

**West Virginia Water Research Institute
Annual Technical Report
FY 2015**

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 fifteen full-time and one part-time staff. We are adding two more full time staff positions this year. The Institute also supports numerous students; typically 3-4 GRA's and 2-3 undergraduate students within the WWRI 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

The WVVRI has four completed research projects to report on this year. They are:

Use of Chemical Signatures as Diagnostic Tools to Identify Bromide Contamination Sources - Y. Thomas He, Ph.D., Principal Investigator

Development of a Drinking Water Well Sampling Protocol to Establish Baseline Data Prior to Horizontal Drilling of Gas Wells (Phase I) and Implementation of a Drinking Water Well Sampling Protocol (Phase II) - Jennifer Hause, Principal Investigator

Bioelectrical Treatment for Softening and Desalination of Produced Water from Oil and Shale Production - Lance Lin, Ph.D., Principal Investigator

Modeling the Hydrologic Response in Surface Mining Watersheds with Redesigned Reclamation Practices - Leslie Hopkinson, Principal Investigator

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

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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.
4. Hopkinson, L., A.E. Sears, M. Snyder, E. O'Leary, N. DePriest, J. Quaranta, and P. Ziemkiewicz. 2015. Simulating the hydrologic response when streams are incorporated in valley fill design. Journal of Mining, Reclamation, and Environment. doi: 10.1080/17480930.2015.1105180.

Final Report

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

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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.

Research results related to each objective are outlined in the following sections.

Obj. 1: Generate geomorphic valley-fill designs.

This work extended previous work that began the process of creating geomorphic landform designs for valley fills. In that previous work, the process for creating regional geomorphic landform designs for Central Appalachia valley fills was developed (Sears et al., 2013; Buckley et al., 2013, Sears et al., 2014). We developed new designs to evaluate in this work.

Valley pond design

Surface water runoff retention structures were included in this design. The design was created to consider wildlife and vegetation benefits as well as potentially create perennial stream channels on the site. Three valley ponds (constructed on the surface of the land) were included in the regional valley-fill design that satisfied the drainage density requirements (Figure 1). These structures will be used to retain surface water runoff, create wetland areas, and discharge water year-round to create perennial stream flow. Figure 2 illustrates a close-up of one of the created valley ponds.

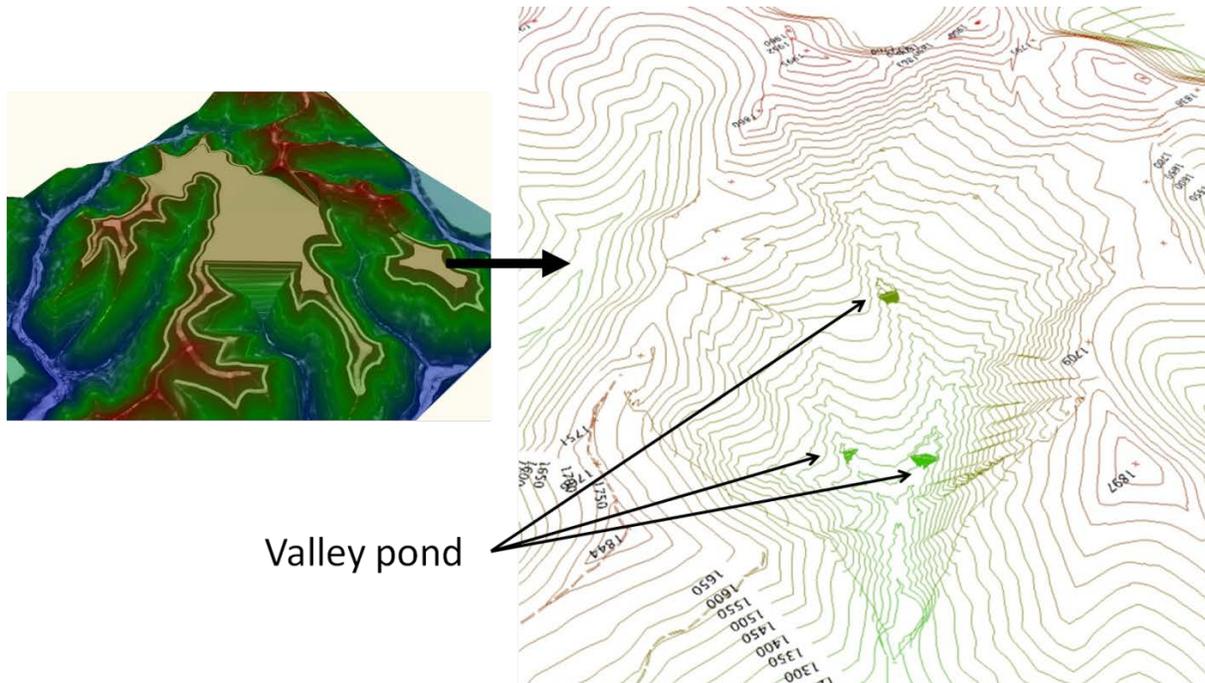


Figure 1. GLD with Regional Data and Valley Ponds



Figure 2. Valley pond, close-up view

Bench pond design

The bench ponds were created on the geomorphic landform designed valley fill and were designed by creating a top of dam of a specified width, and then projecting inward to model the pond, and outward to model the slopes to match to the target surface. The bench pond structures mimic wetlands and are located beside stream channels that were created on the valley fill site. Three bench ponds were spaced over the 241 acre area (1.4 km²) (Figure 3).

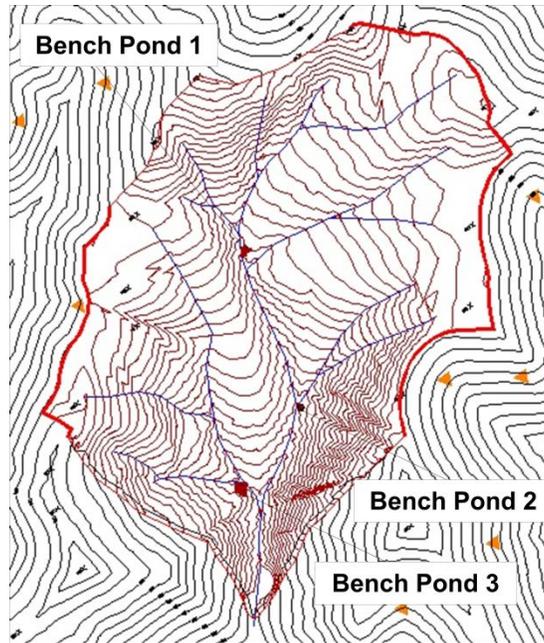


Figure 3. Created bench pond design

Retrofit design

The valley fill surface design was completed using geomorphic landform principles (Figure 4). The original surface of the valley fill was level at an elevation of 1693 ft (516 m) and the land-use was specified as pastureland. The GLD surface of the valley fill includes stream channels, ridges, and valleys. The GLD corresponds with government regulations including no flow over the valley-fill face. Features of the GLD included complex slope profiles and a dendritic drainage pattern potentially resulting in improved surface water control and topography creating a natural appearance. The design resulted in $6.7 \times 10^7 \text{ m}^3$ of cut volume and $5.7 \times 10^7 \text{ m}^3$ of fill volume and approximately 8.4 km of stream length.

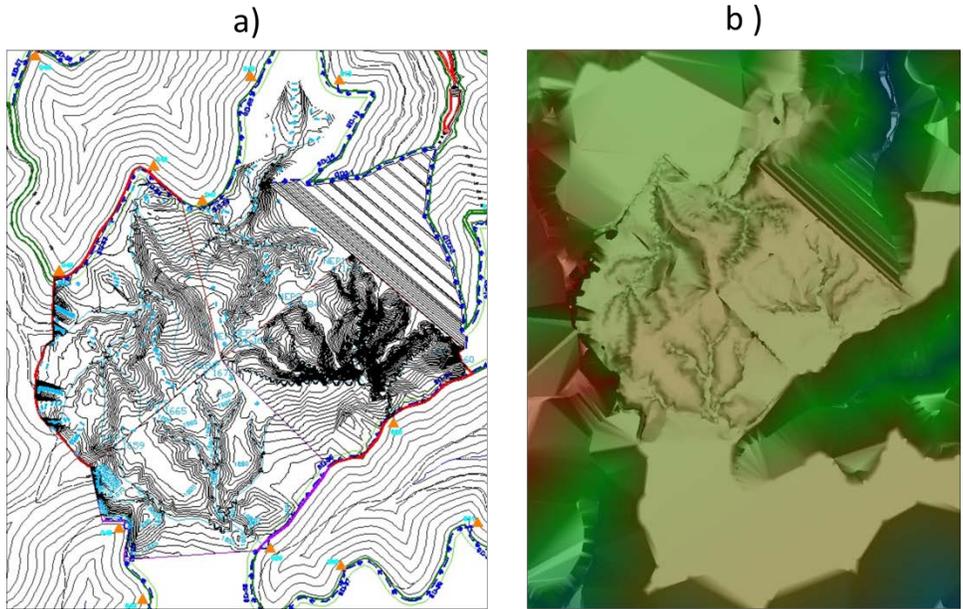


Figure 4. Retrofit design of permitted valley fill in (a) 2D and (b) 3D.

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

Curve Numbers

Curve numbers were calculated for three watersheds in southern WV that had varying levels of mining activity. The watershed data used to calculate the curve numbers of watersheds with active mountaintop removal mining (MTRM) was acquired from stream gage stations maintained by the USGS. Hydrograph data provided by the stream gages were used to calculate the amount of runoff generated by selected 24-hour storm events. The precipitation values of these storm events were acquired from the National Oceanic and Atmospheric Administration (NOAA) website. The values calculated for this research (Table 1) are compared to published values in Table 2.

Table 1: Calculated Curve Numbers (CN) for watersheds with varying degrees of mining

Watershed	Area (mi²)	Description	CN
Panther	31	Undisturbed	65-72
Clear Fork	62.7	7% MTRM	67-81
Laurel Creek	33	9% MTRM	70

Table 2: Curve numbers (CN) for watersheds impacted by MTRM

Reference	Location	Condition	NRCS Reference Condition	CN
Talyor et al., 2009	KY	Reclaimed Mine Site	-	60- 90
Warner et al., 2010	KY	Reclaimed Mine Site	-	62-94
Bonta et al., 1997	OH	Reclaimed Mine Site	-	87-97
Ritter and Gardner, 1991	PA	Reclaimed Mine Site	-	72-89
Permit S-5008-09	WV	Pre-Mining/Undisturbed	Woods – Poor – B	66
-	-	Active mining/not seeded or mulched	Dirt – Poor – B	82
-	-	Reclamation > 5 yrs	Brush/Weed/Grass Mixture – Poor – B	67
-	-	Reclamation < 5 yrs	Pasture – Fair – B	69

Hydrologic Modeling

The objective of this research was to predict the hydrologic response of a mine site reclaimed using geomorphic methods for a location in southern West Virginia. The methods and results are summarized in the following sections.

Methods. Three alternative geomorphic reclamation designs were modeled using Aquaveo's Watershed Modeling System: i) a geomorphic reclamation of the valley fill ("GLD"); ii) a geomorphic reclamation of the valley fill with three detention ponds ("Pond design"; and, iii) a geomorphic retrofit design ("Retrofit"). Results were compared to the response of both the original, undisturbed topography and a conventional valley fill (Figure 5). The peak flowrate, time to peak, and runoff volumes were evaluated at three stages of reclamation (during mining, post-mining (< 5 years), and post-mining (> 5 years)) for a range of storm events (1- through 500-year, 24-hour).

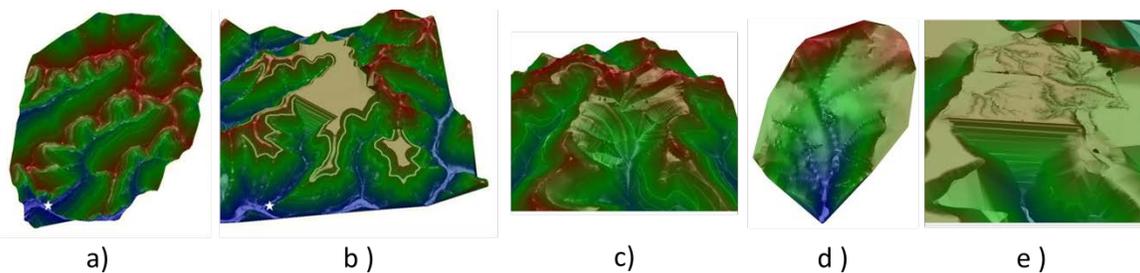


Figure 5. Landforms for hydrologic response comparison: a) undisturbed topography, b) conventional valley fill, c) geomorphic landform design, d) pond design, and e) retrofit design.

Comparison of reclamation designs to the original topography. The GLD for during mining conditions generated higher peak discharge and runoff volume values and lower time of peak values when compared to the original topography (Table 3). During mining conditions resulted in peak discharge values on average 340% higher, average time of peak values 1% lower, and average runoff volume values 140% higher than the original topography (Table 11).

Table 3. Comparison between the hydrologic response of the GLD watershed and the original topography for during mining conditions

Return Period	Peak Discharge (cfs)		Time of Peak (min)		Volume (ft ³)	
	GLD	Original	GLD	Original	GLD	Original
1-year	521	54	732	738	1.82×10 ⁶	4.69×10 ⁵
2-year	686	104	732	738	2.34×10 ⁶	7.34×10 ⁵
5-year	1037	246	732	738	3.43×10 ⁶	1.38×10 ⁶
10-year	1369	398	732	738	4.45×10 ⁶	2.04×10 ⁶
25-year	1725	580	732	738	5.53×10 ⁶	2.79×10 ⁶
50-year	1904	678	732	738	6.08×10 ⁶	3.19×10 ⁶
100-year	2205	849	732	738	6.98×10 ⁶	3.87×10 ⁶
500-year	3,225	1,256	726	738	9.07×10 ⁶	5.45×10 ⁶

The GLD for post-mining conditions generated peak discharge and runoff volume values that closely resembled the values generated by the original watershed (Table 4). When compared to the original, undisturbed watershed, the GLD post-mining values most closely matched the peak discharge values of the original topography with an average peak discharge 2% lower and runoff volume 7% higher than those produced by the original topography (Table 11). Average time of peak values were no different than the values for the original watershed (Table 11).

Table 4: Comparison between the hydrologic response of the GLD watershed and the original topography for post-mining conditions

Return Period	Peak Discharge (cfs)		Time of Peak (min)		Volume (ft ³)	
	GLD	Original	GLD	Original	GLD	Original
1-year	56.7	54	750	738	5.20×10 ⁵	4.69×10 ⁵
2-year	105	104	744	738	8.02×10 ⁵	7.34×10 ⁵
5-year	238	246	744	738	1.47×10 ⁶	1.38×10 ⁶
10-year	372	398	744	738	2.16×10 ⁶	2.04×10 ⁶
25-year	542	580	738	738	2.94×10 ⁶	2.79×10 ⁶
50-year	634	678	738	738	3.35×10 ⁶	3.19×10 ⁶
100-year	795	849	738	738	4.05×10 ⁶	3.87×10 ⁶
500-year	1,383	1,256	732	738	5.71×10 ⁶	5.45×10 ⁶

The detention pond reclamation design generated peak discharge values that more closely resembled the original watershed values than the GLD for during mining conditions (Table 5). Average peak discharge values were 250% higher than the peak discharge values generated by the original watershed for all rainfall return periods (Table 11). The GLD and detention pond design produced similar average runoff values. Both reclamation designs generated 140% more runoff volume than the original topography (Table 11). Average time of peak values were 2% lower for the detention pond design than the original topography (Table 11).

Table 5. Comparison between the hydrologic response of the designed watershed and original topography for during mining conditions

Return Period	Peak Discharge (cfs)		Time of Peak (min)		Volume (ft ³)	
	Detention Pond	Original	Detention Pond	Original	Detention Pond	Original
1-year	440	54	726	738	1.85×10 ⁶	4.69×10 ⁵
2-year	572	104	726	738	2.39×10 ⁶	7.34×10 ⁵
5-year	850	246	726	738	3.52×10 ⁶	1.38×10 ⁶
10-year	1,104	398	726	738	4.58×10 ⁶	2.04×10 ⁶
25-year	1,370	580	726	738	5.69×10 ⁶	2.79×10 ⁶
50-year	1,498	678	726	738	6.25×10 ⁶	3.19×10 ⁶
100-year	1,725	849	726	738	7.19×10 ⁶	3.87×10 ⁶
500-year	2,188	1,256	720	738	9.21×10 ⁶	5.45×10 ⁶

The detention pond design produced lower peak discharge and total runoff volume and higher time of peak values than the original watershed for short-term (< 5 years) post-mining conditions (Table 6). Peak discharge values were, on average, 45% lower than values generated by the original watershed (Table 11). Average time of peak values were 1% higher and total runoff volume was 15% lower than the original watershed (Table 11).

Table 6. Comparison between the hydrologic response of the designed watershed and original topography for short-term, post-mining conditions

Return Period	Peak Discharge (cfs)		Time of Peak (min)		Volume (ft ³)	
	Detention Pond	Original	Detention Pond	Original	Detention Pond	Original
1-year	36	54	756	738	4.54×10 ⁵	4.69×10 ⁵
2-year	63	104	750	738	6.72×10 ⁵	7.34×10 ⁵
5-year	136	246	747	738	1.17×10 ⁶	1.38×10 ⁶
10-year	216	398	747	738	1.70×10 ⁶	2.04×10 ⁶
25-year	308	580	747	738	2.29×10 ⁶	2.79×10 ⁶
50-year	356	678	747	738	2.60×10 ⁶	3.19×10 ⁶
100-year	439	849	747	738	3.13×10 ⁶	3.87×10 ⁶
500-year	625	1,256	744	738	4.32×10 ⁶	5.45×10 ⁶

The detention pond design generated even lower peak discharge and total runoff volume values than those generated by the original watershed for long-term (> 5 years), post-mining conditions (Table 7). Average peak discharge and total runoff volume values were 73% and 44% lower respectively (Table 11). Average time of peak values were 3% greater than time of peak values generated by the original topography (Table 11).

Table 7. Comparison between the hydrologic response of the designed watershed and original topography for long-term, post-mining conditions

Return Period	Peak Discharge (cfs)		Time of Peak (min)		Volume (ft ³)	
	Detention Pond	Original	Detention Pond	Original	Detention Pond	Original
1-year	9	54	777	738	2.35×10 ⁵	4.69×10 ⁵
2-year	20	104	762	738	3.77×10 ⁵	7.34×10 ⁵
5-year	59	246	759	738	7.43×10 ⁵	1.38×10 ⁶
10-year	109	398	756	738	1.15×10 ⁶	2.04×10 ⁶
25-year	173	580	756	738	1.63×10 ⁶	2.79×10 ⁶
50-year	207	678	756	738	1.88×10 ⁶	3.19×10 ⁶
100-year	269	849	753	738	2.33×10 ⁶	3.87×10 ⁶
500-year	412	1,256	753	738	3.37×10 ⁶	5.45×10 ⁶

For during mining conditions, the retrofit reclamation design generated peak discharge, time of peak, and total runoff volume values lower than those generated by the GLD or detention pond design at during mining conditions, but greater than those generated by the original watershed (Table 8). Average peak discharge and total runoff volume values were 117% and 58% greater respectively (Table 11). Average time of peak values were 1% higher than those generated by the original topography.

Table 8. Comparison between the hydrologic response of 2B of the retrofit watershed and original topography for during mining conditions

Return Period	Peak Discharge (cfs)		Time of Peak (min)		Volume (ft ³)	
	Retrofit	Original	Retrofit	Original	Retrofit	Original
1-year	262	54	744	738	1.20×10 ⁶	4.69×10 ⁵
2-year	345	104	744	738	1.55×10 ⁶	7.34×10 ⁵
5-year	521	246	744	738	2.27×10 ⁶	1.38×10 ⁶
10-year	688	398	744	738	2.94×10 ⁶	2.04×10 ⁶
25-year	867	580	744	738	3.66×10 ⁶	2.79×10 ⁶
50-year	957	678	744	738	4.02×10 ⁶	3.19×10 ⁶
100-year	1,108	849	744	738	4.62×10 ⁶	3.87×10 ⁶
500-year	1,434	1,256	744	738	5.91×10 ⁶	5.45×10 ⁶

The short-term (< 5 years), post-mining conditions of the retrofit design produced peak discharge and runoff volume values lower and time of peak values higher than those generated by the original watershed (Table 9). Average peak discharge and total runoff volumes were 46% and 30% lower respectively while average time of peak values were 4% higher than those generated by the original watershed (Table 11).

Table 9. Comparison between the hydrologic response of 2B of the retrofit watershed and original topography for post-mining, short-term conditions

Return Period	Peak Discharge (cfs)		Time of Peak (min)		Volume (ft ³)	
	Retrofit	Original	Retrofit	Original	Retrofit	Original
1-year	33.9	54	780	738	3.40×10 ⁵	4.69×10 ⁵
2-year	61.7	104	768	738	5.25×10 ⁵	7.34×10 ⁵
5-year	141	246	768	738	9.69×10 ⁵	1.38×10 ⁶
10-year	214	398	768	738	1.42×10 ⁶	2.04×10 ⁶
25-year	300	580	768	738	1.94×10 ⁶	2.79×10 ⁶
50-year	346	678	768	738	2.22×10 ⁶	3.19×10 ⁶
100-year	425	849	768	738	2.68×10 ⁶	3.87×10 ⁶
500-year	620	1,256	762	738	3.74×10 ⁶	5.45×10 ⁶

Under long-term (> 5 years), post-mining conditions the retrofit design generated peak discharge and runoff volume values lower than the both the short-term conditions and the original watershed (Table 10). Time of peak values increased with respect to the short-term conditions (Table 10). Average peak discharge and total runoff volume values were 74% and 55% lower respectively and average time of peak values were 4% higher (Table 11).

Table 10. Comparison between the hydrologic response of 2B of the retrofit watershed and original topography for post-mining, long-term conditions

Return Period	Peak Discharge (cfs)		Time of Peak (min)		Volume (ft ³)	
	Retrofit	Original	Retrofit	Original	Retrofit	Original
1-year	8.35	54	792	738	1.48×10 ⁵	4.69×10 ⁵
2-year	19.1	104	780	738	2.69×10 ⁵	7.34×10 ⁵
5-year	59.6	246	780	738	5.90×10 ⁵	1.38×10 ⁶
10-year	112	398	780	738	9.50×10 ⁵	2.04×10 ⁶
25-year	177	580	780	738	1.38×10 ⁶	2.79×10 ⁶
50-year	207	678	780	738	1.60×10 ⁶	3.19×10 ⁶
100-year	261	849	780	738	2.00×10 ⁶	3.87×10 ⁶
500-year	404	1,256	768	738	2.93×10 ⁶	5.45×10 ⁶

Table 11. Average percent difference between original topography at CN=66 and various reclamation designs for peak discharge, time of peak, and total runoff averaged over all rainfall return periods

	Condition	GLD	Detention Pond	Retrofit*
Average Peak Discharge Difference	DM	340%	250%	120%
	SR	-2%	-45%	-46%
	LR	-2%	-73%	-74%
Average Time of Peak Difference	DM	-1%	-2%	1%
	SR	0%	1%	4%
	LR	0%	3%	6%
Average Total Runoff Difference	DM	140%	140%	58%
	SR	7%	-15%	-30%
	LR	7%	-44%	-55%

Note: DM=during mining; SR = short-term reclaimed (< 5 years); LR = long-term reclaimed (>5 years). The retrofit reclamation design has a smaller drainage basin discharging to the outlet than the other two reclamation designs.

These results indicate that the GLD may be the most suitable design for the reclamation of the mountaintop removal mine site being investigated. The detention pond and retrofit design appear to perform better than the GLD for during-mining conditions in regards to peak discharge, however for post-mining conditions the two designs generate both peak discharge and total runoff volumes considerably lower than the original topography.

Comparison of GLD reclamation to conventional reclamation. The during-mining peak discharge values of every reclamation design were much higher than the peak discharge values generated by the conventional design. The GLD generated peak discharge values as much as 3,240% higher than the discharge values generated by the conventional design (Table 12). The retrofit and detention pond designs yielded similar results with peak discharge values 1,579% and 2,721% respectively higher at the 1-year return period (Table 12). The during-mining peak discharge values generated by the alternative reclamation designs more closely resembled the values generated by the conventional design as the rainfall return period increased. Post-mining peak discharge values were closer to the conventional design peak discharge values for each reclamation design. The GLD generated peak discharge values larger than the conventional design for the 1-, 2-, and 5-year return period rainfall event, but at the 10-year and greater return period the GLD generated lower peak discharge values (Table 12). The retrofit and detention pond designs followed similar patterns for the short-term reclamation though they generated lower peak discharge values than the GLD reclamation design (Table 12). Long-term peak discharge values for the retrofit and detention pond design were lower than the conventional design peak discharges for all return periods (Table 12).

Table 12. Percent difference of peak discharge in comparison with the conventional reclamation

Return period (yrs)	Time of Reclamation	GLD (%)	Retrofit (%)	Detention (%)
1	DM	3,240	1,579	2,721
	SR	263	117	131
	LR	263	-46	-42
2	DM	2,274	1,094	1,879
	SR	263	113	118
	LR	263	-34	-31
5	DM	810	357	646
	SR	109	24	19
	LR	109	-48	-48
10	DM	220	61	158
	SR	-13	-50	-50
	LR	-13	-74	-75
25	DM	119	10	74
	SR	-31	-62	-61
	LR	-31	-78	-78
50	DM	103	2	59
	SR	-33	-63	-62
	LR	-33	-78	-78
100	DM	89	-5	48
	SR	-32	-64	-62
	LR	-32	-78	-77
500	DM	98	-12	34
	SR	-15	-62	-62
	LR	-15	-75	-75

Note: DM=during mining; SR = short-term reclaimed (< 5 years); LR = long-term reclaimed (>5 years). The retrofit reclamation design has a smaller drainage basin discharging to the outlet than the other two reclamation designs.

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. 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 was 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 were 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 were 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 6). 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 6). 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 6). 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.

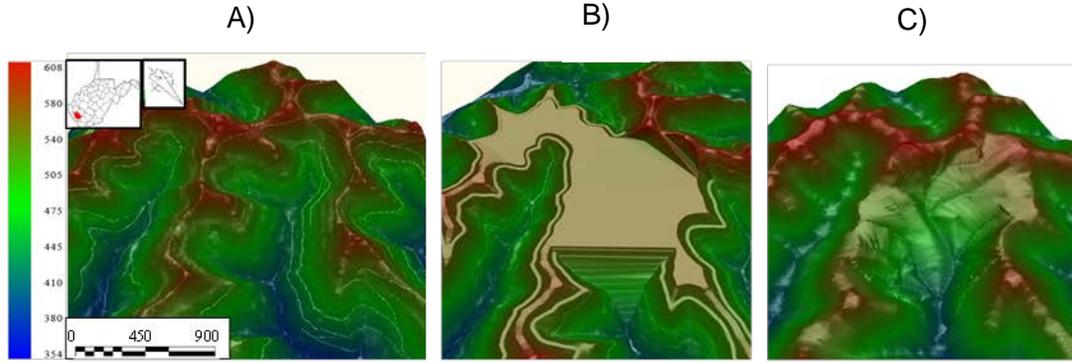


Figure 6. a) Original Topography, b) conventional Fill, c) geomorphic landform design (elevation and scale in m)

Description of Factors. 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 was 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 was 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 were taken from the nearest station (WV465353; Logan, WV; 19 km from study site). Twenty-three years of hourly rainfall data were collected and used for the calculation of MFI and R -factor. The R -factor was 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 ($\text{MJ mm ha}^{-1} \text{ h}^{-1} \text{ year}^{-1}$) 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 was determined based on soil texture, structure, organic matter content, and permeability (Demirci and Karaburun, 2012; Kouli et al., 2009). The K -factor was 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 were estimated using the

soil survey and literature. Soil properties of the spoil were obtained from Russell (2012), where soil classification and analysis were performed on the spoil material at the study site. The soil properties were 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 was calculated by using the following equation in the GIS environment:

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

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 were 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 was 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 was equal to one for this study for all modeling scenarios.

Results

Undisturbed, Pre-Mining Conditions. The undisturbed, pre-mining condition resulted in an estimated average annual soil loss rate (*A*) of 35.4 t ha⁻¹ yr⁻¹ (Figure 7) The lowest erosion rates (<20 t ha⁻¹ yr⁻¹) occurred along ridgelines, following the location patterns of the low *LS*-factor values. The highest soil loss rates (>50 t ha⁻¹ yr⁻¹; maximum of 1,654.3 t ha⁻¹ yr⁻¹) mimicked the highest *LS*-factor locations along the stream channels and valleys. The undisturbed area had approximately 4480 m of ridgelines (35-1,240 m range) and 6210 m of valleys/channels (35-860 m range) identified in the *LS*-factor and soil loss rate distributions.

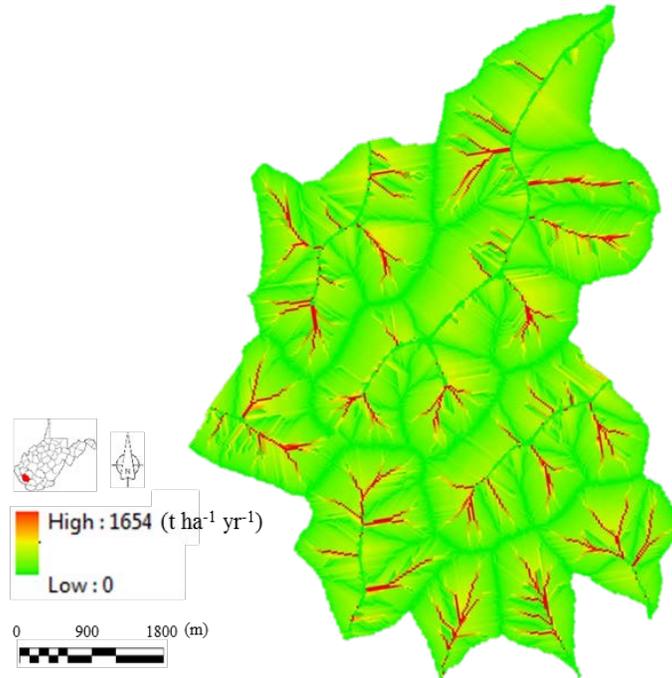


Figure 7. Average annual soil loss rate (A) for the undisturbed, pre-mining condition of the experimental watershed

Conventional Valley Fill Post-Mining, Pre-Vegetation Condition. The study site as the conventional valley fill post-mining, pre-vegetation condition had an estimated A of $123.2 \text{ t ha}^{-1} \text{ yr}^{-1}$ (standard deviation of $726.9 \text{ t ha}^{-1} \text{ yr}^{-1}$). Low soil loss rates ($<30 \text{ t ha}^{-1} \text{ yr}^{-1}$) occurred along the ridgelines and the valley-fill crest. The highest erosion rates ($>100 \text{ t ha}^{-1} \text{ yr}^{-1}$; maximum of $47,538.7 \text{ t ha}^{-1} \text{ yr}^{-1}$) were estimated to be at the entire valley-fill face, Surface Water Run-Off Analysis (SWROA) ditch locations, and highwall locations (Figure 8). The area surrounding the conventional fill had approximately 2,475 m of ridgelines (35-450 m range) and 4,950 m of valleys/channels (30-435 m range) identified in the LS-factor and soil loss rate distributions. The conventional fill area had 3,109 m of SWROA ditches along the perimeter of the fill, and the area did not have any ridgelines.

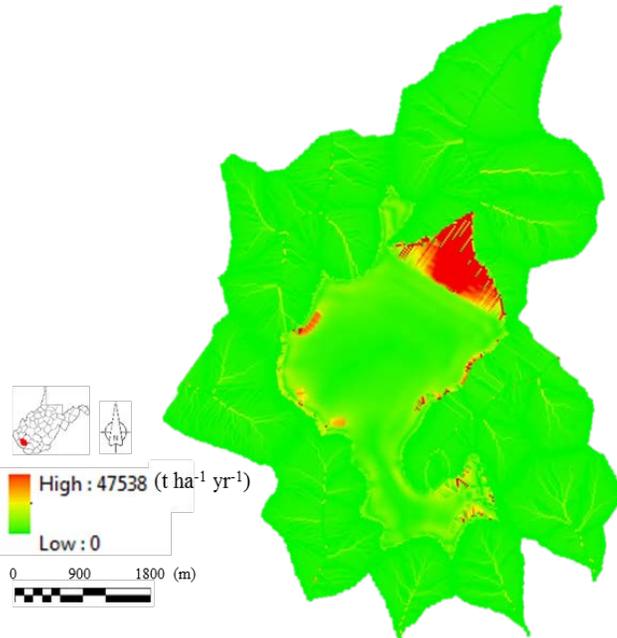


Figure 8. Average annual soil loss rate (A) for the conventional valley fill, pre-vegetation condition of the experimental watershed

Conventional Valley Fill Post-Reclamation, Long Term Condition Results. The conventional valley fill post-mining, long term condition resulted in a predicted A of $35.6 \text{ t ha}^{-1} \text{ yr}^{-1}$ with a standard deviation of $89.7 \text{ t ha}^{-1} \text{ yr}^{-1}$. Low erosion rates ($<30 \text{ t ha}^{-1} \text{ yr}^{-1}$) occurred along the ridgelines and the valley-fill crest, which mimicked the low soil loss locations in the conventional valley fill, pre-vegetation condition. The highest soil loss rates ($>50 \text{ t ha}^{-1} \text{ yr}^{-1}$; maximum of $4,627.7 \text{ t ha}^{-1} \text{ yr}^{-1}$) were estimated to be at the entire valley-fill face, SWROA ditches, highwalls, and stream channels (Figure 9).

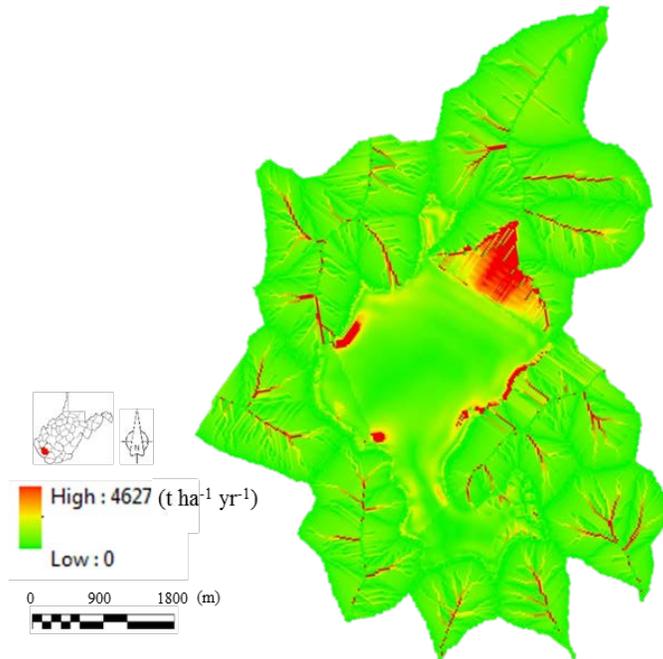


Figure 9. Average annual soil loss rate (A) for the conventional valley fill, post-reclamation, long term condition of the watershed

Groundwater Modeling

Three-dimensional groundwater and contaminant transport was modeled for reclamation alternatives of a valley fill. The objective of groundwater modeling was 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 was 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 were obtained from reclamation alternatives for a southern WV valley fill (Figure 10). The pre-mining undisturbed valley was used as the lower boundary of the models. The existing conventional reclamation plan was used for the surface geometry of the conventional valley fill. The geometry of the geomorphic fill was taken from a conceptual design that has been generated as an alternative to the existing valley fill. 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).

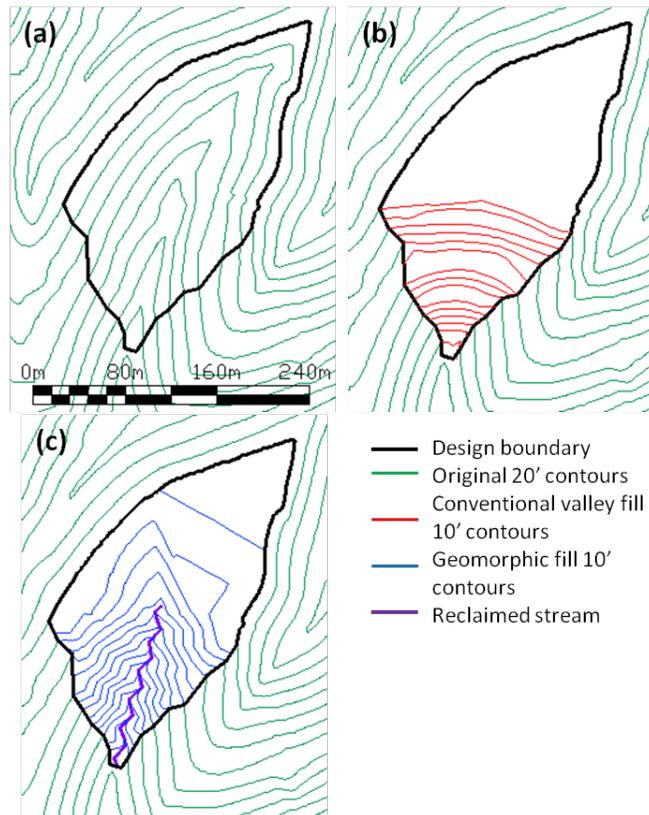


Figure 10. Contours used for geometry of model: (a) original valley; (b) conventional valley fill reclamation; and (c) geomorphic design.

Groundwater was 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 were collected from soil testing and literature. 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) estimation of the permeability function. Hydrologic data were 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 was a function of landform slope/shape and surface properties. The conventional fill experienced 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 varied by location based on slope. The portion of the geomorphic fill covered by the recreated stream was modeled with a low infiltration capacity to promote surface flow. Over time, the following groundwater properties were documented: infiltration volume, storage volume, discharge rate and volume, groundwater flux rate, degree of saturation, pore-water pressure, and total head.

Due to limitations in the modeling software, contaminant transport was 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 were taken from soil testing data. Over time, the volume of water that travelled through and discharged from each fill was 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 was selenium release over time from fill alternatives.

Results

Groundwater. The steady-state, three-dimensional geomorphic groundwater model exhibited lower normalized infiltration volume than the conventional fill (23% reduction), lower normalized discharge rate (11% reduction), and comparable degree of saturation (1.7% increase). Saturated thicknesses were small, and the majority of flow was through unsaturated blasted rock (Figure 11).

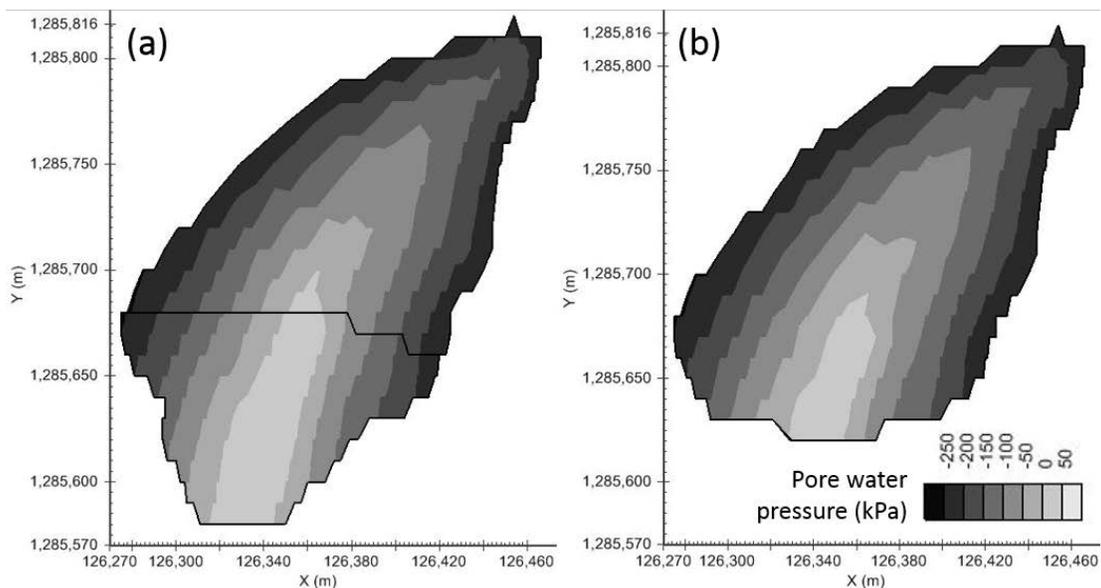


Figure 11. Pore pressure distribution in three-dimensional models of reclamation alternatives: (a) conventional fill; and, (b) geomorphic fill. Lightest shade in distribution corresponds to positive pore pressure (location of groundwater table).

The transient geomorphic groundwater model exhibited reductions in infiltration volume, discharge rate and volume, and difference between infiltration and discharge volumes as compared to the conventional fill (Table 13). The most significant reduction was in the difference between infiltration and discharge volumes. Reducing the magnitude by which infiltration volume exceeded discharge volume resulted in a condition with reduced groundwater contact time with internal fill materials.

