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Geochemical behavior and isotopic signature of chromium cycling in estuaries: Insights from two rivers in southwestern Japan

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An investigation into chromium (Cr) cycling in estuarine environments is essential for accurately evaluating its ecological risks in aquatic systems. In estuaries, the removal and remobilization of Cr are influenced by numerous factors, including partitioning with suspended solid (SS), precipitation and dissolution of metal oxides due to redox and salinity changes, and diffusive release from sediment porewater. The stable isotope ratio of Cr (δ^{53}Cr) fluctuates mainly due to changes in oxidation states between Cr(III) and Cr(VI), reflecting redox reactions. To better understand the geochemical behavior of Cr in estuarine environments, we have determined total Cr, Cr(VI) concentrations, and δ^{53}Cr values in water, SS, and porewater samples collected from two rivers in southwestern Japan. One of these rivers has organic-rich, anoxic sediments, while the other has less organic matter and is considered oxic.

In both rivers' freshwater, Cr(VI) predominated, and δ^{53}Cr values increased with decreasing total Cr concentration, suggesting Cr(VI) was reduced to Cr(III) and light Cr isotopes were preferentially scavenged by riverbed sediment or SS. As salinity increased, δ^{53}Cr values gradually decreased, indicating conservative behavior that can be attributed to the mixing of freshwater and seawater or the merging of low salinity tributary with light δ^{53}Cr values downstream. The Cr(VI)/Cr-total ratio in porewater was higher (0.3-0.9) in oxic sediments and lower (<0.1) in anoxic sediments. The Eh-pH conditions indicated that in oxic sediments, Cr(III) was re-oxidized to Cr(VI) by MnO_2, whereas in anoxic sediments, the reduction of Fe(III)-Cr(III) oxides was linked to Cr(III) release. δ^{53}Cr values in porewater ranged from +0.24‰ to +0.99‰ in oxic sediments and were lower (-0.06‰) in anoxic sediments, consistent with trends in Cr isotope fractionation due to redox reactions observed in previous studies. A positive correlation between the calculated Cr(III) concentration in anoxic sediment porewater and the concentrations of Cu, Fe, and Pb suggests that Cr(III) may form dissolved complexes with organic matter, such as humic substances, which have a high affinity for these heavy metals. During periods of high tidal fluctuations, the observation of low Cr(VI)/Cr-total ratios in anoxic estuarine water suggests the release of Cr(III)-organic complexes into the water through sediment agitation.