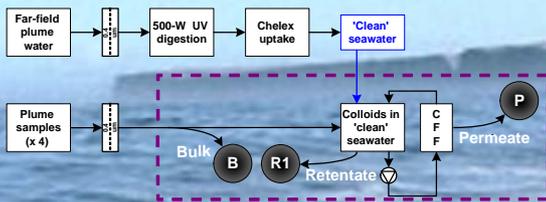


- Climate and hydrological models tell us that we can expect significant changes in the quality and quantity of dissolved organic matter (DOM) supplied by rivers to the ocean at higher latitudes. Currently we know little about the current fate of terrestrial DOM and associated bioactive metals (e.g. Fe and Cu) in the coastal ocean.
- River Thurso drains deep peat soils, creating a humic-rich plume in adjoining coastal waters. Its composition is more representative of peat-draining boreal rivers than any other in the UK. Its high pH, short flushing time and low suspended load result in a conservative mixing behaviour of most elements in the estuary ($S = 0-30$).
- In the present study, we have tracked changes in the bulk and size fractionated properties of terrestrial humic substances in the high-salinity ($S = 30-35$) region of the plume, as it travels away from the river mouth and undergoes both ageing and dilution by ocean water.



Methods

Cross-flow filtration (CFF) protocol



- CFF in the concentration mode yielded the low molecular weight ($MW < 5$ kDa) fraction = P (Permeate)
- CFF in the diafiltration mode yielded the high molecular weight fraction ($MW > 5$ kDa) = R (Retentate)
- Diafiltration allows replacement of the original seawater matrix for either metal-clean offshore seawater (R1) or low ionic strength buffer solution (R2)

Analytical scheme

- Core variables measured on the bulk samples (B) included S, pH, TA, absorption coefficient at 355 nm (a_{355}) and fluorescence index ($FI = I_F(\text{Ex}370/\text{Em}450) / I_F(\text{Ex}370/\text{Em}500)$).
- Chemical variables directly measured by adsorptive cathodic stripping voltammetry (ACSV) on each fraction of each of the 4 plume samples included $[\text{Fe}_T]$, $[\text{Cu}_T]$, $[\text{Fe-HS}]$, $[\text{FeTAC}_0]$, $[\text{FeTAC}_{14}]$.
- Metal binding parameters calculated from the ACSV titration procedures (see below) were $(K'_{\text{FeL}}, [L_T])$ for iron and $[\text{Cu}_{\text{labile}}]$, $(K'_{\text{CuL}_1}, [L_1])$, $(K'_{\text{CuL}_2}, [L_2])$ for copper.

Glossary

- $[\text{Fe}_T]$, $[\text{Cu}_T]$ Total dissolved iron, copper concentrations
- $[\text{Fe-HS}]$ Concentration of iron naturally complexed with humic substances (voltammetric detection)
- $[\text{FeTAC}_t]$ Concentration of iron bound by the added synthetic ligand TAC (and therefore detectable by ACSV) after an equilibration time of t hours
- K' Conditional stability constant of any of the naturally occurring complexes FeL , CuL_1 or CuL_2
- $[L_T]$ Total concentration of iron-binding ligand L
- $[L_1]$, $[L_2]$ Concentrations of strong (L_1) and weak (L_2) natural copper binding ligands

Results and Discussion

Chemical distributions across the far-field plume

DOC, $[\text{Fe}_T]$, and $[\text{Fe-HS}]$ decreased linearly with salinity in each size fraction

- 1) Terrestrial inputs of Fe-binding HS occur in both the LMW and HMW fractions
- 2) No net exchange takes place between the fractions during plume mixing

Size fractionation and binding strength of organic ligands

Fe and Fe-binding ligands were mostly found in the colloidal phase
Cu and Cu-binding ligands were mostly found in the soluble phase

When progressing towards the open sea...

- $\log K'_{\text{FeL}}$ values for complex formation with colloidal ligands remained constant at 21.3 ± 0.3 , and were not influenced by ionic strength
- $\log K'_{\text{CuL}_1}$ values for complexation by soluble and colloidal Cu-binding ligands increased from about 15.1 ± 0.2 ($S = 30$) to 16.0 ± 0.2 ($S = 35$), probably due to a progressive contraction of the humic assemblages, trapping Cu inside
- The origin of the weaker Cu-binding ligand L_2 ($\log K'_{\text{CuL}_2} = 11.8-12.6$) appeared to be neither the river nor the open ocean (Thurso Bay sediments?)
- Because the strong ligand L_1 was saturated with Cu, L_2 was instrumental in bringing $[\text{Cu}_{\text{labile}}]$ to the very low levels observed (see below)

Labile metal pools and kinetics of metal-ligand dissociation

The colloidal fraction of iron (\blacktriangle or \blacktriangledown) contributed to the total exchangeable iron $[\text{FeTAC}_{14}]$ to a greater extent than to the labile iron $[\text{FeTAC}_0]$

This indicates that the rate of dissociation of the Fe-HS colloidal associations was delayed compared to that of soluble iron complexes

Despite this kinetic limitation the entire pool of colloidal iron was successfully modelled as being in equilibrium with a single ligand L, except at—or near—the marine end-member

The relative constancy of $[\text{Cu}_{\text{labile}}]/[\text{Cu}_T]$ (right), both across the salinity range and between size fractions, means that the equilibrium assumption between labile Cu, CuL_1 and CuL_2 is also valid

- How representative is this system of large scale boreal river plumes?
- How does the behaviour of these humic colloidal carriers change under high river flow regime?

