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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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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 km² 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 SUVA₂₅₄ and E₄/E₆ indicated DOC in both streams had similar aromaticity and fulvic:humic acid for most of the time, but SUVA₄₁₀ and E₂/E₄ 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 SUVA₂₅₄ (less total aromatic material) and SUVA₄₁₀ (fewer humic substances). The decreased E₂/E₄ in both streams indicated the total aromatic carbon decreased more than humic substances content. Moreover, the larger E₄/E₆ 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.

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.

Keywords

Dissolved organic carbon; peatland; wind farm; deforestation; SUVA, UV-vis spectrophotometry; Fe

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 ($\text{pH} < 2$) 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

89 this approach we use here, drawing on the large body of research that has interpreted DOM
90 composition (see Table 1), and from this environmental understanding of controls on
91 composition (e.g. Mao et al., 2017). This approach to considering HS should still offer a
92 framework for future reinterpretation if it is considered too simple.

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

103 The visible wavelengths 400 nm and 665 nm are considered to provide DOM
104 compositional information (Chen et al., 1977; Hongve and Åkesson, 1996; Hautala et al.,
105 2000). Peak absorption above 400 nm indicates more-complex conjugated and aromatic
106 structures (such as HS, including both HAs and FAs), and reflects organic materials resulting
107 from the humification process. Peak absorbance above 600 nm is indicative of even more
108 complex conjugated associations, and strongly-humified materials with a high degree of
109 aromatic, condensed groups (Zbytniewski and Buszewski, 2005; Albrecht et al., 2011), such
110 as HAs.

111 The ratios between absorbance at different wavelengths can provide qualitative
112 information about the aqueous DOC composition. For example, HS are thought to generate
113 most of the brown colour in DOC samples (Hautala et al., 2000; Frimmel, 2005) and have
114 strong UV-visible absorption at about 400 nm (resulting in yellow-brown colours). Therefore,
115 $SUVA_{410}$ (Abs_{410} divided by [DOC]) is used to reveal the changes in proportion of HS which
116 contain complex aromatic structures. In addition, the ratio between absorbance at 254 nm and
117 410 nm (E_2/E_4) reflects the intensity of UV-absorbing aromatic rings to HS colour (Zepp and
118 Schlotzhauer, 1981; Selberg et al., 2011; Graham et al., 2012), and so provides some insight
119 about proportions of HS in total aromatic carbon. Waters which contain a greater proportion
120 of HS have lower E_2/E_4 values (Graham et al., 2012). Additionally, HAs and FAs absorb light
121 in different amounts at 465nm and 665nm, thus, the ratio between absorbance at 465 nm and
122 665 nm (E_4/E_6) is used to infer differences in the proportion of humic and fulvic acids between
123 samples (Thurman, 1985; Hautala et al., 2000; Spencer et al., 2007; Moody et al., 2013). A
124 lower E_4/E_6 reflects a larger proportion of HAs, a higher degree of aromatic condensation and
125 a higher level of organic material humification (Zbytniewski and Buszewski, 2005). Between
126 aquatic humic and fulvic acid samples, E_4/E_6 has been observed to be higher for fulvic acids
127 and lower for humic acids (Thurman, 1985). Fig.1 demonstrates how optical parameters can
128 be used for understanding DOC composition.

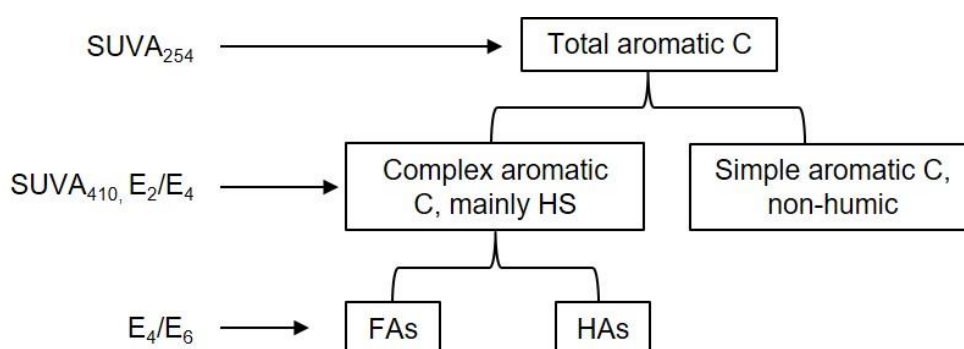


Fig. 1. The relationship between total aromatic C, simple aromatic C, HS, HAs and FAs. The four optical parameters can be used to indicate the composition of DOC.

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 & 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., 2013; Glatzel et al., 2003). For example, in peat, soil organisms, primarily bacteria and fungi, metabolize the non-coloured, small-molecular-weight non-humic substances in preference to the coloured, larger and more biologically-resistant HS (Dawson et al., 2001; Hope et al., 1994; Thomas, 1997; Thurman, 1985; Wallage et al., 2006). A change in balance in these processes could affect the DOC composition.

Fluvial export of DOC is a key lateral transport process in the global carbon cycle, with uncertainty as to how much is exported to the ocean versus transformed to CO_2 where it can be degassed to the atmosphere en route (e.g., Long et al. 2015). This transformation will be compositionally dependent and as such it is important to consider the processes that control fluvial DOC composition and its stability seasonally. In a peaty catchment, where part of the catchment has been used for wind farm construction and another part of the catchment felled, we assessed if land use differences influenced the concentration and composition of DOC in

161 catchment drainage. Over one annual cycle we measured fluvial [DOC] and characterized its
162 composition using UV-spectrophotometry to explore: 1) if land use caused any difference in
163 [DOC] of catchment drainage and 2) if this released DOC differed in composition. This
164 understanding explores the influence of land use on DOC export. The insight gained may
165 ultimately inform understanding of the fate of DOC in streams.

166 167 **2. Materials and methods**

168 **2.1. Study sites and sampling strategy**

169 **2.1.1. Drumtee**

170 Drumtee Water (55°41'16"N, 4°23'37"W) is a third order 5.7 km² catchment in central
171 Scotland, UK, draining the edge of the Whitelee wind farm, which is Europe's second largest
172 and the UK's largest onshore wind farm. The land use in Drumtee is rough grazing and
173 maximum elevation within the catchment is 260 m. Whitelee is located mostly on peat-rich
174 soils, with an average peat depth of 190 cm ± 134 cm. Peat is defined as soil where the
175 uppermost soil horizon has > 60% organic matter and exceeds 50 cm in thickness (Soil Survey
176 in Scotland, 1984; SNH 2014). Historic imagery of the catchment (see for example Google
177 Earth™) suggests a mosaic of historical drainage, but the most recent disturbance of a large
178 scale across the site was for wind farm construction and felling. Wind farm construction
179 activities took place from October 2006 and the original 140 turbines became fully operational
180 in 2009. By 2013, the wind farm had been extended with a further 75 turbines. The wind farm
181 disturbance comprised mostly forest clearance, peat excavation, access road construction
182 (thus drainage), and turbines and associated infrastructure erection. The main disturbance in
183 the Drumtee Water was forest-felling and some excavation and road construction for the eight
184 turbines that lie within the catchment footprint (Fig. 2A).

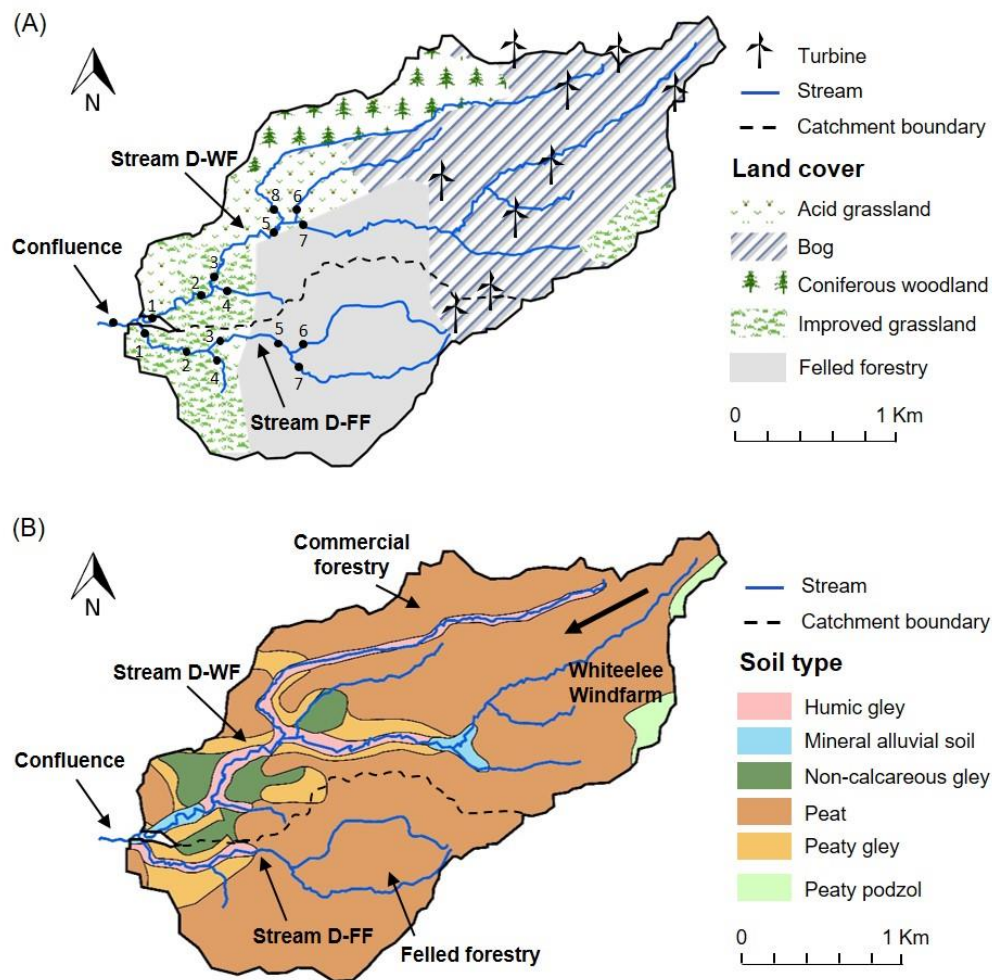


Fig. 2. Map of Drumtee Water catchment indicating different land uses (A) and soil type (B). Drumtee is draining part of the western edge of Whitelee Wind Farm, and consists of two sub-catchments (separated by the dashed black line in both A and B). Each of the sub-catchments contains one main stream (D-WF in the north and D-FF in the south). There is a similar dominance of peat coverage in each catchment, but land uses differ, with D-FF dominated by deforestation while D-WF hosts more turbines. There are six turbines in D-WF (and another one very close, which could have affected drainage in D-WF) and two in D-FF. One small tributary from Stream D-WF originates in felled forestry. Sampling sites are presented by black dots and labelled by number (A).

