THE OCCURRENCE AND IMPACTS OF SELENIUM IN AQUATIC SYSTEMS DOWNSTREAM OF A MOUNTAINTOP MINING OPERATION IN CENTRAL APPALACHIA[1]

R.R. Maggard[2]

Abstract: The occurrences of low levels of selenium (<25 µg/l) were detected in central Appalachian streams during the data collection for the Mountaintop Mining Environmental Impact Study. The study was conducted as part of a settlement in a lawsuit alleging "Clean Water Act" and "SMCRA" violations related to the construction of valley fills. Most of the areas east of the Mississippi River have been characterized as being low or even deficient in selenium. During the past twenty-five years the role of selenium has changed from being considered a toxic element to now being considered a necessary micronutrient that is important for biological functions. The current water quality standard for selenium is 5 µg/l, which is lower than the levels measured in some streams in the study area of central Appalachia. Typically, areas west of the Mississippi River have higher naturally occurring soil selenium concentrations. In a few areas some streams have selenium concentrations as high as 500 to 1000 µg/l. The sources of selenium in the central Appalachian area are related to several anthropogenic activities. These sources can range from the weathering of exposed soil and rock created from various surface disturbance activities to runoff from domestic animal feedlots. The concentrations in soil, rock, and coal can range from < 0.5 mg/kg to as high as 21 mg/kg. The exact path in which the selenium becomes part of the water column is currently being evaluated. The impacts of these low levels of selenium on aquatic life are nearly indistinguishable from other contaminants (high suspended solids or high total dissolved solids), which also occur in these streams. Elevated levels of these parameters will usually result in more significant aquatic degradation than can be correlated with low selenium concentrations.

Additional Key Words: valley fill, total suspended solids, total dissolved solids, anthropogenic activities, coal mining.

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[2] Randall R. Maggard, Manager of Environmental Compliance, Argus Energy WV LLC. Rt. 1, Box 155, Dunlow, WV 25511

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Introduction

A great deal of controversy has been generated over the "discovery" of low levels of selenium (<25 µg/l) in small streams downstream of several mountaintop mining operations in southern West Virginia. This discovery occurred as a result of water quality data collected for part of the Mountaintop Mining Environmental Impact Study. This incident occurred because analysis down to the part per billion (ppb) or microgram (µg/l) level for selenium had never been performed as part of ongoing NPDES or SMRCA permitting activities. More common contaminants like iron, manganese, and aluminum are typically more of a concern downstream of coal extraction activities. Selenium had typically been associated with coal combustion byproducts such as bottom ash and fly ash. With the selenium content of coals well documented and the concentrations being increased as a result of burning, this parameter was usually seen as a problem for the electrical utilities. In hindsight, it is not surprising that when analyzed down to the part per billion level that detectable amounts of selenium were found downstream of coal extraction areas. The levels of selenium contained in coals and the organic shales associated with them can reach concentrations as high as 20 mg/kg. Now the concern is whether these levels of contamination cause adverse impacts and whether these impacts are measurable.

Objectives

The purpose of this paper is to share the results of an investigation of potential sources of selenium that could be associated with a coal extraction operation and the results of any measurable impacts on the aquatic systems downstream of the facilities. The focus of the analytical work was the source of the selenium so no speciation of selenium has been performed to date.

Methodology for Selenium Analysis

The solid samples (coals, overburdens, soils, substrates) were composites collected using methods approved for coals and soils. The samples were prepared for analysis using SW-846

Method 3050B. This is an acid digestion involving nitric acid, hydrogen peroxide and the application of heat. After digestion, the resulting extract is then analyzed for selenium using method SW 7740. This method utilizes Graphite Furnace Atomic Absorption Spectroscopy. The minimum detection level for this procedure was 0.5 mg/kg.

The water column samples were grab samples collected at various locations near the mining operation. The samples were preserved with nitric acid and transported to the laboratory by approved methods. The samples were digested for total selenium using EPA Method 200.2. This is an acid digestion that utilizes nitric and hydrochloric acids and the application of heat. The resulting extract can then be analyzed for selenium using any one of EPA Methods 270.2 (Graphite Furnace Atomic Absorption Spectroscopy), 200.9 (Stabilized Temperature Graphite Furnace Atomic Absorption Spectroscopy) or 200.8 (Inductively Coupled Plasma-Mass Spectroscopy). The minimum detection level for these procedures was 2µg/l.

The Selenium Source

The analytical data presented in this paper was gathered at a large-scale coal mining facility located in southern West Virginia. This facility uses several mining methods that range from conventional room and pillar underground mining to surface contour and mountaintop mining. The operation also contains a preparation plant, coarse refuse fill, slurry impoundment, and numerous haul roads and valley fills. This operation encompasses several thousand acres and has been ongoing for over 17 years with over 35 million tons of coal extracted. This facility also conducts detailed bio-monitoring each spring and fall, which involved analysis of habitat, water chemistry, benthic macroinvertebrates, and fisheries. After the issue of selenium arose, an analysis of various potential sources was conducted with practically all samples of solid material being reported as non-detect (<0.5 mg/kg) except from the coal and refuse samples. The results of the coal and refuse samples varied from 1.5 mg/kg to a high of 21 mg/kg of selenium (see Table 1).

