydroxide phases.

A USEPA study was conducted between 1975 and 1979 at an abandoned sand pit near Boguszowice, Poland to determine the extent of groundwater deterioration due to coal mine refuse disposal (USEPA, 1983). Groundwater and leachates were monitored and laboratory testing was conducted. Leaching experiments revealed that pollutants may be divided into three groups: most easily leached (chloride, sulfate, sodium, potassium), medium leachability (copper, zinc, mercury, strontium, cadmium, manganese, molybdenum, cyanide), and slowest leaching (magnesium, aluminum, chromium, arsenic, lead, ammonia, calcium). Colloidal sediments were shown to be flushed from the coal waste. This report concluded that coal refuse disposal in an abandoned open pit in contact with an underlying aquifer deteriorated groundwater

quality at the site. The report also pointed out that the level of groundwater contamination depends on the leachability of the wastes, the amount of precipitation, and the self-sealing of the disposal site bottom by the fine clays washed out from the waste. Also, it was observed that significant pollution occurred only in the direction of the greatest declination in the groundwater table. Finally, the report divided coal waste into two subgroups: dry and wet wastes, of which the wet waste has a greater potential for groundwater contamination because of its fine granulation.

Regarding underground coal slurry injection, it is noteworthy that chemical models predict that the high pH associated with coal slurries would prevent acid leaching of toxic metals by precipitation of metal oxides, hydroxides, and carbonates. In addition, underground injection of coal slurry is likely to result in reducing conditions due to consumption of oxygen by chemical reactions and metabolism of heterotrophic microorganisms. Reducing conditions will further contribute to the immobilization of metals by formation of insoluble sulfides.

### ***Coal Slurry Injection Considerations***

Very little information is available regarding potential contamination of groundwater by organic compounds from coal slurry. Madsen et al. (1996) investigated the transport of naphthalene from buried subsurface coal tar and observed a 400-m migration via groundwater to an organic matter-rich seep area. Using laboratory analyses, the authors determined that neither toxicity nor nutrient limitation was the cause of naphthalene persistence. They suggested that oxygen limitation was the most

probable cause for lack of naphthalene biodegradation, even though diffusion or sorption reactions might also play a role.

Even though leaching of organic compounds from coal slurry is an understudied phenomenon, evidence is accumulating that sorption of organic chemicals to carbonaceous materials, including coal and kerogen, may exceed absorption in amorphous organic matter by a factor of 10 to 100. Presence of such carbonaceous materials can explain that sorption of organic materials to soils and sediments is up to two orders of magnitude higher than expected on the basis of sorption to organic matter only. Also, higher sorption of organics on carbonaceous materials may explain low observed biota to sediment accumulation factors and limited potential for microbial degradation (Cornelissen et al., 2005).

### **Microbiology of Coal-Related Compounds**

Bioleaching of toxic metals, such as aluminum and iron from coal fly ash, is known to be mediated by acidophile bacteria such as *Thiobacillus thiooxidans* (Johnson and Hallberg, 2003). Laboratory-scale studies of the interactions between bacteria, metabolic coal fly ash particles, and metal leaching, Seidel et al. (2001) showed that coal could mitigate metal leaching through the release of alkaline components that causes a rise in the pH and inhibition of bacterial growth by attachment of the cells to both sulfur particles and coal ash particles.

Bacteria isolated from selenium-contaminated Lake Macquarie, Australia sediment were able to transform selenite to elemental selenium. While most isolates

grew on media containing selenate, no elemental selenium was formed from this species (Peters et al., 1999).

Prokaryotes, including bacteria and archaea, are known to play potentially important roles on the chemistry of coal and coal refuse (Faison, 1991). Heterotrophic aerobic microbes are expected to use abundant organic material as electron donors, which results in oxygen depletion and anoxic conditions. In the absence of oxygen, heterotrophic anaerobes use alternate electron acceptors, such as sulfate, which generate toxic sulfides (Stoner et al., 1993).

The overall effect of microbial activity on underground coal slurry injection is unpredictable in the absence of comprehensive, specific investigation. Some beneficial effects can be considered, including immobilization, sequestration, and biodegradation of toxic organic contaminants (Fakoussa and Hofrichter, 1999; Filcheva et al., 2000).

Although aerobic degradation is faster, it has been shown that some hydrocarbons are efficiently degraded under anaerobic conditions by bacteria using a variety of electron acceptors (Foght, 2008). Aromatic hydrocarbons enter the environment through various human activities, including crude oil spillage, fossil fuel combustion, and coal mining and coal refuse dumping. Aromatics (such as benzene and toluene), PAHs (such as naphthalene and pyrenes), and numerous alkyl-substituted isomers impact both aerobic and anaerobic environments such as aquifers, freshwater bodies, soils, and sediments. It has been recently observed that anaerobic biodegradation of aromatic and saturated hydrocarbons is a widespread activity that can occur under nitrate-, iron-, manganese- and sulfate-reducing, and methanogenic conditions.



Using fluorescent in situ hybridization (FISH), Bakermans and Madsen (2002) detected intracellular messenger ribonucleic acid (mRNA) coding for naphthalene dioxygenase, a key enzyme involved in bacterial biodegradation of naphthalene, in coal tar waste-contaminated groundwater. This study suggests the presence of the potential for naphthalene biodegradation in coal contaminated environments.

## **Summary**

Because specific documentation about potential or reported health effects resulting specifically from underground coal slurry injection is scarce, information about coal-related products and activities, coal mining, and other mining activities have been included in the review. Extension of environmental and health effects reported below about coal and/or mining activities to the specific cases of underground coal slurry injection must be pursued with caution since potential leaching mechanisms and environmental and human exposure routes may be different.

## ***Toxic Components of Coal, Coal Refuse, and Coal Combustion Products***

Coal slurry typically consists primarily of coal fines, containing carbon, hydrocarbons, complex organic compounds, sulfur, silica, iron oxide, calcium oxide, sodium, and traces of metals (Landsberger et al., 1995; Hower et al., 1996). Toxicities of coal slurry potentially arise from coal components, such as PAHs and salts of heavy metals (Griest et al., 1982; Liu et al., 2000; Manerikar et al., 2008), and from coal processing chemicals, such as acrylamide which was used as a monomer historically in coal processing. This process has changed. Today, acrylamide can be present in trace amounts from mining activities and also from traces of acrylamide monomer present in

the quantities of partially polymerized polyacrylamides now used in coal cleaning (ATSDR, 2006).

Although very little research on the possible health impacts of organic substances in coal slurry has been performed, the greatest environmental impact from coal slurry is likely due to heavy metals. Available literature strongly suggests that the likeliest environmental and health concerns of coal slurry injection will be related to heavy metals that have the potential to migrate into nearby aquifers and potentially contaminate water supplies and private wells. According to the National Research Council, the elements of greatest concern in coal are arsenic, boron, cadmium, mercury, molybdenum, lead, and selenium (NRC, 1980).

### ***Toxicity and Environmental Impact of Coal and Coal-Related Compounds***

It is widely recognized that the intensive coal mining in the Appalachian region for more than 200 years has led to extensive surface and groundwater contamination (USGS, 2006). This background of contamination makes it very difficult to isolate the specific impact of underground coal slurry injection on the environment and human health. For instance, coal mining activities are known to generate AMD, an acidic water containing high levels of sulfate and metals that contaminates many streams in West Virginia and Pennsylvania (USGS, 2000). Analysis of VOCs in the northern Appalachian coal region show that toxic chemicals, such as benzene, toluene, ethylbenzene, and xylene (BTEX), halogenated compounds, and tetrahydrofuran, were detected in mined areas. However, there is no evidence that these observations are specifically related to underground coal slurry injection.

Analyses of hot water tank water from homes in an area contaminated by coal slurry following impoundment failure (Martin County, Kentucky, 2000) showed that water samples taken from both impacted and reference areas often exceeded USEPA drinking water guidelines for several metals, including arsenic, cadmium, chromium, copper, iron, manganese, and lead. Analysis of well water quality in the vicinity of the Sprouse Creek Slurry Impoundment showed that primary drinking water standards were exceeded for lead, arsenic, barium, beryllium, and selenium and secondary drinking water standards were exceeded for iron, manganese, aluminum, and zinc (Stout and Papillo, 2004).

Many reports focus on the environmental impact of coal combustion residues. Although they are not coal slurry *per se*, coal combustion residues potentially contain chemicals that are found in coal slurries (Elmogazi et al., 1988). Generally speaking, release of combustion residues of coal into the aquatic environment has resulted in deleterious effects, such as the accumulation of toxic metals in aquatic organisms (Rowe et al., 2002; Gupta et al., 2002; Reijnders, 2005).

A previously mentioned USEPA report included data on Class V underground injection wells. It intended to evaluate the risk posed to underground sources of drinking water (USEPA, 1999) and is of special interest to this study. A distinct section specifically dedicated to the injection of “coal-cleaning waste” is particularly relevant. The report cites the example of two mines injected with coal slurry: New Elk Mine (Colorado) with coal slurry exceeding drinking water standards for arsenic and total suspended solids (TDS), and Kindall mine (Indiana) with coal slurry and slurry leachate exceeding drinking water standards for arsenic, cadmium, lead, TDS, sulfate, and

manganese. However, the report indicates that no incidents of contamination of a drinking water supply have been documented that are directly attributable to injection into mine backfill wells.

### ***Transport and Mobility of Coal-Associated Contaminants***

Evidence of toxic metal leaching has been obtained from the study of impoundments used for coal fly ash storage. For instance, it was estimated that at pH 7.0, a significant fraction of toxic elements, such as chromium, mercury, and arsenic, are leachable and may contaminate groundwater (Wasay, 1992). A previously mentioned USEPA study conducted at an abandoned sand pit used for coal mine refuse disposal (in Poland) concluded that contaminants susceptible to be leached may be divided into three groups: most easily leached (e.g., sulfate, sodium), medium leachability (e.g., copper, zinc, mercury, cadmium, manganese), and slowest leaching (e.g., aluminum, chromium, arsenic, lead). It is uncertain to what degree these data are reliably useful in practice, as there were insufficient measures to provide proof of principle.

## **Analysis of Phase I Data**

### **Introduction**

In order to assess the potential impact of underground coal slurry injection on the environment and human health, Phase I of this investigation conducted quantitative analyses of chemicals present in coal slurries collected at six different locations. The selection of the sampling sites was made by consensus of the SCR-15 study team with input from citizens and environmental groups concerned about the coal slurry issue.

### ***Southern Minerals***

Southern Minerals, located in McDowell County, is the oldest active injection site in the state of West Virginia. There are two large public water supplies near the site that could be potentially affected by the coal slurry injection points.

### ***Loadout***

Loadout, LLC in Boone County was selected because it is the only site in the State where no other mining activity occurred in the watershed prior to slurry injection. That means a major part of the watershed was unaffected by mining and, therefore, this site provides potentially useful data to infer a baseline comparison.

### ***Panther***

Panther, LLC located in Kanawha County, was chosen regarding the water quality concerns brought by environmental groups and residents of the area.

### ***Power Mountain***

Power Mountain, located in Nicholas County, was chosen because, after Southern Minerals, it is the oldest slurry injection point, being the most disturbed by mining activity. In addition, water quality problems in wells located near this injection point have been reported.

Two additional slurry sites were selected in order to have a broader set of locations that allow evaluating the variability of slurry composition only.

## **Coresco**

Coresco, Inc., located in Monongalia County, was selected to assess the variability of slurry in the State. However, Coresco is the only plant in the State of West Virginia that does not use chemicals in coal processing. It is unique.

## **Marfork**

Another slurry composition-only site, Marfork, is located in Raleigh County, and does actually not use slurry injection.

Determining the public health and environmental impacts of coal slurry requires information about the constituents in coal slurry which can potentially be released into the environment. Analysis of the liquid phase of the slurry and leachate was performed in order to provide information about the chemical composition of coal slurry.

Samples of coal slurry and run-of-mine coal were collected at sites where injection activities occurred and were analyzed for a suite of organic and inorganic constituents. The liquid phase of the sample was separated at the lab through settling the solids and decanting the liquid. The solid and liquid portions (phases) of the slurry were then analyzed separately. To further understand the composition of the slurry, a solid coal and simulated coal leachate were also analyzed.

A total of 175 different parameters were analyzed for each sample (see Table 3). These parameters were grouped into five different categories including *metals* (e.g., aluminum, arsenic, chromium, selenium), *general chemistry* (e.g., nitrogen, fluoride, alkalinity, pH), *volatile organic compounds* (e.g., acetone, benzene, xylene), *semi-volatile organic compounds* (e.g., naphthalene, phenol), and *miscellaneous* (e.g.,

acrylamide, cyanide, bacteria). Complete results of the analysis performed during Phase I of this investigation are presented in Appendix-O of the Phase I report (WVDHHR, 2009). Maps of the extent of underground mining are also available for each site in the Phase I report (WVDEP, 2009).

### **Relationship of Well Water, Surface Water, and Supply Water Chemicals to Groundwater Content**

Reasonable estimation of the extent to which groundwater, surface water, and supply water are impacted by nearby leaching wastes is limited by many factors. These include migration potential of contaminants, hydrogeology of the site, and reactivity or biodegradation of contaminants. In addition, this situation is further complicated by the fact that it is virtually impossible to isolate contaminants leaching from underground coal slurry from specific indigenous soil, background, and other contaminants coming from other sources in areas heavily impacted by coal mining activities.

In this investigation, we chose to adopt the most conservative approach with respect to health protection. Contaminants of concern (substances selected for consideration) were selected based on the hypothesis that concentrations measured in the liquid phase of coal slurry samples of the different sites under study could potentially result in equal, but not higher, concentrations in soil, stream water, and drinking water, through the contamination of private wells and water supplies. Although it is possible that chemical reactions between water constituents could increase the concentrations of those constituents, the assumption that higher concentrations would not be found was made because higher concentrations could only be found if there was another source of contamination other than the coal slurry itself. Due to the large number of different

constituents of coal slurry, the amount of possible chemical reactions among slurry constituents could not be accurately modeled and as such, were beyond the scope of this investigation.

### **Selection of Chemicals to be Reviewed**

The first step in the assessment of human health risk is the selection of chemicals to be reviewed. This process compares data from the sites under study to relevant media-specific environmental guideline comparison values (CVs). CVs have been established on the basis of an evaluation of toxicology literature for a given substance and they are used as screening tools. The comparison values used for this investigation were obtained from the USEPA and the ATSDR.

Exposure to a chemical below its corresponding CV indicates that adverse health effects are unlikely based on current knowledge (historic trends suggest we may raise or far more often lower safe thresholds as mechanisms of toxicity are newly understood). Many safety factors are included in the derivation of these values; they are designed to be conservative (i.e., protective of public health), although the historic trend toward lower thresholds provides a perspective on the limits of our understanding at any time. Chemicals found at a concentration above a CV are considered chemicals to be reviewed. However, exposure to chemicals above a CV *does not necessarily mean* that an adverse health effect will result. Exposure above a CV simply indicates *a need for further evaluation* to determine if the exposure *could have caused* adverse health effects at this site (ATSDR, 2009a). Furthermore, in the absence of historical data, Phase II researchers are discussing the potential for an exposure above a threshold. It



is unknown with certainty that such exposure has occurred. Under working assumptions, modeling indicates that it can.

When more than one CV was available for one chemical, it was considered as contaminant of concern if its concentration exceeded at least one of the CVs. Some chemicals have both carcinogenic and non-carcinogenic CVs. For chemicals with both carcinogenic and non-carcinogenic CVs, the most conservative CV (i.e., the lowest) is selected.

Concentrations of different contaminants in samples collected at coal and coal slurry-contaminated sites during Phase I of this investigation were compared to different CVs. Results are presented in Table 4. For all contaminants analyzed in the liquid phase of coal slurry in Phase I of this investigation, Table 4 presents the concentrations determined in each sample (if detected), the corresponding environmental and health guidelines developed by ATSDR and/or USEPA, and whether the contaminant belongs to the 2007 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) priority list of hazardous substances (<http://www.atsdr.cdc.gov/cercla/07list.html>). Chemicals found at concentrations above a CV (i.e., chemical of concern) are highlighted in bold italics.

According to the comparison presented in Table 4, the metals that are of environmental concern for the different sites include: aluminum, antimony, arsenic, iron, lead, and manganese. Note that all of these except manganese were predicted from the literature review concerning coal waste more generally. However, that list also predicted metals such as cadmium and strontium, which do not appear here. In the category of general chemistry, it was found that nitrogen (nitrite), chloride, fluoride, sulfate, TDS,

and pH are of environmental concern. These were all predicted in the literature search. Although most volatile or semi-volatile organic compounds were not detected during Phase I analyses, concentrations determined for a few of them were found to be below the environmental guideline values. The following VOCs were detected: 2-butanone, acetone, acrolein, benzene, *m,p*-xylene, methylene chloride, *o*-xylene, and toluene. The following semi-volatile compounds were detected: *bis*(2-ethylhexyl)phthalate, naphthalene, and phenanthrene. All organics detected are listed as CERCLA list of priority pollutants. However, their detected concentrations are below the environmental and health guidelines so they are not considered in this study as contaminants of concern.

Environmental guideline CVs used in this screening are the following (USEPA, 2006; USEPA, 2009):

- ***Drinking Water Equivalent Level (DWEL)***: A lifetime exposure concentration protective of adverse, non-cancer health effects that assumes that all of the exposure to a contaminant is from drinking water.
- ***Health Advisory (HA)***: 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.
  - ***One-Day HA***: The concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for up to one day of exposure. The One-Day HA is normally designed to protect a 10-kg child consuming 1 liter of water per day.

- **Ten-day HA:** The concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for up to ten days of exposure. The Ten-Day HA is also normally designed to protect a 10-kg child consuming 1 liter of water per day.
- **Lifetime HA:** The concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for a lifetime of exposure. The Lifetime HA is based on exposure of a 70-kg adult consuming 2 liters of water per day. The Lifetime HA for Group C carcinogens includes an adjustment for possible carcinogenicity.
- **$10^{-4}$  Cancer Risk:** The concentration of a chemical in drinking water corresponding to an excess estimated lifetime cancer risk of 1 in 10,000.
- **Maximum Concentration Limits (MCLs):** The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to the MCLG (Maximum Concentration Limits Goal) as feasible using the best available analytical and treatment technologies and taking cost into consideration. MCLs are enforceable standards.
- **Secondary Drinking Water Regulations (SDWR):** Non-enforceable Federal (USEPA) guidelines regarding corrosion control and cosmetic effects (such as tooth discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water. While the regulatory intent of SDWR is non-health and non-enforceable, it should be noted that measures of potential health concern are covered, including manganese, sulfate, and TDS.

## Exposure Pathway Analysis in Human Risk Assessment

An exposure pathway consists of five parts:

1. A source of contamination (in the context of a coal slurry risk assessment, this includes the potential toxins in the coal slurry).
2. The “medium” of exposure, including the movement of the contaminant(s) into and through the environment (in soil, air, groundwater or surface water, and onto land) to bring it into contact with people.
3. A point of exposure, or a place where humans could be exposed to the contaminant(s).
4. A way for humans to be exposed to the contaminant(s) (such as by drinking contaminated water or breathing contaminated air).
5. A receptor population or one or more people who may have been or may be in contact with the contaminant(s).

Exposure pathways are considered complete when all five of these elements existed, in series, at some point in the past, exist in the present, or are predictably *likely* to occur in the future. Exposure pathways are considered potential when one or more of the elements is missing or uncertain but could have existed in the past, could be occurring now, or could exist in the future. Pathways are considered eliminated when one or more of these five items does not exist or where conditions make exposures highly unlikely. A completed pathway means that people have been exposed to chemicals. However, the existence of a completed pathway *does not necessarily mean that a public health hazard existed* in the past, exists currently, or is likely to exist in the future. Chemicals found in the completed pathways are evaluated to determine whether

adverse health effects could have occurred in the past, are occurring in the present, or could occur in the future (ATSDR, 2009b).

### **Uncertainties of Pathway Exposure**

A limitation with this kind of analysis is that it is done once, and designed to evaluate future risk in terms of probabilities. Scientists want and citizens deserve long-term assurances; risk assessments address recent historic measurements and attempt to make reasonable projections based on these. Experts are required to make reasonable projections and, therefore, reject unlikely possibilities. Yet, over long time periods, some unlikely events will also happen, although it is nearly impossible to predict which unlikely events will occur. Changes in environmental conditions and population activities are also partly unpredictable over long time periods (ATSDR, 2009b).

Chemicals can enter the body in three ways:

- The chemicals can be ingested, either in food or drinking water, and using the water for cooking. Small amounts of contaminants encountered through normal hand-to-mouth activities are known as incidental ingestion.
- The chemicals can enter the body through the skin. This is called dermal exposure. The skin presents an important barrier to metals in most (but not all) of their forms. Dermal exposure also includes the absorption of chemicals through the mucous membranes.

- The chemicals can enter the body by breathing air containing chemicals or particles that are small enough to get into the part of the lung where they can be absorbed. This is called *inhalation*.

## **Identification of Potential and Completed Exposure Pathways in Humans**

### ***Ingestion of and Dermal Exposure to Chemicals in Water: Completed Pathways for the Past, Present, and Future***

Metals and elements found in groundwater, well water, supply water, and surface water at the vicinity of slurry injection sites may be naturally occurring or may be related to past coal mining activities. Metals and elements in home supply water may also result from the corrosion of metal objects, such as the metal well casing, water pumps, hot water tanks and their anodes, fittings, and valves, and water pipes in contact with the water. These metals and elements may be either dissolved in the water, found as small particles in the water, or may be attached to small particles in the water such as clay or sand (silica). People who use this water can come in contact with these chemicals when the water is ingested, when food is eaten that has absorbed chemicals from this water, or by incidental ingestion. The drinking water pathway is considered for the well water and water supply only. Although the chemicals reported in the Phase I report do not readily pass through the skin into the body, the dermal pathway is also evaluated for chemicals that can pass through the skin barrier or cause skin disease by direct contact (ATSDR, 2005; ATSDR, 2006).

Chemicals from the sampling sites could move into the groundwater and soil through leaching or through vaporization. Contaminants could be ingested if present in the drinking water or, from small amounts of ingestion of locally contaminated soil.

Contaminants could be inhaled if the chemicals vaporize, i.e., easily move into the air from contaminated water or soil or are aerosolized in the home (showering activity). Contaminants on the skin (dermal contact) could occur by contact with contaminated water or soil.

For the present investigation, the different elements of exposure are identified as follows:

- **Source of contamination:** The sources of the contamination are the potential toxins identified in coal slurry injected underground, including coal products (metals and hydrocarbons), overburden materials in the slurry, and coal cleaning agents.
- **Release mechanism into water, soil, air, food chain (biota) or transfer between media:** Release mechanisms involve leakage from the site of storage, including the mine pool and anywhere else injected slurry may travel, into groundwater, into surface water, and soil contamination. Transfer mechanics involve migration in the ground with groundwater flow, possibly contacting drinking water and surface water.
- **Exposure points or areas:** Exposure points involve drinking water wells, residential yards, recreational waters, streams, and privately or publicly owned community water supplies.
- **Exposure route:** Exposure routes include ingestion through drinking water, consuming foods from private yards or affected farms, as well as incidental ingestion of a diverse nature (e.g., children playing and gardening at any age),

dermal contact with drinking water, stream water, and the soil, and the potential for inhalation in homes (for example, during showering/bathing).

- ***Potentially exposed population:*** The exposed population involves local residents and those employed at local businesses or attending local schools, the population served by a potentially contaminated water supply, as well as the population in contact with stream and surface water downstream points of contamination.

## **Summary**

During Phase I of this investigation, chemical analyses were conducted on samples collected at six different sites in West Virginia where coal slurry has been injected underground. Samples of coal slurry and run-of-mine coal were collected and analyzed for a suite of organic and inorganic constituents (177 different parameters). The phase I investigation did not measure and was not designed to measure the entrance of coal slurry into drinking water. At 4 sites, over a limited time period, it did not show a likely direct hazard.

## ***Relationship of Well Water, Surface Water, and Supply Water Chemicals to Groundwater Content***

A reasonable estimation of the extent to which groundwater, surface water, and supply water could be impacted by nearby underground injection of coal slurry is determined by numerous physical, chemical, hydrological, geological, and climatic factors. In this investigation, we adopted a conservative approach with respect to health protection: contaminants of concern were selected based on the hypothesis that



concentrations measured in the liquid phase of coal slurry from the different sites under study could potentially result in equal, but not higher, concentrations in soil, stream water, and drinking water.

### **Selection of Chemicals to be Reviewed**

The selection of chemicals to be reviewed was based on the comparison of the concentrations detected in the coal and coal slurry samples in Phase I of this investigation with relevant media-specific environmental guideline CVs defined by the USEPA (e.g., MCLs and HAs). Chemicals found at a concentration above one or more CVs were considered as chemicals to be reviewed (ATSDR, 2009a). Based on this analysis, five metals, aluminum, antimony, arsenic, iron, lead, and manganese are considered as contaminants of concern. In the category of general chemistry, nitrogen (nitrite), chloride, fluoride, and sulfate were identified as chemicals to be reviewed. Also, TDS and pH were detected at levels higher than the CVs. The following volatile and semi-volatile organic compounds were detected: 2-butanone, acetone, acrolein, benzene, *m,p*-xylene, methylene chloride, *o*-xylene, toluene, *bis*(2-ethylhexyl)phthalate, naphthalene, and phenanthrene. Although these organics are listed as CERCLA list of priority pollutants, their concentrations were significantly below the CVs, so they are not considered in this study as contaminants of concern.

### **Summary of Exposure Pathway Analysis in Human Risk Assessment**

A complete exposure pathway requires the five following elements to be present: A source of contamination, a medium of exposure, a point of exposure, a way for humans to be exposed, and a receptor population. Exposure pathways are considered

complete when all five of these elements existed, in series, at some point in the past, exist in the present, or are predictably likely to occur in the future. After review of the different elements potentially involved in the pathway of exposure to contaminants in underground coal slurry, the authors of the present investigation conclude that it is reasonable to believe that a complete exposure pathway(s) can/could have existed in theory and may in the future, although measurements did not detect such events in the Phase I report. The reasons why we make this conservative assumption begin below.

### **Human Exposure Analysis: Chemicals to be Reviewed**

Exposure doses are estimates of how much of a chemical may get into a person's body based on the person's actions and habits. Selection of the chemicals in coal slurry to be reviewed for non-carcinogenic effects were based on the comparison to the estimated dose of exposure with health-based CVs, such as ATSDR minimum risk levels (MRLs) and USEPA references doses (RfDs). Chemicals for which the estimated exposure doses were below health-based CVs were eliminated from further review. This means that exposures to these chemicals at these levels are not expected to result in adverse health effects. In the present study, the exposure doses were calculated based on the concentrations of contaminants in the samples analyzed in Phase I of the investigation and reasonable hypotheses regarding body weight and ingestion of drinking water in worst case scenarios as previously described. The selection of a chemical of concern in this type of conservative approach does not mean that we know it to be a health hazard from coal slurry injection. Instead, it means that we thought it prudent to make worst case assumptions in the absence of data, and we included

chemicals which might exceed a threshold in the worst case. The following chemicals were found to have exposure doses equal to or exceeding health guidelines CVs for children: antimony, arsenic, cadmium, chromium, molybdenum, silicon, sodium, strontium, nitrite, and fluoride. The following chemicals were found to have exposure doses equal to or exceeding health guidelines CVs for adults: antimony, arsenic, molybdenum, silicon, sodium, strontium, and fluoride.

### ***Estimating Exposure doses***

Exposure doses are estimates of how much of a chemical may get into a person's body based on one's actions and habits. The calculations rely on assumptions that identify how much, how often, and how long a person may be exposed to chemicals in the water, as well as environmental sample data that accurately reflect the chemical composition of the water. The review of the possible health consequences from chemical exposures examined estimated exposure doses from both ingestion and dermal exposures.

### ***Selection of Chemicals to be Reviewed for Non-Carcinogenic Effects***

Health-based CVs, such as ATSDR MRLs and USEPA RfDs, are calculated concentrations of a toxin, in specific media (such as water), designed to be protective of public health. Where estimated exposure doses are below these health-based CVs, the chemical of concern is eliminated from further review in risk assessment (ATSDR, 2004). This means that exposures to these chemicals at these levels are not expected to result in adverse health effects. Chemicals to be reviewed for which estimated

exposure doses are over the health-based CVs, or for which no health-based CV had been established, are selected for further review.

The review for possible adverse health effects is accomplished by comparing the estimated exposure doses for these chemicals to research such as that outlined in the ATSDR toxicological profiles (<http://www.atsdr.cdc.gov/toxpro2.html>). An exposure dose where no effects are observed is known as the no-observed-adverse effect level (NOAEL). The lowest exposure dose where an adverse health effect is observed is called the lowest-observed-adverse effect level (LOAEL).

### ***Selection of Chemicals to be Reviewed for Carcinogenic Effects***

Theoretical cancer risks are calculated on the basis of current environmental data. Cancers can develop over many years. Exposures for each age group are averaged over a 70-year lifetime. The estimates obtained for each age group are added together. This gives a theoretical excess cancer risk for a person who is exposed to the chemical over the total exposure time noted in the exposure frequency assumptions. This number is multiplied by the cancer slope factor (CSF). The theoretical excess cancer risks obtained using this method are only estimates of risk because of the uncertainties and conservative assumptions made in calculating the CSFs. The actual risk of cancer is probably lower than the calculated number. The true risk is unknown and could be as low as zero. However, the method assumes no safe level for exposure to a carcinogen. Lastly, the method computes the 95% upper bound for the risk, rather than the average risk. Therefore, the risk of cancer is likely actually lower than the conservative computation, perhaps by several orders of magnitude. One order of

magnitude is 10 times greater or lower than the original number, two orders of magnitude are 100 times, and three orders are 1,000 times. In the Phase I report, West Virginia Department of Health and Human Resources (WVDHHR) ranked the theoretical excess cancer risks using the following criteria. Theoretical cancer risks less than 1 in 10,000 were considered very low risk and are not discussed in the text. Theoretical cancer risks between 1 and 9.9 in 10,000 were classified as a low risk, 10 and 99 as a moderate risk, and greater than 99 in 10,000 as a significant risk (ATSDR, 2006). A weakness of this approach is the tendency to have better data for well-recorded outcomes such as cancer that permit a robust assessment. Developmental, neurotoxic, and immunologic outcomes provide examples of chronic conditions whose severity is less likely to be based on yes/no considerations of cancer histopathology (“less binary”) and whose recording and the related geographic context are far less robust for risk-assessment purposes. These health outcomes can be equally as important as cancer. They can pertain to some of the chemicals to be reviewed listed above. However, the methodology for consideration is less well developed.

In the present study, the exposure doses were calculated based on the concentrations of contaminants in the samples analyzed in Phase I of the investigation. Results are presented in Tables 4 and 5. For all contaminants in the samples analyzed in Phase I of this investigation (if detected), Tables 4 and 5 present the calculated exposure doses, the corresponding health guideline CVs developed by ATSDR. Chemicals for which calculated exposure doses equal or exceed at least one health guideline CV are highlighted in bold italics. Table 5 shows the estimates of the exposure doses calculated for a child. The following chemicals were found to have exposure

doses equal to or exceeding health guidelines CVs for children: Antimony, arsenic, cadmium, chromium, molybdenum, silicon, sodium, strontium, nitrite, and fluoride. It should be noted that, with the exception of chromium and sodium, these appeared as possibilities based upon the literature review of coal and coal-related waste. Some predicted chemicals, such as lead, also appeared in the literature review but not in Phase I CVs above thresholds. Table 6 shows the estimates of the exposure doses calculated for an adult. The following chemicals were found to have exposure doses equal to or exceeding health guidelines CVs for adults: Antimony, arsenic, molybdenum, silicon, sodium, strontium, and fluoride.

The calculation of estimated exposure doses noted in Tables 4 and 5 and in the section below assumes that a child weighs 10 kilograms (kg) (about 22 lb) and drinks 1 liter of water a day (about 1 quart). The calculation assumes that an adult weighs 70 kg (about 154 lb) and drinks 2 liters of water a day (about 2 quarts). The calculation assumed that exposure to the chemical occurred every day (meaning that the exposure factor was 1). The estimated exposure dose, in milligrams per kilogram per day (mg/kg/day), is calculated by multiplying the maximum concentration of the contaminant detected (in milligrams per liter) by the amount of water ingested in a day (in liters) divided by the body weight (in kilograms).

In the present investigation, the estimated exposure doses were compared to the following health guidelines (ATSDR and USEPA):

- ***Minimal Risk Levels (MRLs)***: MRLs are an estimate of the daily human exposure to a substance that is likely to be without appreciable risk of adverse health effects during a specified duration of exposure.

- **Chronic Reference Dose (RfD):** An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

### **The Precautionary Principle in the Context of Underground Injection of Coal Slurry**

When environmental exposure and health outcome concerns arise that are difficult to interpret because of uncertainty about either the exposures or the health outcomes, one frequently refers to the *precautionary principle*. First, what is the precautionary principle? In 2005, the United Nations Educational, Scientific and Cultural Organization (UNESCO) and the World Commission on the Ethics of Scientific Knowledge and Technology (COMEST) brought together an expert group that developed a working definition of the precautionary principle (Dolan and Rowley, 2009): *When human activities may lead to morally unacceptable harm that is scientifically plausible but uncertain, actions shall be taken to avoid or diminish that harm.* This definition also clarifies the elements of harm, uncertainty, and proportionate responses. The COMEST concludes that "the grounds for concern that can trigger the precautionary principle need to be plausible or tenable and that the scientific uncertainty should be considerable." Finally, the COMEST also states that the precautionary principle is not based on *zero risks* but aims to achieve lower or more acceptable risks or hazards.

Two questions that risk assessment raises in general and this report raises in relationship to coal slurry injection are: (1) Does the precautionary principle apply in the

context of underground injection of coal slurry; and (2) If so, what does this principle imply in terms of environmental risk assessment, public policy, and, ultimately, coal slurry disposal practice? It should be noted that the precautionary principle is a human response to absence of data or to theoretical reasons for concern. It is based on absence of knowledge about safety, rather than on presence of certain knowledge about hazard.

In the context of coal slurry, this implies that scientific evidence must be provided that potential, although uncertain, environmental and/or health hazard *may* occur following underground injection of coal slurry. The evidence collected through Phase I of this investigation, as well as data from extensive literature review, leads to the following published-literature and data summary:

- 1) Coal and coal waste, including coal slurry, contains significant levels of toxic chemicals, notably heavy metals and also aromatic hydrocarbons.
- 2) These contaminants have the potential to leach and contaminate groundwater to various extents that depend on the nature of the contaminant and the site conditions. One Federal reference to such historic leaching does exist, specifically related to coal slurry injection (US EPA, 1985b). In addition, the National Academy of Science has noted that the success of underground injection is likely to be site specific (NAS, 2002).
- 3) Contaminated groundwater can impact surface water and reach private wells and water supplies, thereby threatening the environment and human health, even though the complexity of groundwater hydrogeology often makes such predictions very difficult.



- 4) There is no reported peer-review-level evidence that underground injection of coal slurry has resulted directly in adverse effect on human health, although a large degree of uncertainty exists.

In addition, several publications from USEPA and the U.S. Geological Survey (USGS) report the negative impact of coal mining and coal waste disposal on wildlife and the quality of surface and groundwater. Although there is limited to no information currently available about the actual harmful effects of underground injection of coal slurry on the environment and human health, there is certainly the *potential* for such effects to occur. Considering the clear existence of a gap in available data and the complexity of the problem, the authors of the present report consider that a large uncertainty exists about the impact of underground injection of coal slurry on the environment and human health.

In this setting, in which data gaps are known to be more prominent than available data, risk assessments generally lead to the following types of recommendations:

- 1) Further environmental and health risk assessment investigations should be conducted. In the specific setting of coal slurry injection, this includes hydrogeological site studies with further routine monitoring so that proof of principle, that coal slurry injection does not harm surface or drinking water, is established over time by actual measurements rather than by a single limited study.
- 2) For coal slurry in general, it also applies further chemical characterization and toxicology testing as a complex mixture with high potential to affect populations.

- 3) Awaiting further scientific evidence about the potential effects of underground injection of coal slurry on the environment and human health, regulatory and technical means should be used in order to characterize, and minimize any effects on the environment, as well as establish proof of principle that the practice works as well over time as individual measurements in limited circumstances may indicate.

## **Coal Slurry Chemical Risk Assessment**

### **Introduction**

The purpose of reviewing is to consider the toxicity of elements, chemicals, or mixtures which are reasonable to consider as chemicals to be reviewed following coal slurry injection. Some assumptions are inevitable when this kind of work is done. One assumption made is about the route of exposure, especially for elements and their salts. For example, coal slurry may contain significant quantities of selenium. In turn, that selenium can exist in many forms, but only some of those forms are relevant. For example, very extreme heating of a concentrated specimen could, in theory, create selenium dioxide, a potent respiratory irritant. However, unless there is a likely episode of extreme heating leading to a specific selenium species which would then have an important toxicity following a likely respiratory route of exposure, then the authors have generally not included respiratory toxicity for an element species such as selenium. That is because the significant route of exposure, outside of certain workplaces, is oral. The respiratory hazards are highly unlikely to arise from current or foreseeable coal slurry injection practices. The consideration of selenium exposures is limited to forms and

routes of exposure that may come from coal slurry, such as contamination of potable water, or crops affected by contaminated water. (Contaminated potable water may create routes of inhalation from showering; that would not be an important consideration for selenium whereas it might be for a volatile organic solvent. The difference is the degree of heating required. Furthermore, the available data implicate metals rather than solvents as chemicals to be reviewed. If solvents were chemicals to be reviewed in this analysis, then consideration of inhalation through hot water and showering/bathing would be more important.) The strengths and weaknesses of assumptions that underlie the risk assessment process are recapitulated with each substance examined.

### **Summary of assumptions and limitations**

1. Oral exposures are by far the most important population exposures for injected coal slurry waste.
2. Organics may be important, but data are lacking and the specific chemicals will vary and be hard to predict. Rather than making assumptions about specific organic chemicals, we will approach this problem through recommendations for broad-based monitoring.

The above assumptions are consistent with what is known about each of the substances covered in this section.

### **Metals and Nonmetallic Elements Adjacent to Coal Soils: A Problem of Tracking Sources**

Metals adjacent to coal soils have already been discussed. Mining, and especially abandoned mines, present the opportunity for long-term exposure of surface and groundwater to oxidizing surfaces; metal oxides available to enter human drinking

water supplies may increase dramatically when mines are abandoned. Also discussed is that the burden of pollution from soils, or from abandoned mines, cannot be easily distinguished from the same types of burden that come from coal slurry once injected into an abandoned mine. It is possible to instrument sites scientifically, and to record the mining practices and measure the pollutants in adjacent surface and groundwaters over time. Even then, conclusions about original sources of pollution may still be inferences, in part, because mine pool water is in contact with multiple sources.

There are no existing designed studies which specifically address human health in the context of coal slurry or coal slurry injection.

Based on measures and models, chemicals to be reviewed are reviewed with reference to potential health effects. It is important to understand the meaning and limitations of this exercise.

1. The designation of a chemical of concern does not mean that the existing data show with certainty that a health hazard exists. Instead, the modeled data indicate the potential for a hazard.
2. The brief reviews here are, in many cases, of the substances with the lowest tolerances and, therefore, most likely to be considered in a public health context if an additional burden is created.
3. If a chemical which can be in coal slurry is not designated as a chemical of concern, this does not rule out some unpredictable occurrence of a health hazard. It means that such occurrence is not likely or predicted.
4. The chemicals to be reviewed are briefly reviewed for reader convenience. These reviews are not meant to be complete. ATSDR complete reviews of

individual chemicals are book-length efforts and are available online. The extensive literature on these substances is continuously updated. Those needing the latest data are referred to ATSDR reviews and the subsequent, extensive literature which is available in abstract form with links at National Library of Medicine.

Contaminants to be considered are aluminum, antimony, arsenic, cadmium, chloride, chromium, fluoride, lead, manganese, molybdenum, nitrite, selenium, sulfate, silicon, sodium as sodium chloride, and strontium, listed alphabetically. An indicator of water quality, total dissolved solids (TDS), while not a contaminant of concern, is also a topic for consideration. Among the contaminants of concern, aluminum, arsenic, iron, lead, manganese, selenium, and sulfate are most likely to occur in slurry water. Arsenic, cadmium, lead, and mercury, are considerably more toxic than others considered, and the toxicologic knowledge involving ingested manganese is the least understood and most uncertain.

### ***Aluminum***

Aluminum is a common, light metal, frequently existing in combined states with other elements in the earth. Aluminum is not an essential element for human health; it is not known to have any beneficial role in human metabolism. However, it is used in large concentrations in some oral medicines and even in buffered intravenous solutions. Aluminum is also used to make cans, sidings, foils, and lightweight alloys, and it is used in water treatment. Antiperspirants are a common form of substantial skin contact.

Because of its abundance in the earth, aluminum ions can be found as dissolved oxides, sulfides, silicates, hydroxides, or halides in water, even though aluminum is not very soluble in neutral pH water. Aluminum is more soluble in acid or alkaline water. While most atmospheric sources of aluminum have their origin in volcanoes and in the natural weathering of rocks, coal burning and aluminum smelting can create important regional exceptions and can also widely distribute aluminum particles. Aluminum can be also released to the water environment by mining activity in general.

### **Exposure**

Aluminum is not generally biomagnified in the food chain. It is nevertheless commonly present in many foods, and food is responsible for most human exposure to aluminum in nonoccupational settings. This is particularly the case for processed foods such as cheese, cake, biscuits, bread, pizza, and soy-based infant formula. Tea and crayfish represent examples of food with naturally high concentrations of aluminum. Buffered medical products (especially antacids, as well as antidiarrheal agents, aspirin, and buffered intravenous fluids) may contain very substantial concentrations of aluminum (ATSDR, 2008). Cooking in aluminum containers, or aluminum foil, can cause detectable inputs (still small compared to inputs from processed-food sources).

For most of us, exposure to drinking water represents a minority of daily encounters with the ubiquitous element aluminum. Most US drinking water contains < 0.1 mg/L (ATSDR, 2008). However, concentrations in drinking water can vary quite

widely in different geographies, and there can be many exceptions in the amount of drinking-water exposure. The chief determinant of aluminum in drinking water is generally whether or not coagulation treatments using “alums” (aluminum sulfates) are required to maintain water quality. Less than 1% of a typical ingested dose is absorbed. However, this percentage may go up substantially when the gastrointestinal tract is bypassed, as in intravenous introduction of dialysis fluids or parenteral nutrition. Manufacturers of modern dialysis fluids generally make efforts to reduce aluminum concentrations in order to mitigate this problem.

Median aluminum concentrations in the drinking water of 186 surveyed communities were 0.045 mg/L in finished water when alums were not used, and 0.112 mg/L when alums were used (Miller et al., 1984), with higher mean levels (Letterman and Driscoll, 1988). Surface-water sources generally have higher concentrations than ground-water sources. In addition, acid mine drainage is specifically considered to add to the aluminum burden of impacted water systems (Filipek et al., 1987).

While health hazards of aluminum exposures at ambient, nonoccupational environmental concentrations are still a research subject with few consensus facts (see health hazard section), there is a rich exploratory literature suggesting the possibility that reducing exposures could be beneficial. Human daily intakes range from 1-10 mg/day and vary by diet and culture, particularly intake of processed food, with US estimated of mean intake ranging from 0.10 mg/Kg for infants to 0.35 mg/Kg for two-year-olds (ATSDR, 2008). Because of their slightly higher intake, toddlers may be a

susceptible population. Use of buffered medical products such as aspirin or antacids may increase exposures above these levels in some instances.

### **Aluminum in Humans**

Small individual variations in aluminum concentrations in human tissues are subject to laboratory quality control issues. As such, the study of these small variations are difficult to extrapolate to the general population and are thus best understood as a research topic. In contrast, historic very high concentrations which can be associated with dialysis, in the setting of kidney failure, are easily detected. Modern dialysis techniques generally minimize this historic risk. Human (nonoccupational) population serum concentrations are generally < 0.01 mg/L, with a mean urine concentration of 0.005 (range 0.001-0.097 mg/L) (ATSDR, 2008).

Hair is likely not a viable marker of exposure outside of highly controlled experimental studies, since endogenous uptake into hair cannot be reliably distinguished from exogenous sources (Wilhelm et al., 1989) by standard techniques. This warning seems particularly pertinent in coal-burning regions.

### **Health Hazards of Aluminum**

The literature concerning human aluminum exposure is dominated by (1) occupational studies, with respiratory exposures and with primarily respiratory



outcomes; (2) associated occupational cancer investigations that may relate more to process exposures (other chemicals associated with making aluminum products); (3) neurotoxic occupational studies, which find intermittent and inconsistent associations of aluminum respiratory exposure with subtle neurologic deficits; and (4) iatrogenic (caused by a doctor) exposures of kidney-failure patients exposed to aluminum in dialysis fluids, with primarily neurologic outcomes. Dialysis encephalopathy is accompanied by and likely caused by aluminum accumulation in the brain. It occurs in a specific situation, with a medical introduction of high-dose aluminum directly into the bloodstream. In this setting plasma levels of aluminum are usually greater than 100 µg/L (orders of magnitude higher than background normal) (Alfrey, 1993). Until doctors learned how to control this exposure problem, aluminum-induced dementia was also associated with hemolytic anemia and osteomalacia.

In addition to the occupational and kidney failure studies, numerous ecologic and some designed studies have also investigated the relationship between aluminum in regional water and neurodegenerative outcomes such as Alzheimer's disease. These are more pertinent to this risk assessment because of the similarity of route of exposure and dose. The majority of these studies have suggested the potential for a relationship between aluminum in potable water and dementia. However, results are inconsistent. Importantly, higher exposures to teas, and buffered medical products taken orally, which expose humans to far more aluminum, have not been shown to be associated with encephalopathy. Frequent antacid users consume one to three orders of magnitude more aluminum than the average adult. However, the gastrointestinal bioavailability of

different forms of aluminum is still a matter of scientific study, so direct comparisons such as this might also be misleading. Heavy antacid use also interferes with phosphate metabolism, and may be associated with osteomalacia (changes in phosphate-calcium metabolism leading to softer bones), especially in those who consume antacids consistently and also have kidney disease.

The example of neurotoxic dementia following iatrogenic exposures to aluminum in dialysis treatment of renal failure, and the demonstration of aluminum in the neurofibrillary tangles of Alzheimer's disease, present associative evidence that environmental aluminum could be a primary contributing cause of Alzheimer's disease. This association is supported in some geographic or ecologic studies (Martyn et al., 1980; Graves et al., 1990; McLachlan et al., 1996; Ferreira et al., 2009), and the evidence base includes at least one well-designed prospective study (Rondeau et al., 2009). Of course, there are also studies which fail to find relationships (Martyn et al., 1996). And, studies of exposed workers do not reveal excess Alzheimer's disease or development of presenile dementia (Salib and Hiller, 1996; Iregren et al., 2001).

Aluminum and phosphorylated tau protein colocalize in the neurofibrillary tangles characteristic of Alzheimer's disease, providing an anatomic level of biologic plausibility for the hypothesis that aluminum is a cause of dementia in the general population. However, aluminum is not the only element known to interact with beta-amyloid precursor proteins; zinc and iron can also do this. And, only a small proportion of the aluminum in the human body originates in drinking water, so there is a serious question about biologic plausibility. If aluminum in water is a plausible agent of dementia, then

some hypothesis related to increased bioavailability will likely need to be invoked to explain how a minor contributor to body burden is involved, while major contributors such as medicines or worker inhalation are absolved. Animal models of aluminum neurotoxicity have been sought; monkeys fed high-aluminum, low-calcium diets develop motor neuron pathology (Garruto et al., 1991), an important yet very distinct outcome that provides neither proof of principle nor reassurance that the hypothesis is wrong. Consensus opinions from literature reviews suggest a need for more research, and generally do not indict aluminum in drinking water as a currently known cause of dementia (Rondeau, 2002; Frisardi et al., 2010). The suspicion of causation is neither accepted nor rejected, and the possible contribution of aluminum to Alzheimer's disease, alone or in combination with other metals such as copper, iron, and zinc, remains an important consideration of unknown importance.

A summary of important health effects for aluminum, pertinent to drinking water and risk assessment, includes the certainty of neurotoxicity at high intravascular doses, and the controversial possibility of contributions to neurodegenerative disease such as Alzheimer's at environmentally ambient exposures.

### **Exposure Limits**

Using a NOAEL/LOAEL approach, based on thresholds for reproductive effects in rodents, and accounting for possible differences in bioavailability of medicinal compounds, an MRL of 1 mg Al/Kg/d has been derived (ATSDR, 2008) (Table 7). The

EPA has not developed a health reference dose, but there is an SMCL of 0.05-0.2 mg/L based on odor and taste.

### ***Antimony***

Antimony is a metal used in some specialty metal alloys. It can be found in trace quantities associated with coal or coal overburden. (For this reason, coal-fired power plants are a source of antimony in the air and soil.) Most surface waters contain less than 5 ppb antimony. Foods also contain only trace amounts of antimony. Outside of workplace exposures, or medical uses, antimony toxicity is rare.

Because workplace exposures have been most relevant, the human toxicology literature concerning environmental (nonmedical) antimony is documented by inhalation studies, particularly early studies of pneumoconiosis and reproductive loss in women exposed by inhalation at work. The acute effects of an unusual toxin group, stibenes, are not relevant to risk assessments of water or soil pollution.

Antimony is not known to be essential for human nutrition, but antimony compounds have been used in health care, notably and at present for the treatment of schistosomiasis and leishmaniasis.

### **Health Effects**

Oral exposure to antimony is most commonly to antimony oxides (such as antimony trioxide) or to organic antimony. Based on animal studies, less than 10% of an oral dose is believed to be absorbed. Animal studies indicate that antimony is then taken up in red blood cells and distributed to a number of tissues, including liver, kidney, bone, lung, and skin. Antimony is excreted in urine and feces. In acute overdoses, such

as accidental or intentional mixture to drinks containing 0.5 mg/Kg, adult males vomited. This reaction is consistent with animal toxicology studies. (ATSDR, 1992). Studies of chronic effects of exposure to compounds which may appear in water have been conducted in water-contamination episodes. Important outcomes are not reported.

Health effects are found at higher exposures, characteristic of medical treatments, including changes in cardiac conduction, myocardial damage, anemia, vomiting, diarrhea, and muscle pain.

### **Exposure Limits**

Possibly because toxicity is rare at environmental doses, MRLs have not been developed for antimony. Scant information is available about the use of antimony in urine as a biomarker following oral exposures.

### ***Arsenic***

Arsenic is a “metalloid” element (it has some properties of metals) which is most commonly found in the environment as an oxide, chloride, or sulfur-containing compound (inorganic arsenic). Arsenic compounds occur naturally in rocks and may be found in coal overburden. Many arsenic compounds are soluble in water. Thus arsenic may move through the water table or surface water into drinking water and croplands.

The fate of arsenic in either surface or groundwater is complex. High or low pH, sulfide, iron, and salt content affect the fate of arsenic, and easy predictions are not available for West Virginia’s waters, which may reflect these conditions. Depending on the amount of arsenic in surrounding soils, undisturbed surface water and groundwater generally contain approximately 1 ppb arsenic (>80% of drinking water supplies in the

U.S. contain <2 ppb), but can in rare circumstances contain much more. Food is the largest source of arsenic in the normal human diet, especially seafood, and crustaceans such as lobster in particular. In contrast to organic lead or organic mercury, naturally occurring organic arsenics are generally much less harmful to humans than inorganic arsenic compounds. In the food chain, and especially in seafood, arsenic compounds may be combined with carbon atoms (organic arsenic). Most of these compounds are of low toxicity.

Recently developed models suggest that, under “general population” conditions, U.S. citizens ingest about 14 times more total arsenic from food sources than from drinking water, and about twice as much inorganic arsenic from food (Xue et al., 2010). From a human health perspective, the inorganic arsenic comparison is more important, and it does suggest that both contribute, especially where water systems may be contaminated. For most of us, food contributes about twice the biological burden of hazardous species of arsenic than water. For populations at high risk, however, this relationship reverses. Arsenic-poisoned populations, other than workplace populations, are generally poisoned by their water.

### **Arsenic Health Effects**

Arsenic is among the oldest of known poisons. It has also been used as a medicine, yet this use is limited by toxicity. Intentional high dose arsenic poisoning is characterized by vascular collapse followed by death. This presentation is not representative of chronic arsenic exposure, which occurs almost exclusively by ingestion under non-industrial conditions.

Arsenic is not known to be an essential element; it is not required for human existence. Arsenic causes deleterious effects for most human organs. Early clinical effects of chronic ingestion involve hyperkeratinization and hyperpigmentation of the skin. These may appear at chronic exposure levels of 0.002 mg arsenic/Kg/d (presented in relationship to kilograms of human body weight). Such lesions typically appear first on palms and soles, and can resemble corns or warts. Chronic arsenic poisoning from naturally contaminated areas in the Bengal region (northeast India, and especially Bangladesh) provide substantial data about these manifestations. Graphic pictures of arsenic-related skin changes from inhabitants of contaminated areas can be viewed at [PathologyOutlines.com](http://PathologyOutlines.com).

Arsenic also affects the vasculature. Like lead, it is a cause of hypertension and alterations in cardiac rhythm. Unlike lead, and at slightly higher exposure levels, it also contributes to peripheral vascular disease. A severe form seen in Taiwan, "black foot disease," presents with distal limb cyanosis and eventually gangrene. It has been attributed to a combination of arsenic and humic acids in drinking water. Arsenic in drinking water also affects lung function.

Findings of excess diabetes with U.S. population-level increases in arsenic exposure (see, for example, Navas-Acien et al., 2008) have been challenged by reanalysis of the same data, using different assumptions about the significance of organic mercury in urine (Steinmaus et al., 2009; Note; part of the discussion is about which toxin, not about the outcome of toxicity.) Reanalysis by the original authors, over a long time period, controlling for seafood intake, again indicated that population drinking water levels of arsenic are associated with diabetes (Navas-Acien et al.,

2009a). The authors pointed out that there was other literature also noting similar associations. An accompanying editorial and the general need for prudence in risk assessment both support the need to consider that arsenic exposures below current regulatory tolerances in drinking water may be associated with small increased risks for diabetes in populations. If the associations are proven to be real and causal, substantial numbers of people are affected.

Arsenic-contaminated drinking water causes symptoms very similar to lead exposures such as gastrointestinal distress, including nausea, vomiting, diarrhea, and abdominal pain. And, also similar to lead, arsenic is an important reproductive toxin causing fetal loss and low birth weight, as well as neurobehavioral decrements in children who were exposed in utero. Also, in common with lead, chronic arsenic exposure can lead to distal symmetrical peripheral neuropathy, and anemia/leukopenia.

A consistent population concern is the carcinogenicity of arsenic. Arsenic contamination of drinking water increases the incidence of cancers of the skin, bladder, liver, kidney and, to a lesser extent, lung. (Lung cancer is also noted in workers exposed by inhalation.) Most of the environmental cancer data comes from population studies in areas of the world where arsenic poisoning is substantial, such as Bangladesh.

An often overlooked aspect of arsenic toxicity is the effect upon the immune system. Possibly, the reason it is not discussed for purposes of standard setting is that the most direct among potential outcomes, frequency and severity of routine infectious diseases, is seldom captured in population studies of chronic diseases. Consistent evidence suggests alterations of in vitro cellular immune function, even at exposure



levels consistent with or below the current USEPA standard of 10 ppb. The question arises whether this finding has meaning for whole organisms. Mice, fed a diet which included 100 ppb arsenic in drinking water, experienced much more influenza morbidity than did influenza-infected control mice. Undesirable outcomes included an initially delayed and subdued immune response, followed by a late and destructive chronic inflammation (Kozul et al., 2009). This represents a small safety factor between health effects in animals and regulation in water.

### **Arsenic Exposures and Biomonitoring**

Except in workforces exposed to arsenic, population exposures are from food and water. Skin contact is irritating, but does not cause absorption. Inhalation occurs in industry and, in rare community events such as when wood treated with chromate copper arsenate (CCA) is burned indoors for heating. The mean population daily exposures, which come almost exclusively from ingestion, are shown in Table 8.

Of the total sources of oral arsenic intake, an estimated 1-20  $\mu\text{g}/\text{d}$  is inorganic (inorganic forms of arsenic are more capable of producing harm). Cereals and grain are important natural contributors to the total load of dietary inorganic arsenic.

Typical groundwater contains  $<2 \mu\text{g}/\text{L}$  in the U.S. Higher natural levels are commonly encountered in some U.S. regions, including western states where 12% of groundwater supplies exceed  $20 \mu\text{g}/\text{L}$ . It is unusual for U.S. surface water to contain more than  $10 \mu\text{g}/\text{L}$  arsenic, the drinking water standard (DWS). Parts of Taiwan, Chile, and especially West Bengal (India) and Bangladesh may have much higher exposures, with drinking water concentrations exceeding  $100 \mu\text{g}/\text{L}$ .

The U.S. DWS is heavily influenced by arsenic's carcinogenicity. The USEPA has calculated a drinking water "unit risk" of  $5 \times 10^{-5} (\mu\text{g/L})^{-1}$  based primarily on cancer outcomes. A definition of unit risk is the upper-bound excess lifetime cancer risk of a continuous exposure of 1  $\mu\text{g/L}$  in drinking water (or, for other exposures in which air is the medium exposure, in air). A question for policy makers is whether associations with vascular response, immune response, and diabetes deserve additional policy considerations.

Acute arsenic toxicity is usually diagnosed in biomonitoring specimens by urine collection, with 50  $\mu\text{g/L}$  in a spot sample or 100  $\mu\text{g}$  in a 24-hour urine sample as common thresholds. For any biomonitoring, avoidance of seafood in the 48 hours before testing is important, or else speciation of arsenic types (with attendant costs and numerous scientific uncertainties) into specific organic and inorganic forms is required.

The most common source of arsenic exposure is seafood. However, this organic arsenic form is relatively harmless and excreted quickly, largely without entering cells or causing cell damage. (This is a contrast to the organic mercury in seafood, which is hazardous.)

For skin pigmentation/keratosis outcomes, the generally cited exposure level is  $>0.02 \text{ mg arsenic/Kg/d}$ . However, associations at lower levels of exposure have been reported, as low as  $0.0043 \text{ mg arsenic/Kg/d}$ . This lowest-recorded exposure level associated with non-cancer human health effects corresponded to a peak water concentration of  $0.115 \mu\text{g/L}$ .

Absorbed arsenic is rapidly cleared from blood and either excreted via the kidneys or widely distributed to tissues. Biomonitoring of arsenic is an imprecise

measure of either current or historic exposure. It can be done, and it does serve limited purposes with measurements of arsenic in nails, hair, urine, or serum/whole blood. Biomonitoring for environmental exposures is best done in population context and very hard to apply to individuals. This limitation does not apply to episodes of intentional poisoning. They are easy to detect at the individual level, provided the test selection is appropriate and timed to the exposure. Recent seafood meals greatly influence urinary and serum arsenic but the organo-arsenics detected are not generally regarded as very toxic, so arsenic bio-monitoring is more easily performed in populations which do not eat seafood (NRC, 1999).

For non-seafood-eating populations, or those who have recently abstained from eating seafood, blood levels of arsenic range from 0.1 to 0.4  $\mu\text{g}/\text{mL}$ ; levels in populations exposed to arsenic in water can be an order of magnitude higher (Lauwerys and Hoet, 2001). Arsenic in urine mostly reflects the previous 48 hours of exposure. In U.S. adults who do not consume seafood and who are not selected for occupational exposure, mean urine arsenic excretion is 3 to 4  $\mu\text{g}/\text{L}$  (NRC, 1999). A threshold value of 35  $\mu\text{g}/\text{g}$  creatinine has been used to monitor for excess urinary excretion, signifying excess exposure, in industrial populations at the end of a work week (ACGIH, 2006). A minority of ingested inorganic arsenic is excreted as inorganic arsenic; humans metabolize most inorganic arsenic to organic forms readily but variably from person to person. Thus, population studies may measure inorganic arsenic (arsenite and arsenate), methyl arsenate, dimethyl arsenate, and arsenobetaine (which was principally but not exclusively from seafood) in order to provide a biomarker of arsenic exposure (Navas-Acien et al., 2009c).