There are two sub-catchments in Drumtee Water. The stream D-WF in the north sub-catchment (3.9 km²) mainly drains an area with six turbines in the headwater and intact commercial forestry, although one tributary originates in the felled area and another transits through it. The stream D-FF in the south sub-catchment (1.8 km²) mainly drains felled forest with only two turbines (Fig. 2A). The soils in Drumtee Water are mainly blanket peat, comprising 74 % of the area of D-WF and 88 % of D-FF. A further 8 % of each catchment is peaty gley area, and the remainder is composed of humic gleys, mineral alluvial soils, non-calcareous gleys and peaty podzols (Fig. 2B). Across the study area the slope is gentle, < 6° generally except for the river channels where it can be up to 10°, and this topography is similar between sub-catchments. The similar soil type and topography, but different land uses,

between the two sub-catchments allows the impact of land use on stream DOC to be explored.

Eight sites were sampled on Stream D-WF and seven sites on Stream D-FF (Fig. 2A). The confluence site is an 'anchor' site, having been monitored approximately monthly for water quality since June 2006 (Murray, 2012; Phin, 2015; Waldron et al., 2009). Discharge at the confluence site was recorded at half-hourly intervals by an ISCO flow logger, and this was used to generate a hydrograph, except for the period 25/06/2014 – 20/08/2014. Here discharge monitored at the closest Scottish Environment Protection Agency (SEPA) gauging station Newmilns (station reference: NS 53252 37188) was used to reconstruct the hydrograph from the relationship between Newmilns and Drumtee (Coleman, 2017). The discharge data shows our sampling was carried out during base flow and wet periods (Fig. 3).

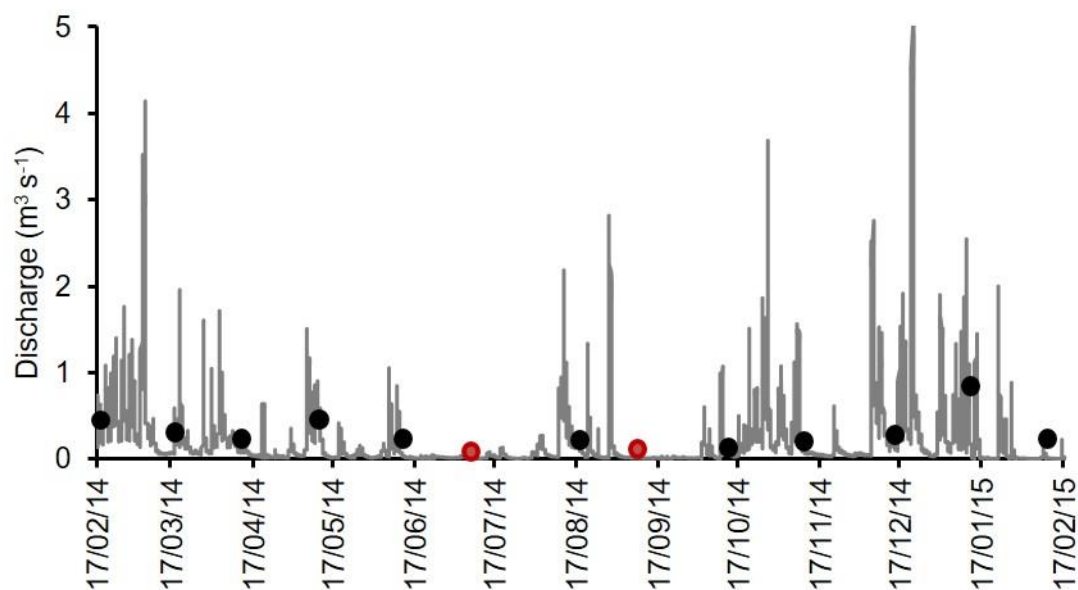


Fig. 3. Discharge from February 17, 2014 to February 17, 2015 at the long-term sampling point just downstream of the confluence of two streams. Sampling dates are indicated by spots. July and September 2014 sampling represented the lowest flows (red spots), and December 2014 sampling represented the highest flow.

2.1.2. Sampling

Samples were collected approximately every four weeks from February 2014 to February 2015 from the 15 sampling points along Streams D-WF and D-FF in Drumtee (Fig. 2B). All samples were collected within six hours. 330 ml drinking water bottles (PETE, polyethylene terephthalate) were used for field sample containers. Of many different bottles tested these had negligible UV-absorbance material release. Bottles were rinsed with deionized water in the lab and with stream water in the field three times each before collecting samples. Field samples were kept in a cool box and on return to the laboratory they were stored in the cold room at 4°C until filtering that same day. Samples were filtered using a Whatman GF/F 0.7 µm filter paper, which had been pre-combusted at 450°C for 8 h and rinsed with deionized water, previously tested to generate a negligible UV absorbance blank after 125 ml rinse. Filtered samples were stored in the cold room to minimize bacterial decomposition and were analyzed as soon as possible, typically within three days. This timeline was acceptable as we tested the

impact of storage length on DOC UV absorbance and found $< 0.01\text{cm}^{-1}$ difference ($n = 7$, $SD = 0.008\text{ cm}^{-1}$) was observed among filtered samples before and after being stored for a month. No difference in [DOC] was observed in samples stored for up to 30 days if the samples had been filtered (Gulliver et al., 2010).

2.2. [DOC] and UV-visible absorbance measurements

[DOC] was measured on a Thermalox TOC analyser which combusted organic carbon at 680°C to CO_2 , which was subsequently detected by a non-dispersive infra-red sensor. Before combustion, dissolved inorganic carbon (DIC) was removed by acidifying samples with 0.01M H_2SO_4 to pH 3.9 using a Mettler DL 20 Autotitrator, and degassing for 20 min in an ultrasonic bath. Triplicate measurements were made of each sample, with the mean [DOC] accepted when the coefficient of variance was $< 2\%$.

UV-visible absorbance of filtered field samples was measured at the following wavelengths using a Hitachi U-1100 spectrophotometer: 254 nm, 340 nm, 410 nm, 465 nm, 665 nm and 800 nm. Water samples were placed in a 10 mm quartz cuvette. All samples were warmed to room temperature prior to measurement as otherwise the low temperature can affect accuracy. Deionized water was used as blank and its absorbance (usually close to zero) was subtracted from the field sample absorbance.

Fe^{3+} absorbs UV light and therefore the accuracy of SUVA_{254} and E_2/E_4 can be compromised by dissolved iron (Weishaar et al., 2003; Peacock et al., 2014). Thus, we made a correction for iron interference in UV absorbance measurements by spiking samples with a known amount of Fe^{3+} and measuring its influence on absorbance. Inorganic salt $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ was dissolved in deionized water to prepare 100 mg l^{-1} Fe^{3+} solution. Deionized water and filtered DOC samples collected from Stream D-WF and D-FF were mixed with 5 ml 0.01M HCl and sufficient sample from 100 mg l^{-1} Fe^{3+} solution, to make up 50 ml solutions with 0.001 M HCl and 0 mg l^{-1} , 1 mg l^{-1} , 2 mg l^{-1} , 3 mg l^{-1} , 4 mg l^{-1} and 5 mg l^{-1} Fe^{3+} amendment. Deionized water with the same Fe^{3+} amendment ($0 - 5\text{ mg l}^{-1}$) and HCl (0.001 M) amendment was regarded as a blank. Two replicates were made of each $[\text{Fe}^{3+}]$ solution. The total Fe concentration of each solution was measured using a Perkin-Elmer AAnalyst 100 Atomic Absorption Spectrophotometer, and Fe standard solutions with concentrations from $1 - 6\text{ mg l}^{-1}$ were prepared using 1000 mg l^{-1} Fe stock. UV absorbance at 254nm and 410nm of each solution was measured using a Hitachi U-1100 spectrophotometer. The $[\text{Fe}^{3+}]$ -absorbance measurements generated a relationship, from which field sample absorbance was corrected for Fe^{3+} interference following measurement of $[\text{Fe}]$.

2.3. Statistical analysis and data treatment

Sub-catchment temporal variation was considered by calculating the mean and the standard deviation (SD) of all stream sampling points for each sampling trip. This was undertaken to provide more confidence that the variation in a sub-catchment composition was captured in a single point average. This approach has a degree of pseudoreplication. However, approximately 50% of sampling points did not receive water from upstream and so were independent of one another, and all sites received new water and so we used this field sampling strategy to generate details, as has been done with many other catchment studies (e.g. Yates et al., 2016). From this pooled data, one-way analysis of variance (ANOVA) was

applied to investigate if there were significant differences between the two streams for all optical parameters. Before any ANOVA analysis, the Anderson-Darling method was applied to examine the normality of each dataset in both D-WF and D-FF groups. All datasets in this study were normally distributed. All normality and ANOVA analyses were conducted using Minitab® 17 statistical software. A p value < 0.05 was considered as significantly different.