We see that in the region of MTM/VF mining, the coals can contain an average of 4 ppm of selenium, normal soils can average 0.2 ppm and the allowable water quality limits are 5 µg/l (0.005 ppm). Disturbing coal and soils during MTM/VF mining could be expected to result in violations of the water quality limit for selenium (Bryant, et. al, 2002). Based on this information, similar concentrations can be expected below any land-disturbing activity in the Appalachian region.

TABLE 1. Results of selenium analysis on various solid samples at a coal extraction facility. MDL 0.5 mg/kg.

Sample Identification	Date	Selenium (mg/kg)
Maynard Slurry	11/17/2003	10.8
Maynard Slurry	9/10/2003	1.4
Maynard Slurry	10/17/2003	5.3
Mixed Refuse (Pyrite Nodule)	9/10/2003	21.5
5-Block Rider	10/17/2003	<0.5
5-Block Raw Mix	9/10/2003	3.9
5-Block Raw Mix	10/17/2003	4.1
Coal Mix (clean)	9/10/2003	3.3
Coal Mix (clean)	10/17/2003	3.8
Coalburg Raw Mix	9/10/2003	3.9
Coalburg Raw Mix	10/17/2003	4.2
Mixed Coarse Refuse	9/10/2003	9.2
Mixed Coarse Refuse	10/17/2003	10.1
5-Block Sandstone	9/10/2003	<0.5
A-Horizon Soil	9/10/2003	<0.5
B-Horizon Soil	9/10/2003	<0.5
Magnalime (alkaline amendment)	9/10/2003	<0.5
Limestone Road Gravel	9/10/2003	<0.5
Steel Slag Road Gravel	9/10/2003	<0.5
Road Sump Mud	9/10/2003	<0.5

During the analysis of various potential sources for selenium, water column samples were also collected. An interesting finding was that even though both the coarse and fine refuse contained from 1.5 mg/kg to 10.5 mg/kg of selenium, the water in the pool of the refuse impoundment and emanating from the toe of the embankment reported results of non-detect (<2 µg/l). It would appear that any selenium detected downstream of such facilities may be associated with suspended fine particles of coal or clays.

The substrate of the streams upstream and downstream of the mining operations were also sampled and analyzed for total selenium. Samples were collected at the same locations where the bio monitoring was being conducted. A sample was collected at a riffle area and a sample was collected in a pool area to represent various substrates present in a stream system. All of the samples except one, which was located on an unmined reference stream, resulted in non-detect (<0.5 mg/kg). This indicates that very little, if any, of the selenium released during mining activity was being retained in the substrate.

Selenium in Aquatic Systems

Selenium is one chemical for which 304(a) aquatic life criteria have been derived, but which is currently undergoing review by USEPA. Selenium exhibits a number of chemical and toxicological properties that complicate the derivation of numeric aquatic life criteria. Among these are: (1) its existence in at least four different oxidation states in the environment, (2) its propensity to bioaccumulate in aquatic food webs, and (3) its ability to convert to different chemical forms (USEPA, 1998). Based on these statements, using data from coal combustion ash ponds to correlate to potential toxic effects at coal extraction facilities is very presumptuous. The effects of combustion on selenium forms are probably very relevant to their potential toxicity. Very little, if any, data has been published relating to selenium entrained within the natural coal matrix, or the toxic effects, if any, in aquatic systems. The cases of reproductive failure in fishes cited by Lemly (1999) in coal ash disposal ponds cannot be correlated to coal extraction facilities. A fisheries study conducted by USGS on Kanawha River streams as part of the Mountaintop Mining EIS (USEPA, 2003) clearly demonstrates that selenium concentrations have not adversely affected the fish community in that watershed.

Fisheries studies conducted at the coal mining facility located in southern West Virginia provided similar results. The studies were performed at several locations in the streams above and below discharges from the mining and processing operations. This facility has been on going since 1987 and the fisheries studies cited here were conducted in April 2001. Considering that this mining complex has been in operation for 14 years, any cumulative effects of selenium discharges should be easily found.

A survey by REI Consultants (2001) indicated the stream has an abundant and healthy fisheries community. It noted 26 taxa with a species diversity of 3.80 and an Index of Well-Being (IWB) score of 12.64. Over fifty water chemistry samples collected in the watershed as recently as January 2004 range from <1µg/l to a high of 10µg/l, which is above the water quality criterion of 5µg/l.

Another survey performed by United States Department of the Interior, Fish and Wildlife Service (USFWS) during the spring and summer of 2003 was made available to the author in January 2004. This study (USFWS 2004) was conducted in some of the same streams studied by REI Consultants in 2001. The purpose of the USFWS study was to determine if the waterborne selenium downstream of valley fills was accumulating in fish tissues to ecologically relevant levels. A portion of the survey included East Lynn Lake and Beech Fork Lake and one stream in each of their watersheds (Trough Fork and Miller’s Fork, respectively). The East Lynn watershed is heavily mined by the same large scale mining facility previously mentioned in this paper, while the Beech Fork watershed is relatively undisturbed by mining. The sampling in the lakes targeted bluegill, large mouth bass, gizzard shad, and white crappie. The samples included whole fish, fillet (left side, skin on, scaled), and eggs. The samplings in the stream fish targeted primarily creek chubs and blacknose dace and were sampled as whole fish.

