

## Fluxes of sulfide-derived sulfate in the Rio Grande valley

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Sulfide oxidation is an important weathering pathway in surface environments. However, few data are available to address the contributions and fluxes of sulfide-derived  $\text{SO}_4^{2-}$  in hydrologic systems. In order to better understand this process, we measured the seasonal fluxes of  $\text{SO}_4^{2-}$  and the  $\delta^{34}\text{S}$ - $\delta^{18}\text{O}$  of riverine  $\text{SO}_4^{2-}$  as well as sulfate-rich salt efflorescences in three watersheds connected to the upper Rio Grande valley. In this region, the  $\delta^{34}\text{S}$  of hydrothermal and biogenic sedimentary sulfides differ by 20-30 ‰ compared to S from evaporites. Therefore, the contribution and fluxes of sulfide-derived  $\text{SO}_4^{2-}$  can be estimated using S isotope mass balance constraints.

In the Red River, a small tributary to the Rio Grande within the Taos Plateau in northern New Mexico, sulfide-rich mineralization in the form of hydrothermal veins and disseminated pyrite undergoes oxidation in natural alteration scars and abandoned mine waste piles. In April and August of 2010, the measured  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  of riverine  $\text{SO}_4^{2-}$  varied from -2.5 to +1.3 ‰ and from -7.1 to -4.0 ‰, respectively. These variations were consistent with the previously reported  $\delta^{34}\text{S}$  of pyrite (-13.6 to +2.7 ‰), and the  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  values of gypsum/jarosite (-12.1 to +2.6 ‰ and -9.3 to +3.1 ‰) formed by surface oxidation of hydrothermal sulfides. In the Red River valley, nearly 100 % of aqueous  $\text{SO}_4^{2-}$  appears to be sourced by sulfide oxidation. The measured flux of sulfide-derived  $\text{SO}_4^{2-}$  was higher during the snowmelt in April (19.3 tons/day) compared to baseflow conditions in August (15.2 tons/day).

In the Rio Chama and Rio Puerco, tributaries to the Rio Grande in western and central New Mexico, sulfides occur as biogenic pyrite in Cretaceous shale and coal formations. Sulfate-rich salt efflorescences are common weathering products in surface outcrops of these formations. Analysis by X-ray diffraction shows that these are largely Mg, Na, and Ca sulfates (e.g., starkeyite or hexahydrite, thenardite, and gypsum) and  $\delta^{34}\text{S}$  analyses indicate that the sulfate in these phases formed by sulfide oxidation. Between 2009 and 2011, the contribution of sulfide-derived  $\text{SO}_4^{2-}$  to the total S load varied widely in the Rio Chama (from 48 to 95 %). S isotopes indicated mixing of  $\text{SO}_4^{2-}$  from the dissolution of salt efflorescence (-25.2 to -9.5 ‰) and Jurassic evaporites (+15.1 to +17.7 ‰). In the lower reaches of the Rio Chama, the fluxes of sulfide-derived  $\text{SO}_4^{2-}$  varied widely between Nov 2009 (10.5 tons/day) and Apr 2010 (134.3 tons/day). These variations, however, were to some degree controlled by water releases from upstream reservoirs. Similar contributions of sulfide-derived  $\text{SO}_4^{2-}$  were calculated for the semi-arid Rio Puerco (68 % of the total S load) during the snow melt season. Because less water is available in the Rio Puerco, the fluxes of sulfide-derived  $\text{SO}_4^{2-}$  were significantly lower (~3.8 tons/day) compared to the Rio Chama. This investigation indicates that much of the  $\text{SO}_4^{2-}$  (>50 %) in the upper Rio Grande valley is derived from sulfide oxidation in the surrounding watersheds.