

**West Virginia Water Research Institute
Annual Technical Report
FY 2014**

Introduction

West Virginia Water Research Institute

The West Virginia Water Research Institute is dedicated to the preservation and restoration of the natural environment through research and outreach with industry, government agencies, academia and the public.

Introduction

Water is one of West Virginia's most precious resources. It is essential for life and our economic prosperity, yet so many of the activities that keep our economy alive, and growing, also threaten our water resources. Energy generation, mineral extraction, agricultural production and other industrial activities all impact our water, making it increasingly necessary to find new ways to protect and restore this vital commodity as our economic activity accelerates. For over 40 years, the West Virginia Water Research Institute (WVWRI) has been leading the important work of addressing these issues and is the go-to organization for solving West Virginia's water-related problems.

While much of the work we do is focused on exploring and implementing technologies to improve and protect the quality of our State's water resources, we are also dedicated to expanding the understanding of threats and opportunities related to this critically important resource. We strive to bring together a diverse cross section of stakeholders to participate in water-related research throughout West Virginia. We encourage a constructive and respectful dialog about the future of our lakes, rivers and streams as well as our groundwater supplies.

Today, the WVWRI continues to grow its established programs and develop new initiatives to address emerging problems affecting the State's environmental and economic health. With financial support from State and Federal partners, private foundations and industry, and through the efforts of our staff and collaborating researchers, the WVWRI continues to work for real improvements to West Virginia's water resources.

Water Research for West Virginia: A Team Approach

In 1967, under Federal legislation, the United States Geological Survey established the West Virginia Water Research Institute (WVWRI) to conduct research related to water issues in the State. Today, the WVWRI develops state water research priorities with oversight and guidance from the West Virginia Advisory Committee for Water Research, a committee represented by members of Federal and State agencies, academia and industry. Our programs and projects develop strong, multi-disciplinary research teams through collaboration with West Virginia University colleges and divisions, higher education institutions across the country and industry professionals. This team approach offers the best expertise available to address West Virginia's water issues and allows the WVWRI to perform research in a number of areas at any given time. More information on WVWRI programs, research, projects, initiatives and publications can be found at www.wvwri.org.

Funding Strategy

The Institute uses funding received from the U.S. Geological Survey Clean Water Act section 104b program and State funding to develop research capabilities in priority areas and to provide service to State agencies, industry and citizen groups. Our strategy relies on using the USGS section 104b funding to develop competitive capabilities that, in turn, translate into successful proposals funded by a broad spectrum of Federal and State agencies.

Our strategy also relies on maintaining a broad cadre of researchers within WVU and other institutions within the state. We also work with faculty from institutions across the country to form competitive research partnerships. As West Virginia University is the State's flagship research institution, its researchers have played the dominant role. Our funding strategy relies on successful competition for Federal dollars while teaming with State agency and industry partners. The latter provide test sites, in-kind support and invaluable background data. The institute has 13 full time staff. We are adding two more full time staff positions this year. The Institute also supports numerous students; typically 4-6 GRA's and 1-3 undergraduate students within the WVWRI and more through other departmental projects. All but two positions are supported entirely on external grant funds. Roughly two-thirds of the Institute staff is directly engaged in research projects; the remaining is engaged in community economic redevelopment, outreach, and administration.

Research Program Introduction

This year we have four USGS 104b and one USGS 104g research projects on which to report.

Modeling the hydrologic response in surface mining watersheds with redesigned reclamation practices

Basic Information

Title:	Modeling the hydrologic response in surface mining watersheds with redesigned reclamation practices
Project Number:	2012WV200G
USGS Grant Number:	G12AP20156
Start Date:	9/1/2012
End Date:	8/31/2015
Funding Source:	104G
Congressional District:	First
Research Category:	Engineering
Focus Category:	Hydrology, Models, Management and Planning
Descriptors:	None
Principal Investigators:	Leslie Hopkinson, Ben Mack, John D. Quaranta

Publications

1. Snyder, M.W. 2013. Hydrologic response of alternative valley fill reclamation design. MS Thesis. Civil and Environmental Engineering Department, West Virginia University.
2. Snyder, M.W. 2013. Hydrologic response of alternative valley fill reclamation design. MS Thesis. Civil and Environmental Engineering Department, West Virginia University.
3. O Leary, E.E. 2014. Floodplain mapping in response to surface mine reclamation. MS Thesis. Civil and Environmental Engineering Department: West Virginia University.

Annual Report

Title: Modeling the hydrologic response in surface mining watersheds with redesigned reclamation practices

Reporting Period Start Date: 03/01/2014

Reporting Period End Date: 02/28/2015

Principal Authors: L. Hopkinson, J. Quaranta

Date Report Issued: May 2015

USGS Award Number: G12AP20156

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1. Research

The goal of this research is to evaluate the potential application of geomorphic design in surface mining reclamation, focusing on the water supply in Central Appalachia. Specific objectives include the following:

- Obj. 1: Generate geomorphic valley-fill designs.
- Obj. 2: Determine the hydrologic function of a redesigned valley-fill site in southern West Virginia.
- Obj. 3: Predict differences in floodplain mapping downstream of redesigned reclamation, resulting from extreme meteorological events.
- Obj. 4: Predict the hydrologic response of watersheds with redesigned reclamation at the landscape scale.

In this reporting period, there was technical progress for objectives 2, 3, and 4. Specific technical progress is outlined in the following sections.

Obj. 2. Determine the hydrologic function of a redesigned valley fill site in southern WV

Erosion

The objective of this portion of the research is to estimate soil erosion at the watershed scale of the created geomorphic landform design (GLD), conventional design, and the undisturbed land to predict the potential impact of land use change, particularly different surface mining and reclamation techniques, on sediment load to nearby rivers and streams. Proposed methods and results are reported in the following sections

Methods. The Revised Universal Soil Loss Equation (RUSLE) estimates average annual soil loss by sheet and rill erosion on the portions of landscape profiles where erosion is occurring using the empirical equation:

$$A=R*K*LS*C*P \quad (1)$$

where A is the average soil loss per unit area during a unit period of time, R is the rainfall-runoff erosivity factor, K is the soil erodibility factor, LS is the slope length and steepness factor, C is the cover-management factor, and P is the supporting practices factor (Renard et al., 1991). In this study, RUSLE will be utilized in a distributed GIS framework to assess erosion and estimate sediment load for each of five design scenarios (i. undisturbed, pre-mining condition; ii. conventional valley fill post-mining, pre-revegetation condition; iii. conventional valley fill post-reclamation, long term condition; iv. GLD post-mining, pre-revegetation condition; and, v. GLD post-reclamation, long-term condition). The values of the factors will be determined from the soil survey, topography, meteorological data, land cover, land use, and literature pertaining to the study watershed and surrounding area. The factors used in RUSLE will be represented by raster layers in a GIS environment and then multiplied together to estimate the soil erosion rate in the study area for each of the five scenarios (Fernandez et al., 2003; Ranzi et al., 2011; Demirci and Karaburun, 2012).

Study Site. The study site is located in Logan County, West Virginia, USA and undisturbed topography consisted of steep, complex slope profiles with slopes reaching up to 27.5% (Figure 1). The area was in the Central Appalachian ecoregion (USEPA, 2013) with an average precipitation of 1.18 m and average annual temperature of 13 °C (US Climate Data,

2014). The pre-mining study watershed hydrology included one main perennial channel with four contributing tributaries likely ranging from ephemeral to intermittent (Hopkinson et al., 2014). The main valley slope was 10.1%, and the geology was dominated by sandstone (Russell, 2012). Pre-mining vegetation was predominately dense core forest with a dominant land use of forestland.

Design scenarios. The permitted valley-fill design (1.4 km²; 6.9x10⁶ m³ fill material) for the site consists of conventional valley-fill features including a benched valley fill face (11 benches: 6.1-6.4 m wide every 15.2 vertical meters in elevation), rock core underdrain, and Surface Water Runoff Analysis (SWROA) ditches located around the perimeter of the fill (Figure 1). The top of the fill was reclaimed to a planar surface that sloped away from the fill face (1-2%) in accordance with an Approximate Original Contour (AOC) variance permit to support the post-reclamation land use of pastureland. The pastureland (commercial cow-calf operation) included 65% of the fill area and was predominately reclaimed with grass. The remaining 35% of fill area was permitted to be reclaimed as forestland. The conventional fill resulted in the burial of approximately 3,130 m of original stream length.

An alternative valley-fill design based on geomorphic landform design (GLD) principles and including on-site stream channels, as described in Sears et al. (2014), was created for the study site (0.98 km²) (Figure 1). The software design tool (Carlson[®] Natural Regrade[®] with GeoFluv[™]) and regional data inputs (Sears et al., 2014; Buckley et al., 2013) were used for the creation of mature, stable landforms. The GLD resulted in sub-basins that directed flow to stream channels (main channel and 12 tributaries) as opposed to the control structures and SWROA ditches in the conventional design. The stream channels (5,466 m total combined length; 131-1,440 m length range; type A and type C (Rosgen, 1994)) were designed to mimic the original dendritic drainage (Sears et al., 2014). The elevation ranged from 338 m to 608 m and the main valley slope was 12.7%. Proposed features of the design described by Sears et al. (2014) included complex slope profiles (concave-convex), improved hydrology and groundwater movement, decreased infiltration and contaminant desorption, and decreased flooding risk.

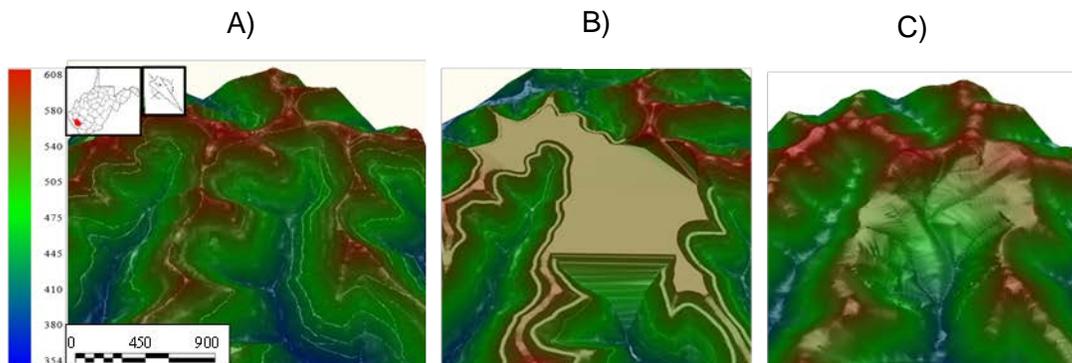


Figure 1. a) Original Topography, b) conventional Fill, c) geomorphic landform design (elevation and scale in m)

Description of Factors. In RUSLE, the rainfall-runoff erosivity factor, R , represents the erosivity occurring from rainfall and runoff at a particular location (Renard et al., 1991; Demirci and Karaburun, 2012). In many studies, the R -factor has been determined to be the most related to soil loss and erosion (Kouli et al., 2009; Yu and Rosewell, 1996; Renard and Freimund, 1994). The value of the R -factor will be calculated from the collected rainfall data as well as the Modified Fournier's Index (MFI), a widely used parameter for rainfall erosivity (Demirci and Karaburun, 2012; Renard and Freimund, 1994; Arnoldus, 1980). MFI will be

calculated as the sum of the squared monthly precipitation divided by the annual precipitation (Renard and Freimund, 1994):

$$MFI = \frac{\sum_{i=1}^{12} p_i^2}{P} \quad (2)$$

where p_i (mm) is the average monthly precipitation and P (mm) is the average annual precipitation (Kouli et al., 2009; Arnoldus, 1980). Precipitation data will be taken from the nearest station (WV465353; Logan, WV; 19 km from study site). Twenty-three years of hourly rainfall data will be collected and used for the calculation of MFI and R -factor. The R -factor will be calculated using MFI in Equation 3 (Renard and Freimund, 1994).

$$R - factor = 95.77 - (6.081 * MFI) + (0.477 * MFI^2) \quad (3)$$

for $P > 850$ mm, where R -factor ($MJ \text{ mm ha}^{-1} \text{ h}^{-1} \text{ year}^{-1}$) is the rainfall-erosivity factor, and MFI is the Modified Fournier's Index (mm).

The soil erodibility factor, K , represents the erodibility of the soil or surface material at the study location (Renard et al., 1991; Demirci and Karaburun, 2012). The K -factor is determined based on soil texture, structure, organic matter content, and permeability (Demirci and Karaburun, 2012; Kouli et al., 2009). The K -factor is calculated using the soil erodibility nomograph (Wischmeier and Smith, 1978). The soil erodibility nomograph solves Equation 4 for soils containing less than 70% silt and very fine sand.

$$100K = 2.1M^{1.14}(10^{-4})(12 - a) + 3.25(b - 2) + 2.5(c - 3) \quad (4)$$

where M is the particle size parameter defined as the percent silt and very fine sand (0.002-0.1 mm) times the quantity 100 minus percent clay (<0.002 mm), a is the percent organic matter, b is the soil structure code used in soil classification, and c is the profile permeability class (Wischmeier and Smith, 1978). Soil properties of the undisturbed soil will be estimated using the soil survey and literature. Soil properties of the spoil will be obtained from Russell (2012), where soil classification and analysis were performed on the spoil material at the study site. The soil properties will be used to calculate the K -factors for each scenario.

The overall topography contributes two factors to soil erosion in RUSLE (Renard et al., 1997; Demirci and Karaburun, 2012). The LS -factor depends on slope percentage and length and is defined as a ratio of soil loss under given conditions to those at the study site (Demirci and Karaburun, 2012). The LS -factor will be calculated by using the following equation in the GIS environment:

$$LS = (Flow \text{ Accumulation} * \frac{Cell \text{ Size}}{22.13})^{0.4} * (\frac{\sin \text{ Slope}}{0.0896})^{1.3} \quad (5)$$

where flow accumulation is the grid layer expressed as the number of grid cells, and cell size is the length of a cell side (Demirci and Karaburun, 2012). The LS factors will be computed from a DEM of the study site in ArcGIS (Fernandez et al., 2003; Demirci and Karaburun, 2012).

The cover and management factor (C) represents the effects of management practices and ground cover on the soil erosion rate (Demirci and Karaburun, 2012). Values for C can range from near zero for a very well protected soil to 1.5 for a finely tilled, ridged surface that produces large amounts of runoff and leaves the soil highly susceptible to rill erosion (Renard et al.,

1991). Values for *C* are a weighted average of soil loss ratios (SLRs) that represent the soil loss for a given condition at a given time and vary throughout the year as soil and land cover change (Renard et al., 1991). In RUSLE, SLRs are computed as a function of four subfactors: prior land use, canopy, ground cover, and within-soil effects (Renard et al., 1991). The *C* factor will be determined by matching the land cover of the study area with the *C* factor values for each scenario (Goldman et al., 1986).

The supporting practices factor, *P*, represents how surface conditions affect flow paths and flow hydraulics (Renard et al., 1991). The *P*-factor values were determined by the extent of individual conservation practices including contouring, strip cropping, and terracing or a combination of these (Fernandez et al., 2003). Implemented conservation practices typically decreased the erosive impact of rainfall and runoff and therefore were accounted for in the *P*-factor (Renard et al., 1997; Fernandez et al., 2003). No supporting practices were implemented within the study site; therefore, the *P*-factor will be equal to one for this study for all modeling scenarios.

Expected Results. The average annual sediment yield for the five design scenarios (i. undisturbed, pre-mining condition; ii. conventional valley fill post-mining, pre-revegetation condition; iii. conventional valley fill post-reclamation, long term condition; iv. GLD post-mining, pre-revegetation condition; and, v. GLD post-reclamation, long term condition) will be determined and a comparison of the results will be performed to determine which designs provide the least erosion. The comparison results will assist in the determination of the ability of reclamation using geomorphic landform principles to be successfully implemented in Central Appalachia.

Groundwater Modeling

Three-dimensional groundwater and contaminant transport will be modeled for reclamation alternatives of a valley fill. The objective of groundwater modeling is to compare the groundwater movement (both in velocity and quantity) over time between a conventional valley fill and a geomorphic reclamation in response to differences in landform design and infiltration. The objective of contaminant transport modeling is to compare the long-term release of selenium from reclamation alternatives as a result of desorption from the mine spoil used to construct valley fills.

The case to be modeled consists of the following features: an existing foundation ground surface; fill material consisting of sandstone overburden; infiltration into the surface of the fill material; water table with variable location within the fill material; pond at toe of fill with specified head. The existing ground surface is the undisturbed valley being filled in reclamation. The fill material surface varies depending on the reclamation technique (planar for conventional fill, curvilinear for geomorphic fill). Infiltration into the fill also varies depending on hydrologic inputs, reclamation technique, slopes, and soil properties. The fill material is unsaturated with a variable water table due to unconfined aquifer conditions. The interface between the fill material and existing valley is considered impermeable due to a drastic decrease in permeability.

Model geometries will be obtained from reclamation alternatives for a southern WV valley fill (Figure 2). The pre-mining undisturbed valley (Figure 2a) will be used as the lower boundary of the models. The existing conventional reclamation plan will be used for the surface geometry of the conventional valley fill (Figure 2b). The geometry of the geomorphic fill will be taken from a conceptual design that has been generated as an alternative to the existing valley fill (Figure 2c). The geomorphic design incorporated a stream on the fill surface using a drainage density of

61.7 ft/ac (DePriest et al., 2015). The channel was designed to be stable at floodprone flow, consistent with the most successful designs from DePriest et al. (2015).

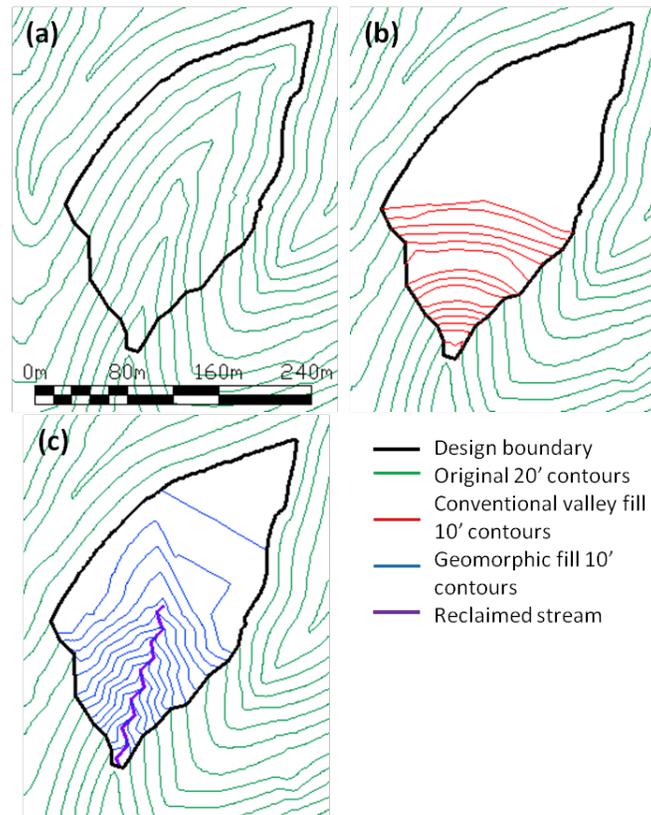


Figure 2. Contours used for geometry of model: (a) original valley; (b) conventional valley fill reclamation; and (c) geomorphic design.

Groundwater will be modeled using SoilVision Systems Ltd. (Saskatoon, Saskatchewan, Canada) SVOOffice Geotechnical Software Suite due to the software's ability to model unsaturated flow. Necessary soil properties for groundwater modeling include saturated hydraulic conductivity, anisotropy ratio, porosity, and specific gravity, and will be collected from soil testing and literature. Unsaturated soil property functions will be determined using the Fredlund and Xing (1994) equation for the soil-water characteristic curve and the Fredlund et al. (1994) estimation of the permeability function. Hydrologic data will be obtained from the National Oceanic and Atmospheric Administration (NOAA) Precipitation Frequency Data Server (PFDS) and used to determine the normal flux boundary conditions applied to the surface of each fill profile. The closest weather station to the field design site is Madison, WV (Site ID: 46-5563) (NOAA, 2014). Infiltration into the surfaces of reclamation alternatives will be a function of landform slope/shape and surface properties. The conventional fill will experience a high infiltration rate across the flat crest and benches, with a lower infiltration rate on the sloped face. Infiltration into the hillslopes of the geomorphic fill will vary by location based on slope. The portion of the geomorphic fill covered by the recreated stream will be modeled with a low infiltration capacity to promote surface flow. Over time, the following groundwater properties will be documented: infiltration volume, storage volume, discharge rate and volume, groundwater flux rate, degree of saturation, pore-water pressure, and total head. It is expected that the geomorphic fill with a recreated stream will have improved groundwater movement through lower infiltration and discharge volumes, as well as faster movement of groundwater through the fill.

Due to limitations in the modeling software, contaminant transport will be manually calculated by combining selenium leaching data with the groundwater modeling results. Required soil properties for contaminant transport calculation are bulk density, porosity, distribution coefficient (K_d), and contaminant starting concentration, and will all be taken from soil testing data. Over time, the volume of water that has travelled through and discharged from each fill will be related to the volume of internal fill materials that water has contacted and the rate at which selenium desorbs from the contacted fill materials. The output of these calculations will be selenium release over time from fill alternatives. It is expected that the geomorphic fill will exhibit lower selenium release due to lower volumes of groundwater and decreased contact time of groundwater with internal fill materials.

Obj. 3: Predict differences in floodplain mapping downstream of redesigned reclamation, resulting from extreme meteorological events.

This work resulted in a MS thesis and preliminary results were presented at an international meeting. In the reporting period we completed the unsteady modeling, and the results from that analysis are summarized in the following sections. Results of the steady analysis were reported in the previous annual report.

The unsteady analysis results of the study reach (downstream of the GLD study site) for a 24-hour period are presented in the following sections. We compared conditions: i. undisturbed, pre-mining condition; ii. conventional valley fill as represented in the permit file; iii. GLD during mining; and iv. GLD post-mining, long-term condition.

Pre-mining

The pre-mining cross-sectional outputs are presented in Table 1. Modeled inundation areas and flood depths are shown in Figures 3-6.

Table 1: Maximum water surface pre-mining condition unsteady flow analysis results

Rainfall Return Period (yr)	Flood Extents ^a (m)	Max. Depth (m)	Cross-Sectional Flow Area ^a (m ²)	Average Velocity (m/s)	Flood Surface Area (km ²)
2	11.6 (5.7-27.1)	1.0	4.1 (1.4-16.5)	1.0	22.9
50	18.9 (8.2-41.0)	1.9	12.4 (4.8-42.7)	1.6	37.1
100	20.4 (8.7-44.6)	2.1	14.5 (5.7-48.4)	1.8	39.7
500	24.1 (9.7-54.9)	2.5	19.2 (7.4-61.5)	2.0	45.9

^amean and range in parentheses



Figure 3: Pre-Mining 2-yr unsteady max water level flood extents and depth



Figure 4: Pre-Mining 50-yr unsteady maximum water level flood extents and depth



Figure 5: Pre-Mining 100-yr unsteady maximum water level flood extents and depth



Figure 6: Pre-Mining 500-yr unsteady maximum water level flood extents and depth

Conventional

Unsteady analysis results for the conventional reclamation condition are displayed in Table 2 and Figures 7-10. Modeled channel depths corresponding to the maximum water levels from conventional reclamation varied in comparison to pre-mining conditions depending on the return period. The 2-yr storm event produced lower channel depths (-22%), whereas the 50-yr, 100-yr, and 500-yr maximum channel depths increased by 15%, 12%, and 8%, respectively, compared to those of the pre-mining condition.

The conventional reclamation condition inundated areas for the 2-yr, 50-yr, 100-yr, and 500-year were 18.4, 36.5, 41.0, and 49.4 km², respectively. In comparison to the pre-mining condition, the 2-yr and 50-yr storm events resulted in decreased areas of 20% and 2%., respectively. The larger storms resulted in increased flood surface areas; the 100-yr storm increased by 3%, and the 500-yr storm increased by 8% (Figures 7-10).

Table 2: Maximum water surface conventional condition unsteady flow analysis results

Rainfall Return Period (yr)	Flood Extents ^a (m)	Max. Depth (m)	Cross-Sectional Flow Area ^a (m ²)	Average Velocity (m/s)	Flood Surface Area (km ²)
2	9.4 (4.7-24.6)	0.78	2.5 (0.7-11.2)	0.9	18.4
50	18.5 (8.0-42.1)	2.2	12.0 (4.5-41.7)	1.6	36.5
100	20.9 (8.7-48.4)	2.3	15.0 (5.6-50.9)	1.8	41.0
500	25.0 (9.7-61.9)	2.7	20.1 (7.5-65.5)	2.0	49.4

^amean and range in parentheses

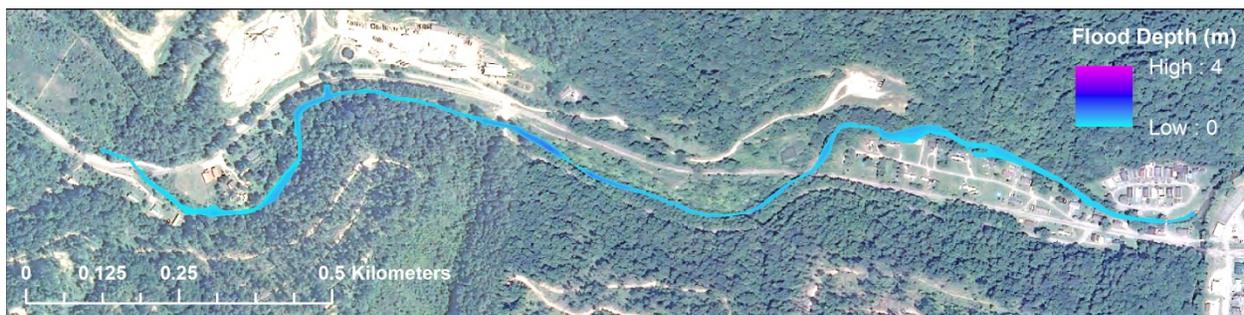


Figure 7: Conventional 2-yr maximum unsteady flood extents and depth



Figure 8: Conventional 50-yr maximum unsteady flood extents and depth



Figure 9: Conventional 100-yr maximum unsteady flood extents and depth



Figure 10: Conventional 500-yr maximum unsteady flood extents and depth

GLD (During mining)

Unsteady flow analysis results of the GLD (During mining) condition are shown in Table 3 and Figures 11-14. All modeled storm events resulted in increased maximum channel depths in comparison to the pre-mining condition results. The 2-yr, 50-yr, 100-yr, and 500-yr channel depths increased by 102%, 72%, 66%, and 61%, respectively.

The inundation areas from the unsteady analysis of the GLD (During mining) condition increased for every modeled storm event. The 2-yr storm event inundation area increased by 62%, 50-yr increased by 50%, 100-yr increased by 51%, and 500-yr increased by 54%.

Table 3: Maximum water surface GLD (During mining) condition unsteady flow analysis results

Rainfall Return Period (yr)	Flood Extents ^a (m)	Max. Depth (m)	Cross-Sectional Flow Area ^a (m ²)	Average Velocity (m/s)	Flood Surface Area (km ²)
2	18.9 (8.2-42.3)	2.0	12.5 (4.8-42.3)	1.6	37.1
50	30.3 (10.6-80.3)	3.2	26.7 (9.3-85.7)	2.2	55.7
100	33.2 (10.9-86.4)	3.5	30.1 (10.0-96.3)	2.3	60.1
500	37.9 (11.4-97.6)	4.0	38.5 (11.3-119.0)	2.5	70.8

^amean and range in parentheses



Figure 11: GLD (During mining) 2-yr maximum unsteady flood extents and depth



Figure 12: GLD (During mining) 50-yr maximum unsteady flood extents and depth



Figure 13: GLD (During mining) 100-yr maximum unsteady flood extents and depth



Figure 14: GLD (During mining) 500-yr maximum unsteady flood extents and depth

GLD (Post-mining)

The GLD (Post-mining) unsteady analysis results are displayed in Table 4 and Figures 15-18. The maximum channel depths increased for each modeled storm event compared to pre-mining condition channel depths. The channel depths increased for the 2-yr, 50-yr, 100-yr, and 500-yr storm events by 2%, 4%, 3%, and 2%, respectively. The inundation areas of the GLD (Post-mining) reclamation condition also saw slight increases for all each modeled storm event. The 2-yr inundated area increased by 2%, and the 50-yr, 100-yr, and 500-yr inundated areas each increased by 1% compared to pre-mining inundation.

