ARSENIC, SELENIUM, AND ANTIMONY: FROM COAL FIRED POWER PLANTS TO THE CHATTAHOOCHEE RIVER

M. Patrick Lesley and Philip N. Froelich

AUTHORS: School of Earth & Atmospheric Sciences, Georgia Institute of Technology, 311 Ferst Dr., Atlanta, GA 30332-0340.
REFERENCE: *Proceedings of the 2003 Georgia Water Resources Conference*, held April 23-24, 2003, at the University of Georgia. Kathyrn J.Hatcher, editor, Institute of Ecology, The University of Georgia, Athens, Georgia.

Abstract. Dissolved arsenic (As), selenium (Se), and antimony (Sb) fluxes in rivers below ash ponds of coal fired power plants (CFPP) are of magnitude above natural levels. We have estimated the release of As, Se, and Sb from CFPPs to rivers to be 0.73 mg, 0.30 mg, and 0.15 mg respectively per kilogram of coal combusted. Mass balance calculations have revealed that the main sink of metalloids in contaminated rivers is biological removal. Comparison of our release estimates to EPA Toxic Release Inventory estimates suggests that the modeling estimates of metalloid release from CFPPs are too low .

INTRODUCTION

Work conducted by Froelich in the 1980's revealed a large flux of the metalloid germanium (Ge) from CFPPs to rivers. Ge is a trace element in coal along with its toxic cousins As, Se, and Sb. Froelich and Lesley (2001) hypothesized that the processes of ash disposal that mobilized Ge would similarly mobilize As, Se, and Sb.

The main method of fly ash disposal for CFPPs on the Chattahoochee River is wet ash disposal. CFPPs using this system wet sluice ash to holding lagoons situated on the bank of the Chattahoochee River. The pH of these ponds is raised to precipitate hazardous metals such as Cu, Cd, Zn, and Ni. This basic pH mobilizes metalloid elements from solid ash into the dissolved reactive phase. Overflow from ash ponds is drained into local surface. This discharge includes solid ash material as well as liquid effluent.

From May 2001 to June 2002 dissolved metalloid and particulate As, Se, and Sb, and nutrient samples were collected on the Chattahoochee River approximately every 6 weeks (Lesley 2002). The sample sites ranged from north of metropolitan Atlanta at Buford Dam to south of West Point Reservoir in

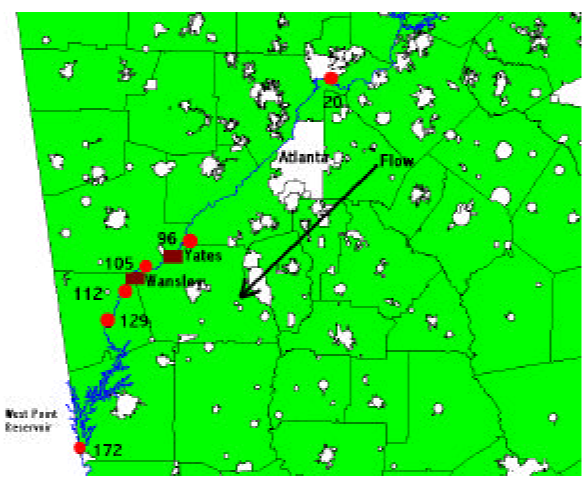

Fig. 1. The Chattahoochee River sampling transect. Brown squares represent CFPPs; red dots represent sampling sites. Sites are labeled using their km points downstream of Buford Dam.

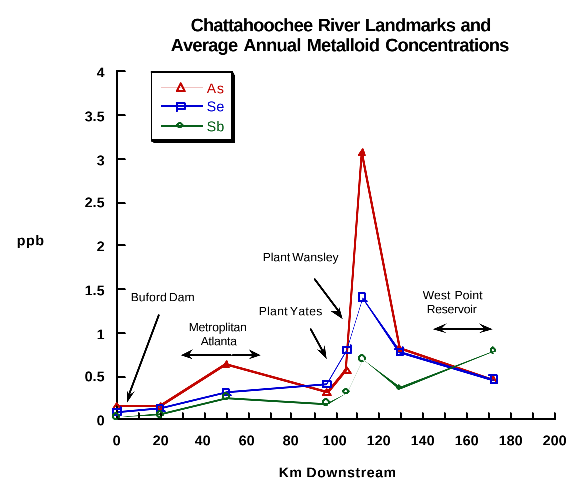

Fig. 2. Profiles of average annual dissolved As, Se, and Sb concentrations in the Chattahoochee River from Buford Dam to West Point, GA.