Table 13. Normalized percent change in three-dimensional transient groundwater modeling results from conventional fill to geomorphic fill: volume of infiltrating water (V_i), instantaneous flow rate at toe (Q_t), cumulative volume of water that has discharged

through toe (V_o), total volume of water in fill (V_w), and difference in infiltration and discharge volumes ($V_i - V_o$).

Time (d)	5	180	365	1460	3650
V_i (m^3)	-23	-23	-23	-23	-23
Q_i (m^3/d)	-14	-25	-22	-28	-28
V_o (m^3)	-12	-21	-23	-26	-27
V_w (m^3)	-0.9	-4.0	-2.4	-1.3	-1.3
$V_i - V_o$ (m^3)	-88	-68	-60	-48	-44

The geomorphic model exhibited shorter residences times for groundwater that affected larger fill volumes (Figure 12). Groundwater contacting large fill volumes required approximately twice as long to travel through and discharge from the conventional fill. The conventional fill exhibited a consistent increase in the volume of fill contacted by discharging water over time due to the steady infiltration and discharge of groundwater flow paths; the amount of time needed for a flow path to travel through the fill and discharge through the toe steadily increased with increased distance between the infiltration point and the toe. The geomorphic fill exhibited an initial sharper increase in fill volume contacted by discharging water, followed by a shallower, steady increase. The sharp increase was due to longer flow paths associated with larger fill volumes traveling through the fill and discharging from the toe at a faster rate than the conventional fill. Differences in fill volume contacted by water over time are tabulated can be found in DePriest (2015).

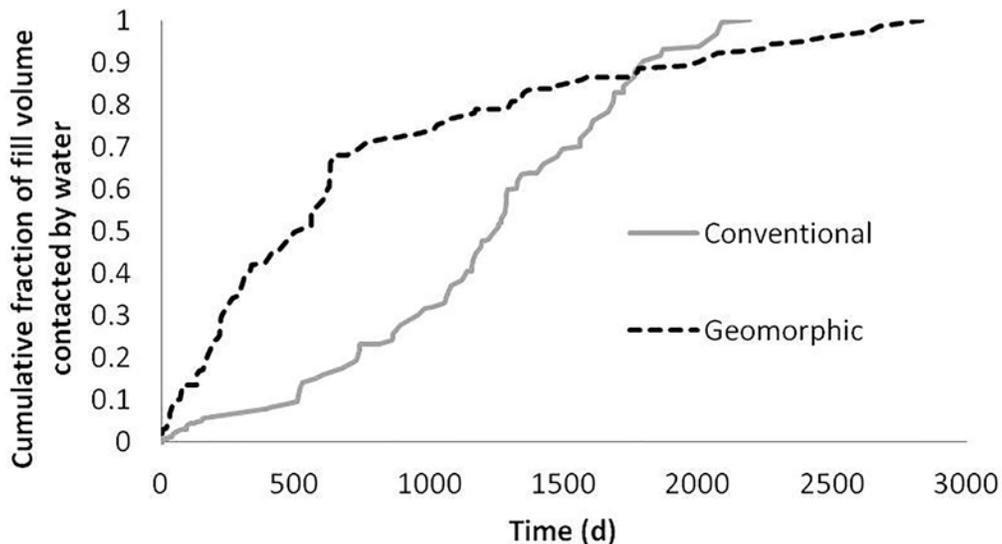


Figure 12. Cumulative fraction of three-dimensional fill volume contacted by discharging water over time in fill alternatives.

Calculation for Desorbed Se Mass. Desorption of Se based on three-dimensional groundwater models is shown in Table 13, Figure 13, and Figure 14. Se desorption was reduced in the geomorphic fill, and the highest desorption of Se occurred in the first few passes of water. A slight increase in Se desorption occurred after the ninth pass through, and was attributed to the slight increase in Se desorption in the laboratory study (Hopkinson et al., 2015). In general, Se desorbed from reclamation alternatives decreased in correspondence with decreased Se desorption rates in a laboratory study (Hopkinson et al., 2014).

The reduction in Se desorption for the geomorphic fill can be directly attributed to two characteristics of geomorphic reclamation apparent from groundwater modeling: decreased infiltration and decreased groundwater residence time. Decreased infiltration and groundwater residence times were possible through the application of geomorphic slopes to the entire fill surface and minimal construction of shallow sloping, high infiltration areas.

Table 14. Percent change in normalized selenium desorption in three-dimensional model of geomorphic fill compared to conventional fill as a result of consecutive passes of water, both individually and cumulatively.

Pass through	Normalized desorbed Se		Percent change (%)	
	Conventional	Geomorphic	Individual	Cumulative
1	0.02190	0.01344	-38.6	-38.6
2	0.02520	0.01546	-38.7	-38.6
3	0.01717	0.01053	-38.7	-38.6
4	0.01616	0.00991	-38.7	-38.7
5	0.01077	0.00660	-38.7	-38.7
6	0.00437	0.00268	-38.7	-38.7
7	0.00414	0.00254	-38.7	-38.7
8	0.00392	0.00240	-38.7	-38.7
9	0.00695	0.00426	-38.7	-38.7
10	0.00695	0.00426	-38.7	-38.7
11	0.00555	0.00340	-38.7	-38.7
12	0.00545	0.00334	-38.7	-38.7
13	0.00589	0.00361	-38.6	-38.7
14	0.00484	0.00297	-38.6	-38.7

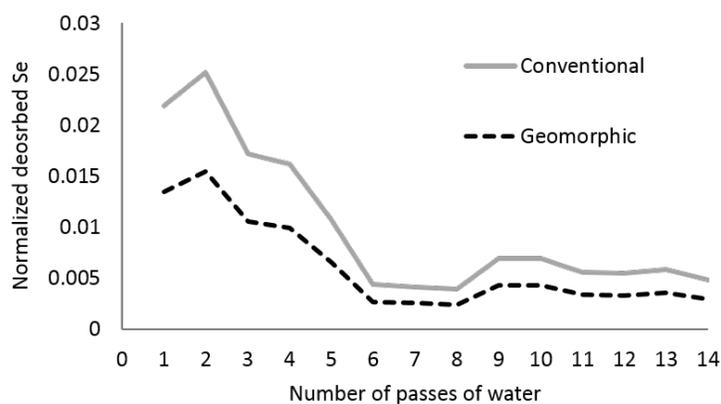


Figure 13. Normalized desorption of selenium from individual passes of water assuming passes occur in succession in three-dimensional models of reclamation alternatives.

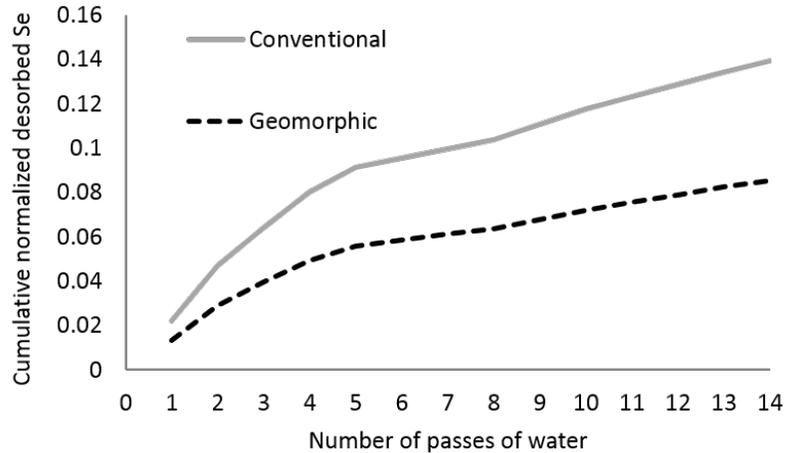


Figure 14. Cumulative normalized desorbed selenium from consecutive passes of water in three-dimensional models or reclamation alternatives.

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

The objective of this portion of the work was to evaluate the extent of downstream flooding related to geomorphic reclamation. 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 14. Modeled inundation areas and flood depths are shown in Figures 15-18.

Table 15: 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 15: Pre-Mining 2-yr unsteady max water level flood extents and depth



Figure 16: Pre-Mining 50-yr unsteady maximum water level flood extents and depth



Figure 17: Pre-Mining 100-yr unsteady maximum water level flood extents and depth



Figure 18: 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 16 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, 410, 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 19-22).

Table 16: 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 19: Conventional 2-yr maximum unsteady flood extents and depth



Figure 20: Conventional 50-yr maximum unsteady flood extents and depth



Figure 21: Conventional 100-yr maximum unsteady flood extents and depth



Figure 22: 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 17 and Figures 23-26. 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 17: 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 23: GLD (During mining) 2-yr maximum unsteady flood extents and depth



Figure 24: GLD (During mining) 50-yr maximum unsteady flood extents and depth



Figure 25: GLD (During mining) 100-yr maximum unsteady flood extents and depth



Figure 26: 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 18 and Figures 27-30. 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 18: 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 27: GLD (Post-mining) 2-yr maximum unsteady flood extents and depth



Figure 28: GLD (Post-mining) 50-yr maximum unsteady flood extents and depth



Figure 29: GLD (Post-mining) 100-yr maximum unsteady flood extents and depth



Figure 30: 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 31).

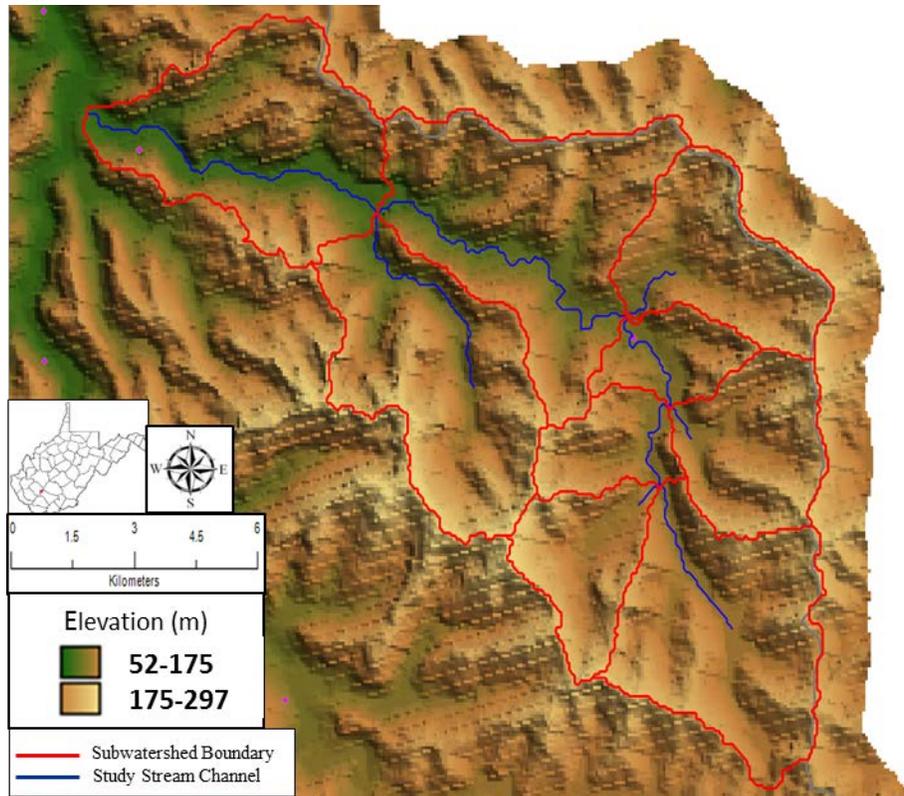


Figure 31. Study Area with Delineated Watershed

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.

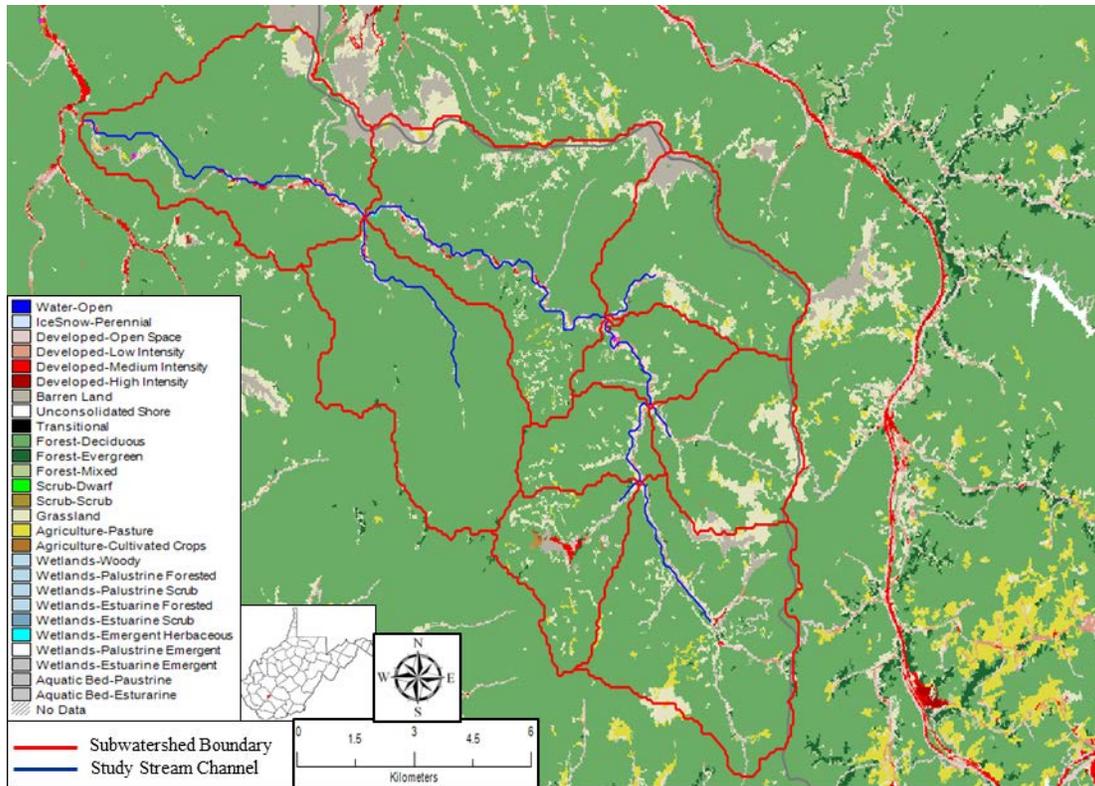


Figure 32. Study Area with 2001 Land Use

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 19). 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 19. 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 20.9 km 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 20) 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, 61 km from the study watershed. However, calibration errors exceeded allowances, except for the total flow error (Table 20). 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 20).

Table 20. 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 21). 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 20.9 km away from meteorological station, and

HSPF relying heavily on calibration (Brun and Band, 2000; Ferrari et al., 2009). The validation model was accepted.

Table 21. 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).

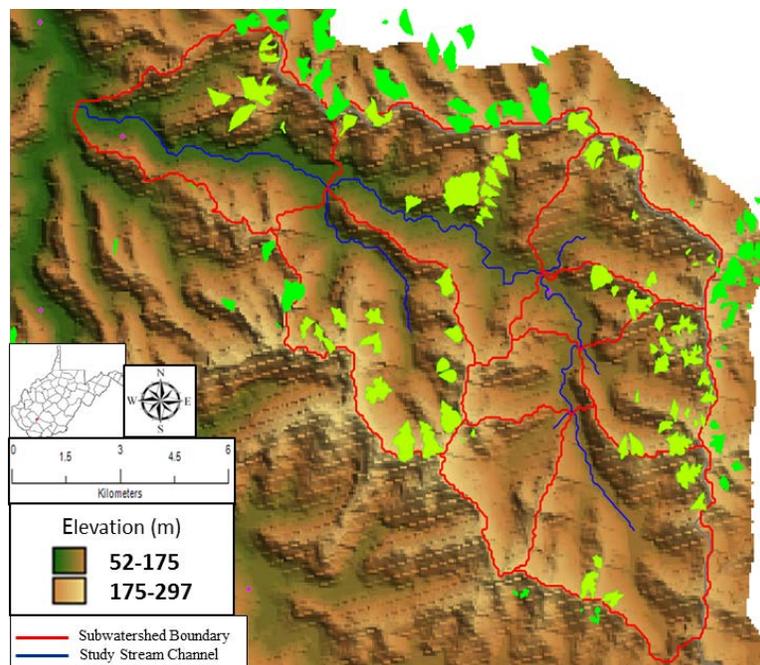


Figure 33. Study Subwatersheds with Elevation and 2014 Valley Fills (Inside of Watershed in Yellow and Outside of Watershed in Green)

Table 22. 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=Geomorphoc Landform Design

Results

The HSPF model predicted the hydrologic impact of altering the traditional valley-fill reclamation to the innovative geomorphic landform reclamation approach. Five hydrologic response prediction simulations were completed, i) current hydrologic response given conventionally reclaimed valley fills; ii) current hydrologic response given GLD valley fills; iii) future hydrologic response given conventionally reclaimed valley fills; iv) future hydrologic response given GLD valley fills; and v) future hydrologic response given no land disturbance occurred in the watershed (Table 22), and the results were compared based on reclamation type and time frame.

HSPF Prediction Model Results: Predictions 1 and 2. Model simulations 1 and 2 predicted the current hydrologic responses within the study watershed for GLD valley-fill reclamation and traditional reclamation methods (Figure 34). Results indicated no substantial difference (<1.1% difference) in daily flow or volume when the two valley-fill reclamation techniques were compared. The total flow, lowest 50% flow, highest 10% flow, mean storm volume, and mean storm peak flow were lower (-0.27% to -1.10% difference) for the watershed when geomorphic valley-fill reclamation was modeled as opposed to conventional valley-fill reclamation (Table 23).

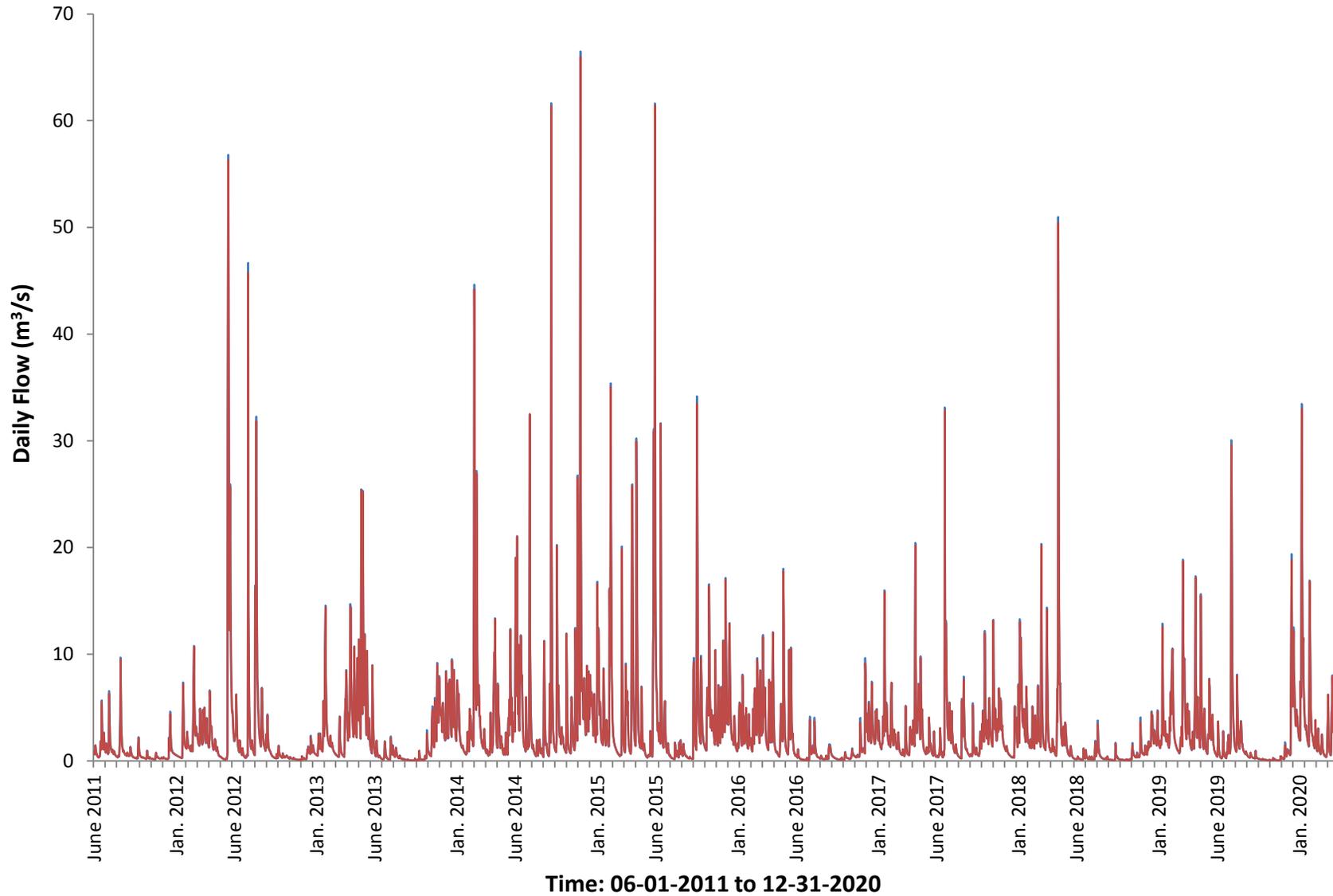


Figure 34. Model predictions 1 and 2 daily flow comparison for 2011-2020 (traditional flow in blue and GLD flow in red)

Table 23. Model predictions 1 (traditional) and 2 (GLD) comparison

Prediction Criteria	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: $D\% = (X_{1,Trad} - X_{2,GLD}) / X_{2,GLD}$; where $X_{1,Trad}$ = variable from simulation 1; $X_{2,GLD}$ = variable from simulation 2

Flood frequency analysis was performed for the prediction scenarios compared to the observed values. Predicted annual peak stormflow values, from daily flow data, were used to predict the same year stormflows for model predictions 1 and 2. No substantial difference (0-18 m³/s) resulted among the traditional and GLD predicted 5-, 10-, 25-, and 50-yr stormflows. However, the GLD 100- and 200-yr stormsflows were substantial higher than the traditional stormflows (100-yr: 90.1 m³/s difference; 200-yr: 368.1 m³/s difference). Flood discharge trends were similar for the observed, current traditional, and current GLD simulations (Figure 35).

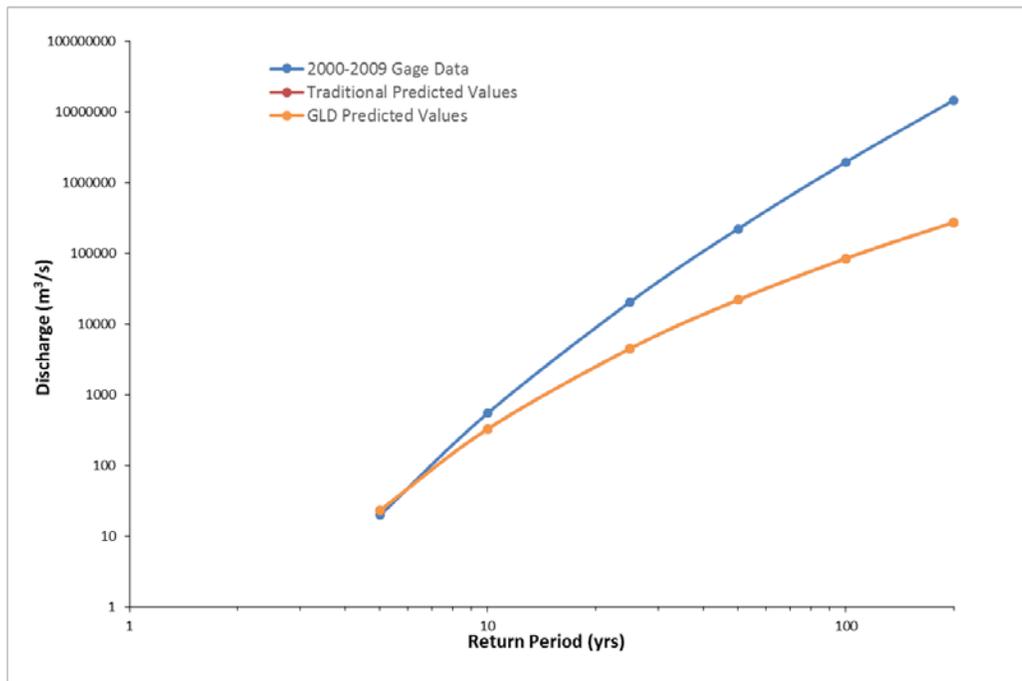


Figure 35. Flood frequency analysis for Clear Fork watershed using log-Pearson type III analysis using observed, current traditional predicted, and current GLD predicted annual peak stormflow values (log-log scale)

HSPF Prediction Model Results: Predictions 3, 4, and 5. Prediction simulations 3 and 4 estimated the future hydrologic responses within the experimental watershed with conventional and GLD valley-fill reclamation. Model predictions 3 and 4 resulted in no substantial difference in daily flow or volume (Figure 36). Total flow, lowest 50% flow, highest 10% flow, mean storm volume, and mean storm peak flow decreased (-0.34% to -3.33% difference) for the geomorphic valley-fill reclamation compared to the traditional valley-fill reclamation (Table 24). Prediction simulations 3 and 4, resulted in larger differences (-0.34% to -3.33% difference) in flow and volume compared to prediction simulations 1 and 2, percent differences (-0.27% to -1.1% difference).

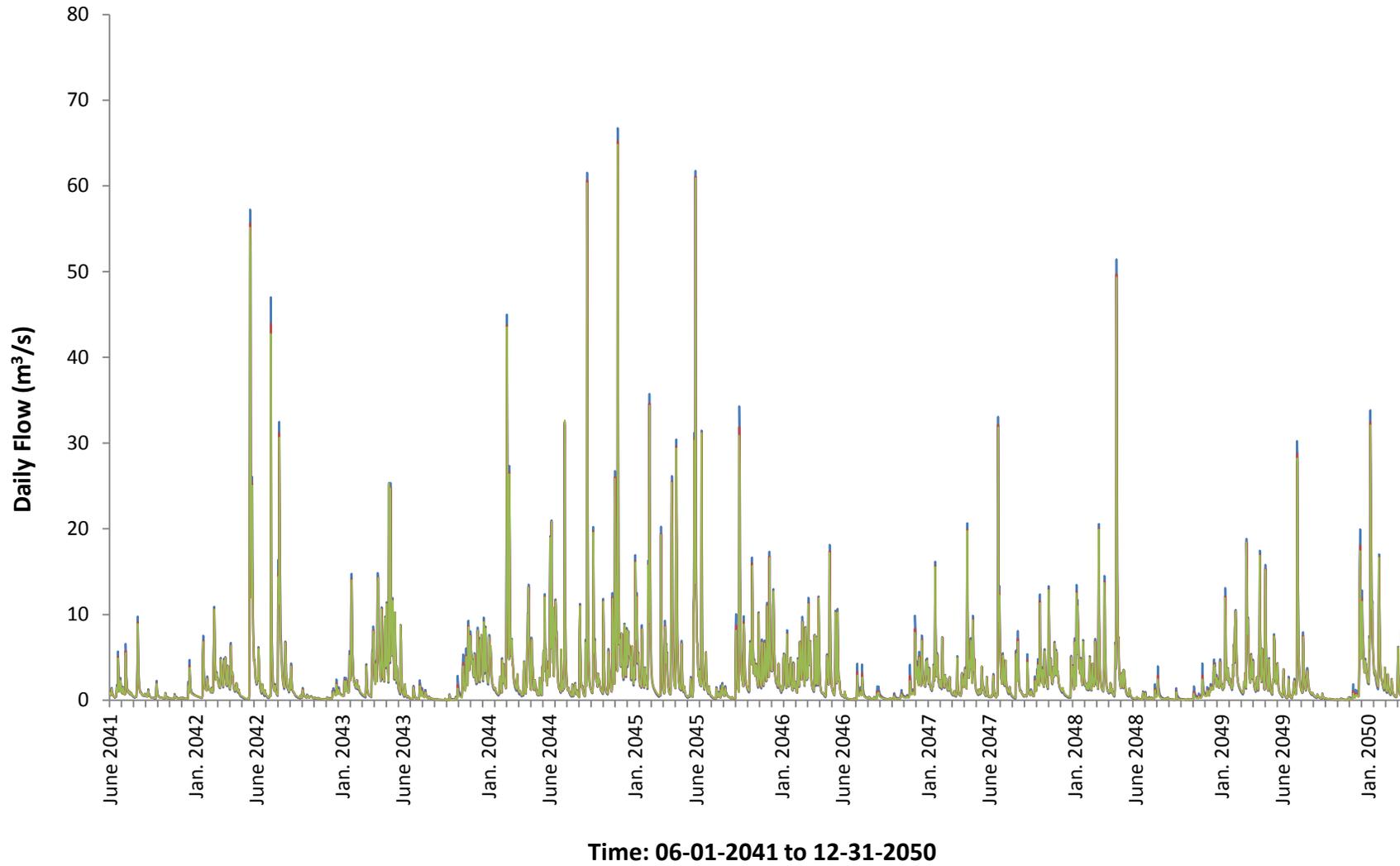


Figure 36. Model predictions 3, 4 and 5 daily flow comparison for 2041-2050 (traditional flow in blue, GLD flow in red, and NLD flow in green)

Table 24. Model predictions 3 (traditional) and 4 (GLD) comparison

Prediction Criteria	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: $D\% = (X_{3,Trad} - X_{4,GLD}) / X_{4,GLD}$; where $X_{3,Trad}$ = variable from simulation 3; $X_{4,GLD}$ = variable from simulation 4

Flood frequency analysis was performed using log-Pearson type III analysis for the observed model and model predictions 3 (traditional), 4 (GLD), and 5 (NLD). Observed annual peak stormflow values, using daily flow data, were used to determine 5-, 10-, 25-, 50-, 100-, and 200-year stormflows for the experimental watershed. Predicted annual peak stormflow values were used to predict the stormflows for model predictions 3, 4, and 5. The predicted 100- and 200-yr stormflows for the traditional, GLD, and NLD scenarios varied substantially. The 100-yr GLD stormflow was 5,003 m³/s greater than the 100-yr traditional stormflow and 4,969 m³/s less than the 100-yr NLD stormflow. The 100-yr GLD stormflow was 20,852 m³/s greater than the 100-yr traditional stormflow and 20,993 m³/s less than the 100-yr NLD stormflow. Flood frequency trends were similar for the observed, future traditional, future GLD, and future NLD simulations (Figure 37).

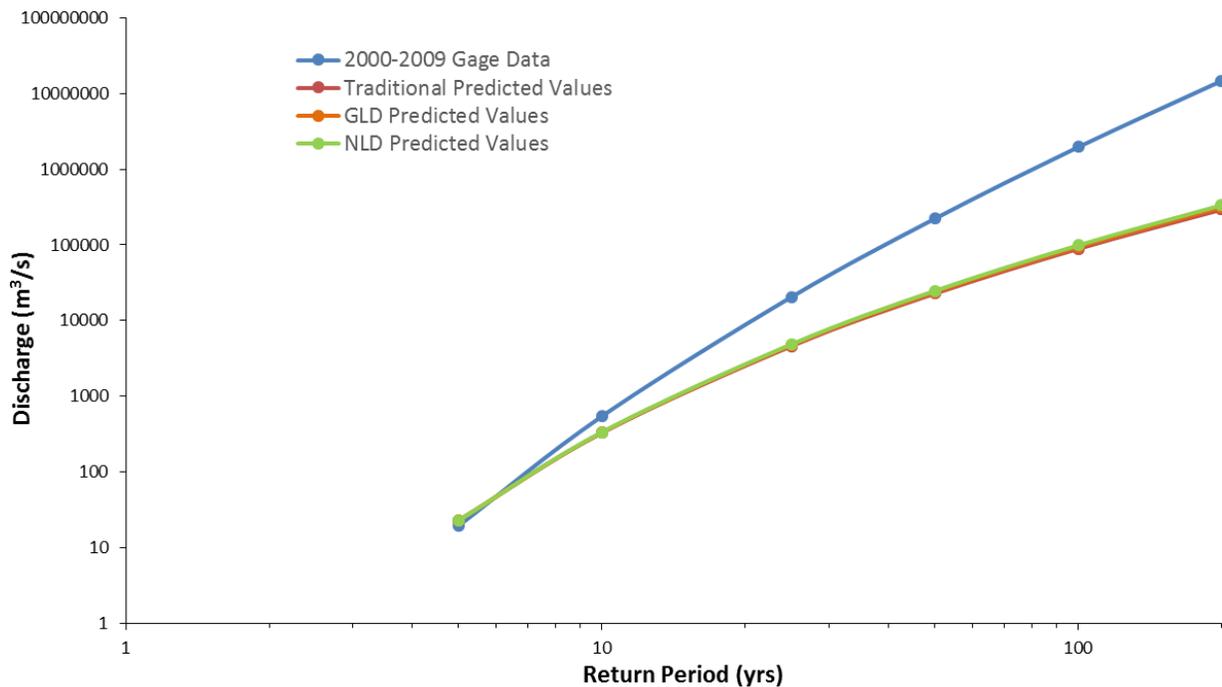


Figure 37. Flood frequency analysis for Clear Fork watershed using log-Pearson type III analysis using observed, future traditional predicted, future GLD predicted, and future NLD predicted annual peak stormflow values (log-log scale)

Prediction simulations 3 and 5 resulted in similar future hydrologic responses within the study watershed for conventional valley-fill reclamation compared to the no land disturbance (NLD) simulation (Figure 36). The total flow, lowest 50% flow, highest 10% flow, mean storm volume, and mean storm peak flow were higher for the watershed when conventional valley-fill reclamation was modeled as opposed to no land disturbance (0.32% to -4.36% difference; Table 25).

Table 25. Model predictions 3 (traditional) and 5 (no land disturbance) comparison

Prediction Criteria	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: $D\% = (X_{3,Trad} - X_{5,NLD}) / X_{5,NLD}$; where $X_{3,Trad}$ = variable from simulation 3; $X_{5,NLD}$ = variable from simulation 5

A comparison of prediction simulations 4 and 5 showed the future hydrologic impact was similar for the valley fills reclaimed using geomorphic reclamation methods compared to the no land disturbance simulation (Figure 36). The total flow, highest 10% flow, mean storm volume, and mean storm peak flow were higher for the watershed when geomorphic valley-fill reclamation was modeled as opposed to if no land disturbance had occurred in the watershed (0.51% to 0.89% difference). The lowest 50% flow was lower for the geomorphic valley-fill model compared to the no land disturbance model (-0.03% difference; Table 26).

Table 26. Model predictions 4 (GLD) and 5 (No Land Disturbance) comparison

Prediction Criteria	GLD vs NLD
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: $D\% = (X_{4,GLD} - X_{5,NLD}) / X_{5,NLD}$; where $X_{4,GLD}$ = variable from simulation 4; $X_{5,NLD}$ = variable from simulation 5

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2. Publications

Journal Articles (*graduate student)

1. Sears*, A., L. Hopkinson, and J. Quaranta. Predicting erosion at valley fills with multiple reclamation techniques in mountainous terrain. Paper to be resubmitted for peer-review in May 2016.
2. DePriest*, N.C., Hopkinson, L.C., and Quaranta, J.D. Three-dimensional modeling of unsaturated groundwater seepage and selenium desorption in blasted rock fills of central Appalachia, USA implementing alternative surface reclamation techniques. *Geotechnical and Geological Engineering*. (Accepted)
3. Hopkinson, L. Sears*, A.E., Snyder*, M., O'Leary*, E., DePriest*, N., Quaranta, J., and Ziemkiewicz, P. 2015. Simulating the hydrologic response when streams are incorporated in valley fill design. *Journal of Mining, Reclamation, and Environment*. doi: 10.1080/17480930.2015.1105180.

Conference Proceedings

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.
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)

Theses and Dissertations

1. Sears, A. 2015. Hydrologic response and erosion modeling of geomorphic landform reclamation designs in mountainous terrain. PhD Dissertation. Civil and Environmental Engineering Department West Virginia University.
2. DePriest, N.C. 2015. Chapter 5: Groundwater modeling and selenium desorption comparison of geomorphic and conventional valley fill alternatives. In, Assessing geomorphic landform design as an alternative for conventional valley fill surface mine reclamation. PhD Dissertation. 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.
4. Snyder, M.W. 2013. Hydrologic response of alternative valley fill reclamation design. MS Thesis. Civil and Environmental Engineering Department: West Virginia University.

3. Information Transfer Program

Oral Presentations

1. **Hopkinson, L.** and **J. Quaranta.** 2016. Geomorphic design. WVDEP-AML & Special Reclamation Training. January 12-14. Stonewall Resort: Roanoke, WV. (*invited*)
2. **Snyder, M.***, and L. Hopkinson. 2013. The hydrologic response of valley fills with alternative reclamation methods. 88th Annual West Virginia Academy of Science Meeting, April 6. Canaan Valley Institute: Davis, WV.

Poster Presentations (*Graduate student, **Undergraduate 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.
2. **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.
3. **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.
4. **O’Leary, E.***, Hopkinson, L. 2014. Floodplain mapping in response to surface mine reclamation. Environmental Connection 2014. International Erosion Control Association Annual Conference, Nashville, TN. Feb. 23-28, 2014.
5. **Sears, A.***, Hopkinson, L., Quaranta, J., and Bise, C. 2013. Enhanced surface mine reclamation using geomorphic landform principles. American Geophysical Union Fall Meeting. December 9-13. Moscone Center: San Francisco, CA. (published abstract)

Project listed on WVVRI website (<http://wwwri.org>)

4. Student Support

- Four graduate students have worked on research related to this project: Alison Sears (PhD, graduated December 2015), Nathan DePriest (PhD, graduated December 2015), Mike Snyder (MS, graduated December 2013), Erin O’Leary (MS, graduated December 2014).

Category	Number of students supported with USGS base grant	Number of students supported with matching funds	Total number of students supported
Masters	2	2	2
Ph.D.	2	2	2
Total	4	4	4

- Two undergraduate students completed a research course for three hours of credit (CE 497 Civil Engineering Research Projects for Undergraduates). The semester-long research projects were related to this work.

CE 497, Students Supervised:

	Name	Major	Semester	Topic
1	H. Billian	CEE	S14	Erosion on reclaimed surface mine sites
2	C. Snyder	CEE	S14	Pond design for stormwater control

5. Student Internship Program

NA

6. Notable Achievements and Awards.

The following achievements were completed:

- Two graduate students graduated with PhDs in December 2015.
- One graduate student graduated with a MS in December 2014.
- One graduate student graduated with a MS in December 2013.
- Three graduate students presented results at professional meetings
- Two undergraduate students presented results at a professional meeting.
- Two undergraduate students completed a research course related to this work.
- MS student, Erin O'Leary, was selected as a student moderator for an international conference:
 - Erin O'Leary, Student Moderator, International Erosion Control Association (IECA) 2014 Environmental Connection Conference, February 25-28, 2014, Nashville, TN. (awarded travel and registration costs)
- PhD student, Alison Sears, won a Student Research Enhancement Award to present at an international, professional meeting:
 - Alison Sears, 2013. Student Research Enhancement Award, "Improvement of Water Supply on Reclaimed Appalachian Surface Mine Sites", 2013-2014 Student Research Enhancement Award, WVU Women in Science and Engineering (WiSE), \$1,250.

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:	2/28/2016
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

Final Report:
March 1, 2014-May 20, 2016

Principal Authors:
Y. Thomas He

Submission Date:
May 20, 2016

USGS Award #:
2014WV212B

Submitted by:
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Abstract

Bromide (Br) contamination is a relatively new water quality issue in West Virginia. Potential sources of elevated bromide that could impact Br concentration include agricultural runoff, coal mining, shale gas development, or other human activities. It is important to identify the origin of bromide in drinking water sources since the inability to identify contamination sources limits our ability to effect appropriate control measures.

This study examined chemical signatures that can be used as a diagnostic tool to identify origins of bromide sources. Water chemistry data from shale gas flowback, produced water from conventional hydrocarbon development, formation brine, produced water from coal bed methane, coal mine drainage from surface and deep mines, a large river and one of its tributaries were examined. The results show a generally linear Br versus Cl relationship, and with Br versus Cl concentrations of different sources clustering at different concentration ranges. The range of Br/Cl ratio is large within individual water sources, but the difference among different water sources is relatively small and stays in a narrow range. The range of SO_4/Cl versus Br is large and widely spread within individual water sources. The SO_4/Cl versus Br relationship can be classified into two groups. Oil and gas related produced waters generally have low SO_4/Cl ratio, and coal mining related wastewaters generally have high SO_4/Cl ratio. TDS in examined water sources generally increases as Br concentration increases. Concentration of Na is strongly correlated with Br across all water sources examined. The concentration of Na also increases as Br concentration increases. In uncontaminated surface water, the correlation between Na and Br is weak due to very low Br concentrations. Geochemical modeling showed a linear increase of Br concentration through mixing as the percentage of wastewater increased in the receiving streams.

The Br-Cl and Na-Br relationship could be useful in identifying Br sources. The SO_4/Cl versus Br relationship may have limited use in differentiating coal related wastewater sources from oil and gas associated wastewaters. Other chemical signatures did not show a clear and/or consistent relationship with Br concentration, and are not likely to be useful as diagnostic tools for identifying bromide sources.

