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Toward understanding organic matter fluxes and reactivity in surface waters: Filtering impact on DOC and POC degradation

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Running head: Filtering impact on DOC and POC degradation

Abstract

Peatlands cover a very small area of the Earth, but store globally significant quantities of carbon and export disproportionate quantities of fluvial organic carbon, especially when the peatlands are degraded or disturbed. Peatland headwater catchments with high concentrations of dissolved and particulate organic carbon (DOC and POC) provide an opportunity to investigate the possibility of competing effects that could lead to enhanced or diminished turnover of DOC in the presence of POC. Both POC and DOC can be degraded by light and microbes, producing smaller molecules and releasing CO_2 and CH_4 to the atmosphere, and POC can inhibit light penetration, stabilise DOC by providing adsorption sites and providing surfaces for microbes to interact with DOC. However, the majority of peatland fluvial carbon studies are conducted using filtered water samples, and measure only the DOC concentration, so the impact of the particulate organic matter (POM) on in-stream processing of organic carbon is relatively unknown. It is therefore possible that studies have underestimated carbon transformations in rivers as they have not considered the interaction of the particulate material on the dissolved concentrations; there could be higher losses than previously estimated, increasing the contribution of peatland headwaters to GHG emissions. In this study we assessed if the current approach of DOC degradation studies accurately represent the impact of POM on DOC degradation, by quantifying DOC production from POM, and therefore POC, over time in water with manipulated POM concentrations. Both filtered and unfiltered water lost 60% of the DOC over 70 hours, whereas the treatment with additional POM lost only 35%. The results showed that filtering does not significantly impact the DOC degradation rates; however, when the POC concentration was doubled, there was a significant reduction in DOC degradation, suggesting that filtering would still be necessary to get accurate rates of DOC transformations in waters with high POC concentrations.

Keywords

POM, filtered water, peatland stream, carbon assessment

1. Introduction

Peatlands cover approximately 3% of the Earth's land area, but store a disproportionate amount of carbon (500 ± 100 Pg C; Loisel et al., 2017). Consequently, peatlands are important sources of fluvial carbon, and disturbed, degraded or eroded peatlands export large quantities of organic carbon to streams and rivers relative to other ecosystems (Ward et al., 2017). In the UK, peatlands cover 2.3 million hectares, but around 1.8 million hectares (78%) are estimated to be disturbed, degraded or eroded (Bain et al., 2011). Goulsbra, Evans and Allott (2016) showed that eroded peatlands are hotspots for export of fluvial carbon, both as particulate organic carbon (POC) and dissolved organic carbon (DOC). In several countries, particularly the UK, peatland catchments supply water to drinking water reservoirs, and high POC and DOC concentrations cause increased treatment and energy costs to water companies (Kothawala, Köhler, Östlund, Wiberg, & Ahrens, 2017).

The importance of organic carbon as a critical water quality characteristic is widely recognized (Kaplan and Newbold, 2000). Aquatic organic carbon is an important energy source, impacting the productivity, ecosystem exchange, and food cycles of terrestrial waters (Ask et al., 2009; Cory et al., 2011). Forms of organic carbon in surface waters include particulate organic carbon (POC), referring to particles that are in suspension and could settle out; and dissolved organic carbon (DOC), including colloidal and dissolved material that will not settle out. These are operationally defined as the organic carbon that will pass through (DOC) or be retained on (POC) a filter. Though the standard classification of dissolved constituents in natural waters is typically passed through a 0.45 µm filter, some studies of organic matter require use of a binder-free glass-fibre filter, where 0.7 µm is the smallest nominal pore size available (Cory et al., 2011; Stimson, Allott, Boult, & Evans, 2017).

In surface waters, DOC and POC molecules can be modified by in-stream processes (Hope, Billett, Milne, & Brown, 1998). Both DOC and POC can be broken down by light and microbes, producing smaller organic carbon molecules and releasing CO_2 and CH_4 to the atmosphere, contributing to increasing atmospheric greenhouse gases, and therefore to climate change (Evans & Thomas 2016). Estimates of CO_2 losses from rivers, streams, lakes and reservoirs are as high as 3.9 Pg C year^{-1} (Drake, Raymond, & Spencer 2017). The DOC molecules in surface waters can also flocculate, forming larger molecules of POC (von Wachenfeldt, Sobek, Bastviken, & Tranvik, 2008). When there is an increased POC load in the river, the POC can interact with DOC in a number of ways: inhibiting light penetration; stabilising DOC by providing adsorption sites; and providing surfaces for microbes to interact with DOC (He, Chen, Schlautman, & Hur, 2016). Light-mediated flocculation of DOC to POC (von Wachenfeldt et al., 2008; Porcal, Dillon, & Molot, 2013) is considered a less important pathway in upland waters in the UK, because of the iron catalyst hypothesized to be needed. Iron concentrations are typically low in surface waters, but iron becomes more soluble at lower pH, like those found in ombrotrophic peatland waters (Neal et al., 2008), and so light-mediated flocculation of DOC to POC may also occur in these waters.

