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Fluvial dissolved organic carbon composition varies spatially and seasonally in a small catchment draining a wind farm and felled forestry

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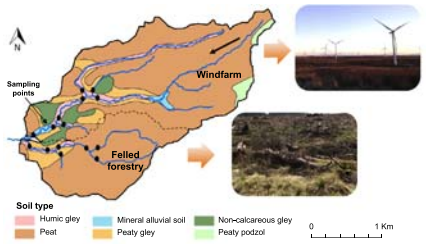
HIGHLIGHTS

- The influence of land use on the concentration and composition of fluvial DOC in a peat-rich catchment was investigated.
- There was greater fluvial [DOC] in the felled catchment than in the wind farm catchment.
- Fluvial DOC was similarly aromatic, but more humified in the wind farm catchment.
- In the dry months, DOC became more humified in the felled catchment, indicating DOC might be from different peat layers.

GRAPHICAL ABSTRACT



	Weather	Land Use	Monthly Mean [DOC]	DOC Aromaticity	DOC Humification
Inter-stream Comparison	Not-dry	Windfarm	Lower	Similar	Larger
		Deforestation	Higher	Similar	Smaller
Change from the previous month	Dry (only July & Sept.)	Windfarm	Decreases	Decreases	Decreases
		Deforestation	Decreases	No change	Increases

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ABSTRACT

Assessing whether land use, from activities such as wind farm construction and tree-felling, impacts on terrestrial C delivery to rivers has focused on quantifying the loss of dissolved organic carbon (DOC), and not the composition changes. Here we explore how land use influences DOC composition by considering fluvial DOC concentration, [DOC], and spectrophotometric composition of a river draining a peat-rich catchment. We find that in this 5.7 km^2 catchment differences occur in both the concentration and composition of the DOC in its sub-catchments. This is attributed to differences in how land was used: one tributary (D-WF) drains an area with wind farm construction and forestry in the headwaters, and one tributary (D-FF) drains an area with felled plantation trees. Generally, [DOC] in both streams showed similar seasonal variation, and autumn maxima. However, the felled catchment had greater mean [DOC] than the wind farm catchment. The $SUVA_{254}$ and E_4/E_6 indicated DOC in both streams had similar aromaticity and fulvic:humic acid for most of the time, but $SUVA_{410}$ and E_2/E_4 indicated less DOC humification in the felled catchment. This may be due to young DOC from the breakdown of residual branches and roots, or more humification in soils in the wind farm area. During the dry months, DOC composition showed more spatial variation: the D-WF DOC had smaller $SUVA_{254}$ (less total aromatic material) and $SUVA_{410}$ (fewer humic substances). The decreased E_2/E_4 in both streams indicated the total aromatic carbon decreased more than humic substances content. Moreover, the larger E_4/E_6 for D-WF in summer indicated that the humic substances were richer in fulvic acids than humic acids. Soil disturbance associated with forestry-felling likely contributed to the higher [DOC] and release of less-humified material in D-FF. This research indicates drivers of different DOC concentration and composition can exist even in small catchments.

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1. Introduction

Peatlands are a significant terrestrial carbon store and a principal source of dissolved organic carbon (DOC) to the fluvial systems (Wallage et al., 2006). In the past decade it has been observed that DOC concentrations, [DOC], in surface waters have increased in Europe and North America, attributed primarily to reduced acid deposition no longer suppressing terrestrial DOC production (Monteith et al., 2007), and supporting increased DOC mobility (Clark et al., 2005). However, land use change can also release C from peat soils. Afforestation can lead to higher [DOC] for peat-covered catchments, and forestry effects on [DOC] appear largest following felling (Neal et al., 1998). On peaty-mineral soils, timber-felling generally causes an increase in [DOC] in stream water which may persist for a few years, particularly at a local scale (e.g. Neal et al., 2004). In Europe large areas of peat have been drained to improve grazing, lowering the water tables and stimulating DOC production (Holden et al., 2004). However, little is known about how the composition of DOC in fluvial systems may reflect land use, and if this composition varies considerably, but this is also important to understand the fate of DOC in a fluvial system.

DOC consists of a variety of molecules considered to range in size and structure, from simple acids and sugars to complex humic substances (HS) (Thurman, 1985). Traditionally, HS are thought to comprise the dominant fractions of dissolved organic matter (DOM), and are heterogeneous mixtures formed by humification, the process where the biochemical and chemical reactions occur along with the decay and transformation of plant and microbial materials (Kastner and Hofrichter, 2001). Further, it is thought there are two main sources of aquatic HS: 1) land-derived material from soil and plants (allochthonous substances) and 2) from biological activities within aquatic systems (autochthonous substances) (Frimmel, 2005). In peat land drainage systems the terrestrial source typically dominates (Tipping et al., 2010).

HS have never been separated into pure components (Hautala et al., 2000; Muscolo et al., 2013), but have been generally divided into two main fractions based on chemical extraction processes: humic acids (HAs) and fulvic acids (FAs) (International Humic Substances Society; Frimmel, 2005; Muscolo et al., 2013). HAs are categorized as the fraction that is not soluble in water under acidic conditions (pH < 2) but are soluble at higher pH values. Generally HAs have a larger molecular weight and contain more carbon with fewer oxygen-containing functional groups (Stevenson, 1994; Weng et al., 2006; Gungor and Bekbolet, 2010; Tang et al., 2014). They have a greater proportion of hydrophobic (mainly aromatic) moieties (Piccolo, 2001; Šmejkalová and Piccolo, 2008), and are more stable as they have more conjugated bond systems. Therefore, HAs are more complex and microbially-resistant than FAs. The structural difference suggests HAs to be more humified and aromatic than FAs. These properties allow the use of spectrophotometric methods to infer structural characteristics, as aquatic DOM strongly absorbs light in the UV–visible wavelength range, with compositional differences influencing absorbance at specific wavelengths (Korshin et al., 1997; Helms et al., 2008; Selberg et al., 2011; Peacock et al., 2014).

