Aquatic Sciences

RESEARCH ARTICLE

Dynamics of dissolved organic matter in headwaters: comparison of headwater streams with contrasting DOM and nutrient composition

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Abstract

Dissolved organic matter (DOM) in freshwaters is recognised as a significant and active component of the global carbon budget. DOM exported from terrestrial ecosystems may be compositionally and functionally altered by chemical and biological reactions as it is transported downstream. The processes affecting DOM in headwater streams remain uncertain but are potentially highly variable depending on DOM composition and nutrient availability as a function of soils, land-use, and human pressures. To investigate variability of DOM reactivity we took water samples from two contrasting headwater catchments, considered functional 'end-members' for DOM export: one rich in aromatic DOM and low in inorganic nutrients (peatland), and another (nearby) catchment characterized by less aromatic DOM and high nutrient loadings (agricultural grassland). Under controlled laboratory conditions, we evaluated the effects of light, presence/absence of aquatic biota and nutrient enrichment on short-term changes in DOM quantity and quality in these samples. For the peat stream, exposure to sunlight (with UV) resulted in net abiotic DOM removal, whereas in the agricultural stream it led to net biological DOM production. Nutrient addition accelerated DOM production in both streams. We conclude that in-stream changes in DOM quantity and quality represent the net effect of multiple consumption and production processes whose relative importance is strongly influenced by source-dependent DOM composition and environmental factors such as inorganic nutrient content and sunlight exposure. Our findings suggest that headwater streams may be more active processors of carbon and nutrients than presumed hitherto.

Keywords Dissolved organic carbon DOC · Biogeochemical cycling · Headwaters · Photo-degradation

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Introduction

Recent estimates suggest that CO_2 emissions from inland waters are comparable to net absorption of CO_2 by the terrestrial and oceanic biosphere (Battin et al. 2008; Biddanda 2017; Ciais et al. 2013). Characterising carbon transformations in inland waters are crucial to properly evaluate the effects of global changes on the carbon cycle (Tranvik et al. 2009), and have therefore received more attention in recent years. While the importance of lake processes has been emphasised (Berggren et al. 2018; Cole et al. 2007; Evans et al. 2017; Holgerson and Raymond 2016), the inferred importance of running waters, in particular headwaters, varies between studies. Some studies (Kothawala et al. 2015; Wollheim et al. 2018 2015) have suggested that short transit times limit DOM processing in streams and rivers, whereas others (Berggren and del Giorgio 2015; Cory et al. 2014; Creed et al. 2015) observed significant modifications of DOM concentrations by in-stream processes over

relevant timescales. Headwaters constitute potential hotspots of carbon processing as they comprise the majority of total river length in many areas (Bishop et al. 2008), have high ratios of surface area to water volume, and often receive high inputs of freshly exported terrestrial DOM (Agren et al. 2007; Raymond et al. 2016). Process rates in these short residence time systems may be under-estimated by studies of larger downstream systems, because the reactivity of DOM declines with increasing water residence time (Catalán et al. 2016; Evans et al. 2017). Although biological activities in the benthic zone are usually considered a major driver of ecosystem processes in headwaters (Gardner and Doyle 2018), water column processes can contribute to a significant part of annual respiration and primary production, up to 25% according to Rovelli et al. (2017).

In such headwaters, dissolved organic matter (DOM) leached from the terrestrial system may be mineralised by photodegradation (Cory et al. 2014; Koehler et al. 2014; Köhler et al. 2002; Moody et al. 2013; Pickard et al. 2017; Spencer et al. 2009; Winter et al. 2007; Worrall and Moody 2014), or heterotrophic respiration (Battin et al. 2008; Franke et al. 2013; Mulholland and Hill, 1997). DOM can also be produced in these systems by autotrophic production (Fuß et al. 2017). Storage via flocculation and adsorption, and their reversal, may also affect the dynamics of downstream DOM transport. According to the 'river continuum' concept (Vannote et al. 1980), headwaters are dominated by heterotrophy, while autotrophy typically dominates downstream. Allochthonous inputs of DOM received by streams, however, can equal or exceed those derived from primary productivity (Bernhardt et al. 2018). Among these headwaters, the bio- and photo-degradability of DOM varies as a function of its origin within the terrestrial system; and autotrophic DOM production varies with nutrient (nitrogen, N and phosphorus, P) availability (Aitkenhead and McDowell 2000; Fuß et al. 2017; Graeber et al. 2015; Riedel et al. 2016; Winterdahl et al. 2014; Evans et al. 2017) as a function of catchment soils and land-use (Gucker et al. 2016; Heathwaite and Johnes, 1996). Moreover, photo-degradation can affect the bioavailability of residual DOC that is not converted into CO_2 (Anesio et al. 2005; Cory et al. 2014; Moran and Zepp, 1997). Therefore, it is likely that the relative importance of different DOM transformation processes, their interaction, and the overall rate of DOM removal and associated CO_2 production, vary broadly among headwater catchments as a function of soils and land management regime.

Few studies have investigated the interactions simultaneously between photo-degradation, biological processes affecting DOM and their modulation by nutrient availability for a range of stream waters. Madsen-Østerbye et al. (2018) studied both microbial and photochemical processing of DOM in a humic lake and its groundwater inflow.

