**Dissolved Organic Matter Cycling in the Tyne Estuary, U.K.**

R. G. M. Spencer¹, A. K. Anestis¹, A. Baker², G. L. Cowie³, G. Uher¹ and R. C. Upstill–Goddard¹

¹Ocean Research Group, School of Marine Science & Technology, University of Newcastle-upon-Tyne, NE1 7RU, UK.
²Centre for Land Use & Water Resources, University of Newcastle-upon-Tyne, NE1 7RU, UK.
³Department of Geology and Geophysics, University of Edinburgh, UK.

1. **BACKGROUND**

Dissolved organic matter (DOM) is the most abundant form of organic matter in the ocean and one of the largest reactive carbon reservoirs on earth. Its influence on physical, chemical and biological processes in the oceanic carbon cycle is widely recognised. The optical properties of DOM are dominated by a complex mixture of chromophores (molecules that absorb UV and visible light) and fluorophores (molecules that re-emit absorbed light at longer wavelengths). Absorption and fluorescence measurements are used routinely to characterise the chromophoric components of aquatic DOM (CDOM). Light absorption by CDOM decreases approximately exponentially throughout the near – UV and visible wavelength regimes in aquatic systems (Fig 1).

**Fig. 1.** Light absorption spectra for natural waters from the Tyne estuary.

- Two distinct DOM fluorescence signals (fluorophores) have been observed in aquatic samples, classified on the basis of their wavelength-independent excitation/emission (EX/EEM) maxima. The first (fluorophore H) has an `EX/EEM of 380/425 nm`. This feature may be associated with terrestrial (T) or marine (M) depending on its `EX/EEM maxima`. However, for simplicity it will here be referred to as fluorophore H (EX/EEM of 340/425, Fig 2(a)). Fluorescence of fluorophores H and A indicating humic and fulvic rich river water. Both fluorophores and fluorophore A also appears to be of humic origin. Study of CDOM can therefore yield important information on the nature of HMW humic removal during estuarine mixing.

2. **DOM RESULTS & DISCUSSION**

**Fig. 2.** Fluorescence EEM measurements from an estuarine transect. R. Tyne water (a) shows high fluorescence of fluorophores H and A indicating humic and fulvic rich river water. Both fluorophores decrease in intensity during estuarine mixing (b), until (c) where they are found at low intensities in North Sea water. Fig. 2 (a) also shows the impact of a sewage works by the increase in fluorophore T. The linear feature is Rayleigh–Tytodk scatter when excitation wavelength equals emission wavelength.

**Fig. 3.** Non – conservative mixing of CDOM absorption in the Tyne estuary. Dashed lines represent apparent dilution lines extrapolated from CDOM absorption at higher salinities.

**Fig. 4.** Non – conservative mixing of FDOM in the Tyne Estuary.

FDOM in the Tyne estuary also shows non-conservative behaviour. Levels of FDOM appear to be dependant on river flow, indicating that riverine DOM is the dominant DOM source in the Tyne estuary. Fig 4a shows a small removal of fluorophore A whereas fluorophore H shows non-conservative mixing in the Tyne estuary.

**Fig. 5.** Conservative mixing behaviour of DOC in the Tyne estuary, axial transect 11/07/02.

**Fig. 6.** HMW and LMW fractions of DOC in the Tyne estuary axial transect 11/07/02.

**CDOM shows non-conservative mixing in the Tyne estuary.** At low river inflow (Fig 3a) CDOM shows a high dilution line, whereas at high inflow (Fig 3b) CDOM removal is evident at lower salinities as for the case in Fig 3a. Fig 3c also shows net CDOM addition in the upper estuary but in contrast does not show CDOM removal.

- DOC levels are high in the Tyne compared to other U.K. estuaries. Fig 4 shows a small deviation from conservative mixing close to salinity 30, attributable to Howdon sewage works. A small DOC removal at around salinity 10 corresponds to the region of CDOM removal in Fig 3a.
- The molecular weight composition of DOM in the Tyne estuary was investigated using Tangential flow ultrafiltration. Bulk water samples (25L) were fractionated and concentrated 30 fold using a 10kDa cut-off membrane. The procedure caused nominal gain or loss of DOC (mass balance 104 ± 5%) and Fig 6 shows the low molecular weight (LMW) fraction to follow the same trend as total DOC and it appears that the DOC input from Howdon sewage works is LMW. This is as expected because the absorbance of waters around Howdon typically have deep spectral slopes, suggesting them to contain lower levels of aromatic and HMW carbon compared to riverine CDOM.

3. **REFERENCES**

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