For the data analysis, not all sites were grouped by sub-catchment. In stream D-WF, there was one tributary, D-WF4 which had [DOC] and composition more similar to D-FF group (Fig. S1). This site, unlike others in D-WF, had its source within, and mostly drained the felled area. As this research explores if land-use affects DOM composition, it was considered more appropriate to pool this data with the D-FF samples. Doing this reduced the standard deviation of D-WF dataset, but did not cause obvious changes in those of D-FF group (Fig. S2, Table S1). The results and discussion hereafter treat D-WF4 as part of the D-FF catchment.

3. Results

3.1. Seasonal DOC concentration in two streams

Across the catchment and annual cycle, [DOC] ranged from 6.6 to 86.3 mg l⁻¹ (Fig. 4, Fig. S1). All [DOC] showed little variation between sites within either stream. The range in [DOC] in both streams was large, with D-FF having greater [DOC], ranging from 14.1 – 86.3 mg l⁻¹ compared to from 6.6 – 49.0 mg l⁻¹ for D-WF. Generally, [DOC] in the two streams shared the same seasonal pattern with the highest concentrations in the summer and the lowest concentration in winter. There were obvious [DOC] decreases in the catchment from June to July (D-WF: from 48.5 ± 2.8 to 21.4 ± 3.0 mg l⁻¹; D-FF: 77.3 ± 7.0 to 62.7 ± 17.9 mg l⁻¹) and from August to September (D-WF: from 49.0 ± 4.0 to 28.7 ± 3.1 mg l⁻¹; D-FF: from 81.6 ± 9.5 to 67.6 ± 13.5 mg l⁻¹), which as discharge evidences were the drier periods in 2014 (Fig. 4).

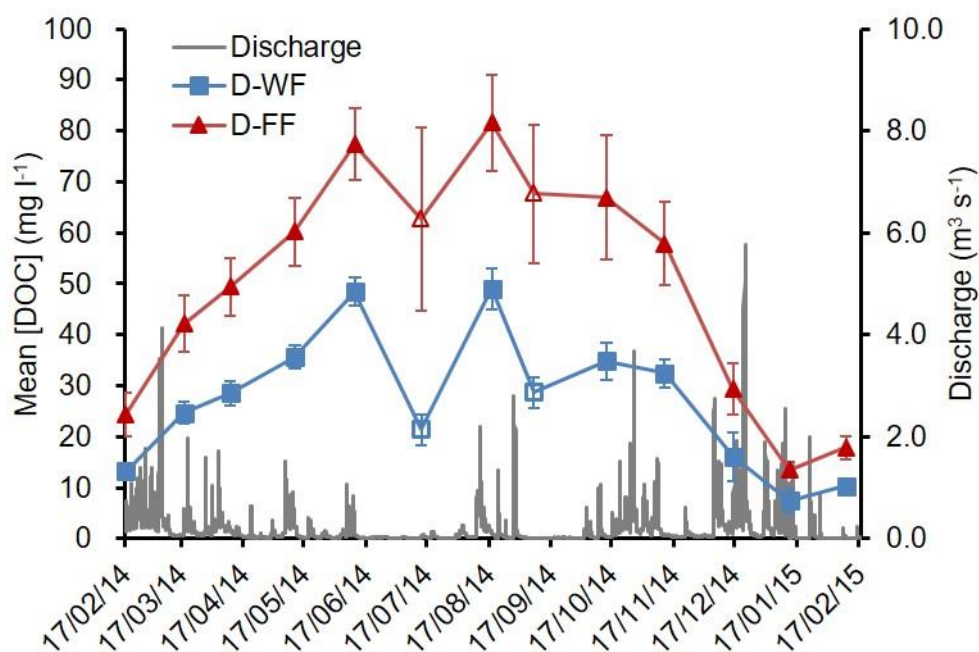


Fig. 4. Stream D-WF and D-FF mean [DOC] from February 2014 to February 2015. Each sample point is the mean ± SD of all stream sampling points on that day. July and September samples are represented by empty symbols.

3.2. Fe³⁺ interference

In the control samples, UV absorbance at 410 nm (Abs₄₁₀) was negligible (0 - 0.001 cm⁻¹) for all [Fe³⁺] amended solutions, but at 254nm (Abs₂₅₄) positively increased as [Fe³⁺] increased from 0 – 5 mg l⁻¹ (Fig. 5A). Similarly, Abs₂₅₄ increased linearly with increasing total Fe³⁺ concentration (Fig. 5B) in the matrix whole water samples from Drumtee catchment. The absorbance difference between streams reflects different starting [DOC], but the slopes of these relationships are very similar (D-WF: 0.054; D-FF: 0.064) reflecting the [Fe³⁺] contribution. The gradients of the D-WF and D-FF [Fe³⁺]-Abs₂₅₄ were thus used to correct Abs₂₅₄ of field samples, using the measured sample [Fe³⁺] to guide the correction. Abs₂₅₄ of samples from all sites across both tributaries ranged from 0.27 – 3.51 cm⁻¹ and [Fe³⁺] from 0.11 – 6.14 mg l⁻¹ during the study period (data not presented). The Fe³⁺ interference in the two tributaries was from 0.01 – 0.39 cm⁻¹, comprising 2.1 – 15.9 % of the un-corrected Abs₂₅₄. After correction Abs₂₅₄ in the two tributaries ranged from 0.26 – 3.18 cm⁻¹.

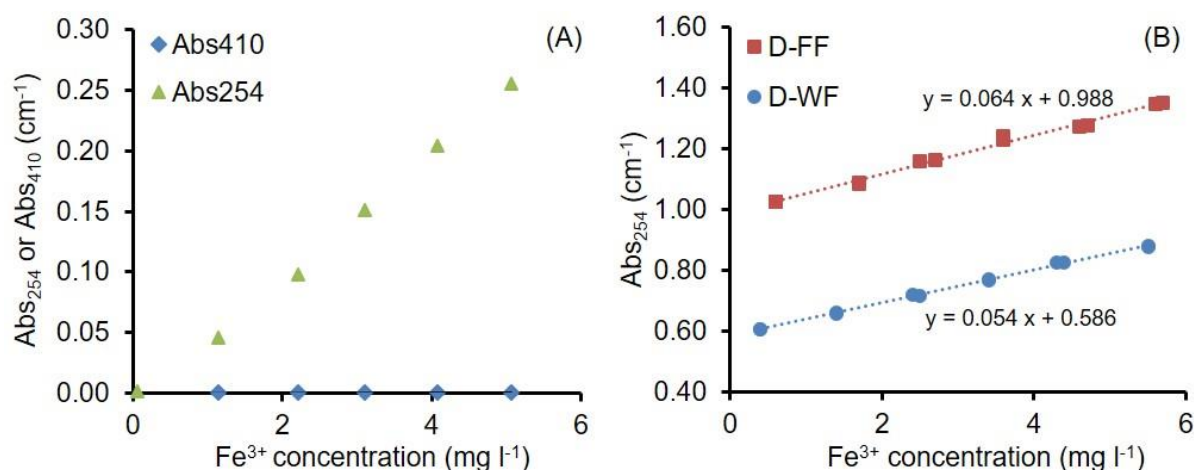


Fig. 5. The effect of Fe³⁺ concentration (0 – 5 mg l⁻¹) on Abs₂₅₄ and Abs₄₁₀ of blank control waters (A), and only on Abs₂₅₄ of D-FF and D-WF stream waters (B). In the blank solutions, a positive relation between Abs₂₅₄ and [Fe³⁺] was observed, while Abs₄₁₀ was constantly negligible across all amended blank solutions. Closely parallel lines were generated in the [Fe³⁺] amended stream waters, indicating a similar linear relationship between [Fe³⁺] and Abs₂₅₄. Equations were used for further UV absorbance correction.

3.3. DOC quality: aromaticity; HS proportion; HA: FA

SUVA₂₅₄ in the Drumtee catchment ranged from 2.8 to 4.6 l mg⁻¹ m⁻¹ and the average (3.7 ± 0.32 l mg⁻¹ m⁻¹) was within the range of diverse surface freshwater SUVA₂₅₄ (Table 1), but is towards the higher end of the range, indicating the fluvial DOC was rich in aromatic carbon. Generally, DOC in the two streams had similar aromaticity with little variation throughout the year ($p > 0.05$) (Fig. 6A). However, the D-WF DOC aromaticity decreased noticeably from 3.9 ± 0.0 to 2.8 ± 0.3 l mg⁻¹ m⁻¹ in July 2014 (the dry period) when there was a slight increase (from 3.7 ± 0.1 up to 3.8 ± 0.3 l mg⁻¹ m⁻¹) in D-FF. D-WF DOC SUVA₂₅₄ increased to 4.5 ± 0.3 l mg⁻¹ m⁻¹ in January 2015 after a period of the highest flow, but did not change in D-FF. Most of time D-WF had a higher SUVA₄₁₀ (0.50 ± 0.05 l mg⁻¹ m⁻¹) than D-FF (0.45 ± 0.05 l mg⁻¹ m⁻¹) ($p < 0.05$) (Fig. 6B). Higher SUVA₄₁₀ in D-WF may indicate a larger amount of more-complex

aromatic materials. Generally, there is no clear seasonal pattern in either stream, but similar to $SUVA_{254}$, there was a decrease in D-WF in the July sampling (from 0.53 ± 0.01 to 0.39 ± 0.07 $\text{l mg}^{-1} \text{m}^{-1}$) and an increase in D-FF (from 0.45 ± 0.03 to 0.49 ± 0.06 $\text{l mg}^{-1} \text{m}^{-1}$). In this month the standard deviations of the data overlapped between D-WF and D-FF. Generally in July in both streams the inter-stream profile in SUVA shows least synchronicity, i.e. the similarity in $SUVA_{254}$, and the relative difference in $SUVA_{410}$ between catchments, are not present.