Sulfhydryl groups are an important constituent of keratin, which comprises hair and nails. And, sulfhydryl groups bind trivalent inorganic arsenic (and they bind organic arsenic from seafood much less well). Therefore, hair and nails have theoretical advantages for measuring chronic arsenic exposure including the longer growth life of hair and nails, which may permit detection of past exposures and estimation of chronic doses. However, the technical difficulties of this approach are easy to underestimate, and insufficient skepticism is given to the probable lack of validity and reproducibility of inexpensive tests commonly available from alternative health care providers who routinely measure a variety of metals in hair and nails as part of a “nutritional screen.” In particular, hair measurements will be uninterpretable in parts of the world where coal is burned or metal smelting occurs (Lauwerys and Hoet, 2001).

Researchers looking for a detailed summary of arsenic health effects and risk levels can find them in the ATSDR Toxicological Profile for Arsenic (ATSDR, 2007). Arsenic oral intake guidelines can be found in Tables 7 and 9.

### ***Barium***

Barium is a nonessential (i.e., the human body does not need it) alkaline earth metal element that can be present in coal and in coal overburden. It is a common element in coal slurry in mineral form. The two common subsurface forms of barium, barium sulfate and barium carbonate, are not water soluble. Therefore, barium typically does not travel as far in contaminated water as do some other elemental pollutants. For the same reason, barium compounds, once present, may persist for a long time in a polluted area. Barium pollution from mining activities can also be present in less

common, more soluble forms, such as barium hydroxide or barium sulfide. Thus, sites such as coal slurry impoundments or underground slurry injections can become a source of primarily local barium contamination, especially in immediately adjacent well water.

Coal mining is not the only local source of barium contamination in Appalachian coal bearing regions. Barium compounds are used in the drilling “muds” of oil and natural gas exploration. Barium can enter surface and subsurface water from drilling operations as well.

### **Barium Exposure**

Most uncontaminated surface and public water supplies in the U.S. contain <0.04 ppm barium (average 30 µg/L). While human barium exposures can occur via oral, inhalation, or skin absorption, the predominant route of human population exposure is considered to be oral, and water is the commonly implicated non-medical source. The USEPA drinking water standard is 2 ppm (2.0 mg/L), far above the level of the average water supply, implying a large margin of regulatory safety for most water supplies. Some seafoods and nuts (such as Brazil nuts) are potential dietary sources of barium. However, dietary barium is not generally considered hazardous.

Barium in its most common forms, such as barium sulfate, is generally regarded as low toxicity. In fact, it is sufficiently non-toxic that it can be used in medical diagnostics because it is radio-dense (shows up on x-ray) and poorly absorbed by the gut. While barium sulfate is relatively poorly absorbed and regarded as minimally toxic, the more soluble forms of barium (barium acetate, barium chloride, barium hydroxide,

barium nitrate, barium sulfide) are better absorbed and, therefore, more toxic. Barium carbonate, while not very water soluble, is nevertheless soluble in the human gastrointestinal tract and therefore also toxic. The absorbable barium salts can cause gastrointestinal, cardiac, and CNS toxicity, and even death. These health effects are generally associated with very substantial exposures compared to common environmental levels. The lethal oral dose for adults is 2-4 grams (CDC, 2003) The oral MRL for barium is listed in Table 7.

### **Barium Toxicity**

Large quantities of ingested barium can cause hypokalemia (low serum and cellular potassium) and thereby alter nerve conduction, causing acute and potentially fatal cardiac arrhythmias in humans. Large quantities of barium can also cause severe gastrointestinal hemorrhage. Other acute or sub-acute symptoms, at lower but still substantial doses, include abdominal cramping, watery diarrhea, nausea/vomiting, hypotension, numbness (notably, facial numbness), and muscle weakness (ATSDR, 2007). Barium is not classified as a human carcinogen.

There are no study data to confirm or deny the presence of susceptible populations, but it is reasonable to be concerned about cardiac rhythm in those with pre-existing rhythm disturbances, in those already taking drugs which can independently cause hypokalemia, and it is reasonable to think about greater susceptibility to diarrhea in the very young or elderly. And, a likely susceptible population will be those with inflammatory bowel disease, cancer, or other causes of a non-intact gastrointestinal tract. Any source of gut mucosal compromise may increase

absorption. Individuals who are already hypokalemic (for example, from diuretic medications) may be more susceptible to arrhythmias following exposure because the drug and the barium may have additive effects.

Animal studies in rodent species also suggest a need to be respectful of possible chronic kidney damage at repeated high-intake doses, as well as other organ changes, including decreased pup birth weight (Dietz et al., 1992) following maternal exposure. There are also some human anecdotal case reports suggesting this possibility of a reproductive hazard (NTP, 1994) from high environmental barium exposures.

An ecologic study of a population consuming barium-contaminated drinking water associate excess cardiovascular disease within a modeled exposure of 0.06-0.3 mg barium/Kg/day (Brenniman and Levy, 1985) among the elderly ( $\geq$  age 65). A limitation of ecologic data is that they are generally considered appropriate for creating but not for testing hypotheses about etiology (causation). A human exposure study involving adult males exposed to barium chloride for four weeks did not detect changes in electrocardiogram or in blood pressure (Wones et al., 1990).

### **Permissible Exposures to Barium**

Based on the information that can be gleaned from human case reports, and based on wide variations in the demonstration of end-organ (mostly kidney) damage in laboratory rodents, the assigned MRL is 0.9 mg barium/Kg/day for intermediate-length exposures (15-364 days).

## **Barium Biomarkers**

Barium is present in human blood and excreted in both feces and urine. In parallel with many elements featuring a +2 valence, it is sequestered in bone and teeth. A geometric mean urine value of 1.5 µg/L has been cited (CDC, 2005). Because of its complicated compartment metabolism, biomonitoring, to the degree useful is most useful during or shortly (days to weeks) after exposure.

## ***Cadmium***

### **Cadmium Exposure and Susceptible Exposure Populations**

Cadmium is a blue-white corrosion-resistant metal present in soils, including soils adjacent to coal mining activity. Its most prominent current industrial use is in batteries. Cadmium is not an essential element for human nutrition (i.e., cadmium is not known to be needed for human biological activity). In common with arsenic and lead, it is a pure toxin without a known physiologic benefit for humans. When cadmium infiltrates local soil from any source of pollution, a concern is the very efficient rate of soil-to-plant transfer (Franz et al., 2008). In particular, cadmium bioaccumulates in tobacco, the most common source of major exposures in the U.S. It can also accumulate in other crops when there is a soil source. Because a common exposure source is tobacco, a common route of exposure is voluntary inhalation of burning vegetable matter and involuntary exposures of bystanders. Uptake is very efficient via the lungs.

The Provisional Tolerable Weekly Intake (PTWI) established by the World Health Organization (WHO) was set at 400-500 µg/person/week two decades ago (WHO, 1989), or about 7 µg/Kg/week for a 70Kg adult, yet more for a child! Because children



may be more likely than adults to absorb cadmium, some investigators have suggested lower thresholds for children (Horiguchi et al., 2004), a suggestion common to many toxins. Several studies have identified more cadmium in the tissues of women than in those of men (Satarug et al., 2010). Thus, children and women are potentially sensitive subgroups based on exposure characteristics.

Current thresholds have been criticized as insufficiently protective. A review of the literature shows that exposure levels of 25-30  $\mu\text{g}/\text{d}$  were modeled to produce kidney disease in as much as 1% of the population (Satarug et al., 2010). If this model is instructive, then the WHO PTWI is more than an order of magnitude above the modeled health effect.

The PTWI often accounts one of two thresholds in sensitive species, either the LOAEL, or the Benchmark Dose (BMD). Using a BMD model, European food safety recommendations have been lowered to 2.5  $\mu\text{g}/\text{Kg}$  body weight (ESFA, 2009). Recent reviews demonstrate that it is unclear whether this is low enough (Satarug et al., 2010).

### **Cadmium Disease**

Cadmium's classic target organs are kidney and bone. In addition, cadmium has been associated with diabetes, diabetic nephropathy, hypertension, peripheral arterial disease, myocardial infarction, periodontal disease, and age-related macular degeneration (a cause of blindness). Cadmium is also a carcinogen, primarily identified as a lung carcinogen, but probably also operating in other body systems (Satarug et al., 2010).

Chronic kidney disease can be caused by cadmium. The best-designed U.S. population study, based on NHANES (1999-2006) data, recorded sociodemographic risk factors, chronic kidney disease risk factors, and obtained sufficient data to compute standard measures of kidney function (Navas-Acien et al., 2009b). The commonly used markers of kidney function are the serum creatinine, the calculated glomerular filtration rate (GFR), and albumin (a protein) in urine. In the NHANES study, standard techniques were used to adjust for risk factors other than cadmium and lead in the serum (blood) of participants. Those in the highest quartile of serum cadmium had more proteinuria (albumin in their urine, odds ratio [OR] 1.92, 95% confidence interval [CI] 1.52, 2.43), and GFR low enough to be considered clinically reduced (OR 1.32, 95% CI 1.04, 1.68), and both of these indicators of chronic kidney disease together (albuminuria and low GFR, together) (OR 2.91, 95% CI 1.76, 4.81) when compared to those in the lowest quartile (Navas-Acien et al., 2009b). Because the cadmium serum values in the NHANES study are broadly representative of the entire U.S. population, and consistent with the well established deleterious effect of cadmium on kidney function, it is uncertain whether or where there are safe thresholds for cadmium exposure. The data also are preliminary, and the association could be interpreted with a plausible possibility of “reverse causation,” a scenario in which those with existing kidney disease accumulate more cadmium. However, for a variety of technical and toxicologic reasons, causation is more plausible and cannot be dismissed. The implication is that each substantive addition of cadmium to the water supply could result in additional chronic kidney disease in the exposure population.

## **Chromium**

Chromium is a blue-white metallic element which occurs naturally in rocks and soil and which is present adjacent to coal and in coal overburden. It has many uses in industry, and it can also be encountered from metal alloy foundries, parts cleaning, paints, wheel bearings, aircraft engine parts, and operating or abandoned tanneries. Older pressure-treated wood from decks and playgrounds can be a source of chromium. Chromium is typically present in US drinking water within a 0.4-8.0 µg/L range, and soils often contain around 400 ppm (Pellegrin and Booker, 2000). Humans can be exposed to chromium in drinking water, many foods, and by inhalation. Adults absorb less than 10% of ingested chromium. Workers in chromium industries, who are exposed primarily by inhalation, tend to have far higher exposures than the general population. A medical source of substantial exposures can be from chromium-alloy joint prostheses. Chromate compounds may also be absorbed through skin.

Natural chromium exists in several valence states, of which chromium III and chromium VI are of practical importance. Most chromium VI is from anthropogenic (industrial) sources.

Chromium III is possibly essential. Human health may suffer in the absence of sufficient chromium, and most adults ingest 20-45 µg chromium (III)/d. Myocardial infarction may be causally associated with low chromium intake (Guallar et al., 2005). Some individuals take chromium III compounds as nutritional supplements in the expectation that chromium will improve glucose metabolism, energy levels, aid in weight loss, and prevent diabetes. Actual clinical trials of chromium compounds yield contradictory and uncertain results about these hypothesized benefits. And, chromium

III may have some health risks, in parallel with chromium VI. In contrast, chromium VI is not an essential element, and it is a known cause of gastrointestinal (oral exposure) cancer, lung cancer, and nasal septum perforation in exposed workers (inhalation exposure). For reasons that are not yet clear, the carcinogenicity of chromium VI appears to be potentiated by ascorbic acid (vitamin C). Chromium VI is also a source of allergic skin-contact dermatitis as well as skin ulceration, and respiratory contact can cause asthma. Some ingested chromium VI will be reduced to the presumably less toxic chromium III before it is absorbed. Absorbed chromium VI is distributed to red blood cells, where it is partially detoxified to chromium III, and eventually to kidney, bone, teeth, hair, and nails. Chromium can be excreted in urine, and can also be transferred from mother to fetus (placental transfer) or mother to baby in breast milk.

### **Biological Monitoring**

Biomonitoring of chromium can be done with blood, urine, hair, or nails. Particular care about use of hair must be taken in areas with coal-fired power plants, or foundries, or other industrial sources of atmospheric chromium, as all of these can deposit chromium onto the surface of hair. Urine is most commonly used. Chromium from environmental sources such as soil is generally insufficient to alter urine levels, and biomonitoring does not accurately distinguish chromium III from chromium VI sources. Even 200 µg/d for three days does not alter detectable levels in urine (Lauwerys and Hoet, 2001). The reference value is 0.5 µg/g creatinine. Higher and different biological exposure indices are noted for exposed workers.

## **Health Effects of Oral Exposures**

The majority of human chromium toxicity literature describes inhalation or dermal exposures, often in industrial settings. A 1965 case report describes a Chinese village whose well water was poisoned by a nearby alloy foundry at 20 mg chromium (VI)/L (ATSDR, 2000). The 156 inhabitants were said to experience oral ulcers, diarrhea, and other gastrointestinal symptoms. Rodents fed water at a calculated dose of as low as 0.77 mg chromium VI/Kg/d were found to have cellular changes in the duodenum (ATSDR, 2000), as well as changes in red blood cell indices. (Reproductive and developmental effects occur in rodents at a much higher dose.) A small population residing on the site of a former chromium slag landfill did not experience detectable kidney damage (Wedeen et al., 1996).

Sensitive populations do exist. Skin and respiratory allergy are thought to affect about 0.5-1% of the nonworker population. These routes of exposure may be dismissed as irrelevant to waterborne exposures; however, asthmatic patients are more often treated by nebulization. For the sensitized patient, this can provoke a new attack, or worsen an existing bout of asthma.

The most feared outcome of chromium VI exposure is cancer. In humans, this has been amply demonstrated by industrial populations exposed by inhalation. In rodents, increased gastrointestinal cancers may appear after doses around 2.4 mg chromium (VI)/mg/Kg/d.

While chromium carcinogenicity is its most feared effect, allergic sensitivity is actually common and can be associated with inexpensive jewelry, or with residual tanning products found in leather goods (such as shoes). Threshold doses are not

established (or establishable) for humans. Rodents can be sensitized with intradermal injection series as low as 0.004 mg chromium (III) Kg. Whether intradermal injection is a realistic model is questionable.

### **Established Oral MRLs**

The oral chronic ( $\geq$ /year) MRL is .001 mg chromium (VI)/Kg/d (Table 7). This is based on gastrointestinal dose-response as measured by histologic reactions in animal studies. However, there are suggestions that stomach cancer rates may be higher in areas of China with higher chromium in well water (Beaumont et al., 2008). This kind of general observation adds weight to MRL, but does not assist with establishing the actual level.

For chromium III, MRLs are not established, and it is thought that humans should have some minimum intake.

### ***Diesel***

Diesel is a fuel composed of distillates obtained through the refining of crude petroleum and is used in motor vehicles (US Energy Information Administration, 2010). It is not fully characterizable, as it is a mixture with general characteristics, which vary with geography and with intended uses. That is, significant variations depend on the geographical source of the crude oil, or the type of engine application. Transportation, agricultural, and mining equipment may each use different formulations. Furthermore, diesel formulations have changed over time to accommodate evolving engine designs. Definitions of diesel generally mention a mixture of C8-C21 aliphatic hydrocarbons with a boiling range of 160-360 degrees C, accompanied by less than 25% aromatic

compounds. This may vary. And, additives in small quantities such as biocides may have their own toxicity, and also vary by application. While it is often assumed that diesel in coal slurry comes from equipment leaks, the possibility of diesel discharge due to coal processing or diesel disposal cannot be ruled out.

### Health Effects

There is obviously no nutritional requirement for this manmade mixture. Exposure is most commonly by the respiratory route to diesel exhaust as a complex combustion product. This important and vast literature concerning diesel exhaust is not directly relevant to the consideration of diesel in water.

Acute ingestion of concentrated diesel product is most dangerous because of the potential for unintended aspiration into the lungs, particularly aspiration that may follow from the nausea and vomiting that can follow acute ingestion of fuels. The danger is chemical pneumonitis, which is potentially fatal. It should be clearly understood that this danger relates to the concentrated product, not the concentrations normally characteristic of pollution. In addition, gastrointestinal irritation with nausea and vomiting are possible in oral poisoning episodes (Health Protection Agency, 2007). A limitation of the available literature concerning the oral route of exposure is that inferences concerning diesel are frequently made based upon the much richer literature concerning kerosene (ATSDR, 1995). However, kerosene is more volatile, likely more acutely dangerous following ingestion, and may not contain the same additives.

Direct skin exposure to diesel can cause dermatitis. Diesel fuel is partially absorbable via skin exposure, and that may include exposure to vaporized diesel

(ATSDR, 1995). There are rare case reports of acute renal failure after diesel was used to wash hair or hands (Barrientos et al., 1977; Crisp et al., 1979).

There are no useful data concerning chronic human oral exposure to diesel. Rabbits fed 4 to 8 m/Kg/d for 10 of 14 days developed dose-dependent dermal irritation and anorexia, with cachexia and death in the higher-dose group (Health Protection Agency, 2007).

There is no human information about susceptible populations, but it is possible that children are at higher risk. In animal studies, young rats are more susceptible to kerosene toxicity than older rats (ATSDR, 1995).

#### Other Considerations

Because diesel is rapidly photo-oxidized in sunlight, the formation of peroxy radicals and hyperperoxides is possible in aqueous solutions or suspensions. However, the degree to which this occurs or the potential importance is not known.

A review of EPA, CDC, and National Library of Medicine sites, including the toxicology sites, finds that exposure to diesel in drinking water is sometimes mentioned, and potential acute poisoning hazards acknowledged, but chronic clinical exposures and disease are addressed only in context of respiratory exposures. The reason for this hole in the literature is absence of relevant data. As a result, meaningful thresholds for humans are not established, and biomonitoring is unexplored.

Comment: When a significant common exposure is not well addressed, the plausible reason is absence of significant examples of toxicity in practical settings.



## **Fluoride**

Fluorine is a highly reactive halogen element often found in nature as a salt, or silicate, or complexed with aluminum, iron, or silica. Fluoride is the reduced form of fluorine which can exist in nature as an organic or inorganic compound. Fluoride salts, silicates, and other minerals are generally quite stable, in contrast to the highly reactive element. Fluorine has innumerable industrial uses. From a public health perspective, the most important use is the addition of fluoride to drinking water (“fluoridation”) in order to prevent dental caries (cavities). In developed countries, fluoridation (and associated preventive benefit against dental decay) is more common in urban than in rural areas (Yarmolinsky et al., 2009). Fluoridation of municipal water supplies is generally accomplished by the addition of a silicic acid or silicate form of fluoride. Fluoride is also unintentionally released to the atmosphere in substantial quantities from coal burning, to a lesser degree from waste incineration, and naturally in very substantial quantities from volcanoes. A 650-megawatt coal-burning power plant has a modeled release of 180,000 pounds of hydrogen fluoride annually (Rubin, 1999). These estimates vary with the type of coal burned. Power plant “scrubbers” can limit direct releases to air. Scrubbing uses water, which captures pollutants such as hydrogen fluorides and sulfur oxides, and which must then be released. The fluoride captured by scrubbing is redirected from air release directly to surface water.

In addition to natural and industrial sources, the amount of fluoride in surface water or groundwater is influenced by preexisting aluminum concentration, calcium

concentration, and pH. Fluoride complexes with aluminum and may stay in solution; mildly acid soils and water have higher water-soluble fluoride and aluminum levels. Waters low in hardness and high in alkalinity have generally higher levels still. In contrast, in limestone areas, the calcium carbonate in water tends to complex with fluoride and precipitate out of solution. The equilibria models of fluoride in solution are extremely complex. Among the many considerations, fluoride-silicates are extremely important because of their deliberate introduction for the purpose of improving dental public health.

### **Human Exposure to Fluoride**

Humans encounter fluoride in food, in water (and more when water is fluoridated for public health reasons), and in toothpastes and other dental applications. Foods or beverages particularly high in fluoride include tea, bone meal, seafoods, particularly canned fish, with lower but still substantial quantities in cereals (Fung et al., 1999). Rice cooked in fluoride-rich water becomes a fluoride-rich food (Takizawa et al., 2010). Fluoride and aluminum-processing industry workers may be exposed via inhalation. Most of us have drinking water and toothpaste as our principal sources of exposure. Some dental products are > 1% fluoride (> 10,000 ppm), but most are around 0.1 ppm. For heavy tea drinkers, the tea can be the principal source.

The average surface-water fluoride concentration is 200 µg/L, with a wide range (1-6500 µg/L) (ATSDR, 2003a). Most groundwater in the US contains 200-1500 µg/L

fluoride, but parts of West Texas feature water with > 5000 µg/L fluoride. West Virginia is generally not considered a problem area for fluoride in water. Public drinking water fluoridated to optimum levels of exposure in the US (0.7-1.2 mg/L) would amount to drinking intakes of 1.2-2.4 mg/d from water alone (ATSDR, 2003a). This correlates to an estimated Canadian average adult intake of 1.8 mg/d fluoride with a range of 0.35 mg/d for children ages 1-3 to 3.03 mg/d for males ages 40-64 (Dabeka and McKenzie, 1995), with comparable estimates at the high end of this range for intake in US cities with fluoridated water (ATSDR, 2003a). The range of daily exposure is quite wide because of differences in water, diet, and dental exposures, with less than 1 mg/d in adults with unfluoridated water and no toothpaste or tea exposures. Exposures to workers can be much higher; these are principally inhalation. Children need fluoride for development of healthy bones and teeth.

Children ages 6 months to 2 years consume about 0.21-0.61 mg/d (NRC, 1993; Ophaug et al., 1985). Beverage consumption and fluoride concentration in water are the most important predictors of childhood intake. ATSDR (2003a) has provided an “adequate intake” table based on previous Institute of Medicine (IOM, 1997) data, ranging from .01 mg/d for 0-6 months, to >4 mg/d in males older than 18. The concentration of fluoride in water can be different from the concentration of fluoride ion, so it is important to focus on what is actually being measured when following the fluoride literature.

### **Fluoride Biomonitoring in Humans**

The consideration of exposure to total fluorides should attempt to account for the bioavailability. Some but not all of an ingested concentration of fluoride will be absorbed. The plasma or serum level peaks about an hour after exposure. The nature of the fluoride complex affects bioavailability, and fluoride ingested with food is better absorbed than fluoride in water. In general, adults absorb around 75% of ingested fluoride (NRC, 1993). Serum fluoride levels in humans are a mean of .0089 mg/L and a median of .0076 mg/L in Danish adults (Poulsen et al., 1994).

Fluoride levels can also be measured in extracted or lost teeth for purposes of dental and environmental research. And, fluoride is frequently measured in hair, but the clinical value is questionable because of differences in hair growth rate and the unavoidable atmospheric deposition of fluoride on hair. The consideration of external deposition is particularly important in coal-burning regions. The presence of fluoride on the hair implies the need for a standard, effective cleaning method, and no accepted standard exists. Urine fluoride measures are potentially valuable for accessing recent exposures, such as in populations of exposed workers, or in highly exposed populations with post-shift worker values of 2.7 m/L (Dinman et al., 1976), and urine fluoride concentrations in the 0.75-10.36 mg/L level in highly exposed populations on the Indian subcontinent (Nayak et al., 2009). Because fluoride accumulates in bone yet has a short half-life in serum, plasma, and urine, these are better markers for quite recent exposure than for body burden.

The introduction of perfluorocarbon chemicals (PFCs) to industrial processes and household products began around 1950. Some of these chemicals are long-lived in the environment and the human body. They may be present in surprisingly high concentrations, and can cause confusion if all fluoride compounds are considered. PFCs may have health consequences, but they behave very differently from other fluorides and are not a topic for consideration in this document except for the need to distinguish PFCs from other types of fluoride in humans.

Fluoride inhalation is a very serious problem in industry, particularly for gases and acid fluoride mists. This route of exposure is largely industrial in nature, has very different implications than oral fluorides, and is not a topic related to coal slurry.

### **Health Effects of Fluoride**

Fluoride may be an essential element for human health. Bone and dental health may be adversely affected in fluoride-deficiency states. Fluoride added to toothpaste, dental hygiene products, and drinking water has been demonstrated to prevent dental caries and gum disease. (Prevention of dental diseases by fluoride supplementation in turn prevents gingival inflammation; there is an emerging literature linking dental inflammation to possible cardiovascular and neurovascular disease.)

The other end of the spectrum is too much fluoride. The best-recognized problem of excess human fluoride exposure is fluorosis, which causes deformity of bones (and

mottled appearance of teeth if exposure is before tooth eruption). The mottled appearance of teeth when exposed to excess fluorine before tooth eruption (in children) is a complex problem, as enamel fluorosis is associated with a lower incidence of dental caries (Iida and Kumar, 2009). Fluoride-rich water and fluoride-rich foods/beverages can cause fluorosis; both causes are rare in the United States. In addition to cosmetic effects on teeth, fluorosis can lead to brittle bones, inhibited bone growth, and joint deformity. "Brick tea"-consuming populations in parts of Asia have been documented to suffer from fluorosis (Cao et al., 1996). The associated skeletal deformities have been documented to be more severe in those exposed in utero and in childhood, defining a susceptible population. Reviews of published papers reveal that the damage to physiologic sites is more widespread than enamel and bone; it also affects dentin, peripheral nervous system, and central nervous system. Some authorities believe the neurologic findings are secondary to mechanical aspects of skeletal deformities rather than a direct toxicity of fluorine (Reddy, 2009). Exposure in children can lead to skeletal growth arrest and joint deformity. Some of these outcomes in Indian and other Asian populations may be due to the confluence of high fluoride exposure with underlying malnutrition. It is unclear whether fluoride alone is the culprit in these dramatic, high-concentration population exposures; cadmium may also be implicated in some cases (Tang et al., 2009).

At less dramatic exposure levels, population studies have raised the question of increased risk of hip fracture at drinking water fluoride concentrations of > 4 mg/L (Li et al., 2001). However, US studies show only weak, gender-specific associations between

the level of fluoridation and childhood bone mineral density (Levy et al., 2009), suggesting a mostly positive association with bone health.

Population studies have also raised questions concerning fluoride in municipal drinking water and decreased population fertility, developmental decrements such as diminished population measures of intelligence, and especially with cancer. These studies have been considered exploratory. Outcomes have not been uniform, and study designs have often been weak. Currently, fluorine in water is being studied for carcinogenic potential, but the weight of evidence has so far not designated it as a human carcinogen at relevant population exposures.

### **Minimal Risk Levels**

The adequate required intake for a possibly essential element informs thinking about levels of fluoridation but should not be confused with minimum risk levels (MRL). For fluoride, the chronic-duration oral MRL is 0.05 mg/Kg fluoride/day (Table 7). (This number is exclusive of exposures to fluorides with long half-lives, such as PFCs; that is a different topic.) This MRL is based in part on the Li (2001) study, which found a LOAEL of 4.32-7.97 mg/L, and a NOAEL of 2.62-3.56 mg/L water (ATSDR, 2003a). Li and colleagues (2001) reported a U-shaped dose response for fractures, with more fractures in populations consuming the lowest and the highest fluoride concentrations in their water, and fewer fractures in those with intermediate concentrations of fluoride, in the vicinity of 1 mg/L.

## ***Iron***

Iron is an abundant element, but pure iron is rarely seen on the earth's surface because of oxidation. Mined iron has many uses, notably in the manufacture of steel. Iron is an essential element for human metabolism, and iron deficiency is a serious problem in malnourished populations.

Coal related activities can increase iron content in surface water and in the water table. The outcome is not specific to coal slurry. Iron is a common element around coal mining. Once a mine void has been established, water which moves through the mine environment can transfer iron to surface and groundwater in several forms. This occurs commonly in West Virginia.

Iron in surface water or in groundwater can affect water quality in many ways. Iron oxides are corrosive and can affect water pipes. In addition to creating a rust environment, this corrosion can harbor bacteria, archea, and viruses or fungi. Bio-films are complex and mutually supportive colonies of different types of microorganisms which are organized with a mucous protective layer. The formation of bio-films makes it extremely difficult to extirpate the undesired growth.

In addition, the metabolites of iron-loving microorganisms can generate sulfate-reducing bacteria which can lead to the production of sulfide compounds. This in turn produces a characteristic "rotten egg" smell that is undesirable in drinking water as is the characteristic dark (red, brown, or black) particulate staining from pipe corrosion. Associated health conditions such as diarrhea or loose stools are not necessarily directly related to iron. They stem from microorganisms and their chemical by-products.



The average adult has about 4 g of iron; men generally have more than women because menstruation and breastfeeding transfer iron from the body. About 70% of body iron is in blood. Iron is essential to the operation of hemoglobin and myoglobin.

The USEPA considers that iron-related health outcomes are not directly toxicologic. Instead, they are either aesthetic (such as staining of fixtures or laundry and metallic taste of water) or physical, related to iron build-up, microbial overgrowth, and corrosivity. For this reason, iron is regulated as a secondary contaminant at 0.3 mg/L National Secondary Drinking Water Regulations (NSDWR). From a health perspective, most humans can tolerate considerably more than this concentration in drinking water because our bodies handle iron efficiently. However, there is a sensitive population for whom that may not be the case.

### **Sensitive or Susceptible Populations**

Primary hemochromatosis, a genetically inherited disease arises from a “founder” gene mutation that appears to have originated in the Celtic population. Hemochromatosis is by far the most common hereditary condition of Caucasians (with lower rates in Hispanics and African-Americans, and virtually no appearance in West Asians). Individuals who carry both copies of the abnormal gene (genetic recessive condition) can, but do not always, suffer from the effects of iron overload in the liver because they lack the ability to excrete iron. (There is actually a common and a less common abnormal gene variant, and double heterozygote carriers may also manifest the disease.) Most texts indicate that the recessive condition is present in about 1 in 200 Caucasians. Although men and women have the genetic condition with equal

frequency, men are affected at younger age and more often because women of child-bearing age are protected, to some degree, by iron loss through menstruation. Many people who have the genetic recessive susceptibility never get the clinical condition, so genetic testing is not (yet) recommended. Patients are detected by routine screening of iron status, or else because of presenting symptoms. Presenting symptoms can include arthritis, diabetes, fatigue, heart problems, darkened skin, testicular atrophy, and cirrhosis of the liver.

Individuals with clinically significant hemochromatosis are treated by periodic phlebotomy (bloodletting), one of the few known indications for this ancient treatment. Phlebotomy is surprisingly effective for mitigating and even reversing the progression of clinical hemochromatosis. The arthritis tends to remain after treatment.

### **Iron exposure from water in the setting of hemochromatosis**

Most humans get the majority of their iron from food. Iron supplementation is also increasingly common, especially in developed countries; iron is a frequent addition to multivitamins. Special diets and avoidance of vitamin supplementation are part of the medical regimen for hemochromatosis. Whether water is a significant source of iron compared to food is not really known, but at least one reputable website (Medicine.net) has made the point that patients with hemochromatosis should avoid water that is high in iron. The possibility that inputs to iron content of drinking water can affect susceptible people is a risk consideration. However, consensus threshold recommendations for iron in water have not been established for this sensitive population.

## ***Lead***

### **Sources of Lead**

Lead is an extremely heavy, dull, gray-black metal usually found as an oxide, salt, or sulfide in the earth's crust, generally in a 2+ oxidation state. It may also be found as the mineral lead carbonate. It has numerous uses in industry, and historic human exposures in the U.S. have usually been from leaded gasoline, from lead-based paint or glaze, and from lead pipes in older water systems. Household plumbing fixtures were required to greatly reduce lead content in solders and fittings following a 1998 revision to the Safe Drinking Water Act (SDWA). (Well pumps may contain up to 8% lead, however.) The potential sources of human exposure in the household and on the job are quite diverse. Modern humans have been exposed to far more lead than their pre-industrial ancestors. We can infer this from the amount of lead deposited into ice cores through the centuries and test it definitively by measuring the concentrations of lead in ancient and modern bones.

Lead, present in coal in very small quantities, and in coal overburden, is a chemical of concern because it is so extraordinarily toxic, even at low doses, without a known threshold for safe exposure, and not because it is a major contaminant of coal or coal slurry. Health studies show that even small inputs are problematic. Lead adheres to sediment and soil particles very well, and lead in soil that can be transported on shoes or vehicles and tracked back into the home is a potentially important source of exposure that will not be emphasized in this section. Lead in soil was not determined to be a long-lasting problem in the Martin County event. Acid rain, characteristic of the Appalachian environmental conditions in coal-burning regions, may also leach lead from

soil and sediment into nearby surface water. Most surface and groundwater contains only small concentrations of lead, typically less than 0.005 ppm (ATSDRc, 2007). Fewer than 1% of U.S. public water systems have lead levels over 5 µg/L. Acid water supplies can leach lead from plumbing fixtures, however, so the concentration of lead from tap water can exceed the concentration from source water in some water systems and in individual homes.

### **Human Exposure and Uptake: Exposure Susceptibility**

Adult volunteers absorb a mean of 6% ingested lead, but this may increase to 60-80% if the gut encounters lead after a greater-than-24-hours fast. And, the gastrointestinal tract of children absorbs calcium and lead much more easily than that of adults, with an absorption rate of approximately 50% in small children. The gastrointestinal apparatus of young children normally absorbs calcium and other elements with “plus two valence” far better than the same process in adults. This creates an obviously greater susceptibility for children based on relative exposures. Furthermore, iron deficiency (more common in women and in breast-fed infants) may increase the efficiency of absorption of plus two valence compounds such as lead. Women of childbearing age and especially children are sensitive populations for greater exposure than the same concentration presented to the gut of adult males.

Once in the body, lead tends to first enter the bloodstream. The half-life for residence in the bloodstream is approximately equal to the half-life of the red blood cell, which is slightly longer in adults than in children. While in the bloodstream, lead is also presented to soft tissues, such as the brain, peripheral nerves, and kidneys. From the

bloodstream, lead is concentrated in bones and teeth, where it may reside for a half-life of a decade or more. However, there are health conditions which can mobilize lead from bone back to bloodstream, including degenerative bone disease, such as osteoporosis and Paget's disease, as well as normal conditions such as bone healing and pregnancy.

### **Health Effects of Lead, Including Susceptible Populations (Children)**

Lead is an impressive toxin, with a protean list of health effects; a more dramatic effect on susceptible populations (infants and children), and lifelong negative outcomes at low doses. Virtually all human organ systems can be affected by lead exposure. The following paragraphs list only the most important of many known outcomes of lead exposure, which center primarily on neurologic, cardiovascular, and renal decrements to health.

By far the most important outcomes of human lead exposure relate to documented central nervous system capacity. While this definitively occurs in both children and adults, substantial human population data from multiple races, cultures, and nations indicate that infants and children are more susceptible to permanent damage, and at lower doses. Children who have been lead poisoned consistently perform worse than other children in measures of intellectual and social achievement, and are more likely to suffer from poor social attainment in numerous ways (ATSDRc, 2007). For example, IQ (Chen et al., 2005; Canfield et al., 2003), math/reading skills (Lanphear et al., 2000), and social behavior (Chiodo et al., 2004) are all negatively associated with blood lead. Infant development is negatively associated with first-trimester maternal plasma lead (Hu et al., 2006). These findings are robust to

adjustment for race, parental education, and markers of family socioeconomic status. Reverse causation has been ruled out by well designed studies; the associations are causal. Put simply, lead poisoning of children robs them and society of potential achievements. In a population context, when lead poisoning affects many children, the societal burden is inferred to be substantial.

### **Low-Level Lead: Dose-Response Studies of Human Performance**

Target blood lead levels (BLL) have been revised and revisited since the 1960s. The latest target recommendation of acceptable BLL levels has been <10 micrograms/deciliter ( $\mu\text{g}/\text{dl}$ ) since 1991. Since then various studies have established the persistence of population health risks even below the acceptable limit of <10  $\mu\text{g}/\text{dl}$ . It is unclear whether there is an established safe threshold. Recommendations for still lower levels in biomonitoring blood are surfacing.

Canfield and others (2003) measured blood lead concentrations in 172 children at 6, 12, 18, 24, 36, 48, and 60 months of age and administered the Stanford-Binet Intelligence Scale at the ages of 3 and 5 years. The results showed that the blood lead concentration was significantly and inversely associated with IQ. It was statistically derived that IQ declined by 7.4 points as lifetime average blood lead concentrations increased from 1 to 10  $\mu\text{g}/\text{dl}$ . The lifetime average BLL was measured to be 7.7  $\mu\text{g}/\text{dl}$  at 3 years and 7.4  $\mu\text{g}/\text{dl}$  at 5 years. This model of persistent adverse health effects even below the acceptable levels of 10  $\mu\text{g}/\text{dl}$  is consistent with other studies. The degree of performance decrement may vary among studies (this example is higher than many);

the presence of deleterious effects does not. Virtually all studies document diminished neurocognitive performance in relationship to blood lead.

Min and others (2009) evaluated the impact of early postnatal lead exposure measured at age 4 on children's IQ and academic achievement up to 11 years of age. Their analyses of subgroups of children with blood lead levels  $<10 \mu\text{g}/\text{dl}$  showed detrimental lead effects even at the  $5 \mu\text{g}/\text{dl}$  level, adding evidence to the detrimental effects of low-level exposure to lead.

Jedrychowski and colleagues (2008) assessed the neurocognitive status of 6-month-old infants whose mothers were exposed to low but varying amounts of lead during pregnancy. Their results led to a recommended cutoff for cord blood lead levels at  $\leq 1.67 \mu\text{g}/\text{dl}$ . The basis for this recommendation stems from finding that the infants scored lower by 1.5 points, as measured by instruments of intelligence testing appropriate for age, for every increase by one unit ( $1 \mu\text{g}/\text{dl}$ ) of lead concentration in cord blood. Further, the risk of the presence of a diagnosis of developmental delay was twofold greater among those children with higher cord blood levels.

### **Blood Pressure, Kidney, and Vascular**

In adults, higher blood and bone lead levels (as measured by KXRF in human tibias) correlate with elevated blood pressure (Hu et al., 1996; Nash et al., 2003). While most studies of blood pressure have been done on adult populations, it is also the case that lead poisoning in childhood is associated with an excess incidence of hypertension in adulthood. And, higher prenatal lead in mothers is associated with higher resting blood pressure in childhood, even at background population levels (Gump et al., 2005).

Similarly, when age and other covariables are accounted, decreased kidney function as measured by calculated GFR is associated with lead exposure as measured in blood or bone, even biomonitored exposures as low as 10 µg/dl or lower (Payton et al., 1994; Kim et al., 1996; Tsaih et al., 2004).

Studies on other organ systems have noted similar detrimental effect of chronic and cumulative low levels of lead exposure. Menke and others (2006) measured blood lead levels in a nationally representative sample of 13,946 adult participants of the third NHANES, who were recruited in 1988 to 1994 and followed for up to 12 years for all-cause and cause-specific mortality. The lower quartile of BLL was <1.94 µg/dl, and the upper quartile was >3.62 µg/dl, which fell well within the acceptable standards. However, when analyzed for all-cause mortality among the subjects, the hazard ratio was 1.25 for the upper quartile as compared to the lower quartile, the difference was statistically significant. For cardiovascular mortality, the hazard ratio was 1.55, and blood lead level was significantly associated with both myocardial infarction and stroke mortality at blood levels >2 µg/dl). No association was found between blood lead levels and cancer in this study, although lead is potentially a weak carcinogen.

In the cardiovascular system, it has been found that blood lead levels were strongly associated with the elevation of both systolic and diastolic blood pressure, at a level below the current U.S. occupational exposure limit guidelines (Nash et al., 2003). In this study, women aged 40 to 59 years were the age group most vulnerable to developing low-level lead-related hypertension.

Munter and others (2003) concluded that even low levels of exposure to lead in individuals suffering from hypertension can lead to chronic kidney disease (CKD).



Among persons with and without hypertension, mean blood lead was 4.21 and 3.30 µg/dL respectively, and the prevalence of CKD was 10% and 1%, respectively. Reverse causation is a consideration in this study design, but this study does not stand alone. Additional evidence of low-level lead as a major factor in the development of CKD exists in multiple studies (Ekong et al., 2006).

### **Reproduction and Endocrine**

Fertility is affected by low-level blood lead exposure. Chang and colleagues (2006) investigated the risk for infertility in women after low-level lead exposure. After controlling for age, body mass index, smoking, Chinese herbal medicine use, and irregular menstruation, it was concluded that the risk of infertility among women with BLL >2.5 µg/dl was three times greater than in women with BLL ≤2.5 µg/dl. Dundar and others (2006) also described the effect of low-level lead exposure on thyroid hormones, specifically FT4.

### **Uric Acid and Saturnine Gout**

Shadick and others (2000) confirmed that the long term accumulation of lead is associated with an increased uric acid level in middle-aged and elderly men. The association of lead with gout has been recognized for centuries, but the recognition of stepwise associations of increasing uric acid, the major risk factor for one kind of gout, with increasing biomonitored dose, is a new finding.

## **Cellular Effects**

Lead also has increased toxicological and population effects on hemoglobin synthesis and human red blood cell function (Schwartz et al., 1990). Hemoglobin is the molecule that allows red blood cells to capture oxygen from the lungs and to then deliver oxygen to points of use in the body—essentially all organs and tissues. By interfering with the formation of hemoglobin, lead poisoning can lead to ineffective blood cell formation, enhanced speed of cycling red blood cells, and anemia. Lead poisoning is characterized as both a cause and an outcome of anemia. Young children exposed to lead produce more of the hormone erythropoietin, which in turn stimulates a compensatory production of new red blood cells, and their guts absorb more lead.

The possibility that lead, at general population levels of exposure, may increase periodontal bone loss (Dye et al., 2002) is an important consideration for Appalachian mining regions, with their historic pattern of poor oral health.

There is increasing evidence that oxidative mechanisms play an important role in the development of many diseases. There is also evidence that low-level lead exposure can induce oxidative stress. Ahamed and others (2006) have found that such exposure induces oxidative stress by alteration of glutathione in blood and catalase in red blood cells (RBCs). The levels of these enzymes also correlate with delta-aminolevulinic acid dehydratase (delta-ALAD) inhibition. Similar effects were noted by Oktem and others (2004), who noted that lead-induced oxidative stress might have a detrimental effect on renal function as well.

## **Cancer**

Although cancer is among the less impressive toxicological attributes of human lead exposure, lead is considered a human carcinogen by the International Agency for Research on Cancer (IARC).

## ***Manganese***

Manganese is a transition metal element which occurs naturally in rocks and soils, combined with oxygen, silica, sulfur, or chlorine in mineral forms. It is used in industry as a metal alloy in steel, in welding, in batteries, fertilizers, paints, rubber and wood preservatives, cosmetics, and fungicides. Manganese has been used as an anti-knock additive to improve the octane rating of gasoline. An unusual use is as a contrast enhancer in magnetic resonance imaging (MRI).

Manganese is an essential trace element; the human body needs small amounts of manganese for normal functions. Manganese is essential to the function of enzymes that build or repair bones and cartilage, for the energy role of mitochondria, for the metabolism of glucose, and for the production of energy. Deficiency states or inherited errors of metabolism that prevent these enzymes from functioning properly can cause disease. Most humans have oral ingestion of food and drink as their principal source of exposure. Some people supplement natural exposures with additional manganese for health reasons. The risks and benefits of this practice are not well characterized.

Human populations at large are exposed because manganese is present in many foods, especially tea, nuts, or organ meats such as kidney or liver (Browning, 1961). Contributions from air pollution, and skin exposure are also possible, with a number of worker populations (metal miners, welders) at particular risk. Although small concentrations of manganese are essential to health, and the human body is known to have a wide tolerance to manganese exposure, high concentrations of manganese are known to be toxic. Manganese is demonstrated to cause devastating occupational disease, described below, among heavily exposed miners. Mining activity is a known source of manganese introduction to the environment (ATSDR, 2009c).

### **Human Exposure to Manganese**

The health literature concerning manganese exposure is dominated by inhalation, and especially occupational inhalation exposures, or else exposures in residential areas that are adjacent to industrial emissions. This is because inhaled manganese is the route of exposure clearly associated with toxicity. The human body handles oral manganese doses very well, and food intake is the primary source of exposure for most of us. The routine oral consumption range in adult humans is reported to be 0.7-10.0 mg/d, and higher in vegetarians if they eat a diet rich in nuts (ATSDR, 2009c). Nevertheless, oral toxicity has been reported in several settings, including contamination of drinking water.

Manganese is ubiquitous in soil. As a result, surface waters contain a median 24 µg/L (Smith et al., 1987), with a 99<sup>th</sup> percentile of < 800 µg/L. Groundwaters may contain more; median values are reported as 5-150 µg/L, and the 99<sup>th</sup> percentile is < 5600 µg/L. Most American public water supplies provide concentrations of < 50 µg/L (ATSDR, 2009c).

Natural sources are not the only contributors to environmental manganese. Iron, steel, and fossil fuel-based energy production provide important additions to the atmosphere and subsequently to soils and surface water (EPA, 2003). For most populations, exposures from water are far less substantial than exposures from food. The EPA has modeled a daily adult absorbed exposure from a 3.8 mg/d (3800 µg) total exposure. An absorbed dose approximates 0.24 µg from water, 0.46 µg from air, and 114 µg from food (EPA Table in ATSDR, 2009c). The difference between exposure and absorbed dose reflects the relatively low rate (3-5%) of gastrointestinal absorption. Exposures from air are negligible compared to diet. However, there is a specific concern that inhaled manganese can be transported directly into the brain (Elder et al., 2006), so central nervous system bioavailability could be much higher by the inhalation route. Occupationally exposed groups and populations living near foundries may be experiencing varying degrees of inhalation exposure, and there are theoretical reasons to consider whether inhalation exposures may be more neurotoxic than food and water exposures.

Manganese in water is generally measured as dissolved manganese, yet suspended solids may be a potential source of exposure. The gastrointestinal uptake of suspended manganese has not been explored, so “dissolved only” measurements of surface drinking-water sources may underestimate exposures. Among US regions, the Ohio River drainage basin has higher concentrations of manganese than many other areas, 232 µg/L (Kopp and Kroner, 1967).

### **Manganese in Humans**

Manganese in the blood of nonoccupationally exposed humans ranges from 4-15 µg/L (Barceloux, 1999). Mean urinary manganese is 1.10 µg/L in nonoccupational adult US populations (Paschal et al., 1998). Breast milk (collected in Germany) had a mean manganese level of 6.2 µg/L (Dorner et al., 1989), substantially less than manganese in infant formula. Leading experts have convincingly demonstrated that blood or plasma measures of manganese have very limited utility as biomarkers of manganese exposure in humans (Smith et al., 2007). Research means to quantify manganese in hair (Olmedo et al., 2010) have been developed, and complex approaches to understanding the implications of manganese in hair have been used in research studies (Haynes et al., 2009). However, the clinical hair-manganese tests occasionally seen in outpatient practice should be viewed with skepticism.

### **Sensitive Exposure Populations**

Pregnant women and neonates are likely to retain a higher proportion of an oral dose (Hafeman et al., 2007). The presence of manganese in infant formulas may be a concern for formula-fed infants.

### **Manganese and Human Health**

A historic, devastating, and seldom-seen neurologic disease known as manganism is frequently compared (misleadingly) to parkinsonism. It is characterized by muscle weakness, speech impairment, diminished coordination, impotence, tremor, paresthesia (abnormal sensory perceptions), salivation, emotional deterioration, “mask-like” facial expression, muscle rigidity, and gait disorder. Characteristic victims have been ore miners, with manganese inhalation exposures of  $> 5 \text{ mg/m}^3$  (Rodier, 1955; Cook et al., 1974). Manganism and parkinsonism are extrapyramidal neurodegenerative diseases located in anatomically distinct parts of the basal ganglia of the brain.

Acute oral inebriation is occasionally reported, especially in the context of cholecystatic disease requiring long-term parenteral nutrition that bypasses the gut's poor uptake and also its excretory role (Fell et al., 1996). Substance abusers who manufactured their own stimulant/euphoric drug methcathinone in a permanganate solution also experienced extrapyramidal symptoms suggestive of manganese toxicity (Stepens et al., 2008). High-dose occupational respiratory exposures can also cause pneumonia and respiratory problems; concern may also pertain to residents living near ferroalloy industries.

Classic manganism is proof of manganese high-dose toxicity. It is also rare, and its chief relevance to a water-pollution risk assessment lies in the ongoing and important scientific study of subtler manganese toxicity outcomes at much lower, long-term exposure levels.

There is a rich and hotly debated literature concerning neuropsychologic decrements in long-term, lower-level worker exposures, such as for welders. An important, current research question is whether welders suffer from a much subtler form of manganese inhalation-induced toxicity. To investigate this question, studies address precise measures of rapid hand movements, balance and coordination, and ability to concentrate. The vast majority of these studies address workplace inhalation exposures. The best-designed occupational exposure studies generally find subtly poorer performance associated with higher inhalation doses; a limitation is that the specifically abnormal tests and relationship to exposure times/doses are not necessarily consistent among studies.

A related question is whether manganese exposure in the workforce or in locally exposed populations increases the diagnosis of parkinsonism (presumably, a misdiagnosis for undetected manganism). A controversial study by Lucchini et al. (2007) detecting a higher prevalence of Parkinson's disease in the general vicinity of ferroalloy factories, with associated higher levels of manganese in local dust, has raised substantial interest, and a variety of follow-up studies are under way. Preliminary study



of residents living in proximity to a ferroalloy plant in Ohio shows an association with poorer postural stability (Standridge et al., 2008). There are studies suggesting still subtler neurologic change following chronic ingestion of contaminated drinking water. Kondakis et al. (1989) found increased neurologic signs in elderly Greek residents drinking water with 1.2-2.3 mg/L manganese, compared to residents in an area with much lower exposure. ATSDR (2009c) has pointed out numerous limitations in this report. A better-designed study from Bangladesh revealed an association of poorer ten-year-old-child performance on several neuropsychological tests in association with manganese exposure (Wasserman et al., 2006) in a population drinking water containing from 4-3908 µg/L manganese. To reach its conclusion, this study had to account for co-exposures to arsenic. A Chinese study of 92 children, 11-13 years of age and exposed to drinking water containing manganese at 240-350 µg/L, also found associations with diminished performance in neurobehavioral testing (He et al., 1994). A pilot study in Quebec found an association between contaminated drinking water (610 µg/L) and hair manganese, as well as associated lower scores on certain neuropsychologic tests (Bouchard et al., 2007).

### **Regulations, Reference Doses, and Guidelines**

The adequate and safe daily intake of manganese is considered to be 2-5 mg/day (NAS, 1980). The World Health Organization has established a water-based manganese standard of 400 µg/L. The US EPA issues a drinking water health advisory for manganese exposure of 300 µg/L in drinking water for a lifetime.

The historical NOAEL in drinking water (11 mg) has derived from a conflation of findings in food and water (IOM, 2001) and does not distinguish between the exposure/absorption rates of children and adults. Concerns have been raised that the current approach has been excessively permissive, of manganese-containing infant formula, and possibly in drinking water (Ljung and Vahter, 2007).

### **Summary**

It is currently believed that humans tolerate oral manganese well, and it is understood that most of us are primarily exposed to manganese in food. However, there are research questions raised about populations exposed to high levels of manganese in drinking water.

### ***Molybdenum***

Molybdenum is a transition metal element which is not found in its elemental form in nature. It exists in nature in several different ore forms, such as molybdenite ( $\text{MoS}_2$ ) and molybdenum trioxide. It is reasonably abundant and is found dissolved in ocean water. It is used as an alloy in steel, in ceramics, pigments, as a catalyst in some types of pollution control, and as an antiwear lubricant on metal surfaces. Molybdenum is essential to the activity of some bacterial and human enzymes, including xanthine oxidase and sulfite oxidase. A rare hereditary (or cofactor deficiency) condition impedes

the human ability to utilize molybdenum-dependent enzymes. This condition is characterized by build-up of serum sulfites and urate, leading to neurologic damage.

### **Human Exposure to Molybdenum**

Most exposure is from food rich in molybdenum, such as meat, eggs, beans, and cereals. Gastrointestinal absorption of molybdenum in food or water depends on water solubility. Molybdenum trioxide and calcium molybdate are well absorbed; water-insoluble forms such as molybdenum disulfide are not absorbed. About 38-77% of an ingested dose will be absorbed (USEPA, 1990). Once absorbed, molybdenum is excreted via urine and, to a lesser degree, in bile (and therefore feces). Molybdenum is retained in the body in growth cartilage, bone diaphyses, and kidney. A recommended daily intake of 25-250 g/day for adults was set by the National Research Council (1989). Several popular modern diets are believed to be molybdenum-deficient (Calton, 2010).

Generally, molybdenum exposures come from foods. High concentrations are found in leafy vegetables and legumes (Vyskocil and Viau, 1999). Molybdenum concentrations in drinking water range from 0-20 µg/L, and contribute about 20% of the intake. Molybdenum and other metal mining effluents can increase this concentration appreciably (US DOE, 1993).

## **Biomonitoring of Molybdenum**

Absorbed molybdenum appears rapidly in blood and in other organs. The highest concentrations are found in kidney, liver, and bone. Excretion is primarily renal, and occurs rapidly. The human biological half-life is not known but believed to be on the order of several days to two weeks. In nonoccupationally exposed populations, urine concentrations average 23 µg/100 ml (Lauwerys and Hoet, 2001). Biomonitoring for molybdenum is not generally performed because useful distinctions are not generally found.

## **Health Effects**

As an essential element, molybdenum is required for a number of normal body functions including the breakdown of purines to uric acid, and the control of cholesterol levels, among a list of critical functions. Molybdenum toxicity is rare and is said to resemble copper deficiency; it is treatable with copper supplementation. Copper-deficient populations (such as those with rare inherited enzyme abnormalities) represent a population at special risk. Molybdenum toxicity can also be induced by high doses of molybdenum even when copper supplies are adequate and copper-dependent enzymes are working normally. Increased levels of uric acid and gout-like symptoms have been reported in exposed workers (inhalation) and affected communities in parts of Armenia and India (oral intake of vegetables, with uptake from high concentrations of molybdenum in soil) (Vyskocil and Viau, 1999).

Meeker and colleagues (2009, 2010) observed an inverse relationship between several circulating metals in male humans, including molybdenum, and serum prolactin and testosterone levels. The significance of this finding is not known. They also found a negative association with human sperm concentration and a positive association with abnormal morphology (Meeker et al., 2008). Replication or refutation of these findings will obviously be important to populations voluntarily exposed to supplements and in areas of the world with molybdenum-rich soil.

Reference doses, NOAELs, and LOAELs have not been established. Despite provocative research about male reproductive toxicity, the toxicity of molybdenum is generally considered to be low.

### ***Nitrate (and Nitrite)***

Nitrate ions have the general formula  $\text{NO}_3^-$ . They form inorganic salts which are soluble in water and organic compounds (explosives used in mining are often organic nitrates). Nitrate compounds are common in the natural environment, and highly mobile in water in their common soluble forms. They may also be introduced to surface or subsurface waters by agricultural use of fertilizers, intensive feed lots and animal waste, sewage or septic tanks, erosion of natural depositions, and mining activities. West Virginia's Eastern Panhandle farmers have received particular scrutiny because of the Potomac River's nitrogen contributions to Chesapeake Bay (WVU Extension Service).

Nitrates are also present in many foods, such as green leafy vegetables (spinach, beets, broccoli, rhubarb, cabbage, and lettuce are the classic examples) (NAS, 1966), and they are added to food as a food preservative. Nitrites ( $\text{RNO}_2^-$ ) are much more acutely toxic to humans than nitrates; however, some conversion of less-harmful nitrates to more-harmful nitrites does occur by normal human metabolism. Nitrates ingested as part of a normal human diet (i.e., in a balanced vegetarian diet) are not generally considered harmful to adults, but dietary experts do recommend reducing nitrates, nitrites, and nitrosamines that enter the diet from sources such as preservatives and cooked meats.

### **Human Exposure to Nitrates**

Nitrate in shallow wells can be a concern in farming and even in suburban areas. Parts of the United States (not West Virginia) also have very high soil natural nitrate levels that can affect supplies generally. An estimated 8200 private wells in the US (2.4% of private wells) and 1.2% of municipal wells exceed the nitrate standard (ATSDR, 2010; USEPA, 2002). The risk is accentuated because few private wells receive routine testing.

### **Human Exposure, Metabolism, and Biomonitoring**

Estimated adult intake is about 75 mg/d, with a range of about 40-140 mg/day. Infants and children have correspondingly less exposure, but are considered a

susceptible population because (1) higher pH stomach acid normally found in infants can react with food proteins to form N-nitroso compounds, increasing exposure to a carcinogen; and (2) higher levels of nitrate are found in infant formulas than in most water sources.

Nitrate is almost completely absorbed in the small intestine (ATSDR, 2007) and excreted in saliva and urine.

Biomonitoring is done in specific medical circumstances, such as in schistosomal infections and bladder cancer (Mohsen et al., 1999). It is not performed as a biomarker of exposure.

### **Health Effects**

Nitrates can be metabolized to nitrites ( $\text{NO}_2^-$ ) and ammonia ( $\text{NH}_3$ ) in the human body. The nitrite is a physiologic concern. In sufficient exposure concentrations, nitrite exposures oxidize the iron in hemoglobin within the bloodstream. Hemoglobin is the compound that carries oxygen from the lungs to all other organs. So, the presence of sufficient nitrate in drinking water can lead to the presence of sufficient nitrite to reduce the effective amount of oxygen delivered to all organs in the human body, a condition called methemoglobinemia. Obviously, direct ingestion of nitrite can do the same thing. Infants and small children have been considered to be at much higher risk (e.g., the “blue-baby syndrome” of high-nitrate-exposure areas). Children and adults with a rare

inherited mutation for hereditary methemoglobinemia, and those with inherited mutations for common hemoglobinopathies (such as thalassemia and sickle cell, among many possible examples) may be considered populations at special risk. In fact, anemia of any cause can increase the risk that methemoglobinemia will lead to symptomatic outcomes.

Normal humans have < 2% blood methemoglobin. As this level begins to increase to 10%, the skin and lips can take on a blue tinge. Humans generally do well until methemoglobin levels are higher than this, although methemoglobinemia can be a serious condition in susceptible individuals. The reference dose (RfD) for nitrate is based on exposures that will result in no more than 10% methemoglobin. It is unusual to base a reference dose on an exposure concentration which can create a visible physical manifestation and symptoms in susceptible humans; the explanation may be that methemoglobinemia is unusual in the way it is tolerated at lower exposures, and nitrates are hard to eliminate from all water supplies.

Methemoglobinemia can result in hypotension and in pregnancy complications. There is a literature suggestive that prenatal nitrate exposure causes development abnormalities (Fan et al., 1996), especially neural tube defects (Ward et al., 2005), or increased risk of diabetes (Virtanen et al., 1994; Parslow et al., 1997). These are topics of current research, and research reviews generally regard the presence/absence of these outcomes following exposure as inconclusive (Manassaram et al., 2006).



Nitrosamines are known carcinogens. Nitrates can react with amino acids to form nitrosamines. There are associated elevated risks of several cancers including non-Hodgkin's lymphoma, colon, stomach, esophageal, nasopharyngeal, bladder, and prostate cancer (Cantor, 1997; Eichholzer et al., 1998; Ward et al., 1996; Ward et al., 2005; Barrett et al., 1998). The research topic of nitrate exposure and human cancer is controversial; there are many well-performed studies which do not find relationships (Zeegers et al., 2006). The current weight of evidence does suggest a possible relationship, which may operate at or below regulatory limits, but the extent and outcomes are not well characterized (Ward et al., 2005).

Animal studies have proven that high-dose nitrate exposure can inhibit iodine uptake and induce hypertrophic changes in the thyroid. Ecologic studies of human populations support the possibility that this may also be occurring in humans (van Maanen et al., 2000). An increasing number of respected researchers (Powlson et al., 2008) have raised the question of whether current nitrate exposure levels are sufficiently protective of human health.

### **Permissible Exposure**

The Joint Expert Committee on Food Additives (JECFA) of the United Nations Food and Agriculture Organization has set an Acceptable Daily Intake (ADI) of 0-2.7 mg nitrate (in some form)/kg body weight. The US EPA RfD is 0.9 mg nitrite nitrogen/Kg

body weight (0.33 nitrite ion/Kg body weight/d) (from ATSDR website at [http://www.atsdr.cdc.gov/csem/nitrate/no3standards\\_regulations.html](http://www.atsdr.cdc.gov/csem/nitrate/no3standards_regulations.html)).