Table 4: Maximum water surface GLD (Post-mining) condition unsteady flow analysis results

Rainfall Return Period (yr)	Flood Extents ^a (m)	Max. Depth (m)	Cross-Sectional Flow Area ^a (m ²)	Average Velocity (m/s)	Flood Surface Area (km ²)
2	11.9 (5.8-27.5)	1.0	4.4 (1.5-17.1)	1.0	23.4
50	19.1 (8.3-42.0)	1.9	12.7 (4.9-43.7)	1.7	37.5
100	20.6 (8.8-45.5)	2.2	14.8 (5.7-49.4)	1.8	40.1
500	24.6 (9.7-56.6)	2.6	19.5 (7.5-62.9)	2.0	46.4

^amean and range in parentheses



Figure 15: GLD (Post-mining) 2-yr maximum unsteady flood extents and depth



Figure 16: GLD (Post-mining) 50-yr maximum unsteady flood extents and depth

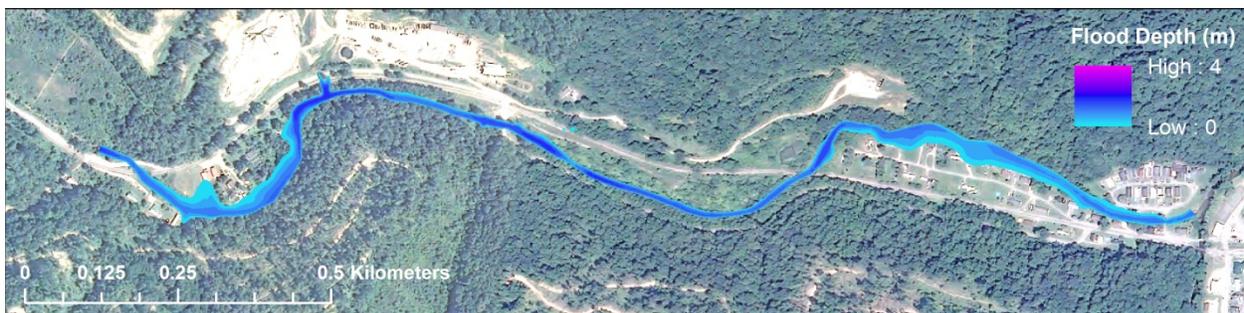


Figure 17: GLD (Post-mining) 100-yr maximum unsteady flood extents and depth



Figure 18: GLD (Post-mining) 500-yr maximum unsteady flood extents and depth

Obj. 4: Predict the hydrologic response of watersheds with redesigned reclamation at the landscape scale.

The leading land use change in Central Appalachia is due to surface mining and reclamation, which relies on valley-fill construction to facilitate spoil material placement (Ferrari et al., 2009). Recent research presented the use of geomorphic landform principles in an innovative reclamation technique for surface mined lands and valley fills with the potential to improve the hydrologic impact within the affected watershed (Sears, 2012; Russell et al., 2014; Sears et al., 2013; Sears et al., 2014). The hydrologic impact of reclaiming valley fills in Central Appalachia using geomorphic landform principles compared to conventional reclamation techniques has been identified but not quantified at the landscape scale. Hydrologic responses have important implications for the mitigation of possible flood damage to human life, property, and wildlife (Ferrari et al., 2009).

Two objectives were identified for this research. The first objective was to estimate the current hydrologic impact within a watershed in Central Appalachia if the valley-fill reclamation method was changed from conventional to geomorphic landform design. The second objective was to predict the future hydrologic impact within the same watershed if no land disturbance had occurred or if mining continued at the current rate and the land use was changed from conventional to geomorphic landform design.

Methods. The hydrologic responses for three reclamation scenarios were predicted using Hydrologic Simulation Program-FORTRAN (HSPF) in conjunction with Better Assessment Science Integrating Point and Nonpoint Sources (BASINS) for a watershed in Central Appalachia. The three reclamation scenarios included: i. no land disturbance; ii. all valley fills reclaimed using traditional techniques; and, iii. all valley fills reclaimed using GLD methods. The changes in hydrologic response were compared among the three scenarios.

Study Area and Land Use. The watershed for which the hydrologic responses were predicted was located among steep, rugged terrain in southern West Virginia. It is serviced by USGS 03198350 Clear Fork at Whitesville, WV (37°57'58" N, 81°31'28" W) and had a drainage area of 166.8 km². The entire watershed was used for modeling because it was important to consider the changes in hydrologic response at the watershed scale as opposed to a single design, which has been analyzed in the past (Negley and Eshleman, 2006; Bonta et al., 1997). The watershed was delineated into nine subwatersheds using BASINS (Figure 19).

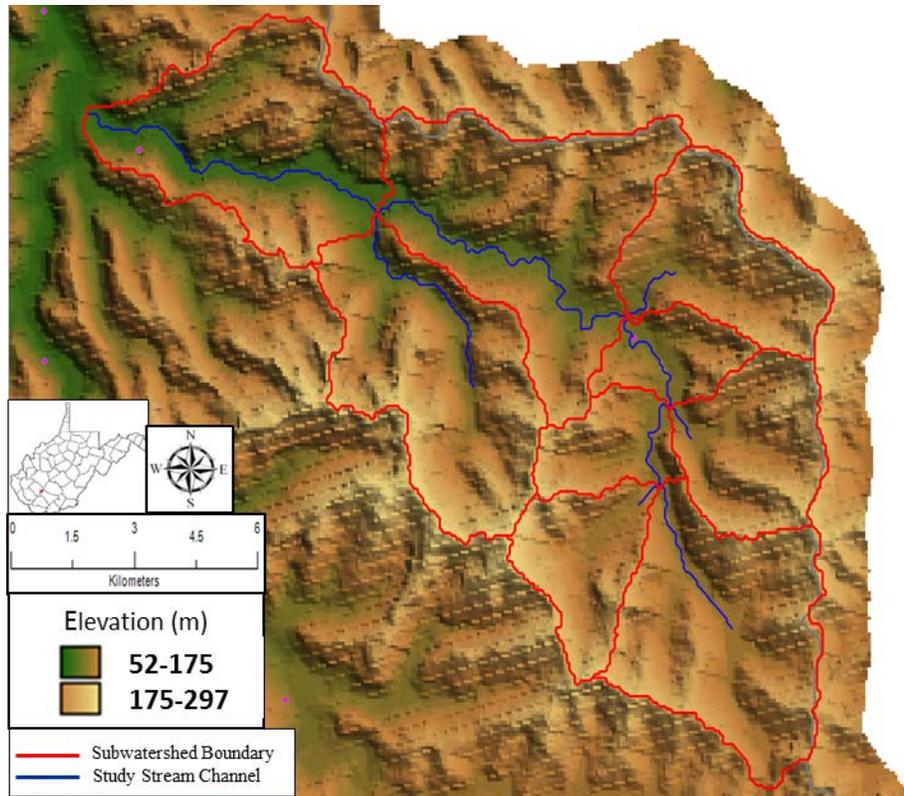


Figure 19. Study Area with Delineated Watershed

The undisturbed vegetation of the study watershed consisted of predominately deciduous forest with the dominant land use of forestland and minimal estimated long-term erosion (Figure 20). The 2001 land use areas for the study watershed were consolidated within five land use/land cover conditions (urban/build-up, agricultural land/grassland, forest, barren land, and wetlands/water). All land use conditions were estimated to be permeable with the urban or built-up land condition estimated to be 50% pervious due to roadways, buildings, parking lots, etc. Therefore, there was a permeable land condition and an impermeable land condition for each urban or built-up land condition within each of the nine subwatersheds.

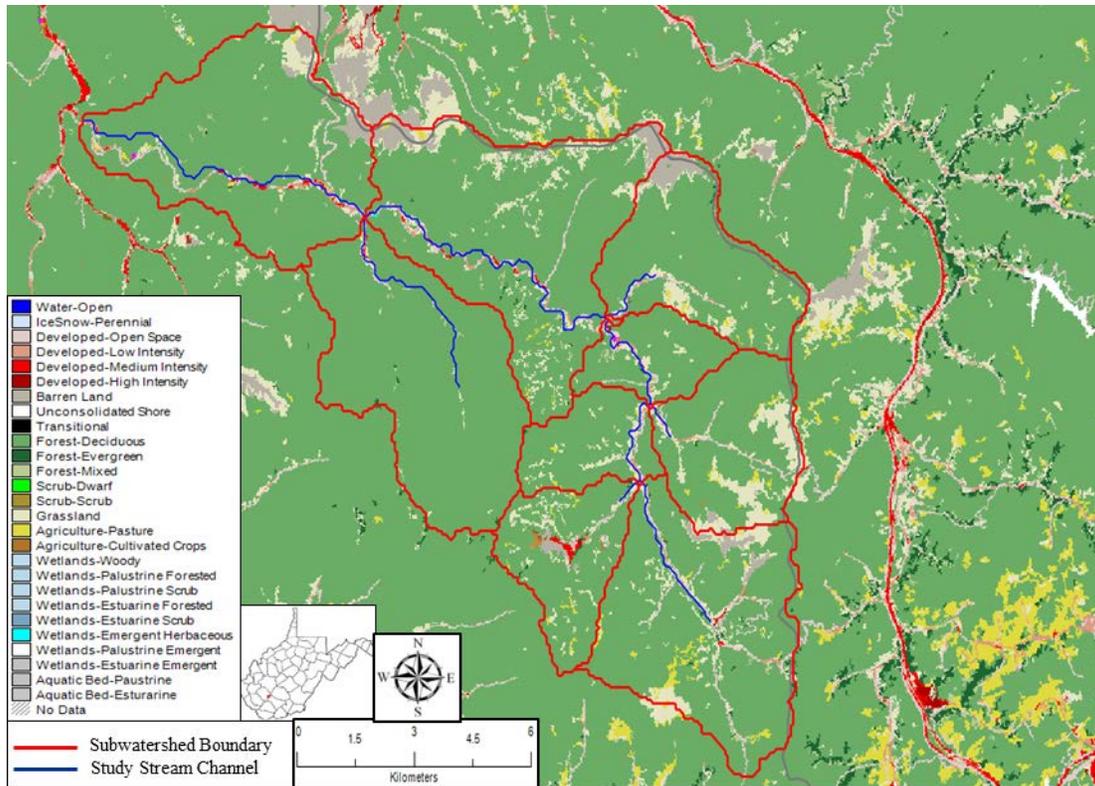


Figure 20. Study Area with 2001 Land Use

Surface mining and reclamation were the leading source of land use change within the watershed. Approximately 30% of the watershed was disturbed by mining with 21% of the disturbed area defined as valley fills. The watershed had 11.0 km² of completed valley fills constructed through 2014. The valley fills were constructed using traditional reclamation techniques involving end-dumping overburden material into nearby valleys to create engineered fill structures with planar slopes and a benched face. The removal of vegetation, prolonged soil exposure, and predominant re-vegetation of grass result in changes in hydrologic response of the site and surrounding area including increased surface water runoff, excess sedimentation, and erosion (Ferrari et al., 2009; Zhang et al., 2009).

Watershed Modeling Using BASINS and HSPF. Hydrologic Simulation Program-FORTRAN (HSPF) was used in conjunction with Better Assessment Science Integrating Point and Nonpoint Sources (BASINS) to model the hydrologic response of the study watershed (Table 5). Site specific data including elevation, precipitation, and streamflow were downloaded within BASINS to create the user control input (UCI) file for the HSPF simulations.

Table 5. Data For HSPF Model

Description	Source
3-m Digital Elevation Model (DEM)	BASINS
Mining Permit Boundaries	WV DEP Technical Applications and GIS Unit
Meteorological Stations and Data	BASINS
Land Use	BASINS; Multi-Resolution Land Characteristics Consortium (MRLC)
Streamflow	BASINS; USGS

Model Calibration. Meteorological data for the Dry Creek weather station (approximately 13 miles from study watershed) was available for 2000-2009 and was used for calibration. Calibration followed standard modeling procedures as advised by established criteria (Atkins et al., 2005; Ferrari et al., 2009). The calibration period was chosen to be June 2000 through December 2004 and was simulated with land use parameters from 2001. The error allowances described in Atkins et al. (2005) and Ferrari et al. (2009) (Table 6) were used as criteria for model calibration and validation acceptance.

Initially, HSPF input parameters were implemented into WinHSPF based on the input parameters used in Atkins et al. (2005) for the USGS Clear Fork station at Clear Fork, WV, 38 miles from the study watershed. However, calibration errors exceeded allowances, except for the total flow error (Table 6). Therefore, further calibration of input parameters was required. Parameters including AGWRC (groundwater recession rate parameter), CEPSC (interception storage capacity), INFILT (index to the infiltration capacity of the soil), INTFW (interflow inflow parameter), IRC (interflow recession parameter), LSUR (length of the assumed overland flow plane), LZETP (lower zone evapotranspiration parameter), and NSUR (Manning's n for the overland flow plane) were altered from the initial input values during the calibration process to meet error allowances. Calibration continued until each of the calibration error allowances were met indicating a successful model calibration (Table 6).

Table 6. Calibration Error Allowances

Calibration Criteria	Limit or Range	Initial	Final
Total Flow Error (%)	± 10	8.87	6.84
Lowest 50% Flow Error (%)	± 10	49.70	9.33
Highest 10% Flow Error (%)	± 15	-23.81	3.50
Mean Storm Volume Error (%)	± 15	15.04	5.11
Mean Storm Peak Flow Error (%)	± 15	32.06	-0.83
Overall Water Balance Error (%)	-1.3-32.9 ^a	^b	7.24
Mean Yearly Water Balance Error (%)	-2.1-27.8 ^a	^b	3.30
Mean Monthly Water Balance Error (%)	0.7-83.9 ^a	^b	-78.23 ^c

Note: Adapted from Atkins et al. (2005) and Ferrari et al (2009)

^aWater balance error limits were not specified in Atkins et al. (2005) or Ferrari et al. (2009), so published values of these errors were used

^bWater Balance not calculated due to other error allowances not met

^cExcessive mean monthly water balance error due to single day error outlier of -4941%; Mean monthly water balance = 11.83% excluding outlier

Model Validation. Daily discharge data were available for the USGS station Clear Fork at Whitesville, WV and were used for validation of the calibrated HSPF model. The model was validated with the 2006 land-use condition for years 2005-2009 and the same input parameters used for the calibration were used for the validation. The same error allowances described in Table 6 were used for the validation process.

All of the error allowances were met with the exception of the lowest 50% flow error (Table 7). This error difference could have been attributed to the large differences (-31% to 37% difference) in the average annual precipitation for the nine year span compared to the overall historical average annual precipitation of the site. Other probable error difference contributions included comparing a fixed land use to empirical data over a period with non-stationary land use, using meteorological data that may not have accurately reflected the weather pattern of the watershed due to being located approximately 13 miles away from meteorological station, and HSPF relying heavily on calibration (Brun and Band, 2000; Ferrari et al., 2009). The validation model was accepted.

Table 7. Validated Model Run Results

Validation Criteria	Limit	Model Results
Total Flow Error (%)	± 10	3.12
Lowest 50% Flow Error (%)	± 10	52.11
Highest 10% Flow Error (%)	± 15	-12.93
Mean Storm Volume Error (%)	± 15	-3.11
Mean Storm Peak Flow Error (%)	± 15	3.62
Overall Water Balance Error (%)	-1.3-32.9 ^a	9.74
Mean Yearly Water Balance Error (%)	-2.1-27.8 ^a	5.74
Mean Monthly Water Balance Error (%)	0.7-83.9 ^a	25.28

Note: Adapted from Atkins et al. (2005) and Ferrari et al (2009)

^aWater balance error limits were not specified in Atkins et al. (2005) or Ferrari et al. (2009), so published values of these errors were used

Prediction Models. The hydrologic responses for three reclamation scenarios were predicted for the study watershed. The three reclamation scenarios included: i) no land disturbance; ii) all valley fills reclaimed using traditional techniques; and, iii) all valley fills reclaimed using GLD methods. Prediction simulations were performed using the nine years of meteorological data available (2000-2009). A nine year span was selected to incorporate a wide variety of atmospheric driving conditions for hydrologic response, specifically for peak flow events. The nine year span included average annual percent differences of -31% to 37% when compared to the overall average annual precipitation of 1.16 m at Whitesville, WV.

Prediction models were performed to estimate the future hydrologic response of the watershed from 2011 to 2020 and from 2041 to 2050. Predictions were completed by changing the HSPF model land use parameters to mimic the proposed land use conditions. Valley fills reclaimed using traditional techniques were estimated to respond similar to grassland, while valley fills reclaimed using geomorphic landform principles were estimated to respond similar to forest (Snyder, 2013). The no land disturbance scenario included modeling all disturbed land as forest, the pre-disturbed land use. Each prediction simulation began with the 2011 estimated land use for the watershed, then the barren, forest, and grassland land uses were altered. All remaining land use areas remained unchanged.

The first two prediction simulations performed in HSPF estimated the hydrologic responses of the study watershed to the year 2020. Each of the models used the total area of constructed valley fills within the watershed in 2014 for input alteration (Figure 21). The 2011 land use area inputs were altered based on the reclamation technique being modeled.

The HSPF scenario of traditional valley-fill reclamation was modeled by changing the valley-fill area within each subwatershed from barren land use to the reclaimed land use of grassland (Snyder, 2013). If the barren land use area was depleted before all of the valley-fill area was subtracted, the remaining valley-fill area was subtracted from the forest land use area, assuming the disturbance occurred after 2011 and was classified as forest land use in 2011 (Table 8). The GLD valley-fill reclamation scenario was modeled using the same land use alteration technique except for the barren land use area, which was changed to the reclaimed land use of forest (Snyder, 2013). If the barren land use area was depleted, the remaining valley-fill area was subtracted from grassland, assuming the land had been re-vegetated and was classified as grassland in 2011 (Table 8).

The last three prediction simulations performed in HSPF estimated the hydrologic responses of the study watershed to the year 2050. Aerial photography was used to evaluate the year major land use changes began within the study watershed. Surface mining land disturbance and valley-fill construction began in approximately 1996 within the study watershed, still occurs today, and was projected to occur in the future. The valley-fill construction rate that occurred from 1996 to 2014 was predicted to remain steady for future decades. Therefore, the projected (2050) valley-fill area was estimated to be triple the current (2014) valley-fill area (WVDEP TAGIS, 2014) for each subwatershed. The projected valley-fill area was used in the models for input alteration.

The traditional and GLD valley-fill reclamation scenarios 3 and 4 were modeled using the same principles applied for the 2020 prediction model. The traditional reclamation model land use inputs were altered by changing the predicted valley-fill area from barren to grassland. If the barren land use area was depleted, the remaining valley-fill area was subtracted from the forest area, assuming the disturbance occurred after 2011 and was classified as forest land use in 2011 (Table 8). The GLD reclamation model land use inputs were altered by changing the predicted valley-fill area from barren to forest. If the barren land use area was depleted, the remaining valley-fill area was subtracted from grassland, assuming the land had been re-vegetated and was classified as grassland in 2011 (Table 8).

The HSPF scenario of no land disturbance was modeled by altering the barren, grassland, and forest land use areas within each subwatershed. All of the barren and grassland areas were depleted and added to the forest area to simulate no land disturbance had occurred within the study watershed through 2050 (Table 8).

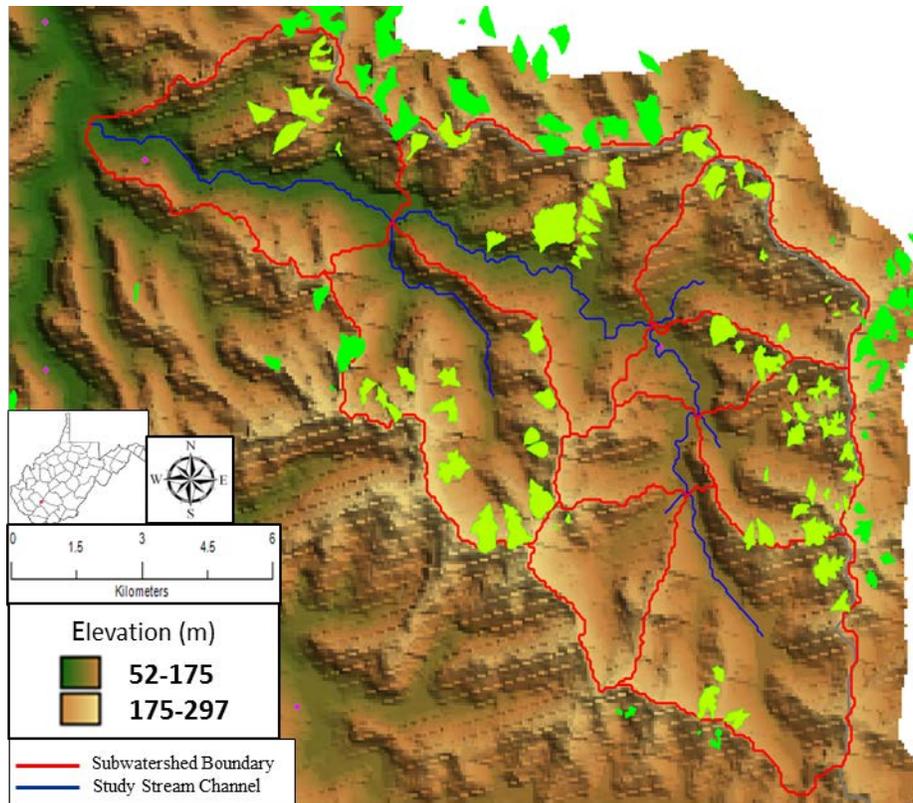


Figure 21. Study Subwatersheds with Elevation and 2014 Valley Fills (Inside of Watershed in Yellow and Outside of Watershed in Green)

Table 8. Prediction Simulations 1 and 2: Traditional and GLD

Prediction Simulation	Meteorological Data Years	Simulation Years	VF Area Date	Land Use Date	Reclamation Technique	How Land Use Was Altered	If Land Use Depleted
1	2000-2009	2011-2020	2014	2011	Traditional	VF area subtracted from barren and added to grassland	Remaining VF area subtracted from forest
2	2000-2009	2011-2020	2014	2011	GLD	VF area subtracted from barren and added to forest	Remaining VF area subtracted from grassland
3	2000-2009	2041-2050	Projected 2050	2011	Traditional	VF area subtracted from barren and added to grassland	Remaining VF area subtracted from forest
4	2000-2009	2041-2050	Projected 2050	2011	GLD	VF area subtracted from barren and added to forest	Remaining VF area subtracted from grassland
5	2000-2009	2041-2050	N/A	2011	N/A	All barren and grassland depleted and added to forest	N/A

Note: VF = Valley Fill, N/A = Not Applicable, GLD=Geomorphic Landform Design

Results

Prediction simulations 1 and 2 resulted in similar current hydrologic responses (-0.27% to -1.1% difference) within the study watershed for GLD valley-fill reclamation compared to traditional reclamation methods (Table 9). The current hydrologic impact of the valley-fill construction within the watershed was estimated to be reduced when GLD reclamation was implemented as opposed to traditional reclamation practices.

Table 9. Percent differences ($D_{\%}$) comparing simulation 1 (traditional) and 2 (GLD)

	$D_{\%}$
Total Flow	-0.57
Lowest 50% Flow	-0.27
Highest 10% Flow	-0.85
Mean Storm Volume	-0.67
Mean Storm Peak Flow	-1.10

Note: $D_{\%} = (x_{\text{Trad}} - x_{\text{GLD}})/x_{\text{GLD}}$; where x_{Trad} = variable from simulation 1; x_{GLD} = variable from simulation 2.

Prediction simulations 3 and 4 resulted in greater future differences in hydrologic response (-0.34% to -3.33% difference) compared to predicted current hydrologic responses (-0.27% to -1.1% difference) within the study watershed for GLD valley-fill reclamation compared to traditional reclamation methods (Table 10). The estimated hydrologic impact of the valley-fill construction within the watershed was estimated to be reduced when GLD reclamation was implemented as opposed to traditional reclamation practices.

Table 10. Percent differences ($D_{\%}$) comparing simulation 3 (traditional) and 4 (GLD)

	$D_{\%}$
Total Flow	-1.72
Lowest 50% Flow	-0.34
Highest 10% Flow	-2.64
Mean Storm Volume	-2.11
Mean Storm Peak Flow	-3.33

Note: Note: $D_{\%} = (x_{\text{Trad}} - x_{\text{GLD}})/x_{\text{GLD}}$; where x_{Trad} = variable from simulation 3; x_{GLD} = variable from simulation 4.

When comparing prediction simulations 3 and 5, the future hydrologic impact was greater (0.32% to 4.36% difference) for the valley fills reclaimed using traditional methods compared to the no land disturbance (NLD) simulation (Table 11).

Table 11. Percent differences ($D_{\%}$) comparing simulation 3 (traditional) and 5 (no land disturbance)

	$D_{\%}$
Total Flow	2.26
Lowest 50% Flow	0.32
Highest 10% Flow	3.53
Mean Storm Volume	2.88
Mean Storm Peak Flow	4.36

Note: Note: $D_{\%} = (x_{\text{Trad}} - x_{\text{NLD}})/x_{\text{NLD}}$; where x_{Trad} = variable from simulation 3; x_{NLD} = variable from simulation 5.

When comparing prediction simulations 4 and 5, the future hydrologic impact was similar (-0.03% to 0.89% difference) for the valley fills reclaimed using GLD methods compared to the no land disturbance simulation (Table 12). The estimated hydrologic impact was greater for the GLD reclamation scenario when compared to the NLD scenario for all prediction criteria except the lowest 50% flow, in which the GLD scenario hydrologic impact was less than the NLD scenario.

Table 12. Percent differences ($D_{\%}$) comparing simulation 4 (traditional) and 5 (no land disturbance)

	$D_{\%}$
Total Flow	0.51
Lowest 50% Flow	-0.03
Highest 10% Flow	0.79
Mean Storm Volume	0.70
Mean Storm Peak Flow	0.89

Note: Note: $D_{\%} = (x_{\text{Trad}} - x_{\text{NLD}})/x_{\text{NLD}}$; where x_{Trad} = variable from simulation 4; x_{NLD} = variable from simulation 5.

Overall, prediction model results indicated that the current and future hydrologic impacts within the watershed were reduced when valley-fill reclamation was completed using the geomorphic landform reclamation technique as opposed to the conventional reclamation method (-0.34% to -3.33% current difference and -0.27% to -1.1% future difference). Results also showed that the future hydrologic response of the impacted watershed closer resembled the pre-mining hydrologic state when the valley-fills were reclaimed using geomorphic landform techniques (-0.03% to 0.89% difference) compared to traditional methods (0.32% to 4.36% difference).

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2. Publications

Articles (*graduate student)

1. Hopkinson, L.C., Sears, A.E.* , Snyder, M.* , O'Leary, E.* , DePriest, N.* , Quaranta, J.D., and Ziemkiewicz, P.F. Simulating the hydrologic response when streams are incorporate in valley fill design. In Review.
2. Sears, A.* , and Hopkinson, L. 2015. Predicting hydrologic response at the landscape scale when streams are included in valley-fill design. American Society of Agricultural and Biological Engineers Annual Meeting. July 26-29, 2015. (Conference paper in preparation)
3. DePriest, N.* , Hopkinson, L., Quaranta, J., Sears, A.* , Russell, H. Snyder, M.* , O'Leary, E.* , Eddy, J.* , Mack, B., and Hause, J. 2014. Developments in valley fill reclamation in Central Appalachia: the design of stable and sustainable landforms. Advances in Geomorphic Reclamation at Coal Mine Sites. A Technical Interactive Forum and Field Tour. Office of Surface Mining Reclamation and Enforcement. May 20-22. Albuquerque, NM. 6 pages. (not peer-reviewed, invited paper)

Theses

1. O'Leary, E.E. 2014. Floodplain mapping in response to surface mine reclamation. MS Thesis. Civil and Environmental Engineering Department: West Virginia University.

3. Information Transfer Program

Poster Presentations (*Undergraduate student, presenter in bold)

1. **Billian**, H.* , Sears, A., and Hopkinson, L. 2014. Evaluating the effects of geomorphic landform design on erosion potential. 89th Annual West Virginia Academy of Science Meeting, April 12. Shepherd University: Shepherdstown, WV. poster
2. **Snyder**, C.* , DePriest, N., and Hopkinson, L. 2014. Sizing ponds for a surface mine reclamation valley fill. 89th Annual West Virginia Academy of Science Meeting, April 12. Shepherd University: Shepherdstown, WV. Poster

Accepted Abstracts (*Graduate student, presenter in bold)

1. Sears, A.* , and **Hopkinson**, L. 2015. Predicting hydrologic response at the landscape scale when streams are included in valley-fill design. American Society of Agricultural and Biological Engineers Annual Meeting. July 26-29, 2015.

4. Student Support

- Four graduate students have worked on research related to this project: Alison Sears (PhD, continuing), Nathan DePriest (Continuing), Mike Snyder (MS, graduated December 2013), Erin O'Leary (MS, graduated December 2014).

5. Student Internship Program

NA

6. Notable Achievements and Awards.

The following achievements were completed in this reporting period:

- One graduate student graduated with a MS in December 2014.
- Two undergraduate students presented results at a professional meeting.
- One abstract was accepted to present at professional meetings.
- Technical progress continues for all objectives.

