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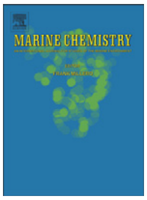

Size fractionation and optical properties of colloids in an organic-rich estuary (Thurso, UK)

Silvia Batchelli [a], François L.L. Muller [a,*], Mohamed Baalousha [b], Jamie R. Lead [b]

[a] *Environmental Research Institute, Castle Street, Thurso, Caithness KW14 7JD, UK*
[b] *School of Geography, Earth and Environmental Science, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

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ABSTRACT

The optical characteristics of a black water river estuary from the north coast of Scotland were examined in the filtered (0.4 µm), ultrafiltered (5 kDa) and colloid-enriched fractions of estuarine samples. The samples were collected over the full salinity range during a period when the pH was relatively constant (8.2–8.5) throughout the estuary, allowing the influence of salinity on estuarine colloidal processes to be distinguished. The properties examined in the bulk, the low molecular weight (LMW) and the colloidal fraction (HMW) were UV–visible absorption, 3-D fluorescence excitation–emission matrix (EEM) spectrum, inorganic and organic carbon, mean size (by dynamic light scattering), and size distribution by flow field-flow fractionation analysis (FlFFF). The combined results of these analyses support the view that river-borne, humic-rich colloids underwent two types of transformation upon mixing with the seawater end member. The first one resulted in an apparent increase in the abundance of LMW constituents and may be explained by coiling of the individual humic macromolecules. The second one resulted in an increase in the mean size measured in both the lower and higher colloidal size ranges, and may be explained by aggregation of colloids to form entities that were still mostly colloidal i.e., smaller than 0.4 µm. The LMW contribution to the bulk optical properties increased with increasing salinity. Very similar findings were obtained from simulated mixing experiments using a Nordic Reference NOM extract as a source of freshwater colloids. This indicates that changes in the molecular architecture and molar mass of river-borne colloids—not changes in their chemical nature—were responsible for the observed variations in the spectral characteristics of CDOM in this estuary.

1. Introduction

Coloured or chromophoric dissolved organic matter (CDOM), historically known as “Gelbstoff” or “yellow matter,” is that portion of the dissolved organic matter (DOM) that strongly absorbs light in the blue and ultraviolet (UV) part of the light spectrum. This photochemical active fraction plays an important role not only in the optical properties of natural waters, e.g. by reducing light levels available for algal growth or shielding aquatic organisms from harmful UV radiation, but also in the transport and reactivity of bioactive metals and organic compounds. Remotely sensed features of CDOM are used to track DOM in the coastal environment and have the potential to improve our understanding of its source, composition and fate, with important implications for CO_2 dynamics, ecosystem functioning and other environmental processes (Coble et al., 2004). In the last few years, extensive studies and reviews on CDOM characteristics have been published (Blough and Del Vecchio, 2002), yet neither its composition nor its highly variable optical properties (both in time and space) are fully understood. Recent studies (Boehme and Wells, 2006; Floge and Wells, 2007) have shown that a significant fraction of DOM falls within the colloidal size range (1–1000 nm), and that this fraction includes highly reactive components in relation to both biodegradation and aggregation processes. This reactivity means that the turnover of colloidal organic carbon in coastal waters can be quite fast (hours to days), and therefore may contribute to the variability found in the optical signatures of surface waters. Independent observations by the same authors suggest that optical characteristics, and especially fluorescence, come from chromophoric constituents that are indeed spread heterogeneously through the dissolved organic matter (DOM) pool, including a very significant contribution from colloidal constituents that fluctuates with the colloidal size spectrum (Floge and Wells, 2007). This and many other factors—not least the ionic composition of the carrier solution—can potentially affect empirical relationships between optical signatures and DOM concentration, and so may account for the lack of robustness found in these relationships (Ferrari et al., 1996; Ferrari, 2000; Rochelle-Newall and Fisher, 2002; Chen et al., 2004; Floge and Wells, 2007). Taking into account the increasing importance of remote sensing in many areas, such as the study of the carbon cycle and climate change, there is a clear need to improve our fundamental knowledge of how CDOM transformations, especially size-related, can affect the interpretation of satellite data.

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* Corresponding author. Tel.: +44 1847 889585; fax: +44 1847 890014.
E-mail address: francois.muller@thurso.uhi.ac.uk (F.L.L. Muller).

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Estuaries are areas of particular interest for the study of dissolved organic matter, as they constitute an interface between the terrestrial and the marine environment where, due to the abrupt change in environmental conditions, DOM is subject to complex biological, physical and chemical transformations. However, since estuaries are spatially and temporally complex, considerable difficulty still exists in assigning observed changes in the spectral properties of CDOM to biogeochemical transformations of DOM (Boyd and Osburn, 2004). In this study, the first critical steps were taken towards understanding the effects of salinity changes in an estuarine mixing zone on UV–visible absorption and fluorescence characteristics of DOM. This was achieved through (i) the choice of a model estuary (black water river with short residence time of water and flow conditions that ensured a constant pH), (ii) an independent examination of the spectral changes that would be anticipated during simulated estuarine mixing of a freshwater NOM Certified Reference Material, and (iii) the fractionation (by cross-flow filtration) of the DOM matrix between colloidal and dissolved constituents and the measurement of spectral properties in the bulk (0.4-µm filtered), permeate (<5 kDa) and retentate (colloid-enriched) fractions of every sample. This analytical scheme enabled us to examine the effects of salinity changes alone on the spectral optical properties of low molecular weight (LMW, <5 kDa) and colloidal (operationally defined here between 5 kDa and 0.4 µm) DOM. In addition, compositional variations induced by dilution with seawater were examined. Since humic and fulvic substances make up a large fraction of DOM in this estuary, each experiment was run with both natural estuarine samples and carrier solutions of the same ionic composition as the natural samples but containing known concentrations of Nordic Reservoir NOM obtained from the International Humic Substances Society (IHSS). To better constrain our results, we systematically compared the spectral optical properties of the bulk (0.4-µm filtered) samples with those of the low molecular weight and colloidal fractions using absorption, fluorescence and field-flow fractionation (FlFFF) detection techniques.