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Executive Summary

Bromide contamination 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) formed by chlorination or bromination of methane compounds. 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 in the Appalachian region include agricultural runoff, coal mine water, hydrocarbon formation waters, or flowback and produced water from shale gas development. Identification of bromide sources in water may allow for the development of appropriate control measures.

In this study, we examined the water chemistry data of waste streams from the hydrocarbon extraction (shale gas, conventional oil and gas, coal bed methane) and coal mining industries. We also examined water chemistry of receiving streams in the Appalachian region. Based on literature review, a range of chemical signatures (including Cl, Br, Cl/Br, Cl/Br versus Br, Cl/Br versus Cl, SO_4/Cl versus Br, SO_4/Br versus Cl, Na, Ca, Ba and Sr versus Br, *etc.*) were screened and examined for their relationship to Br concentration. Geochemical modeling was used to simulate how the waste streams may impact the Br concentration and water quality in the receiving streams.

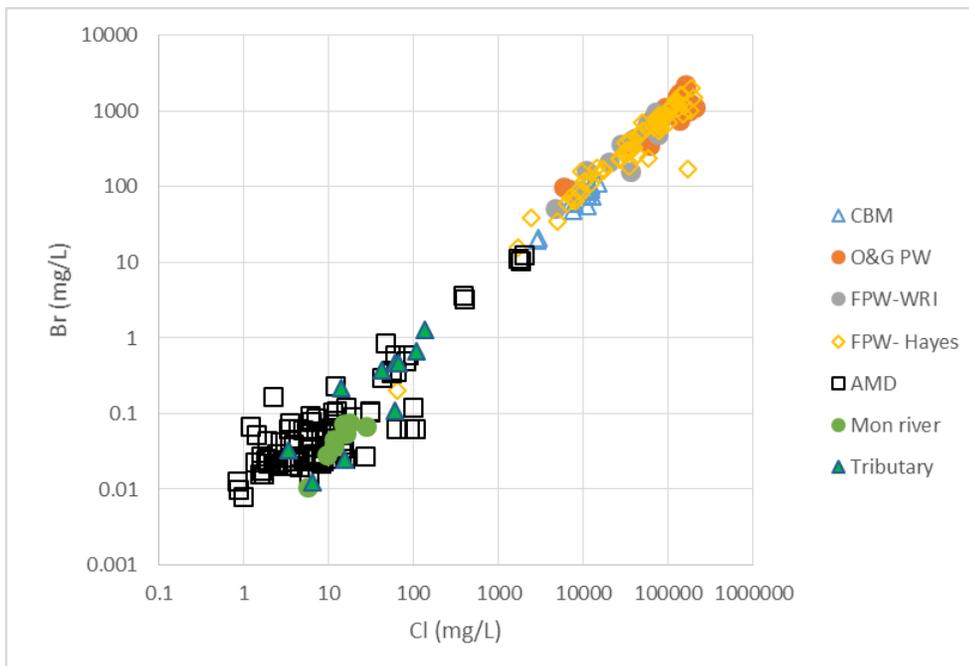


Figure 1. Log $[\text{Br}^-]$ versus log $[\text{Cl}^-]$ in water from different sources.

We found a generally linear relationship between Cl versus Br in waters from different sources. Linear correlation for Br versus Cl spans across eight orders of concentration range in both bromide and chloride among the water sources. However, different water sources tend to cluster at different spaces in the Br-Cl plot (Figure 1). The range of Br/Cl ratio is large within individual water sources, but the difference among different water sources is relatively small and stays in a narrow range. The range of SO_4/Cl versus Br is large and widely spread within individual water sources. The SO_4/Cl versus Br relationship can be classified into two groups. Oil and gas related produced waters generally have low SO_4/Cl ratio, and coal mining related wastewaters generally have high SO_4/Cl ratio. TDS increases as Br concentration increases. The mean TDS concentration increases from receiving streams, to AMD, to FPW, with O&G PW having the highest concentration. Concentration of Na is strongly correlated with Br across all water sources examined. The concentration of Na increases as Br concentration increases. In uncontaminated surface water, the correlation between Na and Br is weak due to very low Br concentrations in these sources. Several other parameters have also been examined to investigate their potentials as a tool to differentiate Br sources. Ca versus Br, Mg versus Br, and Sr versus Br show strong correlation in some examined water sources. However, weak or no correlations is observed in other sources. No consistent relationship is observed for these chemical signatures across different water sources, thus they are not useful as a diagnostic tool in identifying Br sources.

Geochemical modeling results show a linear increase of Br concentration through mixing as the percentage of wastewater increases in the receiving streams. Depending on the Br concentration in the wastewater, Br may exceed MCL even with only 5% wastewater streams mixed in uncontaminated surface water.

The results of this study indicate that chemical signatures Br versus Cl, Na versus Br have potential to be used to differentiate sources of Br. SO_4/Cl versus Br has limited use in the Appalachian region, as it can differentiate water sources from coal related industry versus oil and gas related industry. Br/Cl ratio is not useful because of the narrow range among the sources. Other signatures are not likely to be useful as diagnostic tools since no consistent trends have been observed. These diagnostic tools may be used to identify and differentiate among bromide contamination sources. This will assist regulators in making informed decisions for effective bromide contamination control and management.

Problem and Research Objectives

Bromide contamination 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. Elevated concentrations of Br⁻ in drinking water sources are cause for concern because of its potential to be oxidized to bromate (BrO₃⁻) or to interact with organic carbon forming brominated trihalomethane (THM) disinfection byproducts (DBPs), primarily as a consequence of ozonation or chlorination (U.S. Environmental Protection Agency, 2003; Parker *et al.*, 2014). DBPs are carcinogenic and teratogenic (NCI, 1976; USEPA, 1998), and brominated DBPs are associated with increased human health risk compared with chlorinated DBPs (Plewa *et al.*, 2004; Richardson *et al.*, 2003, 2007, 2008). While the relationships between source water halogens and DBP formation are complex and poorly understood, it is important to understand potential sources of bromide in order to better manage their concentrations in drinking water.

Bromide is found in all fresh water, generally at very low concentrations [0.014–0.2 mg/L (Bowen, 1966, 1979)]. Bromide concentrations in freshwater depend on the geochemistry of the materials that come into contact with water, e.g., aquifer formations that contain natural salts, runoff from road salt applications (Kjensmo, 1997), or localized addition of the fumigant methyl bromide (Wegman *et al.*, 1983; Wilson *et al.*, 2014). In the Appalachian region, potential sources of elevated bromide include agricultural runoff, coal mine water, hydrocarbon formation waters, or other fluids. With the development of shale gas in the region, Br from produced water is a concern for contamination of receiving streams.

Chloride and bromide salts are highly soluble (**Table 1**), only forming minerals under hypersaline conditions at or above halite saturation (Cartwright *et al.*, 2006; Alcalá and Custodio, 2008).

Table 1. Solubility of alkali and alkali earths chlorides and bromides.

Chlorides	Water solubility (mg/L)	Temperature (°C)	Bromides	Water solubility (mg/L)	Temperature (°C)
NaCl	357,000		NaBr	1,160,000	25
KCl	347,000	20	KBr	534,800	25
CaCl ₂	745,000	20	CaBr ₂	1,420,000	25
MgCl ₂	542,500	20	MgBr ₂	1,015,000	0
SrCl ₂	538,000	20	SrBr ₂	1,000,000	0
BaCl ₂	587,000	20	BaBr ₂	1,041,000	0

Source: CRC Handbook of Chemistry and Physics, 1976.

Cl and Br ions dissolved in natural water are tracers close to the ideal conservative behavior due to their hydrophilic character and small ionic size (Davis *et al.*, 1998, 2004). Neither of them take part in significant ion exchange reactions at low temperatures, nor are they adsorbed onto mineral surfaces. They are highly soluble and only form minerals during extreme evaporation

conditions when halite starts to precipitate (Fontes and Matray, 1993; Herczeg *et al.*, 2001; Cartwright *et al.*, 2006). This means that the physical processes taking place in soil (dilution, evaporation, transpiration, *etc.*) can change their absolute concentrations, but do not significantly modify the Cl/Br ratio of groundwater (Alcala and Custodio, 2008).

Management of Br⁻ requires an understanding of the origin of Br⁻ and associated constituents, specifically for the Appalachian region, whether the Br⁻ originates naturally from the bedrock formations subjected to mining, or if the Br⁻ is the result of wastewater disposal practices from shale gas industries. The objectives of this study are to collect 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 different potential sources.

Methodology

The basic approach of this study is to collect water chemistry data from Appalachian region energy related industries and receiving streams, screen the chemical signature of different wastewaters from the energy industry, and explore their potential as diagnostic tools to differentiate origins of bromide source in receiving waterbodies.

During the study, we analyzed chemical signatures (concentration of Br⁻, Cl⁻, Cl/Br ratio, other parameters) in collected water data from waste streams of energy industry and the receiving water body in West Virginia. These data sources included energy industry waste streams such as flowback (WVWRI, 2012; Hayes, 2009), produced water (Dressel and Rose, 2010), coal bed methane water (Unpublished data), coal mine drainage water (surface, underground deep, underground shallow) (Cravotta, 2014), as well as receiving streams (tributary and Monongahela River) (WVWRI, 2014). Linear correlation and ANOVA analysis were conducted to examine the significance of these trends in these chemical signatures among different waste streams.

We also used geochemical modeling to investigate how major types of wastewater from the energy industry in West Virginia interact with water chemistry parameters in the receiving water body, focusing on modeling change of chemical signatures (Br and Cl concentrations, Cl/Br ratio) during the mixing of wastewater with receiving streams; and impact on other water quality parameters in receiving streams.

Principal Findings

1. Bromide concentration in wastewaters

In the Appalachian region, potentially important sources of halogens include conventional oil and gas produced water, unconventional oil and gas flowback and produced water, coal-bed methane (CBM) produced water, and acid mine drainage (AMD). Halogens are elevated in conventional and unconventional oil and gas produced water. **Table 2** summarizes the mean

concentration and range of data from different sources and the data indicate a wide range in chemical compositions and ionic concentrations.

In their study of flowback water from shale gas development, Ziemkiewicz and He (2015) found that ion concentrations in general increased throughout the flowback reaching concentrations of 1,500 mg/L Br and 80,000 mg/L Cl. Dresel and Rose (2010) and Haluszczak *et al.* (2013) reported similar or higher concentrations of chloride and bromide in produced waters from conventional oil and gas wells in Pennsylvania. The major halogen ions in CBM produced waters range from 20 to 112 mg/L Br and 2,800 to 14,700 mg/L Cl.

Various halogen (Cl, Br, I), alkali earth (Na, K, Li), and alkaline earth (Sr, Ba) elements tend to be elevated in oil and gas brines or connate fluids (Dresel and Rose, 2010; Haluszczak *et al.*, 2013), elevated concentrations of these elements are not typically identified with AMD. Nevertheless, such brine constituents, notably bromide (Br⁻), have been documented in AMD samples from selected sites in Pennsylvania (Cravotta, 2008; Cravotta and Brady, 2015). Cravotta *et al.*, (2014) reported Br⁻ concentrations for the 182 untreated AMD samples collected in 1999 and 2011 range from <0.003 to 12.8 mg/L, with a median of 0.036 mg/L. The AMD samples with elevated Br⁻ concentrations tend to originate from deep mines or from associated waste rock piles. These samples also have elevated Cl⁻, I⁻, Na⁺, and K⁺. Although these brine constituent concentrations are dilute in AMD compared to oil and gas brines or other sources of salinity, the Br/Cl ratios indicate many of the deep mine waters have enriched Br⁻ compositions that are consistent with residual brine diluted with meteoric water (Cravotta *et al.*, 2014). While halogen concentrations in AMD are much lower than in oil and gas produced waters, the discharged volumes from coal mines are substantially higher, thus the overall impact can still be significant.

Figure 2 shows the medium and range of bromide concentrations across different water sources. Flowback and produced water have the highest Br concentrations. CBM is in the intermediate range. Br concentration in AMD is generally low, but it may be impacted by brine contact in deep mines. Bromide concentration in the tributary is elevated and is likely impacted by discharge from coal mine drainage. Br concentration in the Monongahela River is lowest, which is expected in uncontaminated surface water. As shown in **Table 3**, ANOVA analysis show significant difference in Br concentrations among the examined waste streams ($p < 0.001$). Only the Br concentration in FPW-WRI and FPW-Hayes datasets show no significant difference ($p = 0.333$).

Table 2: Chemistry of water from different sources (mg/L).

Source	Parameter															
	TDS		Cl		Na		SO ₄		Mg		Ca		K		Br	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Seawater ¹	35083	n/a	19400	n/a	10800	n/a	2712	n/a	1290	n/a	411	n/a	392	n/a	67	n/a
CBM ²	14751.83	11529.9-17973.7	9205.08	6799.9-11610.3	5942	4645.2-7238.8	12.52	5.3-19.7	111.27	77.5-145	328.4	166.7-490.1	30.33	8.6-52.1	67.36	48.8-85.9
O&G PW ³	177000	145000-209000	104543.6	88031-121056	45572.7	37565-53581	171.5	106-237	2079.15	1750-2408	17626.36	13994-21259	858.21	416-1300	997.44	829-1166
FPW-WRI ⁴	71103.3	41336.9-100869.7	40656.7	23440.6-57872.8	18469.2	13246-18469.2	42	16.0-67.9	733.8	371.7-1095.8	6408.3	3170.1-9646.6	241.1	173.7-308.4	424.8	232.2-617.4
FPW-Hayes ⁵	103011.8	221-345000	63602.2	50669.8-76535.6	25884.3	20745.5-31023.2	53.24	0.8-348	745.81	586.4-905.2	8302.06	6404.6-10199.6	584.51	382.7-786.4	574.18	455.6-692.8
AMD ⁶	2479.81	139-15792	82.98	13.87-152.08	192.14	81.97-302.3	1620.76	1189.4-2052.12	112.3	87.25-137.35	244.69	196.98-290.70	5.66	4.38-6.94	0.53	0.09-0.97
Mon River ⁷	188.52	97.44-279.6	14.44	8.82-20.07	25.11	18.25-31.97	99.58	57.1-142.05	8.03	2.0-19.0	31.28	10.0-43.0	n/a	n/a	0.05	0.03-0.07
Tributary ⁸	1196.7	0-2543.26	51.38	19.62-83.13	226.86	0-525.91	836.65	0-1716.57	11.6	1.0-18.0	42.3	4.0-63.0	n/a	n/a	0.37	0.08-0.65
Source	Parameter															
	Sr		Al		Ba		Fe		Mn		Alkalinity		pH			
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range		
Seawater ¹	8	n/a	3	n/a	0	n/a	0	n/a	0	n/a	n/a	n/a	n/a	n/a		
CBM ²	46.85	22.1-71.5	2.96	1.2-4.7	17.71	4.6-30.8	41.06	14.6-67.5	0.58	0.3-0.9	n/a	n/a	n/a	n/a		
O&G PW ³	2120.21	916-3324	n/a	n/a	877.37	378-1377	196.03	142-250	24.29	1750-2408	158.47	52-265	6.43	6-7		
FPW-WRI ⁴	1167.5	402.4-1932.6	0.4	0-1.0	405.1	0-884.4	60.6	31.8-89.4	5.2	3.2-7.1	191.3	157.7-224.8	6.61	6.3-8.11		
FPW-Hayes ⁵	1830.41	1371.4-2289.4	1.5	0.2-47.2	1494.54	859.7-2135.4	n/a	n/a	n/a	n/a	130	5.0-588	6.6	5.9-8.2		
AMD ⁶	0.001	0-0.005	0.01	0-0.12	0.03	0.02-0.04	0.14	0-4.1	11.52	6.59-16.45	n/a	n/a	6.6	6.15-7.04		
Mon River ⁷	n/a	n/a	0.06	0.01-0.11	n/a	n/a	0.09	0.01-0.14	0.06	0.01-0.13	45.64	5.0-64.0	7.36	6.99-8.36		
Tributary ⁸	n/a	n/a	0.09	0-3.0	n/a	n/a	0.18	0-4.0	0.22	0-3.0	64.91	35.0-128.0	7.4	6.17-8.46		

Note:

n/a: not available

1. Turekian, 1976
2. Unpublished data
3. Dressel and Rose, 2010
4. WVVRI, 2012
5. Hayes, 2009
6. Denicola, 2013/ Carovatta, 2014
7. WVVRI, 2014
8. WVVRI, 2014

Table 3. *p* values from ANOVA analysis (alpha=0.05).

Parameter	All waste streams	CBM versus CMD	O&G PW versus FPWs	O&G PW versus FPW-WRI	FPW-WRI versus Hayes	O&G versus CBM	O&G versus AMD	FPWs versus AMD
TDS	<0.001	<0.001	<0.001	<0.001	0.205	<0.001	<0.001	<0.001
Br	<0.001	<0.001	<0.001	0.001	0.333	<0.001	<0.001	<0.001
Na	<0.001	<0.001	<0.001	<0.001	0.24	<0.001	<0.001	<0.001
Cl/Br	0.001	0.269	0.428	0.836	0.488	<0.001	0.005	0.005
SO4/Cl	<0.001	0.045	0.654	0.256	0.761	0.831	<0.001	<0.001

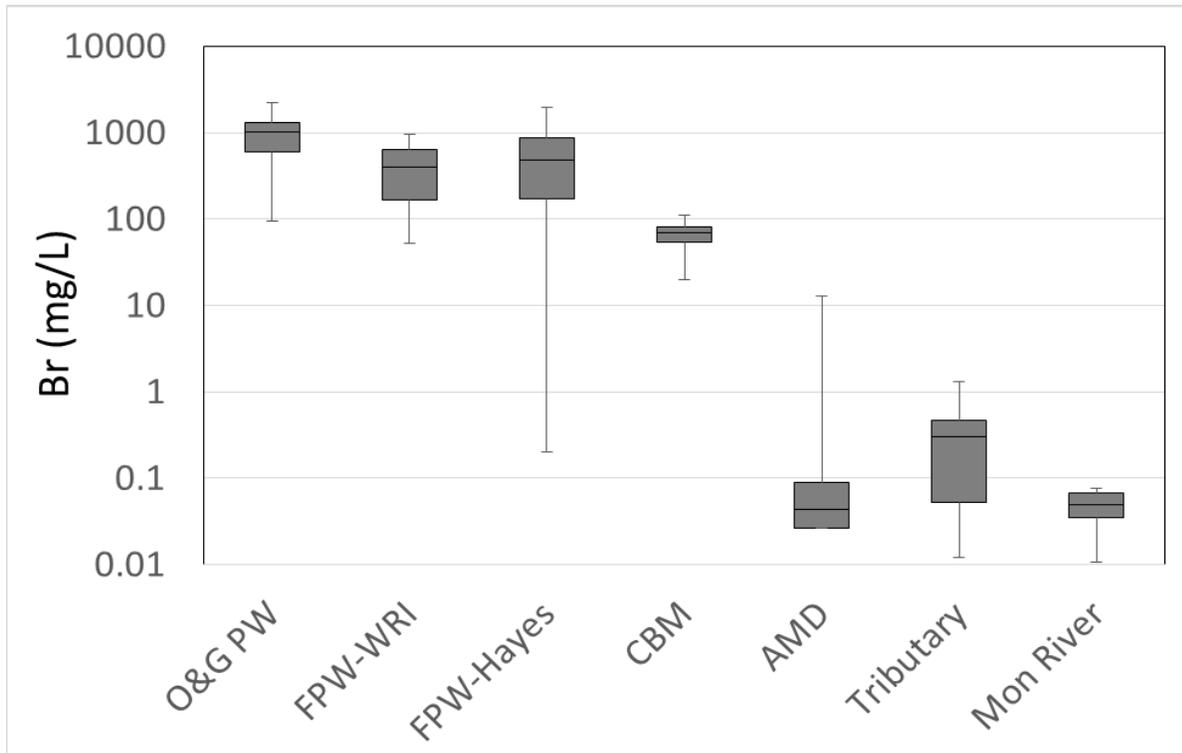


Figure 2. Bromide concentration in different water sources.

2. Br versus Cl relationship

Chloride and bromide ions have been used to discriminate among various sources of anthropogenic and naturally occurring contaminants in groundwater. Plots of chloride concentrations 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).

Figure 1 is a composite plot showing Br versus Cl relationship of different water sources. A linear relationship between Br versus Cl is observed for all water sources (**Figures 1, 3-9**). Both bromide and chloride concentrations span eight orders across the water sources examined. Even though there is overlap among different sources, Br versus Cl tends to cluster within a range for a specific water source. The Br versus Cl relationship has potential to be used to discriminate and identify sources of Br contamination in water.

Across a wide range of concentrations, the trends for O&G PW and shale gas flowback/produced water suggest a common source of Br for these waters (**Figures 3-5**). AMD data has wide spread Cl and Br ranges. This is likely due to the fact that the AMD dataset includes data from surface mine, deep mine and refuse (three sources). The tributary has significantly higher Br concentration than the Monongahela River. The higher Br concentration in the tributary is likely originated from mixing discharge from coal mine drainage in this area with tributary water.

In **Figure 3**, log Cl versus log Br of flowback lies below the seawater evaporation trajectory, indicating dilution of original brine with freshwater or injected fracturing fluid. The Hayes (2009) FPW data overlap with FPW from other Marcellus sources and also lies below the seawater evaporation line. A comprehensive study examining the geochemistry of deep basinal brines in Pennsylvania was conducted by Dresel and Rose (2010) and they concluded that the brines originated as evaporated seawater that has subsequently been diluted to current concentrations. Late stage Marcellus shale FPW have similar major ion chemistries with formation waters from the overlying and underlying Devonian formations and show similar Na-Cl-Br ratios (Osborn and McIntosh, 2010; Rowan *et al.*, 2010). The overlap of flowback and produced water from conventional wells in upper Devonian rock in Figure 3 suggests similar processes or a similar origin for both.

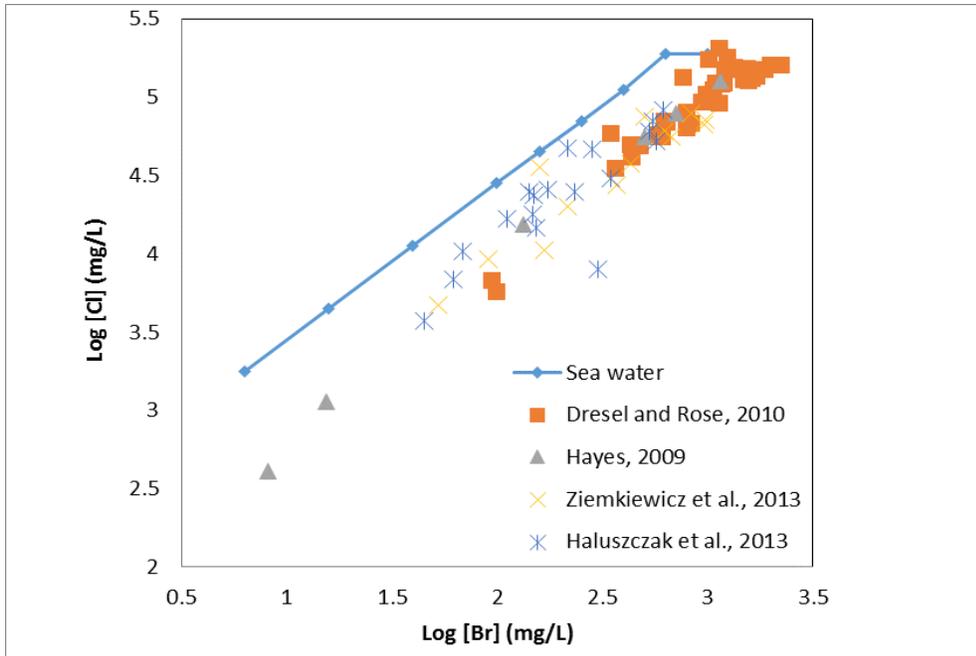


Figure 3. Correlation of Br with Cl in flowback. Sea water data and produced water data in conventional well from Upper Devonian is from Dresel and Rose (2010). Data from Hayes (2009) is an average value of 19 well sites. Data from Ziemkiewicz *et al.* (2013) is from 6 well sites in north central West Virginia, and data from Haluszczak *et al.* (2013) used 22 BOGM samples from PADEP.

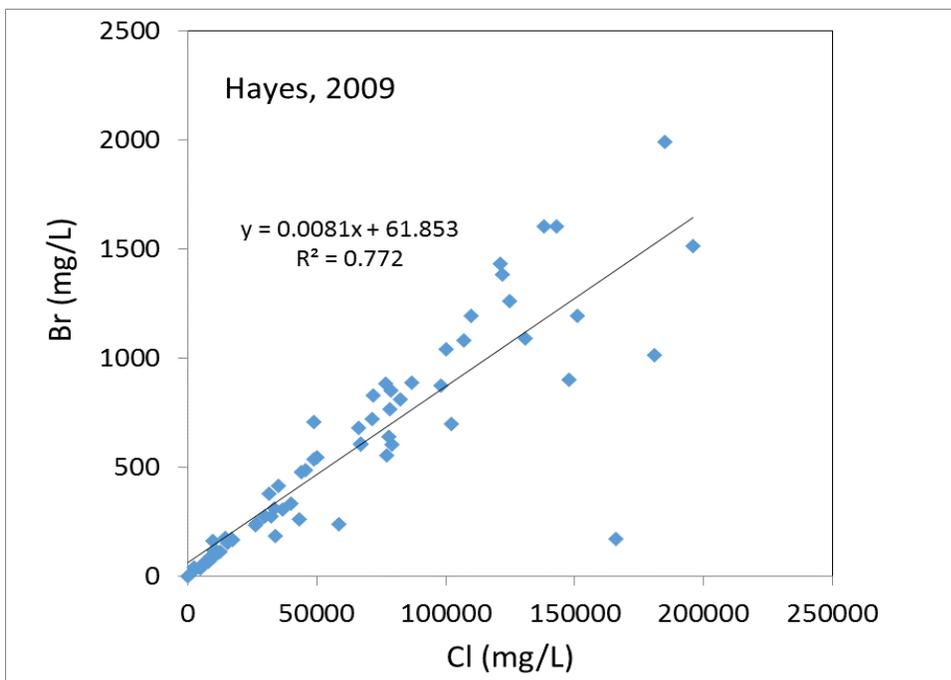


Figure 4. Br versus Cl in flowback and produced water from Marcellus shale gas development (data source: Hayes, 2009).

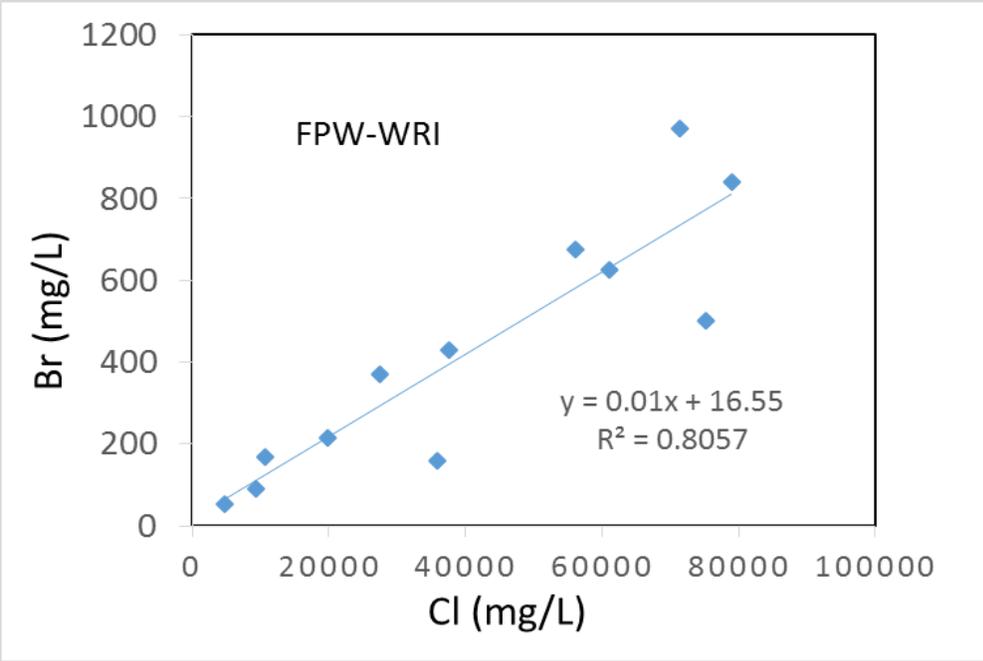


Figure 5. Br versus Cl in flowback from Appalachian region (Data source: WWRI, 2012).

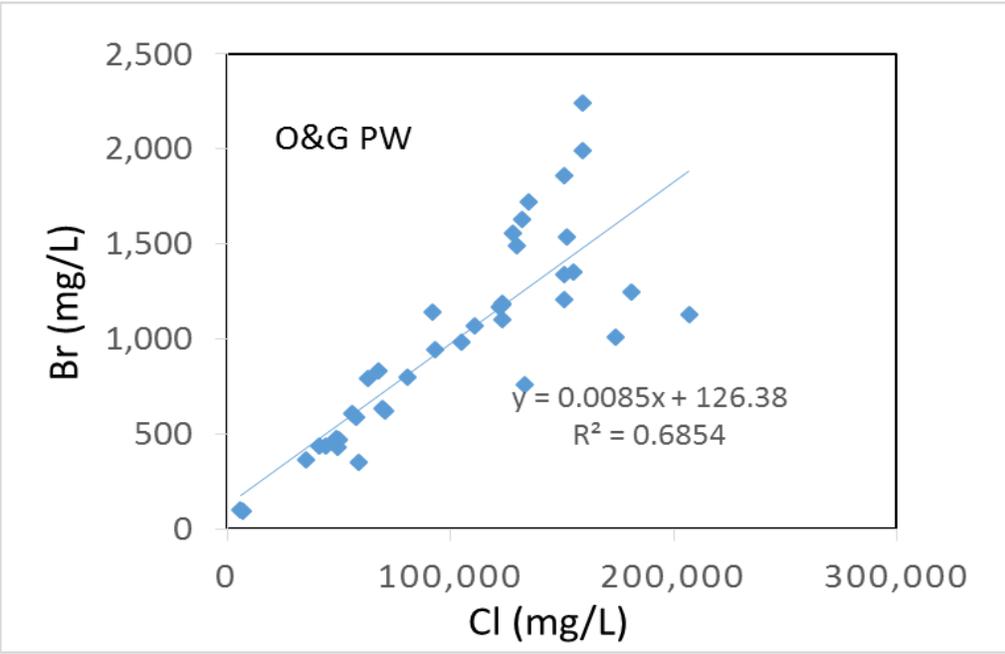


Figure 6. Br versus Cl in produced water from O&G PW in Appalachian region (data source: Dresel and Rose, 2010).

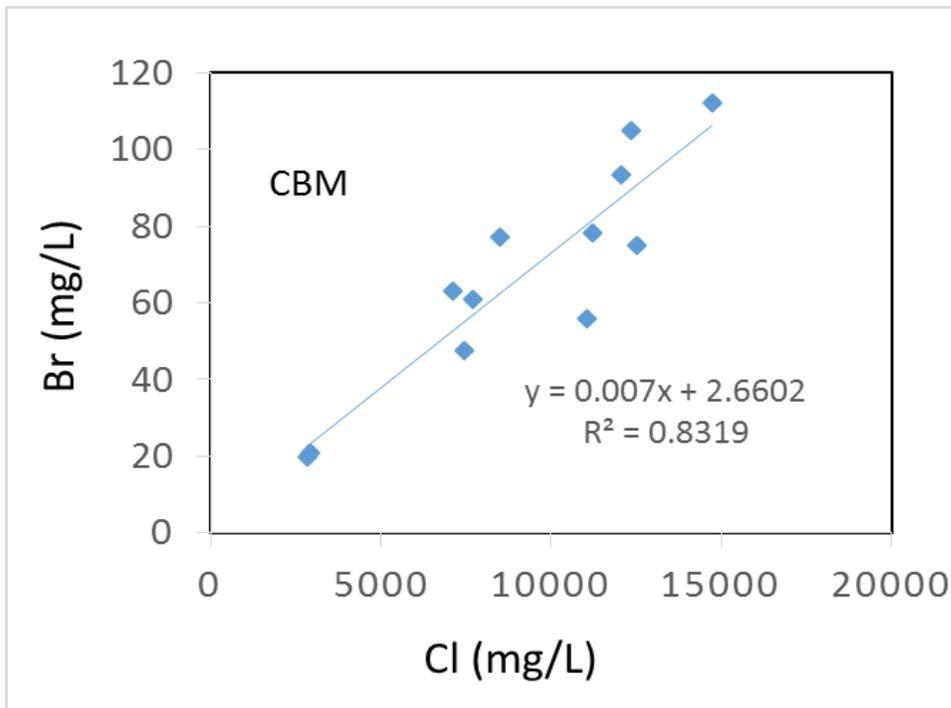


Figure 7. Br versus Cl in coal bed methane produced water (Data source: unpublished data).

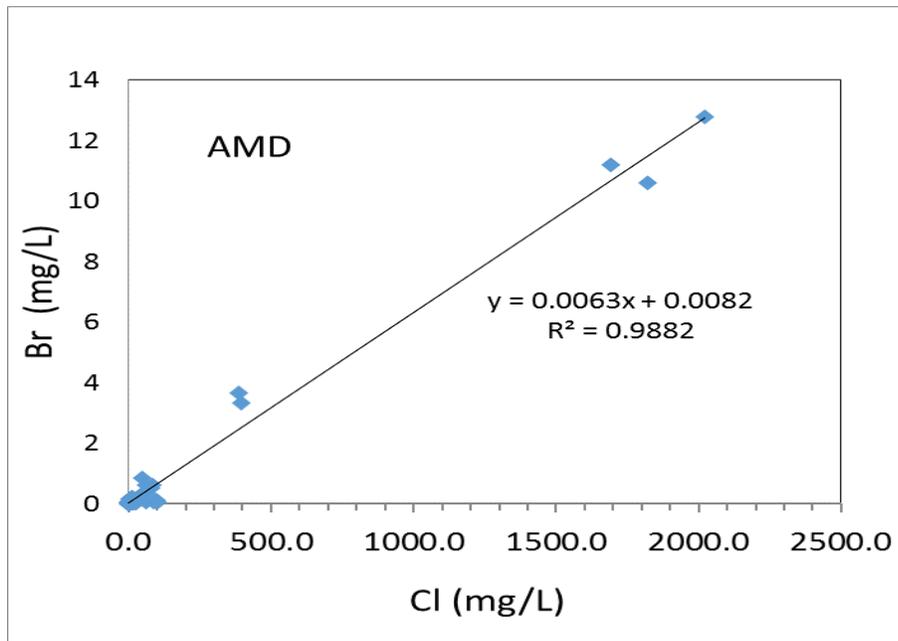


Figure 8. Br versus Cl in acid mine drainage in Appalachian region (data source: Cravotta, 2014).

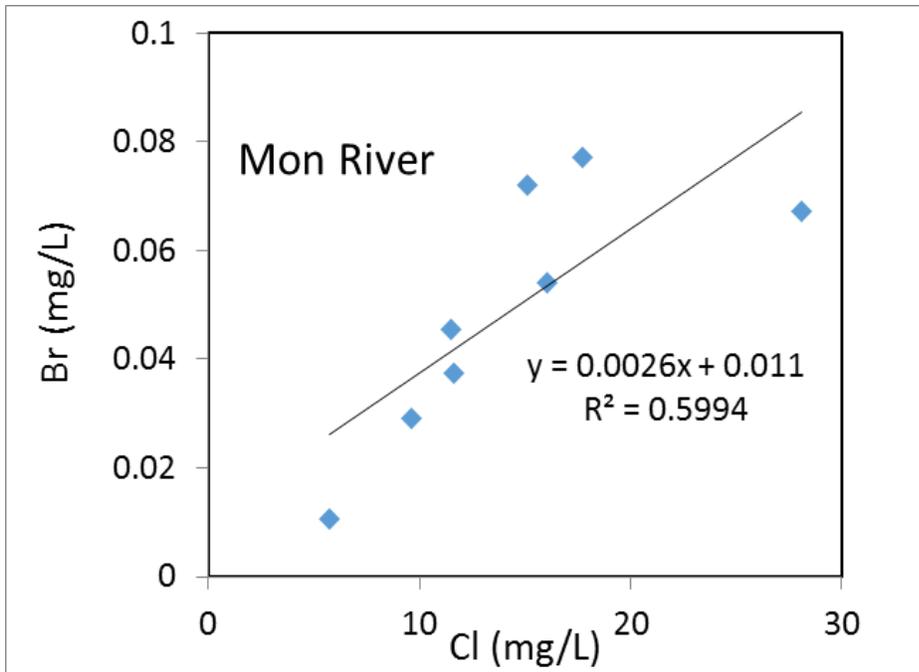


Figure 9. Br versus Cl in receiving stream Monongahela River (Data source: WVVRI 2012).

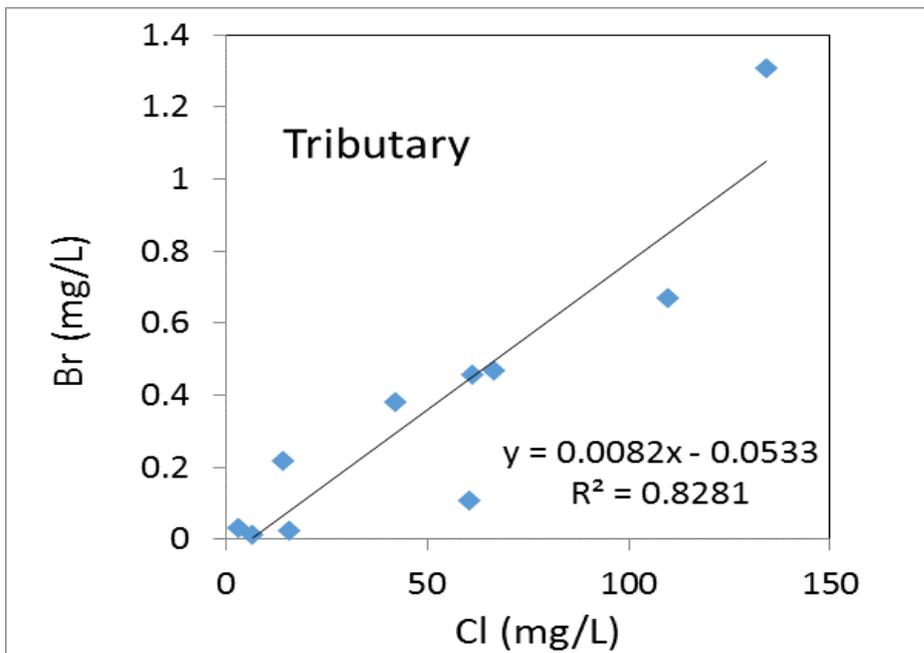


Figure 10. Br versus Cl in a tributary of Monongahela River in Appalachian region (Data source: WVVRI, 2014).

3. Cl/Br ratio

The conservative behavior of Br⁻ and Cl⁻ during water transport makes halides and their ratios especially useful in determining water movement. Several studies have reported distinct ranges of Cl/Br ratios for various end members that control salinity processes in groundwater. Cl/Br ratios in wastewater, such as septic-tank effluent and treated municipal wastewater, tend to have larger ranges due to variations in source water, salt intake, and other anthropogenic factors (Katz *et al.*, 2011). Chloride/Br ratios show characteristic ranges for several sources. Water from the unsaturated zone and unaffected groundwater show the smallest Cl/Br ratios. Road salt had comparatively large Cl/Br ratios as did the water affected by road salt (Panno *et al.*, 2006). The Cl/Br mass ratio has been used successfully to study the origin of saline groundwater and brines from relatively deep geologic formations, and to characterize atmospheric precipitation, shallow groundwater, and domestic sewage (Richter and Kreitler, 1993; Davis *et al.*, 1998; Panno *et al.*, 2006). Bromide and bromide-to-chloride ratios have also been used to identify pollution sources from agriculture applications (Wegman *et al.*, 1981, 1983) and shale gas-produced water contamination to shallow groundwaters (Siegel and Kight, 2011; Wolford, 2011; Wilson *et al.*, 2014).

However, because of the similarities of the ranges of Cl/Br ratios for different sources and geochemical processes that can affect the Cl/Br ratio, the technique is not always definitive. For example, other studies have shown that sorption of Br on clays and iron oxides in the soil can affect Cl/Br ratios in water (Fabryka-Martin *et al.*, 1991; Whittemore and Davis, 1995). Other processes can modify the Cl/Br ratio in groundwater including decomposition of organic matter that can add Br to solution (Gerritse and George, 1988; Fabryka-Martin *et al.*, 1991; Cartwright *et al.*, 2004), seawater intrusion and upconing of brines (Wilson and Long, 1993; Davis *et al.*, 1998), and fluids derived from evaporite mineral dissolution (Vengosh and Pankratov, 1998). There can also be large ranges of Cl/Br ratios for wastewater (Davis *et al.*, 1998; Dumouchelle, 2006) that may overlap somewhat with Cl/Br ratios from other sources (Vengosh and Pankratov, 1998). Mixing of groundwater affected by wastewater or water affected by other sources such as road salt (Brown *et al.*, 2009) or halite (Cartwright *et al.*, 2004) can result in high Cl/Br ratios. Mixing with oil-field brines (Cl/Br 110–400) would also result in lower Cl/Br ratios (Eberts *et al.*, 1990; Thomas, 2000; Jagucki and Darner, 2001; Katz *et al.*, 2011).

