

**West Virginia Water Resources Research Institute  
Annual Technical Report  
FY 2007**

# Introduction

The West Virginia Water Research Institute (WVWRI) addresses the key water resource issues facing policy makers, agency staff and the public. Our research program is guided by the West Virginia Advisory Committee for Water Research. It includes representatives from the following:

- \$ West Virginia Department of Natural Resources
- \$ West Virginia Department of Health & Human Resources
- \$ West Virginia Chamber of Commerce
- \$ West Virginia Coal Association
- \$ West Virginia Department of Environmental Protection
- \$ West Virginia Farm Bureau
- \$ U.S. Federal Bureau of Investigation
- \$ U.S. Geological Survey
- \$ U.S. Environmental Protection Agency
- \$ U.S. Department of Energy – National Energy Technology Laboratory
- \$ U.S. Army Corps of Engineers – Huntington, WV District
- \$ West Virginia University

The Advisory Committee develops the Institute's research priority list, reviews its progress and selects startup projects at its annual meeting. With this direction, the Institute recruits new researchers to study emerging water research issues. Because the Advisory Committee understands future regulatory and economic driving factors, these issues tend to grow in importance and have often led to follow-on funding from their agencies.

## Funding Strategy

The Institute receives a grant of roughly \$92,000 annually through the U.S. Geological Survey CWA section 104b program. We use this funding to develop research capabilities in priority areas and to provide service to State agencies, its industry and citizen groups. As a result of successful leveraging, we supported a program with an average yearly value of over \$3M since 2003. 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. Over the past 15 years over 50 WVU faculty members have been supported by WVWRI projects while over 25 faculty from other State institutions have participated in the program. Our funding strategy relies on successful competition for Federal dollars while teaming with State agency and

industry partners. They later provide test sites, in-kind support and invaluable background data.

## Research Capability

The bulk of our research is undertaken by academic faculty. Since West Virginia University is the flagship research institution in the State, its faculty have received the bulk of Institute funding. Over 50 WVU researchers have been supported by the WVVRI representing 20 departments. In addition, the Institute has a staff of 12, with three research contractors. Roughly half of the Institute is directly engaged in research projects.

## Successes

Three successful policy initiatives: • Our research led the West Virginia Department of Environmental Protection to use our center and our planning technology to implement the newly reauthorized abandoned mine land program's set aside funds for watershed remediation. This is a \$300M fund that will be used to systematically evaluate and remediate priority watersheds that are impacted by historic mine drainage. • WVVRI research on stream mitigation banking was presented to the WV Legislature and we have been directed to work with the Natural Resources Conservation Service, U.S. Army Corps of Engineers and WVDEP to incorporate our approach into a mitigation banking framework for the State. • WVVRI research and organizational capability led to the creation by the WV Legislature of Brownfield Assistance Centers to help communities gain access to brownfield development opportunities. Two were created and WVVRI manages the northern WV Brownfield Assistance Center. Thus far this center has developed two successful grants worth \$400,000.

## Future Direction

The following programs of the WVVRI are expected to continue to remain stable and grow modestly into the future:

\$National Mine Land Reclamation Center

\$Combustion Byproducts Recycling Consortium

\$Hydrology Research Center

\$Northern WV Brownfields Assistance Center

\$Watershed Assistance Center

## Outreach

The WVVRI performs outreach through meetings, workshops, conferences, site visits, web site, newsletters, and publications.

## West Virginia Water Conference 2007

A conference was held in November, 2007 in which the WVVRI served as co-sponsor. The Virginia Water Resources Research Institute at Virginia Tech took the lead in this event. This weeklong event including several workshops, oral presentations, and panel sessions was held at the Virginia Tech Skelton Center in Blacksburg, Virginia. There were over 80 presenters and approximately 175 attendees.

## WWRI Web Site

A web site (<http://wwri.nrcce.wvu.edu>) contains information on all the WWRI programs and projects. This site is updated on an on-going basis as new information becomes available.

# Research Program Introduction

With diversified funding and support, the WVVRI develops strong, multi-disciplinary research teams by collaborating with various West Virginia University colleges and divisions, other higher education institutions, private firms, and consultants. This team approach brings the best expertise available to address water issues. It also allows the WVVRI to perform research in a number of areas at any given time.

# Evaluation of the Environmental Hazard of Selenium in Coal-Associated Rocks of the Southern WV Coal Basin (WRI-83)

## Basic Information

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<b>Principal Investigators:</b>	Ronald B Smart, Jack Renton

## Publication

Title: Evaluation of the Environmental Hazard of Selenium in Coal-Associated Rocks of the Southern WV Coal Basin

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## ABSTRACT

Mountaintop removal-valley fill coal mining involves the removal of the mountain top and the filling of nearby valleys with overburden to result in a level surface that can be used for a variety of purposes. According to a USEPA report, (Bryant et al. 2002) selenium concentrations in several streams and rivers associated with mountaintop removal-valley fill mining areas in southern West Virginia were found to contain up to 50 ng /L , a concentration that is ten times the West Virginia stream standard (5 ng /L). Pre-mining data indicated that the valley fills were responsible for the elevated selenium levels.

Our study focused on comparative ultrasound-assisted kinetics of the leaching of selenium and arsenic from pulverized samples of rock that are associated with coal mining activities. Most traditional batch extraction methods utilize lengthy mechanical shaking or soxhlet extractions that may take hours or days for a single extraction to be performed. For the ultrasound method, a five-minute application of ultrasound energy to a pulverized rock sample mixture in a 1:10 solid to solution ratio was found to produce useful results for a single extraction. The rock samples were collected from a core supplied by the West Virginia Geological and Economic Survey (WVGES). The samples were collected from Kayford Mountain in Kanawha County, West Virginia (USA).

The amount of arsenic extracted with ultrasound was three orders of magnitude greater than the selenium. No arsenic was previously detected in the stream waters (Bryant et al. 2002), even though the accelerated rate constants appeared to be ten times greater than those for selenium (Table 4), which suggests that arsenic is sequestered from the aqueous phase by a different mechanism compared to selenium. The rate of release of total arsenic and total selenium did not depend on their respective concentrations in rocks but rather on the type of rocks analyzed.

The reactivity and toxicity of arsenic and selenium depend on their oxidation states. The primary arsenic species found in the environment are inorganic As (III), arsenite, and As (V), arsenate, as well as several organoarsenic compounds. Selenium species include Se (IV), selenite, and Se (VI), selenate, Se (0) and Se (-II), as well as several organic forms. The most toxic species are Se (IV) and As(III), and Se (VI) and As (III) are more bioavailable compared to the other oxidation states. Sequential extractions of BT700 indicated that most of the extractable is Se (IV) whereas in BT571 the predominant extractable form is Se (VI).



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## **Introduction**

Temperature controlled ultrasound extractions provide important kinetic data that can be useful in describing the chemistry at the solid-solution interface. The solid – solution chemistry can then be used to infer the bioavailabilities of metals released into associated aquatic systems. Most traditional batch extraction methods utilize lengthy mechanical shaking or soxhlet extractions that may take hours or days for a single extraction to be performed. For the ultrasound method, a five-minute application of ultrasound energy to a pulverized rock sample mixture in a 1:10 solid to solution ratio was found to produce useful results for a single extraction. Ultrasonic extraction enhances dissolution process by causing acoustic cavitations that result in bubble formation and subsequent collapse generating high-pressure gradients, thereby increasing reactivities (Brunori et al. 2004; Suslick 1989).

The use of ultrasonic energy has been proven to be an easy, convenient, and fast way of desorbing inorganic (Luque-Garcia and de Castro 2003; Perez-Cid and Bola 2001; Perez-Cid et al. 1999) and organic pollutants (Tse and Lo 2002) from sediments, soil and biological samples (Arruda et al. 2003; Mierzwa et al. 1997). Focused ultrasonic probes enable efficient adjustment and monitoring of temperature in a water-jacketed extraction vessel and this methodology was used in this study to study the kinetic releases of arsenic and selenium from pulverized samples of rocks associated with coal mining activities. Since natural rock dissolution is a lengthy process (Sparks 1989), ultrasound extraction was used to mimic the natural weathering of coal associated rocks on a much shorter time scale.

Mountaintop removal-valley fill coal mining involves the removal of the mountain top and the filling of nearby valleys with overburden to result in a level surface that can be used for a variety of purposes. According to a USEPA report, (Bryant et al. 2002) selenium concentrations in several streams and rivers associated with mountaintop removal-valley fill mining areas in southern West Virginia were found to contain up to 50 ng /L , a concentration that is ten times the West Virginia stream standard (5 ng /L). Pre-mining data indicated that the valley fills were responsible for the elevated selenium levels.

Although low concentrations of selenium and arsenic are dietary essentials, higher concentrations pose a serious health risk to terrestrial and aquatic organisms (Jukes 1983; Yih et al. 2005). Elevated concentrations of these metalloids have also been shown to stunt the growth of some plants (Lejeune et al. 1996; Terry et al. 2000) which could inhibit a critical process required in the remediation of filled sites.

Our study focused on comparative ultrasound-assisted kinetics of the leaching of selenium and arsenic from pulverized samples of rock that are associated with coal mining activities. The most common models used to describe the kinetics for the release of inorganic and organic substances from solids into solution are parabolic diffusion, Elovich, power function and first and second order kinetic models. (Aharoni et al. 1991; Goh and Lim 2004; Kithome et al. 1998; Shimizu et al. 2004). These models are often used to approximate the overall chemical kinetics of intricate reactions occurring in complex matrices that are often unknown. Although the first order and parabolic diffusion models are both very important in describing the surface film diffusion or intraparticle diffusion of materials from rocks into solution (Sparks 1989), the first order

kinetic model was found to be most useful in comparing the rates of accelerated rock disintegration and the concomitant release of arsenic and selenium from coal-associated rocks. Thus, the ultrasound assisted extraction rate is proportional to the following parameters: 1) the mobility of the selenium and arsenic compounds from the solid to liquid phase, 2) the chemical potential of these species, 3) lithology of rocks extracted, 4) the surface area of particles, and 5) the level of ultrasonication power.

### **Methods and materials**

An Ultrasonic Sonicator (Misonix, Model XL 2020) with a 0.3 mm diameter titanium probe was used to deliver sound energy ( $200 \text{ W/cm}^2$ ) to a mixture of 1g of pulverized sample and 10 mL water. A 38-ml capacity water-jacketed extraction vessel (22mm ID x 10 cm quartz tube) was designed. The ultrasonic power was measured by calorimetry (Contamine et al. 1995; Mason et al. 1992). A thermocouple was immersed into the extraction solution to monitor the temperatures during extraction and ultrasound energy measurement processes. The water/pulverized rock mixture was ultrasonicated for a period of five minutes followed by centrifugation for 20 minutes at 3400g. The supernatant solution was decanted and placed in a 25-mL polyethylene vial. The solid residue was returned back to the sonication vessel followed by the addition of a fresh 10-mL aliquot of water for the second ultrasonication step. The process was repeated seventeen times for a total 90 minutes of sequential extraction. Each extract was analyzed for total selenium and arsenic by graphite furnace atomic absorption spectrophotometry and Se (IV) and As (III) were measured by hydride generation atomic spectrophotometry. A Varian atomic absorption spectrometer (Model 55B) was used to analyze all the samples.

The total arsenic and selenium concentrations in the unextracted rocks were determined after microwave digestion. Each of the three samples (0.5g) were digested in triplicate using 5 ml concentrated HNO<sub>3</sub> , 5 ml concentrated HF and 3 mL concentrated HCl in a microwave oven (CEM Corporation MARS-5- Explorer version 194A04) followed by analysis of digests using graphite furnace atomic absorption spectrophotometry.

## **Sampling**

The rock samples were collected from a core supplied by the West Virginia Geological and Economic Survey (WVGES). The samples were collected from Kayford Mountain in Kanawha County, West Virginia (USA). The core was obtained by drilling from the mountaintop down to 270 m below the surface. Three samples (BT60, BT571 and BT700) were analysed. These samples were collected at depths of 18 meters (BT60), 174 meters (BT571) and 214 meters (BT700), respectively. Each sample was subdivided lengthwise, pulverized and passed through a 60 mesh sieve. The sieved rock powders were then subjected to ultrasonic extraction.

## **Mineralogical examination of pulverized rocks**

Lithologic analyses of the rocks were performed by analysts at WVGES. The results obtained indicated that BT60 was sandstone, while BT571 and BT700 were claystones. Sample BT60 was comprised of 81% SiO<sub>2</sub> , most of which was present as quartz as shown in Tables 1 and 2. Samples BT571 and BT700 had 62.25 % and 63.83 % SiO<sub>2</sub> of which about half of BT571 and about a third of BT700 was quartz. The two claystone samples had about six times the percentage of illite as that in BT60. There were

no significant differences in kaolin composition in the three samples as indicated in Table 1. The  $\text{Fe}_2\text{O}_3$  and % chlorite compositions in BT60 were below 0.01% as shown in Tables 1 and 2.

## **Results and discussion**

### **Comparison of extraction methods**

Most kinetic batch extraction experiments reported in the literature are carried out at aqueous concentrations that are higher than those found in natural environments. In these studies pure solids (e.g. kaolin, silica, illite, iron oxides) are equilibrated with organic or inorganic substances of interest to allow them to adsorb onto the solid surfaces prior to performing desorption experiments. Because ionic concentrations used in such adsorption and desorption experiments are too high, kinetic studies are limited due to equilibrium conditions that are quickly established during the onset of extractions (Skopp 1986). The reason most workers in this area prefer to use continuous flow methods is that there is no flow back or re-adsorption of the materials that had been released earlier into the solution (Barry et al. 1993; Huertas et al. 1999; 2002). The initial extractions in kinetic batch experiments are known to release most of the metals being extracted, therefore during the first extraction, there is a greater chance of establishing equilibrium between the adsorbed and free metals in solution. Thus, concentrations so obtained cannot be used to describe the kinetics of extraction but rather only provide equilibrium conditions (Sabbah et al. 2005). Such conditions prompted the use of temperature-jump experiments (Zhang and Sparks 1990) to study the adsorption and desorption kinetics of selenate and selenite at the goethite surface.

In order to establish that equilibrium was not reached during the first 5 minutes of ultrasonic extraction, results for 120 minutes of continuous sonication were compared with those obtained from the initial 5 minutes of sonication of a 90-minute sequential extraction experiment consisting of 5 minute ultrasonifications. The concentrations of total arsenic and selenium obtained by different extraction methods and microwave digestions are summarized in Table 3.

Although there was a large initial increase for both the arsenic and selenium concentration obtained during the first five minutes of the 90-minute sequential extraction, there is a statistically significant difference in the values obtained after first 5 minutes of the 90 minute sequential extraction to the Se concentration that was extracted after 120 minutes of continuous sonication ( $P \leq 0.11$ ,  $n = 9^*$ ). Based on this, it can be concluded that the concentration of both metals in solution obtained after five minutes would not have reached equilibrium with arsenic and selenium still encapsulated, sorbed or remaining within the pulverized rock particles.

There is an apparent three orders of magnitude (ng/g vs.  $\mu\text{g/g}$ ) difference between the Se and As concentrations extracted from the rock samples. The values obtained after 2 hours of continuous sonication were smaller than the values obtained by the 90-minute sequential sonication. These data indicate equilibration and/or reabsorption could have been established during the course of the 2-hour extraction. In order to promote the non-equilibrium conditions needed for kinetic studies it was found necessary to use the sequential extraction method. Thus the observed non-equilibrium conditions at 5 minutes of ultrasonication time could be described in terms of a slow reabsorption process of the released metals compared to a faster desorption rate at  $200\text{W/cm}^2$  of ultrasonication

power. These extraction conditions were used to simulate the accelerated kinetic release of selenium and arsenic from valley fills into streams.

The amount of arsenic extracted with ultrasound was three orders of magnitude greater than the selenium as shown in Figures 2 and 3. No arsenic was previously detected in the stream waters (Bryant et al. 2002), even though the accelerated rate constants appeared to be ten times greater than those for selenium (Table 4), which suggests that arsenic is sequestered from the aqueous phase by a different mechanism compared to selenium.

Sample BT60 was found to have the lowest concentrations of arsenic and selenium compared to BT571 and BT700 as shown in Table 1. Although BT700 had the highest total and extractable arsenic and selenium species, the rates of their releases from the solid into the solution were smaller than those of BT571 and BT60 as shown in Table 4.

The rate of release of total arsenic and total selenium did not depend on their respective concentrations in rocks but rather on the type of rocks analysed. Sample BT60, a sandstone had the lowest amounts of selenium yet it was all extracted during the first three extractions. Jenkins and Schaer (2005) found that darker overburden with large amounts of humic and fulvic substances had the highest selenium concentrations. These observations were consistent with our findings in that the claystones (BT700 and BT571) were dark in appearance and had the highest amounts of selenium and arsenic (Table 3).

Organic acids which originate from dead plants are often incorporated into rock lattices during rock formation. Any selenium that is bound to organic acids will become part of the rock and some of this sorbed selenium can become bioavailable as the rocks



weather (Liu et al. 2006). In the rocks analysed, it appears there are two forms of organic bound selenium, with one weakly sorbed and the other strongly sorbed. The weakly sorbed forms are readily available and the strongly sorbed take more time and energy to become bioavailable. This information could explain the fact that samples BT571 and BT700 had more selenium which was not readily leachable compared to BT60.

Peak and Sparks (2002) found that selenate and selenites both bind strongly to iron oxides and this could be the reason the selenium in BT60 was easily extracted compared to BT571 and BT700 (Table 2). Such kinetic information is useful in determining procedures that are necessary to be undertaken when disposing different types of mining waste. Another complication is that the toxicity and bioavailability of the released metalloids depend on chemical speciation which suggests the need to differentiate the selenium and arsenic compounds released.

The reactivity and toxicity of arsenic and selenium depend on their oxidation states. The primary arsenic species found in the environment are inorganic As (III), arsenite, and As (V), arsenate, as well as several organoarsenic compounds. Selenium species include Se (IV), selenite, and Se (VI), selenate, Se (0) and Se (-II), as well as several organic forms. The most toxic species are Se (IV) and As(III), and Se (VI) and As (III) are more bioavailable compared to the other oxidation states.