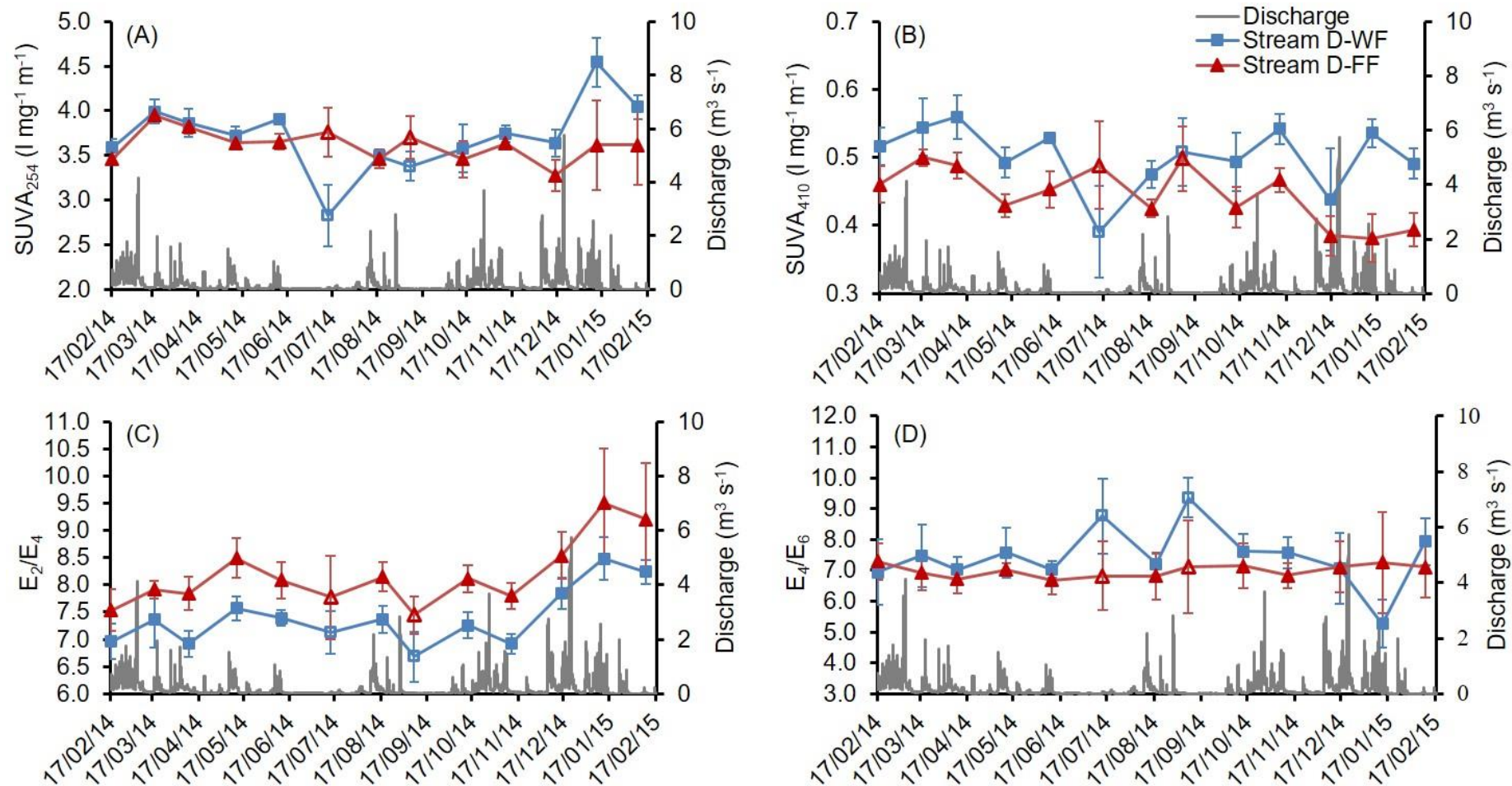


Fig. 6. D-WF and D-FF water from February 2014 to February 2015: mean (A) SUVA_{254} , an indicator of aromaticity, (B) SUVA_{410} , an indicator of more complex aromatic rings from the humification, (C) E_2/E_4 , an indicator of HS proportion, and (D) E_4/E_6 , an indicator of FA:HA. SUVA_{254} and E_4/E_6 were variable in D-WF but more stable in D-FF. July and September samples are represented by empty symbols. Similar patterns between the two streams were generally observed in SUVA, but most clearly in E_2/E_4 . Higher SUVA_{410} and smaller E_2/E_4 in D-WF indicate the DOC is more humic, as the result of having a larger proportion of HS.

351 E_2/E_4 ranged from 6.68 – 8.62 in the catchment with an average of 7.4 ± 0.5 in D-WF and
352 8.2 ± 0.6 in D-FF, which indicates HS in Drumtee water is dominated by terrestrial sources
353 (Table 1). Spatial variation in E_2/E_4 between the two streams was apparent and significant (p
354 < 0.05): E_2/E_4 in D-FF is constantly larger than in D-WF (Fig. 6C), suggesting the DOC in D-
355 FF had a smaller proportion of HS. Seasonally DOC in both streams showed similarly constant
356 E_2/E_4 patterns from Feb. – Nov. 2014, followed by an increase in the winter coincident with
357 increased discharge and a large storm event. In September, a dry month, E_2/E_4 decreases
358 were observed in both streams, suggesting the HS proportion increased.

359 The FA:HA in HS is represented by E_4/E_6 (Fig. 6D), and this was more variable in D-WF
360 over the year (from 5.3 – 9.4, mean 7.4 ± 1.0) than D-FF, which was more constant (6.7 – 7.3,
361 mean 7.0 ± 0.2). The ratios were not significantly different between the streams ($p > 0.05$),
362 suggesting at most times of the year, FA:HA was similar in the HS pools. However, unlike D-
363 FF, the relative proportion of FA and HA in D-WF was fairly sensitive to hydrological conditions
364 (Fig. 6D), as the ratio increased in July and September (the dry months) but decreased in
365 January (a wet month).

Measurements	Other studied DOM	Field ranges	Authors	Drumtee
SUVA ₂₅₄ (l mg ⁻¹ m ⁻¹) Positively related to DOC aromaticity	OM isolates from ocean to dark water	0.6 – 5.3		
	Aquatic isolated FAs	0.6 – 3.9	(Weishaar et al., 2003)	
	Aquatic isolated HAs	5.1 – 5.3		
	New Zealand peat pore water	1.9 – 3.5	(Moore and Clarkson, 2007)	D-WF: 3.7 ± 0.4 D-FF: 3.6 ± 0.2 (p > 0.05)
	Yukon river	2.2 – 3.6	(Wickland et al., 2012)	
	SUVA ₂₈₅ deforested peatland pore water	3.5 – 6.1	(Gandois et al. 2013)	
	Peatland well water	3.65 ± 0.04	(Olefeldt et al., 2013)	Similar aromaticity between streams
	Peatland ditch water	4.58 ± 0.89		
	Pore water from blanket bog	4.00 ± 0.47	(Peacock et al., 2014)	
	Bog lake	4.58 ± 1.16	(Selberg et al., 2011)	
	Stream water from a peatland headwater	4.6	(Goulsbra et al., 2016)	
SUVA ₄₁₀ (l mg ⁻¹ m ⁻¹) Positively related to more complex aromatic C	Discharge from surface soil in peat	~0.35		
	Discharge from -10 cm water depth in peat	~0.39	(Lou et al., 2014)	D-WF: 0.50 ± 0.05 D-FF: 0.45 ± 0.04 (p < 0.05)
	Discharge from -20 cm water depth in peat	~0.5		
	Streams and drains before peat drain-blocking	0.54	(Worrall et al., 2007)	
	Streams and drains after peat drain-blocking	0.67		D-WF DOC contains more complex aromatic C
E ₂ /E ₄ Inversely related to HS proportion	Terrestrial DOM	4 – 11	(Selberg et al., 2011)	D-WF: 7.4 ± 0.5 D-FF: 8.2 ± 0.6 (p < 0.05)
	Ditch water from blanket bog	6.42 ± 0.73	(Peacock et al., 2014)	
	Pore water from blanket bog	6.77 ± 0.45		
	Downstream water from a peaty catchment	15.5	(Graham et al., 2012)	D-WF DOC contains more HS than D-FF
E ₄ /E ₆	HAs extracted from soils	≤ 5.0	(Kononova, 1966)	D-WF: 7.4 ± 1.0

Positively related to FA:HA	FAs extracted from soils	6.0 – 8.5	(Thurman, 1985)	D-FF: 7.0 ± 0.2
	HAs extracted from soils	2 – 5		(p > 0.05)
	FAs extracted from soils	8 – 10		
	Blanket peat headwater in England	2.8 – 7.3	(Worrall et al., 2002)	Similar HA:FA between streams
	Blanket peat headwater in England excluding storm events	~5 – 6		
	Stream water from a peatland headwater	6.5		
	Ditch water from blanket bog	5.99 ± 3.76	(Peacock et al., 2014)	
	Pore water from blanket bog	7.37 ± 4.04		

366 **Table 1** A summary of the application of the spectrophotometric characterization used in this study, interpretation of each parameter, field ranges
367 in other research and the key findings of two Drumtee streams. ANOVA was applied for testing the significance of variance between two streams
368 and it shows the mean values of SUVA₂₅₄ and E₄/E₆ were not statistically different between D-WF and D-FF with a p > 0.05.

4. Discussion

4.1. Spatial and temporal variation of DOC quantity

The seasonal pattern of changing [DOC] has been observed previously in this catchment (Murray, 2012; Waldron et al., 2009) and in other temperate blanket peatland systems (e.g. Worrall et al. 2006; Dawson et al. 2011), with highest [DOC] in late summer. The concentration maximum in summer is likely to be caused by greater terrestrial productivity and lower water table promoting DOC production (Freeman et al., 2001), with pore water DOC flushed into streams when the water table rises (Tipping et al., 2007).