Jones et al. (2016) sampled contrasting stream waters in the Conwy catchment, North Wales, and measured DOC transformations under a range of experimental treatments. Based on controlled light experiments, combined with ^{14}C-DOC measurements, they concluded that peat-derived DOM was highly sensitive to photochemical degradation, and that stream water samples from agricultural catchments and estuarine samples experienced a net production of DOC, which was attributed to their higher nutrient concentrations.

Building on this study, we report on a set of mesocosm experiments that were undertaken to assess the influence of nutrients (N and P) on the reactivity of DOM in water samples from two headwater streams with contrasting DOM and nutrient inputs (Cooper et al. 2014; Emmett et al. 2016). Water draining from peatland is composed of highly aromatic and photosensitive DOM, but typically has low inorganic nutrient concentrations, whereas water draining from agricultural grassland contains DOM with lower aromaticity and low light absorbance, and higher nutrient concentrations. Samples were exposed to different light conditions, in the presence and absence of biota to discriminate light/dark and biotic/abiotic processes, under ambient and elevated nutrient levels.

Material and methods

Sampling sites

Water samples were collected from two headwater streams in the Conwy catchment, North Wales, UK. The first sampling location (Fig. 1) was on the Nant y Brwyn, a stream draining a 1.1 km^2 subcatchment of upland blanket peat with low intensity sheep-grazing, characterised by high DOC concentrations and very low nutrient levels. The second was the Hiraethlyn, a stream draining a catchment of 7.4 km^2 dominated by improved grassland on mineral soils, with a high density of sheep and cattle, moderate DOC and relatively high inorganic nutrient concentrations. The range of concentrations of water quality variables in the two streams is shown in Table 1, based on monthly samples collected during 2014 (Cooper et al. 2013). Both streams have been monitored for over a decade as part a distributed catchment-scale research programme led by the Centre for Ecology and Hydrology, and have been identified as effective 'end-members' at this scale based on their soils, land-use and water quality attributes (e.g. (Brailsford et al. 2017; Cooper et al. 2013; Emmett et al. 2016)).

Experimental design

For each study stream, a four litre water sample was collected in early summer 2014 and returned immediately to
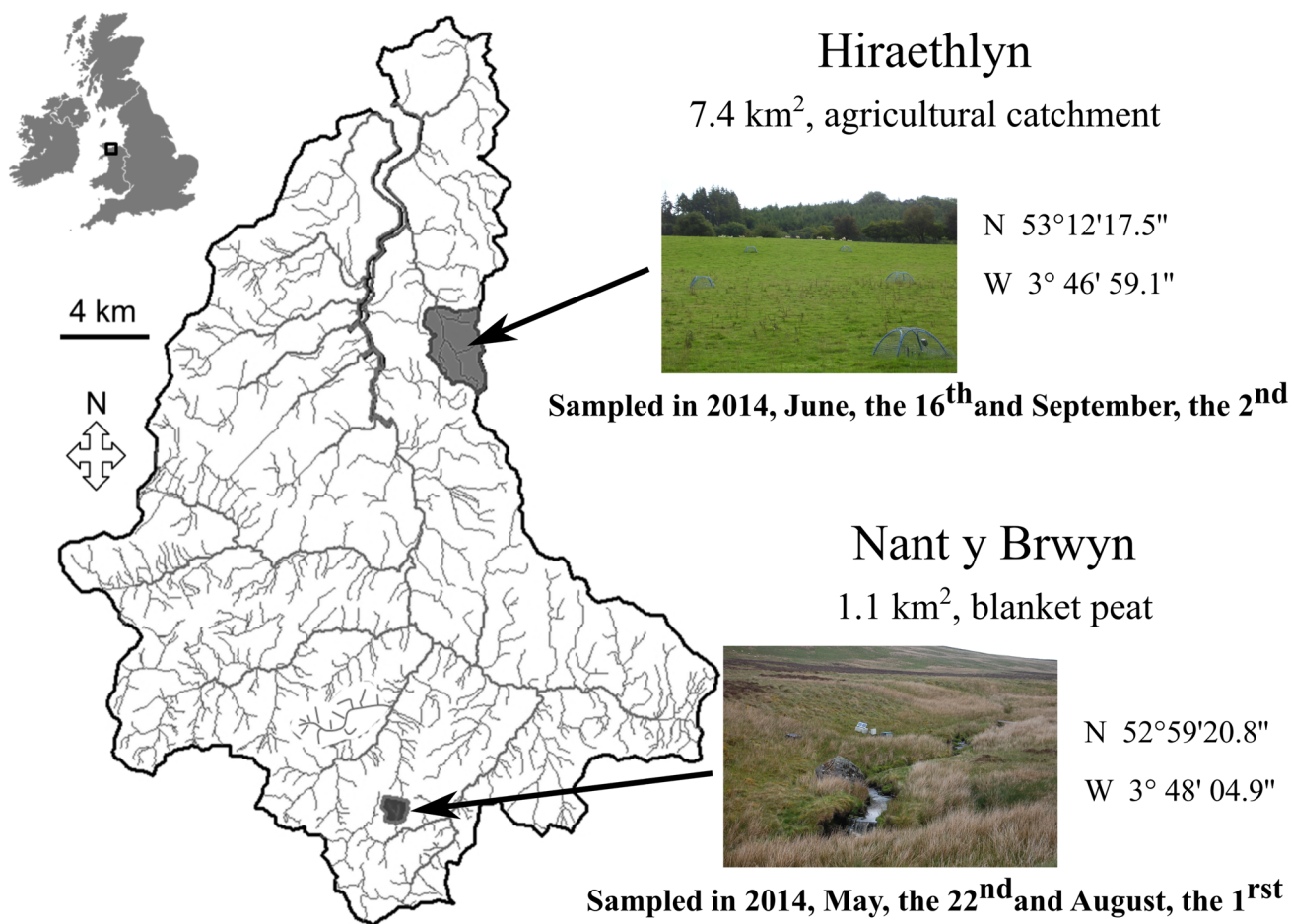
Fig. 1 Location of the Conwy catchment and sampling points. Sampling dates are provided for the samples used for this study, however, monthly sampling was also performed on these stations and elsewhere within the Conwy catchment during the years 2013–2014