### **Effects of ultrasonic power on the speciation studies for Se (IV)/ Se (VI) and As (III)/As (V)**

In order to determine the effects of ultrasonic power on the stability of arsenic and selenium, 10 ml of 5 ng/mL solutions of As (III)/As (V) and Se (IV)/Se (VI) in a 1:1 ratio were separately monitored as a function of ultrasonication time using 200W/cm<sup>2</sup> power

intensity. A fresh 10-ml solution of 5 ng/L arsenic /selenium was sonicated for each of the following sonication times (5 min, 10 min, 15 min ... up to 2 hours). All experiments were done in triplicates. As illustrated in Figure 4, As (III) concentration decreased by 70% after only five minutes of sonication followed by a slow decrease to reach values that are 96 % lower than the initial concentration within a period of two hours. Solutions containing 1:1 mixtures of 5, 10 and 15 ng/mL of As (III) and As (V) also showed similar trends. Hence, ultrasonication extraction cannot be applied for the speciation studies of As in rocks. Analysis of the total arsenic in the ultrasonicated solutions revealed no arsenic losses due to evaporation.

On the other hand Se (IV) concentration remained constant over the entire 120 minutes of continuous sonication. No significant changes in total selenium concentrations were observed after a two-hour continuous sonication of 5, 10 and 15 ng/mL of 1:1 Se (IV)-Se (VI) mixtures. Hence, Se (IV) solutions are not easily oxidized under the experimental conditions used.

### **Comparison of the extraction of Se (IV) and total Se in samples**

Sequential extractions of BT700 indicated that most of the extractable is Se (IV) whereas in BT571 the predominant form is Se (VI), as shown in Figures 5 and 6. The Se (IV) concentration increased in the order BT60 < BT571 < BT700.

### **Conclusions**

Ultrasound dissolution is a useful tool for the kinetic extraction of arsenic and selenium and the speciation of selenium from coal-associated rocks. The release of arsenic and selenium from coal-associated rocks depend both the type of rock and the

concentrations found in rocks. These metalloids are released at different rates indicating that they bound at different sites and by different mechanisms.

The extracted arsenic concentrations are 3 orders of magnitude higher than selenium concentrations, and the speciation of the extracted selenium is also dependent on the rock material. Additional work is currently in progress to determine the type of binding and the locations of arsenic and selenium in these coal-associated rocks as well as the fate of arsenic and selenium that has been leached from valley fills.

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**Table 1:** X-ray diffraction results

Sample	Lithology	% Quartz	% Orthoclase Feldspars	% Plagioclase (Na/K Feldspar)	% Illite	% Kaolinite	% Chlorite
BT60	Sandstone	81.0	3.2	< 0.1	6.8	9.1	< 0.01
BT571	Claystone	32.1	0.4	0.5	40.1	12.2	14.7
BT700	Claystone	22.6	0.5	0.9	46.6	7.5	21.9

*Courtesy, West Virginia Geological and Economic Survey*

**Table 2:** X-ray fluorescence results

	% MnO	% K <sub>2</sub> O	% SiO <sub>2</sub>	% Al <sub>2</sub> O <sub>3</sub>	% Fe <sub>2</sub> O <sub>3</sub>	% Na <sub>2</sub> O	% MgO	% TiO	% CaO
BT60	0.01	2.48	81.05	15.28	< 0.01	0.07	0.48	0.86	0.22
BT571	0.04	4.91	62.25	23.95	5.17	0.05	2.15	1.34	0.04
BT700	0.03	5.52	63.83	23.28	4.16	0.19	1.97	1.27	<0.01

*Courtesy, West Virginia Geological and Economic Survey.*

**Table 3:** Comparison of extraction techniques

Sample	Total available Selenium	Total Selenium Extracted			Total available Arsenic	Total Arsenic extracted		
	Microwave digestion ng/g	120 min continuous sonication* ng/g	Partial 5 minute of the 90 minute sequential sonication* ng/g	Total 90 minute sequential sonication ng/g	Microwave digestion µg/g	120 min continuous sonication* µg/g	Partial 5 minute of the 90 minute sequential sonication* µg/g	Total 90 minute sequential sonication µg/g
BT60	93.3 ± 3.7	78.4 ± 3.1	69.7 ± 2.5	93.2 ± 3.4	5.05 ± 0.15	2.19 ± 0.55	0.78 ± 0.11	4.15 ± 0.4
BT571	1088 ± 18	261.1 ± 15	208.3 ± 35	387.0 ± 14.5	48.2 ± 5.9	8.71 ± 1.07	9.07 ± 0.67	11.6 ± 1.4
BT700	1126 ± 122	153.8 ± 9.6	101.7 ± 10.1	428.8 ± 20.2	61.8 ± 5.4	15.7 ± 1.4	4.55 ± 1.76	27.7 ± 2.21

**Table 4:** Accelerated first order kinetic modeling for the extraction of total Se and total As

Sample	Se		As	
	<sup>b</sup> Rate constant min <sup>-1</sup>	R <sup>2</sup> value	<sup>b</sup> Rate constant min <sup>-1</sup>	R <sup>2</sup> value
BT60 <sup>a</sup>	-	-	0.050 ± 0.003	0.9404
BT571	0.0089 ± 0.0002	0.9474	0.013 ± 0.003	0.9847
BT700	0.0052 ± 0.0001	0.9949	0.034 ± 0.001	0.9950

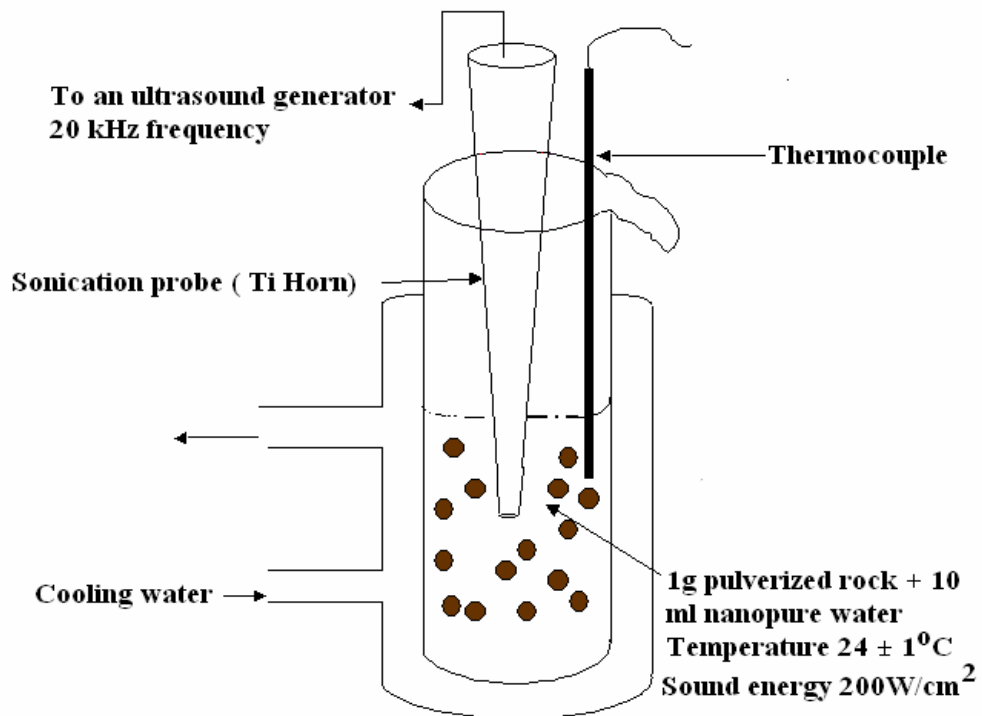
<sup>a</sup>Not enough data points were available for total Se kinetic modeling. All Se was leached out in the first three extractions.

<sup>b</sup>Accelerated extraction rate constant ± standard error of the slope obtained from First order model  $\ln(1 - C_t / C_\infty) = -kt$ , where  $C_t$  is the concentration of extracted species at sonication time  $t$  and  $C_\infty$  is the extracted species concentration at infinite sonication,  $k$  is the accelerated extraction rate constant

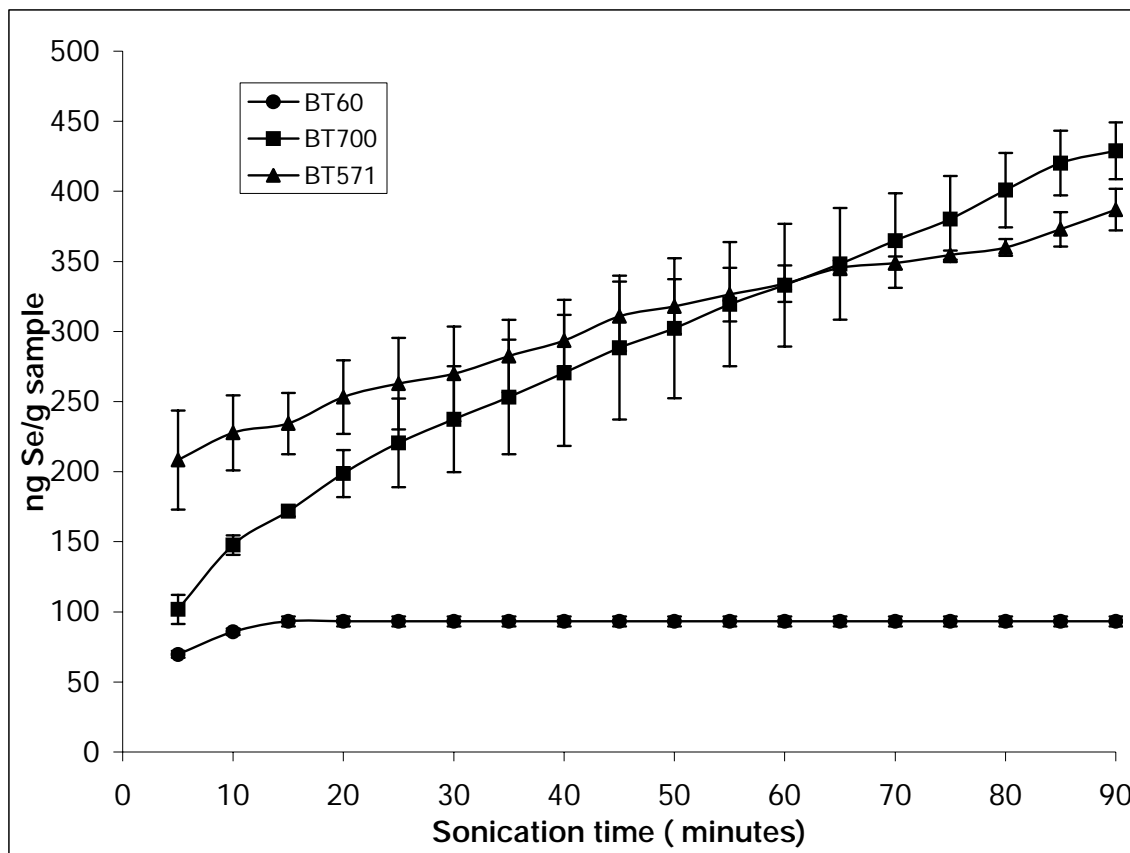


**Table 5:** First order kinetic modeling for the release of Se (IV)

Sample	Rate constant (min <sup>-1</sup> )	R <sup>2</sup> value
BT571	0	0.9837
	.034 ± 0.002	
BT700	0.026 ± 0.001	0.9905

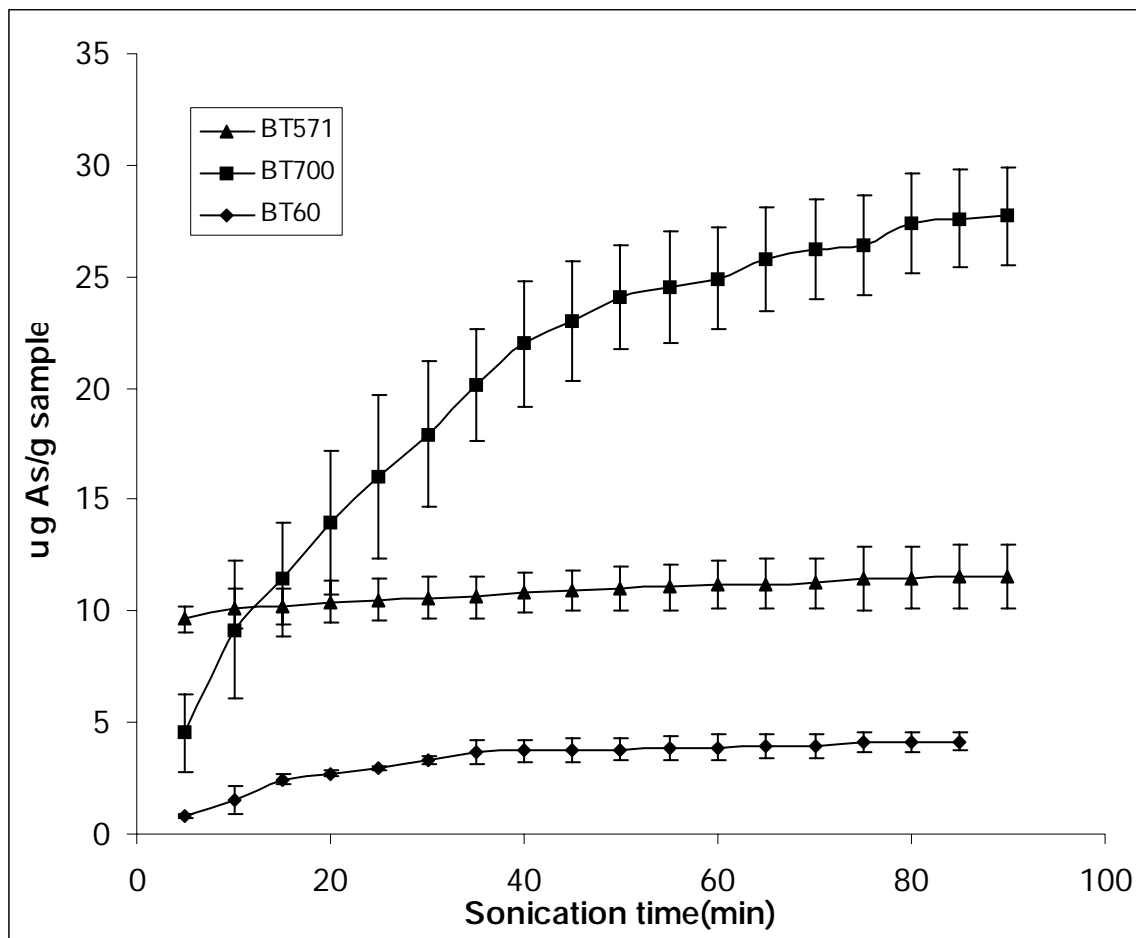


**Figure 1: Ultrasound extraction experimental set up**



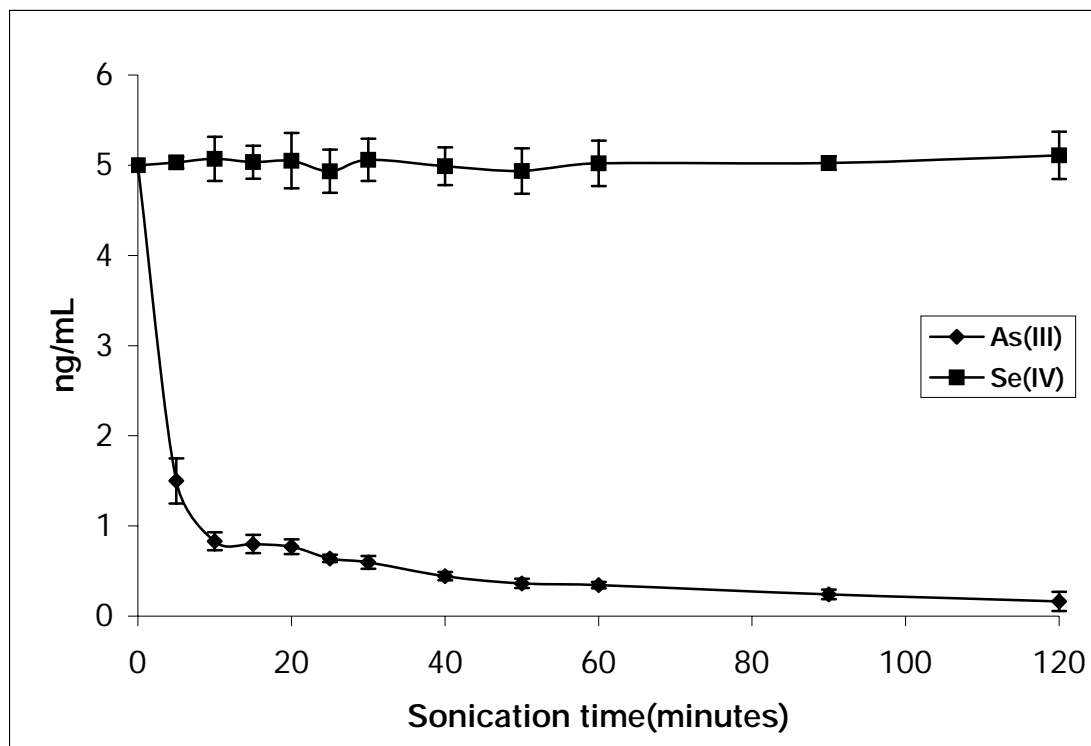
**Figure 2:** Release of total Se (ppb) as a function of sonication time

**Conditions:** Sequential five minute ultrasonic extractions, ultrasound pulse 40 %, probe diameter 0.3 cm, sonication power 200 watts/cm<sup>2</sup>, temperature 24 ± 1°C. 1 g sample in 10 mL nanopure water.