The [DOC] range across the catchment was large from 7.5 – 86.3 mg l⁻¹. Although only one year of study, the ‘anchor’ sampling point showed a similar range (8.6 – 60.4 mg l⁻¹) to observed in 2007 – 2010 (7.7 – 57.1 mg l⁻¹) (Murray, 2012). The similarity in [DOC] (and composition), for the different sampling points within a sub-catchment on a given date (Fig. S1), suggests no net loss. This is observed in both sub-catchments, and suggests that difference in catchment size is not a strong control on [DOC] – if transit times varied we would perhaps see differences longitudinally.

The [DOC] range is comparable to other studied peatland catchments in UK but is close to the higher end of the range. For example different peatland sites across Scotland were observed to have [DOC] from approximately 2 to 88 mg l⁻¹ (Billett et al., 2006; Dawson et al., 2011, 2004; Grieve and Gilvear, 2008), and smaller for some peatland catchments in England and Wales, ranging from around 1 to 60 mg l⁻¹ (Goulsbra et al., 2016; Jones et al., 2016; Moody and Worrall, 2016; Pawson et al., 2012; Worrall et al., 2007). Six years after wind farm construction was complete, Drumtee catchment still has high [DOC]. This may be due to wind farm-related peat disturbance, or a DOC driver unrelated to the wind farm given the concentration has stayed relatively constant with time. However, with two different landscapes (turbines emplacement vs. felled forestry), we can further explore whether wind farm construction-related land use difference has influenced exported DOC.

The two streams drain from mainly dystrophic blanket peat with similar peat coverage, so it is not likely the [DOC] difference was an effect of soil difference (the proportion of peatland in a catchment is considered a key control on aquatic DOC loading, Kortelainen, 1993; Mattsson et al., 2005). Both deforestation (Zerva and Mencuccini, 2005; Schelker et al., 2014) and wind farm development (Mitchell et al., 2010) cause disturbance to soil. Peat excavation and vegetation removal that has occurred in the turbine-covered area could leave an exposed surface more susceptible to C losses (e.g., Glatzel et al., 2003), but [DOC] in Stream D-WF are lower than D-FF. Clear-felling and mulching leaves large residues of tree litter and dying tree roots, which are easily decomposed (Zerva and Mencuccini, 2005). Meanwhile the removal of forest canopy can increase soil and surface temperatures (Hoffmann et al., 2003; Jauhiainen et al., 2012), and the decomposition of branches often releases a flush of nutrients to the soils (Kreutzweiser et al., 2008). This can enhance peat and wood litter decomposition (Gandois et al., 2013), important in peat due to the low nutrient content (Nieminen, 2004). Therefore surface soil in deforested areas can have a large carbon flux associated with root turnover and exudation (Hansson et al., 2010). In this dystrophic blanket peat-dominated area, these conditions very likely stimulate microbial activity, thereby altering rates of peat decomposition and generation of new DOC from felled material. Thus, it appears possible that the high [DOC] in D-FF is a result of drainage for commercial forestry and now deforestation

residue breakdown. This may suggest that deforestation can cause higher [DOC] than the excavation disturbance associated with the wind farm turbine, cabling and road emplacement.

4.2. Spatial and temporal variation of DOC quality

The Drumtee DOC had SUVA₂₅₄ in the range of other fluvial environments (0.6 – 5.3 l mg⁻¹ m⁻¹ for organic matter isolates from oceans to dark water; 2.9 – 3.9 l mg⁻¹ m⁻¹ for most aquatic FAs, Weishaar et al. 2003; Table 1) and towards the higher end of the range. It is also similar to pore waters from blanket bog (4.00 ± 0.47 l mg⁻¹ m⁻¹, Peacock et al. 2014; Table 1) but less than the SUVA₂₅₄ of water from a bog lake (4.58 ± 1.16 l mg⁻¹ m⁻¹, Selberg et al. 2011; Table 1). This indicates DOC in the catchment is rich in complex heterogeneous aromatic OM (Selberg et al., 2011), although less aromatic than some bog lakes, and the source of DOM in both streams is largely derived from soil pore water.

SUVA₂₅₄ varied little between sites except for July and September in 2014 and January in 2015, showing that the DOC was mostly of similar aromaticity between sites and throughout the year. The lack of difference suggests soil aromaticity between sub-catchments is broadly similar. This understanding is refined by the SUVA₄₁₀. In July, September and December SUVA₄₁₀ was similar between catchments, but for most of the year, SUVA₄₁₀ was higher in D-WF (p < 0.05). This may indicate more of the DOC contains complex aromatic materials (mainly HS), formed from the DOC humification process.

The lower E₂/E₄ composition in D-WF is consistent with more DOC humification and thus a greater proportion of HS (HAs and FAs) (Kalbitz et al., 1999). Further the similarity in E₄/E₆ between two streams at most times of year (Fig. 6D) suggests a similar proportion of HA in their humic substance pool. These parameters collectively suggest, the greater content of HS in D-WF, although with a similar proportion of HAs, shows the DOC was more humic, and thus likely to be more resistant to decomposition than D-FF (Fig. 7).

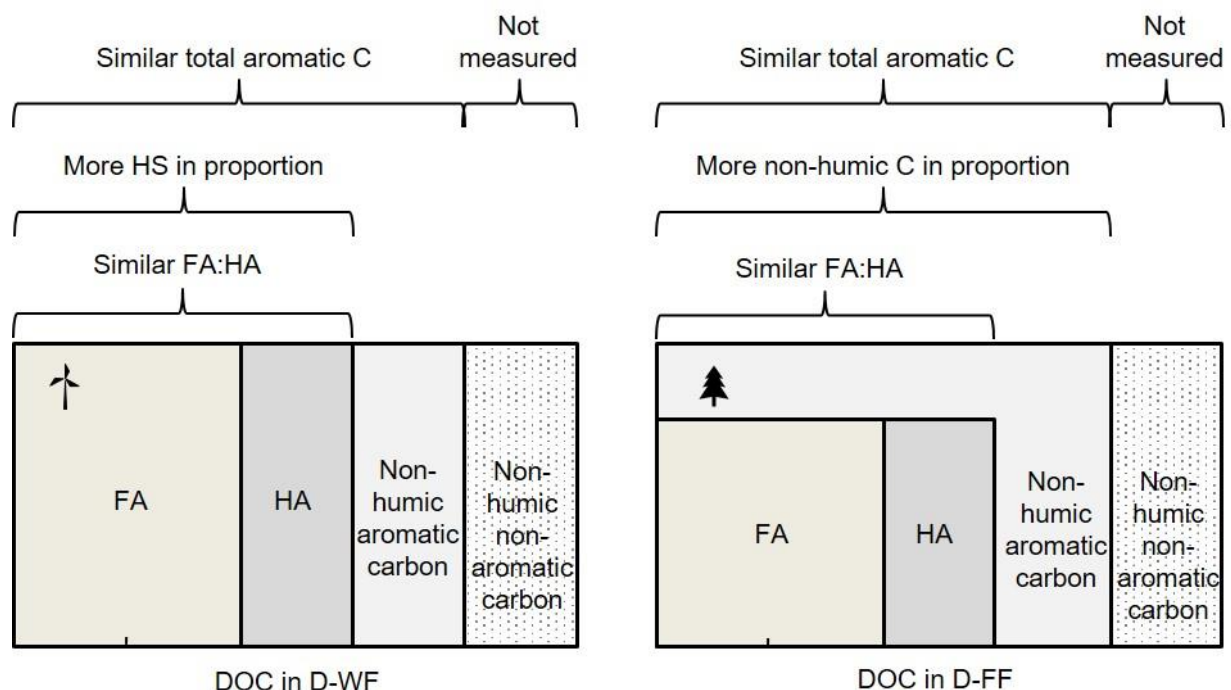


Fig. 7. Schematics showing the different proportions of HS in DOC produced from the two streams with the relative areas hypothesised to represent broadly the proportional composition

of the DOC pool.

The more aromatic DOC in D-WF can arise as either less humic material is entering D-FF or more HS are entering D-WF. There are two mechanisms for this. Firstly, more non-HS were produced in D-FF catchment as a result of deforestation. Leachates from fresh litter are usually dominated by low-molecular-weight (LMW) carbohydrates, while those from humified organic soils, such as peat, often have a significant contribution from highly aromatic high-molecular-weight (HMW) humic and fulvic acids (Kalbitz et al., 2003; Wickland et al., 2007; Olefeldt et al., 2013). The decomposition of tree branches and dying roots in felled area may have produced 'young' DOC consisting of more non-humic substances. There are no measurements of water table changes in this study, but due to the reduction in evapotranspiration, the depth to water tables beneath clear-felled stands can be comparatively higher and the soil can have a higher water content (Adams et al., 1991; Smethurst and Sadanandan Nambiar, 1995; Zerva and Mencuccini, 2005). Thus, younger DOC with more non-humic substances from the upper soil layer may become an important source of stream DOM. Secondly, the wind farm construction disturbance (mainly peat excavation and potentially drainage) may have lowered the water table for a period of time, exposing deeper DOC to an aerobic environment. This may result in the reduction of phenolic compounds in response to oxygenation and trigger an 'enzymic-latch' mechanism, which accelerates further DOC humification, and produces 'older' and more resistant DOC, even after the water table rises (Freeman et al., 2001; Worrall and Burt, 2005). Increased humification is suggested by the larger SUVA₄₁₀ (observed except during the dry months) and smaller E₂/E₄ in D-WF. It is not possible to tell which mechanism is more likely, or if both happened simultaneously.