Understanding variations in isotopic and molecular compositions of stray gas in areas of accelerating shale gas development

Basic Information

Title:	Understanding variations in isotopic and molecular compositions of stray gas in areas of accelerating shale gas development
Project Number:	2013WV205B
Start Date:	3/1/2013
End Date:	2/28/2015
Funding Source:	104B
Congressional District:	
Research Category:	Water Quality
Focus Category:	Water Quality, Geochemical Processes, Hydrogeochemistry
Descriptors:	
Principal Investigators:	Shikha Sharma

Publications

1. Sharma, S., M. Mulder, A. Sack, K. Schroeder, and R. Hammack. 2013. Isotope approach to assess hydrologic connections during Marcellus Shale drilling. Groundwater. DOI: 10.1111/gwat.12083.
2. Soeder, D.J., S. Sharma, N. Pekney, L. Hopkinson, R. Dilmore, B. Kutchko, B. Stewart, K. Carter, A. Hakala, and R. Capo. 2014. An approach for assessing engineering risk from shale gas wells in the United States. International Journal of Coal Geology. DOI: 10.1016/j.coal.2014.01.004.
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Understanding variations in isotopic and molecular compositions of stray gas in
areas of accelerating shale gas development

Final Report

Reporting period: March 1, 2013-February 28, 2015

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Report Issue Date: May 27, 2015

USGS Award: 104b grant

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Research

Abstract

Accurate spatial and geochemical characterization of stray gas is imperative as shale gas production rapidly increases in basins around the world, including the Appalachian basin. To achieve economic gas production from shale, a technique known as hydraulic fracturing, or “fracking” is adopted. During the hydraulic fracturing process a mixture of water, proppant and chemicals is injected thousands of feet underground at high pressure which induces fractures in the source rock to release trapped gas. Under natural conditions, the water and gases occurring within the shale and other deep formations do not mix with shallow fresh water aquifers due to the barrier provided by several thousand feet of impermeable rocks. However, there are concerns that the hydraulic fracturing process can create new fracture networks or connect existing fracture networks which could augment hydraulic pathways between previously isolated formations. Additionally, well casing or grouting failures intersecting with pre-existing faults can allow dissolved gases and brine waters to contaminate shallow fresh water sources. Gas migrating into shallow aquifers, particularly methane, is a concern because the corresponding explosion risks, suffocation potential, and the negative impact on air quality. The preliminary data collected by the WVU Stable Isotope Lab and USGS collaborators at WV Water Science Center indicate that dissolved methane concentrations can be naturally high in some fresh water sources in North central West Virginia. The isotopic and molecular composition of dissolved methane, concentration of dissolved CO₂ and the carbon isotope signature of dissolved inorganic carbon suggest that methane in these groundwaters is not produced by biogenic processes at shallow depths but instead produced by CO₂ reduction and thermogenic processes in deeper geological formations. There is no prior or recent oil/gas drilling or coal mining activity in the study area. Hence, we propose that methane in these aquifers could be naturally migrating along natural faults and fractures from deeper coalbeds, Marcellus Shale and/or deeper Silurian and Ordovician oil and gas reservoirs over geological time scales. It is important to note that concentration, isotopic, and molecular composition of dissolved gas in water can also be significantly affected by changes in sampling methodologies and environmental conditions at time of sampling. With public awareness and concern about stray gas incidents on the rise, a complete understanding of spatial baseline stray gas concentrations and their relationships with natural faults and fractures is a necessity.

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Executive Summary

One of the primary concerns associated with shale gas development is stray gas migration into shallow aquifers during gas well drilling and stimulation through the creation of new hydrologic connections or the reactivation of ancient fracture networks. Under natural conditions, the fluids occurring within the shale and other deep formations do not mix with shallow fresh water aquifers due to the barrier provided by several thousand feet of impermeable rocks present between the two end-members. However, during well drilling, casing or grouting failures, existing subsurface fractures, and fractures created during hydraulic fracking can generate or augment hydraulic pathways between previously isolated formations. While stray gas may migrate from gas wells, other sources of stray gas include coalbeds, storage gas fields, abandoned oil and gas wells, and coalbed methane wells. In addition to these sources of stray gas, methane may also be produced through biogenic pathways within the aquifer. Isotopic and geochemical analyses can be used to aid in the determination of stray gas sources in shallow groundwater. This study is a deeper exploration of results from a project completed in the summer of 2011 where 4 out of 41 groundwater wells sampled had methane concentrations >10 mg/L. Results from this study also indicated that the stray gas in these shallow aquifers is not produced by biogenic processes in shallow aquifers but is probably sourced from deeper oil/gas containing geological formations. However, high methane concentrations could not be related to old oil/gas/coalbed methane drilling activities or recent shale gas drilling in the study area.

The aim of this study is to determine the source of the stray gas present in these shallow aquifers by targeting the area around the high dissolved methane wells (Mulder, 2012) and attempt to isolate potential pathways for this fluid migration. This will be accomplished by completing the following objectives:

- 1) Understand the isotopic and molecular composition of natural gas in major coalbed and oil and gas reservoirs in the study area to assess the potential sources for the stray gas in this area.
- 2) Understand the relationship between dissolved methane, water quality parameters and stable isotope (C, O and H) signatures of ground waters sampled for this study. The results will help in the development of robust isotopic models to evaluate stray gas incidents in areas of active shale gas drilling.
- 3) Determine potential source of stray gas through isotopic and geochemical analyses as well as mapping of potential migration pathways.

Out of 35 wells sampled the majority of the sampled wells have low methane levels (89% of wells have concentrations less than 1 mg/L), three wells, Ran-02, Ran-23 and Ran-12 have concentrations of 40.0, 14.0 and 9.7 mg/L respectively. Our preliminary results indicate that stray gas migration in this area is likely controlled by highly localized structural controls such as natural faults or fractures creating pathways or conduits for deep fluid to migrate from depth. More work is needed to map the study area in order to determine precise fracture trends, but preliminary lineament tracing and field observations indicate that there is the potential for fractures to create the necessary pathway.

Introduction

Previous Work: Previous groundwater sampling was completed in 2011 before active shale gas drilling occurred throughout north central West Virginia (Sharma et al., 2013, Mulder, 2012). This project highlighted that methane concentrations in groundwater are extremely variable throughout north central West Virginia and several relationships were considered to explain occurrences of high methane. These included; topographic lows (as described by Molofsky et al., 2012), structural faults, gas storage fields, landfills and marshes, abandoned oil and gas wells and abandoned/active coal mining activity. Mulder (2012) identified two locations in Randolph County, WV (Ran-0276 and Ran-0278) that had high methane concentrations and no relationship with prior energy development. However, both Ran-0276 and Ran-0278 are located within a river valley and are in proximity to a Precambrian fault (figure 1). From these results, it is hypothesized that high concentrations of stray gas occur naturally in proximity to faults or areas with dense underlying fracture networks.

Purpose: The purpose of this study is to complete targeted, high-density sampling in an area with extensive faulting and naturally high concentrations of stray gas unrelated to previous energy development. Geochemical and isotopic data will be used to determine potential source as well as post-formation mixing and migration trends of stray gas.

Study Location and Geology: The study site for this project is a section of the Tygart River valley located in central Randolph county and extending south into northern Pocahontas county, West Virginia (figure 1).

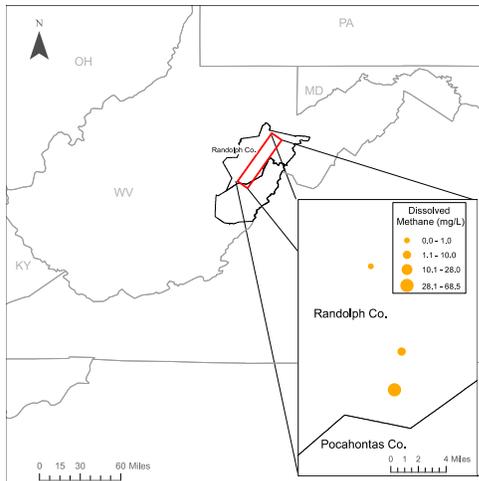


Figure 1: Study location spanning northern Pocahontas and Randolph counties, West Virginia. Inset shows locations and corresponding concentrations of dissolved methane from study by Mulder, 2012.

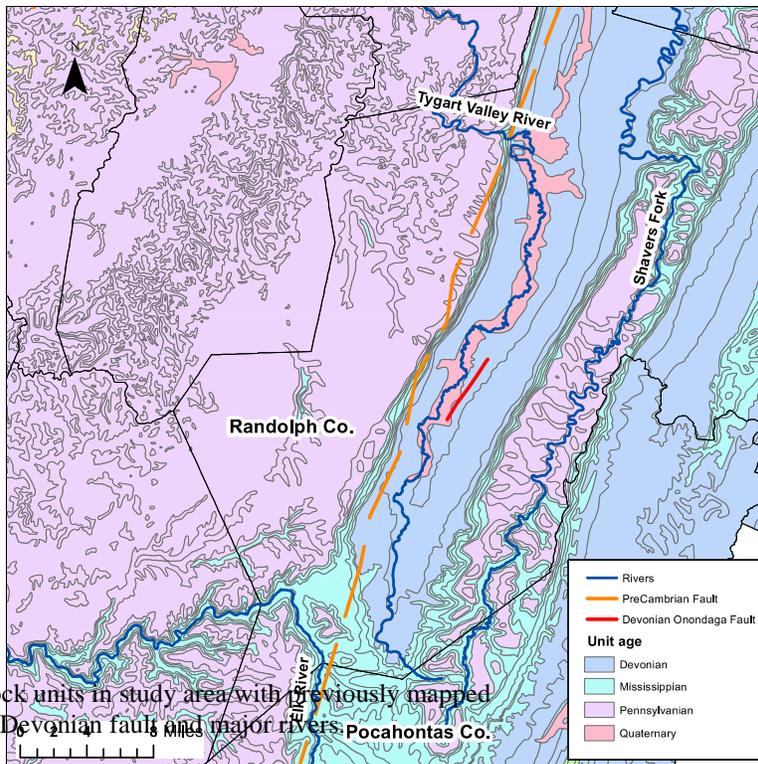
The extent of the study area is approximately 35 miles in length and 5 miles in width. Land use is generally residential with some agricultural activity (predominantly cattle grazing). The study area lies within the Tygart and Cheat watersheds with the southern section extending into the Elk watershed. The three main rivers are the Tygart Valley river which essentially bisects the study area, the Elk river in the southern section of the study area and Shaver's fork to the east.

The majority of the study area is located along the Deer Park anticline (also called the Elkins Valley anticline) which runs South 12° West through Randolph county and extends into Pocahontas county (Reger, 1931). The Elkins Valley anticline lies within the Allegheny plateau province and is located approximately 20 miles to the east of the Allegheny structural front (Ryder et al., 2008). The anticline was formed as a result of the Alleghenian

orogeny which resulted in dramatic deformation in the Valley and Ridge province with less deformational impact in central and eastern West Virginia. While less deformationally dramatic, the Appalachian High plateau is distinguished by high-amplitude folds with thrust faults sometimes occurring within the anticlinal cores. The thrust faults occurring within the folds

increases the overall fold amplitudes which results in the topographic variation observed in Randolph and Pocahontas counties (Renton, 2004). The Elkins Valley anticline has experienced multiple thrust faults originating from the Harrell shale acting as the zone of detachment.

A common feature of the Appalachian high plateau, the axis of the Elkins Valley anticline has eroded and the units exposed at the surface in Randolph County primarily consist of the Upper Devonian-age Portage and Chemung series. The Genesee series and Catskill Series also outcrop along the anticline in shorter intervals. To the east of the anticline the Pennsylvanian-age Pottsville series is the dominant rock type (Reger, 1931). Also occurring in the center of the valley are deposits of Quaternary alluvium (figure 2).



Closer to the Pocahontas border the outcrops become Mississippian in age which includes the Pocono, Maccrady, Greenbrier and Mauch Chunk series. In Pocahontas County the surface geology within the study area is definitively Mississippian with the Greenbrier and Mauch Chunk series dominating (Reger, 1931) (figure 2).

The aquifers in the study area generally occur within the rock that composes the surface geology of the particular location due to the thickness of units compared to an average groundwater well depth. This potentiates that the likely aquifers in the study area are Tygart valley alluvium,

Devonian sands, and in the southern part of the study area Mississippian limestones (figure 2). The alluvium, while high in productivity, likely contains high amounts of clay and silt which may impact potability of the groundwater. However, some shallow wells that were sampled may be accessing water from this unit. The Devonian aquifers make up a majority of the study area and are a clastic fractured bedrock type aquifer with characteristically high transmissivity. The Greenbrier limestone to the south of the study area could potentially have conduit flow within the aquifer which complicates the understanding of localized aquifer characteristics but is overall understood to be a productive aquifer. Complicating the understanding of groundwater flow in the study area are the thrust faults cutting through the anticlinal hinge as these can create major pathways for groundwater flow (Kozar and Mathes, 2001).

Natural gas production hasn't to date been successful or intensive in Randolph or Pocahontas county. Interest in drilling for natural gas and oil in Randolph county began in the early 1900s but the anticline limbs complicated the driller's ability to complete a straight well and the wells weren't as productive as other locations in the state (Reger, 1931). Vertical wells continued to be drilled in the mid-1900s but the current status of most wells within the study area

is abandoned or plugged. However, with vertical wells permitted in the study area and horizontal Marcellus wells encroaching from the west the timing of this study becomes apropos (WVDEP Office of Oil and Gas permit locations, accessed February, 2014).

Experimental Method

For this study, business and homeowners are contacted that are within the desired area and state that they have groundwater wells or spring water supplying their property. The well/spring owners also must confirm that the water is not exposed to air (i.e. headspace in a spring box) before coming out of the sampling port, experiences no treatment (i.e. chlorinators, softeners etc.) and that there is a working pump in the well. Attaining representative groundwater well samples is difficult due to complications such as pump variability and sample flow rates (Gorody, 2012) but efforts were made to limit varied environmental conditions and collect samples in a consistent and deliberate fashion. A total of 27 private and public groundwater wells and springs were sampled between October, 2013 and December, 2013.

Field Parameters: The purpose of monitoring field parameters is two-fold; firstly, parameters such as pH, temperature and conductivity are important for calculations that describe the water geochemistry. Secondly, monitoring relative differences in field parameters over the pre-collection and sample collection time period is important in understanding whether changes are occurring that may impact sample quality. For example, if a spike in dissolved oxygen is observed, it is assumed that drawdown has occurred to the point where water is cascading from a fracture above the water level in the well, and time should be allowed for the well to recover so as to prevent degassing. For this study, field parameters are monitored constantly from when water began to flow from the well to the completion of sampling.

A YSI Professional Plus handheld multiparameter meter is used in conjunction with a Professional Series pH/ORP combo sensor inserted into a 203 mL standard flow cell. The YSI is calibrated for pH and conductivity in the field to ensure accurate measurement. Parameters are logged every 30 seconds from when water begins flowing through the cell until every sample is collected (figure 7).

When possible, depth to water is also measured using a Solinst 101 P2 water level meter to determine initial water level and change in water level throughout the pumping period (figure 8). This is to ensure that drawdown doesn't occur too quickly; this could result in damage to the pump if it were to start drawing in air or sediment. At sites where monitoring water level wasn't possible, the owner was interviewed about the recharge to the well, depth of the well, and perceived initial water level so that flow rate could be adjusted appropriately.

Geochemistry: Alkalinity is measured in the field using a Hanna Instruments handheld colorimeter and replicated in the lab with a Metrohm 848 Titrino plus autotitrator using 0.1 normal Hydrochloric acid. The Hanna meter has a precision of ± 5 ppm and replication occurs in the field until consecutive samples are within 5 ppm of each other. Samples for titration are collected in the field in pre-rinsed 125 mL narrow mouth HDPE bottles. The bottle is filled from a 60 mL Luer-lock syringe fitted with a .45 μm Whatman nylon filter until a positive meniscus is observed so that no headspace occurs within the sample. To confirm precision of methods, field alkalinity measurements and autotitrations are compared with manual titrations (table 2). From this comparison, it was determined that using the Hanna meter in the field followed by a measurement done in the lab within 48 hours after collection using the autotitrator is an accurate characterization of alkalinity for the purposes of this study.

Samples are collected for cation and anion analysis using a pre-rinsed 60 mL Luer-lock syringe and .45 μm Whatman nylon filter. Cation samples are collected in pre-rinsed 60 mL HDPE narrow mouth bottles and are acidified with approximately 1 mL of 65% Omni Trace Nitric acid (figure 9). Anion samples are collected in pre-rinsed 30 mL narrow mouth HDPE bottles. Both cation and anion samples are collected with no headspace. The samples are then shipped to a geochemical lab for analysis.

Water Isotopes: Isotope samples are collected for measuring $\delta^{13}\text{C}_{\text{DIC}}$, $\delta\text{D}_{\text{H}_2\text{O}}$, and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$. Samples for $\delta\text{D}_{\text{H}_2\text{O}}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ are collected in a 8 mL glass screw-top vial using a pre-rinsed 60 mL Luer-lock syringe with no headspace. The vials are then wrapped in parafilm to prevent leaking or contamination. For $\delta^{13}\text{C}_{\text{DIC}}$, the same syringe is fitted with a .45 μm glass/nylon filter and water is filtered into a 10 mL glass bottle and topped with 3 drops of benzalkonium chloride as a preservative. The bottle is then crimped shut with a 20 mm Teflon septa and aluminum cap with no headspace.

The three stable isotopes are analyzed at the WVU Stable Isotope lab using a Finnigan Delta Advantage continuous flow isotope ratio mass spectrometer connected with a ThermoQuest Finnigan GasBench II. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\delta\text{D}_{\text{H}_2\text{O}}$ are measured from the same aliquot of sample water, but different flushing gases and equilibration methods are used. A platinum catalyst is used to enhance equilibration for $\delta\text{D}_{\text{H}_2\text{O}}$ samples. The precision rate for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ is $\pm 0.02\%$ and the precision rate for $\delta\text{D}_{\text{H}_2\text{O}}$ is $\pm 1\%$. The $\delta^{13}\text{C}_{\text{DIC}}$ samples are run in different vials separately from O and H and are acidified to enhance equilibration. The precision rate for $\delta^{13}\text{C}_{\text{DIC}}$ is $\pm 0.02\%$.

Dissolved gases and methane isotopes: Gas samples are collected in a 1 liter plastic Isotech dissolved gas bottle with a Teflon septa cap and a benzalkonium chloride capsule that releases into the water after sample collection to prevent microbial activity. The bottle is submerged into a clean 5-gallon bucket without the cap and the sample water tube is submerged at the bottom of the bottle (figure 10). The water flows at a rate of approximately 1 liter/min (control on flow velocity was varied at each site) into the bottle and sample water is cycled into the bottle until 3 sample volumes are exchanged. The bottle is then capped quickly underwater. The cap is wrapped in parafilm and samples are stored upside down to prevent gas from escaping.

Dissolved gas compositions and isotopes of methane and ethane are analyzed at Isotech laboratory. The gas analysis is performed using a headspace equilibration method. Water is removed through the septum at the top of the bottle and then an equivalent amount of helium is added to create between 30-60 mL of headspace at a dilution factor of 0.68. The bottle is then shaken for two hours to allow equilibrium of gases between the water and headspace. Gas composition is measured using a Shimadzu 2010 GC system and then concentrations of dissolved gas are calculated using Henry's Law. Gas composition analyses have a precision rate of $\pm 5\%$ for C_{1-4} and $\pm 10\%$ for C_{5-6+} .

For isotopes of methane and ethane, both an online and offline prep system are used depending on the concentrations of methane or ethane. When the concentrations are higher, an offline prep system is used that combines a Finnigan MAT Delta S Isotope Ratio Mass Spectrometer for carbon measurement and a Finnigan Delta Plus XL Isotope Ratio Mass Spectrometer for hydrogen. When concentrations are lower, a HP6890 GC connected to a ThermoFinnigan Delta Plus Advantage is used for measuring carbon, and a HP6890/7890 is

connected with a Thermo Scientific Delta V Plus for measuring hydrogen. When the concentrations of methane are below 0.5% and the ethane concentrations are below 0.3% the analysis is performed with the online system. Higher concentrations of methane are required relative to ethane due to the increased number of carbons in the ethane molecule. The precision rate for offline preparation of gas isotopes is $\delta^{13}\text{C}_{\text{C1-2}}$ is $\pm 0.2\%$ and $\pm 2.0\%$ for $\delta\text{D}_{\text{C1-2}}$. The precision rate for online preparation of the gas isotopes is $\delta^{13}\text{C}_{\text{C1-2}}$ is $\pm 0.3\%$ and $\pm 5.0\%$ for $\delta\text{D}_{\text{C1-2}}$.

Results and Discussion

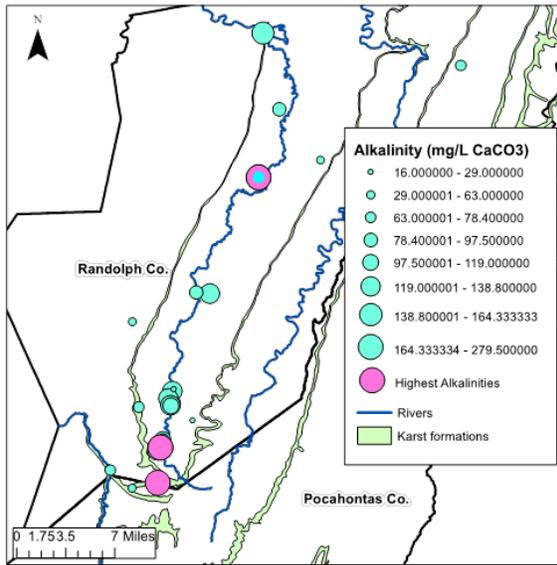


Figure 3: Alkalinity concentrations in sampled wells

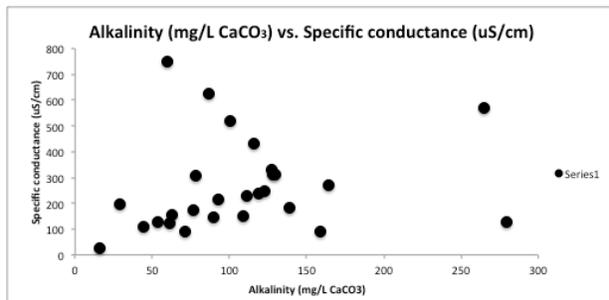


Figure 4: Plot of Alkalinity (mg/L CaCO_3) vs. Specific Conductance (uS/cm)

all of the wells with Na-HCO_3 type water only ~14% have methane levels above 10 mg/L. When compared with data from a previous study done by our lab (Mulder 2012), out of the four wells with dissolved methane concentrations greater than 10 mg/L, 3 have Na-HCO_3 type water. Na-HCO_3 type water seems to correlate with high dissolved methane concentrations in the study area and also within the larger region sampled by Mulder in 2012. High Li concentrations in conjunction with Na, Cl, and Br could be indicative of a brine signature. Ran-02 and Ran-23

Geochemistry: Alkalinity and specific conductance were the two field parameters that showed variability throughout the study area. It is presumed that due to the occurrence of carbonate rock in the study area, this is the predominant source of alkalinity (figure 3). However, alkalinity shows no spatial trends related to limestone/karst occurrence. This indicates that there could either be another source of alkalinity in the study area (i.e. iron or phosphate) or there are more localized/well specific controls on alkalinity. Further geochemical analysis of the samples will help illuminate this trend.

Alkalinity and specific conductance were plotted to understand whether Ca and Mg (potential sources of alkalinity) would show a positive linear correlation. While there is some indication that the Ca and Mg may be a source of ions in some of the wells (shallow positive linear correlation at low alkalinities) there is also a negative linear correlation between specific conductance values of 400-800 uS/cm (figure 4). This indicates that in these wells (Ran-19, Ran-21 and Ran-25) there are ions present that have little contribution to alkalinity. Methane

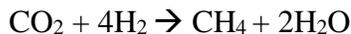
concentrations greater than 10 mg/L are found within Na-HCO_3 type waters. However, out of

have the two highest Li concentrations (382 mg/L and 200 mg/L respectively) along with high Na and Cl and are also the two wells with dissolved methane concentrations above 10 mg/L.

Dissolved Gas: Proper end member characterization of natural gas in situ is the most effective way to understand gas signatures occurring out of geologic context (Breen et al., 2005, Gorody, 2012). Methane occurring in groundwater can be produced in a variety of settings through numerous processes. The production of methane can generally be subdivided into three different categories; microbial, thermogenic and abiogenic methane (Coleman, 1995, Gorody, 2012). Microbial methane can be further divided into two different production methods: the CO₂ reduction process and acetate fermentation process (Baldassare and Laughrey, 1997, Breen et al., 2005, Coleman 1995, Martini et al., 1998, Révész et al, 2010, Whiticar, 1999, Whiticar et al., 1986). Each of these gas production categories results in methane with distinct signatures that can help us identify the potential source of stray occurring within wells in the study area.

δ¹³C-CH₄ and δ²H-CH₄: Carbon and hydrogen isotopes of methane are the most defining and widely used characteristic to determine the source of stray gas. Methane produced thermogenically is influenced by the pressure and temperature conditions at the time of gas formation as well as the type of organic material that the gas was produced from (Coleman, 1995). Potential sources of thermogenic gases in the study area include the Devonian Harell and Marcellus shales. Thermogenic gases native to the Appalachian basin have δ¹³C_{CH₄} values that range from -55.1‰ to -27.2‰ and δ²H_{CH₄} values that range from -303‰ to -150‰ (Baldassare and Laughrey, 1997). Maturity of thermogenic gases can also be assessed using gas isotopes with δ¹³C_{CH₄} values becoming increasingly enriched with increasing thermal maturity (Whiticar, 1999).

Microbial gas can be produced by either CO₂ reduction or acetate fermentation (Baldassare and Laughrey, 1997, Coleman 1995, Martini et al., 1998, Révész et al, 2010, Whiticar, 1999, Whiticar et al., 1986). CO₂ reduction occurs when microbes use CO₂ and H₂ present in formation water to create methane in the following reaction:



This process generally occurs in a marine setting and results in more depleted δ¹³C_{CH₄} and δ²H_{CH₄} values than observed in thermogenic gas (Martini et al., 1998, Révész et al., 2010). CO₂ reduction methane produces gases with δ¹³C_{CH₄} signatures of approximately -62‰ to -90‰ and δ²H_{CH₄} signatures of about -180‰ to -240‰ (Breen et al., 2005). Relative to methane produced

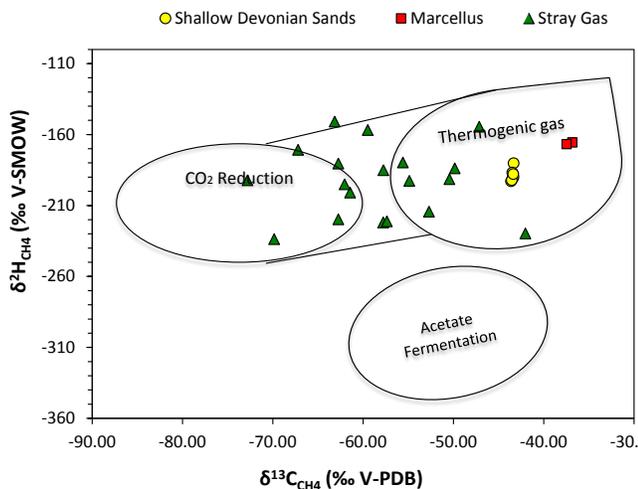
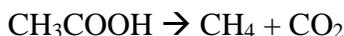


Figure 5: General classification of natural gas sources based on isotope compositions. Though carbon and hydrogen isotopes are somewhat diagnostic, more geochemical evidence must be integrated before defining source (Coleman, 1995). Plotted for comparison are GW sites (Mulder, 2012), Shallow Devonian sands gases and Marcellus shale gases.

by acetate fermentation, CO₂ reduction methane $\delta^{13}\text{C}_{\text{CH}_4}$ tends to be more depleted and the $\delta^2\text{H}_{\text{CH}_4}$ tends to be slightly more enriched. Acetate fermentation occurs when methanogens, generally in a freshwater system, breakdown an organic compound that results in the production of CO₂ and CH₄ in the following reaction:



(Révész et al., 2010, Whiticar, 1999). In the acetate fermentation process, the hydrogen is slightly more depleted than during CO₂ reduction because the majority of the hydrogen atoms in the CH₄ molecules are derived from organic matter. In comparison, hydrogen is derived from formation water in the CO₂ reduction process (Révész et al., 2010, Whiticar, 1999, Whiticar et al., 1986). Acetate fermentation produced methane results in a $\delta^{13}\text{C}_{\text{CH}_4}$ signature of approximately -40‰ to -62‰ and a $\delta^2\text{H}_{\text{CH}_4}$ signature of -270‰ to -350‰ (Breen et al., 2005). Abiogenic, or mantle gas, is very uncommon and therefore is unlikely to be a source of stray gas (Coleman, 1995). The carbon and hydrogen isotopes are frequently used to distinguish between the thermogenic and biogenic origin of gases.

When stray gas samples from the study area are plotted on the dual carbon and hydrogen isotope plot the samples fall in the CO₂ reduction, thermogenic and mixed regions (figure 5). None of the sample fall in acetate fermentation category which is prominent pathway of biogenic methane formation in shallow freshwater aquifers. While CO₂ reduction is generally assumed to take place in marine settings, it can occur in freshwater settings with low acetate availability (i.e. at depth) (Chanton et al. 2005). Because the hydrogen atom from the formation water is incorporated into the methane molecule during CO₂ reduction, there should be a 1:1 relationship between the isotopic signatures of the hydrogen in methane and hydrogen of the formation water (Chanton et al. 2005, Schoell 1980, Sharma et al. 2014). If this correlation is observed within the samples, this would indicate that CO₂ reduction is producing methane within the aquifers that were sampled. However, the hydrogen isotope composition of the water does not show any relationship with hydrogen isotope composition of methane indicating methane was likely not produced in the sampled aquifer. CO₂ reduction also can enrich the $\delta^{13}\text{C}_{\text{DIC}}$ of the groundwater through the preferential removal of the lighter ¹²C as methane is produced. The $\delta^{13}\text{C}_{\text{DIC}}$ signatures all plot below 0‰, further indicating it is unlikely that CO₂ reduction is occurring in the sampled aquifers. To further understand methane source and post genetic effects natural gas composition can be used in conjunction with isotopic data.