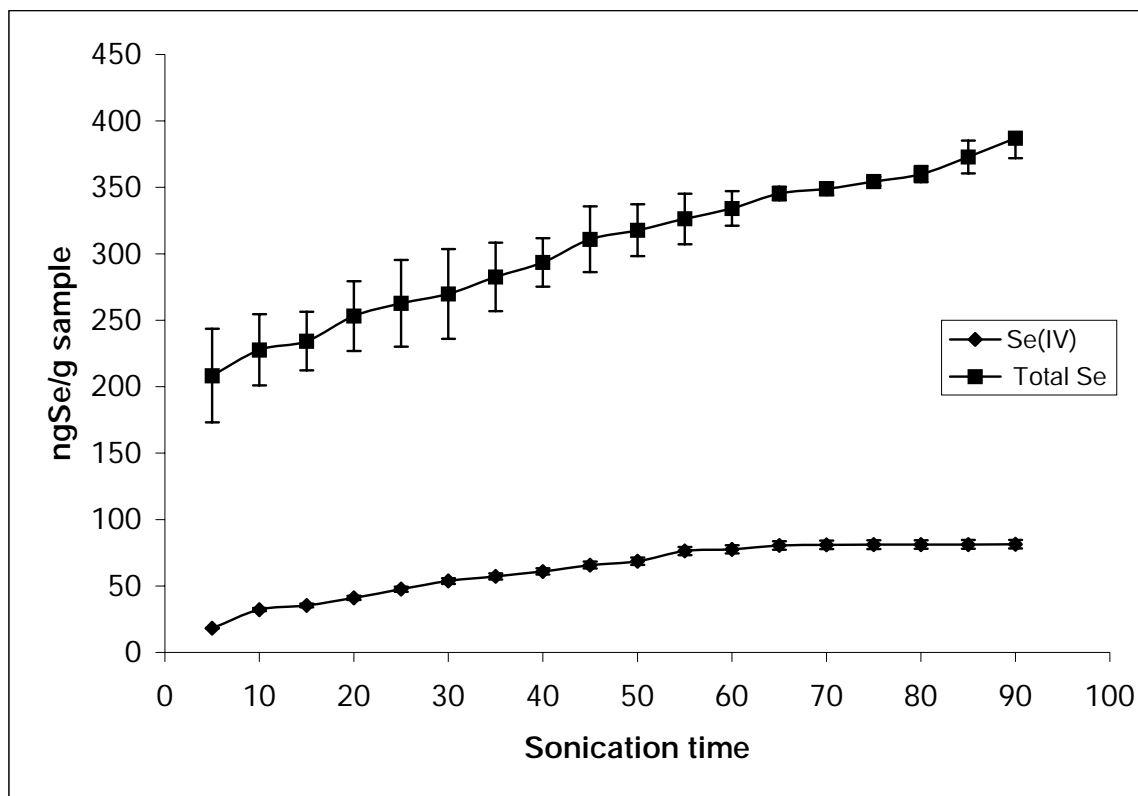
**Figure 3:** The release of total Arsenic (ppm) as a function of sonication time

**Conditions:** Sequential five minute ultrasonic extractions, ultrasound pulse 40 %, probe diameter 0.3 cm, sonication power 200 watts/cm<sup>2</sup>, temperature 24 ± 1°C. 1 g sample in 10 mL nanopure water.



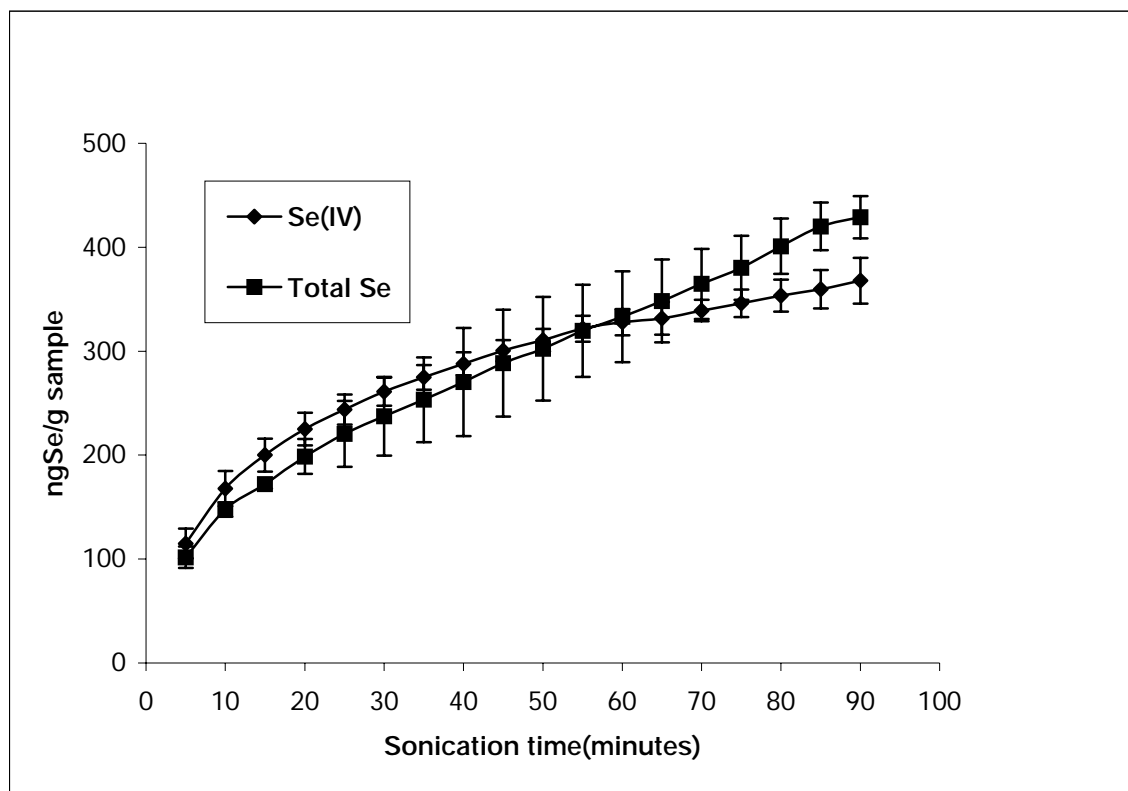
**Figure 4:** Variation of Se (IV) and the disappearance of As (III) as a function of sonication time

**Conditions:** 10 ml solutions of 5 ng/ml of 1:1 Se (IV)/Se (VI) and As (III)/As (V) sonicated at  $200\text{W}/\text{cm}^2$ , continuous sonication, ultrasound pulse 40 %, probe diameter 0.3 cm,  $24 \pm 1^\circ\text{C}$ .



**Figure 5:** The release (ppb) of total Se and Se (IV) from BT571 as function of sonication time

**Conditions:** Sequential five minute sonications, sonication pulse 40 %, probe diameter 0.3 cm, Sonication power 200 watts/cm<sup>2</sup>, temperature 24 ± 1°C. 1 g sample in 10 mL nanopure water.



**Figure 6:** The release of total and Se (IV) from BT700 as a function of sonication time.

**Conditions:** Sequential five minute ultrasonifications, sonication pulse 40 %, probe diameter 0.3 cm, Sonication power 200 watts/cm<sup>2</sup>, temperature 24 ± 1°C. 1 g sample in 10 mL nanopure water.

# In-Stream Turbidity and Suspended Sediment Changes Following Improvements to a Forest Road and Harvesting (WRI-82)

## Basic Information

<b>Title:</b>	In-Stream Turbidity and Suspended Sediment Changes Following Improvements to a Forest Road and Harvesting (WRI-82)
<b>Project Number:</b>	2006WV76B
<b>Start Date:</b>	3/1/2006
<b>End Date:</b>	2/28/2008
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	WV 01
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Non Point Pollution, Sediments, Water Quality
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Jingxin Wang, Pamela Edwards, Joseph F. McNeel, Lawrence E. Osborn

## Publication

1. Publications: "In -stream turbidity changes resulting from forest haul road construction" Planned for submission to Journal of the American Water Resource Association. Currently out for external review prior to journal submission, as per Forest Service requirements. A masters thesis and at least 2 resulting journal articles from that thesis are anticipated within the next ~6 months. Thesis completed in May 2007. "Changes to in-stream turbidity following construction of a forest road in a forested watershed in West Virginia". Presented at the 2007 Virginia/West Virginia Water Research Symposium. "Effects of Hill-slope Attributes and Road Construction on Sediment Movement in Forested Watersheds in West Virginia". In proceedings of ASABE annual meeting in Providence, RI June 29-July 2 2008.



**Title: Changes to In-Stream Turbidity Following Construction of a Forest Road in a Forested Watershed in West Virginia**

Report: Final Report

Investigators: Jingxin Wang and Pamela J. Edwards

Reporting Period Start Date: January, 2006

Reporting Period End Date: February 28, 2007

Principal Authors: Jingxin Wang, Pamela Edwards, William F. Sharp and Gregory Hamons

Date Report was issued: June, 2008

USGS award number: WRI-82

Name and address of submitting department: Division of Forestry and Natural Resources.  
206-B Percival Hall, PO Box 6125, Morgantown, WV 26506-6125.

**Research:**

**Executive Summary:**

A forest road was constructed through a watershed in summer 2002 and was left in poor condition from fall 2002 through mid-summer 2003. During mid-summer of 2003 the condition of the road was improved through installation of water control features, sediment traps, seeding of the fill slopes and cut banks, and graveling of the driving surface.

Turbidity and suspended sediment levels in both the control and treatment watersheds fell within expected ranges during the 3 pretreatment years prior to road construction. Both parameters increased to very high levels on the treatment watershed prior to its finalization. After road improvements were made, reductions in turbidity and suspended sediment were observed on the treatment watershed.

The objectives of this study were to:

- 1) describe turbidity before and after haul road construction,
- 2) determine if or when in-stream turbidity levels decreased after construction of a haul road in the treatment watershed,
- 3) assess soil movement created from road construction, and
- 4) if possible, given the short pre and post treatment periods, evaluate if recovery was linear, exponential, or if turbidity levels off at a level higher than pretreatment at some point in time.

**Introduction:**

The introduction of a forest management treatment into an undisturbed forested watershed can result in considerable site disturbance and has the potential to change the rate of soil erosion and movement at that site. Nearly all modern harvesting operations

employ the use of heavy equipment, which typically disturbs the litter layer (Steinbrenner and Gessel 1955, Lull 1959, Froehlich 1979). Depending on the site and equipment used some forest management operations can cause soil surface disturbance ranging from removal of the protective organic litter to the complete removal of the topsoil and even disturbance of the subsoil (Dyreness 1965). The construction of roads and landings for a forest management application are the major disturbances that can increase soil erosion during management (Hatchell et al. 1970, Pope 1991, Croke and Hairsine 2006); however, they are necessary to complete nearly all forest management treatments.

An estimated 3.6 billion metric tons of sediment is carried to streams, ponds, lakes and rivers each year in the United States (Florida Department of Environmental Regulation 1988). In the mid-1980s the damage to water resources from non-point source pollution was estimated to be between \$7 and \$9 billion a year (Ribauda 1986, Klapproth 2000). Soil particles that have been transported across the forest floor and into a stream channel can lead to excessive sediment deposition when the energy of the water lowers and the majority of the sediment is deposited onto the stream bottom. Excessive sediment deposition can cause damage to aquatic life, obstruct the navigation of streams, reduce available hydrological capacities of streams, and increase flood crests (Corbett et al. 1978, Pope 1991, Klapproth 2000, Croke and Hairsine 2006); which can result in an increase in stream temperatures, loss of aquatic life and habitat, increased damage during flooding, and an overall reduction of stream and site production (Pope 1991, Klapproth 2000, Croke and Hairsine 2006).

Road construction and use are recognized as the primary sources of sediment production during forest operations (Hornbeck and Reinhart 1964). Roads accelerate erosion, affects run-off, and increases effective channel lengths in headwater watersheds (Reinhart 1964, Binkly and Brown 1993, Jones and Grant 1996, Wemple et al. 1996). One year after road construction in north central West Virginia, treatment watershed maximum turbidity exceeded maximum reference watershed turbidity by 3,700 JTU (Jackson turbidity units) (Hornbeck and Reinhart 1964). Turbidity increases were primarily attributed to the poorly located skid roads and skidding in streams (Kochenderfer and Hornbeck 1999).

Turbidity is the primary water quality parameter used to assess water quality in the East. “West Virginia water quality regulations permit no more than a 10 NTU increase from baseline conditions, specifically, “No point or non-point source to West Virginia's waters shall contribute a net load of suspended matter such that the turbidity exceeds 10 NTU's over background turbidity when the background is 50 NTU or less, or have more than a 10% increase in turbidity (plus 10 NTU minimum) when the background turbidity is more than 50 NTUs. This limitation shall apply to all earth disturbance activities and shall be determined by measuring stream quality directly above and below the area where drainage from such activity enters the affected stream. Any earth disturbing activity continuously or intermittently carried on by the same or associated persons on the same stream or tributary segment shall be allowed a single net loading increase.” (USEPA 2006).

## **Experimental Methods:**

In-stream suspended sediment, turbidity, and streamflow (i.e. stage and velocity) in two headwater streams were measured since 1999. Both streams are located within the Clover Run Watershed, Monongahela National Forest, north central West Virginia (Fig. 2.1). This design adopts the typical paired watershed design (e.g. reference and treatment watersheds) to evaluate the effects of road construction on water quality (i.e. turbidity and suspended sediment).

Monitoring stations (Fig. 2.2) were constructed in both watersheds to facilitate this study. The monitoring stations were constructed at the watersheds outlet to house automated samplers, which collected suspended sediment samples and stream stage and velocity measurements. Silt fences (Fig 2.3) around the active stream channels were installed in both watersheds, from the monitoring stations to the upper most portions of their drainage networks. Silt fence was used to capture and quantify the sediment being delivered to the stream channels from the adjacent hill-slopes. Selected silt fence sections were permanently numbered. These numbers were used to identify specific silt fence sections, so when samples were collected their locations would be known and could be associated with contributing attributes upslope.

In the beginning, the primary goal of this study was to measure to-stream sediment delivery, hence, the silt fence lining the stream channels, although, due to a number of events that led to a substantial amount of sediment being deposited in the stream channel, which is thoroughly described in a later section, the primary focus of this study shifted towards measuring changes to in-stream suspended sediment.

Data from a weather station (1973-2004) located approximately 3.4 air kilometers away (operated by the US Forest Service's Northern Research Station), indicate the average precipitation for the area is approximately  $161 \text{ cm yr}^{-1}$ . The months of April through July generally receive the most precipitation, while September through November generally receives the least precipitation. The largest rainfall events are typically the result of tropical storms and hurricanes moving inland from the Atlantic Ocean. In addition, convective thunderstorms commonly produce intense periods of rainfall during the summer. Snowfall is common between November and March although can occur earlier or later. During the dormant season, a snow pack can remain on the ground for the majority of the winter or periodic rain-on-snow or fluctuating temperatures can produce intermittent ground coverings (Edwards, P.J. Submitted).

Water samples have been collected and streamflow (i.e., stage and velocity) has been measured in the treatment and reference streams since 1999. Housing for stream gauging and sampling equipment (Fig. 2.2) was constructed in both watersheds near their mouths. Five-minute streamflow velocity and stage readings were recorded at both stations using an American Sigma 950 flow meter. Stream water samples were collected for turbidity analyses. Daily samples were collected with an American Sigma model 900s automatic sampler in each watershed. Stormflow samples were collected with an Isco model 2700 automatic sampler in each watershed. The Isco model 2700s were actuated using precipitation rather than stage and then sampled on pre-set time intervals following the first sample to obtain a better representation of sediment responses during storms (Edwards and Owens 1995). Funnels

Stormflow sampling started November 2, 1999 and lasted until June 4, 2002 in both watersheds. One-hundred and fifty-three storms were sampled during pretreatment. Of these 70 were paired storms – that is, they were sampled on both the treatment and reference watershed. Stormflow sampling in the reference watershed started again on November 1, 2002 and lasted until April 30, 2005. Treatment watershed storm sampling started again on October 15, 2002 and lasted until April 30, 2005. One-hundred and thirty-four storms were sampled during post-treatment. Of these forty-two were paired storms. Samples were not collected from June 4, 2002 to October 15, 2002 for safety purposes during construction.

Stream velocity and stage measurements were made on 5-minute intervals since October 1, 1999. The velocity measurements from the American Sigma equipment were unstable and inaccurate, but the stage readings remained quite stable following calibration. Consequently, discharge was estimated from the stage measurements using Manning's equation in HEC-RAS software ([www.hec.usace.army.mil/software/hec-ras/](http://www.hec.usace.army.mil/software/hec-ras/)). These calculations were made by the Forest Service. Stage < 2.0 cm (0.8 in) could not be measured accurately because of equipment limitations. Samples collected during these streamflows represented anywhere from 8 to 45 percent of the routine and storm samples during pre and post-treatment periods. These samples are referred to as samples collected when streamflow was below detection limits. Streamflow also could not be calculated when the streams were frozen or when samplers malfunctioned (Edwards, P.J. Submitted). Turbidity analysis relative to streamflow was nonexistent due to some large variations in streamflow regressions and peak streamflow comparisons. Streamflow is presented in liters per second ( $L s^{-1}$ ).

The construction of the 1.9 km haul road began in July of 2002 and was not finished until summer 2003. Unfortunately, the road was left in a disturbed condition, with very few BMPs in place over the winter. During the summer of 2003 cross drain culverts and broad-based dips were installed and the road was graded and graveled with 10-cm limestone which improved road drainage substantially (Bills 2005). There were initially four culvert-and-fill type stream crossings within the treatment watershed along the haul road. The first and second crossings were later combined (July 2003) upslope of the road surface to create a single combined crossing. During road construction, areas near stream crossings had fill material mechanically pushed down to the silt fences which resulted in large quantities of sediment material captured near the stream crossings.

The initial seeding and mulching of the disturbed areas, which occurred in November, 2002, mostly failed due to the onset of winter conditions. Double reseeding and mulching was completed in May 2003 and vegetation established quite well on the fill slopes but establishment was noted as poor on the cut slopes. All areas were hydroseeded with Kentucky 31 fescue (*Festuca arundinacea*), orchard grass (*Dactylis glomerata*), and Ladino clover (*Trifolium repens*); then limed, and fertilized, and chopped mulch was blown onto these areas.

Water samples were processed for turbidity at the US Forest Service's Timber and Watershed Laboratory in Parsons, West Virginia. Turbidity, in nephelometric turbidity units (NTU), was determined using a Hach Ratio Turbidimeter, which was calibrated using formazin standards (Edwards, P.J. Submitted). The samples were first shaken to distribute the sediment throughout the bottle. A sub sample was then poured into a small glass tube.