Table 1 Average values and [min; max] range obtained from the monthly water quality monitoring in 2013–2014 ($n = 16$) from (Cooper et al. 2013)

Parameter	Unit	Peat stream	Agricultural grassland
pH	pH unit	5.3 [3.8; 6.7]	7.10 [6.6; 7.7]
Alkalinity	µeq L^{-1}	23 [− 100; 230]	882 [500; 1400]
EC	µS cm^{-1}	41 [25; 70]	240 [180; 300]
[DOC]	mg C L^{-1}	13.3 [5; 20]	9.8 [3; 15]
$SUVA_{254}$	10^2 L mg^{-1} m^{-1}	5.2 [4.7; 5.9]*	2.4 [1.7; 3.0]*
NO_3	mg N L^{-1}	0.0014 [0.01; 0.04]	2.7 [2; 3]
NH_4	mg N L^{-1}	0.02 [0.01; 0.05]	0.19 [0.03; 0.6]
PO_4	mg P L^{-1}	0.008 [0.0015; 0.03]	0.07 [0.02; 0.14]

*$SUVA_{254}$ was not recorded in Cooper et al. (2013), these average, min and max values are estimated from our samplings (2 dates)
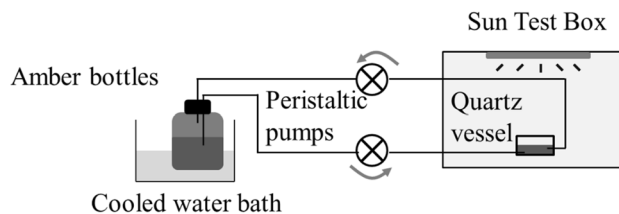

Fig. 2 Experimental set-up used to investigate the DOM reactivity in each combination of stream water and treatment

the laboratory. The sample was split into twelve 300 mL sub-samples with each transferred into a 500 mL amber-coloured glass bottle without filtration. The bottles were placed in a cooling bath to maintain a water temperature below 10 °C.

The laboratory experiment comprised a closed water recirculation system (Fig. 2, also described in Jones et al. (2016)) which was used to expose samples to a controlled sunlight irradiation dose in the presence or absence of inorganic nutrients and aquatic biota. Four of the bottles were

subject to each of three treatments. The bottles were connected via Marprene® tubes (Watson-Marlow Ltd., Falmouth, UK) to a 22 mL quartz vessel placed in a SunTest Atlas CPS + (SunBox; Atlas Material Testing Technology, Mount Prospect, IL, USA), and subjected to a controlled level of visible and UV light exposure. Two peristaltic pumps were used to continuously circulate water between the amber bottle and the quartz vessel (flow rate of 2 mL min⁻¹). Subsamples were collected from the tubes connecting the vessel back to the amber bottle via a side port, to minimise disturbance and to keep the system as closed as possible. Given the number of quartz vessels that could be accommodated within the SunBox at any one time, experiments were run sequentially for the two study streams, using samples collected immediately prior to the start of each experiment (Dates are given in Fig. 1).

In a first set of experiments, samples were subjected to three treatments in order to identify the effect of irradiation on DOM in the presence or absence of biota. Treatments for this experiment comprised (i) irradiated with aquatic biota present ('light'); (ii) dark with aquatic biota present ('dark'), and (iii) a sterilised irradiated treatment, in which 0.42 mL of a biocide, $HgCl_2$, was added in order to kill any microorganism present in the sample ('light + $HgCl_2$'). This sterilisation method, described by Spencer et al. (2009), has been used in previous controlled experiments and is not thought to affect photo-reactivity of Chromophoric DOM (CDOM) or UV visible spectra (Helms et al. 2008). In the light treatment, the vessel was exposed continuously to 765 W m⁻² in the SunBox over a 5 days period. Taking into account the irradiation dose, the duration of the experiment and the volume of water contained in the vessel relative to the total sample volume, this represents a cumulative irradiance dose of about 33,000 kJ m⁻², which is slightly higher than the irradiance dose associated with one clear summer day at the latitude of the study site. In the dark treatment, vessels were covered with tin foil and therefore always maintained in darkness, but with the same circulation conditions as in the irradiated treatments. The amber bottle reservoir was used to keep a part of the volume in the dark to limit the cumulative irradiance dose to realistic levels, to avoid possible sterilization of the sample by UV radiation, and to (crudely) reproduce the effects of mixing within the water column.