Knowing how much carbon is exported via streams and rivers is important to obtaining accurate carbon budgets of peatlands. However, to fully quantify the impact of peatlands on larger scale carbon and greenhouse gas budgets, such as the river catchments, or the global carbon cycle, it is important that the ultimate fate of this transported carbon is known (Brown, Goulsbra, & Evans, 2019). Additionally, little is known about how much of the carbon exported undergoes in-stream processing, and how much reaches the marine environment. The contribution of peatlands to global greenhouse gas fluxes, and the potential of peatland restoration methods to decrease the atmospheric load of carbon depend on the accuracy of carbon budgets, and further highlights the urgency of research in this topic.

Peatland headwater catchments with high concentrations of DOC and POC provide an opportunity to investigate the possibility of competing effects that could lead to enhanced or diminished turnover of DOC in the presence of POC (Attermeyer et al., 2018). DOC can flocculate to form larger molecules that could be sufficiently large to act as particulates and so settle out or attenuate light penetration, therefore impacting the DOC's photo-induced turnover (von Wachenfeldt et al., 2008). However, the majority of lab-based peatland fluvial carbon studies filter the sampled water and measure only the DOC concentration (e.g., Dean, Garnett, Spyrakos, & Billett, 2019; Evans et al., 2018; Stimson et al., 2017), so the impact of the particulate material

(> 0.45 µm) on in-stream processing of organic carbon is relatively unknown. It is, therefore, possible that studies of fluvial organic carbon have underestimated carbon transformations in rivers as they have not considered the interaction of the particulate material on the dissolved concentrations (Brailsford et al., 2017). Lab-based studies, such as those listed above, are often used to assess the lability and degradability of DOC, and measure evasion of CO_2 from water. Without considering the interaction and transformation of DOC and POC in the water, these experiments risk under or over estimating the lability and degradability of DOC, and the subsequent evasion of CO_2 to the atmosphere.

This study aims to assess how filtration (the removal of particulates) impacts DOC degradation. The impact of POC concentration on DOC degradation will be measured, to determine if high concentrations of POC inhibit DOC loss by increasing conversion of POC to DOC.

2. Methods

2.1. Approach

Experiments were conducted to measure DOC and POC concentrations over 70 hours in water with manipulated particulate organic matter (POM) concentrations. These experiments were carried out using deionised water with POM added, and separately with stream water from a headwater catchment in northern England, with manipulated POM concentrations. The term 'POM' is used to describe the particulate material collected from the study catchment, as it contained more than just organic carbon (so cannot be called 'POC') but is still almost 100% organic matter, due to its source being a peat-covered catchment.

The approach of both the deionised water and stream water experiments was the same. After POM manipulation, the DOC and POC concentrations were measured every few hours for approximately 70 hours. The stream water experiment was repeated seven times, with water collected from the study site approximately monthly, between May and October 2014.

2.2. Study catchment

This study used stream water and POM collected from Cottage Hill Sike (CHS; 54.689, -2.399, 545-560 m asl), a small peatland stream (catchment area: 0.2 km^2, with 100% blanket peat cover) within the Moor House National Nature Reserve in the UK, part of the Environmental Change Network monitoring programme (Rennie et al., 2017). The mean annual temperature at Moor House is 5.9°C, and the mean annual rainfall is 1931 mm (20 year average from 1993 to 2013; Moody, Worrall, & Burt, 2016). The Cottage Hill Sike catchment is dominated by *Calluna* (heather), *Eriophorum* (cotton grass) and *Sphagnum* moss, and is grazed by sheep. The peat is up to 4 m thick, and the water table is high (typically within 5 cm of the surface; Clark, Lane, Chapman, & Adamson, 2008). Over the study period (May to October 2014) the average DOC concentration measured in the stream was 45 times higher than the average POC concentration (DOC range: 20.9 to 113.9 mg C L^{-1}; POC range: 0.0 to 4.9 mg C L^{-1}; Figure S1). The conductivity ranged from 31.9 to 46.4 µS cm^{-1}, and the pH from 3.85 to 4.58. The stream flow was visually assessed on each site visit, and followed a seasonal pattern, with low flow recorded in June, July and August, medium flow record in May and September, and high flow in October.

2.3. Deionised water experiment

An experiment was conducted to examine the rate of transformation of POC into DOC. POM was collected from the study catchment in October 2014 – 2 L of CHS stream water was filtered through 0.7 µm glass fibre filters and the POM collected as the residue. The POM was rinsed with DI water, to flush any DOC from the material, then weighed (0.77 g) and added to deionised water (1 L). The concentration of POM was similar to the concentration used in Brown et al. (2019; 0.8 g L^{-1}) which is described as a typical POM concentration from a peatland stream in the UK. However, as Brown et al (2019) also acknowledge, this is higher concentration of POM than found in non-eroding or disturbed catchments in the UK, such as those measured in NE Scotland and Mid-Wales by Dawson, Billett, Neal and Hill (2002; range < 0.01 to 7.22 mg C L^{-1}). The DI water in this experiment contained no DOC; however rinsing the POM with DI water will not have removed microbes from the POM – therefore this water is not ‘sterile’ and abiotic and biotic transformation of POC to DOC was possible. The water was stirred, then 50 mL of this POM solution was poured into 20 vials. The vials were made of a quartz glass tubing, stoppered with a rubber bung at the end, and loosely stoppered at the top (approximate volume 100 mL). Quartz glass allows all light wavelengths to pass through it. These vials were then placed outside under monitored ambient light and temperature conditions. Replicates were included, with two vials for each of ten sampling times. The experiments spanned approximately 70 hours with sacrificial sampling taking place at hour 1, 2, 8, and then at dawn and dusk (approximately 8:00 and 18:00 in October; 10 hours of daylight) on day 2, 3 and 4 (hours 20, 30, 44, 54 and 68). Over the 70 hours of the experiment, the average air temperature was 11.6 °C (range 10.1 to 14.1 °C).