The scientific community is now considering whether HS exist and if this terminology appropriately captures the degradation processes prevalent in soil that may also shape fluvial DOC (Lehmann and Kleber, 2015). This is an exciting consideration and it may herald a new approach to interpreting DOC composition. However spectrophotometric characterization has been informed by molecular composition consideration (e.g. Weishaar et al., 2003) and it is this approach we use here, drawing on the large body of research that has interpreted DOM composition (see Table 1), and from this environmental understanding of controls on composition (e.g. Mao et al., 2017). This approach to considering HS should still offer a framework for future reinterpretation if it is considered too simple.

Spectroscopic approaches are based on the following understanding. Conjugated double bond systems in aromatic materials will lead to strong absorption in the near UV (200–380 nm), while other electron structures do not absorb in this range of the UV spectrum (Weishaar et al., 2003). The measurement termed specific UV absorbance ($SUVA_{254}$), calculated by dividing the absorbance of a water sample at 254 nm by its DOC concentration, is considered to be strongly-related to DOC aromaticity (Weishaar et al., 2003), particularly the proportion of the total carbon in aromatic rings (Zbytniewski and Buszewski, 2005). It should also be noted here that although non-humic substances are generally not aromatic, the amino acids phenylalanine, tryptophan and tyrosine do have aromatic rings and UV absorption peaks in the region 200–300 nm, thus $SUVA_{254}$ characterizes all aromatic C.

The visible wavelengths 400 nm and 665 nm are considered to provide DOM compositional information (Chen et al., 1977; Hongve and Åkesson, 1996; Hautala et al., 2000). Peak absorption above 400 nm indicates more-complex conjugated and aromatic structures (such as HS, including both HAs and FAs), and reflects organic materials resulting from the humification process. Peak absorbance above 600 nm is indicative of even more complex conjugated associations, and strongly-humified materials with a high degree of aromatic, condensed groups (Zbytniewski and Buszewski, 2005; Albrecht et al., 2011), such as HAs.

The ratios between absorbance at different wavelengths can provide qualitative information about the aqueous DOC composition. For example, HS are thought to generate most of the brown colour in DOC samples (Hautala et al., 2000; Frimmel, 2005) and have strong UV–visible absorption at about 400 nm (resulting in yellow-brown colours). Therefore, $SUVA_{410}$ (Abs_{410} divided by [DOC]) is used to reveal the changes in proportion of HS which contain complex aromatic structures. In addition, the ratio between absorbance at 254 nm and 410 nm (E_2/E_4) reflects the intensity of UV-absorbing aromatic rings to HS colour (Zepp and Schlotzhauer, 1981; Selberg et al., 2011; Graham et al., 2012), and so provides some insight about proportions of HS in total aromatic carbon. Waters which contain a greater proportion of HS have lower E_2/E_4 values (Graham et al., 2012). Additionally, HAs and FAs absorb light in different amounts at 465 nm and 665 nm, thus, the ratio between absorbance at 465 nm and 665 nm (E_4/E_6) is used to infer differences in the proportion of humic and fulvic acids between samples (Thurman, 1985; Hautala et al., 2000; Spencer et al., 2007; Moody et al., 2013). A lower E_4/E_6 reflects a larger proportion of HAs, a higher degree of aromatic condensation and a higher level of organic material humification (Zbytniewski and Buszewski, 2005). Between aquatic humic and fulvic acid samples, E_4/E_6 has been observed to be higher for fulvic acids and lower for humic acids (Thurman, 1985). Fig. 1 demonstrates how optical parameters can be used for understanding DOC composition.

As most fluvial DOC comes from the catchment soils, differences in fluvial DOC concentration and composition may reflect differences in the catchment soil reservoir, including how the land is managed. For example, [DOC] was observed to increase immediately during peat bog harvesting as a result of the ecosystem disturbance, but decrease afterwards, considered to reflect the reduced content of stored DOM in the soil (Glatzel et al., 2003). In a degraded peat, higher $SUVA_{285}$ (a similar approach to $SUVA_{254}$), together with a red shift in fluorescence spectra (another approach to considering DOC composition, Miano and Senesi, 1992), in extracted DOC indicated increased aromaticity and humification (Kalbitz et al., 1999).

A land use change prevalent today is the disturbance of peat soils for the construction of wind farms, potentially impacting water quality (Drew et al., 2013). For example, a small but significant negative impact of construction on water chemistry (pH, alkalinity and ANC only) has been observed during and after wind farm construction in the upper part of a Scottish catchment (Millidine et al., 2015). Soil disturbance to the depth of bedrock and extensive deforestation can be required for wind farm construction and thus these activities may be expected to increase [DOC]. Indeed short-term increases have been observed (e.g. Grieve and Gilvear, 2008; Waldron et al., 2009). Whether this also induces compositional changes in DOC is unknown. The DOC composition reflects its origin (microbial production, vegetation and soil leaching), and unveils carbon cycling processes in the peat (Fellman et al., 2008; Gandois et al.,