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Fractionation of Cu and Zn isotopes in antifouling paints during dissolution and adsorption in marine environment

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Antifouling paints (AFPs) applied to ships could be an important source of metals in the coastal environment. It is therefore necessary to determine indicators of AFP-derived metals in environmental samples. The elemental and isotopic (δCu and δZn) characteristics of 34 AFP samples from 4 types of paint, the isotopic fractionation during the dissolution of AFPs by seawater, and the subsequent adsorption of isotopes onto coastal fine-grained sediments were investigated to identify potential indicators (metal ratios and isotopes) for tracking metal contamination from AFPs.

Metal ratios (Zn/Cu, Cu/Fe, and Zn/Fe) could be used for the discrimination of AFP metals from background sediments, but there were only small differences among the different types of paints from different manufacturers. The δCu and δZn values for 34 AFPs could be divided into 2 groups, 0.49 ± 0.09‰ (n = 23) and -0.01 ± 0.07‰ (n = 9), and 0.07 ± 0.09‰ (n = 23) and 0.03 ± 0.07‰ (n = 9), regardless of the type of paint or manufacturer. Dissolution by seawater induced substantial fractionation (the $\Delta^{65}Cu_{soln\text{-}solid}$ and $\Delta^{66}Zn_{soln\text{-}solid}$ values were -1.54‰ and -0.52‰ in the low leached fraction), but δCu and δZn approached the bulk AFP values when the leached fraction increased (> 0.14% Cu and > 2.7% Zn). The adsorption of metals onto marine sediments resulted in substantial fractionation ($\Delta^{65}Cu_{soln\text{-}solid}$ = 0.91 ± 0.30‰ and $\Delta^{66/64}Zn$ = -0.11 ± 0.04‰), but the δCu values in sediments were similar to those in bulk AFP because almost all of the Cu adsorbed to marine sediments within 12 h. However, because a portion of the dissolved Zn did not adsorb to marine particles, less isotopic fractionation occurred, with the extent of fractionation being smaller than -0.11‰. Therefore, the δCu value could be used as an indicator because Cu in the dissolved and particulate phases derived from AFPs could be determined and was indicative of the levels in bulk AFPs.