Cu and Zn isotope fractionation along the Scheldt estuary

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Our study presents trace metal and Cu and Zn isotope geochemistry of the Schledt estuary (Belgium- Netherlands) which is a 100 km long and polluted estuary characterized by high freshwater residence time.

Surface sediments and Suspended Particulate Matter (SPM) are collected during 8 cruises from November 2002 to February 2006, with systematic monitoring of water-column parameters. 100 mg of crushed and calcinated sample powder are dissolved by HF/HNO_3 acid digestion. Cu and Zn are separated and purified by chromatography on ion-exchange resin. Cu and Zn isotopic ratios are measured by a Nu-Plasma MC-ICP-MS (ULB). Instrumental mass bias is simultaneously corrected by SSB and external normalisation assuming an exponential law of mass fractionation. Long term reproducibility of in-house standards, characterized relative to international reference materials Cu NIST and Zn JMC, give 0.00 ± 0.07 ‰ (2SD, n=100) for both $\delta^{65}Cu$ and $\delta^{66}Zn$. Spectral and non-spectral interferences - including relevant major (Ca, Mg, Na, Fe, Ba and Si) and trace (Ti, Co, Cr) elements are assessed, as well as effects of variable concentrations on mass discrimination, for both dry and wet plasma conditions.

$\delta^{66}Zn$ and $\delta^{65}Cu$ variations of 30 samples cover a range of 0.99 and 1.80 ‰, respectively. Zn isotopes show significant differences between sediments and SPM, as well as a fractionation trend relative to the upstream-downstream profile, which might reflect a granulometry dependence. The highest concentrations are recorded in the Estuarine Turbidity Maxima (ETM, 5-10 psu) and further dilutions are observed downstream. Marine sands show heavy Zn isotopic signature (up to 1.12 ‰) while loamy sediments in the ETM have light Zn isotopic signature (down to 0.21 ‰). In contrast, SPM displays smaller $\delta^{66}Zn$ variations (0.23 in the ETM to 0.66 ‰ at the mouth). Inside the estuary, variations in Zn isotopic composition are consistent with a qualitative model of transport dynamic for particulate materials. Variations of Cu isotopic compositions in sediments mimic those of Zn. However, $\delta^{65}Cu$ in SPM may show abrupt shifts from +1 in the upper estuary to -1 ‰ in the middle estuary likely reflecting redox processes.