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Mo isotopes as tracers of river-ocean mixing in the Amazon and Pará estuaries

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Rivers are a major source of trace elements to the ocean, but their contribution is difficult to quantify due to transformations occurring at the river–ocean interface. To better understand these processes, we investigate molybdenum (Mo) abundances and isotopes across the salinity gradient in the Amazon and Pará estuaries, the world's largest system for freshwater and metal input to the ocean. Molybdenum is stable under oxic conditions, so its dissolved concentration and isotopic composition are expected to follow conservative mixing between river water and seawater along the salinity gradient. However, deviations in δ^{98}Mo may reveal non-conservative behaviour caused by processes such as adsorption onto Fe-Mn oxides [1].

Dissolved water samples (< 0.2 µm) were collected during the M206 cruise (GApr21, December 2024, RV *Meteor*). Molybdenum concentration and isotopic composition were measured using a Neptune Plus MC-ICP-MS following pre-concentration and purification [2]. Analytical precision is ± 0.04 ‰ (2 SD) for δ^{98}Mo in seawater samples.

In both estuaries, Mo concentrations vary conservatively with salinity ($R^2 > 0.99$). In the Amazon estuary, δ^{98}Mo versus 1/[Mo] also defines a strong linear relationship ($R^2 > 0.99$) between the riverine endmember (S = 0.08) and the seawater endmember (S = 36), consistent with conservative mixing. In contrast, the Pará estuary exhibits δ^{98}Mo values above the Amazon mixing line and a weaker correlation ($R^2 = 0.76$). This offset may indicate either a distinct riverine endmember for the Pará (which we were not able to sample) or non-conservative behaviour, potentially reflecting partial removal of isotopically light Mo through adsorption onto Fe–Mn oxides at intermediate salinities. These observations provide new insights into Mo behaviour in these estuarine systems.

[1] Archer, C., & Vance, D. (2008). The isotopic signature of the global riverine molybdenum flux and anoxia in the ancient oceans. *Nature Geoscience*, *1*(9), 597–600.

[2] Sun, M., Archer, C., & Vance, D. (2021). New Methods for the Chemical Isolation and Stable Isotope Measurement of Multiple Transition Metals, with Application to the Earth Sciences. *Geostandards and Geoanalytical Research*, *45*(4), 643–658.