The sides were wiped free of fingerprints and other dirt, and the glass tube was placed in the turbidimeter. After approximately 5 seconds, the turbidity value was recorded.

After measuring turbidity, the sub-sample was poured back into the original bottle so suspended sediment concentrations could be calculated. Before measuring suspended sediment concentrations, the entire sample was weighted. The bottle, lid, and sample were weighed then subtracted from the known bottle and lid weight to obtain the weight and of the water/sediment sample. Each sample was filtered through one or more pre-dried and pre-weighted ashless GF/C glass microfiber filters using vacuum filtration. The bottles were rinsed several times, and each time the rinse water was filtered. The number of filters needed depended on the amount of sediment in the bottle. Although, most samples required only 1-3 filters, a few required 30 or more. All samples were then dried at 100 °C (212°F) for 2 hours then re-weighed. This weight minus the initial dry filter weight is the combination of the organic and inorganic material (g/L). The filters were then combusted in a muffle furnace for 1 hour at 550 °C (1022°F) and then re-weighed. This weight plus a 0.001 filter correction for filter loss during combustion, minus the initial dry filter weight, is the amount of inorganic material (g). The dry weight minus the combusted weight plus a 0.001 filter correction is the amount of organic material. These samples were determined using U.S. EPA method 160.2. All analysis involving suspended sediment concentrations used both organic and inorganic material.

Statistical Analysis Systems (SAS 1988) was used to analyze these data. Nonparametric methods primarily were used because the data were not normally distributed. Wilcoxon signed-rank tests and median scores (Proc NONPAR1WAY) were used to transform the data to an ordinal scale to make statistical conclusions about the location differences (higher lower or no difference (random)) between both watersheds' turbidity. Median scores were used to test for differences between watersheds turbidity.

The relationship between turbidity and SSC (TS ratio) was created to compare the turbidity of a sample to the suspended sediment concentration. This ratio compares two different types of water clarity measurements and samples between watersheds were of different volumes, therefore, any conclusions formed should be viewed with skepticism. However, sample volumes averaged by month and by storm were not significantly different between watersheds pretreatment and post-treatment periods. Parametric analyses were used on non-normal untransformed data in the form of regression analysis only. Log base 10 transformations were used to increase data normality and express changes to variability. Statistical significance was tested at 0.05 level.

## **Results and Discussion:**

The reference watershed's storm and routine samples prior to construction were statistically more turbid than the treatment watershed's. The reference watershed's routine samples contained more sediment by weight relative to its turbidity index. Storm samples and TS ratios were similar between watersheds. The reference watershed produced less turbidity per sediment than the treatment watershed. This is probably the result of past disturbance in the reference watersheds (i.e. roads, farming, and timbering) as the reference watershed generally had larger median substrate than the treatment watershed (Bills 2005).

Substantial variation to streamflow occurred from pretreatment to post-treatment. Several studies have measured changes to streamflow following timber removal (Hornbeck

et al. 1993, Jones and Grant 1996). Few studies have intensively measured streamflow changes due to road construction, therefore, streamflow responses due to road construction are uncertain. Roads theoretically increase the efficiency of water transfer from hillsides to stream channels by intercepting subsurface streamflow and precipitation then directing the intercepted water directly to stream channels and/or in more concentrated levels onto the hillside below (Reinhart 1964, Wemple et al. 1996). Streamflow measurements and classes were not used rigorously to analyze turbidity because streamflow was modeled and deviated substantially from predicted values. For example, one predicted peak stormflow level differed between watersheds by  $280 \text{ L s}^{-1}$  (10 cfs) when the average streamflows were less than  $28 \text{ L s}^{-1}$  (1 cfs). The Forest Service employees who created the model would be better suited to evaluate any changes to streamflow due to road construction, therefore any analysis that uses streamflow such as turbidity and streamflow relationships and/or SSC and streamflow relationships should be viewed with skepticism.

The results of this study demonstrated the effects of road construction on water quality. Several studies have identified roads as the primary source of to-stream sediment during forest operations and have identified road to stream interactions as the most problematic within the road network (Irvin and Sullivan unpublished data, in Bilby et al. 1989, Wemple et al. 1996). This study isolated most of the road network from the stream channel (e.g. silt fence), therefore, the majority of sediment that entered the treatment watershed's stream channel was the result of stream crossing construction. FS 973 occupies 4.1 percent of the treatment watershed and stream crossings occupy less than one percent of the treatment watershed.

Average and median turbidities for these watersheds were below 5 NTU during pretreatment. Turbidity is noticeable around 5 NTU (Strausberg 1983, in Edwards Submitted) therefore, these streams normally have clear water. Prior to treatment, the treatment watershed's stream samples (2680) exceeded 25 NTU 29 times or 1 percent of the time and the reference watersheds samples (3059) exceeded 25 NTU 55 times or 2 percent of the time.

Maximum pretreatment turbidities were less than 400 NTU in both watersheds. They occurred during the largest storm events or during summer thunderstorms. Turbidities were elevated throughout the summer months during pretreatment. Stormflows that produced larger turbidities were relatively short-lived and storms samples overall produced clockwise hysteresis. Clockwise hysteresis is an indicator of a sediment supply limitation.

In July 2002 road construction was initiated within the treatment watershed. Very few samples were collected between July 2002 and July 2003, therefore, changes to in-stream turbidity during the 1<sup>st</sup> year post-treatment are unknown. Several studies site that the largest deviations to background levels occur within the first few months following disturbance (Hornbeck and Reinhart 1964, Fredriksen 1970), however, this may not be the case here as mitigation structures could have trapped and stored and disturbed sediment. However, sediment that does reach the stream channel during disturbances typically flushes quickly during the first couple of storms. In Oregon, sediment concentrations were measured 250 times expected levels during the first storm post-treatment, 9 times larger 2 months later, and remained elevated 2 to 3 times expected levels 2 years later (Fredriksen 1970). In West Virginia, average turbidity was 12.9 and 149.5 times larger during forest operations than first year after treatment from a clearcut and diameter limit harvest,

respectively. Average turbidity was 38.0 and 6.0 times larger after the first year post-treatment than the second year post-treatment (Hornbeck and Reinhart 1964).

These samples were too few or occurred during insignificant times to provide an adequate account of turbidity during the first few storms post-treatment. However, if pretreatment values were increased to the same magnitude as in Hornbeck and Reinhart 1964 during treatment, then average turbidity values could have been as high as 255 and 525 NTU for routine and storm samples respectively. These values would be deemed excessively high by all the past literature however, it does show the potential changes to both stormflow and routine during the first few storms during treatment.

The reference watershed stayed within normal background levels after treatment even though the treatment watershed's average and median turbidities were above 5 NTU. Fourteen percent of the turbidities exceeded 25 NTU in the treatment watershed. Elevated turbidities were the result of stream crossing construction. Areas in stream crossings were less than 1 percent of the treatment watershed using 10 m aerial photographs.

Maximum turbidity in the treatment watershed following treatment reached 2,352 NTU and occurred during the initiation of a storm event. The treatment watershed's turbidities were less seasonally dependent, that is, the largest average monthly turbidity, occurred more so in late fall and during the winter months. The treatment watershed's stormflow turbidities were substantially elevated during the initiation of all storm events and are believed to be the result of precipitation impact remobilizing easily suspended channel sediment. Stormflows produced larger peak, average, and median turbidity values. Stormflow turbidities were relatively longer-lived and even maintained and increased after peak stormflow. Several storms produced counter-clockwise hysteresis towards the end of the 1<sup>st</sup> year post-treatment. Counter-clockwise hysteresis is an indicator of an energy limited situation and an abundance of sediment in the stream channel.

## **Conclusions:**

Sedimentation in these two forested watersheds was dominated by a few primary sources within each study watershed. In the treatment watershed peak sediment delivery occurred during and directly after the haul road construction process. The majority of sediment came from the road fillslopes located just downslope of the approaches to the stream crossings. The primary sediment sources within the treatment watershed were identified as the fillslopes associated with the roads, primarily the fillslopes which were  $\leq 25$  m from the stream channel, and the bare soil areas  $\leq 2$  m of the stream channel. The primary sediment sources within the control watershed were, similarly, the largest areas of exposed soil within that watershed, that is, the soil associated with tree falls (typically  $\leq 4$  m from the silt fence), and the bare soil areas ( $\leq 2$  m from the silt fence).

This study illustrates that significant increases to average turbidity during forest operations are not exclusively the result of similar increases to average SSC. For example, the treatment watershed routine and storm samples average SSC was 1.4 and 1.0 times the pretreatment levels post-treatment while average turbidity was 4.5 and 9.9 times the pretreatment levels post-treatment, respectively. By comparison, the reference watershed routine and storm samples average SSC were 0.7 and 0.5 times the pretreatment levels post-treatment while average turbidity were 1.0 and 1.2 times the pretreatment levels post-treatment, respectively. SSC measurements are an inadequate indicator of water quality as

decreases to water clarity were probably the result of smaller inorganic and organic sediment that weighed less than average pretreatment sediments.

The TS ratio indicated that the treatment watersheds turbidities were significantly lower during pretreatment although less sediment per weight produced them. The reference watershed was transporting relatively more sediment with less turbidity. After treatment, the TS Ratio increased to 1.4 as the majority of turbidity values were larger than the SSC values. Towards the end of the post-treatment sampling period the TS ratio drops to around 0.5 as the majority of the turbidity values were half the SSC values. This indicates a considerable shift to sediment properties that influenced turbidity and SSC concentrations. The TS ratio went from the highest levels to the lowest levels relative to pretreatment levels in 2 years or by the 3<sup>rd</sup> year post-treatment. Although, turbidity is a better predictor of SSC than streamflow, the relationship between SSC and turbidity changed substantially between sample types, pretreatment and post-treatment periods, and levels of turbidity to warrant the use of several different regression relationships.

Prior to treatment, average daily rainfall was a statistically significant predictor of average stormflow turbidity. Average daily precipitation explained 11 and 38 percent of the variation to average stormflow turbidity during pretreatment. Average daily precipitations were not a statistically significant predictor of average stormflow turbidity during post-treatment. The relationship did not return to pretreatment values for the duration of this study. There was no statistical significance between the two parameters in the reference watershed.

Stream crossing have to be constructed with better soil conservation practices. This road extended throughout the treatment watershed before the crossings were finalized. Time study analysis may be useful to help contractors increase road production and efficiency while decreasing costs associated with road construction while increasing soil conservation. Although, these crossings are legally defined as non-point sources of pollution, this study illustrates that very specific points along the road network were mainly responsible for water quality degradation.

The variability in sediment generations, illustrates that sediment sources are discrete and local in their extent. Consequently, sedimentation control should be most effective when it is focused on the discrete areas responsible for the majority of the sediment inputs. Being able to better identify and target important contributors will not only make controlling sediment more effective but also more cost effective.

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**Publications:**

“In –stream turbidity changes resulting from forest haul road construction” Planned for submission to Journal of the American Water Resource Association. Currently out for external review prior to journal submission, as per Forest Service requirements.

A masters thesis and at least 2 resulting journal articles from that thesis are anticipated within the next ~6 months. Thesis completed in May 2007.

“Changes to in-stream turbidity following construction of a forest road in a forested watershed in West Virginia”. Presented at the 2007 Virginia/West Virginia Water Research Symposium.

“Effects of Hill-slope Attributes and Road Construction on Sediment Movement in Forested Watersheds in West Virginia”. In proceedings of ASABE annual meeting in Providence, RI June 29-July 2 2008.

**Information Transfer Program:**

**Student Support:**

William Sharp, M.S. Student (Graduated May 2007)  
 Gregory Hamons, M.S. Student (Graduated December 2007)

Category	Number of Students supported With 104b Base grant	\$ Value of students supported With 104b base grant	Number of students supported With matching funds	\$ Value of student support with matching funds	Total number of students supported	Total \$ value of student support
M.S.	2	\$12,000	2	\$15,000	2	\$27,000

A M.S. in Forestry Science was earned for each student.

**Noticeable Achievements and Awards:**

# Chloride Sorption to Acid Mine Drainage Solids (WRI-84)

## Basic Information

<b>Title:</b>	Chloride Sorption to Acid Mine Drainage Solids (WRI-84)
<b>Project Number:</b>	2006WV81B
<b>Start Date:</b>	3/1/2006
<b>End Date:</b>	2/28/2008
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	1
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Quality, Treatment, Surface Water
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Louis M McDonald, Paul Ziemkiewicz

## Publication

# Final Report: Chloride Sorption to Acid Mine Drainage Solids

Project Number: 2006WV81B

Louis M. McDonald

Division of Plant & Soil Sciences

West Virginia University

## **Introduction**

Reports suggest that chloride concentrations are increasing in mine water and surface waters affected by mining operations. Chloride concentrations above the in-stream limit of  $250 \text{ mg L}^{-1}$  would require treatment, but chloride is a particularly difficult ion to remove from aqueous solution. The results of this project would be of interest to the State Department of Environmental Protection, Coal Operators and others interested in meeting existing and emerging water quality standards.

## **Stated Nature, Scope and Objectives**

Because of the need to control experimental conditions, all experiments will be conducted in the laboratory using fully characterized solutions and solids. Chloride and sulfate sorption to AMD solids will be characterized using competitive sorption isotherms. Experimental conditions will span the range of anticipated field conditions. The objectives are 1) to quantify chloride sorption to AMD solids as a function of sulfate concentration, pH, and the absence and presence of the specifically sorbing cation  $\text{Mn}^{2+}$ . Aluminum will be included because it often occurs in AMD. 2) To determine the extent to which chloride is part of the occluded water in AMD precipitates.

## **Actual Nature, Scope and Objectives**

An earlier WWRI had suggested that chloride could be removed from AMD by sorption to precipitating solids. However, before proceeding to the full experiments described above, preliminary experiments were conducted to confirm these results.

## Materials and Methods

One liter of each experimental solution was prepared as shown in Table 1. Iron was added as  $\text{Fe}(\text{NO}_3)_3$ , sulfate as  $\text{Na}_2(\text{SO}_4)$ , chloride as  $\text{NaCl}$ . Sodium nitrate ( $\text{NaNO}_3$ ) was added as an indifferent electrolyte to control ionic strength. The remaining solution was adjusted to approximately pH 2 and then titrated to pH 10 with  $\text{NaOH}$  in nine increments using an Accumet pH meter (Model No. 15, Fisher Scientific, Pittsburgh, PA) and a Ross Sure-Flow combination electrode (Fisher Scientific, Pittsburgh, PA). At each pH increment, visible absorbance at 450 nm was determined with a fiber-optic dip probe attached to a spectrophotometer (Cary 50 UV-Vis, Varian Inc., Palo Alto, CA) to determine the onset of precipitation. Chloride activity was determined at each titration point using a chloride specific electrode (Accumet, Fisher Scientific, Pittsburgh, PA). Maximum chloride removal was calculated by difference and assuming that all initial iron in solution precipitated.

Table 1. Ion concentrations and ionic strength for each experimental solution.

Solution	Iron (III)	Chloride	Sulfate	Nitrate	Sodium	Ionic Strength
		----- mM -----				----- M -----
A	10	1.7	10	30	21.7	0.047
B	10	1.7	0	60	31.7	0.047
C	10	1.7	20	30	41.7	0.077
D	10	1.7	0	90	61.7	0.077

## Results

For all solutions precipitation was essentially complete by pH 3 (data not shown). When comparing solution A to B and Solution C to D (Table 2), it is apparent that the presence of sulfate in solution depressed chloride removal. The average maximum

amount of chloride removed from solution, under these experimental conditions was 0.046 mg per gram Fe(III) precipitated.

Table 2. Maximum chloride removed at constant ionic strength.

Solution	I	Sulfate	Chloride Removed
		----- mM -----	-----mg Cl/g Fe -----
A	0.047	0	0.044
B	0.047	10	0.038
C	0.77	0	0.060
D	0.77	20	0.040

### Conclusions

A second year of funding to investigate AMD flocs as a removal technology for chloride was not requested. In our preliminary work with iron-sulfate flocs, using a chloride selective electrode for chloride determinations, the average chloride removal was 0.046 mg chloride per g iron precipitated, an amount considered too low for a practical treatment technology. In addition chloride removal was strongly inhibited by the presence of sulfate.

# WRI 99 Selenium Speciation & Removal

## Basic Information

<b>Title:</b>	WRI 99 Selenium Speciation & Removal
<b>Project Number:</b>	2007WV105B
<b>Start Date:</b>	3/1/2007
<b>End Date:</b>	2/28/2008
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	First
<b>Research Category:</b>	Water Quality
<b>Focus Category:</b>	Water Quality, Treatment, Surface Water
<b>Descriptors:</b>	None
<b>Principal Investigators:</b>	Louis M McDonald, Richard Herd

## Publication

# **WRI-99 Selenium Speciation and Removal Final Report**

**Louis M. McDonald**

**Division of Plant and Soil Sciences, West Virginia University**

## **Introduction/Background**

Selenium (Se) has been detected in mine drainage waters in southern West Virginia above the current water quality limit of  $5 \mu\text{g L}^{-1}$  total Se. Although an essential element, Se has a very small threshold between essentiality and toxicity. The common dissolved forms of Se are free or complexed selenite ( $\text{SeO}_3^{2-}$ ) and selenate ( $\text{SeO}_4^{2-}$ ). Because toxicity and treatment strategy depend on speciation, a robust, reliable method for the quantification of selenite and selenate is needed. Relatively little work has been done on Se determination in mine drainage waters.

A Zero Valent Iron-Steel Wool (ZVI-SW) treatment technology has emerged as a promising technique to remediate selenium contaminated waters. Field scale studies have shown near complete removal of selenium within 24 hrs. However, a more complete understanding of the removal kinetics, especially the effects of initial Se speciation and other influent water quality parameters is needed to design site-specific treatment systems. There is also a need to know the forms of Se following treatment. Two selenium removal mechanisms can be postulated. First, selenate/selenite reduction to elemental selenium, coupled to the oxidation of iron in the steel wool, and second, selenite (and to a lesser extent, selenate) adsorption to iron oxide corrosion products on the steel wool. Synchrotron-based spectroscopy can provide molecular evidence for the oxidation state of elements in environmental samples (Hayes et al., 1987; Manceau and Charlet, 1994; Myneni et al., 1997) and thus can be used to determine the reaction products of treatment reactions.

