Proceedings America Society of Mining and Reclamation, 2004

A PRELIMINARY STUDY ON THE SPECIATION OF SELENIUM IN A WEST VIRGINIA WATERSHED[1]

Dorothy J. Vesper[2], Gary Bryant, Paul F. Ziemkiewicz

Abstract. The presence and chemistry of selenium (Se) has undergone considerable investigation in the western U.S. coal mining regions and in irrigated agricultural lands. Se is also present in West Virginia coals but its distribution and transport has received little attention to date. The recently completed Environmental Impact Statement (EIS) on Mountaintop Mining and Valley Fills (MTM/VF) reported Se in stream waters at concentrations up to 50 µg/L (USEPA, 1999). The streams with the elevated Se concentrations are located in watersheds impacted by MTM/VF in south-central West Virginia. Our ongoing work reviews the literature on Se in mine settings, and applicability of this largely western U.S. literature to the Appalachian geologic setting. This paper also reports our preliminary data for Se speciation in streams in southern West Virginia.

Additional Key Words: trace metals, coal mining

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[1] Paper was presented at the 2004 National Meeting of the American Society of Mining and Reclamation and The 25th West Virginia Surface Mine Drainage Task Force, April 18-24, 2004. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502

[2] Dorothy J. Vesper, Assistant Research Professor of Geology and WV Water Research Institute, West Virginia University, Morgantown, WV, 26506 Gary Bryant, Consulting Research Associate, WV Water Research Institute, Morgantown, WV 26506 Paul F. Ziemkiewicz, Director, WV Water Research Institute/National Mine Land Reclamation Center, Morgantown, WV, 26506.

Proceedings America Society of Mining and Reclamation, 2004 pp 1950-1959
DOI: 10.21000/JASMR04011950
`https://doi.org/10.21000/JASMR04011950`

Introduction

Selenium (Se) is a pervasive trace metal in geologic materials and the environment. It is an essential nutrient at low concentrations and toxic at high concentrations (McNeal and Balistrieri, 1989). To date, much of the research considering Se in the U.S. has been conducted in reference to two areas in which elevated concentrations of Se have been identified: irrigated lands and coals in the western U.S. Although Se is also known to be present in West Virginia coals (WVGES, 2003), the focus to date has been on total Se concentrations and not on its mobility and environmental fate.

Objectives

There were two primary objectives to this work. The first objective was to evaluate the existing literature on Se speciation in western U.S. settings and compare it to WV coals and environmental settings. Our second objective was to begin to determine the transport and mobility of Se in association with WV coal mines and associated valley fills.

Background

Most of the Se research conducted to date has focused on either agricultural drainage water or western U.S. coal mines. California's Kesterson Reservoir, located in the Kesterson National Wildlife Refuge, received Se-containing agricultural drainage water from the San Joaquin Valley. The toxic effect of Se on waterfowl in the reservoir was identified in the early 1980s (Fujii and Deverel, 1989; Weres et al., 1989). Since that time, numerous studies have been conducted regarding the source of the Se, its mobility, and its speciation and cycling within the reservoir (Weres et al., 1989). The storage of Se within the reservoir sediments has been attributed largely to its association with organic carbon. Solubility of Se has been shown to increase with the presence of organic compounds, polysulfide ions, and increasing pH (Weres et al., 1989).

While Se in coal has been investigated throughout the western U.S., the Powder River Basin has been a focus of numerous studies. Recent work by Vance et al. (1998) considered the sources and mobility of Se from backfilled overburden materials. Using a selective extraction procedure they identified seven possible forms in which Se may be held by the backfill. Most of the Se was water soluble, bound into organic matter, associated with iron oxides/acid-volatile sulfides, or in the crystalline sulfides/refractory minerals. The distribution between the forms varied with location. The Se in these materials can be released when the backfill is subjected to different chemical conditions (redox, pH, saturation) and its mobility is then controlled by the formation of organic/inorganic species, sorption/desorption, and precipitation/dissolution (Vance et al., 1998). Dreher and Finkelman (1992) conducted a similar study of backfilled overburden and found that the most common forms of Se were water soluble, ion exchangeable and organically-bound. In this study the authors concluded that the Se in ground water was from two sources: oxidation of Se-pyrites when they are moved from their original location and dissolution of soluble salts when they are exposed to water. In another study of overburden in the Powder River Basin (Naftz and Rice, 1989) the authors conducted a factor analysis of the overburden chemistry in which they identified two primary factors: (1) Se association with detrital material in the coal – the Se is interpreted to have been transported into the system in a dissolved form in association with the clastic detrital material, (2) Se association with organic carbon. The second factor is further corroborated by a statistically significant correlation between the Se concentration and the organic carbon content.