Natural gas compositions: Chemical compositions of natural gas can also be used as an indicator of whether the stray gas in the study area has a thermogenic or microbial origin. Thermogenic natural gas generally produces a larger volume of higher chain hydrocarbons such as ethane, propane and butane. Microbial processes generate a higher percentage of methane, with lower percentages of C₂₊ hydrocarbons (Coleman, 1995, Osborn et al, 2011, Whiticar, 1999). A plot that combines $\delta^{13}\text{C}_{\text{CH}_4}$ values with natural gas compositions is another way to distinguish the origin of gas occurring within wells in the study area (figure 6). As discussed in previous section it does not appear that methane was produced by acetate fermentation within the shallow aquifer or by CO₂ reduction in the sampled aquifer, this gas must have migrated from another formation. Regardless of whether the gas was initially produced through CO₂ reduction or thermogenic processes in deeper formations the migrated gas sampled in the aquifer will be isotopically depleted and enriched in C₁ gas compared to original source This post genetic modification can impart what appears as biogenic gas signatures to migrated thermogenic gas complicating the interpretation of the origin of the gas.

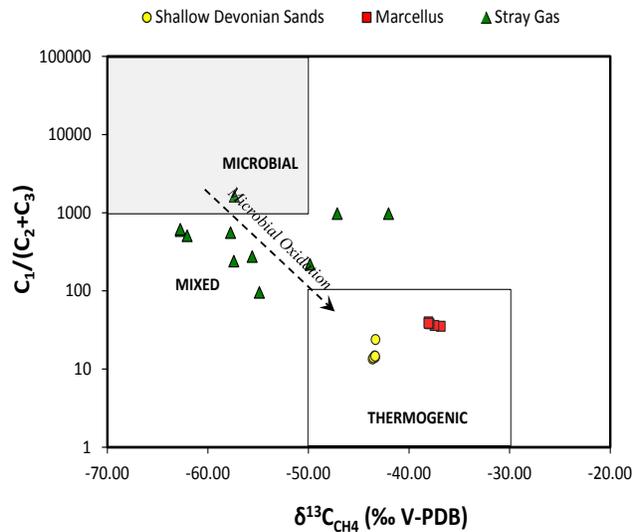


Figure 6: Plot of $\delta^{13}\text{C}_{\text{CH}_4}$ vs. concentration of $\text{C}_1/\text{C}_2+\text{C}_3$ hydrocarbons. Stray gas samples fall into the microbial and mixed areas of the plot which could indicate either the oxidation of microbial gas or the migration of thermogenic

preliminary fracture mapping and structural interpretation indicate that a complex fracture network or the anticlinal axis may be providing gas migration pathways or increased opportunity for mixing with deep fluids. This study emphasizes the importance of rigorous baseline stray gas characterization due to the high spatial variability of dissolved methane concentrations in this region.

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Conclusions

Initial results show extreme variability in the geochemical and isotopic composition of dissolved gases and waters throughout the study area. The isotopic and molecular compositional analyses indicate that the stray gas is either of thermogenic and/or CO_2 reduction origin probably produced in deeper geological formations. There is no old/recent oil, gas, coalbed methane or shale gas drilling activity in the region. Therefore, it appears that gas has migrated into the shallow freshwater aquifers from the deeper formations through natural faults and fractures probably over geological time scales. With very little robust structural data for the study area, understanding fault and fracture systems is very difficult. However,

Conference, San Francisco, CA & Society of Petroleum Engineers Continuing Education Seminar “Engineering Applications for Michigan”, Mt. Pleasant, MI.

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Information Transfer Program

Student Support

Category	Number of students supported with 104b base grant	\$ Value of students supported with 104b base grant	Number of students supported with matching funds	\$ Value of student support with matching funds	Total number of students supported	Total \$ value of student support
Undergraduate	1					
Masters	1					
Ph.D.	0					
Post-Doc	0					
Total	2					

NOTABLE ACHIEVEMENTS AND AWARDS

- Two publications in peer-review international journals and one in process
- 1 MS thesis
- \$2 M collaborative research funding award from NSF to understand microbial methanogenesis in geological formations
- \$ 250K funding award from DOE-NETL to better understand gas migration pathways

Using geomorphic landform design principles to reduce selenium loads from West Virginia valley fills

Basic Information

Title:	Using geomorphic landform design principles to reduce selenium loads from West Virginia valley fills
Project Number:	2013WV208B
Start Date:	3/1/2013
End Date:	2/28/2015
Funding Source:	104B
Congressional District:	First
Research Category:	Water Quality
Focus Category:	Water Quality, None, None
Descriptors:	
Principal Investigators:	Ben Mack, Leslie Hopkinson, John D. Quaranta

Publications

1. Hopkinson, L., N. DePriest, J. Quaranta, and P. Ziemkiewicz. "Characterizing selenium leaching and transport from southern West Virginia valley fill alternatives". In review for volume published by Society of Mining, Metallurgy and Exploration.
2. DePriest, N.*, Hopkinson, L., Quaranta, J., Sears, A.*, Russell, H. Snyder, M.*, O Leary, E.*, Eddy, J.*, Mack, B., and Hause, J. 2014. Developments in valley fill reclamation in Central Appalachia: the design of stable and sustainable landforms. Advances in Geomorphic Reclamation at Coal Mine Sites. A Technical Interactive Forum and Field Tour. Office of Surface Mining Reclamation and Enforcement. May 20-22. Albuquerque, NM. 6 pages. (not peer-reviewed, invited paper)

Report title: Using geomorphic landform design principles to reduce selenium loads from West Virginia Valley fills

Type of report (annual or final): Final

Reporting Period Start Date: March 1, 2013

Reporting Period End Date: February 28, 2015

Principal Author(s): Leslie Hopkinson, John Quaranta

Date Report was issued (Month and Year): May 2015

USGS award number: G11AP20114

Name and address of submitting department(s):

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Abstract

Selenium is found in southern West Virginia coal seams and overburden. This selenium is leached into watersheds and is toxic in excessive concentrations. The objective of this study was to characterize leaching of mobile selenium for two West Virginia (WV) valley fills and to predict the transport of selenium from two design alternatives (conventional valley fill and geomorphic fill alternative). Unsaturated column leaching tests were performed on coal overburden samples from two southern WV surface mines. Duplicate columns containing each soil were periodically leached with simulated rain water similar in pH to southern WV rainfall. Leachate water was tested for dissolved selenium, dissolved metals, pH, specific conductance, sulfate, acidity, and alkalinity. Saturated tests were performed by filling a series jars with each soil, saturating the jars, and collecting water samples after certain time intervals. The samples were tested for the same parameters as the unsaturated test. Experimental results were used for the contaminant transport predictions. Results indicated that conductivity ranges were 100-1132 $\mu\text{S}/\text{cm}$ and 503-2940 $\mu\text{S}/\text{cm}$ for the unsaturated and saturated tests, respectively. Maximum selenium concentrations occurred in the unsaturated tests during the first two samples (0.071-0.185 mg/L). Selenium (Se) desorption was reduced through geomorphic fill design, most significantly when a reclaimed stream with reduced infiltration was applied to the fill profile. Geomorphic profiles exhibited lower infiltration rates and volumes of water travelling through and exiting the fill. The calculation of mass of Se desorbed from each fill was limited by the following assumptions: two-dimensional models, homogeneous distribution of Se, constant infiltration rate into fills, no effect due to groundwater velocity, uniform desorption rate within each flux section, and no desorption due to fully saturated conditions. Future Se desorption modeling will consider a more detailed analysis accounting for more discrete water flux calculations, variable infiltration rates and desorption rates, groundwater velocities, water residence time, and saturated/unsaturated zones.

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Introduction

Selenium is a water quality concern because it can be toxic in excessive concentrations. It is a naturally occurring element in the sedimentary rock and coal seams in Central Appalachia and can be released through mining practices (Vesper et al., 2008; Ziemkiewicz and Lovett, 2012). Overburden rock composed of organic shale has selenium concentrations four times that of sandstone (Vesper et al., 2008). Approximately 25% of the total selenium found in overburden is mobile (Roy, 2005).

For WV coal mines, selenium discharges must meet the chronic aquatic life standard of 5 $\mu\text{g/L}$ (WVDEP, 2011). Many surface mines and tailings facilities require treatment to meet this value. Ziemkiewicz and Lovett (2012) proposed that selenium concentrations will reach this level within 25 years after initial mining.

The objective of this study was to characterize leaching of mobile selenium for two West Virginia (WV) valley fills. The transport of selenium from the two design alternatives were predicted and compared. First, experimental results are presented to understand leaching from overburden. Then, results from groundwater and contaminant transport modeling are presented.

Experimental Methods

Laboratory study

Site Description

Overburden samples were collected from two active surface mines in southern West Virginia (July 9, 2013). Both samples had been relatively recently uncovered from their natural geological locations at the time of collection.



Figure 1. Area where overburden sample was obtained: Mine A



Figure 2. Overburden pile where sample was obtained: Mine A



Figure 3. Area where overburden sample was obtained: Mine B



Figure 4. Overburden pile where sample was obtained: Mine B

Sampling Methods

When collecting the material, caution was taken to obtain as high a portion of shale as possible. The shale was passed through a 2 in (5 cm) metal sieve prior to collection (Figure 5). The pieces of rock that did not pass the sieve were broken by hand as much as possible while using little effort. Large particles were removed from the sample.



Figure 5. Two inch sieve being held over overburden collection tubs

Soil Testing

The following tests were performed on the two soil samples to determine their physical and engineering properties: Soil Classification-USCS (D-2487), Sieve/hydrometer (D-422), and Specific Gravity (D-854).

Unsaturated tests

A 1.5 ft. long (0.46 m), 6 in (15.2 cm) inside diameter PVC pipe was used for this leaching study as suggested by ASTM E2242. A 0.5 in (1.3 cm) hole was drilled through the center of the PVC end cap to allow drainage of the effluent from the bottom of the column setup. An Oatey 5 in (12.7 cm) stainless steel drainage grate with 0.375 in (0.95 cm) square openings was placed inside the end cap followed by a 6 in (15.2 cm) diameter piece of HB Wick Drains MD-88 wick drain filter fabric with US Sieve #170 pore size. The fabric was secured and the edge was sealed by applying a bead of silicone caulk between its edge and the side of the end cap. The stainless steel grate served to hold the weight of the soil above the drainage hole and allow free drainage of the soil. The filter fabric kept any soil particles from draining with the effluent and clogging the drain. The pipe was inserted into the end cap until secure. A 4 in (10.2 cm) long, 0.5 in (1.3 cm) outside diameter piece of flexible vinyl tubing was inserted to the bottom of the end cap and water sealed with grease sealant. A 6 in (15.2 cm) diameter piece of the wick drain filter fabric was placed on top of the soil once it was added. Four columns were setup in this configuration for the unsaturated leaching tests: two for each of the mine site soils (Figures 6 and 7).

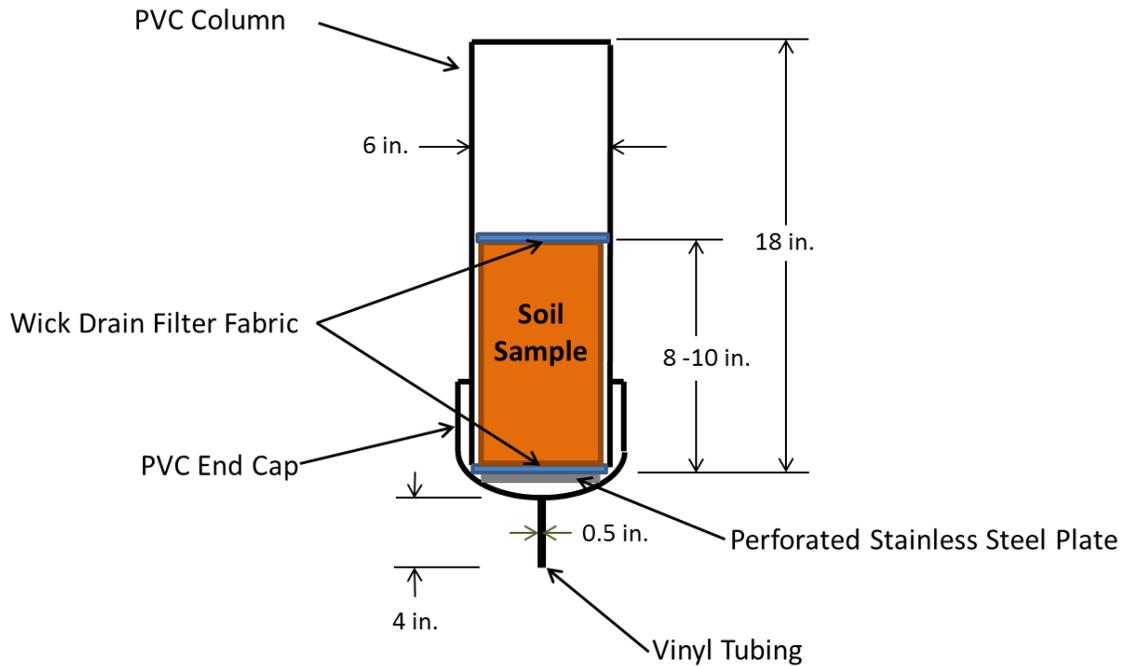


Figure 6. Schematic of unsaturated testing column.



Figure 7. Unsaturated column setup

A test sample was obtained from the overburden material collected from the mine site. To follow ASTM E2242, only the material that passed through a 2 in. sieve by hand-breaking was brought back to the lab. Five kilograms of overburden by dry weight were used for each unsaturated test. To obtain the actual weight (W_T) needed for 5 kilograms by dry weight (W_s), the following relationships were utilized:

$$W_w = w \times W_s \quad (1)$$

$$W_T = W_s + W_w \quad (2)$$

where W_w = weight of water;
 W_s = weight of solids;
 W_T = total weight; and,
 w = moisture content (Punmia et al. 2005).

The overburden sample was transferred to the column on top of the drainage plate and filter fabric at the bottom. Caution was used to prevent and excessive compaction or breaking of the soil particles by dropping the soil in diagonally or from a low drop (less than 20 cm). Once the soil was in place, a 6 in (15.2 cm) diameter piece of wick drain filter fabric was placed above the sample.

A series of pours was performed on two columns of each sample. Simulated rainwater was utilized for the testing to match the acidity of typical Appalachian precipitation (~5.2). A 2-yr, 12-hr storm of 5.5 cm for Madison, WV (NOAA Station 46-5563) was chosen for rainfall simulation. The weather station is close to both of the mine sites due to proximity (both within 16 km). Also, this volume of pour ensured sufficient effluent was collected to perform the lab testing. This pour of 1,010 mL was performed twice per week for each column (Table 1). The effluent was then filtered and sent to the WVU National Research Center for Coal and Energy Analytical Laboratory where it was analyzed for pH (EPA Method 150.1), alkalinity (SM2310A), acidity (SM2310B), sulfate (EPA Method 375.4), specific conductance (SM2510B), and dissolved Fe, Al, Ca, Mg, and Mn (EPA Method 200.7). REIC Consultants (Beaver, WV) analyzed the effluent for selenium (SM3114B). Values less than the detection limit were recorded as half of the detection limit (USEPA, 1998).

Table 1. Unsaturated leaching schedule of 1,010 mL of simulated rainwater

AU1*	AU2*	BU1*	BU2*
8/13/13	8/13/13	8/13/13	8/13/13
8/15/13	8/15/13	8/15/13	8/15/13
8/20/13	8/20/13	8/20/13	8/20/13
8/27/13	8/27/13	8/27/13	8/27/13
9/3/13	9/3/13	9/3/13	9/3/13
9/10/13	9/10/13	9/10/13	9/10/13
9/12/13	9/12/13	9/12/13	9/12/13
9/17/13	9/17/13	9/17/13	9/17/13
9/19/13	9/19/13	9/19/13	9/19/13
9/25/13	9/25/13	9/25/13	9/25/13
9/27/13	9/27/13	9/27/13	9/27/13
10/1/13	10/1/13	10/1/13	10/1/13
10/8/13	10/8/13	10/8/13	10/8/13
10/11/13	10/11/13	10/11/13	10/11/13

*AU1=Mine A, unsaturated, replication 1; AU2=Mine A, unsaturated, replication 2; BU1=Mine B, unsaturated, replication 1; and, BU2=Mine B, unsaturated, replication 2.

Saturated tests

For the saturated tests, 3.8 L jars were filled with soil, starting with the largest rocks (Figure 8). The remaining soil was passed through a large 1 in (2.54 cm) sieve in order to obtain the rest of the largest particles (Figure 9). The portion retained was divided into the jars. This process was repeated with a 0.5 in (1.27 cm) sieve. The rest of the available soil was placed on top of the already added soil in the jars. The large pieces were added first to make sure that the top surfaces of the soil horizons in the jars were as flat and uniform as possible. This allowed for a more definite saturation volume when filling the jars with the simulated rain water. Mine A jars contained approximately 3.7 kg of soil, and Mine B jars contained approximately 4.4 kg of soil.

Jars were filled to the observed saturation point with simulated rainwater (pH~5.2). As the jars were being filled, the sides were lightly tapped and shaken to remove any air bubbles that remained. After saturation, jars containing the samples were sealed (Figure 10). Water samples were collected at predetermined intervals with one replicate per soil type (Table 2).



Figure 8. Saturated jars being filled with soil



Figure 9. Soil being put through a 1 in sieve



Figure 10. Soil filled jar saturated with simulated rain water

Table 2. Saturated sampling schedule

Sample IDs				Date of Fill	Date of Sampling	Number of Days Saturated
AS1-1	AS2-1	BS1-1	BS2-1	12/19/13	12/19/13	0.083 (2 hrs)
AS1-2	AS2-2	BS1-2	BS2-2	12/19/13	12/19/13	0.25 (6 hrs)
AS1-3	AS2-3	BS1-3	BS2-3	1/16/14	1/17/14	0.5 (12 hrs)
AS1-4	AS2-4	BS1-4	BS2-4	12/9/13	12/10/13	1
AS1-5	AS2-5	BS1-5	BS2-5	12/9/13	12/11/13	2
AS1-6	AS2-6	BS1-6	BS2-6	12/9/13	12/12/13	3
AS1-7	AS2-7	BS1-7	BS2-7	12/9/13	12/13/13	4
AS1-8	AS2-8	BS1-8	BS2-8	12/9/13	12/16/13	7
AS1-9	AS2-9	BS1-9	BS2-9	12/9/13	12/19/13	10
AS1-10	AS2-10	BS1-10	BS2-10	12/23/13	1/6/14	14
AS1-11	AS2-11	BS1-11	BS2-11	12/23/13	1/10/14	18
AS1-12	AS2-12	BS1-12	BS2-12	12/17/13	1/8/14	22
AS1-13	AS2-13	BS1-13	BS2-13	12/9/13	1/8/14	30
AS1-14	AS2-14	BS1-14	BS2-14	11/22/13	1/8/14	47

*AS1=Mine A, saturated, replication 1; AS2=Mine A, saturated, replication 2; BS1=Mine B, saturated, replication 1; and, BS2=Mine B, saturated, replication 2.

To collect the sample, mesh strainers with a coffee filter were used to minimize the amount of larger particles getting into the lab sampling bottles. Like the unsaturated experiment, WVU National Research Center for Coal and Energy Analytical Laboratory analyzed the samples for pH (EPA Method 150.1), alkalinity (SM2310A), acidity (SM2310B), sulfate (EPA Method 375.4), specific conductance (SM2510B), and dissolved Fe, Al, Ca, Mg, and Mn (EPA Method 200.7). REIC Consultants (Beaver, WV) analyzed the second sample for selenium (SM3114B). Values less than the detection limit were recorded as half of the detection limit (USEPA, 1998).

Groundwater Modeling

A geomorphic landform with one channel on the surface of the valley fill was generated as an alternative to an existing conventional valley fill at Mine A (Figure 11). Profiles on the centerline of each of the two fills were selected for two-dimensional groundwater modeling. The original valley foundation surface served as the lower boundary of the model (Figure 12). For all three profiles, the elevation extent was 290 m to 335 m and the longitudinal extent was 0 m to 273 m. In the conventional valley fill, the profile extended through the benched face and horizontal area (1%-2% slope). For the geomorphic reclamation, the profile cut through the centerline of the landform that included the recreated channel. The head of the reclaimed stream was at an elevation of 321m and extended to the outlet of the fill. The fill volumes (profile area times unit width) of the conventional and geomorphic profiles were 4725 m³ and 3009 m³, respectively. The properties of the fill material are presented in Table 3.

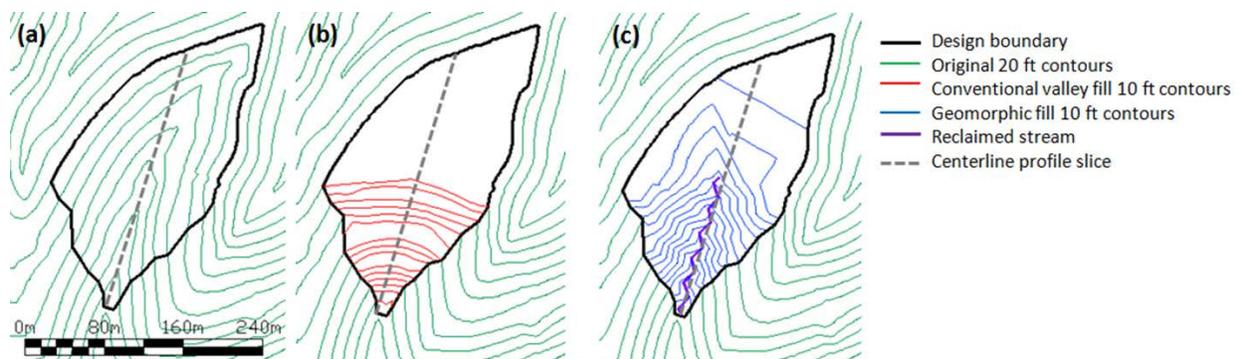


Figure 11. Contours used for geometry of model with location of two-dimensional profile slice for (a) original valley; (b) conventional valley fill reclamation; and (c) geomorphic design.

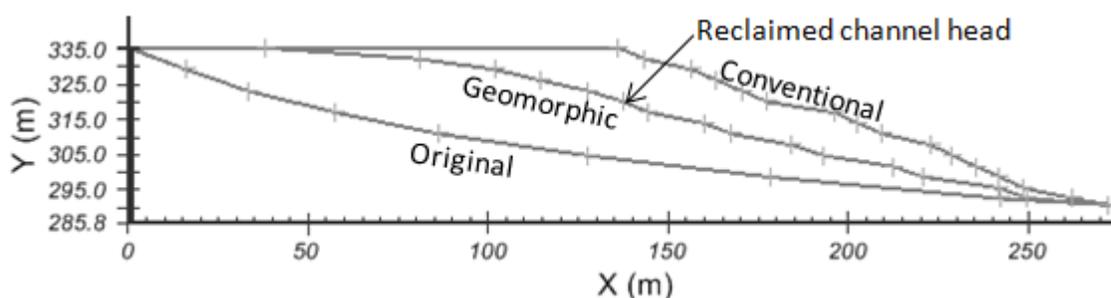


Figure 12. Two-dimensional profiles along centerline slice for original valley, conventional valley fill reclamation, and geomorphic design.

Table 3. Fill material properties necessary for groundwater modeling

Property	Expected value	Range
Saturated hydraulic conductivity (K_{sat}) (m/d)	1.47	0.86-46.7
Anisotropy ratio (K_H/K_V)	10	2.0-20
Porosity (n)	0.30	0.30-0.43
Specific gravity (G_s)	2.69	N/A

Sources: Mine permit file; Peterson et al. (2004); Wels et al. (2012); Abdelghani et al. (2009); Mao et al. (2006), Ataie-Ashtiani (2007), Fredlund et al. (1997); Domenico and Schwartz (1990); Russell (2012)

Due to the steep lower phreatic boundary of the model and high hydraulic conductivity values, the seepage analysis was modeled under unsaturated conditions. Unsaturated soil property functions were determined using the Fredlund and Xing (1994) equation for the soil-water characteristic curve and the Fredlund et al. (1994) permeability estimation function. Soil-water characteristic curve fitting parameters a_f , n_f , m_f , and h_r were estimated using the Torres (2011) model for granular materials using laboratory data on grain size distribution of valley fill overburden (Russell 2012). A D_{10} particle diameter of 0.11 mm resulted in the following fitting parameters: $a_f = 9.62$, $n_f = 4.72$, $m_f = 0.79$, $h_r = 100$.

Twenty years of precipitation data (1993-2012) from the NOAA Station 46-5563 were used to calculate an average precipitation rate of 0.0039 m/d. For the conventional fill,

infiltration into the surface was calculated as 55% of the total infiltration precipitation (0.0022 m/d), determined from the ranges reported for reclaimed surfaces (Wels et al. 2012; Meek and O'dell 2012; Ritter and Gardner 1993).

For the geomorphic fill, two boundary condition cases were modeled, with infiltration varying by location along the slope profile. First, infiltration was equal to 0.0022 m/d for the entire profile, consistent with the boundary condition applied to the conventional fill. The purpose of this model was to compare the two fills based on the fill volume and profile shape, while keeping infiltration constant. For the second geomorphic model, infiltration into the uncovered portion of the fill was equal to the rate applied to the conventional fill surface (55% of total precipitation), while the infiltration rate for the portion of the fill having a stream length was equal to 10% of total precipitation. The infiltration rate associated with 10% of total precipitation was consistent with consolidated bed material with high silt-clay content (USDA 2007).

A review boundary condition was modeled near the toe of the fill (Figure 5). Due to the sharp convergence of the profile at the toe of the slope, applying a specified head at the toe pond elevation resulted in the water table elevation being forced lower at the toe than it would be expect in the field. Due to these convergence issues, the model was conceptually cut vertically near the toe (at a location where fill height was approximately 3 m), and a review boundary condition was applied to solve for the location at which the water table would exit without being affected by profile convergence. This numerical modeling technique was located where the fill height occurred at a horizontal station of 249 m and 242 m for the conventional fill and geomorphic fill, respectively. The flow rate and volume discharging from the modeled face represented the flow exiting at the toe of each fill.

All models considered unsaturated conditions, homogeneous fill material, and isotropic hydraulic conductivity. Models were first completed under steady state flow conditions. Results from steady state models served as initial conditions for transient modeling. Transient conditions were modeled over a range five days to ten years and the following outputs were documented: infiltration volume, storage volume, discharge rate and volume, groundwater flux rate, degree of saturation, pore-water pressure, and total head.

Selenium Loads

Selenium (Se) leaching data from Mine B were coupled with the groundwater model results to calculate the mass of Se desorbed from each fill. Mine B was used because the sample consisted mostly of sandstone, the type of material expected to make up the majority of the fill. The initial Se concentration in rock of 1.26 mg/kg for Mine B was applied homogeneously to each fill model where 30% of the total Se in each fill was considered mobile (Ziemkiewicz et al. 2011), resulting in the total calculated initial leachable masses of Se of 2.503 kg and 1.954 kg in the conventional and geomorphic fills, respectively.

Each fill was divided into seven flux sections to determine the number of pore volumes of water that flowed through each section over a ten year period. A period of ten years was modeled to obtain large enough numbers for Se desorption comparison. For each flux section, the number

of pore volumes that had flowed through the fill volume was used to predict the percentage of leachable Se that had been desorbed (as informed from the laboratory tests). The total mass of Se desorbed was then calculated for the 10 year period for each fill.

Results and Discussion

Soil

Acid digestion of Mine A soil produced a total selenium concentration of 4.84 mg/kg. Acid digestion of Mine B soil produced a total selenium concentration of 1.26 mg/kg.

Unsaturated tests

For parameters selenium, pH, conductivity and total dissolved solids, equilibrium was reached by a leached volume of 10.1 L (Figures 11-14). Selenium concentrations (0.0038-0.18 mg/L) were on the same order of magnitude for each of the mine sites, AU and BU. Concentrations of Se were greater than the chronic aquatic life standard of 5 µg/L. Three outliers occurred for BU2 (samples 6-8) that were exactly one order of magnitude less than expected (Figure 13).

The pH values followed similar trends for both mine sites; the only variation occurred during the first two samples. The pH values reached an equilibrium value of 6.9 after the tenth sample (i.e. 10.1 L) (Figure 14).

Conductivity values for BU samples (240-1131 µS/cm) were on average approximately two times the values for AU (100-418 µS/cm) (Figure 15). TDS values were also greater for BU than AU (Figure 16). These differences are likely attributed to the differences in SO₄, Mg, Mn, and Ca. Average concentrations of SO₄, Mg, Mn, and Ca for BU were 2.6, 2.8, 5.0, and 2.0 times greater than AU, respectively. Concentrations of dissolved Fe were less than the detectable limit (0.02 mg/L) for 78% of AU samples and 61% of the BU samples. Concentrations of dissolved Al were less than the detectable limit (0.2 mg/L) for 81% and 92% of the samples for AU and BU, respectively (Tables 7-10).