As can be seen from **Figures 11 and 12**, the range of Cl/Br ratio within each water source is large for most water sources. The range is especially large for AMD. This is likely due to AMD dataset inclusion of data from surface mine, deep mine and refuse (three sources). On the other hand, Cl/Br ratio range across different water sources is relatively small. Cl/Br ratio only spans three orders in comparison to eight orders of Br concentration difference among different sources. Because of the spread of data within each source, it does not show a clear trend among different sources (Figures 11 and 12). However, the mean Cl/Br versus Br from each source shows a decreasing Cl/Br trend as Br concentration increases, with the ratio for FPW and O&G PW the lowest (**Figure 13**). ANOVA analysis (Table 3) indicate no significant differences between CBM and AMD ($p=0.269$), O&G PW versus FPWs ($p=0.428$), FPW-WRI versus FPW-Hayes ($p=0.488$), and FPW-WRI versus AMD ($p=0.112$). The only significant difference is between AMD versus FPW-Hayes ($p=0.005$), and O&G PW versus CBM ($p<0.001$).

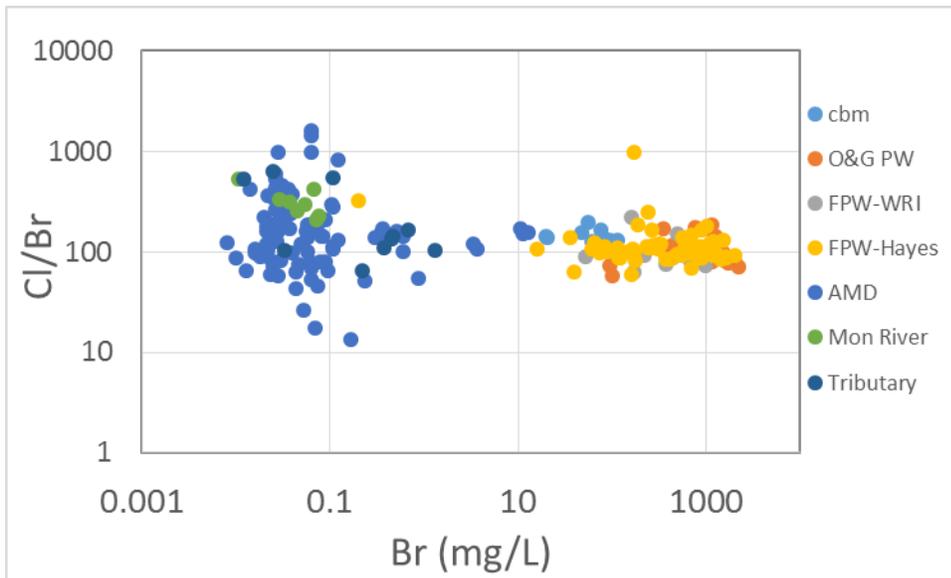


Figure 11. Cl/Br versus Br across different water sources.

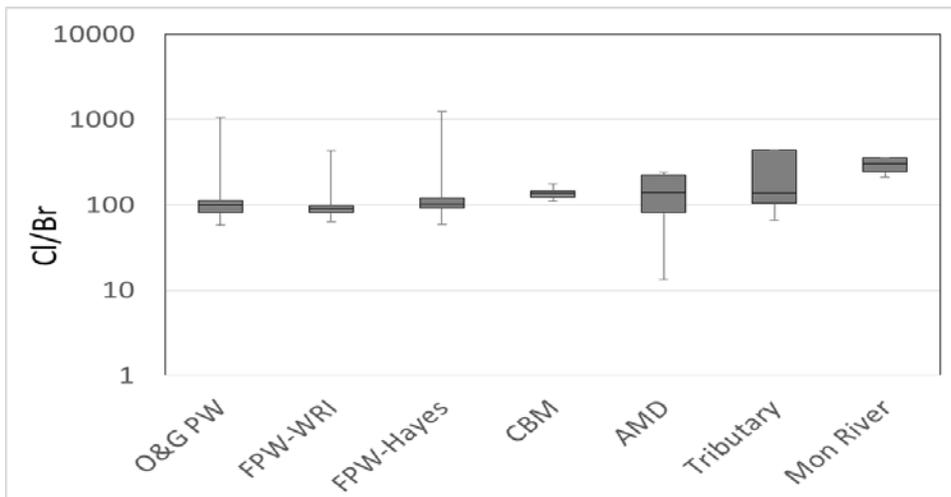


Figure 12. Cl/Br ratio from different water sources.

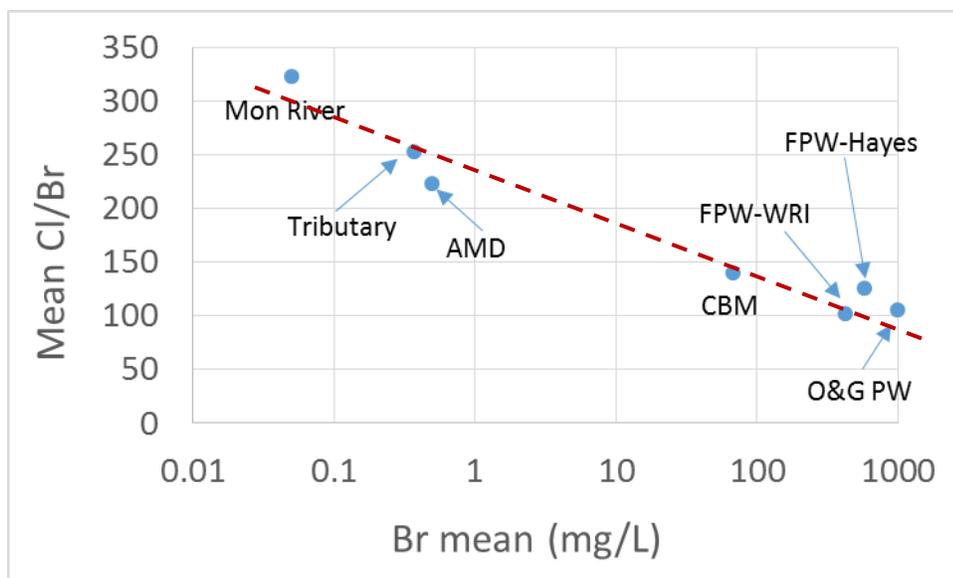


Figure 13. Mean Cl/Br versus mean Br concentration from different water sources.

4. Na versus Br

Similar to Cl and Br in anions, Na shows conservative properties as a cation, and the solubility of Na salts in water are typically high (Table 1).

Strong correlations have been found between Na and Br concentration for most water sources (**Figures 15-20**). However, correlation between Na and Br is not very strong in reference streams (**Figures 21-22**). This is likely due to the very low Br concentration and low Na concentration in the tributary and Monongahela River.

Figure 14 shows the general trend of Na versus Br across different water sources. In general, Na concentration increases as Br concentration increases. For coal mining related wastewaters, Na concentration spans five orders, while Br concentration only spans three orders. This is likely due to inclusion of surface mine, deep mine and refuse samples in AMD data examined in this study. As shown in Table 3, ANOVA analysis shows a significant difference in Na concentration among the waste streams (all $p < 0.001$), with the exception of no significant difference between FPW-WRI versus FPW-Hayes ($p = 0.24$). This is expected as they are the same type of wastewater from different sampling locations.

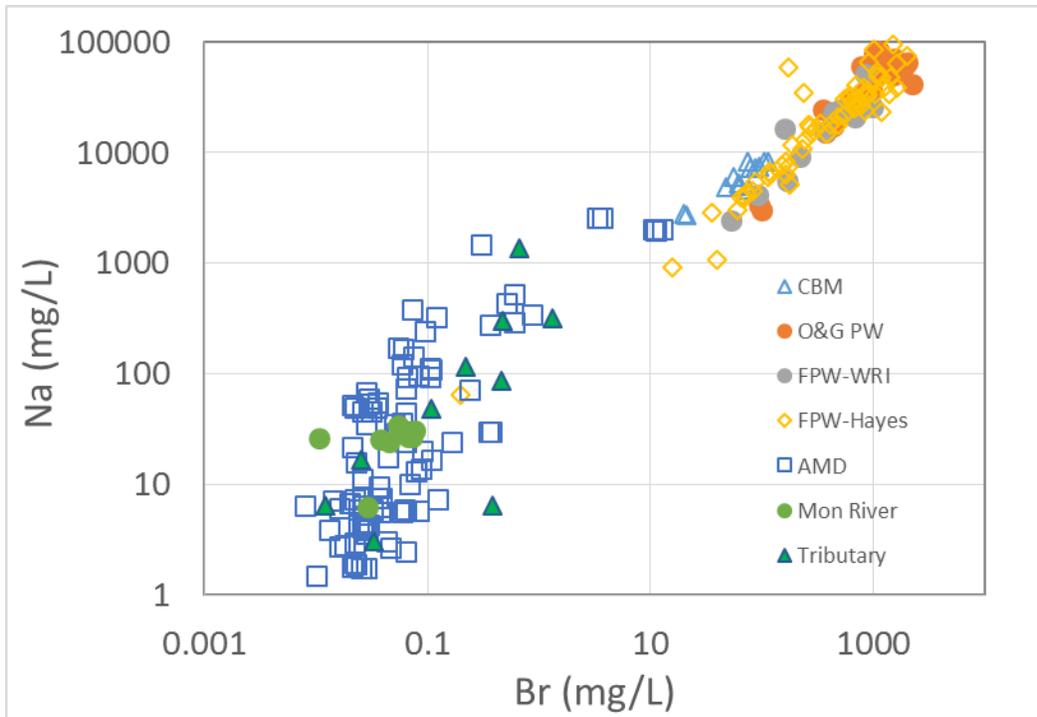


Figure 14. Na versus Br across different water sources.

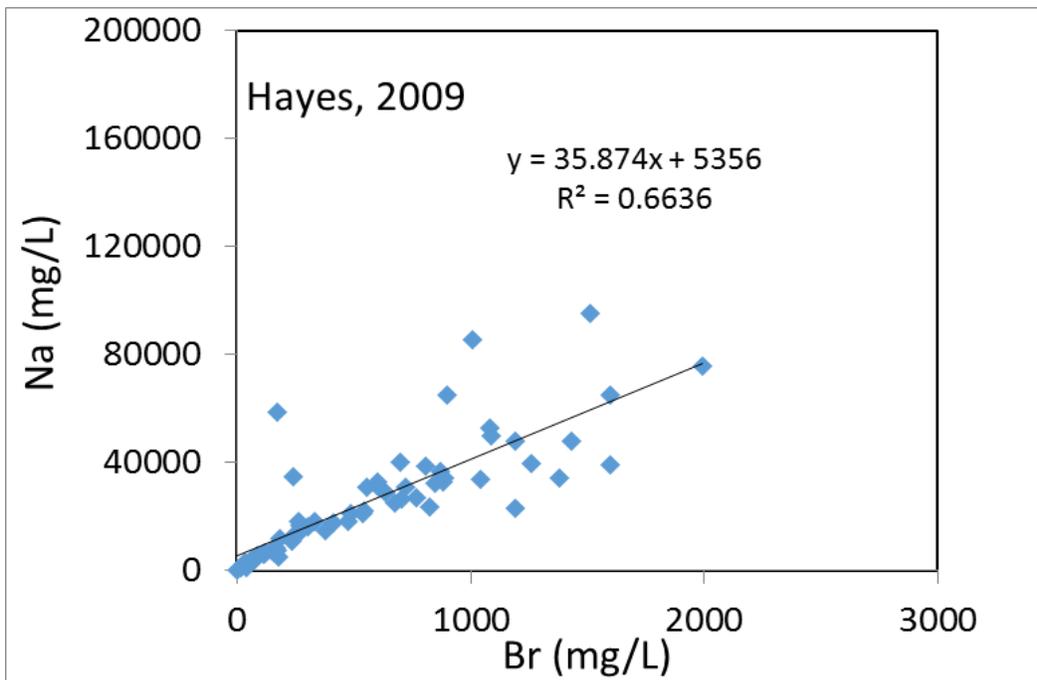


Figure 15. Na versus Br in flowback and produced water from Marcellus shale gas development (data source: Hayes, 2009).

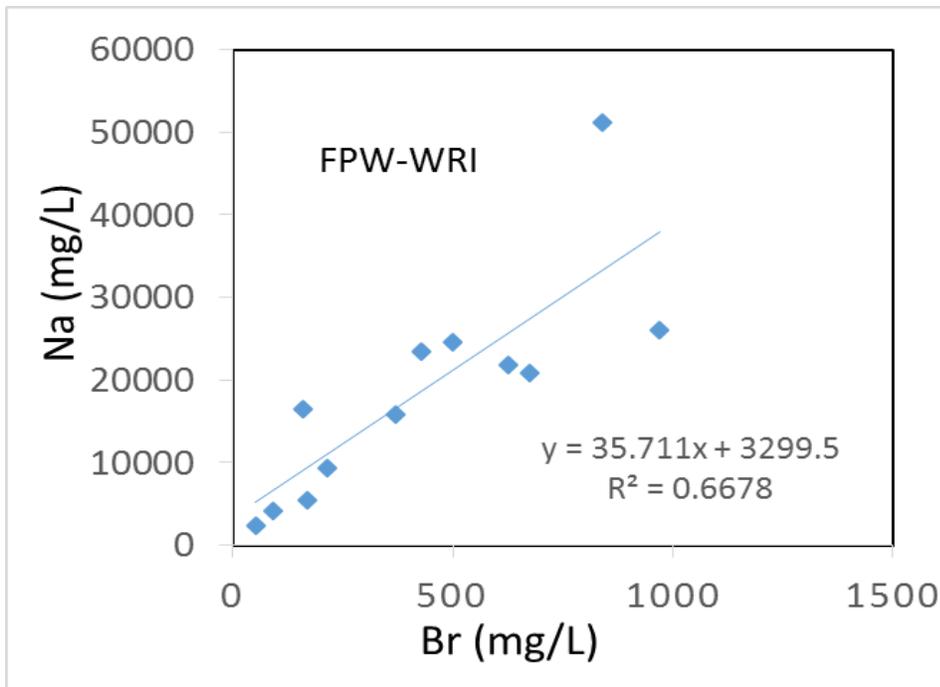


Figure 16. Na versus Br in flowback and produced water from Marcellus shale gas development (data source: WVVRI, 2012).

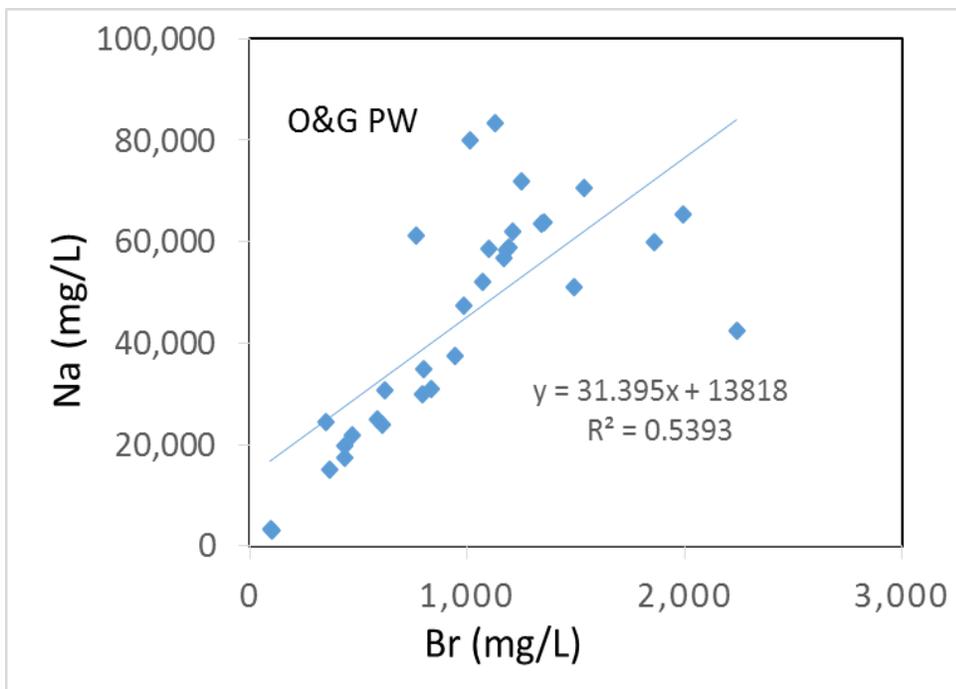


Figure 17. Na versus Br in O&G produced water from Marcellus shale gas development (data source: Dresel and Rose, 2010).

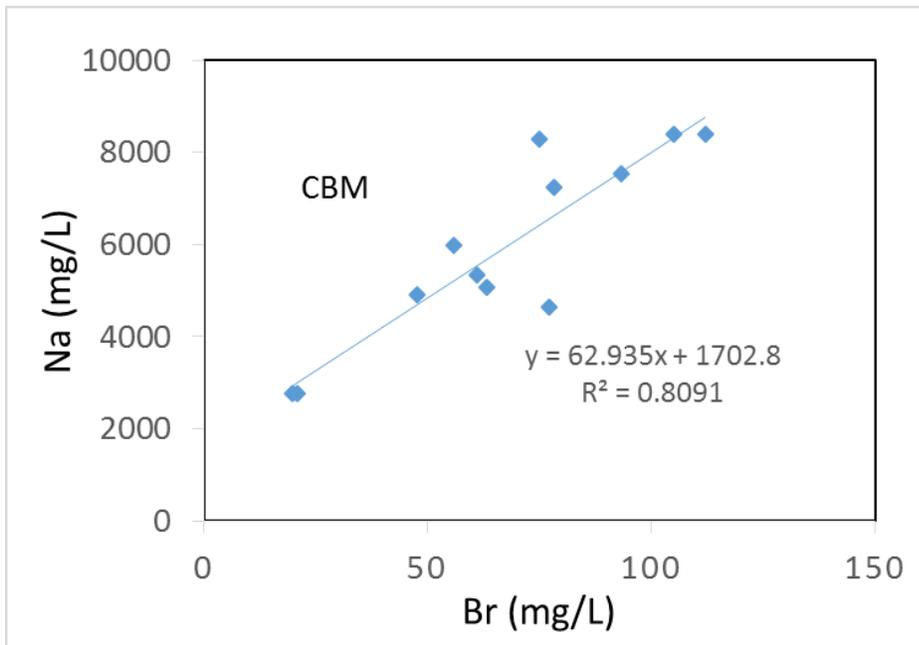


Figure 18. Na versus Br in CBM produced water from Marcellus shale gas development (data source: unpublished data).

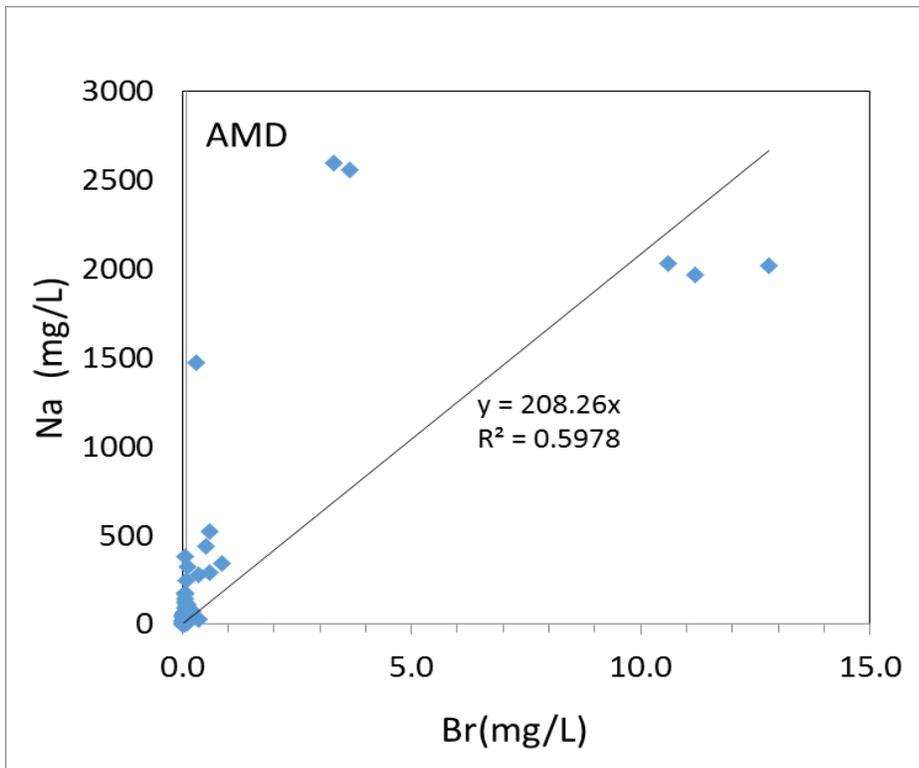


Figure 19. Na versus Br in acid mine drainage (data source: Cravotta, 2014).

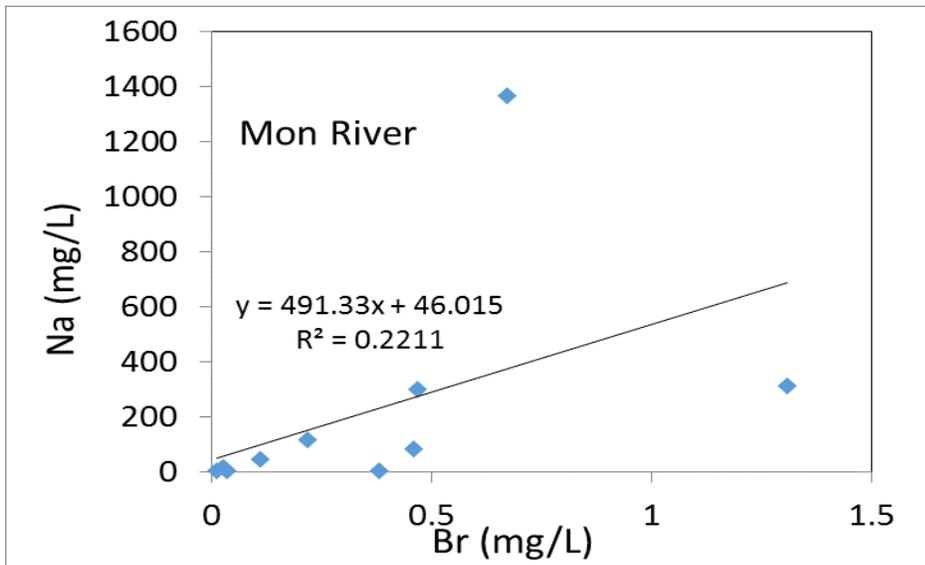


Figure 20. Na versus Br in reference stream Monongahela River (data source: WVVRI, 2014).

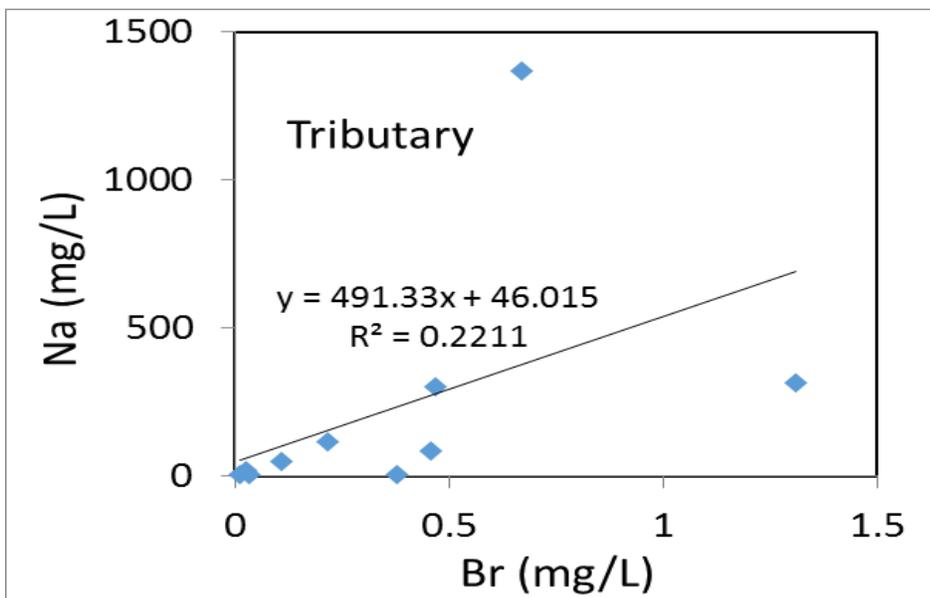


Figure 21. Na versus Br in a tributary to Mon River (data source: WVVRI, 2014).

5. TDS versus Br

As shown in **Table 2**, O&G produced water has the highest total dissolved solids (TDS) concentration, significantly higher than the FPWs. The difference in concentrations is due to the mixture of early stage flowback and later stage produced water in FPW; produced water refers to the wastewater during the production phase. The former reflected the injected fluids in the

hydraulic fracturing process which was gradually replaced by more concentrated produced waters resulting in increasing ion concentrations from initial flowback through the production cycle (Ziemkiewicz and He, 2015). The conventional O&G produced waters, on the other hand, were from vertical wells that were not stimulated by hydraulic fracturing. Thus, their ionic concentrations more accurately reflected formational pore waters.

Figures 22-23 show TDS concentration trends across different water sources. TDS increases as the mean Br concentration of each source increases (Figure 22). A general increasing trend of TDS from reference streams to AMD, CBM, and FPW/O&G produced water can be observed in Figure 23. ANOVA analysis results in Table 3 show a significant difference in TDS concentration among different waste streams (all $p < 0.001$). Only TDS of FPW-WRI versus FPW-Hayes shows no significant difference ($p = 0.205$), which is expected.

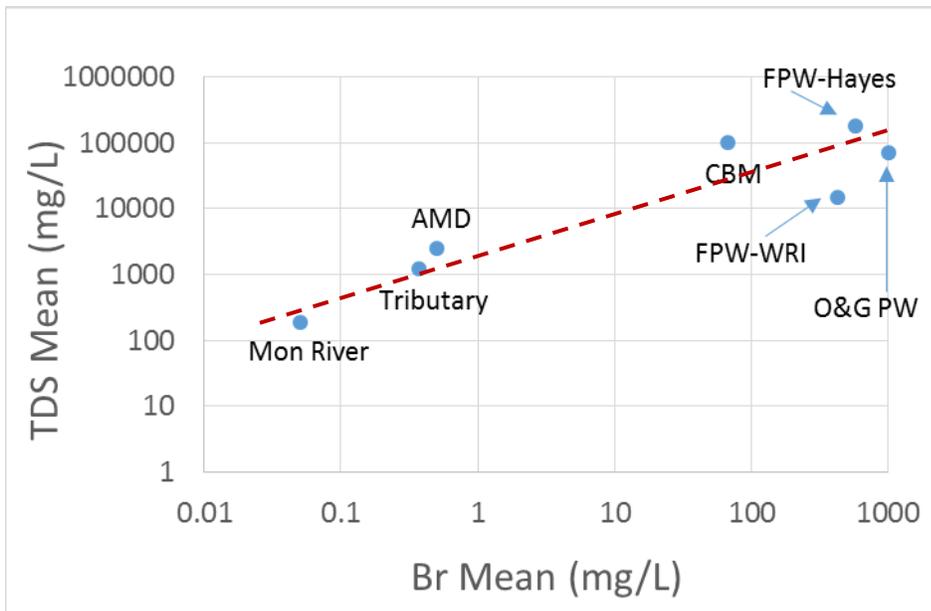


Figure 22. Mean TDS versus mean Br concentration across different water sources.

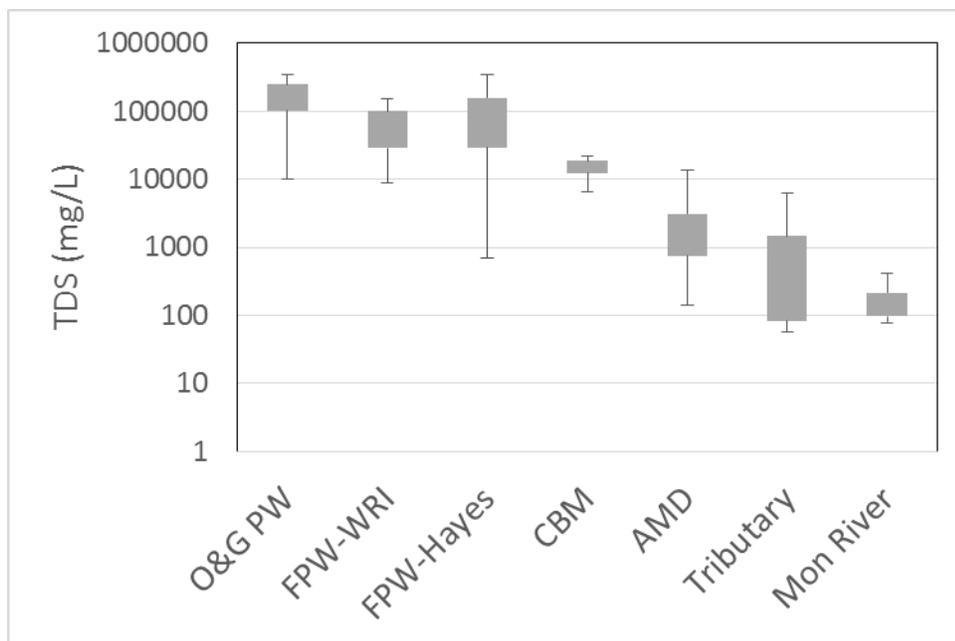


Figure 23. TDS concentrations from different sources.

6. SO_4/Cl versus Br

Sulfate and chloride are major anions in natural and waste waters. However, their concentrations vary significantly depending on sources of water. Coal in the Appalachian region is high in sulfur content (Milici and Dennen, 2009); therefore, coal-related wastewaters in the region would be expected to contain significant amounts of sulfate. Historical acid mine drainage in the region has been reported to contain high concentrations of sulfate (Cravotta 1993, 2008). As expected, coal-associated wastewaters are enriched in sulfate compared to natural waters, and statistically significantly different from oil and gas wastewaters. Conventional and Marcellus produced waters are similar in sulfate concentration (Wilson *et al.*, 2014).

Considering the SO_4/Cl ratio for coal-related wastewaters and oil and gas-produced waters, coal-related wastewaters are enriched in sulfate relative to chloride, and oil and gas-produced waters are enriched in chloride relative to sulfate. Thus, coal-related wastewaters have a significantly higher median SO_4/Cl ratio than oil and gas-produced waters (by five orders of magnitude), and natural waters (by two orders of magnitude). Similarly, oil and gas-produced waters are significantly different from coal-related wastewaters and natural waters. However, there is no statistically significant difference in SO_4/Cl for Marcellus Shale gas well-produced water and conventional gas well-produced water or between all gas well-produced water and oil well-produced water. This suggests that SO_4/Cl cannot be used to distinguish among gas and oil well-produced waters, but it can be used to distinguish between coal-related wastewaters and oil and gas-associated wastewaters (Wilson *et al.*, 2014).

Figure 24 shows a general decreasing trend of SO_4/Cl versus Br concentration across different water sources. However, within the water source, the correlation between SO_4/Cl versus Br is relatively weak. This could be seen from the wide spread of data points within each water source.

The SO_4/Cl versus Br in different water sources can be generally categorized into two groups. High SO_4/Cl for AMD, tributary and Monongahela River and low SO_4/Cl ratio for produced water and flowback. This was likely due to low sulfate concentration and extremely high Cl concentration in these water sources (**Figures 24-26**). ANOVA analysis results (Table 3) show no significant difference between O&G PW versus FPWs ($p=0.654$), and FPW-WRI versus FPW-Hayes ($p=0.76$). However, significant difference in SO_4/Cl ratio are observed between O&G PW versus AMD ($p<0.001$), FPW-Hayes versus AMD ($p<0.001$), and CBM versus AMD ($p=0.045$).

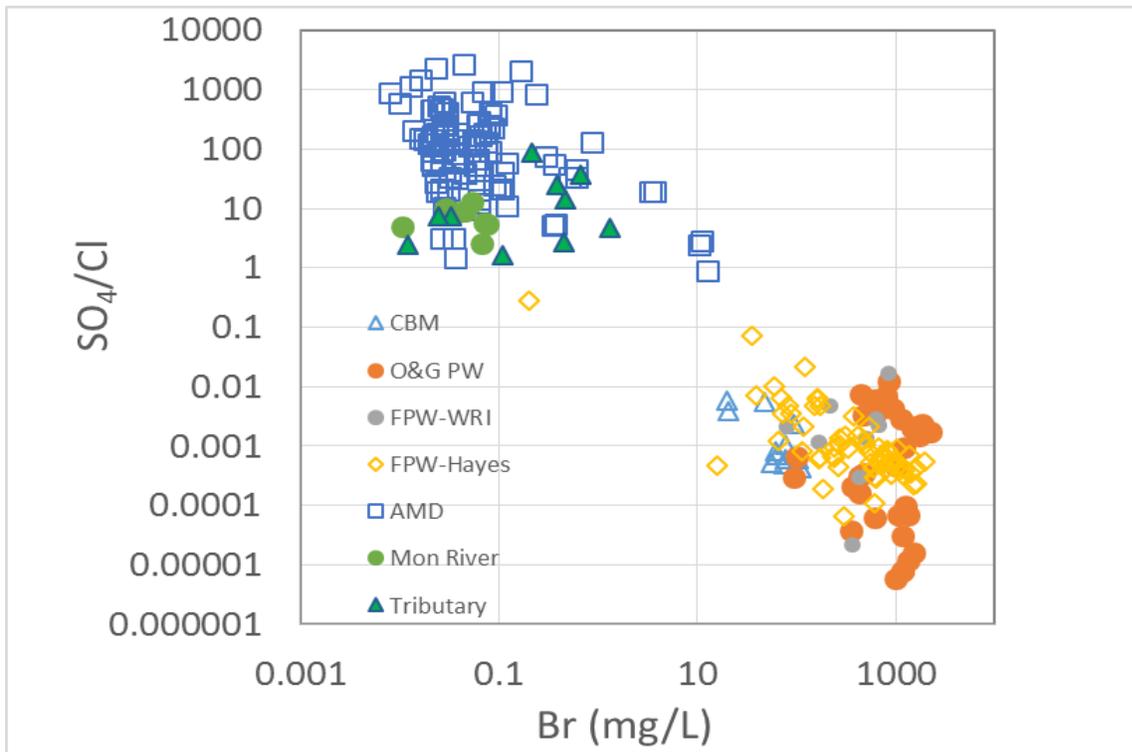


Figure 24. SO_4/Cl versus Br across different water sources.

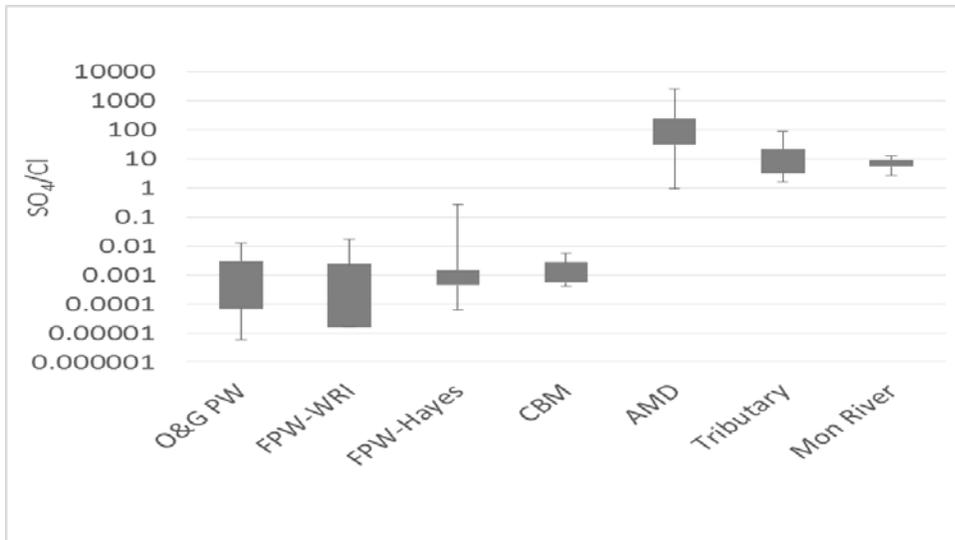


Figure 25. SO₄/Cl ratio across different water sources.

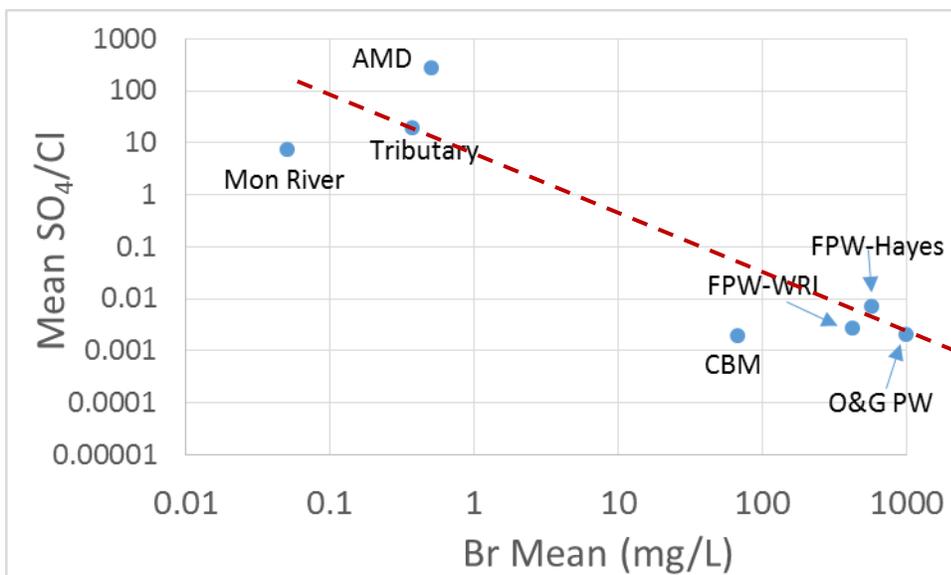


Figure 26. Mean SO₄/Cl versus mean Br concentration across different water sources.

7. Other chemical signatures

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

Ca versus Br, Sr versus Br, and Mg versus Br show strong correlation in low sulfate water sources (i.e., FPW, O&G PW) (Figures 27-31). Weak correlations have been observed in SO₄/Br versus Br, and Ba versus Br.

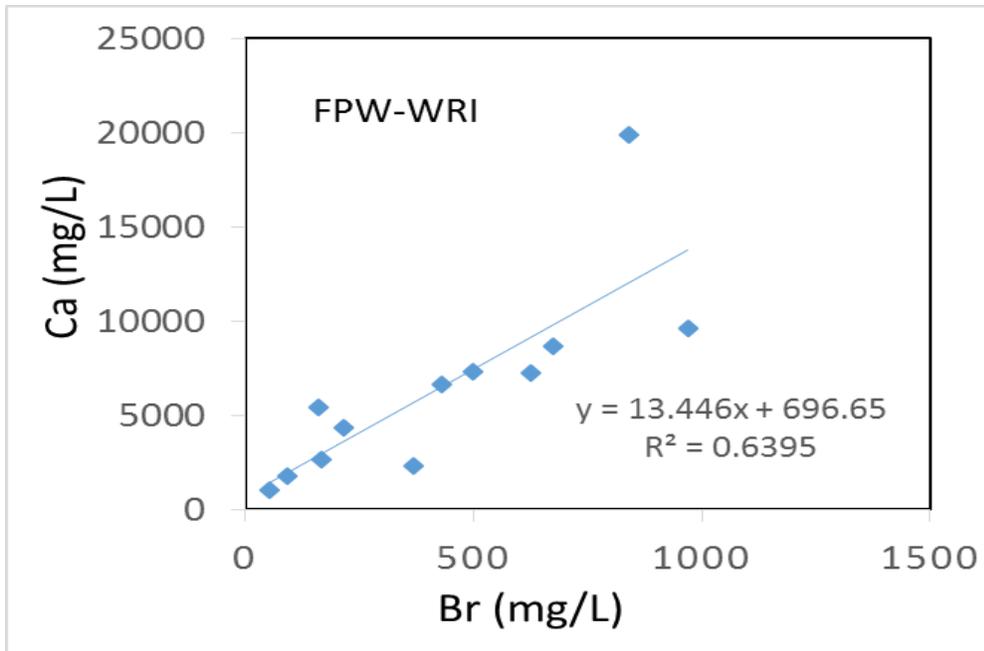


Figure 27. Ca versus Br in flowback from Marcellus shale gas development (data source: WVVRI, 2012).

