

# Natural Selenium Attenuation at the Lab, Outlet, and Watershed Scales

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## Abstract

In Appalachian coal overburden, nearly all selenium occurs in a reduced state in largely unweathered, sedimentary rock. The rate and period of selenium leaching is poorly understood. Selenium discharge is regulated in the United States and this knowledge is critical in estimating financial and environmental liabilities. This study estimated the dynamics of selenium leaching by analyzing its release at three scales: laboratory humidity cells, discharges from mined spoil aged 6 to 25 years and streams affected by mining over the same interval. The two field studies took place on a 6,000 ha coal mining complex in southern West Virginia. Both indicated that selenium was released rapidly from mine spoil and that its rate of attenuation was rapid (about 0.05%/day after 145 weeks). Selenium was depleted from mine spoil to the extent that concentrations were generally less than the regulated limit of 5 µg/L within 25 years. Laboratory humidity cell results indicated a similar profile for selenium concentration over a much shorter interval. Adjustment of the laboratory results to estimate field values was accomplished by multiplying concentration by 6.4 and by multiplying time in years by 7.0. With this adjustment, humidity cell results were similar to those from the field at a given time.

By segregating a large number of field observations according to age class, this study identified a procedure for conducting long-term weathering studies with data collected over relatively short (six-year) sampling intervals. Statistical analysis indicated that experimental error was minor and that temporal trends in selenium concentration were readily identified.

Keywords: selenium, coal mining, attenuation

## Introduction

Predicting the amount of pollutant that will be released from a unit of mine spoil requires an understanding of the total amount present in the rock, the proportion that is potentially mobile, the rate of mobilization, sequestration within the spoil mass and finally the leaching or release rate. Vesper et al. (2008) reported selenium concentrations in southern West Virginia coal overburden rock ranging from about 0.84 in sandstone to 4.10 mg/kg in organic shale with higher selenium concentrations coinciding with the highest sulfide levels. Selenium-rich rock units are highly segregated and 90% of an overburden profile's selenium is typically found in less than 15% of the rock mass (Mullenex, 2005). The proportion of selenium that is subject to mobilization was estimated by Roy (2005) and Pumure et al. (2010) who used extreme methods to accelerate selenium release from rock. Roy (2005) used modified sequential extraction to estimate that roughly one half of total selenium was non-extractable while another quarter of the total selenium was bound in organic form. Neither of these selenium forms was shown to contribute significantly to the mobile fraction. Sequential extraction was developed for soils and the extent to which it is able to mobilize the organically bound fraction in coal related rock is not well understood. It is possible that much of the non-extractable fraction in this study was, in fact, organically bound. Most of the remaining selenium that could be potentially mobile in the environment occurred in association with sulfides and, to a lesser extent, as exchangeable ions. Thus, only about 25 to 35% of the total selenium found in total overburden analysis was found to be mobile.

Similar results were obtained using a sonication extraction method intended to estimate bioavailable or mobile selenium (Pumure et al. 2010) in shale. Samples were sonicated in deionized water for ninety minutes in five-minute increments with total replacement of the water for each five-minute extraction.

The authors reported that 35 and 38% of total selenium in two similar organic shales from southern West Virginia was mobile. In theory, sonication enhanced the oxidation of reduced selenium forms via cavitation and released soluble selenium.

Diehl et al. (2005) determined selenium in pyrite in southern Appalachian coals by a variety of micro-analytical techniques. Up to 670 mg/kg of selenium was found in pyrite samples. The minimum sulfur to selenium ratios in their pyrite samples were near  $10^3$ . Whole coal values for selenium ranged from 25 to 247 mg/kg. At one to two percent sulfur content (estimated, sulfur content was not reported), the pyrite contained roughly 2 to 20% of the selenium in the coal. The selenium percentage found in pyrite correlates well with the fraction found in the sulfidic extract by Roy (2005), who found 8 percent of the total selenium in the pyrite fraction of coal and 13 percent in shale. Diehl et al. (2005) concluded that trace element enrichment was post depositional to pyrite formation.