## **Research Objectives**

1. Develop and validate a method to determine trace levels of selenate and selenite in mine drainage waters.



2. Quantify the effects of solution properties and initial selenium species on the kinetics of removal by ZVI-SW in bench-scale experiments.
3. Use synchrotron-based spectroscopy to determine the forms of selenium following reaction with ZVI-SW.

## **Methodology**

### *Inorganic Selenium Speciation*

A flow injection – hydride generation – inductively coupled plasma spectroscopic (FI-HG-ICP) method was used to determine selenite. Selenite is reduced to the volatile hydride form in an acidic medium, swept into the ICP with an inert carrier gas and determined at 196.026 nm. To speciate selenite and selenate (in a sample containing both) two determinations are required. Selenite is determined in one aliquot as described above. A second aliquot is digested in hot, concentrated HCl to reduce selenate to selenite (total Se). Selenate is then calculated by difference.

### *Selenium Removal Kinetics*

All experiments were conducted in a water-jacketed, glass reaction flasks designed to allow for control of gas partial pressures and periodic sample collection. Constant mixing speed was maintained by overhead stirring with Teflon coated paddles. All experiments were conducted at 30°C in duplicate. Treatments were salt type ( $\text{Ca}(\text{NO}_3)_2$  or  $\text{CaCl}_2$ ) and ionic strength (0.01 to 25 mM), selenite or selenate, and open or  $\text{N}_2$  purged systems. All chemicals were of at least reagent-grade quality. Selenium was added as either  $\text{Na}_2\text{SeO}_3$  or  $\text{Na}_2\text{SeO}_4$  and ionic strength was adjusted using either  $\text{Ca}(\text{NO}_3)_2$  or  $\text{CaCl}_2$ . Samples were collected with time, filtered (0.45  $\mu\text{m}$ ) and selenite concentrations determined as described above.

### *Synchrotron-Based Spectroscopy*

Untreated, fine grade (#0) steel wool (0.1 g) was reacted with 50 mL of 5 mg L<sup>-1</sup> Se (as  $\text{Na}_2\text{SeO}_3$  or  $\text{Na}_2\text{SeO}_4$ ) in screw cap centrifuge tubes. There were two factors, selenium species at two levels, Se(IV) or Se(VI), and aeration at two levels, nitrogen-purged or unpurged, for a total of four samples. For the unpurged samples, no attempt was made to exclude any gases from the solution. For the  $\text{N}_2$ -purged samples, wool was added to the Se-containing solutions and then purged for 5 minutes. Tubes for all

treatments were capped tightly and those that were purged were wrapped with parafilm to minimize gas exchange. Preliminary experiments and previous studies have shown nearly complete selenium removal by steel wool within 24 hours and within 5 hours with iron powders (Mondal et al., 2004). Therefore, after at least 24 hours, steel wool samples were removed from tubes and placed into specially prepared Plexiglass sample holders. Supernatant solution was added to fill the cell completely and immediately sealed on both sides with Kapton tape. Samples were prepared individually and placed immediately in the X-ray sample compartment. It was not possible to keep samples from being exposed to air during preparation, and Kapton tape is not gas tight. The time period from the start of sample preparation to the first exposure to synchrotron radiation was less than three minutes.

Se K-Edge XANES spectra were collected at Beamline X18B at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY, using a multi-element Ge detector, at room temperature with 0.3 eV step size through the XANES region. Selenium foil was used for the Se(0) standard; liquid Se(IV) and Se(VI) standards were prepared as 10 mM solutions of Na<sub>2</sub>SeO<sub>3</sub> and Na<sub>2</sub>SeO<sub>4</sub>. Data (two to three scans) were averaged normalized, and background subtracted using standard procedures in the program ATHENA (Newville, 2001).

## **Principal Findings**

### *Inorganic Selenium Speciation*

The FI-HG-ICP selenite calibration curve was linear ( $R^2 > 0.999$  up to 3 mg L<sup>-1</sup>) although greater precision and lower detection limits could be achieved with lower concentration standards. For the range 0 to 500 µg L<sup>-1</sup> ( $R^2 = 0.9999$ ) the detection limit was 5.2 µg L<sup>-1</sup> with a relative standard deviation (RSD) of 7.2 % at 1 µg L<sup>-1</sup> and an average RSD of 1.9% (range 0.98 – 3.1%) above 1 µg L<sup>-1</sup>. The detection limit could be reduced to 1.2 µg L<sup>-1</sup> by calibrating from 0 to 50 µg L<sup>-1</sup>. Selenate was quantitatively reduced to selenite and recovered.

### *Selenium Removal Kinetics: Salt Type and Concentration Effects*

Selenate removal appeared to proceed in two phases (Figure 1). There was a lag phase of approximately 12 hrs when no selenium was removed from solution, followed by a rapid removal phase lasting from 12 to 24 hours. Neither the length of the lag phase and the rapid removal rate appear to be affected by ionic strength.

In contrast, selenite removal was dependent on ionic strength (Figure 2), and at constant ionic strength (Figure 1 and 2), much slower (longer lag phase). This result is not what was expected and deserves more study; typically selenite removal is much faster than selenate. Selenite removal rate appears to be dependant on salt type, with faster removal in  $\text{CaCl}_2$  (Figure 3) than in  $\text{Ca}(\text{NO}_3)_2$  (Figure 2).

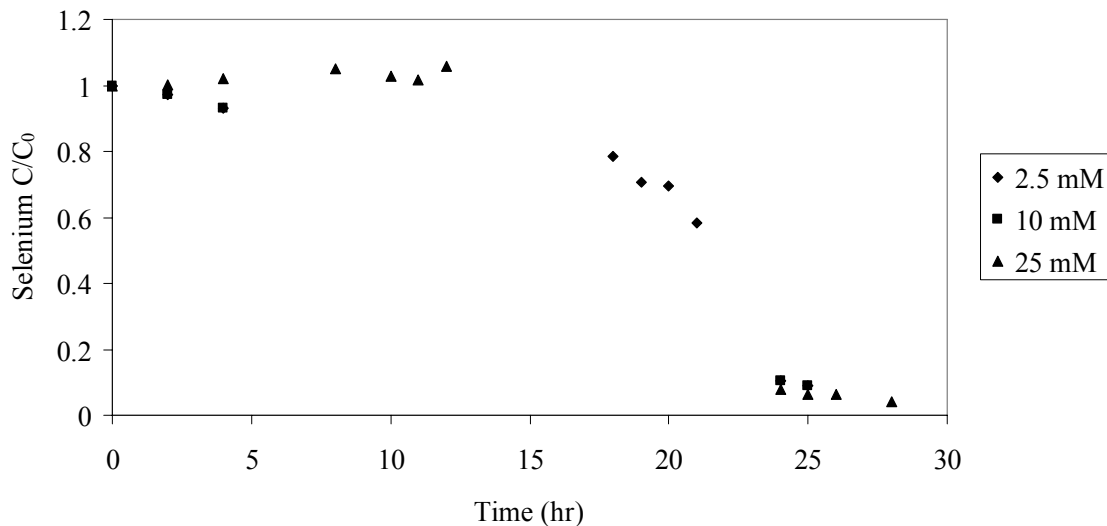


Figure 1. Selenate removal with ZVI-SW as a function of salt concentration in an open system. Initial selenate concentration  $2 \text{ mg L}^{-1}$ ; background salt  $\text{Ca}(\text{NO}_3)_2$ .

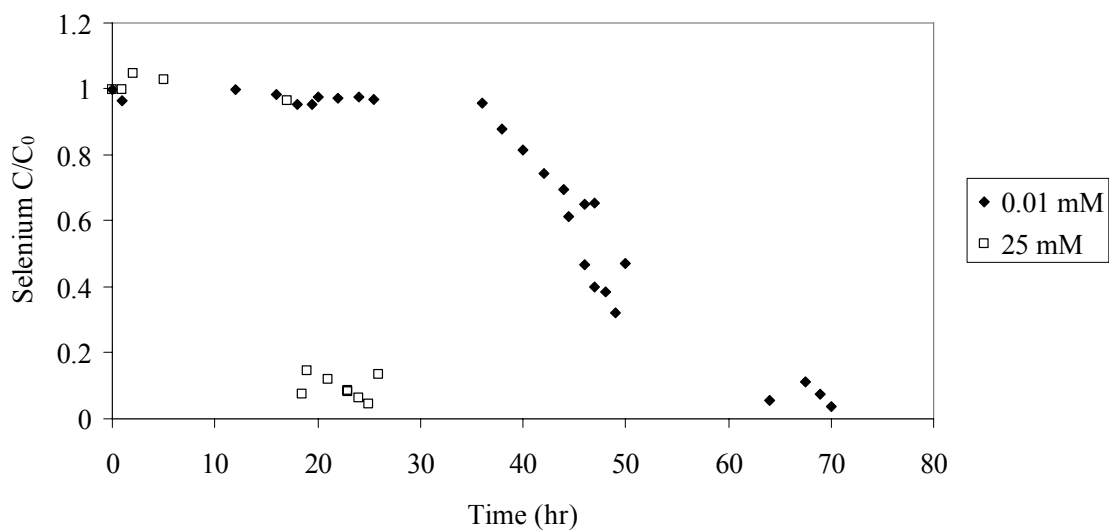


Figure 2. Selenite removal with ZVI-SW as a function of salt concentration in an open system. Initial selenite concentration  $2 \text{ mg L}^{-1}$ ; background salt  $\text{Ca}(\text{NO}_3)_2$ .

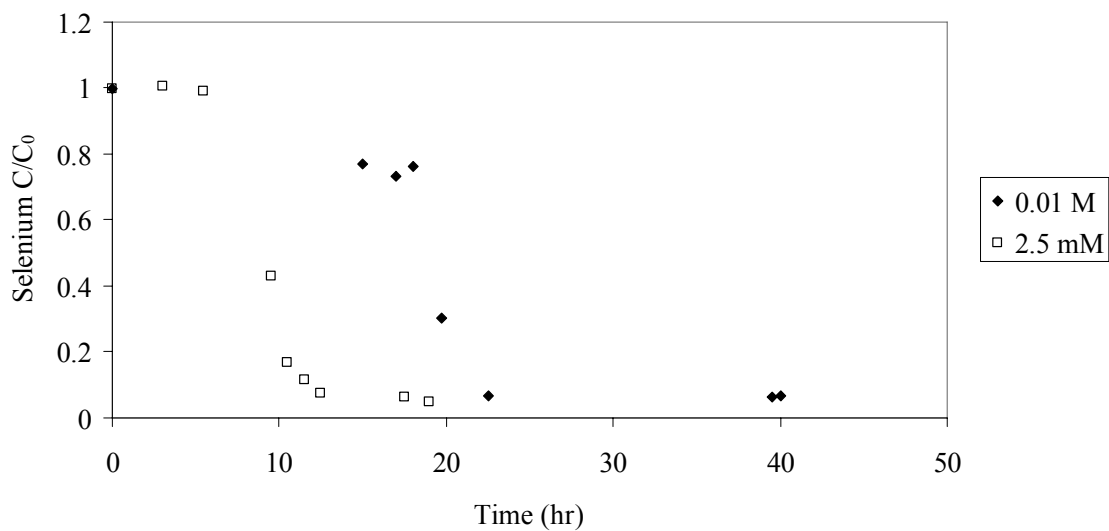


Figure 3. Selenite removal with ZVI-SW as a function of salt concentration in an open system. Initial selenite concentration  $2 \text{ mg L}^{-1}$ ; background salt  $\text{CaCl}_2$ .

### Selenite Removal Kinetics: Initial Selenite Concentration Effects

Selenite removal at the lowest initial concentration ( $1 \mu\text{g L}^{-1}$ ) tested was dependent on ionic strength (Figure 4), but not at the higher initial concentrations of 2 or  $4 \mu\text{g L}^{-1}$  (Figures 5 and 6).

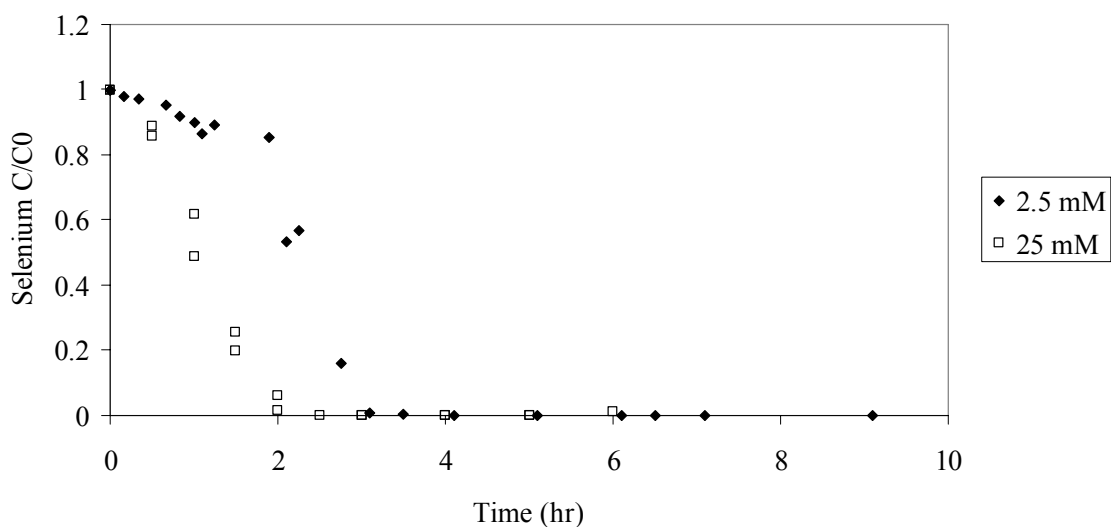


Figure 4. Selenite removal with ZVI-SW as a function of salt concentration in  $\text{N}_2$  purged system;  $1 \text{ mg L}^{-1}$  initial Se, background salt  $\text{Ca}(\text{Cl})_2$ .

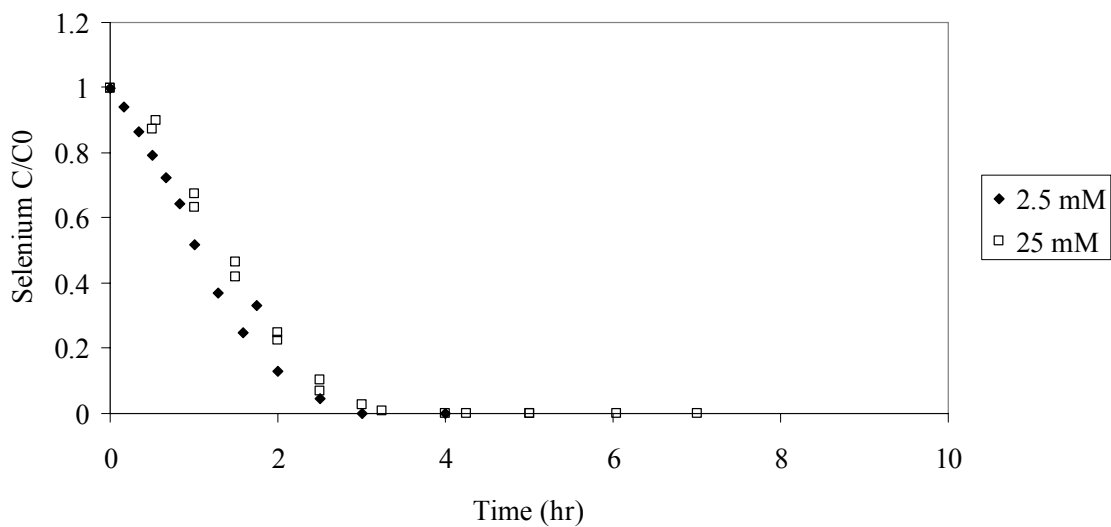


Figure 5. Selenite removal with ZVI-SW as a function of salt concentration in  $\text{N}_2$  purged system;  $2 \text{ mg L}^{-1}$  initial Se, background salt  $\text{Ca}(\text{Cl})_2$ .

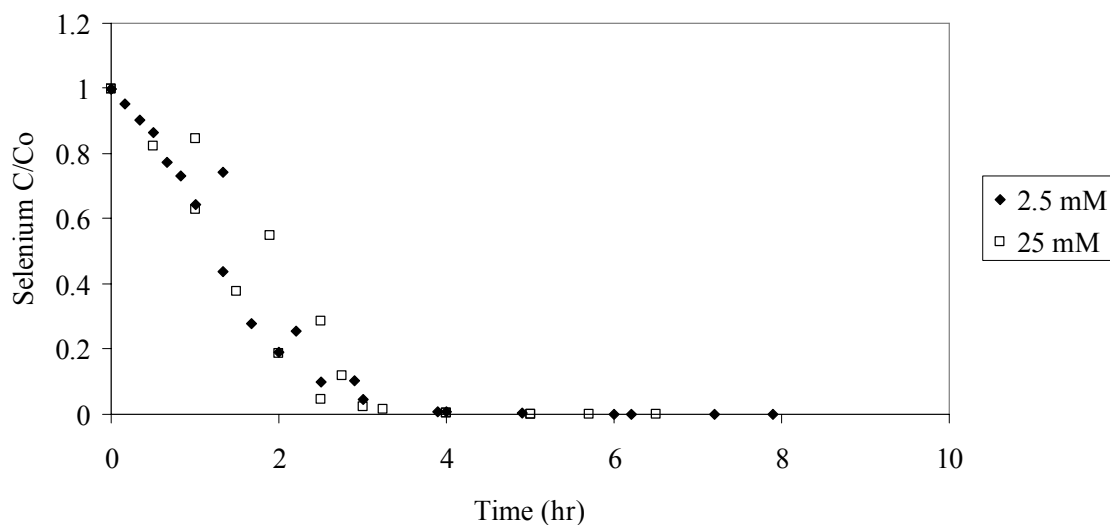


Figure 5. Selenite removal with ZVI-SW as a function of salt concentration in  $N_2$  purged system;  $4 \text{ mg L}^{-1}$  initial Se, background salt  $\text{Ca}(\text{Cl})_2$ .