A second set of experiments was conducted using samples collected from each of the streams during late summer 2014. The procedures used were identical to those described above (using the same volumes, duration and exposure), with three different treatments to assess the effect of nitrogen (N) and phosphorus (P) availability on the processing of DOM. The growth of primary producers in temperate freshwaters is considered to be limited by either P or co-limited by P and N though local variations exist (Dodds and Smith 2016). The treatments in this experiment were (i) irradiated ('light'), as

in the first experiment, used as the reference; (ii) combined irradiation plus P addition ('light + P'), achieved by injecting NaH_2PO_4 into the sample at the beginning of the run; and (iii) irradiation, P and N addition ('light + P + N'), following the same procedure plus N addition using $NaNO_3$. The number of replicates per treatment was reduced to three in this experiment to accommodate the additional treatments, which are not reported here. The amount of nutrient addition was calculated a priori to be sufficient to remove any nutrient limitation.

Analytical measurements

Samples were collected for analysis of DOC concentrations at the start of the experiment, and daily thereafter until the end of the experiment on day 5. All collected sub-samples were filtered at 0.45 μm using Whatman cellulose nitrate filters. Carbon concentrations were measured on a Thermalox TC/TN Analyser (Analytical Sciences UK, Cambridge, UK). Total carbon (TC) was determined by thermal oxidation (680 °C) with detection of CO_2 by an NDIR (Non Dispersive Infra-Red) sensor. Non Purgeable Organic Carbon (NPOC) was determined following the same procedure as for TC after first spiking samples with 1 M HCl and sparging for 60 s with O_2 gas to remove inorganic carbon. Total inorganic carbon (TIC) was determined as for TC, but with a lower furnace operating temperature of 120 °C and phosphoric acid added to the reactor tube as a catalyst. For the stream draining the peatland, DOC was measured as NPOC, while for the stream draining improved grassland, DOC was measured as the difference between TC and TIC. This protocol has been chosen according to previous analyses (Cooper et al. 2014) including comparison of both methods on each water types that enabled us to identify the most reliable method for DOC determination considering differences between samples (in DIC concentration and portion of volatile organic compounds).

Additional analyses for concentrations of major anions were conducted on the initial and the final samples (days 0 and 5), again on samples filtered at 0.45 μm. Major anion concentrations were determined by ion chromatography on a Dionex DX-120 instrument (Dionex Corp., Sunnyvale, CA, USA). Anions were measured with an Ionpac AS4A-SC column using 1.7 mM $NaHCO_3$ and 1.8 mM Na_2CO_3 as the eluent.

All filtered samples were also analysed for absorbance, at wavelengths from 200 to 700 nm, using a Spectramax M2e plate reader (Molecular Devices, Sunnyvale, CA, USA). A Milli-Q blank reading was used to subtract the background from each sample. Specific Absorbance to UV ($SUVA_{254}$) was computed as the ratio between absorbance at 254 nm (in m⁻¹) and DOC concentration (in mg L⁻¹), and considered

a proxy for DOM aromaticity according to (Weishaar et al. 2003).

All analyses were conducted in the CEH Bangor laboratory, which subscribes to the Aquacheck International Testing scheme for Chemical Analytical Laboratories. If storage was necessary prior to analysis, samples were kept in the dark below 5 °C. Control analyses were conducted on subsamples after addition of $NaNO_3$, NaH_2PO_4 and $HgCl_2$ to check that those additions did not have unexpected effects on measured water quality parameters (see SI tables S1 and S2). Data are deposited in Fovet and Evans (2017).

Statistical analysis

We used a repeated measures statistical analysis of the data, allowing for successive sampling from the same bottle. Exploratory graphical analysis of the data suggested that DOC concentrations in each bottle tended towards an asymptote, from a similar starting concentration at the beginning of the experiment. We used the nlme routine in the R package MASS to fit a non-linear mixed effects model to the DOC measurements for each experiment, taken as a function of irradiance. After conversion of irradiance to days, we fitted the following model:

$$DOC = DOC_{Fin} + (DOC_{Ini} - DOC_{Fin})e^{(-k \times days)} \quad (1)$$

This is selected for convenience as a model which is capable of fitting the limited data available, unlike, for example, a simple quadratic. This is not to suggest the model provides a complete representation of underlying processes, particularly under extrapolation. A fuller dataset might reveal, for example, power law rather than exponential behaviour. In the model, the parameter DOC_{Fin} is the DOC concentration at the asymptote, i.e. the final DOC concentration towards which the incubation was converging. The parameter DOC_{Ini} is the initial concentration and k a parameter governing the rate at which the asymptote is approached, thus here a descriptor for decay rates. The parameters DOC_{Fin} and DOC_{Ini} were set as random effects, with all three parameters as fixed effects in an initial model. Exploratory data analysis indicated that the inclusion of random effects for k led to over-parameterisation. Fixed effect dependence on treatment was introduced through each of the parameters DOC_{Fin}, DOC_{Ini} and k, testing models through the Akaike Information Criterion (AIC; Akaike 1973). Inclusion of treatment dependence was found not to be justified for parameter DOC_{Ini} for any of the models, which is consistent with the lack of treatment effect at the start of the experiment. While there was some evidence of a dependence of k on treatment, we have excluded this dependence in the interests of parsimony. The model fitted for all experiments therefore included DOC_{Fin} and DOC_{Ini} as random effects, and DOC_{Fin}, DOC_{Ini} and k as fixed effects, with dependence on treatment for DOC_{Fin}. We fitted a model with the same structure to the $SUVA_{254}$ data for two of the experiments.