Selenium in waste rock can exist in soluble forms, such as selenite or selenate, which will be released immediately upon exposure to water, or in solid forms that become mobile upon exposure to oxygen and water. Very little is known about the actual selenium forms in rock. The concentration of selenium is too low to determine for all but the most sophisticated analytical equipment, but the most commonly presumed species is the selenium analog of pyrite. The Pourbaix diagram for iron-selenium (Figure 1)

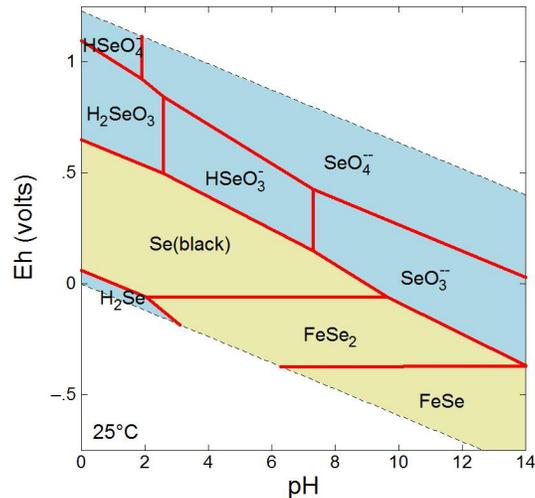


Figure 1. Pourbaix diagram of  $10^{-6}$ M (79  $\mu$ g/L) selenium and  $10^{-3}$ M (56 mg/L) iron. Solid forms are indicated by buff shading. Soluble species are indicated by blue shading.

shows areas of thermodynamic stability for elemental selenium in addition to more reduced iron compound forms. In natural systems, ferroselite ( $\text{FeSe}_2$ ), ferrous selenide ( $\text{FeSe}$ ) or elemental selenium ( $\text{Se}^0$ ) may comprise the dominant solid form. The differences in the oxidation mechanisms and kinetics for these solids are unknown. Figure 1 also shows that with increasing reduction/oxidation potential ( $E_H$ ), the first stable, soluble species is selenite ( $\text{SeO}_3^{2-}$ ) and its protonated forms. The oxidation of selenite to selenate is slow. As an example, Vesper et al. (2004) showed that the proportion of selenate to selenite gradually increased downstream of coal mines, indicating both initial release of selenite and slow oxidation. Selenite is often the primary species found in various power plant ash materials (Huggins et al. 2007), although Hyun et al. (2006) found significant selenate.

Iron oxyhydroxide or ferrihydrite, a byproduct of pyrite oxidation is known to preferentially sorb selenite over the more oxidized selenate oxyanion. Iron oxyhydroxide removed 95% of selenite at pH 4, 80% at pH 9 (Merrill et al. 1985). Su and Suarez (2001) studied amorphous iron oxide and goethite,  $\alpha\text{-FeOOH}$ , and reached similar conclusions for each material, although the data for amorphous iron oxide were less

definitive. Zhang and Sparks (1990) had previously studied selenate and selenite sorption on goethite and, unlike Su and Suarez (2001), concluded that whereas selenite formed an inner sphere complex, selenate formed a less stable outer sphere complex. Ziemkiewicz et al. (2011) added ferrihydrite to weathering, selenium-containing mine spoil and found that roughly 70% of selenium was immobilized relative to untreated controls. Presumably, most of the adsorbed selenium was in the selenite form.

While laboratory leaching results provide insight into weathering and leaching mechanisms under ideal conditions, the important issue to the mining and regulatory sectors is the concentration of selenium that will discharge from operating mines over time. Selenium discharge dynamics under field conditions are poorly understood, largely due to: the long-term nature of field weathering processes and the relatively short-time interval since selenium has been monitored. In fact, selenium was not considered a pollutant in Appalachian coal mining until about 2003. Thereafter, some large, surface coal mines were obliged to sample and report selenium discharged via their regulated outlets.

Overburden is unmined rock that is moved to access the coal seam. After mining, it is known as spoil. Large scale surface coal mining in the highly dissected Appalachian plateau involves horizontal, multiple seams and a mixture of sedimentary rock types. Roughly half of the overburden is moved by blast casting with the remainder moved by dragline or shovel to truck haulage. The latter generally dump on an advancing face with the rock distributed down slopes that can be 10 to 50 m long. All of these overburden handling methods result in a high degree of overburden blending. Weathering begins immediately after mining. Spoil age refers to the length of time since a rock unit was mined. While each rock type will behave differently with regard to selenium production, the mining process dictates that we recognize spoil units that are of mixed composition and ages within the constraints of an individual mine permit.

### Proposed selenium weathering model

Based on the above studies, a working model for selenium weathering, sequestration and release was developed (figure 2).