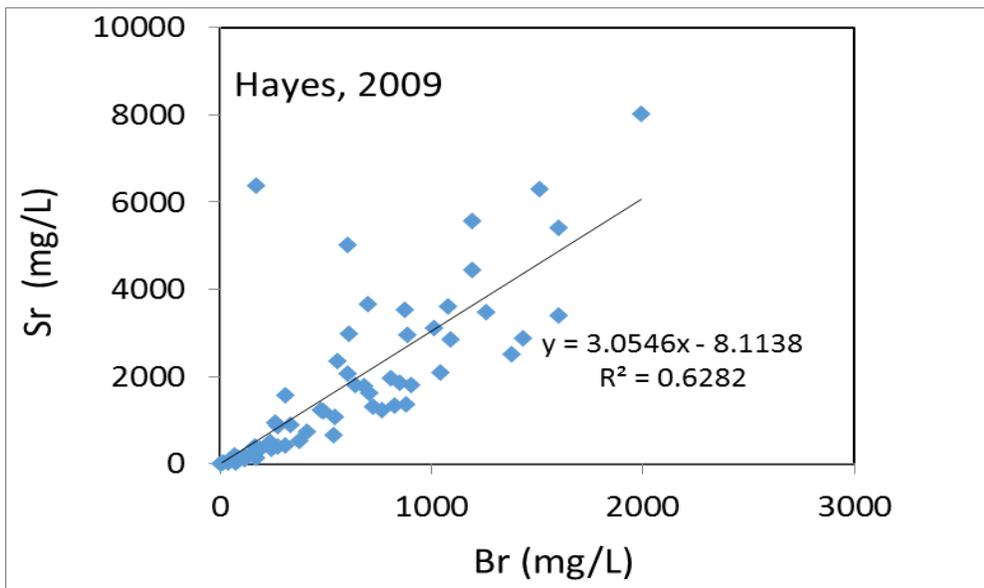


Figure 28. Sr versus Br in flowback and produced water from Marcellus shale gas development (data source: Hayes, 2009).

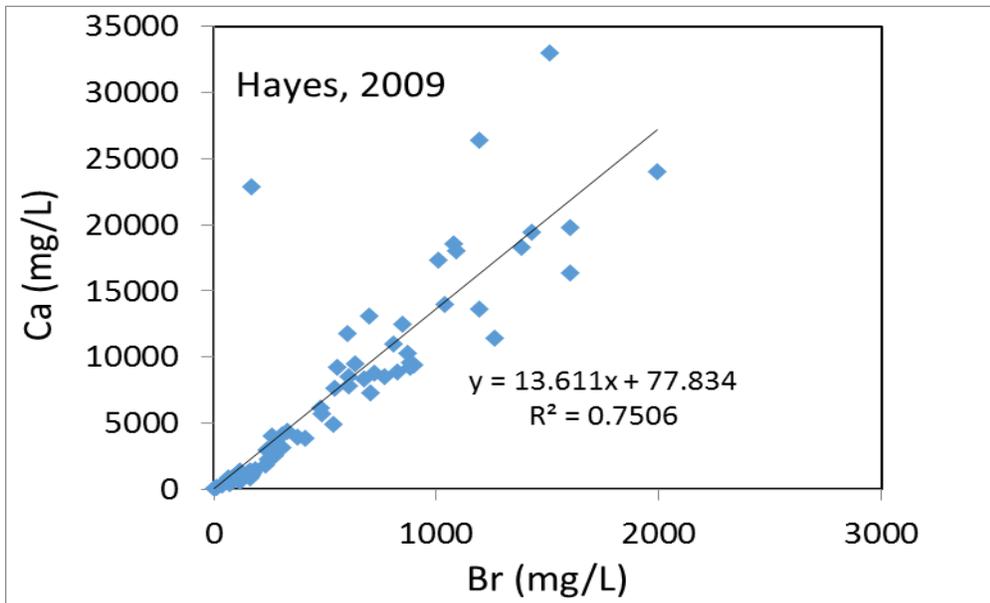


Figure 29. Ca versus Br in flowback and produced water from Marcellus shale gas development (data source: Hayes, 2009).

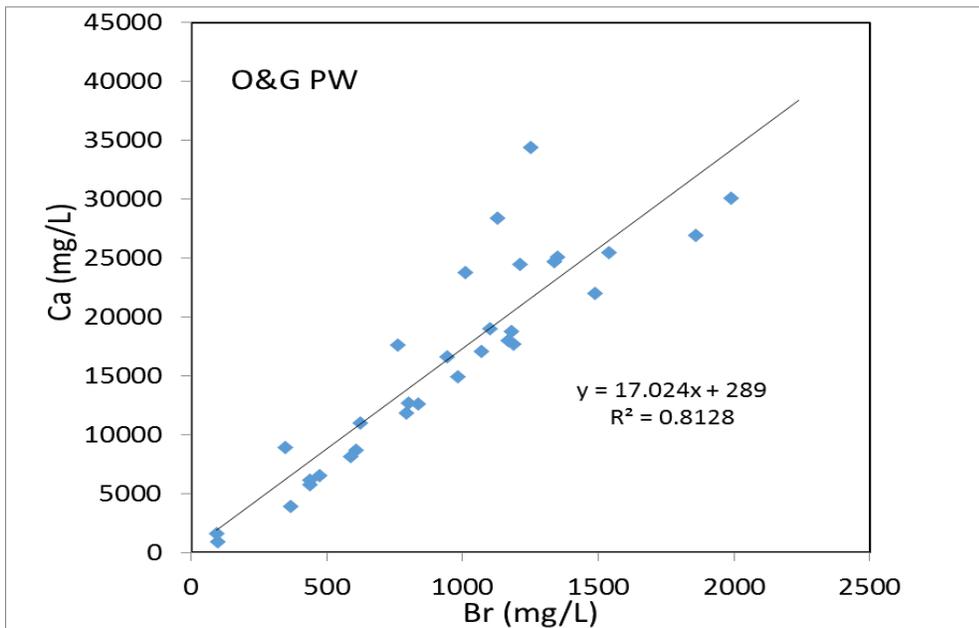


Figure 30. Ca versus Br in O&G produced water from Marcellus shale gas development (data source: Dresel and Rose, 2010).

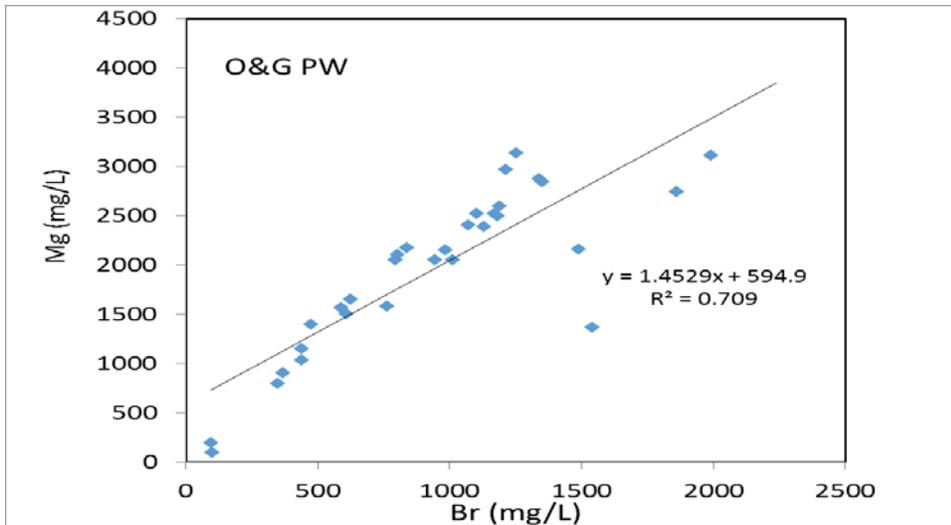


Figure 31. Mg versus Br in O&G produced water from Marcellus shale gas development (data source: Dresel and Rose, 2010).

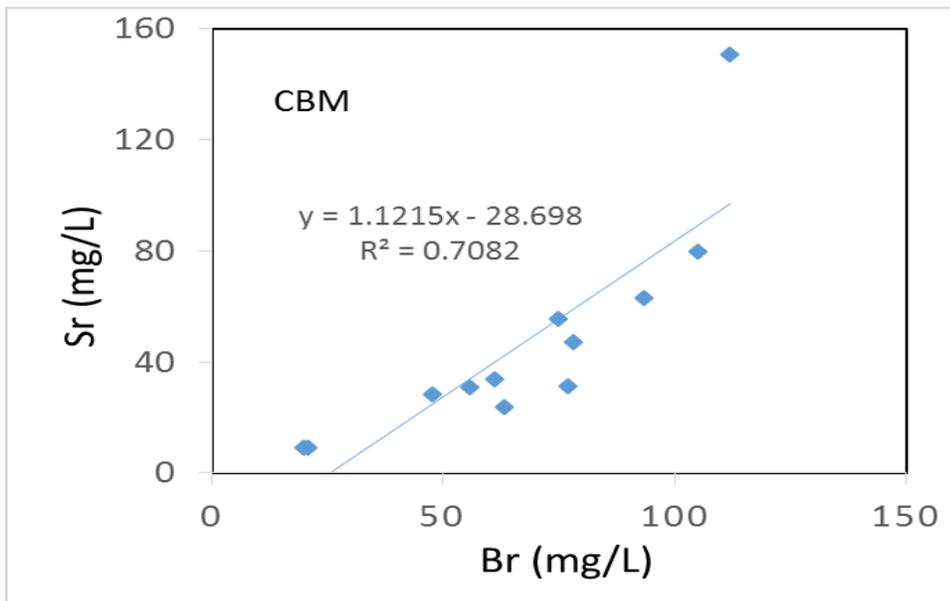


Figure 32. Sr versus Br in CBM produced water (data source: unpublished data).

8. Geochemical modeling

Vengosh and Pankratov (1998) found that it was possible to detect and distinguish sewage contamination from marine ratios in groundwater when a sewage contribution of 5–15% is mixed with regional groundwater, particularly where the background bromide concentration in groundwater is low. Panno *et al.* (2006) demonstrated that the trends displayed by the Cl/Br versus Cl⁻ scatter diagram appeared to reflect the evolution of water and trends of mixing (as the water samples increased in Cl⁻) from background levels (precipitation, unsaturated zone water, pristine groundwater) to the levels found in the sources.

Geochemical modeling using PHREEQC was conducted to examine mixing of shale gas produced water and other energy industry related wastewater with receiving streams (Monongahela River water) at different fractions 5%, 10%, 20%, and 30%. Water quality data used in the modeling is listed in Table 2. Changes in Br and Cl concentrations and impact on water quality is examined based on modeling results. Water quality data from modeling results is listed in **Table 4**.

Water quality change in general depends on the wastewater quality and percentage of wastewater mixed with receiving streams. Due to the conservative nature of Cl and Br, Br concentration increases linearly with percentage of wastewater mixed with receiving streams (**Figures 33-34**). Even with 5% of wastewater, Br concentration in receiving streams will likely exceed 100 µg/L.

Interaction of ions in wastewater and ions in receiving streams is not significant. However, interaction with solid phase was not considered in the modeling work in this study. Under natural conditions, this may have an important impact on the concentrations of some constituents.

Comparison of tributary water quality data with AMD mixing with Monongahela River water (Figure 34) indicate that tributary water may be impacted by AMD discharge in the area, even though the extent of impact was difficult to quantify in many circumstances.

Examining the modeling results in **Table 4**, we can see that 5% of waste streams (10% for AMD) will likely cause the Br concentration to exceed MCL in the receiving streams. Concentration of chemical constituents in receiving streams increases with percentage of waste streams mixed with receiving streams. Water chemistry is mainly changed by physical mixing; no significant chemical reactions were observed during mixing.

Table 4. Predicted water Chemistry after mixing Mon River water with wastewater at different ratios.

Source Ratio	Parameter													
	pH	pe	Br	Cl	Na	K	Ca	Mg	Ba	Sr	Fe	Al	Mn	SO4
O&G PW														
5%	7.04	2.62	60.5	6350	2790	52	1100	134	53.2	129	12	0.06	1.53	105
10%	6.93	2.79	121	12700	5550	104	2160	259	106	257	23.9	0.05	3	110
20%	6.82	3.03	242	25400	11100	208	4300	510	213	514	47.7	0.05	5.94	121
30%	6.76	3.19	363	38000	16600	312	6430	762	319	771	71.5	0.04	8.88	132
FPW-WRI														
5%	7.03	3.11	22.9	2200	1020	12.9	374	47	21.7	62.7	3.34	0.08	0.34	96.8
10%	6.91	3.34	45.7	4380	2010	25.9	716	86	43.5	125	6.6	0.1	0.61	94.1
20%	6.8	3.58	91.26	8741.9	3986.1	51.77	1401	163.95	86.98	250.7	13.11	0.13	1.16	88.64
30%	6.75	3.72	137	13100	5970	77.7	2090	242	130	376	19.6	0.17	1.72	83.2
FPW-Hayes														
5%	7.33	4.36	32.1	3560	1470	32.6	493	49.2	83.3	102	0.09	0.06	0.06	97.5
10%	7.31	4.51	64.1	7100	2910	65.2	954	90.4	167	204	0.08	0.05	0.05	95.5
20%	7.28	4.69	128	14200	5790	130	1880	173	333	408	0.07	0.05	0.05	91.5
30%	7.26	4.83	192	21300	8680	195	2800	255	500	612	0.06	0.04	0.04	87.5
AMD														
5%	6.65	3.82	0.07	17.9	33.5	0.28	42	13.3	0	0.04	7.08	0.58	0.63	176
10%	6.62	3.83	0.1	21.3	41.9	0.57	52.7	18.5	0	0.07	14.1	1.1	1.21	252
20%	6.61	3.86	0.15	28.2	58.6	1.13	74.1	28.9	0.01	0.15	28.1	2.13	2.36	404
30%	6.6	3.88	0.19	35.1	75.4	1.7	95.5	39.4	0.01	0.22	42	3.17	3.51	557
CBM														
5%	7.37	4.84	3.47	481	326	1.54	46.4	13.3	0.9	2.38	2.17	0.21	0.09	95.2
10%	7.39	4.86	6.89	948	626	3.08	61.5	18.5	1.8	4.76	4.26	0.36	0.11	90.9
20%	7.45	4.77	13.7	1880	1230	6.16	91.8	29	3.6	9.52	8.43	0.65	0.17	82.2
30%	7.51	4.65	20.6	2820	1830	9.24	122	39.5	5.4	14.3	12.6	0.94	0.22	73.5

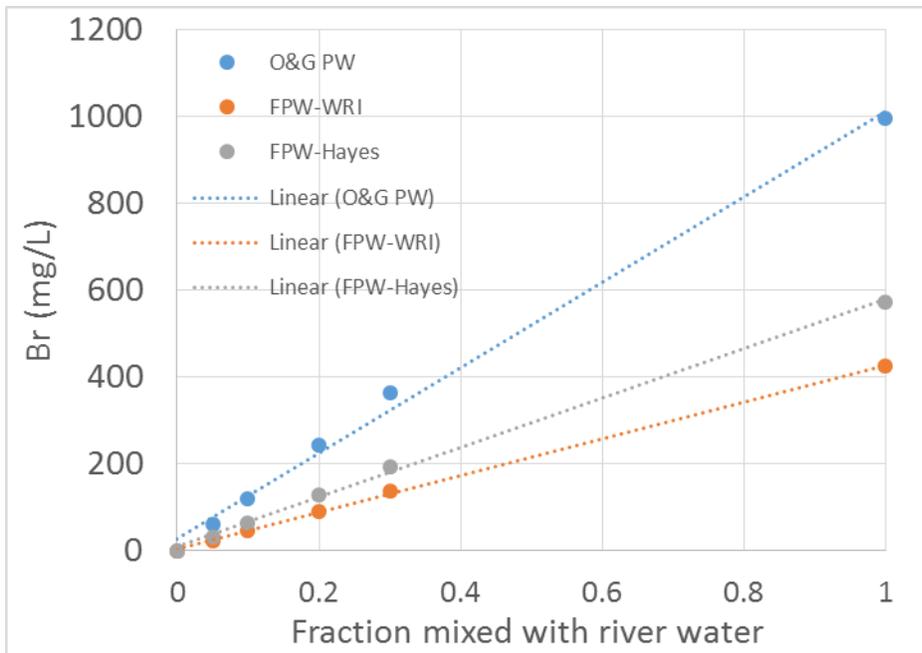


Figure 33. Predicted Br concentration at different fraction of produced water mixed with Monongahela River water.

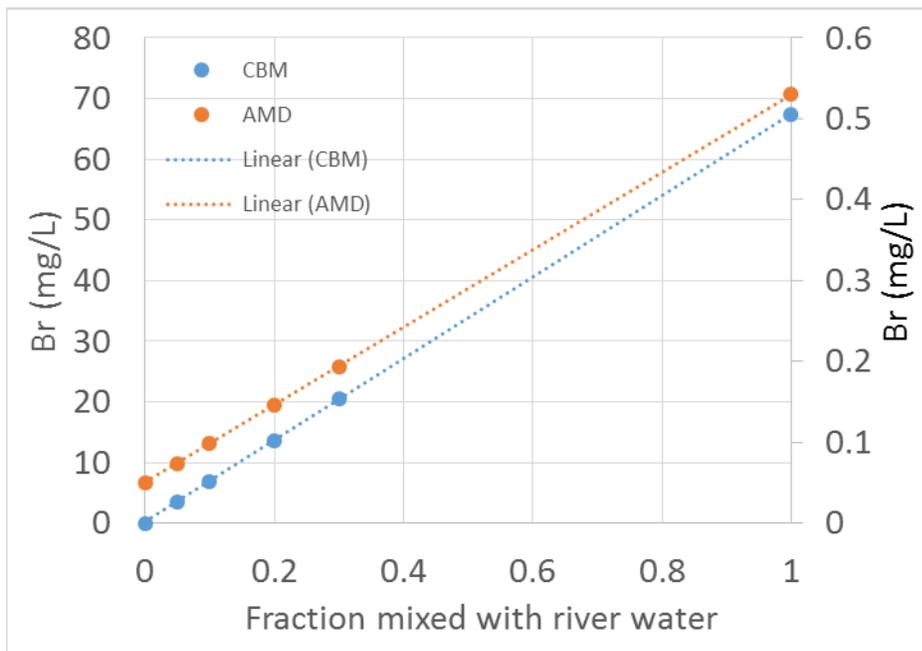


Figure 34. Predicted Br concentration at different fraction of coal related wastewater mixed with Monongahela River water (AMD on secondary Y axis).

9. Summary of key findings

- Controlling Br concentration in source water is important for drinking water treatment plants. Br concentration in different wastewater streams ranged widely in the Appalachian region. The Br concentration in receiving streams depends on the wastewater source and extent of mixing of wastewater with receiving streams. Similar to Cl, Br is mobile in the environmental media because of its conservative nature.
- Strong correlation between Br and Cl (and log Br versus Log Cl) was observed among all water sources examined. Linear correlation for Br versus Cl spans across eight orders of concentration range in both bromide and chloride among the water sources. However, each source only occupies certain concentration domain across the range.
- The range of Br/Cl ratio is large within individual water sources, but the difference among the different water sources is relatively small and stays in a narrow range.
- The SO₄/Cl versus Br range is large and widely spread within individual source. The SO₄/Cl versus Br relationship for the water sources examined could be grouped into two classes. Oil and gas related produced waters have a low SO₄/Cl ratio; coal mining related wastewaters have a high SO₄/Cl ratio.
- The concentration of TDS increases as Br concentration increases. TDS increased from receiving streams, to AMD, to FPW, with O&G PW having the highest TDS concentration.
- Concentration of Na is strongly correlated with Br across all water sources examined. Na concentration increases as Br concentration increases. In uncontaminated surface water, the correlation is weak due to very low Br concentrations.
- Several other parameters have been examined to investigate their potentials as a tool to differentiate water sources. Ca versus Br, Mg versus Br, Sr versus Br showed strong correlation in some examined water sources. However, weak or no correlations were observed in other sources. No consistent relationship was observed for these chemical signatures across different water sources, thus they are not likely to be useful as a diagnostic tool in identifying Br source.
- Geochemical modeling results show a linear increase of Br concentration through mixing as percentage of wastewater increases in the receiving streams due to conservative nature of Br. Br will likely exceed standard even with 5% wastewater (10% for AMD) mixed in uncontaminated surface water.
- The results of this study indicate that chemical signatures Br versus Cl, Na versus Br have potential to differentiate source of Br from different industry. SO₄/Cl versus Br has limited use, it can differentiate water sources from coal related industry versus oil and gas related industry. Br/Cl ratio is not useful because of the narrow range among the sources. Other signatures are not useful as no consistent trends can be identified.

Significance of the Project

This study investigated one of the newer environmental issues (Br contamination) in the Appalachian region. The use of the diagnostic tools such as Br versus Cl, Na versus Br 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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Publications

- Y. Thomas He and Paul Ziemkiewicz. Chemical signatures to differentiate bromide source in water in the Appalachian region. In Preparation.

Information Transfer Program

WVWRI will submit abstracts and/or papers to conferences and journals for consideration.

Student Support

A graduate student that was originally recruited to assist with project activities left school unexpectedly.

Notable Achievements and Awards

No awards to report at this time.

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

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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 (Phase I) and Implementation of a Drinking Water Well Sampling Protocol (Phase II)

Final Report

March 1, 2012 – February 29, 2016

Principal Authors:

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Abstract

The Marcellus Shale, one of the largest natural gas reserves, requires horizontal drilling and hydraulic fracturing to release the natural gas from the formation. Upwards of four million gallons of a water-based fluid is used in the hydraulic fracturing (fracing) process with upwards of 20% of this fluid flowing back over time leading operators to deal with huge amounts of water. To effectively manage these waters, operators need to know what they are dealing with – what are the characteristics of the supply waters used to frac a well and what are the characteristics of the water that comes back up once the well starts producing. Small amounts of additives are mixed in with the supply waters to frac a well. Each gas company has their own “recipe” of friction reducers, corrosion and scaling inhibitors, biocides, etc. to add with the water and sand mixture making up their fracing fluid. The flowback water will contain these compounds along with salts, metals, organic compounds and other constituents of concern picked up from the formation. The increased activity with the Marcellus Shale has heightened attention and raised questions about potential impacts on nearby environmental and public health, specifically surrounding the water streams associated with the gas wells and impacts on nearby groundwater. Given the sheer number of additive compounds that are used during the drilling process and those that could be mixed with supply waters to frac a well, and the water quality of the supply water, it becomes an overwhelming task to determine what water quality parameters need to be monitored to protect nearby groundwater sources that may serve as drinking water supplies. Once the fracing fluid mixes in with the shale formation and the water begins to flow back, additional water quality parameters become of concern thus adding to the list.

The objective of this study was to look at the chemical make-up of drilling fluids, muds and cuttings and fracing and flowback waters throughout the Marcellus Play in northern West Virginia and determined a manageable list of parameters industry and homeowners can follow to monitor groundwater and drinking water wells near a gas well. Working closely with industry and state agencies, gas well sites were identified and accessed to obtain drilling fluids, muds and cuttings and fracing and flow back waters were sampled.

Information on the source waters that made up the fracing water and copies of the fracturing fluid composition were obtained. Comparisons were made of all water streams at each gas well site with the EPA’s contaminants of concern list, focusing more on organic compounds. A list of parameters to monitor for each well were developed along with a monitoring plan and sampling schedule. Analytical results were reviewed and used as the basis for the development of a monitoring protocol for sampling and analyzing nearby groundwater and drinking water wells.

This study was comprised of two phases. Phase I, “*Development of a Drinking Water Well Sampling Protocol to Establish Baseline Data Prior to Horizontal Drilling of Gas Wells,*” focused on developing a drinking water well sampling protocol. Samples from various horizontal gas well sites in West Virginia were collected from drill cuttings and muds, hydraulic fracturing fluids, and flowback/produced water (FPW). These samples were analyzed for several organic, inorganic, and radiological parameters to characterize these water and waste streams. Results were compared to

similar research projects' results to verify findings were within normally observed ranges. Parameters of concern, those with the greatest potential to be found in nearby water resources, were identified and used as the basis to begin establishing a drinking water well monitoring protocol.

Phase II, "*Implementation of a Drinking Water Well Sampling Protocol*," focused on implementing the monitoring protocol. Drinking water wells were monitored in multiple study areas, an active area of horizontal gas well development, and a non-active area – area with no horizontal gas well development activity. Drinking water well monitoring results of the active and non-active study areas were compared to determine if: 1) the monitoring protocol consists of the appropriate water quality indicators when considering potential human health effects; 2) negative impacts to drinking water well(s) resulted from shale gas development; and 3) results of sampled parameters are the consequence of pre-existing in situ environmental conditions. Findings of Phase II provided a field-tested, cost-efficient, and effective drinking water well protocol option for well owners. The protocol may also provide guidance to industry and regulatory agencies to refine their own groundwater monitoring protocols/programs.

During phase II of the study, various recommendations exist for water quality testing of private drinking water wells from regulatory agencies, private laboratories, and environmental groups. For general use and maintenance, these recommendations are fairly similar. However, when you insert new industrial development into the surrounding area, such as the recent Marcellus Shale gas development, water quality testing becomes very complex and costly to the average homeowner (well owner). The well owner wants to ensure their drinking water has not been compromised; but, they often end up with more questions than answers. What parameters should be monitored, how often should sampling occur, when should sampling start, how long should samples be taken, and how much is this going to cost, are just a few of the frequently asked questions.

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Executive Summary

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 used recently within the Marcellus Shale Formation has greatly escalated. Horizontal wells, unconventional gas 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 may pose an increased potential to impact nearby water resources. Of most concern to the general public are potential contamination threats to nearby private drinking water wells during shale gas development activities. Most horizontal shale gas well development occurs outside populated areas in rural areas of the countryside. Many homeowners living in these 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 quality 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. Various recommendations exist for water quality testing of private drinking water wells. For general use and maintenance, these recommendations are fairly similar. However, when you insert new industrial development into the surrounding area, such as the recent Marcellus Shale gas development, water quality testing becomes very complex and costly to the average homeowner (well owner). The well owner wants to ensure their drinking water has not been compromised; but, they often end up with more questions than answers. What parameters should be monitored, how often should sampling occur, when should sampling start, how long should samples be taken, and how much is this going to cost, are just a few of the questions asked repeatedly.

Phase I, *“Development of a Drinking Water Well Sampling Protocol to Establish Baseline Data Prior to Horizontal Drilling of Gas Wells,”* focused on developing a drinking water well sampling protocol. Samples from various horizontal gas well sites in West Virginia were collected from drill cuttings and muds, hydraulic fracturing fluids, and FPW. These samples were analyzed for several organic, inorganic, and radiological parameters to characterize these water and waste streams. Results were compared to similar research projects’ results to verify findings were within normally observed ranges. Parameters of concern, those with the greatest potential to be found in nearby water resources, were identified and used as the basis to begin establishing a drinking water well monitoring protocol.

Phase II, *“Implementation of a Drinking Water Well Sampling Protocol,”* focused on implementing the monitoring protocol. Drinking water wells were monitored in two study areas, one active area of horizontal gas well development, and one non-active area – area with no horizontal gas well development. Drinking water well monitoring results of the active and non-active study areas were compared to determine if: 1) the monitoring protocol consists of the appropriate water quality indicators when considering potential human health effects; 2) negative

impacts to drinking water well(s) have resulted from shale gas development; and 3) sampled parameters are the result of pre-existing in situ environmental conditions.

The monitoring protocol (or plan) provided a concise list of contaminants to monitor drinking water wells located in close proximity to unconventional shale gas well development. Results from this study indicated the drinking water wells were not negatively impacted by nearby gas well development.

Problem and Research Objectives

Development of shale gas resources promises to be an important opportunity for the United States; thus, drilling activities have escalated over the past few years due to the use of horizontal drilling and hydraulic fracturing techniques. Although these methods have been in practice for decades in other areas of the country, they are considered new to the Marcellus Shale region. The accelerated rate at which these methods have been applied and the volumes of water necessary for their use, have elevated concerns of potential environmental impacts. Drilling fluids and muds may consist of water, mineral oil or a 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. FPW 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 and waste streams associated with the development of a shale gas well requires knowing the characteristics of those streams. This study first focused on sampling and analyzing drilling fluids, muds and cuttings, along with hydraulic fracturing fluids and FPW of shale gas wells in northern West Virginia and determining which of their compounds, if they were to reach groundwater resources, are of concern for potential contamination. Results of these activities provided the initial framework to address *what must a well owner living near shale gas development do to recognize if their well has been negatively impacted and how to protect themselves if their water becomes contaminated*. A monitoring protocol for sampling nearby individual drinking water wells was 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 monitoring protocol was also compared to research studies that have sampled drinking water wells located in close proximity to planned and active Marcellus Shale gas wells. The next step was to “field-test” the protocol to determine if it would provide a cost-effective and efficient tool for homeowners to monitor the quality of their drinking water wells and detect contaminant intrusion.

This project was a field-based research effort to examine the effects of large-scale horizontal shale gas development on surrounding water resources (surface and ground water resources) and to provide a monitoring protocol for drinking water well owners to follow to address these concerns.

Phase I

Objective 1: Define the concerns with potential groundwater contamination that may be caused by gas well development. Determine how groundwater sources are protected during the well drilling process. Identify the major natural gas players within the Monongahela River Basin and identify the composition of the drilling fluids, muds and cuttings and the “frac recipe” being used for each well in the study area.

Objective 2: Compare the make-up of drilling fluids and muds, fracing and flowback waters to the EPA’s list of contaminants of concern associated with the shale gas development industry. Determine what are the “real” indicators or “parameters of concern” to analyze based on the make-up of the drilling fluids and muds, and fracing and flowback waters.

Objective 3: Define sampling frequency and duration to monitor the drilling fluids, muds and cuttings along with the fracing and flowback waters, starting with an initial sampling plan to collect at least one sample of the drilling fluids, muds and cuttings during the drilling process and upon drilling completion. Frac water samples will be collected on the first day of fracing and days 1, 14, 30, 45 and 90 of flowback water. Based on results, the sampling plan will be adjusted accordingly.

Objective 4: Explore the feasibility of having sampling results added to the pre-established MonRiver Quest GIS platform or develop an independent GIS platform for this study.

Objective 5: Garner cooperation from stakeholders in developing a monitoring protocol for drinking water wells based on the results of this study. Stakeholder groups may include West Virginia Department of Health and Human Resources, West Virginia Department of Environmental Protection, and energy companies active in the region.

Objective 6: Looking at basic water chemistry parameters and identified parameters of concern from this study, especially organic compounds, develop a monitoring protocol for sampling and analyzing drinking water wells located in close proximity to horizontal gas wells. The monitoring protocol should identify a list of parameters to analyze and how often samples should be taken during the course of planning (for baseline data), development and production (for determination if water quality changes during gas well activity) of a gas well.

Phase II

Objective 1: Identify study areas to implement monitoring protocol developed in Phase 1.

Objective 2: Identify potential partners (watershed associations, homeowner associations, etc.) willing to assist with the implementation of the monitoring protocol by allowing access to drinking water wells for water sampling.

Objective 3: Implement monitoring protocol, collect samples, and compare findings of active versus non-active study areas. Adjust monitoring protocol according to results, if needed.

Objective 4: Input data into 3RQ GIS system.

Methodology

Phase I

Objective 1: Define the concerns with potential groundwater contamination that may be caused by gas well development. Determine how groundwater sources are protected during the well drilling process. Identify the major natural gas players within the Monongahela River Basin and identify the composition of the drilling fluids, muds and cuttings and the “frac recipe” being used for each well in the study area.

Researchers identified several public concerns with potential groundwater contamination that may be caused by gas well development to include: aquifer and drinking water well contamination; waste storage pit leakage; spills of hydraulic fracturing fluids; handling of flowback streams; water use and supply; drilling waste disposal; stormwater runoff; and blowouts. These concerns stem from two related activities: 1) well development and completion, and 2) management of water and waste streams (handling, storage and disposal). Identifying the cause of contamination of a nearby drinking water well can be difficult. Characterization of flowback and produced water chemistry and isotopic composition is typically employed to identify migration of hydraulic fracturing wastes into drinking water supplies.

Drinking water wells need to be properly drilled and cased to protect against any potential contamination from nearby activities such as agriculture, industry, and even discharges from onsite septic systems. Baseline monitoring or sampling is necessary for drinking water well users. Baseline sampling is the establishment of a benchmark to use as a foundation to compare future sampling or monitoring results. Pre-activity and post-activity drinking water well samples should be taken to identify any changes in water quality that may be linked to the nearby development activity.

Researchers identified the major natural gas players within the Monongahela River Basin and identified the composition of the drilling fluids, muds and cuttings, and the “frac recipe” being used for each well in the study area.

Objective 2: Compare the make-up of drilling fluids and muds, fracing and flowback waters to the EPA’s list of contaminants of concern associated with the shale gas development industry. Determine what are the “real” indicators or “parameters of concern” to analyze based on the make-up of the drilling fluids and muds, and fracing and flowback waters.

Researchers compared the make-up of drilling fluids and muds, fracing and flowback water to the EPA’s list of contaminants of concern associated with the shale gas development industry.

WVWRI developed an initial list of analytes for sampling and characterizing water and waste streams associated with the various stages of unconventional shale gas well development. The list was based on 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, Pennsylvania, and Ohio.

Objective 3: Define sampling frequency and duration to monitor the drilling fluids, muds and cuttings along with the fracing and flowback waters, starting with an initial sampling plan to collect at least one sample of the drilling fluids, muds and cuttings during the drilling process and upon drilling completion. Frac water samples will be collected on the first day of fracing and days 1, 14, 30, 45 and 90 of flowback water. Based on results, the sampling plan will be adjusted accordingly.

Marcellus Shale gas wells located in northern West Virginia were identified and samples were collected of water and waste streams. A monitoring plan and sampling schedule was developed. Samples were collected following standard methods and procedures. Samples were sent to a certified laboratory for analysis with proper chain-of-custody paperwork and trip blanks. Samples of drilling fluids, muds and cuttings were collected during the horizontal drilling stage. Hydraulic fracturing fluids and makeup water were sampled during the fracing stage of well development. Flowback/Produced water (FPW) samples were collected on the first day of production, once per week for the first month, followed by sampling every-other-week for the next three months of production.

Objective 4: Explore the feasibility of having sampling results added to the pre-established MonRiver Quest GIS platform or develop an independent GIS platform for this study.

Data was entered into the Mon River Quest GIS platform upon review of the data whenever the data was determined to be an added benefit to the existing water quality platform.

Objective 5: Garner cooperation from stakeholders in developing a monitoring protocol for drinking water wells based on the results of this study. Stakeholder groups may include West Virginia Department of Health and Human Resources, West Virginia Department of Environmental Protection, and energy companies active in the region.

Researchers within the WVU School of Public Health participated with the initial review of contaminants and the development of a drinking water sampling plan.

Objective 6: Looking at basic water chemistry parameters and identified parameters of concern from this study, especially organic compounds, develop a monitoring protocol for sampling and analyzing drinking water wells located in close proximity to horizontal gas wells. The monitoring protocol should identify a list of parameters to analyze and how often samples should be taken during the course of planning (for baseline data), development and production (for determination if water quality changes during gas well activity) of a gas well.

Based on the results of this study, a monitoring protocol for sampling and analyzing nearby groundwater and drinking water wells was developed. The monitoring protocol has a defined set of water quality parameters to analyze and a sampling schedule. The sampling schedule reacts to the schedule of gas well development activity by obtaining pre-stage and post-stage water quality samples for each stage of gas well development. Once a well is producing, water quality samples should be taken on a regular basis, dependent upon results obtained throughout the gas well development stage and any changes in water quality noted during these stages.

Phase II

Objective 1: Identify study areas to implement monitoring protocol developed in Phase 1.

Control study sites were selected based on research knowledge of nearby areas without a previous coal mining or natural gas exploration – Preston County, West Virginia. Active study sites were selected based on the intensity of natural gas development in the surrounding area – Susquehanna County, Pennsylvania. Specific sampling locations were identified in an area that included a permitted natural gas well without close proximity of previously developed natural gas wells.

Objective 2: Identify potential partners (watershed associations, homeowner associations, etc.) willing to assist with the implementation of the monitoring protocol by allowing access to drinking water wells for water sampling.

Control site partners were identified through prior communications/inquiries regarding water related studies in Preston County, WV. Active site partners were identified through a related air monitoring study through WVU – homeowners participating in the air monitoring study were contacted regarding participation in this water research study. Information regarding participants in the study is confidential. Simple nomenclature (i.e. W-01) serves to identify sampling locations.

Objective 3: Implement monitoring protocol, collect samples, and compare findings of active versus non-active study areas. Adjust monitoring protocol according to results, if needed.

Field measurements included: temperature, dissolved oxygen, specific conductivity, and total dissolved solids. Grab samples were collected using proper techniques for each analyte (Table 2) and submitted to an analytical laboratory for analysis.

Objective 4: Input data into 3RQ GIS system.

To publicly share data without compromising confidentiality of homeowners, the resultant study data was provided to the Three Rivers Quest (3RQ) program. The 3RQ is processing data for upload to their online data map. Users will have the ability to see data without being able to zoom in closely to reveal specific sampling locations.

Principal Findings

Table 1 details the parameter list and analytical results based on 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, Pennsylvania, and Ohio.

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

Parameter	Units	Freshwater Impoundment	HF Fluids	Drilling Muds	Drill Cuttings	FPW	Waste Storage
Aluminum	mg/l	ND – 0.0236	ND – 0.80	0.969 – 4550	4740 – 12100	ND – 13.3	ND – 2.78
Arsenic	mg/l	ND	ND – 0.0022	ND – 37	2.35 – 19.2	ND- 0.62	ND
Barium	mg/l	0.032 – 0.0565	0.03 – 12.4	2.13 – 5900	23.9 – 5920	23.1 – 2580	10.2 – 572
Bromide	mg/l	ND – 0.11	0.235 – 126	1.60 – 37.5	ND – 10.8	370 – 970	52.5 – 675
Calcium	mg/l	20.8 – 44.4	35 – 1260	1090 – 52000	781 – 152000	2200 – 19900	1010 – 8670
Chloride	mg/l	12.8- 26.5	48 – 9500	ND – 131000	876 – 20000	27500 – 79000	4700 – 56000
Chromium	mg/l	ND	ND – 0.0065	0.268 – 19.0	6.367 – 32.8	ND – 0.16	ND – 0.144
Iron	mg/l	ND – 0.0244	0.174 – 30.9	1.09 – 30000	6670 – 30400	14.7 – 340	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 – 2700	1920 – 7090	310 – 2260	107 – 944
Manganese	mg/l	0.0025 – 0.022	0.147 – 1.76	0.064 – 435	91.9 – 714	1.715 – 14	1.38 – 7.56
Mercury	mg/l	ND	ND	ND – 0.196	ND – 0.173	ND	ND
Nickel	mg/l	ND	ND	ND – 140	10.3 – 41.4	ND – 0.79	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	118 – 1100	44.2 – 315
Selenium	mg/l	ND	ND – 0.0005	ND – 16	ND – 3.14	ND – 0.5	ND
Silver	mg/l	ND	ND – 0.00005	ND – 0.54	ND – 0.397	ND – 0.05	ND
Sodium	mg/l	8.46 – 27.1	62 – 3990	364 – 44900	543 – 12400	12000 – 119000	2440 – 20800
Strontium	mg/l	0.122 – 0.239	0.32 – 136	10.6 – 1600	4.22 – 508	530 – 4660	117 – 1460
Sulfides	mg/l	4.19 – 30.3	4.47 – 33	ND – 9450	1410 – 12800	ND – 303	ND – 38.7
Zinc	mg/l	ND – 0.0075	ND – 1.74	ND – 480	2.22 – 89.7	ND – 0.58	0.06 – 0.352
Conductivity	µmhos/cm	315 – 483	1030 – 33100	9100 – 222000	1150 – 77000	48000 – 230000	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 – 330	118 – 234
TDS	mg/l	170 – 277	420 – 20400	6600 – 119000	NM	45400 – 154000	8840 – 93700
TSS	mg/l	ND – 6	14 – 260	18300 – 162000	NM	ND – 1200	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 – 8400	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 – 0.0025	ND – 262	NM	ND – 0.74	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	5.14 – 83	14.9 – 23770	17.3 – 30.1	168 – 4664	34 – 1349
Radium-226	pCi/l	0 - .725	1.44	6.45 – 9.715	0.95 – 3.114	178 – 10299	15.4 – 1194
Radium-228	pCi/l	0.189 – 0.354	1.23	0.486 – 4.95	0.715 – 1.929	49.1 – 461	53.5 - 216

ND = not detected NM = not measured

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 the elimination of parameters not detected and thus would not appear in drinking water well sampling results unless reported during prior water quality testing. Public health professionals were enlisted to evaluate the shale gas water and waste stream characterization sampling results and identify potential pollutant markers. This exercise led to the development of a sampling list when testing drinking water wells located near shale gas development activities, **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, BTEX = benzene, toluene, ethylbenzene, xylene

Baseline sampling is conducted prior to any nearby gas well development activity beginning. *Baseline sampling* is the establishment of a benchmark to use as a foundation to compare future sampling results and should consist of at least the parameters listed in **Table 2** above. What is *nearby*? States and industry define nearby differently. For this project, it is considered the distance (or radius) from the center of the wellhead extending outward 360° and can range from 500 feet to over 3000 feet. Well owners should have at least one set of baseline results on hand for comparing future testing results they may have done or the energy company may have done.

