

## ABSTRACT

### Selenium Biogeochemistry in Rivers Receiving Direct Coal Ash Input

Selenium in natural waters as a dissolved ion exists in several oxidation states (-II, selenide; IV, selenite; VI, selenate) and chemical forms within a given oxidation state (e.g., organic and inorganic). This chemical speciation is highly relevant given that its biotic and abiotic reactivity/bioavailability vary with the chemical form. Significantly, the toxicity of dissolved Se is also affected by its chemical speciation. In the particulate state, Se is found in these various oxidation states (plus the elemental form, Se(0)), and studies of particulate Se's bioavailability and trophic transfer through the food web show a strong dependence on chemical speciation. Thus, any study of Se in natural waters must consider chemical speciation in both the particulate and dissolved phases. The 22 December 2008 release of coal ash (fly and bottom ashes) from the Tennessee Valley Authority's Kingston (Tennessee) Fossil Plant into the Emory and Clinch Rivers represents a potentially large input of toxic trace elements to this aquatic ecosystem. Oxyanions such as selenium are particularly soluble in coal combustion products due to the alkaline nature of the materials, and therefore this spill may be a major input of selenium to these rivers. However, the biogeochemical cycling of selenium in lotic (rivers and streams) waters has received little attention, with most research being on lakes and reservoirs (lentic), and the ocean.

Due to the fact that most studies of selenium cycling related to coal-fired power plants have dealt largely with lentic systems, and only considered dissolved inputs, the Kingston Fossil Plant/Emory River incident is rather unique and requires a modified approach to that used with lakes and reservoirs. In this respect, the particulate input from the coal ash release has to be the focus since most of it will enter river sediments and represents a long term source of contamination. Moreover, the net effect of transformation processes for selenium in the aquatic environment and their rates will be highly modified by the water residence times (e.g., flow rates). Therefore, a 3 year study of the Emory and Clinch Rivers system (upstream of the spill to act as a control, and downstream to highlight contamination processes) is proposed as an environmental test bed that will carefully integrate field and lab work to address the Overall Objective: **Qualitatively describing the processes affecting selenium cycling and quantitatively determining the rates of processes for this cycle in a freshwater aquatic system that has received selenium inputs via direct coal ash deposition.** Within this objective, several Questions will be addressed: (1) What is the speciation of dissolved and particulate selenium in this aquatic system and can it be used to trace ash input? (2) Is the biogeochemical cycle of selenium in a lotic system fundamentally different than that in lentic waters? (3) What are the rates of processes in selenium's biogeochemical cycle (e.g., regeneration of particulate organic selenide to dissolved organic selenide) and are they functions of environmental variables such as temperature and oxygen concentrations? To meet this objective and answer the questions, seasonal field work will include sampling waters for dissolved and particulate selenium species and ancillary parameters, and sediments for solid phase selenium speciation, dissolved porewater selenium, and relevant ancillary parameters. Laboratory experiments will measure the rates of selenium release from suspended matter, sediment-water fluxes, and related variables. At its conclusion, the ultimate goal of this research will be to allow effective management and remediation of future coal ash inputs.