The EPA nitrate MCLG of 10 mg/L (10 ppm) and nitrite MCLG of 1 mg/L is based upon calculations of methemoglobinemia toxicity (EPA Drinking water contaminants website at <http://www.epa.gov/safewater/contaminants/index.html>). In contrast, the allowable concentration of nitrate in smoked fish and cured meat is 200 ppm. EPA acknowledges that the carcinogenic potential of nitrate is not considered in the standards (US EPA, 2002). And, experts doing research on human populations point out that the existing research base is inconclusive about presence/absence of risk at current permissible exposure levels, and that current levels of permissible exposure do not build in a safety factor. There is a possible, but not proven, additional hazard not accounted in current safety standards (Ward et al., 2005; Manassaram et al., 2006).

### ***Selenium***

Selenium is a non-metallic element naturally present in the overburden materials associated with coal mining operations, and small amounts of selenium are directly associated with coal. Also, many forms of selenium are not readily soluble in water. Once dissolved in water, however, selenium compounds can be highly mobile. Humans can be exposed to selenium that originates in coal slurry through drinking water or from uptake by plants or animals that are food sources.

## **Selenium Health Effects**

Selenium is an essential trace element; humans need small amounts for thyroid metabolism and for the operation of cellular anti-oxidation defense mechanisms. Geographies (such as parts of China) with selenium deficient soils and food experience health problems, which are probably due to the selenium deficiency. The best known medical condition associated with selenium deficiency is Kashin-Beck disease, a combination of severe, deforming osteoarthropathy and cardiomyopathy, appearing in young children in selenium deficient regions of China and Tibet (Stone, 2009). The disease and its dramatic effects are partly reversible with selenium supplementation. Selenium deficiency is an underlying cause, but mycotoxins from grain and other sources of oxidative stress are considered to play a role.

Because selenium is an essential trace element with antioxidant properties, it may theoretically be useful in greater than minimum amounts for the prevention of cancer or other chronic disease. Cancer prevention has been evaluated in a number of studies of selenium supplementation. Some data support a cancer prevention role for selenium, whereas others do not. In practice, such benefits have not been definitively established, and recent epidemiologic evidence suggests there is actually a potential risk in supplementation. A very well done study from national databases shows that serum selenium concentrations are positively associated with adult-onset diabetes (Laclaustra et al., 2009). The highest population quartile of serum selenium ( $> 146 \mu\text{g/L}$ ) had more risk (OR 7.64; CI 3.34-17.46) than the lowest quartile ( $<124 \mu\text{g/L}$ ). While the direction of association is not clear from this study alone, oral supplementation trials are associated with increased risk in populations (Stranges et al., 2007). Also, the available

studies about bioavailable selenium and peripheral arterial disease suggest (but do not prove) a “U-shaped” association with possible benefits up to normal physiologic levels and then vascular disease risks at higher levels (Bleys et al., 2009). Selenium supplementation may also increase the risk of non-melanoma skin cancer (Duffield-Lillico et al., 2003).

Acute selenium toxicity is rare outside of poorly controlled selenium workplaces. Very high acute doses have been reported to cause diarrhea and tachycardia. Long-term intake of exposures 10-20 times the recommended daily allowance (RDA) causes brittle, abnormal appearing nails, hair loss, tooth discoloration and decay, and a neurologic syndrome characterized by unsteady gait which may progress to paralysis. The oral exposures required to cause selenosis, including nail deformation, in Chinese adults was an estimated daily intake of 0.91 mg/d (Yang et al., 1989a).

Small exposures to selenium compounds have been demonstrated to be necessary for thyroid metabolism, whereas larger exposures (several times the RDA or more) can be shown to reduce serum T<sub>3</sub> hormone. However, hypothyroidism as a result of selenium exposure has not been documented.

Epidemiologic studies show associations between selenium and dental caries (Hadjimarkos, 1969) as well as mottled teeth (Yang et al., 1989b), loss of hair, and nail deformities. Interactions between selenium and fluoride have been proposed as a mechanism. Very high intakes of selenium (in China) have been associated with peripheral neuropathy and arthralgia (Yang et al., 1983). High-concentration skin exposures can be irritating.

One form of selenium, selenium sulfide, causes cancer in laboratory rodents when they are fed this compound in daily doses at very high levels. This particular form of selenium is regarded as unusual in most environments because it does not readily dissolve in water; the presence of sulfides in coal slurry and in mine drainage may be a consideration. Selenium element also disrupts normal sperm formation and reproductive cycles in laboratory rodents. The significance of these findings for humans is not known; no reproductive problems associated with selenium exposure are documented so far for humans. Selenium does cross the placenta to enter the fetal circulation. However, no reliable studies to date show selenium exposure to be associated with birth defects in humans. Volunteers fed high selenium diets did experience small decreases in sperm motility, but these decreases were inconsistent over time (Hawkes and Turek, 2001).

By far the most complete discussion of selenium toxicity is the ATSDR Toxicological Profile (2003b), which is available online from the CDC. However, important data about diabetes associations was developed after publication. And, no population studies address the recently raised question of relevant concentrations of selenium in water and diabetes.

### **Selenium Exposure and Biomonitoring**

Blood selenium in humans does correspond to recent selenium exposures, but there is no good bio-monitoring test for chronic burden from past exposures. Individual tests for selenium as a biomarker of health or toxicity are probably not generally useful unless poisoning is suspected, or in the context of wider, thoroughly designed population studies. Population studies can use blood, urine, or nails. (There is a

significant potential problem with using an external biomarker such as hair, with its large surface area, in a coal-burning region. Selenium is emitted to the atmosphere when coal is burned, and coal measured on hair or nails can be in or on the sample. Because of the larger relative surface area and greater surface adherence, this is likely a more significant problem for hair than for toenails.)

### **Selenium Exposures: Recommendations and Tolerances**

In general, most human exposure to selenium comes from food sources, and water sources become most important when they affect locally grown crops. Because many health-conscious individuals voluntarily take selenium supplements in hopes of obtaining an antioxidant benefit, there are also substantial supplementation exposures from non-food sources. The likely forms of selenium encountered in food (and in food supplements) are selenate, and selenium element. In specific areas where there is substantial water pollution, drinking water is also an important source. Selenate and selenite are the typical forms in water runoff from polluted areas. Selenium in selenite is in the +4 oxidation state and occurs as the oxyanion  $\text{SeO}_3^{2-}$ . This form is considered more biologically active (and more toxic). It sorbs readily to sediments such as ferrihydrate. It also undergoes oxidation to selenate. For these reasons, selenite is predicted to travel less far in groundwater than selenate. However, an ATSDR review (2003b) suggests that selenite and selenate are equally common in surface waters. Selenium in selenate occurs as the oxyanion  $\text{SeO}_4^{2-}$  and is in the +6 oxidation state. Sodium selenate is a particularly mobile selenate compound. In contrast, selenium element has low solubility, and may not travel far in water.

Common sources of dietary selenium are cereals, breads, pasta, nuts, eggs, and meat. The estimated U.S. population daily intake is 0.071-0.152  $\mu\text{g}/\text{d}$ , with an estimated mean of 0.114  $\mu\text{g}/\text{d}$  for all ages and sexes (ATSDR, 2003b; USDHHS, 2002). Lower levels of selenium are found in milk and in breast milk. Childhood blood levels of selenium do appear to vary with the amount of selenium in soil (Yang et al., 1989b), at least under high-exposure conditions. Selenium supplementation products can contain 200  $\mu\text{g}/\text{tablet}$ ; this is a higher supplemental dose than is generally considered prudent. Home use of selenium supplements is thought to pertain to adults much more than to children. Home products such as selenium shampoos are not considered to be a skin-absorption hazard.

For adults, the RDA of selenium is 55  $\mu\text{g}/\text{d}$  or 0.8  $\mu\text{g}/\text{Kg}/\text{d}$ . The U.S. National Academy of Sciences (NAS) has recommended a Tolerable Upper Intake Level (UL) of 400  $\mu\text{g}/\text{d}$  for adults. (Recent data concerning diabetes may prompt re-evaluation and exert downward pressure on recommended tolerable limits; however, readers should recognize this thought as speculative because it precedes the activities of future review groups.) Based primarily on the Chinese population, a LOAEL of 0.023 mg/selenium/Kg/d, a NOAEL of 0.015 mg selenium/Kg/d, and an MRL of 0.005 mg selenium/Kg/d have been proposed (ATSDR, 2003b) (Table 7).

There are also recommended guidelines for drinking water intake, 0.9  $\mu\text{g}/\text{Kg}$  body weight in adults (WHO, 2001), as well as USEPA guidelines. The USEPA guidelines for selenium uptake are provided in Tables 10 and 11.

## **Silicon**

Silicon is an abundant metalloid element which is widely found in soils/dusts as silicon dioxide (silica) or as silicate minerals. Silica is a key component of sand. Silicon has numerous industrial uses, including several that are historically important in West Virginia, such as the creation of glass, ceramics, and cements. And, silicon is the mainstay of the semiconductor industry, appearing in a variety of semiconductor devices. It is also found abundantly adjacent to coal seams, where its presence as crystalline silica can represent a significant inhalation health hazard. Inhaled silica in its crystalline form leads to a serious lung fibrosis called silicosis, and related conditions such as Caplan's syndrome (accelerated rheumatoid arthritis in silicosis victims). Inhaled crystalline silica plays a role in coal workers' pneumoconiosis, or "black lung." Silica inhalation is also a contributing risk for lung cancer. Silica is present in coal ash, so it may be introduced to subsurface waters by coal slurry injection, where it can lead to ingestion of silica.

Ingested silicon in several forms is incorporated, in trace amounts, into bones, ligaments, and tendons in the human body. It is thought to stimulate protein synthesis in the formation of collagen, and increased concentrations of silicon appear around healing fractures.



## **Oral Exposure**

The topic of inhalation exposure to silicon is very important, and features very specific toxicity in important work settings (such as mining or surface drilling) and in natural events (such as sandstorms and volcanoes). This route of exposure is not the topic of this report. Similarly, there are research questions about skin exposure to silica in cosmetics, creams, and sunscreens, and possible relationships to autoimmune disease. That, too, is not the topic of this report. And, asbestos (in its several forms) is a silicate mineral whose inhalation leads to pulmonary fibrosis and several forms of pulmonary cancer, and whose oral ingestion may be related to oral and/or gastrointestinal cancer. However, asbestos is not relevant to coal slurry and is therefore not considered in this report.

Silicon enters drinking water by natural aging and transport of silicon-containing minerals such as silica and feldspar, as well as by mining and industrial activity. Sand filtration is used for purifying water in municipal water systems; that can theoretically add to the amount of exposure. However, because toxicity is considered low, water concentrations of silicon are infrequently measured, and relevant standards have not been set.

Manufactured silica nanoparticles are becoming important in industry. Early indications are that silica aggregates into micrometer-sized particles in aqueous solution, and therefore does not pose an additional risk to health (Iso et al., 2010).

Oral silica is encountered in vegetables and fruits which take up silica from soil, notably cereals, string beans and bananas, and in beverages made from vegetables high in silica content, such as beer (which may account for about half of all silica uptake in beer drinkers) (Powell et al., 2005), and in water. The average Western adult diet, including water sources, includes a mean intake of 18.6 mg/d in postmenopausal women (McNaughton et al., 2005), and a range of 13-62 mg silicon intake (Jugdaohsingh R et al., 2002) for adults. Although evidence for health benefits is uncertain, there are indicators of some benefits and numerous consumers who seek silica supplements in the belief of benefits for prevention of dementia, for longevity, or for improved appearance of hair and nails. Silicon-containing powders are used to formulate the coatings and binders of pharmaceutical agents. Silica is added to beverages as an anticaking agent. It is also in toothpaste as an abrasive agent.

Monomeric silicates are well absorbed, and polymeric silicates are less well absorbed with increasing polymerization (Sripanyakorn S et al., 2009). Once absorbed, silicon compounds are rapidly excreted as silicic acid in urine or incorporated into target organs such as bone. Biomonitoring has not been performed.

### **Health Effects**

There is limited and controversial evidence that silica protects against hypothesized damage from oxidative, neurodegenerative exposures to aluminum in

drinking water (Frisardi et al., 2010), and animal data suggests possible protection by silica against hepatotoxic chemicals (Hsu et al., 2010).

While there is no definitive data, a number of epidemiologic studies (Jugdaohsingh et al., 2004; Tucker et al., 2009), and animal investigations (Maehira et al., 2009) suggest the possibility that oral silicon is good for bone health, and emerging data support its use in the treatment of osteoporosis (Spector et al., 2008). Health risks may exist, but they have not been detected in good studies.

### **Minimal Risk Levels**

Minimal risk levels have not been established for oral intake at doses relevant to drinking water.

### ***Sodium***

Sodium is a metallic element. The elemental form is highly reactive and not encountered in nature. Instead, sodium is encountered commonly as a salt, especially as sodium chloride (table salt, or common salt) or as an ion. Soluble sodium is found in water, and insoluble forms such as sodium-aluminum-potassium silicates are found in the earth's crust. Sodium is an essential element for most or all animal life, and humans are among the species which have a taste receptor for table salt.

Sodium compounds have innumerable uses in industry; most people recognize the oldest use—as a condiment for food. Humans are exposed to salt in food via oral ingestion of processed food to which salt has been added in processing, naturally salty food, and table salt which we voluntarily add to food. In the absence of sodium in our diet, humans become “hyponatremic” and are unable to maintain control over our fluid balance. However, most cases of hyponatremia are due to medical conditions rather than to inadequate sodium intake. Instead, medical literature reveals common concern about an opposing and more common problem, increasing evidence that most Americans ingest too much salt.

### **Guidance for Reduced Intake**

In a recent report, the Institute of Medicine (IOM) recommended that the US EPA set standards for the salt content of processed (and restaurant) foods (IOM, 2010). The recommendation is for sodium, not for chloride. The recommendations are specific to food. However, a concern is that sodium ingestion from drinking water will also be relevant to total exposure. The report, which has been highly publicized, is intended to develop strategies to reduce population salt intake. The reduction in salt intake was also recommended in another, less publicized federal document (IOM, 2004). That document recommended limiting total daily adult sodium intake to less than 2300 mg/d (about a teaspoon), and noted that 1500 mg/d is adequate. The projected decrease in mortality from achieving this goal was said to be 100,000 deaths per year (IOM, 2010).

Most humans maintain salt balance easily; the World Health Organization (2003) recommends “slightly more than 1g of table salt per person per day.”

At current high salt doses, the data supporting reductions are partly based upon treatment of chronic disease with salt restriction. Reduced salt intake is clinically proved to be useful for managing several chronic diseases or risk factors, such as salt-sensitive hypertension and congestive heart failure. There are also critics of the recommendations because projected reductions in mortality are based, in part, on ecologic studies whose outcomes are not always consistent (Alderman et al., 2010).

As a result of the concern about Americans’ overall salt intake, the US EPA has included sodium on the Contaminant Candidate List (CCL). EPA clearly announces its scientific conflict (<http://www.epa.gov/safewater/ccl/sodium.html>). On one hand, EPA believes that the current guidance (DWEK, or Drinking Water Equivalency Level) needs updating. On the other hand, EPA publicly reports that the current level is, if anything, too low. In the climate of recommendations to decrease intake, this may seem surprising. Close inspection of the EPA posting in this regard notes that the language of the statement, while strong, also contains an internal contradiction suggesting that there are exceptions (quoted below from the EPA web site).

**“Should I be concerned about sodium in my drinking water?”**

“No. Sodium levels in drinking water from most public water systems are unlikely to be a significant contribution to adverse health effects.”

An interpretation of the EPA document is that it is for most consumers, but possibly not for the ones who have high levels of sodium in their drinking water.

Sodium (and chloride) may enter water from natural sources, from sodium ion-exchange water-treatment systems (water softeners), from water-system disinfection using sodium hypochlorite, from road deicing, inorganic fertilizers, landfill leachates, industrial and mining effluents, irrigation drainage, and seawater intrusions. Although sodium is generally considered the relevant ion for human health, the World Health Organization has also created a document for chlorides (2003), and frames its recommendations in terms of common salt.

### **Human Exposure to Sodium**

The US EPA web site states that most Americans consume 4,000-6,000 mg of sodium per day. For about three-fourths of municipal water systems, the average adult consuming eight glasses of municipal water per day would consume less than 100 mg of that intake from water. This comparison, < 100 mg from water versus 4,000-6000 mg total, appears to form the basis of EPA's assurance that water is not an important source of sodium.

However, it is also clear that current recommendations call for much lower sodium intake (about one-third of the EPA's official estimate of average intake). As little as 120-400 mg/d of sodium will meet the minimum developmental needs of children,

and 500 mg/d will meet the needs of adults. Ideal recommendations are on the order of < 2500 to < 1500 mg/d for adults. It is clear that some water systems or wells feature concentrations of > 100 mg/L, so it is also the case that high-sodium drinking water, while contributing less than food, may still represent an appreciable fraction of the salt in specific instances of those who need to reduce their sodium intake for health reasons.

### **Health Effects of Salt**

Adequate intake of sodium and chloride is essential to “homeostasis,” the body’s regulation of its fluids. Rapid changes in salt content of body fluids in either direction can lead to muscle cramps, dizziness, heart rhythm problems, and death. Animal data consistently demonstrate that hypertension (high blood pressure) can be created in different species fed diets high in salt. While this phenomenon is less clear (and harder to study) in humans, it is well known that hypertensive humans and those suffering from some of the consequences of hypertension (such as congestive heart failure or chronic kidney disease) do benefit from a salt-restricted diet. Therefore, humans with salt-sensitive hypertension, and with congestive heart failure or chronic kidney disease, represent sensitive populations.

A striking observation is that “non-Westernized” populations consuming diets low in salt feature a very low population prevalence of hypertension, including absence of the increase in blood pressure with aging that is noted in developed countries (WHO, 1996). This sort of ecologic data clearly points to a Western problem, but it alone does

not specify that the source of the problem is just one or two dietary element(s). Many aspects of diet could also contribute. Based on many additional studies of numerous study designs, most experts, including those who write for the Cochrane Collaboration, a respected international review mechanism for “evidence-based medicine,” have concluded that higher lifetime salt intake does result in an increase of adult hypertension (He and MacGregor, 2005).

Hypertension is not the only disease associated with high salt intake. For example, there is historic concern that salted fish and salted meat are associated with epidemic gastric cancer, and that the historic decreases in gastric cancer are associated with the advent of refrigeration (and the decreased need to salt meat and fish once refrigeration became available). However, less salt curing is not the only change that came with refrigeration, so this association is uncertain.

For purposes of thinking about thresholds in consumable water, hypertension is the human health outcome of greatest interest. In considering the role of water, it is important to remember that most of us get more than 90% of our sodium from food (and can likely improve our health by wiser choices of food and condiments (He and MacGregor, 2010). Water intake becomes a significant factor when there is contamination.

### ***Strontium***

Strontium is an element which is found in a number of minerals in nature. The strontium in nature that can be associated with coal and coal overburden is mostly non-



radioactive. Strontium enters the environment when coal is burned or cleaned, or when water runs through minerals bearing strontium. Most but not all strontium minerals can be dissolved or suspended in water. Strontium in small quantities is also naturally present in food, especially grains, leafy vegetables, and milk.

Most drinking water in the U.S. has less than 1 ppm strontium. The radiation from strontium in water is generally very small, less than 0.1 pCi/L (or .004 Bq/L). (Picocuries [pCi] and becquerels [Bq] are standard measures of ionizing radiation, named for scientists.)

### **Strontium Exposure and Metabolism**

Most public health considerations of strontium involve inhalation, because strontium is easily inhaled in dust and easily absorbed via the lungs. In contrast, strontium is not well absorbed via the gut. However, and in common with lead, infants and small children may be a susceptible population for greater exposure as there is some evidence that they are more exposed from dairy products such as milk, and they absorb strontium better because their guts absorb calcium better than adults. Strontium is also slightly permeable through skin; however, this is not considered an important route of exposure in most circumstances.

Because the human body handles strontium in ways similar to calcium, strontium is rapidly distributed in the blood once absorbed and then the blood effectively distributes the strontium to other parts of the body. Over time, much of the absorbed strontium will be deposited on the surface of bones or teeth. And, like calcium, the strontium in bone is reabsorbed and in equilibrium with strontium in the blood.

Thus, strontium is also gradually excreted over time. This description of strontium metabolism resembles the description of what happens when humans ingest lead.

### **Strontium and Health**

Strontium is not considered an essential element; it is thought that humans can survive without it. On the other hand, there are some potential health benefits of strontium. Calcium absorption may be slightly better in the presence of strontium. Strontium has been used in successful clinical trials to improve the bone density of patients suffering from osteoporosis.

Strontium is not a known toxin in its common, non-radioactive form in the local coal environment. Because most strontium is in the coal-processing waste stream, there is no reason to consider strontium as a significant hazard in most circumstances. A possible exception to this statement is that one form of strontium mineral, strontium chromate, can be toxic. However, the toxicity is inherently from the chromate compound, not the strontium. There is a separate consideration for chromium toxicity. In calcium-deficient children, too much strontium can contribute to brittle bones. The USEPA drinking water designation of 4 mg/L accounts for this risk. Details about strontium toxicity in the context of risk assessment can be seen at <http://www.atsdr.cdc.gov/toxprofiles/phs159.html>. Strontium also has an oral MRL of 2 mg/kg/day (Table 7).

## **Sulfates**

Sulfate ( $\text{SO}_4^{(2-)}$ ) is a molecule that can be ionically bound to elements such as sodium which are soluble in water, and, less commonly, in insoluble compounds such as barium or lead sulfate. Sulfates occur naturally in innumerable minerals. A small geographic area northwest of Lewisburg, WV, is famous for high-sulfate-bearing water, including related thermal springs (Heller and Rauch, 1986). The lead-acid battery is the best-recognized industrial use, but fertilizers are the biggest intentional sulfate introduction to the environment. "SO<sub>x</sub>" aerosol emissions (in numerous permutations) from fossil-fuel power generation and pulp or paper processing are the best-known unintended form of sulfate pollution. Aluminum sulfate is used as a sedimentation agent in drinking-water processing. Magnesium sulfate is a common intravenous pharmaceutical. Sulfate is a natural constituent of drinking water and coal overburden. Coal contains varying amounts of sulfur, and coal slurry therefore contains sulfates. As addressed elsewhere in this document, acid mine drainage contributes sulfate to surface waters and subsurface water.

### **Human Exposure to Sulfate**

Sulfate is present in most natural water supplies. It is a dissolved component of rain, especially in regions which burn substantial quantities of high-sulfur coal (or to a lesser degree petroleum products), or have large industrial operations, or where vehicular traffic is dense. Sulfate minerals in rocks and soils can be dissolved and move

into ground or surface water. In addition, sulfates from abandoned mine operations commonly enter surface and subsurface waters, through processes described elsewhere in this document.

Typical sulfate concentrations in fresh water are around 20 mg/L, but can range up to 630 mg/L in rivers (WHO, 2004).

The estimated daily consumption for US adults is around 450 mg in food (NAS, 1972) and about 500 mg total (WHO, 2004).

A number of common prescribed and self-selected drugs are in sulfate form. Chondroitin sulfate, an over-the-counter remedy with supposed benefits for degenerative joint disease, is a prominent example.

### **Health Effects of Sulfate**

Most humans can notice the distinctive taste of sulfate in water at 250-500 mg/L (WHO, 2004). The Centers for Disease Control surveyed several populations in areas with wide-ranging sulfate concentrations (< 100 mg/L to > 1g/L) for sulfate use and diarrhea outcome, as well as smaller numbers of travelers who entered areas where sulfate concentrations were higher than those where they lived. Important associations with diarrhea were sought and not found (CDC, 1999). A weak association at the highest exposure concentration fell short of statistical significance.

Although infants are designated a susceptible population, CDC concluded from their data that few women who received water high in sulfate concentration in their home intended to feed it to their infants. (The possibility of survey-information bias was not discussed.) The actual threshold sulfate concentration that causes diarrhea in susceptible humans such as infants and travelers is not known (Backer, 2000).

Although this section is addressed to human health, agricultural extension recommendations for cow-calf operations note that bovine diarrhea may occur at about 1g/L, reducing herd economic performance (Cooperative Extension Service website, 2010).

### **Drinking Water Reference Value**

The EPA SMCL is 250 mg/L (ppm) based upon aesthetic considerations such as taste/odor. (This rationale is partly misleading because of laxative health effects, as sulfate-rich waters can be a cause of diarrhea.) EPA estimates that about 3% of the US public water systems exceed the SMCL (EPA Sulfate in Drinking Water website, 2010).

The European Union has suggested a lower (250 mg/L) standard than the current EPA standard (WHO has the same standard as the EPA).

## ***Total Dissolved Solids***

Total dissolved solids (TDS) is defined as the measure of all inorganic salts and organic solids dissolved or colloidally suspended in water. TDS is generally measured by filtration and is related to but not the same as another general measure of water quality, conductivity. (In practice, some field devices that report TDS actually measure conductivity.) TDS is distinguished from total suspended solids (TSS) by filter pore size. By definition, a sum of unknown components is obtained and the actual composition of the individual components is not measured, so the concept of TDS does not correlate well with how we try to define health hazards. TDS is therefore a secondary drinking-water standard (secondary standards are based on taste, or potential effects on water-system components, and other “nonhealth” outcomes such as odor).

Nevertheless, TDS is potentially useful because it is inexpensive to measure and broad-based in its ability to monitor for changes in drinking-water quality. The potential principal anions and cations comprising TDS include coal slurry components such as sodium chloride, sulfates, and nitrates, as well as others. TDS can come from natural sources (including storm runoff), sewage, fertilizer, animal waste, fish farming, road salt, as well as industrial and mining sources. Coal-pile leachates are known to contribute to TDS in surface water (Carlton and Carlson, 1994) and in groundwater (Ebraheem et al., 1990). The potentially useful thing about TDS is that most anions or cations will be measured, so large variances can be detected. The limitation is that the specific

components are not measured, and constant TDS may disguise significant but unmeasured changes in toxic concentrations.

The representation that TDS is not a health hazard can also be misleading, and relates, in part, to differences in how water-quality experts frame problems (compared to, for example, air-quality experts). TDS is a broad-based indicator of water quality in the same way that carbon dioxide is used as an indicator gas in determining building indoor-air quality. Although a high CO<sub>2</sub> reading (for example, 1300 ppm) in a building does not itself represent a health hazard, most environmental specialists would not hesitate to use the high indicator-gas reading as clear evidence of sufficiently poor circulation to predict symptom health outcomes and productivity problems in a building that consistently featured this reading. This prediction would be based on experience buttressed by peer-reviewed studies. Similar studies are lacking for TDS as an indicator; water-quality research has not used indicators to the same extent in research studies. However, there are studies from developing nations that do indicate potential usefulness. Research from Rajasthan (India) showed that water samples with high TDS also had high levels of other contaminants, indicating nonpotability for humans (Batheja et al., 2002). Thus, TDS is potentially useful as a health indicator, but sufficient research has not been done to predict specific health outcomes. And, where groundwater is salty, TDS can provide a warning of toxic metal exposures (Buschmann et al., 2008).

## **Human Exposure to Total Dissolved Solids**

Municipal water-treatment plants substantially reduce the water burden of dissolved and colloidally suspended solids. Nevertheless, water concentrations of important toxic elements such as lead and copper do correlate with TDS in river water (Newchurch and Kahwa, 1984).

No biomonitoring approach is possible. Humans maintain an electrolyte milieu that is far higher than the water we drink.

## **Health Effects**

The World Health Organization (2003) reviewed existing studies and noted that a number of early studies (published in the 1960s and 1970s) showed higher rates of cardiovascular disease and all-cause mortality associated with *lower* levels of TDS in drinking water. An ecologic study design of cancer death rates in the 100 largest US cities showed a statistically significant correlation between both TDS and electrical conductivity with cancer death rates (Burton and Cornhill, 1977). In general, health effects of drinking water have been studied in the context of specific exposures rather than general measures of coarse and colloidal burdens. And, recent high-quality studies have not been done in regions where mining or drilling operations, or encroaching sea water, may provide opportunities to study whether observations in TDS correlate with changes in human health status.



## **Reference Standard**

EPA secondary regulations advise an MCL of 500 mg/L TDS (500 ppm). This is based primarily on the presence of salt and on odor/taste. (EPA Secondary Drinking Water Regulations Website, 2010).

## **Summary of Health Effects**

Existing data, while sparse, suggest that arsenic, cadmium, and lead are potential chemicals of concern and candidates for ongoing monitoring, in the context of possible contamination by coal slurry. Because of their known toxicity, these have low (lead and arsenic), and potentially low (cadmium) thresholds for inducing unfavorable changes in human health. Exposures to these elements can result in several kinds of detrimental changes in human population health if introduced into drinking water. Furthermore, small changes in water quality are theoretically capable of causing human health effects when enough people are exposed. That judgment is based on health literature. Small increments to oral exposures are reported to have caused population health effects, in well-designed studies, in some part of the world. In no case is that circumstance known to be from coal slurry, however.

A fourth element, iron, also presents a potential health risk limited to a susceptible population. The susceptible population comprises people who have inherited two genes for a condition known as hemochromatosis. They are homozygous or double heterozygous for either of the two recessive genes that diminish the normally excellent human capability to safely handle and excrete environmental iron. Those

susceptible may suffer from liver disease if exposed to sufficient iron; they benefit from reductions in exposure to iron. The population at risk is descended from northern Europeans (such as Scots-Irish), and the gene frequency is high enough so that the disease, hemochromatosis, is actually seen. Thus iron contamination of water is a potential contributor to a public health concern in West Virginia.

The Wheeling Jesuit University data suggest that arsenic, barium, cadmium, iron, lead, and selenium may enter southern West Virginia water in excess of drinking water standards. Slurry liquid is a potential source, based on concentrations documented in the Phase I, SCR-15 report. We do not have concrete evidence that slurry injection alone has substantially contributed to or caused the exposures of greatest concern within data sets reviewed. In fact, the Phase I data indicate that the sites monitored are not important recent sources of such exposures, but important data gaps must be acknowledged. The Wheeling Jesuit University report is evidence that such exposures do occur, regardless of sources. Although slurry water is demonstrably a potential source, the specific sources of contamination are unclear. (We do not have sufficient measures to reliably identify, separate, implicate, or absolve sources; this is a data gap.)

Of the chemicals reviewed, arsenic, cadmium, and lead are universally hazardous. Iron is hazardous to a population subset, and all are found in drinking water. Table 12, a review of drinking-water regulations, illustrates the nature of water-consumer protection, including the absolute vulnerability of those who rely on wells, and the relative vulnerability of small and even medium-sized municipal systems.

Another data gap arises when studying the organic dataset from the Phase I report. The existing literature on organics in coal slurry does not provide specific guidance on what compounds to analyze for, how to sample them, or how to interpret the results. Because of this, as well as the expense of analysis, only a small fraction of the possible organic compounds were reviewed. Many potentially harmful compounds were not included in the Phase I report.

### **Comparison of Drinking-Water Sampling Frequencies to Potential Health Hazards**

The Federal plan for protecting consumers of drinking water (summarized in Table 12) does not invariably protect the public from intermittent, unintentional introduction of hazards such as arsenic, cadmium, or lead. In addition, federal and state regulation of chemicals found in coal slurry is often difficult due to multiple reasons. Chemicals vary by chemical supplier and chemical feed into the slurry, technology has changed the chemicals used in the coal preparation process, and the type of coal mined is different among processing plants.

Private wells are not regulated. Water systems that serve small populations may be checked by infrequent sampling (every three years) in the case of lead, or no sampling for other potentially important intermittent pollutants.

Intermittent exposures to elements of health importance, when they do occur, are not necessarily accompanied by odor, visual, or taste warning properties. When sampling is seldom, or never, reliance on drinking-water monitoring is incompletely protective in the setting of potential intermittent introductions of the most important chemicals under consideration. These are the chemicals of concern: arsenic, cadmium,

and lead, as well as iron because of the potential harm to a susceptible population. When a new or intermittent hazard is introduced to seldom- or never-sampled water supplies, other means to secure drinking-water security should be a consideration.

## **Coal Slurry Underground Injection Control Data Evaluation**

### **Coal Slurry Production**

#### ***Coal Processing***

When coal is initially removed from the mine, it is called raw or run-of-mine (ROM) coal. It contains coal and associated shales removed by the excavation equipment. Depending on the customer's requirements, it may be cleaned by crushing, sieving and washing to remove impurities such as shale and pyrites. Coal cleaning is accomplished in a wash, or preparation plant, and results in clean coal for shipment to the customer and rejected rock, known as refuse or tailings.

The first step in the preparation process is characterization of the ROM coal. In this step, wash-ability studies are performed in order to determine how much coal can be produced at a certain size and specific gravity. Step two, the liberation process, occurs through the size reduction of the ROM coal. Grinding the coal to a finer size allows removal of increasing proportions of impurities. Coal from various seams may be cleaned and blended at the preparation plant resulting in a more homogeneous mixture of coal. Step three is the separation of the liberated particles. The ROM coal is made into slurry by adding water and additives and using various machinery (such as jigs and cyclones) to achieve the separation of the coal from its associated impurities. The fourth and final step in coal processing involves transporting the clean coal to market

and disposing of refuse. Refuse disposal is governed by environmental rules and regulations (NAS, 2007). In general, the refuse consists of about 1/3 fines and 2/3 coarse refuse. Coarse refuse is generally sized between coarse sand (2 mm) and 3 inches in diameter. Coarse refuse is transported in rock trucks or conveyors to the disposal facility. Fine refuse (smaller than sand size) is then transported hydraulically to a surface impoundment or an underground disposal site. This discussion focuses on the refuse fines or slurry fraction of coal tailings that have been placed in the open void space left after underground coal mining.

Coal slurry consists of both solid and liquid fractions. The rocks, minerals, and soil removed from the coal, as well as the water used to wash the coal, are the major constituents of coal slurry (Nicol, 1997). In addition to the minerals in coal slurry that were exposed by coal preparation, other chemicals may be present that were used to facilitate the washing and other preparation processes used in the coal preparation plant. To permit dewatering of the slurry under controlled conditions, it is placed either in surface impoundments or in underground coal mine voids. Each approach has its advantages and disadvantages.

Limited data permit a range of interpretations regarding the pollution potential of coal slurry. Testing of water in four underground slurry injection sites in southern West Virginia determined that two of the four sites were influenced by the injected material. Although some slurry constituents were found to have migrated from the slurry to the mine pool, there was no evidence that any of these pollutants had migrated into the surrounding surface water (WVDEP, 2009).

There are also some useful historic data. Libicki et al. (1983) found that pollutants from coal refuse stored in abandoned mining pits had migrated into the surrounding groundwater. The migration of such pollutants is predicted by column studies. Pollutants could be divided into three-column study categories: most leachable (chlorine, sulfate, sodium, and potassium), medium leachability (copper, zinc, mercury, strontium, cadmium, boron, manganese, molybdenum, and cyanide), and least leachable (magnesium, aluminum, chromium, arsenic, lead, ammonia, and calcium). The level of groundwater contamination was found to be due to two main factors: the leachability of the waste and the sealing of the bottom of the pit by clay particles washed from the top of the waste pile. Self-sealing by clay particles was observed in the column studies, but could not be proven in the field because the bottom of the pit was not sampled and water levels were unknown.

Seven sites were researched by Smith (1987) to determine if injection of coal slurry had any impact on nearby groundwater. She found that the concentrations of various parameters in the mine pool groundwater were influenced by the initial pH of the mine pool. Injection of coal slurry into alkaline mine pools generally decreased metal concentrations and increased sulfate concentrations.

The migration of aqueous slurry can also be influenced by the depth and structure of the target mine voids. If a mine is below drainage (below the local water table), then it will eventually flood when mining ceases. Upon flooding, the mine pool will achieve pressure equilibrium with water in the unmined strata thus slowing the migration of slurry that was injected into the mine (WVDEP, 2009).

Surface impoundments are the most common form of slurry disposal. Coal slurry injection into underground voids is the alternative to surface impoundments. Surface impoundments usually occupy the heads of stream valleys. Surface impoundments disrupt habitat and may be long-term sources of AMD. They may also pose a long-term geotechnical risk and may require indefinite maintenance, or at least monitoring, to ensure that the integrity of the containment structure is maintained.

Underground slurry injection has the advantage, in comparison to surface impoundments, of placing the most geo-technically unstable fraction of the tailings underground where, if the site is chosen carefully and the injection works as planned, it will not exit to the surface. Depending on the degree of flooding, underground coal mines may become anoxic and thus constrain further oxidation of pyrite. This constraint on iron oxidation, in turn, limits production of acidity and metal leachates. These are advantageous attributes. The disadvantage of underground slurry injection is that its flow path within the mine voids and its effect on mine and surrounding groundwater chemistry are poorly understood and potentially difficult to measure, especially without substantial advance planning. In West Virginia, 10-15% of coal slurry is injected underground (WVDEP, 2009).

### **Factors That Affect Slurry Chemistry**

Since coal slurry consists of a solid and an aqueous phase, it is important to distinguish their properties and chemistries. Due to the nature of their different chemical environments, compounds found in the solid refuse particles may not be found in the aqueous phase, and vice versa.

With the exception of the chemicals added during coal processing, the chemistry of coal slurry is very similar to coal itself. The specific chemistry of coal slurry is determined by the characteristics of the coal, the associated rock, and the quality of the water used in the coal cleaning process. In addition to the fine coal refuse and water found in slurry, a heterogeneous mixture of many other chemicals may be found as well. Unfortunately, many of these chemicals are proprietary and the manufacturers are often unwilling to disclose exactly what is in the chemical. This trade secrecy constrains the completeness of risk assessment efforts for any means of slurry disposal.

The State of West Virginia has a list of 237 chemicals that are allowed in coal slurry when it is injected underground. These chemicals are permitted for injection because they do not meet the definition of a hazardous material under the Resource Conservation and Recovery Act (RCRA). Only those constituents listed in the Underground Injection Control (UIC) permit may be part of the injectate (WVDEP, 2009).

### ***Coal Slurry Matrices Considered***

#### ***Aqueous Phase***

The aqueous (liquid) phase consists of water, additives, and elements that dissolve out of the solid phase. Many of the compounds added during coal cleaning are organic. They are often difficult to analyze accurately and analytical results may be confounded by the fact that additives used may bind to coal and that coal itself releases a number of similar organic compounds. In an aqueous environment, chemical reactions are influenced by the dipolar nature of the water molecule. Because a water



molecule has both positive and negative sites, it can associate with both anions and cations. Depending upon solubility and the hydrophobic/hydrophilic nature of the substance, water may totally or partially dissolve the substance. In addition to soluble compounds, the aqueous phase includes colloids. Colloids typically consist of suspended particles which can pass through the typical laboratory filtration. Colloids are mixtures in which one substance is evenly dispersed in another. They contain particles in the size range between  $10^{-9}$  m and  $10^{-6}$  m (Hiemenz and Rajagopalan, 1997), typically less than 0.45 microns. Since these particles will pass through the typical laboratory filtration process, they are accounted for in the dissolved analyses. The total analysis, on the other hand, will account for precipitated, suspended solids as well as dissolved and colloidal fractions. For this reason, water samples are analyzed for both dissolved and total concentrations.

In the case of coal slurry, the aqueous phase consists of fine coal, minerals, and additive chemicals from the coal preparation process in a solution of water. As a result, the extent to which these additives pass into the aqueous phase of coal slurry can only be estimated by analyzing the resulting aqueous phase chemistry.

The aqueous phase of slurry is much more mobile than the solid phase particles and much more likely to migrate from its original location since it will be transported as a dissolved or suspended constituent of water. Because of this, there is concern that groundwater supplies may become contaminated by coal slurry. In the Phase I study, testing of water in four underground slurry injection sites in southern West Virginia (Southern Minerals, Loadout, Panther, and Power Mountain) determined that two of the four mine pool sites were influenced by the injected material (WVDEP, 2009). Although

some slurry constituents were found to have migrated from the slurry to the slower moving groundwater in the mine pool, there is no irrefutable evidence that these pollutants had migrated from the mine pool into the surrounding surface water (WVDEP, 2009). Table 13 summarizes the aqueous phase of five coal slurries studied in SCR-15 Phase 1.

### ***Solid Phase***

To determine the composition of solid phase coal slurry, the material is filtered, dried, crushed and digested to release elements trapped inside the coal/rock matrix. The digestion process uses chemicals that dissolve the coal and rock matrix. Those elements that remain in the solid phase after going through the coal cleaning process are resistant to weathering. Results of the digestion and analysis are reported as mg/kg. Buttermore et al. (1978) explained that the typical size of the solid phase of coal refuse is greater than 1/16." These larger materials have a relatively low surface area and do not weather quickly. Solid phase coal chemistry consists of many elements that do not leach into the aqueous phase because they are bound in stable minerals such as long, organic chain and ring compounds. When evaluating the solid phase of a substance, mobility and availability of the constituents in the environment are not taken into account.

In its Phase I report, the WVDEP (2009) analyzed the solid phase of coal slurry from 6 different sites for over 175 different parameters. In order to further understand the slurry composition, they also analyzed the raw coal and a simulated coal slurry leachate for the same analytes. The coal slurry leachate was made by crushing the raw

coal, adding de-ionized water, and tumbling the solution for 24 hours. Most of the organic compounds found in the solid slurry were in the PAH group. Eight chemicals were found in the slurry that were not found in the corresponding coal sample. However, only one sample was taken, which does not provide a large enough sample set to determine the exact source of these compounds. Table 14 summarizes the organic coal and slurry composition.

The inorganic chemistry analysis of five of these Phase I report samples (Tables 13 and 14), compared to threshold values, found that iron was an important metal in the slurry, while aluminum, antimony, arsenic, cadmium, iron, lead, and manganese reached thresholds as contaminants of concern. Sulfates were a prominent finding, highest at the Coresco site and lowest at the Southern Minerals site, which may be due to the initial sulfur content of the coal. Fluoride, nitrogen, and total dissolved solids were also contaminants of concern based on slurry data.

Historic research on the solid phase of coal slurry has shown that various factors may influence its chemistry. Wewerka et al. (1976) determined that Al, Si, Fe, Ca, and Mg dominate the coal-associated minerals. Table 15 details the trace elements found in coal refuse alone. Some of the minerals that were found associated with these trace elements included: quartz, chlorite, illite, calcite, pyrite, and muscovite, among others.

Concentrations of trace elements in slurry can be affected by the coal preparation process; waste rock handling affects slurry chemistry. Wewerka et al. (1976) showed that drainage from coarse coal refuse piles was much more concentrated with respect to boron, barium, chromium, manganese, and strontium, than was drainage from underground mining because the exposed waste being much more

susceptible to leaching and oxidation. Another factor that may influence slurry chemistry is whether the slurry is exposed to an alkaline or acidic environment. Many of the metals associated with the coal waste have low solubility at higher pH values, meaning that they are less mobile in the alkaline environment. Some of the metals studied in this research included: cadmium, copper, iron, lead, nickel, silver, and zinc (Cobb et al, 1999).

### **Slurry Physical Characteristics**

The physical characteristics of coal slurry are determined by the coal preparation process and the mineralogy of the coal. These characteristics may be quite variable. By its nature, coal slurry is a mixture of many different substances. The three major product streams from a coal preparation plant are coal, waste, and middlings, or coal with too many impurities to be burned in a power plant (Osborne, 1988). These materials are often separated from one another in a flotation tank. The middlings and the waste settle to the bottom of the tank while the coal, which is hydrophobic, associates with bubbles in the tank, causing it to float to the surface. Often, both the middlings and the waste rock are disposed of as coal slurry. Because of this, particle size, specific gravity, porosity, viscosity, etc. can be very different among different coal wastes. A comparison of coal, fresh coal waste, and weathered coal waste can be found in Table 16.

Although the Phase I report did not describe the physical characteristics of the coal slurry they sampled (WVDEP, 2009), other research has been performed on this topic. Buttermore et al. (1978) divided coal slurry into two different sizes categories:

1. Gob: particles greater than 1/16", mostly rock and waste coal.
2. Fines: particles less than 1/16" diameter, material in slurry solution.

Other researchers place the cutoff between coarse and fine material at 28 mesh (0.02 in.; USEPA, 1980) and 1 mm (NSF, 1975). Particle size of the coal refuse is important because it affects how quickly the refuse settles out of solution. This in turn affects waste-handling procedures at coal preparation plants. Eggert et al. (1980) determined that large pieces of slurry would settle out first because of a reduction in fluid velocity as the slurry was discharged from a pipe. Remaining coarse tailings were deposited as the slurry flowed across the surface of the storage area. The fluid velocity dropped again when the slurry reached the standing water of the impoundment. At this point, only clay-sized particles still remained in suspension. Eggert et al. (1980) also estimated that roughly half of the particles were in the size range 0.0965-0.1067 mm. Particles this small create material handling problems due to the large amount of moisture they absorb. Faster weathering and mobilization of pollutants would also occur due to the small particle size.

## **Exposure Pathways in the Environment**

### **Southern West Virginia Streams**

#### ***Background Chemistry of Mined Watersheds***

The WVDEP performed some in-stream sampling as part of the SCR-15 Phase I report. For this report, data from the in-stream samples were categorized by whether or not the watersheds had a history of mining. In all, two in-stream samples from mined watersheds (Southern Minerals and Panther) were collected from three different

sampling locations (WVDEP, 2009). Neither of the two locations were affected by slurry injection activities, as they were either up-gradient of slurry injection or sampled from a different part of the watershed. For the “background chemistry of mined watersheds” section of this report, “background water chemistry” data are defined as those data which are affected by mining activities, but not by slurry injection. These data are important because they enabled the research team to observe the water quality conditions previous to slurry injection.

### Southern Minerals

There was one background chemistry sample site (SM-4) in the Southern Minerals sampling area. SM-4 was chosen as representative of the background water chemistry because no slurry injection occurred upgradient of this sample point. This site was located on Elkhorn Creek. The dominant ions that influenced this water were calcium-sodium-bicarbonate. Bicarbonate concentrations at SM-4 contributed to high alkalinity (204 mg/L) and a pH value of 8.0. The geology surrounding SM-4 is largely shale. Sampling showed no contamination by organic compounds, with the exception of a trace amount of Total Petroleum Hydrocarbons. Regarding dissolved metal concentrations for SM-4, most analytes were below quantification limits, but above detection limits. As such, the reported result is an estimate. With the exception of calcium, magnesium, potassium, silicon, sodium, and strontium, concentrations of all ions were less than 0.3 mg/L. General chemistry at SM-4 was typical of mine-impacted water in this region, with sulfate concentrations of 99 mg/L, chloride concentrations of 4.96 mg/L, and Total Dissolved Solids (TDS) of 331 mg/L. No other background

chemistry data was available within the delineated Southern Minerals area (WVDEP, 2009).

### Panther

One background chemistry sample site was taken in the Panther sampling area (PL-4) as part of the sampling for SCR-15. PL-4 was located upstream of the Wet Branch Refuse area, which also placed it upstream of any slurry injection. Water at PL-4 was found to be a weak magnesium-sulfate (magnesium-sulfate) water type. No Volatile Organic Compounds (VOCs) or Semi-Volatile Organic Compounds (SVOCs) were detected at PL-4. Dissolved metal concentrations were either undetectable or below 0.1 mg/L, with the exception of calcium, magnesium, potassium, silicon, and sodium. A pH of 6.78 at PL-4 was the lowest of all sample sites in the Panther sampling area. However, the conductivity and TDS were the lowest values among all Panther sampling area sites (WVDEP, 2009).

Some historic data were available for the Wet Branch Watershed (Table 17) Sites 001 and 002 are associated with previously permitted mines and were sampled as part of the permitting process. Site 001 is located in the headwaters of Wet Branch, while Site 002 is at the mouth of Wet Branch. USWB (Up Stream Wet Branch) and DSWB (Down Stream Wet Branch) were also sampled during the permitting process for a previous coal mine in this area. Although the locations of the upstream in-stream site USWB and the downstream site DSWB do not coincide with Sites 001 and 002, they are similar because they detail the historical water quality of Wet Branch before slurry injection. Although the data does not show any specific trend, it illustrates water quality

changes between 1981 and 2007 (WVDEP, 2009). Since slurry injection did not occur in this area until 1996, Site 001, Site 002, USWB, and DSWB provide water quality data within the Wet Branch watershed that are unaffected by slurry injection.

### Power Mountain

Two in-stream samples were taken at Power Mountain. However, both of these are downstream of slurry injection activities. Because of this, no samples from the SCR-15 report adequately represent “background” water chemistry at this site. However, historic data within the Twentymile Creek watershed was taken before slurry injection occurred. Two in-stream samples (Sites #9 and #10) were taken downstream and upstream, respectively, of the confluence of Sugarcamp Branch and Twentymile Creek in 1983 while mining was occurring. One other sample (Up Stream Twentymile Creek, or USTC) was taken upstream of the Hutchinson Branch No. 1 mine, which drains into Spruce Run. Although the sample point USTC was sampled after slurry injection began, it was taken upstream of any injection activities. The historic data taken in the Twentymile Creek watershed is described in Table 18.

### Loadout LLC

Although there was no sampling performed as part of SCR-15 in the Loadout project area that could represent baseline data, historic data were collected in this area for proposed mining permits and permit amendments. No organic chemistry data was collected at any point prior to the SCR-15 study in the Fork Creek watershed. Aqueous chemical sampling was conducted prior to the O-513-99 permit amendment. All analytes were below detection limits, except selenium which was detected at a



concentration of 3.0 µg/L in a sample collected below a coal preparation plant. Other baseline data were collected for mining permits. Mining in the Fork Creek watershed did not begin until 1996, so both pre-mining and post-mining data were available. A general trend of increasing levels of TDS, conductivity, alkalinity, and sulfate was found in this data, particularly below mining activities. This trend appeared to occur as mining progressed over time in the watershed.

### ***Other Baseline Data***

Another source of baseline stream chemistry data for the southern part of West Virginia outside of the SCR-15 Phase I report is a report contracted by the WVDEP to Ackenheil Engineers Geologists (AEG). This report was written to determine the feasibility of a water line extension along Prenter Road in Boone County, West Virginia. AEG performed a Phase I preliminary investigation to determine if, and to what extent, mining operations had affected groundwater in the area. The AEG Phase I report determined that mining was associated with significant groundwater impacts. In January of 2008, AEG conducted a Phase II Grant Supporting investigation to provide supporting information to the WVDEP regarding the quality of the local groundwater. Water chemistry samples from wells, streams, and mine openings were obtained to support the generation of the report. Twenty-eight sites were sampled, with six of these being in-stream, baseline samples (ST-1 through ST-6; AEG, 2008).

Five of the six stream samples were determined to be affected by mining activities. Four (ST-1 through ST-4) were all magnesium-calcium-sulfate water types, one (ST-5) was sodium-magnesium-sulfate-chlorine-bicarbonate, and one (ST-6) was

magnesium-calcium-sulfate- bicarbonate. Organic chemistry parameters were not sampled as part of this report. All of the samples were alkaline with the exception of ST-6. At this site, a pH of 4.9 and an acidity concentration of 139 mg/L were found. The acidic conditions found at site ST-6 were likely due to differences in the local geology. With the exception of site ST-3, iron, aluminum, and manganese concentrations were low. Conductivity and sulfates were higher at sites ST-3 and ST-5. This is likely because these two sites were closest to active mining, which has a larger effect on water chemistry than pre-existing mining (AEG, 2008).

### ***Background Chemistry of Unmined Watersheds***

In addition to samples collected in mined watershed as part of the SCR-15 Phase I report, one of the samples collected at Loadout is representative of an unmined watershed (site LL-4). No surface mining was conducted in the headwaters of Wilderness Fork until after 1996. Site LL-4 is situated in a tributary of Wilderness Fork that has remained unmined since 1996 (WVDEP, 2009). Site LL-4 was located upstream of the dewatering borehole for the Nellis mine. While the Nellis mine does inject slurry, the injection point is downgradient of site LL-4. Thus, this sample may be used as representative of an unmined watershed and serve as a background sampling point.

Site LL-4 was deemed to be a calcium-magnesium-sodium-sulfate-bicarbonate water type. No organic compounds were detected at this site. Dissolved metal concentrations were either undetectable or below 0.3 mg/L, with the exception of calcium, magnesium, potassium, silicon, sodium, and strontium. General chemistry

taken at site LL-4 was indicative of a site that had not been mined. Sulfate (16 mg/L) and TDS (180 mg/L) were both fairly low. Sulfate concentrations below 30 mg/L and TDS concentrations below 120 mg/L are common for unmined watersheds in this region (WVDEP, 2009).

### ***Other Related Studies***

A study was initiated by the West Virginia Department of Natural Resources to evaluate the effects of coal slurry injection into underground coal mines in southern West Virginia (Smith and Rauch, 1987). The authors concluded that “the injection of slurry into alkaline mine pools seems to generally improve the water quality within the mine pool by decreasing iron, manganese and total suspended solids and increasing pH and alkalinity. Sulfate, however, increased in concentration from the injected slurry effect.”

During the period 2004-2005 a study was conducted near Williamson, Mingo County, West Virginia by Wheeling Jesuit University (WJU). Data from the 2004 sampling was included in a draft report (WJU, 2004). The 2005 data were not published but were evaluated in this study. Collectively, the 2004 and 2005 data prepared by WJU will be referred to as the WJU study. The WJU data are presented in Table 19 and summarized in Table 20. Samples were taken from various sources, including pressure tanks, hot water tanks, and domestic wells. The WJU data make it clear that many of the sampled water sources were affected by sewage. Reduction/oxidation potential was measured at 67 sources and 60% of those were reducing. The average reduction/oxidation potential was -130 mV for those samples in the reducing category.

Such strongly reducing conditions require an effective electron donor. Although coal may be degraded both aerobically and anaerobically, labile organic matter as found in sewage is the likely source. Coal, on the other hand, is highly recalcitrant (otherwise it would not have survived for 220 million years) and is not an effective reducing agent. The WJU study revealed that 90% of the water sources were contaminated with coliforms and 40% of all samples were contaminated with fecal coliforms. In addition, the samples were contaminated to varying degrees with metal and other ions that exceeded USEPA DWS. Among the primary drinking water standard exceedences, lead was the most common at 15% followed by barium and arsenic at 4% and selenium and cadmium at 2% and 1%, respectively. Not all of the samples in the WJU study were water that came from the tap. A number of samples were supernatant liquids from sludges that accumulated at the bottom of hot water tanks. While those samples accounted for many of the higher secondary contaminant concentrations, they accounted for none of the primary contaminant exceedences and only about 10% of the aluminum, iron and manganese exceedences.

The WJU study identified no cases where the following contaminants exceeded either primary or secondary DWS: chromium, beryllium, thallium, copper, antimony, silver and mercury. Table 21 summarizes the slurry liquid concentrations of contaminants that were detected in the WJU study and the average values of those exceedences. Both dissolved and total slurry liquid analyses are presented. With few exceptions, the average concentrations reported in the WJU study were substantially higher than those found in the undiluted slurry liquids. All samples from this study were analyzed by an EPA certified laboratory.

The results of the WJU study and the slurry concentrations identified in SCR-15 pointed to a set of contaminants of concern: arsenic, lead, selenium, aluminum, iron and manganese.

Another study was conducted to evaluate drinking water issues related to mining and processing in the same area of Mingo County, West Virginia (ATSDR, 2005). It concluded that, while domestic wells in the study area were polluted with coliforms and metals common in mining (iron, manganese, aluminum), there was no evidence pointing to coal slurry per se as a health risk.

### ***Southern West Virginia Groundwater***

Groundwater flow in this region of West Virginia is mainly controlled by three factors: the distribution and type of recharge that infiltrates into the groundwater basin, topography of the recharge area, and the hydraulic conductivity of the material through which the groundwater flows (WVDEP, 2009). These factors may in turn be affected by a host of other elements, including soils, climate, lithology, and geologic structure, among others. Both surface and underground mining can drastically alter these factors in a variety of ways. For example, groundwater recharge rates can be altered depending on the degree of compaction of the surface material, as well as how the site is revegetated. Post-mining topography will impact groundwater recharge as well. Surface topography can be altered from its original contours depending on the final reclamation plan. Hydraulic conductivity of a surface mining site can be greatly affected by the overburden, which must be removed and replaced as mining progresses. Mine spoil may be more conductive than parent material by several orders of magnitude due

to larger void spaces between pieces of mine spoil (Hawkins, 1995). In underground mining, hydraulic conductivity also can be significantly altered by collapsed and fractured roof rock (Kendorski, 1993).

The direction of groundwater flow is determined by differences in hydraulic head. Groundwater flows from areas with higher hydraulic head to areas with lower hydraulic head as the water system attempts to reach equilibrium. In an unconfined aquifer, water table elevation can be used to determine the distribution of hydraulic head and indicate the direction of groundwater flow. The local topography, coupled with spring (discharge area) and possibly well (water level) mapping, are used to estimate the direction of groundwater flow. In an open, flooded mine pool, the groundwater flow system is often radically different than the aforementioned undisturbed strata. The mine water will flow relatively unimpeded down -dip along the floor of the mine until a barrier is encountered. These barriers are usually in the form of a coal barrier or a previously flooded section of the mine. Once flooded, the mine water flow system is then dominated by the significantly lower hydraulic conductivities of the coal and overlying geologic units (WVDEP, 2009).

Aquifers may be categorized by their hydraulic conductivity (permeability). The two types of permeability are primary and secondary. Primary permeability refers to the intergranular spaces of the transmitting medium. It may be more significant in unconsolidated sediment types, but is less important in the consolidated bedrock of the Appalachian Plateau. Secondary permeability is the permeability in a rock strata developed after its deposition, typically from the weathering and fracturing of the rock strata (Williamson and Carter, 2001). Abandoned underground coal mine voids may

serve as large secondary permeability pathways. Flow in an underground mine is different from typical intergranular and fracture flow. Due to the scale of the operations, underground mines may impact the hydrology of a given area to a greater extent than a surface mine. Interbasin transfer of groundwater is a common event associated with underground mines. The voids created during mining act as a large sink which draws in groundwater. At the conclusion of mining, the mine void becomes a highly permeable aquifer which can alter the local flow regime both physically and chemically. Due to the interconnected nature of many mine-void aquifers, there is a high possibility of postmining transfer of the resulting mine-pool water throughout the interconnected mine workings (WVDEP, 2009).

### ***Acidic Mine Pool Water Background Chemistry***

The geology in this region is from the Pennsylvanian Age. The majority of the rock is sandstone, with layers of coal, limestone, and shale interspersed among the sandstone. Groundwater in Southern West Virginia is often found in sandstones and carbonates, which impart to groundwater a higher pH and lower metal concentrations (National Research Council Committee on Groundwater Resources in Relation to Coal Mining, 1981). Because of the large amount of alkaline material found in the geology, acidic groundwater is often more difficult to find in southern West Virginia than in the northern part of the State, where the geology is much more likely to be acidic. This applies to mine drainage in southern West Virginia as well. As coal and its associated minerals are exposed to the atmosphere during the mining process, the carbonate minerals located in the nearby geology cause alkaline mine drainage.

Although none of the sample sites in the SCR-15 study were taken from acidic mine pools, other data that are from acidic environments are available for this region of West Virginia. AEG (2008) sampled 18 residential wells and 4 mine drainage sites to determine the viability of a water line extension in eastern Boone County, West Virginia within the Laurel Creek watershed. Of the sampled sites, two acidic mine drainage sites and 4 residential wells were located. Table 22 gives the data for these sample points. The two sites labeled MD-3 and MD-4 are mine drainage sites sampled at a mine portal, while WL-12, 13, 14, and 15 are samples drawn from residential wells.

All six sample sites had a pH below 5.0. Metal concentrations were mostly low, with the exception of aluminum concentrations in MD-3 and MD-4. Sulfates were also fairly low, with the exception of MD-4 and WL-12.

Stiff diagrams were also constructed for each sample site. A Stiff diagram is a graphical comparison of the relative concentrations of specific anions and cations of several different samples (WVDEP, 2009). The direction and length of each corner of the diagram illustrates sample chemistry. Stiff diagrams can help the researcher identify samples that have similar or dissimilar compositions.

The shape of the plots for both MD-3 and MD-4 were similar. However, MD-3 had much smaller peaks, meaning that this site was not dominated as heavily by any specific ion group. MD-3 plotted as a sodium-calcium-magnesium-sulfate-chlorine water type and MD-4 was a calcium-magnesium-sulfate water type. WL-12 and WL-15 also had similar Stiff diagrams, with both waters described as magnesium-bicarbonate-sulfate. The dominating ions in WL-13 and WL-14 were quite different from the other



sample sites. WL-13 was a magnesium-calcium-bicarbonate-sulfate water type and WL-14 was a sodium-calcium-chlorine-bicarbonate (AEG, 2008).