Some parameters (spectral slope obtained over the wavelength range 320–520 nm, position and intensity of fulvic fluorophores) turned out to be sensitive to the increase in molecular weight (MW) brought about by the formation of larger colloidal assemblages, while others (McKnight's index, DOC-normalised absorption coefficient) appeared more useful in revealing information on the actual chemical composition of the colloids. Although bulk CDOM behaved conservatively through the Thurso River estuarine mixing zone, the combination of optical and fractionation techniques used here revealed a trend towards the formation of both smaller (by contraction) individual macromolecules and larger (by aggregation) colloidal assemblages during the mixing process.

2. Methods

2.1. Site description and sampling

The River Thurso is located in the Far North of Scotland (UK), near a passage (Pentland Firth) running from the North Atlantic to the North Sea. It drains a peatland catchment of 413 km^2 which constitutes one of the largest regions of unbroken blanket bog in the northern hemisphere, and flows north through a short section of agricultural land before entering the Pentland Firth at the town of Thurso. The river is approximately 36 km long and has an average freshwater flow of 10.8 m^3 s^{-1}, as measured 10 km south of Thurso by the Scottish Environment Protection Agency (SEPA). Daily mean flows have fallen between 1 and 70 m^3 s^{-1} for 99% of the time over the last 30 years. This river is not representative of most high latitude river systems because of its relatively high pH (7.0–8.5), low turbidity and remarkably conservative mixing behaviour of Fe, Mn and Al across the full salinity gradient of the estuarine zone. These conditions are brought about by the combination of high fulvic and humic concentrations derived from the blanket bog vegetation upstream and relatively high alkalinity generated in the last 10 km of its course from sandstones, mudstones, calcareous flags and limestone. The groundwater there is also rich in calcium bicarbonate. Due to these conditions, the River Thurso Estuary provides an excellent natural laboratory for examining the effects of salinity on the functional properties of DOM, as flocculation processes are negligible and pre-formed or resuspended inorganic particles such as clay minerals occur in low concentrations.

Table 1
Water chemistry characteristics at the Thurso Estuary sites on the sampling dates and corresponding characteristics of the composite freshwater/seawater (fw/sw) solutions where the freshwater component had been amended with 30 mg L^{-1} of Nordic Reference NOM (from the IHSS).

Sampling date	1-kDa filtered fw (mL)	1-kDa filtered sw (mL)	Salinity	pH
Thurso Estuary samples				
23/05/07	–	–	0.1	8.4
24/05/07	–	–	4.0	8.2
27/05/07	–	–	12.6	8.6
29/05/07	–	–	33.8	8.3
Nordic NOM solutions				
–	1500	0	0.1	8.2
–	1350	150	4.3	8.0
–	950	550	12.7	8.1
–	100	1400	33.3	8.5

Thurso Estuary water samples were collected from two footbridges that provided access to the full estuarine salinity range, during May 2007 (Table 1). Each sample was collected in a 4-L, acid cleaned low density polyethylene (LDPE) bottle which had been previously rinsed with sample water before filling. Once in the laboratory, it was immediately and sequentially filtered through a 0.8-µm cellulose acetate filter and a 0.4-µm hydrophilic polyethersulfone membrane filter (Sartorius). This was achieved through gentle vacuum filtration into an acid cleaned fluorinated ethylene propylene (FEP) container held inside a Class 100 laminar flow cabinet (Bassaire). The filtrate was then stored in the dark at 4 °C until ultrafiltration the next day.

2.2. Preparation of the Nordic NOM solutions and compositional properties

Nordic NOM Reference Material from the Vallsjøen water reservoir, Sør-Odal, Norway, was obtained through the International Humic Substances Society (IHSS) and used as a source of terrestrial NOM from a humic-rich environment. A stock solution of 30 mg L^{-1} was prepared by dissolving the NOM isolate in 1-kDa cross-flow filtered River Thurso water that had been collected at the same time as the estuarine samples so as to reproduce the same major ion composition. This 1-kDa filtrate may still have contained small amounts of DOM but this is likely to have been swamped by the much larger amount of added NOM. The value of 30 mg L^{-1} was chosen in order to approximately reproduce the original organic carbon content found in the River Thurso. From this solution, different dilutions were prepared with 1-kDa cross-flow filtered seawater to acquire the different ionic strength values close to the ones obtained in the natural Thurso Estuary samples (Table 1). Nordic NOM samples prepared in this way were also filtered sequentially through a 0.8-µm cellulose acetate filter and a 0.4-µm hydrophilic polyethersulfone membrane filter, following the same protocol as for the natural samples.

2.3. Ultrafiltration system: cleaning, conditioning and operating parameters

All samples were ultrafiltered using a Sartoflow® Slice 200 benchtop cross-flow filtration system equipped with a peristaltic pump, a 500-mL polysulfone feed reservoir, and a 5 kDa Hydrosart® filter cartridge which had been stored in 0.1 M NaOH in a closed container and thoroughly rinsed with Arium (Sartorius) ultra-pure water prior to each experiment. During typical operation, cross-flow filtration was performed in