### *Synchrotron-Based Spectroscopy*

Spectra for Se all standards were comparable to published Se spectra. For simplicity, spectra white line positions (peaks) are used for comparison rather than edge positions (near edge inflection points). Both Se(VI) treatments (purged and unpurged) showed evidence of elemental Se (Figure 1). The stronger elemental Se peak for the purged sample may be the result of the removal of oxygen from the solution. The peaks at eV less than that for Se(VI) may indicate the presence of selenite sorbed to the iron oxide produced during the reaction. Selenite has been shown to bond to iron oxides (Neal and Sposito, 1991).

That elemental Se was formed in both the purged and unpurged samples is consistent with previous studies that indicated that there was no effect on Se removal from chloride (100mM), nitrate (10 mM), sulfate (5 mM), or bicarbonate (5 mM) in solution, and only small effects from sulfate at 50 and 100 mM, and bicarbonate at 10 mM (Zhang et al., 2005).

For solutions containing selenite, only the purged samples show evidence for the formation of elemental Se (Figure 3). This suggests that some component of the unpurged solution is interfering with the reduction process. The unpurged spectra is very noisy

compared to all other collected spectra because the concentration of Se(IV) in solution is very low;  $5 \text{ mg Se L}^{-1}$  is too low to obtain reliable spectra; this signal may represent adsorbed but unreacted selenite. Note that once dissolved Se is reduced to and precipitated as Se(0), its effective concentration in the beam is increased.

The most likely component of an unpurged solution to interfere with Se reduction is dissolved oxygen. The formation of an oxidized iron coating on the surface of the wool could prevent the transfer of electrons necessary for the redox reaction to occur and/or selenite sorption to these oxides may slow the reduction process (Neal and Sposito, 1991). However, an inspection of the sample tubes before analysis indicated no evidence of iron oxidation on the surface of the wool or in solution for the unpurged selenite treatment. To minimize the possibility that this observation was an artifact, new samples were prepared as described above, with the same result.

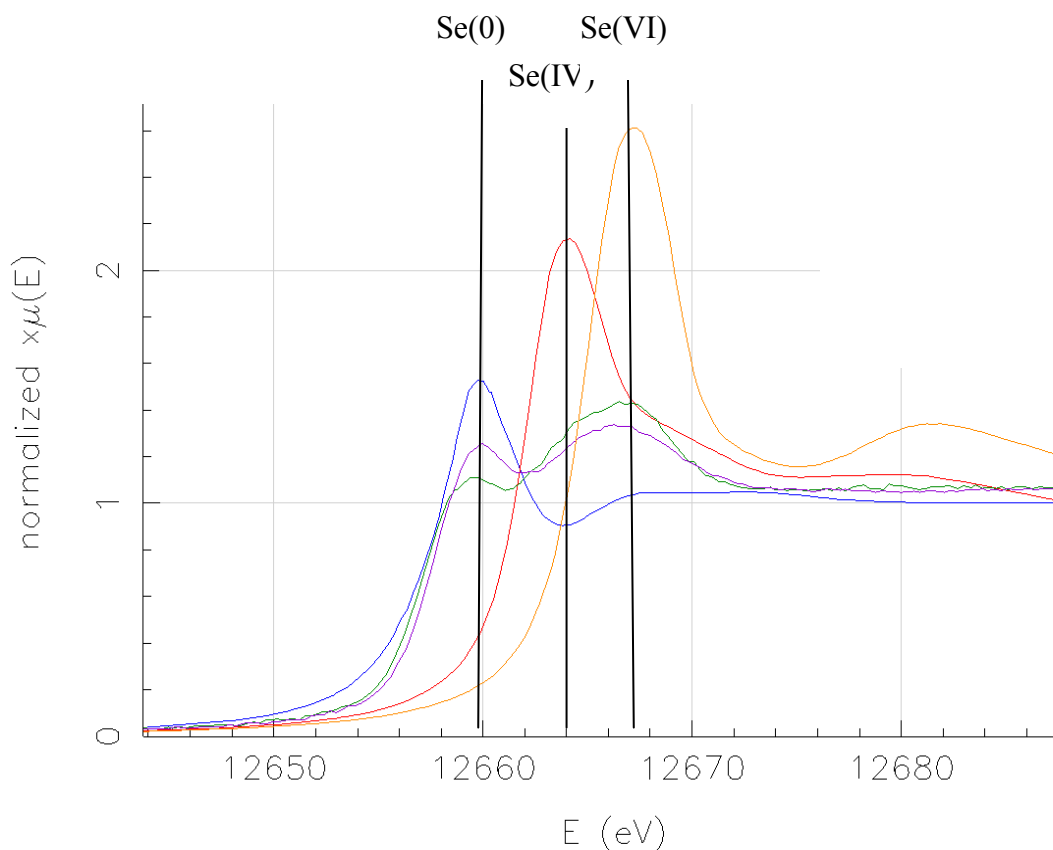


Figure 6. Selenate solutions (Ar-purged, purple and unpurged, green) after reaction with steel wool for 24 hrs. White lines (peaks) are indicated for each Se species. Both purged and un-purged treatments show peaks at 12658 eV indicating the presence of elemental Se.

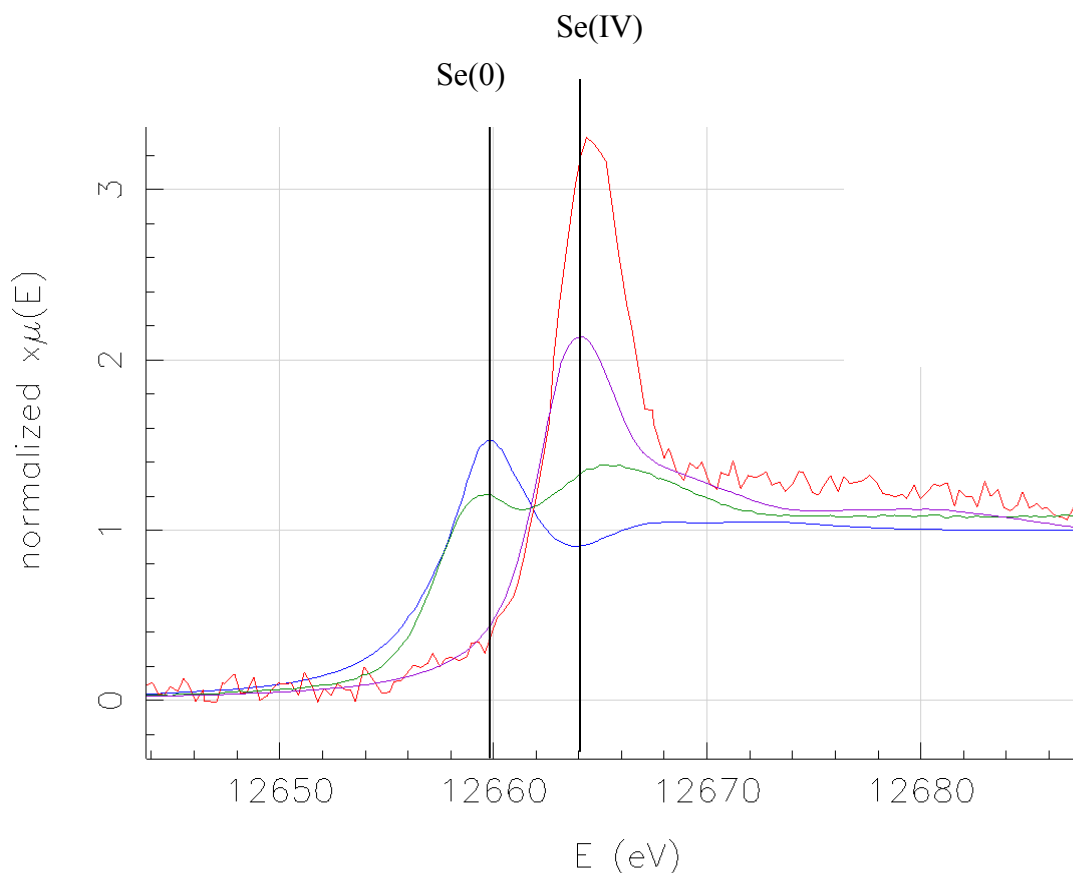


Figure 7. Selenite solutions (Ar-purged, green and unpurged, red) after reaction with steel wool for 24 hrs. White lines (peaks) are indicated for each Se species. Only the purged solution has a peak at 12658 eV indicating the presence of elemental Se.

### Significance of the Project

Because the current water quality standard for Se is written as total Se, that is what commercial laboratories provide. However, because toxicity and treatment system design and efficiency will depend on Se speciation, the implementation of a relatively inexpensive, reliable FI-HG-ICP method to speciate Se will be valuable for research, regulatory, and treatment design needs.

The observation that selenite removal was slower than selenate removal (batch kinetic and spectroscopic results) is opposite of what is typically observed. The most likely explanation for this is the overall reaction dependence on ionic strength and salt type (Cl vs  $\text{NO}_3$ ). Removal rate dependence on initial selenite concentration and open or



closed system indicates that selenium reduction by ZVI-SW is a complex process and that additional research is needed to understand the effects of other water quality parameters on removal rates.

### **Student Support:**

Donglin (Lynn) Huang Ph.D. Student (1<sup>st</sup> year)

### **Publications**

In Preparation

### **Literature Cited**

Hayes, K.F., A.L. Roe, and G.E.B. Jr. K.O. Hodgson, J.O. Leckie, and G.A. Parks. 1987.

In situ x-ray absorption study of surface complexes of selenium oxyanions on  $\alpha$ -FeOOH. *Science* 238:783–786.

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Newville J. 2001. IFEFFIT: interactive XAFS analysis and FEFF fitting. *J Synchrotron Radiat.* 8:322-324.

Zhang, Y. J. Wang, C. Amrhein and W.T. Frankenberger, Jr. 2005. Removal of selenate from water by zerovalent iron. *J. Environ. Qual.* 34:487-495.

# WRI 96 – Experimental Investigation into the Changes in Hydrologic and Environmental Quality Associated with Valley Fills

## Basic Information

<b>Title:</b>	WRI 96 – Experimental Investigation into the Changes in Hydrologic and Environmental Quality Associated with Valley Fills
<b>Project Number:</b>	2007WV96B
<b>Start Date:</b>	3/1/2007
<b>End Date:</b>	2/28/2009
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	WV-1
<b>Research Category:</b>	Climate and Hydrologic Processes
<b>Focus Category:</b>	Hydrology, Water Quality, Floods
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Todd Petty, J Todd Petty, Paul Ziemkiewicz

## Publication

2. Publication Citations (Presentations) Merriam, E., G. Merovich, and J. T. Petty. 2008. Poster. Factors influencing water quality and ecological condition in an intensively mined southern West Virginia watershed. 2008 Spring Meeting Southern Division of the American Fisheries Society, Oglebay Resort and Conference Center, Wheeling, WV, February 28–March 2. Abstract: Large scale surface mining in southern West Virginia results in significant impacts to headwater catchments. It is unclear, however, the extent to which these impacts influence conditions in downstream ecosystems, especially in watersheds affected by historic mining activities and more typical urbanization activities. We initiated a study in the upper Pigeon Creek watershed in south, central West Virginia. The objectives of this study are to: 1) characterize spatial variation in habitat quality, water quality, and ecological condition; 2) attribute instream conditions to spatial variation in landscape conditions (residential development and mining); and 3) identify spatially–explicit restoration and protection priorities. Our preliminary results indicate high levels of ecological impairment within this watershed, with condition ratings ranging from a high of 85 to a low of 22. Furthermore, variation in water quality appears to be a predominant factor influencing ecological conditions. For example, conductivity levels exceeding 1200 were commonly observed. Finally, spatial variation in water quality and ecological condition is strongly associated with residential development and untreated human waste. Residential structure density was significantly correlated with sodium and nitrate concentrations and ecological condition scores. Consequently, effectively managing impacts from new mine development must address the prevalence of non–mining related impacts in this watershed. Minter, M. S., Merovich, Jr., G. T., and J. T. Petty. 2008. Poster. Flow Variability, Water Quality, and Organic Matter Processing in Intensively Mined Headwater Catchments in Southern West Virginia. 2008 Spring Meeting Southern Division of the American Fisheries Society, Oglebay Resort and Conference Center, Wheeling, WV, February 28–March 2. Abstract: Mountaintop removal /valley fill (MTR/VF) mining is a controversial process that may have far–reaching impacts on central Appalachian watersheds. Our project applies current knowledge of organic matter processing to

Pigeon Creek, an intensively mined sub-watershed of the Tug Fork River in southern West Virginia. The long-term goal of our research is to restore and protect ecosystem functions in watersheds of the MTR/VF region of West Virginia. The specific objective of this study is to quantify organic matter retention and decomposition across a broad temporal and stream size gradient. To accomplish this we: 1) quantified the effects of valley fills on water quality, flow variability, structural complexity, and organic matter processing rates in small perennial streams; and 2) Quantified organic matter processing rates in an entire drainage across a size gradient ranging from ephemeral to large perennial streams. Our study consists of 28 sites where we released artificial leaves and sticks, and placed leaf packs to measure decomposition. Flow variability was measured with continuous flow gages, and water quality measurements were based on seasonal, whole water samples analyzed for all major anions, cations, and metals. After one season of data collection (Fall 2007), we observed significant, but highly variable, effects of drainage area and structural complexity on organic matter retention. Small perennial streams below valley fills possessed higher overall flows than comparable reference sites, which resulted in slightly higher rates of decomposition. Our preliminary results suggest a variable, but measurable, interactive effect of mining, drainage area and stream channel complexity on overall stream function as it relates to organic matter processing. Our study will greatly improve our understanding of organic matter processing within Pigeon Creek and may be applicable to intensively mined watersheds throughout southern West Virginia.

## **ANNUAL REPORT: WRI-96**

### **Experimental Investigation into the Changes in Hydrologic and Environmental Quality Associated with Valley Fills**

#### **Introduction/Background**

Mountaintop removal/valley fill (MTR/VF) mining is a common method of mining in southern West Virginia. MTR/VF mining essentially results in the reconfiguration of headwater catchments. These large-scale landscape alterations may have far-reaching effects on environmental and ecological processes such as hydrologic and organic matter dynamics in headwater stream ecosystems. Hydrologic dynamics includes water flow, retention, and delivery downstream. Organic matter dynamics includes retention, transport, and decomposition of coarse particular organic matter.

Effects of valley fill mining on ecosystem-level processes in headwater streams are very important to understand, because headwaters supply water and nutrients downstream, thereby forming the basis for stream food webs in the watershed. Natural stream channels in an unaltered state are physically complex at multiple spatial scales, thereby acting to retain water from precipitation events and moderate the delivery of this water downstream. On the other hand, structurally simplified stream channels and watersheds (i.e., channelized, detached from their floodplains, dredged; denuded of riparian vegetation) are less likely to retain precipitation and moderate flows downstream, thereby creating more frequent, large-scale, intense flood events. In addition, structurally complex stream channels tend to retain organic matter. This is important because it makes decomposition more likely, thereby contributing to nutrient cycling on a smaller scale and supporting diverse productive stream food webs.

Many studies have suggested that organic matter dynamics may be used as a sensitive ecosystem-level measure of stream function and integrity. With respect to organic matter processing in streams, it is still unknown how large-scale surface mining may affect headwater function in this capacity. We also do not know to what degree altered and reconstructed channels mimic natural ones in terms of headwater function including water delivery and retentiveness, and organic matter dynamics. Understanding the function of headwaters in a MTR/VF region will improve our knowledge of stream ecosystem processes and provide new insight for developing mitigation strategies.

The Pigeon Creek watershed in Mingo County is one example of an intensively mined watershed in southern WV. Our studies are in progress in the upper half of this watershed, which is a sub-watershed of the Tug Fork River. The watershed has been actively mined for multiple years and contains numerous MTR/VF jobs.

#### **Problem and Research Objectives**

The *long-term goal* of our research is to develop the information needed to restore and protect ecosystem functions in watersheds of the MTR/VF region of West Virginia. The *overriding objective* of our current study is to quantify aspects of ecosystem function in Pigeon Creek over time and across a stream size gradient. The *rationale for the study* is that the research will first help us understand how MTR/VF mining affects watersheds

and consequently aid the improvement of stream mitigation efforts. We have two specific objectives outlined that will allow us to meet our overall objective. *Specific Objective 1:* Quantify the effects of valley fills on water quality, hydrologic dynamics, and organic matter processing rates in headwater perennial streams. *Specific Objective 2:* Quantify organic matter processing rates in the watershed across a stream size gradient.

## **Methodology**

To quantify the effects of MTR/VF mining on organic matter and hydrologic dynamics, we chose eight perennial headwater streams, all of similar sizes, in the Pigeon Creek watershed. Four are below valley fills and four are control sites containing no large-scale mining upstream. We also chose 21 additional sites along a basin area continuum to quantify how a mined watershed varies in terms of organic matter dynamics.

### Organic Matter Dynamics

In our study, organic matter dynamics refers to the variation in retention/transport and decomposition of coarse particular organic matter in stream ecosystems over time and across streams of different sizes. Retention and decomposition are measured during each season.

Organic matter transport/retention—Dowel rods are used to imitate small sticks and pieces of square construction paper are used to imitate leaves. These artificial sticks and leaves are released in the channel to estimate the capacity of the stream to transport or retain coarse particulate organic matter. The artificial leaves are used to measure instantaneous transport distance because their distance traveled is measured after 30 minutes of being released into the stream channel. The artificial sticks are left in the channel for a period of six weeks and distance traveled is measured every other week. This gives a measure of long-term transport. We also record the stream feature that retains the artificial sticks and leaves.

Organic matter decomposition—Twelve leaf packs, each consisting of ten grams of dry pin oak leaves, are used at each site to estimate the capacity for in-stream decomposition. Six packs are retrieved after 75 days; the last six are left for an additional 45 days. Water temperature data are collected continuously at each decomposition site as well to account for the effects of temperature on decomposition rates. After the packs are retrieved, leaves are processed (ash-free dry mass) to determine remaining biomass and rate of decomposition. Any macroinvertebrates found in leaf packs are identified to genus and enumerated.