### ***Alkaline Mine Pool Water Background Chemistry***

All groundwater samples taken as part of SCR-15 were from alkaline sources. There were 18 groundwater samples taken as part of this study. Three sites were sampled in the Southern Minerals sampling area, six in the Loadout area, three in the Panther area, and six in the Power Mountain area (WVDEP, 2009).

### **Southern Minerals**

The locations of the samples taken at the Southern Minerals study area are shown in Figure 1. The three groundwater samples taken in this study area were sites SM-5a/b (also named GW-1), SM-6, and SM-7. The major ions indicate the water type for sample site GW-1 (SM-5a and SM-5b) to be sodium bicarbonate (Figure 2). GW-1 was previously used as a groundwater monitoring well, but for the past several years had also been used as a slurry injection site. The well is an open borehole that is cased to a depth of about twenty feet. Two zones for the well were sampled. SM-5a, which was identified as the deep zone of the well, consisted of the settled solids. SM-5b was identified as the shallow zone and represented the supernatant, or liquid portion found above the slurry sediment (WVDEP, 2009).

GW-1 is likely part of an intermediate zone in which chloride has been removed by flushing with infiltrated surface waters. However, significant concentrations of sodium remain that are likely adsorbed to clays and similar materials in the sediment.

This chemistry would lead to the Sodium Bicarbonate water that was found at this site. The elevated sodium is a result of cation exchange, with sodium released from the exchange sites and replaced by calcium and magnesium (WVDEP, 2009).

Only two individual semi-volatile organic compounds and no individual volatile organic compounds were detected in these two samples. Both samples also had detectable concentrations of Total Petroleum Hydrocarbons (TPH's), which are made up of both volatile and semi-volatile compounds. The Phase I report did not distinguish between volatile and semi-volatile compounds when reporting TPH. As such, only total TPH results are given. Tables 23 and 24 describe selected organic and inorganic water chemistry results, respectively. Sites SM-6 and SM-7 are artesian discharges. SM-6 surfaces along U.S. Route 52 and SM-7 is a downdip discharge from the adjacent abandoned Pocahontas Capels Mine. The major ions indicate the water type for both sample sites SM-6 and SM-7 as sodium-bicarbonate (Figures 3 and 4). These two sites represent the hydrologically interconnected discharges from the flooded Pocahontas No.3 and No.4 seam mine voids. Water chemistry for these sites indicates that deep groundwater is mixing with fresh water from the surface within the deeper circulation of the mine pool, which is characterized by the Sodium Bicarbonate water type (WVDEP, 2009).

Chemistry results from the lab detected no semi-volatile or volatile organic compounds for either site. Elevated dissolved iron and alkalinity concentrations were found at SM-6 as well as fairly high sulfate concentrations at both sites. Table 25 details selected general and inorganic chemistry results for SM-6 and SM-7. No other baseline chemistry data was available for this sampling area (WVDEP, 2009).

## Loadout

The six groundwater samples taken in the Loadout sampling area were sites LL-1, LL-7, LL-8a, LL-8b, LL-12, LL-13, and LL-14. Samples LL-1, LL-7, LL-8a, LL-8b, and LL-12 all represent groundwater associated with mine pools in the Eagle coal seam. Sample LL-13 is from a deep mine, located in the #2 Gas seam which lies above the Eagle Coal seam. Sample LL-14 was taken from the Nellis mine. Table 26 and Figure 5 give locations and descriptions of the water sampling sites in the Loadout sampling area.

Direction of groundwater movement in the Fork Creek watershed is controlled by fractures near the surface at shallow depths (<200 feet), as well as the dip of the mine voids (Wyrick and Brochers, 1981). The most extensive and deepest of these existing mines is the Eagle Seam mine works. These mine works are shown in Figure 5 as the yellow outlines. The Eagle Seam mine works underlie much of Fork Creek watershed, causing them to have a large impact on groundwater movement in this watershed. Within these open mine voids, groundwater will flow in a down dip direction.

None of the Loadout groundwater sampling points detected any organic constituents, with the exception of 1,2,4-Trimethylbenzene at point LL-7. This compound was detected at a low concentration of a 0.6 µg/L. A possible source of this chemical is as a fuel material that was used during the mining process.

Inorganic and general chemistry showed generally higher concentrations in groundwater than in surface water. This is likely due to the passage of the groundwater through the mineralized environment of the various Eagle Seam deep mines in the Loadout sampling area. High levels of sodium, potassium, carbonate and sulfates were

found in the groundwater samples (Tables 27 and 28). Strontium was also found in elevated concentrations in several groundwater samples that were associated with abandoned deep mine works in the Eagle Seam. These Eagle Seam mine works also had elevated iron and manganese concentrations. Aluminum concentrations were also elevated in many samples, most notably at sites LL-1 and LL-12 (Table 27). Sample LL-12 appears to illustrate alkaline mine drainage contamination. It is visibly stained with iron and has elevated levels of iron, manganese, beryllium, aluminum, nickel and sulfate. Sample LL-12 also shows an elevated lead concentration of 0.0106 mg/L (Table 27; WVDEP, 2009).

Baseline sampling data was also taken by the Fork Creek mining company as part of its mining permit. Four samples (BGW-22 through BGW-25) were taken during 1997-1998. All four sites were taken from abandoned mine pools (Table 29). No testing was performed for either organic compounds or heavy metals at any of these sites. Similar to current water chemistry, this data from the four abandoned mine pool sites showed elevated concentrations of total dissolved solids, sulfates, iron, and aluminum (Tables 30-33).

### Panther

Locations of the sampling points are shown in Figure 6. Three groundwater points were sampled in the Panther sampling area. These sites were named PL-5, PL-2, and PL-6. Sample site PL-5 was considered both a ground and surface water site. PL-5 represents surface water which began as a seep on top of a refuse pile. The seep then drained through the pile (where it became groundwater) and discharged from the

toe of the refuse. It is likely that the water from the seep mixed with other groundwater sources within the pile. PL-5 was characterized as a sodium-sulfate water type (Figures 7 and 8; WVDEP, 2009).

No Volatile Organic Compounds (VOCs) or Semi-Volatile Organic Compounds (SVOCs) were found at PL-5. Selected inorganic and general chemistry is summarized in Table 34. PL-5 shows the highest concentrations of all three sites regarding sodium, chloride, sulfate, and conductivity. This is likely due to the mineralization of the water after it has infiltrated through the refuse pile (WVDEP, 2009).

PL-2 is a mine dewatering borehole for mine UO-391. The water type for this sample was determined to be Sodium Bicarbonate, with weak influences by chloride and sulfate (Figures 7 and 9). No VOCs or SVOCs were found at PL-2 with the exception of TPH compounds. The concentrations of the TPH chemicals were as follows: Diesel Range (0.92 mg/L), Oil Range (4.16 mg/L), and Oil and Grease (2.20 mg/L). PL-2 had the highest concentration of bicarbonate among the three groundwater sites (Table 34; WVDEP, 2009).

PL-6 is the residential well of Owen Stout. The water type for this sample was determined to be Calcium-Bicarbonate (Figures 7 and 10). No VOCs or SVOCs were found at PL-6. PL-6 had the highest concentrations of manganese, iron, silicon, and acidity among the three groundwater sites (Table 34; WVDEP, 2009).

One historic groundwater sample site was available for comparison to the current Panther groundwater data. The Mollie Bailey well was sampled as part of mining permit #O-112-83 (WVDEP, 2009). This well was located within the current Wet Branch Refuse Area. Table 35 shows that the water chemistry of the Mollie Bailey well is

significantly different from the three current Panther sample sites taken at sample points PL-2, PL-5, and PL-6. Historical permit data from the Mollie Bailey monitoring well was available, but current data from this well were not available, because the well has been buried (WVDEP, 2009).

### Power Mountain

Groundwater was sampled at eight different points in the Power Mountain sampling area. However, PM-1 and PM-2 were excluded as baseline water quality points because they are below coal slurry injection sites. The remaining six baseline sites were named PM-6, PM-9, PM-10, PM-11, PM-13, and PM-14. Table 36 gives descriptions of the sample points and Figure 11 shows their locations (WVDEP, 2009).

PM-6 was a sample taken from a monitoring well in the Flying Eagle mine pool. This sample has a water type of Sodium-Sulfate (Figure 12). The only organic compounds detected at PM-6 were microgram concentrations of benzene (0.3 ug/L) and toluene (0.3 ug/L). The source of these compounds may be from leachate of the coal seam within the mine or remnants of equipment left in the mine. High concentrations of sulfate, sodium, and strontium, as well as high conductivity and TDS, are indicative of mining-influenced water. Table 37 gives more water chemistry results for PM-6 (WVDEP, 2009).

PM-9 was taken from the Naylor's well. This sample is a magnesium-sulfate water type (Figure 13). No organic compounds were detected at PM-9. Metal concentrations in this sample are also low (Table 38). However, sulfate is elevated

compared to historic groundwater data seen in Table 39. It is likely that the observed elevated sulfate concentrations are due to mining impacts (WVDEP, 2009).

PM-10 was taken from the Corbetts' well. This sample is a sodium-bicarbonate water type, which suggests that this water source is not impacted by mining (Figure 14). No organic compounds were detected at PM-10. Although still fairly low, iron, aluminum, and manganese are highest at this site when compared to the other two residential wells (Table 38). Iron and aluminum concentrations are above the Federal secondary drinking water standards at PM-10. However, sulfates were not detected in this sample (WVDEP, 2009).

PM-11 was taken from the Mullins' well. Although PM-9 and PM-11 are near one another, their water quality is vastly different. This sample is a sodium-bicarbonate water type, which suggests that this water source is not impacted by mining (Figure 15). No organic compounds were detected at PM-11. PM-11 had much lower overall metal concentrations than PM-9. PM-11 did have a high sodium concentration (Table 38). Sulfates were also very low (WVDEP, 2009).

PM-13 was taken from a seep downslope of the Rhonda Eagle mine. This sample is a calcium-sulfate water type (Figure 16). No organic compounds were detected at PM-13. This site is characterized as having elevated metal concentrations, sulfate, and TDS (Table 37), which are consistent with results of groundwater from mining impacted areas in southern West Virginia. This water chemistry may also be influenced by slurry injection that has taken place within the mine (WVDEP, 2009).

Historical mine pool data is also available for other mines near the Rhonda Eagle mine. TDS and sulfate concentrations are lower in these historic data before slurry

injection (Table 40). A review of some historical data on mine pool water quality for selected mines prior to slurry injection. The table also shows water data for the mine pool at the Jerry Fork Mine, an adjacent mine on the Eagle coal seam where slurry injection did not occur. Water quality of the Jerry Fork Mine shows lower sulfate and TDS concentrations than those samples from the other mines (Table 40). The sample from the Jerry Fork mine is therefore more representative of baseline groundwater quality in this region (WVDEP, 2009).

PM-14 was sampled from the entry of the Radar Eagle mine. This sample is a weak calcium-sulfate water type (Figure 17). No organic compounds were detected at PM-14. This site is characterized as having low metal concentrations (Table 37). TDS and sulfates are also low. This water quality is indicative of an unmined watershed. This may be because of shallow ground cover, which gives the groundwater a short flow path. The infiltrating groundwater may be short circuiting the mine (WVDEP, 2009).

#### **Additional sources of information**

Another source of baseline groundwater data is the Prenter Waterline Feasibility Study (AEG, 2008). This site was not included in the SCR-15 Phase I report and is located in a different area of the state. Groundwater sampling consisted of 18 residential wells (WL-1 through WL-18) and 4 mine pool samples (MD-1 through MD-4). Water chemistry results for all sample points are shown in Table 41 and Piper Diagrams showing water types for each sample are described in Figures 18 and 19.

Piper diagrams detail clusters of data points which indicate if a specific water sample has a similar composition to another sample. Piper diagrams are created by plotting the major cations and anions as percentages of milliequivalents in two base



triangles. The data in these triangles is projected to a diamond graph which may reveal useful trends and relationships for large sample groups (WVDEP, 2009).

Although all samples were taken in a mined watershed, none of the WL samples showed impacts from mining as evidenced by where they plotted on the Piper Diagram (Figures 18 and 19). This may be due to the wells accessing water that is in a shallow bedrock aquifer and thus do not have a high level of communication with area streams. All wells sampled were also fairly distant from mining. Mining took place at least 1,000 feet upslope from the wells, which gave the groundwater an opportunity to flow through the geologic strata before it was pumped out of the well. The geology in this area is not conducive to poor groundwater quality.

## **Mass Balance Model**

### ***Underground Mine Pools***

There are no studies that systematically and temporally evaluate the effect of slurry injection on mine water chemistry in southern West Virginia. That is, there are no studies that characterize a mine pool prior to, during and after slurry injection while documenting the quality and quantity of injected slurry. However, SCR-15 sampled mine pools up and downgradient of slurry injection. Another study by WJU sampled 97 domestic water sources (mainly private wells) in Mingo County, West Virginia in 2004 and 2005. The intention was to determine whether well chemistry pointed toward coal slurry as a source of contamination. While not conclusive with respect to the source of contamination, the WJU study was useful in that it identified a suite of inorganic contaminants that occurred at levels in excess of USEPA DWS in domestic wells near

mining and slurry activities. Those exceeding the primary DWS included: arsenic, barium, cadmium, lead and selenium. Secondary drinking water exceedences included: coliforms, TDS, pH, aluminum, iron, manganese and zinc. These will be taken as the initial contaminants of concern.

Analyses of coal slurry liquids presented in the SCR-15 report indicated that the Southern Minerals, Panther and Coresco slurry liquids exceeded the primary DWS for antimony while the Panther slurry liquid also exceeded the primary DWS for arsenic. Among the secondary drinking water standards, only aluminum, iron and manganese were exceeded. While total analyses were invariably higher than dissolved concentrations, there were few differences between the two with respect to whether the drinking water limit was exceeded (Table 13).

A subset of contaminants identified in the WJU study was subjected to a mass balance analysis to estimate whether enough was injected with slurry to cause the receiving mine pool to exceed drinking water standards. The concentrations of all of these contaminants in coal slurry were evaluated and those that did not originate in coal slurry or did not occur in the slurry samples at concentrations above DWS were eliminated. In fact, most did not exceed DWS but the following were subject to the mass balance analysis: arsenic, lead, selenium, aluminum, iron, manganese, sulfate and TDS. The WJU study did not include sulfate but it was included in the mass balance analysis since it results from pyrite oxidation and is a common indicator of mine drainage.

Among the organic contaminants that were evaluated in SCR-15 Phase 1 only diesel appeared to be directly traceable to coal slurry and present in a large number of samples. It was, therefore, chosen as the organic marker across the four study mines.

Concentrations of dissolved contaminants in the slurry were used in the mass balance analysis since it was hypothesized that the dissolved fraction best estimates the mobile fraction of the slurry. Chemical analysis of the solid fraction of the coal slurry does not indicate which ions will become mobile or what concentrations they would achieve. It was anticipated that comparison of slurry affected mine pool chemistry to results of the mass balance analysis would provide a test of this hypothesis.

The mass balance analysis was developed to estimate the maximum contaminant concentrations that could develop as a result of slurry injection. The analysis was conducted on the four mines studied in detail in the SCR-15 Phase I report: Southern Minerals, Loadout LLC, Panther, LLC and Power Mountain. The mass balance analysis used site-specific data such as slurry contaminant concentration, injection rate, period of injection and mine area (Table 42). The analysis calculated the volume of water injected as slurry and the mass of the dissolved constituents (the mobile fraction). In an underground mine, the mass of contaminant injected with slurry will be diluted by the volume of groundwater infiltrating into the mine. The volume of infiltrating groundwater was estimated on the basis of the mine's surface area and an assumed infiltration rate of 0.25 gpm/acre/year. That value is at the low end of the generally assumed infiltration range of 0.2 to 1.0 gpm/acre/year. Thus, a conservative dilution factor was used. All of these mines were small, ranging from 2.0 to 5.12 square miles. Infiltration rates indicated that even if 100% of the mine voids were available to

fill with water, then the pools would be replaced in between a shortest time span of 1.3 years for Panther and a longest time span of 3.1 years for Southern Minerals. Planned injection periods would exceed all of those numbers. Since the flooded volumes of the mines were not known and the pool replacement times were short, dilution of the existing mine pool was not considered. There were no data to indicate the degree of mine void flooding or concentrations of contaminants in either the mine pools or the infiltrating water, so the analysis assumed that slurry was the only source of contaminant. Thus, estimated parameter reflected the net effect of slurry addition on mine pool water quality. We do not know the degree of flooding in the mines or the extent to which there is open access of atmospheric gas exchange. Thus, it must be assumed that pyrite oxidation continues and, even though there may be sufficient alkalinity to maintain an alkaline pH, secondary contaminants, sulfate, iron, manganese and aluminum will continue to be produced.

If contaminant ions do not come out of solution in the mine pool by mechanisms such as precipitation or sorption, then their equilibrium concentrations would be dominated by dilution with groundwater infiltrating into the mine. Since the mass balance model only accounts for dilution, the difference between the model estimate and the observed values should reflect the extent to which either additional ions are liberated from solids in the mine (net gain) or the extent to which ions are removed from solution by the above mechanisms (net loss). If ions are conservative and slurry is the only source, then during the slurry injection period contaminant concentrations will increase to a level where the mine pool chemistry is dominated by dissolved ions in the slurry. After slurry injection ceases, those levels will decline as infiltration water flushes

contaminants out of the mine voids. Since injection into all of these mines is expected to extend for at least 10 years, no decay curve was included in the mass balance model. It was also assumed that all study ions are conservative. That means that there was no attempt to identify how much of the contaminant would sorb to solids or react to form insoluble precipitates. In reality, many of the contaminants would tend to precipitate based on pH and redox conditions. For example, most of the aluminum will precipitate as a hydroxide at pH greater than 4.5 while arsenic and selenium (selenite) would sorb to ferrihydrite, the result of iron precipitation in oxidizing conditions. However, estimation of the extent of sorption and the resulting ion solubilities would require sophisticated geochemical sampling and modeling that would be beyond the scope of this study. Thus, the assumptions favor conditions that would yield maximum contaminant concentrations.

The mass balance analysis assumed that the soluble contaminants in the slurry will be diluted by largely uncontaminated water infiltrating through the roof of the mine. The output of the mass balance analysis was compared to the water quality upgradient and downgradient of slurry injection sites identified in SRC-15 (Table 43). The table indicates contaminant concentrations in groundwater samples that are presumed to be unaffected by (upgradient of) slurry injection and slurry liquids and samples that are presumed to be affected by (or downgradient of) slurry injection. Average values are given for the affected samples and they are compared to the results of the mass balance analysis. The results are discussed below and separately for each of the four study mines.

## **Surface Water**

A mass balance analysis was not undertaken for surface water since no flow data are available. Therefore, discussion of the effects on surface water rely on observed concentrations and comparison with aquatic life standards.

The analyses discussed above are based on SCR-15 data which represents unreplicated samples taken over a several year period. Ideally, multiple samples of surface water, groundwater and slurry would be available so that sampling error and population variance could be calculated. While these limitations should be taken into consideration when assessing the results, they are to some extent, compensated by the fact that four mines were studied, yielding a sort of replication. It should also be remembered that mine flow pathways are not straightforward. Chemical characterization of a mine pool without slurry injection is difficult and can yield very different results in different parts of the mine.

## **Effects of Coal Slurry Injection**

### **Groundwater**

Table 43 summarizes the results of groundwater monitoring upgradient and downgradient of slurry injection. It also includes slurry chemistry and the results of the mass balance analysis. The results are compared to primary and secondary USEPA DWS. The results are discussed below.

### Southern Minerals

The slurry at this site exceeded the secondary DWS for aluminum and iron. However, none of the primary drinking water contaminants: arsenic, lead, selenium

exceeded their DWS in either the upgradient, downgradient or slurry liquid samples. The upgradient sample exceeded the secondary DWS for manganese and TDS. Half of the downgradient samples complied with DWS while one of the other two exceeded secondary DWS for iron, manganese and TDS and a fourth sample exceed secondary DWS for iron and manganese. On average the downgradient wells exceeded secondary DWS for iron, manganese and pH. The mass balance analysis correctly predicted no effect on primary contaminants from slurry injection and identified manganese as a secondary contaminant. The model predicted an iron concentration of 0.2586 mg/L, slightly below the secondary DWS of 0.3 mg/L. The higher levels of iron, aluminum and manganese in the downgradient wells suggest ongoing pyrite oxidation in the mine voids. The rate of pyrite oxidation is likely very slow as the model predicted 45 mg/L of sulfate while 53 mg/L were observed. Diesel was not observed in the upgradient well or the slurry but appeared in two of four downgradient samples averaging 0.215 mg/L.

### Loadout LLC

Like the Southern Minerals site, no exceedences of primary DWS were observed in upgradient, downgradient or slurry samples. Mass balance model predictions were consistent with these observations. Upgradient groundwater samples exceeded most of the secondary drinking water parameters including pH. Downgradient of slurry injection, pH increased which probably accounted for lower concentrations of aluminum and iron. On average, the downgradient samples exceeded secondary DWS for iron and manganese. The model incorrectly predicted an exceedence for aluminum and was

likely wrong because it did not account for the higher pH in the mine pool which would have precipitated aluminum as a hydroxide. The model yielded reasonable predictions of iron concentrations: observed 0.332 versus 0.264 mg/L and manganese: observed 0.096 versus 0.031 mg/L. Diesel was observed in the slurry in a concentration of 16.6 mg/L. However, it was not detected in any of the downgradient samples.

### Panther LLC

While the other three mine sites had multiple groundwater samples, monitoring at this site consisted of one upgradient and one downgradient well. This was the only site where slurry liquids exceeded primary DWS. Arsenic was present in the upgradient well but both arsenic and lead concentrations, were zero in the downgradient sample. The mass balance model predicted concentrations greater than zero, yet below DWS. The lower, observed values may be the result of arsenic sorption to ferrihydrite and precipitation of lead hydroxide at the higher pH in the mine pool. Otherwise, only TDS exceeded the secondary DWS. Iron and manganese concentrations were both higher in the upgradient than in the downgradient well. The mass balance model predicted a TDS of 490 mg/L (the secondary DWS is 500 mg/L) while the observed value was 791 mg/L. While diesel was not detected in the slurry, it was detected in the downgradient well at a concentration of 4.16 mg/L.

### Power Mountain

Neither arsenic, nor lead, nor selenium exceeded their respective primary DWS in the upgradient, downgradient or slurry samples. However, arsenic increased downgradient of slurry injection (to 13% of the primary DWS) yet it was not detected in



the slurry. This was the only case where arsenic was higher in the mine pool water than in the slurry. In fact, other than a slightly higher lead concentration in Southern Mineral's mine pool water than in the slurry liquids (0.0008 mg/L slurry versus 0.0013 mg/L average in the mine pool) this was the only case where mine water concentrations exceeded concentrations found in slurry liquids for arsenic, lead or selenium. This suggests that the liquid fraction is a robust predictor of the mobile fractions of these elements. Levels of both aluminum, iron, manganese, sulfate and TDS all increased downgradient of slurry injection well beyond the concentrations predicted by the mass balance model suggesting ongoing pyrite oxidation in the mine voids. While diesel was observed in the slurry, it was absent in the upgradient and downgradient samples.

### ***Surface Water***

Streams were sampled upgradient and downgradient of slurry injection sites in SCR-15. The results are summarized in Table 44. The same parameters were used in this analysis as in the previous section on groundwater effects. Dissolved ion analyses are used throughout this discussion except for slurry where the data indicate the total analysis of the aqueous fraction. The data are compared to West Virginia water quality criteria for warm water fishery (WWF). Concentrations above WWF are considered exceedences. There are no WWF criteria for sulfate, TDS or diesel.

### **Southern Minerals**

The upstream sample did not exceed any of the WWF criteria. The slurry at this site exceeded the WWF criterion for selenium with a concentration 0.008 mg/L and one downstream sample measured 0.007 mg/L. The WWF criterion for selenium is 0.005

mg/L. The other downstream sample was 0.002 mg/L. No other WWF criteria were exceeded either in the slurry or in the downstream samples.

#### Loadout LLC

One of the upstream samples at this site exceeded the WWF criterion for selenium and the slurry liquids exceeded the WWF criteria for selenium and aluminum. However, none of the downstream samples exceeded the WWF criteria.

#### Panther LLC

There were no upstream exceedences of WWF criteria at this site. Slurry exceeded WWF criteria for lead and selenium. The downstream sample did not exceed any of the WWF criteria. The only exceedence occurred downstream of a surface slurry impoundment where the selenium concentration was measured at 0.007 mg/L. Otherwise all WWF criteria were met at this site. Diesel was not detected in either the stream samples or the slurry.

#### Power Mountain

One of the two upstream samples exceeded WWF criteria for selenium and manganese at this site. The slurry exceeded WWF criteria for selenium and there were no downstream exceedences of WWF criteria. Diesel was detected in the slurry but not in the downstream sample.

In summary, the data show no in-stream exceedences of WWF criteria downgradient of slurry injection in a underground mine. The only exceedence of a WWF criterion was in the discharge from a surface refuse impoundment at Panther.

The above discussion is based on stream samples that were analyzed for dissolved ions except for sulfate and TDS which were total analyses. Slurry ion concentrations were all based on total analyses (Table 44). Table 45 was prepared to evaluate whether using total ion analyses would change the conclusions. While concentrations of several ions were higher than in the dissolved fraction, they did not result in any additional exceedences of WWF criteria.

## **Comparison of Contaminant Concentrations with Water Quality Standards**

### ***Primary Drinking Water Standards (DWS)***

Only the Panther slurry liquids exceeded primary DWS. Specifically, arsenic in the Panther liquid fraction was 0.0113 mg/L while the primary DWS is 0.010 mg/L. Lead was 0.0775 mg/L while the primary DWS is 0.015 mg/L. The mass balance model estimated low levels of arsenic and lead below the drinking water limit. However, the water sample from the well downgradient from the Panther slurry injection site was below the detection limit with respect to both arsenic and lead. This may be explained by sorption and precipitation of lead and arsenic within the mine, reducing concentrations below estimates based solely on dilution with infiltrating groundwater.

The mass balance model predicted that none of the primary DWS for arsenic, lead and selenium would be exceeded in the four mines. Observations confirmed these predictions (Table 43). The mass balance model did not predict any exceedences of the primary DWS for arsenic, lead or selenium. The mass balance model tended to overestimate the concentrations of arsenic, lead and selenium. Seventy five percent of the mass balance predictions exceeded the observations, suggesting either systematic

sampling error or precipitation/sorption of contaminants in the mine. In the absence of evidence to suggest that the pH or redox status of the mines would change dramatically, it is expected that this sequestration would be permanent. Only three upgradient groundwater samples were at a pH 6 or below: PM 9, LL 12 and LL 13. PM 9 was from an updip mine that had not received slurry injection while LL 12 was a seep on the updip cropline of an injection mine and LL 13 was a domestic well outside the mine boundaries. All other upgradient and downgradient groundwater samples had a pH greater than 6.5. This suggests that the acid/base balance in the mines is alkaline.

### ***Secondary Drinking Water Standards (DWS)***

At least one of the secondary drinking water contaminants exceeded secondary DWS upgradient and downgradient of slurry injection in all of the mines. Manganese exceeded the secondary DWS upgradient of slurry injection in all of the mines while iron, aluminum and TDS exceeded the secondary DWS in half of the mines. Downgradient of slurry injection, TDS, exceeded the secondary DWS in all mines while iron and manganese exceeded the secondary DWS in 75% of the mines. Aluminum exceeded the standard in half of the mines. In nearly all cases the predicted secondary contaminant levels were lower than the observations. Since most of these were products of pyrite oxidation they are likely produced in the unflooded portions of the mines. However, the low concentrations of sulfate indicate that pyrite concentrations are very low.

Diesel was detected in three groundwater samples representing two mines. In both cases, diesel was not detected in the slurry injected into those mines.

## **Summary and Conclusions**

### ***Groundwater***

Two primary sources of data were evaluated in this section: the WJU study and the SCR-15 Phase 1 report. The WJU study was useful in identifying a list of three primary drinking water contaminants for detailed study: arsenic, lead, selenium and six secondary drinking water contaminants: aluminum, iron, manganese, sulfate, TDS, pH. Diesel was also studied though it is not subject to a DWS. The SCR-15 report provided four case studies of slurry injection into mines. In preparing the SCR-15 report the slurry injected into each mine was characterized and surface and groundwater samples were taken upgradient and downgradient of slurry injection. The results did not indicate any exceedences of primary DWS as a result of slurry injection. The elements comprising the secondary DWS are associated with alkaline mine drainage. Thus, while pyrite oxidation was active, acidity was neutralized by alkaline, leaving sulfate, TDS, manganese, iron and aluminum in solution. Secondary DWS were commonly exceeded both upgradient and downgradient of slurry injection. Downgradient concentrations were generally greater than was predicted by the mass balance model suggesting continuing pyrite oxidation although at a slow rate as indicated by the low sulfate concentrations. Downstream of slurry injection, concentrations of secondary contaminants increased at Power Mountain and did so to a lesser extent at Southern Minerals. On the other hand, secondary contaminants decreased at both Loadout and Panther. The data show no general increase in secondary contaminants as a result of slurry injection.

Diesel was detected in three groundwater samples representing two mines. In both cases, diesel was not detected in the slurry injected into those mines. The SCR-15 report indicated that the analytical similarities between the organic compounds associated with coal and the analytical results for diesel make conclusions difficult if not impossible. That, coupled with the inconsistent appearance of diesel in the sampling results make it impossible to draw any conclusions other than the fact that the appearance of diesel downgradient of slurry injection did not coincide with the detection of diesel in the slurry.

### ***Surface Water***

Analysis of the effects of slurry injection on groundwater was based on the four case studies in the SCR-15 report. Consistent with the objective of identifying adverse effects of aquatic life, surface water was assessed in comparison to the WWF standard. It is important to note that the WWF for selenium is 0.005 mg/L versus the 0.050 mg/L primary DWS. Thus selenium appears out of compliance more commonly with regard to stream samples than in groundwater samples. In fact, all four slurry liquids exceeded WWF for selenium. Selenium exceeded the WWF in two of the upstream samples but both were surface mine discharges that were not associated with coal slurry. The only downstream samples that exceeded the WWF for selenium were discharges from surface slurry storage areas. None of the stream samples were out of compliance with regard to selenium or any other WWF contaminant (Table 44). That conclusion was the same whether total or dissolved ion analysis was used (Table 45).

In summary, the results based contaminants identified in the WJU study and the data generated through SCR-15 and summarized in this section are straightforward. The data do not identify a link between slurry injection in any of the four study mines and exceedences of primary DWS for arsenic, lead or selenium in the mine pool water downgradient of slurry injection. Contaminants associated with alkaline mine drainage: aluminum, iron, manganese, sulfate and TDS, however, often exceeded secondary drinking water standards upgradient, in the slurry liquids and downgradient of slurry injection. Their concentrations were generally much higher than could be accounted for through slurry injection alone suggesting ongoing pyrite oxidation in the mines.

These conclusions reflect data collected at four slurry injection sites: Southern Minerals, Loadout, Panther and Power Mountain. The data represent single sampling events. That prevented statistical testing to determine the confidence interval about the data points. However, the consistency of the results among the four mines suggests that the results may be representative of slurry injection in southern West Virginia underground mines.

## **Recommendations**

The type of monitoring network established in SCR-15 is fundamentally sound. Slurry chemistry was characterized and groundwater sampling stations were established upgradient and downgradient of each mine's slurry injection point. Similarly, surface water was sampled upstream and downstream of the slurry injection points. The study mines were mapped, the general direction of groundwater flow was identified and the sampling stations and injection points were identified.

However, there were shortcomings with the monitoring program that should be rectified in any future studies. For example, a slurry monitoring program should include regular and repeated sampling with respect to chemistry, volume and the proportions of liquid to solid fractions. It should involve thorough characterization of the receiving mine: area, interconnections with other mines, flooded area and pre-injection chemistry.

The mass balance approach used in this study correctly predicted exceedences of the primary contaminants: arsenic, lead and selenium. Mass balance modeling was less successful in estimating secondary contaminant exceedences due to the high background concentrations and the likelihood of ongoing generation of aluminum, iron, manganese, sulfate and TDS. However, it indicates the extent to which slurry injection contributes to the concentrations of these parameters. Also, the mass balance approach should be used to estimate the potential for primary contaminant exceedences in advance of slurry injection.



## **How the Known or Suspected Hazards of Injection Compare to Other Means of Dealing with Slurry from Coal Operations**

### **Background of Coal Refuse**

Coal refuse is noncombustible material that is separated from coal during the mining or cleaning process. Refuse includes waste rock, clays, fine dust size particles, and by-products from coal cleaning including slimes (additives used in dewatering) (Arnold et al., 2007). The source of the refuse begins with the material mined from underground coal seams that is both above and below the coal, including the sediments within the coal seam. Surface coal mining produces refuse from the removal of overburden and rock, excavated material from shafts, and from other working space within the mine. Coal waste is commonly categorized into Coarse Refuse and Fine Refuse. Both of these divisions are discussed below.

### ***Coarse Coal Refuse (CCR)***

Beginning at the mining of raw coal, commonly referred to as ROM coal, the coal is divided into separate size fractions for cleaning. The modern course size is graded dimensionally with particle sizes up to 3 inches and has a small percentage of fines (<10%; MSHA, 2007). However, the historical hand-picked coal and slate sizes would fall into dimension ranges larger than those produced by modern automated processes with sizes approaching 6 inches (Arnold et al., 2007). The coarse refuse material is by its nature a reject material. This material is produced after ROM coal is fed to a preparation plant for cleaning and it is the first level of separated, non-combustible, material rejected from the plant cleaning circuit. Coarse refuse is either trucked or belted to an approved refuse site.

### ***Fine Coal Refuse (FCR)***

The fine refuse begins as fragments of ROM coal and coarse refuse produced in the preparation plant by the screening, cyclone separation, wet cleaning processes, and other processes. These material sizes range very fine (<1mm, No. 200 sieve) and to ultra fine size ranging less than 1 mm. The accumulation of fines in slurry waters are of such a small size that further separation is extremely difficult. This fine reject is usually capable of being pumped to a disposal site.

The cleaning process may use chemical additives to assist in coal/waste separation. These additives include magnetite slurry, flocculants as thickeners, and coagulants. The magnetite is washed off of the material in the wet cycle operation and the process water is then recycled in the plant. However, coal refuse may leave the plant with surface moisture contents of 8 to 15 percent (MSHA, 2007). The implications of the fine particle sizes can be most significant when the fine clays bond cations from the additives or from naturally occurring geologic materials to form slimes. The slimes can have physical properties which result in increased water retention that renders dewatering and particle consolidation more difficult and time dependent.

### **Existing Methods for Disposal of Coal Waste**

The disposal of coal waste consists of two basic types: i) Impounding structures, and ii) Non-impounding structures. Impounding structures by their nature impound water, sediment, or slurry to regulated elevations and volumes. Non-impounding structures include piles and fills, and do not impound water or slurry.

The implementation of the impounding refuse storage facilities depends on several factors. The most important factor is the projected production volume of refuse (fine and coarse) from the mine(s). The production capacity will determine the necessary fill volume and determine the size of the facility. Disposal of coal waste is dependent on the final physical condition of the reject material, volume, and amount of water to separate from the fine tailings inconsideration of production. The current and historical methods for the final disposition of coal waste include:

- Impoundments (dams and embankments, incised ponds, diked ponds)
- Coal Refuse fills
- Coal Refuse Piles (Coarse, Combined, Segmented)
- Slurry Cells
- Underground Injection

The above listing specifically does not include physical separation methods such as mechanical filter separation for dewatering slurry or dry cleaning method alternatives. These methods also produce fines which must be disposed of as well. The fine coal refuse may be initially dewatered using technologies including the addition of thickener chemicals which transform the slurry into a thickened paste. Mechanical dewatering equipment includes: belt filters, vacuum, press, plate, and frame filters. (MSHA, 2007)

## **Impounding Facilities**

### ***Coal Waste Impoundments***

Coal waste impoundments are impounding facilities and hold coarse and fine refuse, slurry, and process water. There is a legacy of reclaimed coal refuse piles and

impoundments going back to the 1850's. In West Virginia a WVU study was performed in 2003 (Quaranta et al., 2004) to identify and assess safety aspects of the State's coal waste impoundments. From this initial study approximately twenty percent of the then total permitted impoundments were visited and three distinct categories of impoundments were identified and are presented as follows:

Category I: Impoundments designed, constructed, operated, and reclaimed prior to 1972.

Category II: Impoundments designed, permitted, constructed, and operated prior to 1972 then renovated between 1972 and 1977 for compliance with the Surface Mining Control and Reclamation Act (SMCRA), and which continue to be permitted and remain open, or reclaimed, and

Category III: Impoundments designed, permitted, constructed, and operated / reclaimed post SMCRA.

The Category I sites were the oldest sites and two of these were visited. Each had major remedial repair performed within the past two years. These sites were under the authority of the WVDEP. The Category II sites observed were either significantly renovated during operation by the mine owners for compliance with WVDEP and MSHA regulations; were not permitted for further expansion/use due to non-compliance with underground mining variances; or are permitted but nonactive and continue to impound water. The Category III sites visited were in full operation and these sites also exhibited innovative design approaches for the engineering of drainage and water removal systems. The Category III sites appear to be the soundest impoundments within the state.

The coal impoundment facility is actually a storage and water holding system that is designed to separate coarse and fine coal refuse and retain process wash water for reuse.

Coal waste impoundments which incorporate coarse refuse as the embankment fill material routinely use cross-valley construction in West Virginia. Besides cross-valley impoundments, other configurations can include side-hill impounding embankments, and incised and diked ponds. The cross-valley impounding structures using coarse refuse as the majority of the fill are built as embankment dams with layered fills of coarse refuse. The embankment dam then has fine slurry and water placed behind the structure. This cross-valley configuration is illustrated in Figure 20 (from MSHA, 2007).

The cross-valley impoundments may be constructed using one of three distinct method variations: i) Upstream construction, ii) Centerline construction, and iii) Downstream construction. Each variation has unique attributes that offer the owners options on fill volume placement and relative proportions of coarse and fine refuse, and process water use.

### ***Incised Impoundments***

An incised impoundment is constructed by excavating into the natural ground surface or into an engineered fill surface. This type of impoundment is completely underground. The facility may be used to dispose of fine coal refuse and to consolidate slurry material.

### ***Non-Impounding Facilities***

Non-impounding facilities include configurations of material stored in valley-fills, side hills, ridge-dumped, and heaped.

### ***Coarse Refuse Embankments and Piles***

The coarse refuse embankments are designed for separate disposal of the coarse refuse from the fine refuse. Coarse refuse embankments do not include zones for fine refuse disposal. Coarse refuse embankments are designed to generally be constructed of coarse materials having a range of grain size distribution and when all compacted reach an engineered design strength for structural stability.

### ***Combined Refuse Piles***

Combined refuse piles and embankments are designed for co-disposal of coarse and fine coal refuse. The refuse may be both combined or blended but may also be zoned or segregated within the pile. Combined piles have many challenges with operation due to the higher moisture contents of the fine refuse. In order to properly handle the combined refuse, large areas are required in order to dry the material prior to final placement. The combined refuse drying is also challenged by seasonal precipitation and cold temperatures which reduce the evaporative cycle and prevent material placement.

### ***Slurry Cells***

Slurry cells are classified by MSHA (MSHA, 2007) as small ponds constructed within coarse refuse piles or embankments that may receive fine refuse and slurry. The

disposal of the fine refuse and slurry is done on a small scale and usually multiple cells are operated concurrently. The primary function of a slurry cell is to dewater and consolidate the water saturated fine coal refuse. After the fine refuse is dewatered the cell may be covered with a layer of coarse refuse. Another option is for the slurry to be excavated and blended to a coarse refuse for co-disposal in a larger pile.

### **Underground Injection**

Underground injection is limited to disposal of fine coal refuse into abandoned underground mine workings. The objective of this type of material disposition is to site an injection point where there is unobstructed injection volume and a mine structure that exists where the liquid may be contained. There are two classifications of underground slurry disposal: i) Controlled Flushing and ii) Blind Flushing.

#### ***Controlled Flushing***

Controlled flushing is a method used when mined refuse materials are backfilled into abandoned underground mines. The mines may be either dry or wet and are open to mine personnel for work. This technique involves hydraulically flushing a slurry of crushed coal fines blended with water and pumped from well head locations into a piping distribution network for placement. The method can distribute a slurry having 30 to 50 percent solids mixed with water. Depending on the settling of the fine refuse fraction the process water may be recovered and reused in the process to minimize makeup water use.

The controlled flushing is operated by miners installing a pipe network within the mine workings in order to distribute the slurry injectate. The mine personnel are able to

direct the slurry fill into the desired zones and maintain the pipe network. The technique enables point source deposition and process water recovery is possible. For water recovery the slurry deposition methodology incorporates controlled seepage techniques through leaky bulkheads and sumps. The leaky bulkheads are constructed at existing openings and consist of wooden timbers arranged to form a wall. This timber wall will retain the pressure of the solid slurry materials and will have gaps or spaces where water can seep. The water may then be collected in sumps.

The collected water may then be pumped to the surface to be re-blended with crushed refuse and re-injected. Using this method it is possible to develop horizontal distribution zones of 600 feet measured from the injection source.

### ***Blind Flushing***

Blind flushing is a method of slurry disposition used when access to underground workings is either unsafe or impossible. The disposal approach involves developing a detailed plan identifying a grid of injection borehole wells. The borehole wells are arranged to intersect the abandoned mine openings which were previously used as haul routes, air supply / return routes, or openings from room and pillar mining.

The slurry is pumped from the surface into a borehole well with little control of placement possible. The pumping will continue until no more slurry can be placed.

This type of storage requires larger volumes of water compared with controlled flushing. This is because the higher water volume and injection flow rate would be used to disperse and fan out the distribution of the refuse fines. Widening the distribution zone will minimize the concentrated deposition at the immediate borehole injection area.



Studies on borehole injection report that slurry solids are also reduced to ranges of 17 percent as compared to 30 to 50 percent for Controlled Flushing. Figure 21 is a borehole plan layout for a proposed mine injection project illustrating the location of a borehole and abandoned mine workings.

### **Exposure Characterization of Existing Coal Waste Systems**

This section addresses the potential mechanisms and pathways for the introduction of coal slurry or process water introduction into the environment from coal waste facilities.

The introduction of coal refuse slurry, impounded process water, and surface water impounded from natural precipitation storage into the subsurface depends on many factors including the geology and hydrogeology of the specific site source, and the potential for subsidence of overburden structure into abandoned mine workings. Impounded facilities may be separated into two zones which include the impoundment dam foundation zone and the basin zone. The foundation zone is well characterized by geotechnical engineering studies and field construction. The groundwater seepage and strength aspects of this zone would not be expected to provide a significant source of water into the subsurface and is, therefore, not further considered. The basin zone includes the areas of the impounded facility which store water where the drainage elevation permits water or slurry flow into subsurface voids.

#### ***Slurry Seepage from Impounded Facilities into Basin Geology***

This section addresses the potential for impounded slurry, process water, and precipitation storage to seep through the natural openings within the basin soil and rock.

The NRC (2002) identified that the site geology within the storage basin at an impounded storage facility located in the Appalachian Plateau is strongly fractured and yet has a low porosity.

The regulatory permit requirements are the driver for the impoundment basin area construction practices. The perimeter of the impoundment basin is stripped of its vegetation, topsoil and loose rock overburden during the progressive construction of the refuse placement lift elevations. Therefore as the impoundment rises in elevation the pool water is placed in direct contact with the exposed rock. The steep topography typical of an impoundment basin would expose the cracks, faults, coal seam outcrops, and other preferential pathways for water and coal slurry seepage.

The NRC (2002) cites references which present geologic conditions under which slurry or impounded water would enter the groundwater system within the exposed rock faces of a basin. The NRC discusses that the exposure of regional joints and fractures on shallow near-surface fracture system produce a myriad of groundwater flow paths. The majority of this seepage water in the coal-bearing rock is transmitted in features including fractures, joints, bedding planes, and coal cleats. These permeable features can extend from bedrock surfaces to depths of 200 feet.

### ***Subsidence***

Mine subsidence is the ground movement resulting from collapse of subsurface rock strata into a mine opening. Subsidence occurs in working and abandoned mines and causes weakness in strata and may accompany water flow from overlying layers of high permeability or water storage. Mine subsidence causes vertical cracks in strata

and bed separation. In the horizontal plane the subsidence results in rock joint separation. Both of these subsidence induced effects would provide permeable zones for water and slurry transport into strata layers confining the regional groundwater.

### ***Slurry Infiltration & Mobilization from Impounded Facilities Into Coal Mine Workings***

Surface coal slurry impoundment and slurry cell discharges into the subsurface, surface, and underground mine workings are possible. Failure mechanisms have been documented by the OSM based on investigations of mine inundations. The failure mechanisms are caused by active and permitted impoundments having considerable water pool depths or reclaimed impoundments with saturated slurry. The following mechanisms apply to impoundments (OSM, 2001).

### ***Failure of Sealed Underground Mine Openings***

This infiltration could be caused by the mine opening seal made of rock and soil or other material which would fail and allow slurry to directly enter abandoned mine workings. Mine openings include punch-outs, portals, horizontal drainage ventilation conduits, and auger holes that connect with underground mines.

- Breakthrough at an unsealed underground mine opening: This source of water and slurry would entail the direct inundation of workings from mine openings which had not been permanently sealed.
- Breakthrough at coal barriers: Barriers include ground contours between underground mines, soil/rock barriers between auger holes and underground mines, and shallow drift mines with underground mines. Hydraulic pressures of

slurry and water stressing small or thin sections of soil/rock barriers allowing slurry to uncontrollably enter a mine.

- Breakthrough at Strata overlying the coal seam: Water and slurry entering a mine or subsurface opening into a mine through natural fractures and joints, and mining-induced fractures from roof falls, sinkholes, and subsidence.

### ***Slurry Distribution from Underground Injection***

The distribution of slurry either using controlled or blind flushing results in an increase to the hydraulic head within the flooded portions of the mine. Methods to contain the slurry are limited to bulkhead construction and sustainability between the open mine passages. Another option is to collect the seepage water into sumps and transfer to the surface for subsequent reuse.

## Summary and Conclusions

Current methods of coal refuse disposal (coarse and fine materials) include underground (injection) and above ground (impoundments) methods. Each method possesses attributes which have competing risks for exposure. Injection disposal into underground mine voids first places coal slurry, specifically the liquids fraction, into a zone where the hydrogeology becomes complex and there can be a loss of control of the liquids from contacting distributive networks leading to spreading and diluting. Underground injection can be more dispersive to the distribution of slurry liquids by the portability of placement of the injection well heads relative to other water supply sources.

Above-ground systems in contrast are stationary and they offer an operational capability to slurry or liquid management that underground injection cannot. The construction and management of coal refuse impoundments do have competing risk factors such as dam failure modes and consequences of failure which however may be more consequential to the loss of life than just to the contamination of subsurface drinking waters.

The control and management of slurry liquids is the most important factor when considering exposure pathways. When considering underground injection the WV DEP Phase I report identified an absence or lack of regulatory control of the chemistry and volumes of injected liquids. With surface impoundments, slurry seepage into basin geology is a condition which can be an uncontrolled source of introducing slurry liquids into the subsurface via cracks in geologic formations and even through mine workings.

Surface impoundments do offer the opportunity to control liquid volumes and introduction to the subsurface by the use of geomembrane liners which are similarly used in hazardous waste landfills.

## **Conclusions**

Chemical analysis of coal slurry indicate that injection may cause surface and subsurface pollution that could affect human health. However, there is no existing, accessible data which proves that coal slurry injection specifically has done this. There is ample proof that contributions from coal mining can affect drinking water, but separating out the specific components of mining operations that contribute pollution has not often been done, with the notable and important exception of the Phase 1 Report. That document provides reliable evidence that the contributions of coal slurry injection, if they exist, cannot be distinguished from other coal sources of pollution at four sites studied in a limited time frame and begun well after operations had begun.

The limitations of the available data are compelling for several reasons. The National Academy of Sciences has pointed out pollution from slurry injection is possible and that each site contemplated for this practice will have unique considerations. No one site will be broadly representative of other sites, nor do we consider it prudent to assume that limited time frames will represent the longer time frame of any site which was studied from before the beginning to the end of operations, and for some time after

We conclude that the data gaps are very large. It is currently not possible to distinguish the absence of proof of specific contributions attributable to coal slurry waste injection from the larger contributions of all sources of the coal industry cycle. The

excellent start created by the Phase 1 report is the kind of work which should accompany the large- scale efforts to move waste that coal slurry injection represents. We think that the practice, if it is to continue, deserves routine quality control.

Our expert reviewers have encouraged us to consider what that effort might look like. Presently, the State of Virginia, Department of Mines, Minerals and Energy, Division of Mined Land Reclamation has developed guidelines for slurry injection into underground mine voids under §4VAC25-130-816.41(i) and §4VAC25-130-817.41(h), as well as incorporating existing guidance from the Federal Environmental Protection Agency UIC requirements.

### ***Monitoring Plan for Slurry Injection Programs***

The objective of a slurry injection monitoring program is to determine with reasonable certainty whether injection benefits, has no effect, or degrades ground and surface waters.

The following elements are considered essential for an underground injection control program for coal slurry and include concepts from the State of Virginia's program:

Site characterization:

- GIS mapping of the target mine and surrounding mines with detail to penetration of multiple overlying mine voids; and correlation with underground mine maps
- GIS mapping of streams up- and down-gradient of target mine with detail to above drainage discharge locations

- Identification of sampling stations to characterize water quality and flow up- and down-gradient of mine
- Characterization of water quality and flow at stream-sampling stations
- Determination of mine void volume
- Injection well design, casing, sealing at undesired injection locations, and closure plans
- Installation of monitoring wells in mine and down gradient of mine
- Identification of flooding level
- Characterization of mine-pool water quality
- Identification of discharge points
- Identification of existing wells
- Water quality of existing wells
- Summarize mine history: period of mining, any previous slurry injection
- Identification of constructed barriers and their stability
- Presence of regional groundwater users
- Location of regional aquifers

Injection plan:

- Characterize the chemical and physical properties of the slurry
- Investigate risk release pathways, human exposure pathways, and environmental receptors
- Investigate risk associated with blowout potential



- Identify injection points and sources of dilution water if required
- Identify injection rates, periods of injection, pressure controls, piping construction and routing design, and injection well design requirements and safeguards
- Develop emergency response plan to include a spill prevention, control, and countermeasures plan; and secondary containment plan
- Worker training, spill response training
- Develop operational contingency plans for shut down, secondary dewatering and slurry conveyance designs for potential slurry removal, and location of secondary disposal sites

#### Monitoring:

- Develop monitoring plan, including sampling interval, sampling and analytical protocols, reporting plan, and action levels of key parameters
- Correlate sampling methods, detection limits, and analytical methods to detect specific injectate chemistry
- Conduct regular sampling of monitoring wells and slurry characterization
- Conduct regular sampling of surface streams
- Develop and submit reports for WVDEP
- Identify readings that are in excess of action/triggering levels
- Identify regional groundwater user wells and historic water quality values
- Visual inspection of all potential release locations

- Understanding of the fate and transport of slurry chemical additives relevant to underground placement

Parameters:

The key parameters should include, at minimum:

- pH, acidity, alkalinity
- Representative approach to organics: diesel-range organics
- Primary drinking water contaminants: antimony, arsenic, lead, selenium
- Secondary drinking water contaminants: aluminum, iron, manganese
- Other parameters in excess of DWS identified in the liquid fraction of the slurry

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## APPENDIX A

### TABLES

**Table 1: Characteristics of Six Sites Studied in the Project Report**

<b>Name of mine</b>	<b>County</b>	<b>Years of slurry operation</b>	<b>Pool type</b>	<b>Confounders*</b>	<b>Coal sulfur proportion</b>	<b>Reason for selection</b>
Southern Minerals	Raleigh	30+ (1970's to present)	Alkaline	Extensive regional mining. Surface runoff may go into the pool.	low	Long dwell time; nearby public water supplies, including two drawing from the same mine.
Loadout	Boone	1996-2006	Alkaline		low	No mining activity preceded slurry injection-associated activity  Locally unspoiled areas for comparison
Panther	Kanawha	2002-04 (unauthorized 1996)	Alkaline		low	Local water quality concerns
Power Mountain	Nicholas	20? (1990-present)	Alkaline	Includes 5 mines, one of which receives slurry injection.	low	Nearby domestic wells reported problems. Environmental audits requested.
Coresco	Monongalia		Alkaline		low	Plant did not use chemicals.
Marsh Fork	Raleigh				low	Did not use slurry injection

\*presence of other sources of coal refuse pollution.

