Topic WQ-4

White Paper Topic: Prediction and Treatment of Selenium

Development Team: Hugh Bevans, Steve Parsons, Paul Ziemkiewicz, Bill Winters, et al.

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A FRAMEWORK FOR SELENIUM STUDIES IN THE APPALACHIAN PLATEAUS

Introduction

A recent Environmental Impact Study (EIS) on the effects of mountaintop coal mining in West Virginia showed that concentrations of selenium (Se) in small streams and sediment ponds receiving drainage from valley fills can exceed the aquatic wildlife standard of 5 micrograms per liter (µg/L). Deleterious impacts of this finding have not been observed in the Appalachian Plateaus, but can be implied from other research.

During the past 20 years, scientists from the U.S. Geological Survey (USGS) and the U.S. Fish and Wildlife Service (USFWS) have collaborated on studies to understand the occurrence and impacts of Se in the environment. Initial studies were conducted during 1982-85 at the Kesterson Reservoir, National Wildlife Management Area in the Central Valley of California, where Se leached by irrigation of desert soils caused severe health problems for aquatic wildlife. Studies at Kesterson Reservoir led to the development of the Department of Interior Irrigation Drainage Program in 1985 to investigate impacts of irrigation drainage throughout the western United States.

Se is an essential micronutrient for animals, but it is also known to be the most toxic to mammals of all biologically essential elements; fish and birds are very sensitive to Se contamination in an aquatic environment. Se is passed from parents to offspring in eggs and, during critical stages of development and growth, is substituted for sulfur in amino acids that form structural and functional proteins. As Se exposure increases, toxic effects can range from suppression of the immune system, to reduced juvenile growth, to embryo mortality, to mass wasting in adults, to teratogenesis (lethal or sub-lethal deformities) in juveniles, to juvenile mortality, and finally to adult mortality.

Previous studies have shown that predators are more at risk than their prey. Aquatic organisms strongly bioaccumulate Se, maybe up to thousands of times the water concentration, but are unaffected by residues in their tissues that can cause reproductive failure when consumed by predator fish and aquatic birds. Bioaccumulation in aquatic food chains is the most important rout for the transfer of toxic levels of Se to upper trophic level species, including humans. However, some forage plants accumulate Se from contaminated soils or wastes and are toxic when ingested by grazing animals.

Although there is a significant body of scientific literature on the occurrence and impacts of Se, most of the studies have been in the western United States where climatic conditions generally are drier and there is less biodiversity. This paper will present a framework for investigating Se in the Appalachian Plateaus region of the eastern United States.

SELENIUM RESULTS FROM THE EIS ON MOUNTAINTOP COAL MINING AND OTHER STUDIES

Selenium in Stream Water and Bottom Sediments

Se was analyzed in 213 stream-water samples as part of the EIS; 66 samples, all collected downstream from valley fills, exceeded the aquatic wildlife standard of 5 µg/L. The median concentration of Se detected at EIS sites downstream from valley fills was 11.7 µg/L while the median concentration for un-mined sites was below the detection limit of 3 µg/L. Subsequent sampling by the West Virginia Department of Environmental Protection (WVDEP) detected Se in 126 of 909 stream-water samples and resulted in nine streams being placed on West Virginia's 2002 303(d) list; four are in the Coal River Basin (Beech Creek, Left Fork Beech Creek, Rockhouse Creek, and Buffalo Fork) where 121 of the 126 Se detections occurred, four are in the Guyandotte River Basin, and one is in the Gualey River Basin. During July 2002 through June 2003 all 11 samples from Left Fork Beech Creek exceeded the 5 µg/L Se aquatic-wildlife standard; all four samples collected during February through June 2002 exceeded 35 µg/L (WVDEP). Se detections were most common during low flow; 95 of 126 detections were associated with total suspended solids concentrations (TSS) of 5 milligrams per liter (mg/L) or less; the highest seven Se concentrations were associated with TSS < 3 mg/L. In contrast, when TSS exceeded 50 mg/L (indicating overland runoff) there were only three associated detections of Se.

An ongoing study by West Virginia University (WVU) determined that most (90%) of the Se in water samples from the Mud River is selenate (SeO4 2-) while a Se in water from a sediment pond at the toe of a valley fill was less oxidized, with about 70% selenate. Selenate is generally mobile and occurs in the dissolved state in water.