Apart from the seasonal changes, DOC composition changed in the dry periods. Here lower stream discharge indicated a reduced contribution from soil water, particularly upper soils, so deeper soil waters and groundwater may contribute more to fluvial DOM and thus DOC may become more aromatic. Increases in coloured and aromatic DOC were previously observed in peatland soil water under lower water tables (Lou et al., 2014). This interpretation is supported in our study by a decreased E₂/E₄ in D-FF in the dry September 2015 (Fig. 6C), which may indicate more HS content (humification increases with increased soil age and depth).

However, we also found in drier months that DOC derived from deeper peat exported to D-WF was less aromatic (decreased SUVA₂₅₄ and SUVA₄₁₀, Fig. 6A, B). In a tropical deforested peatland SUVA₂₈₅ of pore water DOC increased from the surface to 30 cm depth, then decreased to 180 cm, and this was interpreted to represent aromatic molecules accumulation around 30 cm depth (Gandois et al., 2013). SUVA₂₈₅ was used here instead of SUVA₂₅₄ as the high DOC concentration induced saturation of the spectrophotometer at 254 nm, but as based on similar principles and within the 200-300 nm range, they are comparable. In D-WF, the water table may have dropped below where aromatic materials accumulated in the dry period, but less so in D-FF as the tree mulch and reduced evaporation would support a higher water table. Further, the spectrophotometric composition of DOC in D-FF is more constant (e.g. SUVA₂₅₄) suggesting that fluvial DOC in D-WF is more sensitive to rainfall and soil water depth. Finally, the compositional differences may suggest drainage from mineral soil layers may be more important in D-WF: there are more humic and non-calcareous gley along Stream D-WF (indicated in Fig.2B), and in these layers more DOC is less-humified.

5. Conclusion

This research shows that even with a small catchment there can be considerable differences in fluvial DOC concentration and composition within different tributaries of one drainage system. Whilst concentration varies seasonally, reflecting the integration of catchment production and export, this is not synchronous with pronounced seasonal changes in DOC composition within-sub catchments. Rather the changes that occur reflect less water being delivered from the surface soils as the catchment becomes drier and sources of organic C change. The higher concentration and 'fresher' composition in stream DOC draining the felled forestry suggests that this activity causes more widespread disturbance than preparation of land for turbine emplacement. Although the sub-catchment hosting the wind farm is subject to disturbance, there is not the residue of younger C in the catchment and so the DOC released here is 'older' and when from deeper peat has a composition of material that has already undergone decomposition. As a result of their low nutrient content and sensitivity to water table level, organic-rich soils such as peat can be more sensitive to forest activities (e.g. clear-felling) than mineral soils and this could affect the DOC pool. Further, for many years after the roots can still act as a source of DOC (Hansson et al., 2010). An interesting next step would be to consider if these compositional differences affect the fate of C in the fluvial system.

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753

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

Supplementary Information (SI)

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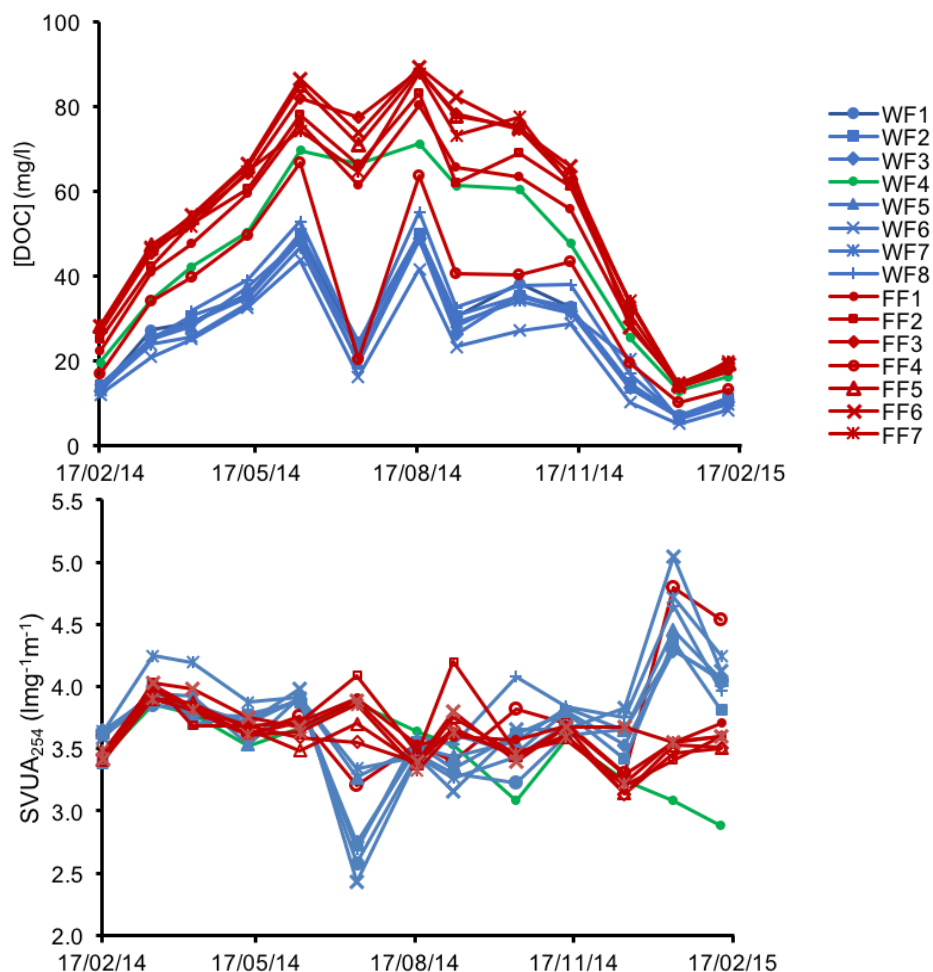
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This document contains information to support the approach to the grouping of sites in sub-catchments (point 1) and to increase confidence that the observations in the year of study are representative of a longer-term response (point 2):

1. The concentration and compositional time series for all sites from February 2014 to February 2015 are presented (Fig. S1) and the data are then pooled for each sub-catchment to allow comparison of the mean sub-catchment composition when D-WF4 is grouped with other D-WF sampling points (group 1), or with the D-FF sampling points (group 2) (Fig. S2).

Fig. S1 shows that for all sampling occasions, [DOC], SUVAs and E ratios for D-WF4 are more similar to D-FF site profiles. Fig. S2 shows that when D-WF4 is considered within the population of the other D-WF sites, the standard deviation in the population considerably increases (compare the SD errors bars between group 1 and group 2 for D-WF, Table S1 also), suggesting more variation within a population. However, addition of D-WF4 to D-FF hardly changes the population variation. This supports an interpretation that the D-WF4 DOM pool is more similar composition to D-FF sites, and not the D-WF sites. Further, from the catchment land use map (Fig. 2), it is clear that the D-WF4 tributary is draining mostly land that has been deforested (more similar to D-FF catchment land use than D-WF). Thus, to allow most insight into how DOM compositional changes may be influenced by land use, these two considerations suggest it is appropriate that D-WF4 is grouped with D-FF.