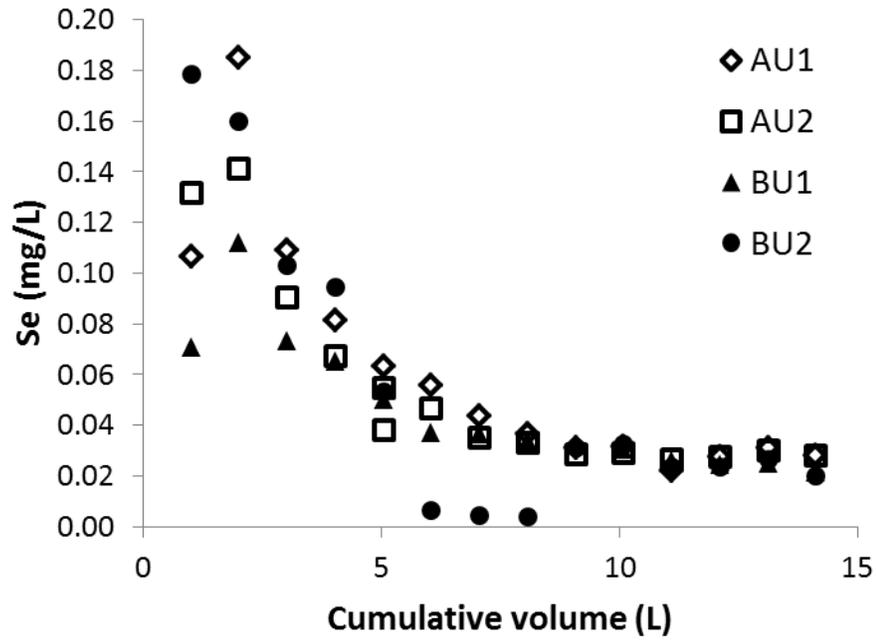


Figure 13. Selenium concentrations (unsaturated tests)

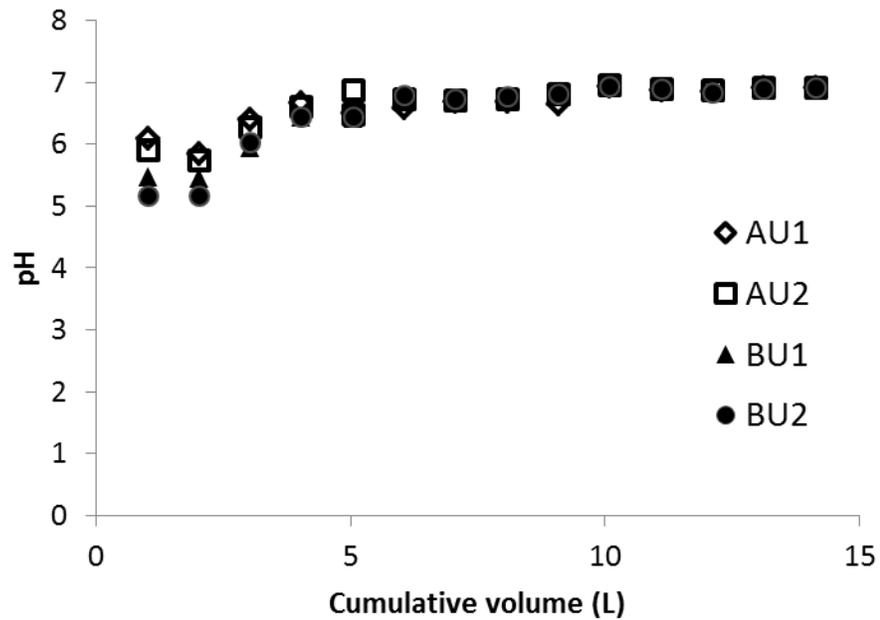


Figure 14. Distribution of pH values (unsaturated tests)

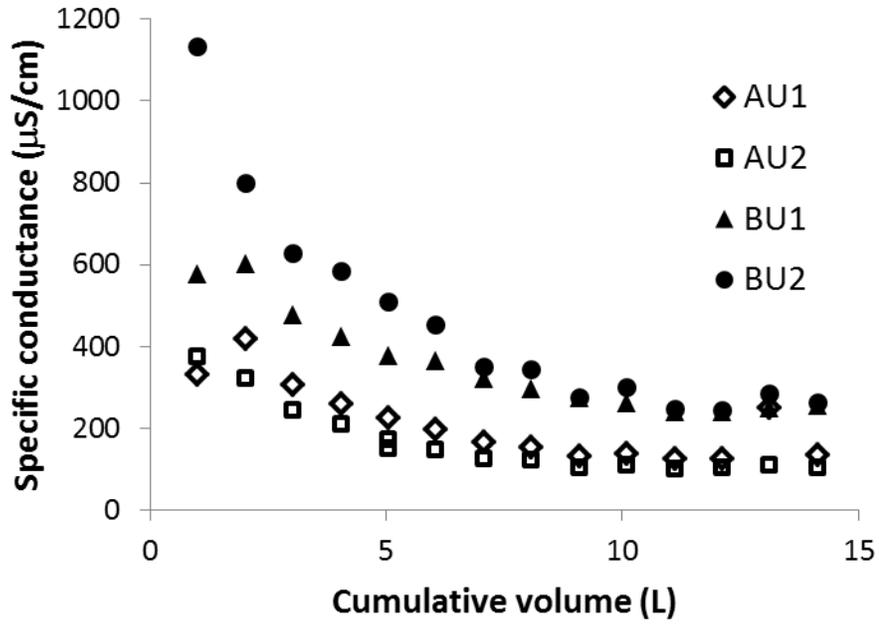


Figure 15. Distribution of conductivity (unsaturated tests)

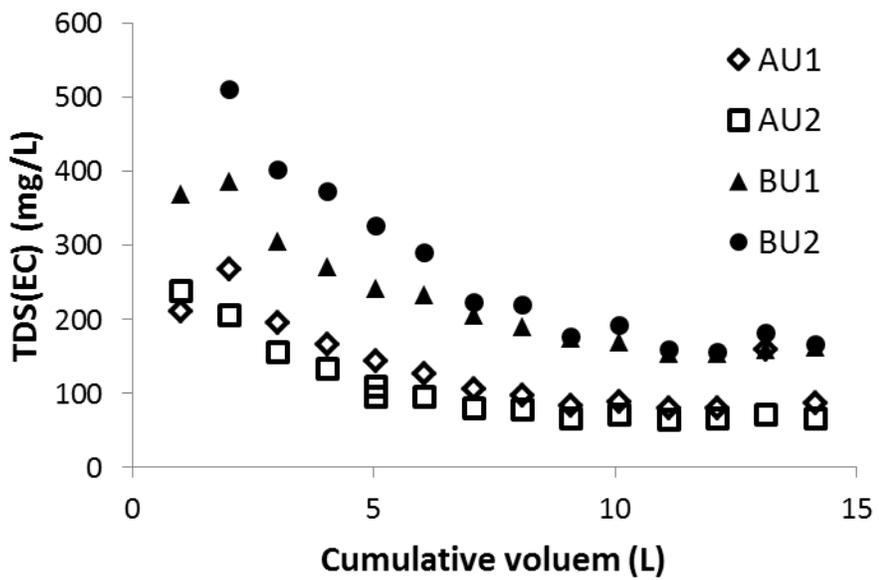


Figure 16. Distribution of total dissolved solids (unsaturated tests)

Saturated tests

Selenium concentrations increased substantially within the first day after saturation for all samples, reaching a value of 0.76 mg/L, 0.88 mg/L, 0.57 mg/L, and 0.50 mg/L for AS1, AS2, BS1, and BS2, respectively. While Se concentrations had a decreasing or stabilizing trend after the first 5-7 days, there was much variability (standard deviation (σ): $\sigma_{AS1} = 0.21$ mg/L, $\sigma_{AS2} = 0.23$ mg/L, $\sigma_{BU1} = 0.16$ mg/L, $\sigma_{BU2} = 0.23$ mg/L). Like the unsaturated tests, all selenium concentrations were greater than the chronic aquatic life standard (Figure 17). Desorption coefficients were calculated with these data. Preliminary results indicated that the desorption coefficient for AS is on the order of 10^1 mL/g while the desorption coefficient for BS is on the order of 10^2 mL/g.

pH values (5.4-7.2) reached equilibrium 12-14 days after saturation for all samples. The equilibrium value was 7.2, 7.2, 6.9 and 6.8, for AS1, AS2, BS1, and BS2, respectively (Figure 18). These values are close to the 6.9 value reached in the unsaturated experiments.

Like the unsaturated tests, conductivity values for BS samples (1190-2940 μ S/cm) were, on average, two times the values for AS (503-1335 μ S/cm) (Figure 19). TDS values were also greater for BS than AS (Figure 20). These differences are also attributed to the differences in SO_4 , Mg, Mn, and Ca. Average concentrations of SO_4 , Mg, Mn, and Ca for BS were 2.5, 2.5, 5.0, and 1.9 times greater than AS, respectively; these differences are similar to the unsaturated results. Sixty percent of the Fe concentrations for AS were at or above detectable limits (average concentration = 0.13 mg/L). More than 90% of the Fe concentrations for BS were above detectable limits (average concentration = 1.0 mg/L). The majority of Al samples met detectable limits. The average Al concentrations for AS and BS were 0.54 and 0.50 mg/L, respectively (Tables 11-14).

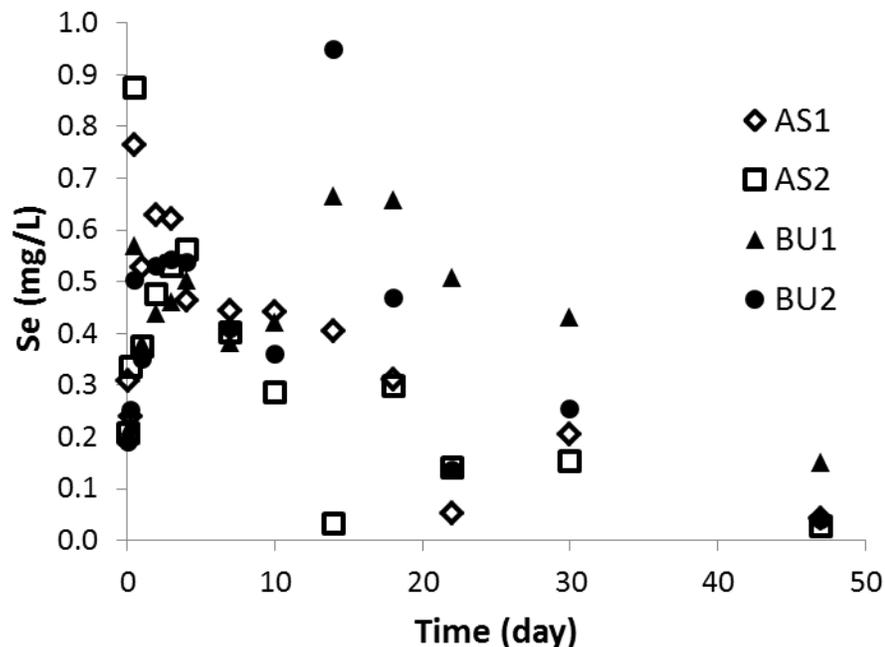


Figure 17. Selenium concentrations (saturated tests)

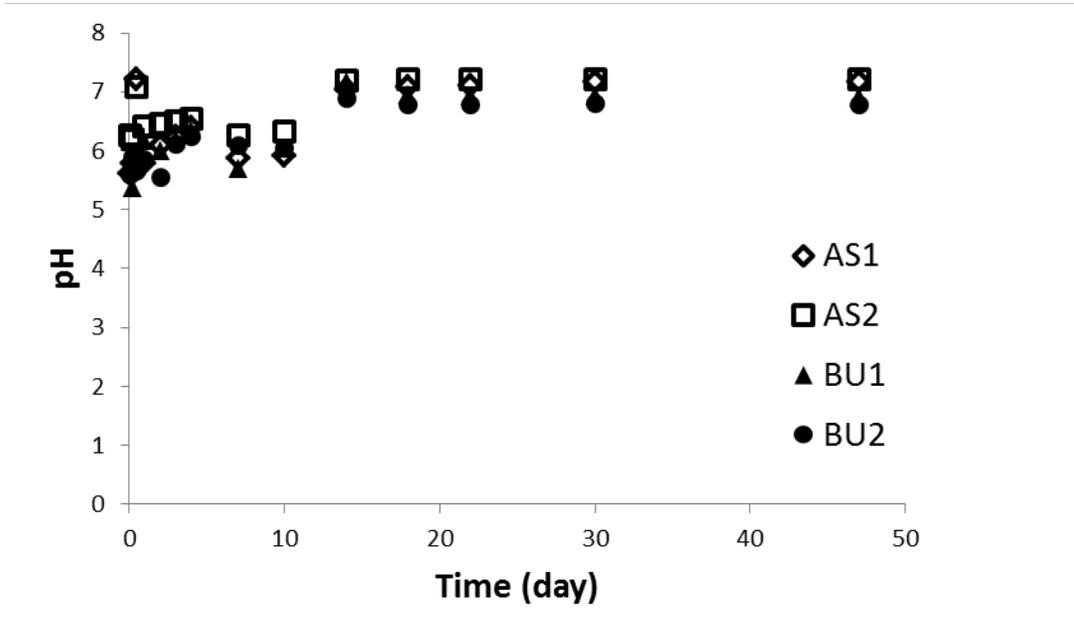


Figure 18. Distribution of pH values (saturated tests)

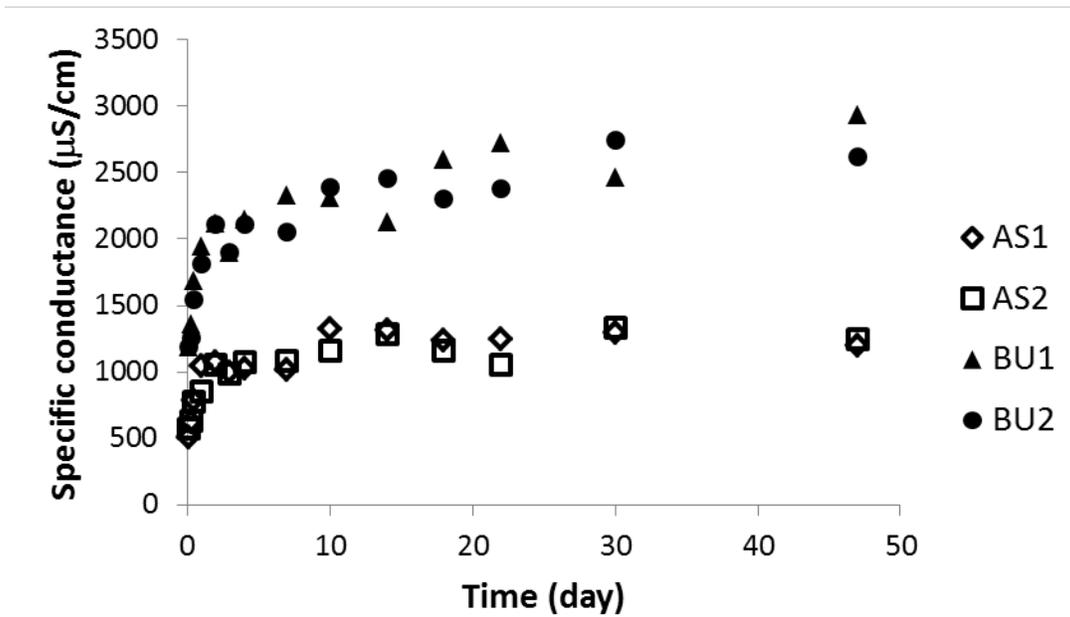


Figure 19. Distribution of conductivity (saturated tests)

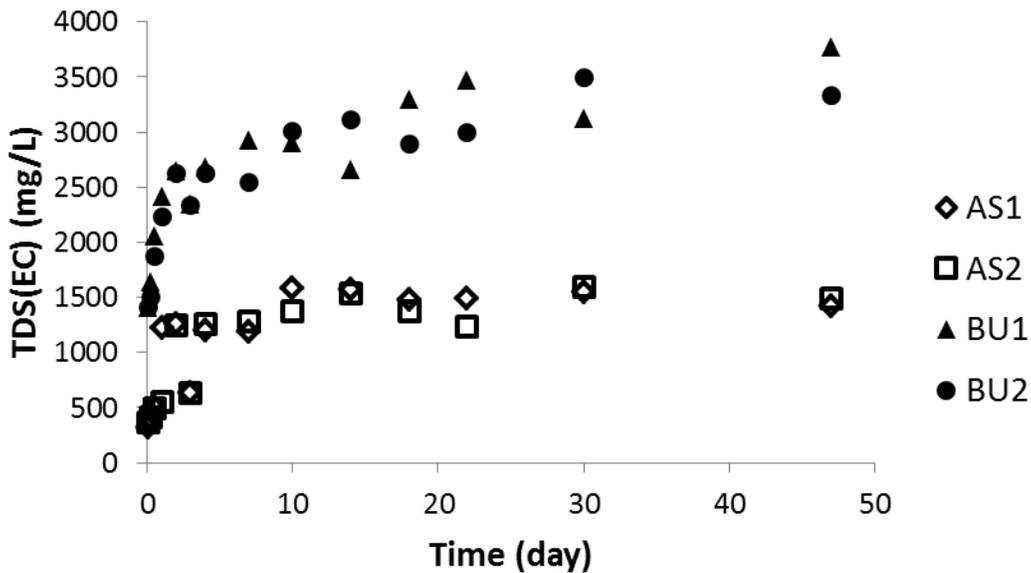


Figure 20. Distribution of total dissolved solids (saturated tests)

Groundwater Modeling

Infiltration into the geomorphic fill without and with a stream was 5.6% and 47.9% lower, respectively, than infiltration into the conventional fill. The degree of saturation for each fill was comparable. For the geomorphic fills, discharge rates at the toe were closer to the infiltration rate than for the conventional fill (Table 4). Lower water volumes in the geomorphic fills were due to lower total fill volumes and/or reduced infiltration.

Table 4. Steady state modeling results for conventional fill, geomorphic fill without stream, and geomorphic fill with reduced infiltration stream

Model	V_i (m ³ /d)	S (%)	Q_t (m ³ /d)	V_w (m ³)
Conventional	0.5947	34.7	0.4770	492.0
Geomorphic without stream	0.5612	39.1	0.5112	353.3
Geomorphic with stream	0.3096	35.5	0.3008	320.3

* V_i =volume of infiltrating water, S=degree of saturation, Q_t =flow rate at toe, V_w =total volume of water in fill

All three models reached steady state conditions after four years. Infiltration volume, discharge volume at the toe of the fill, volume of water in the fill, and the difference between water volumes entering and exiting the fill were all lower in geomorphic fill models than in the conventional fill (Table 5). The lowest values for these criteria were found in the geomorphic fill with the stream, showing the highest percent change from the conventional fill. As compared to the traditional fill, the percent change in total volume of water in the fill remained relatively constant for all time periods (25.3-28.2% lower for the geomorphic fill with no stream, 30.9-34.9% lower for the geomorphic fill with stream).

The magnitude of percent change between the geomorphic fills and the conventional fill with respect to discharge volume increased as time increased. Less water infiltrated into geomorphic fills, and had a shorter residence time within the fill. The geomorphic fill with a stream was the quickest to reach a condition in which water was discharging from the fill at or higher than the

rate at which water was infiltrating (Figure 21), resulting in the least contact with internal fill materials. Establishing a stream on the surface of a geomorphic fill to reduce infiltration appears to be necessary to have a significant impact on groundwater movement. Simply altering the two-dimensional profile had less or insignificant impact on groundwater movement.

Table 5. Transient modeling results for conventional fill, geomorphic fill, and geomorphic fill with reduced infiltration stream

Time (d)	0	5	180	365	1460	3650
<i>Conventional</i>						
V_w (m ³)	492.0	517.2	505.2	491.4	486.5	486.5
$V_i - V_o$ (m ³)	0	-0.7	5.2	10.3	117.1	340.5
<i>Geomorphic without stream</i>						
V_w (m ³)	353.3	386.2	370.8	354.2	350.1	350.1
$V_i - V_o$ (m ³)	0	0.3	8.2	15.4	141.3	398.9
<i>Geomorphic with stream</i>						
V_w (m ³)	320.3	357.5	341.9	324.14	318.9	318.9
$V_i - V_o$ (m ³)	0	0.2	-10.5	-26.8	-22.5	-3.3

* V_w =total volume of water in fill; $V_i - V_o$ =difference in infiltrating and discharge volumes

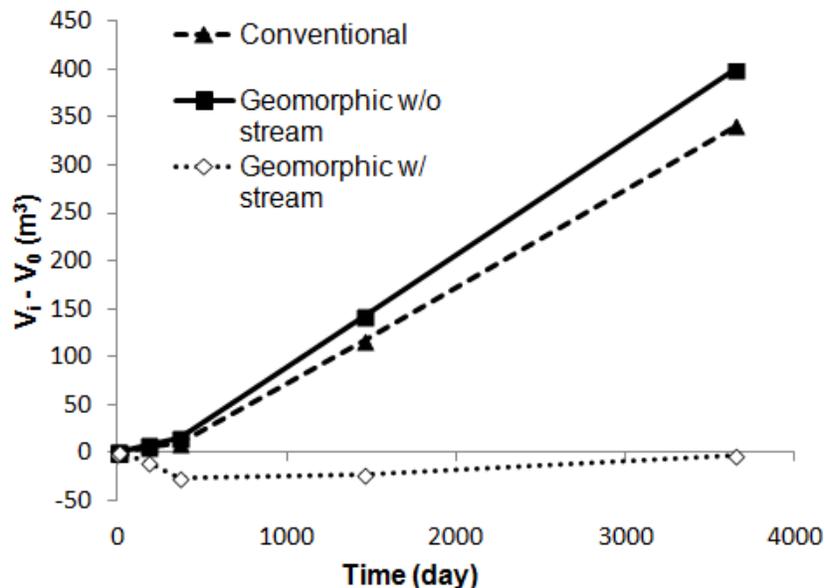


Figure 21. Difference in infiltration volume and discharge volume over time for each fill.

Selenium loads

Groundwater movement in the geomorphic profiles resulted in a reduction in Se desorption due to lower fluxes of water through the fill (Table 6). Infiltration volume into the geomorphic profile without a stream was comparable to infiltration volume into the conventional profile, but the curvilinear shape of the geomorphic profile provided less fill area over which infiltrating water could flow. The geomorphic fill with a stream was more effective at reducing Se desorption

through reduced infiltration into the area of the fill covered by the stream. Less water came in contact with the fill materials below the stream, reducing desorption in those areas. This was seen in that the water fluxes through the upper flux sections in the geomorphic profile with a stream were comparable to those through the same sections in the profile without a stream. The lower sections exhibited lower fluxes of water for the geomorphic fill with a stream. While the reduction in Se desorption from the geomorphic profiles may be attributed to less available Se to be desorbed, total Se desorbed from the geomorphic profiles was still lower as a percentage of total leachable Se than in the conventional profile (62% lower for the geomorphic fill without a stream, 73% lower for the geomorphic fill with a stream).

Table 6. Mass of selenium desorbed and percent reduction compared to the conventional fill

Model	Mass Se desorbed (g)	Percent reduction in desorption (%)
Conventional	103.3	-
Geomorphic without stream	83.0	19.6
Geomorphic with stream	59.7	42.2

Conclusions

Experimental leaching studies were completed for two mine soils under both unsaturated and saturated conditions. Selenium, the main parameter of concern, reduced significantly within the first five leaching pours for the unsaturated condition; however, concentrations remained above the chronic aquatic life standard. There was a large amount of variability in the saturated selenium results.

Geomorphic profiles exhibited lower infiltration rates and volumes of water travelling through and exiting the fill. Improvements in groundwater movement through contaminated fill materials resulted in less desorption, both in total mass of Se desorbed and as a percentage of available mobile Se. The calculation of mass of Se desorbed from each fill was limited by the following assumptions: two-dimensional models, homogeneous distribution of Se, constant infiltration rate into fills, no effect due to groundwater velocity, uniform desorption rate within each flux section, and no desorption due to fully saturated conditions. Future Se desorption modeling will consider a more detailed analysis accounting for more discrete water flux calculations, variable infiltration rates and desorption rates, groundwater velocities, water residence time, and saturated/unsaturated zones.

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Appendix: Concentration Data

Table 7. Unsaturated data for Mine A, sample 1; detection limit in italics

Sample	Se (mg/L)	pH	Alk (mg/L)	Acd (mg/L)	SO ₄ (mg/L)	Cond. (μS/cm)	D.Fe (mg/L)	D.Al (mg/L)	D.Ca (mg/L)	D.Mg (mg/L)	D.Mn (mg/L)
<i>Detection</i>	<i>0.001</i>		<i>1.00</i>	<i>1.00</i>	<i>0.12</i>	<i>2.20</i>	<i>0.02</i>	<i>0.02</i>	<i>0.06</i>	<i>0.03</i>	<i>0.02</i>
AU1-1	0.1063	6.09	15.46	8.92	125	330					
AU1-2	0.1848	5.84	15.66	7.03	161	418	0.01	0.01	39.31	16.76	0.42
AU1-3	0.1091	6.4	12.96	8.63	128	305	0.02	0.05	30.35	12.1	0.36
AU1-4	0.0815	6.66	14.61	13.92	100	260	0.01	0.02	25.63	9.94	0.26
AU1-5	0.0632	6.51	16.36	5.36	77.3	226	0.01	0.01	21.6	8.36	0.23
AU1-6	0.0555	6.58	13.46	11.58	79	197.4	0.03	0.01	16.47	6.98	0.15
AU1-7	0.0438	6.69	12.95	8.13	61.3	164.7	0.04	0.02	13.03	5.69	0.15
AU1-8	0.0367	6.68	15.17	8.88	53.4	152.4	0.03	0.01	12.05	5.28	0.09
AU1-9	0.0309	6.64	15.2	10.04	46.2	131.8	0.03	0.01	9.92	4.51	0.08
AU1-10	0.0318	6.93	16.21	10.55	40.2	138.5	0.09	0.02	11.79	5.16	0.12
AU1-11	0.0218	6.87	16.45	5.24	35	125.4	0.03	0.01	10.14	4.59	0.09
AU1-12	0.0275	6.86	16.71	8.56	33.7	126.2	0.03	0.01	10.3	4.72	0.09
AU1-13	0.0308	6.91	5.71	19.5	102	249	0.03	0.01	19.36	11.72	0.63
AU1-14	0.0278	6.92	16.86	8.45	36.9	135.6	0.03	0.01	11.27	5.2	0.09

* Values less than the detection limit were recorded as half of the detection limit (USEPA, 1998).

Table 8. Unsaturated data for Mine A, sample 2; detection limit in italics

Sample	Se (mg/L)	pH	Alk (mg/L)	Acd (mg/L)	SO ₄ (mg/L)	Cond. (μS/cm)	D.Fe (mg/L)	D.Al (mg/L)	D.Ca (mg/L)	D.Mg (mg/L)	D.Mn (mg/L)
<i>Detection</i>	<i>0.001</i>		<i>1.00</i>	<i>1.00</i>	<i>0.12</i>	<i>2.20</i>	<i>0.02</i>	<i>0.02</i>	<i>0.06</i>	<i>0.03</i>	<i>0.02</i>
AU2-1	0.1316	5.9	17.71	9.49	144	374					
AU2-2	0.1414	5.74	14.49	11.24	116	321	0.01	0.04	30.07	12.011	0.39
AU2-3	0.0903	6.28	9.81	11.03	96.8	244	0.01	0.01	22.88	8.81	0.17
AU2-4	0.0674	6.6	8.76	10.29	81.4	209	0.01	0.01	18.46	7.55	0.16
AU2-5a	0.0382	6.49	6.31	10.61	54.7	150.5	0.01	0.01	12.14	5.13	0.1
AU2-5b*	0.0545	6.88	17.06	10.84	56.4	171.1	0.06	0.01	16.13	5.64	0.11
AU2-6	0.0464	6.72	7.86	13.42	54.9	148.6	0.05	0.01	11.31	4.81	0.11
AU2-7	0.0349	6.71	8.81	11.69	48.6	125.3	0.03	0.01	9.29	4.01	0.08
AU2-8	0.033	6.72	10.61	13.39	42.6	121.3	0.03	0.01	8.74	3.82	0.08
AU2-9	0.0284	6.8	8.26	10.83	36.1	104.3	0.03	0.01	7.55	3.31	0.08
AU2-10	0.0289	6.95	12	15.81	30.8	110.9	0.02	0.01	8.89	3.78	0.09
AU2-11	0.0264	6.9	11.66	14.13	26.1	100	0.03	0.01	7.67	3.27	0.09
AU2-12	0.0275	6.87	10.06	11.71	27.1	102.4	0.03	0.01	7.92	3.4	0.09
AU2-13	0.0302	6.91	10.31	27.95	31	111.3	0.03	0.01	8.71	3.76	0.11
AU2-14	0.0278	6.92	12.33	11.03	27.8	104.6	0.03	0.01	8.06	3.48	0.09

*Two samples analyzed due to increased pour volume

** Values less than the detection limit were recorded as half of the detection limit (USEPA, 1998).

Table 9. Unsaturated data for Mine B, sample 1; detection limit in italics; detection limit in italics

Sample	Se (mg/L)	pH	Alk (mg/L)	Acd (mg/L)	SO ₄ (mg/L)	Cond. (μS/cm)	D.Fe (mg/L)	D.Al (mg/L)	D.Ca (mg/L)	D.Mg (mg/L)	D.Mn (mg/L)
	<i>0.001</i>		<i>1.00</i>	<i>1.00</i>	<i>0.12</i>	<i>2.20</i>	<i>0.02</i>	<i>0.02</i>	<i>0.06</i>	<i>0.03</i>	<i>0.02</i>
BU1-1	0.071	5.47	2.51	26.31	262	576					
BU1-2	0.112	5.46	3.75	20.63	274	603	0.23	0.01	51.46	28.85	1.03
BU1-3	0.0734	5.95	3.5	17.93	204	478	0.02	0.01	43.89	23.86	0.89
BU1-4	0.0652	6.44	3.01	16.09	187	423	0.01	0.01	37.59	21	0.85
BU1-5	0.0504	6.42	3.21	14.79	164	378	0.01	0.01	31.22	18.1	0.73
BU1-6	0.0372	6.73	4.41	17.43	163	364	0.03	0.01	28.24	16.65	0.72
BU1-7	0.0365	6.75	4.52	19.02	133	322	0.03	0.01	24.35	14.4	0.63
BU1-8	0.0341	6.77	4.56	19.24	121	298	0.09	0.03	21.37	13.11	0.61
BU1-9	0.0328	6.85	3.95	20.02	112	274	0.03	0.01	20.39	12.48	0.57
BU1-10	0.0305	6.93	4.97	24.84	110	264	0.03	0.01	19.98	12.02	0.61
BU1-11	0.0261	6.92	5.76	17.29	99.7	242	0.03	0.01	18.46	11.04	0.57
BU1-12	0.0245	6.89	5.56	21.88	97.6	240	0.07	0.06	18.54	11.17	0.64
BU1-13	0.0248	6.91	5.71	19.5	102	249	0.03	0.01	19.36	11.72	0.63
BU1-14	0.0216	6.95	5.76	24.8	103	255	0.03	0.01	19.33	11.46	0.64

* Values less than the detection limit were recorded as half of the detection limit (USEPA, 1998).

