

Non-conservative behaviour of Li isotopes in a low salinity estuary

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Lithium in seawater is largely derived from continental silicate weathering, and is primarily transported to the oceans by rivers through estuaries. Effects of estuarine mixing can affect the behaviour of elements, potentially impacting the elemental and isotopic fluxes to the oceans.

Dissolved and suspended particulate Li concentrations and isotopic compositions ($\delta^7\text{Li}$) have been measured along a low-salinity gradient for two stably stratified estuaries: the Kalix and Råne estuaries (Northern Sweden). In both estuaries, dissolved [Li] increases with depth and follow a conservative mixing trend with a seawater-like Bothnian Bay end-member, but lower [Li] of 2.3 μM .

Dissolved $\delta^7\text{Li}$ compositions span a range of values from $\sim 23\text{--}28\text{‰}$ in surface waters to $\sim 31\text{‰}$ (global seawater compositions) at depth. Suspended particulate $\delta^7\text{Li}$ span a range in compositions extending from detrital compositions $\sim 5\text{‰}$ to compositions approaching that of seawater ($\sim 29\text{‰}$). Surprisingly, simple conservative mixing between freshwater and seawater/Bothnian Bay end-members cannot explain the isotopic data. The non-conservative behaviour of Li is likely related to interactions with the suspended particulate material in the low-salinity zone. TEM images show the presence of poorly crystalline Fe oxides such as goethite, amorphous organic matter and sheet silicate clay minerals. Such highly reactive secondary minerals are known to fractionate Li isotopes. The suspended particulate $\delta^7\text{Li}$ reflects the isotopic signature of a detrital component plus an additional component from the water within the estuary, implying rapid exchange within the estuary rather than inheritance of additional Li from the source region.

This has implications for palaeoweathering studies, where changes in weathering regimes may be reflected in the secondary mineralogy, providing an additional sink for Li. This highlights the potential importance of estuarine processes in modifying the riverine Li fluxes into the ocean.