2.4. Peatland stream water experiments

The purpose of this experiment was to measure the impact of POM in the presence of natural concentrations of DOC, using three treatments:

I. POM0: the stream water was filtered through a 0.7 µm glass fibre filters to remove the POM and so create a POM-free sample. This treatment was carried out to investigate the dynamics of DOC in the absence of POC, and quantify any conversion of DOC to POC.
II. POM1: the ‘control’ treatment – the stream water was unfiltered, to show the effect of the ‘normal’ interaction between DOC and POC
III. POM2: when the water was filtered for POM0, the POM removed from the water was collected and added to the POM2 treatment, making the POM concentration in this water double that of the POM1 treatment, to show effect of a high POC concentration on the DOC and POC dynamics.

The same approach (and vials) were used in this experiment as in the deionised water experiment, above. The water in each treatment was stirred, then 50 mL of each treatment solution was poured into each of 20 vials. The first day of the experiment was conducted at the field site so the samples were exposed to the same light and temperature conditions as the river. At dusk all vials were taken to the laboratory and placed outside so they would continue to experience natural light and temperatures. This experiment was repeated seven times, with water collected from the field site approximately monthly, between May and October 2014. Water was collected across a range of meteorological conditions, and a range of natural DOC and POC concentrations (Figure S1). A sample of the initial water was collected before any treatments were applied (t_0).

Replicate vials were included within each experiment. No zero time (t_0) samples were replicated, but 41% of all other measurements were replicated (162 of 393 samples). Replication was limited by practical constraints of the amount of equipment available and the time taken to process DOC analysis to ensure the maintenance of the short sampling timescales at the beginning of the experiment.

As in the deionised water experiments, the stream water experiments spanned approximately 70 hours with sacrificial sampling taking place at hour 1, 2, 4, 8, and then at dawn and dusk on day 2, 3 and 4. Fixed numbers of hours since the start of each experiment were not used across all months of the study because change in day length would mean that samples in daylight for one experiment may be in darkness in a subsequent month, and so samples were taken relative to dawn and dusk for each month of the study. The number of hours since the beginning of the experiment were averaged, resulting in 10 'sampling times', each with a standard error: 0, 1, 2, 4, 7.2 ± 0.2, 19.7 ± 0.1, 31.3 ± 0.1, 43.7 ± 0.1, 55.1 ± 0.2, and 67.7 ± 0.1. All sampling times are referred to as 't_x' where x is the average number of hours since the beginning of the experiment e.g. the beginning and end points of the experiments are referred to as t_0 and t_{68}. Due to equipment and laboratory issues, the first experiment only ran for 30 hours, and therefore the t_{30} DOC and POC concentrations were used as the end point of the experiment.

2.5. Water sampling and analysis

In both the deionised and stream water experiments, the vials were placed outside to be exposed to natural day/night cycle and temperatures for 70 hours, and the vials were lain at an angle to prevent rainfall entering and the sample evaporating or pouring out. The angle of the tubes also stopped the water samples being shaded by the top bung and exposed a larger surface area of water to natural light. The vials were loosely stoppered to allow air inflow and prevent anoxic conditions. A data logger with a PAR (photosynthetically active radiation) meter and thermocouple recorded the radiation levels and air temperature at 15-minute intervals throughout the 70-hour period of each experiment. The PAR and temperature data recorded during each experiment were summed to give the total PAR and temperature experienced by any sample. The PAR and temperature measurements were treated in this way because a sample after 70 hours may have experienced the same average radiation as a sample after 1 day but will have received a larger total radiation dose. The total sum of PAR experienced by each months' experiment varied from 738 to 8782 μmol m^{-2} s^{-1} (highest in June). The total sum of air temperature experienced by each months' experiment varied from 691 to 1163 °C (highest in June). In the warmest month, June, the average air temperature was 18.4 °C, whereas in the coldest month, October, the average air temperature was 11.4 °C.

At each sampling time, two vials (replicates) were sacrificially sampled. The water was agitated to re-suspend any settled OC, and a small volume (< 10 mL) of the 50 mL of water from each vial was filtered (0.45 µm Whatman, 28 mm diameter, syringe filter), and then acidified with concentrated sulphuric acid. The DOC concentrations were analysed using the wet oxidation method described in Bartlett and Ross (1988). The UV-Vis spectrophotometer was calibrated using standards of oxalic acid of known concentrations. For the deionised water experiment, the calibration had an R^2 of 0.9941. For the stream water experiments, the R^2 of the calibrations were 0.9955, 0.9960, 0.9967, 0.9926 and 0.9941. In all calibrations, the measurements from duplicate standards were within 95-105 % of each other, and the relative standard error across all calibrations were less than 5 % at each concentration.

The quality and colour of the DOC was analysed by UV-Vis spectrophotometry. The absorbance at 400, 465 and 665 nm were measured, and used to calculate the specific UV absorbance at 400 nm ($SUVA_{400}$; an indicator of DOC aromaticity) and the E4:E6 ratio (465/665 nm; an indicator of the humic/fulvic nature of the DOC).