Once gas well development activity begins, a drinking water well owner should have their well tested for the same suite of parameters after the completion of each shale gas well development stage: land clearing and well pad construction; vertical drilling; horizontal drilling; and hydraulic fracturing. Once the gas well begins to flow back water and gas, a drinking water well owner may consider having his well periodically tested over the course of the next few years depending upon their proximity to the gas well, geography and geology of the area, and if additional gas wells in the area are being planned for development.

Two general locations were identified for this 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 the northeast and southwest regions of

Pennsylvania. The *active group* is located near Montrose in Susquehanna County, Pennsylvania. The *control group* is located near Cranesville in Preston County, West Virginia.

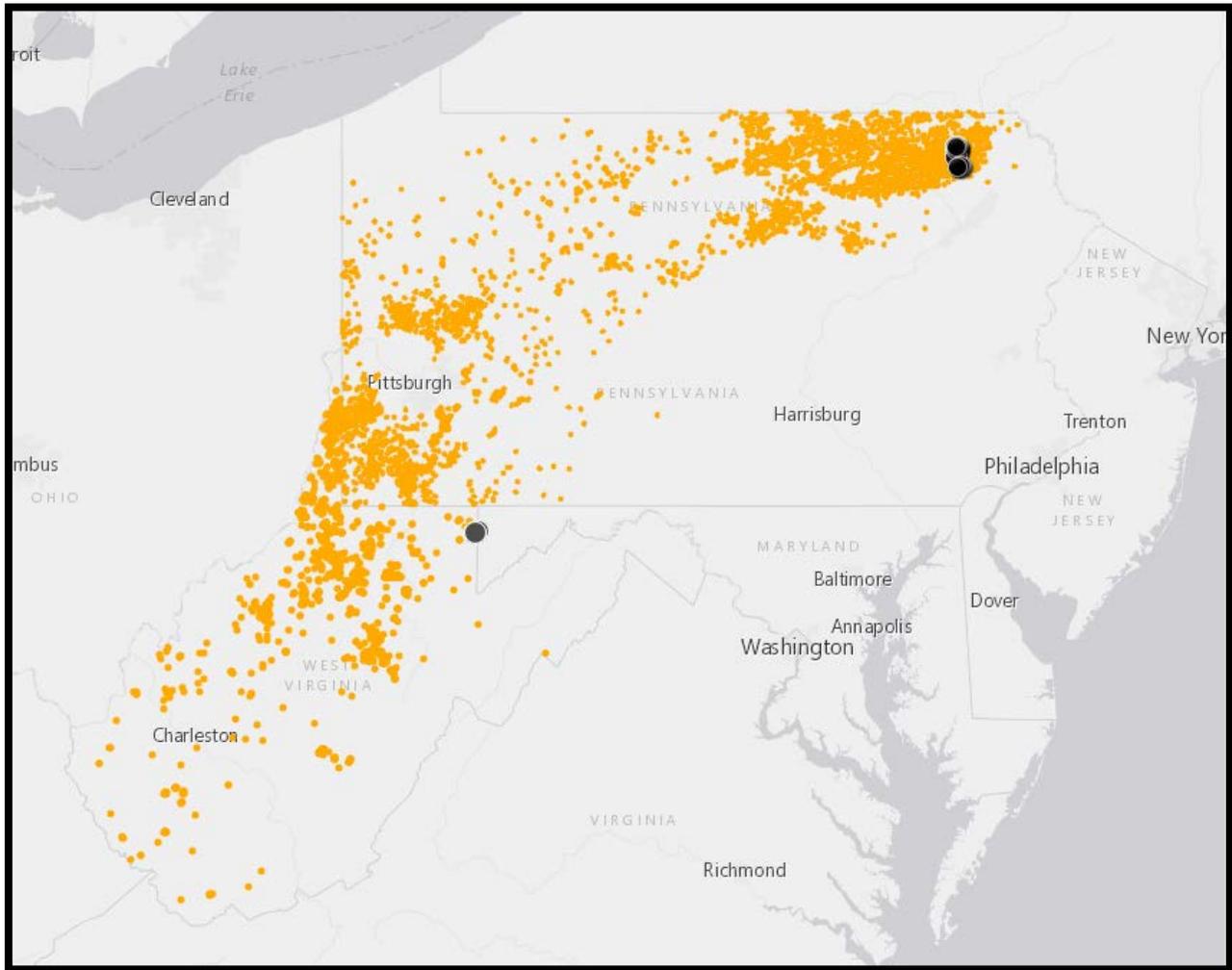


Figure 1. Permitted shale gas sites (orange), and control and active site sample locations (black).

Sampling Locations

Active Site Sampling

Development of the Marcellus Shale through horizontal drilling techniques has been intense in Pennsylvania with over 9,000 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 2 is a closer look at unconventional gas well development in Susquehanna County. While intense activity is present in Susquehanna County, the research team identified homeowners that were near a permitted, but not yet drilled well (API #115-21822). **Figure 3** identifies surface water monitoring sites (7A, 6C, 5A, P-01, P-02, SP-A, SP-B, SP-C, UNT 44288) and groundwater monitoring (drinking water well) sites (W-01, W-02, W-03, W-04) selected for the study.

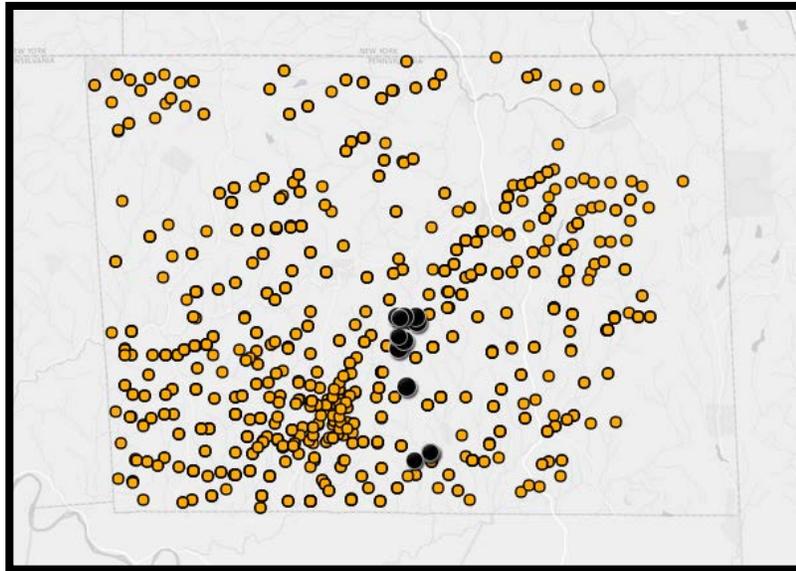


Figure 2. Unconventional wells drilled (orange) and active site sampling locations (black) in Susquehanna County, Pennsylvania.

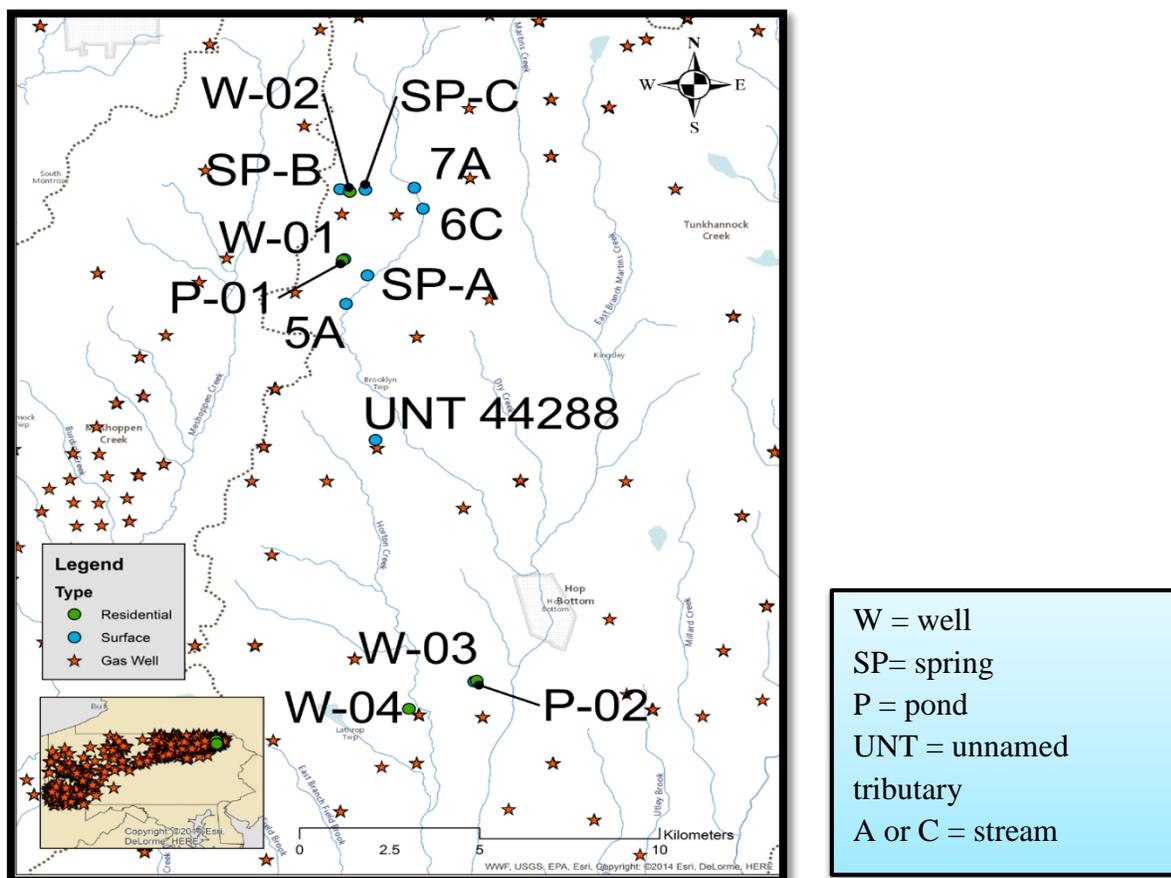


Figure 3. Active site sampling locations and well locations in Susquehanna County, Pennsylvania.

Groundwater samples were taken from residential drinking water wells. Samples were drawn from the pressure tank prior to any treatment (e.g. water softening) as noted in **Figure 4**. Water valves were opened to allow water to run for at least 3 to 5 minutes prior to sample collection.



Figure 4. Groundwater was sampled mostly from pressure tanks in residences.

Figure 5 shows two of the spring locations that were also sampled. Spring SP-A was accessible to the public along Hop Bottom Road and many residents would depend upon this spring for cooking and drinking purposes using their private drinking water well for other water usage. Estimated flow for Spring SP-A ranged from a high of 36 gallons per minute (gpm) to a low of 8 gpm.



Figure 5. Spring sampling sites SP-A (left) and SP-B (right).

Surface water sampling points along Hop Bottom included upstream and downstream points where potential runoff from the development of the nearby permitted gas well site may impact the stream. **Figure 6** depicts site 7A along Hop Bottom, upstream of the soon-to-be developed unconventional gas well.



Figure 6. Surface water sampling point 7A upstream of permitted gas well.

Figure 7 is the first sampling location, 6C, immediately downstream where potential runoff may impact Hop Bottom.



Figure 7. Sampling location 6C downstream of gas well site.

Control Site Sampling

Groundwater (drinking water well) samples were collected at six residencies in Preston County, West Virginia and Garrett County, Maryland shown in **Figure 8**. The nearby permitted unconventional gas well: API # 4707700580 is approximately 2,000 meters (just over 6,500 feet) from the closest sampling 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 site* highlighted yellow in **Figure 8**.

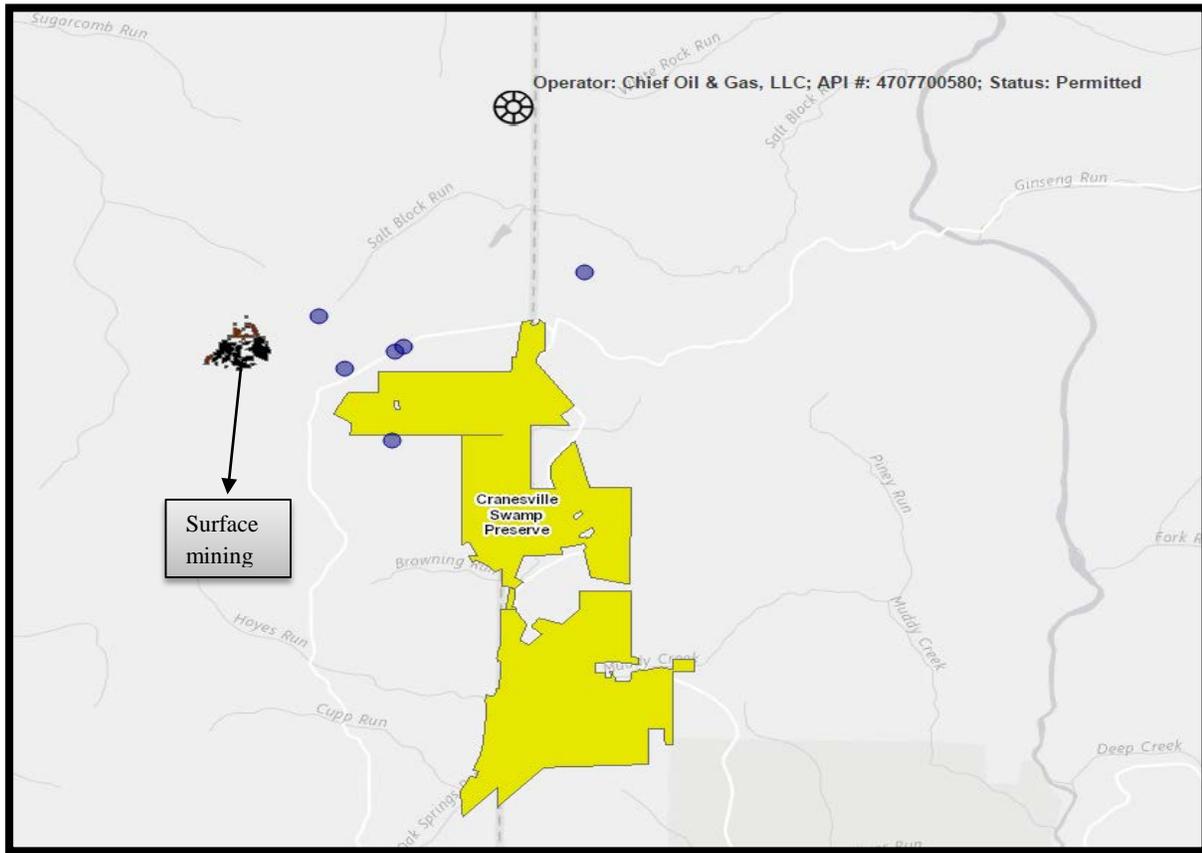


Figure 8. Control site sampling locations (blue circles) in Preston County, West Virginia.

The six residencies, identified as CW-01 through CW-06 in **Figure 9**, make up the *control site* for the study. Depths of drinking water wells at the control site ranged from 20 feet to just under 200 feet. Sampling activities for these residencies were conducted similar to the collection activities at the *active site*.

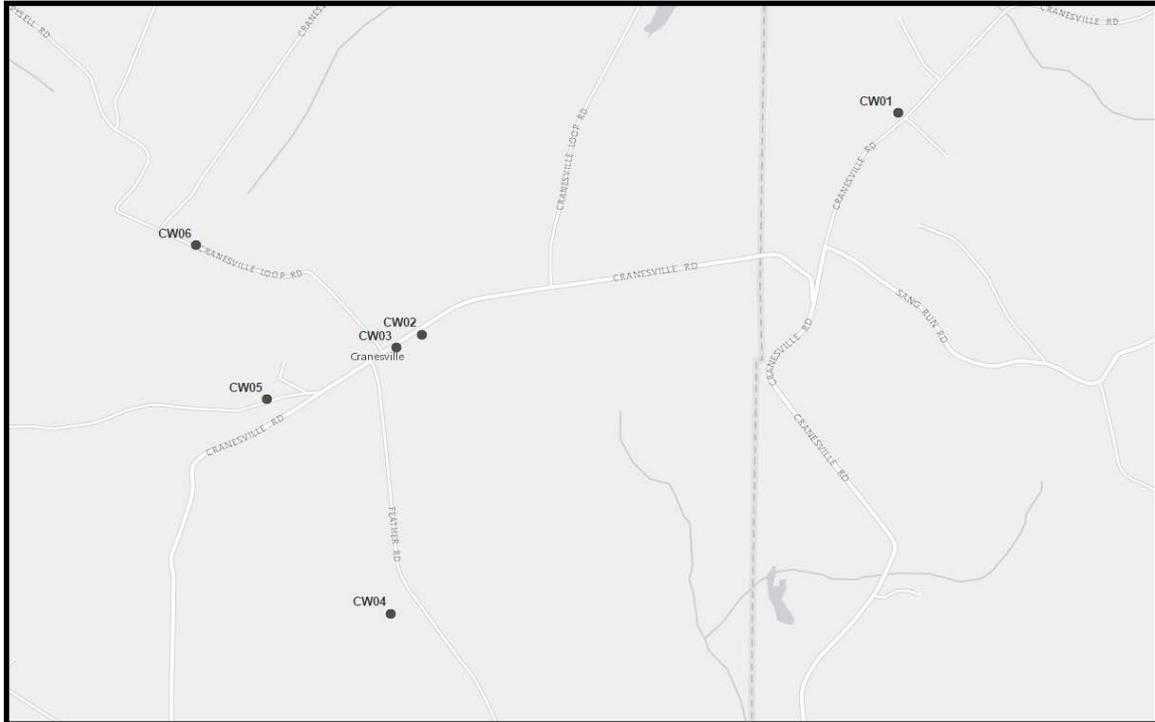


Figure 9. Residential drinking water wells sampled as the control site. CW01 closest sampling point to permitted gas well.

Sampling Parameters

During each sampling event, field measurements for pH, specific conductivity, total dissolved solids, and dissolved oxygen were recorded with an YSI 550 multi-probe instrument. Additionally, grab samples were collected via standard operating procedures and submitted with chain-of-custody documentation to a certified analytical laboratory for analysis within specified hold times. A trip blank was also submitted for analysis. **Table 3** identifies the water quality parameters tested along with laboratory methods used and reporting limits. The results of the collaboration with public health officials, regulatory officials, and industry representatives have yielded a concise list of parameters with the greatest potential to be found in nearby groundwater resources. This list incorporates most states highest tier of recommended water quality testing for well owners living in an active shale gas development area. The cost for one water sample will run around \$550, not very cost effective; however, a one-time investment to obtain good baseline data (data prior to gas well development) may prove beneficial. Well owners may then periodically have “*indicator*” parameters monitored while the gas well is drilled, completed, and producing gas. These *indicator* parameters may include: bromide (Br), chloride (Cl), sodium (Na), sulfate (SO₄), conductance, and total dissolved solids (TDS). The cost for one water sample analyzed for these parameters will run around \$70. Elevated readings of any of these *indicator* parameters may signal the drinking water well has been compromised and further testing would be needed to confirm.

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				Hg d
	0.0002			Hg
8260 MSV UST				Benzene
				Ethylbenzene
				Toluene
				Total-Xylene
				Surr: 1,2 - Dichlorethane -d4
		%REC		Surr: 4-Bromofluorobenzene
				Surr: Toluene -d8
2540C				TDS
E300.0	0.02	mg/L	Anions by Ion Chromatography	Br
SM4500CLE	3			Cl
ASTM D516-9002	10			SO4
Field Readings		°C		Temp.
		µS/cm	Field Readings	Conductivity
		(mg/L)		TDS
		pH		pH
	(mg/L)	DO		
Radiologicals		pCi/L	Radiologicals	Gross Alpha
				Gross Beta
				Radium-226
				Radium-228
				Potassium-40

Results: Active versus Non-Active Sites

Unconventional gas well development (active site) began in the latter part of October 2014. Development was temporarily halted after drilling was completed for most of the 2015 calendar year with completions occurring in late 2015. The United States Environmental Protection Agency (USEPA) has established mandatory (primary) and non-mandatory (Secondary) drinking water standards. Primary drinking water standards are enforceable and are called maximum contaminant levels (MCLs) established to protect the public against consumption of drinking water contaminants that present a risk to human health. An MCL is the maximum allowable amount of a parameter to be present in drinking water. Secondary drinking water standards are non-mandatory water quality standards but exist for aesthetic considerations such as color, taste, and odor. **Table 4** provides the list of parameters monitored during this study and corresponding primary (MCLs) or secondary drinking water standards. These standards are applicable to water systems and serve as a water quality guide to private, individual well owners when considering the quality of their drinking water well and determining if treatment may be necessary prior to consumption. This information serves as reference for reviewing monitoring results presented in proceeding figures. Overall, results of drinking water well analyses showed no impact from unconventional gas well activities. **Figures 10** through **17** show various parameters for each of the drinking water wells sampled over the course of 17 months. Refer back to **Figure 3** for location of wells in relation to the unconventional gas well.

Table 4. National primary (1°) and secondary (2°) drinking water standards for contaminant measured.

Contaminant		Standard	Contaminant		Standard	Contaminant		Standard
Aluminum (Al)	2	0.05 – 0.2 mg/L	Selenium (Se)	1	0.05 mg/L	Alkalinity		
Arsenic (As)	1	0.01 mg/L	Silver (ag)			TDS	2	500 mg/L
Barium (Ba)	1	2 mg/L	Sodium (Na)			Bromide (Br)		
Calcium (Ca)			Strontium (Sr)			Chloride (Cl)	2	250 mg/L
Chromium (Cr)		0.1 mg/L	Zinc (Zn)	2	5 mg/L	Sulfate (SO4)	2	250 mg/L
Iron (Fe)	2	0.3 mg/L	Mercury (Hg)	1	0.002 mg/L	Alpha (α)	1	15 pCi/L
Lead (Pb)	1	0.015 mg/L	Benzene	1	0.005 mg/L	Beta (β)	1	4 mr/yr
Magnesium (Mg)			Toluene	1	1	Radium (Ra)-226 & 228	1	5 pCi/L
Manganese (Mn)	2	0.05 mg/L	Ethylbenzene	1	0.07 mg/L	Potassium (K)-40		
Nickel (Ni)			Xylene	1	10 mg/L			
Potassium (K)			MBAS					

■ No standard, 1 = primary standard, 2 = secondary standard
 mg/L = milligrams per liter, pCi/L = pico curies per liter, mr/yr = millirems per year

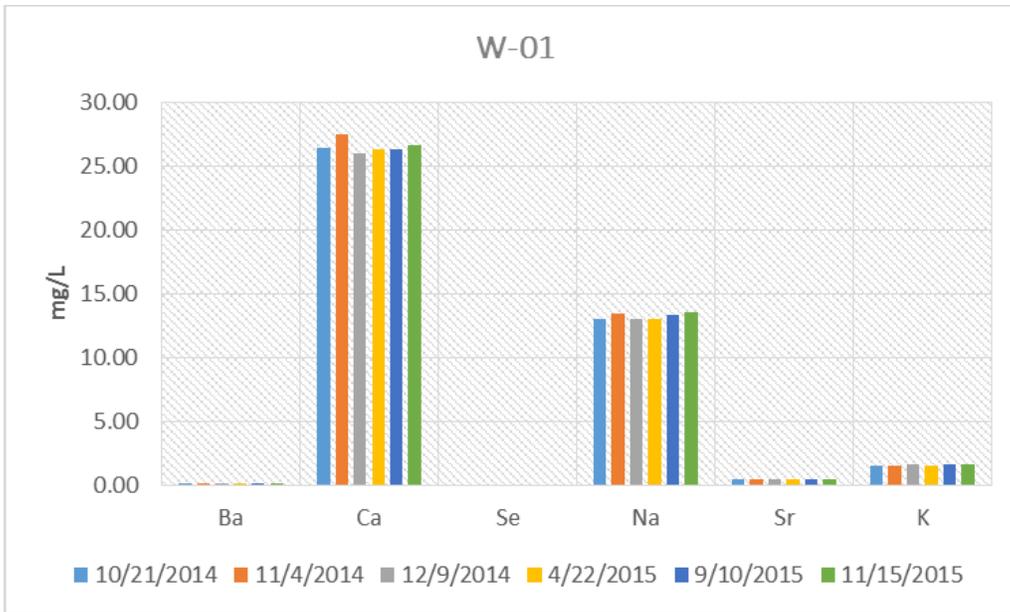


Figure 10. Various inorganic cations for drinking water well W-01.

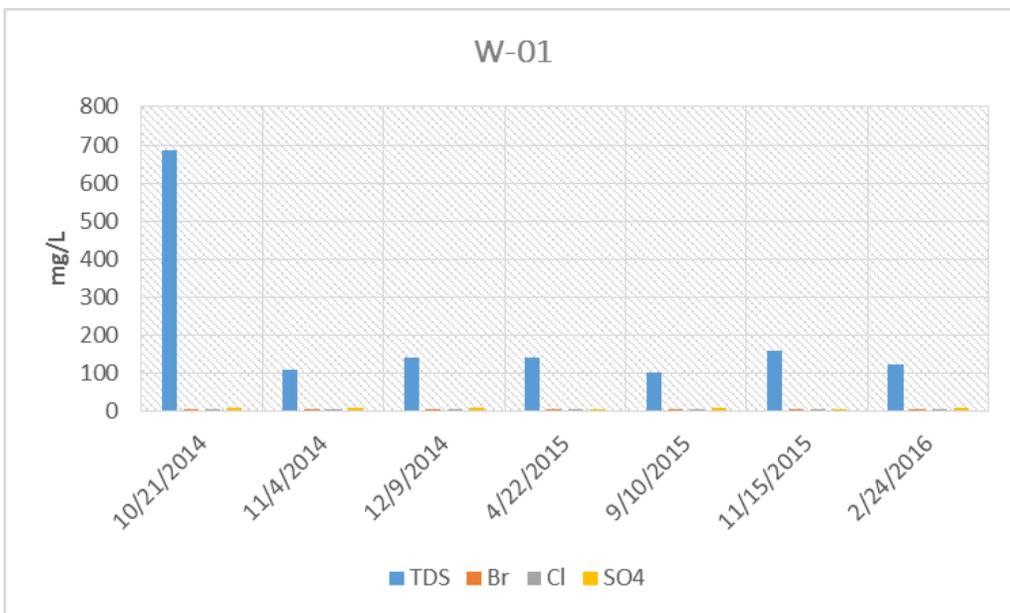


Figure 11. TDS and anions for drinking water well W-01.

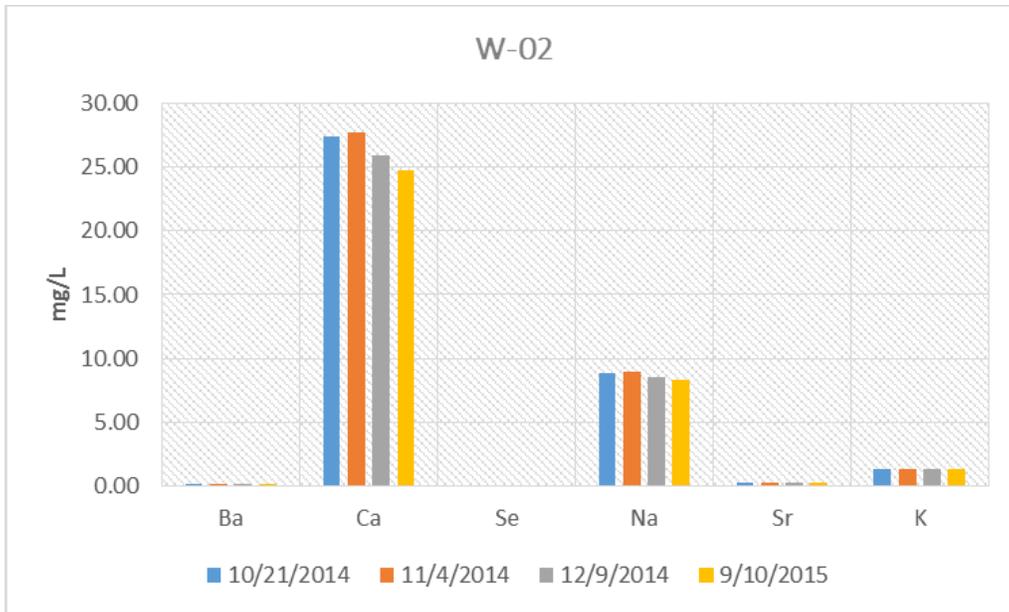


Figure 12. Various inorganic cations for drinking water well W-02.

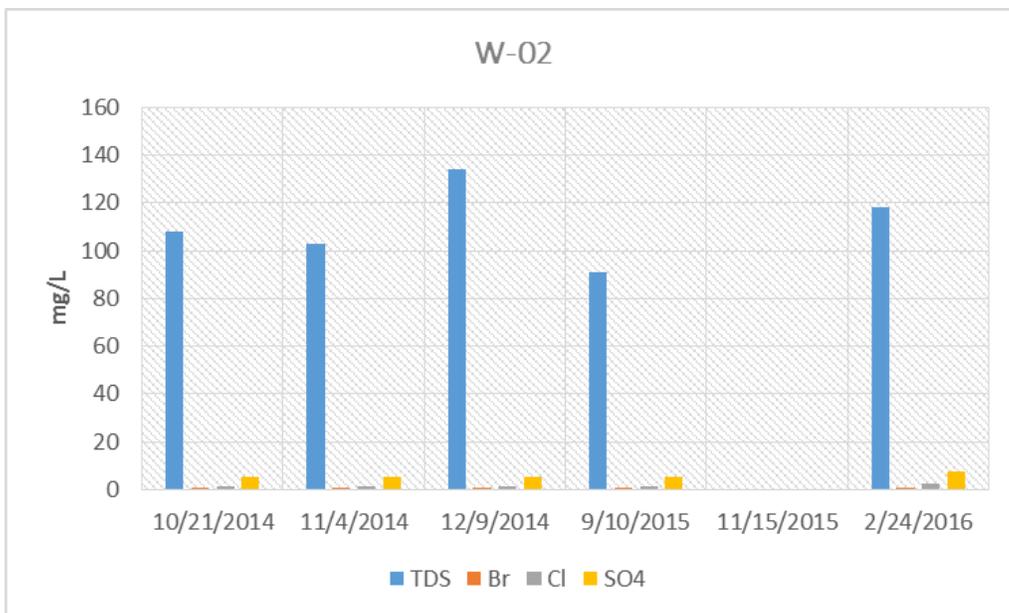


Figure 13. TDS and anions for drinking water well W-02.

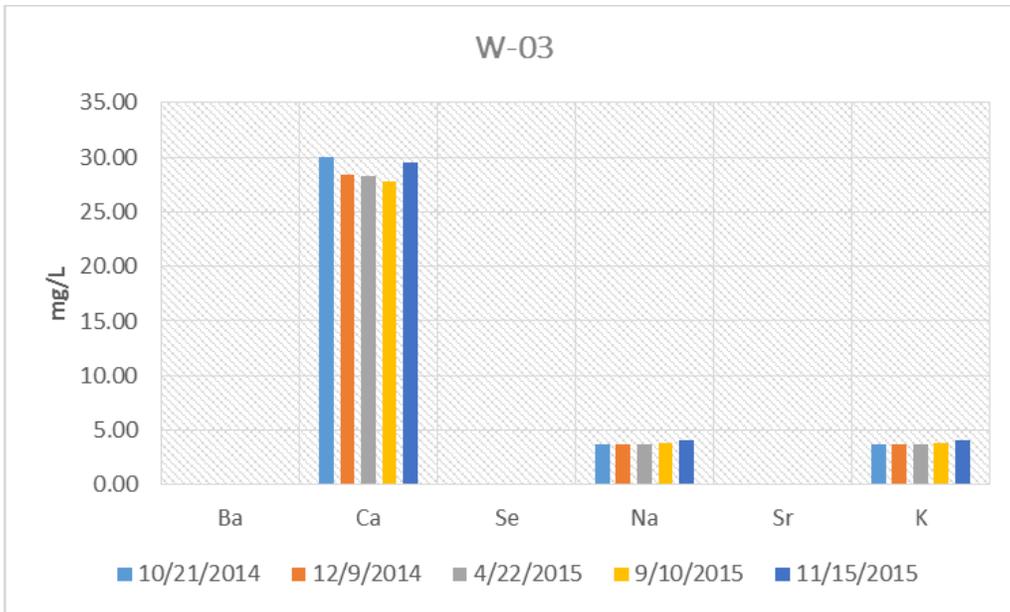


Figure 14. Various inorganic cations for drinking water well W-03.

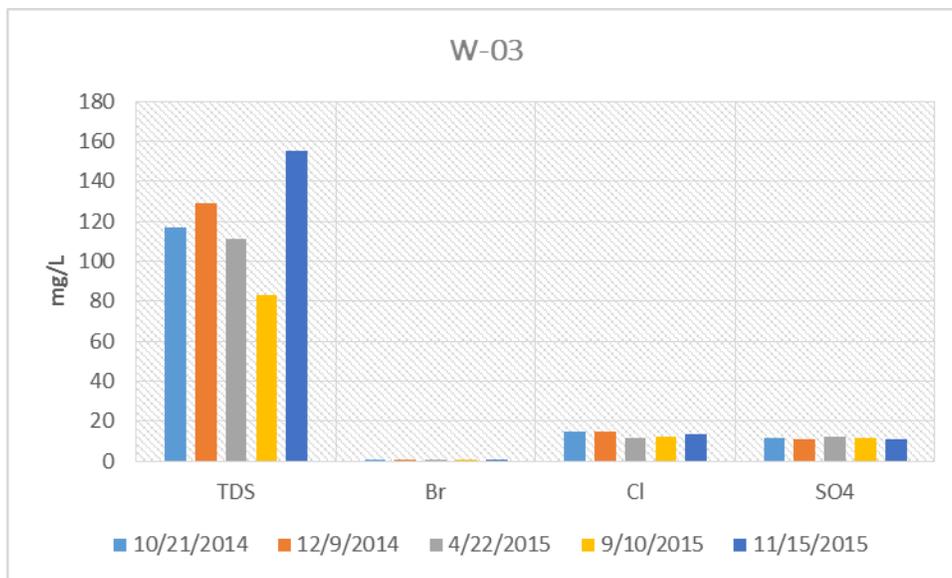


Figure 15. TDS and anions for drinking water well W-03.

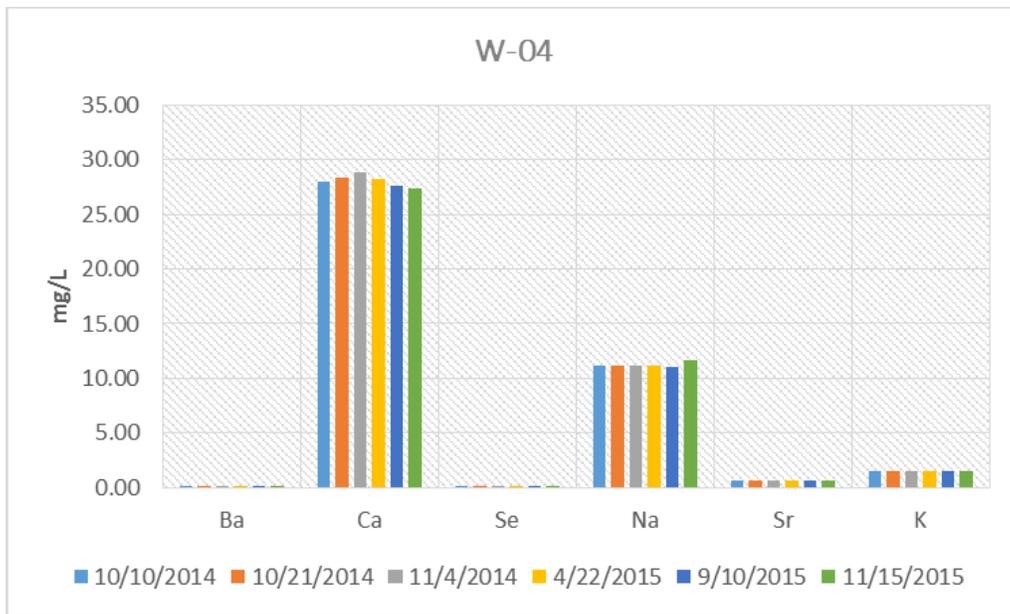


Figure 16. Various inorganic cations for drinking water well W-04.

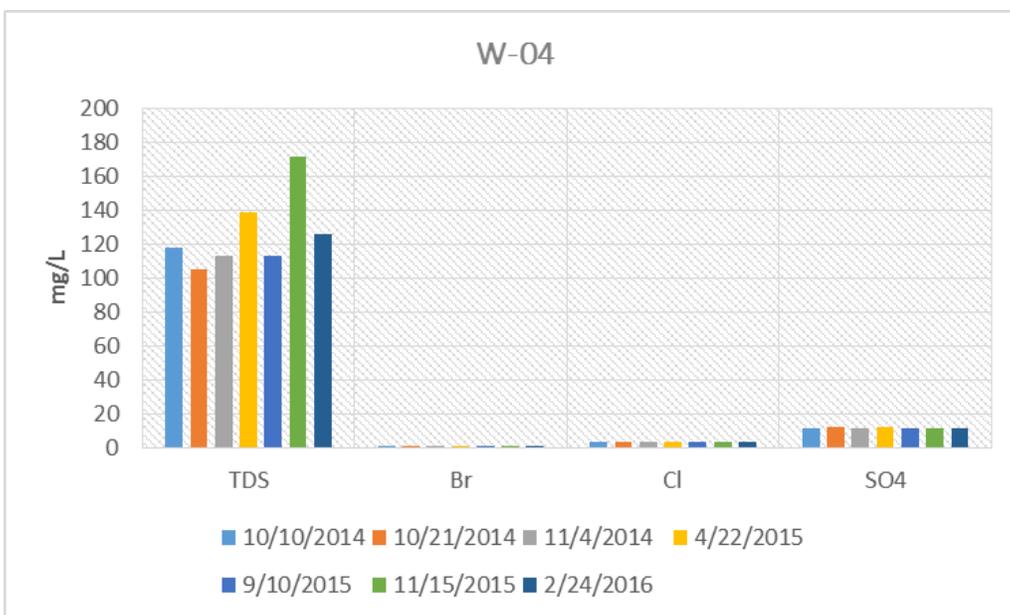


Figure 17. TDS and anions for drinking water well W-04.

Looking at the same parameters for the control site drinking water wells, measurements of most parameters were overall lower than those observed for the active site drinking water wells, see **Figures 18** through **20**. However, this does not necessarily indicate active site drinking water wells were impacted by nearby unconventional gas well development. One would have to have record of water quality prior to any nearby gas well development activity showing measurements lower than this project’s baseline data. Requests were made to the well owners to provide this data but was not made available. Also, geology plays a big role when attempting to compare sites.

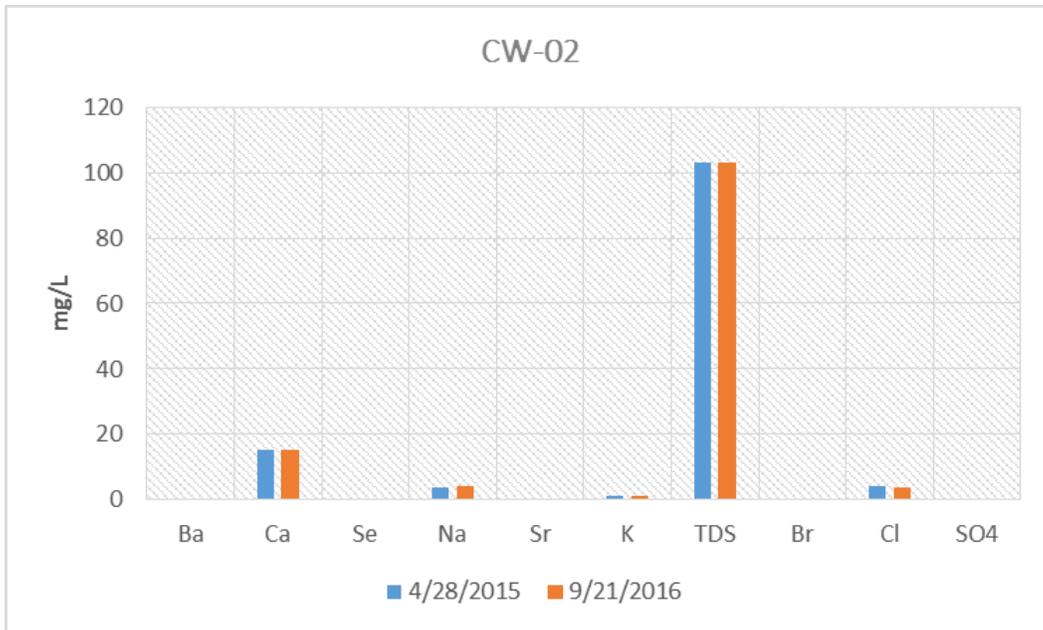


Figure 18. Inorganics from control site drinking water well CW-02.