Coleman et al. (1993) reviewed the Se data from 9000 coal samples throughout the U.S. and found the highest concentrations of Se in coal were in Texas and Mississippi. In fact, the average concentrations of Se in Appalachian coals were higher than those from the Powder River Basin (Table 1). Fourteen bituminous coals from Virginia and West Virginia were included. Their Se concentrations did not correlate with ash yield, pyritic sulfur or organic sulfur even though the sulfur parameters are strongly correlated to Se concentration in coal data from the Power River Basin (Coleman et al., 1993).

The West Virginia Geologic and Economic Survey, (WVGES, 2003) reports Se concentrations from 845 coals with an average concentration of 4.2 mg/kg which is higher than the regional average reported by Coleman et al. (1993). The highest concentrations were generally from middle to upper Pennsylvanian rocks and are typically found in the south-central regions of the state (esp. the middle Pennsylvanian Allegheny and upper Kanawha coals). The WVGES findings agree with the conclusions based on regional data: that Se concentrations do not correlate with ash yield, total sulfur or pyritic sulfur.

Table 1. Concentrations of Se in coals according to Coleman et al., (1993)

Location	Number of Samples	Geometric mean (mg/kg)	Arithmetic mean (mg/kg)	Maximum (mg/kg)
Power River Basin	819	0.66	1.1	13
Northern Appalachians	1654	2.9	3.8	75
Central Appalachians	1921	2.9	3.8	18
Southern Appalachians	1039	1.9	3.3	20

The source of Se in the coals can be from detrital materials, original organic sources, volcanic ash deposition, or interaction with water (Coleman et al., 1993). The distributed forms of Se in the studies by Vance et al. (1998) and Dreher and Finkelman (1992) indicate that each of these plays a role in the current distribution of Se in the mined coals and backfills (with the exception of volcanic contributions which were not directly addressed). Se is often interpreted to be associated with sulfur because the ions are similar in both ionic size and electronegativity (Berrow and Ure, 1989). The association can be either as Se substitution into sulfide minerals or into organic compounds. However, if oxidation occurs and the Se is released, both Se and S will be present in water in the anionic form and hence their chemical cycles are typically decoupled and their post-weathering mobility is not necessarily related (Berrow and Ure, 1989).

Preliminary Study of Se Speciation in South-Central West Virginia Watersheds

Sample Collection and Laboratory Methods

The recent EIS on Mountaintop Mining and Valley Fills in Appalachia (USEPA, 1999) identified Se in surface watersheds in south-central West Virginia. Total (digested) Se was detected in streams and impoundments over an 8-month period at concentrations up to nearly 50 μg/L. The highest concentrations were found in creeks containing valley fills and in sediment control structures.

For our preliminary study, we sampled five locations that matched those in the EPA EIS report in the Mud River Watershed (Fig. 1). All locations were from surface streams except for MT-24 which was collected from a settling pond at the toe of a spoil pile. The samples were field filtered and thus the samples represent the “dissolved” concentration. A split sample was collected at each location and submitted to Sturm Environmental Services laboratory for analysis of dissolved-inorganic Se to compare with the speciation data.

Selenium concentrations were measured at West Virginia University using a Varian hydride-generation atomic adsorption spectroscopy (HG-AAS). The advantage to using the HG-AAS is that it achieves low detection limits (~0.5 μg/L) and only detects selenite (Se^{4+}).

