Applying Zn isotopes as tracers of electroplating wastes in a Brazilian lagoon system

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The Sepetiba Bay is a coastal lagoon system located in Rio de Janeiro State (Brazil), which has been impacted by smelting and metallurgic plants over the last decades. This area is a perfect setting to study the trace metal cycling in estuaries under these impacts and to test the application of metal stable isotopes to identify metal sources and fates. Sediment cores, suspended particulate matter and rocks from the study area, and willemite ores samples (used for Zn refining) were collected for the determination of Zn isotopes by MC-ICP-MS. The results show a relatively wide range of isotope ratios $(\delta^{66/64}Zn)$ for the natural samples from Sepetiba Bay, ranging from +0.21 to +1.15% relative to JMC-Lyon reference standard. Sediments directly impacted by a large metallurgic tailing source showed heavier $\delta^{66/64}$ Zn values (0.68 to 1.15%). Willemite ores showed lighter compositions (-0.10 to 0.14‰), indicating high fractionation induced by industrial processes. Sediments collected close to the mouth of the major freshwater source and near the open sea showed lighter isotope signatures and lower Zn concentrations in deeper layers, with heavier isotope signatures and higher Zn concentrations in top layers. The $\delta^{66/64}$ Zn values and Zn enrichment factor in relation to local background are highly correlated in four of five cores. A two end members mix model was used to estimate the relative contributions of the major anthropogenic Zn source. It was observed a decrease of electroplating waste contributions to Zn input in the last years. Zinc isotopic data provided support to (i) identify and quantify different sources and fates of Zn in the study area; (ii) reconstruct the temporal evolution of the anthropogenic Zn input and (iii) undestand the influence of hydrodynamics on anthropogenic Zn dispersion in the bay.