Results

Dark, light and sterile light treatments

Figure 3 shows the changes in DOC concentrations over the course of the first experiment for each treatment and each stream water type. Results of our statistical analysis of DOC and $SUVA_{254}$ responses to experimental treatment are presented for the peatland and grassland streams in Table 2. Measured changes in DOC concentrations over time are shown in Fig. 3a-b, while changes in SUVA254 and nutrient concentrations are shown in Table S3. For each experiment, results are presented as the difference between initial and final DOC concentrations (or $SUVA_{254}$) for each treatment, and the difference between final concentrations between treatments (Table 2).

For the peatland stream water, the data show highly significant ($p \leq 0.001$) differences between initial and final DOC concentrations for all three treatments. In all three treatments, DOC concentrations declined, with the smallest reductions in for the dark treatment and the greatest in the 'light + $HgCl_2$' treatment. Changes in $SUVA_{254}$ during the experiment were non-significant for the Dark and Light treatments, but a significant ($p < 0.001$) reduction in SUVA254 was observed in the Light + $HgCl_2$ treatment. Comparing the final concentrations for each treatment, we observed significantly lower DOC concentrations in both the Light and Light + $HgCl_2$ treatments when compared to the Dark treatment, but significantly lower final $SUVA_{254}$ was only observed for the Light + $HgCl_2$ treatment. The Light and Light + $HgCl_2$ treatments did not have significantly different DOC concentrations, but again $SUVA_{254}$ was significantly lower in the Light + $HgCl_2$ treatment.

In the grassland stream water samples, we again found significant changes in DOC concentration ($p < 0.001$) over the course of the experiment for all three treatments, but in this case all changes were positive. In contrast, $SUVA_{254}$ significantly decreased in all treatments. We observed no significant differences in final DOC concentrations or between the Light and Dark treatments, but there was evidence of lower final DOC concentration for the Light + $HgCl_2$ treatment compared to both the Light and Dark treatments ($p < 0.001$). No differences in final $SUVA_{254}$ were observed between any treatments.

Concentrations in NO_3^- and PO_4^{3-} were at all times below the limit of quantification in the peatland stream, while in the grassland stream both nutrient concentrations decreased during the experiment in the Dark and Light
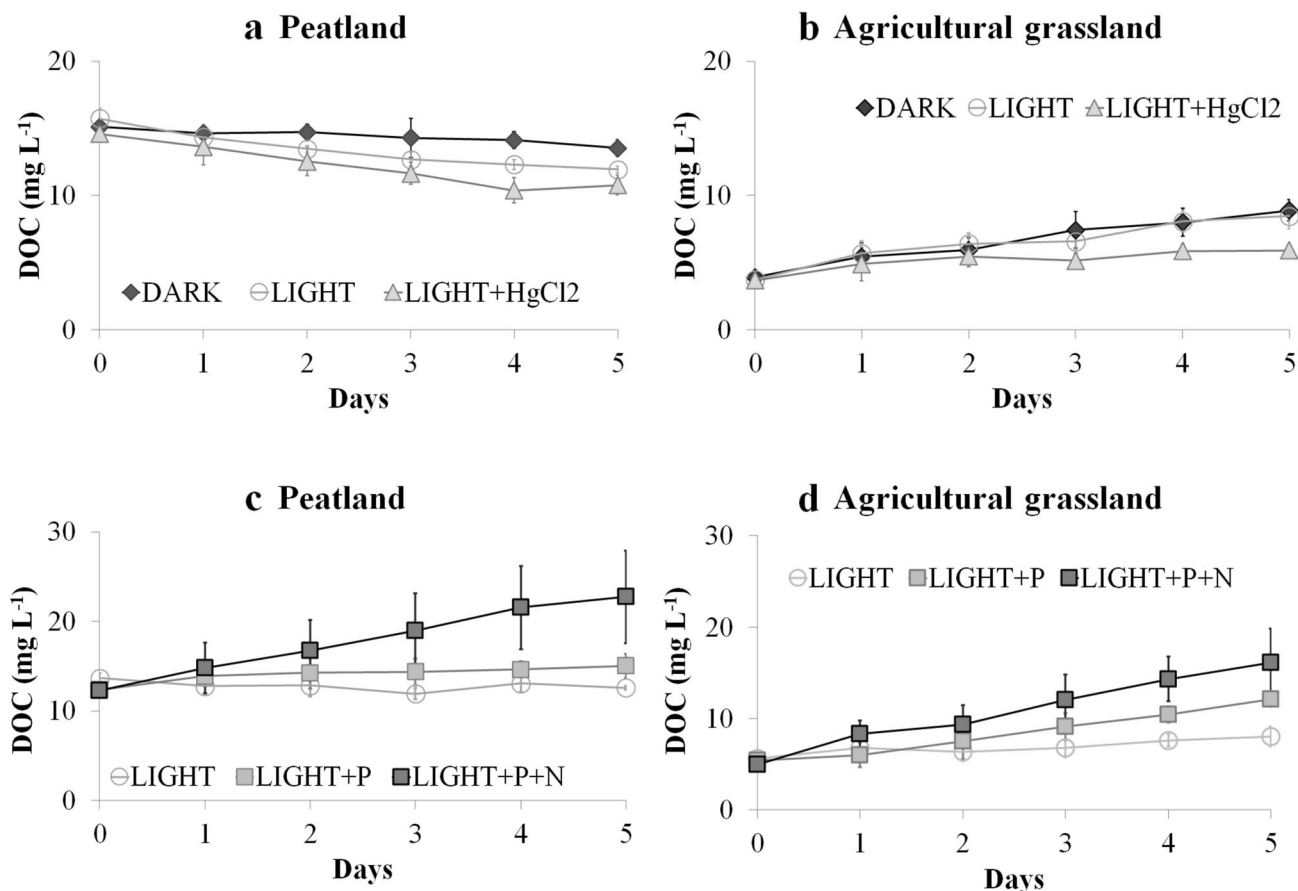
Fig. 3 Dynamics of DOC concentration in the light (± biocide) manipulation experiment (**a**, **b**) and in nutrient addition experiments (**c**, **d**) for the water draining peatland (**a**, **c**) and grassland (**b**, **d**). Dots, diamond, triangles and squares represent the average among replicates and error bars the associated standard deviation

