Using boron isotopes to trace sources of nutrient loading in water systems (Oreti River catchment, New Zealand)

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Boron is an essential micro-nutrient that is ubiquitous in crustal settings and commonly added to manufactured products, including fertilizer, detergents and is naturally elevated in animal excreta. Due to its soluble nature, boron redistributes into aqueous environments where it is commonly associated with nutrient-rich solutes. Boric acid and borate dominate the speciation of boron in acidic and alkaline water, respectively. The two naturally occurring stable isotopes of boron are preferentially sequestered in opposite species, ^{11}B in boric acid and ^{10}B in borate. Isotopic fractionation occurs as the result of adsorption/ desorption reactions, mineral precipitation and dissolution, evaporation, and biological processes. Stable isotope fingerprinting is commonly used to trace contamination sources and to distinguish the primary mechanisms of fractionation in a water system. Isotopic compositions of geogenic contributors and anthropogenic boron provide a basis to test whether contamination can be ascribed to natural sources. In the Oreti River catchment in Southland, New Zealand, nutrient loading has resulted in a decline in regional water quality. Eutrophication is associated with a long history of intensive land use, including a more recent shift from sheep to irrigated dairy farming. Boron isotopic values in surface water samples from the catchment decrease with distance from the coast (+20 to +40‰ $\delta^{11}B_{Coast}$; +5 to +30‰ $\delta^{11}B_{Inland}$), and with increasing elevation (+12 to +40‰ $\delta^{11}B_{MSL}$; +5 to +30‰ $\delta^{11}B_{Mtns}$), suggesting a marine influence in accord with the values of seawater aerosols (+40‰). Widespread variance in the $\delta^{11}B$ values implies that there is an anthropogenic and/or geological component to fractionation in the catchment. Isotopic compositions of tile-drainage samples (+15 to +35‰), representative of an agricultural influx, suggest that the waters are contaminated by cattle manure (+28.6‰), phosphate fertilizer (+14.8‰), or nitrate fertilizer (-2- to +0.7‰). The $\delta^{11}B$ scatter in the tile-drainage samples points to anthropogenic contributors as the primary source of contamination in the middle to lower reaches of the Oreti catchment, but ratio variations in surface water north of the glacio-alluvial plains suggest that there is a stronger lithological component in the upper reaches due to the greater diversity in rock type (from metasedimentary to ultramafic units). Given that nutrient loading is a global issue, the Oreti River catchment can be used as a model to assess the controls on contamination therefore improving water quality through enhanced resource management in hydrologic systems worldwide.