West Point, GA (Fig. 1). There are two major CFPPs on this transect, Plant Yates (1250 MW) and Plant Wansley (1730 MW). All samples were analyzed for metalloid content by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

METALLOID CONCENTRATIONS AND FLUXES ON THE CHATTAHOOCHEE RIVER

Average annual arsenic, selenium, and antimony concentrations on the Chattahoochee River increase from 0.16 ppb, 0.13 ppb, and 0.06 ppb respectively upstream of Atlanta at Holcomb Bridge (km 20) to 3.07 ppb As, 1.41 ppb Se, and 0.70 ppb Sb below Wansley and Yates CFPPs (km 112) (Figure 2). This increase in concentration is due to effluent from CFPP ash ponds. The relative concentrations of As, Se, and Sb reflect that in coals. occur from greatest to least in that order. This pattern of relative concentrations is found in waters impacted by fly ash pond discharge.

We made quantitative estimates of metalloid discharge from CFPPs to the Chattahoochee River using our concentration data and river flows from the USGS NWIS program. Metalloid concentration (mg/L) is multiplied by river flow (L/s) to obtain flux (mg/s). The difference between upstream and downstream metalloid fluxes gives an estimate of the input or loss of metalloids from the Chattahoochee River. River fluxes of As, Se, and Sb increase from 4 mg/s, 4 mg/s, and 1 mg/s respectively at Holcomb Bridge (km 20) to 159 mg/s As, 69 mg/s Se, and 34 mg/s Sb below Yates and Wansley CFPPs (km 112) (Figure 3). All individual (quasi-monthly) metalloid flux profiles of the Chattahoochee River show a characteristic increase below Yates and Wansley CFPPs.

The difference between up and downstream fluxes is the net input or loss of metalloids over that stretch of river. This is a quantity we term Delta Flux-Δ Flux (Figure 4). Δ Flux profiles of the Chattahoochee River show a positive Δ Flux across CFPPs Yates and Wansley. The Δ Flux below the CFPPs also show the same characteristic ratios of As, Se, and Sb, adding one more piece of evidence that this is a signal from ash pond effluent, not natural rock weathering or effluent from another industrial source.

By summing the Δ Fluxes from Plants Yates and Wansley a total CFPP Δ Flux can be calculated. This total Δ Flux is 130 mg/s As, 55 mg/s Se, and 27 mg/s Sb, corresponding to a total dissolved release of 4.1 tons (metric) As, 1.7 tons Se, and 0.9 tons Sb to the Chattahoochee River from May 2001 to June 2002.

Using these aquatic releases and coal combustion data from Georgia Power, aquatic escape efficiencies for As, Se, and Sb can be calculated. The aquatic escape efficiency is the ratio of the aquatic metalloid release (mg/s) to the amount of coal burned by the power plants (kg/s). The yields the escape efficiency in mg metalloid released per kg coal burned. The aquatic escape efficiencies for As, Se, and Sb are 0.73 mg/s,

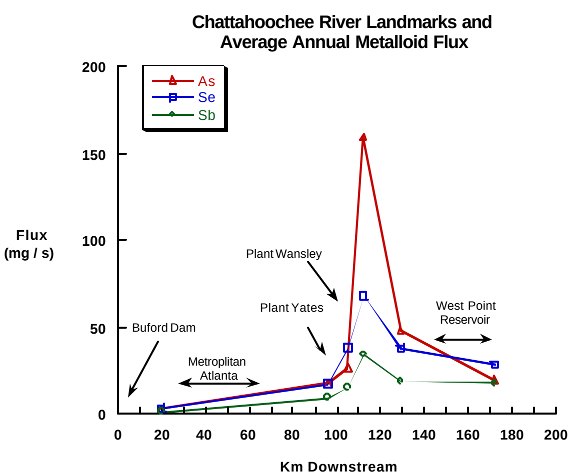

Fig. 3 Profiles of As, Se, and Sb fluxes on the Chattahoochee River from Buford Dam to West Point, GA.

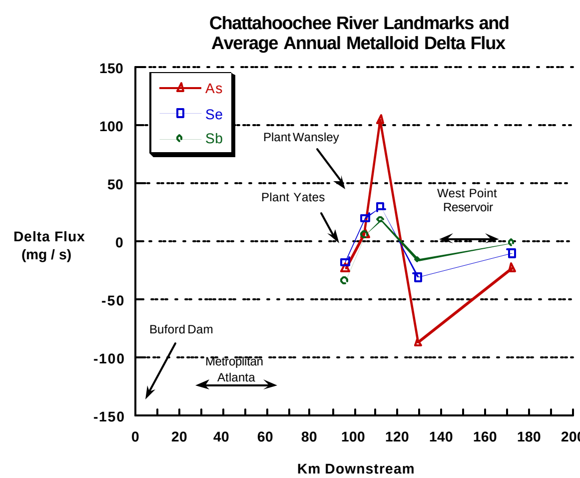

Fig. 4. Profiles of As, Se, and Sb D Fluxes on the Chattahoochee River. A positive D Flux indicates a net input of metalloids to the river. A negative D Flux indicates a net loss of metalloids from the river.