The remaining sample in both replicate vials was combined (to ensure there was enough water for reliable results), and was used to measure the POM and POC concentrations. For analysis of POM and POC concentration, the remaining volume of water was filtered through pre-weighed, 0.7 µm, glass fibre filters (Whatman, 47 mm diameter, glass fibre); dried to 105°C for 8 hours, and the filter paper re-weighed to give the concentration of suspended sediment. The filter papers were then put in a furnace for 4 hours at 550°C, and then re-weighed. The mass lost in the furnace equates to the mass of POM, and 47.5% of this was assumed to be POC (Worrall, Burt, & Howden, 2016). This method of sampling resulted in two DOC measurements (one from each replicate vial), but only one POC measurement, per sampling time per treatment.

2.6. Statistical analysis

Prior to any statistical analysis the data were tested for normality using the Anderson-Darling test, if necessary the data were log-transformed and re-tested – no further transformations were found necessary. An analysis of variance (ANOVA) was used to assess the significance of two factors: the treatment and sample time, and where possible the interaction between these two factors. Results were expressed as least squares means as these are better estimates of the mean for that factor level having taken account of the other factors, interactions and covariates that were included in the analysis. Results are reported as significant at the 5% probability ($p < 0.05$) of being zero (95% probability of being different from zero). A small number of significant results were further analysed using Fisher's Least Significant Differences post-hoc test.

3. Results

3.1. Deionised water experiment

This experiment examined the rate of transformation of POM into DOC, and the interaction between POC and DOC, in deionised water where the only source of DOC was the added POM. Assuming 47.5% of the added POM was carbon, the initial mass of POM in the deionised water treatment (0.77 g L^{-1}) equates to 365.75 mg L^{-1} of POC. The measured POC concentration in the initial water, after the treatment was applied, but before the experiment started, was 255.27 mg L^{-1}, 70% of the theoretical POC concentration. This difference may challenge the assumption that all suspended sediment collected from the stream (CHS) is truly organic, therefore all POM, or the calculated proportion of POM from the stream that is POC (as outlined in the methods, 47.5% used in this study; and Worrall et al., 2016).

In this experiment, any DOC present was produced from the POM as there was no DOC present in the initial water (this was confirmed by measurement). The first samples taken after 1 hour had an average DOC concentration of 19.6 ± 0.4 mg C L^{-1} (mean ± standard error; Figure 1). The highest rates of DOC production were during the first two hours, coinciding with the largest drop in POC concentration. The DOC concentration generally decreased over time and was 6.7 ± 2.6 mg C L^{-1} at t_{68}. However, there were three times during the experiment when the DOC concentration increased between sampling times (between t_7 and t_{20}, t_{30} and t_{44}, and t_{55} and t_{68}). The POC concentration started at 255.3 mg L^{-1} but rapidly decreased and after 1 hour the concentration was only 10.7 mg C L^{-1}. Overall, the POC concentration decreased, and was 0.95 mg C L^{-1} at t_{68}. Even though the POC concentration decreased overall, there were several times during the experiment when the POC concentration increased between sampling times (between t_1 and t_2, t_4 and t_7, t_{20} and t_{31}, t_{44} and t_{55}). The POC concentration alternated between increasing and decreasing at almost every sampling time, and at t_2 and t_{30}, the POC concentration was higher than at t_1. The organic carbon content (OC) in the water showed that there was an overall loss of OC, however (as shown in the DOC and POC concentrations) there were three times during the experiment where the measured OC concentration was higher than at the preceding sampling time (between t_1 and t_2, t_{20} and t_{31}, and t_{55} and t_{68}).

There was a weak but significant positive linear relationship for the production of DOC from POC in the deionised treatment ([DOC produced] = 0.60 [POC] + 7.02; $R^2 = 0.28$; n = 9; p = 0.03); higher POC concentrations produced higher DOC concentrations (Figure 2). The gradient of the relationship (0.60) shows that for each 10 mg L^{-1} of POC, there was 6 mg L^{-1} of DOC produced. The intercept value (7.02) showed that even when no POC was present, the DOC concentration would be 7.02 mg L^{-1}; however it was shown there was no DOC present in the initial water sample (before POM addition). A slightly higher R^2 value was obtained from a non-linear regression ([DOC produced] = 7.16 [log POC] + 6.63; $R^2 = 0.32$; p = 0.02). This model showed a steeper relationship between DOC and POC when POC concentrations were low – more DOC was produced per mg L^{-1} of POC when the POC concentration was below ~ 7 mg L^{-1}. There was a less steep relationship when the POC and DOC concentrations were higher. This model suggested a faster conversion of POC to DOC as the most labile POC fractions are converted first, followed by a slower rate of POC to DOC conversion, possibly as the OC reaches an equilibrium.

These experiments show that there was very fast (1-2 hours) conversion of POC to DOC, then a slower rate of loss (24-48 hours) of both DOC and POC, indicating that the POM collected from the stream was very labile and degradable.