Selenium was present in all fish samples. As a guideline for evaluating the ecological significance of the selenium concentrations, the report cited Lemly (2002). Based on a synthesis and interpretation of scientific literature, Lemly has established “toxic effect thresholds for selenium in aquatic ecosystems,” which he describes as “levels at which toxic effects begin to occur in sensitive species of fish and aquatic birds. They are not levels that signify the point at which all species die from selenium poisoning” (p.31). Lemly’s values and associated biological effects in fish are 8 ppm dry weight (dw) for fillets (reproductive failure); 10 ppm for eggs (reproductive failure); and 4ppm for whole fish (mortality of juveniles and reproductive failure). For reproductive failure in birds, Lemly cites 7 ppm in food chain organisms.

No fish or fish eggs collected from Beech Fork Lake (Table 2) or East Lynn Lake (Table 3) contained selenium at concentrations above Lemly's thresholds. Selenium concentrations in creek chub samples from both Trough Fork and Miller's Fork (Table 4) were low relative to Lemly's thresholds.

These fisheries studies seem to conflict with earlier studies regarding selenium toxicity. Some previous studies state that 1 to 5 µg/l can bioaccumulate in aquatic food chains and become a concentrated dietary source of selenium that is highly toxic to fish and wildlife (Lemly and Smith, 1987, Lemly 1993, Lemly 1997). This scenario of poisoning has occurred in reservoirs contaminated by selenium leached from fly ash at coal-fired electricity generating stations in the Eastern U.S. (Garret, 1984, Lemly, 1985). As mentioned before, selenium exhibits a number of chemical and toxicological properties that complicate the derivation of numeric aquatic life criteria (USEPA, 1998). The comparison of selenium concentrations in a water column in a fly ash disposal pond to samples collected in a stream receiving discharges from coal extraction facilities should be reevaluated.

TABLE 2. Beech Fork Lake selenium fish tissue analysis. June 2003 (USFWS, 2004)

Fish species and tissue	Mean fish size (mm)	Tissue Se (ppm, dw)
Bluegill -5 whole fish	100	0.600
Bluegill -3 gravid females	149	0.635
Largemouth bass -3 whole fish	328	0.871
White crappie -5 fish	125	0.600
Largemouth bass - fillets from 1 gravid female	455	1.76 dw, 0.422 ww
Largemouth bass - fillets from 1 gravid female and 1 male	400 (f) 370 (m)	1.26 dw, 0.490 ww
Bluegills-eggs from 3 fish	153	1.08
Largemouth bass -eggs from 1 fish (same fish used for fillet, above)	455	2.06
Largemouth Bass- eggs from 1 fish	400	2.48

TABLE 3. East Lynn Lake selenium fish tissue analysis. June 2003 (USFWS, 2004)

Fish species and tissue	Mean fish size (mm)	Tissue Se (ppm, dw)
Bluegill -5 whole fish	89 - 113	1.60
Gizzard shad- 5 whole fish	89 - 100	3.29
Largemouth bass - 1 whole fish (female, eggs removed)	260	1.72
Largemouth bass - 2 whole fish	272	3.84
White crappie - 2 whole fish	201	0.863
Largemouth bass - fillets from 5 fish	337	3.25 dw 0.772 ww
Gizzard shad - eggs from 1 fish	285	3.54
Largemough bass - eggs from 1 fish (remainder analyzed whole -see above)	260	3.17
Largemough bass - eggs from 3 fish	343	4.73

TABLE 4. Trough Fork and Millers Fork selenium fish tissue analysis. June 2003 (USFWS, 2004)

Fish species and tissue	Mean fish size (mm)	Tissue Se (ppm, dw)
Creek chub - 5 fish (Trough Fork)	7.5 – 10	0.564
Creek chub-5 fish (Millers Fork)	7.5 – 85	0.713

Conclusion

Since the issuance of the 1987 chronic criterion of 5 µg/l, considerable information has come forth regarding the route of exposure of selenium to aquatic organisms. Studies have shown that diet is the primary route of exposure that controls chronic toxicity in fish. The diet control of selenium chronic toxicity in the environment and water-only exposures requires unrealistic aqueous concentrations in order to elicit a chronic response. A water-based criterion is not appropriate for selenium because diet is the most important route of exposure for chronic toxicity (EPA, 2002). Based on these statements and other information presented in the report—that water column concentrations of selenium are not correlated to fish—then the application of the current water quality criteria of 5 µg/l for selenium should be reconsidered.

Further studies should be performed to gather more information on the concentrations and forms of selenium in coals and whether these types of selenium have any toxic effects if released during the coal extraction and processing procedures. Any actions taken to enforce or maintain the current selenium standard of 5 µg/l at coal extraction or processing facilities should be carefully reconsidered.

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