Table 2 Summary results of statistical analysis of DOC and SUVA$_{254}$ changes over the course of each light/biota manipulation experiment, and between-treatment differences in the final (asymptotic) concentration values

Stream	Comparison	Treatment	DOC (mg L^{-1})		SUVA$_{254}$ (10^2 L mg^{-1} m^{-1})	
			Difference	p-value	Difference	p-value
Peatland	Change during experiment	Dark	− 1.48	0.001	− 0.48	0.124
		Light	− 3.91	<0.001	− 0.29	0.358
		Light + HgCl$_2$	− 4.91	<0.001	− 1.21	<0.001
	Between-treatment comparison	Light vs Dark	− 2.43	<0.001	0.19	0.556
		Light + HgCl$_2$ vs Dark	− 3.43	<0.001	− 0.74	0.028
		Light + HgCl$_2$ vs Light	− 1.00	0.081	− 0.93	0.007
Grassland	Change during experiment	Dark	5.38	<0.001	− 1.20	<0.001
		Light	5.06	<0.001	− 1.25	<0.001
		Light + HgCl$_2$	2.26	<0.001	− 1.12	<0.001
	Between-treatment comparison	Light vs Dark	− 0.32	0.527	− 0.05	0.697
		Light + HgCl$_2$ vs Dark	− 3.12	<0.001	0.08	0.486
		Light + HgCl$_2$ vs Light	− 2.80	<0.001	0.13	0.290

For details of statistical analysis see text, and for full statistical results see Supplementary Tables S5 and S6

treatments, but not in the Light + HgCl$_2$ treatment. In both the Dark and Light treatments PO$_4$$^{3-}$ was consumed to below the limit of detection, whereas NO$_3$$^-$ concentration declined by 57 to 75% (see Supplementary Table S3).

Nutrient addition treatments

Results of the statistical analysis are presented in Table 3, and DOC changes over the experiment in Fig. 3c, d. Because of gaps in the SUVA$_{254}$ data, (due to a temporary unavailability of the device), the statistical model was not applied to the SUVA$_{254}$ results in the nutrient addition treatments. For the peatland stream water samples, we observed no significant changes in DOC in either the Light or Light + P treatments. However, a very large and highly significant increase in DOC (> 12 mg L^{-1}, $p < 0.001$) was observed in the Light + P + N treatment. Differences in final DOC concentration between this treatment and the other treatments were also highly significant ($p \leq 0.001$).

For the grassland stream water samples, we observed a tendency for DOC concentrations to increase in all treatments, but this was not significant ($p = 0.10$) in the Light-only treatment. In the Light + P treatment DOC increased by 9.6 mg L^{-1}, and in the Light + P + N treatment it increased by 14.8 mg L^{-1}. Final DOC concentrations were significantly different between all three treatments.

For the peat stream water samples, both NO$_3$$^-$ and PO$_4$$^{3-}$ were below detection limits in the original stream sample. The PO$_4$$^{3-}$ added in both the Light + P and Light + P + N treatments was rapidly consumed, with measured concentrations decreasing by 86% in the Light + P treatment, and falling below detection limits in the Light + P + N treatment. In the Light + P + N treatment, we did not observe significant NO$_3$$^-$ removal, although mean concentrations were slightly lower at the end (1.11 mg L^{-1}) than at the start (1.75 mg L^{-1}) of the experiment (see Supplementary Table S3).

