

***Supplement to: Conservative transport of dissolved sulfate across the Rio Madre de Dios floodplain in Peru***

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**I. Cl-based mass balance for hot spring contribution to Rio Madre de Dios**

To determine the role of hot springs in the regional  $\text{SO}_4^{2-}$  budget of the Madre de Dios watershed, a chloride based mass balance was used:

$$[\text{Cl}^-]_{\text{downstream hot springs}} = f_{\text{hot springs}}[\text{Cl}^-]_{\text{hotsprings}} + f_{\text{upstream hotsprings}}[\text{Cl}^-]_{\text{upstream hotsprings}}$$

$$\text{and } f_{\text{hot springs}} + f_{\text{upstream hotsprings}} = 1,$$

where  $f$  is the fractional contribution to discharge. In May 2019 the fractional contribution of hot springs to riverine discharge was 0.01% and in March 2019, the contribution was undetectable. Given their low contribution to discharge and low  $\text{SO}_4^{2-}$  (~6-10 mg/L, compared to 8-12 mg/L in the Rio Alto Madre de Dios), we conclude that the hot springs do not have a significant impact on the regional  $\text{SO}_4^{2-}$  budget.

**II. Explanations for evolution of  $\delta^{18}\text{O}_{\text{SO}_4}$  across the Madre de Dios floodplain**

Figure 3 illustrates the oxygen isotope composition of riverine  $\text{SO}_4^{2-}$  from mountain to floodplain. In all sampling campaigns,  $\delta^{18}\text{O}_{\text{SO}_4}$  increased across the floodplain, i.e., from the foothills of the Andes (~2000 m median catchment elevation, site D in Fig. 1B) to Los Amigos (~450 m median catchment elevation, site E in Fig. 1B). The magnitude of these floodplain increases is annotated on Fig. 3B for each season.

To explore possible causes of the observed changes in  $\delta^{18}\text{O}_{\text{SO}_4}$  across the floodplain, we consider three scenarios (main text Fig. 3C-E): (1) mixing of  $\text{SO}_4^{2-}$  derived from oxidative weathering of pyrite (OWP) and evaporite weathering, (2) reduction of  $\text{SO}_4^{2-}$  and removal via a reduced phase ( $\text{H}_2\text{S}$  or secondary sulfide mineral) and (3) reduction and re-oxidation of  $\text{SO}_4^{2-}$  at lower elevation, similar to the mechanism invoked to explain  $\text{SO}_4^{2-}$  isotope composition in lower reaches of the Amazon River by Longinelli and Edmond, 1983.

In the first case (Figure 3C), weathering source mixing calculations followed a two endmember mixing model, with  $\delta^{18}\text{O}_{\text{SO}_4} = 10\text{-}20\text{‰}$  for the evaporite weathering endmember (Claypool et. al, 1980):

$$\delta^{18}\text{O}_{\text{SO}_4, \text{River}} = \delta^{18}\text{O}_{\text{SO}_4, \text{OWP}} F_{\text{SO}_4, \text{OWP}} + \delta^{18}\text{O}_{\text{SO}_4, \text{Evaporite}} F_{\text{SO}_4, \text{Evaporite}},$$

where  $F_{\text{SO}_4}$  is the fraction of  $\text{SO}_4^{2-}$  from OWP or evaporite weathering.

In the second case (Figure 3D), Rayleigh fractionation is used to model the isotopic impacts of sulfate reduction and removal as a reduced phase. A range of separation constants are used from the literature ( $\alpha = 0.990$ , Mandernack et al., 2003;  $\alpha = 0.995$  and  $\alpha = 0.996$ , Turchyn et al., 2013).

In the third case (Figure 3E), calculations of the effect of reduction and re-oxidation were carried out as follows: we calculated a theoretical  $\delta^{18}\text{O}_{\text{SO}_4, \text{Floodplain, predicted}}$  value using a floodplain water isotope composition (i.e., assuming all  $\text{SO}_4^{2-}$  is reduced and reoxidized in the floodplain). The fractionation factor between  $\text{SO}_4^{2-}$  and source water oxygen isotopes was assumed to be 9‰ (an average literature value from Taylor & Wheeler, 1993 and Van Stempvoort & Krouse, 1993; e.g., within the range in Fig. 2B). The fraction of oxygen in sulfate from atmospheric  $\text{O}_2$  was varied from 10-20%.

The fraction of reduction and re-oxidation needed to explain the observed change in  $\delta^{18}\text{O}_{\text{SO}_4}$  from the foothills of the Andes to the floodplain was calculated as:

$$F_{\text{re-oxidation}} = (\delta^{18}\text{O}_{\text{SO}_4, \text{Floodplain, measured}} - \delta^{18}\text{O}_{\text{SO}_4, \text{Foothills, measured}}) / (\delta^{18}\text{O}_{\text{SO}_4, \text{Floodplain, predicted}} - \delta^{18}\text{O}_{\text{SO}_4, \text{Foothills, measured}}),$$

where  $F_{\text{re-oxidation}}$  is the fraction of the  $\text{SO}_4^{2-}$  pool that was reduced and re-oxidized,  $\delta^{18}\text{O}_{\text{SO}_4, \text{Floodplain, measured}}$  is the measured oxygen isotope composition of the Rio Madre de Dios (site E, Fig 1B)  $\delta^{18}\text{O}_{\text{SO}_4, \text{Floodplain, predicted}}$  is a predicted oxygen isotope composition that would result from total re-oxidation of  $\text{SO}_4^{2-}$  with a floodplain source water isotope composition, and  $\delta^{18}\text{O}_{\text{SO}_4, \text{Foothills, measured}}$  is the measured oxygen isotope composition of  $\text{SO}_4^{2-}$  as it leaves the Andes mountains and enters the floodplain (site D, Fig 1B).

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10