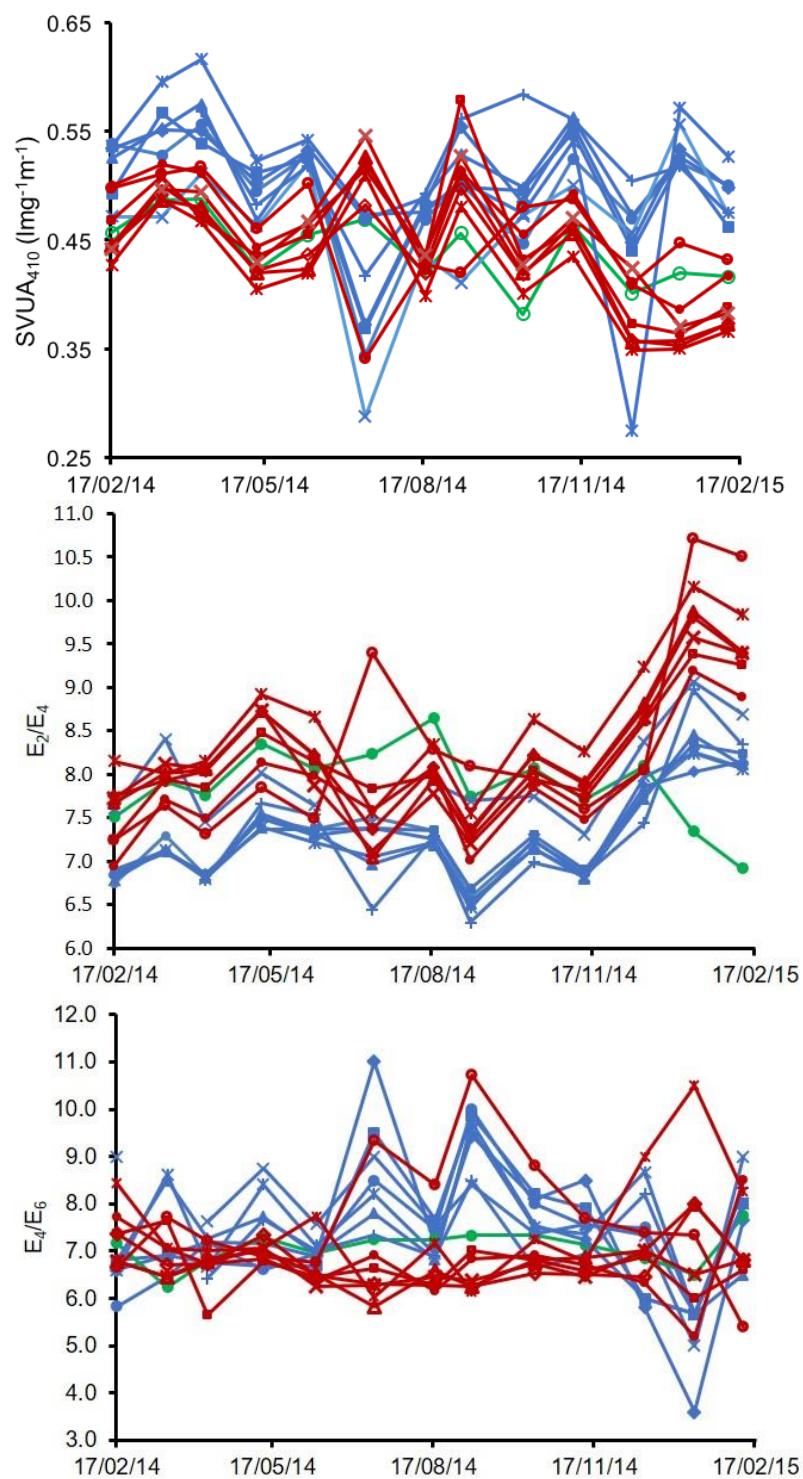
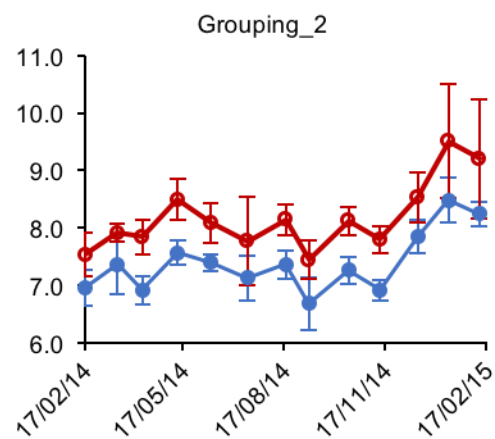
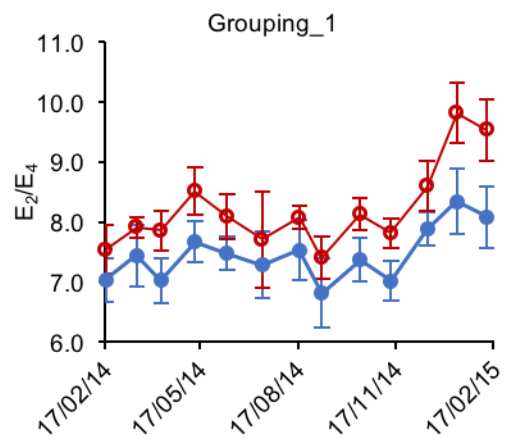
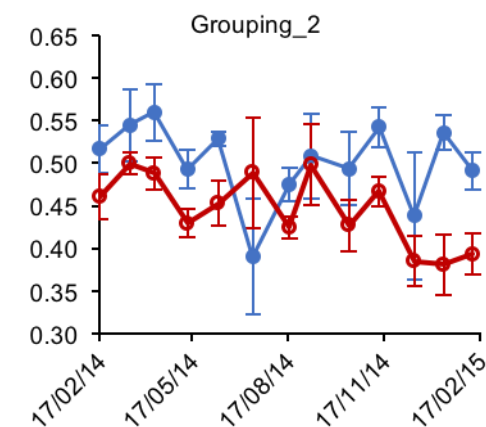
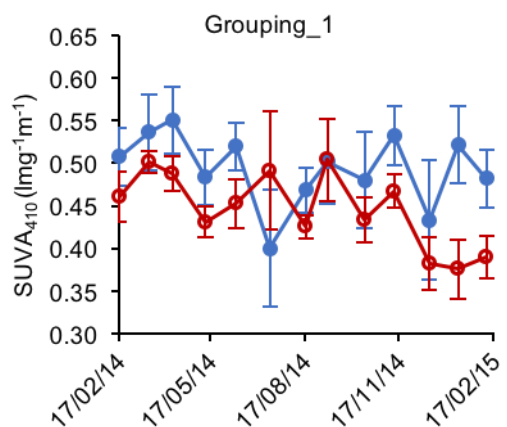
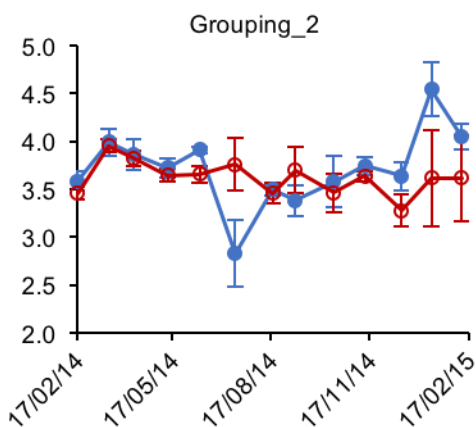
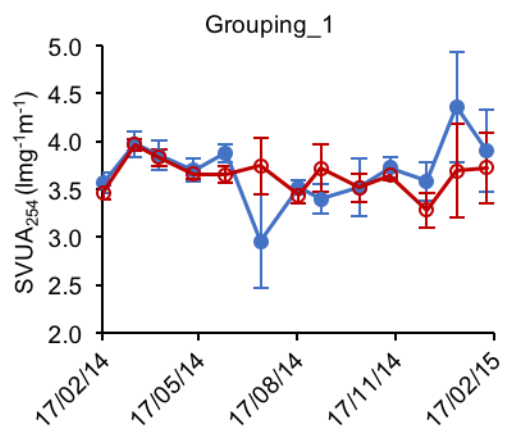
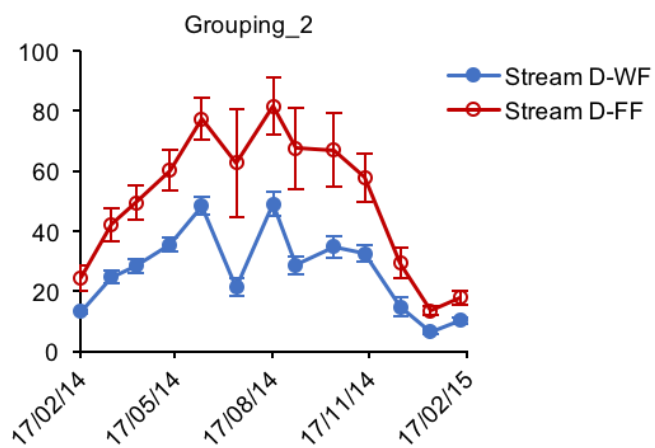
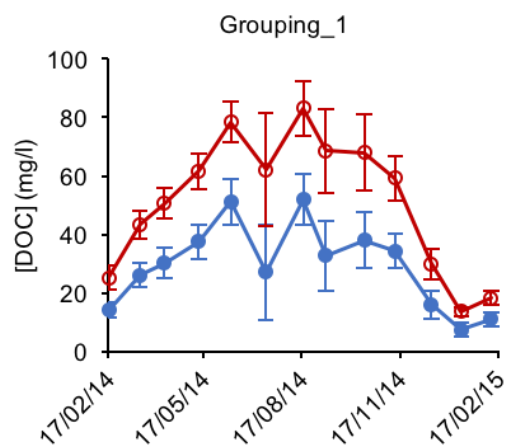


Fig. S1. DOC concentration, SUVA and E ratios of all samples collected from Drumtee streams during Feb. 2014 – Feb. 2015. The D-WF group is coloured in blue, and D-FF in red. Site D-WF4 is represented by the green symbol, and is clearly more similar to D-FF than D-WF.



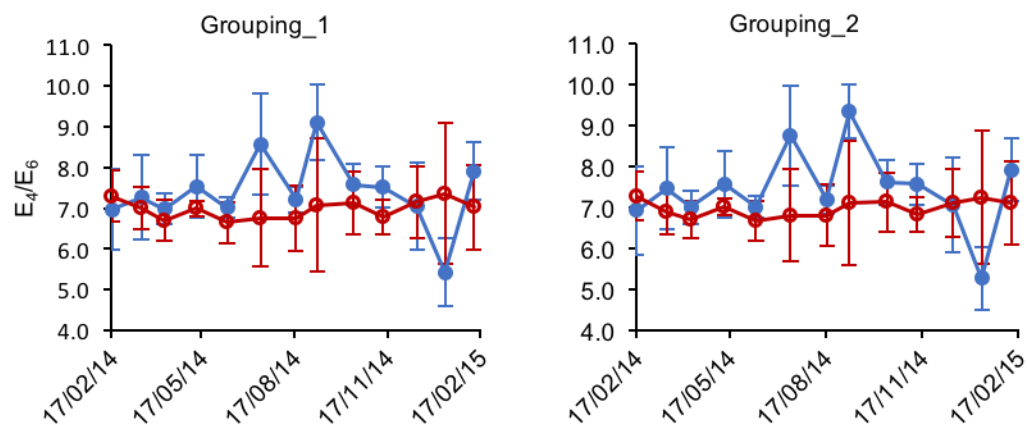


Fig. S2. The comparisons between different grouping methods. Grouping_1 has no change applied to the data division. Grouping_2 represents the method used in the study: D-WF4 is pooled with D-FF sites. By applying method 2, the SDs decreased in [DOC] for the observation period, and were similar, or smaller in UV-vis parameters for most months. No clear change is observed in D-FF after merging with D-WF4.