3.2. Peatland stream water experiments

3.2.1. Initial water DOC and POC concentrations

The initial water chemistry (t_0), measured before the treatments were applied, had an average DOC concentration of 68.5 mg C L^{-1} (range: 20.9 to 113.9 mg C L^{-1}; Figure S1) and an average POC concentration of 1.5 mg C L^{-1} (range: 0.0 to 4.9 mg C L^{-1}). Applying the treatments did not change the initial DOC concentrations, so the t_0 concentrations were used as the starting DOC concentration for all three treatments, and results are presented as a percentage of the t_0 DOC concentration. Applying the treatments did change the POC concentrations, so the t_1 POC concentrations were used as the starting POC concentrations for each separate months' experiment. The t_1 POC concentrations show that the treatments altered the POC as intended (Table 1) – there was no POC detected in the POM0 water, there was a 'normal' POC concentration

(1.2 mg C L^{-1}) in the POM1 water, and almost exactly a ‘double’ concentration in the POM2 water (2.5 mg C L^{-1}).

The initial DOC concentrations cover a wide range of concentrations, probably due to the varied stream discharge conditions over the sampling time (May to October), including a very dry summer. The initial DOC concentration varied by month, and was higher in May, June and July than the other months (Figure S1). The initial DOC concentration in the stream water had a positive relationship with the DOC concentration at the end of the experiments in each treatment (Table 1). Experiments with higher initial DOC concentrations (summer months) had higher overall losses of DOC in all three treatments – however this relationship was only significant in the POM2 treatment (Table 1).

The initial water chemistry also showed some variation in DOC quality indicators, including $SUVA_{400}$ and E4:E6, whereas the absorbance at 400 nm was relatively similar across the sampling months. The E4:E6 and $SUVA_{400}$ followed a similar pattern – higher in May and October and generally lower in the summer months. High E4:E6 and $SUVA_{400}$ indicate the DOC was more fulvic than humic in nature, and had a higher aromaticity than in the summer months, whereas the water colour (absorbance at 400 nm) was relatively similar across all months.

3.2.2. DOC and POC concentrations throughout the experiments

On average, the DOC concentrations decreased over the 70-hour experiments (Figure 3). Between the beginning and end to the experiments, in the POM0 water, the average DOC concentration decreased by 67%; in the POM1 water, the average DOC concentration decreased by 65%; and in the POM2 water, the average DOC concentration fell by 35% (Table 1). The largest average decrease in a single hour in DOC concentration occurred in the POM0 treatment where there was a 41% decrease in DOC concentration between t_0 and t_1. The initial loss of DOC from the POM1 and POM2 treatments was not as great as that for POM0; both treatments lost 14% of the DOC in the first hour. Despite these initial similarities between the POM1 and POM2 treatments, POM0 and POM1 had both lost over 60% of the total DOC by t_{68}, whereas the POM2 treatment had only lost 35%. Each months’ individual experiment showed variation in the DOC concentration with time (Figure S2); however the DOC consistently fell between the beginning and end of each experiment.

The ANOVA showed significant differences in the DOC concentrations between the sample times ($p < 0.01$) and treatments ($p < 0.01$). Fisher's Least Significant Differences post-hoc test showed there were significant differences in the DOC concentration between all of the treatments, with DOC concentrations greater in the order POM2 > POM1 > POM0. The interaction between treatment and sample time was not significant, i.e. in all three treatments DOC concentration behaved in the same way over the course of the experiment. This result is supported by a simple linear regression of the average DOC concentrations in each treatment over time: the gradient of the relationship was similar, varying from 0.26 to 0.48 mg C L^{-1} hr^{-1} (Figure 3). The intercepts of the relationship varied from 44.6 (POM0) to 58.4 (POM2) mg C L^{-1}, reflecting the differences found between treatments in the ANOVA.

The total DOC lost each month in each treatment was compared to the sum of the PAR (the total PAR the water was exposed to over the 70 hours of each experiment). There was a positive relationships in all three treatments: higher PAR, higher total DOC loss. The R^2 and gradient were highest in the POM0 treatment, showing a stronger relationship between PAR and DOC loss without POM present. The gradient was lowest in the POM2 treatment, reflecting the lower total loss of DOC over the experiments.

The POC concentrations increased, rather than decreased, over the 70-hour experiments (Figure 4). In the POM0 water, the average POC concentration increased from 0.00 to 0.43 mg C L^{-1} (range 0.00 to 1.57 mg C L^{-1}); in the POM1 water, the average POC concentration increased by 28% (range 0.19 to 3.61 mg C L^{-1}); and in the POM2 water, the average POC concentration increased by 131% (range 0.00 to 19.81 mg C L^{-1}; Table 1). Each months' individual experiment showed variation in the POC concentration with time (Figure S3); some months' show very varied results, especially in the POM1 and POM2 treatments.

Of the 55 POC data points in the POM0 treatment, 38 were 0.00 mg C L^{-1}. The POC concentration in the POM1 treatment in the first stream water experiment was 0.00 mg C L^{-1} on two occasions (t_4 and t_{20}), and was very low for the whole experiment (highest concentration 1.14 mg C L^{-1}). Likewise, in the POM2 treatment in the first stream water experiment, the POC concentration was 0.00 mg C L^{-1} between t_4 and t_{30} (the end of the experiment). These results indicate the POC present in the stream water when it was collected was particularly labile, and was easily broken down to DOC or lost to the atmosphere in 30 hours.