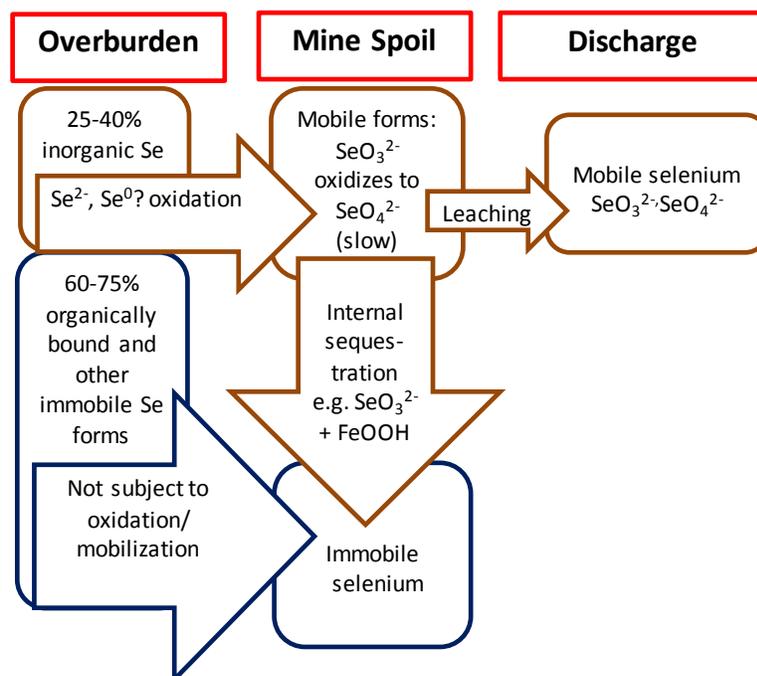


Figure 2. A model was developed to illustrate our current understanding of the selenium weathering process in coal related spoil.

While the knowledge to describe and quantify the model components is lacking, it is reasonable to partition the system into three components: unweathered overburden, mined and weathering spoil and discharge containing soluble selenium. Both Roy (2005) and Pumure et al. (2011) identified, on average, about 33% of the total overburden selenium as potentially mobile. That proportion was used in this study to approximate the potentially mobile selenium fraction. Diehl et al. (2005) identified a strong association between selenium and iron sulfides in coal overburden. So, it is postulated that overburden contains a potentially mobile fraction of largely inorganic selenium consisting of selenides and possibly elemental selenium. The immobile fraction contains organically bound and otherwise recalcitrant selenium. Mining introduces oxygen and water which initially produces selenite. It can either oxidize to selenate and exit the spoil as discharge or bind with sorption agents such as ferrihydrite (FeOOH). Selenium sequestration within the mine spoil likely increases in significance with increasing iron sulfide and thus ferrihydrite production. Mobile selenium leaves the system as either selenite or selenate while the immobile selenium sink consists of non- or slowly-weathered selenium and selenite which has been sorbed to agents such as ferrihydrite. Oxidation of selenite to selenate is slow and a significant amount of selenite may exit the spoil.

Some of the key components of coal spoil involve ranges of mineral types rather than specific mineralogies. For example, ferrous sulfides include iron monosulfides (FeS) through pyrite and marcasite (Fe<sub>2</sub>S). Iron oxidation products include a number of amorphous, variously hydrated oxyhydroxides including ferric hydroxide, ferrihydrite and goethite. For simplicity, the former will be referred to as pyrite and the latter as ferrihydrite.

## **Methods**

In this study, the release kinetics of selenium from coal overburden rock was estimated at three scales: in laboratory humidity cells, regulated discharges from a large surface mine and in receiving streams.

### **Laboratory scale study**

Samples of a selenium-rich (1.55 mg Se/kg) organic shale were subjected to weathering and leaching in humidity cells for 145 weeks. Results up to week 96 (Ziemkiewicz, et al. 2011) estimated the rate of selenium mobilization and leaching under laboratory conditions. Field selenium concentrations were estimated by multiplying the observed selenium concentrations from the humidity cells by a factor of 6.4. This factor was developed by comparing selenium and chloride concentrations in the humidity cells with the same parameters at a large waste rock dump comprising similar rock. The 6.4 factor appeared to account for the dilution resulting from the high liquid to solid ratio in the humidity cells (2:1) and yielded concentrations of both selenium and chloride that were similar to those observed in the field (Ziemkiewicz et al. 2011).

### **Mine outlet study**

In order to estimate the temporal trends in selenium concentration, mine outlets from a large (6,000 ha) surface mining complex in southern West Virginia were studied. Selenium concentration had been monitored over a period of up to seven years (2004 through 2010) for regulatory reporting. The mine extracts coal from the Stockton/Coalburg zone within the Pennsylvanian age Kanawha Formation. Overburden consists of a horizontally bedded mixture of sandstone, organic and non-organic shale. A single core from the property indicated an average concentration of 0.262 mg Se/kg with selenium concentrated in organic shale units. Spoil upstream of each outlet would contain a mixture of those rock units with unknown degrees of homogenization.

