

## Source, transport, and matrix controls on metal bioavailability in floodplain soils

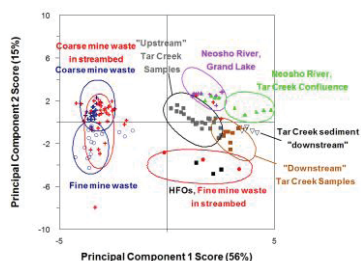
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With the deposition of metal-bearing sediments from upstream sources, floodplains have the potential to serve as an exposure vector for heavy metals. Not only are floodplains frequently located proximate to population centers, transported metals may also be present in more bioavailable forms (adsorbed or in secondary mineral phases) than in source material. Thus, a complex set of transport and biogeochemical transformation processes determines the spatio-temporal distribution of metal-bearing phases. Given that complexity, which variables (source, transport, matrix, aging) control metal speciation and the fraction of metals that are bioavailable by ingestion and inhalation pathways?

We examine this question for lead-, zinc-, and cadmium-bearing soils in the Neosho-Tar Creek floodplain system in Miami, Oklahoma, USA. To identify the source of metals within floodplain soils we have combined major and trace element geochemistry with multivariable statistical analysis (PCA) to develop fingerprints for distinct metal sources (Figure 1). By combining this approach with X-ray diffraction (XRD) to broadly characterize soil mineralogy we have developed endmembers for mixing models that apportion the relative contribution of various metal-bearing phases (detrital primary ore minerals versus secondary iron oxides and hydroxides (FeOx) minerals).



**Figure 1:** PCA of bulk element concentrations from floodplain soil and river sediment samples that demonstrate endmember sources and mixing relationships

Floodplain soil and sediment coring additionally allow us to reconstruct historic flood events and the temporal changes in metal flux, distribution, and speciation. We examine the role that shallow burial plays on the aging and in-situ weathering processes that result in FeOx mineral transformations. This combined approach will aid in estimating current and future risks associated with this evolving pool of bioavailable metals.

## Calcite (CaCO<sub>3</sub>) growth as a function of calcium-to-carbonate ratio in the presence of strontium: implications for the mechanism of inhibition

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One potential remediation method for toxic contaminants that has been proposed is to sequester the contaminant as an impurity in the crystal lattice of a mineral which incorporates the impurity. For example, radioactive strontium is present as a contaminant in a number of U.S. DOE sites and it may be possible to sequester it *in situ* through the engineered growth of calcium carbonate.<sup>1</sup> To enable targeted precipitation without porosity clogging and scale formation, separate injection wells of calcium and carbonate containing solutions have been proposed.

To understand this phenomenon, here we use atomic force microscopy (AFM) to examine the effect of strontium on calcite growth rates under solutions containing variable ratios of aqueous calcium-to-carbonate. Growth rates of the obtuse and acute step orientations on calcite were measured at two saturation indices as a function of the aqueous calcium-to-carbonate ratio and various aqueous strontium concentrations ranging from 0 – 9 × 10<sup>-3</sup> M. It was found that the amount of strontium necessary to inhibit growth correlated with the aqueous calcium concentration, but no correlation or inverse correlation was observed for carbonate. This suggests strontium is inhibiting attachment of calcium but not carbonate attachment or detachment.

At an average strontium-to-calcium ratio of 1.1 for the obtuse step orientation and 1.4 for the acute step orientation, the average step velocity decreases to half of the maximum step velocity, which corresponds to the ratio where the concentration of strontium and calcium on the step at kink propagation sites is the same.<sup>2</sup> We propose that this corresponds to the cation exchange coefficient for calcium and strontium bound to precursor sites on the step.

The implications of this study are two-fold. Firstly, to ensure calcite growth is not inhibited by strontium, the concentration of calcium should be kept approximately higher than the cation exchange coefficient. Secondly, extensions of existing analytical models are unable to capture all the salient features of observed growth rates, indicating that improvement in analytical expressions can still be made.

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[1] Tartakovsky, A. M. et al. (2008) *Wat. Resour. Res.*, **44**, W06S04.

[2] De Yoreo, J. J. et al. (2009) *Cryst. Growth Des.* **9**, 5135-5144.