**Table 2: Historic Estimates of Trace Elements of Coal and Coal Refuse  
(in ppm)**

<b>Element</b>	<b>Coal</b>	<b>Coal Refuse</b>
Be	0-31	0.2-3
Na		150-375
Mg		500-8000
Al		> 25,000
Si		> 25,000
K		500-1200
Ca		50-2000
Sc		3-25
Ti		300-3000
V		25-250
Cr		3-25
Mn	6.0-181	65-1300
Fe		7500-41,000
Co		3-25
Ni	0.4-104	25-250
Cu	2.0-185	12-50
Zn	0-6000	30-85
Ga		3-25
Y	0.1-59	3-25
Zr		3-25
Ag		0.3-2.5
Cd	0.1-65	0.25-1.0
Pb	4.0-138	20-150
As	0.5-106	
Se	0.4-8	
Hg	0.01-1.6	

*From Smith DM, 1987, citing: Wewercka et al., 197; and Busch et al., 1974.*



**Table 3: Critical Parameters Studied in the Phase 1 Report**

<b><u>What</u></b>	<b><u>Where</u></b>
175 chemicals (organic and inorganic)	coal; coal slurry; surface water; groundwater
<b><u>Metals Tested</u></b>	
Aluminum (Al)	
Antimony (Sb)	
Barium (Ba)	
Calcium (Ca)	
Chromium (Cr)	
Iron (Fe)	
Lead (Pb)	
Magnesium (Mg)	
Manganese (Mn)	
Molybdenum (Mo)	
Selenium (Se)	
Silver (Au)	
Strontium (Sr)	
Thallium (Tl)	
<b><u>Organics Tested</u></b>	
Acetone	
Butanol	
2-butanone	
Butyl benzene	
Chloromethane	
Diesel-range organics	
Ethyl benzene	
Gasoline-range organics	
Oil-range organics	
Naphthalene	
n-propyl benzene	
Pyrene	
Toluene	
<b><u>Other</u></b>	
Acidity	
Alkalinity and pH	
Cyanide	
Dissolved solids	
Potassium	
Sodium	
Specific conductivity	
Sulfates	

**Table 4. Concentration of Analytes Determined in Phase I and Corresponding Environmental and Health Comparison Values. Metals, General Chemistry, Semivolatile Organic Compounds, and Miscellaneous units are given in mg/L and Volatile Organic Compound units are given in ug/L**

Contaminant	CERCLA Priority List Y/N	EPA Standards			Health Advisory			ug/L at 10 E-4 Cancer Risk	Contam. of Concern (***)
		MCL (a)	MCLG (b)	SDWR (c)	10-kg Child		DWEL (d)		
					1 day	2 days			
<b>Metals (mg/L)</b>									
Aluminum	Y			0.05 - 0.2					Y
Antimony	Y	0.006			0.01	0.01	0.01	0.006	Y
Arsenic	Y	0.010					0.01	0.002	Y
Barium	Y	2			0.7	0.7	7		
Beryllium	Y	0.004			30	30	0.07		
Cadmium	Y	0.005			0.04	0.04	0.02	0.005	
Calcium		-							
Chromium	Y	0.1			1	1	0.1		
Cobalt	Y	-							
Copper	Y	1.3		1.0					
Iron				0.3					Y
Lead	Y	0.015							Y
Magnesium									
Manganese	Y			0.05	1	1	1.6	0.3	Y
Mercury	Y	0.002			0.002	0.002	0.01	0.002	
Molybdenum					0.08	0.08	0.2	0.04	
Nickel	Y				1	1	0.7	0.1	
Potassium									
Selenium	Y	0.05					0.2	0.05	
Silicon									
Silver	Y			0.1	0.2	0.2	0.2	0.1	
Sodium									
Strontium					25	25	20	4	
Thalium					0.007	0.007	0.002	0.0005	
Vanadium	Y								
Zinc	Y			5	6	6	10	2	
<b>General Chemistry (mg/L)</b>									
Nitrogen, Nitrate	Y	10							
Nitrogen, Nitrite	Y	1							Y
Chloride				250					Y
Fluoride	Y	4.0							Y
Sulfate				250					Y
Nitrogen, Ammonia	Y								
Specific Conductance (**)									
Total Dissolved solids				500					Y
Total Suspended Solids									
Acidity, Total									
Alkalinity, Bicarbonate									
Alkalinity, Carbonate									
Alkalinity, Total									
pH (**)				6.5 - 8.5					Y
<b>Volatile Organic Compounds (ug/L)</b>									
2-Butanone	Y								
Acetone	Y								
Acrolein	Y								
Benzene	Y	5.000			200	200	100	100	
m,p-Xylene	Y	10000 (*)			40000 (*)	40000 (*)	7000 (*)		
Methylene Chloride	Y								
o-Xylene		10000 (*)			40000 (*)	40000 (*)	7000 (*)		
Toluene	Y	1000.000			20000	2000	3000		
<b>Semivolatile Organic Compounds (mg/L)</b>									
bis(2-ethylhexyl)phthalate	Y								
Naphthalene									
Phenanthrene	Y								
<b>Miscellaneous (mg/L)</b>									
TPH (Diesel Range)									
TPH (oil Range)									
Sulfate-Reducing Bacteria (**)									

Contaminant	Southern Minerals		Loadout, LLC			Panther, LLC		
	SM Slurry (Liquid )		LLSlurry (Liquid )		LL Coal Leachate	PLSlurry (Liquid )		PLCoal Leachate
	Dissolved	Total	Dissolved	Total	Dissolved	Dissolved	Total	Dissolved
<b>Metals (mg/L)</b>								
Aluminum	0.1950	0.651	0.1500	2.37	0.0540	0.029	0.0460	0.398
Antimony	0.0220	0.0215	0.0057	0.0059	0.0019	0.0146	0.016	0.0012
Arsenic	0.0039	0.0043	0.0042	0.0047	0.0041	0.0104	0.0113	0.012
Barium	0.0809	0.114	0.0974	0.133	0.0055	0.243	0.269	0.0129
Beryllium	0.0002	0.0004	ND	ND	ND	ND	ND	ND
Cadmium	ND	ND	ND	ND	ND	ND	0.0011	ND
Calcium	51.4	51.7	62.10	63.7	2.42	2.83	3.51	0.464
Chromium	0.0013	0.0016	ND	ND	0.0013	0.0272	0.0342	ND
Cobalt	0.0021	0.0024	ND	0.0016	ND	0.0142	0.0161	ND
Copper	0.0012	0.0018	0.0016	0.0034	ND	0.0248	0.0278	ND
Iron	ND	0.91	ND	0.828	ND	0.068	0.089	ND
Lead	ND	0.0008	ND	0.0016	ND	0.0762	0.0775	ND
Magnesium	20.8	21	19.8	20.6	0.705	0.591	0.771	ND
Manganese	0.0141	0.0177	0.0860	0.097	ND	0.021	0.028	ND
Mercury	ND	ND	ND	ND	ND	ND	ND	ND
Molybdenum	0.0176	0.0178	0.0447	0.0466	0.0090	0.198	0.217	ND
Nickel	0.0043	0.0052	0.0067	0.0073	ND	0.0386	0.0432	ND
Potassium	6.90	7.07	13.9	14.3	5.02	5.38	7.05	1.23
Selenium	0.0082	0.0082	0.0268	0.0278	0.0195	0.0224	0.0255	0.0087
Silicon	3.3	3.76	2.3	8.54	11.1	0.346	0.358	0.384
Silver	ND	ND	ND	ND	0.0005	ND	ND	ND
Sodium	58.8	55.5	265	267	4.88	266	341	10.1
Strontium	1.16	1.17	1.44	1.47	0.0159	0.571	0.632	0.0222
Thalium	ND	0.0002	0.0003	0.0004	ND	ND	ND	ND
Vanadium	0.0018	0.0021	0.0013	0.0025	0.0044	0.0103	0.0131	0.007
Zinc	0.016	0.027	ND	0.008	0.008	0.019	0.014	ND
<b>General Chemistry (mg/L)</b>								
Nitrogen, Nitrate	0.45		1.85		0.07	0.59		0.03
Nitrogen, Nitrite	2.32		0.35		0.17	ND		ND
Chloride	0.18		84.80		1.45	423.00		7.12
Fluoride	8.39		ND		0.55	1.53		0.51
Sulfate	157.00		849.00		7.40	261.00		2.60
Nitrogen, Ammonia	0.18		1.27		0.34	1.96		0.44
Specific Conductance (**)	702.00		1840		57.20	5000.00		170.00
Total Dissolved solids	423.00		933.00		21.00	2540.00		87.00
Total Suspended Solids	5440.00		191.00		1.00	74.00		6.00
Acidity, Total	6.80		6.90		ND	ND		ND
Alkalinity, Bicarbonate	180.00		102.00		25.50	412.00		42.00
Alkalinity, Carbonate	1.40		ND		6.00	7.10		14.30
Alkanlinity, Total	181.00		103.00		32.70	420.00		58.20
pH (**)	7.93		7.88		9.40	8.26		9.56
<b>Volatile Organic Compounds (µg/L)</b>								
2-Butanone	ND		ND		ND	68.4		ND
Acetone	ND		ND		ND	16.7		9.9
Acrolein	ND		7		14.8	ND		ND
Benzene	ND		ND		ND	1.8		1.6
m,p-Xylene	ND		ND		ND	0.8		0.4
Methylene Chloride	ND		1.4		1.0	ND		ND
o-Xylene	ND		ND		ND	0.6		0.3
Toluene	ND		0.6		0.7	2.8		2.1
<b>Semivolatile Organic Compounds (mg/L)</b>								
bis(2-ethylhexyl)phthalate	ND		ND		ND	ND		ND
Naphthalene	ND		0.0143		ND	ND		ND
Phenanthrene	ND		0.061		ND	ND		ND
<b>Miscellaneous (mg/L)</b>								
TPH (Diesel Range)	ND		16.60		ND	0.5100		ND
TPH (oil Range)	ND		19.40		ND	ND		ND
Sulfate-Reducing Bact. (**)	NA		NA		ND	ND		ND

Contaminant	Power Mountain			Coresco			Marfork		
	PM Slurry (Liquid )		PM Coal Leachate	CLSlurry (Liquid )		CL Coal Leachate	MF Slurry (Liquid )	MF Coal Leachate	
	Dissolved	Total	Dissolved	Dissolved	Total	Dissolved	Dissolved/ Total	Dissolved	Total
<b>Metals (mg/L)</b>									
Aluminum	0.509	0.564	0.214	0.532	0.644	0.356	NA	0.146	1.190
Antimony	0.0004	0.0005	0.0018	0.0069	0.0071	0.0005	NA	0.0015	0.0011
Arsenic	ND	ND	0.0141	ND	ND	0.0019	NA	0.0198	0.246
Barium	0.0523	0.0634	0.0079	0.0677	0.0713	0.0047	NA	0.0227	0.695
Beryllium	ND	ND	ND	ND	ND	ND	NA	ND	0.002
Cadmium	ND	ND	ND	ND	ND	ND	NA	ND	ND
Calcium	124.00	123.00	0.552	111	115	4.820	NA	0.2840	1.260
Chromium	ND	ND	ND	ND	ND	ND	NA	ND	0.0054
Cobalt	0.0037	0.0039	ND	0.0027	0.0029	ND	NA	ND	0.0067
Copper	0.0015	0.0016	ND	0.0021	0.0021	ND	NA	ND	0.0248
Iron	0.030	0.195	0.038	ND	0.174	0.022	NA	0.050	13.200
Lead	ND	0.0004	0.0004	ND	ND	ND	NA	0.0003	0.2170
Magnesium	81.40	82.20	ND	38.90	40.00	0.29	NA	ND	2.21
Manganese	0.921	0.921	ND	0.133	0.138	ND	NA	0.001	0.142
Mercury	ND	ND	ND	ND	ND	ND	NA	ND	ND
Molybdenum	0.0023	0.0024	0.0035	0.0290	0.0297	0.0020	NA	0.0029	0.0021
Nickel	0.0092	0.0096	ND	0.0073	0.0074	ND	NA	ND	0.011
Potassium	15.50	15.50	0.380	5.01	5.16	1.080	NA	0.321	0.925
Selenium	0.0057	0.0059	0.0082	0.0024	0.0024	0.0019	NA	0.0043	0.0040
Silicon	3.27	5.31	7.59	1.14	3.91	0.43	NA	13.20	71.00
Silver	0.0006	0.0006	ND	ND	ND	ND	NA	ND	ND
Sodium	236.0	237.0	75.5	272.0	279.0	12.6	NA	48.1	6.7
Strontium	1.63	1.74	0.0043	31.9	3.27	0.16	NA	0.115	0.135
Thalium	0.0002	0.0003	ND	ND	0.0002	ND	NA	0.0002	0.0004
Vanadium	ND	ND	0.0052	ND	ND	0.0015	NA	0.0031	ND
Zinc	0.032	0.041	ND	ND	ND	0.003	NA	ND	0.038
<b>General Chemistry (mg/L)</b>									
Nitrogen, Nitrate	3.45		ND	0.83		ND	NA	ND	
Nitrogen, Nitrite	ND		0.14	0.16		ND	NA	0.10	
Chloride	77.10		1.71	32.80		0.60	NA	1.43	
Fluoride	0.56		0.42	ND		ND	NA	0.31	
Sulfate	853.00		3.44	1110.00		14.00	NA	4.55	
Nitrogen, Ammonia	1.16		0.35	0.72		0.14	NA	0.10	
Specific Conductance (**)	2110		100	ND		ND	NA	86.7	
Total Dissolved solids	1470		21	1340		51	NA	15.0	
Total Suspended Solids	9		1	22		1	NA	1	
Acidity, Total	8.7		ND	5.4		ND	NA	ND	
Alkalinity, Bicarbonate	146.0		34.3	143.0		32.1	NA	23.2	
Alkalinity, Carbonate	ND		10.0	ND		6.8	NA	6.0	
Alkalinity, Total	147.0		45.8	144.0		40.0	NA	30.6	
pH (**)	7.75		9.49	7.71		9.35	NA	9.44	
<b>Volatile Organic Compounds (µg/L)</b>									
2-Butanone	ND		ND	ND		ND	NA	ND	
Acetone	ND		ND	ND		ND	NA	ND	
Acrolein	ND		ND	ND		ND	NA	ND	
Benzene	ND		ND	ND		ND	NA	ND	
m,p-Xylene	ND		0.4	ND		ND	NA	ND	
Methylene Chloride	ND		ND	ND		ND	NA	ND	
o-Xylene	ND		0.3	ND		ND	NA	ND	
Toluene	ND		1.9	ND		ND	NA	0.2	
<b>Semivolatile Organic Compounds (mg/L)</b>									
bis(2-ethylhexyl)phthalate	ND		0.0091	ND		ND	NA	0.0108	
Naphthalene	ND		ND	ND		ND	NA	ND	
Phenanthrene	ND		ND	ND		ND	NA	ND	
<b>Miscellaneous (mg/L)</b>									
TPH (Diesel Range)	0.26		ND	ND		ND	NA	ND	
TPH (oil Range)	ND		ND	ND		ND	NA	ND	
Sulfate-Reducing Bact. (**)	NA		NA	NA		5500	NA	NA	

Remarks:

(a) MCL: Maximum Contaminant Level

(b) MCLG: Maximum Contaminant Level Goal

(c) SDWR: National Secondary Drinking Water Regulation

(d) DWEL: Drinking Water Equivalent Level

(\*) The values is given in mg/L for total xylenes

(\*\*) The specific conductance is given in umhos/cm, the pH is given in SU, and the bacterial numbers are given in CFU/mL

(\*\*\*) Analytes for which the concentration has been observed at least once above one the health or environmental guideline

***Values marked in bold-italic are above the comparison values***

Yellow: Inorganic contaminants detected at least once higher than one guideline value

**Table 5. Exposure Dose Estimated for a Child for Analytes Determined in Phase I and Corresponding Health Comparison Values**

Contaminant	Minimal Risk Level (MRL) mg/kg/d	Chronic Ref. Dose (RfD) mg/kg/d	Estimated exposure dose for a child mg/kg/d (*) Southern Minerals		Estimated exposure dose for a child mg/kg/d (*) Loadout, LLC			Estimated exposure dose for a child mg/kg/d (*) Panther, LLC		
			SM Slurry (Liquid )		LL Slurry (Liquid )		LL Coal Leachate	PL Slurry (Liquid )		PL Coal Leachate
			Dissolved	Total	Dissolved	Total	Dissolved	Dissolved	Total	Dissolved
<b>Metals</b>										
Aluminum	1.000E+00		1.950E-02	6.510E-02	1.500E-02	2.370E-01	5.400E-03	2.900E-03	4.600E-03	3.980E-02
Antimony		4.000E-04	2.200E-03	2.150E-03	5.700E-04	5.900E-04	1.900E-04	1.460E-03	1.600E-03	1.200E-04
Arsenic	3.000E-04	3.000E-04	3.900E-04	4.300E-04	4.200E-04	4.700E-04	4.100E-04	1.040E-03	1.130E-03	1.200E-03
Barium	2.000E-01	2.000E-01	8.090E-03	1.140E-02	9.740E-03	1.330E-02	5.500E-04	2.430E-02	2.690E-02	1.290E-03
Beryllium	2.000E-03	2.000E-03	2.000E-05	4.000E-05						
Cadmium	1.000E-04	5.000E-04							1.100E-04	
Calcium			5.140E+00	5.170E+00	6.210E+00	6.370E+00	2.420E-01	2.830E-01	3.510E-01	4.640E-02
Chromium	1.000E-03	3.000E-03	1.300E-04	1.600E-04			1.300E-04	2.720E-03	3.420E-03	
Cobalt	1.000E-02		2.100E-04	2.400E-04		1.600E-04		1.420E-03	1.610E-03	
Copper	1.000E-02		1.200E-04	1.800E-04	1.600E-04		3.400E-04	2.480E-03	2.780E-03	
Iron				9.100E-02		8.280E-02		6.800E-03	8.900E-03	
Lead				8.000E-05		1.600E-04		7.620E-03	7.750E-03	
Magnesium			2.080E+00	2.100E+00	1.980E+00	2.060E+00	7.050E-02	5.910E-02	7.710E-02	
Manganese		1.400E-01	1.410E-03	1.770E-03	8.600E-03	9.700E-03		2.100E-03	2.800E-03	
Mercury										
Molybdenum		5.000E-03	1.760E-03	1.780E-03	4.470E-03	4.660E-03	9.000E-04	1.980E-02	2.170E-02	
Nickel		2.000E-02	4.300E-04	5.200E-04	6.700E-04	7.300E-04		3.860E-03	4.320E-03	
Potassium			6.900E-01	7.070E-01	1.390E+00	1.430E+00	5.020E-01	5.380E-01	7.050E-01	1.230E-01
Selenium	5.000E-03	5.000E-03	8.200E-04	8.200E-04	2.680E-03	2.780E-03	1.950E-03	2.240E-03	2.550E-03	8.700E-04
Silicon	2.000E+00		3.300E-01	3.760E-01	2.300E-01	8.540E-01	1.110E+00	3.460E-02	3.580E-02	3.840E-02
Silver		5.000E-03					5.000E-05			
Sodium	5.000E-02		5.880E+00	5.550E+00	2.650E+01	2.670E+01	4.880E-01	2.660E+01	3.410E+01	1.010E+00
Strontium		6.000E-01	1.160E-01	1.170E-01	1.440E-01	1.470E-01	1.590E-03	5.710E-02	6.320E-02	2.220E-03
Thalium		7.000E-05		2.000E-05	3.000E-05	4.000E-05				
Vanadium	3.000E-03		1.800E-04	2.100E-04	1.300E-04	2.500E-04	4.400E-04	1.030E-03	1.310E-03	7.000E-04
Zinc	3.000E-01	3.000E-01	1.600E-03	2.700E-03		8.000E-04	8.000E-04	1.900E-03	1.400E-03	
<b>General Chemistry</b>										
Nitrogen, Nitrate		1.600E+00	4.500E-02		1.850E-01		7.000E-03	5.900E-02		3.000E-03
Nitrogen, Nitrite		1.600E-01	2.320E-01		3.500E-02		1.700E-02			
Chloride			1.800E-02		8.480E+00		1.450E-01	4.230E+01		7.120E-01
Fluoride	5.000E-02		8.390E-01				5.500E-02	1.530E-01		5.100E-02
Sulfate			1.570E+01		8.490E+01		7.400E-01	2.610E+01		2.600E-01
Nitrogen, Ammonia			1.800E-02		1.270E-01		3.400E-02	1.960E-01		4.400E-02
Total Dissolved Solids			4.230E+01		9.330E+01		2.100E+00	2.540E+02		8.700E+00
Total Suspended Solids			5.440E+02		1.910E+01		1.000E-01	7.400E+00		6.000E-01
Acidity, Total			6.800E-01		6.900E-01					
Alkalinity, Bicarbonate			1.800E+01		1.020E+01		2.550E+00	4.120E+01		4.200E+00
Alkalinity, Carbonate			1.400E-01				6.000E-01	7.100E-01		1.430E+00
Alkanlinity, Total			1.810E+01		1.030E+01		3.270E+00	4.200E+01		5.820E+00
<b>Volatile Organic Compounds</b>										
2-Butanone								6.840E-03		
Acetone	2.000E+00							1.670E-03		9.900E-04
Acrolein	4.000E-03				7.000E-04		1.480E-03			
Benzene	5.000E-04	4.000E-03						1.800E-04		1.600E-04
m,p-Xylene	2.000E-01	2.000E-01						8.000E-05		4.000E-05
Methylene Chloride	6.000E-02				1.400E-04		1.000E-04			
o-Xylene	2.000E-01	2.000E-01						6.000E-05		3.000E-05
Toluene	2.000E-02	8.000E-02			6.000E-05		7.000E-05	2.800E-04		2.100E-04
<b>Semivolatile Organic Compounds</b>										
bis(2-ethylhexyl)phthalate										
Naphthalene	6.000E-01	2.000E-02			1.430E-03					
Phenanthrene					6.100E-03					
<b>Miscellaneous</b>										
TPH (Diesel Range)					1.660E+00			5.100E-02		
TPH (oil Range)					1.940E+00					

Contaminant	Estimated exposure dose for a child mg/kg/d (*) Power Mountain			Estimated exposure dose for a child mg/kg/d (*) Coresco			Estimated exposure dose for a child mg/kg/d (*) Marfork		
	PM Slurry (Liquid )		PM Coal Leachate	CLSlurry (Liquid )		CL Coal Leachate	MFSlurry (Liquid )	MF Coal Leachate	
	Dissolved	Total	Dissolved	Dissolved	Total	Dissolved		Dissolved	Total
<b>Metals</b>									
Aluminum	5.090E-02	5.640E-02	2.140E-02	5.320E-02	6.440E-02	3.560E-02		1.460E-02	1.190E-01
Antimony	4.000E-05	5.000E-05	1.800E-04	<b>6.900E-04</b>	<b>7.100E-04</b>	5.000E-05		1.500E-04	1.100E-04
Arsenic			<b>1.410E-03</b>			1.900E-04		<b>1.980E-03</b>	<b>2.460E-02</b>
Barium	5.230E-03	6.340E-03	7.900E-04	6.770E-03	7.130E-03	4.700E-04		2.270E-03	6.950E-02
Beryllium									2.000E-04
Cadmium									
Calcium	1.240E+01	1.230E+01	5.520E-02	1.110E+01	1.150E+01	4.820E-01		2.840E-02	1.260E-01
Chromium									<b>5.400E-04</b>
Cobalt	3.700E-04	3.900E-04		2.700E-04	2.900E-04				6.700E-04
Copper	1.500E-04	1.600E-04		2.100E-04	2.100E-04				2.480E-03
Iron	3.000E-03	1.950E-02	3.800E-03		1.740E-02	2.200E-03		5.000E-03	1.320E+00
Lead		4.000E-05	4.000E-05					3.000E-05	2.170E-02
Magnesium	8.140E+00	8.220E+00		3.890E+00	4.000E+00	2.900E-02			2.210E-01
Manganese	9.210E-02	9.210E-02		1.330E-02	1.380E-02			1.000E-04	1.420E-02
Mercury									
Molybdenum	2.300E-04	2.400E-04	3.500E-04	2.900E-03	2.970E-03	2.000E-04		2.900E-04	2.100E-04
Nickel	9.200E-04	9.600E-04		7.300E-04	7.400E-04				1.100E-03
Potassium	1.550E+00	1.550E+00	3.800E-02	5.010E-01	5.160E-01	1.080E-01		3.210E-02	9.250E-02
Selenium	5.700E-04	5.900E-04	8.200E-04	2.400E-04	2.400E-04	1.900E-04		4.300E-04	4.000E-04
Silicon	3.270E-01	5.310E-01	7.590E-01	1.140E-01	3.910E-01	4.300E-02		1.320E+00	<b>7.100E+00</b>
Silver	6.000E-05	6.000E-05							
Sodium	<b>2.360E+01</b>	<b>2.370E+01</b>	<b>7.550E+00</b>	<b>2.720E+01</b>	<b>2.790E+01</b>	<b>1.260E+00</b>		<b>4.810E+00</b>	<b>6.700E-01</b>
Strontium	1.630E-01	1.740E-01	4.300E-04	<b>3.190E+00</b>	3.270E-01	1.600E-02		1.150E-02	1.350E-02
Thalium	2.000E-05	3.000E-05			2.000E-05			2.000E-05	4.000E-05
Vanadium			5.200E-04			1.500E-04		3.100E-04	
Zinc	3.200E-03	4.100E-03				3.000E-04			3.800E-03
<b>General Chemistry</b>									
Nitrogen, Nitrate	3.450E-01			8.300E-02					
Nitrogen, Nitrite			1.400E-02	1.600E-02				1.000E-02	
Chloride	7.710E+00		1.710E-01	3.280E+00		6.000E-02		1.430E-01	
Fluoride	<b>5.600E-02</b>		4.200E-02					<b>3.100E-02</b>	
Sulfate	8.530E+01		3.440E-01	1.110E+02		1.400E+00		4.550E-01	
Nitrogen, Ammonia	1.160E-01		3.500E-02	7.200E-02		1.400E-02		1.000E-02	
Total Dissolved solids	1.470E+02		2.100E+00	1.340E+02		5.100E+00		1.500E+00	
Total Suspended Solids	9.000E-01		1.000E-01	2.200E+00		1.000E-01		1.000E-01	
Acidity, Total	8.700E-01			5.400E-01					
Alkalinity, Bicarbonate	1.460E+01		3.430E+00	1.430E+01		3.210E+00		2.320E+00	
Alkalinity, Carbonate			1.000E+00			6.800E-01		6.000E-01	
Alkanlinity, Total	1.470E+01		4.580E+00	1.440E+01		4.000E+00		3.060E+00	
<b>Volatile Organic Compounds</b>									
2-Butanone									
Acetone									
Acrolein									
Benzene									
m,p-Xylene			4.000E-05						
Methylene Chloride									
o-Xylene			3.000E-05						
Toluene			1.900E-04					2.000E-05	
<b>Semivolatile Organic Compounds</b>									
bis(2-ethylhexyl)phthalate			9.100E-04					1.080E-03	
Naphthalene									
Phenanthrene									
<b>Miscellaneous</b>									
TPH (Diesel Range)	2.600E-02								
TPH (oil Range)									

Remarks:

(a) MRL: Maximum Risk Level (<http://www.epa.gov/>)

(b) RfD: Chronic reference dose (<http://www.atsdr.cdc.gov/mrls/>)

(\*) Based on an average child weight of 10 kg and a daily drinking water consumption of 1 liter

***Values marked in bold-italic are above one or more reference doses***

Yellow: Inorganic contaminants detected at least once higher than one guideline value

Blue: Organic contaminants detected at least once higher than one order of magnitude lower than one guideline value



**Table 6. Exposure Dose Estimated for an Adult for Analytes Determined in Phase I and Corresponding Health Comparison Values**

Contaminant	Minimal risk Level (MRL) mg/kg/d	Chronic Reference Dose (RfD) mg/kg/d	Estimated exposure dose for an adult mg/kg/d (*) Southern Minerals		Estimated exposure dose for an adult mg/kg/d (*) Loadout, LLC			Estimated exposure dose for an adult mg/kg/d (*) Panther, LLC			
			SM Slurry (Liquid)		LLSlurry (Liquid)		LLCoal Leachate	PLSlurry (Liquid)		PLCoal Leachate	
			Dissolved	Total	Dissolved	Total	Dissolved	Dissolved	Total	Dissolved	
<b>Metals</b>											
Aluminum	1.000E+00		5.571E-03	1.860E-02	4.286E-03	6.771E-02	1.543E-03	8.286E-04	1.314E-03	1.137E-02	
Antimony		4.000E-04	<b>6.286E-04</b>	<b>6.143E-04</b>	1.629E-04	1.686E-04	5.429E-05	4.171E-04	4.571E-04	3.429E-05	
Arsenic	3.000E-04	3.000E-04	1.114E-04	1.229E-04	1.200E-04	1.343E-04	1.171E-04	2.971E-04	<b>3.229E-04</b>	<b>3.429E-04</b>	
Barium	2.000E-01	2.000E-01	2.311E-03	3.257E-03	2.783E-03	3.800E-03	1.571E-04	6.943E-03	7.686E-03	3.686E-04	
Beryllium	2.000E-03	2.000E-03	5.714E-06	1.143E-05						3.143E-05	
Cadmium	1.000E-04	5.000E-04									
Calcium			1.469E+00	1.477E+00	1.774E+00	1.820E+00	6.914E-02	8.086E-02	1.003E-01	1.326E-02	
Chromium	1.000E-03	3.000E-03	3.714E-05	4.571E-05			3.714E-05	7.771E-04	9.771E-04		
Cobalt	1.000E-02		6.000E-05	6.857E-05		4.571E-05		4.057E-04	4.600E-04		
Copper	1.000E-02		3.429E-05	5.143E-05	4.571E-05	9.714E-05		7.086E-04	7.943E-04		
Iron				2.600E-02		2.366E-02		1.943E-03	2.543E-03		
Lead				2.286E-05		4.571E-05		2.177E-03	2.214E-03		
Magnesium			5.943E-01	6.000E-01	1.378E-05	1.798E-05		1.689E-02	2.203E-02		
Manganese		1.400E-01	4.029E-04	5.057E-04	2.457E-03	2.771E-03		6.000E-04	8.000E-04		
Mercury											
Molybdenum		5.000E-03	5.029E-04	5.086E-04	1.277E-03	1.331E-03	2.571E-04	<b>5.657E-03</b>	<b>6.200E-03</b>		
Nickel		2.000E-02	1.229E-04	1.486E-04	1.914E-04	2.086E-04		1.103E-03	1.234E-03		
Potassium			1.971E-01	2.020E-01	3.971E-01	4.086E-01	1.434E-01	1.537E-01	2.014E-01	3.514E-02	
Selenium	5.000E-03	5.000E-03	2.343E-04	2.343E-04	7.657E-04	7.943E-04	5.571E-04	6.400E-04	7.286E-04	2.486E-04	
Silicon	2.000E+00		9.429E-02	1.074E-01	6.571E-02	2.440E-01	3.171E-01	9.886E-03	1.023E-02	1.097E-02	
Silver		5.000E-03					1.429E-05				
Sodium	5.000E-02		<b>1.680E+00</b>	<b>1.586E+00</b>	<b>7.571E+00</b>	<b>7.629E+00</b>	<b>1.394E-01</b>	<b>7.600E+00</b>	<b>9.743E+00</b>	<b>2.886E-01</b>	
Strontium		6.000E-01	3.314E-02	3.343E-02	4.114E-02	4.200E-02	4.543E-04	1.631E-02	1.806E-02	6.343E-04	
Thalium		7.000E-05		5.714E-06	8.571E-06	1.143E-05					
Vanadium	3.000E-03		5.143E-05	6.000E-05	3.714E-05	7.143E-05	1.257E-04	2.943E-04	3.743E-04	2.000E-04	
Zinc	3.000E-01	3.000E-01	4.571E-04	7.714E-04		2.286E-04	2.286E-04	5.429E-04	4.000E-04		
<b>General Chemistry</b>											
Nitrogen, Nitrate		1.600E+00	1.286E-02		5.286E-02		2.000E-03	1.686E-02		8.571E-04	
Nitrogen, Nitrite		1.600E-01	6.629E-02		1.000E-02		4.857E-03				
Chloride			5.143E-03		2.423E+00		4.143E-02	1.209E+01		2.034E-01	
Fluoride	5.000E-02		<b>2.397E-01</b>				1.571E-02	4.371E-02		1.457E-02	
Sulfate			4.486E+00		2.426E+01		2.114E-01	7.457E+00		7.429E-02	
Nitrogen, Ammonia			5.143E-03		3.629E-02		9.714E-03	5.600E-02		1.257E-02	
Total Dissolved solids			1.209E+01		2.666E+01		6.000E-01	7.257E+01		2.486E+00	
Total Suspended Solids			1.554E+02		5.457E+00		2.857E-02	2.114E+00		1.714E-01	
Acidity, Total			1.943E-01		1.971E-01						
Alkalinity, Bicarbonate			5.143E+00		2.914E+00		7.286E-01	1.177E+01		1.200E+00	
Alkalinity, Carbonate			4.000E-02				1.714E-01	2.029E-01		4.086E-01	
Alkanlinity, Total			5.171E+00		2.943E+00		9.343E-01	1.200E+01		1.663E+00	
<b>Volatile Organic Compounds</b>											
2-Butanone								1.954E-03			
Acetone	2.000E+00							4.771E-04		2.829E-04	
Acrolein	4.000E-03				2.000E-04		4.229E-04				
Benzene	5.000E-04	4.000E-03						5.143E-05		4.571E-05	
m,p-Xylene	2.000E-01	2.000E-01						2.286E-05		1.143E-05	
Methylene Chloride	6.000E-02				4.000E-05		2.857E-05				
o-Xylene	2.000E-01	2.000E-01						1.714E-05		8.571E-06	
Toluene	2.000E-02	8.000E-02			1.714E-05		2.000E-05	8.000E-05		6.000E-05	
<b>Semivolatile Organic Compounds</b>											
bis(2-ethylhexyl)phthalate											
Naphthalene	6.000E-01	2.000E-02			4.086E-04						
Phenanthrene					1.743E-03						
<b>Miscellaneous</b>											
TPH (Diesel Range)					4.743E-01			1.457E-02			
TPH (oil Range)					5.543E-01						

Contaminant	Estimated exposure dose for an adult mg/kg/d (*) Power Mountain			Estimated exposure dose for an adult mg/kg/d (*) Coresco			Estimated exposure dose for an adult mg/kg/d (*) Marfork		
	PM Slurry (Liquid )		PM Coal Leachate	CLSlurry (Liquid )		CLCoal Leachate	MFSlurry (Liquid )	MFCoal Leachate	
	Dissolved	Total	Dissolved	Dissolved	Total	Dissolved		Dissolved	Total
<b>Metals</b>									
Aluminum	1.454E-02	1.611E-02	6.114E-03	1.520E-02	1.840E-02	1.017E-02		4.171E-03	3.400E-02
Antimony	1.143E-05	1.429E-05	5.143E-05	1.971E-04	2.029E-04	1.429E-05		4.286E-05	3.143E-05
Arsenic			4.029E-04			5.429E-05		5.657E-04	7.029E-03
Barium	1.494E-03	1.811E-03	2.257E-04	1.934E-03	2.037E-03	1.343E-04		6.486E-04	1.986E-02
Beryllium									5.714E-05
Cadmium									
Calcium	3.543E+00	3.514E+00	1.577E-02	3.171E+00	3.286E+00	1.377E-01		8.114E-03	3.600E-02
Chromium									1.543E-04
Cobalt	1.057E-04	1.114E-04		7.714E-05	8.286E-05				1.914E-04
Copper	4.286E-05	4.571E-05		6.000E-05	6.000E-05				7.086E-04
Iron	8.571E-04	5.571E-03	1.086E-03		4.971E-03	6.286E-04		1.429E-03	3.771E-01
Lead		1.143E-05	1.143E-05					8.571E-06	6.200E-03
Magnesium	2.326E+00	2.349E+00		1.111E+00	1.143E+00	8.286E-03			6.314E-02
Manganese	2.631E-02	2.631E-02		3.800E-03	3.943E-03			2.857E-05	4.057E-03
Mercury									
Molybdenum	6.571E-05	6.857E-05	1.000E-04	8.286E-04	8.486E-04	5.714E-05		8.286E-05	6.000E-05
Nickel	2.629E-04	2.743E-04		2.086E-04	2.114E-04				3.143E-04
Potassium	4.429E-01	4.429E-01	1.086E-02	1.431E-01	1.474E-01	3.086E-02		9.171E-03	2.643E-02
Selenium	1.629E-04	1.686E-04	2.343E-04	6.857E-05	6.857E-05	5.429E-05		1.229E-04	1.143E-04
Silicon	9.343E-02	1.517E-01	2.169E-01	3.257E-02	1.117E-01	1.229E-02		3.771E-01	2.029E+00
Silver	1.714E-05	1.714E-05							
Sodium	6.743E+00	6.771E+00	2.157E+00	7.771E+00	7.971E+00	3.600E-01		1.374E+00	1.914E-01
Strontium	4.657E-02	4.971E-02	1.229E-04	9.114E-01	9.343E-02	4.571E-03		3.286E-03	3.857E-03
Thalium	5.714E-06	8.571E-06			5.714E-06			5.714E-06	1.143E-05
Vanadium			1.486E-04			4.286E-05		8.857E-05	
Zinc	9.143E-04	1.171E-03				8.571E-05			1.086E-03
<b>General Chemistry</b>									
Nitrogen, Nitrate	9.857E-02			2.371E-02					
Nitrogen, Nitrite			4.000E-03	4.571E-03				2.857E-03	
Chloride	2.203E+00		4.886E-02	9.371E-01		1.714E-02		4.086E-02	
Fluoride	1.600E-02		1.200E-02					8.857E-03	
Sulfate	2.437E+01		9.829E-02	3.171E+01		4.000E-01		1.300E-01	
Nitrogen, Ammonia	3.314E-02		1.000E-02	2.057E-02		4.000E-03		2.857E-03	
Total Dissolved solids	4.200E+01		6.000E-01	3.829E+01		1.457E+00		4.286E-01	
Total Suspended Solids	2.571E-01		2.857E-02	6.286E-01		2.857E-02		2.857E-02	
Acidity, Total	2.486E-01			1.543E-01					
Alkalinity, Bicarbonate	4.171E+00		9.800E-01	4.086E+00		9.171E-01		6.629E-01	
Alkalinity, Carbonate			2.857E-01			1.943E-01		1.714E-01	
Alkanlinity, Total	4.200E+00		1.309E+00	4.114E+00		1.143E+00		8.743E-01	
<b>Volatile Organic Compounds</b>									
2-Butanone									
Acetone									
Acrolein									
Benzene									
m,p-Xylene			1.143E-05						
Methylene Chloride									
o-Xylene			8.571E-06						
Toluene			5.429E-05					5.714E-06	
<b>Semivolatile Organic Compounds</b>									
bis(2-ethylhexyl)phthalate			2.600E-04					3.086E-04	
Naphthalene									
Phenanthrene									
<b>Miscellaneous</b>									
TPH (Diesel Range)	7.429E-03								
TPH (oil Range)									

Remarks:

(a) MRL: Maximum Risk Level (<http://www.epa.gov/>)

(b) RfD: Chronic reference dose (<http://www.atsdr.cdc.gov/mrls/>)

(\*) Based on an average adult weight of 70 kg and a daily drinking water consumption of 2 liters

***Values marked in bold-italic are above one or more reference doses***

Yellow: Inorganic contaminants detected at least once higher than one guideline value

Blue: Organic contaminants detected at least once higher than one order of magnitude lower than one guideline value

**Table 7. Oral Minimal Risk Levels (MRLs) for seven elements**

<b>Substance</b>	<b>Minimal Risk Level</b>	<b>Identified Endpoint</b>
<i>Aluminum</i>	Int. 1.0 mg/kg/day	Neurologic
	Chr. 1.0 mg/kg/day	Neurologic
<i>Arsenic</i>	Acute 0.005 mg/kg/day	Gastrointestinal
	Chr. 0.0003 mg/kg/day	Dermal
<i>Barium, soluble salts</i>	Int. 0.2 mg/kg/day	Renal
	Chr. 0.2 mg/kg/day	Renal
<i>Chromium (VI)</i>	Int. 0.005 mg/kg/day	Heme
	Chr. 0.001 mg/kg/day	Gastrointestinal
<i>Fluoride, Sodium</i>	Chr. 0.05 mg/kg/day	Musculoskeletal
<i>Selenium</i>	Chr. 0.005 mg/kg/day	Dermal
<i>Strontium</i>	Int. 2 mg/kg/day	Musculoskeletal

\*Values and endpoints adapted from ATSDR, available at [http://www.atsdr.cdc.gov/mrls/mrls\\_list.html](http://www.atsdr.cdc.gov/mrls/mrls_list.html)

**Table 8. U.S. Population Mean Daily Arsenic Exposures**

<b>Daily Total Arsenic Exposures</b>		
	<b><i>Adult Females (<math>\mu\text{g}/\text{d}</math>)</i></b>	<b><i>Adult Males (<math>\mu\text{g}/\text{d}</math>)</i></b>
<b>Mean</b>	50.6	58.5
<b>Range</b>	1.01 – 1,081	0.21 – 1,276

*From ATSDR Toxicological Profile for Arsenic (ATSDR, 2007)*

**Table 9. Arsenic Oral Intake Guidelines**

<b>Arsenic Guidelines</b>	<b>Oral Intake</b>
Acute MRL	0.005 mg/Kg/d (14d)
MCLG (chronic MRL, also RfD)	0.0003 mg/Kg/d ( $\geq 365$ d) <sup>+</sup>
LOAEL	0.05 mg/Kg/d*
NOAEL (ATSDR)	0.0008 mg/Kg/d
DWEL	0.01 mg/Kg/d

<sup>+</sup>From ATSDR, *Toxicological Profile for Arsenic* (ATSDR, 2007)

\*Based on Japanese reports of contaminated soy oil.

**Table 10. Tolerable Upper Intake Level for Selenium**

<b>Population Group</b>	<b>Selenium UL (in µg/d)*</b>
Men	0.055
Women	0.055
Pregnant women	0.060
Lactating women	0.070
Infants (0-6 months)	0.015
Infants (7-12 months)	0.020
Children (1-3 years)	0.020
Children (4-8 years)	0.030
Children (9-18 years)	0.040

*\*WHO UL and FDA RDS's for daily intake correspond for selenium.*

**Table 11. USEPA Selenium Guidelines**

<b>Selenium Guidelines</b>	<b>mg/L</b>
MCLG	0.50
MCL	0.05
DWEL	0.20
Health Advisory – Lifetime	0.05
Groundwater monitoring (PQL)	0.75 (750 µg/L)
Groundwater monitoring (concentration limits)	0.01
EPA water-quality standards:	
Freshwater maximum	0.20 (200 µg/L)
Freshwater continuous	0.05 (50 µg/L)



**Table 12. Municipal Water Measurements**

<b>Municipal Water System Size</b>	<b>Surface/Groundwater source?</b>	<b>Measures Taken</b>	<b>Periodicity</b>
<b>Very Small (population 25-500)</b>	Surface Water and Groundwater	Total Coliform	One sample per month. TNCWS and NTNCWS one sample per quarter.
	Surface Water and Groundwater	Copper	Population 25-100: 5 samples / Monitoring Period (MP). No reduced monitoring schedule. Population 101-500: 10 samples / MP, 5 samples / MP on reduced schedule. MP=6 month calendar period for two consecutive periods, then reduced to annual. After three years, one sample taken per three years if copper action level is not met.
	Surface Water and Groundwater	Lead	Population 25-100: 5 samples / Monitoring Period (MP). No reduced monitoring schedule. Population 101-500: 10 samples / MP, 5 samples / MP on reduced schedule. MP=6 month calendar period for two consecutive periods, then reduced to annual. After three years, one sample taken per three years if lead action level is not met.
	Surface Water and Groundwater	All secondary Drinking Water Contaminants	Not enforced in West Virginia
	Surface Water and Groundwater	Turbidity	Sampled every four hours or continuously dependent on filter type.
	Surface Water	Inorganic contaminants	One sample per nine years if the treatment entity has a waiver or one sample annually if the

Groundwater	Inorganic contaminants	treatment entity has no waiver One sample per nine years if the treatment entity has a waiver or one sample every three years if the treatment entity has no waiver
Surface Water and Groundwater	Synthetic Organic Contaminants	No sampling required if the treatment entity has a waiver or one sample every three years if no waiver
Surface Water	Volatile Organic Contaminants	One sample every nine years if the treatment entity has a waiver or one sample every year if no waiver
Groundwater	Volatile Organic Contaminants	One sample required every nine years if the treatment entity has a waiver or one sample every three years if no waiver
Surface Water and Groundwater	Nitrate	One sample every year if there were four quarters of results <1/2 of MCL. Groundwater sources may be reduced to one sample every two years.
Surface Water and Groundwater	Nitrite	Systems must monitor at a frequency specified by the primacy agency if <1/2 of MCL OR one sample per year if consistently below MCL OR one sample per quarter if >1/2 MCL
Surface Water and Groundwater	Radionuclides	Quarterly samples for the first year of treatment, then one sample per nine years if < detection limit OR one sample every six years if greater than detection limits OR one sample every three years if >50% of MCL, but still below MCL.

**Small (population 501-3,300)**

Surface Water and Groundwater	Asbestos	No sampling required if the treatment entity has a waiver or one sample every nine years if no waiver
Surface Water and Groundwater	Disinfection Byproducts	Varies by monitored parameter.
Surface Water	Total Coliform	Population 501-1,000: One sample per month. TNCWS and NTNCWS one sample per quarter. Population 1,001-3,300: Two-three samples/month
Surface Water and Groundwater	Copper	20 samples/Monitoring Period (MP). Reduced monitoring schedule: 10 samples/MP. MP=6 month calendar period for two consecutive periods, then reduced to annual. After three years, one sample taken per three years if copper action level is not met.
Surface Water and Groundwater	Lead	20 samples/Monitoring Period (MP). Reduced monitoring schedule: 10 samples/MP. MP=6 month calendar period for two consecutive periods, then reduced to annual. After three years, one sample taken per three years if lead action level is not met.
Surface Water and Groundwater	All secondary Drinking Water Contaminants	Not enforced in West Virginia.
Surface Water and Groundwater	Turbidity	Sampled every four hours or continuously dependent on filter type.
Surface Water	Inorganic contaminants	One sample per nine years if the treatment entity has a waiver or one sample annually if the treatment entity has no waiver

Groundwater	Inorganic contaminants	One sample per nine years if the treatment entity has a waiver or one sample every three years if the treatment entity has no waiver
Surface Water and Groundwater	Synthetic Organic Contaminants	No sampling required if the treatment entity has a waiver or one sample every three years if no waiver
Surface Water	Volatile Organic Contaminants	One sample every nine years if the treatment entity has a waiver or one sample every year if no waiver
Groundwater	Volatile Organic Contaminants	One sample every nine years if the treatment entity has a waiver or one sample every three years if no waiver
Surface Water and Groundwater	Nitrate	One sample every year if there were four quarters of results <1/2 of MCL. Groundwater sources may be reduced to one sample every two years.
Surface Water and Groundwater	Nitrite	Systems must monitor at a frequency specified by the primacy agency if <1/2 of MCL OR one sample per year if consistently below MCL OR one sample per quarter if >1/2 MCL
Surface Water and Groundwater	Radionuclides	Quarterly samples for the first year of treatment, then one sample per nine years if < detection limit OR one sample every six years if greater than detection limits OR one sample every three years if >50% of MCL, but still below MCL.
Surface Water and Groundwater	Asbestos	No sampling required if the treatment entity has a waiver or

<b>Medium (3,301-10,000)</b>	Surface Water and Groundwater	Disinfection Byproducts	one sample every nine years if no waiver
	Surface Water	Total Coliform	Varies by monitored parameter. Four-10 samples/month depending on served population
	Surface Water and Groundwater	Copper	40 samples/Monitoring Period (MP). Reduced monitoring schedule: 20 samples/MP. MP=6 month calendar period for two consecutive periods, then reduced to annual. After three years, one sample taken per three years if copper action level is not met.
	Surface Water and Groundwater	Lead	40 samples/Monitoring Period (MP). Reduced monitoring schedule: 20 samples/MP. MP=6 month calendar period for two consecutive periods, then reduced to annual. After three years, one sample taken per three years if lead action level is not met.
	Surface Water and Groundwater	All secondary Drinking Water Contaminants	Not enforced in West Virginia
	Surface Water and Groundwater	Turbidity	Sampled every four hours or continuously dependent on filter type.
	Surface Water	Inorganic contaminants	One sample per nine years if the treatment entity has a waiver or one sample annually if the treatment entity has no waiver
	Groundwater	Inorganic contaminants	One sample per nine years if the treatment entity has a waiver or one sample every three years if the treatment entity has no waiver
	Surface Water and Groundwater	Synthetic Organic Contaminants	Two samples taken in two quarters

			not more than one year apart in a three year period. Can be reduced to one sample per nine years.
	Surface Water	Volatile Organic Contaminants	One sample every nine years if the treatment entity has a waiver or one sample every year if no waiver
	Groundwater	Volatile Organic Contaminants	One sample every nine years if the treatment entity has a waiver or one sample every three years if no waiver
	Surface Water and Groundwater	Nitrate	One sample every year if there were four quarters of results <1/2 of MCL. Groundwater sources may be reduced to one sample every two years.
	Surface Water and Groundwater	Nitrite	Systems must monitor at a frequency specified by the primacy agency if <1/2 of MCL OR one sample per year if consistently below MCL OR one sample per quarter if >1/2 MCL
	Surface Water and Groundwater	Radionuclides	Quarterly samples for the first year of treatment, then one sample per nine years if < detection limit OR one sample every six years if greater than detection limits OR one sample every three years if >50% of MCL, but still below MCL.
	Surface Water and Groundwater	Asbestos	No sampling required if the treatment entity has a waiver or one sample every nine years if no waiver
	Surface Water and Groundwater	Disinfection Byproducts	Varies by monitored parameter.
<b>Large (10,001-100,000)</b>	Surface Water	Total Coliform	10-100 samples/month depending

Surface Water and Groundwater	Copper	on served population 60 samples/Monitoring Period (MP). Reduced monitoring schedule: 30 samples/MP. MP=6 month calendar period for two consecutive periods, then reduced to annual. After three years, one sample taken per three years if copper action level is not met.
Surface Water and Groundwater	Lead	60 samples/Monitoring Period (MP). Reduced monitoring schedule: 30 samples/MP. MP=6 month calendar period for two consecutive periods, then reduced to annual. After three years, one sample taken per three years if lead action level is not met.
Surface Water and Groundwater	All secondary Drinking Water Contaminants	Not enforced in West Virginia
Surface Water and Groundwater	Turbidity	Sampled every four hours or continuously dependent on filter type.
Surface Water	Inorganic contaminants	One sample per nine years if the treatment entity has a waiver or one sample annually if the treatment entity has no waiver
Groundwater	Inorganic contaminants	One sample per nine years if the treatment entity has a waiver or one sample every three years if the treatment entity has no waiver
Surface Water and Groundwater	Synthetic Organic Contaminants	Two samples taken in two quarters not more than one year apart in a three year period. Can be reduced to one sample per nine years.
Surface Water	Volatile Organic Contaminants	One sample every nine years if the treatment entity has a waiver or

<b>Very Large (100,001+)</b>	Groundwater	Volatile Organic Contaminants	one sample every year if no waiver One sample every nine years if the treatment entity has a waiver or one sample every three years if no waiver
	Surface Water and Groundwater	Nitrate	One sample every year if there were four quarters of results <1/2 of MCL. Groundwater sources may be reduced to one sample every two years.
	Surface Water and Groundwater	Nitrite	Systems must monitor at a frequency specified by the primacy agency if <1/2 of MCL OR one sample per year if consistently below MCL OR one sample per quarter if >1/2 MCL
	Surface Water and Groundwater	Radionuclides	Quarterly samples for the first year of treatment, then one sample per nine years if < detection limit OR one sample every six years if greater than detection limits OR one sample every three years if >50% of MCL, but still below MCL.
	Surface Water and Groundwater	Asbestos	No sampling required if the treatment entity has a waiver or one sample every nine years if no waiver
	Surface Water and Groundwater	Disinfection Byproducts	Varies by monitored parameter.
	Surface Water	Total Coliform	100 - 480 samples/month depending on served population
	Surface Water and Groundwater	Copper	100 samples/Monitoring Period (MP). Reduced monitoring schedule: 50 samples/MP. MP=6 month calendar period for two consecutive periods, then reduced to annual.



Surface Water and Groundwater	Lead	After three years, one sample taken per three years if copper action level is not met. 100 samples/Monitoring Period (MP). Reduced monitoring schedule: 50 samples/MP. MP=6 month calendar period for two consecutive periods, then reduced to annual. After three years, one sample taken per three years if lead action level is not met.
Surface Water and Groundwater	All secondary Drinking Water Contaminants	Not enforced in West Virginia
Surface Water and Groundwater	Turbidity	Sampled every four hours or continuously dependent on filter type.
Surface Water	Inorganic contaminants	One sample per nine years if the treatment entity has a waiver or one sample annually if the treatment entity has no waiver
Groundwater	Inorganic contaminants	One sample per nine years if the treatment entity has a waiver or one sample every three years if the treatment entity has no waiver
Surface Water and Groundwater	Synthetic Organic Contaminants	Two samples taken in two quarters not more than one year apart in a three year period. Can be reduced to one sample per nine years.
Surface Water	Volatile Organic Contaminants	One sample every nine years if the treatment entity has a waiver or one sample every year if no waiver
Groundwater	Volatile Organic Contaminants	One sample every nine years if the treatment entity has a waiver or one sample every three years if no

<b>Private Wells-not regulated by the EPA</b>	Surface Water and Groundwater	Nitrate	waiver One sample every year if there were four quarters of results <1/2 of MCL. Groundwater sources may be reduced to one sample every two years.
	Surface Water and Groundwater	Nitrite	Systems must monitor at a frequency specified by the primacy agency if <1/2 of MCL OR one sample per year if consistently below MCL OR one sample per quarter if >1/2 MCL
	Surface Water and Groundwater	Radionuclides	Quarterly samples for the first year of treatment, then one sample per nine years if < detection limit OR one sample every six years if greater than detection limits OR one sample every three years if >50% of MCL, but still below MCL.
	Surface Water and Groundwater	Asbestos	No sampling required if the treatment entity has a waiver or one sample every nine years if no waiver
	Surface Water and Groundwater	Disinfection Byproducts	Varies by monitored parameter.
	Groundwater	EPA recommends testing for nitrates and coliform bacteria. Other testing is dependent on where in the United States the landowner resides	Test for nitrates and coliform bacteria annually. Test for other parameters as needed.

**Table 13. Inorganic chemical analyses of coal slurry liquids from five processing plants. Both dissolved and total amounts are given. All data are in mg/L. ND=Non-Detect: below detection limit. Yellow shading=exceeds primary drinking water standard. Pink shading=exceeds secondary drinking water standard. The MCLG for arsenic and lead is zero.**

	Southern Minerals		Load Out LLC		Panther LLC		Power Mountain LLC		Coresco	
	SM-Slurry (Liquid)		LL Slurry (Liquid)		PL-Slurry (Liquid)		PM-Slurry (Liquid)		CL-Slurry Liquid	
	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total	Dissolved	Total
Aluminum	0.195	0.651	0.15	2.37	0.029	0.046	0.509	0.564	0.532	0.644
Antimony	0.022	0.0215	0.0042	0.0047	0.0146	0.016	0.0004	0.0005	0.0069	0.0071
Arsenic	0.0039	0.0043	0.0042	0.0047	0.0104	0.0113	ND	ND	ND	ND
Barium	0.0809	0.114	0.0974	0.133	0.243	0.269	0.0523	0.0634	0.0677	0.0713
Beryllium	0.0002	0.0004	ND	ND	ND	ND	ND	ND	ND	ND
Cadmium	ND	ND			ND	0.0011	ND	ND	ND	ND
Calcium	51.4	51.7	62.1	63.7	2.83	3.51	124	123	111	115
Chromium	0.0013	0.0016	ND	ND	0.0272	0.0342	ND	ND	ND	ND
Cobalt	0.0021	0.0024	ND	0.0016	0.0142	0.0161	0.0037	39	0.0027	0.0029
Copper	0.0012	0.0018	0.0016	0.0034	0.0248	0.0278	0.0015	0.0016	0.0021	0.0021
Iron	ND	0.91	ND	0.828	0.068	0.089	0.03	0.195	ND	0.174
Lead	ND	0.0008	ND	0.0016	0.0762	0.0775	ND	0.0004	ND	ND
Magnesium	20.8	21	19.8	120.6	0.591	0.771	81.4	82.2	38.9	40
Manganese	0.0141	0.0177	0.086	0.097	0.021	0.028	0.921	0.921	0.133	0.138
Mercury	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Molybdenum	0.0176	0.0178	0.0447	0.0466	0.198	0.217	0.0023	0.0024	0.029	0.0297
Nickel	0.0043	0.0052	0.0067	0.0073	0.0386	0.0432	0.0092	0.0096	0.0073	0.0074
Potassium	6.9	7.07	13.9	14.3	5.38	7.05	15.5	15.5	5.01	5.16
Selenium	0.0082	0.0082	0.0268	0.0278	0.0224	0.0255	0.0057	0.0059	0.0024	0.0024
Silicon	3.3	3.76	2.3	8.54	0.346	0.358	3.27	5.31	1.14	3.91
Silver	ND	ND	ND	ND	ND	ND	0.0006	0.0006	ND	ND
Sodium	58.8	55.5	265	267	266	341	236	237	272	279
Strontium	1.16	1.17	1.44	1.47	0.571	0.632	1.63	1.74	3.19	3.27
Thallium	ND	0.0002	0.0003	0.0004	ND	ND	0.0002	0.0003	ND	0.0002
Vanadium	0.0018	0.0021	0.0013	0.0025	0.0103	0.0131	ND	ND	ND	ND
Zinc	0.016	0.027	ND	0.008	0.019	0.014	0.032	0.041	ND	ND

From An Evaluation of the Underground Injection of Coal Slurry in West Virginia Phase I: Environmental Investigation (WVDEP, 2009).

Table 14. Solid Phase Coal and Slurry Organic Composition for Six Study Areas

Analyte	Unit	Loadlout, LLC		Panther	
		Slurry Solid	Coal	Slurry Solid	Coal
TPH (Diesel Range)	mg/Kg	282	746	144	NA
TPH (Oil Ranger)	mg/Kg	469	525	159	NA
<b>Volatile Organic Compounds</b>					
1,2,4-Trimethylbenzene (C9H12)	ug/kg	ND	64.1	216	NA
1,3,5-Trimethylbenzene (C9H12)	ug/kg	ND	60.1	76.8	NA
Acetone (C3H7O)	ug/kg	267	ND	ND	NA
Acrolein (C3H4O)	ug/kg	ND	ND	ND	NA
Benzene (C6H6)	ug/kg	ND	16.6	166	NA
Carbon disulfide (CS2)	ug/kg	ND	36.7	ND	NA
Chloromethane (CH3Cl)	ug/kg	ND	ND	ND	NA
Ethylbenzene (C8H10)	ug/kg	ND	24.9	122	NA
Isopropylbenzene (C9H10)	ug/kg	ND	62.2	30.2	NA
m,p-Xylene (C8H10)	ug/kg	ND	92.6	585	NA
Methylene chloride (CH2Cl2)	ug/kg	ND	ND	ND	NA
Naphthalene (C10H8)	ug/kg	ND	ND	259	NA
n-Propylbenzene (C9H12)	ug/kg	ND	ND	45.5	NA
o-Xylene (C8H10)	ug/kg	ND	53	284	NA
sec-Butylbenzene (C10H14)	ug/kg	ND	ND	8.5	NA
Toluene (C7H8)	ug/kg	27.6	205	1040	NA
<b>Semivolatile Organic Compounds</b>					
2,4-Dimethylphenol (C8H10O)	mg/Kg	0.482	1.24	0.167	NA
Acenaphthene (C12H10)	mg/Kg	0.07	0.227	ND	NA
Benzo(a)anthracene (C18H12)	mg/Kg	0.136	0.563	0.036	NA
Benzo(a)pyrene	mg/Kg	0.162	0.834	0.07	NA
Benzo(b)fluoranthene (C20H12)	mg/Kg	0.176	0.859	0.082	NA
Benzo(g,h,i)perylene (C22H12)	mg/Kg	0.513	2.07	0.155	NA
Benzo(k)fluoranthene (C20H12)	mg/Kg	0.065	0.298	ND	NA
Bis(2-ethylhexyl)phthalate (C24H38O4)	mg/Kg	ND	0.239	ND	NA
Chrysene (C18H12)	mg/Kg	0.198	0.76	0.206	NA
Dibenzo(a,h)anthracene (C22H14)	mg/Kg	0.042	0.251	0.032	NA
Fluoranthene (C16H10)	mg/Kg	0.119	0.525	0.07	NA
Fluorene (C13H10)	mg/Kg	0.184	0.675	0.202	NA
Indeno(1,2,3-c,d)pyrene (C22H12)	mg/Kg	0.074	0.371	ND	NA
m,p-Cresol (C7H8O)	mg/Kg	0.21	0.428	0.089	NA
Napthalene (C10H8)	mg/Kg	2.69	9.61	1.5	NA
Nitrobenzene (C6H5NO3)	mg/Kg	ND	ND	ND	NA
n-Nitrosodiphenylamine	mg/Kg	0.171	ND	ND	NA

o-Cresol (C7H8O)	mg/Kg	0.207	0.434	ND	NA
Phenanthrene (C14H10)	mg/Kg	0.947	3.77	0.903	NA
Phenol (C7H6O)	mg/Kg	0.068	0.087	0.045	NA
Pyrene (C16H10)	mg/Kg	0.225	0.966	0.095	NA

ND = Not Detected

NA = Not Analyzed

Analyte	Unit	Southern Mineral		Power Mountain	
		Slurry Solid	Coal	Slurry Solid	Coal
TPH (Diesel Range)	mg/Kg	280	NA	222	927
TPH (Oil Ranger)	mg/Kg	391	NA	382	782
<b>Volatile Organic Compounds</b>					
1,2,4-Trimethylbenzene (C9H12)	ug/kg	ND	NA	25.2	398
1,3,5-Trimethylbenzene (C9H12)	ug/kg	ND	NA	ND	183
Acetone (C3H7O)	ug/kg	ND	NA	ND	ND
Acrolein (C3H4O)	ug/kg	ND	NA	ND	ND
Benzene (C6H6)	ug/kg	ND	NA	ND	330
Carbon disulfide (CS2)	ug/kg	ND	NA	ND	ND
Chloromethane (CH3Cl)	ug/kg	ND	NA	ND	ND
Ethylbenzene (C8H10)	ug/kg	ND	NA	ND	139
Isopropylbenzene (C9H10)	ug/kg	ND	NA	29.9	132
m,p-Xylene (C8H10)	ug/kg	ND	NA	44.6	976
Methylene chloride (CH2Cl2)	ug/kg	ND	NA	ND	23.2
Naphthalene (C10H8)	ug/kg	ND	NA	34.4	99.3
n-Propylbenzene (C9H12)	ug/kg	ND	NA	ND	61
o-Xylene (C8H10)	ug/kg	ND	NA	28.7	473
sec-Butylbenzene (C10H14)	ug/kg	ND	NA	ND	ND
Toluene (C7H8)	ug/kg	ND	NA	51.6	8670
<b>Semivolatile Organic Compounds</b>					
2,4-Dimethylphenol (C8H10O)	mg/Kg	ND	NA	ND	0.466
Acenaphthene (C12H10)	mg/Kg	ND	NA	ND	0.072
Benzo(a)anthracene (C18H12)	mg/Kg	ND	NA	ND	0.127
Benzo(a)pyrene	mg/Kg	0.167	NA	0.463	0.329
Benzo(b)fluoranthene (C20H12)	mg/Kg	ND	NA	ND	0.261
Benzo(g,h,i)perylene (C22H12)	mg/Kg	0.092	NA	0.346	0.982
Benzo(k)fluoranthene (C20H12)	mg/Kg	0.191	NA	ND	0.278
Bis(2-ethylhexyl)phthalate (C24H38O4)	mg/Kg	ND	NA	ND	0.217
Chrysene (C18H12)	mg/Kg	0.528	NA	0.248	1.16
Dibenzo(a,h)anthracene (C22H14)	mg/Kg	ND	NA	ND	0.183
Fluoranthene (C16H10)	mg/Kg	0.078	NA	0.144	0.288
Fluorene (C13H10)	mg/Kg	0.327	NA	0.18	0.852

Indeno(1,2,3-c,d)pyrene (C22H12)	mg/Kg	ND	NA	ND	0.175
m,p-Cresol (C7H8O)	mg/Kg	ND	NA	ND	0.175
Napthalene (C10H8)	mg/Kg	0.069	NA	1.41	7.54
Nitrobenzene (C6H5NO3)	mg/Kg	ND	NA	ND	ND
n-Nitrosodiphenylamine	mg/Kg	ND	NA	ND	ND
o-Cresol (C7H8O)	mg/Kg	ND	NA	ND	0.224
Phenanthrene (C14H10)	mg/Kg	0.949	NA	1.09	4.99
Phenol (C7H6O)	mg/Kg	ND	NA	ND	0.075
Pyrene (C16H10)	mg/Kg	0.136	NA	1.69	0.447

ND = Not Detected

NA = Not Analyzed

Analyte	Unit	Cresco		Marfork	
		Slurry Solid	Coal	Slurry Solid	Coal
TPH (Diesel Range)	mg/Kg	712	1020	179	535
TPH (Oil Ranger)	mg/Kg	765	740	258	640
		<b>Volatile Organic Compounds</b>			
1,2,4-Trimethylbenzene (C9H12)	ug/kg	87.9	86.9	26.7	166
1,3,5-Trimethylbenzene (C9H12)	ug/kg	35.4	78.6	22.6	94.3
Acetone (C3H7O)	ug/kg	ND	398	ND	ND
Acrolein (C3H4O)	ug/kg	ND	356	ND	ND
Benzene (C6H6)	ug/kg	ND	ND	ND	ND
Carbon disulfide (CS2)	ug/kg	ND	ND	ND	ND
Chloromethane (CH3Cl)	ug/kg	ND	ND	ND	ND
Ethylbenzene (C8H10)	ug/kg	20.2	ND	ND	24.5
Isopropylbenzene (C9H10)	ug/kg	107	162	34.4	100
m,p-Xylene (C8H10)	ug/kg	71.4	44.4	ND	163
Methylene chloride (CH2Cl2)	ug/kg	ND	ND	ND	ND
Napthalene (C10H8)	ug/kg	ND	ND	40.4	ND
n-Propylbenzene (C9H12)	ug/kg	22	ND	ND	23.7
o-Xylene (C8H10)	ug/kg	72.6	66.8	ND	114
sec-Butylbenzene (C10H14)	ug/kg	ND	ND	ND	ND
Toluene (C7H8)	ug/kg	64.3	25.1	ND	178
		<b>Semivolatile Organic</b>			

