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Fluxes and isotopic compositions of Zn and Cd in an estuary severely impacted by acid mine drainage

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It has been estimated that the acid mine drainage (AMD) impacted Odiel river basin in southern Spain supplies 15% of the global riverine flux of Zn to the oceans [1]. However, the behaviour of Zn in the Ria of Huelva estuary, which connects the Odiel and Tinto watersheds with the Gulf of Cadiz, has yet to be investigated. Furthermore, very few studies have investigated Cd and Zn isotope behaviour in estuaries worldwide. This study presents Zn and Cd concentrations and isotopic compositions for the Ria of Huelva estuary and surroundings, sampled in 2017 and 2019. Uniform riverine signals of about +0.17‰ for δ^{66}Zn and +0.02‰ for δ^{114}Cd indicate that tracing of individual mining regions using Zn and Cd isotope systems is not feasible. The variability of dissolved δ^{66}Zn values, including AMD, the estuary, and the Gulf of Cadiz spanned -0.12‰ to +0.35‰ (n=28), including both 2017 and 2019 data. The same geographical and temporal scope for Cd yielded a mean δ^{114}Cd of 0.00 ± 0.13‰ (n=25, 2SD; excludes one AMD outlier, at +0.48‰). In May 2017, a large spill from an abandoned mine resulted in a drastic increase in the concentrations of trace metals reaching the estuary compared to 2019, but no impact of this mine spill on Cd or Zn isotope compositions is observed. Overall, Cd concentrations and isotope compositions in the estuary are largely consistent with conservative mixing behaviour. By contrast, Zn behaviour is non-conservative, with removal of 49 to 97% of dissolved riverine Zn in the estuary during the period 2017 to 2019, associated with a relatively small isotopic shift to lighter Zn isotope compositions. Removal of Zn to the particulate phase in the Ria of Huelva estuary therefore largely attenuates high riverine Zn fluxes from AMD, indicating that previously estimated Odiel river basin Zn fluxes are too high. Nevertheless, the variable but distinct light AMD Zn and Cd isotope compositions, coupled with high dissolved concentrations, suggest that Zn and Cd isotopes may be useful tracers of regionally averaged AMD inputs to the Gulf of Cadiz and beyond.

[1] Sarmiento et al., 2009, Applied Geochemistry 24(4):697-714.