For the grassland stream water samples, PO$_4$$^{3-}$ and NO$_3$$^-$ concentrations were both above detection limits at the start of the experiment. P addition increased initial PO$_4$$^{3-}$ concentrations by 174–207%, while N addition increased NO$_3$$^-$ concentrations by 305%. For the Light treatment, all of the initial PO$_4$$^{3-}$ in the sample (0.040 mg L^{-1}) was removed during the experiment, along with 81% of the NO$_3$$^-$ (1.64 mg L^{-1}). In the Light + P treatment, 92% (0.175 mg L^{-1}) of initial PO$_4$$^{3-}$ was removed, along with all (2.1 mg L^{-1}) of the NO$_3$$^-$. In the Light + P + N treatment, PO$_4$$^{3-}$ removal was similar (94%, 0.2 mg L^{-1}) to the Light + P treatment. Although some NO$_3$$^-$ remained at the end of the experiment for this treatment (82% reduction) the total amount of NO$_3$$^-$ removed (7.1 mg L^{-1}) was much higher than in the Light + P treatment (2.1 mg L^{-1}).

Discussion

Our results clearly show that the concentration and composition of DOM in headwater streams has the potential to be highly dynamic, depending on a range of biotic and abiotic conditions. Depending on these conditions, both net consumption and net production of DOM are possible. Here we discuss the main processes influencing DOM removal, DOM production, their interactions, and the overall implications of our results for understanding of organic matter turnover in aquatic systems.

DOM degradation

Net DOM degradation was only observed in the samples collected from the peatland stream. Reductions of DOC

Table 3 Summary results of statistical analysis of DOC changes over the course of each nutrient addition experiment, and between-treatment differences in the final (asymptotic) concentration values

Stream	Comparison	Treatment	DOC (mg L^{-1})	
			Difference	p-value
Peatland	Change during experiment	Light	− 0.58	0.771
		Light + P	2.49	0.217
		Light + P + N	12.21	< 0.001
	Between-treatment comparison	Light + P vs Light	3.07	0.278
		Light + P + N vs Light	12.79	< 0.001
		Light + P + N vs Light + P	9.72	0.001
Grassland	Change during experiment	Light	2.53	0.101
		Light + P	9.64	< 0.001
		Light + P + N	14.82	< 0.001
	Between-treatment comparison	Light + P vs Light	7.11	0.002
		Light + P + N vs Light	12.29	< 0.001
		Light + P + N vs Light + P	5.18	0.019

For details of statistical analysis see text, and for full statistical results see Supplementary Table S7

were smallest in the dark treatment, and largest in the Light + HgCl$_2$ treatment. In both light treatments, DOC reductions were accompanied by a decline in SUVA$_{254}$, implying a proportionally greater reduction in the chromophoric, aromatic fraction of total DOM (Helms et al. 2008). These observations are all consistent with photodegradation representing a major mechanism for breakdown of DOM in peatland runoff, as has been suggested previously (Jones et al. 2016; Köhler et al. 2002; Moody et al. 2013; Pickard et al. 2017). The lower reduction in DOC concentration in the dark treatment supports the expectation of low microbial degradability relative to photo-chemical degradability in peatland runoff, albeit for the specific incubation time, light and temperature levels in the experiments.

In comparison, DOM exported from agricultural landscapes is typically expected to have higher biodegradability, given its lower aromaticity and more stoichiometrically favourable C:N and C:P ratios (Graeber et al. 2015). No apparent photo-degradation was observed in the + HgCl$_2$ treatment, and we did not observe any net removal of DOM in the agricultural stream samples, even in the dark treatment, where DOC concentration actually increased during the five days of incubation whether under light or dark conditions.

Biological production of DOM

Net production of DOM is clearly indicated by the increase in DOC concentration observed in samples with ambient nutrient levels collected from the grassland stream, in both the light manipulation and nutrient manipulation experiments (Fig. 3b, d). This tendency for DOM to increase during the incubations for the more eutrophic stream was enhanced by P addition, and further increased by N addition. These findings strongly suggest that DOM production in samples collected from this stream was nutrient-driven, a conclusion also supported by the rapid depletion of PO4^{3-} and NO$_3^-$ over the course of the incubations in both ambient and elevated nutrient treatments. In the peat stream, addition of nutrients was sufficient to alter the system from a net sink for DOM (Fig. 3a) into a net source (Fig. 3c). The much larger DOM increase in the treatment in which both N and P were added, compared to the P-only treatment, suggests that this stream was N-limited at the time of sample collection, although an N-only treatment would be needed to rule out co-limitation. The almost immediate response of DOM in the peat stream to N + P addition suggests that the microbial community was able to rapidly exploit additional nutrients to support biomass growth and produce additional DOM, despite the oligotrophic conditions to which this community is adapted. From the experiments involving addition of N and P, we were able to estimate a 'pseudo Redfield ratio' of the microbial community, based on the amount of