There were significant differences in the POC concentrations between the treatments ($p< 0.01$), but not between sample times, i.e. there was no statistical justification to say POC changed over time in these peatland stream water experiments. Equally, the interaction of treatment and sample time was also not significant. The post-hoc test showed there were significant differences in the POC concentration between all of the treatments, where POM2 > POM1 > POM0.

The relationship between DOC and POC in each treatment was analysed by simple linear regression. In POM0, there was no significant relationship ($p = 0.15$, $R^2 = 0.03$). In POM1, there was a very weak but significant positive relationship ($p = 0.03$, $R^2 = 0.08$). In POM2 there was a significant and stronger positive relationship ($p < 0.01$, $R^2 = 0.30$). For the two significant relationships found, when the POC concentration was high, the DOC concentration was also high.

The indicators of DOC quality and colour showed varied results. Absorbance at 400 nm increased significantly ($p < 0.01$) over time in all three treatments. The $SUVA_{400}$ increased significantly ($p = 0.03$) over time too, indicating the DOC was becoming more coloured, and more aromatic. In both the $SUVA_{400}$ and absorbance and 400 nm there were no significant differences between treatments. The E4:E6 ratio varied over time, but the difference was not statistically significant. The E4:E6 decreased to t_{30}, midway through the experiment, then increased to t_{68}, indicating the DOC started out more fulvic in nature, became more humic at t_{30}, and then returned to a fulvic nature.

4. Discussion

4.1. Deionised water experiment

This study aimed to assess if current water sampling methods accurately represent the impact of POC on DOC degradation. The deionised water experiment showed how much DOC can be produced from a very high concentration of labile POM in a short amount of time. The highest rate of DOC production from POM in the deionised water experiment occurred during the initial hour of the experiment and was 19.6 mg C L^{-1} hr^{-1}; however at the end of the 70 hours there was a total loss of over 250 mg C L^{-1} POC with only an overall gain of 6.7 mg C L^{-1} as DOC. There was clearly rapid conversion of POC to DOC, with apparent subsequent loss of organic carbon as CO_2, as very little of the initial OC (organic carbon) was present in the final water samples. Rapid turnover (less than 24 hours) and loss of organic carbon from water was reported by Bengtson and Bengtsson (2007) in their study of DOC respiration. They suggest that the limit on DOC loss wasn’t initial DOC concentration, but the rate of DOC production. This finding supports the loss of organic carbon in our study as there was a high concentration of POC available to produce DOC. However, the concentration of POC used in the deionised water experiment was much higher than POC concentrations typically found in peatland streams (and those found in the peatland stream of this experiment), except in areas of peatland that have been badly disturbed, or have high rates of erosion; these results should not be extrapolated to all peatland streams.

4.2. Stream water experiments

The results of the peatland stream water experiments showed the addition of POM resulted in lower losses of DOC from the water. Unexpectedly, the filtered water and unfiltered water (with 'natural' POM and POC concentrations) had the same overall loss after 70 hours in the degradation experiment. There were differences in the DOC concentration in the filtered and unfiltered during the earlier stages of the experiment (Figure 3). Filtering the water would have removed the larger microbes and aquatic animals that may be responsible for biodegradation of DOC, and so once the initial photodegradable DOC had been broken down, there were fewer microbes available to biodegrade the resulting compounds, resulting in a slower rate of loss after the first 12 hours. In the unfiltered water, with the 'normal' POC concentration, there was no net effect on the DOC concentration. It is likely there was DOC production from POC, buffering lower losses of DOC by photodegradation, resulting in an overall net reduction that was no different to the filtered stream water. When the POC concentration was doubled (POM2 treatment), there was an inhibition of DOC loss, perhaps by reduced light penetration leading to lower photodegradation. There also may have been more microbes present in the water than in the POM1 treatment (although this was not analysed), and so the rates of DOC loss by biodegradation would be expected to be higher. Attermeyer et al (2018) found the microbial degradation rates of POC were higher than those of DOC in unfiltered, dark incubations of peatland, stream, river and reservoir water over 7 days. The POC was preferably degraded, and had a significantly shorter half-life than DOC (Attermeyer et al., 2018). Light penetration in natural water has been shown to impact the rates of photo-induced DOC losses (Ask et al., 2009) and reduced primary production (Kankaala et al., 2019). The rate of change of DOC in the stream water experiments varied from 0.26 to 0.48 mg C L^{-1} hr^{-1} in the three treatments (Figure 3). Despite the rates being relatively similar, extrapolating shows that the DOC concentration would reach 0 mg C L^{-1} after 121, 113 and 225 hours (in the POM0, POM1 and POM2 treatments respectively). However, it is unlikely that the rate of DOC loss would remain constant, as the lability and degradability of the DOC is highly variable (Evans et al 2017).