		Compounds			
<b>2,4-Dimethylphenol (C8H10O)</b>	mg/Kg	ND	ND	ND	0.424
<b>Acenaphthene (C12H10)</b>	mg/Kg	ND	ND	ND	0.197
<b>Benzo(a)anthracene (C18H12)</b>	mg/Kg	ND	ND	ND	ND
<b>Benzo(a)pyrene</b>	mg/Kg	0.747	0.797	ND	0.231
<b>Benzo(b)fluoranthene (C20H12)</b>	mg/Kg	ND	ND	0.087	0.227
<b>Benzo(g,h,i)perylene (C22H12)</b>	mg/Kg	ND	ND	0.098	0.42
<b>Benzo(k)fluoranthene (C20H12)</b>	mg/Kg	ND	ND	ND	0.213
<b>Bis(2-ethylhexyl)phthalate (C24H38O4)</b>	mg/Kg	ND	ND	ND	0.227
<b>Chrysene (C18H12)</b>	mg/Kg	0.73	0.873	0.32	1.1
<b>Dibenzo(a,h)anthracene (C22H14)</b>	mg/Kg	ND	ND	ND	0.132
<b>Fluoranthene (C16H10)</b>	mg/Kg	ND	ND	0.096	0.348
<b>Fluorene (C13H10)</b>	mg/Kg	0.843	1.14	0.135	1.04
<b>Indeno(1,2,3-c,d)pyrene (C22H12)</b>	mg/Kg	ND	ND	ND	0.08
<b>m,p-Cresol (C7H8O)</b>	mg/Kg	ND	ND	ND	0.151
<b>Napthalene (C10H8)</b>	mg/Kg	4.1	5.24	0.234	4.8
<b>Nitrobenzene (C6H5NO3)</b>	mg/Kg	ND	ND	ND	ND
<b>n-Nitrosodiphenylamine</b>	mg/Kg	ND	ND	ND	ND
<b>o-Cresol (C7H8O)</b>	mg/Kg	ND	ND	ND	0.229
<b>Phenanthrene (C14H10)</b>	mg/Kg	4.22	6.2	0.604	4.76
<b>Phenol (C7H6O)</b>	mg/Kg	ND	ND	ND	ND
<b>Pyrene (C16H10)</b>	mg/Kg	ND	ND	0.121	0.462

ND = Not Detected

NA = Not Analyzed



**Table 15. Comparison to Historic Minimum and Maximum Concentrations of Trace Elements in West Virginia Coal Refuse (Wewerka et al., 1976)**

Element	Minimum Concentration (mg/L)	Maximum Concentration (mg/L)
Be	0.2	3
Na	150	375
Mg	500	8000
Al %	>2..5	--
Si %	>2.5	--
K	500	1200
Ca	50	2000
Sc	3	25
Ti	300	3000
V	25	250
Cr	3	25
Mn	65	1300
Fe %	0.75	4.1
Co	3	25
Ni	25	250
Cu	12	50
Zn	30	85
Ga	3	25
Y	3	25
Zr	3	25
Ag	0.3	2.5
Cd	0.25	1
Pb	20	150

**Table 16. Comparison of Coal, Fresh Coal Waste, and Weathered Coal Waste (NAS, 1975)**

<b>Parameter</b>	<b>Coal</b>	<b>Fresh Waste</b>	<b>Weathered Waste</b>
Specific Gravity	1.23-1.72	Varies considerably from pile to pile range = 1.6-2.7 average = 2.2	Varies considerably, primarily by coal content range = 1.4-2.7 average = 2.0
Size	Varies; dust - 6 inches	Size range variable, but the pile is usually well-graded Coarse: normally 4 in., rarely 8 in.	More fines and fine coal than coarse refuse
Moisture Content	range 1- 40% average 3 - 6%	Dry refuse 5 - 10% Prep plant refuse 10-40% Slurries and sludge 25 - 70% (30% solids)	10 - 20%
Carbon & volatile content (dry basis)	80 - 95%	range 7 - 25%	10 - 45%
BTU per pound	10,000 - 15,000	1,500 - 6,000	Higher BTU in general than fresh refuse: 3,000 - 10,000
Sulfur content	1 - 5%	range 3 - 15% average 5 - 10%	Less sulfur the longer the refuse is leached
Permeability	in situ: $10^{-1}$ - $10^{-3}$ cm/s	Uncompacted - high permeability Compacted: $10^{-2}$ - $10^{-4}$ cm/s	High permeability; varies with the configuration of the pile
Shear Strength	block of coal: 200 - 1,000 psi average 700 psi	Angle of drained shearing resistance 25.5° - 41.5° average = 30° compacted = higher angle	average drained shearing strength 30° saturated average 11°
Compressive Strength	500 - 6,000 lb/in <sup>2</sup>	100 - 500 psi compacted	50 - 150 psi
Drained Cohesive Strength	N/A	Zero	Zero
Ash	range 3 - 12% average 8%	----	----
Other Constituents	Clay, silica, carbonates	Primarily - clays, micas, carbonaceous materials  Often - quartz, pyrite, hematite	The same as fresh refuse with slag material and sulfates

		<p>Occasionally - calcite, ankerite, apatite, garnet, rutile, sphene, tourmaline, and zircon</p> <p>Primarily - silica, aluminum, carbon</p> <p>Secondarily - calcium, sulfur, magnesium, sodium, iron, potassium</p> <p>Occasionally - manganese, phosphorous</p> <p>Rarely - copper, nickel, zinc</p>	
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**Table 17. Summary of Historical and Current Water Quality Data for the Panther site: Wet Branch (WVDEP, 2009). \*= Samples that were taken before slurry injection. NS=Not Sampled. Data above the red line are upstream samples and data below the red line are downstream samples**

Site*	Date	pH	Acidity	Alkalinity	TSS	Total Iron	Sulfate	EC
	Range	s.u.	mg/L	mg/L	mg/L	mg/L	mg/L	μS/cm
*Site 001	May-Nov 1981	6.1-7.7	0-16	3-176	8-234	0.1-0.15	NS	NS
*USWB	Dec '94-Jan '95	6.29-8.4	2.0-40	<0.2-8	1.0-19	<0.01- 0.59	35-108	123-463
*Site 002	May-Nov 1981	6.6-8.3	0-4	7.0-17	1.0-15	<0.02-68	NS	NS
*DSWB	Dec '94-Jan '95	6.9-7.37	<0.2-4	8.0-24	1.0-65	0.19-0.83	73-205	188-525
PL-4	1/23/2008	7.21	1-Jan	32.8	2	0.053	106	463

**Table 18. Historic data from the Twentymile Creek watershed. NS=Not Sampled. ND=Not Detected**

Site	Date	pH	EC	Alk.	Acidity	TSS	Fe	Mn	Al	SO <sub>4</sub>	TDS
			us/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
#9	6/1/83	6.43	101.99	20	16	10	0.05	10	0	26.32	52
#10	6/1/83	6.7	117.18	10	0	10	0.12	0	NS	30.24	NS
	3/12/84	7.2	110.58	25	3	4	0.17	0.19	NS	27.2	NS
USTC	12/13/03	6.66	NS	NS	NS	NS	0.06	NS	NS	NS	95
	6/15/04	6.61	266	12.93	ND	6	0.01	0.01	ND	108.14	392

**Table 19. Summary of Drinking Water Supply Analyses Conducted by Wheeling Jesuit University (WJU) in 2004 and 2005. Analyses exceeding either primary (yellow) or secondary (tan) USEPA drinking water standards or MCL guidelines (blue) are indicated**

Type	1	pressure tank sludge
	2	downstream of pressure tank
	3	how water tank sludge
	4	Other
	5	domestic well

	primary	0	0	15	10	2000	50	5	100	4	2	1300	6
	secondary												
	MCL guidelines			0	0								
id	type	Coliforms *		Pb	As	Ba	Se	Cd	Cr	Be	Tl	Cu	Sb
		fecal	total	ppb	ppb	ppb	ppb	Ppb	ppb	ppb	ppb	ppb	ppb
7526	1			4.8	4.5	677	2	0	4	0	0	248	0
4806	2	0	80	0.2	0.7	336	2	0	0	0	0	0	0
7383	2			0.1	1.0	477	2	0	0	0	0	1	0
7398	2	0	26	0.3	0.6	346	0	0	0	0	0	5	0
7375	2			0.4	0.7	340	1	0	0	0	0	1	0
4766	2			0.2	0.7	337	0	0	0	0	0	3	0
4796	2	6	1000	0.4	0.6	320	1	0	0	0	0	6	0
7393	2			0.0	0.7	367	1	0	0	0	0	2	0
7413	2			0.0	0.7	344	0	0	0	0	0	0	0
7407	2			0.2	0.6	340	0	0	0	0	0	1	0
7531	2			0.1	0.8	368	0	0	0	0	0	3	0
4831	3			188.0	150.0	3000	646	0	29	1		390	

4813	3			22.0	8.4	400	0	0	8	0		131	
4845	3			23.0	3.2	100	0	0	7	0		0	
7508	3			3.5	2.4	255	3	35	3	0	0	59	1
7406	4	0	8	0.1	0.5	484	0	0	0	0	0	2	0
4816	4			0.0	0	0	0	0	7	0		0	
4824	4			16.0	0.0	0	0	0	3	0		0	
4835	5			12.0	7.6	500	0	0	17	0		0	
4795	5	0	0	0.4	11.4	422	1	0	0	0	0	1	0
7506	5			2.1	0.1	62	0	6	0	1	0	226	0
7050	5	0	22	0.3	2.3	135	0	0	0	0	0	1	0
4798	5	0	12	0.2	8.2	255	1	0	0	0	0	1	0
4842bi	5			110.0	5.0	400	0	0	18	1		758	
7528	5			2.9	6.4	256	3	3	1	0	0	197	0
4817	5			0.0	0.0	300	0	0	0	0		53	
7529	5			2.5	2.0	339	2	1	1	0	0	143	0
4823	5			0.0	340.0	500	0	0	4	0		0	
7382	5	0	22	9.5	1.3	576	2	0	1	0	0	86	0
4801	5	196	1000	1.4	1.5	239	1	0	0	0	0	9	0
7404	5	2	1000	45.0	1.3	500	1	0	2	0	0	619	0
4808	5			10.0	0.0	200	0	0	6	0		0	
4799	5	0	0	0.3	1.4	144	1	0	0	0	0	6	0
7402	5	0	14	0.2	4.8	176	0	0	0	0	0	1	0
7392	5	0	0	0.5	3.8	133	4	0	5	0	0	3	0
4856	5			0.0	0.0	900	0	0	3	0		0	
7381	5	0	112	1.3	2.2	175	1	0	0	0	0	70	0
4977	5	4	8	0.8	2.7	483	0	0	0	0	0	2	0
4811	5	0	1000	12.1	0.8	342	1	0	1	0	0	119	0
4825	5			9.0	44.0	500	0	0	2	0		0	

7532	5			0.3	0.7	347	1	0	0	0	0	14	0
7523	5			1.7	0.5	79	0	0	0	0	0	23	0
7054	5	0	40	5.2	1.3	193	0	0	1	0	0	11	0
4827	5	6	1000	0.2	0.5	352	0	0	0	0	0	2	0
7538	5			5.1	1.2	213	0	0	1	0	0	5	0
4793	5	0	0	0.3	1.5	373	0	0	0	0	0	1	0
7397	5	50	1000	1.1	2.4	53	0	0	4	0	0	15	0
7035	5	26	1000	0.7	0.7	117	0	0	0	0	0	2	0
7242	5	0	8	0.1	0.5	1233	0	0	0	0	0	2	0
4829	5			10.0	4.2	200	0	0	4	0		0	
7127	5	0	2	0.3	0.1	234	0	0	0	0	0	7	0
7535	5			3.4	0.6	37	0	0	1	0	0	15	0
7384	5	2	1000	9.6	0.2	105	2	0	1	0	0	10	1
7390	5	114	1000	0.4	0.4	1235	0	0	0	0	0	8	0
7389	5	4	1000	34.0	1.9	347	0	0	0	0	0	116	0
4836	5			20.0	0.0	100	65	0	9	0		0	
7200	5			1.1	1.0	380	0	0	1	0	0	117	0
4790	5	96	1000	2.5	0.6	1218	0	0	0	0	0	2	0
4802	5			6.0	0.0	200	0	0	6	0		0	
4841	5			16.0	0.0	2400	0	0	0	0		0	
7022	5	0	14	1.4	0.6	1553	0	0	6	0	0	75	0
7326	5	0	112	0.4	7.7	2069	8	0	2	0	0	5	2
7224	5	20	68	16.8	0.2	441	0	0	0	0	0	758	1
7388	5	0	0	0.3	0.7	157	1	0	0	0	0	4	0
4844	5			19.0	0.0	0	0	0	7	0		0	
7323	5	0	16	1.3	0.6	744	0	0	1	0	0	2	0
7394	5	1000	1000	5.4	0.5	38	1	1	1	0	0	23	0
7449	5			0.8	0.1	152	1	0	1	0	0	10	0
7023	5			1.8	0.4	76	1	0	2	1	0	13	0
7163	5	0	10	0.2	0.4	748	0	0	0	0	0	12	0



7453	5			0.1	0.3	477	0	0	3	0	0	8	0	
7530	5			14.2	0.5	169	0	0	1	0	0	22	1	
4815	5	0	44	86.0	4.9	3802	2	0	0	0	0	34	0	
4826	5			16.0	0.0	100	0	0	4	0		0		
4803	5	0	114	0.1	0.6	8	1	0	0	0	0	1	0	
4838	5			30.0	0.0	0	0	0	24	7		0		
4852	5			0.0	0.0	500	0	0	0	0		0		
7092	5	18	1000	0.1	0.6	292	0	0	0	0	0	1	0	
7509	5			1.5	0.1	453	0	0	1	0	0	293	0	
7227	5	36	1000	0.3	0.1	84	1	1	1	1	0	38	0	
4797	5	6	114	1.3	0.2	59	1	0	1	0	0	5	0	
4807	5	0	74	2.2	0.4	26	2	0	0	0	0	64	0	
4821	5			0.0	0.0	0	0	0	0	0		0		
7527	5			6.9	0.2	620	1	0	0	0	0	127	0	
7524	5			0.4	0.6	393	0	0	0	0	0	3	0	
4822	5	0	66	0.3	0.2	62	1	0	0	0	0	8	0	
7539	5			0.3	0.0	514	0	0	1	0	0	1	0	
7072	5	368	1000	0.2	0.2	577	0	0	0	0	0	3	0	
7540	5			0.6	0.0	40	0	0	0	0	0	3	0	
7391	5	0	30	16.4	1.2	3	0	0	0	0	0	442	0	
4792	5	0	1000	0.6	0.1	48	1	0	0	0	0	6	0	
4809	5	0	52	0.4	0.2	74	2	0	0	0	0	4	0	
4818	5			0.0	0.0	700	0	0	0	0		0		
7232	5	1000	1000	4.3	0.2	115	0	0	0	0	0	20	0	
7324	5	18	1000	0.5	0.1	61	2	0	0	0	0	24	0	
4789	5	0	1000	0.2	0.1	548	0	0	0	0	0	1	0	
7525	5			1.2	0.1	37	0	0	0	0	0	6	0	
4819	5			0.0	0.0	400	0	0	0	0		0		
4824	5			16.0	0.0	0	0	0	3	0		0		
* only 5% of samples per month can exceed 0 colonies/100 ml														

	Primary								
	Secondary	300	50	0.50	200	6.5-	5000	100	2
	Guidelines					8.5			
		<b>Fe</b>	<b>Mn</b>	<b>TDS</b>	<b>Al</b>	<b>pH</b>	<b>Zn</b>	<b>Ag</b>	<b>Hg</b>
<b>id</b>	<b>type</b>	<b>ppb</b>	<b>ppb</b>	<b>g/L</b>	<b>ppb</b>		<b>ppb</b>	<b>ppb</b>	<b>ppb</b>
7526	1	6225	215		264		264	0	0
4806	2	591	57	0.64	26	7.7	3	0	0
7383	2	497	236		7		2	0	0
7398	2	321	76	0.65	10	7.4	8	0	0
7375	2	293	57	0.64	112	7.7	4	0	0
4766	2	243	63	0.66	19	7.9	3	0	0
4796	2	204	59	0.63	8	7.9	5	0	0
7393	2	143	102		5		1	0	0
7413	2	98	78		4		1	0	0
7407	2	92	51	0.58	7	7.7	2	0	0
7531	2	77	104	0.38	2	7.2	3	0	0
4831	3	557700	27260		200		2118		
4813	3	27327	387		70		388		
4845	3	25280	435		50		67		
7508	3	8608	48	0.66	105	7.4	105	0	0
7406	4	358	41	0.16	11	7.1	13	0	0
4816	4	14	0		0		0		
4824	4	0	35		30		0		

4835	5	57588	511		70		419		
4795	5	55901	1574	0.55	4	6.8	53	0	0
7506	5	41300	73	0.31	11	6.5	190	0	0
7050	5	28453	44	0.43	2	6.9	45	0	0
4798	5	25360	93	0.48	2	6.9	42	0	0
4842bi	5	25059	2953		50		5658		
7528	5	11948	323	0.34	34	6.2	592	0	0
4817	5	10550	308		60		49		
7529	5	9715	289	0.15	182	7.2	261	0	0
4823	5	9701	452		40		70		
7382	5	9154	239	0.66	118	7.4	14	0	0
4801	5	8550	307	0.20	36	6.4	122	0	0
7404	5	8229	355	0.71	333	6.9	39	0	0
4808	5	7586	2890		170		1000		
4799	5	6718	285	0.34	2	7.0	54	0	0
7402	5	6098	257	0.31	3	6.8	4	0	0
7392	5	5785	38	0.19	19	6.7	24	0	0
4856	5	5339	269		50		15		
7381	5	4807	1982	0.54	12	7.2	86	0	0
4977	5	4579	20	0.14	6	6.8	14	0	0
4811	5	4371	193	0.53	48	6.7	162	0	0
4825	5	4214	82		30		62		
7532	5	4183	81		1		182	0	0
7523	5	4070	38	0.24	13	6.6	98	0	0
7054	5	3989	182	0.15	313	6.8	133	0	0
4827	5	3341	336	0.23	19	6.6	14	0	0
7538	5	3311	33	0.26	364	6.5	680	0	0
4793	5	2938	1252	0.33	3	6.8	32	0	0
7397	5	2733	333	0.59	61	7.0	56	0	0

7035	5	2652	115	0.28	8	6.5	43	0	0
7242	5	2377	324	0.46	9	7.4	2	0	0
4829	5	2203	171		70		74		
7127	5	1854	210	0.29	2	7.1	351	0	0
7535	5	1759	52	0.07	672	5.8	39	0	0
7384	5	1693	291	0.52	10	6.9	59	0	0
7390	5	1656	156	0.46	4	7.5	84	0	0
7389	5	1655	322	0.26	8	7.0	93	0	0
4836	5	1569	2999		60		239		
7200	5	1276	56	0.71	92	8.2	35	0	0
4790	5	1271	346		91	7.3	62	0	0
4802	5	1257	67		60		137		
4841	5	1221	157		0		61		
7022	5	1207	152	0.42	29	7.0	22	0	0
7326	5	1169	2239	4.42	15	6.9	7	0	0
7224	5	1147	116	0.23	11	7.1	69	0	0
7388	5	1097	3266	0.24	9	6.9	202	2	0
4844	5	1015	57		0		48		
7323	5	880	179	0.31	288	7.2	10	0	0
7394	5	803	32	0.25	582	5.9	208	0	0
7449	5	643	50	0.56	2	7.3	3	0	0
7023	5	607	1614	0.43	1103	6.3	42	0	0
7163	5	541	137	0.29	8	7.6	10	0	0
7453	5	512	24	0.26	7	6.8	4	0	0
7530	5	487	3	0.31	5	8.0	560	0	0
4815	5	475	63	1.35	21	7.3	9	0	0
4826	5	473	55		0		26		
4803	5	454	3	0.46	2	7.3	9	0	0
4838	5	371	4063		8030		712		
4852	5	364	29		0		25		

7092	5	335	46	0.52	7	8.3	3	0	0
7509	5	323	144	0.27	16	7.1	63	0	0
7227	5	313	2257	0.42	439	6.3	165	0	0
4797	5	281	11	0.26	113	6.8	8	0	0
4807	5	281	45	0.61	5	6.1	97	0	0
4821	5	271	0		10		64		
7527	5	257	127	0.31	2	7.3	31	1	0
7524	5	256	53	0.32	1	7.5	12	0	0
4822	5	137	12	0.23	9	6.7	16	0	0
7539	5	136	140	0.27	3	7.1	61	0	0
7072	5	135	23	0.39	6	7.6	8	0	0
7540	5	134	29	0.09	77	5.2	73	0	0
7391	5	133	3	0.32	19	6.8	639	0	0
4792	5	131	1	0.35	7	6.3	17	0	0
4809	5	122	1	0.49	6	5.8	44	0	0
4818	5	120	23		60		0		
7232	5	88	6	0.15	69	6.8	16	0	0
7324	5	84	3	0.40	2	6.4	31	0	0
4789	5	81	67	0.37	6	7.9	5	0	0
7525	5	62	6	0.19	5	7.2	9	0	0
4819	5	39	52		50		0		
4824	5	0	35		30		0		

		No EPA Drinking water standards								
		<b>ORP</b>	<b>Mo</b>	<b>Ni</b>	<b>V</b>	<b>Co</b>	<b>Sr</b>	<b>Ti</b>	<b>Sn</b>	<b>U</b>
<b>id</b>	<b>type</b>	<b>mV</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>ppb</b>	<b>Ppb</b>
7526	1		2	5	1	2	1000	5	1	0

4806	2	-392	0	1	0	0	807	1	0	0
7383	2		1	1	0	0	872	1	0	0
7398	2	-288	0	0	0	0	685	0	0	0
7375	2		0	1	0	0	781	2	0	0
4766	2	-295	1	0	0	0	684	0	1	0
4796	2	-245	1	0	0	0	740	1	1	0
7393	2		1	0	0	0	804	0	1	0
7413	2		1	0	0	0	806	0	1	0
7407	2		0	0	0	0	666	0	1	0
7531	2	-111	1	0	0	0	825	0	1	0
4831	3			0	91	0	1210			
4813	3			0	0	0	680			
4845	3			0	22	0	660			
7508	3	48	2	10	1	1	0	3	1	0
7406	4	-168	0	1	0	0	517	0	0	0
4816	4			0	0	0	1500			
4824	4			0	10	0	700			
4835	5			0	0	0	0			
4795	5	-102	0	1	0	0	157	2	0	0
7506	5	-101	0	3	0	0	462	1	0	0
7050	5	-101	0	1	0	0	455	1	0	0
4798	5	-105	0	1	0	0	698	1	1	0

4842bi	5			0	0	0	0			
7528	5	-61	0	2	0	0	571	1	0	0
4817	5			0	13	0	760			
7529	5	-140	0	2	1	0	0	5	0	0
4823	5			0	0	0	600			
7382	5	-259	0	6	0	2	1424	1	4	0
4801	5	-5	0	2	0	1	253	1	0	0
7404	5	-237	0	12	0	6	1551	2	13	0
4808	5			0	0	0	0			
4799	5	-64	1	2	0	0	798	1	0	0
7402	5	-131	0	1	0	0	749	1	0	0
7392	5	153	0	6	0	4	796	1	0	0
4856	5			0	0	0	840			
7381	5	-211	0	1	0	0	543	1	1	0
4977	5	-15	1	1	0	1	471	1	1	0
4811	5	-198	0	2	0	0	918	1	1	0
4825	5			0	0	0	510			
7532	5		0	1	0	0	0	1	0	0
7523	5	54	0	9	0	1	2683	1	1	0
7054	5	-94	0	5	1	1	161	4	0	0
4827	5	6	0	1	0	0	535	1	0	0
7538	5	-78	0	2	1	1	0	7	1	0
4793	5	-30	0	2	0	0	214	1	0	0
7397	5	-71	1	4	0	0	3990	2	0	0
7035	5	136	0	1	0	0	206	1	0	0
7242	5	-115	0	0	0	0	1141	1	0	0

4829	5			0	0	0	640			
7127	5	-71	0	1	0	0	807	1	1	0
7535	5	97	0	2	2	1	0	6	0	0
7384	5	-118	0	2	0	0	3684	1	0	0
7390	5	43	0	1	0	0	1257	1	1	0
7389	5	-112	0	3	0	1	753	1	2	0
4836	5			0	16	0	0			
7200	5	-92	0	3	0	0	408	1	1	0
4790	5		0	5	0	1	1552	1	0	0
4802	5			0	0	0	650			
4841	5			0	0	0	2580			
7022	5	138	1	8	0	0	642	1	6	0
7326	5	62	0	5	0	1	9992	4	1	0
7224	5	-131	0	2	0	0	390	1	1	0
7388	5	1	0	1	0	0	204	0	0	0
4844	5			0	0	12	2210			
7323	5	131	0	7	0	2	607	3	0	0
7394	5	89	1	4	1	1	152	6	0	0
7449	5	-216	0	1	0	0	0	1	1	0
7023	5	84	1	50	1	3	343	3	0	0
7163	5	-147	0	1	0	0	1254	0	1	0
7453	5	111	0	2	0	0	5450	0	0	0
7530	5	97	1	1	1	0	0	0	1	0
4815	5	139	1	1	0	1	4811	2	2	0
4826	5			0	0	0	0			
4803	5	37	0	2	0	0	5	1	0	0



4838	5			285	0	179	0			
4852	5			0	35	0	0			
7092	5	-252	0	0	0	0	274	0	0	0
7509	5	256	0	3	0	0	281	1	0	0
7227	5	-198	0	17	0	8	267	2	0	0
4797	5	59	0	3	0	0	964	2	0	0
4807	5	40	0	7	0	0	1915	2	2	1
4821	5			0	10	0	0			
7527	5	-80	0	1	0	0	2019	0	2	0
7524	5	-5	0	1	0	0	0	0	1	0
4822	5	74	0	3	0	0	587	1	0	0
7539	5	-171	0	1	0	0	0	0	1	0
7072	5	-3	0	1	0	0	944	0	0	0
7540	5	256	0	1	0	0	59	1	0	0
7391	5	-84	0	240	0	0	12	1	2	0
4792	5	111	0	2	0	0	351	1	1	0
4809	5	38	0	4	0	0	947	2	1	0
4818	5			0	0	0	930			
7232	5	166	0	2	0	0	0	0	0	0
7324	5	111	0	3	0	0	412	2	0	0
4789	5	127	0	1	0	3	952	0	0	0
7525	5	-14	0	1	0	0	0	0	1	1
4819	5			0	0	0	720			
4824	5			0	10	0	700			

**Table 20. Summary of Drinking Water Standard Exceedences from WJU Study**

			samples	
			that exceed	% of
Primary	n		DW std	total
coliforms				
	total	48	43	90%
	fecal	48	19	40%
Pb	97		15	15%
Ba	97		4	4%
As	97		4	4%
Se	97		2	2%
Cd	97		1	1%
Secondary				
Fe	97		76	78%
Mn	97		53	55%
Al	97		9	9%
Zn	97		1	1%
TDS	70		20	29%
pH	75		9	12%

**Table 21. SCR 15 Phase 1 Data: Metal Ions in the Liquid Fraction of Coal Slurry with Comparison to USEPA Drinking Water Standards and Average Exceedences Recorded by the WJU Study**

							<b>WJU data:</b>
<b>Primary</b>	<b>USEPA</b>	<b>Dissolved ion analysis (µg/L)</b>					<b>Average of</b>
<b>contaminants</b>	<b>DW std.</b>	<b>SM</b>	<b>LL</b>	<b>PL</b>	<b>PM</b>	<b>CL</b>	<b>Exceedences</b>
Arsenic	10	4	4	10	ND	ND	136
Barium	2000	81	97	243	52	68	2,818
Cadmium	5	ND		ND	ND	ND	35
Lead	15	ND	ND	76	ND	ND	46
Selenium	50	8	27	22	6	2	356
<b>Secondary</b>							
<b>contaminants</b>							
Aluminum	200	195	150	29	509	532	1,239
Iron	300	ND	ND	68	30	ND	14,742
Manganese	50	14	86	21	921	133	940
Zinc	5000	16	ND	19	32	ND	5,658
ND=non detect							
<b>Primary</b>	<b>USEPA</b>	<b>Total ion analysis (µg/L)</b>					
<b>contaminants</b>	<b>DW std.</b>	<b>SM</b>	<b>LL</b>	<b>PL</b>	<b>PM</b>	<b>CL</b>	
Arsenic	10	4	5	11	ND	ND	136
Barium	2000	114	133	269	63	71	2,818
Cadmium	5	ND	0	1	ND	ND	35
Lead	15	1	2	78	0	ND	46
Selenium	50	8	28	26	6	2	356
<b>Secondary</b>							
<b>contaminants</b>							
Aluminum	200	651	2370	46	564	644	1,239
Iron	300	910	828	89	195	174	14,742
Manganese	50	18	97	28	921	138	940
Zinc	5000	27	8	14	41	ND	5,658
ND=non detect							

**Table 22. Selected Data from Six Sample Sites in Boone County, West Virginia (AEG, 2008)**

<b>Site</b>	<b>pH</b>	<b>Acidity</b>	<b>Alkalinity</b>	<b>Iron</b>	<b>Al</b>	<b>Mn</b>	<b>SO<sub>4</sub></b>
	<b>SU</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>
MD-3	4.5	20	<1	0.37	0.92	0.19	21
MD-4	4.3	528	<1	0.42	1.22	0.18	155
WL-12	4.2	203	<1	0.06	0.05	0.02	100
WL-13	4.7	146	26	<0.05	<0.05	<0.01	51
WL-14	4.9	109	3	0.27	<0.05	0.04	22
WL-15	4.8	148	27	0.19	<0.05	<0.01	47

**Table 23. Selected Organic Chemistry Results for SM-5a and SM-5b. ND=Non Detect, TPH=Total Petroleum Hydrocarbons**

<b>Sample Site</b>	<b>Diethylphthalte</b>	<b>Phenol</b>	<b>TPH (Oil Range)</b>	<b>TPH (Diesel Range)</b>
	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>
SM-5a	0.0056	0.0024	0.71	1.81
SM-5a	ND	ND	0.15	0.37

**Table 24. Selected Inorganic and General Chemistry Results for SM-5a and SM-5b**

<b>Sample Site</b>	<b>Sodium</b>	<b>Specific Conduc.</b>	<b>Sulfate</b>
	<b>mg/L</b>	<b>Umhos/cm</b>	<b>mg/L</b>
SM-5a	49.2	269	11
SM-5b	40.6	228	10.2

**Table 25. Selected Inorganic and General Chemistry Results for SM-6 and SM-7**

<b>Sample Site</b>	<b>Iron mg/L</b>	<b>Alkalinity mg/L</b>	<b>Specific Conduc. Umhos/cm</b>	<b>Sulfate mg/L</b>
SM-6	2.85	422	1090	138
SM-7	0.36	558	1370	141

**Table 26. Water Sample Sites in the Loadout Sampling Area**

<b>Name</b>	<b>Notes</b>	<b>Old Name</b>	<b>Point X</b>	<b>Point Y</b>	<b>Date</b>	<b>Sample Type</b>
LL-1	Active Mine Raw		431893.9	4228991.7	9/25/2007	Groundwater
LL-2	Upstream of Refuse Pile	URF-2	433042.3	4228694.6	6/17/2008	Surface Water
LL-3	Downstream of Refuse Pile	URF-2	432453.0	4229104.3	6/17/2008	Surface Water
LL-4	Upstream of Pump	UDF-1	433373.0	4223899.7	9/25/2007	Surface Water
LL-5	Downstream near mine pump	DWF	432091.6	4225565.4	9/25/2007	Surface Water
LL-6	Refuse pile discharge	5	432977.8	4228756.5	9/25/2007	Surface Water
LL-7	Nellis Mine pump	6	432216.7	4225161.6	9/25/2007	Groundwater
LL-8	Hole 17 - a=lower pool b=upper pool	223	432076.3	4224022.1	9/25/2007	Groundwater
LL-12	Possible seep		434084.7	4222549.5	9/25/2007	Groundwater
LL-13	Private well		434149.3	4222465.7	9/25/2007	Groundwater
LL-14	Bricktown deep mine flow		434543.5	4223902.5	6/17/2008	Groundwater
LL-Slurry	Raw slurry		431854.2	4229393.8	6/17/2008	Slurry



**Table 27. Inorganic Chemistry Data for Groundwater Samples in the Loadout Sampling Area.**  
**All concentrations are dissolved. ND=Non-Detect**

<b>Site</b>	<b>Al</b>	<b>Be</b>	<b>Fe</b>	<b>K</b>	<b>Mn</b>	<b>Na</b>	<b>Ni</b>	<b>Pb</b>	<b>Sr</b>
	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>
LL-1	0.422	ND	0.034	2.6	0.02	129	ND	0.0005	0.183
LL-7	0.126	ND	0.095	5.18	0.072	301	ND	0.0003	0.465
LL-8a	0.065	ND	0.389	3.94	0.152	337	ND	ND	0.281
LL-8b	0.07	ND	0.808	3.57	0.138	316	ND	ND	0.287
LL-12	1.65	0.0092	42.8	8.11	20.7	68.2	0.77	0.0106	2.78
LL-13	0.383	0.0004	0.034	7.47	11.5	64.3	0.249	ND	2.05
LL-14	0.233	ND	0.539	3.7	0.082	11.8	0.0021	ND	1.16

**Table 28. Selected General Chemistry Data for Groundwater Samples in the Loadout Sampling Area**

<b>Parameters</b>		<b>LL-1</b>	<b>LL-7</b>	<b>LL-8A</b>	<b>LL-8B</b>	<b>LL-12</b>	<b>LL-13</b>	<b>LL-14</b>
	<b>Unit</b>							
Chloride	mg/L	33.1	62.5	72.5	72	21.8	19	1.57
Fluoride	mg/L	0.44	0.44	0.66	0.6	ND	ND	0.28
Sulfate	mg/L	52.1	38.6	67.8	66.6	2340	1940	87.5
Cyanide	mg/L	ND	ND	ND	ND	ND	ND	ND
Nitrogen, Ammonia	mg/L	ND	ND	0.89	0.97	0.57	ND	0.2
Specific Conductance	umhos/cm	674	1410	1500	1500	2880	2440	502
Total Dissolved Solids	mg/L	434	798	906	807	2000	1710	249
Total Suspended Solids	mg/L	92	2	8	5	213	19	7
Acidity, Total	mg/L	4.9	23.4	9.6	13	291	85.4	20.5
Alkalinity, Bicarbonate	mg/L	240	611	617	611	9	10.5	167
Alkalinity, Carbonate	mg/L	2.2	2.5	4.3	5.5	ND	ND	ND
Alkalinity, Total	mg/L	242	613	621	616	9.1	10.5	167
pH	SU	7.99	6.86	7.57	7.75	6.53	8.66	7.64

**Table 29. Site Descriptions for Five Historic Groundwater Sampling Points in the Loadout Sampling Area**

<b>Sampling site</b>	<b>Description</b>	<b>Latitude</b>	<b>Longitude</b>	<b>Elevation</b>	<b>Source/Aquifer</b>
BGW-22	Old Zella #4 mine	38 11 31	81 43 52	720	#2 Gas Seam
BGW-23	Old Welch mine	38 10 38	81 43 49	750	#2 Gas Seam
BGW-24	Nellis #2 Gas mine slope	38 10 17	81 46 26	800	#2 Gas Seam
BGW-25	Flowing well	38 10 51	81 46 40	754	Unknown
BGW-26	Lewis "Bob" Smith well	38 13 08	81 49 26	640	Unknown

**Table 30. Inorganic and General Water Chemistry for Historic Sampling Site BGW-22. NP= Not Provided**

<b>Sample Date</b>	<b>pH</b>	<b>Acidity</b>	<b>Alkalinity</b>	<b>Total Fe</b>	<b>Total Mn</b>	<b>Total Al</b>	<b>Sulfate</b>	<b>TSS</b>	<b>TDS</b>	<b>Spec. Cond.</b>
	<b>SU</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>Mhos</b>
12/3/97	7.80	0	13	0.47	<0.02	0.25	8.0	NP	53	62
12/17/97	NP	0	9.7	0.11	<0.02	<0.10	18.2	NP	50	58
1/24/98	7.7	0	27	0.53	0.02	0.68	19	12	60	64.4
2/19/98	6.7	0	6.7	0.54	<0.02	0.31	21.8	3	46	77
3/20/98	6.8	2.4	4.8	1.92	0.06	2.29	15.7	30	50	58.8
4/24/98	7.3	0	23	0.30	0.02	0.36	13	4	60	100
5/26/98	6.5	0	9.9	1.12	0.02	1.02	17.2	16	64	69.7

**Table 31. Inorganic and General Water Chemistry for Historic Sampling Site BGW-23. NP= Not Provided**

<b>Sample Date</b>	<b>pH</b>	<b>Acidity</b>	<b>Alkalinity</b>	<b>Total Fe</b>	<b>Total Mn</b>	<b>Total Al</b>	<b>Sulfate</b>	<b>TSS</b>	<b>TDS</b>	<b>Spec. Cond.</b>
	<b>SU</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>Mhos</b>
12/3/97	7.9	0	65	0.4	0.06	0.19	163	NP	540	708
12/17/97	NP	0	56	0.04	0.02	0.20	392	NP	572	711
1/24/98	7.8	0	59	0.19	<0.02	<0.1	231	<2.8	350	499
2/19/98	7.4	0	30	0.2	<0.02	<0.1	132	3	200	320
3/20/98	7.1	0	31	0.53	0.03	0.6	96	12	190	261
4/24/98	7.2	0	23	0.25	<0.02	0.36	61	4	140	215
5/26/98	7.0	0	40	0.13	<0.02	0.4	179	<2.8	270	450

**Table 32. Inorganic and General Water Chemistry for Historic Sampling Site BGW-24. NP= Not Provided**

Sample Date	pH	Acidity	Alkalinity	Total Fe	Total Mn	Total Al	Sulfate	TSS	TDS	Spec. Cond.
	SU	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	Mhos
12/3/97	7.4	0	680	0.03	0.07	0.12	377	NP	717	1100
12/23/97	7.8	0	700	0.14	0.07	0.31	15.3	NP	674	1000
2/2/98	7.4	5	5.7	0.07	<0.02	<0.10	15.7	<2.8	56	57
2/25/98	7.6	0	590	0.04	0.09	0.43	100	<2.8	690	990
3/23/98	7.7	0	560	0.1	0.07	0.27	<1.20	<2.8	650	1010
4/24/98	7.8	0	580	0.13	0.08	0.36	45	3	540	1120
5/27/98	7.8	0	560	0.09	0.08	0.24	19	<2.8	690	1100

**Table 33. Inorganic and General Water Chemistry for Historic Sampling Site BGW-25. NP= Not Provided**

<b>Sample Date</b>	<b>pH</b>	<b>Acidity</b>	<b>Alkalinity</b>	<b>Total Fe</b>	<b>Total Mn</b>	<b>Total Al</b>	<b>Sulfate</b>	<b>TSS</b>	<b>TDS</b>	<b>Spec. Cond.</b>
	<b>SU</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>mg/L</b>	<b>Mhos</b>
12/23/97	7.8	0	200	0.27	0.04	0.198	<1.20	NP	130	330
2/2/98	7.6	0	200	0.42	0.03	<0.10	<1.20	<2.8	200	358
2/25/98	7.6	0	170	0.27	0.04	<0.10	3	<2.8	200	330
3/23/98	7.6	0	170	0.28	0.04	0.33	<1.20	<2.8	200	348
4/24/98	7.7	0	170	0.31	0.04	0.19	1.9	<2.8	210	380
5/27/98	7.7	0	170	0.29	0.03	0.25	1.9	<2.8	200	390

**Table 34. Analysis of Groundwater for PL-2, PL-5, and PL-6. Bicarbonate value for PL-5 is 303 mg/L**

<b>Name</b>	<b>Unit</b>	<b>PL-2</b>	<b>PL-5</b>	<b>PL-6</b>
Sample ID		PL-2	PL-5	PL-6
Date		1/23/2006	1/23/2006	1/23/2006
Manganese	mg/L	0.024	0.78	0.915
Aluminum	mg/L	0.111	0.142	0.067
Calcium	mg/L	4.13	24.2	10.4
Iron	mg/L	0.146	0.039	10.5
Magnesium	mg/L	1.55	9.36	3.02
Potassium	mg/L	1.38	3.69	1.26
Silicon	mg/L	0.514	0.654	1.04
Sodium	mg/L	98.6	174	3.39
Sulfate	mg/L	78.1	334	18.3
Bicarbonate	mg/L	532	3303	123
Carbonate	mg/L	1.3	2.4	0.5
Chloride	mg/L	69.9	194	16.5
Nitrate	mg/L	0.08	2.24	0.02
Conductivity	umhos/cm	1430	3100	309
Acidity	mg/L CaCO <sub>3</sub>	40.5	4.7	74.6
Dissolved Solids	mg/L	791	1660	161



**Table 35. Historical and Current Groundwater Data from Wet Branch**

<b>Site</b>	<b>Date</b>	<b>pH</b>	<b>Acidity</b>	<b>Alkalinity</b>	<b>TSS</b>	<b>Fe total</b>	<b>Sulfate</b>	<b>EC</b>
	Or Range	su	mg/L	mg/L	mg/L	mg/L	mg/L	umhos
Mollie Bailey	May-August 1982	6.1 - 8.0	3 to 8	9 to 20	2 to 7	0.17 - 1.19	N/A	67 - 86
Mollie Bailey	4/11/1997	6.8	12	45	1	8.93	89	457
PL-2	1/23/2008	7.4	40.5	532	2	0.5	78	1430
PL-5	1/23/2008	7.93	4.7	303	7	0.4	334	3100
PL-6	1/23/2008	6.52	74.6	123	40	27.9	18.3	309

**Table 36. Sample Site Descriptions for all Points in the Power Mountain Sampling Area**

<b>Site ID</b>	<b>Site name</b>	<b>Site Details</b>
PM-1	TE-DH-1	Hutchenson pump - mine pool - downgradient
PM-2	FE-DH-1	Flying Eagle pump - mine pool - downgradient
PM-3	Midstream Twentymile Creek	Instream - below confluence with Robinson Fork
PM-6	FE-MW-2	Flying Eagle well - mine pool - upgradient
PM-7	Downstream Twentymile Creek	Instream - below confluence with Robinson Fork & Sugarcamp Branch
PM-8	Sugar Camp VF Pond	Pond Spillway - Sugarcamp Branch at confluence with Twentymile Creek
PM-9	Naylor Well	Private water well along Jones Branch
PM-10	Corbett Well	Private water well along Jones Branch
PM-11	Mullins Well	Private water well along Jones Branch
PM-13	Pond 001 O-27-85 (seep)	Seep from Rhonda Eagle mine - mine pool
PM-14	Radar Eagle Discharge	Mine pool - downgradient - control mine
PM-Slurry	Raw Slurry Site	Main prep plant

**Table 37. Inorganic and General Chemistry for Five Groundwater Sampling Sites**

ID	pH	EC	TDS	Alk	SO <sub>4</sub>	Sodium	Calcium	Chlorine	Iron	Manganese	Aluminum	Arsenic	Selenium	Strontium
	Su	umhos/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
PM-1	7.68	2860	1670	572	733	537	41.3	45	3.7	0.326	0.325	0.003	ND	1.13
PM-2	7.56	2810	1540	568	752	536	40.3	46.8	3.06	0.559	0.407	0.003	ND	1.05
PM-6	7.53	2230	1450	377	696	346	81.2	33	0.064	0.06	0.498	0.002	ND	2.09
PM-13	7.57	1340	1040	78.1	544	36.8	165	14.3	1.21	4.31	0.465	0.001	0.003	0.66
PM-14	6.96	211	114	32.8	56	7.58	19.2	5.11	0.091	0.043	0.224	0.001	ND	0.31

**Table 38. Inorganic and general chemistry for PM-9, PM-10, and PM-11**

<b>Sample ID</b>	<b>pH</b>	<b>EC</b>	<b>TDS</b>	<b>Alk.</b>	<b>SO<sub>4</sub></b>	<b>Na</b>	<b>Ca</b>	<b>Cl</b>	<b>Fe</b>	<b>Mn</b>	<b>Al</b>
PM-9	6.02	224	106	17.2	72	4.73	19.7	5.8	0.024	0.083	0.214
PM-10	7.7	336	158	177	ND	58.7	15.7	5.64	0.604	0.196	0.228
PM-11	7.4	394	236	191	3	103	0.2	12.6	0.032	0.024	0.039

**Table 39. Historical Groundwater Data Within Twentymile Creek and Sugarcamp Branch**

Sample	Date	pH	EC	Alk	Acidity	TSS	Total Fe	Diss. Fe	Total Mn	Total Al	Sulfate	TDS	Chlorine
		(lab)	umhos/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
GW-1 (Twentymile Church)	2/2/2004	6.5	303	145.21	NS	23	18.28	ND	0.81	0.03	7.14	192	1.02
	6/9/2004	6.4	286	NS	NS	100	25.36	ND	1.07	0.001	19.17	171	1.62
Spring 2-Sugarcamp Branch	6/11/1983	6.4	86.8	10	6	8	0.1				22.4		
Seep 4-Sugarcamp Branch	6/1/1983		80.29				0.08	0.07			20.72		

**Table 40. Historical Mine Pool Data from Three Different Mines. (F)=Field measurement**

Sample	Date	Flow	pH	EC	Alk	Acidity	Total iron	Diss. Iron	Total Mn	Total Al	Sulfate	TDS	Chlorine
		gpm	su	umhos/cm	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Terry Eagle mine (before slurry injection)	1/30/2004	NS	9.2	NS	NS	NS	NS	0.05	ND	0.09	32.96	354	ND
Terry Eagle mine (during slurry injection)	1/10/2005	NS	7.34 (F)	1912	401.98	ND	0.77	NS	ND	ND	373.92	1157	121.99
William Eagle mine (before slurry injection)	10/22/2000	0.5	6.38	350	110	<2.0	1.33	NS	0.29	0.12	164	252	1.5
Jerry Fork mine (no slurry injection)	3/23/2000	NS	8.4 (F)	515	147	137	NS	0.03	0.01	0.1	37.5	260	NS
	5/12/2000	NS	7.6 (F)	469	104	<2.0	0.07	NS	0.69	0.51	80	320	6.1

**Table 41. Water Chemistry Results for 18 Well Samples and Four Mine Pool Samples**

Sample ID	pH	Acidity	Alk	Total Fe	Total Mn	Ca	Mg	EC	SO <sub>4</sub>	Al	Na	K	Cl	Alk	Pb
WL-1	6.7	<1	115	1.77	<0.01	33.2	10.2	375	25	<0.05	80.4	2.23	25	115	<0.001
WL-2	7.5	<1	218	0.22	<0.01	4.02	1.06	610	<1	<0.05	139	1.32	58	218	<0.001
WL-3	6.6	<1	63	1.21	<0.01	14.4	4.54	147	12	<0.05	51.7	1.9	1.2	63	<0.001
WL-4	6.8	<1	100	0.68	<0.01	18.2	3.1	249	29	<0.05	16.1	1.45	3.3	100	<0.001
WL-5	8.3	<1	164	<0.05	<0.01	5.7	1.35	477	<1	<0.05	99.1	1.37	49.5	158	<0.001
WL-6	6.7	<1	69	0.6	<0.01	20.8	4.82	167	12	<0.05	3.3	0.85	2.2	69	<0.001
WL-7	7.2	<1	87	<0.05	<0.01	23.3	5.51	156	9	<0.05	6.1	1.1	1.4	87	<0.001
WL-8	7.2	<1	130	0.54	<0.01	16.2	3.77	248	<1	<0.05	18.8	1.06	7.6	130	<0.001
WL-9	7.2	<1	98	0.66	<0.01	25.6	6.35	276	37	<0.05	10.4	1.42	4.4	98	<0.001
WL-10	6.4	<1	61	0.83	<0.01	19.2	7.44	255	46	<0.05	9.27	1.77	9.7	61	<0.001
WL-11	7.5	<1	135	<0.05	<0.01	15.5	4.1	287	6	<0.05	20.4	1.45	11	135	<0.001
MD-1	7.6	<1	112	<0.05	<0.01	44.6	28.5	496	149	<0.05	1.73	5.21	1.6	112	<0.001
MD-2	7	<1	120	0.32	<0.01	28.9	10.3	764	255	<0.05	117	5.83	1	120	<0.001
ST-1	7	<1	42	0.54	0.19	41	31.4	446	168	0.85	16	4.2	8.3	42	<0.001
ST-2	6.2	<1	24	0.74	0.64	29.2	20.7	327	123	0.54	2.76	2.8	5.2	24	<0.001
ST-3	6.7	<1	92	2.91	1.33	69.4	71.3	878	377	3.38	12.6	8.31	8.6	92	<0.001
MD-3	4.5	20	<1	0.37	0.19	4.93	2.35	124	21	0.92	7.89	2.84	13.6	<1	<0.001
MD-4	4.3	528	<1	0.42	0.18	20.2	28.8	469	155	1.22	0.73	2.76	1.2	<1	<0.001
ST-4	6.5	<1	56	0.05	<0.01	36.5	23.1	498	185	<0.05	21.6	5.06	6	56	<0.001
ST-5	7.4	<1	181	0.48	0.84	33	48.4	1600	379	0.13	135	6.34	106	181	<0.001
WL-12	4.2	203	<1	0.06	0.02	14.8	15.4	227	100	0.05	1.53	2.62	1.4	<1	<0.001
WL-13	4.7	145	26	<0.05	<0.01	12.5	8.52	157	51	<0.05	3.14	2.88	2.5	26	<0.001
WL-14	4.9	109	3	0.27	0.04	24.2	8.21	568	22	<0.05	75.9	4.44	119	3	<0.001
WL-15	4.8	148	27	0.19	<0.01	9.41	7.74	134	47	<0.05	2.97	1.34	1.3	27	<0.001
WL-16	5	51	139	0.13	0.03	13.4	4.04	265	3	0.15	51.8	1.75	7.6	139	<0.001
ST-6	4.9	139	45	0.17	0.36	22.4	16.4	285	90	0.24	8.13	3.15	5	45	<0.001
WL-17	7.8	<1	62	0.85	0.43	31	15.8	383	112	<0.05	10.5	2.75	24.7	62	0.004

WL-18	7.8	<1	93	0.07	0.02	10.9	3.03	162	<1	0.06	21.3	1.13	1.7	93	<0.001
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**Table 42. Initial mass balance model parameters for four SCR-15 Phase I study areas**

	Southern	Loadout	Panther	Power	
	Minerals	LLC	LLC	Mountain	
Mine area	5.12	4.50	6.15	2.00	sq. mi.
Slurry injection rate	800	1000	417	1000	gpm
Injection period	60	10	10	10	years
Time to replace mine pool	3.1	2.5	4.9	1.3	/year
slurry water/infiltration	40%	47%	24%	61%	

**Table 43. Summary of Groundwater Sampling Data from SCR-15. The slurry sample represents the slurry that is injected at the site. The columns to the left indicate samples upgradient by slurry injection while those on the right are samples downgradient of slurry injection. All data represent the dissolved fraction and are dimensioned as mg/L. Those samples that exceed either the USEPA primary or secondary drinking water standards are shaded either yellow or pink respectively. Results of the mass balance analysis are included**

								average	mass
Drinking	Primary	<b>A. Southern Minerals</b>						slurry	balance
water stds.	Secondary	SM-7	Slurry	SM-5A	SM-5B	SM-6	SM-9	affected	estimate
Arsenic	0.010	0.0014	0.0043	0.0011	0.0000	0.0045	0.0052	0.0027	0.0013
Lead	0.015	0.0000	0.0008	0.0022	0.0028	0.0000	0.0000	0.0013	0.0002
Selenium	0.050	0.0000	0.0082	0.0000	0.0000	0.0000	0.0000	0.0000	0.0023
Aluminum	0.200	0.1540	0.6510	0.0750	0.0510	0.1920	0.1290	0.1118	0.1850
Iron	0.300	0.356	0.910	0.069	0.037	2.850	5.110	2.017	0.2586
Manganese	0.050	0.175	0.018	0.006	0.007	0.304	0.175	0.123	0.0050
Sulfate	250	141	97	11	10	138		53	45
TDS	500	752	423	141	117	655	438	338	120
pH	6.5-8.5	7.4	7.9	9.8	9.7	7.0		8.8	
Diesel		0.000	0.000	0.710	0.150	0.000	0.000	0.215	

SM-7 is a large downdip artesian discharge from the adjacent abandoned Pocahontas Capels Mine.

SM-5A = Deep zone of an old monitoring well now used for slurry injection

SM-5B = Shallow zone of an old monitoring well now used for slurry injection

SM-6 is an artesian spring that surfaces along US Route 52.

