



WATER RESOURCES RESEARCH GRANT PROPOSAL

Project ID: 2003LA18B

Title: Metal Speciation in Particulates in the Mississippi River in Louisiana

Project Type: Research

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Congressional District: 6

Principal Investigator:

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Abstract

Metals are transported in the Mississippi River water principally as dissolved and adsorbed species. Some amount of transport may also take place as small mineral fragments. Adsorbed species are those attached to the suspended particulate matter (SPM) in the water. The SPM includes silt- and clay-sized mineral particles in suspension in the flowing water. Mineralogically, the SPM consists of quartz, feldspars, and clay minerals, the stable silicates and alumino-silicates on the Earth's surface. The mineral grains are often coated with iron and manganese hydroxides which aid the adsorption process. The colloidal fraction, extending in size down to a few nanometers, may also be included in the SPM as it is also important to transportation by adsorption. Most elements are significantly partitioned onto the SPM and thus it is the major carrier of metals in the Mississippi.

The distribution of metals between the dissolved and the adsorbed fractions has mostly been determined by separating water samples into different fractions based on filter size followed by bulk chemical analysis of each fraction. The metal adsorption process can be further characterized by sequentially extracting the metals from the SPM in various (mostly) acidic media. Some speciation information has lately been obtained using voltammetric stripping analysis. All these techniques are operationally defined and the

correspondence between the results obtained by them and actual speciation is unclear. The adsorption processes of various metals are thus not very well understood. It is also suspected that the dissolved fraction contains metals adsorbed onto the colloidal fraction which is too small to be retained on filters (<0.45 or 0.4 μm) normally used.

X-ray absorption spectroscopy (XAS) is an element-specific analytical technique which can be used to probe the local structure around atoms. Speciation information, for example the oxidation state, and the location of an atom relative to other atoms, i.e., whether an atom is adsorbed onto a surface or within a crystal structure, can be obtained by XAS. XAS can be used to study solid, liquid or gaseous samples with practically no sample preparation. Thus Mississippi River water samples can be directly studied. The evidence obtained by this method is more direct than most other techniques. A wide range of elements over a large concentration range can be studied by XAS. The XAS signal from an element in a sample is also additive, thus the phases in which the element is present can be identified and quantified.

Systematically sampled Mississippi River water will be studied by XAS at the J. Bennett Johnston Sr., Center for Advanced Microstructures and Devices. The adsorption processes of heavy metals such as Cr, Cu, Pb, Zn, etc. on the SPM will be investigated. The importance of the coarser SPM, particularly the silicate minerals, the iron and manganese hydroxides, and the colloidal fraction (<0.45 μm) can be clarified. In addition, the transport of P, an important nutrient in the River water, can also be investigated by XAS.

The study will result in an improved understanding of the metal transport processes in the Lower Mississippi River. This understanding will result into better models of the metal transport processes and can also help in improving the quality of the River water.

Some specific problems have been identified for study. Engineered media and barriers, particularly iron- and manganese-coated material for storm water treatment, will be investigated. The effect of variable redox condition on the adsorption of metals such as Cd, Cu and Zn by these media will be examined.