



Binding of iron and copper to humic colloids in the Thurso River plume

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We report on the physicochemical forms of dissolved iron and copper in the high-salinity region (salinity = 28-35) of a coastal plume created by a small river (River Thurso) draining a peat-rich catchment. Speciation information was obtained through a combination of size fractionation by cross-flow filtration (5 kDa) and voltammetric detection of the metal complexes formed upon titration of the fractionated samples with a known competing ligand. Titrations with the metal of interest were also carried out. In this way, it was possible to unravel the contributions of weaker and stronger ligands to the overall binding properties of each sample fraction.

The majority of colloidal (> 5 kDa) iron was present as iron-humic complexes directly supplied by the river and showing uniform conditional stability constants ($\log K = 21.0-21.4$) throughout the plume. Iron present in these humic-rich colloidal assemblages was strongly but reversibly bound to the humic substances. Only in the marine end-member did non-colloidal, or 'soluble', iron accounted for a significant portion (up to 50%) of total dissolved iron. The marine end-member also contained a kinetically inert form of colloidal iron. Humic substances also contributed high-affinity copper binding ligands whose colloid/solution partitioning reflected the changing nature of the inputs of terrestrial DOM. By contrast with iron, the (log of) stability constants of the copper-humic high-affinity complexes found in the colloidal phase increased when progressing towards the open ocean, from 15.4 to 16.1. This was attributed to a slow re-configuration of the humic colloids in response to the increasing salinity.

Under typical spring and summertime river flow conditions (3-12 m³/s), we found no evidence for any significant removal of copper or iron in the river-ocean mixing zone, suggesting that the humic substances can act as very effective carriers of trace metals to the ocean. Further work is planned to examine the cycling of iron, copper and humic substances in the same coastal system but under conditions of high river discharge.