Chemical and isotopic constraints on carbon and sulfur dynamics in Lake Erie nearshore waters

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While phosphorus-induced eutrophication has been studied extensively in freshwater ecosystems, cycling of other essential elements such as sulfur and carbon has not been sufficiently explored. To improve our understanding of the carbon and sulfur dynamics across the land-lake interface, concentrations of chloride (Cl), sulfate (SO₄), dissolved inorganic carbon (DIC), and dissolved organic carbon (DOC), the stable isotopic compositions of water ($d^{18}O$ and $d^{2}H$) and sulfate ($d^{34}S_{SO4}$ and $d^{18}O_{SO4}$), and the stable and radio isotopic compositions of DIC $(d^{13}C_{DIC} \text{ and } D^{14}C_{DIC})$ were measured in water samples from nearshore and offshore sites at Lake Erie, the Detroit River, and other tributaries. The Detroit River and offshore waters were characterized by lower concentrations of Cl and SO₄ but higher values of d¹³C_{DIC} and d³⁴S_{SO4}, whereas other tributaries were featured with higher values of Cl, SO4, and d-excess but lower values of $d^{13}C_{DIC}$, $D^{14}C_{DIC}$, $d^{34}S_{SO4}$, and $d^{18}O_{SO4}$. The nearshore waters of Lake Erie had elevated values of Cl, SO₄, and *d*-excess, and lower values of $d^{34}S_{\rm SO4}$ and $d^{18}O_{\rm SO4}$ than samples from offshore sites, consistently attesting to a strong tributary influence. The average d³⁴S_{SO4} value decreased from the Detroit River to open Lake Erie by as high as 1.5‰, while there was a concomitant increase in d¹⁸O_{SO4} by 2.1‰. These results revealed that the carbon and sulfur dynamics in Lake Erie nearshore waters were not only affected by tributary inputs but also modulated by a range of in-lake biogeochemical processes such as CO₂ degassing, carbonate precipitation, DOC degradation, microbial sulfate reduction, and subsequent reoxidation.