### Hydrologic Dynamics

At each of the control and valley fill impact sites, we deployed a vent-tube free, HOBO water-level logger (OnSet Corporation), for a total of 8 deployed units. These units are placed in the water and they continuously record water level by measuring absolute pressure—atmospheric pressure plus pressure from being under the water column. A ninth unit placed in the watershed in a central location continuously records ambient

atmospheric pressure as a control. In our study, hydrologic dynamics refers to the variation in water level over time, and is essentially the hydrograph for each study site, the pattern of water level variation over time.

### Analytical Procedures

We use two-sample t-tests to compare water level variability, transport distances, and decomposition rates among stream types (valley fill vs. non valley fill) to look for statistical differences. Linear regression is used to relate decomposition rates and transport distances to basin area. Coefficient of variation of water level is used as a measure of flow variability.

### **Principal Initial Findings**

Thus far, our initial data show that variability in water level is statistically higher in control sites than in sites impacted by MTR/VF mining (Fig. 1). Streams below valley fills tend to have greater hydrologic stability than streams that are unaltered by large-scale surface mining.

After one season of leaf pack deployment (winter 2007), decomposition rates of leaves were not statistically different between valley-fill and control sites ( $p > 0.05$ ) (Fig. 2), and there was no relationship between decomposition rates and basin area ( $R^2=0.024$ ) (Fig. 3). Basin area was the best predictor of transport distance for artificial sticks ( $r^2=0.70$ ; Fig. 4a) and artificial leaves ( $r^2= 0.83$ ; Fig. 4b). Across all study sites, transport distance of artificial leaves and sticks in streams increased as basin area increased (Fig. 4). Transport distance did not statistically differ between valley fill and non-valley fill sites (Fig.5).

### **Current Progress**

Water level data continues to be collected by the data loggers. One water level logger and one water temperature logger were lost to vandalism in March. They were replaced with new devices. Currently, we are in the middle of our spring sampling where spring-season decomposition and retention/transport data are being collected.

### **Significance of the Project**

Our study will improve our understanding of organic matter processing within Pigeon Creek and may be applicable to intensively-mined watersheds throughout southern West Virginia. This research will help us develop a system for using organic matter processing as a biological indicator. By comparing MTR/VF-impacted streams and non-impacted streams we will be able to quantify the effects that valley fills have on headwater streams and ecosystem processes. Ultimately, this research will be applied to a watershed mitigation plan in the Pigeon Creek watershed.

## **Publication Citations (Presentations)**

Merriam, E., G. Merovich, and J. T. Petty. 2008. Poster. Factors influencing water quality and ecological condition in an intensively mined southern West Virginia watershed. 2008 Spring Meeting Southern Division of the American Fisheries Society, Oglebay Resort and Conference Center, Wheeling, WV, February 28-March 2.

Abstract: Large scale surface mining in southern West Virginia results in significant impacts to headwater catchments. It is unclear, however, the extent to which these impacts influence conditions in downstream ecosystems, especially in watersheds affected by historic mining activities and more typical urbanization activities. We initiated a study in the upper Pigeon Creek watershed in south, central West Virginia. The objectives of this study are to: 1) characterize spatial variation in habitat quality, water quality, and ecological condition; 2) attribute instream conditions to spatial variation in landscape conditions (residential development and mining); and 3) identify spatially-explicit restoration and protection priorities. Our preliminary results indicate high levels of ecological impairment within this watershed, with condition ratings ranging from a high of 85 to a low of 22. Furthermore, variation in water quality appears to be a predominant factor influencing ecological conditions. For example, conductivity levels exceeding 1200 were commonly observed. Finally, spatial variation in water quality and ecological condition is strongly associated with residential development and untreated human waste. Residential structure density was significantly correlated with sodium and nitrate concentrations and ecological condition scores. Consequently, effectively managing impacts from new mine development must address the prevalence of non-mining related impacts in this watershed.

Minter, M. S., Merovich, Jr., G. T., and J. T. Petty. 2008. Poster. Flow Variability, Water Quality, and Organic Matter Processing in Intensively Mined Headwater Catchments in Southern West Virginia. 2008 Spring Meeting Southern Division of the American Fisheries Society, Oglebay Resort and Conference Center, Wheeling, WV, February 28-March 2.

Abstract: Mountaintop removal /valley fill (MTR/VF) mining is a controversial process that may have far-reaching impacts on central Appalachian watersheds. Our project applies current knowledge of organic matter processing to Pigeon Creek, an intensively mined sub-watershed of the Tug Fork River in southern West Virginia. The long-term goal of our research is to restore and protect ecosystem functions in watersheds of the MTR/VF region of West Virginia. The specific objective of this study is to quantify organic matter retention and decomposition across a broad temporal and stream size gradient. To accomplish this we: 1) quantified the effects of valley fills on water quality, flow variability, structural complexity, and organic matter processing rates in small perennial streams; and 2) Quantified organic matter processing rates in an entire drainage across a size gradient ranging from ephemeral to large perennial streams. Our study consists of 28 sites where we released artificial leaves and sticks, and placed leaf packs to measure decomposition. Flow variability was measured with continuous flow gages, and water quality measurements were based on seasonal, whole water samples analyzed for all major anions, cations, and metals. After one season of data collection (Fall 2007), we observed significant, but highly variable, effects of drainage area and structural complexity on organic matter retention. Small perennial streams below valley fills possessed higher overall flows than comparable reference sites, which resulted in slightly higher rates of decomposition. Our preliminary results suggest a variable, but measurable, interactive effect of mining, drainage area and stream channel complexity on overall stream function as it relates to organic matter processing. Our study will greatly improve our understanding of organic matter processing within Pigeon Creek and may be applicable to intensively mined watersheds throughout southern West Virginia.

### **Student Support**

1. Megan Minter, MS, Fisheries Science, co-funding from grant from Consol Energy
2. Eric Merriam, MS, Fisheries Science, co-funding from grant from Consol Energy

### **Notable Awards and Achievements**

None to report

### **Publications**

No current refereed publications



## Figures

Figure1. Coefficient of variation in water level between headwater streams with valley fills and headwater streams without valley fills upstream (Control).

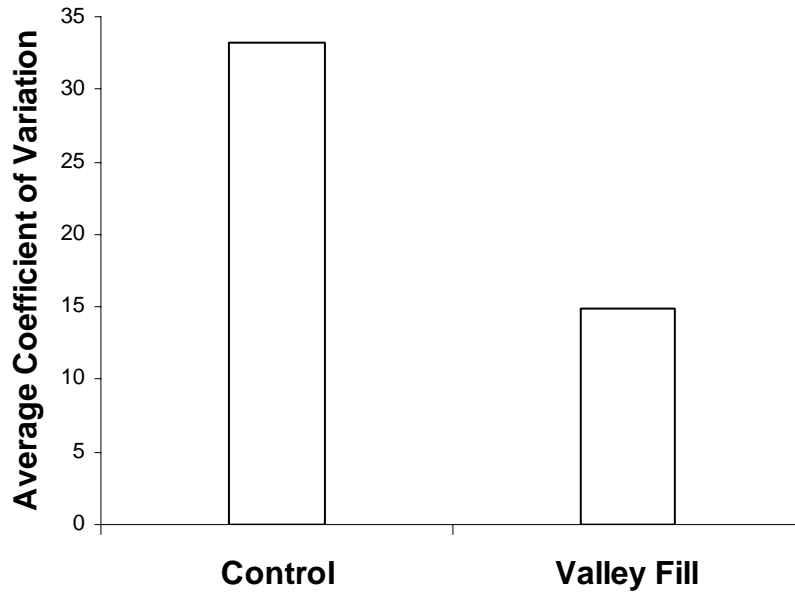


Figure 2. Average decomposition rate of leaves between headwater streams with valley fills and headwater streams without valley fills upstream (Control). Error bars are standard deviations of the mean.

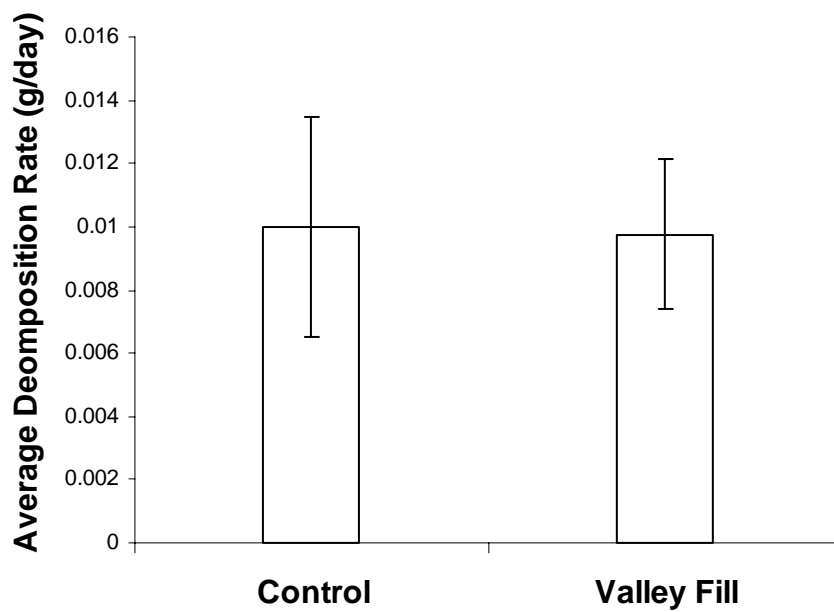


Figure 3. Decomposition rate of leaves across a stream size gradient (basin area) in the Pigeon Creek watershed. Data points are labeled with stream size and treatment (when applicable) categories, i.e., E = ephemeral channels; I = intermittent channels; HW = perennial headwater channels (basin areas < 1,000 acres), HW\_C = HW control sites, and HW\_VF = HW valley fill sites in the valley fill impact study; LT = large tributaries (basin area = 1,000 – 10,000 acres); MS = mainstem channels (basin area > 10,000 acres).

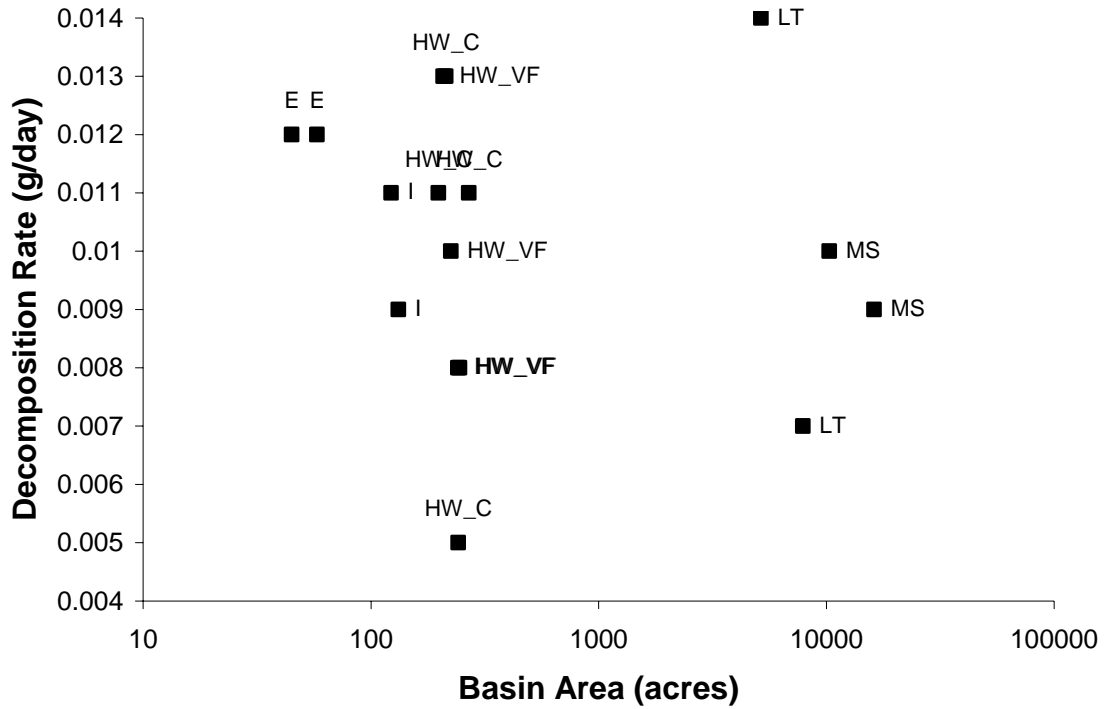


Figure 4. Transport distance of a) artificial sticks (dowel rods in  $m d^{-1}$ ) and b) artificial leaves (average distance in m) across a stream size gradient (basin area) in the Pigeon Creek watershed. The  $R^2$  for each relationship is given on the scatterplot. The best trend line that fit the data is log for the dowel rod data and linear for the leaf data. Note, the x-axis, basin area, is on a log scale.

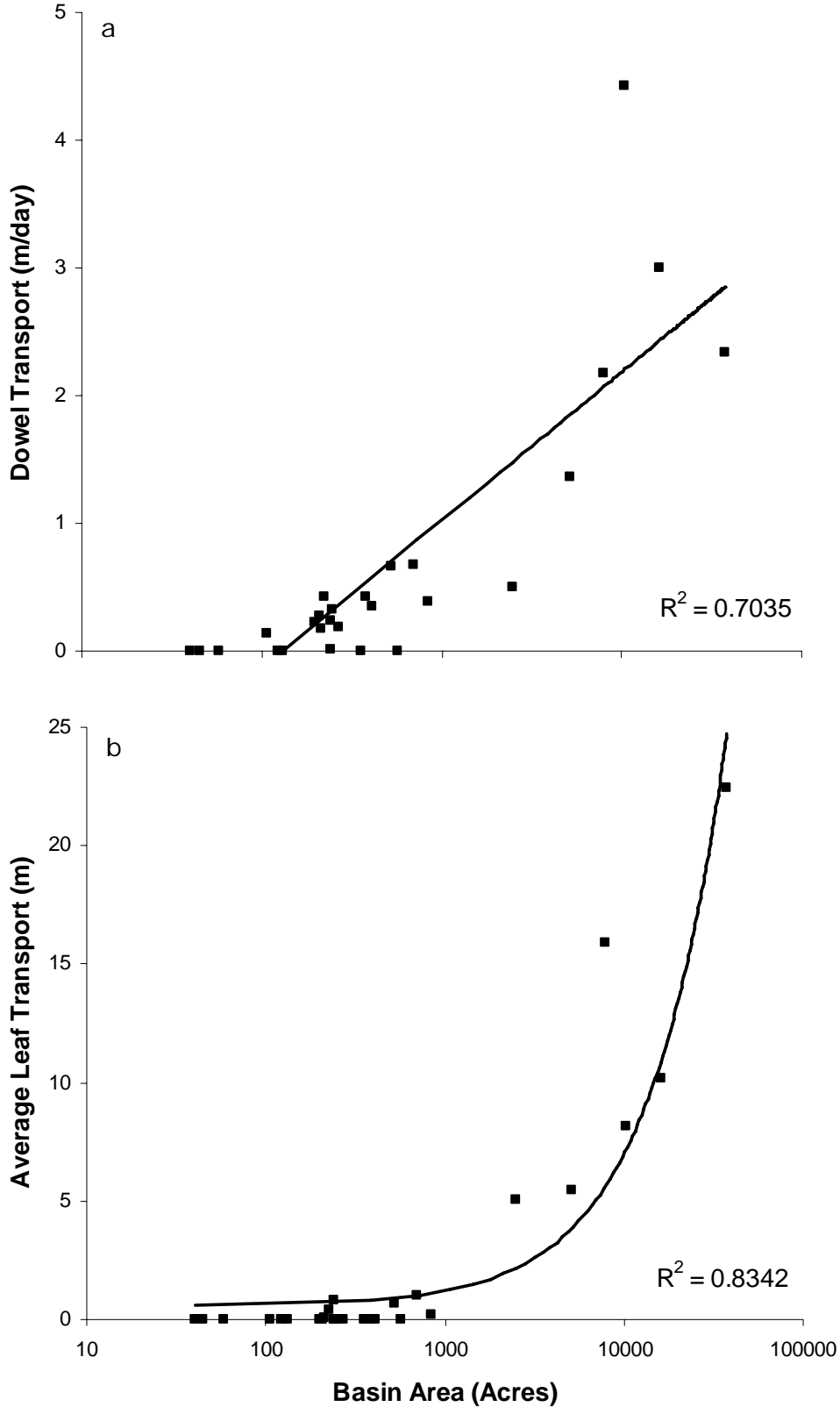
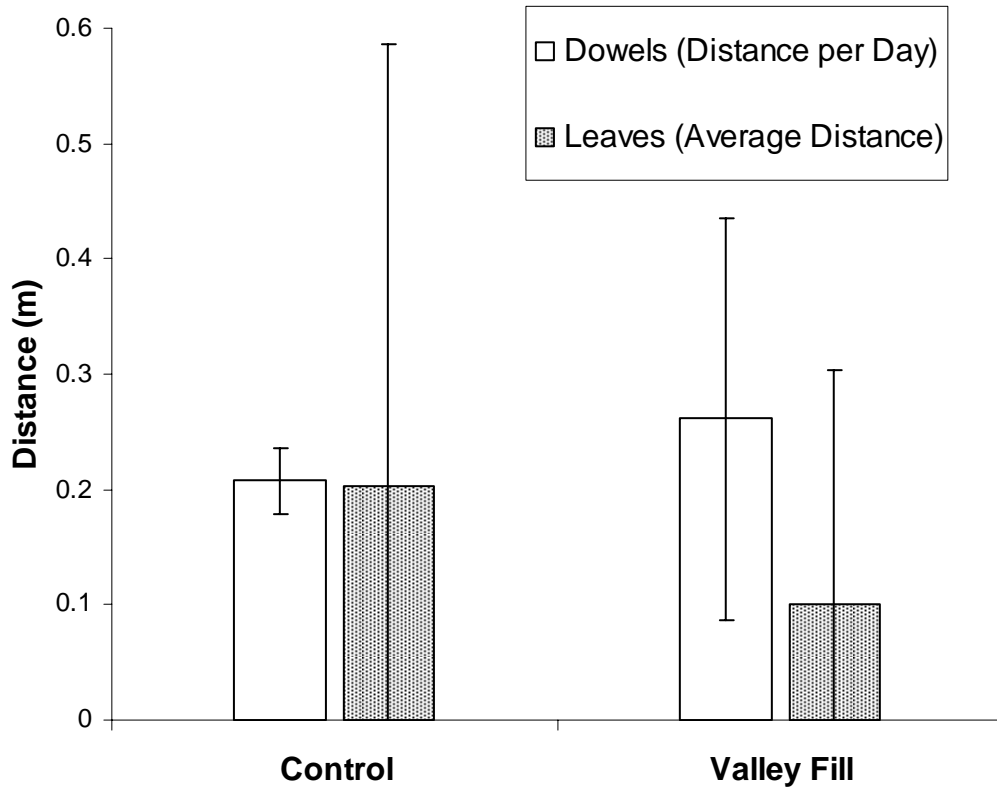


Figure 5. Transport distance data for artificial sticks (dowels) and leaves in the paired control-valley fill study. Error bars are standard deviations.



