Dynamics of dissolved organic matter in a shallow Danish estuary

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This study presents data on dissolved organic matter, collected through an annual cycle in a shallow Danish estuary, Roskilde Fjord. The different DOM fractions initially appeared to behave conservatively when evaluated against salinity. However, isotopic mixing models based on stable isotope ratios of carbon and nitrogen reveal that conservative mixing models based on DOM concentration and salinity mask estuarine processes altering the DOM pool. Our data suggest an accumulation of DON especially in the inner parts of the estuary potentially as release from both sediment and phytoplankton.

Roskilde Fjord, Denmark, is microtidal, and salinity varies from about 7 psu in the innermost part to some 23 psu at the mouth, opening to Kattegat. Roskilde Fjord receives freshwater input from several smallish streams along the whole estuary.

All DOM fractions – DOC, DON and CDOM (expressed as a total) would initially appear to be conservatively mixed – i.e. no production or decomposition in Roskilde Fjord. Note initial disappearance of 20 – 30% of DOC and CDOM.

The δ13C-DOM mixing curve (A and B) follows a non-conservative isotope mixing both in autumn and in spring. The δ15N-DOM mixing curve shows 15N depletion in autumn at the inner stations while the two outer stations follow the expected conservative distribution (C). In spring, DON concentrations at all stations are depleted compared to the expected conservative distribution.

Average estuarine δ15N-DOM and δ13C-DOM values from autumn show that DOM at the inner station (E1) has the highest terrestrial signal. DOM at St. 2, on the other hand, is depleted in 13C which could be explained by autochthonous DOC production. St. 3 and 4 had similar δ13C-DOM values but the DOM at St. 4 was more depleted of 15N. During spring the pattern changed and the isotope composition of DOM at St. 1 and St. 2 (E1 and E2) was enriched in δ13C and depleted of δ15N compared with autumn averages.

Schematic relationship between the ratio of DIN:DOC in loadings and the autochthonous to allochthonous DOC ratio (auDOC:alDOC) illustrating the potential effect of residence time and production rate. The line represents the ratio assuming that autochthonous DOC is produced from DIN at the Redfield ratio (C:N=6.2). The annual average of DIN:DOC loadings for Horsens Fjord and Roskilde Fjord are 0.45 and 0.19 (mol basis), respectively. This is equal to a auDOC:alDOC ratio at Redfield (∙) of 2.68 for Horsens Fjord and 1.22 for Roskilde Fjord. Estimated auDOC:alDOC are approximately 4 in both Roskilde Fjord and Horsens Fjord placing them above the Redfield line (□).

The mechanisms controlling concentrations of DON, DOC and CDOM seem to be dilution most of the year (conservative mixing). However, isotopic mixing models reveal that conservative mixing models based on DOM concentration and salinity mask estuarine processes altering the DOM pool. Isotope analysis of DOM reveals a high terrestrial/refractory signal in November-December whereas biochemical processes alter the DOM pool in spring.