The rates of DOC loss also highlight the importance of the duration and sampling frequency of degradation experiments – the greatest rates of DOC loss occurred during the first few hours of the experiment – detail that would have not been clear if taking daily (rather than hourly) samples. Up to t_2, the DOC concentrations were almost identical in the POM1 and POM2 treatments, while the DOC concentration in the POM0 treatment was almost 20 mg C L^{-1} lower (despite starting from the same average DOC concentration as the POM1 and POM2 treatments). The results from both the DI water and peatland stream degradation experiments are supported by those found by Goulsbra et al., (2018) and Brown et al., (2019). Both studies showed that addition of POM to filtered stream water resulted in rapid emission of carbon as CO_2. The CO_2 emissions were highest from water that had POM added and was irradiated with gamma radiation (to stop biodegradation) showing the significant impact of light on the degradation of POM. The CO_2 emissions were very low from filtered water without POM added (Goulsbra et al., 2018; Brown et al., 2019). Additionally, Goulsbra et al., (2018) showed rapid conversion of POC to DOC in less than 24 hours, a significant relationship between POC and initial DOC concentration, and increased DOC concentrations in water with added POM, similar to the results found in the current study. Brown et al., (2019) simulated erosion into streams and rivers by adding POM to water, and found a rapid release of CO_2, above that found in water without POM addition, and that this relationship was light-dependent.

4.3. Interactions between POC and DOC

In both the deionised water and peatland stream water experiment, the concentrations of DOC and POC increased and decreased over time, showing DOC can flocculate to become POC, and POC can break down to DOC. The increases in overall OC concentration suggest the colloidal pool of carbon (sizes intermediate between DOC and POC, not quantified by this study) may be a more important store and source of OC then previous considered in terrestrial ecosystems (Guo and Macdonald 2006). The changes in OC concentration over time (in both the deionised water and stream water experiment) happened alongside changes in the colour of the water – there were changes in the composition of the DOC during the experiments. In the deionised water experiment, the E4:E6 ratio increased to t_2, then decreased rapidly and stayed very low for the remainder of the time. The $SUVA_{400}$ increased to t_7, was low at t_{20}, and then increased again to its highest point at t_{30} (high aromaticity coinciding with the increased in DOC concentration). The $SUVA_{400}$ then decreased for the rest of the experiment, suggesting the remaining DOC was less aromatic in composition.

The stream water experiment had the lowest E4:E6 ratio at t_{30}, indicating the DOC was more humic in character. It is interesting that the DOC character changed most at t_{30} in both the deionised and stream water experiments – perhaps this is evidence of a change in lability/availability to microbial degradation occurs after approximately 30 hours of in-stream processing. This change in character could also impact on the total OC (measured as POC + DOC concentration) as the varied types of OC molecules may be more difficult to detect using the analytical methods used (Giasson, Averill and Finzi, 2014).

The interaction of DOC and POM significantly impacted the overall loss of DOC: the presence of POC decreased the loss of DOC. It is possible that the POM inhibited light penetration in the water, or that the POM is preferentially degraded by microbes over DOC. The vials were kept at an angle, and so the water in the vials was shallow (approximately 150 mm), but not unrealistically when compare to the stream. Moody and Worrall (2017) estimated that 150 mm represented the 46.5th percentile flow depth of Cottage Hill Sike, and that water of this depth would be exposed to 62.5% light penetration 75% of the time. It is unlikely that the POM present in the vials inhibited the light penetration, and so unlikely that this was the driver behind the differences in DOC losses between treatments in this experiment. The high concentrations of DOC typically found in peatland streams may inhibit light penetration more than the POM concentrations applied in this study.

It is possible that microbes present in the water prefer POM to DOC, and that the degradation of POM by microbes results in modified POM, rather than breaking it down to molecules small enough to be colloidal and smaller than 0.45 µm (the cut-off size for DOC). Some organic matter contains compounds that actively inhibit enzyme activity, such as polyphenols or tannins, and physical accessibility of organic matter was found to be important in decomposition (Dungait, Hopkins, Gregory, & Whitmore, 2012), supporting the idea that the inhibition of DOC breakdown in the presence of POM is due to a physical constraint, such as binding sites on enzymes. Polymers that are heterogeneous in size and chemistry, such as organic matter, are more resistant to breakdown by enzymes (Marschner et al., 2008). Further work on the factors that impact the interaction between DOC and POM would allow for the relative contribution of light attenuation and microbial degradation to be quantified.

The methods of analysis of DOC and POC used in this study were as accurate as possible; however there are still some unavoidable sources of error that contribute to the results. Combining the replicate vials to increase the volume of water for POC analysis meant there were no replicate measurements, but resulted in one measurement that would be more accurate than two gained from smaller volumes of water. Giasson, Averill and Finzi (2014) assessed the Bartlett and Ross (1988) colorimetric method of DOC analysis used in this study, and found that when compared to a measurements from combustion analyser, the Bartlett and Ross method underestimated DOC concentrations in water from peat soils. Applying the correction factor suggested by Giasson, Averill and Finzi (2014) to DOC concentrations reported in this paper resulted in concentrations that were 45 % higher than those previously reported here. The underestimate of DOC concentrations by the Bartlett and Ross method is attributed to oxidation-resistant organic compounds present in DOC.

In our study, we used the operational definition of DOC as anything smaller than 0.45 µm, whereas some studies use smaller cut-off point of 0.22 µm, to remove more of the bacteria present in natural water (e.g. Abbott, Larouche, Jones Jr, Bowden, & Balser, 2014; Guillemette & del Giorgio 2011; Polrovsky et al., 2010). Brailsford et al., (2017) looked into the impact of different filter size, vs no filtering, as methods of assessing DOC concentrations. In dark, lab incubations, they found the size of the filter (0.22 vs 0.45 µm) had no impact on biodegradation in upland water over a period of 168 hours – there was no difference in amino acid, glucose or orthophosphate depletion in the water. However, Brailsford et al., (2017) did find significant depletion of amino acids, glucose or orthophosphate in unfiltered water. These results showed that the microbes and particulates present in the unfiltered water had an impact on the DOC concentration of the water.

