

$\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ behavior across mangrove pollution gradients in Brazil

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Mangrove sediments trap trace metals as a result of sediment accumulation, potentially attenuating the impacts of land-based pollution on the ocean. The cycling of trace metals and the extent of the fate of contaminants in mangrove sediments needs to be better understood to improve environmental service predictions. Stable isotopes are a potential tool to resolve sources and processes controlling the behavior of trace metals within these systems. This study evaluates Cu and Zn stable isotope signatures of mangrove sediments under different degrees of contamination along the Brazilian coast. Data from 5 sediment cores were gathered, including highly contaminated sites (Cubatão and Mangaratiba), a low to moderately impacted bay (Florianópolis), and one non-impacted site (Paraty). The $\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ values varied from -0.31 to 0.57‰ and 0.09 to 0.72‰, respectively. These results are within the ranges previously reported for anthropogenic sources and sedimentary environments. Anthropogenic source tracing with $\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ was feasible in highly contaminated mangrove sediments where isotope values correlated with Al-normalized enrichment factors. However, $\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ were not observed as effective anthropogenic source tracers in the less contaminated areas investigated. In Florianópolis, the inter-relationship between $\delta^{66}\text{Zn}$, Al and Fe, indicate that aluminosilicates and oxyhydroxides control Zn isotopes of bulk samples close an urban area and a natural reserve, respectively. A positive correlation between $\delta^{65}\text{Cu}$ and Fe was observed in Guaratiba, further highlighting the influence of Fe redox cycle when pollution is not overwhelming. In the pristine mangrove of Mamanguá, the correlation between $\delta^{65}\text{Cu}$ and TOC appoint for a Cu biogenic origin. Overall, both $\delta^{65}\text{Cu}$ and $\delta^{66}\text{Zn}$ have contrasting distribution and drivers across the mangrove