Parameter	Grouping Method	17/02/17	18/03/17	10/04/17	12/05/17	11/06/17	14/07/17	18/08/17	08/09/17	14/10/17	12/11/17	16/12/17	13/01/17	10/02/17
[DOC]	1	2.5	4.1	5.3	5.7	8.0	16.2	8.7	11.9	9.7	6.0	4.8	2.3	2.3
	2	0.8	2.1	2.4	2.3	2.8	3.0	4.0	3.1	3.7	2.8	3.2	0.7	1.0
SUVA ₂₅₄	1	0.1	0.1	0.2	0.1	0.1	0.5	0.1	0.2	0.3	0.1	0.2	0.6	0.4
	2	0.1	0.1	0.2	0.1	0.0	0.3	0.1	0.2	0.3	0.1	0.1	0.3	0.1
SUVA ₄₁₀	1	0.03	0.04	0.04	0.03	0.03	0.07	0.03	0.05	0.06	0.03	0.07	0.05	0.03
	2	0.03	0.04	0.03	0.02	0.01	0.07	0.02	0.05	0.04	0.02	0.08	0.02	0.02
E ₂ /E ₄	1	0.36	0.52	0.37	0.34	0.27	0.55	0.50	0.57	0.36	0.33	0.28	0.54	0.51
	2	0.32	0.52	0.24	0.22	0.15	0.39	0.24	0.46	0.24	0.18	0.29	0.39	0.22
E ₄ /E ₆	1	0.98	1.04	0.39	0.76	0.26	1.25	0.32	0.93	0.51	0.49	1.07	0.84	0.70
	2	1.07	1.01	0.41	0.81	0.28	1.22	0.35	0.64	0.54	0.51	1.15	0.78	0.76

Table S1. Standard deviations of all parameters measured for D-WF samples. The grouping methods 1 and 2 are the same as described in Fig. S2. Smaller SDs are coloured in red. By applying method 2, the SDs decreased in [DOC] for the year, and were similar or smaller in UV-vis parameters for most months. SDs for D-FF samples are not presented, as no clear change is observed between different grouping methods.

2. In the course of other research, fluvial samples from two study sampling points (D-WF1 and D-FF1) were collected approximately 7-16 months after this study ended (Fig. S3). Not all sites were sampled and samples were collected quarterly than monthly, and so the data cannot be incorporated into the core manuscript analysis.

However, [DOC] and spectroscopic compositional characteristics for these samples collected later from the two sampling points are almost always within the ranges observed during the earlier study year, and show differences between sub-catchments similar to the year-long study (e.g. [DOC], $SUVA_{254}$, E_2/E_4). This suggests the fluvial DOC pools sampled later have similar compositional and concentration characteristics to earlier and still maintain differences.

If this is the case, it supports the interpretation that although land use is complicated and has changed the influence it imparts may be detected over an extended period (disturbance first started in 2006-9 in this catchment and sampling was 2 years thereafter).

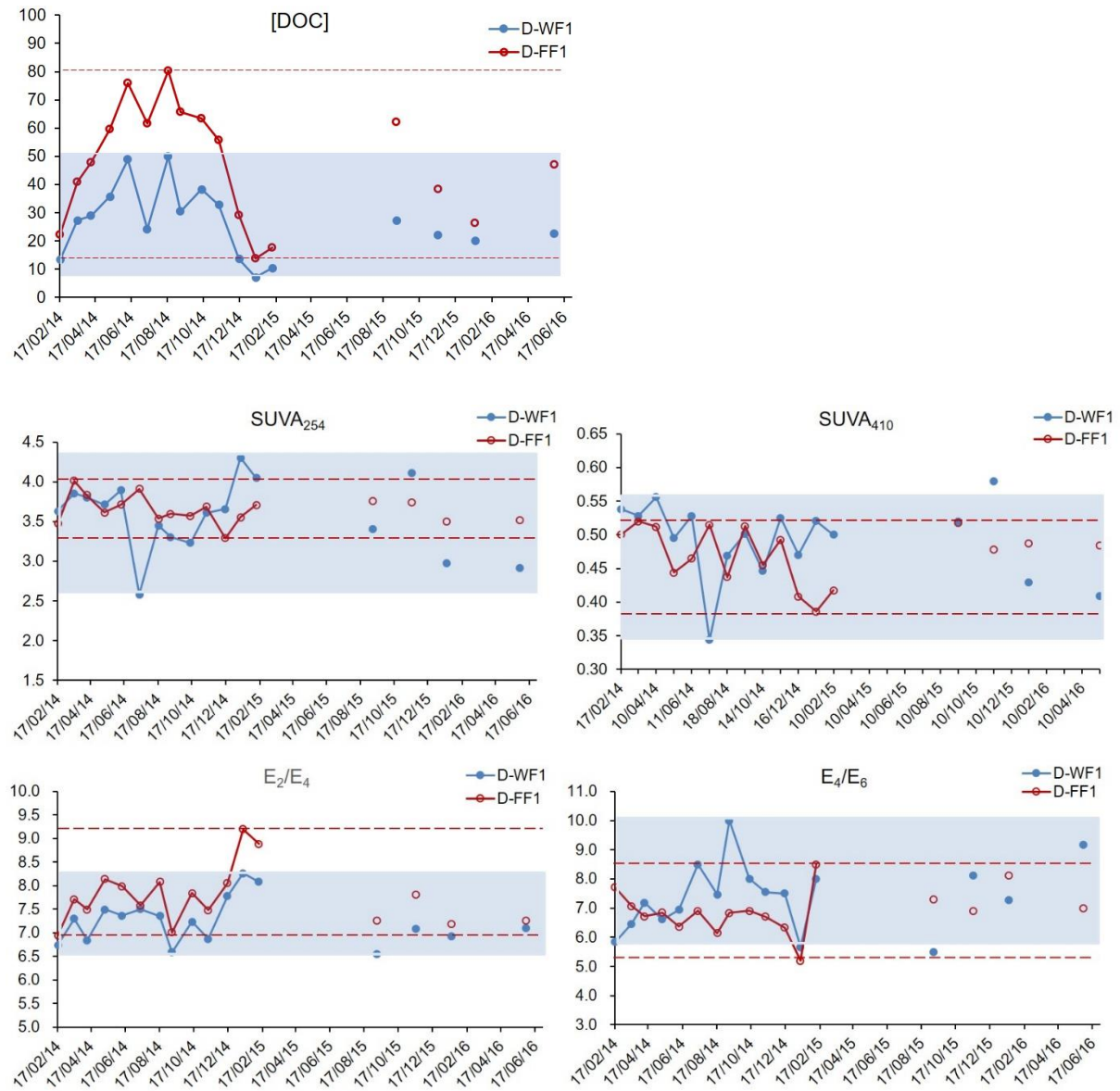
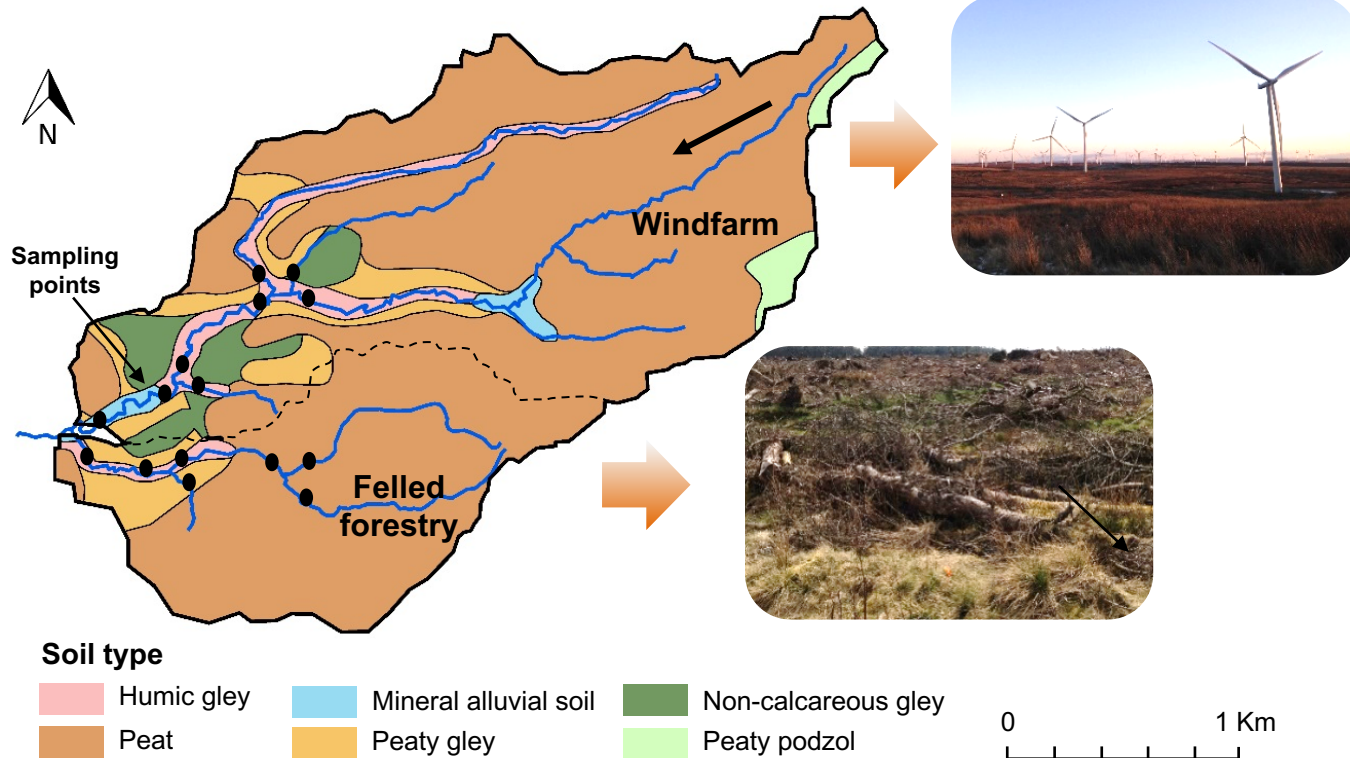


Fig. S3. A longer time series (2014 – 2016) for sample points D-WF1 and D-FF1 only (later data does not exist for the other points). The blue shaded area and red dashed lines represent respectively the maximum and minimum value for each parameter for D-WF1 and D-FF1 during Feb. 2014 – Feb. 2015. With the exception of one $SUVA_{410}$, and one E_4/E_6 , the samples collected later during 2015 and 2016 share the same composition as before, and within-catchment differences still exist.



	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