0.30 mg/s, and 0.15 mg/s respectively, representing 7% if the As, 30% of the Se, and 15% of the Sb concentration in coals. Further research on other CFPPs using wet ash disposal systems can help establish if these numbers are global escape efficiencies or if that are applicable only to the plants in this study.

THE FATE OF METALLOIDS IN CONTAMINATED RIVER SYSTEMS

Mass balance modeling of the metalloid fate in the Chattahoochee River has shown that there are three main reservoirs in the river system and six main fluxes into, between, and out of the reservoirs (Fig. 5) (Lesley 2002). Reservoir A is the water of the Chattahoochee River. Reservoir B is the suspended sediments entrained in the flow of the Chattahoochee River. The arrows represent flow past the power plants towards West Point Reservoir. Reservoir C is the bed of the river. There are two metalloid inputs to the Chattahoochee River from CFPPs (Fig. 5). Flux 1 is the solid ash material from ash pond effluent. This flux is directly to the suspended sediment reservoir. Flux 2 is the dissolved component from the ash ponds which goes into the dissolved reservoir of the river. There are three fluxes between the reservoirs of the river (Fig. 5). Flux 3 represents the settling of particulate material onto the bed of the Chattahoochee River. Flux 4 represents the sorption of dissolved metalloids onto suspended sediment. Flux 5 represents desorption of metalloids off of suspended sediment back into the dissolved phase. Flux 6 represents the flux of metalloids out of the river system through biological uptake.

The most important fluxes in this system are 1, 2, and 6. Table 1 shows that the solid metalloids to the suspended sediment reservoir from ash ponds are comparable to the dissolved inputs. In the case of As,

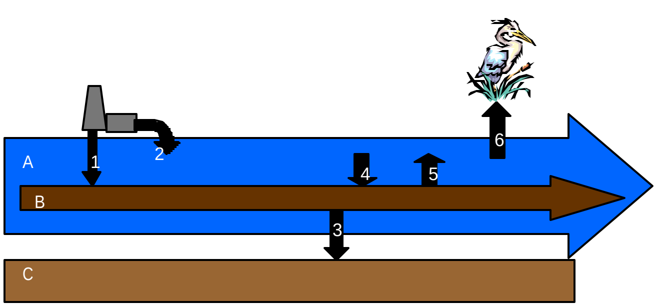

Fig. 5 Diagram of metalloid reservoirs and fluxes on the Chattahoochee River

Table 1. Metalloid fluxes through on the Chattahoochee River. All units are in tons/year.

Flux	1	2	3	4	5	6
As	10.2	4.1	5.3	1.3	5.3	8.8
Se	1.4	1.7	0.7	0.1	1.3	1.5
Sb	0.1	0.9	0.1	0.1	0.1	0.5

the particulate input is greater by more than a factor of 2. This model also predicts that the greatest sink of metalloids in the system is biological uptake. In particular 8.8 tons of arsenic is uptaken by the biological system every year. The settling of metalloid laden sediment onto the stream bed and upper reaches of West Point Reservoir also presents concern as West Point Reservoir is a major source of drinking water for west central Georgia and a major sport fishing locale.

TOXIC RELEASE INVENTORIES (TRI)

Beginning in 1998 the EPA required industrial facilities, including CFPPs, to report their toxic releases under a program called the Toxic Release Inventory (TRI). The basis for CFPP TRI reporting is the mega-watt (MW) of the power plant. Plants larger than 400 MW are required to provide a release estimate for arsenic. For Se the threshold is 1200 MW and for Sb, 4500 MW (Rubin 1999). It is of note that while this study has shown a considerable release of Sb from CFPPs there is no plant in existence larger than 4500 MW, and thus no reporting guideline for Sb.