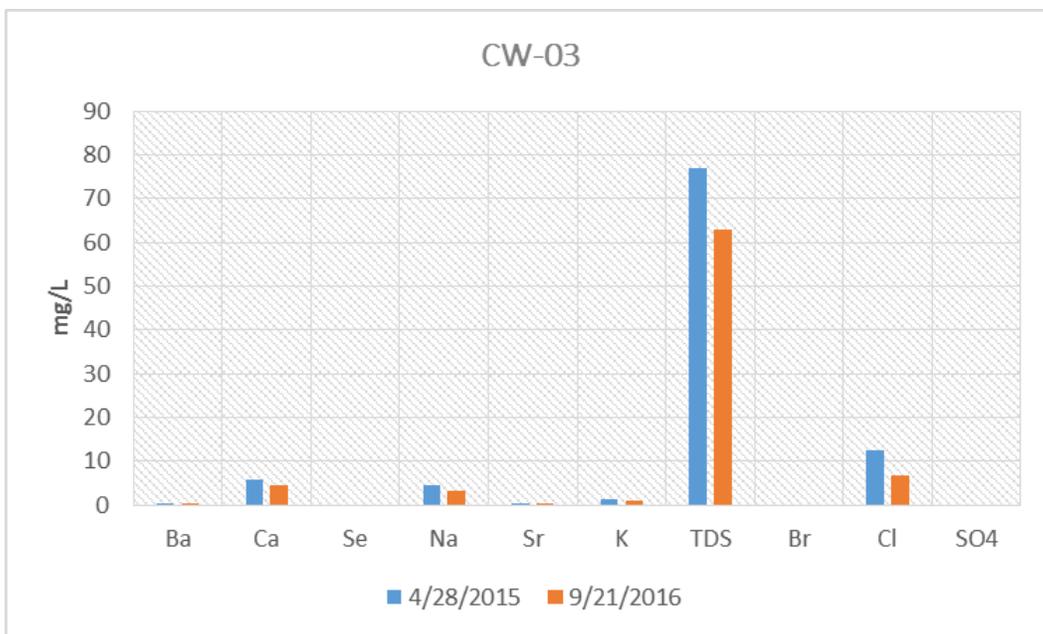


Figure 19. Inorganics from control site drinking water well CW-03.

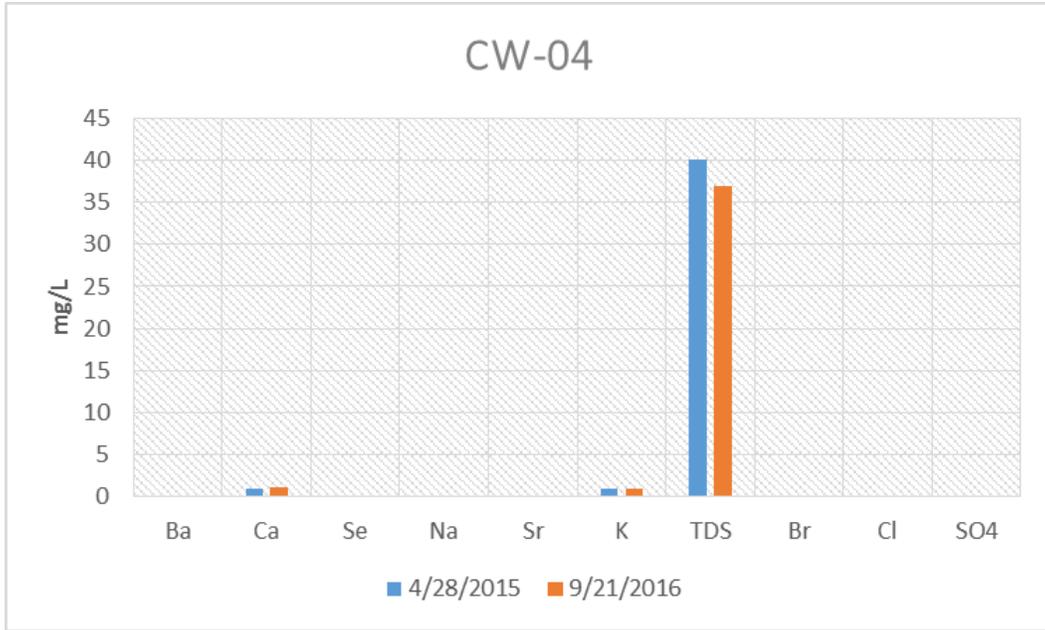


Figure 20. Inorganics from control site drinking water well CW-04.

A comparison of radiological parameters gross alpha and beta for active and control site drinking water wells are provided in **Figures 21** and **22**. Although readings were overall higher for active site drinking water wells, this again does not indicate impact from unconventional gas well development. Pre-existing data prior to any nearby gas well development for the active drinking water wells would need to be available to make a valid comparison. If a conclusion and/or recommendation could be made based on this data, it would be to educate drinking water well owners of the need to have historical records of water quality data for their drinking water well.

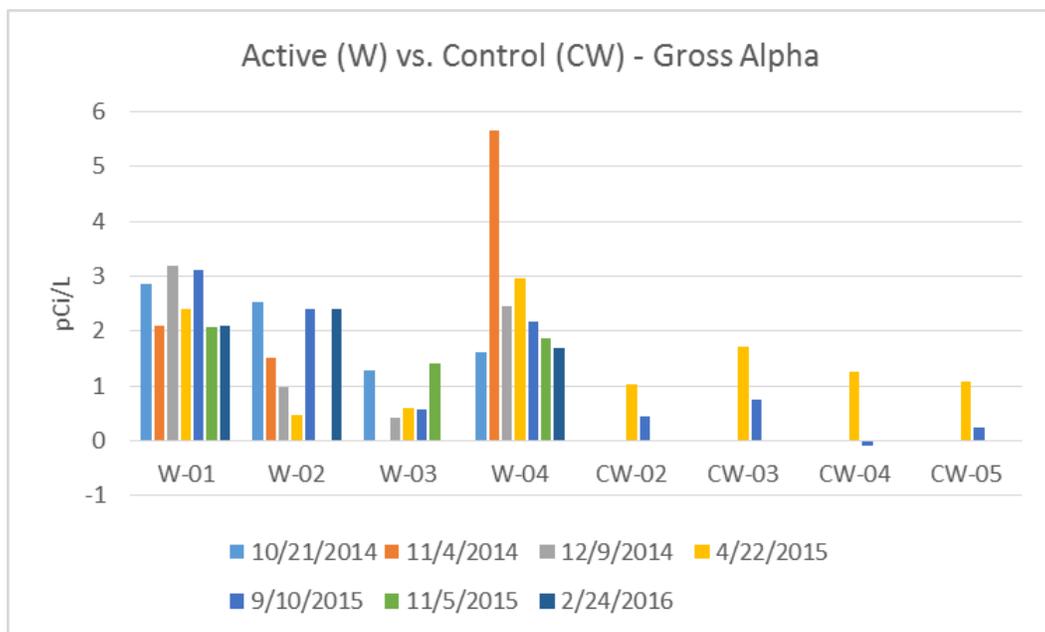


Figure 21. Gross alpha results for active and control site drinking water wells.

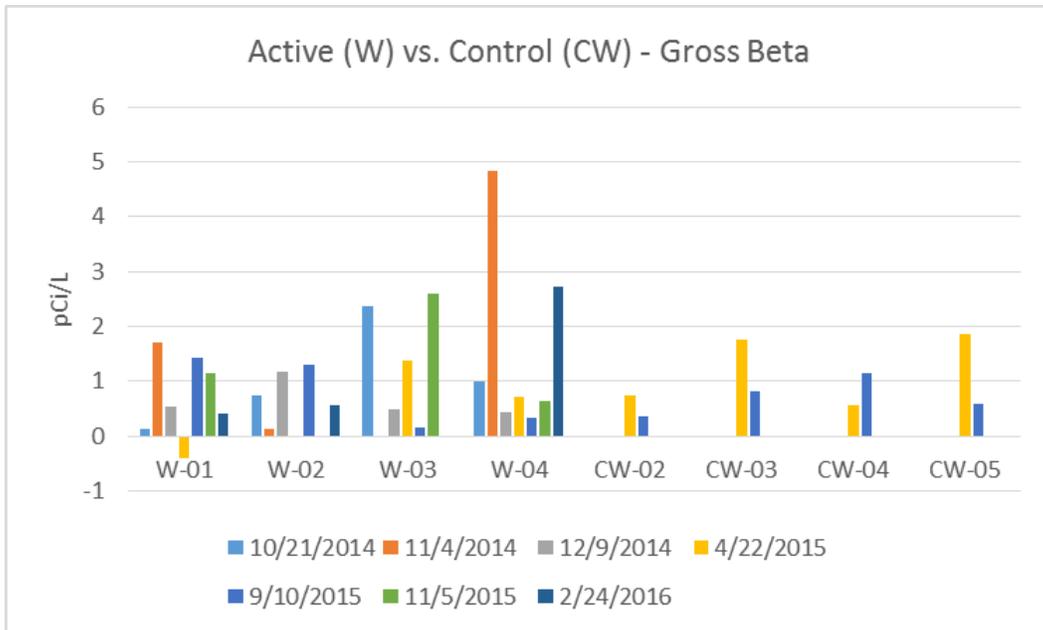


Figure 22. Gross beta results for active and control site drinking water wells.

Each well owner in the study, at both the active and non-active sites, was provided a *well owner report*. The report is divided into the following sections: purpose of the study; project activities; and results; drinking water related definitions, report legend; and results of analyses performed on the water samples collected from their drinking water well during each visit. Examples of three pages from no particular drinking water well is provided in **Figures 23** and **24**.

Drinking Water Related Definitions

Secondary Maximum Contaminant Level (SMCL) – The EPA has established National Secondary Drinking Water Regulations (NSDWRs) that set non-mandatory water quality standards for 15 contaminants. EPA does not enforce these "secondary maximum contaminant levels" or "SMCLs." They are established only as guidelines to assist public water systems in managing their drinking water for aesthetic considerations, such as taste, color and odor. These contaminants are not considered to present a risk to human health at the SMCL.

Maximum Contaminant Level (MCL) – The EPA has established National Primary Drinking Water Regulations (NPDWR) that set mandatory water quality standards for drinking water contaminants. These are enforceable standards called "maximum contaminant levels" or "MCLs", which are established to protect the public against consumption of drinking water contaminants that present a risk to human health. An MCL is the maximum allowable amount of a contaminant in drinking water which is delivered to the consumer. Secondary standards are set to give public water systems some guidance on removing these chemicals to levels that are below what most people will find to be noticeable.

Maximum Contaminant Level Goal (MCLG) – After reviewing health effects studies, EPA sets a Maximum Contaminant Level Goal (MCLG), the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, and which allows an adequate margin of safety. MCLGs are non-enforceable public health goals. Since MCLGs consider only public health and not the limits of detection and treatment technology, sometimes they are set at a level which water systems cannot meet. When determining an MCLG, EPA considers the risk to sensitive subpopulations (infants, children, the elderly, and those with compromised immune systems) of experiencing a variety of adverse health effects.

Health Advisory for Lifetime Exposure (HAL) – The EPA defines the lifetime health advisories as the concentration in drinking water that is not expected to cause any adverse non-carcinogenic effects for a lifetime of exposure.

Dissolved Metals – Dissolved metals results indicate the metals dissolved into the water only. Dissolved metals are more mobile and biologically available, thus pose a greater risk to health than do metals in particulate form.

Total Metals – Total metals results indicate both the metals present as particulates and those metals which have dissolved in the water.

Soft water – The United States Geological Survey (USGS) guidelines classify soft water as 0 to 60 mg/L.

Figure 23. Screenshot of partial definition page from well owner report.

Chloride (Cl)

Drinking water standards:

SMCL: 250 mg/L

What's in your well?

Results for your well:

Cl: 38.20 mg/L

Analytical lab results for chloride were below the SMCL (250 mg/L).

Chromium (Cr)

Drinking water standards (Total Chromium only; no standard for dissolved Cr):

MCL = 0.1 mg/L

MCLG = 0.1 mg/L

Health effects summary:

Chromium can cause stomach ulcers, damage to the liver and kidneys, and an increased risk of cancer.

What's in your well?

Analytical lab results for chromium were below detection limits.

Iron (Fe)

Drinking water standard:

SMCL: 0.3 mg/L

Characteristics:

Forms rust-colored sediment; stains laundry, utensils, and fixtures reddish brown. Objectionable for food and beverage processing. Can promote growth of certain kinds of bacteria that clog pipes and well openings.

What's in your well?

Results for your well:

Fe: 0.44 mg/L

Fe (dissolved): 0.16

Analytical lab results for iron were above the SMCL (0.3 mg/L).

Figure 24. Screenshot of various inorganic parameter details from a well owner report.

Significance of the Project

Various studies have been conducted to characterize water and waste streams generated during the development of an unconventional gas well. Other studies have looked at the effects on local or nearby drinking water wells pre- and post-development of gas wells. This study attempted to identify parameters of concern that exist in the water/waste streams from Marcellus shale gas development, have potential to migrate to nearby groundwater, and exist at concentration levels to negatively impact human health. Once these parameters of concern were identified, they were monitored at selected groundwater sites (wells and springs used for drinking water) near a planned and eventually developed gas well site. Analytical results provide an efficient, and cost-effective plan for well owners to follow if there is concern about their private drinking water supply.

Recommendations for a sampling plan

Results indicate the need for drinking water well owners to have complete records available concerning the quality and quantity of their drinking water prior to any industrial development nearby, in this case, shale gas development. Wells and springs were monitored pre-pad development through the completions stage of the gas well for the full suite of parameters presented. Results indicate baseline monitoring, or sampling of the drinking water source, should consist of the full suite of parameters to provide as much data indicative of the condition of the drinking water source. This suite of analyses can easily run over \$500 mainly because of the costs to analyze for any radiological analytes. For a potentially one-time exercise, many well owners may think it is a worthwhile investment in their health.

A much smaller suite of parameters: chloride, bromide, sodium, sulfate, conductance, and total dissolved solids (TDS) should be analyzed on water samples taken periodically as the gas well development phases progress. Once the gas well is producing gas, analysis of these drinking water quality parameters once a year should be more than sufficient. This smaller suite of parameters (water quality screening) should cost around \$70 to \$80 dollars. Results of the water quality screening tests need to be compared to the baseline results each time. Any parameter significantly higher (at least a one to two orders of magnitude higher, depending on the parameter), may signal the water supply has been compromised and further testing should be conducted. The well owner would then consider having the full suite of parameters analyzed to verify the screening results and then contact appropriate state authorities for further investigation into the cause of change in water quality.

Publications

No articles have been submitted for publication consideration to date. However, WVVRI plans to submit abstracts and/or papers to relevant publications now that the project is final.

Information Transfer Program

Drinking water well owners who participated in the study were provided preliminary reports midway through the project and will be provided final reports within the next 30 to 60 days. Review of the drinking water quality parameters will be conducted on a regular basis as additional studies similar to the scope of this project are conducted across the country. Adjustments will be made as needed and shared with public health officials for recommendations to include/exclude parameters.

An interactive data map was created using arcgis.com. A screenshot is provided in **Figure 26**. This provides viewers with data on nearby wells, site locations, etc. and can be cross-referenced to water quality data from similar monitoring projects. The map is not yet available to the public; however, once data from current WVVRI projects have been included, a link will be available on the WVVRI website at WVVRI.org.

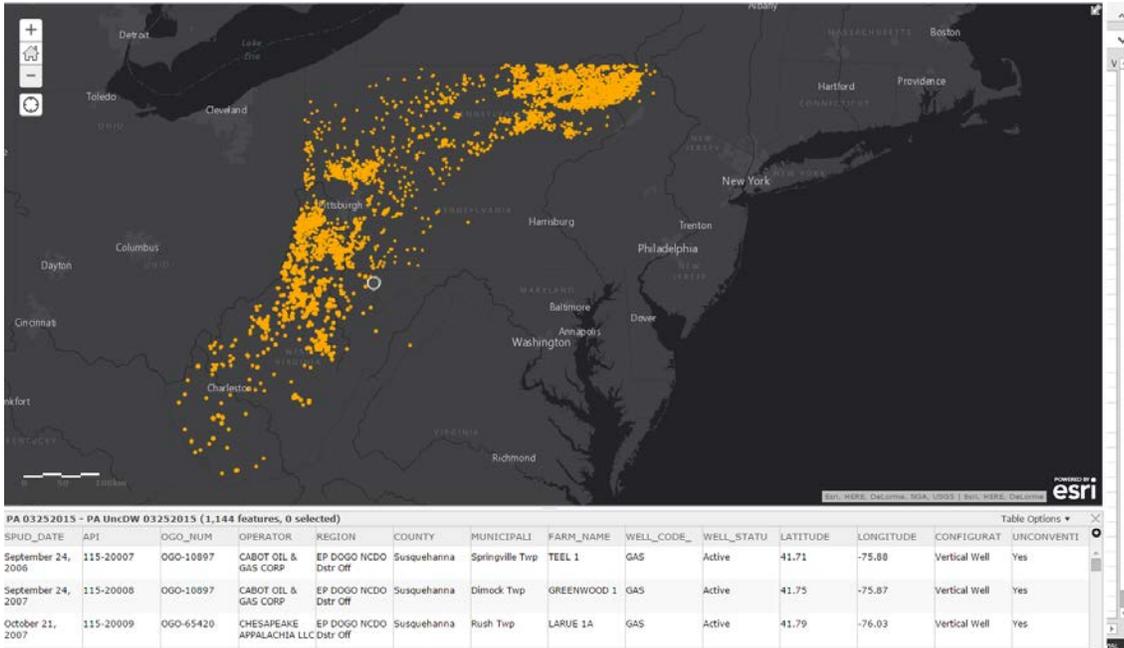


Figure 25. Interactive data project map.

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 WWRI field technician with collection of samples, data analysis, and development of homeowner (well owner) reports.

Notable Achievements and Awards

No awards to report at this time.

Development of Microbial Desalination Cells as an Innovative Low-cost Desalination Method for Produced Water Treatment

Basic Information

Title:	Development of Microbial Desalination Cells as an Innovative Low-cost Desalination Method for Produced Water Treatment
Project Number:	2015WV220B
Start Date:	3/1/2015
End Date:	2/29/2016
Funding Source:	104B
Congressional District:	WV-001
Research Category:	Water Quality
Focus Category:	Wastewater, Treatment, Water Quality
Descriptors:	None
Principal Investigators:	Lian-Shin Lin

Publications

There are no publications.

**Bioelectrochemical Treatment for Softening and
Desalination of Produced Water from Oil and Shale
Production**

Final Report

Start Date: March 1, 2015

End Date: February 29, 2016

**Lance Lin, Associate Professor
Hoil Park, Post-doctoral researcher
Department of Civil and Environmental Engineering
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Morgantown, WV 26506-6103**

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Date Submitted on

MAY 20, 2016

Project Number. 2015WV220B

Abstract

Hydraulic fracturing for oil and gas (O&G) production results in generation of more than 20 billion barrels of produced water each year. One troublesome aspect of the produced water is its high salinity and organic contents, which often require treatment before disposal or reuse of the water. At present, the major barriers to produced water recovery and reuse are the high cost of existing technology, difficulties adapting water treatment techniques to high salinity environments, and lack of a regulatory framework and motivation for adoption. The goal of this USGS/104b funded project is to develop a low-cost innovative technology employing bioelectrochemical mechanisms for treatment of produced water. It capitalizes on an ongoing multi-disciplinary research program, Marcellus Shale Energy and Environmental Laboratory (MSEEL), funded by DOE National Energy Technology Laboratory (NETL) through sharing resources and produced water samples from a research well pad in Morgantown WV.

This study evaluated an innovative method for produced water treatment using bioelectrochemical systems (BESs) and targeting water reuse and potentially surface water discharge. Using produced water samples collected from the MSEEL site, various designs of BES were tested under a range of applied voltage and electric current. Several designs tested early in the study were found to be not effective. A treatment method involving two treatment steps including softening (i.e., removal of multi-valent scale forming cations) and desalination (mono-valent ions removal) showed promising results. In lieu of addition of alkaline chemicals required in conventional water softening processes, a two-chambered BES was used to create a pH imbalanced condition and generate high-pH catholyte for produced water softening. The supernatant from the softening treatment was treated in a three-chambered microbial desalination cell (MDC) to remove mono-valent ions (i.e., Na and Cl).

The study demonstrated technical feasibility of the treatment concept and the results were encouraging and warrant further investigations of the treatment kinetics, the process factors that control the treatment efficiency, and the overall cost-effectiveness. The treatment method for produced water is novel and can provide more options for produced water treatment and management for varied end uses (irrigation water, reuse in energy production, safe surface discharge). It also has broader applications, including desalination of industrial and agricultural wastewaters and brines.

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Executive Summary

Hydraulic fracturing for oil and gas (O&G) production results in generation of more than 20 billion barrels of produced water each year. One troublesome aspect of the produced water is its high salinity and organic contents, which often require treatment before disposal or reuse of the water. At present, the major barriers to produced water recovery and reuse are the high cost of existing technology, difficulties adapting water treatment techniques to high salinity environments, and lack of a regulatory framework and motivation for adoption. The goal of this USGS/104b funded project is to develop a low-cost innovative technology employing bioelectrochemical mechanisms for treatment of produced water. It capitalizes on an ongoing multi-disciplinary research program, Marcellus Shale Energy and Environmental Laboratory (MSEEL), funded by DOE National Energy Technology Laboratory (NETL) through sharing resources and produced water samples from a research well pad in Morgantown WV.

This study evaluated an innovative method for produced water treatment using bioelectrochemical systems (BESs) and targeting water reuse and potentially surface water discharge. Using produced water samples collected from the MSEEL site, various designs of BES were tested under a range of applied voltage and electric current. Several designs tested early in the study were found to be not effective. A treatment method involving two treatment steps including softening (i.e., removal of multi-valent scale forming cations) and desalination (mono-valent ions removal) showed promising results. In lieu of addition of alkaline chemicals required in conventional water softening processes, a two-chambered BES was used to create a pH imbalanced condition and generate high-pH catholyte for produced water softening. The supernatant from the softening treatment was treated in a three-chambered microbial desalination cell (MDC) to remove mono-valent ions (i.e., Na and Cl).

With assistance of an applied external current, the two-chambered BES generated catholyte pH as high as 11.8, sufficiently high to induced chemical precipitations (e.g., CaCO_3 and $\text{Mg}(\text{OH})_2$). Mixtures of the raw produced water with the catholyte (1:1 – 1:10 volumetric ratios) resulted in 32% - 70% removal for Ca and 56% - 99% removal for Mg. Driven by a 2 mA electric current, the MDC resulted in further removal of Ca^{2+} (666 mg/L to 11 mg/L, 98%) and Mg^{2+} (55.6 mg/L to 4 mg/L, 93%) from the supernatant from the softening treatment. Removal of monovalent ions were also significant with sodium concentration decreased from 4,890 mg/L to 86.6 mg/L (98%) and chloride concentration from 126.3 mg/L to 12.7 mg/L (90%).

Overall, the results were encouraging and warrant further investigations of the treatment kinetics, the process factors that control the treatment efficiency, and the overall cost-effectiveness. The treatment method for produced water is novel and can provide more options for produced water treatment and management for varied end uses (irrigation water, reuse in energy production,

safe surface discharge). It also has broader applications, including desalination of industrial and agricultural wastewaters and brines.

1. Problem and Research Objectives

Advances in drilling techniques, including hydraulic fracturing, have dramatically increased oil and gas production in the U.S. in the last decade and provided economic boosts to many states. These new techniques, however, often are very water-intensive, both in their requirements for freshwater and in the production of formation water (or produced water) extracted from subsurface reservoirs along with the oil and gas. Along with freshwater consumption, oil and gas production results in the generation of large volumes of wastewater, a combination of flowback and formation water known as produced water. More than 3 billion cubic meters of produced water are generated yearly in the United States (Veil and Clark, 2011). This produced water can contain a wide variety of chemicals: dispersed oil and other organic components, minerals (including heavy metals and radioactive materials), production chemicals, production solids, and dissolved gases (Fakhru'l-Razi et al., 2009; Bomgardner, 2012; Arthur et al., 2005; Benko and Drewes, 2008). Produced waters are also typically highly saline (high total dissolved solids, or TDS), a result of interactions between reservoir water and the formation materials.

Management of produced water thus requires both the optimization of stimulations and water injection techniques to reduce dependence on freshwater sources and the development of treatment strategies to reuse or safely dispose the high volume of produced water. In many states, disposal of hydraulic fracturing flowback and produced waters has traditionally occurred through deep-well injection. However, this practice has come under scrutiny because of suspected links with seismic events, and concerns over potential drinking water contamination. New treatment strategies are needed that recover this wastewater for surrounding environment. At lower levels of treatment, produced water could be reused as a substitute for more valuable fresh water in further oil & gas operations. This strategy reduces demand for limited freshwater resource and lessens competition between energy production and other water-intensive industries. With additional treatment, produced water may be made suitable for higher-value uses after additional levels of treatment. At present, the difficulties lie with adapting water treatment techniques to high salinity environments, and lack of a regulatory framework and motivation for adoption.

The goal of this project is to develop a cost-effective softening and desalination technology employing innovative electrochemical mechanisms for treatment of produced water from O&G production. The proposed research builds upon previous research on produced water treatment using a capacity deionization unit powered by serially connected three microbial fuel cells (MFCs). It is designed to improve the previous design for removing scale-forming cations and enhanced desalination efficiency. The project represents a multi-disciplinary collaboration and is designed to capitalize an ongoing research program, Marcellus Shale Energy and Environment Laboratory (MSEEL), funded by DOE's National Energy Technology Laboratory (NETL). Research tasks of this study include characterization of produced water collected at the MSEEL site, bioelectrochemical system designs and electrochemical properties characterization, water softening, and desalination of the produced water.

2. Methodology

2.1 Produced water collection and characterization

Raw produced water samples were collected from the MSEEL well site in the Morgantown Industrial Park, Morgantown, WV. Various water quality parameters of the produced water samples were analyzed in the Environmental Engineering Laboratory of the Department of Civil and Environmental Engineering. The raw water samples were also pretreated with an activated carbon filter to remove organic content. Both the raw produced water and pretreated samples were used in this study.

2.2. Characterization of electrochemical properties

Standard electrochemical methods (cyclic voltammetry, electrochemical impedance spectroscopy) was performed using a Gamry 3000 system and using 3-electrode electrochemical cells. In all experiments, a Pt flag was used as the counter electrode. The reference electrode was either a silver/silver chloride reference electrode or a silver wire quasi-reference electrode. Potential limits were adjusted to detect the onset of water reduction, thus allowing potentials to be determined with respect to the standard hydrogen electrode.

The first part of the electrochemical studies focused on characterizing the carbon-based electrodes (carbon felt with and without a platinum coating, carbon brush) in a clean aqueous electrolyte (NaCl buffered with phosphate). The second part focused on characterizing the electrochemistry of the produced water, both untreated and treated.

2.3. Bioelectrochemical system (BES) designs

A number of BES designs were tested for produced water desalination in this study. A series of experiments driven by voltages or electric currents using several earlier designs including two-chambered microbial desalination cell (MDC) and electrodialysis were found not to be effective. Only two designs that showed promising results for softening (i.e., removal of multi-valent scale forming cations) and desalination (mono-valent ions removal) were described and discussed in this report.

2.3.1. Two-chambered BES for softening

A two-chambered BES similar to typical microbial fuel cell designs was constructed for produced water treatment (Figure 1). It consisted of an anode and a cathode chambers separated by a cation exchanged membrane (Membrane International Inc., Ringwood, USA). Each chamber contained graphite felt electrodes (geometric dimension of 6 x 6 cm², 0.5 cm thick, Electrosynthesis Inc., Lancaster, PA, USA). Platinum wires inserted through the felt electrodes were used to connect the electrodes to the electronics. The anode and cathode chamber each had a working volume of 160 mL. An Ag/AgCl electrode (BASI, Inc.) was placed in the anode

chamber as a reference electrode. The anode chamber was inoculated with a mixture of primary wastewater and sludge collected at a local wastewater treatment plant (Star City, WV) and a produced water sample, followed by feeding of an artificial wastewater for microbial enrichment. The synthetic wastewater contained 0.56 g NH_4Cl , 0.20 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 15 mg CaCl_2 , 1 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 20 mg $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 0.42 g NaHCO_3 , and 10 mL of a trace mineral solution, and 2 g sodium acetate as carbon sources in 940 mL distilled water.

The two-chambered BES was driven by an electric current using a potentiostat/galvanostat (Gamry Reference 3000) to create a pH imbalance condition between the anode (fed with the synthetic wastewater in a flow-through mode, retention time = 36 hrs) and cathode (fed with a 0.01 M NaCl in a recirculating mode). The catholyte was continuously bubbled with air to maintain a constant oxygen level. The pH imbalance resulted in a low-pH anolyte and high-pH catholyte. In this study, 8 mA and 9 mA currents were applied using a chronopotentiometry method. The anolyte and catholyte pHs were monitored during the experiments. The catholyte with elevated pH (e.g., 11) was then used to treat the raw produced water samples with a range of volumetric mixing ratios to study its effectiveness for softening.

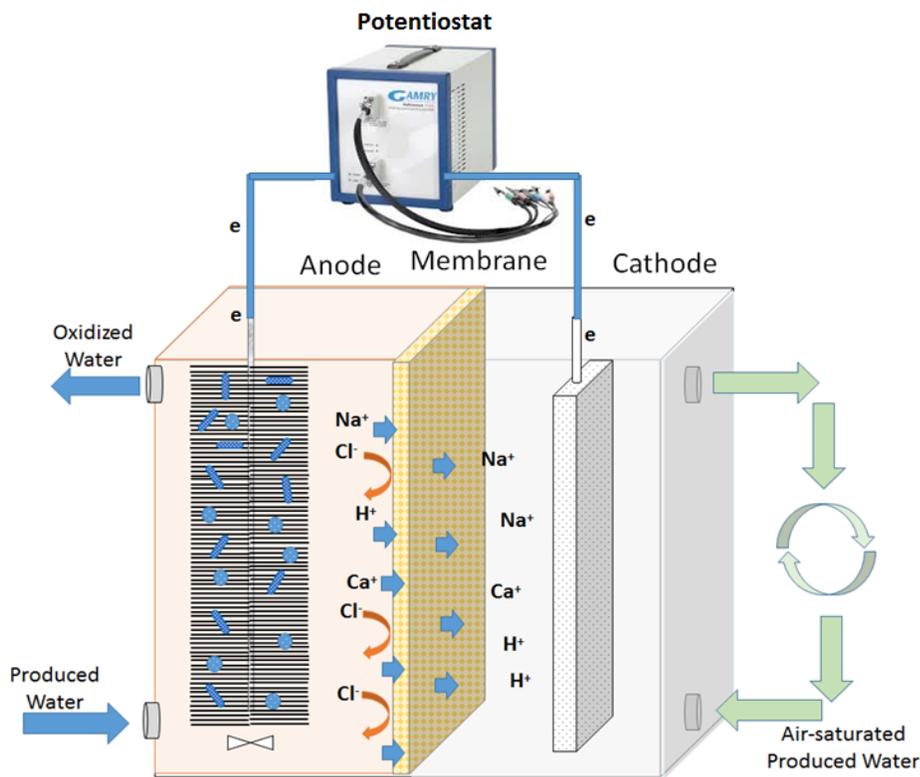


Figure 1. Schematic diagram of the two-chambered bioelectrochemical system (BES)

2.3.2. Three-chambered microbial desalination cell (MDC)

A three-chambered MDC was constructed to treat the supernatants from the softening treatment. The system consisted of an anode and cathode chambers (working volume = 160 mL) separated by a central chamber (working volume = 60 mL). An anion exchange membrane (AEM) was used to hydraulically separate the anode and the central chambers, and a cation exchange membrane (CEM) was used to separate the central and cathode chambers. The central chamber was filled with the supernatant and operated in a fed-batch mode for desalination. The anode was fed with the synthetic wastewater (flow-through with retention time = 36 hrs) and the cathode was fed with a well aerated 0.1 N NaCl solution (recirculation). An electric current was applied across the anode and cathode electrodes to drive ion movements to achieve desalination (i.e., anions move across the AEM from the central to the anode chamber, and cations from the central to the cathode). Overall, the two-step treatment process (i.e., softening and desalination) is illustrated in Figure 2.

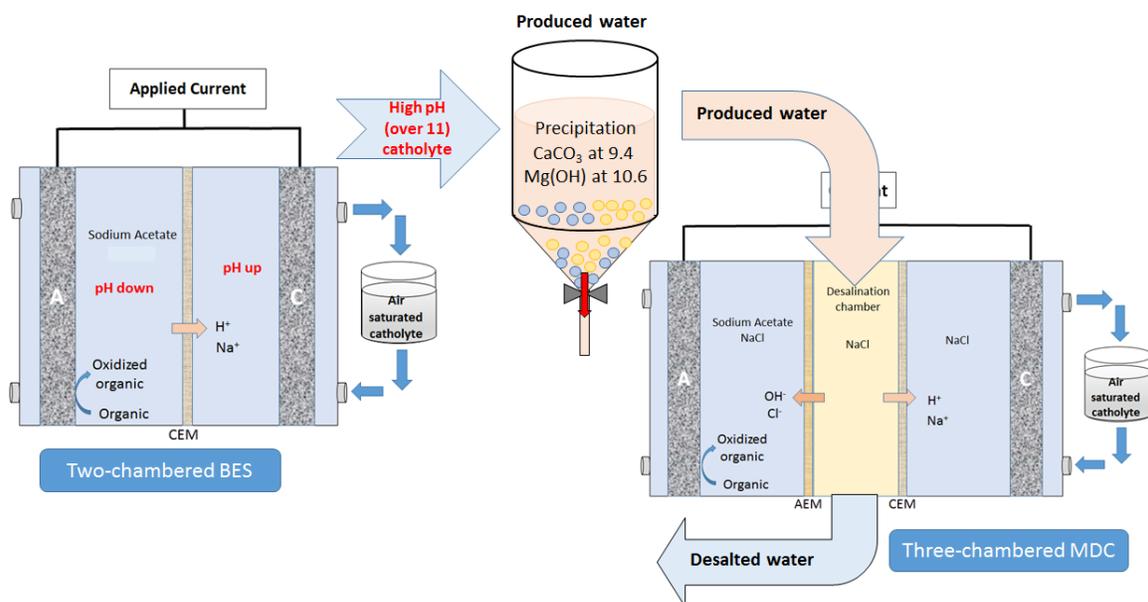


Figure 2. Schematic diagram the softening and desalination treatments.

2.4. Chemical analyses

Chemical parameters were measured following the Standard Methods (21st edition, APHA AWWA WEF). Specifically, metal concentrations in water samples were analyzed using an atomic absorption spectrometry (PerkinElmer, model 3100, Shelton, CT, USA). Chemical oxygen demand (COD) was measured using a modified closed reflux colorimetric method.

Chemical precipitation generated in the softening process was analyzed by scanning electron microscope (SEM, Hitachi S-4700) and X-ray photoelectron spectroscopy (PHI 5000 Versa Probe XPS).

3. Results and Discussion

3.1 Produced water characterization

Table 1 lists chemical constituents of a produced water sample collected at the MSEEL site and the produced water after activated carbon filtration. The produced water was weakly acidic as a result of metal hydroxide precipitations (e.g., $\text{Fe}(\text{OH})_3$) and highly electrically conductive resulting from high levels of mono-valent ions (Na^+ and Cl^-) and multi-valent cations (Ca^{2+} , Mg^{2+} , Sr^{2+} , and Ba^{2+}). The iron concentration was significant and of concern because of its low solubility and scale-forming potential. The water samples were used in softening and desalination experiments.

Table 1. Chemical characterization of a raw produced water and pretreated produced water from the MSEEL site.

Parameter	Unit	Raw produced water	Pretreated produced water with carbon
pH		4.6	8.7
COD	mg/L	958	441
Alkalinity	mg CaCO_3/L	649	717
Acidity	mg CaCO_3/L	300	100
Conductivity	mS/cm	109	104
Sulfate (SO_4^-)	mg/L	0.8	0.6
Chloride (Cl)	mg/L	30040	30470
Sodium (Na)	mg/L	19930	18930
Calcium (Ca)	mg/L	7175	6825
Magnesium (Mg)	mg/L	1310	1067
Iron (Fe)	mg/L	44.6	0.7
Strontium (Sr)	mg/L	2420	2200
Aluminum (Al)	mg/L	3.0	0
Manganese (Mn)	mg/L	4.0	3.6

3.2. Electrochemical properties of the graphite electrodes

3.2.1 Electrochemical characterization with synthetic solutions

The electrolyte in these studies was 0.63 M NaCl with 0.1 M phosphate, pH 7. The electrolyte was saturated with respect to air. Carbon felt electrodes were contacted using a Pt wire inserted along the long axis. The contribution of the Pt wire to the voltammetry was demonstrated to be negligible. The felt electrodes had to be rinsed several times with electrolyte to remove trapped gases.

The Pt-coated carbon felt electrode behaves much like a pure Pt electrode. Figure 3a shows a cyclic voltammogram of a pure Pt electrode (area 3 cm²). At the negative potential limit of -0.6 V vs Ag QRE, the sharply rising current marks the onset of water reduction and the potential of a SHE. Water oxidation starts at +1 V vs QRE. In between, the Pt electrode exhibits hydrogen adsorption waves at -0.4 to -0.5 V vs QRE, Pt oxidation at +0.6 to +0.8 V vs QRE, and oxygen reduction at potentials negative of +0.2 V vs QRE. The oxygen reduction peak current appears at 0.0 v vs QRE. The larger cathodic peak at -0.1 V vs QRE corresponds to reduction of the oxide layer formed on Pt during the positive potential scan.

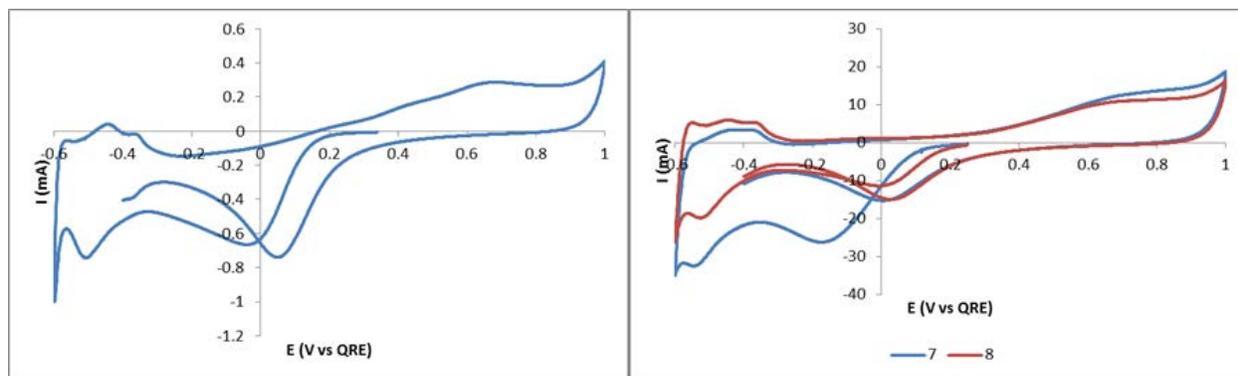


Fig. 3a

3b

Figure 3b is the corresponding cyclic voltammogram of the Pt-coated carbon felt electrode (dimensions 3.0 x 2.0 x 0.6 cm). All of the processes found using the pure Pt electrode are visible in this voltammogram. In particular, reduction of molecular oxygen starts at +0.1 V vs QRE and exhibits a peak current at -0.2 V vs QRE. Scan 7 (blue) is the initial voltammogram and Scan 8 (red) is the subsequent voltammogram. The smaller O₂ reduction in the second scan are attributed to depletion of oxygen within the volume of the carbon felt electrode. Because dissolved oxygen in the electrolyte is slow to diffuse into the bulk volume of the carbon felt, current at a constant applied potential of -0.4 V vs QRE rapidly decayed to less than 2 mA. For future work, it is desirable to replace this immersed carbon felt cathode with a gas-diffusion cathode.

The carbon felt electrode (dimensions 3.0 x 2.0 x 0.6 cm) without a Pt coating does not exhibit any well-defined electrochemical processes (Fig. 3c, Scan 6). In particular, oxygen reduction does not occur until potentials negative of -0.4 V vs QRE. Scan 5 in that figure is the Pt wire current collector in the same electrolyte to illustrate its negligible contribution to the voltammogram.

