Assessing the utility of hydrogen isotopic composition as a tracer for terrestrial dissolved organic matter in estuaries

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Estuaries are the interfaces between river systems and oceans where freshwater and its terrestrial dissolved organic matter (DOM) mixes with seawater and marine-derived DOM. Terrestrial DOM can be a key source of energy and nutrients for estuarine ecosystems, as it comprises ~60% of riverine organic matter input to marine environments. This is especially important where concentrations of riverine DOM are high, such as at boreal and arctic latitudes. The role of terrestrial DOM in regulating estuarine ecosystem processes is poorly understood in part because of difficulties in tracking terrestrial DOM in marine environments. Analysis of multiple stable isotopes (C, N, and S) is often required due to poor separation of the carbon isotope signatures of marine and terrestrial sources. However, hydrogen isotopes exhibit greater fractionation. We propose that hydrogen isotopes may be an excellent tool for tracking terrestrial DOM, because of the large differences that exist between marine (0 per mil) and terrestrial (up to −270 per mil) organic hydrogen isotopic signatures.

Riverine discharge into marine environments introduces

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terrestrial DOM to water of different physicochemical and isotopic compositions. Hydrogen isotopes can undergo exchange between water and organic matter, which may obscure terrestrial signatures. We investigated the magnitude of this effect by exposing terrestrial DOM to freshwaters with hydrogen isotopic compositions up to +1000 per mil for as long as two months. As much as 15% of organic hydrogen exchanged, and enrichments of up to 40 per mil were observed. We are now investigating measurement of the non-exchangeable fraction to compensate for this by equilibrating samples with waters varying in known isotopic composition. We also use surface water samples along a salinity transect at the Salmonier Arm, Newfoundland, Canada, to investigate the effects of changes in water mass conditions (pH, salinity and water isotopes) and recovery techniques on terrestrial DOM elemental and isotopic composition. Initial results indicate that the size range of recovered DOM is correlated with its isotopic signature and therefore results from different techniques are not directly comparable.

Hydrogen isotopes have the potential to provide high resolution separation of terrestrial and marine DOM signatures in a single measurement rather than the multiple analyses required currently. This could be a very useful tool for assessing both estuarine ecosystem health and quantifying the carbon cycling that occurs in these environments, however, careful consideration of isolation technique and H isotopic exchange is important when exploiting this approach.

