Organic Sulfur Fluxes and Isotope Mass Balance in Rivers

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The transport of particulate organic matter in rivers and its subsequent burial in marine depocenters are important fluxes in the global cycles of carbon, sulfur, iron, and dioxygen. However, it is challenging to characterize the nature and isotopic composition of organic and inorganic sulfur phases in river systems due to the existence of multiple sulfur cycle processes associated with river catchments, including microbial sulfate reduction and sulfide oxidation, and a host of assimilatory processes related to the terrestrial biosphere. Moreover, lithological heterogeneity in weathering bedrock typically complicates attempts to constrain isotope mass balance. The Efi Haukadalsa river catchment in Northwestern Iceland is dominated by uniform basaltic lithology of known, homogenous sulfur isotopic composition; this river system, which does not contain hydrothermal waters, provides an ideal environment for accurately characterizing sulfur mass fluxes associated with weathering and sediment transport, including floodplain storage and cycling associated with the biosphere. We employed microprobe X-ray Absorption Near Edge Spectroscopy (XANES) and multiple energy mapping at the sulfur K-edge of both suspended sediment and cored floodplain deposits collected from the Efi Haukadalsa to quantify and image the abundance and redox state of sulfur in a wide range of sedimentary products. We combined XANES measurements with sulfur isotope ratios from multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and elemental analyses from ion chromatography (IC) of river and rainwaters, the latter to constrain aerosol fluxes. Our observations reveal few or no sulfide-bearing phases in the sediments. However, the river hosts relatively large fluxes of diverse organic sulfur phases with mixed oxidation states. Preliminary calculations suggest subequal fluxes of organic and inorganic species, indicating that rivers potentially transport as much organic sulfur as they do sulfate, and predominantly as sulfonate phases. While our current data is limited to a controlled setting in Northwestern Iceland, ongoing research with samples from Oregon will help test if organic sulfur fluxes are a substantial, but overlooked, component of rivers globally.