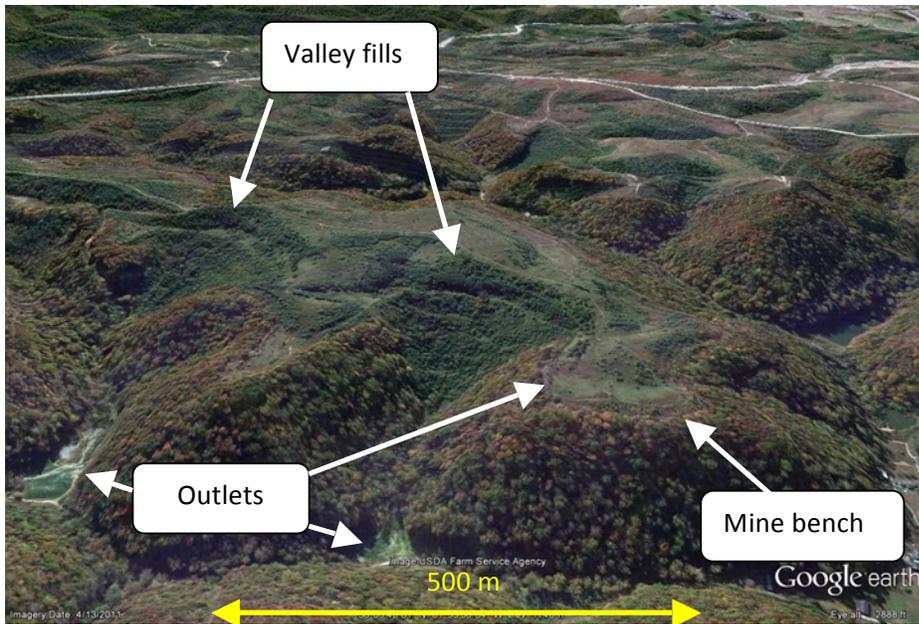


Figure 3. Typical arrangement of a mountaintop mine showing outlet locations below valley fills and on mine benches. The coal is horizontally bedded in this region and the mine bench represents the lowest extent of mining. Spoil is placed on the mine bench and in valley fills.

This water quality dataset included sixty seven outlets with approximately monthly samples. The outlets represented five National Pollution Discharge Elimination System (NPDES) permits and nineteen surface mining permits of approximately 100 to 200 ha each. The time interval between issuance of each mining permit and the discharge sampling date was used to estimate spoil age. Each sample was then assigned a value representing age to the nearest year. While sampling occurred over a seven-year period, the mine permit areas feeding these outlets were as old as 25 years. Within a mine permit area, the progression from mining to surface regrading and revegetation was typically linear over a period of three to five years. Based on limited, historical, aerial imagery, this appeared to be generally true. However, the imagery indicated that one discharge represented a site that was partly re-excavated subsequent to regrading. Its initial mining date was adjusted accordingly.

Outlets were sampled by the company and reported to the state regulatory agency. All chemical determinations were conducted by state-certified analytical laboratories. Outlets were added to the sampling program at various times as mining expanded and were typically sampled at monthly intervals. The number of samples within a given spoil age class ranged from 25 to 578 and averaged 216. The highest selenium discharges tended to be sampled most often. Minor discharges, determined by either intermittent flow or low selenium concentrations, were sampled less frequently. Only samples from flowing discharges were included in this study.

A total of 5,388 water quality samples were included in this study. Given the wide range of sample sizes among age classes, precision was determined by applying Student's *t* statistic according to Ostle (1963) to identify upper and lower confidence limits for mean selenium concentrations within each age class. The precision of the estimated mean values thus indicate the importance of uncontrolled variables such as vertical and horizontal spoil heterogeneity within age classes.

## Watershed study

Four tributaries that receive discharge from the mine complex had been sampled by a research team from West Virginia University over the period June 2009 to November 2010. Mining had moved across these watersheds from 1985 to the present. Between fourteen and seventeen monthly samples were taken in each tributary. The date of initial mining was determined by the average of the upstream surface mine permits and subtracted from 2009 to estimate the age of mining in each tributary's watershed. The mean values and confidence intervals were determined. In addition, two historical sources of selenium data were obtained for two of the tributaries. They included the Mountaintop Mining EIS (USEPA, 2004) and the Guyandotte River TMDL (USEPA, 2002). These agency data were reported as means of multiple samples but the individual sample results were not available and, thus, confidence intervals could not be determined.