Table 10. Unsaturated data for Mine B, sample 2; detection limit in italics

Sample ID	Se (mg/L)	pH	Alk (mg/L)	Acid (mg/L)	SO ₄ (mg/L)	Cond. (μS/cm)	D.Fe (mg/L)	D.Al (mg/L)	D.Ca (mg/L)	D.Mg (mg/L)	D.Mn (mg/L)
	<i>0.001</i>		<i>1.00</i>	<i>1.00</i>	<i>0.12</i>	<i>2.20</i>	<i>0.02</i>	<i>0.02</i>	<i>0.06</i>	<i>0.03</i>	<i>0.02</i>
BU2-1	0.1783	5.17	4.4	13.21	597	1132					
BU2-2	0.1600	5.16	4.44	19.01	380	798	0.11	0.01	76.29	44.32	1.63
BU2-3	0.1028	6.03	4.65	16.33	274	628	0.02	0.01	67	35.74	1.41
BU2-4	0.0943	6.44	4.46	17.6	250	584	0.01	0.01	54.93	30.18	1.27
BU2-5	0.0532	6.44	5.71	13.72	214	510	0.01	0.01	43.97	24.6	1.15
BU2-6	0.0063	6.78	6.06	18.16	256	454	0.03	0.01	37.03	21.21	1.01
BU2-7	0.0043	6.73	6.06	16.46	143	349	0.03	0.01	27.19	15.72	0.77
BU2-8	0.0038	6.76	8.31	18.13	137	342	0.03	0.01	25.89	15.27	0.84
BU2-9	0.0313	6.81	7.51	20.65	108	276	0.03	0.01	19.98	11.86	0.68
BU2-10	0.0324	6.93	7.96	16.34	125	300	0.02	0.01	23.88	13.6	0.79
BU2-11	0.0235	6.90	8.41	16.54	98.1	248	0.03	0.01	19.14	10.99	0.67
BU2-12	0.0237	6.84	9	15.85	93.5	244	0.03	0.01	18.72	10.92	0.72
BU2-13	0.0263	6.9	9.91	23.56	116	284	0.03	0.01	22.84	13.15	0.86
BU2-14	0.02	6.92	8.76	17.72	104	261	0.02	0.01	20.33	11.83	0.79

* Values less than the detection limit were recorded as half of the detection limit (USEPA, 1998).

Table 11. Saturated data for Mine A, sample 1; detection limit in italics

Sample	Se (mg/L)	pH	Alk (mg/L)	Acid (mg/L)	SO ₄ (mg/L)	Cond. (μS/cm)	D.Al (mg/L)	D.Ca (mg/L)	D.Fe (mg/L)	D.Mg (mg/L)	D.Mn (mg/L)
	<i>0.001</i>		<i>1.00</i>	<i>1.00</i>	<i>0.12</i>	<i>2.20</i>	<i>0.02</i>	<i>0.06</i>	<i>0.02</i>	<i>0.03</i>	<i>0.02</i>
AS1-1	0.3076	5.61	12.82	22.48	214	503	0.11	40.87	0.01	19.5	0.34
AS1-2	0.2394	5.79	16.26	19.18	280	625	0.46	53.7	0.01	25.6	0.35
AS1-3	0.764	7.22	23.26	38.91	356.5	782	0.06	84	0.06	35.13	0.53
AS1-4	0.5285	5.78	14.56	30.83	595	1043	0.05	147.68	0.18	61.9	1.08
AS1-5	0.6293	6.08	21.56	25.04	555	1075	0.04	149.9	0.08	62.84	1
AS1-6	0.6214	6.23	22.51	19.75	437	995	0.03	131.55	0.09	55.94	0.84
AS1-7	0.4645	6.38	21.76	19.38	525	1024	0.03	142.04	0.1	61.87	0.98
AS1-8	0.4436	5.87	28.1	9.26	472.5	1013	0.01	102.03	0.01	46.67	0.83
AS1-9	0.4414	5.91	23.95	16.04	665	1320	0.01	145.86	0.01	69.36	1.58
AS1-10	0.4042	7.03	39.45	19.2	660	1314	4.43	166.13	0.68	70.15	1.4
AS1-11	0.3107	7.09	41.26	4.12	626	1238	0.36	154.88	0.03	66.37	1.23
AS1-12	0.0509	7.11	44.71	1.12	632	1251	0.3	167.66	0.02	72.44	1.54
AS1-13	0.2055	7.16	56.21	0.5	655	1298	0.74	162.05	0.08	70	1.51
AS1-14	0.042	7.18	54.96	0.5	577	1198	0.76	143.75	0.09	63.39	1.54

* Values less than the detection limit were recorded as half of the detection limit (USEPA, 1998).

Table 12. Saturated data for Mine A, sample 2; detection limit in italics

Sample	Se (mg/L)	pH pH	Alk (mg/L)	Acid (mg/L)	SO₄ (mg/L)	Cond. (μS/cm)	D.Al (mg/L)	D.Ca (mg/L)	D.Fe (mg/L)	D.Mg (mg/L)	D.Mn (mg/L)
	<i>0.001</i>		<i>1.00</i>	<i>1.00</i>	<i>0.12</i>	<i>2.20</i>	<i>0.02</i>	<i>0.06</i>	<i>0.02</i>	<i>0.03</i>	<i>0.02</i>
AS2-1	0.2075	6.26	9.71	24.02	232.5	574	0.01	51.77	0.01	23.94	0.42
AS2-2	0.3359	6.2	11.06	33.52	252	635	0.01	58.35	0.01	27.72	0.4
AS2-3	0.8752	7.08	17.36	23.5	396	775	0.01	85.49	0.01	36.04	0.6
AS2-4	0.3748	6.41	15.96	18.77	398.5	852	0.03	113.09	0.08	46.79	0.68
AS2-5	0.4769	6.46	19.46	26.48	525	1057	0.03	147.08	0.1	61.48	0.92
AS2-6	0.5299	6.49	23.46	14.56	492.5	987	0.06	137.52	0.11	59.13	0.86
AS2-7	0.5624	6.54	23.25	17.23	545	1073	0.04	150.38	0.08	64.13	1.03
AS2-8	0.403	6.26	27.89	13.66	535	1087	0.74	117.52	0.07	54.07	0.79
AS2-9	0.2851	6.33	48.86	0.5	550	1162	0.01	128.08	0.01	60.01	0.93
AS2-10	0.0325	7.2	37.16	9.79	659	1288	2.86	158.96	0.42	66.77	1.25
AS2-11	0.2985	7.21	37.36	4.04	583	1164	0.28	138.67	0.01	58.95	1.28
AS2-12	0.1407	7.21	38.75	3.45	502	1056	0.07	127.57	0.01	54.26	1.21
AS2-13	0.1526	7.21	48.81	0.5	670	1335	0.37	168.59	0.02	71.88	1.58
AS2-14	0.0278	7.21	42.36	4.67	610	1249	0.17	156.14	0.01	66.7	2.02

* Values less than the detection limit were recorded as half of the detection limit (USEPA, 1998).

Table 13. Saturated data for Mine B, sample 1; detection limit in italics

Sample ID	Se (mg/L)	pH pH	Alk (mg/L)	Acid (mg/L)	SO₄ (mg/L)	Cond. (μS/cm)	D.Al (mg/L)	D.Ca (mg/L)	D.Fe (mg/L)	D.Mg (mg/L)	D.Mn (mg/L)
<i>Detection</i>	<i>0.001</i>		<i>1.00</i>	<i>1.00</i>	<i>0.12</i>	<i>2.20</i>	<i>0.02</i>	<i>0.06</i>	<i>0.02</i>	<i>0.03</i>	<i>0.02</i>
BS1-1	0.2	5.74	6.9	43.75	650	1192	0.19	107.9	0.42	59.38	1.72
BS1-2	0.2225	5.38	6.56	51.72	715	1363	0.01	113.72	0.93	73.76	2.24
BS1-3	0.5693	5.96	7.75	65.52	991	1686	0.01	195.62	0.05	105.67	3.13
BS1-4	0.3787	6.18	6.72	53.45	1190	1949	0.05	283.13	0.45	155.14	4.64
BS1-5	0.439	6.01	7.06	53.18	1340	2120	0.05	315.92	1.03	171.71	5.36
BS1-6	0.4602	6.2	8.31	45.25	1160	1902	0.06	276.52	0.21	153.25	4.47
BS1-7	0.5034	6.34	6.77	73.32	1360	2150	0.07	335.39	0.7	188.05	5.98
BS1-8	0.3819	5.7	6.91	55.24	1400	2330	0.01	244.84	0.31	156.38	5.49
BS1-9	0.4217	6.05	8.17	53.96	1350	2310	0.01	246.11	0.01	158.78	5.97
BS1-10	0.6661	7.18	12.91	63.39	1320	2130	3.26	216.43	1	115.97	4.35
BS1-11	0.6579	6.95	12.95	62.66	1700	2600	1.31	266.28	0.66	145.17	6.51
BS1-12	0.5072	6.94	16.29	55.29	1608	2720	1.52	281.26	0.46	156.3	7.09
BS1-13	0.4319	6.93	18.26	48.71	1590	2470	0.34	267.51	0.64	152.54	7.05
BS1-14	0.1502	6.9	29.96	54.1	1910	2940	0.55	329.41	0.3	193.08	10.49

* Values less than the detection limit were recorded as half of the detection limit (USEPA, 1998).

Table 14. Saturated data for Mine B, sample 2; detection limit in italics

Sample	Se (mg/L)	pH pH	Alk (mg/L)	Acd (mg/L)	SO₄ (mg/L)	Cond. (μ S/cm)	D.Al (mg/L)	D.Ca (mg/L)	D.Fe (mg/L)	D.Mg (mg/L)	D.Mn (mg/L)
<i>Detection</i>	<i>0.001</i>		<i>1.00</i>	<i>1.00</i>	<i>0.12</i>	<i>2.20</i>	<i>0.02</i>	<i>0.06</i>	<i>0.02</i>	<i>0.03</i>	<i>0.02</i>
BS2-1	0.1907	5.58	6.78	45.25	610	1190	0.29	105.2	0.28	57.72	1.67
BS2-2	0.2511	5.89	8.4	39.1	665	1260	0.23	109.73	0.2	63.05	1.7
BS2-3	0.5035	5.66	8.18	56.56	854	1542	0.01	174.17	0.14	93.34	2.72
BS2-4	0.3494	5.84	6.38	56.48	1230	1812	0.05	262.07	2.06	143.63	4.1
BS2-5	0.5311	5.54	6.86	80.63	1430	2110	0.05	301.15	12.17	166.67	5.09
BS2-6	0.5432	6.11	7.16	46.85	1170	1895	0.06	291.92	1.18	162.26	4.55
BS2-7	0.5383	6.24	8.61	50.93	1330	2110	0.07	331.91	0.38	185.01	5.86
BS2-8	0.4087	6.08	10.65	46.7	1220	2050	0.01	200.08	0.43	117.48	3.65
BS2-9	0.3605	6.04	10.46	57.21	1440	2390	0.01	261.58	0.01	166.07	6.12
BS2-10	0.9477	6.88	13.16	53.96	1540	2460	1.42	260.79	0.38	144.01	5.51
BS2-11	0.4685	6.77	11.05	50.82	1440	2300	0.45	233.64	0.79	128.58	5.21
BS2-12	0.135	6.77	20.11	44.55	1490	2380	0.14	250.07	0.64	138.56	5.85
BS2-13	0.2537	6.8	24.62	53.08	1800	2740	0.16	304.69	0.21	172.41	8.49
BS2-14	0.0397	6.77	17.01	58.21	1670	2620	0.23	262.32	2.07	148.42	8.47

* Values less than the detection limit were recorded as half of the detection limit (USEPA, 1998).

1. Publications:

- Hopkinson, L., N. DePriest, J. Quaranta, and P. Ziemkiewicz. "Characterizing selenium leaching and transport from southern West Virginia valley fill alternatives". In review for volume published by Society of Mining, Metallurgy and Exploration.
- DePriest, N. *, Hopkinson, L., Quaranta, J., Sears, A. *, Russell, H. Snyder, M. *, O'Leary, E. *, Eddy, J. *, Mack, B., and Hause, J. 2014. Developments in valley fill reclamation in Central Appalachia: the design of stable and sustainable landforms. Advances in Geomorphic Reclamation at Coal Mine Sites. A Technical Interactive Forum and Field Tour. Office of Surface Mining Reclamation and Enforcement. May 20-22. Albuquerque, NM. 6 pages. (not peer-reviewed, invited paper)

2. Information Transfer Program:

- Abstract accepted to present at the "Environmental Considerations in Energy Production" conference in September 2015, Pittsburgh, PA.
- Hopkinson, L. C., and J. Eddy. 2014. Characterizing selenium leaching from southern West Virginia valley fills. June 9-11. Francis Marion Hotel: Charleston, SC. *Poster* (abstract published).
- Eddy, J., Hopkinson, L. 2014. Characterizing selenium leaching from southern West Virginia valley fills. 89th Annual West Virginia Academy of Science Meeting, April 12. Shepherd University: Shepherdstown, WV. *poster* (abstract published).

3. Student Support:

Category	Number of students supported with 104b base grant	\$ Value of students supported with 104b base grant	Number of students supported with matching funds	\$ Value of student support with matching funds	Total number of students supported	Total \$ value of student support
Undergraduate						
Masters	1				1	
Ph.D.						
Post-Doc						
Total	1				1	

4. Notable Achievements and Awards:

Use of Chemical Signatures as Diagnostic Tools to Identify Bromide Contamination Sources

Basic Information

Title:	Use of Chemical Signatures as Diagnostic Tools to Identify Bromide Contamination Sources
Project Number:	2014WV212B
Start Date:	3/1/2014
End Date:	2/28/2015
Funding Source:	104B
Congressional District:	1
Research Category:	Water Quality
Focus Category:	Water Quality, Wastewater, Geochemical Processes
Descriptors:	None
Principal Investigators:	Yongtian Thomas He, Joseph j. Donovan

Publications

There are no publications.

Use of Chemical Signatures as Diagnostic Tools to Identify Bromide Contamination Sources

Annual Status Report:
March 1, 2014-February 28, 2015

Principal Authors:
Yongtian He
Joseph Donovan

Submission Date:
May 2015

USGS Award #:
2014WV212B

Submitted by:
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Abstract

Bromide is a relatively new water quality issue in West Virginia. While there are no drinking water or aquatic life standards for bromide ion, there is a Safe Drinking Water Act (SDWA) standard of 80 $\mu\text{g/L}$ for disinfection byproducts such as trihalomethanes (THM) which include chlorinated and brominated methane compounds. This standard applies to the water that water systems deliver to their customers. It is believed that higher concentrations of bromide in a water treatment plant's feed water will result in higher THM concentrations. Potential sources of elevated bromide include agricultural runoff, coal mining, shale gas development, or other human activities. It is important to identify origin of bromide in drinking water sources since inability to identify contamination sources limits our ability to effect appropriate control measures.

This study examines chemical signatures that can be used as a diagnostic tool to identify origins of bromide contamination. Water chemistry data from shale gas flowback, produced water from conventional hydrocarbon development, formation brine, coal mine water from surface and deep mines, a large river and one of its tributaries are examined. The results show a generally linear Br vs Cl relationship, and with Br vs Cl concentrations of different sources clustering at different levels of concentration (Figure 1). This Br-Cl relationship could be useful in identifying Br sources. Other chemical signatures do not show a clear relationship with Br concentration, and are not likely to be useful as diagnostic tools for identifying bromide source.

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Executive Summary

Bromide is a relatively new water quality issue in West Virginia. While there are no drinking water or aquatic life standards for bromide ion, there is a Safe Drinking Water Act (SDWA) standard of 80 µg/L for disinfection byproducts such as trihalomethanes (THM) formed by chlorination or bromination of methane compounds. This standard applies to the water that water systems deliver to their customers. It is believed that higher concentrations of bromide in a water treatment plant's feed water will result in higher THM concentrations. Potential sources of elevated bromide include agricultural runoff, coal mine water, hydrocarbon formation waters, or other fluids. Identification of bromide water sources may allow identification of appropriate control measures.

In this study, we examine the water chemistry of waste streams from the hydrocarbon extraction (shale gas, conventional coal bed methane) and mining industries, we also examine chemistry of receiving streams in the Appalachian region. Based on literature review, a range of chemical signatures (including Cl, Br, Cl/Br, Cl/Br vs Br, Cl/Br vs Cl, SO₄/Cl vs Br, SO₄/Br vs Cl, Na, Ca, Ba and Sr vs Br, etc.) were screened for their relationship to Br concentration. Geochemical modeling is used to investigate how the contaminated water impacts the Br concentration and water quality in receiving streams.

We found a generally linear relationship between Cl vs Br and log [Br] vs Log [Cl] in waters from different sources. The Br vs Cl relationship from different water sources tend to cluster at different spaces (Figure 1).

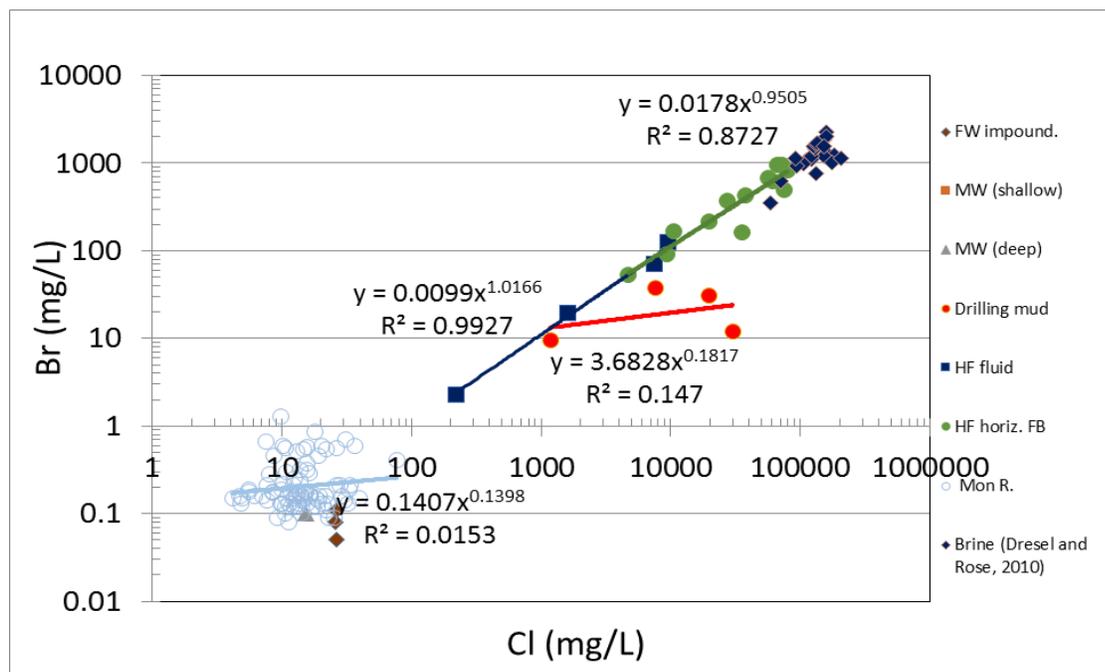


Figure 1: Log [Br⁻] vs. log [Cl⁻] in water from different sources

Other chemical signatures examined (such as Cl/Br vs Br, Cl/Br vs Cl, SO₄/Cl vs Br, SO₄/Br vs Cl, Na, Ca, Ba and Sr vs Br, etc.) do not show a consistent relationship with Br for different source water. Thus it is difficult to use as a diagnostic tool.

These diagnostic tools will help to identify and differentiate among bromide contamination sources. This will assist regulators to make informed decisions for effective bromide contamination control and management.

Problem and Research Objectives

Bromide is a relatively new water quality issue in West Virginia. While there are no drinking water or aquatic life standards for bromide ion, there is a Safe Drinking Water Act (SDWA) standard of 80 µg/L for disinfection byproducts such as trihalomethanes (THM) which include chlorinated and brominated methane compounds. This standard applies to public water systems only. It is believed that higher concentrations of bromide in a water treatment plant's feed water will result in higher THM concentrations. Potential sources of elevated bromide include agricultural runoff, coal mine water, hydrocarbon formation waters, or other fluids. Identification of bromide water sources may allow identification of appropriate control measures.

The objectives of this study are to collect and examine water chemistry data in energy related industries (including shale gas, conventional hydrocarbon, coal bed methane, and coal mining) and to identify chemical signatures that can discriminate bromide contamination from potential sources.

Methodology

The basic approach of this study is to collect water chemistry data from energy related industries and receiving streams, screen the chemical signature of different waste waters from the energy industry, and develop a diagnostic tool to differentiate origins of bromide contamination in receiving waterbodies.

Methods for the study include:

- (1) To analyze chemical signature (concentration of Br⁻, Cl⁻, Cl/Br ratio, other parameters) in collected water data from waste streams of energy industry and receiving water body in West Virginia. These data include energy industry waste streams such as flowback, produced water, coal bed methane water, coal mine water (surface, underground deep, underground shallow), as well as reference streams, and receiving streams.
- (2) To use geochemical modeling to investigate how major types of waste water from the energy industry in West Virginia interact with water chemistry parameters in receiving water body, focusing on modeling change of chemical signatures (Br and Cl concentrations, Cl/Br ratio) during mixing of waste water with receiving streams; and impact on other water quality parameters in receiving streams.

Principal Findings

1. Br vs Cl relationship

Due to their hydrophilic character and small ionic size, Cl and Br ions dissolved in natural water exhibit nearly ideal conservative behavior (Davis et al., 1998). Neither of them take part to a significant degree in ion exchange reactions at low temperatures, nor are they adsorbed onto mineral surfaces. They are highly soluble, only forming minerals under hypersaline conditions

at or above halite saturation (Cartwright et al., 2006; Alcalá and Custodio, 2008). The conservative properties of Br and Cl make them ideal tracers in environmental studies.

Chloride and bromide ions have been used to discriminate among various sources of anthropogenic and naturally occurring contaminants in groundwater. Plots of chloride concentrations and the mass (or molar) ratio of chloride to bromide (Cl/Br) have been used to distinguish pristine groundwater from wastewater and other anthropogenic and natural salinity sources such as road salt, seawater, and deep basin brines (Vengosh and Pankratov, 1998; Davis et al., 1998; Thomas, 2000; Dumouchelle, 2006; Panno et al., 2006; Alcalá and Custodio, 2008; Brown et al., 2009; Katz et al., 2011). The Cl/Br ratio has also been used as a tracer to determine the origin and evolution of groundwater, surface water and brines in oil and gas exploration (Rittenhouse, 1967; Freeman, 2007). It has become an effective aid in hydrogeological studies of surface and groundwater with low-to-moderate salinity (Davis et al., 1998; Cartwright et al., 2006) and in determining the contribution of salinity to lakes and rivers, such as Lake Kinnereth and the Jordan River (Kolodny et al., 1999; Panno et al., 2006; Alcalá and Custodio, 2008).

A linear relationship between Br vs. Cl is observed for waters from different sources (Figures 2-7). Figure 1 is a composite plot showing Br vs Cl relationship of different water sources. Even though there is overlap among different sources, Br vs Cl tends to cluster within specific source groups. The Br vs Cl relationship has potential to discriminate and identify sources of Br contamination in water.

Across a wide range of concentrations, the trends for formation brine, conventional hydrocarbon, and shale gas flowback/produced water suggest a common source of Br for these waters (Figures 2-4).

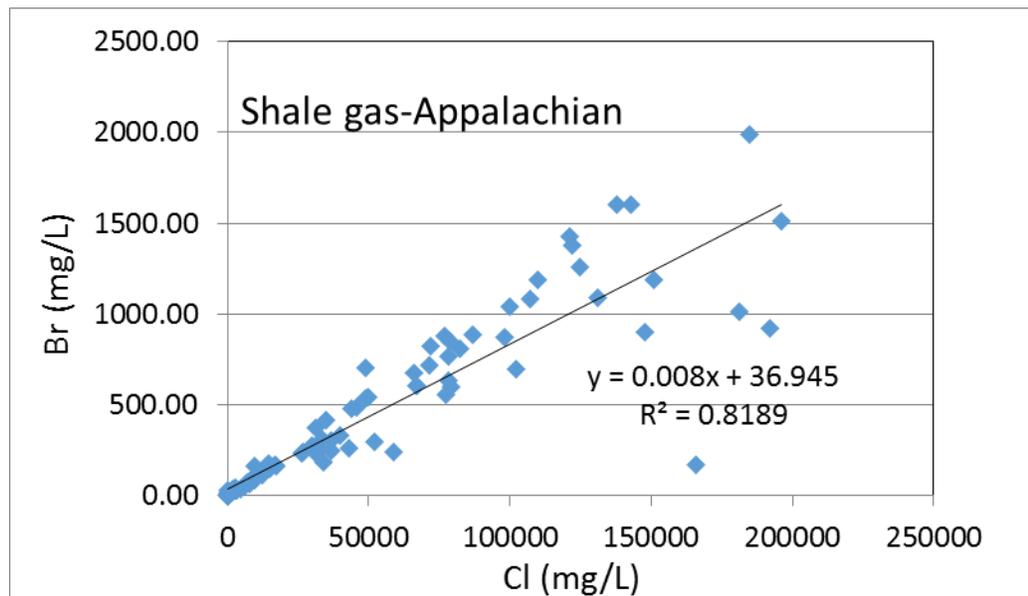


Figure 2: Br–Cl relationship in produced water from Marcellus shale gas development (data source: USGS)

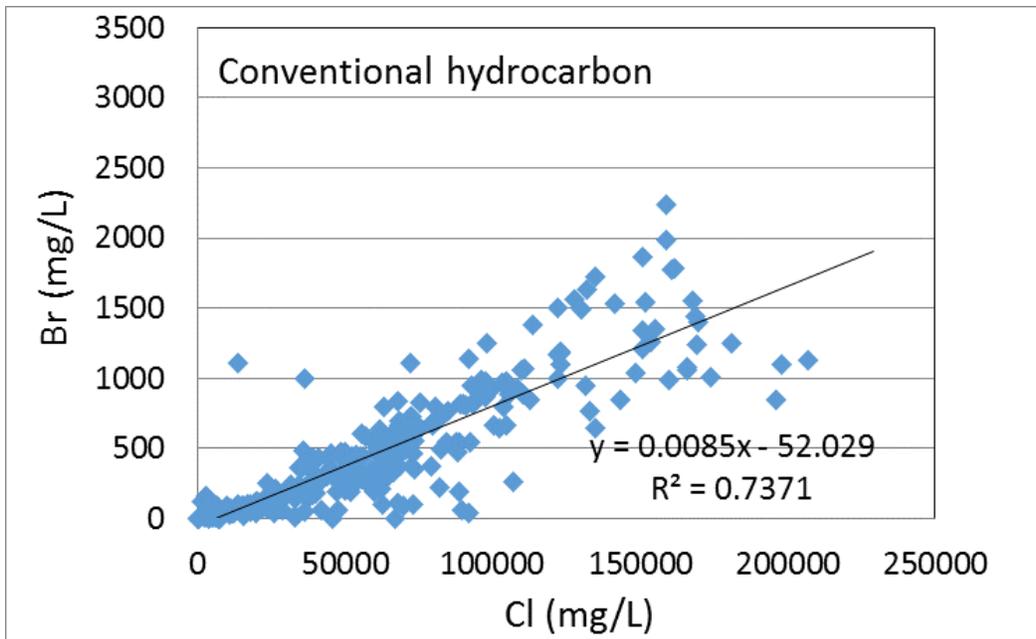


Figure 3: Br–Cl relationship in produced water from conventional hydrocarbon development in Appalachian region (data source: USGS)

