



Terrestrial dissolved organic matter distribution in the North Sea

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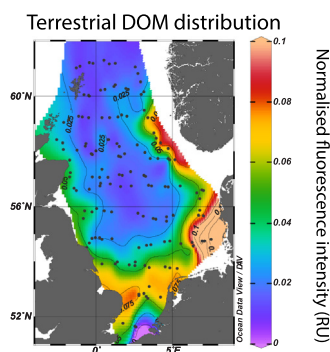
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HIGHLIGHTS

- North Sea fluorescent DOM field sampled to map terrestrial inputs and distributions.
- DOM pool characterised via absorbance and excitation-emission fluorescent spectra.
- Three distinct FDOM fluorophores identified.
- No clear evidence found for significant terrestrial DOM export to the Atlantic Ocean.
- North Sea terrestrial DOM distributions appear stable over multi-decadal timescales.

GRAPHICAL ABSTRACT



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ABSTRACT

The flow of terrestrial carbon to rivers and inland waters is a major term in the global carbon cycle. The organic fraction of this flux may be buried, remineralized or ultimately stored in the deep ocean. The latter can only occur if terrestrial organic carbon can pass through the coastal and estuarine filter, a process of unknown efficiency. Here, data are presented on the spatial distribution of terrestrial fluorescent and chromophoric dissolved organic matter (FDOM and CDOM, respectively) throughout the North Sea, which receives organic matter from multiple distinct sources. We use FDOM and CDOM as proxies for terrestrial dissolved organic matter (tDOM) to test the hypothesis that tDOM is quantitatively transferred through the North Sea to the open North Atlantic Ocean. Excitation emission matrix fluorescence and parallel factor analysis (EEM-PARAFAC) revealed a single terrestrial humic-like class of compounds whose distribution was restricted to the coastal margins and, via an inverse salinity relationship, to major riverine inputs. Two distinct sources of fluorescent humic-like material were observed associated with the combined outflows of the Rhine, Weser and Elbe rivers in the south-eastern North Sea and the Baltic Sea outflow to the eastern central North Sea. The flux of tDOM from the North Sea to the Atlantic Ocean appears insignificant, although tDOM export may occur through Norwegian coastal waters unsampled in our study. Our analysis suggests that the bulk of tDOM exported from the Northwest European and Scandinavian landmasses is buried or remineralized internally, with potential losses to the atmosphere. This interpretation implies that the residence time in estuarine and coastal systems exerts an important control over the fate of tDOM and needs to be considered when evaluating the role of terrestrial carbon losses in the global carbon cycle.

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1. Introduction

The flow of terrestrial organic matter (tOM) through aquatic ecosystems is a significant and increasing component of the global carbon cycle (Ciais et al., 2013) and appears to be increasing in some regions, notably Northern Europe (Monteith et al., 2007). Spatial variations in tOM flux are controlled by regional climate, soil type, vegetation and land use, with the fraction of tOM that ultimately reaches the coastal ocean dependent upon additional biotic and abiotic production and removal processes along the land-sea continuum (Yamashita et al., 2011a; Graeber et al., 2012; Ward et al., 2017). However, the relative importance and future evolution of these processes remain poorly understood with key processes relevant to the transport and transformation of tOM missing from Earth System models, despite its recognised importance (Ciais et al., 2013).

Presently, a total global carbon (C) flux from the land to the ocean of approximately 0.9 Pg C occurs annually consisting of ~0.2 Pg as dissolved organic carbon (DOC), 0.3 Pg as dissolved inorganic carbon (DIC) and up to 0.4 Pg as particulate organic carbon (POC) (Bianchi, 2011; Dai et al., 2012; Ciais et al., 2013). The magnitude of this total terrestrial carbon flux is equivalent to approximately one-third of the total annual oceanic CO₂ drawdown (~2.6 Pg C yr⁻¹; Le Quere et al., 2016). Yet despite the terrestrial DOC flux being capable of turning over the entire marine DOC pool of ~700 Pg C on millennial timescales (Hansell et al., 2009), there is only limited evidence for a significant terrestrial contribution to the open ocean DOC pool which suggests rapid removal of tOM inputs in coastal and shelf waters (Hedges et al., 1997; Opsahl and Benner, 1997; Bianchi, 2011).

Most tOM derives from plant exudation, the decomposition of recent litter or soil organic matter (SOM), although some may derive from the breakdown of older SOM, particularly in disturbed soils (Evans et al., 2014; Butman et al., 2015). A significant fraction of this tOM is removed or recycled within inland waterways (Tranvik et al., 2009) but a substantial proportion reaches estuaries and near coastal waters, where it may be subject to further chemical or biological modification, aiding rapid biological utilization and eventual loss to the atmosphere (Bianchi, 2011). The total terrestrial carbon flux of ~0.9 Pg C yr⁻¹ that reaches the coastal ocean, is therefore significantly less than the total carbon flux actually lost from terrestrial soils. Estimates vary widely for the various carbon pools, but for the UK it has been estimated that >70% of soil derived DOC entering inland waterways is respired or otherwise lost before it reaches coastal waters (Worrall et al., 2012), which is similar to a global estimate of total organic carbon removal in inland waters obtained by Tranvik et al. (2009). Globally, it is thought that around 25% of soil derived DOC is removed in estuaries alone (Dai et al., 2012). Thus, the global land to ocean DOC flux of ~0.2 Pg C yr⁻¹ is acutely sensitive to changes in biotic and abiotic processes which could have significant implications for the proportion of tOM reaching coastal waters. The fate of river borne POC is similar with 30–50% of terrestrially derived POC buried within deltaic sedimentary systems and the remainder rapidly respired in coastal waters (Hedges and Keil, 1995; Burdige, 2005). At present a significant fraction of tOM is prevented from entering the ocean due to processes occurring in freshwater and estuarine systems.