## Results and Discussion

### Laboratory scale study

The selenium leaching rate was characterized as the percent mobile selenium that was removed from the humidity cells per day. The mobile fraction was estimated to be 33% of total selenium as reported by Roy (2005) and Pumure et al. (2010). The leaching rate initially declined rapidly, then after about 50 weeks entered a prolonged, gradual decline from 0.07%/day to 0.05%/day by week 145. A power function (equation 1) was found to approximate the observations with an  $R^2$  value of 0.96.

$$y=0.0045x^{-0.452} \quad \text{Equation 1.}$$

Where: Y=the selenium leaching rate in % of remaining selenium per day  
X=weathering interval in weeks

The observed values and the predicted values are shown in Figure 4. The prediction curve is extrapolated to 550 weeks at which time the leaching rate is predicted to be 0.026%/day.

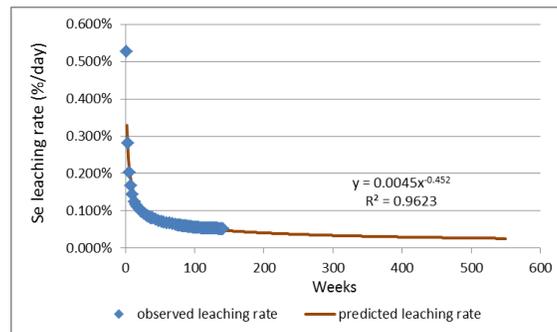


Figure 4. The observed and predicted selenium leaching rates in carbonaceous shale placed in humidity cells and observed for 145 weeks. Experimental values are the mean of six replications. A prediction curve (equation 1) was developed and extrapolated to 550 weeks.

The selenium concentration of humidity cell leachate increased rapidly to a maximum of 4  $\mu\text{g/L}$  by week 56 then decreased nearly as rapidly to 0.5  $\mu\text{g/L}$  by week 145 (Figure 5). If, in fact, only 33% of the total selenium is potentially mobile, then 50% of that fraction was removed by week 145. The decline in selenium concentration suggests possibly two mechanisms: depletion of the mobile selenium fraction and/or immobilization of selenite with ferrihydrite produced by pyrite oxidation per figure 2. Extrapolation of the leaching prediction curve suggests that nearly all of the potentially mobile selenium will be removed from the humidity cells by week 550 (10.5 years).

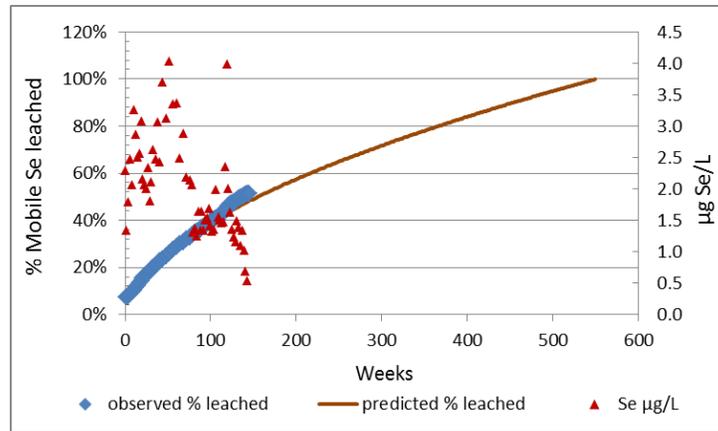


Figure 5. Observed and predicted, cumulative selenium removal amounts from the laboratory study are shown on the left Y axis while estimated field selenium concentrations are indicated on the right Y axis.

The laboratory humidity cells used a liquid to solid ratio of 2:1. Temperatures within the cells reflected ambient laboratory conditions of about 22° C. The humidity cells represent a more aggressive weathering environment and a higher leaching efficiency than a multi-million ton spoil mass. In addition, laboratory temperatures were higher than the ground water temperatures of 10-12° C that are typically found in spoil discharges in West Virginia.

The average concentration ratio of sulfur to selenium released from the humidity cells was 1,764 (Figure 6). Much higher values were noted in leach cycles 1, 2 and 3 (cycle 0 was the initial rinse of the test samples). Other than those initial weathering cycles, the sulfur to selenium ratio remained nearly constant over the subsequent leaching cycles. While not definitive, this suggests a mineralogical, possibly pyritic, co-occurrence of the two elements. Over the 145 weeks of leaching, the average leachate pH was 6.82 and the minimum pH value was 6.13. At this pH range and under oxidizing conditions, ferrihydrite will precipitate. Every mole of sulfur released in pyrite oxidation will release a mole of iron and thus ferrihydrite. So, it is reasonable to expect that approximately 1,764 moles of ferrihydrite would be available for every mole of liberated selenium.