Table 2 compares the TRI aquatic release estimates for 1998-2000 to the aquatic release estimate calculated using the metalloid escape efficiencies determined during this project. The 2000 TRI estimates are the most recent estimates available at this writing. The As and Se TRI estimates for both plants in 1998 and 1999 are orders of magnitude low as compared to the escape efficiency estimate, assuming there has been no significant change in plant operation. The 2000 Se estimate for Plant Wansley also falls under this category. Of interest are the 2000 aquatic release estimates for arsenic. These estimates are more accurate than the As estimates for the preceding years. The 2000 Plant Yates As estimate is within the error (24.6%) of the escape efficiency estimates. The 2000 Plant Wansley As TRI release estimate is statistically different from the escape efficiency estimate, but the increase in estimated relase from 0 kg / year in the preceding years to 1474 kg / yr is significant and may reflect a change in the modeling parameters used to determine power plant emissions.

THE PISCES MODEL

CFPPs calculate annual metalloid release using the Power Plant Integrated Systems: Chemical Emissions Studies (PISCES) model. This is a thermodynamic model that attempts to minimize Gibbs Free Energy through mass and energy balances. The model predicts that As is partitioned almost exclusively onto fly ash which is supported by escape efficiency calculations. PISCES predicts that Se will be lost via gas emission, however measurements show that Se in equally partitioned between gas and ash which may account for the discrepancy between TRI and escape efficiency estimates (Sandelin and Backman 1999). We hypothesize that partitioning cannot be predicted solely with a thermodynamic model due to the changes in temperature and pressure as gasses and ash are transported through the disposal system, a largely kinetic process.

RAMIFICATIONS FOR ASH DISPOSAL

Disposal of fly ash by wet storage has been demonstrated to be an ineffective way to isolated the harmful by-products of coal combustion from the environment. Since 1990 several CFPPs in the southeast have converted from wet ash disposal systems to dry ash disposal systems in the face of large surface and ground water contamination problems.

Table 2. Comparison of yearly TRI aquatic release estimates to the aquatic release estimates calculated with data from this study. All releases are in kg/yr. NA signifies not available. NR signifies that the element is not required by the TRI for this plant.

Power Plant MW	Element	CFPP Aquatic Release (This Study)	1998 TRI Aquatic Estimate (kg/yr)	1999 TRI Aquatic Estimate (kg/yr)	2000 TRI Aquatic Estimate (kg/yr)
Wansley 1730	As	2650	0	0	1474
	Se	1100	507	207	209
	Sb	550	NR	NR	NR
Yates 1250	As	1450	4	4	1573
	Se	600	NA	NA	NA
	Sb	300	NR	NR	NR

Studies of the Hyco Reservoir, a reservoir in North Carolina experiencing Se toxicity from ash pond effluent, have shown a marked decrease in Se concentration in both water and animal tissue samples since the conversion of the Belews CFPP to dry ash disposal (Crutchfield 2000). The authors have discovered a similar case in GA at the Bowen CFPP. Historic samples of surface waters receiving Plant Bowen ash effluent were among the most metalloid contaminated waters in the world. Since conversion of the plant to dry ash disposal the contamination has disappeared.

Fly ash has a number of industrial uses, including dry wall filling, grade under road beds, and fill under new housing developments. Plant Bowen sells 50% of the fly ash it produces and wishes to eventually sell all of it for industrial use.

SUMMARY

This study establishes large fluxes of As, Se, and Sb from CFPP fly ash ponds to the Chattahoochee River. Fluxes of As and Se from power plants to rivers is greater than estimated in TRI reports. We have also shown that there is a significant flux of Sb to rivers from ash ponds that is currently unregulated. Mass balance calculations show that the primary sink of metalloids in contaminated rivers is biological uptake. The transport of ash and metalloid laden sediment downstream to West Point reservoir is also an issue of environmental concern. Evidence from CFPPs in GA and NC suggest that conversion from wet ash disposal to dry ash disposal and the subsequent sale of ash for industrial use may be an effective key to reducing toxic metalloid contamination.

LITERATURE CITED

Crutchfield, J.U. (2000) Recovery of a Power Plant Cooling Reservoir from Selenium Bioaccumulation. *Environmental Science and Policy*, **3**, 145-163.

Froelich, P.N., Lesley, M.P. Tracing Germanium Contamination From Coal Fired Power Plants Down the Chattahoochee-Apalachiacola River: Implications for the Toxic Metalloids Arsenic and Selenium. *Proceedings of the Georgia Water Resources Conference*, 2001.

Lesley, M.P. *The Fluxes and Fates of Arsenic, Selenium, and Antimony from Coal Fired Power Plants to Rivers.* Thesis, 2002.

Rubin, E. (1999) Toxic Releases from Power Plants. *Environmental Science and Technology*, 33, 3062-3067.

Sandelin, K. and Backman, R. (1999) A Simple Two-Reactor Method for Predicting Distribution of Trace Elements in Combustion Systems. *Environmental Science and Technology*, 33, 4508-4513.