SM-9 is an artesian discharge along Elkhorn Creek at Maitland and the

nearest discharge from the active slurry injection site which is approximately one and half mile away.

										average	mass
Drinking	Primary	<b>B. Loadout</b>						slurry	balance		

water stds.	Secondary	LL-12	LL-13	LL-14	Slurry	LL-1	LL-7	LL-8A	LL-8B	affected	estimate
Arsenic	0.010	0.0011	0.0000	0.0000	0.0047	0.0012	0.0000	0.0011	0.0012	0.0009	0.0015
Lead	0.015	0.0106	0.0000	0.0000	0.0016	0.0005	0.0003	0.0000	0.0000	0.0002	0.0005
Selenium	0.050	0.0039	0.0000	0.0000	0.0278	0.0012	0.0000	0.0000	0.0000	0.0003	0.0089
Aluminum	0.200	1.6500	0.3830	0.2330	2.3700	0.4220	0.1260	0.0650	0.0700	0.1708	0.7548
Iron	0.300	42.800	0.034	0.539	0.828	0.034	0.095	0.389	0.808	0.332	0.264
Manganese	0.050	20.700	11.500	0.082	0.097	0.020	0.072	0.152	0.138	0.096	0.031
Sulfate	250	2340	1940	88	849	52	39	68	67	56	270
TDS	500	2000	1710	249	933	434	798	906	807	736	297
pH	6.5-8.5	4.6	5.4	7.0	7.9	8.0	7.6	7.9	8.0	7.9	
Diesel		0.000	0.000	0.000	16.600	0.000	0.000	0.000	0.000	0.000	

LL-12 = Mine seep updip of injection

LL-13 = Residential well updip of injection

LL-14 = Mine discharge from a mine that is updip of injection and had never received slurry injection

LL-1 = Active mine discharge (downstream of slurry injection)

LL-7 = Nellis mine dewatering borehole (This is the mine in which slurry injection occurred)

LL-8A = Lower section of pool downdip of slurry injection in the Nellis mine

LL-8B- Upper section of pool downdip of slurry injection in the Nellis mine

					average	mass
Drinking	Primary	<b>C. Panther</b>			slurry	balance
water stds.	Secondary	PL-6	Slurry	PL-2	affected	estimate
Arsenic	0.010	0.0055	0.0113	0.0000	0.0000	0.0022
Lead	0.015	0.0000	0.0775	0.0000	0.0000	0.0150
Selenium	0.050	0.0000	0.0255	0.0000	0.0000	0.0049
Aluminum	0.200	0.0670	0.0460	0.1110	0.1110	0.0089
Iron	0.300	10.500	0.089	0.146	0.146	0.0172
Manganese	0.050	0.915	0.028	0.024	0.024	0.0054

Sulfate	250	18	261	78	78	50
TDS	500	161	2540	791	791	490
pH	6.5-8.5	6.5	8.3	7.4	7.4	
Diesel		0.000	0.000	4.160	4.160	

PL-6 = Residential well updp of slurry injection

PL-2 = Mine dewatering borehole (same mine in which injection occurred)

											average	mass
Drinking	Primary	D. Power Mountain									slurry	balance
water stds.	Secondary	PM-9	PM-10	PM-11	PM-14	Slurry	PM-1*	PM-2*	PM-6*	PM-13*	affected	estimate
Arsenic	0.010	0.0000	0.0000	0.0000	0.0012	0.0000	0.0034	0.0031	0.0015	0.0013	0.0023	0.0000
Lead	0.015	0.0005	0.0003	0.0004	0.0007	0.0004	0.0000	0.0010	0.0004	0.0000	0.0004	0.0002
Selenium	0.050	0.0000	0.0000	0.0000	0.0000	0.0059	0.0000	0.0000	0.0000	0.0027	0.0007	0.0022
Aluminum	0.200	0.2140	0.2280	0.0390	0.2240	0.5640	0.3250	0.4070	0.4980	0.4650	0.4238	0.2135
Iron	0.300	0.024	0.604	0.032	0.091	0.195	3.700	3.060	5.100	1.210	3.268	0.074
Manganese	0.050	0.083	0.196	0.024	0.043	0.921	0.325	0.559	1.240	4.310	1.609	0.349
Sulfate	250	72	0	3	56	853	733	752	696	544	681	323
TDS	500	106	158	236	114	1470	1670	1540	1450	1040	1425	557
pH	6.5-8.5	6.0	7.7	7.4	7.0	7.8	7.7	7.6	7.5	7.6	7.6	
Diesel		0.000	0.000	0.000	0.000	0.260	0.000	0.000	0.000	0.000	0.000	

**Table 44. Summary of Surface Water Sampling Data from SCR-15. The slurry sample represents the slurry that is injected at the site. The columns to the left indicate samples upstream by slurry injection while those on the right are samples downstream of slurry injection. All data represent the dissolved fraction and are dimensioned as mg/L. Those samples that exceed either the State water quality criteria for warm water fishery (WWF) are shaded. NC=no criteria**

		<b>A. Southern Minerals</b>
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	WWF	SM-4	Slurry	SM-2	SM-3
Arsenic	0.190	0.001	0.004	0.001	0.000
Lead	0.025	0.001	0.001	0.000	0.000
Selenium	0.005	0.002	0.008	0.007	0.002
Aluminum	0.750	0.182	0.651	0.256	0.173
Iron	1.500	0.065	0.910	0.000	0.084
Manganese	1.000	0.017	0.018	0.974	0.026
Sulfate	NC	99	97	932	102
TDS	NC	331	423	1180	362
pH	6-9	8.1	7.9	6.6	8.1
Diesel	NC	0.140	0.000	0.000	0.000

SM-4 = Upstream sampling site in Elkhorn Creek

SM-2 = remnant pond located at base of reclaimed refuse pile

SM-3 = Downstream sampling site in Elkhorn Creek

		<b>B. Loadout</b>					
	WWF	LL-2	LL-4	LL-6	Slurry	LL-3	LL-5
Arsenic	0.190	0.000	0.000	0.002	0.005	0.000	0.000
Lead	0.025	0.000	0.000	0.000	0.002	0.000	0.000
Selenium	0.005	0.000	0.000	0.030	0.028	0.005	0.000
Aluminum	0.750	0.077	0.236	0.264	2.370	0.163	0.071
Iron	1.500	0.072	0.084	0.000	0.828	0.124	0.185
Manganese	1.000	0.023	0.100	0.090	0.097	0.285	0.321
Sulfate	NC	16	16	954	849	189	18
TDS	NC	7	180	1230	933	279	65
pH	6-9	6.9	7.8	8.7	7.9	7.6	6.5
Diesel	NC	0.000	0.000	0.000	16.600	0.000	0.000

- LL-2 = Upstream of mining on River Fork (different stream than slurry injection)
- LL-4 = Upstream of slurry injection on tributary of Wilderness Fork (same tributary as injection)
- LL-6 = Discharge point of mining on River Fork (different stream than slurry injection)
- LL-3 = Downstream of mining on River Fork (different stream than slurry injection)
- LL-5 = Downstream of slurry injection on tributary of Wilderness Fork (same tributary as injection)

		<b>C. Panther</b>			
	WWF	PL-4	Slurry	PL-3	PL-5
Arsenic	0.190	0.000	0.011	0.000	0.000
Lead	0.025	0.000	0.078	0.000	0.002
Selenium	0.005	0.000	0.026	0.000	0.007
Aluminum	0.750	0.077	0.046	0.074	0.142
Iron	1.500	0.000	0.089	0.023	0.039
Manganese	1.000	0.008	0.028	0.033	0.780
Sulfate	NC	39	261	106	334
TDS	NC	86	2540	251	1660
pH	6-9	6.8	8.3	7.2	7.9
Diesel	NC	0.000	0.000	0.000	0.000

- PL-4 = Upstream of slurry injection (sample taken instream)
- PL-3 = Downstream of slurry injection (sample taken instream)
- PL-5 = NPDES discharge from surface refuse storage site

		<b>D. Power Mountain</b>			
	WWF	PM-3	Slurry	PM-7	PM-8
Arsenic	0.190	0.000	0.000	0.001	0.001
Lead	0.025	0.001	0.000	0.000	0.000
Selenium	0.005	0.000	0.006	0.005	0.008
Aluminum	0.750	0.180	0.564	0.467	0.453

Iron	1.500	0.064	0.195	0.161	0.023
Manganese	1.000	0.050	0.921	0.263	2.070
Sulfate	NC	1110	853	1220	777
TDS	NC	1810	1470	1820	1380
pH	6-9	7.9	7.8	8.0	8.2
Diesel	NC	0.000	0.260	0.000	0.000

PM-3 = Instream sample upstream of slurry injection site

PM-7 = Instream sample downstream of slurry injection site

PM-8 = Pond spillway from valley fill of a mine not connected to slurry injection

**Table 45. Summary of Surface Water Sampling Data from SCR-15. The slurry sample represents the slurry that is injected at the site. The columns to the left indicate samples upstream of slurry injection while those on the right are samples downstream of slurry injection. All data represent the total aqueous fraction and are dimensioned as mg/L. Those samples that exceed either the State water quality criteria for warm water fishery (WWF) are shaded. NC=no criteria**

	A. Southern Minerals				
	WWF	SM-4	Slurry	SM-2	SM-3
Arsenic	0.190	ND	0.0043	0.0014	ND
Lead	0.025	0.0004	0.0008	ND	0.0003
Selenium	0.005	0.002	0.0082	0.007	0.0019
Aluminum	0.750	0.211	0.651	0.316	0.22
Iron	1.500	0.108	0.91	0.034	0.223
Manganese	1.000	0.0183	0.0177	0.979	0.0308
Sulfate	NC	99.4	157	932	102
TDS	NC	331	423	1180	362
pH	6-9	8.09	7.93	6.64	8.14

Diesel	NC	0.14	ND	ND	ND
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SM-4 = Upstream sampling site in Elkhorn Creek

SM-2 = remnant pond located at base of reclaimed refuse pile

SM-3 = Downstream sampling site in Elkhorn Creek

		<b>B. Loadout</b>					
	WWF	LL-2	LL-4	LL-6	Slurry	LL-3	LL-5
Arsenic	0.190	ND	ND	0.002	0.0047	ND	ND
Lead	0.025	ND	0.0002	0.0002	ND	ND	ND
Selenium	0.005	ND	ND	0.0301	0.0195	0.0052	ND
Aluminum	0.750	0.073	0.24	0.317	0.054	2.06	0.093
Iron	1.500	0.092	0.349	0.038	ND	0.288	0.128
Manganese	1.000	0.025	0.106	0.227	ND	0.327	0.075
Sulfate	NC	16.1	15.8	954	849	189	18.2
TDS	NC	7	180	1230	933	279	65
pH	6-9	6.86	7.75	8.66	7.88	7.57	6.53
Diesel	NC	ND	ND	ND	16.6	ND	ND

LL-2 = Upstream of mining on River Fork (different stream than slurry injection)

LL-4 = Upstream of slurry injection on tributary of Wilderness Fork (same tributary as injection)

LL-6 = Discharge point of mining on River Fork (different stream than slurry injection)

LL-3 = Downstream of mining on River Fork (different stream than slurry injection)

LL-5 = Downstream of slurry injection on tributary of Wilderness Fork (same tributary as injection)

		<b>C. Panther</b>			
	WWF	PL-4	Slurry	PL-3	PL-5
Arsenic	0.190	ND	0.0113	ND	ND
Lead	0.025	ND	0.0775	ND	0.002



Selenium	0.005	ND	0.0255	ND	0.0079
Aluminum	0.750	0.068	0.046	0.093	0.259
Iron	1.500	0.025	0.089	0.053	0.4
Manganese	1.000	0.014	0.028	0.033	0.777
Sulfate	NC	39.3	261	106	334
TDS	NC	86	2540	251	1660
pH	6-9	6.78	8.26	7.21	7.93
Diesel	NC	ND	ND	ND	ND

PL-4 = Upstream of slurry injection (sample taken instream)

PL-3 = Downstream of slurry injection (sample taken instream)

PL-5 = NPDES discharge from surface refuse storage site

		<b>D. Power Mountain</b>			
	WWF	PM-3	Slurry	PM-7	PM-8
Arsenic	0.190	0.001	ND	0.0015	0.0014
Lead	0.025	ND	0.0004	ND	ND
Selenium	0.005	0.0047	0.0059	0.0051	0.008
Aluminum	0.750	0.449	0.564	0.458	0.482
Iron	1.500	0.095	0.195	0.077	0.114
Manganese	1.000	0.493	0.921	0.255	2.21
Sulfate	NC	1110	3.44	1220	777
TDS	NC	1810	21	1820	1380
pH	6-9	7.87	9.49	7.96	8.23
Diesel	NC	ND	0.260	ND	ND

PM-3 = Instream sample upstream of slurry injection site

PM-7 = Instream sample downstream of slurry injection site

PM-8 = Pond spillway from valley fill of a mine not connected to slurry injection



## Appendix B

### Figures

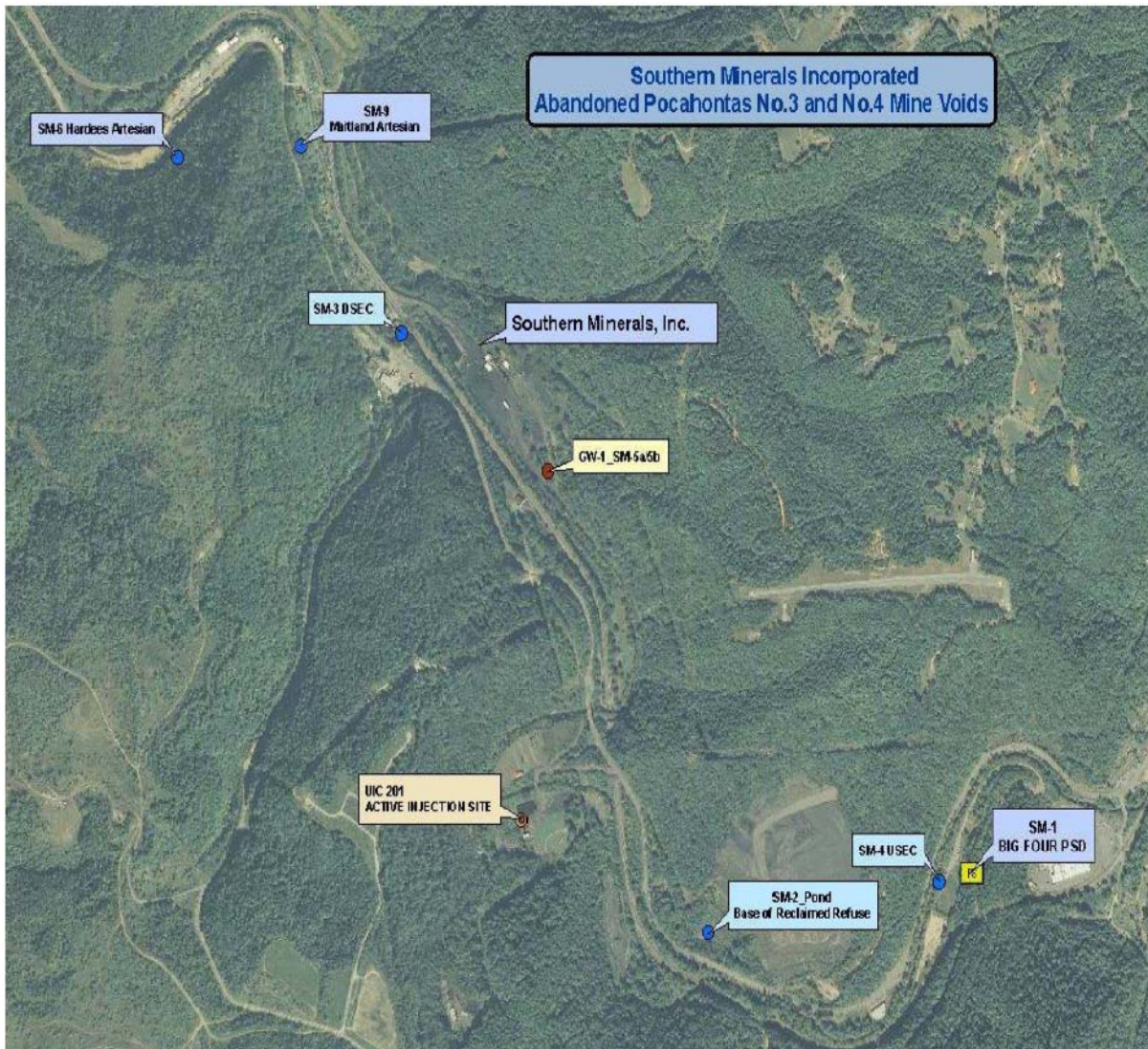


Figure 1. Sample sites in the Southern Mineral study area





Figure 1a. Sample sites in the Southern Minerals study area

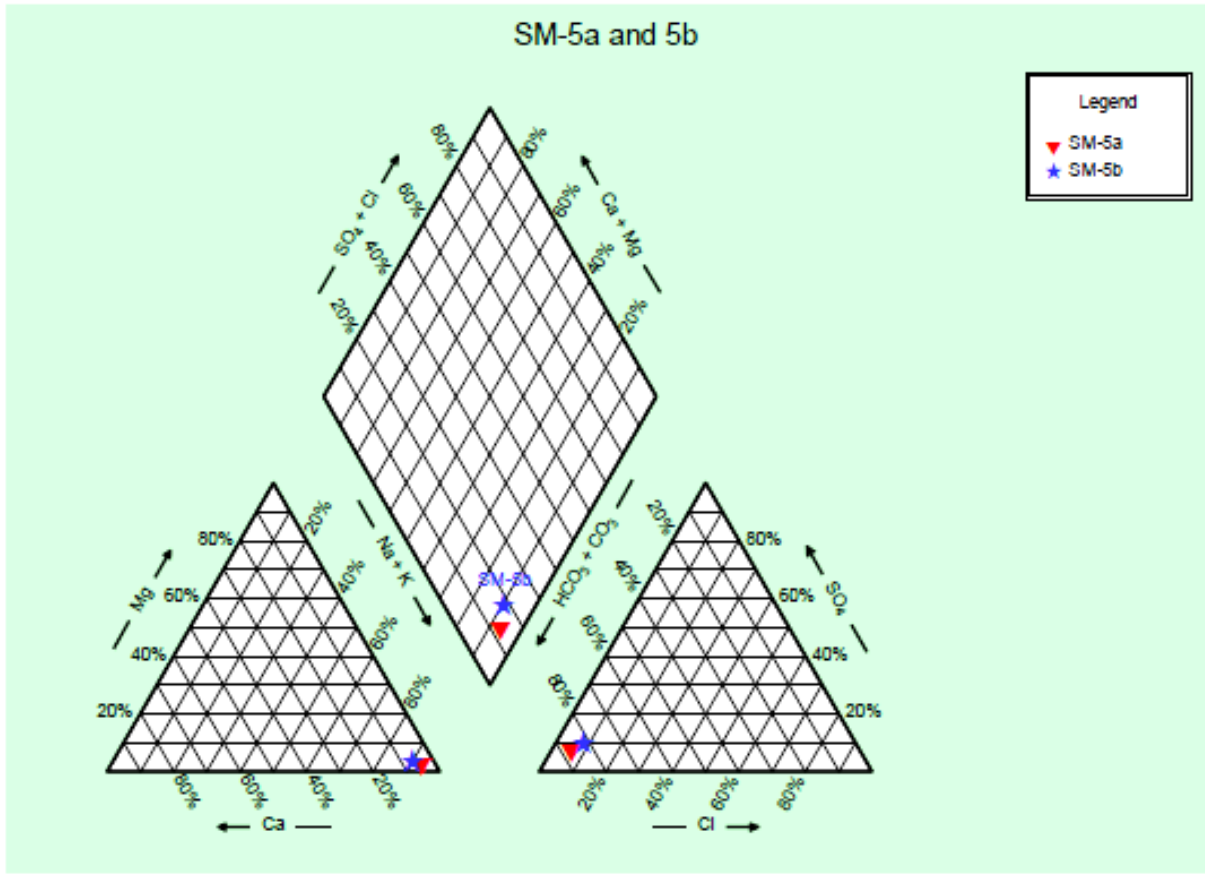


Figure 2. Piper diagram for Southern Minerals groundwater chemistry from sampling locations SM-5a and SM-5b (WVDEP, 2009)

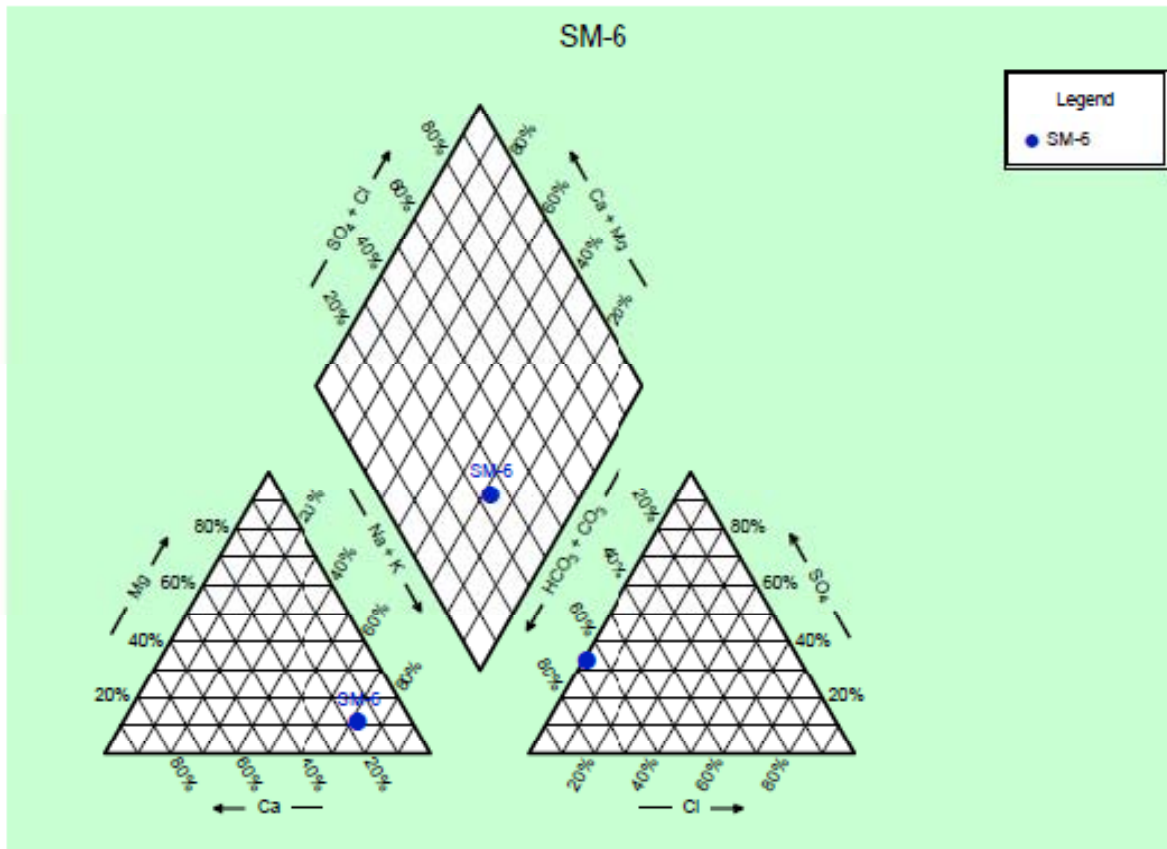


Figure 3. Piper diagram for Southern Minerals underground mine pool sampling location SM-6 (WVDEP, 2009)



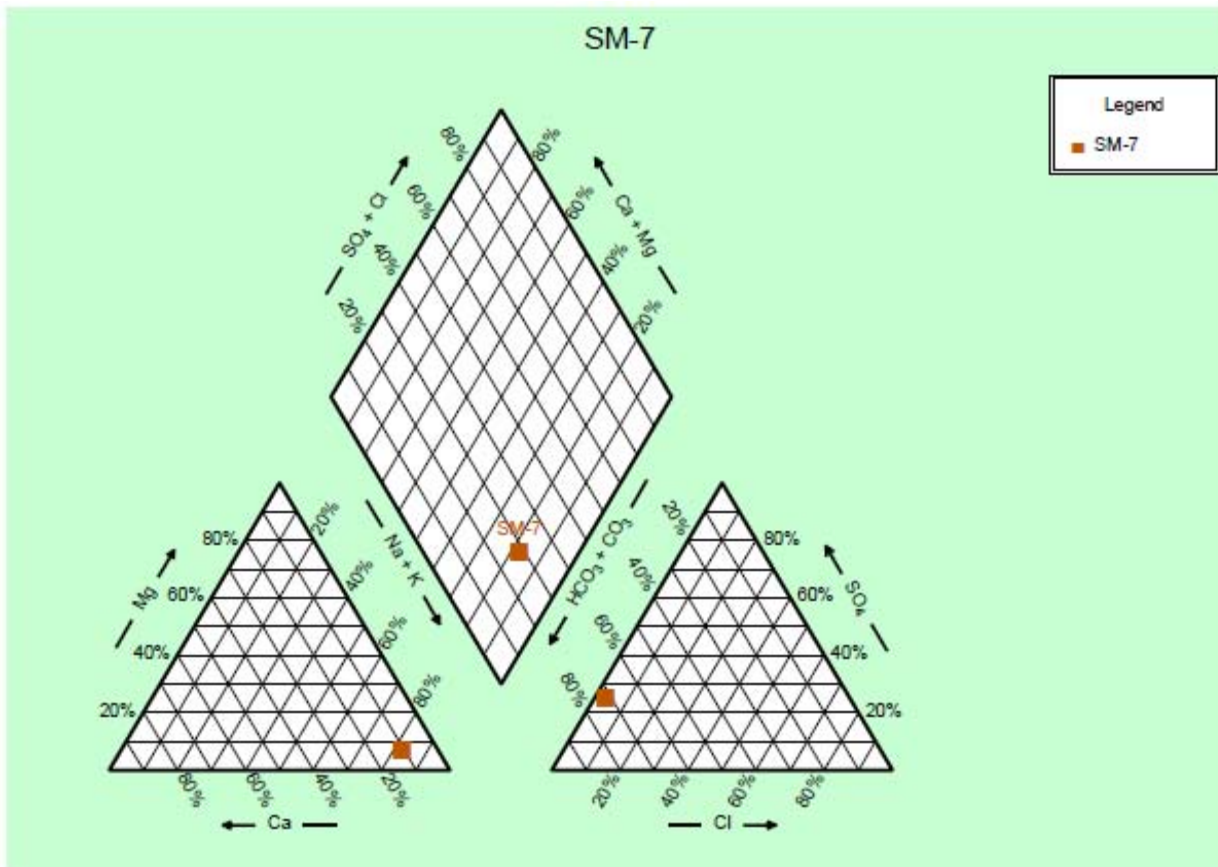
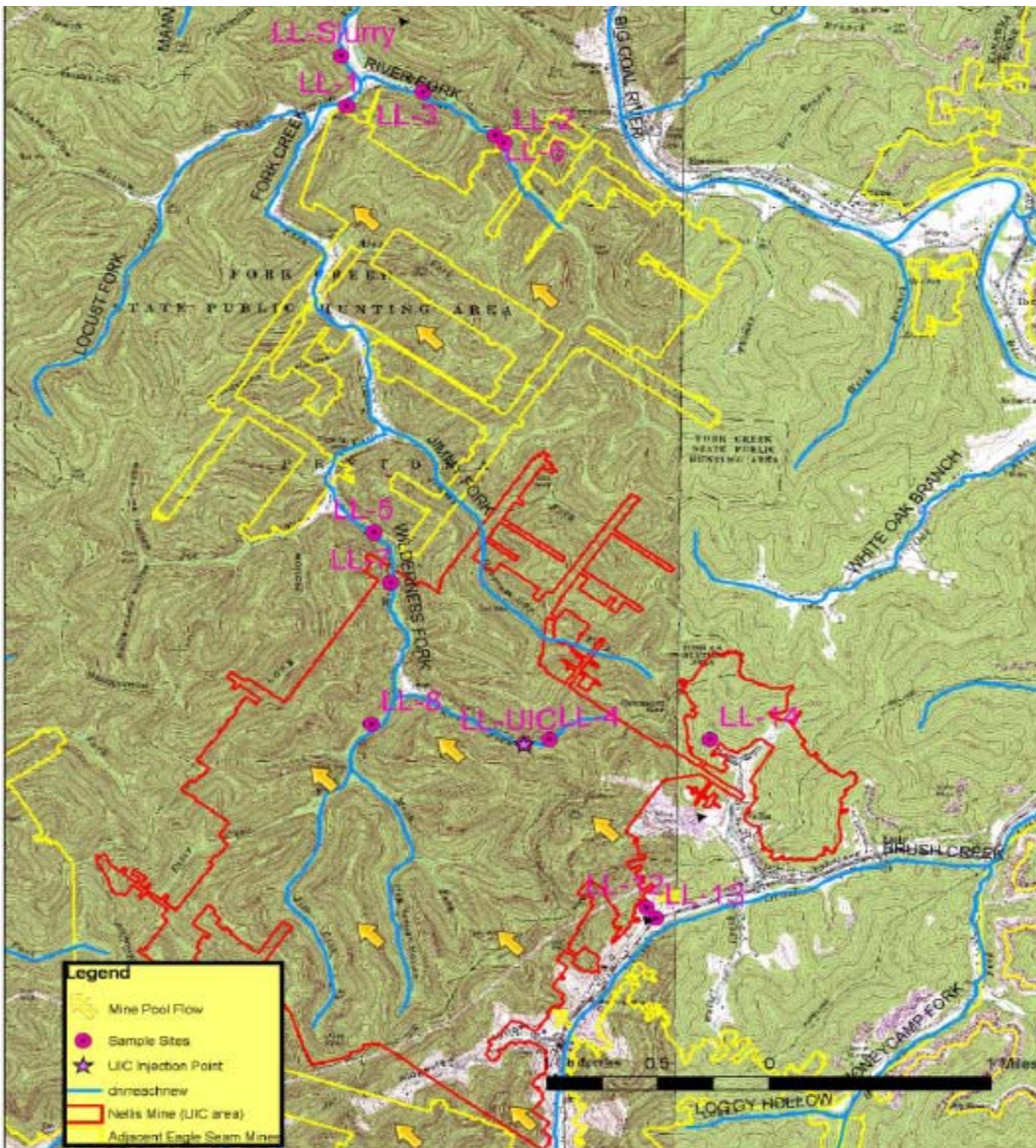


Figure 4. Piper diagram for Southern Minerals sampling location SM-7 (WVDEP, 2009).





**Figure 5. Sample point locations for the Loadout study area (WVDEP, 2009)**

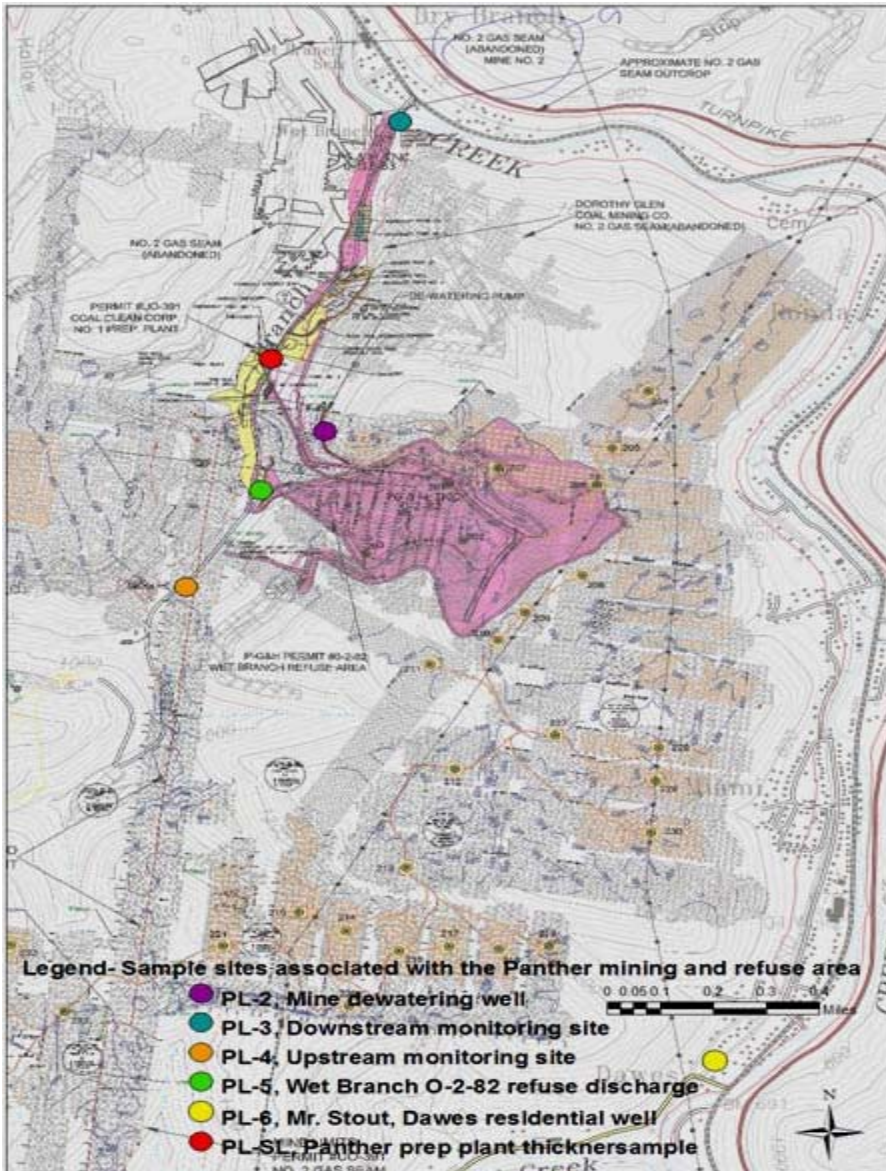


Figure 6. Locations of the sampling points in the Panther study area (WVDEP, 2009)

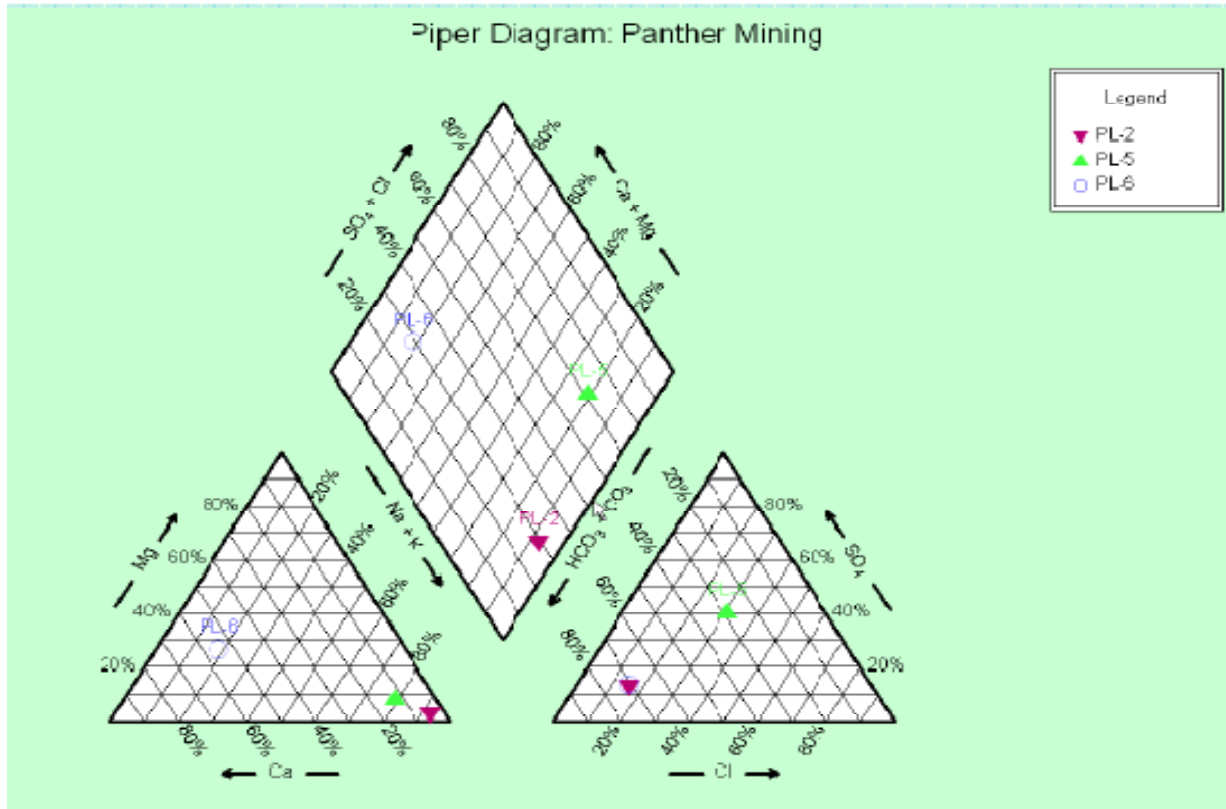
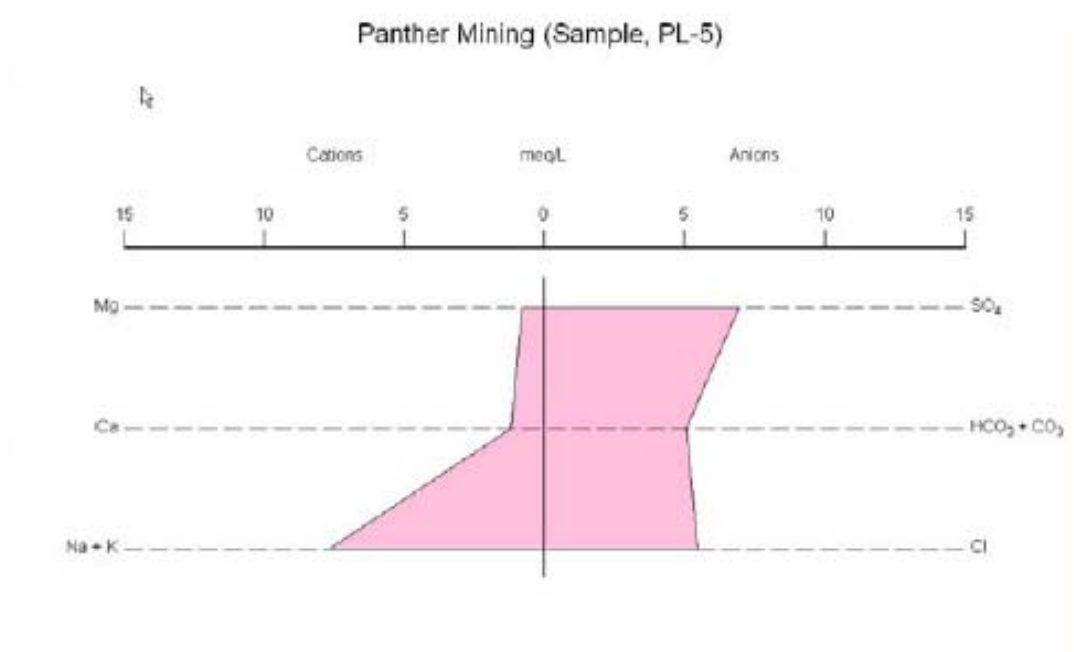


Figure 7. Piper diagram for Panther sampling locations PL-2, PL-5, and PL-6 (WVDEP, 2009)





**Figure 8. Stiff diagram for Panther sampling location PL-5. Cations are represented on the left of the figure and anions on the right (WVDEP, 2009)**

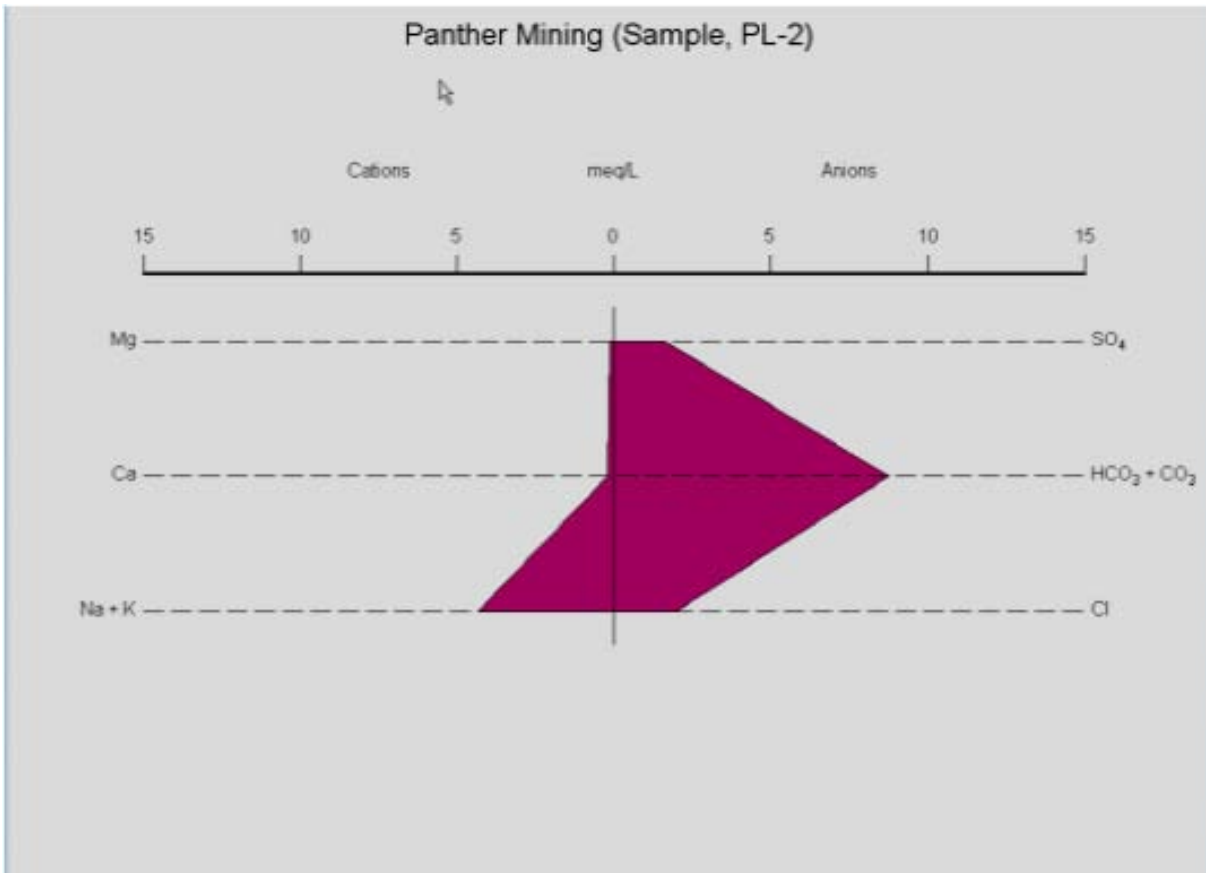


Figure 9. Stiff diagram for Panther sampling location PL-2 (WVDEP, 2009)

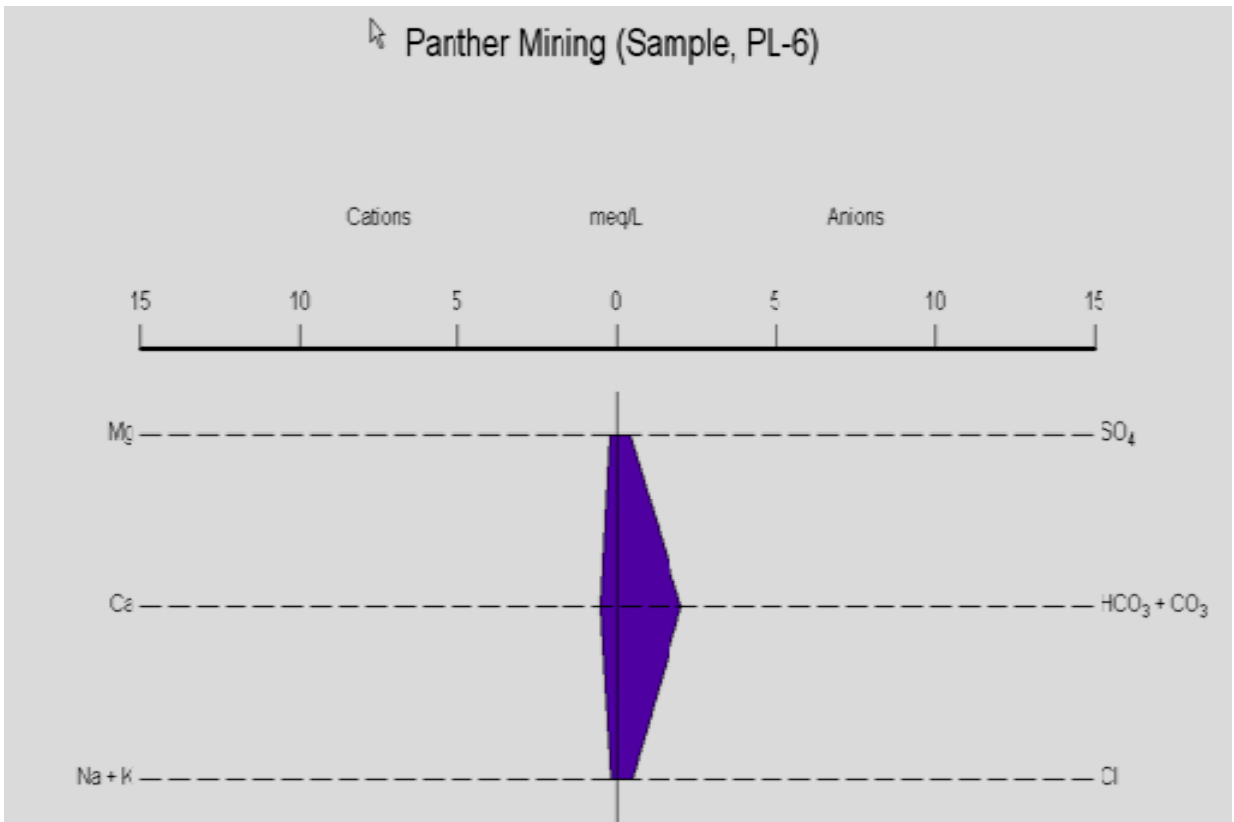


Figure 10. Stiff diagram for Panther sampling location PL-6 (WVDEP, 2009)

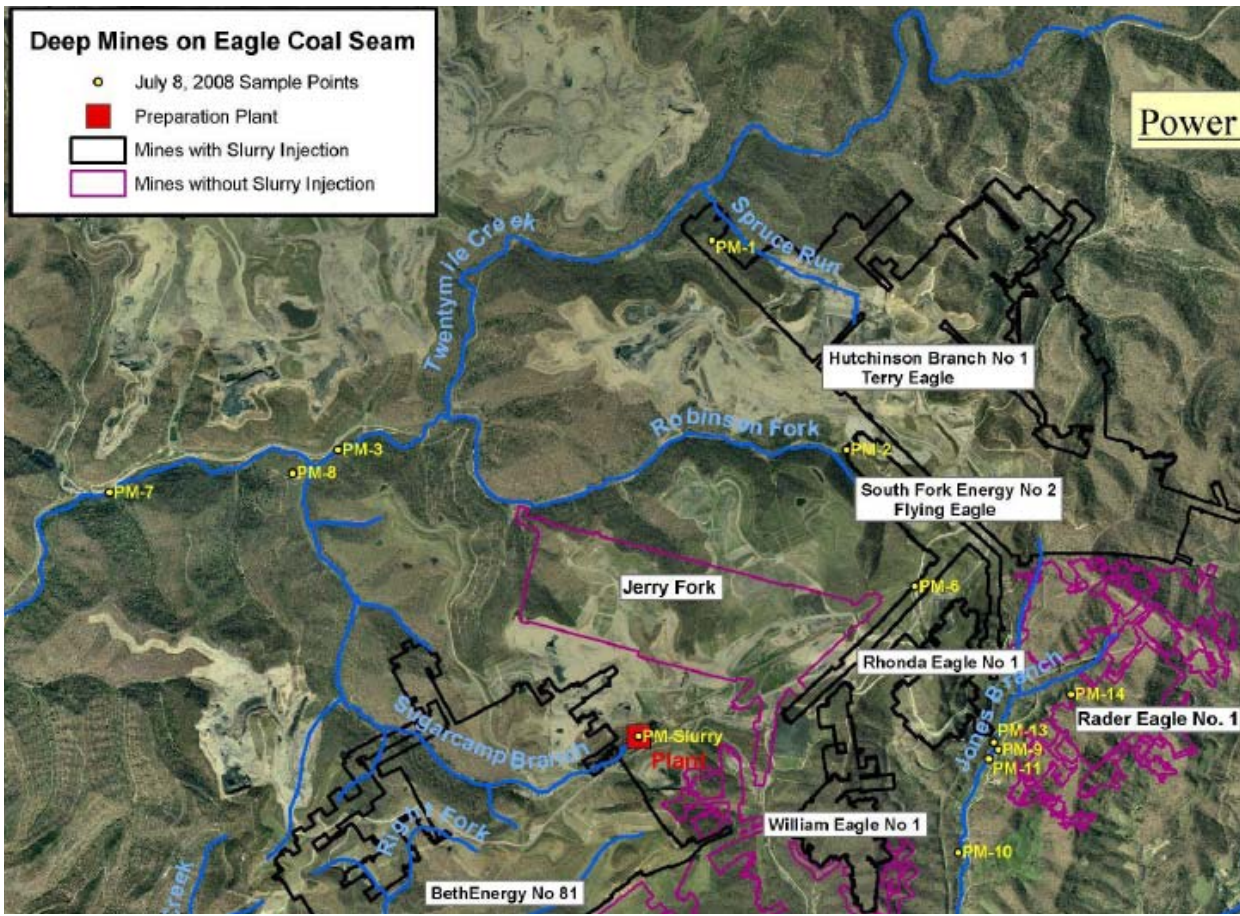


Figure 11. Location of all sampling points in the Power Mountain sampling area (WVDEP, 2009)



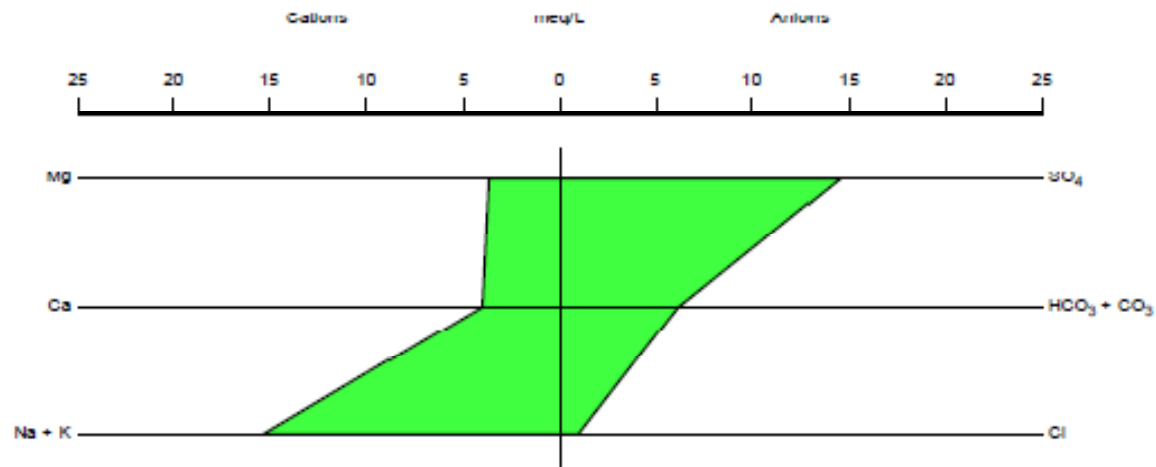


Figure 12. Stiff diagram for Power Mountain sampling location PM-6 (WVDEP, 2009)

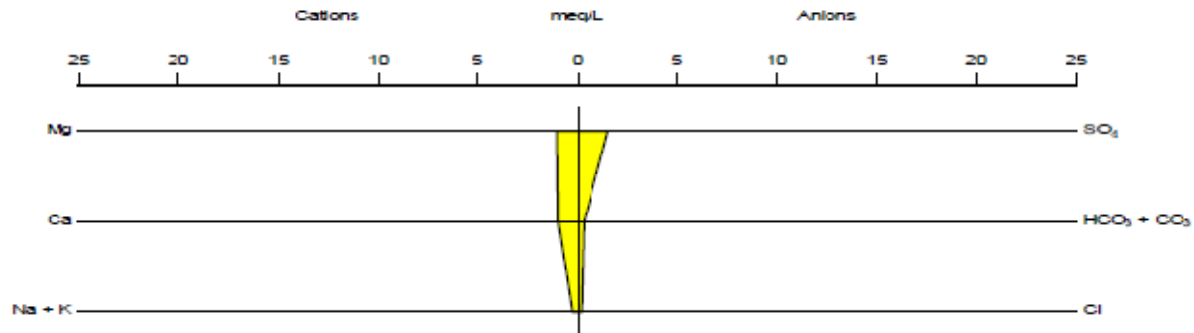


Figure 13. Stiff diagram for Power Mountain sampling location PM-9 (WVDEP, 2009)

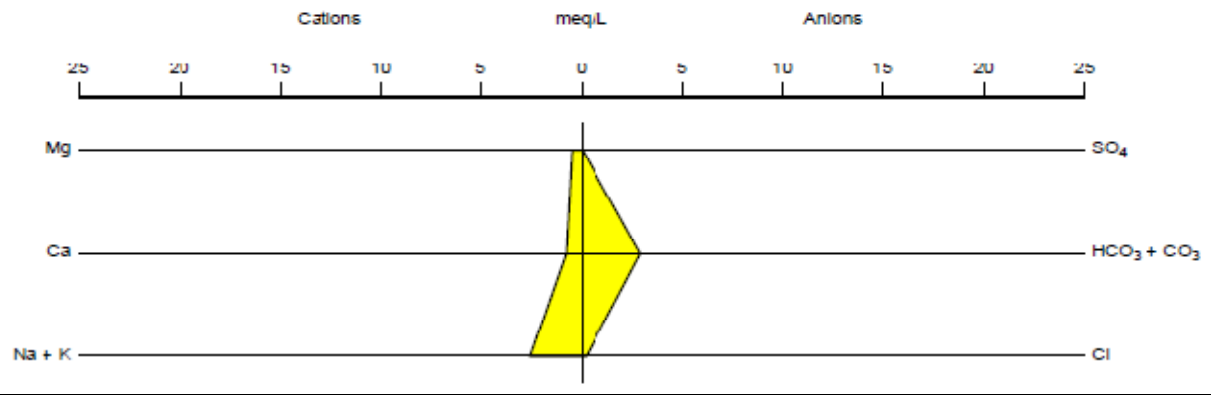


Figure 14. Stiff diagram for Power Mountain sampling location PM-10 (WVDEP, 2009)

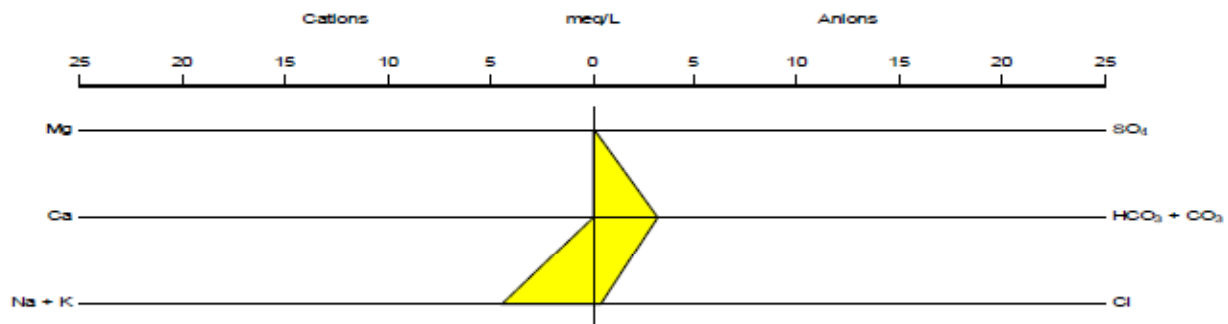


Figure 15. Stiff diagram for Power Mountain sampling location PM-11 (WVDEP, 2009)

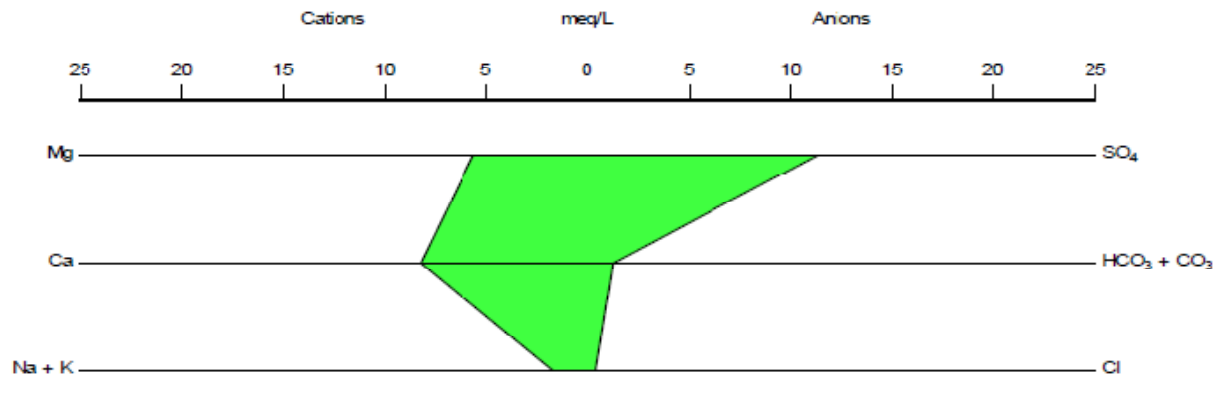


Figure 16. Stiff diagram for Power Mountain sampling location PM-13 (WVDEP, 2009)

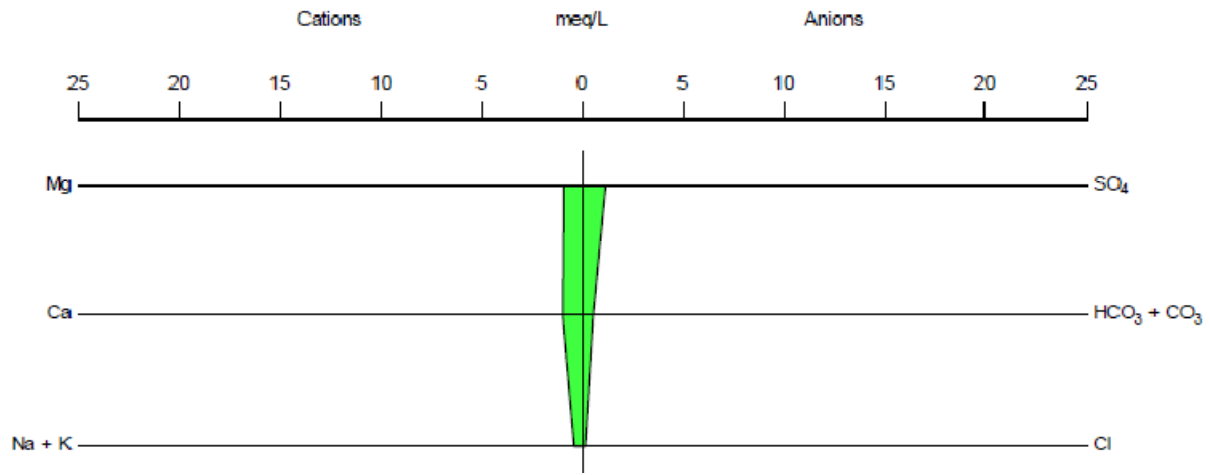


Figure 17. Stiff diagram for Power Mountain sampling location PM-14 (WVDEP, 2009)

- Legend:**
- Mine Drainage
  - Streams
  - Wells

**Piper Trilinear Diagram**

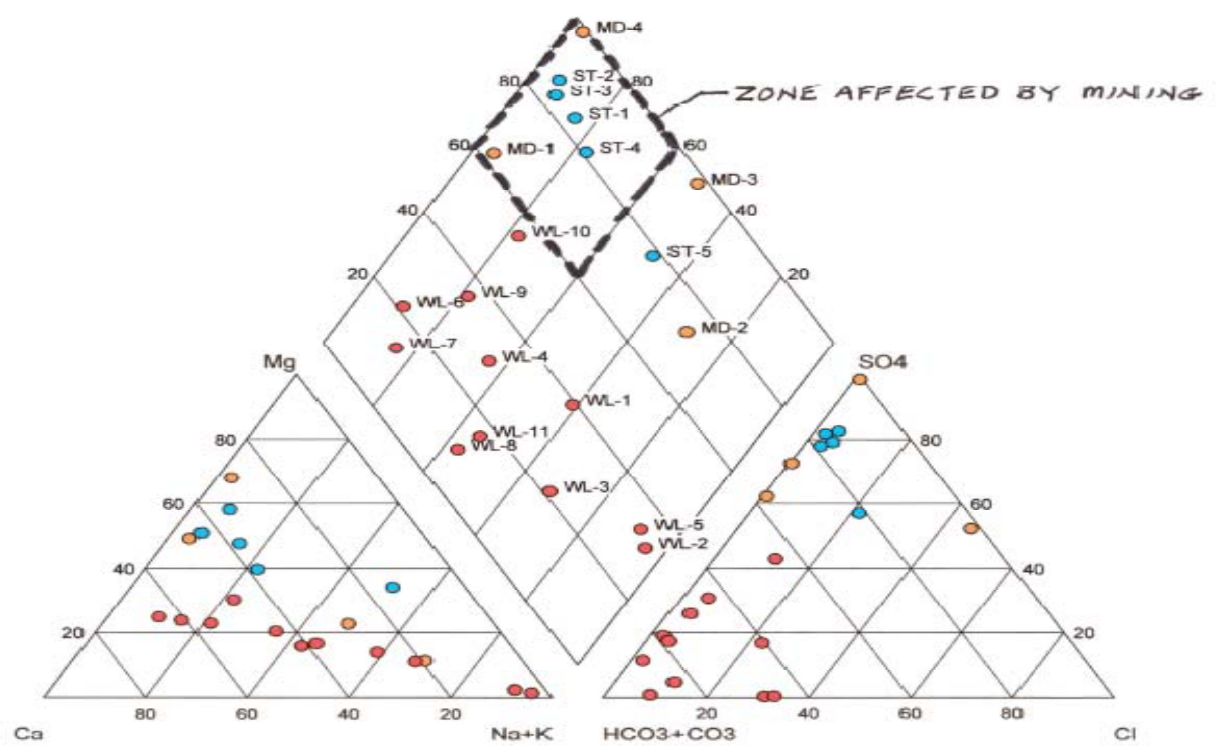


Figure 18. Piper diagram for residential well sampling locations WL-1 through WL-11, stream samples ST-1 through ST-5, and MD-1 through MD-4 (WVDEP, 2009)

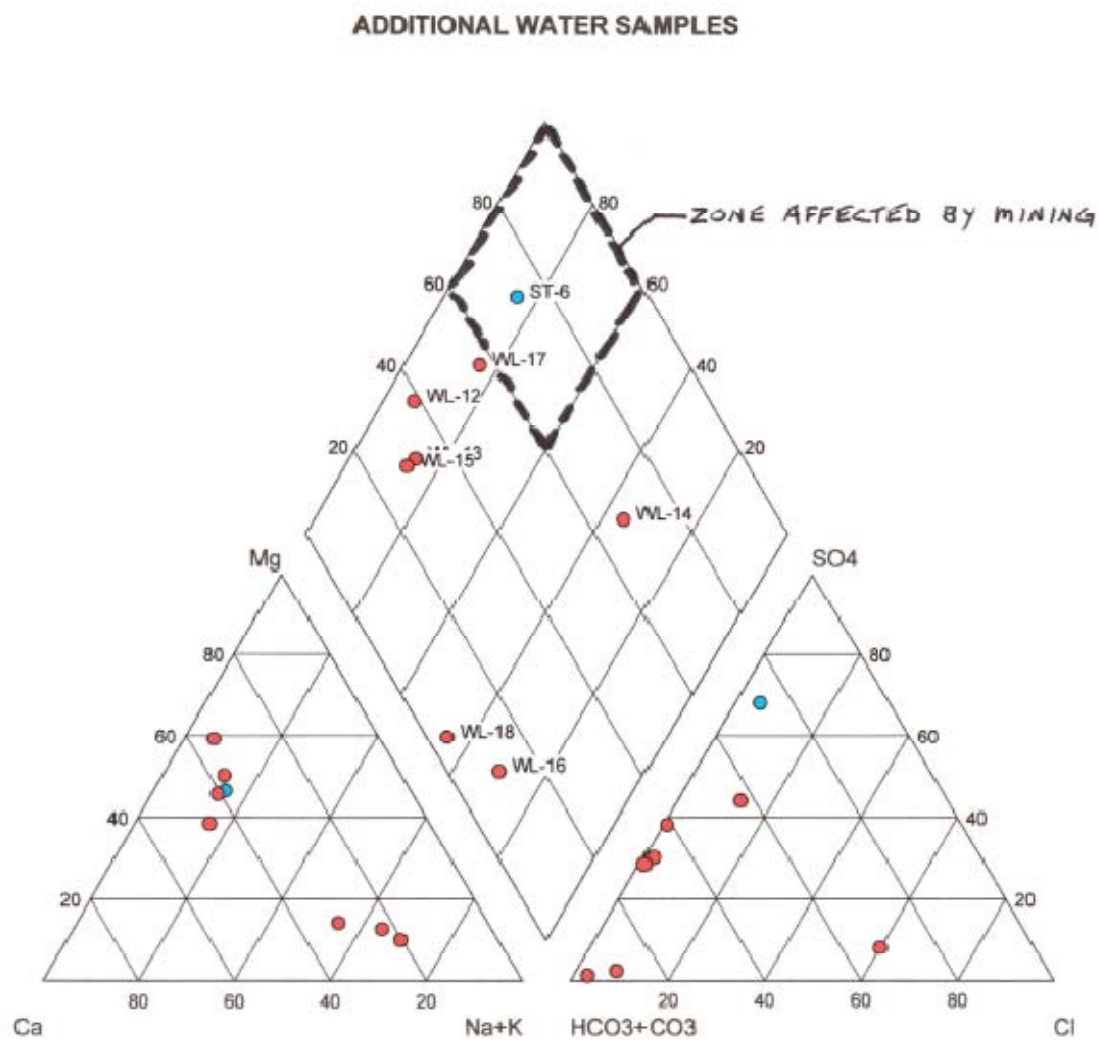




Figure 19. Piper diagram for residential well sampling locations WL-12 through WL-18 and stream sample ST-6 (WVDEP, 2009)

(Source: Figure 3.1 from NRC, 2002)

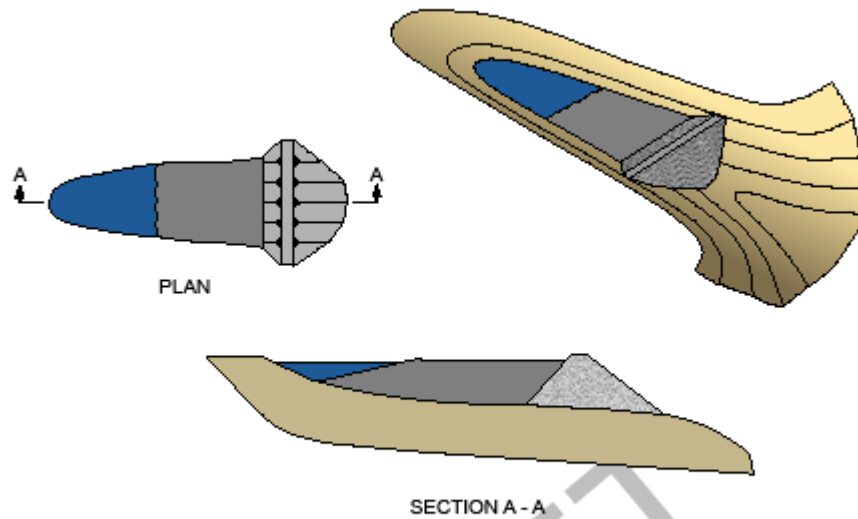


FIGURE 3.1 CROSS-VALLEY IMPOUNDING EMBANKMENT

Figure 20. Cross-valley impounding embankment (NRC, 2002)

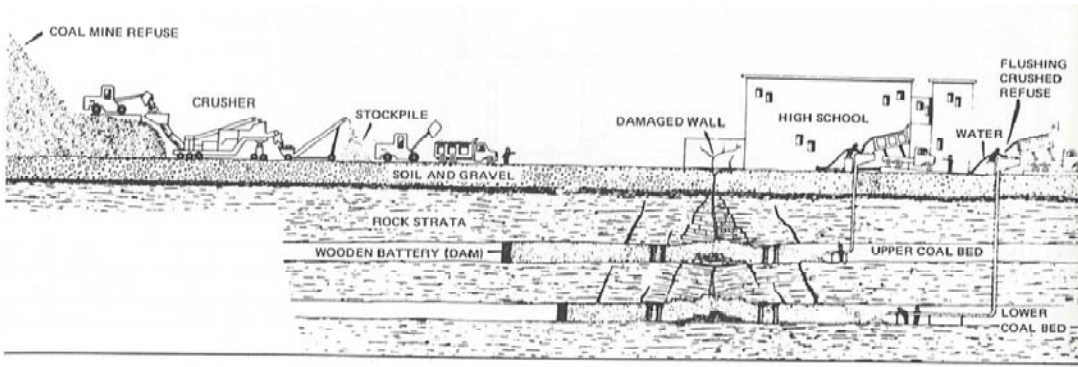


FIGURE 3.11 Controlled flushing (hydraulic). (Bureau of Mines)

Figure 21. Controlled flushing (NAS, 1975)

## **Appendix C**

### **Preparers of Report**

**ALAN DUCATMAN, MD, MSc**  
**Chair, Department of Community Medicine**  
**Project Principal Investigator**

**EDUCATION:**

A.B., Biology, 1972, Columbia College of Columbia University, New York  
M.S., Environmental Health Sciences, 1974, CUNY/Hunter College  
M.D., Medicine, 1978, Wayne State University  
Medical Internship, 1978-1979, Brown University, Providence, Rhode Island  
Medical Residency, 1979-1981, Mayo Clinic, Rochester, Minnesota  
Fellowship, Occupational Medicine, 1981-1982, Mayo Clinic, Rochester, Minnesota

**POSITIONS AND EMPLOYMENT:**

Nov 1997 – present      Professor and Chair, Department of Community Medicine,  
West Virginia University (WVU)  
July 1992 – present      Professor of Community Medicine, Professor of Medicine,  
WVU School of Medicine  
July 1992 – Nov 1997      Director, Institute of Occupational and Environmental Health, WVU School of Medicine  
July 1986 – 1992      Director, Environmental Medical Service, Massachusetts  
Institute of Technology  
July 1983 – June 1986      Director, Professional Occupational Health Branch,  
U.S. Navy Environmental Health Center, Norfolk, VA  
(LCDR, Medical Corps)  
April 1982 – July 1983      Director, Occupational Medical Services, Columbia Park and Brooklyn Park Medical Groups, Columbia  
Park and Brooklyn Park, MN

**OTHER EXPERIENCE AND PROFESSIONAL MEMBERSHIPS:**

April 2005 – Dec 2008      Member, Board of Scientific Counselors, National Center for Environmental Health/Agency for Toxic  
Substances and Disease Registry, Centers for Disease Control and Prevention. Appointed Board Chair,  
August 2007.