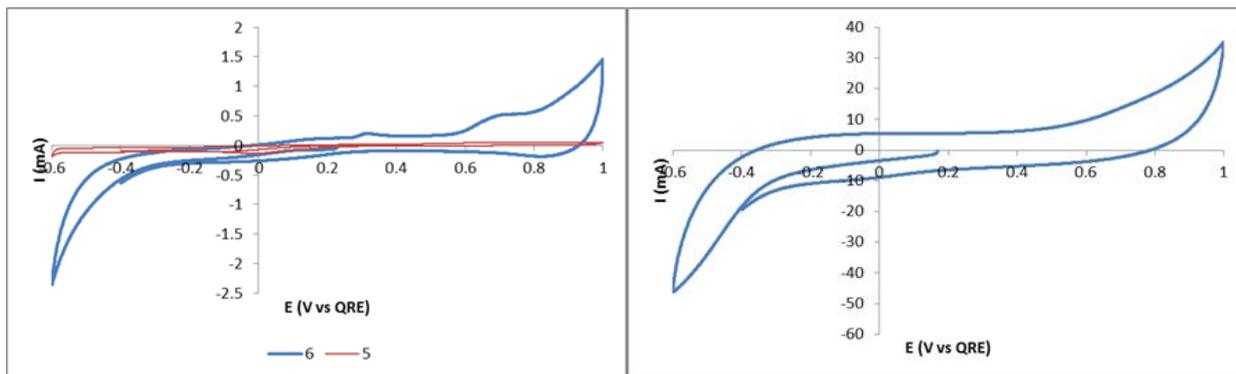


Fig. 3c

3d

Fig. 3d shows the voltammogram of the carbon brush electrode immersed to a depth of 5 cm. As with the carbon felt, oxygen reduction occurs at potentials negative of -0.4 V vs QRE. The large charging currents are consistent with the high surface area of the brush electrode. Both felt and brush electrodes are suitable as supports for microbial films due to their high surface areas.

3.2.2 Electrochemical characterization with the produced water

The electrochemical behavior of a pure Pt electrode, the carbon felt coated with Pt and the carbon felt without Pt were examined in treated and untreated produced water. Because of the high salinity, no added electrolyte was needed. The pH of the treated produced water was estimated to be 4 based on universal pH paper. In this study, a Ag/AgCl reference electrode was used.

Figure 4a shows the voltammogram for a pure Pt electrode (area 2 cm²). Onset of water reduction occurs at -0.8 V vs Ag/AgCl and the onset of oxygen reduction occurs at -0.1 V vs Ag/AgCl. These potentials are shifted negative relative to the values in Fig. 3a, probably because of the change in reference electrodes. In both cases, the onset of oxygen reduction is approximately 0.7 V positive of the onset of water reduction. Pt oxidation is obscured by a new wave of unknown origin near +0.5 V vs Ag/AgCl. Water oxidation occurs positive of +0.8 V vs Ag/AgCl.

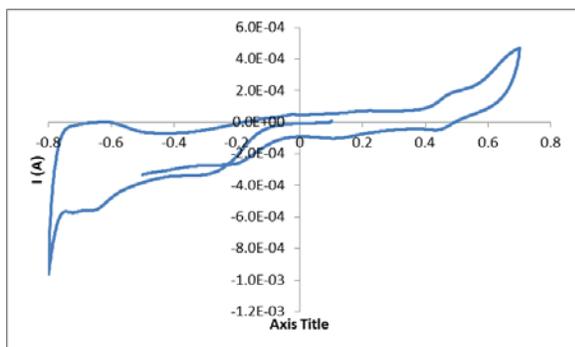


Fig. 4a

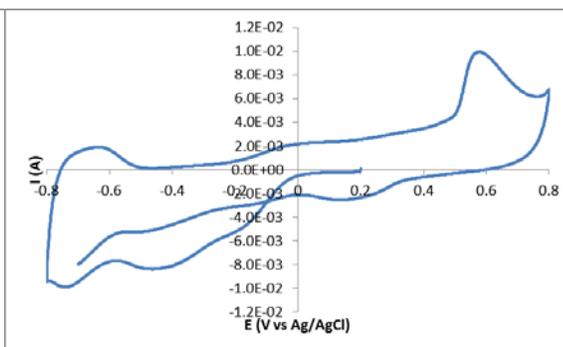


Fig. 4b

The Pt-coated carbon felt electrode (dimensions 1.0 x 1.0 x 0.4 cm) behaves similarly to the pure Pt electrode in the treated produced water (Fig. 4b). Currents are much larger due to the high internal surface area of the foam electrode. Oxygen reduction currents negative of 0 V vs Ag/AgCl are large on the initial scan and smaller on the second scan because of depletion of dissolved oxygen within the felt electrode. An oxidation peak of unknown origin appears at +0.6 V vs Ag/AgCl.

The plain carbon felt electrode (dimensions 1.0 x 1.0 x 0.4 cm) exhibits smaller oxygen reduction currents at more negative potentials than the Pt-coated carbon felt (Fig. 4c). However, the voltammetry is dominated by a large anodic peak at +0.7 V vs Ag/AgCl and a corresponding cathodic peak at +0.2 V vs Ag/AgCl. The large currents suggest the presence of oxidizable substances in the treated produced water that adsorb readily onto the bare carbon surfaces.

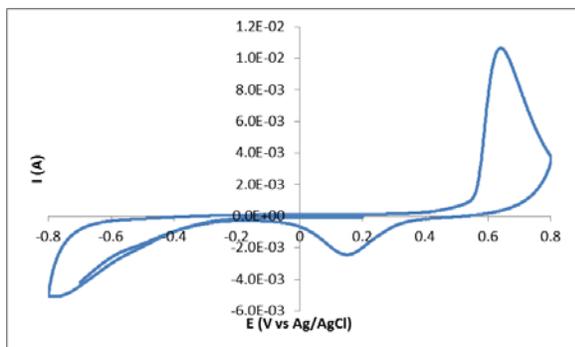


Fig. 4c

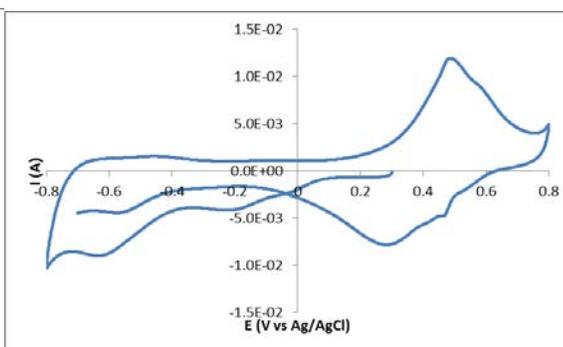


Fig. 4d

The voltammetry of the untreated produced water was similar to that of the treated produced water in terms of peak potentials, suggesting that the pH of the treated and untreated produced water are not different. Fig. 4d shows the voltammogram of the Pt-coated carbon felt electrode in untreated produced water. Comparing Fig. 4d to Fig. 4b, it is evident that the anodic and cathodic peaks at positive potentials are much larger in the untreated produced water. Carbon absorption probably removes much of the oxidizable substances during treatment.

In summary, produced water contains readily oxidizable substances which can contribute to anodic current when the carbon felt electrode potential is positive of +0.2 V vs Ag/AgCl.

3.3. Two-chambered BES for produced water softening

3.3.1. Applied electric currents and voltages

The two-chambered BES was driven by an 8 mA current from day 0 to day 3, followed by an increase of the current to 9 mA from day 4. The corresponding voltage across the cell increased slowly up to 3.2 V with the applied current of 8 mA, and further increased to 3.5 V with 9 mA (Figure 5). Based on the voltammetry reported in section 3.2, this large voltage indicates that both oxygen reduction and water reduction contributed to the faradaic processes at the cathode. Both processes consume protons, thereby raising the electrolyte pH.

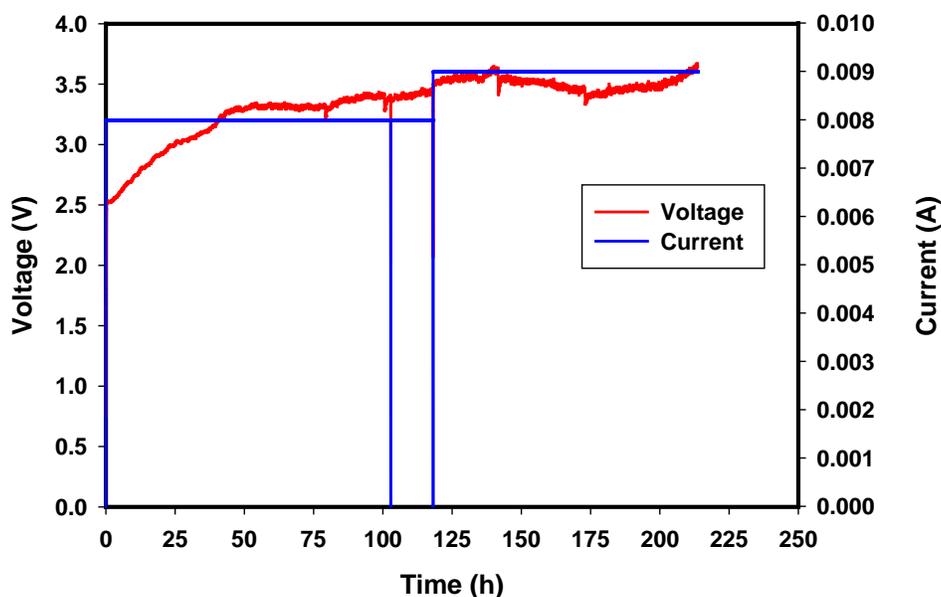


Figure 5. Voltage and current of BES system with applied current.

3.3.2. pH and conductivity

Catholyte pH rapidly increased from initial value of 7.3 to 10.9 during the first day, then slowly to 11.5 on day 4 before the electric current was increased from 8 mA to 9 mA. The higher current further increased the pH to 11.8 on day 9 (Figure 6). The catholyte electric conductivity continuously increased from 6.1 mS/cm to 11.6 mS/cm during the time period. There was a significant pH decrease of the anolyte accompanied with an increase in electric conductivity. The pH decrease is consistent with oxidation of organics and water since both processes generate protons.

The results showed that pH can be reasonably increased to a level sufficiently high for water softening purpose (i.e., 8.5 for calcium removal and 10.5 – 11 for magnesium removal). More frequent monitoring of pH during the first day would allow assessment of the time required to raise the pH for water softening. The pH varied with the applied current. Further studies on such pH-current relationships are required to develop operation guidelines for the BES.

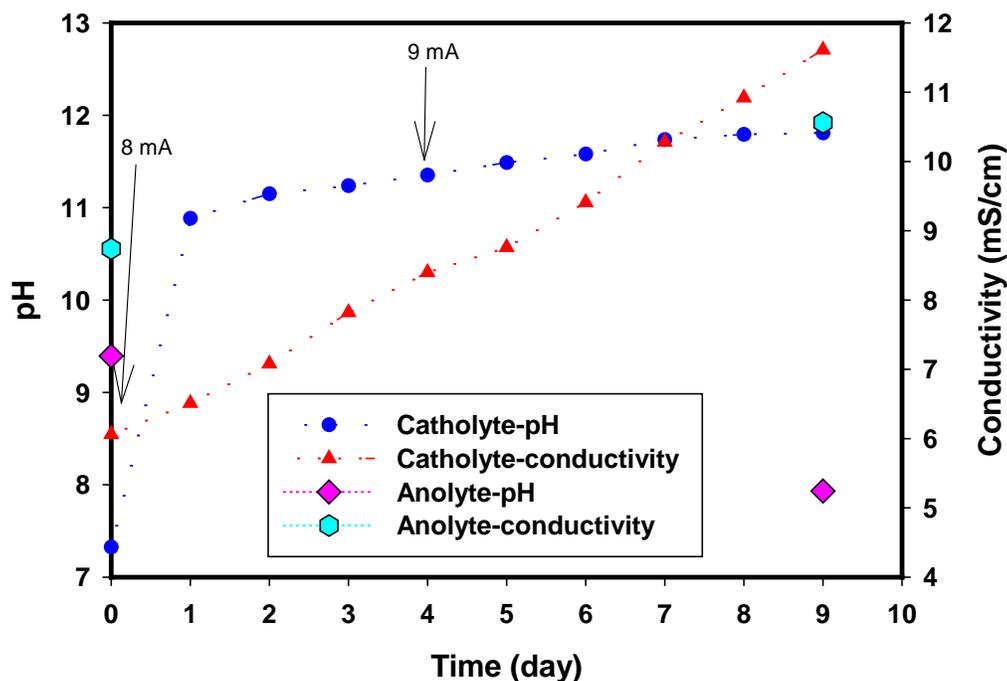


Figure 6. pH and electric conductivity of the anolyte and catholyte of the BES driven by electric current.

3.3.3. Produced water softening

The catholyte (pH = 11.8) was mixed with the raw produced water with a range volumetric ratios (1:1 – 1:10, produced water:catholyte) to examine its softening effects. The mixtures were stirred for 2 mins and the formed chemical precipitations were allowed time to settle, followed by separation of the chemical precipitations from the water using a 0.45 μm filter paper (Figure 7).

TSS (before settlement of the chemical precipitations) of the raw produced water and catholyte were 268 mg/L and 78 mg/L respectively. The mixings resulted in TSS 2,316 mg/L (1:1 produced water: catholyte), 4,600 mg/L (1:2), 23,476 mg/L (1:5), and 11,586 mg/L (1:10) (Figure 8).

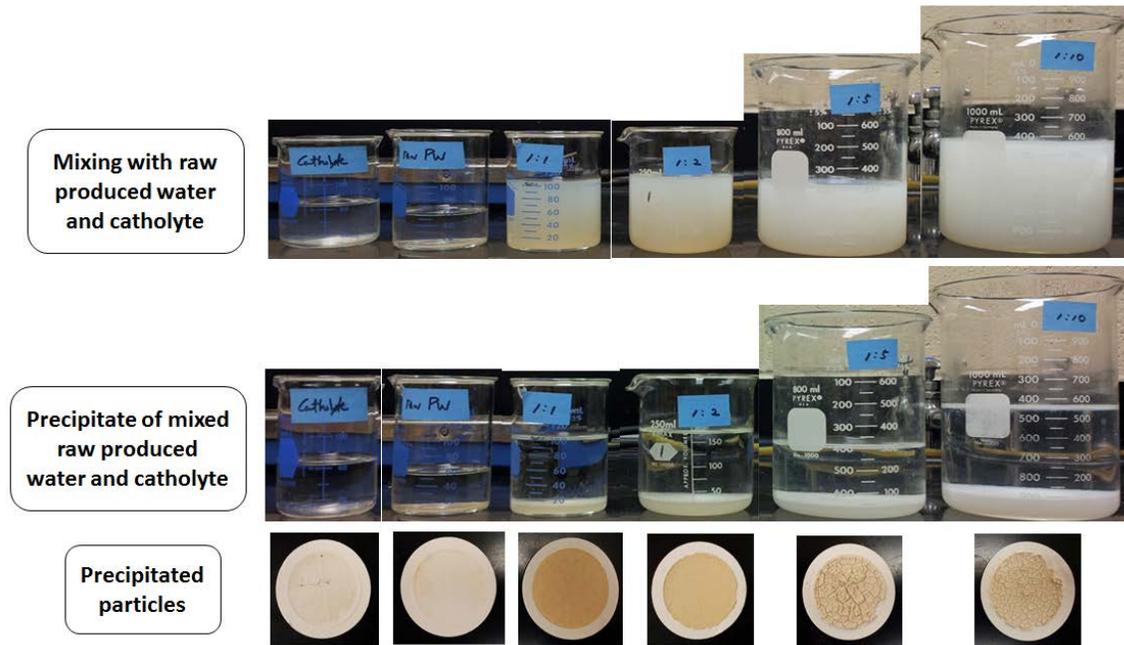


Figure 7. The high-pH catholyte, raw produced water, their mixtures, and resulting chemical precipitations with volumetric ratios from 1:1 (produced water:catholyte) to 1:10.

This softening method uses electrochemical force to create a pH imbalance and use the high-pH catholyte for chemical precipitation of multi-valent cations (e.g., Ca^{2+} and Mg^{2+}), which results in net removal of dissolved ions from the produced water. It has the advantage over conventional water softening treatment because it does not require addition of alkine chemicals. Chemical addition (e.g., $\text{Ca}(\text{OH})_2$, Na_2CO_3 , or NaOH) either increases the quantities of chemical sludge produced or add to the concentration of mono-valent ions to the water, which adds to the burden of following desalination.

The BES softening treatment efficiency can be controlled by the volumetric mixing ratios of the produced water and the catholyte. In addition, calcium removal in the softening treatment would depend on carbonate alkalinity of the produced water and the mixture solutions. Additional of carbonate alkalinity such as sodium bicarbonate will enhance calcium removal, but is a trade-

off because sodium concentration of the mixture will increase, which add to the salt content to be removed by the MDC. Magnesium removal was largely dependent on the mixture pH.

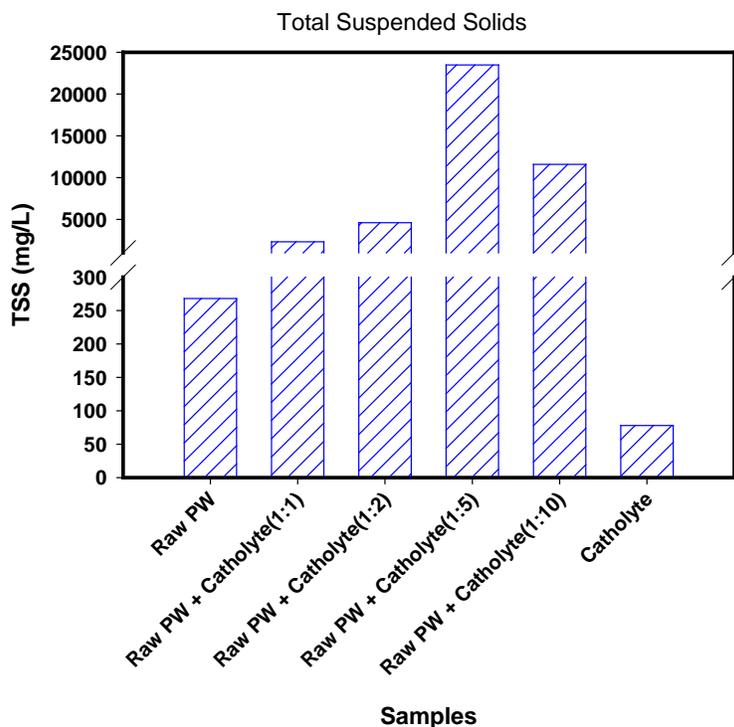


Figure 8. Total suspended solids of the catholyte, raw produced water and their mixtures with volumetric ratios from 1:1 to 1:10 (produced water:catholyte).

The SEM analysis on the chemical sludge of the 1:5 mixture showed globular shape of the precipitation particles (Figure 9). XPS/UPS analysis identified major chemical elements in the globular particles including iron (Fe), calcium (Ca), magnesium (Mg), sulfur (S), and chloride (Cl) (Figure 10). The results showed that the precipitated particles mostly contained multi-valent cations that can be precipitated at the elevated pHs.

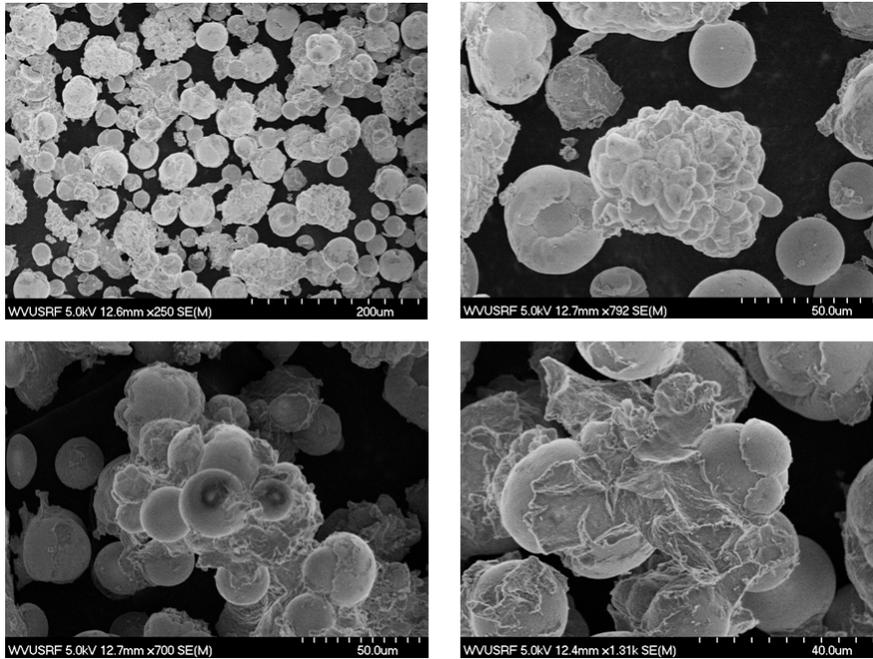


Figure 9. SEM micrograph of the precipitation particles from the raw produced water-catholyte mixture (1:5 volumetric ratio).

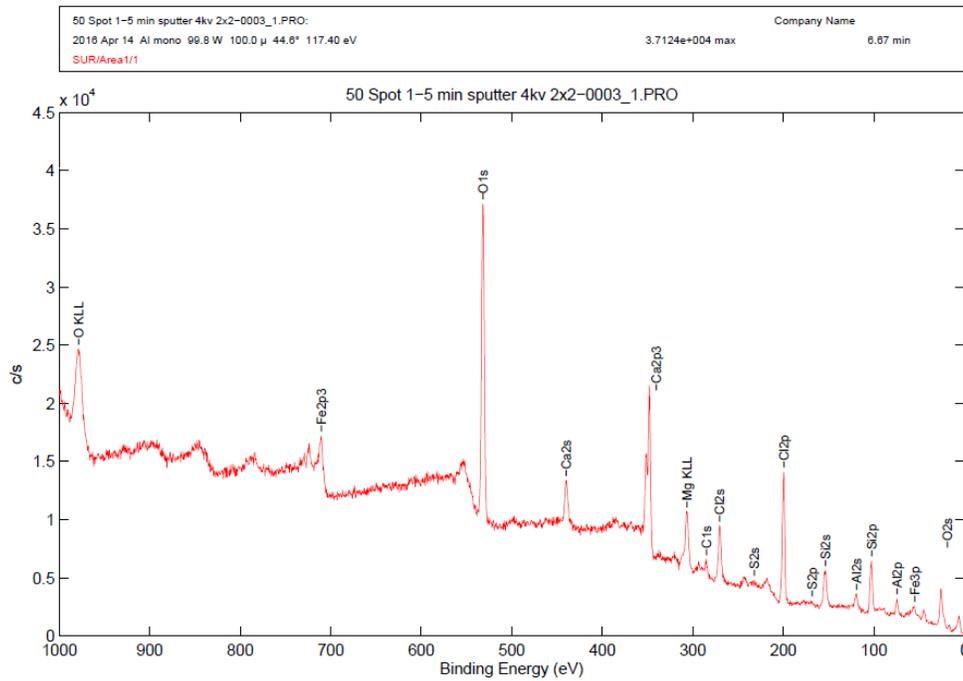


Figure 10. XPS spectrum of the precipitation particles from the produced water-catholyte mixture (1:5 volumetric ratio).

The main two multi-valent cations (i.e., Ca and Mg) were measured in the supernatant of the mixtures and their concentrations showed degrees of removal of the metals as the results of the softening treatment, which ranged from 32% - 70% for Ca and 56% - 99% for Mg (Figure 11). The calcium removal intrinsically depends on carbonate alkalinity in the mixture solutions for calcium carbonate formation. The catholyte pH was sufficiently high to induce magnesium hydroxide precipitations.

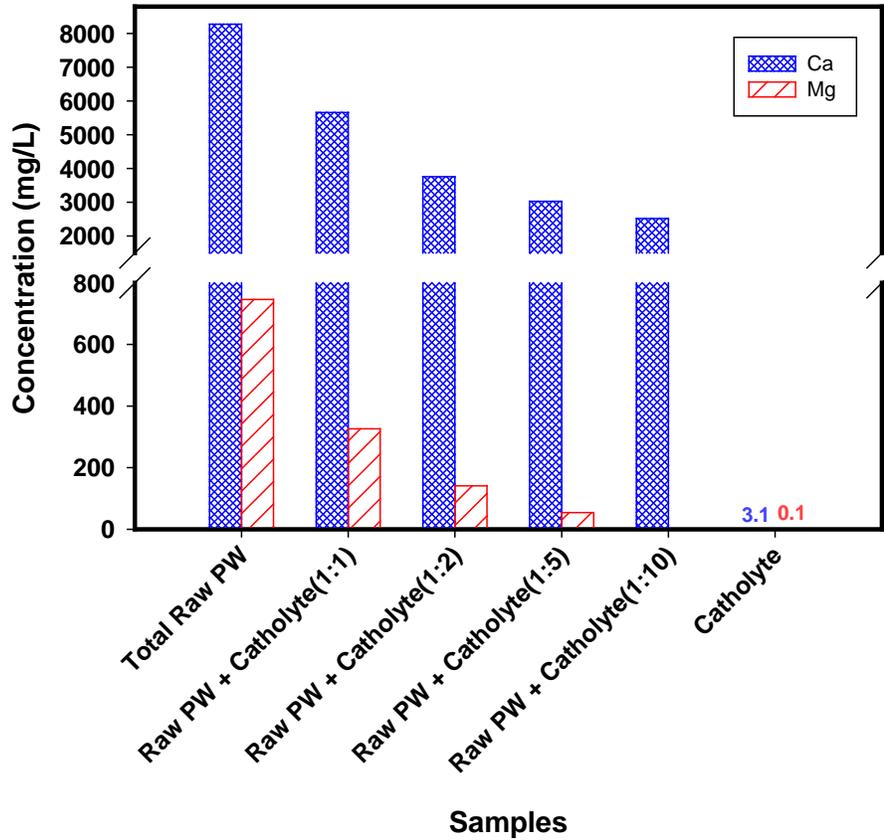


Figure 11. Calcium and magnesium concentrations in mixture supernatants.

3.4. Desalination in the three-chambered MDC

The supernatant from the softening treatment (1:5 raw PW:catholyte) was treated in the three-chambered MDC to further remove dissolved solids. During the desalination, the anode was fed with the synthetic wastewater (flow-through) and the cathode was fed an aerated 0.1 N NaCl solution (recirculation). A fixed voltage or electric current was applied across the anode and cathode to drive ion movements from the central chamber to the anode (anions) and the cathode (cations).

3.4.1. Applied electric current and voltage

The three-chambered MDC was driven by a 2 mA current to evaluate its desalination efficiency. The constant electric current and corresponding voltage across the electrodes are shown in Figure 12. The applied current resulted in voltage rapidly increasing to 1.8 V and leveling off around 2.0 V during an extended operation (5.8 days). The initial rise in voltage can be explained by oxygen depletion inside the carbon felt cathode. At the larger cell voltage, the cathode should be reducing water as well as dissolved oxygen.

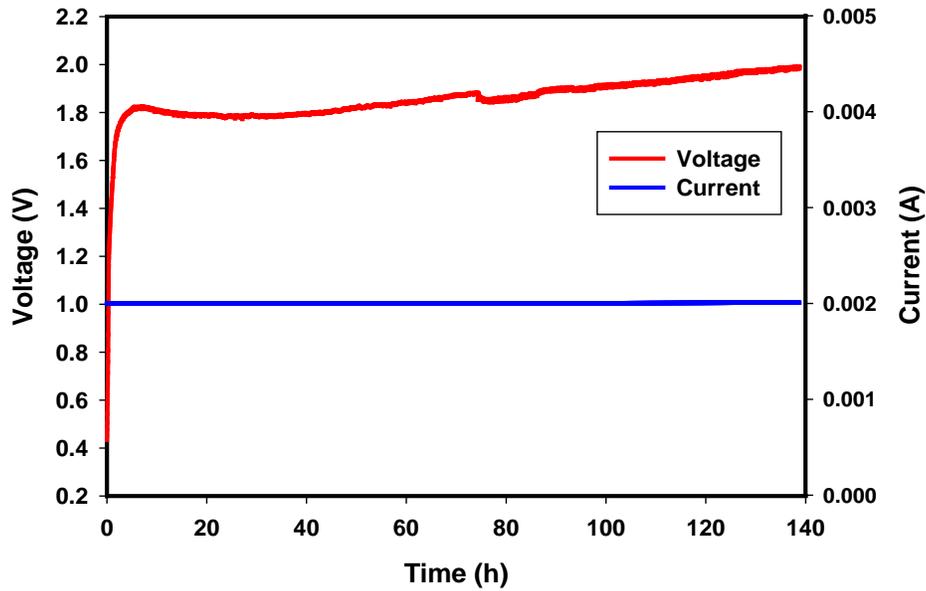


Figure 12. Electric current and voltage applied on the three-chambered MDC for desalination.

3.4.2 Desalination efficiency

The treatment resulted in significant desalination (Figure 13). The pH decreased from 10.3 to 4.6 and electric conductivity from 28.5 mS/cm to 10.7 mS/cm. Removals of Ca^{2+} (666 mg/L to 11 mg/L, 98%) and Mg^{2+} (56 mg/L to 4 mg/L, 93%) were observed in the central chamber. Removal of monovalent ions were also significant with sodium concentration decreased from 4,890 mg/L to 86.6 mg/L (98%) and chloride concentration from 126.3 mg/L to 12.7 mg/L (90%).

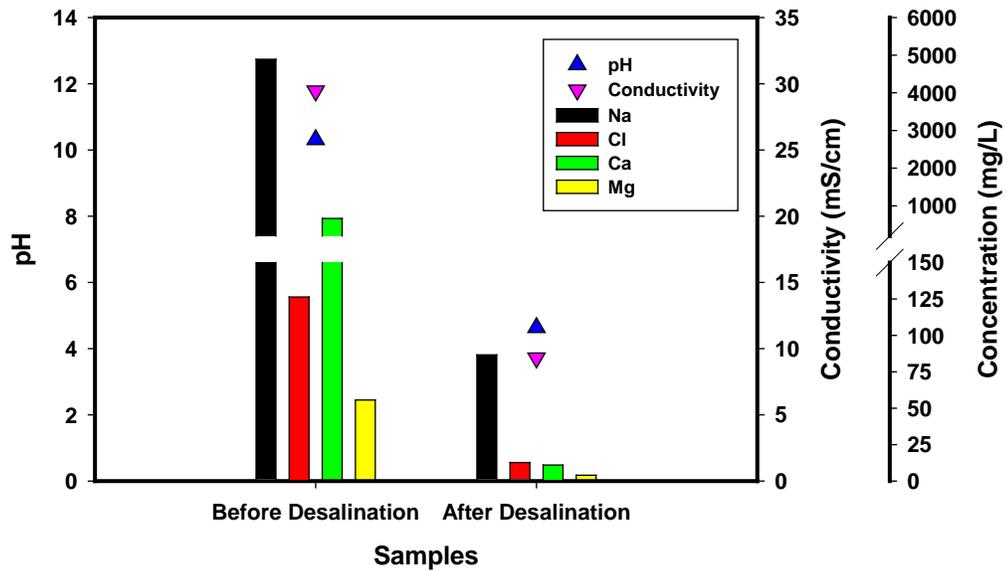


Figure 13. Desalination efficiency in three-chambered MDC.

The desalination treatment resulted in a slight decrease in pH and increase in electric conductivity of the anolyte (Figure 14). The catholyte shows opposite trends of the two parameters. In future field applications, the same softened supernatant can be used as the anolyte and catholyte to avoid the need for different water streams. The anolyte and catholyte from the desalination treatment can be recycled back to the softening unit. The magnitude of the water chemistry changes as a result of the desalination would depend on the working volumes of the anode and cathode chambers and retention times.

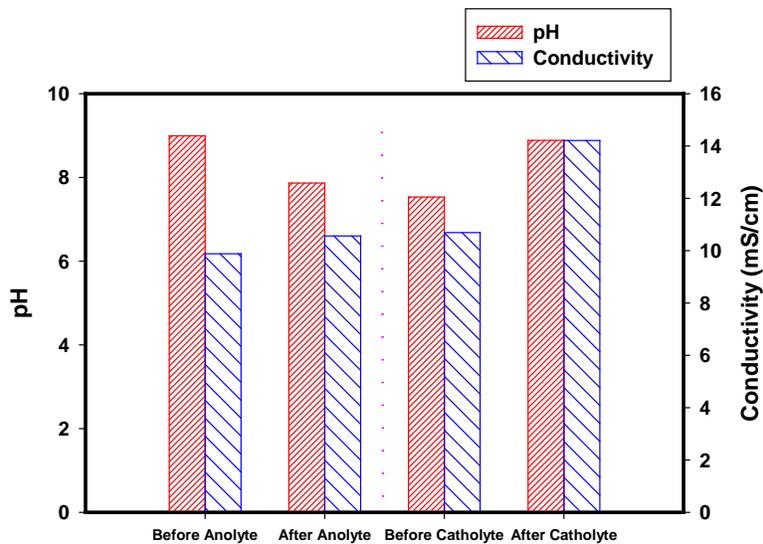


Figure 14. pH and electric conductivity changes as the result of the desalination treatment.

4. Principal Findings

This study evaluated an innovative approach for produced water treatment and has generated results that show promises of the treatment method. Overall, the results were encouraging and warrant further investigations into the treatment kinetics, process factors that control the treatment efficiency, and its cost-effectiveness. Major findings of this study are listed in the followings:

1. The electrochemical characterization of the electrodes with pure electrolyte and with produced water identified potential ranges for the reduction of oxygen, the reduction of water, and the oxidation of water. In addition, produced water contained oxidizable substances that adsorbed onto bare carbon surfaces.
2. The produced water softening and desalination were driven by electric power and require no chemical addition. The treatment resulted in significant net removal of dissolved solids and the chemical sludge would need to be disposed.
3. Using the pH imbalance in the BES to generate high-pH catholytes is feasible. The pH imbalance is conventionally considered as a nuisance for applications of bioelectrochemical systems. In this application, the high-pH catholyte is used and results in net removal of dissolved ions. This method does not require addition of external alkaline chemicals that is typical in the conventional softening processes. Kinetics of the process and relationship between the catholyte pH and the applied current will need to be further investigated to optimize the operation and for continuous produced water treatment.
4. The softening treatment efficiency can be controlled by the volumetric mixing ratios. In addition, calcium removal in the softening treatment would depend on carbonate alkalinity of the produced water and the mixture solutions. Additional of carbonate alkalinity such as sodium bicarbonate will enhance calcium removal, but is a trade-off because sodium concentration of the mixture will increase, which add to the salt content to be removed by the MDC. Magnesium removal was largely dependent on the mixture pH.
5. The three-chambered MDC for desalination of the produced water (after softening) was demonstrated. Similarly, the treatment kinetics, process controlling factors, and system design will need further investigations for optimizing the treatment method.

6. Significance of the Project

Societal needs for food, energy, and water (FEW) are currently met and managed in a piecemeal fashion, resulting in competing water and energy uses among compartmentalized FEW sectors. The disintegrated resource management has resulted in inefficiencies at the FEW nexus, evidenced by increasing energy and water demands and wastes causing adverse ecological and environmental consequences. More than 20 billion barrels of produced water are generated each year as a by-product of oil and gas production within the United States. This project focusing on developing an innovative cost-effective method for produced water treatment to allow reuse of the water and potentially surface discharge. The study has produced promising results that warrant future studies to further develop the treatment technology. The two-step treatment method involves 1) bioelectrochemical mechanisms to create a pH imbalance condition and produce high-pH catholyte for produced water softening, and 2) microbial desalination cell for desalination. This study demonstrated that these treatment can be free from chemical addition, which is typical required for water softening.

The treatment method represents a new treatment method for produced water. Future research is required to further investigate process factors that govern the treatment efficiency for both softening and desalination; develop continuous treatment process; and quantify power consumption. This new treatment method will provide more options for produced water treatment and management for varied end uses (irrigation water, reuse in energy production, safe surface discharge). It will also have broader applications, including desalination of industrial and agricultural wastewaters and brines.

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- Veil, J.A. and C.E. Clark, (2011) Produced-Water-Volume Estimates and Management Practices, *Spe Production & Operations*, 26(03), 234-239.

Publications: None.

Information Transfer Program: None.

Student Support:

Category	Number of students supported with USGS base grant	\$ Value of students supported with USGS base grant	Number of students supported with matching funds	\$ Value of students supported with USGS funds	Total number of students supported	Total \$ value of students supported
Undergraduate						
Masters						
Ph. D.						
Post-Doc	1	\$16,536				
Total	1	\$16,536				

Notable Achievements and Awards:

This research work has provided preliminary results included in a collaborative NSF/EPSCoR proposal with University of Kansas (pending).

Information Transfer Program Introduction

In 2015, the West Virginia Water Research Institute partnered with the Virginia Water Resources Research Center to hold a two day conference on the Water Resources of the Virginias. The event was held in Roanoke, West Virginia and focused on water, energy, and agriculture. More details can be found in the following report.

2015 WV State Water Conference

Basic Information

Title:	2015 WV State Water Conference
Project Number:	2015WV219B
Start Date:	3/1/2015
End Date:	2/29/2016
Funding Source:	104B
Congressional District:	WV-001
Research Category:	Not Applicable
Focus Category:	Agriculture, Toxic Substances, Management and Planning
Descriptors:	None
Principal Investigators:	Tamara Vandivort

Publications

There are no publications.

Information Transfer Program

Final Report

2015 Water Resources Conference of the Virginias October 5-6, 2015

The West Virginia Water Research Institute partnered with the Virginia Water Resources Research Institute to hold a two day Water Resources Conference of Virginias.

The theme was *Water, Energy, Agriculture* and the venue was Stonewall Resort in Roanoke, West Virginia.

A request for abstracts was sent out via email from the participating Institutes. Over 35 abstracts were received.

Keynote speakers included:

- Sen. John Unger II, member of the Joint Legislative Oversight Committee on State Water Resources, West Virginia State Senate.
- Holly Green, Acting Chief, Prevention Branch, Drinking Water Protection Division, Office of Ground Water and Drinking Water, USEPA.
- Tom Bass, Environmental Resources Program Manager, Permitting, Office of Oil and Gas, West Virginia Department of Environmental Protection.
- Dale Skoff, Chair, Marcellus Shale Coalition UIC Well Workgroup.
- Dave Smith, Deputy Chief, Soil Science and Resource Assessment, USDA-NRCS.

The format for day 1 (9am – 9pm) included a plenary session with a keynote presentation by West Virginia Senator John Unger II on the Elk River Chemical Spill a year and a half later, what have we learned, where do we stand and what does the future hold. After a networking break, a panel session was held with Holly Green, Tom Bass and Dale Skoff on Underground Injection Control programs in West Virginia and Virginia.

Following a lunch provided to all participants, two concurrent sessions were held on:

- Water Quality Data; and
- Energy.

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

- Stormwater; and
- Groundwater and Stream Flow.

Following dinner, a networking reception and poster session (seventeen posters) was held from 7:00 pm – 9:00 pm.

On day 2 from 8:00 am – 2:30 pm, the format began with a keynote address by Dave Smith, Deputy Chief, Soil Science and Resource Assessment, USDA-NRCS on the effectiveness of agricultural best management practices, how water research can help and the NRCS Conservation Effects Assessment Program.

Following a networking break, two concurrent sessions were held on:

- Managing Water Resources; and
- Aquatic Life Assessments.

After a lunch provided to all participants, two concurrent sessions were held from 12:45 pm – 2:30 pm on:

- Sourcewater Protection; and
- Impounded Waters.

A website with a specific URL was developed to host information on the event, agenda, online registration, information on the facility, lodging, and other pertinent information.

Presentations from the event were made available on the conference website at:

www.wrcvirinias.org.

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

- Virginia Tech, College of Natural Resources and Environment,
- Virginia Tech, Institute for Critical Technology and Applied Science,
- West Virginia Department of Environmental Protection, Water Use Section,
- West Virginia University, Davis College of Agriculture, Natural Resources and Design,
- USDA-Natural Resources Conservation Service,
- Downstream Strategies,
- Virginia Tech, College of Agriculture and Life Sciences,
- Southeast Rural Community Assistance Project,
- OTT Hydromet; and
- West Virginia Association of Conservation Districts.

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

There were 104 attendees, including presenters. Both West Virginia and Virginia has strong attendance from their states. Attendees included academia, industry, regulatory agencies, city, municipal, state and federal government agencies, legislators, watershed associations, private non-profits, and others. Several students played active roles in presenting results in oral and poster sessions.

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

USGS Summer Intern Program

Basic Information

Start Date:	1/1/2015
End Date:	6/30/2016
Sponsor:	USGS (Ward Sanford)
Mentors:	Joseph j. Donovan
Students:	Jeffrey Cazenias

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

"It was a fantastic experience that was very educational. I was able to learn first hand how to conduct research and work in a professional manner."

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	1	0	1	0	2
Masters	2	2	0	0	4
Ph.D.	0	2	0	0	2
Post-Doc.	1	0	0	0	1
Total	4	4	1	0	9

Notable Awards and Achievements

Some notable achievements and awards include the following:

Project 2015WV220B: This research work has provided preliminary results included in a collaborative NSF/EPSCoR proposal with the University of Kansas (pending).

Project 2012WV200G: Two graduate students graduated with PhDs in December 2015. One graduate student graduated with a MS in December 2014. One graduate student graduated with a MS in December 2013. Three graduate students presented results at professional meetings. Two undergraduate students presented results at a professional meeting. Two undergraduate students completed a research course related to this work. MS student, Erin O'Leary, was selected as a student moderator for an international conference: International Erosion Control Association (IECA) 2014 Environmental Connection Conference, February 25-28, 2014, Nashville, TN (awarded travel and registration costs). PHD student, Alison Sears, won a Student Research Enhancement Award to present at an international professional meeting: Improvement of Water Supply on Reclaimed Appalachian Surface Mine Sites, 2013-2014 Student Research Enhancement Award, WVU Women in Science and Engineering (WiSE), \$1,250.