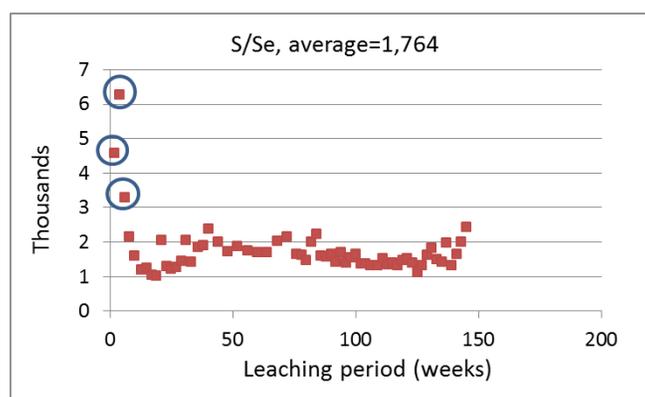


Figure 6. The ratio of sulfur to selenium averaged 1,764 over 145 weeks of leaching. Circled values are the first three leach cycles.

### Mine outlet study

Selenium concentrations increased over the first seven years then declined to less than 5 µg/L by year 25 (Figure 7). Initially about 60% of the samples exceeded 5 µg Se/L. By year five a maximum of 87% exceeded 5 µg Se/L. However, by year 25 only 3% of samples exceeded 5 µg Se/L. The average selenium concentration within age class peaked at year six then declined to less than 2 µg/L by year 24 where the 95% confidence level was also less than 5 µg/L (Figure 8). Both the average selenium concentration and the proportion of samples that were out of compliance with the regulatory limit of 5 µg Se/L reached their maximum values about 6-7 years after issuance of the mining permit. A period of about 20 years followed during which both selenium concentration and the rate of non-compliance decreased.

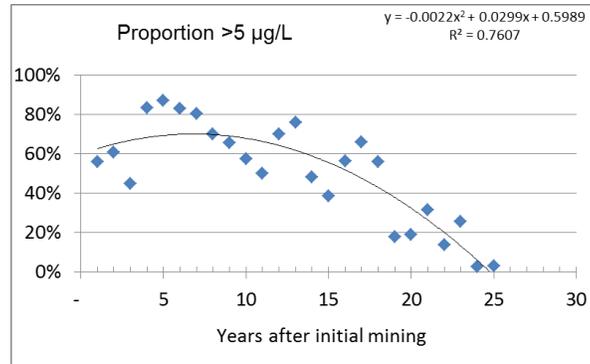


Figure 7. The relationship between the percentage of samples in excess of 5 µg Se/L and age class. The equation for a quadratic model is given, with an  $R^2$  of 0.76.

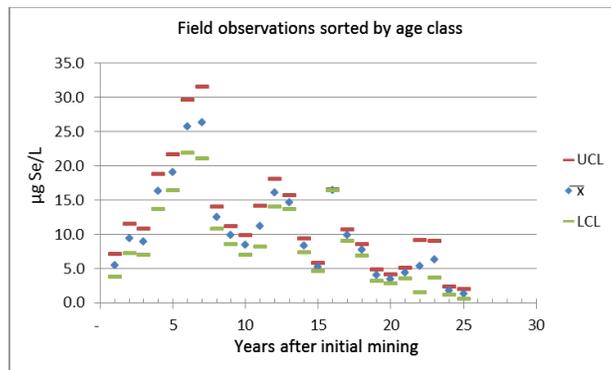


Figure 8. Mean selenium concentrations ( $\bar{x}$ ), with upper and lower confidence levels ( $p=0.95$ ) for mine discharges sorted according to time after initial mining.

The narrow confidence intervals in Figure 8 indicate a strong relationship between time and selenium concentration. This indicates that uncontrolled factors such as geologic and hydraulic heterogeneity were of minor significance.

### Watershed study

Four tributaries to the Mud River drain the southwestern end of the mine. Mining proceeded downstream along the River from south to north. Thus it was possible to identify the interval between initial mining in the tributaries and the date of sampling. In 2009, mining on the tributaries Ballard Fork, Stanley Fork, Sugartree Branch and Berry Branch was, on average, 24, 21, 19 and 8 years old, respectively. These sites were sampled monthly with about fourteen samples each. An unmined tributary of the Mud River (Upton Branch) was also sampled. In addition, stream samples from older studies were available for Stanley

Fork and Sugartree Branch (USEPA, 2002) and (USEPA, 2004). Estimates of sample precision were developed using student's t test at  $p=0.95$ . Data reported from 2000 (USEPA, 2002) and 2003 (USEPA, 2004) sampling included averages and ranges only so precision could not be estimated. Figure 9 illustrates the temporal trend toward selenium concentrations less than 5  $\mu\text{g}/\text{L}$  by year 24.