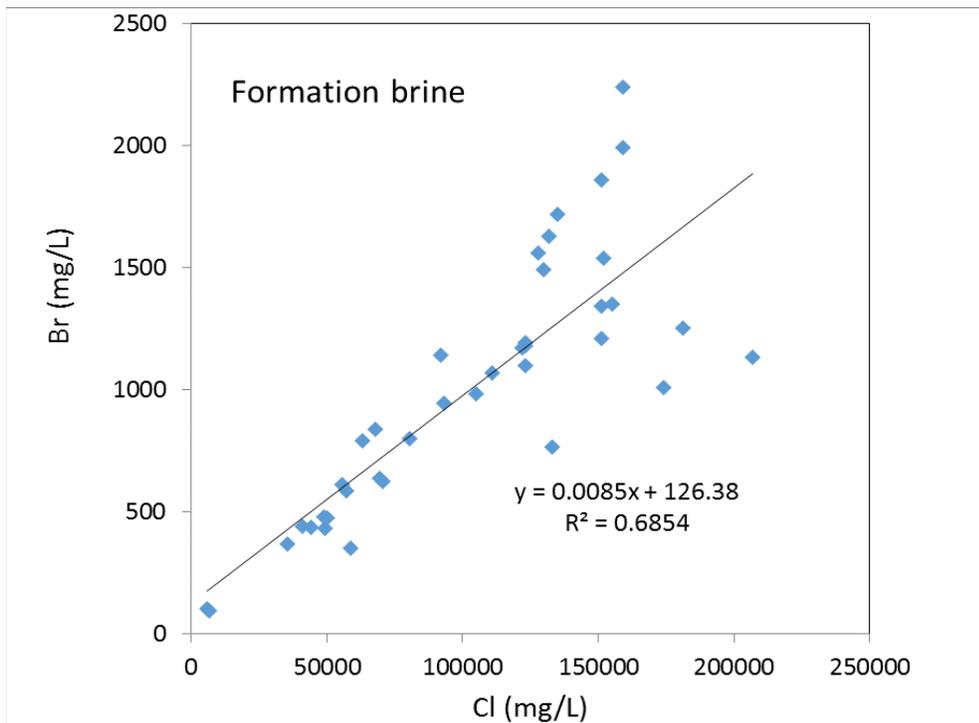


Figure 4: Br–Cl relationship in formation brine in Appalachian region (data source: Dresel and Rose, 2010)

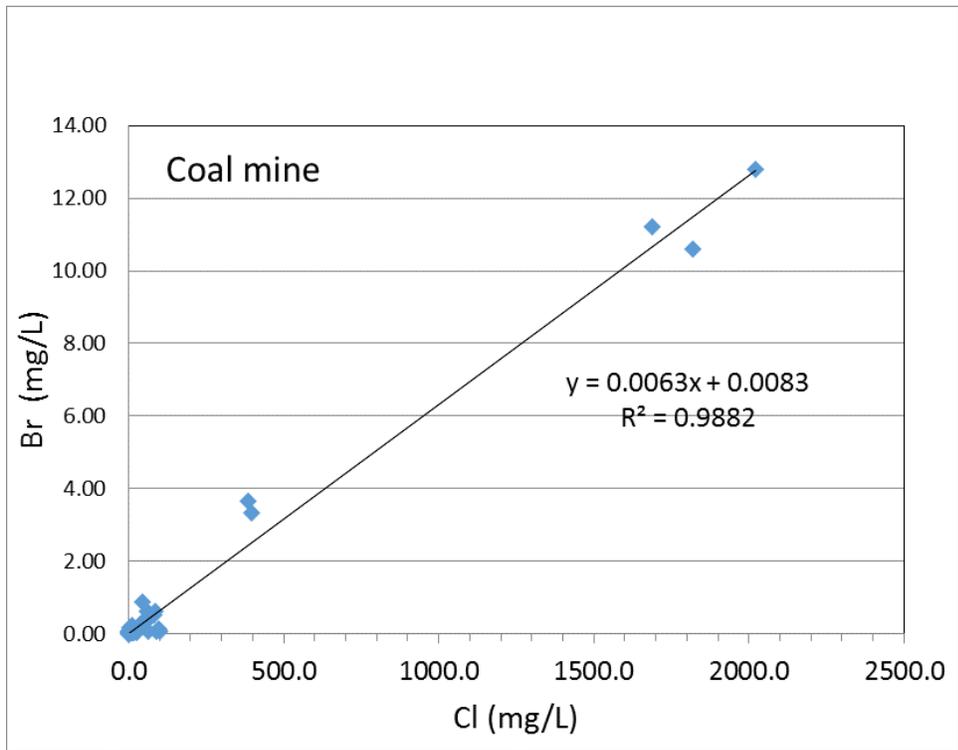


Figure 5: Br–Cl relationship in formation brine in Appalachian region (data source: Cravotta)

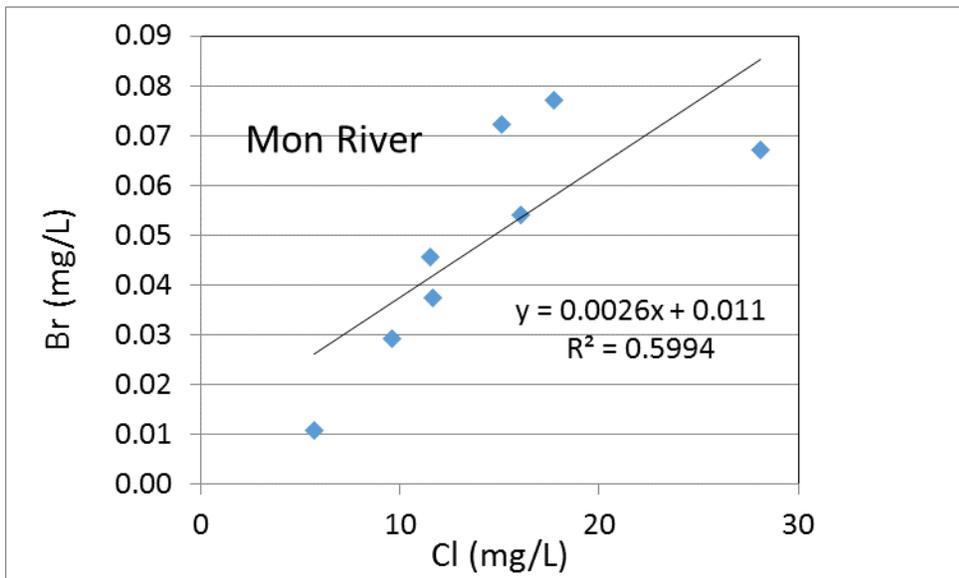


Figure 6: Br–Cl relationship in receiving stream in Appalachian region (Data source: WVVRI)

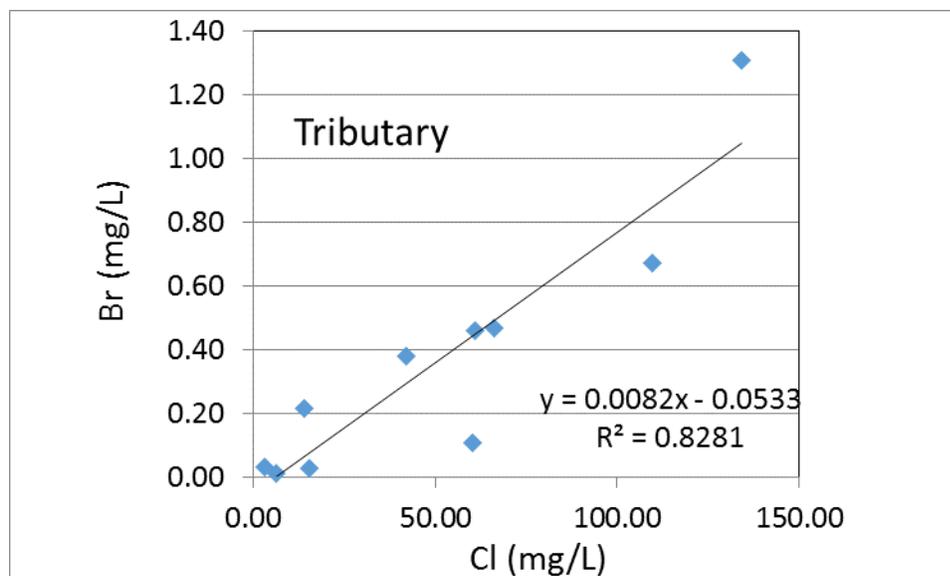


Figure 7: Br–Cl relationship in tributary of Monongahela River in Appalachian region (Data source: WVVRI)

Tributary has significant higher Br concentration than Monongahela River. It is likely originated from mixing with discharge from coal industries.

2. Other chemical signatures

In addition to Br vs Cl, several other chemical signatures that have been used in literature were examined to explore the potential relationship of these chemical signatures with Br concentration profile. These chemical signatures include Cl/Br vs Cl, Cl/Br vs Br, SO₄/Cl vs Br, SO₄/Br vs Br, and cations (Na, Ca, Ba, Sr) vs Br. However, no consistent relationship is found from the examined datasets.

3. Geochemical modeling

This part of work is ongoing. Modeling examine mixing of shale gas produced water with river water at different fractions 5%, 10%, 20% to investigate changes in Br and Cl concentrations and impact on water quality.

Significance of the Project

This study investigate one of the newer environmental issues (Br contamination) in the Appalachian region. The development of the diagnostic tools will help to identify and differentiate among bromide contamination sources, which is important for regulators to make informed decisions for effective bromide control measures.

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<http://www.ncbi.nlm.nih.gov/pubmed/20080279>

Publications

No publication has been submitted yet to date.

Information Transfer Program

The work is ongoing. WVWRI will submit abstracts and/or papers to conferences and journals for consideration.

Student Support

A graduate student is assisting with project activities (including sample collection, water chemistry data analysis and geochemical modeling) on a part-time basis.

Notable Achievements and Awards

No awards to report at this time.

WRI-159: Implementation of a Drinking Water Well Sampling Protocol

Basic Information

Title:	WRI-159: Implementation of a Drinking Water Well Sampling Protocol
Project Number:	2014WV214B
Start Date:	3/1/2014
End Date:	2/28/2015
Funding Source:	104B
Congressional District:	1
Research Category:	Water Quality
Focus Category:	Water Quality, Groundwater, Water Supply
Descriptors:	None
Principal Investigators:	Jennifer Hause, Melissa J. O'Neal, Tamara Vandivort, Paul Ziemkiewicz

Publications

There are no publications.

Development of a Drinking Water Well Sampling Protocol to Establish Baseline Data Prior to Horizontal Drilling of Gas Wells

Annual Status Report
March 1, 2014 – February 28, 2015

Principal Authors:

Jennifer Hause
Tamara Vandivort
Melissa O'Neal

Submission Date:

May 30, 2015

USGS Award #:

G11AP20114

Submitted by:

West Virginia Water Research Institute
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Abstract

Increased use of horizontal drilling and hydraulic fracturing methods to produce natural gas from deep shale beds has raised environmental impact concerns from the general public. Although hydraulic fracturing is not a new technique to release deep deposits of natural gas, the rate of which it has been recently used within the Marcellus Shale Formation has greatly escalated. Of most concern to the general public are potential contamination threats to nearby private drinking water wells during shale gas development activities. In areas with a high level of shale gas drilling in the Marcellus Shale Formation, many homeowners claim their drinking water wells have been negatively impacted by the activities associated with gas well development. However, most homeowners have no baseline data to show the quality of their drinking water has changed since initiation of shale gas development near their property. State agencies provide recommendations for pre-drilling baseline water quality testing. Industry usually takes the recommendations further by testing a more comprehensive suite of parameters. However, the question remains as to whether or not these tests are monitoring the right parameters to identify if nearby drinking water wells are being intruded by drilling or hydraulic fracturing fluids from shale gas well development.

This study proposes to respond to this question by:

1. Characterizing the make-up of drilling muds and cuttings, hydraulic fracturing fluids, and flowback waters of Marcellus Shale gas wells in northern West Virginia,
2. Determining parameters of concern (health-based concerns) found in water and waste streams produced from shale gas development with the greatest potential to be found in nearby groundwater resources,
3. Sampling nearby private drinking water wells for identified parameters of concern, and
4. Finalizing a sampling protocol for private drinking water well owners to follow that provides a level of health protection in a cost-effective and efficient manner.

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Executive Summary

As pressure for fossil fuel production grows, exploration and extraction operations tapping the gas reserves of the Devonian-aged Marcellus Shale Formation are moving closer to residential increasing the concern for human exposure to potential hazards and pollution. The general public is specifically concerned with potential contamination threats to nearby private drinking water wells during shale gas development activities. Horizontal wells in the Marcellus differ from vertical wells due to the large amount of water used and thus wastewater produced; therefore, these shale gas extraction activities pose an increased potential to impact nearby water resources. In areas of active shale gas drilling, many homeowners claim their drinking water wells have been negatively impacted by the activities associated with developing a well site. However, most homeowners have no baseline data to show the quality or quantity of their drinking water has changed since nearby shale gas development started.

Many homeowners living in rural areas depend upon individual (private) groundwater wells as their source of drinking water. When drinking water wells are drilled, flow rates are measured to determine adequate yield and water sampling is conducted to determine if treatment prior to use is necessary. In most cases, homeowners may never have their well water tested again unless they notice a change in color, smell, taste, or if industrial development begins to sprout up around them. State agencies provide recommendations for pre-drilling baseline water quality testing. Natural gas companies usually take those recommendations further by testing a more comprehensive suite of parameters. However, the question remains as to whether or not these tests are monitoring the right parameters to identify if nearby drinking water wells are being intruded by drilling or hydraulic fracturing fluids from gas well development.

This study proposes to respond to this question by characterizing drilling muds and cuttings, hydraulic fracturing and flowback waters of Marcellus Shale gas wells and determining those parameters with the greatest potential to be found in groundwater sources and thus nearby drinking water wells. The need exists to narrow the list of contaminants to potential indicator parameters that are characteristic of water and waste streams associated with horizontal gas well development activities and serve as the basis to develop a sampling protocol for private drinking water wells that is:

- Valid, reliable, and affordable to the homeowner offering a level of protection in the event their water well becomes compromised,
- Identifies adequate baseline water quality,
- Provides a monitoring mechanism to identify upsets in water quality potentially caused by nearby gas well development by monitoring the correct water quality parameters and therefore shortens mitigation response time, and
- Develops a mechanism for the general public, industry, and regulatory agencies to work together.

Problem and Research Objectives

Development of the extensive natural gas reserves contained in the Marcellus Shale Formation promises to be an important opportunity for the United States. Extraction from shale gas reservoirs like the Marcellus Shale Formation requires either vertical or horizontal drilling coupled with hydraulic fracturing to access and release the gas. Rapid application of these technological advancements has increased concern about potential environmental impacts from the general public. Drilling fluids and muds may consist of water, mineral oil or synthetic-based oil compound, weighing agents such as barite or bentonite clay, biocides, lubricants and corrosion inhibitors. The drilling process, through the use of the drilling fluids and cuttings created, increases the threat to groundwater contamination because they also have the potential to include radioactive materials. Flowback and produced water contains salts, metals and organic compounds along with the compounds introduced into the fracturing supply water such as friction reducers, surfactants, gelling agents, scale inhibitors, acids, corrosion inhibitors, antibacterial agents and clay stabilizers.

Efficient management of water streams associated with the development of a shale gas well requires knowing the characteristics of those waters. This study has focused on sampling and analyzing drilling fluids, muds and cuttings along with hydraulic fracturing and flowback waters of Marcellus Shale gas wells in northern West Virginia and determining which of these compounds if they were to reach groundwater resources are of concern for potential contamination that may affect human health. A draft sampling protocol for monitoring nearby individual drinking water wells has been developed taking into account other sampling protocols in existence from various sources such as state agencies, private analytical service providers, and industry (energy companies). The draft sampling protocol has been compared to research studies that have sampled and monitored drinking water wells located in close proximity to planned and active Marcellus Shale gas wells. The next step is to “field-test” the sampling protocol to determine if the sampling protocol will provide a cost-effective and efficient tool for homeowners to monitor water quality of their drinking water wells and detect contaminant intrusion.

Methodology

This study proposes to begin to address public concern of private drinking water well contamination by nearby shale gas well development activities. Tasks 1 and 2 have been completed and Task 3 is almost complete and Task 4 will commence upon the completion of Task 3.

Tasks:

1. Characterizing the make-up of drilling muds and cuttings, hydraulic fracturing fluids, and flowback waters of Marcellus Shale gas wells in northern West Virginia,
2. Determining parameters of concern (health-based concerns) found in water and waste streams produced from shale gas development with the greatest potential to be found in nearby groundwater resources,
3. Sampling nearby private drinking water wells for identified parameters of concern, and
4. Finalizing a sampling protocol for private drinking water well owners to follow that provides a level of health protection in a cost-effective and efficient manner.

Principal Findings

Task 1: Characterize shale gas well water and waste streams

Marcellus Shale gas wells located in northern West Virginia were identified and samples were collected of water and waste streams. The West Virginia Water Research Institute (WVWRI) developed an initial list of analytes for sampling and characterizing water and waste streams associated with the various stages of horizontal gas well development. The list was based on the literature review efforts to identify commonalities among the parameters measured and previous monitoring studies conducted by WVWRI of Marcellus Shale gas wells in West Virginia and Ohio. Table 1 details the parameter list and analytical results.

Table 1. Horizontal gas well water and waste stream analytical results (ranges presented).

Parameter	Units	Freshwater Impoundment	HF Fluids	Drilling Muds	Drill Cuttings	Flowback	Waste Storage
Aluminum	mg/l	ND – 0.0236	ND – 0.335	0.969 – 4550	4740 – 12100	ND – 13.3	ND – 2.78
Arsenic	mg/l	ND	ND	ND – 30.6	2.35 – 19.2	ND	ND
Barium	mg/l	0.032 – 0.0565	0.61 – 12.4	2.13 – 4910	23.9 – 5920	23.1 – 2580	10.2 – 572
Bromide	mg/l	ND – 0.11	2.3 – 126	8.4 – 37.5	ND – 10.8	370 – 970	52.5 – 675
Calcium	mg/l	20.8 – 44.4	49 – 1260	1090 – 47900	781 – 152000	2310 – 19900	1010 – 8670
Chloride	mg/l	12.8 – 26.5	219 – 9500	1180 – 131000	876 – 20000	27500 – 79000	4700 – 56000
Chromium	mg/l	ND	ND	0.268 – 16.2	6.367 – 32.8	ND – 0.068	ND – 0.144
Iron	mg/l	ND – 0.0244	0.174 – 30.9	1.09 – 13600	6670 – 30400	14.7 – 149	19.3 – 57
Lead	mg/l	ND	ND	ND – 84.9	3.5 – 31.5	ND – 0.102	ND
Magnesium	mg/l	4.04 – 8.24	6.85 – 171	2.84 – 2410	1920 – 7090	436 – 2260	107 – 944
Manganese	mg/l	0.0025 – 0.022	0.147 – 1.76	0.064 – 435	91.9 – 714	1.74 – 10.2	1.38 – 7.56
Mercury	mg/l	ND	ND	ND – 0.196	ND – 0.173	ND	ND
Nickel	mg/l	ND	ND	ND – 37.7	10.3 – 41.4	ND	ND
Phosphorus	mg/l	ND – 0.04	0.09 – 11.2	0.6 – 235	100 – 349	ND – 2.36	0.75 – 90
Potassium	mg/l	1.61 – 2.92	2.32 – 63.6	465 – 24900	1930 – 12000	211 – 488	44.2 – 315
Selenium	mg/l	ND	ND	ND – 3.34	ND – 3.14	ND – 0.335	ND
Silver	mg/l	ND	ND	ND – 0.509	ND – 0.397	ND	ND
Sodium	mg/l	8.46 – 27.1	110 – 3990	364 – 44900	543 – 12400	15900 – 119000	2440 – 20800
Strontium	mg/l	0.122 – 0.239	3.92 – 136	10.6 – 839	4.22 – 508	657 – 4660	117 – 1460
Sulfides	mg/l	4.19 – 30.3	4.47 – 33	638 – 9450	1410 – 12800	ND – 303	ND – 38.7
Zinc	mg/l	ND – 0.0075	ND – 1.74	ND – 94.8	2.22 – 89.7	ND – 0.288	0.06 – 0.352
Conductivity	µmhos/cm	315 – 483	1030 – 33100	13200 – 222000	1150 – 77000	74900 – 225000	16800 – 132000
pH		8.09 – 8.75	6.63 – 7.96	7.35 – 12.71	NM	6.49 – 7.07	6.16 – 7.82
Hardness (total)	mg/l	68.4 – 142	150 – 3840	2740 – 6550	NM	196 – 59000	2950 – 25500
Alkalinity (total)	mg/l	48.2 – 188	49.3 – 188	220 – 11100	209 – 54700	139 – 255	118 – 234
TDS	mg/l	170 – 277	568 – 20400	6600 – 119000	NM	45400 – 154000	8840 – 93700
TSS	mg/l	ND – 6	14 – 260	18300 – 162000	NM	ND – 348	143 – 420
Methane	µg/l	ND	ND – 265	ND	NM	1.81 – 8310	187 – 10500
Ethane	µg/l	ND	ND	ND	NM	ND – 2730	ND – 1760
Propane	µg/l	ND	ND	ND	ND	ND – 1130	ND
TOC	mg/l	0.72 – 5.4	4.55 – 217	1050 – 60000	26700 – 82100	3.36 – 588	25.8 – 309
COD	mg/l	12 – 19	31 – 1110	3290 – 11200	526 – 5290	743 – 2660	568 – 2280
Oil & Grease	mg/l	ND	ND – 20.4	ND – 196	ND – 5.13	ND – 39.1	4.6 – 594
Benzene	µg/l	ND	ND – 29.4	ND – 300	ND – 294	ND – 716	ND – 372
Toluene	µg/l	ND	ND – 76.9	ND – 2160	ND – 1640	ND – 2470	ND – 2070
Ethylbenzene	µg/l	ND	ND – 8.7	ND – 513	ND – 404	ND – 220	ND – 235
Xylene (o,m,p)	µg/l	ND	ND – 165.5	ND – 5610	ND – 3164	ND – 4053	ND – 3097
Styrene	µg/l	ND	ND	ND – 9.5	ND	ND	ND – 141
Tetrachloroethylene	µg/l	ND	ND	ND	ND – 63.3	ND	ND
MBAS	mg/l	ND – 0.177	ND	ND – 262	NM	ND – 0.605	ND – 0.473
TPH (diesel)	mg/l	ND	ND – 119	23.1 - 237000	115 - 55900	0.57 – 114	1.9 – 285
Gross Alpha	pCi/l	NM	1.2 – 9.43	3.78 – 173	8.93 – 28.3	18.9 – 20920	8.69 – 5304
Gross Beta	pCi/l	1.48 – 2.25	9.89 – 83	14.9 – 23770	17.3 – 30.1	168 – 4664	34 – 1349
Radium-226	pCi/l	0 - .725	NM	6.45	0.95 – 3.114	178 – 685	15.4 – 1194
Radium-228	pCi/l	0.189 – 0.354	NM	4.95	0.715 – 1.929	49.1 – 85.5	53.5 - 216

ND = not detected NM = not measured

Task 2: Identify Parameters of Concern

A review of drinking water supply studies and various state guidelines for water well testing yielded a fairly comprehensive water quality list of inorganic, organic, and radioactive parameters. Water and waste stream characterization results allowed WVVRI to eliminate parameters that were not detected and thus would not appear in drinking water well sampling results. WVVRI staff enlisted public health professionals to evaluate the shale gas water and waste stream characterization sampling results and identify potential pollutant markers. This exercise led to the development of list of parameters for analysis when sampling drinking water wells located near shale gas development activities, see Table 2.

Table 2. Drinking water well sampling parameters

Parameter				
Inorganics	Arsenic (As)	Aluminum (Al)	Potassium (K)	Strontium (Sr)
	Barium (Ba)	Iron (Fe)	Magnesium (Mg)	Silver (Ag)
	Chromium (Cr)	Manganese (Mn)	Sodium (Na)	Sulfate (SO ₄)
	Lead (Pb)	Zinc (Zn)	Mercury (Hg)	Bromide (Br)
	Selenium (Se)	Calcium (Ca)	Nickel (Ni)	Chloride (Cl)
	Total Dissolved Solids (TDS)	Alkalinity (Alk)		
Organics	Benzene MBAS*	Toluene	Ethylbenzene	Xylene
Radionuclides	Gross alpha	Gross beta	Radium-226	Radium-228

*MBAS = methylene-blue active substances

Task 3: Sample Drinking Water Wells

Two general locations have been identified for study: an “active group” in an area of intense shale gas development, and a “control group” in an area of no shale gas development. As seen in Figure 1, shale gas development is most intense in north east and south west Pennsylvania. The “active group” for this study is located near Montrose in Susquehanna County, Pennsylvania. The “control” group is located near Cranesville in Preston County, West Virginia.

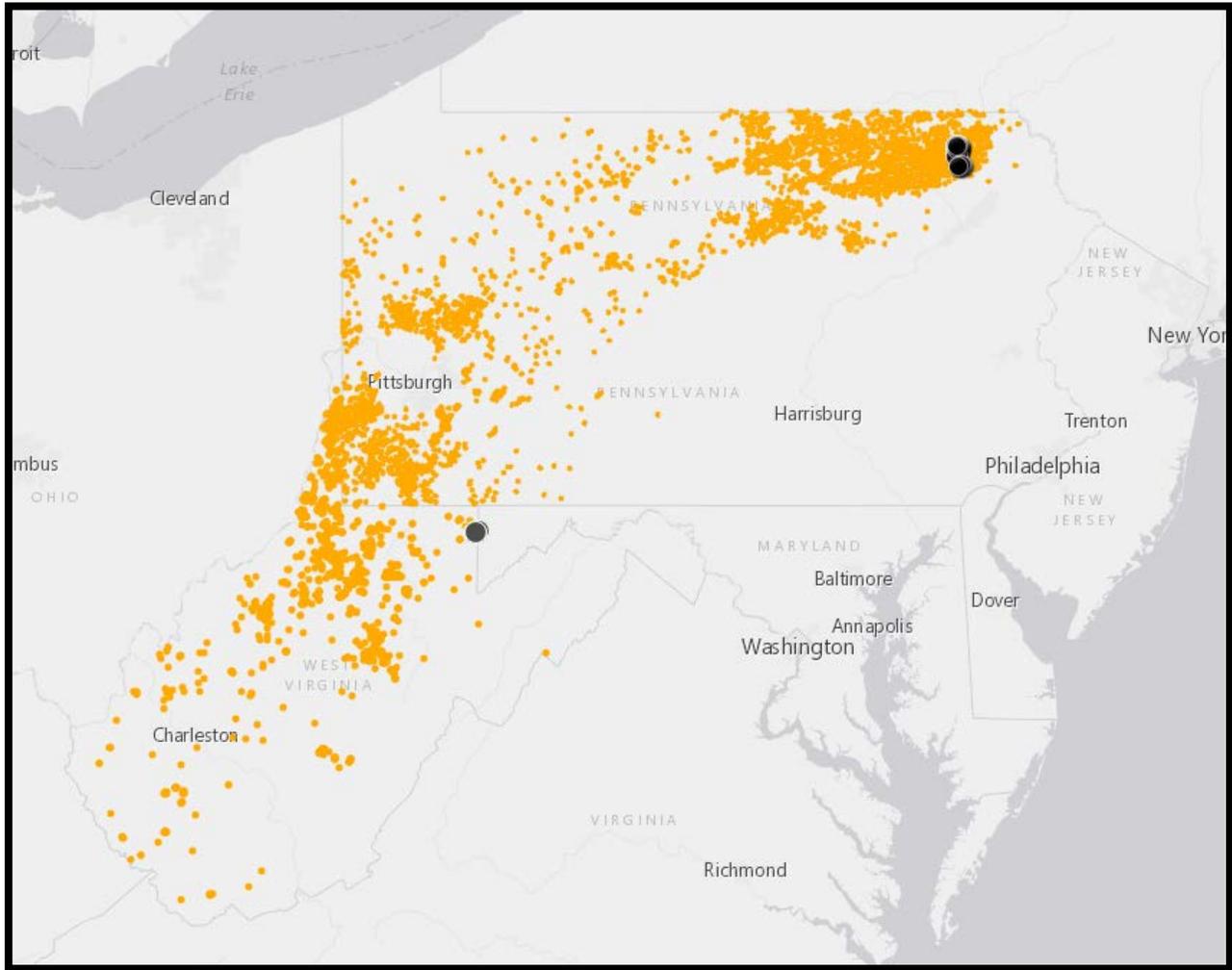


Figure 1. Permitted shale gas sites (orange) and ETD 12 project sample locations (black).

Sampling Parameters

During each sampling event, field measurements of pH, specific conductivity, total dissolved solids, and dissolved oxygen were recorded with an YSI 550 multi-probe instrument. Discharge measurements were taken at surface water locations when possible. Additionally, grab samples were collected via standard operating procedures and submitted with chain-of-custody documentation to the analytical laboratory for analysis within hold times. A trip blank was also submitted for analysis. Resultant data was entered into an excel spreadsheet and graphs were

created for visualizations of results. Results will be included in the final project report to USGS as additional sampling events are planned. Table 3 shows parameters tested along with laboratory methods and reporting limits.

Table 3. Analytical laboratory parameters, reporting limits, and methods.

Method	Reporting Limit	Units		Parameter
SM5540 C	0.1-10	mg/L	Surfactants	MBAS
		g/mol		LAS Molecular Weight
E200.7	0.01	mg/L	Metals by ICP (Total)	Al
	0.005			As
	0.01			Ba
	1			Ca
	0.005			Cr
	0.070			Fe
	0.005			Pb
	0			Mg
	0.005			Mn
	0.01			Ni
	0.50			K
	0.008			Se
	0.006			Ag
	1			Na
	0.01			Sr
0.010	Zn			
E200.7	0.050	mg/L	Metals by ICP (Dissolved)	Al d
	0.005			As d
	0.01			Ba d
	1			Ca d
	0.005			Cr d
	0.070			Fe d
	0.005			Pb d
	2			Mg d
	0.005			Mn d
	0.010			Ni d
	0.500			K d
	0.008			Se d
	0.006			Ag d
	1.00			Na d
	0.005			Sr d
0.010	Zn d			
E245.1	0.0002			Hg d
				Hg
8260 MSV UST				Benzene
				Ethylbenze
				Toluene
				Total-Xylene
				Surr: 1,2 - Dichlorethane -d4
				Surr: 4-Bromoflurobenzene
2540C				Surr: Toluene -d8
				TDS
E300.0	0.02	mg/L	Anions by Ion Chromatography	Br
SM4500CLE	3			Cl
ASTM D516-9002	10			SO4
Field Readings		°C	Field Readings	Temp.
		µS/cm		Conductivity
		(mg/L)		TDS
		pH		pH
Radiologicals		pCi/L	Radiologicals	DO
				Gross Alpha
				Gross Beta
				Radium-226
				Radium-228
				Potassium-40

Information for participants

Fact sheets were developed and provided to landowners and homeowners participating in the study (Figure 2).