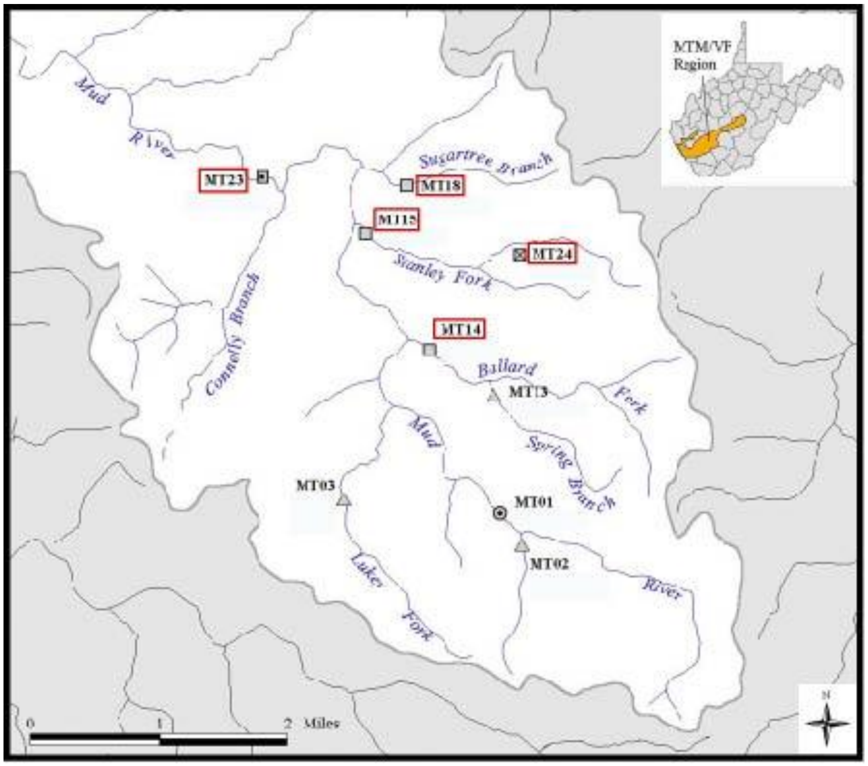

Figure 1. Location of water samples collected during this preliminary study (in red boxes). Locations were selected to match the EIS conducted by the EPA. Map modified from USEPA (1999).

The inorganic speciation was determined by (1) analyzing one sample aliquot on the HG-AAS without modification to obtain the selenite species, and (2) in a second sample aliquot, converting the selenate species to selenite and then analyzing on the HG-AAS to obtain the total inorganic selenium concentration (Fig. 2). Initially, we attempted to reduce the selenate to selenite by adding reagent-strength trace-metal grade HCl to a sample aliquot, and heating the mixture in a 85 C water bath for 20 minutes. This approach is similar to methods used by other researchers (Reddy et al., 1995; Tamari, 1998). Standards for testing the laboratory methods were made for both inorganic species using powdered Na_2SeO_3 and Na_2SeO_4. Based on our initial method tests, we found that the selenate species was not fully reducing to the selenite species. In subsequent tests we found that we obtained full reduction by adding 30 mL of acid to 30 mL of sample, heating the samples to 95C for 60 minutes on a EPI Modblock Heater (rather than in a water bath), and then bringing the sample back to volume.

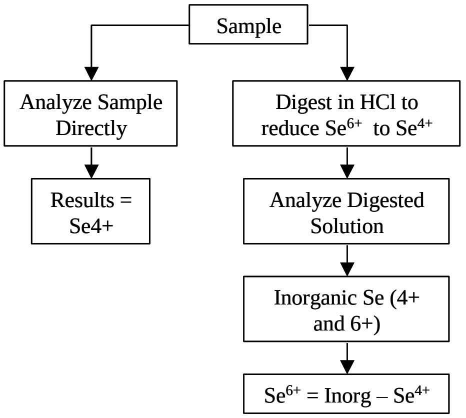

Figure 2. Procedure used to speciate inorganic selenium in water samples.

Results and Discussion

The screening data, historical data from the EPA report, and the inorganic Se concentrations from Sturm Environmental Services are included on Table 2. The results of the speciation study are illustrated on Fig. 3.

Data quality was determined via a filter blank, split samples to a commercial laboratory, blind standards submitted to the speciation process, and replicate field samples. The filter blank was collected in the field with the other samples to determine if either the filter or the ambient conditions caused any sample contamination. It was below detection for Se indicating these issues were not a problem. A split sample from each field location was submitted to Sturm Environmental Services for analysis of inorganic Se. The total inorganic concentration from the speciation study is typically slightly higher then the paired concentration from the commercial laboratory. Accuracy in the method and analysis was determined by including samples of known concentration and speciation in the study (sample T2-1 and T2-2 on Fig. 3). Precision was determined by digesting and analyzing replicate samples. The replicate results had relative standard deviations generally within 25% but with two noticeable outliers. The Se^{4+} concentrations for MT-18 were 27 and 102 μg/L (Sturm detected 26 μg/L Se). The highest value is excluded from Fig. 3 for clarity but it should be noted that the conclusions of the speciation study do not change due to this sample error. The triplicate samples at MT-14 also had a high relative standard deviation for Se^{4+} but the concentrations were at or below the detection limit.

Table 2. Summary of Se in Mud River Watershed, September 2003

Location	Field Data (9-03)				Se (μg/L)	
	Temp (C)	pH	SpC (μS/cm)	Eh (V)	Historic EIS Mean[†]	Sturm[‡]
Filter	---	---	---	---	---	<2
MT-14 (stream)	17.9	7.86	1045	0.479	1.9	<2
MT-15 (stream)	17.3	8.10	1847	0.443	12.1	13
MT-18 (stream)	15.7	7.62	1646	0.342	36.8	26
MT-23 (stream)	16.7	7.13	1008	0.452	12.9	12
MT-24 (near pond)	22.8	7.61	1162	0.475	32.6	6

[†] EIS Mean - EPA Mean is the average value reported in the EPA Mountaintop Mining/Valley Fill EIS (USEPA, 1999). Values below detection not used in calculating average concentrations. These values are for the total (digested) concentration and include all Se species.