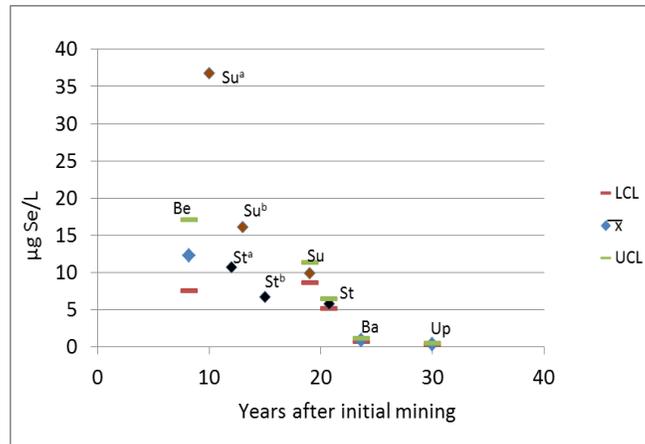


Figure 9. Each of the stream samples was arrayed along a time axis that approximates spoil age in the watershed. Where possible, confidence intervals were included. Be=Berry Branch, Su=Sugartree Branch, St=Stanley Fork, Ba=Ballard Fork, Up=Upton Branch. Superscript 'a' indicates 2000 sampling while superscript 'b' indicates 2003 USEPA sampling.

### Integration of laboratory, outlet and watershed studies

The results of the outlet and watershed studies represent the weathering and leaching of selenium bearing rock under field conditions. Results are dimensioned as selenium concentration at a given year after initial mining. The laboratory data represent weathering and leaching under artificial conditions. Comparison of laboratory and field weathering studies required adjustment of laboratory concentrations and time scales to account for different solid to liquid ratios in the leaching process, higher leaching efficiency in the laboratory versus the field, and the different kinetics associated with higher laboratory temperatures. Large spoil masses are colder; they include preferential flow paths and seasonally variable moisture conditions. Nonetheless, comparison of the trends in the laboratory and field studies (outlet and to a lesser extent the watershed study) provides an opportunity to calibrate findings from the laboratory study.

The comparison required adjustment of two key parameters: selenium concentration and removal rate. The former was adjusted by multiplying the laboratory leachate concentrations by 6.4. The rate parameter was then calibrated by observing that the shapes of the selenium release curves in both field and laboratory studies were similar except that in the laboratory the curve peaked at week 56 (1.08 years) while in the field it peaked at year seven. This suggests that, for the test materials, one year of laboratory leaching was approximately equivalent to seven years of leaching in the field. Laboratory results were thus adjusted to approximate field values by multiplying concentration by 6.4 and time by 7.0. The results are shown in Figure 10A. Figures 10B and 10C show the change in selenium concentration over time in the outlet and watershed studies.

With the exception of several outliers, data from each of the three studies follow a similar temporal trend. The results indicate a rapid increase in selenium concentration over the first seven years followed by a decline over the following sixteen years to less than 5  $\mu\text{g}/\text{L}$ . A secondary peak occurred at year thirteen in the laboratory and outlet results. Whether this is coincidental or indicative of a significant geochemical process is not clear. In the future, it will be worthwhile examining whether, for example the

sharp decline after year seven reflects the maximum production of ferrihydrite and its role as a selenite sink. Ferrihydrite is a product of pyrite oxidation and Meek (1994), reporting on surface coal mine discharges in West Virginia, indicated that the maximum acidity generation and pyrite oxidation occurred between year six and seven after initial mining. The secondary selenium peak at year thirteen may represent exhaustion or saturation of the ferrihydrite sink. Further declines in selenium concentration can be attributed to exhaustion of the spoil selenium pool.

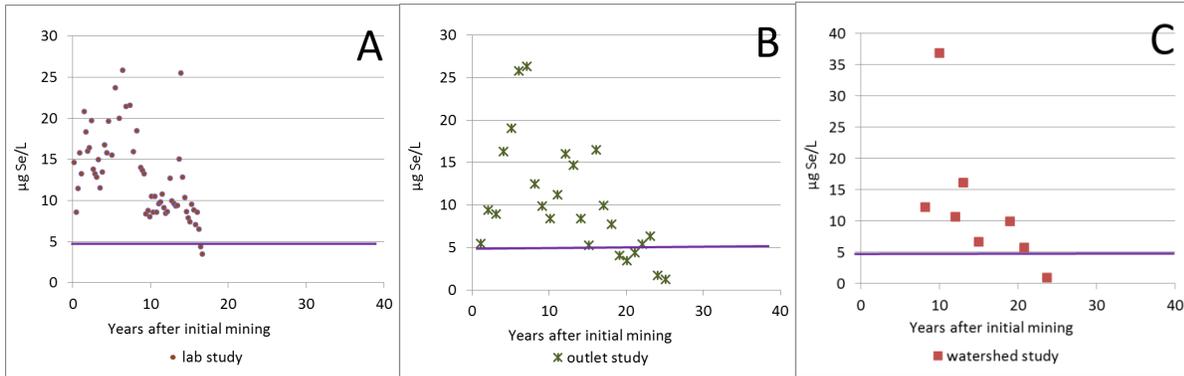


Figure 10. Adjusted results from the laboratory study (A) are compared with the mine outlet (B) and watershed (C) studies. The purple, horizontal line is the chronic aquatic life standard (5 µg Se/L).