1993-2009	Member, West Virginia Poison Center Advisory Board.
1993-2002	Trustee member, American Board of Preventive Medicine (ABPM)
1999-2004	Residency Review Committee; Accreditation Council on Graduate Medical Education-Preventive Medicine, Appointed Vice Chair, 2002; Appointed Chair, 2004.
1993-1995	International Union of Operating Engineers. National HAZMAT Program Board of Scientific Advisors.
1988-1995	American Board of Preventive Medicine/National Board of Medical Examiners. Occupational Medicine Examination Committee.

**RESEARCH SUPPORT:**

*Ongoing Projects*

West Virginia Department of Health and Human Resources	A Ducatman (PI)	4/1/09-3/31/10
<b>GEO 22- Coal Slurry Assessment</b>		
This interdisciplinary project examines human health outcomes of coal slurry injection practices.		

Brookmar, Inc.	A Ducatman (PI)	1/1/06-8/31/08
<b>Data Hosting Project</b>		
This project provides public, summary data for a prevalence study of the relationship of perfluorocarbons (PFCs) to human health of 68,000 exposed participants of all ages.		

National Institutes of Health	A Ducatman (Co-I)	9/28/07-present
<b>National Children's Health Study</b>		

*Projects Closed within Past Three Years*

BrickStreet Mutual Insurance Co.	A Ducatman (PI)	1/1/06-12/31/08
<b>Workers' Compensation Data Analysis Project</b>		
This project evaluated health, cost, disability		



- 1997 Harriet Hardy Award for the physician who exemplifies the highest ideals of occupational environmental medicine. New England College of Occupational and Environmental Medicine.
- 1993 Robert J. Hilker Lectureship Award, American College of Occupational and Environmental Medicine.

**SELECTED PUBLICATIONS:**

- Macneil J, Steenland K, Shankar A, Ducatman A. A cross-sectional analysis of type II diabetes in a community with exposure to perfluorooctanoic acid (PFOA). *Environ Res* 2009; Sep 7 [epub ahead of print].
- Frisbee S, Brooks, AP, Maher A, Flensburg P, Arnold S, Fletcher T, Steenland K, Shankar A, Knox S, Pollard C, Halverson J, Vieira V, Jin C, Leyden K, Ducatman A. The C8 Health Project: design, methods, and participants. *Environ Health Perspect*, doi: 10.1289/ehp.0800378, online July 13, 2009.
- Steenland K, Jin C, MacNeil J, Lally C, Ducatman A, Vieira V, Fletcher T. Predictors of PFOA levels in a community surrounding a chemical plant. *Environ Hlth Perspect* 2009; 117:1083-88.
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- Charumathi S, Shankar A, Li J, Pollard C, Ducatman A. Serum gamma-glutamyl transferase level and diabetes mellitus among US adults. *Eur J Epidemiol* 2009; 24:369-73. Epub May 2009.
- Sun C, Jin C, Martin C, Gerbo R, Wang Y, Atkins J, Ducatman AM. Cost and outcome analyses on the timing of first independent medical evaluation in patients with work-related lumbosacral sprain. *J Occup Environ Med* 2007; 49:1264-8.
- Ducatman AM. Multiple Chemical Sensitivity. In *Environmental and Occupational Medicine* (4<sup>th</sup> ed.) Ed. W Rom. Lippincott-Raven (Philadelphia), 2007. 867-881.
- Haut MW, Kuwabara H, Ducatman AM, et al. Corpus callosum volume in railroad workers with chronic exposure to solvents. *J Occup Environ Med* 2006. 48(6): 615-24.
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- Ducatman AM, Vanderploeg JM, Johnson M, et al. Residency training in preventive medicine: challenges and opportunities. *Am J Prev Med* 2005; 28: 403-412.
- Ducatman BS, Ducatman AM. How expert are the experts? Implications for proficiency testing in cervicovaginal cytology (editorial). *Arch Pathol Lab Med* 2005; 129: 604-605.
- Jin CH, Haut M, Ducatman AM. Industrial solvents and psychological effects. *Clin Occup Environ Med* 2004; 4: 597-620.
- Martin CT, Werntz, CL, Ducatman AM. The interpretation of zinc protoporphyrin changes in lead intoxication: a case report and review of the literature. *Occupational Medicine* 2004; 54(7): 587-591.
- Erdogan MS, Islam SS, Chaudhari A, Ducatman AM. Carbon monoxide poisoning among West Virginia workers' compensation claims: diagnosis, treatment duration, and utilization. *J Occup Environ Med* 2004, 46(6) 577-83.
- Ehrlich PF, McLellan WT, Ducatman A, Helmkamp JC, Islam SS. Understanding work-related injuries in children: a perspective in West Virginia using the state-managed workers' compensation system. *J Pediatric Surgery* 2004; 39: 768-772.
- Abdul-Razzaq WN, Lee V, Islam S, Ducatman AM. Quantification of lead in telephone cord: use of x-ray photoelectron spectroscopy technique. *Appl Occup and Env Hygiene* 2003;18:553-557.
- Li H, Wang ML, Seixas N, Ducatman AM, Petsonk EL. Respiratory protection: associated factors and effectiveness of respirator use among underground coal miners. *Am J Indus Med* 2002;42:55-62.
- Franklin, P, Goldenberg WS, Ducatman AM, Franklin E. Too hot to handle: an unusual exposure of HDI in specialty painters. *Am J Indus Med* 2000;37:431-437.



Ducatman, AM, McLellan R. American College of Occupational and Environmental Health Position Statement. Epidemiologic basis for an occupational and environmental policy on environmental tobacco smoke. J Occup Environ Med 2000;42:575-581.

Meyer JD, Islam SS, Ducatman AM, McCunney RJ. Prevalence of small lung opacities in populations unexposed to dusts: a literature analysis. Chest 1997;111:404-410.

Fleming LE, Ducatman AM, Shalat SL. Disease clusters in occupational medicine: a protocol for their investigation in the workplace. Am J Indus Med 1992;22:33-47.

Ducatman, AM, Bigby M. Systemic contact dermatitis after inhalation of 2-aminothiophenol. Contact Derm 1988;18:57-58.

Ducatman AM, Yang MN, Forman SA. "B-readers" and asbestos medical surveillance. J Occup Med 1988;30:644-647.

**PAUL F. ZIEMKIEWICZ, Ph.D.**  
**Director, West Virginia Water Research Institute**  
**Project Co-Investigator**

**EDUCATION:**

**B.S.** Utah State University, 1969-73. Major: Biology, Minor: Chemistry

**M.S.** Utah State University, 1973-75. Range Ecology

**Ph.D.** University of British Columbia, 1975-78. Forest Ecology

**POSITIONS:**

Since 1978 I have been responsible for developing and managing environmental research programs related to the energy industry: specifically, coal, power generation, oil and gas and oil sands. My current research focuses on mine drainage, water management in the power industry, watershed protection and restoration and brownfields development of mined land. My research program is supported by the USDOE, USEPA, USGS, OSMRE, NRCS, WVDEP as well as the coal, petroleum and power industries.

In addition to my research roles I have served in a regulatory capacity with government agencies. I have developed regulatory and R&D policy and I currently serve on both state and federal policy advisory committees focusing on land reclamation, watershed restoration and mine drainage. I work closely with watershed organizations, the environmental community, state and Federal agencies and the energy industry to find solutions to energy and environmental problems.

**1978-1987:** Director, Reclamation Research, Alberta Energy, Edmonton, Alberta.

**1982-1987:** Deputy Chairman, Development and Reclamation Review Committee, Alberta Energy, Edmonton, Alberta.

**1985-1987:** Senior Research Manager, Alberta Office of Coal Research and Technology, Alberta Energy, Edmonton, Alberta.

**1987-1988:** Director, Research Management, Alberta Technology, Research and Telecommunications, Edmonton, Alberta.

**1988-Present:** Director, National Mine Land Reclamation Center

**1991-Present:** Director, West Virginia Water Research Institute, West Virginia University

**2005-Present:** Subject Matter Expert-Mining and Environment, U.S. Army Corps of Engineers, Engineers Research and Development Center, Hanover, NH



### **CURRENT APPOINTMENTS:**

- Director, National Mine Land Reclamation Center, West Virginia University
- Adjunct Professor, Department of Geology and Geography, West Virginia University
- Adjunct Professor, Cape Breton University, Sydney, Nova Scotia
- Director, West Virginia Water Research Institute
- Member, West Virginia Acid Mine Drainage Task Force
- Member, Eastern Mine Drainage Federal Consortium
- Technical Support Team Leader: Appalachian Clean Streams Initiative/Acid Drainage Technology Initiative
- Member, West Virginia Special Reclamation Fund Advisory Council
- Board of Directors, Upper Mon River Association
- Fellow, USDOE Institute for Advanced Energy Solutions

### **AWARDS:**

- 2005**            **Environmental Conservation Distinguished Service Award,**  
Presented by the Society for Mining, Metallurgy and Exploration
- 1985**            **E.M. Watkin Award for Outstanding Contribution to the Betterment  
of Land Reclamation in Canada,** Presented by The Canadian Land  
Reclamation Association.
- 1977-78**        **University of British Columbia Graduate Research Fellowship**
- 1975-77**        **Kaiser Resources Ltd. Graduate Fellowship**-University of British  
Columbia.

### **PROFESSIONAL AFFILIATIONS:**

- Xi Sigma Pi
- Sigma Xi
- American Association for the Advancement of Science
- Director, Vice President and President of the Canadian Land Reclamation Association. (1980-1987)
- President of the Alberta Chapter of the Canadian Land Reclamation Association. (1979-1986)

- National Executive Committee, American Society for Surface Mine Reclamation. (1988-1992)

**ACADEMIC TEACHING EXPERIENCE:**

- Univ. of Alberta Faculty of Mining and Petroleum Engineering. MinSci 404. Environmental Management in Oil Shale Mining.  
Taught as an adjunct professor with J.D Scott and M.B. Dussault. Fall 1981, 1982.
- Lectures in the WVU Colleges of Agriculture/Forestry and Engineering in mine reclamation and environmental technology.
- Biology Graduate Seminar, West Virginia University

### **PROGRAM DEVELOPMENT:**

Since assuming the directorship of the West Virginia Water Research Institute, it has become one of the strongest research centers at West Virginia University. Over the past 18 years we have developed and managed research projects worth roughly \$75M. Funding has been generated from a variety of federal agencies: Office of Surface Mining, EPA, USGS, USDA, USDOE, USACE, USDOL as well as state and industry sponsors. In the current fiscal year we have 43 projects with an annual budget of \$5.8 million. A detailed summary of sponsored projects is available on request. The Center has a full-time staff of twelve.

### **MAJOR, CURRENT RESEARCH PROJECTS:**

- USACE/Ohio DNR Monday Creek Watershed Restoration Project
- OSMRE Selenium Source Identification/Treatment Project
- USDOE/NETL Identification of Alternate Cooling Water Sources for New Coal-Fired Power Plants
- USDOL/MSHA Risk Assessment of Coal Slurry Impoundments
- USEPA-Region III Development of Water Pollution Credit Trading System
- WVDEP Watershed Restoration Projects: Cheat River, Paint Creek, Tygart River and Ten Mile Creek
- USDOE/NETL Water Recovery from power plant cooling systems
- USDOE/NETL Marcellus frac water treatment for reuse
- USEPA/WVDEP Development of sustainable energy on mined land
- USGS TDS Monitoring program for the Monongahela River
- GenPower, LLC Combined treatment of municipal sewage and treated coal mine drainage to control TDS via sulfate reduction
- OSMRE/Argus Mining Restoration of stream channels and wetlands on Company mountaintop mines: aquatic functional process
- WVDEP Determination of ecological benefits due to stream restoration efforts in southern WV
- Patriot Coal Co./WVDEP Determination of selenium sources and aquatic life impacts in the Mud River
- OSMRE/Patriot Coal Co. In-situ selenium control in selenium rich overburden

- USDOL/MSHA            Geomorphic design of mountaintop mines to enhance stream recovery and aquatic values
- WVDEP                    Monitoring flooding underground mine pools in the Pittsburgh Basin
- Wheeling Jesuit Univ./ MSHA            Geotechnical safety of coal slurry impoundments
- USDA/NRCS                Development of nutrient trading system for the Potomac
- USEPA                      Nutrient trading program for the Kanawha River

## **PUBLICATIONS:**

### *REFEREED JOURNALS:*

Petty, J. T., Fulton, J. B., Merovich, G. T, Jr., Strager, M. P., Stiles, J., and Ziemkiewicz, P. F. IN REVIEW. Landscape indicators and thresholds of ecological impairment in an intensively mined Appalachian watershed. *Journal of the North American Benthological Society*.

Emerson, P., Skousen, J. and Ziemkiewicz, P. 2009. Survival and growth of hardwoods in brown versus gray sandstone on a surface mine in West Virginia. *J. Environ. Qual.* 38:1821-1829

Merovich, G.T., Stiles, J.M., Petty, J.T., Ziemkiewicz, P.F. and Fulton, J.B. 2007. Water chemistry-based classification of streams and implications for restoring mined Appalachian watersheds. *Env. Toxicology and Chem.*, Vol. 26, no. 7, pp 1361-1369.

Skousen, J, Ziemkiewicz, P.F. and Venable, C. 2006. Tree recruitment and growth on 20-year old unreclaimed surface mined lands in West Virginia. *International Journal of Mining, Reclamation and Environment.* Vol. 20, No. 2, June 2006, pp. 142-154.

Ziemkiewicz, P.F., J. Skousen, and J. Simmons. 2003. Long-term performance of passive acid mine drainage treatment systems. *Mine Water and the Environment* 22: 118-129.

Skousen, J, Simmons, J, McDonald, L.M., and Ziemkiewicz, P.F. 2002. Acid-base accounting to predict post-mining drainage quality on surface mines. *J. Environ. Qual.* 31: 2034-2044.

Simmons, J, Ziemkiewicz, P.F. and Black, D.C. 2002. Use of Steel Slag Leach Beds for the Treatment of Acid Mine Drainage. *Mine Water and the Environment* 21: 91-99 Springer-Verlag (2002).

Lenter, C.M., McDonald, L.M., Skousen, J.G., and Ziemkiewicz, P.F. 2002. The Effects of Sulfate on the Physical and Chemical Properties of Actively Treated Acid Mine Drainage Floc. *Mine Water and the Environment* 21: 114-120 Springer-Verlag (2002).



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- Skousen, J., Renton, J., Brown, H., Evans, P., Leavitt, B., Brady, K., Cohen, L., and Ziemkiewicz, P.F., 1997. Neutralization Potential of Overburden Samples containing Siderite. *J. Environ. Qual.* 26: 673-681(1997).
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- Ziemkiewicz, P.F. and Cronin, E.H., 1981. Germination of Seed of Three Varieties of Spotted Locoweed. *J. Range Mgt.* 34 (2): 94-97.
- Ziemkiewicz, P.F. and Northway, S.M., 1978. Species selection technique for Reclamation in British Columbia. *Recl. Rev.* 1:163-166.

*REFEREED PROCEEDINGS/BOOKS:*

- Petty, J. T., Brady Gutta, Richard Herd, Jennifer Fulton, James Stiles, Michael Strager, Julie Svetlick, and Paul Ziemkiewicz. Identifying cost-effective restoration strategies in mining impacted West Virginia watersheds. *Proceedings of the American Society of Mining and Reclamation* 25:837-855.
- Stiles, J., J. T. Petty, Brady Gutta, Richard Herd, Jennifer Fulton, Michael Strager, Julie Svetlick, and Paul Ziemkiewicz. IN PRESS. Mass-balance calculations for various restoration alternatives in AMD impacted watersheds. *Proceedings of the American Society of Mining and Reclamation* 00:000-000.
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- Levitt, B.R., Stiles, J.M., Donovan, J.D., Ziemkiewicz, P.F. 2005. Strategies for Cooling Electric Generating Facilities Utilizing Mine Water: Technical and Economic Feasibility. In. Proceedings of the 22<sup>nd</sup> Annual Int'l Pittsburgh Coal Conference. 12-15 Sep 2005. Pittsburgh PA, USA. ISBN# 1-890977-22-5
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R. Herd, T. Petty, P.F. Ziemkiewicz, J. Fulton, B. Gutta, M. Strager and J. Svetlik. 2008. Optimizing Resources for Restoring Acid Mine Drainage Impaired Watersheds in WV. 2008 Annual Pa Abandoned Mine Reclamation Conference, State College, PA.

Fulton, J.B., P. Ziemkiewicz, and T. Vandivort. 2007. Using flue gas desulfurization solids to control acid mine drainage: a case study. Proceedings of the International Pittsburgh Coal Conference, Johannesburg, South Africa.

Fulton, J.B., T. Vandivort, and P. Ziemkiewicz. 2007. The combustion by-products recycling consortium. Proceedings of the International Pittsburgh Coal Conference, Johannesburg, South Africa.

Strager, M.P., Maskey, V., Petty, J.T., Gutta, B. Fulton, J., Herd, R., Stiles, J., Svetlik, J., and P. Ziemkiewicz. 2008. A Hydrologically Networked Watershed Model for Evaluating AMD Treatment Scenarios. Proceedings of the National Meeting of the American Society of Mining and Reclamation.

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- Ziemkiewicz, P.F. (ed.) 1983. Effects of Coal Mining on the Hydrology of Alberta's Eastern Slopes. Alberta Land Conservation and Reclamation Council Report. #RRTAC 84-4. 123 pp.



- Ziemkiewicz, P.F. 1983. Revegetation of Oil and Gas Disturbances; Seed Mixes, Fertilization and Application Methods. Proc. Can. Land Recl. Assn. 8th Annual Meeting, Waterloo, Ontario, August 1983.
- Ziemkiewicz, P.F. 1982. Reclamation Aspects of Coal Ash Disposal, Proc. Can. Land Recl. Assn. 7th Annual Meeting, Sydney, N.S. August 1982. pp. 197-206.
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- Ziemkiewicz, P.F. 1979. Effects of fertilization on the nutrient and organic matter dynamics of reclaimed coal-mined areas and native grasslands in southeastern British Columbia, Ph.D. Thesis, University of British Columbia. 162 pp.
- Ziemkiewicz, P.F. 1979. The Capacity of Reclamation Plant Communities to supply their own Nutrients: When does maintenance fertilization become unnecessary? Proc. Can. Land Recl. Assn., 4th Annual Meeting, Regina, Sask., August 1979. pp. 195-206.
- Ziemkiewicz, P.F., Dermott, C.A. and Sims, H.P. (eds), 1979. Native Shrubs in Reclamation. Proceedings of an Alberta Land Conservation & Reclamation Council Workshop, Edmonton, Alberta, Nov. 1979. #RRTAC 79-2, 104 pp.
- Ziemkiewicz, P.F. 1975. Reclamation research methods on coal-mining disturbed lands with particular reference to species evaluation and selection. Proc. Can. Land Recl. Assoc., 1st Annual Meeting, Guelph, Ontario, December 1975. pp. 69-76.

**JOHN D. QUARANTA, Ph.D., P.E., Assistant Professor,  
Civil and Environmental Engineering, WVU  
Project Co-Investigator**

**PROFESSIONAL PREPARATION:**

Doctor of Philosophy in Civil Engineering (Ph.D.)

West Virginia University, Department of Civil and Environmental Engineering  
Specialization: Geotechnical and Geoenvironmental Engineering

Master of Science in Civil Engineering (MSCE)

West Virginia University, Department of Civil and Environmental Engineering  
Specialization: Geotechnical and Geoenvironmental Engineering

Bachelor of Engineering (BE)- Civil Engineering

Youngstown State University, Department of Civil and Environmental Engineering

Bachelor of Engineering (BE)- Mechanical Engineering

Youngstown State University, Department of Mechanical Engineering

**APPOINTMENTS:**

- 8/08 – Present:** Assistant Professor – Geotechnical Engineering, Department of Civil & Environmental Engineering, West Virginia University
- 7/03 – 7/08:** Associate Director, West Virginia Water Research Institute, National Research Center for Coal and Energy, West Virginia University
- 9/02 – 5/03:** Research Assistant Professor, Department of Civil Engineering, North Carolina State University
- 4/00 – 9/02:** Engineering Consultant to the US Department of Energy and US Army Corps of Engineers
- 1/98 - 4/00:** Research Assistant Professor, Department of Civil Engineering, North Carolina State University
- 6/96 - 12/97:** Research Assistant Professor, Civil & Environmental Engineering, West Virginia University
- 8/94 - 5/96:** Asst. Director, US Department of Energy Cooperative Agreement, Civil & Environmental Engineering, West Virginia University
- 8/92 - 3/96:** Ph.D. candidate, Civil & Environmental Engineering, West Virginia University
- 6/88 - 7/93:** Project Engineer, EG&G Technical Services, WV
- 6/84 - 6/88:** Structural Design Engineer, Stearns Engineering, Rockville, MD

**REGISTRATION:**

Registered Professional Engineer, State of Ohio.

### **SUMMARY OF CURRENT APPOINTMENT:**

Dr. Quaranta has performed and directed Geoenvironmental and Geotechnical research and development on basic and applied projects for federal and state agencies including: the US Mine Safety and Health Administration, US Department of Defense, the US Department of Energy, and the State of West Virginia. Current research topics include: environmental forensic studies identifying unexploded ordnance and munitions constituents at former firing ranges located in the Monongahela National Forest; geosynthetic filter compatibility of coarse and fine coal refuse; and improving emergency preparedness at coal waste impoundments.

### **SELECT TECHNICAL PUBLICATIONS:**

J.D. Quaranta, H.M. Childers, and P. Myles. "Lessons Learned from Table Top Reviews of Emergency Action Plans for High Hazard Dams in West Virginia, USA." Tailings and Mine Waste' 08, 19-22 October 2008 Vail, CO, CRC Press, pp 325-336.

J.D. Quaranta, L.E. Banta, and J.A. Altobello. "Remote Monitoring of a High Hazard Coal Waste Impoundment in Mountainous Terrain Case Study," Tailings and Mine Waste' 08, 19-22 October 2008 Vail, CO, CRC Press, pp 125-136.

Richard W. Hammack, John D. Quaranta, Vladislav Kaminskiy, Kevin Warner, and William Harbert, "Using Helicopter Electromagnetic Surveys to Identify Potential Hazards at Coal Waste Impoundments," Proceedings of the 2005 Symposium for the Application of Geophysics to Engineering and Environmental Problems, Atlanta, GA, April 3-7, 2005.

J.D. Quaranta, B. Gutta, B. Stout, D. McAteer, and P. Ziemkiewicz, "Improving the Safety of Coal Slurry Impoundments in West Virginia," Tailings 2004, Vail CO

J.D. Quaranta, D. McAteer, J. Papillo, H. Childers, and J.D. Higginbotham, "West Virginia Coal Impoundment Location and Warning System," Tailings 2004, Vail CO

J.D. Quaranta, T. Kunberger, and M.A. Gabr, "WIDE Application for Subsurface Hydraulic Head Control," Geo-Frontiers 23-26 January 2005, Austin, Texas, In Situ Remediation of Contaminated Soils.

John J. Bowders, Mohammed A. Gabr, Omaira M. Collazos, and John D. Quaranta, "Prefabricated Vertical Drains for Enhanced In Situ Remediation," GRI-18 at Geo-Frontiers, 23-26 January 2005, Austin, Texas

Tanya Kunberger, John Quaranta, M.A. Gabr, (2003) "Extraction of JP-4 Using Well Injection Depth Extraction (WIDE): Field Demonstration," Soil Rock America 2003 in Cambridge, USA June 22 - 26, 2003.(page 1575), Editors: P.J. Culligan, H. H. Einstein, and A. J. Whittle, Publisher is VGE - Germany 2003.

K.A. Warren, M.A. Gabr, and J.D. Quaranta. "Field Study to Investigate WIDE Technology for TCE Extraction," Journal of Geotechnical and Geoenvironmental Engineering, ASCE, Volume 132, Issue 9, pp. 1111-1120, September 2006.

J.D. Quaranta and M.A. Gabr, (2000). " Prefabricated Vertical Drains Flow Resistance Under Vacuum Conditions," Journal of Geotechnical and Geoenvironmental Engineering, ASCE,126 (1), 81 – 84

**BENOIT VANAKEN, Ph.D., Assistant Professor  
Civil and Environmental Engineering, Temple University  
Project Co-Investigator**

### **QUALIFICATIONS:**

The Co-PI of the project, Dr. Benoit Van Aken, is an Assistant Professor in the Department of Civil and Environmental Engineering at Temple University. Although he has extensive experience in molecular microbiology, he is a new investigator in the field of waterborne pathogen detection. This proposal, if funded, would help him to establish his research program.

Dr. Van Aken has more than ten years' experience in environmental science research. For two years his team has focused on pathogens and antimicrobial resistance in wastewater. He has expertise in microbiology and molecular biology, including genetic fingerprinting (DGGE, T-RFLP), molecular cloning, gene expression analysis (RT real-time PCR), flow cytometry, DNA sequencing, hybridization, microarray, and bioinformatics. He is the author of 20 publications in peer-reviewed journals.

Dr. Van Aken will spend two academic months on the project. He will supervise all research activities and ensure that the experiments will be conducted according to safety and QA/QC guidelines. He will also be responsible for reporting requirements and publications.

### **REFERENCES CITED:**

- Abdo, Z., Schuette, U. M. E., Bent, S. J., Williams, C. J., Forney, L. J., Joyce, P., 2006. Statistical methods for characterizing diversity of microbial communities by analysis of terminal restriction fragment length polymorphisms of 16S rRNA genes. *Environmental Microbiology* 8, 929-938.
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- Dunbar, J., Ticknor, L.O., Kuske, C.R., 2000. Assessment of microbial diversity in four southwestern United States soils by 16S rRNA gene terminal restriction fragment analysis. *Applied and Environmental Microbiology* 66, 2943-2950.
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- Thies, J.E., 2007. Soil microbial community analysis using terminal restriction fragment length polymorphisms. *Soil Science Society of America Journal* 71, 579-591
- Wu, M., Song, L.S., Ren, J.P., Kan, J.J. and Qian, P.Y., 2004. Assessment of microbial dynamics in the Pearl River Estuary by 16S rRNA terminal restriction fragment analysis. *Continental Shelf Research* 24, 1925-1934

**TAMARA F. VANDIVORT, M.S.**  
**Program Coordinator, West Virginia Water Research Institute**  
**Project Support**

**EDUCATION:**

**M.S.** WVU, Morgantown, West Virginia. Environmental Geology 1995  
**B.S.** WVU, Morgantown, West Virginia. Geology 1992  
**Certificate** WVU, Morgantown, West Virginia. MBA Essentials 2002

**AREAS OF EXPERTISE:**

Program planning, project management; proposal development; budgeting; human resources; employee supervision; water quality; wastewater treatment technologies; environmental remediation; brownfields; technical and business writing; conference coordination; and outreach.

**PROFESSIONAL EXPERIENCE:**

**West Virginia Water Research Institute, WVU, Morgantown, WV** 1999 – present  
*Program Coordinator*

Serves as principal investigator, co-investigator, and/or project manager on projects related to environmental remediation. Responsible for program development, securing funding, proposal development, and budgeting. Responsible for program administration, subcontract implementation, expenditure tracking, monitoring technical progress, developing deliverables, writing technical progress and final reports. Communicates with project researchers, sponsoring agency program officers, representatives from regulatory agencies, watershed associations, and the public. Develops and releases requests for proposals issued by the Institute and supported by funds from such agencies as the U.S. Department of Energy - National Energy Technology Laboratory and the U.S. Geological Survey. Coordinates, moderates, and/or participates in meetings of the West Virginia Water Advisory Committee, the West Virginia Water Gaging Council, and the National Institute for Water Resources and Project Steering Committees. Represents WVWRI at professional meetings and conferences. Writes papers and gives presentations at local, regional, state, national, and international conferences. Coordinates and presents project results at public meetings. Coordinates and oversees outreach activities of the WVWRI, a self-sustaining institute managing over \$3M per year in research programs and projects. Outreach activities include planning, managing, and coordinating an annual state water conference, managing the WVWRI web site, developing a quarterly newsletter, program brochures, fact sheets, and display materials for conference exhibits. Serves as WVWRI human resources liaison following University and Research Corporation hiring procedures to develop position descriptions, chair search committees, interview candidates, draft offer letters, advertisements, etc.

**National Small Flows Clearinghouse, WVU, Morgantown, WV** 1995 - 1999  
*Technical Assistance Specialist*

<b>Appalachian Hardwood Center</b> , WVU, Morgantown, WV <i>Research Assistant</i>	1992 - 1995
<b>Town of Amherst, MA</b> <i>Administrative Support</i>	1988-1989
<b>Virginia Tech, Blacksburg, VA</b> <i>Administrative Support</i>	1977-1987

**PROFESSIONAL AFFILIATIONS:**

2001- present: WVWRI Representative, National Institutes for Water Research  
 2007- present: WVWRI Representative Member, West Virginia Water Gaging Council  
 2001- 2008: WVWRI Representative Member, American Coal Ash Association  
 2005-2006: Secretary/Treasurer, West Virginia Water Gaging Council  
 2005-2006: Secretary/Treasurer, Ohio River Basin Consortium for Research and Education

**ACADEMIC AWARDS:**

- Sigma Gamma Epsilon, W. A. Tarr Award for Outstanding Scholarship in Geology, 1991-1992
- Chevron Corporation, Scholarship for Outstanding Academic Achievement, 1991
- West Virginia University College of Arts & Sciences, Outstanding Senior in Geology, 1991-1992
- West Virginia University, College of Arts & Sciences, Certificates of Achievement for Academic Excellence, 1991, 1992
- West Virginia University, Department of Geology & Geography, Field Camp Scholarship, 1991

**PUBLICATIONS:**

Fulton, Jennifer, Tamara **Vandivort** and Paul Ziemkiewicz. 2007. Combustion Byproducts Recycling Consortium. Paper for the Twenty-fourth Annual International Pittsburgh Coal Conference, Johannesburg, South Africa, September, 2007. 29 p.

**Vandivort**, T. F. and P. F. Ziemkiewicz. 2007. *Potential Uses for Coal Combustion By-products for Sustainable Construction Materials*. Proceedings, Sustainable Construction Materials and Technologies Conference, June 11-13, 2007, Coventry, UK; pp. 171-182.

**Vandivort**, Tamara F. and Paul F. Ziemkiewicz. 2006. *Environmental Concerns Related to the Use of Coal Combustion Byproducts in Mine Placement*. Paper for the Twenty-third Annual International Pittsburgh Coal Conference, September 25-27, 2006, Pittsburgh, PA. 30 p.

Ziemkiewicz, Paul F. and Tamara F. **Vandivort**. 2005. *The United States' Combustion Byproducts Recycling Consortium—Program Update*. Paper



for the Twenty-second Annual International Pittsburgh Coal Conference, September 12-15, 2005, Pittsburgh, PA. 33 p.

Leavitt, Bruce R., James Stiles, Joseph Donovan, Paul Ziemkiewicz, Brenden Duffy, and Tamara **Vandivort**. 2005. *Strategies for Cooling Electric Generating Facilities Utilizing Mine Water: Technical and Economic Feasibility Project*. Paper for the Twenty-second Annual International Pittsburgh Coal Conference, September 12-15, 2005, Pittsburgh, PA. 18 p.

Ziemkiewicz, Paul F. and Tamara F. **Vandivort**. 2004. *The United States' Combustion Byproducts Consortium*. Paper for the Twenty-first Annual International Pittsburgh Coal Conference, September 13-15, 2004. Osaka, Japan. 23 p.

Ziemkiewicz, Paul F. and Tamara F. **Vandivort**. 2001. *The United States' Combustion Byproducts Consortium Program*, Paper for the Eighteenth Annual International Pittsburgh Coal Conference, December 3-7, 2001, Newcastle, Australia. 9 p.

**Vandivort**, T. F. 1999. How to determine the condition of an onsite wastewater treatment system. *Small Flows* 13(1).

**Vandivort**, T. F. and A. M. Lake. 1997. *Drip Irrigation*. *Small Flows* 11(3): 12-13.

Angoli, T. A., and T. F. **Vandivort**. 1997. *What is BOD*. *Small Flows* 11(1):14.

**Vandivort**, T. F., C. C. Hassler and L. E. Osborn. August, 1993. *Waterborne wood finishing technology as an alternative to solventborne products to achieve compliance with volatile organic compound (VOC) emissions regulations*. Appalachian Hardwood Center, West Virginia University, Morgantown, West Virginia. Fact Sheet Series (11):1-4.

**Vandivort**, T. F., C. C. Hassler, T. L. Pahl, and H. C. Sims. April, 1993. *Complying with environmental regulations with emphasis on the Clean Air Act Amendments of 1990*. Appalachian Hardwood Center, West Virginia University, Morgantown, West Virginia. Fact Sheet Series (10): 1-7.

**Vandivort**, T. F., and C. C. Hassler, eds. 1990. *Appalachian Hardwood Center 1989-90 Biennial Report of Research and Extension*, Division of Forestry, College of Agriculture and Forestry, Morgantown, West Virginia.

**Ben Mack, M.S.**  
**Research Associate, West Virginia Water Research Institute**  
**Project Support**

**EDUCATION:**

**Master of Science - 2008**

Plant and Soil Sciences  
West Virginia University

**Bachelor of Science - 2003**

Double Major in Agronomy and Environmental Protection  
West Virginia University

**Bachelor of Arts - 1999**

Technical Theater  
West Virginia University

**EXPERIENCE:**

**Feb. 2009 – Present Research Associate**

*West Virginia University, West Virginia Water Research Institute*

**May 2008-Nov. 2008 Research Assistant**

*West Virginia University, West Virginia Water Research Institute*

**2006- May 2008 Graduate Research Assistant**

*West Virginia University, Division of Agriculture, Forestry, and Consumer Sciences*

**2005 Research Assistant**

*West Virginia University, West Virginia Water Research Institute*

**RESEARCH SUPPORT:**

### ***Roaring Creek Watershed Reclamation Project***

Investigators: Ben Mack, Paul Ziemkiewicz, Brady Gutta  
Funding Source: West Virginia Department of Environmental Protection  
Funding Amount: \$25,000

### ***McCarty Highwall Refurbishment***

Investigators: Brady Gutta, Paul Ziemkiewicz, Ben Mack  
Funding Sources: West Virginia Department of Environmental Protection  
Funding Amount: \$58,932

### **HONORS:**

- American Society of Mining and Reclamation-National Meeting Oral Presentation 3<sup>rd</sup> place-2008
- NASLR scholarship winner- 2007
- Deans List- Fall 1995 and Spring 1997

### **PROFESSIONAL MEMBERSHIPS:**

- American Society of Mining and Reclamation
- National Association of State Land Reclamationists

### **PUBLICATIONS:**

- Mack, B.** and Gutta, B. 2009. An Analysis of Steel Slag and Its Use in Acid Mine Drainage Treatment. Proceedings of the American Society of Mining and Reclamation national conference. Richmond, VA.
- Mack, B.** and Skousen, J. 2008. Water Quality Changes over Time in Above-Drainage Upper Freeport and Pittsburgh Coal Mines in West Virginia. Proceedings of the West Virginia Acid Mine Drainage Task Force annual meeting. Morgantown, WV.
- Mack, B.** and Skousen, J. 2008. Water Quality Changes over Time in Above-Drainage Upper Freeport and Pittsburgh Coal Mines in West Virginia. Proceedings of the National Ground Water Association annual meeting. Denver, CO.
- Mack, B.** and Skousen, J. 2007. Water Quality From Above Drainage Underground Mines Over A 38 Year Period. Proceedings of the National Association of State Land Reclamationists national conference. Asheville, NC.
- Mack, B.** and Skousen, J. 2007. Changes In Water Quality Of 34 Above Drainage Mines In West Virginia. Proceedings of the American Society of Mining and Reclamation national conference. Gillette, WY.

Skousen, J and **Mack, B.** 2006. Water Quality From Above-Drainage Underground Mines Over A 35-Year Period. Proceedings of the International Conference on Acid Rock Drainage. St. Louis, MO.





**STATE OF WEST VIRGINIA  
DEPARTMENT OF HEALTH AND HUMAN RESOURCES**

**Office of the Secretary**

State Capitol Complex, Building 3, Room 206  
Charleston, West Virginia 25305

Telephone: (304) 558-0684 Fax: (304) 558-1130

**Joe Manchin III**  
Governor

**Patsy A. Hardy, FACHE, MSN, MBA**  
Cabinet Secretary

August 2, 2010

The Honorable Earl Ray Tomblin, President  
West Virginia Senate  
Room 227M, Building 1  
State Capitol Complex  
Charleston, West Virginia 25305

The Honorable Richard Thompson, Speaker  
West Virginia House of Delegates  
Room 228M, Building 1  
State Capitol Complex  
Charleston, West Virginia 25305

Dear Mr. President and Mr. Speaker:

In response to Senate Concurrent Resolution 15, dated March 10, 2007, I am pleased to present the Phase Two report prepared for the Department of Health and Human Resources (DHHR) through a contract with West Virginia University (WVU). The WVU team included representatives from the Department of Community Medicine, the Water Research Institute, and the Civil and Environmental Engineering Department.

As you are aware, the study required by SCR-15 was divided into two phases. Phase One required the Department of Environmental Protection (DEP) to develop and conduct a study regarding the chemical composition of coal slurry and the impacts on ground or surface waters from disposing of slurry by underground injection into abandoned coal mines. Phase Two of SCR-15 required DHHR's Bureau for Public Health (BPH) to review data collected from Phase One to determine if slurry injection poses a health threat to coalfield residents.

Under contract and on behalf of BPH, WVU scientists reviewed the environmental data collected during Phase One to determine if there was contamination, the level of contamination, the location, and how people might come into contact with it. They also evaluated whether or not these substances may pose a threat to human health.

The Honorable Earl Ray Tomblin  
The Honorable Richard Thompson  
August 2, 2010  
Page Two

The enclosed final report concludes the BPH activities related to SCR-15. The final report addresses the above issues and additionally provides recommendations for consideration with regard to future monitoring of potential coal slurry injection.

Should your staff need additional information regarding the report, please contact Barbara Taylor, Director of the Office of Environmental Health Services at 304-588-2229 or Randy C. Curtis, Director of the Office's Radiation Toxics and Indoor Air Division at 304-558-6721.

Sincerely,



Patsy A. Hardy  
Cabinet Secretary

PAH:ks

Enclosure

cc: Aaron Allred, Legislative Manager  
Chris Curtis  
Janet Richards  
Barbara Taylor

**AGREEMENT  
BETWEEN  
THE WEST VIRGINIA DEPARTMENT OF HEALTH AND  
HUMAN RESOURCES  
BUREAU FOR PUBLIC HEALTH  
OFFICE OF ENVIRONMENTAL HEALTH SERVICES  
and  
WEST VIRGINIA UNIVERSITY**

**THIS AGREEMENT**, by and between the West Virginia Department of Health and Human Resources, Bureau for Public Health, Office of Environmental Health Services, hereinafter referred to as the DEPARTMENT and West Virginia University, hereinafter referred to as PROVIDER, is effective April 1, 2009 and continues through March 31, 2010 for the purpose of performing the tasks and functions for conducting a Public Health Assessment.

WHEREAS, the West Virginia State Legislature Concurrent Resolution No. 15 (SCR-15) mandated the Department of Environmental Protection (WVDEP) and the DEPARTMENT to jointly design and conduct, or contract to have conducted, a comprehensive study on the effects of underground injection of coal slurry.

WHEREAS, Phase I of this comprehensive study is being conducted by the WVDEP and the federal Office of Surface Mining (OSM), with some assistance from the DEPARTMENT, for the purpose of gathering and presenting environmental and hydrogeological data from Phase I slurry-injection sites.

WHEREAS, the DEPARTMENT is responsible for the oversight of Phase II of the comprehensive study, which is to include analyzing data collected during Phase I and conducting the Public Health Assessment.

WHEREAS, the interagency agreement with the PROVIDER is an excellent example of collaboration between state agencies and the use of the developed facilities at the PROVIDER.

WHEREAS, this collaborative project will allow for the development of a Public Health Assessment necessary to make critical public health decisions.

WHEREAS, the PROVIDER can provide the specialized and unique requirements for developing and conducting a Public Health Assessment.

WHEREAS, the PROVIDER has provided technical support, similar to this request, due to the specialized and unique requirements to other state agencies.



## I. Provisions

- A. The DEPARTMENT will obligate funding in the amount of \$221,519. It shall be mutually understood that should the DEPARTMENT'S funding source for this project not be provided, for any reason, this AGREEMENT shall be declared void with no liabilities on the part of either party.
- B. The PROVIDER shall be responsible for the satisfactory performance of the project goals and accomplishments, and shall submit four (4) written progress reports providing a detailed summary of activities, according to the following schedule:
  - June 30, 2009 (Reporting Period: April 1, 2009 - June 30, 2009)
  - September 30, 2009 (Reporting Period: July 1, 2009 - September 30, 2009)
  - December 31, 2009 (Reporting Period: October 1, 2009 - December 31, 2009)
  - March 31, 2010 (Reporting Period: January 1, 2010 - March 31, 2010)
- C. The PROVIDER shall submit an invoice at the end each reporting period for reimbursement of costs incurred during the period. Funds shall be distributed to the PROVIDER based upon invoices approved by the DEPARTMENT, which itemize actual contract accomplishments and associated costs and expenses. The PROVIDER agrees to maintain adequate financial records and shall hold them open for review by the DEPARTMENT. In addition, any and all subcontracts entered into by the PROVIDER to perform work or provide services in furtherance of the successful completion of this contract shall be subject to the review and approval of the DEPARTMENT.
- D. In addition to progress reports, the PROVIDER shall submit monthly status updates to the DEPARTMENT. These monthly status updates will be shown in tabular form providing percentage complete and expected completion dates for all activities expressed in this AGREEMENT. The DEPARTMENT will provide a template to be used for this purpose.

## II. Activities:

- A. The DEPARTMENT will provide the Phase I environmental and hydrogeological data. The PROVIDER will be responsible for identifying data gaps and making conclusions and recommendations, based on the data provided to it and other publicly available data.
- B. The PROVIDER will be responsible for gathering public health data related to the general topic of slurry injection from whatever peer review (and potentially non-peer review) sources are available. Public health data may be gathered utilizing the following mechanisms:
  - 1. The PROVIDER will create a website for public data collection.
  - 2. The PROVIDER will collect any publicly available data.
  - 3. The PROVIDER will invite federal, state, and local agencies, national foundations, and industry to contribute any human health effects data

that they consider pertinent to the human health effects of slurry injection.

4. The PROVIDER will create and make available a news story to the Central Appalachian media about the effort, and invite public or private submission of data. (Accept all materials submitted, and focus on data.)
- C. The PROVIDER may visit federal and state agencies and up to three foundations as needed for input into report creation.
  - D. The PROVIDER may invite stakeholder visits.
  - E. The PROVIDER will consult with leaders at the Environmental Protection Administration, the Agency for Toxic Substances and Disease Registry, the US Geological Survey, and other relevant federal agencies, and independent risk-assessment experts, as appropriate, to identify reviewers to participate on a expert panel:
    1. The PROVIDER will invite no fewer than three and no more than six reviewers to participate on the expert panel.
    2. The PROVIDER will submit the names of the expert panel to the DEPARTMENT, but the right to request the review and to choose the reviewers remains with the PROVIDER.
  - F. The PROVIDER and affiliated consultants will analyze the Phase I environmental and hydrogeological data and the public health data to draft a Public Health Assessment Report addressing the following five issues.
    1. What are the known health hazards of the components of coal slurry (its major constituent contaminants) on human health? This assessment will be useful in the event that human exposure occurs following slurry underground injection. This component of the review does not presume that sufficient exposures to cause health hazards actually exist. It simply reviews what are the population health hazards should such exposure occur.
    2. What data already exist about human community health hazards from exposures to coal slurries contaminating water, soil, or air? This part of the Phase II study will review existing local, national, or international literature to determine what is currently known about data to determine the actual known or reported effects of coal slurry and its constituent contaminants on public health in communities, where it is determined that coal slurry or its constituent contaminants have migrated from injection sites into ground waters currently or historically used for domestic purposes, or habitated soils, and then into humans, or into air in breathing zones of communities and then into humans.
    3. The study will briefly recapitulate what is known about effects of coal slurry injection on surface water and aquatic ecosystems. This phase of the assessment project is directed at known human health effects, whereas this Phase II study is designed primarily as a human health risk

assessment. Therefore, this section will be a brief overview, and is structured primarily as a human health assessment.

4. Coal slurry injection is not the only choice for disposing of coal slurry. Therefore, a relevant question is, How do the known or suspected hazards of injection compare to other means of dealing with slurry from coal operations? This section of the document will briefly describe and compare what is known about coal slurry injection compared to hazards of coal slurry as surface impoundments.
  5. The Phase II report will enumerate and describe data gaps and their relative significance to the study.
- G. The PROVIDER will format the draft and final Public Health Assessment Report based on the United States Department of Health and Human Services, Centers for Disease Control and Prevention (CDC), Agency for Toxic Substances and Disease Registry (ATSDR) Public Health Assessment Guidance Manual. The DEPARTMENT must approve any significant deviation from the ATSDR, PHA guidance.
- H. The PROVIDER will create an initial draft report based on preliminary findings.
1. The PROVIDER will schedule meeting date, time, and location to present the initial draft report to the DEPARTMENT.
  2. The PROVIDER will schedule meeting date, time, and location to present the initial draft report to other interested parties as approved by the DEPARTMENT.
  3. The PROVIDER will invite additional feedback from the DEPARTMENT and other interested parties and revise the draft report based on the feedback, if necessary.
- I. The PROVIDER will be available to present preliminary findings to the West Virginia State Legislature, if requested.
- J. Upon completion of the draft report, the PROVIDER will submit the draft report to the DEPARTMENT and to the independent expert panel for an external review that may take no more than four weeks.
- K. The PROVIDER will revise the draft report based on comments from the expert panel and the DEPARTMENT. In the event of any final disagreements concerning contents between the PROVIDER and the expert panel, the concerns of the expert panel will be included as an appendix to the report.
- L. The PROVIDER will submit the final Public Health Assessment Report to the DEPARTMENT no later than December 31, 2009. A minimum of forty (40) original bound final Public Health Assessment Reports will be required. In addition the PROVIDER will submit the final report in electronic format.
- M. The PROVIDER shall not distribute the final Public Health Assessment Report prior to the DEPARTMENT'S submittal to the West Virginia State Legislature.

- N. The PROVIDER will participate in presentation of the final Public Health Assessment Report to the West Virginia State Legislature, if requested.

### III. Timeline

A. April 01, 2009-June 30, 2009

1. Receive and review Phase I and any other environmental and hydrogeological data.
2. Gather public health data from all sources.
3. Form expert panel.

B. July 1, 2009-September 30, 2009

1. Analyze data.
2. Identify data gaps, if present.
3. Create an initial draft report based on preliminary findings.
4. Schedule meetings with DEPARTMENT and interested parties to present initial draft report and collect feedback.
5. Revise draft report based on feedback, if necessary.

C. October 1, 2009-October 31, 2009

1. Revise draft report based on feedback.
2. Submit draft report to the DEPARTMENT.
3. Submit draft report to expert panel.

D. November 1, 2009-December 31, 2009

1. Receive comments from the DEPARTMENT and expert panel.
2. Revise draft document based on comments.
3. Submit final report to the DEPARTMENT.

E. January 1, 2010-March 31, 2010

Participate in presentation to West Virginia State Legislature, if requested.

### IV. Terms of AGREEMENT

- A. The PROVIDER further agrees that all subcontracts entered into by the PROVIDER shall be subjected to prior approval of the DEPARTMENT. In addition, any and all subcontracts entered into by the PROVIDER to perform work or provide services in furtherance of the successful completion of this AGREEMENT shall be subject to review and approval of the DEPARTMENT.

- B. This AGREEMENT can be terminated by the DEPARTMENT or PROVIDER at any time during the agreement period if the DEPARTMENT or PROVIDER shows adequate cause that the DEPARTMENT or PROVIDER has not or is not fulfilling its responsibilities as detailed by the terms of the AGREEMENT.
- C. This AGREEMENT can be amended at any time by mutual agreement of the parties hereto, in writing, with such amendments being executed by the designated signatures.
- D. By mutual consent, both parties agree that the initiation of this AGREEMENT shall begin upon the date specified on the face of this document and that those signatory parties identified below have the authority, statutorily or otherwise, to enter into such AGREEMENT for the mutual benefit of their respective agencies and the citizens of the State of West Virginia.

FOR West Virginia University

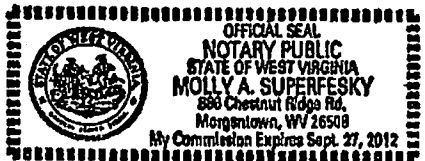
Authorized Signature: *Alan B. Martin* Date: 5/26/09

Printed Name and Title: Alan B. Martin  
Asst. V.P. for Research & Econ. Development

Taken, sworn, and subscribed before me this 26 day of May, 2009

Notary Public Signature: *Molly Superfesy*

My Commission Expires: Sept 27, 2012



FOR West Virginia Department of Health and Human Resources

*James D. [Signature]* 5/28/09  
 Date

**EXHIBIT B  
SOURCE OF FUNDS SCHEDULE**

**Exhibit B**

The Department estimates the funds for this Grant Agreement shall be paid from the following federal and/or state sources:

<b>FEDERAL FUNDS</b>			
<b>1. CFDA Number</b>	<b>2. Account Number (Fund/Activity)</b>	<b>3. WVFIMS Grant Name</b>	<b>4. Amount</b>
<b>TOTAL FEDERAL FUNDS</b>			<b>\$ -</b>

<b>STATE FUNDS</b>			
<b>5. Appropriation Type</b>	<b>6. Account Number (Fund/Activity)</b>	<b>7. Activity Name</b>	<b>8. Amount</b>
Appropriated General Revenue			
Special Revenue: Appropriated or Unappropriated	5139-099	Health Services Fees	\$ 221,519.00
<b>TOTAL STATE FUNDS</b>			<b>\$ 221,519.00</b>

<b>TOTAL FEDERAL AND STATE FUNDS</b>	<b>\$ 221,519.00</b>
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If at the end of the Grant Agreement period the Department determines the funding sources for all payments to the Grantee for this Grant Agreement are different than reflected above, a revised Source of Funds Schedule shall be sent to the Grantee by the Department that reflects the final source of funds.

**EXHIBIT E  
GRANTEE BUDGET**

**Exhibit E**

<b>Budget Category</b>	<b>Amount</b>
A. Personnel	121,744.00
B. Fringe Benefits	28,186.00
C. Equipment	
D. Supplies	6,150.00
E. Contractual Costs	27,301.00
F. Construction	
G. Other	18,000.00
<b>Total Direct Costs</b>	<b>\$201,381.00</b>

H. Indirect Costs	20,138.00
<b>Total Indirect Costs</b>	<b>\$20,138.00</b>

**Total Grant Award** **\$221,519.00**

For informational purposes only:

I. Grantee Supplied Match / Certified Match	
J. Other Grantee Supplied Funds	
K. Program Income (Projected)	

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**EXHIBIT I**  
**NO DEBT REQUIREMENT**

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**Exhibit I**

**West Virginia Code §5A-3-10a states:**

*No contract or renewal of any contract may be awarded by the state or any of its political subdivisions to any vendor or prospective vendor when the vendor or prospective vendor or a related party to the vendor or prospective vendor is a debtor and the debt owed is an amount greater than one thousand dollars in the aggregate.*

**Definitions:**

"Debt" means any assessment, premium, penalty, fine, tax or other amount of money owed to the state or any of its political subdivisions because of a judgment, fine, permit violation, license assessment, defaulted workers' compensation premium, penalty or other assessment presently delinquent or due and required to be paid to the state or any of its political subdivisions, including any interest or additional penalties accrued thereon.

"Debtor" means any individual, corporation, partnership, association, limited liability company or any other form or business association owing a debt to the state or any of its political subdivisions.

"Political subdivision" means any county commission; municipality; county board of education; any instrumentality established by a county or municipality; any separate corporation or instrumentality established by one or more counties or municipalities, as permitted by law; or any public body charged by law with the performance of a government function or whose jurisdiction is coextensive with one or more counties or municipalities.

"Related party" means a party, whether an individual, corporation, partnership, association, limited liability company or any other form or business association or other entity whatsoever related to any vendor by blood, marriage, ownership or contract through which the party has a relationship of ownership or other interest with the vendor, so that the party will actually or by effect receive or control a portion of the benefit, profit or other consideration from performance of a vendor contract with the party receiving an amount that meets or exceeds five percent of the total contract amount.

**Licensing:**

Vendors must be licensed and in good standing in accordance with any and all state and local laws and requirements by any state or local agency of West Virginia, including, but not limited to, the West Virginia Secretary of State's Office, the West Virginia Tax Department, West Virginia Insurance Commission, or any other state agencies or political subdivision. Furthermore, the vendor must provide all necessary releases to obtain information to enable the Director or spending unit to verify that the vendor is licensed and in good standing with the above entities.

Under penalty of law for false swearing (West Virginia Code §61-5-3), Grantee certifies that by signing this grant agreement on the signature page that Grantee and all related parties do not owe any debts.



COMMITMENT COVER SHEET

AUDITOR ENTRY ID: C 1 317145  
DOCUMENT ID: C 317145

STATE ORGANIZATION: 0500  
STATE ORGANIZATION NAME: DEPT OF HEALTH AND HUMAN RESOURCES  
ORGANIZATION CONTACT: WARREN KEEFER  
ORGANIZATION ADDRESS: BUILDING 3  
ROOM 451  
CHARLESTON WV 25305-0000

DATE PREPARED: 05/27/09  
COMMITMENT AMOUNT: 221,519.00  
COMMITTED AMOUNT: 55,379.00  
START DATE: 04/01/09  
END DATE: 03/31/10  
AGENCY REQUISITION NUMBER: G090951  
COMMITMENT TYPE: GRNT  
PROJECTED ENCUMBRANCE DATE: 06/30/09  
CONTRACT NUMBER:  
VENDOR NUMBER: 45835  
VENDOR NAME: WVU

VENDOR ADDRESS: PO BOX 6216

MORGANTOWN WV 26507-6216

CONTACT PERSON: BECKY BYERS  
CONTACT PHONE: 304-558-6505 EXT: 0000

DESCRIPTION: PAY BY IGT GRANT G090951 COMPREHENSIVE STUDY ON  
EFFECTS OF UNDERGROUND INJECTION OF COAL SLURRY

AUTHORIZED SIGNATURE: *Harry J. Rollins*

DATE: 5/28/09

LINE	FUND	FY	ORG	ACT	OBJ	GRANT	PROJ	AMOUNT
001	5139	2009	3190	099	253			55,379.00
								-----
								55,379.00
								-----
TOTAL COMMITMENT AMOUNT								55,379.00



**WEST VIRGINIA DEPARTMENT OF HEALTH AND HUMAN RESOURCES  
GRANT AGREEMENT WITHIN OR BETWEEN STATE AGENCIES**

*(Other than a Federal Subrecipient Agreement within or between State Agencies)*

1. Agreement Number: G 090951

2. WV FIMS Encumbrance Number: C317145

3. Grantee FEIN # 556000842 4. WV FIMS Vendor # 45835 5. Date Prepared April 16, 2009

<p>6. Grantee Name and Address</p> <p>West Virginia University 886 Chestnut Ridge Road Morgantown, WV 26507</p>	<p>7. Spending Unit Name and Address</p> <p>DHHR/BPH/Office of Environmental Health Services Capitol and Washington Streets 1 Davis Square, Suite 200 Charleston, WV 25301-1798</p>
---	---

<p>8. Grantee Remittance Name and Address</p> <p>WVU PO Box 6216 Morgantown, WV 26507-6216</p>	<p>9. Spending Unit Contact Person Name and Telephone Number</p> <p>Program: Walter Ivey (304) 558-6715 Fiscal: Lisa Brightwell (304) 558-8247</p>
--	--

10. Auditor's Information:		State Level		State Level		
Fund	FY	Org	Act	Obj	Amount	
<u>5139</u>	<u>2009</u>	<u>0506</u>	<u>099</u>	<u>025</u>	<u>55,379.00</u>	
<u>5139</u>	<u>2010</u>	<u>0506</u>	<u>099</u>	<u>025</u>	<u>166,140.00</u>	
_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____
<b>Total:</b>					<b>\$221,519.00</b>	

11. Start Date: April 1, 2009 12. End Date: March 31, 2010

13. Description of Program:  
Preparation of a comprehensive study on the effects of underground injection of coal slurry.

14. Spending Unit							
WV FIMS Coding							
Fund	FY	Extended Org	Act	Extended Obj	Grant	Project	Amount
<u>5139</u>	<u>2009</u>	<u>3190</u>	<u>099</u>	<u>253</u>	_____	_____	<u>55,379.00</u>
<u>5139</u>	<u>2010</u>	<u>3190</u>	<u>099</u>	<u>263</u>	_____	_____	<u>166,140.00</u>
_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____	_____	_____
<b>Total:</b>							<b>\$221,519.00</b>

15. Review and Approval Recommended:

GAAR: mk 5/15/09 Grants: Y.N 4/29/09  
 Initials Date Initials Date