[‡] Split samples from Sept 2003 analyzed by Sturm Environmental Services, Inc., Bridgeport WV (using EPA Method 270.2, Graphite Furnace AA). These values are for the dissolved (filtered) concentration and include all Se species.

Overall, although error is present in the speciation process, the variability due to the error is less then the variability between samples (Fig. 3) and thus the data can be used for preliminary interpretation of Se speciation in the field.

In general, the data indicate that the inorganic Se is primarily in the oxidized form. Several similar studies in the Powder River Basin (Dreher and Finkelman, 1992; Naftz and Rice, 1989; Reddy et al., 1995) have also found that Se in ground and surface water is primarily in the oxidized selenate form. This relationship is less true for two samples: MT-14 was more evenly split between reduced and oxidized species – but may be too close to the detection limit for accurate speciation; and MT-24 was collected near a pond at the toe of a spoil pile (this location may not be an exact match to MT-24 in the EPA report). It is possible that the pond chemistry has altered the speciation condition given that pond sediments are often highly reducing. The sediments studied in the Kesterson Reservoir by Fujii and Deverel (1989) typically contain Se in the reduced form (often Se^o).

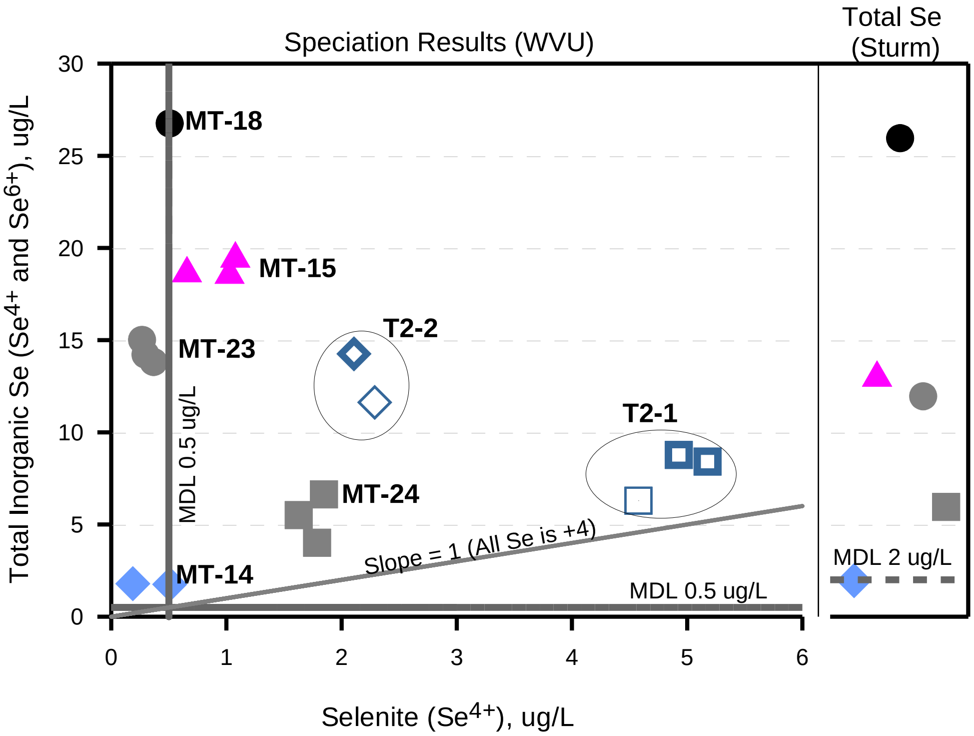

Figure 3. Results of the speciation study and quality control samples. MDL=Method detection limits, T2-1 and T2-2 were prepared standards – the thick-lined symbols are the measured concentrations, the thin-lined symbols are the known concentrations.

Summary

While the chemical relationships (e.g., Se to pyritic-S) are less clear for the West Virginia coals then those from the Powder River Basin, it is clear that the potential sources are the same and the Se mobilization chemistry is consistent. Our data from the Mud River in south-central WV show that the Se in surface water is generally in the oxidized selenate form, a finding consistent with speciation studies of Se in ground and surface water in the Powder River Basin.

Acknowledgements

This work was supported by the U.S. Department of Interior Office of Surface Mining and the National Mine Land Reclamation Center at West Virginia University.

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