Se concentrations in ten bottom-sediment samples collected by the USFWS from the Coal River Basin ranged from < 0.229 to 1.49 parts per million (ppm), with a median concentration of 0.416 ppm. Se concentrations in four bottom-sediment samples from the Mud River Basin ranged from < 0.0679 to 0.192 ppm. Se concentrations in 52 fine-grained (< 63 micrometers) bottom-sediment samples collected during the USGS National Water-Quality Assessment (NAWQA) of the Kanawha-New River Basin ranged from 0.3 ppm to 2.4 ppm, with a medium concentration of 0.95 ppm. Correlation analyses showed that bottomsediment Se concentrations were related to the percent of the basin occupied by quarries, coal strip mines, and gravel pits (r2 = 0.529) and to mean annual coal production during 1980-95 (r2 = 0.271).

Sources of Selenium

Se is often associated with organic-rich deposits including coal and black shale, both of which are present in the Pennsylvanian-age rocks that occur at or near the surface in the Appalachian Plateaus province. Available data on the geochemistry of Pennsylvanian-age coal beds show that those very beds that are included in the mountaintop mining sequence (Clarion, Brookville, No. 5 block, Stockton, Coalburg, and Winifrede) have high concentrations of Se; median concentrations in these coal beds range from about 4.5 to 7 ppm and concentrations exceeding 10 ppm have been observed. Of course, during mountaintop mining, this sequence of coals is removed and, therefore, cannot be the source of Se detected in streams draining valley fills during the EIS.

If a specific rock stratum in the mountaintop mining sequence is enriched in Se, then the release of Se to the environment probably could be controlled by materials handling protocols. However, preliminary geochemical analyses of core sections collected through a joint program by the U.S. Geological Survey (USGS), the West Virginia Geological and Economic Survey (WVGES), and WVU indicate that the entire mountaintop mining geologic interval is enriched with Se and that coarser-grained siltstone has the highest concentrations. If these preliminary results indicating enrichment of Se throughout the mountaintop mining sequence hold true, then controlling the release of Se by materials-handling protocols would be problematic. Se may be enriched in wastes from coal-washing operations and in coal ash from power generation.

Selenium in Aquatic Wildlife

Se concentrations in 16 whole-body composite fish samples (ten creek chub, five blacknose dace, and one bluegill) collected by USFWS from ten sites in the Coal River Basin ranged from 0.845 to 6.89 ppm, dry weight; the median concentration was 3.59 ppm. Se concentrations in seven whole-body composite fish samples (five creek chub and two blacknose dace) collected by USFWS from four sites in the Mud River Basin ranged from < 0.481 to 6.85 ppm, dry weight; the median concentration was 4.13 ppm. Se concentrations in 27 fish-liver samples (19 rock bass, six common carp, one smallmouth bass, and one white sucker) collected from 19 sites during the

USGS Kanawha-New River NAWQA ranged from 1.7 to 15 ppm, dry weight; the median concentration was 5.8 ppm. Correlation analysis showed a relation between Se concentrations in livers of Rock bass and stream-bottom sediment (r2 = 0.568).

QUESTIONS CONCERNING THE OCCURRENCE AND IMPACTS OF SELENIUM IN THE APPALACHIAN PLATEAUS

There are many unanswered questions about the occurrence of Se and its impacts on Appalachian Plateaus ecosystems:

1. What are the relations among rock strata and Se enrichment?
2. Are there other trace elements of concern associated with this geologic interval?
3. What is the geographic extent of the Se-enriched geologic interval?
4. What are the background concentrations of Se in streams draining the enriched area?
5. Have land disturbances in the enriched area released Se to the aquatic environment?
6. What is the amount of Se available for leaching from fill materials?
7. What processes (physical, chemical, and microbiological) control the leaching of Se?
8. What is the rate of Se leaching and does this rate decline through time?
9. Are there quantifiable relations between land disturbances (location, extent, and age) and the occurrence of Se in the aquatic environment?
10. What are the concentrations and loads of Se in water from underground mines?
11. What are concentrations of Se in waters from coal-washing operations?
12. What are Se concentrations in leachate from coal ash from power plants?
13. Can we predict the occurrence and transport of Se in the aquatic environment?

Impacts of Selenium

1. What are the food-web pathways for Se in the Appalachian Plateaus?
2. Are there any quantifiable Se impacts to aquatic wildlife in the mountaintop coal-mining area where aquatic-wildlife standards for Se in water have been exceeded?
3. Are there likely to be impacts to aquatic wildlife as land disturbances continue?
4. Are there quantifiable impacts to grazing animals; is there potential for impacts?
5. Can we predict impacts of Se on aquatic or terrestrial wildlife?