The results of all three studies were plotted on Figure 11. In addition, a prediction model (Equation 2) was developed to encompass most of the data points. The model reflects the initial rapid increase in selenium concentration and its peak at about year seven. Between years seven and thirteen, observations from all studies are substantially less than the predictions. Thereafter, observations again align with the model to less than 5 µg Se/L by year 23 and to about 1 µg Se/L by year 25.

Where:

$$y = 0.009x^3 + 0.489x^2 + 6.230x + 4.308$$

*Equation 2:*

y = predicted selenium concentration  
x = years after initial mining

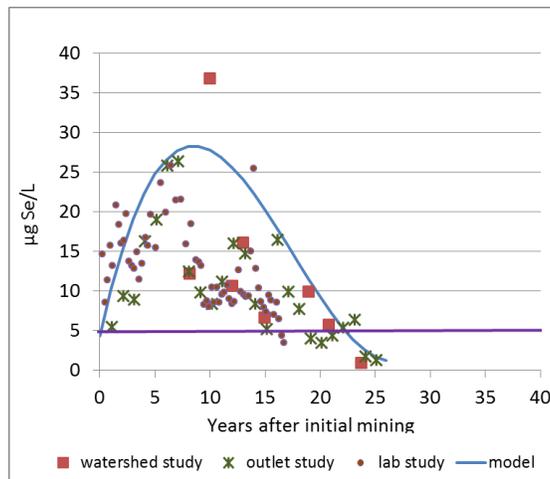


Figure 11. The results of the laboratory and field studies were plotted together. The blue curve is the prediction model according to equation (2). The purple, horizontal line is the chronic aquatic life standard (5 µg Se/L).

## Conclusions

Initial, total selenium content of coal spoil is extremely low (0-5 mg/kg) and the mobile fraction is between 25 and 35% of the total amount. Typical Appalachian coal mine spoil contains between 5,000 to 10,000 times more pyritic sulfur than total selenium. A three-year kinetic study using humidity cells indicated that the average selenium removal rate from coal spoil is about ten times more rapid than sulfur in sedimentary rock (about 0.06%/day vs. 0.006%/day). Thus, a rapid rate of selenium depletion from mine spoil would be expected.

Those expectations were confirmed by two field studies. Both indicated that selenium was released rapidly from mine spoil and, thus, its rate of attenuation was rapid. Laboratory humidity cell results indicated a similar profile for selenium concentration over time. Adjustment of the laboratory results to estimate field values was accomplished by multiplying concentration by 6.4 and by multiplying time in years by 7.0. With this adjustment, humidity cell results were similar those from the field at a given time.

The laboratory study's estimated field selenium concentrations increased to a maximum value of 25.8 µg/L within seven years. Results of the mine outlet study indicated that the average selenium value reached a maximum of 26.3 µg/L. Selenium concentrations in both the laboratory and outlet studies declined after year seven to about half the maximum values by year seventeen. By year 23, nearly all samples had declined to the regulatory limit of 5 µg/L and to near zero by year 25.

The watershed study lacked data from the early stages of mining and the first sample occurred about seven years after initial mining. Nonetheless, from that point forward, selenium concentrations decreased to the compliance level by year 23 and to extinction by year 25.

Twenty three years after initial mining, 97% of samples were below the regulatory compliance level of 5 µg Se/L. After three initial leach cycles, the ratio sulfur:selenium obtained in the laboratory study stabilized at about 1,700:1 for the duration of the study. This suggests a common mineralogy, most likely replacement of sulfur with selenium in Fe<sub>x</sub>S/Se.

This study was conducted on one of the largest surface mines in the eastern United States. It covers 6,000 ha and has been mined since 1977. Sixty seven outlets were sampled over an eight-year period yielding 5,388 mine water samples. While these results are likely robust, analysis of additional coal mines and geologies is encouraged. Study of mine spoil weathering under field conditions has traditionally suffered from the lack of reliable records over the needed time intervals. By segregating a large number of samples according to age class, this study identified a procedure for conducting long-term weathering studies with data collected over relatively short (eight-year) sampling intervals.

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