WEST VIRGINIA
WATER RESEARCH INSTITUTE
A PROGRAM WITHIN THE NATIONAL RESEARCH CENTER FOR COAL AND ENERGY
AT WEST VIRGINIA UNIVERSITY

ASSESSING ENVIRONMENTAL IMPACTS OF HORIZONTAL GAS WELL DEVELOPMENT OPERATIONS & IMPLEMENTATION OF DRINKING WATER WELL SAMPLING PROTOCOL TO ESTABLISH BASELINE DATA PRIOR TO DRILLING GAS WELLS

FUNDED BY:
Environmentally Friendly Drilling Systems Program - The Technology Integration Program & the United States Geological Survey – Water Resources Research Institutes Program

TIME FRAME: October 2014 – October 2015

STUDY LOCATION: In the vicinity of the Diaz Family L.P. well (API #115-21822) Brooklyn Township, Susquehanna County, Pennsylvania

BACKGROUND:
As drilling and production activities to exploit the gas resources of the Devonian Shale increased in recent years, public concern over potential negative impacts of horizontal drilling and hydraulic fracturing also has increased. Although hydraulic fracturing is not a new technique, the accelerated rate at which it is being applied and the volumes of water and chemicals necessary for its use, have elevated concerns of potential environmental impacts. In order for gas development to proceed in a way that grows our economy while protecting our environment, we need to identify all environmental and health risks associated with tapping this vast resource and establish procedures through which regulatory agencies can develop an effective and predictable regulatory scheme allowing industry to operate using approved techniques.

Few studies have been published on the health effects of oil and gas exploration and extraction activities on nearby communities. A lack of evidence does not negate the fact that these operations use and produce contaminants that may adversely affect the health of the surrounding environment and nearby human populations. Further research through field-based environmental monitoring programs is needed.

This field-based research effort is an integrated approach to examine the effects of large-scale horizontal drilling on surrounding air and water resources (surface and groundwater). Researchers will identify a planned horizontal well site to monitor the air, surface waters and groundwater within a predetermined distance from the gas wellhead. Samples to be collected from the well site will include well cuttings and precipitate from filters during drilling of the horizontal section of the well, and produced water. All samples will be analyzed for naturally occurring radioactive materials (NORM). Additional samples will be collected and analyzed from surface and near-surface waters. An air monitoring system will be designed and (cont.)

employed to determine the amount of dust and ultra-fines produced and released into the environment in the vicinity of the well. Sampling techniques to be utilized will be those developed during a recent West Virginia University (WVU) field study requested and funded by the West Virginia Department of Environmental Protection (WVDEP). Analyses will be performed on key parameters determined in this previous study as being the most critical to human and environmental risk.

OBJECTIVES:
The objectives of this study are to (1) compare air quality results to the impact of other industrialized activities and to current environmental standards and health benchmarks; (2) document the physical and chemical characteristics of flowback and produced water and solid waste streams associated with the development of a horizontal shale gas well; (3) compare water quality results to current environmental standards; and (4) evaluate impacts of horizontal gas well activities on nearby groundwater.

INFORMATION FOR PROPERTY OWNERS:
Sites have been selected for sampling of surface water (springs, ponds, streams) and ground water (private drinking wells) within the 3,000ft radius of the identified well pad. Parameters to be tested include a variety of inorganics, organics, and radiologicals. Data collected is to be utilized by WVWRI for research purposes only and results will be shared with individual property owners. Personal information (i.e. names, address, locations) will be used only for right of entry agreement purposes and will not be shared in association with any data collected. Generic names (i.e. well A) will be used to represent locations.

		Suggested analytical parameters			
Indicators	Inorganics	alkalinity	Aluminum	Chloride	Magnesium
		conductivity	Barium	Iron	Manganese
	pH	Bromide	Potassium	Sulfate	
	TDS	Calcium	Lithium	Strontium	
Organics	benzene	xylene			
	toluene	MBAS			
	ethylbenzene				
Radionuclides	Gross α	Radium-226			
	Gross β	Radium-228			

TDS = total dissolved solids, TSS = total suspended solids, α = alpha, β = beta

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FUNDER INFORMATION:
Environmentally Friendly Drilling – The Technology Integration Program
Website- <http://www.afdsystems.org/>

United States Geological Survey – Water Resources Research Institutes Program
Website - <http://water.usgs.gov/wrri/index.php>

WWW.WVWRI.ORG
WWW.NRCCE.WVU.EDU
WWW.WVU.EDU

Figure 2. Screenshot of participant fact sheet.

At the conclusion of the project, participants will be provided a copy of their analytical testing to include an overview of their water quality results. Figure 3. Draft of Homeowner Profile to be provided for participants. Figure 3 is a screenshot of the draft “Homeowner Profile” to be provided to participants at the conclusion of the study.

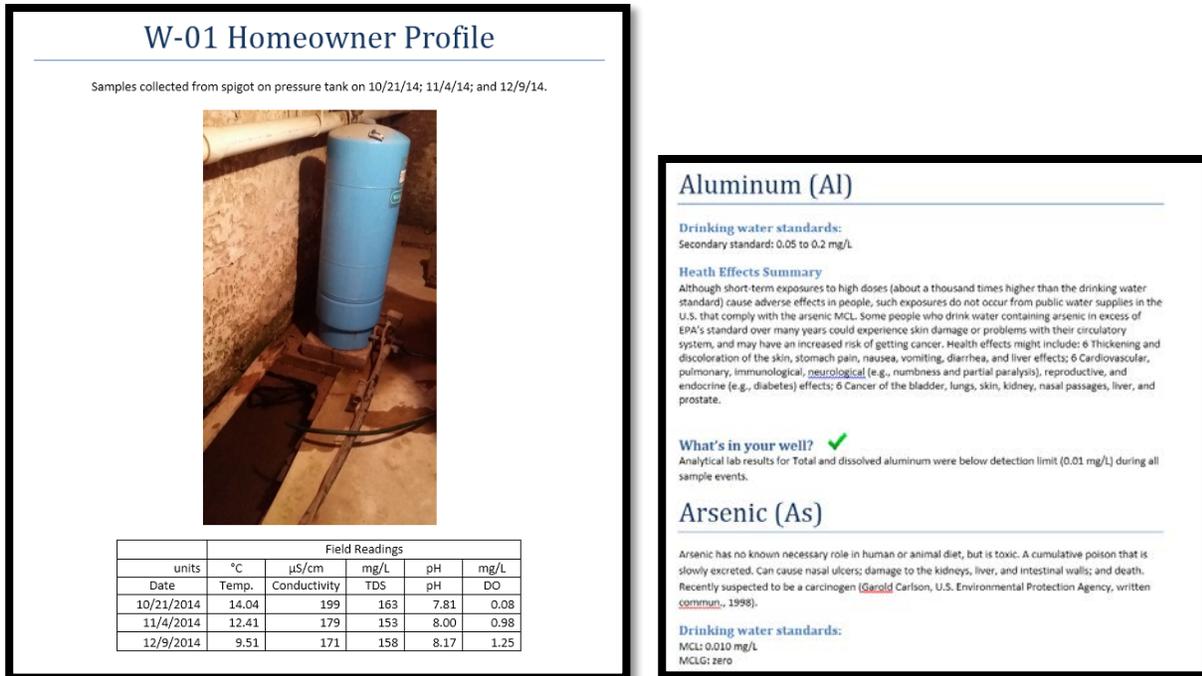


Figure 3. Draft of Homeowner Profile to be provided for participants.

Active Site Sampling

Development of the Marcellus Shale through horizontal drilling techniques has been intense in Pennsylvania with over 9,000 wells unconventional wells drilled since 2005. In particular, over 1,100 unconventional wells have been drilled in the 2,155 km² of Susquehanna County since 2006 (Figure 4).



Figure 4. Unconventional wells drilled (orange) and sampling locations (black) in Susquehanna County, Pennsylvania.

Sampling Locations

While intense activity is present in Susquehanna County, the research team identified homeowners that were nearby to a permitted, but not yet drilled well (API #115-21822). Figure 5 identifies surface water monitoring sites (7A, 6C, 5A, P-01, P-02, SP-A, SP-B, SP-C, UNT 44288) and ground water monitoring sites (W-01, W-02, W-03, W-04) that were selected for the study.

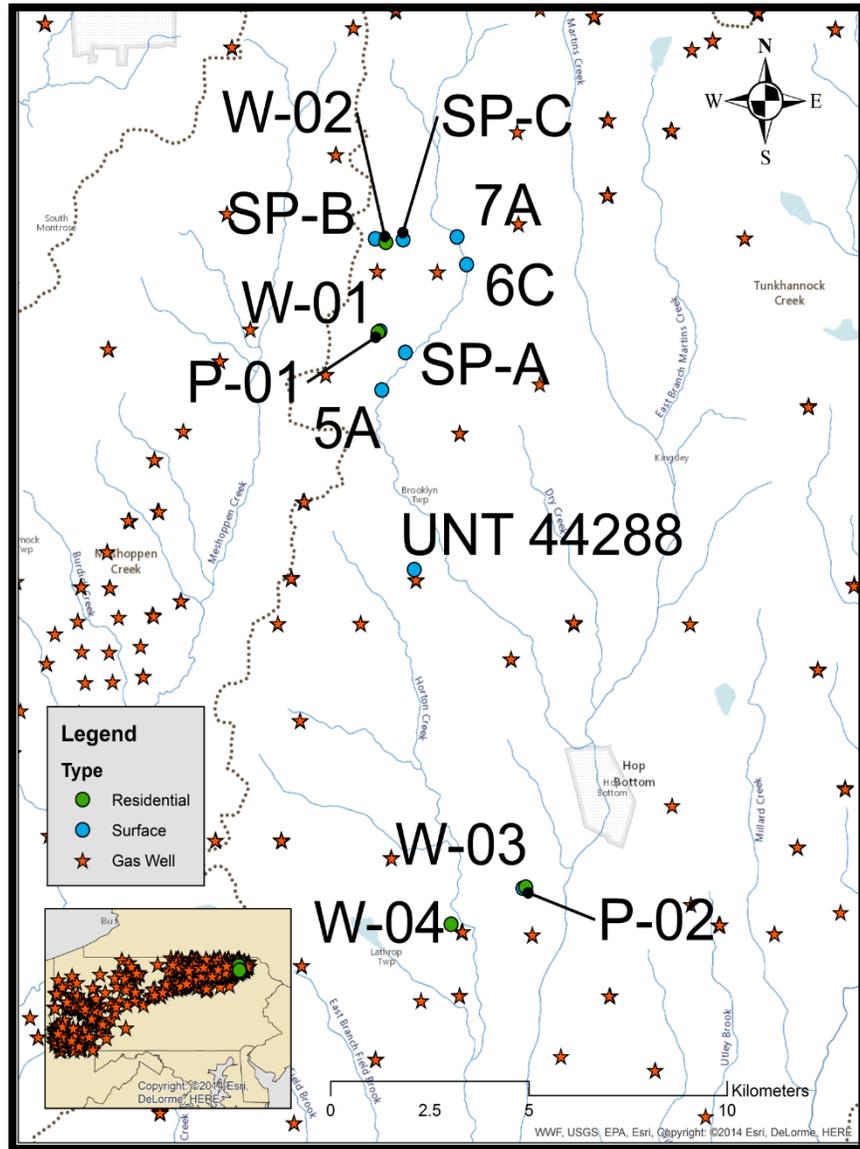


Figure 5. Sampling locations and well locations in Susquehanna County, Pennsylvania.

Sampling Dates

Samples were collected at various stages through the development of the well, to include:

Baseline – October 10, 2014

Drilling – November 4, 2014

Pre- drilling – October 21, 2014

Post-drilling – December 9, 2014

Site Photos

The collection point for groundwater samples was typically the pressure tank locations as noted in Figure 6. The collection point for all samples was prior to any treatment (i.e. water softening).

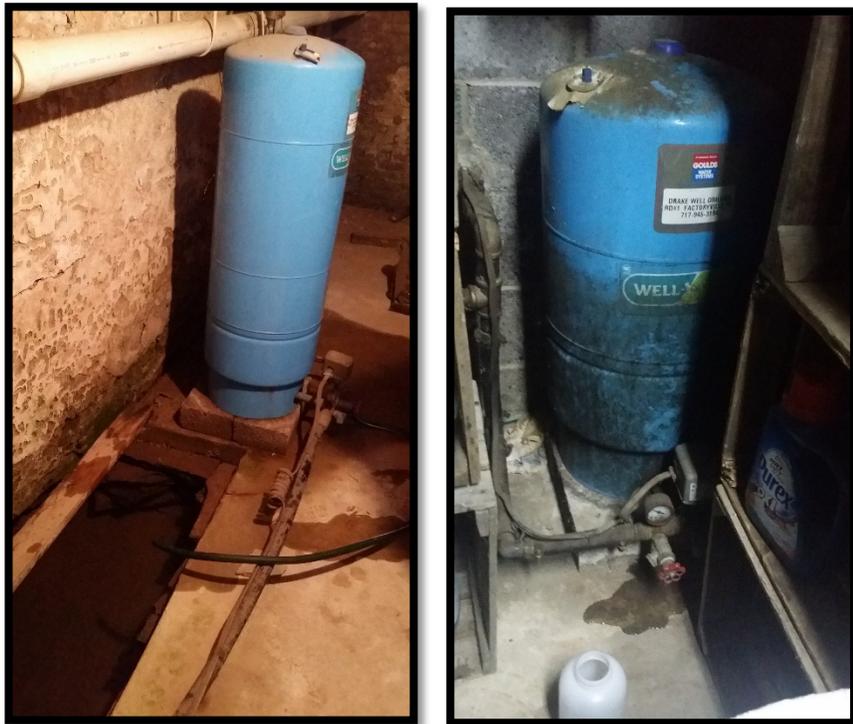


Figure 6. Groundwater was sampled mostly from pressure tanks in residences.

Figure 7 shows two of the spring locations that were also sampled.



Figure 7. Spring sampling sites SP-B (left) and SP-C (right).

Surface water sampling points along Hop Bottom included upstream and downstream of potential runoff from the nearby #API 115-21822. Figure 8 depicts site 6C along Hop Bottom.



Figure 8. Surface water sampling station on Hop Bottom.

Control Site Sampling

Ground water samples were collected at six residential areas on April 28, 2015 (Figure 9) in Preston County, West Virginia and Garrett County, Maryland. These sites serve as a control for the study. The nearby permitted well: API # 4707700580 is approximately 2,000 meters from the closest sample site and shows a status of “permitted”. To date, no activity has taken place on the site. Nearby surface mining is at Cranesville Limestone rock quarry as noted on the map by data from WV Department of Environmental Protection. No evidence of current or legacy coal mining has been found in the area. The Nature Conservancy’s Cranesville Swamp Preserve is in close proximity to the control sample group. At least one more sample collection is planned for the control sites.

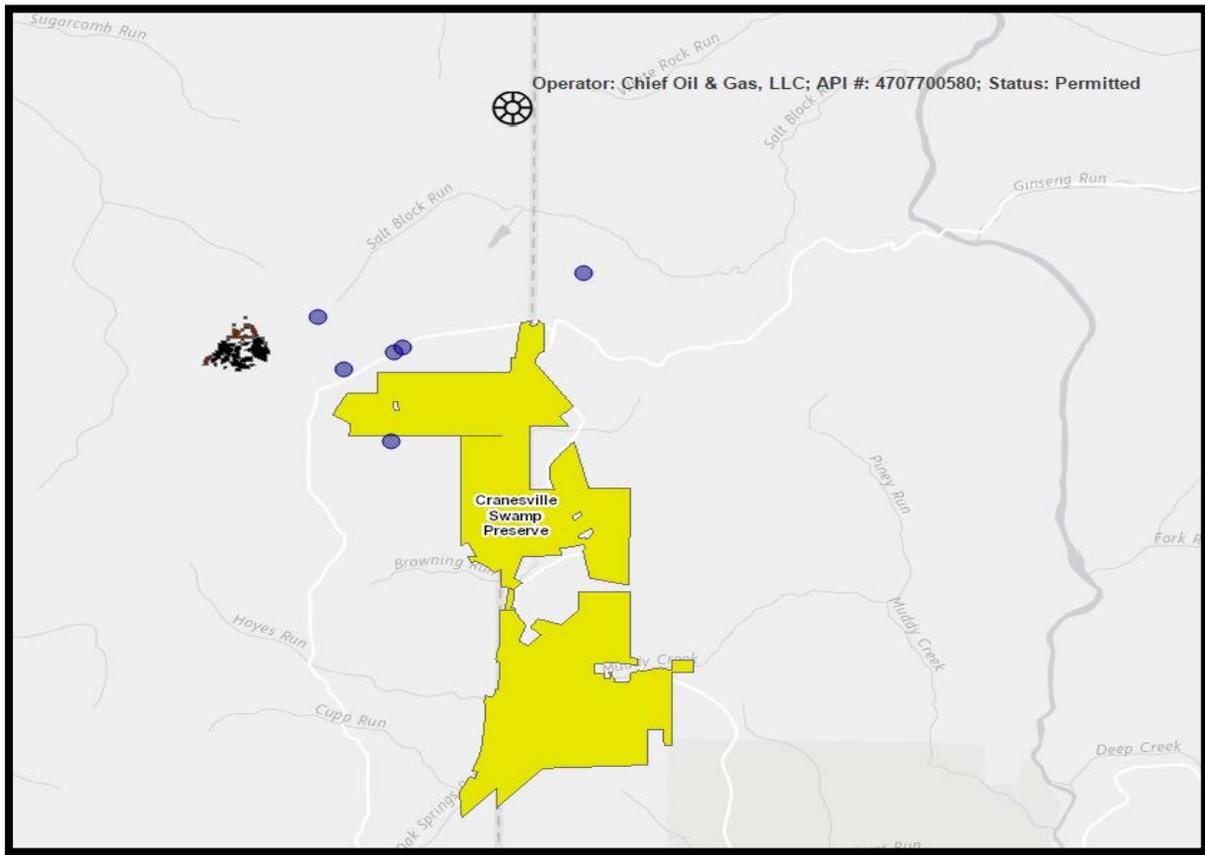


Figure 9. Control site sampling locations in Preston County, West Virginia.

Task 4: Finalize Sampling Protocol

WVWRI will continue to work with public health officials to refine the monitoring recommendations including sampling procedures and water quality parameters. The results of the collaboration with public health officials, regulatory official, and industry representatives will yield a concise list of parameters with the greatest potential to be found in nearby groundwater resources and potential health-related concerns associated with each of the parameters

Significance of the Project

Based on the results, the protocol will be adjusted to provide a plan for private drinking water well owners to follow that offers health protection in a cost-efficient and effective manner.

Publications

No articles have been submitted for publication consideration to date.

Information Transfer Program

Work is ongoing. Once the drinking water well sampling and monitoring protocol has been finalized, WVWRI will submit abstracts and/or papers to relevant publications and conferences for consideration.

Although not yet public, an interactive data map has been created using arcgis.com (Figure 10). This provides the research team with data on nearby wells, site locations, etc.

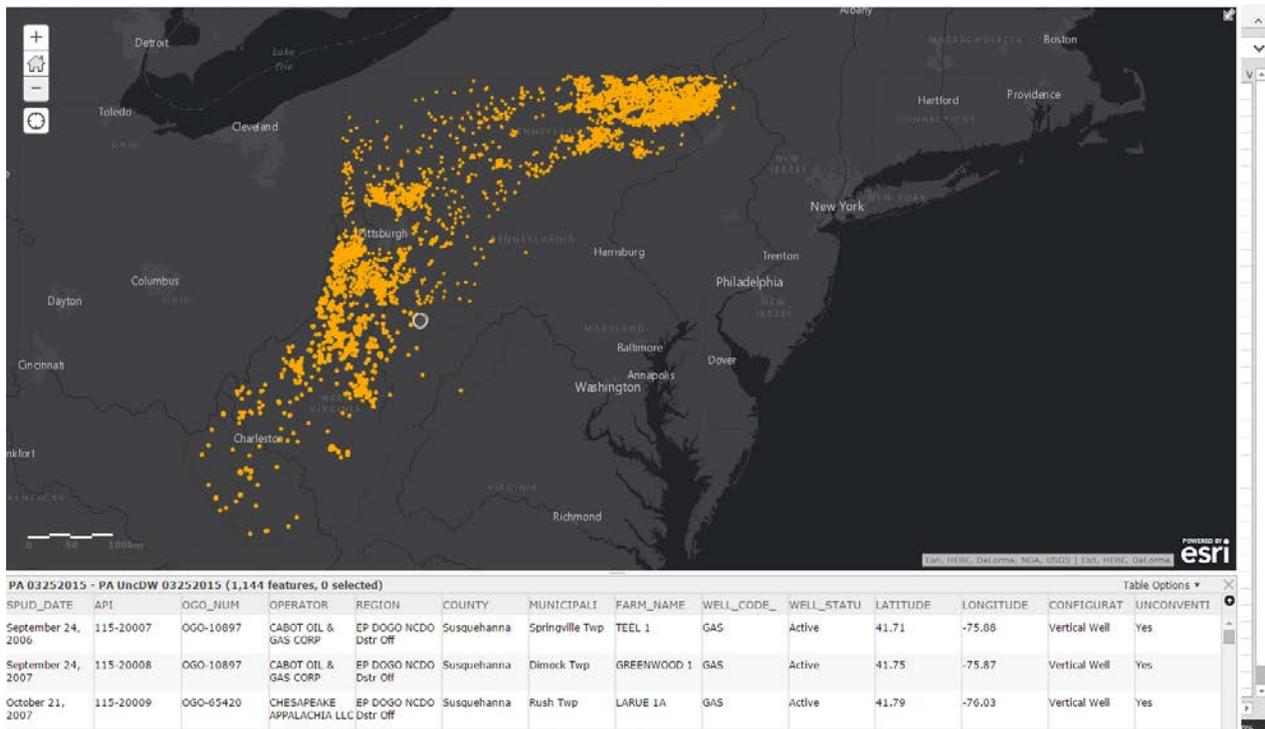


Figure 10. Interactive data project map.

Student Support

Two graduate students have assisted with project activities on a part-time basis. One graduate student assisted in obtaining background information on private drinking water well residences. Two graduate students have assisted the WVVRI field technician with collection of samples and data analysis.

Notable Achievements and Awards

No awards to report at this time.

Information Transfer Program Introduction

A highlight of this year's information transfer was the Mid-Atlantic Water Conference held September 24-25, 2014 in Shepherdstown, West Virginia. West Virginia and Virginia took the lead in coordinating all the Mid-Atlantic Water Resource Research Institutes to develop a two-day program. Representatives from all eight attended and/or participated in the event.

In addition, to giving a presentation at the opening plenary session, Earl Greene, Acting Chief, Office of External Research Coordinator, Hydrologic Networks and Analysis, USGS was interviewed about the 50th Anniversary of NIWR. The result was a short video clip produced and placed on the NIWR.net website.

2014 Mid-Atlantic Regional Water Conference

Basic Information

Title:	2014 Mid-Atlantic Regional Water Conference
Project Number:	2014WV213B
Start Date:	3/1/2014
End Date:	2/28/2015
Funding Source:	104B
Congressional District:	1
Research Category:	Not Applicable
Focus Category:	Water Supply, Law, Institutions, and Policy, Management and Planning
Descriptors:	None
Principal Investigators:	Tamara Vandivort, glenn waldrón

Publications

There are no publications.

Information Transfer Program

Final Report

2014 Mid-Atlantic Regional Water Conference September 24-25, 2014

The West Virginia Water Research Institute partnered with the Institutes for Water Resources Research in the following states to hold a two day Mid-Atlantic Regional Water Conference:

- Virginia
- Washington, DC
- Delaware
- Maryland
- New Jersey
- New York
- Pennsylvania

The theme was *the Future of Mid-Atlantic Infrastructure: Challenges and Solutions* and the venue was the National Conservation Training Center in Shepherdstown, West Virginia.

A request for abstracts was sent out via e-mail from the participating Institutes. Over 50 abstracts were received.

Keynote speakers included:

- Gerald Kauffman, Director, University of Delaware Water Resources Agency
- John Unger II, West Virginia State Senate Majority Leader
- Earl Greene, Acting Chief, Office of External Research, U.S. Geological Survey
- John Kennedy, Director, Virginia Department of Environmental Quality, Office of Ecology and Infrastructure
- John Sheehan, Director of Communications, Adirondack Environmental Council
- Walt Ivey, Director, Office of Environmental Health Services, West Virginia Bureau for Public Health

The format for day 1 (noon – 9 pm) included a plenary session with keynote presentations by Gerald Kauffman on addressing water infrastructure issues in the Mid-Atlantic Region through sustainable watershed management and Earl Greene on the 50th anniversary of the Water Resources Research Institutes. This was followed by a panel session with representatives from all eight Mid-Atlantic Region Water Resources Research Institutes on the infrastructure challenges in the Mid-Atlantic Region.

After a networking break, three concurrent sessions were held on:

- Drinking Water Treatment Methodologies
- Infrastructure Protection through Strategy, Policy, and Legislation

- Green Infrastructure Management and Design

Following a dinner provided to all participants, a networking reception and poster session (ten posters) was held from 7:00 pm – 9:00 pm.

On day 2 from 8:15 am – 10:00 am, the format began with three concurrent sessions were held on:

- Planning and Response to Climate Change & Flooding
- Implications for Drinking Water Safety Nationwide: The Elk River, WV Chemical Spill
- Tools to Plan, Finance, and Manage Stormwater

A plenary session from 10:30 am – noon was kicked off with a keynote address by West Virginia Senator John Unger II on addressing water and energy issues in West Virginia and beyond. This was followed by a panel discussion on protecting water infrastructure from energy-related incidents. Walt Ivy, Director, Environmental Engineering Division, West Virginia Department of Health and Human Resources discussed the Coal Washing Chemical (MCHM) Leak into the Elk River, West Virginia. John Kennedy, Director, Office of Ecology and Infrastructure, Virginia Department of Environmental Quality discussed the coal ash impact to the Dan River, North Carolina. Finally, John Sheehan, Director of Communications, Adirondack Environmental Council spoke on the impacts on water resources from oil tanker derailments.

Following lunch, three concurrent sessions were held from 1:15 pm – 3:30 pm on:

- Water Degradation from Stormwater and Treatment Options
- The Water and Energy Development Conundrum
- Planning for our Future Water Supply

A website with specific URL was developed to host information on the event, agenda, on-line registration, information on the facility, lodging, and other pertinent information. Presentations from the event were made available on the conference website at: www.MidAtlanticWC.org.

In addition to support from the USGS, additional sponsorship support came from:

- NIWR
- Pennsylvania Water Resources Research Center
- Virginia Tech Center for Leadership in Global Sustainability
- ACF Environmental
- EMCO Site Solutions

Registration fees were also charged to cover costs associated with the event.

There were 130 attendees including presenters. At least one person or more attended from each of the eight Mid-Atlantic Region states. Attendees included academia, industry, regulatory agencies, city, municipal, state, and government agencies,

legislators, watershed associations, private non-profits, and others. Several students played active roles in presenting results in oral or poster sessions.

A follow-up survey was sent to participants and the overall response was favorable.

USGS Summer Intern Program

Basic Information

Start Date:	7/7/2014
End Date:	2/28/2015
Sponsor:	USGS
Mentors:	Joseph j. Donovan
Students:	Jeff Casenas

Internship Evaluation

Question	Score
Utilization of your knowledge and experience	Very Good
Technical interaction with USGS scientists	Very Good
Treatment by USGS as member of a team	Very Good
Exposure and access to scientific equipment	Very Good
Learning Experience	Very Good
Travel	About Right
Field Experience Provided	About Right
Overall Rating	A+

Additional Remarks

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	2	0	0	0	2
Masters	8	0	0	0	8
Ph.D.	0	0	0	0	0
Post-Doc.	0	0	0	0	0
Total	10	0	0	0	10

Notable Awards and Achievements

Re. USGS Project No. 2011WV165B: Monitoring for TDS in the Monongahela River Watershed.

Initial sampling and analysis for TDS in the Monongahela River and several tributaries supported by USGS 104b monies led to additional proposals submitted to the Colcom Foundation. We just received a third award from Colcom for \$350,000 making the total from Colcom to date \$1,618,000.

Approximately 30 watershed groups in 4 states (WV, PA, MD, OH) are participating in both voluntary and Colcom-supported monitoring for TDS in the Monongahela, Ohio, and Allegheny River Basins. More details on this project can be found at: 3Riversquest.org.

Re. USGS Project No. 2013WV205B: Understanding Variations in Isotopic and Molecular Compositions of Stray Gas in Areas of Accelerating Shale Gas Development

Results from this USGS-funded project were used to develop proposals and receive additional monies to continue research from both the US Department of Energy - National Energy Technology Laboratory (\$250,000) to better understand gas migration pathways and from the National Science Foundation (\$2,000,000 collaborative research funding) to understand microbial methanogenesis in geological formations.