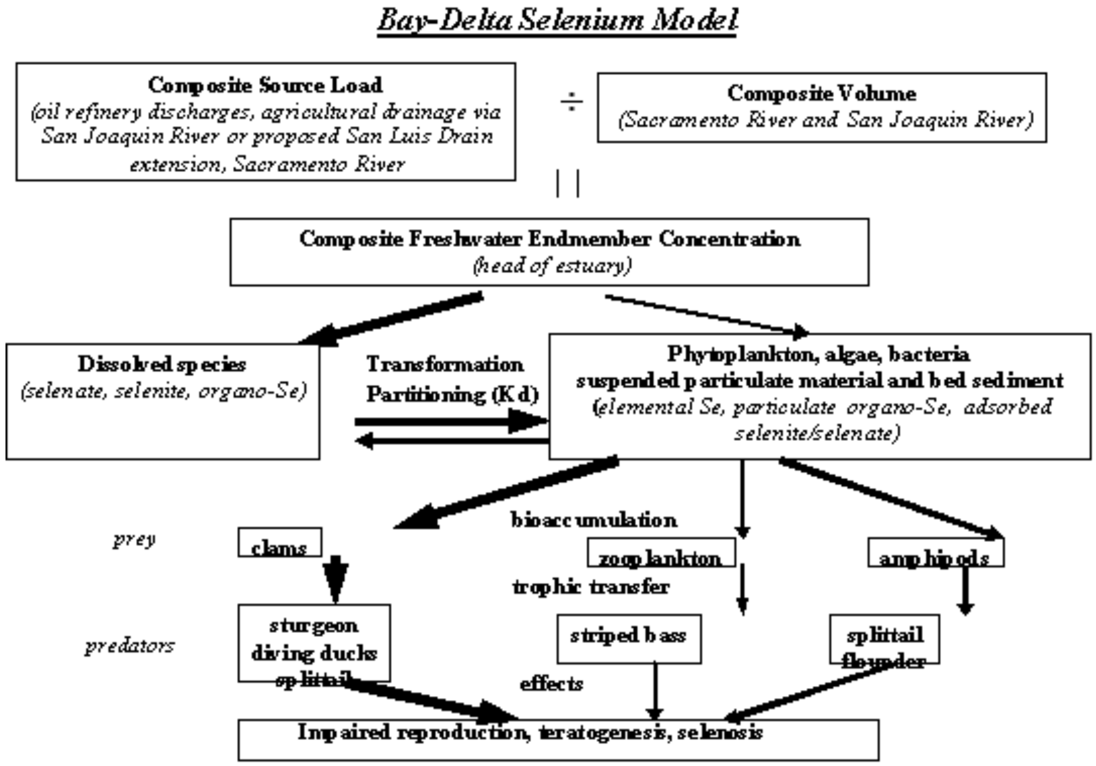
Mitigating / Remediating Selenium Impacts

1. Can Se impacts be mitigated/remediated by materials handling methods?
2. Can Se impacts be mitigated by limiting the extent of disturbances (dilution)?
3. Can Se impacts be mitigated/remediated by water treatments?

FRAMEWORK FOR INVESTIGATING SELENIUM IN THE APPALACHIAN PLATEAUS

An assessment of the occurrence and impacts of Se should:

1. Include the elements of occurrence, impacts, and mitigation discussed above.
2. Encompass the region where surface and near-surface rocks are Se enriched, probably based on coal trace-element and NURE data;
3. Include other trace elements that may be of concern in the region, as identified through a review of available data; and
4. Develop a model for predicting the occurrence and impacts of Se, like the following example for the San Francisco Bay area. A conceptual model for Se in the Appalachian Plateaus Data would be a good framework for designing scientific studies to provide necessary information.
5. Design, implement, and evaluate potential means of remediating Se contamination.



APPROACH

Phase 1 (first year)-- Develop a conceptual "Rock to Duck" Se model; assemble and evaluate available data and literature on Se in coal, rock strata, stream-bottom sediments, and tissues of aquatic and other wildlife; use available data to develop a preliminary model for predicting Se impacts, to estimate the geographic extent of Se enriched geologic sequence, and to evaluate relations among factors controlling the occurrence and impacts of Se; conduct biological impacts reconnaissance; integrate ongoing investigations; plan for Se monitoring and investigations.

Phase 2 (second through fifth years)-- Conduct data-collection activities and studies to provide information necessary to fill in gaps in describing, predicting, and mitigating the occurrence and impacts of Se; complete "Rock to Duck" Se model; report on findings.

Phase 3 (sixth through tenth year)-- Remediate; evaluate remediation; report on findings.

SUPPORT AND FUNDING

Support Pathways

1. Participating Agencies
2. DOI
3. Eastern Mine Drainage Federal Consortium
4. Mid-Atlantic Federal Partners on the Environment
5. Coal Industry

Funding Pathways

1. DOI Initiative
2. Federal Agencies- EPA, OSM, USGS, USFWS, COE, DOT, DOE (NETL)
3. State Agencies
4. Coal Industry
5. Any combination of above sources

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