Here we report a North Sea wide survey of chromophoric and fluorescent dissolved organic matter (CDOM and FDOM, respectively) absorbance and fluorescence properties conducted to 1) investigate the mean distribution of terrestrial dissolved organic matter (tDOM) during summer 2016, 2) identify the major tDOM sources, and 3) determine the likely fate of tDOM entering the North Sea. Collectively, CDOM and FDOM represent 20–70% of the overall DOM pool (e.g. Dittmar and Stubbins, 2014), and as tracers of the tDOM pool can underestimate export fluxes, but CDOM and FDOM distributions are nevertheless considered valuable proxies for tDOM more generally (e.g. Stedmon and Nelson, 2015).

2. Methods

2.1. Regional setting

The North Sea is a semi-enclosed marginal sea of the temperate latitude Northeast Atlantic, and part of the larger northwest European continental shelf (Otto et al., 1990). Oceanic water enters the North Sea via the English Channel to the southwest (~51°N), and directly from the North Atlantic Ocean along its northern boundary (~60°N), with the major outflow occurring via the Norwegian Trench to the northeast (Huthnance et al., 2009). Residence times vary from <100 days for water in the Norwegian Trench to ~4 years for water entering the northwest North Sea (Prandle, 1984; Blaas et al., 2001). Brackish water inputs from the Baltic Sea, via the Kattegat, occur along the eastern edge of the North Sea (Gustafsson and Andersson, 2001). Several major European rivers discharge into the southern North Sea including the rivers Rhine, Meuse, Elbe, Weser and Scheldt and all have been associated with significant tDOM input (Warnock et al., 1999; Astoreca et al., 2009).

2.2. Sampling

Sampling was conducted opportunistically during August–September 2016 onboard the R.V. *CEFAS Endeavour*. Near-surface (~5 m depth) seawater was sampled every 2–3 h during the day and analysed for dissolved inorganic and organic nutrients, salinity, chlorophyll-a concentrations, seawater absorbance, and fluorescent organic matter excitation emission spectra.

2.3. Inorganic and organic nutrient concentrations

Inorganic nutrient samples were syringe filtered through 0.22 μm polyethersulfone filters into acid cleaned and “aged” 60 ml HDPE bottles and frozen at –20 °C for subsequent shore-based analysis. Samples were analysed by colorimetry using a Bran and Luebbe 5-channel AAIII segmented flow autoanalyser using standard analytical techniques (Woodward and Rees, 2001). Detection limits were 0.02, 0.01, 0.01 and 0.02 μmol L⁻¹ for total nitrate (NO₃⁻ + NO₂⁻), NO₂⁻, Si(OH)₄ and PO₄³⁻ respectively. For calculation of mean concentrations, where some measurements were below the detection limit, the detection limit was used in statistical calculations.

Duplicate organic nutrient samples were syringe filtered through 0.22 μm polyethersulfone filters into 125 ml HDPE bottles and frozen at –20 °C for later analysis. DOC concentrations were measured on a Skalar Formacs total organic carbon analyser. Samples were acidified with 3 M HCl and sparged with O₂ to remove dissolved inorganic carbon prior to analysis. Total dissolved nitrogen (TDN) and total dissolved phosphorous (TDP) were measured following UV oxidation of samples as described by Torres-Valdes et al. (2016). Briefly, after defrosting the samples duplicate 10 ml aliquots of seawater were UV-oxidised for 2 h using two Metrohm 705 UV oxidation units. After oxidation, TDN and TDP were measured as total nitrate and phosphate using a SEAL Analytical QuAAtro autoanalyser and standard GO-SHIP protocols (Hydes et al., 2010). A third un-oxidised aliquot of each seawater sample was separately measured for the dissolved inorganic nutrient content (NO₃⁻ + NO₂⁻ and PO₄³⁻). Dissolved organic nitrogen (DON) and dissolved organic phosphorous (DOP) concentrations were subsequently calculated by difference between the total dissolved and inorganic nutrient concentrations (i.e. DON = TDN – (NO₃⁻ + NO₂⁻)). Nutrient reference materials (KANSO, Japan) were analysed regularly to check precision and accuracy (within 1–2%). Analytical detection limits based on measurement standards were 0.02 and 0.01 μmol L⁻¹ for total nitrate (NO₃⁻ + NO₂⁻) and PO₄³⁻ respectively. Analytical uncertainty associated with DON and DOP measurements was estimated as the root-sum-square of total nutrient uncertainty based on replicate sample analysis and inorganic nutrient uncertainty based on the global uncertainty associated

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