Riverine sulfate budget in the light of sulfur isotopes – current understanding and remaining questions for future studies

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Current geochemical models assume that sulfuric acid (H_2SO_4) dissolution via sulfide oxidation is negligible on global scales because of trace/minor sulfide contents in the lithosphere. The assumption is often that much of the sulfate (SO_4) flux comes from non-sulfide sources (e.g., dissolution of marine-origin gypsum/anhydrite). However, recent geochemical studies indicate that previous estimates on sulfide-derived SO_4 fluxes used in elemental cycle models are significantly underestimated. Generally, the reported sulfide-derived SO_4 fluxes appear to span a large range of ~15 to almost 100% in aquatic systems when compared to other SO_4 fluxes from dissolution of evaporites and atmospheric wet/dry deposition. Therefore, sulfide weathering may have important implications on how we understand the Earth's climate and the evolution of biogeochemical sulfur cycle over geological time scales. Despite this importance, there are still only a small number of studies that attempt to quantify sulfide-derived SO_4 fluxes in global riverine systems. It is also uncertain to what extent environmental factors (e.g., physical erosion, bedrock sulfide content) and climate influence these fluxes in aquatic environments.

The Rio Grande watershed (New Mexico, USA) will be used as an example to discuss current understanding and remaining questions related to the importance of sulfide-derived SO_4 in the riverine sulfate budget. The Rio Grande surface water and groundwater samples were collected seasonally (from 2009 to 2011) and analyzed for their major element chemistries and the $\delta^{34}S$ and $\delta^{18}O$ of dissolved SO_4. The observed variation of $\delta^{34}S$ (-4 to +8 ‰) and $\delta^{18}O$ (-2 to +7 ‰) in the Rio Grande mainly resulted from mixing between sulfide- and sulfate-derived SO_4 of volcanic and sedimentary origin. The S isotope mass balance suggests that the average sulfide-derived SO_4 flux usually accounted for 83-94 % (±10-20 %) of the sulfate source in the Upper Rio Grande and decreased to 45-51 % in the Middle Rio Grande. Major factors controlling sulfide-derived SO_4 fluxes were snow melt, recycling of surficial sulfate-rich salts, and elevated bedrock sulfide contents in volcanic and some sedimentary terrains in the Rio Grande basin.