It is important to accurately quantify the interactions of different pools of OC in peatland streams, as these are known to contribute directly to CO_2 losses from rivers, streams, lakes and reservoirs (Raymond et al., 2013). Understanding the interaction between DOC and POC is important to know how lab-based measurements of OC losses relate to those measured in surface waters, and therefore understand the ultimate fate of the OC as it is transported and transformed in the fluvial network (Attermeyer et al., 2018; Brown, Goulsbra, & Evans, 2019). The results of this study showed that in streams where the concentration of POC is high, such as in degraded peatlands like those found in the Peak District, UK, for the first few days of POC transport in the water, POC is likely to buffer the losses of DOC. If the DOC losses are buffered by high POC concentrations, this could result in higher DOC concentrations in inland waters (such as reservoirs) fed by peatland streams, resulting in higher DOC to CO_2 turnover during the residence time of the water (Evans et al., 2017).

As DOC is much more commonly measured than POC in studies of fluvial carbon export, it is difficult to know how many studies could have under- or over-estimated the interactions and concentrations of DOC and POC, if the measurements of DOC loss were based on filtered water samples. If the POC concentration in the sampled stream was high (such as in eroded sites) it is unlikely that measurements of DOC degradation obtained in filtered water lab experiments will be accurate estimates of in-stream DOC degradation (Brailsford et al., 2017). To ensure accurate DOC degradation measurements, we would recommend measuring DOC concentrations in both filtered and unfiltered water, so the impact of particulates on the rates of DOC loss could be quantified, and to gain a better understanding of organic matter reactivity in surface waters, especially in waters with higher than 4 mg C L^{-1} POC concentrations.

5. Conclusion

One of the key limitations to understanding the role of organic matter in shaping water quality is the ability to accurately quantify the interactions and processing of DOC and POC in natural waters. This study aimed to assess if current water filtering methods accurately represent the impact of POC on DOC degradation. The main findings were:

- There was a rapid conversion of POC to DOC and subsequent loss of both forms of organic carbon in the experiments containing only deionised water and POM.
- In natural water, containing both DOC and POC, the loss of organic carbon was not significantly different from filtered water, containing only DOC, showing that filtering (and the consequent absence of POC) did not significantly impact the DOC degradation rates measured in the water.
- Doubling the POM concentration in the water did have a significant impact on the DOC degradation rate, suggesting that filtering would still be necessary to get accurate DOC degradation rates in water with high POC concentrations.
- The impact of POC on the DOC degradation rates was highest in the early summer months – when the initial DOC concentration and PAR were highest. In peatland streams, with high DOC, and relatively low POC and POM concentrations

These findings support the current methods employed in studies of peatland streams, with typically high DOC and relatively low POC concentrations, to filter the water before conducting degradation experiments –

it doesn't affect the DOC degradation rates and prevents the high POC concentrations from potentially impacting the results.

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Data availability statement

The data that supports the findings of this study are available in the supplementary material of this article.

Figure Legends

Figure 1. The DOC, POC and average OC (DOC + POC) concentrations in the deionised water over 70 hours. The initial POC concentration of 255.27 mg C $\mathbf{L}^{-1}$ is not shown to avoid losing detail at lower concentrations.

Figure 2. The relationship between the POC and average DOC concentration at the nine sample times between t_1 and t_{68} in the deionised water.

Figure 3. The average DOC concentration in the three stream water treatments between t_0 and t_{68}. Error bars are the standard errors.

Figure 4. The average POC concentration in the three stream water treatments between t_1 and t_{68}. Error bars are the standard errors.

Table 1. The average (± standard error) initial and end DOC and POC concentrations in the three stream water treatments; and the results and parameter estimates (± standard errors) of linear regression of all the DOC concentrations with the POC concentrations. The relationship between the final DOC and initial DOC concentration are also shown. However, the relationship between the initial and final POC concentrations are not shown, as there were no significant results.

	n	POM0	POM1	POM2
t_0 DOC (mg C L^{-1})	7		68.5 ± 15.4	
t_{68} DOC (mg C L^{-1})	12	22.5 ± 2.6	23.8 ± 5.5	44.6 ± 6.0
% loss of DOC		67	65	35
t_1 POC (mg C L^{-1})	7	0.0 ± 0.0	1.2 ± 0.1	2.5 ± 0.5
t_{68} POC (mg C L^{-1})	6	0.4 ± 0.2	1.6 ± 0.4	5.7 ± 2.1
% increase in POC		-	28	131
relationship with POC	55			
p		ns	0.0333	<0.0001
R^2		-	0.08	0.30
intercept		ns	31.9 ± 6.6	42.2 ± 4.1
POC gradient		ns	10.0 ± 4.6	3.5 ± 0.7
Final DOC concentration relationship with initial DOC	7			
p		0.26	0.09	0.05
R^2		0.24	0.47	0.56
intercept		12.1 ± 7.5	-2.1 ± 12.3	9.8 ± 13.2
t_0 DOC gradient		0.1 ± 0.1	0.3 ± 0.2	0.4 ± 0.2