# WRI 97 – Chemical and Flow Characterization of Mining Impacted Streams Using Continuous Water Quality Monitoring and Watershed Modeling

## Basic Information

<b>Title:</b>	WRI 97 – Chemical and Flow Characterization of Mining Impacted Streams Using Continuous Water Quality Monitoring and Watershed Modeling
<b>Project Number:</b>	2007WV98B
<b>Start Date:</b>	3/1/2007
<b>End Date:</b>	2/28/2009
<b>Funding Source:</b>	104B
<b>Congressional District:</b>	West Virginia District 1
<b>Research Category:</b>	Not Applicable
<b>Focus Category:</b>	Water Quality, Surface Water, Models
<b>Descriptors:</b>	
<b>Principal Investigators:</b>	Jen Fulton, J. Brady Gutta, John D. Quaranta, Paul Ziemkiewicz

## Publication

# **Chemical and Flow Characterization of Mining Impacted Streams Using Continuous Water Quality Monitoring and Watershed Modeling**

**WRI-97**

## **Annual Report**

### **Principal Investigators:**

**Jennifer Fulton, M.S.  
John Quaranta, Ph.D.  
Brady Gutta**

**West Virginia Water Research Institute  
West Virginia University**

**June 27, 2008**

## Introduction

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Efforts to characterize stream water chemistry typically rely upon discrete samples collected over relatively large time intervals. Many important episodic flushing and peak loading events are not captured by these traditional water chemistry sampling protocols. Furthermore, dissolved metal dynamics in mining impacted streams often respond to seasonal and climatic changes (Petty and Barker 2004), and can fluctuate dramatically within a 24 hour period (Nimick et al. 2003). Discrete samples therefore may not adequately represent the true constituent load of the stream, particularly in mining impacted systems (Fytas and Hadjigeorgiou 1995).

Watershed models such as the Watershed Characterization and Modeling System, or WCMS (Strager et al. 2004) also tend to generalize stream water chemistry conditions. WCMS applies loading rates from land use types within a watershed to characterize general stream water quality and flow conditions. Loadings from known mine discharges can be incorporated into the model, producing an estimate of average chemical concentrations in a given stream. The model is based on average annual flow conditions, ignoring extreme loading events that may occur at varying flows throughout the year. WCMS therefore provides only a general estimation of stream water quality.

In order to gain a better understanding of water chemistry dynamics in acid mine drainage (AMD) impacted systems, water chemistry data will have to be collected at significantly smaller time intervals. Advances in instrumentation now allow for nearly continuous monitoring of many water quality parameters. Although sensor technology is not yet available to continuously measure many chemical constituents that may be of concern in these systems, regression models can be used to estimate chemical constituent concentrations and loads from the continuously measured parameters and discrete analytical samples (Christensen et al. 2000). A continuous estimation of chemical concentration will provide a more accurate representation of water chemistry variability in mining impacted systems. Improvement in the accuracy of chemical loading estimates will enable more effective design of AMD treatment systems, and may provide an important tool for TMDL development (Rasmussen et al. 2003).

Continuous monitoring and regression analysis have been used extensively to estimate constituent concentrations in Kansas watersheds (Christensen 2001; Christensen et al. 2000). The parameters of concern in these watersheds included alkalinity, fecal coliform bacteria, total suspended solids, sulfates, nitrates, and phosphorus. These parameters of concern were estimated using pH, specific conductance, temperature, dissolved oxygen, and turbidity data measured hourly with a YSI sonde. The U.S. Geological Survey reported that continuous data collection in these watersheds enabled the identification of important seasonal trends, and provided a more accurate representation of actual chemical loads being transported downstream (Christensen et al. 2000; Rasmussen et al. 2003).

Comparison of continuous water chemistry data to the chemical concentrations predicted by WCMS will enable us to evaluate the predictive ability of WCMS, and will allow us

to place an error bound on the model predictions. The ability of WCMS to predict actual water chemistry parameters has never been evaluated in an AMD system, limiting the utility of WCMS in decision making processes. By associating a measure of error with the model predictions, future WCMS predictions can be made with a known level of accuracy. This will greatly enhance the utility of WCMS in AMD impacted watersheds, particularly in the evaluation of projected load reductions possible with various AMD treatment options.

## **Research Objectives**

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The objectives of the project are to:

- 1) Identify continuously monitored parameters or combinations of parameters that can be used as surrogates for variables of interest in AMD impaired systems, such as acidity, sulfates, iron, and aluminum, and perform regression analysis to estimate constituent concentrations continuously
- 2) Assess the ability of WCMS to predict stream water chemistry based on landscape characteristics and known AMD discharges, and create an error bound for WCMS predictions in a mining impacted watershed
- 3) Use continuous water quality data to examine spatial and temporal variability of water chemistry in a mining impacted watershed

These objectives will be accomplished through the completion of three tasks:

**Task 1** – We will install a continuous water quality monitoring system at four sites in a mining impacted watershed. The instrumentation will record pH, conductivity, temperature, and water level hourly. We will measure stream discharge and analyze water chemistry once a month at each site.

**Task 2** – We will compile existing water quality data for all known mine discharges in the study watershed. Loadings from each discharge will be incorporated into the WCMS model in order to predict chemical concentrations and loadings at each monitoring station in the watershed.

**Task 3** – We will analyze relationships between continuous data and laboratory-analyzed samples in order to provide a continuous estimation of chemical concentrations in the watershed. This continuous data will be used to examine temporal and spatial variability in water chemistry throughout the watershed. We will then compare actual stream data to the WCMS predictions, and produce error bounds for the WCMS model within the study watershed. This information will then be compiled into a final report, and presented at an upcoming West Virginia Water Conference.



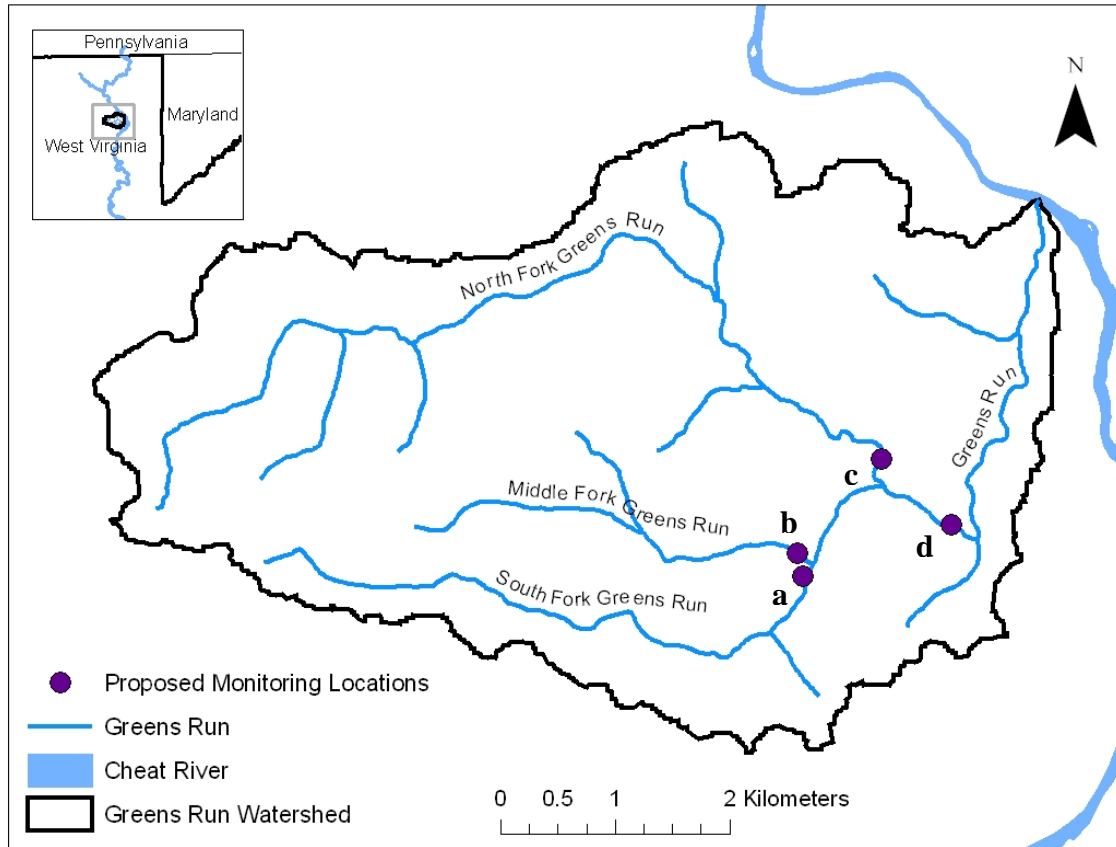
## Methodology

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Greens Run, located in Preston County, WV is a major source of acidity to the lower Cheat River. The watershed drains approximately 11.5 square miles and has 14.9 miles of impaired stream miles. Greens Run has three major tributaries, the North Fork, the Middle Fork, and the South Fork, all of which are heavily impacted by AMD. The three forks contain five recognized abandoned mine sites, as well as one bond forfeited site. The pH of Greens Run below the confluence of these forks is generally less than 3.5. Greens Run was chosen for this project because of the high degree of water chemistry variability observed in the watershed.

Reclamation efforts in the watershed have involved the installation of a doser on the bond forfeiture site by the West Virginia Department of Environmental Protection (WVDEP), as well as two passive treatment installations completed through a cooperative effort with the Friends of the Cheat, the WVDEP, and the National Mine Land Reclamation Center at the West Virginia Water Research Institute (WVWRI). These treatment projects on the Middle Fork and the North Fork help reduce acidity entering Greens Run.

In July 2007, WVWRI installed continuous water quality monitoring systems at the mouth of all forks and below the confluence of the forks, for a total of four monitoring stations (Figure 1). Each monitoring station is comprised of a Eureka multi-parameter sonde with pH, conductivity, temperature, dissolved oxygen, and depth sensors. Similar multi-parameter sondes have been used extensively in water quality research, and their continuous monitoring and logging capabilities are used by many state and federal water quality monitoring programs (Atkinson and Mabe 2006; Christensen 2001; Christensen et al. 2000; Hall and Wazniak 2004). Each sonde was secured to a bridge structure at the site (Figure 2), and is situated at a depth slightly lower than the lowest point in the stream channel. The sondes are programmed to collect data every two hours, and data has been downloaded on a WVWRI laptop computer every month (Figure 3). Probes are cleaned and calibrated monthly (Figure 4).



**Figure 1.** Location of continuous monitoring stations in the Greens Run watershed.



**Figure 2.** Continuous monitoring station on the Middle Fork of Greens Run.



**Figure 3.** Ben Mack downloading data from a Eureka sonde on lower Greens Run.



**Figure 4.** Joseph Kamalesh calibrating a Eureka sonde on the South Fork of Greens Run.

WVWRI staff has collected water samples and measured stream discharge at each monitoring station once per month. Monthly sampling intervals have been found to effectively capture the broad range of temporal and spatial variability of water quality

parameters in mining impacted systems (Petty and Barker 2004). The water samples are analyzed by the analytical lab at the National Research Center for Coal and Energy. Chilled grab samples are analyzed for alkalinity, acidity, and sulfates. Filtered (0.45  $\mu\text{m}$ ), acidified samples are analyzed for dissolved iron, aluminum, calcium, magnesium, and manganese concentrations. Discharge is calculated at each site using an area-velocity technique, by measuring depth and average current velocity (at 60% depth) with a digital Marsh-McBirney flow meter (supplied by WVWRI) in ten equal cells in a cross-section of the stream.



**Figure 5.** Mary Beth Tadj sampling the North Fork of Greens Run

At the completion of the project, the continuous and instantaneous water quality data will be analyzed using stepwise multiple regression in order to produce equations that can be used to estimate chemical concentrations. Monthly discharge calculations will be used to create a stage-discharge rating curve, which will enable estimation of continuous streamflow at each site from the continuous water level data. Chemical load will then be calculated using the estimated instantaneous chemical concentrations and streamflow measurements.

Water quality data for all known mine discharges in the Greens Run watershed will be compiled into a spatially linked database. Using the WCMS feature within the spatial analyst extension of ESRI ArcMap 9.1, we will use the chemical loadings from each known discharge to predict chemical concentrations and loadings at each monitoring station in the watershed. These predictions will then be compared to the continuously-collected data in order to produce error bounds for the WCMS model within the Greens Run watershed.

## Principal Findings

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Continuous data collection began in August on the North Fork, Middle Fork, and lower Greens Run sites. Due to technical problems that required sonde repair, continuous data collection did not begin on the South Fork until October 2007.

As of June 2008, we have collected approximately eight months of continuous water quality data for all sites (Table 1). We have sampled each stream on nine occasions, collecting water samples for analysis and measuring stream discharge at each visit (Table 2).

**Table 1.** Mean sonde water quality measurements through May 2008.

<i>Site</i>	<i>pH</i>	<i>Temp. (°C)</i>	<i>SC (µS/cm)</i>	<i>DO (mg/l)</i>
North Fork	6.97	7.46	178.85	14.24
Middle Fork	3.44	8.17	1069.42	9.72
South Fork	3.30	8.91	841.38	8.51
Greens Run	3.65	24.33	783.97	8.98

**Table 2.** Mean water quality parameters through May 2008. Flow is expressed in GPM and all concentration measurements are expressed in mg/L.

<i>Site</i>	<i>Flow</i>	<i>Acidity</i>	<i>Alk.</i>	<i>SO4</i>	<i>Mg</i>	<i>Ca</i>	<i>Fe</i>	<i>Al</i>	<i>Mn</i>
North Fork	8048	108.08	12.23	40.41	4.17	15.22	0.22	0.17	1.06
Middle Fork	3240	384.96	0.03	559.66	18.89	70.48	44.04	23.99	2.23
South Fork	3201	355.46	0.00	373.98	12.37	44.28	42.59	17.88	3.49
Greens Run	19248	199.35	0.00	235.61	121.14	34.24	16.69	10.15	2.50

## Significance of the Project

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The most important outcome of this project will be the ability to produce continuous concentration estimations for parameters of concern in AMD systems, such as iron and aluminum. This continuous data will greatly enhance our understanding of water chemistry dynamics in acid mine drainage systems. We will be able to produce more accurate estimates of constituent loads, which will be particularly important when designing AMD treatment systems. Continuous water chemistry data will also allow us to produce error bounds for the WCMS model, enabling greater utility of WCMS for predicting benefits of future restoration actions in this watershed.

## Student Support

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Graduate students and undergraduate students have been utilized in the installation of the monitoring equipment, as well as in monthly data downloading and water sampling. This has provided these students and young professionals with knowledge of the design and maintenance of an automatic data logging system, as well as field experience in water chemistry sampling procedures.

### *Graduate Students*

Joseph Kamalesh, M.S. in Civil and Environmental Engineering, August 2008

Ben Mack, M.S. in Plant and Soil Sciences, August 2008

### *Undergraduate Students*

Mary Beth Tajc, B.S. in Chemistry, May 2008

## Project Publications/Notable Awards

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No publications or awards associated with the project are available at this time.

## Citations

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Atkinson, S. F., and J. A. Mabe. 2006. Near real-time monitoring and mapping of specific conductivity levels across Lake Texoma, USA. *Environmental Monitoring and Assessment* 120:449-460.

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Christensen, V. G., X. Jian, and A. C. Ziegler. 2000. Regression Analysis and Real-Time Water-Quality Monitoring to Estimate Constituent Concentrations, Loads, and Yields in the Little Arkansas River, South-Central Kansas, 1995-99. U.S. Geological Survey, 00-4126.

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Hall, M., and C. Wazniak. 2004. Continuous water quality monitoring in the Maryland Coastal Bays. Maryland Department of Natural Resources, Annapolis, MD.

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- Rasmussen, T. J., A. C. Ziegler, P. P. Rasmussen, and T. C. Stiles. 2003. Continuous water-quality monitoring—a valuable tool for TMDL programs. Proceedings of National TMDL Science and Policy 2003 Speciality Conference, Chicago, Illinois.
- Strager, M. P., J. B. Churchill, and V. Maskey. 2004. The Watershed Characterization and Modeling System - A Hydrological Modeling Extension for Environmental Systems Research Institute ArcGIS 9X Software. Natural Resource Analysis Center, Division of Resource Management, West Virginia University, Morgantown, WV.

# Information Transfer Program Introduction

None.



# **USGS Summer Intern Program**

None.

<b>Student Support</b>					
<b>Category</b>	<b>Section 104 Base Grant</b>	<b>Section 104 NCGP Award</b>	<b>NIWR-USGS Internship</b>	<b>Supplemental Awards</b>	<b>Total</b>
<b>Undergraduate</b>	2	0	0	1	3
<b>Masters</b>	2	0	0	0	2
<b>Ph.D.</b>	0	0	0	0	0
<b>Post-Doc.</b>	0	0	0	0	0
<b>Total</b>	4	0	0	1	5

## **Notable Awards and Achievements**

## Publications from Prior Years

1. 2006WV69B ("Evaluation of the Environmental Hazard of Selenium in Coal–Associated Rocks of the Southern WV Coal Basin") – Other Publications – I.Pumure, J.J. Renton, and R.B. Smart, "Accelerated aqueous leaching and speciation of selenium and arsenic from coal–associated rock samples using ultrasound extraction", *Environmental Geology*, submitted for publication, June, 2007. STUDENT SUPPORT Mr. Innocent Pumure, Ph.D. Candidate, West Virginia University, Department of Chemistry, \$4000, Summer, 2006.