DOC produced relative to the amount of N and P consumed. The molar C:N:P ratios obtained were 144:78:1 for the agricultural stream, whereas the C:P ratio was higher and the N:P ratio lower for the peat stream at 204:11:1. However, if photo-degradation releases inorganic N and P as discussed below, this would lead to an underestimate of total N and P supply, especially in the peat stream where photo-degradation is more important. This could explain the higher C:P and lower N:P found for this water type. The differences between the ratios may also be due to differences in the dominant communities in the peat stream; microbial communities C:N:P ratios in freshwaters are highly variable because these organisms are not homeostatic, and will tend to adapt to the nutrient richness of their environment (Makino and Cotner 2004; Lennon and Pfaff 2005; Scott et al. 2012). Both estimated ratios were similar to ratios reported in the literature, for example by Stutter et al. (2018). They found average C:N ratios of 11.3 for moorland peat-derived water and 3.6 for agricultural water which are similar to our estimates (19 for peat stream water and 2 for grassland stream). They found higher C:P ratios (785 for moorlands water and 167 for agricultural water) than our estimates (204 and 144 for peat and grassland streams, respectively). The two datasets are not entirely comparable, because Stutter et al. (2018) calculated ratios based on bioavailable DOC, and also included estimates of bioavailable DON and DOP, whereas we used total DOC and did not account for NH$_4^+$ or organic N and P. However, the comparison nevertheless highlights consistent differences between stoichiometric ratios of peatland and grassland stream waters.

The evidence from our study that net DOM production occurs under high-nutrient conditions is supported by previous work. Jones et al. (2016), also working in the Conwy catchment, observed a DOC increase of 27% in light-exposed samples collected from a streams draining agricultural grassland, and 11% in mixtures of agricultural and peat stream waters. This experimental evidence of aquatic DOM production, and of accelerated production under high-nutrient conditions, is consistent with field data from standing waterbodies showing net DOC increases occurring predominantly in eutrophic systems (Evans et al. 2017). It is likely that this DOM production derives from cell lysis and exudation. Visual observations of biofilm development in final samples from the grassland stream provide some support to this interpretation. In addition, it has to be noted that several studies found some evidence of in-stream diurnal variation in DOM processing (Austnes et al. 2010; Spencer et al. 2007) with minimum levels observed in late afternoon, which would be consistent with some combination of photodegradation and/or biotic DOM uptake. However, such diurnal patterns may also be attributable to other mechanisms such as evapotranspiration or changes in riparian flow (Schwab et al. 2016).

Unexpectedly, DOC concentrations increased in the Dark treatment in samples collected from the grassland streams. This increase was not significantly different from the corresponding Light treatment, and higher than in the light $+$ HgCl$_2$ treatment, suggesting that DOC increases were biologically- (but apparently not light-) driven. Jones et al. (2016) also observed DOC increases in dark-incubated samples containing agricultural stream water, using the same experimental system. By running deionised water blanks, we were able to exclude the possibility of DOC being leached from a component of the experimental system. If DOC production occurred via heterotrophic processes this would require an organic matter substrate, however particulate organic carbon (POC) concentrations measured in the initial water samples ranged from 0.4 to 2.7 mg L^{-1} (see SI Table S4), and thus appear insufficient to fully explain an observed DOC increase of around 5 mg L^{-1}. POC was measured initially but was not measurable at the end of the experiment because volumes kept as low as possible to minimize the duration of the experiment. We were also unable to identify sufficient concentrations of any other reduced compound to support non-photosynthetic carbon fixation processes, although it has been suggested that these are important contributors to biomass production in some lakes (Santoro et al. 2013) and aquifers (Ben Maamar et al. 2015). We cannot exclude the possibility of a shift between auto and heterotrophy depending on the light or dark exposure, but this seems rather unlikely that different processes would result in such similar changes between dark and light samples for the samples from stream draining grassland. The only remaining explanation for this result would be an issue with the experimental setup, e.g. within the Sunbox or the peristaltic pump tubing, that allowed light ingress to the 'dark' samples sufficient to support photosynthetic activity. Since we cannot completely exclude this possibility, we viewed the finding of DOM accumulation in this treatment with caution. We note, however, that any issue with regard to the dark treatment would not affect results from any of the light treatments.

Interaction between photo-degradation and production

The comparison between the Dark, Light and Light $+$ HgCl$_2$ treatments in the peat stream suggests that photo-degradation of DOM may be associated with some new DOM production. In the absence of DOM production, measured DOC change in the light treatment should theoretically have been equal to the sum of DOC losses in the light $+$ HgCl$_2$ (photodegradation only) and dark (biodegradation only) treatments, and therefore have shown the largest overall DOM loss. Previous studies have suggested that partial photo-oxidation may actually enhance the bio-availability

of residual DOM (Anesio et al. 2005; Cory et al. 2014), in which case DOC loss might actually exceed the sum of separate photodegradation and biodegradation. This was not the case however, as final DOC concentrations were lowest in the light $+$ HgCl$_2$ treatment. One possible explanation is that photo- and bio-degradation were effectively competing for the same DOM (Bittar et al. 2015; Obernosterer and Benner 2004), leading to a lower combined removal rate. However, the strongly contrasting susceptibility of organic compounds to biological versus photochemical breakdown (e.g. Benner and Kaiser 2011, Berggren et al. 2018) together with the very limited biodegradation in the dark treatment in the peat stream suggest that the proportion of DOM susceptible to this 'competition' must be small. An alternative explanation for these findings, supported by experimental evidence of strong sensitivity of DOM production to mineral nutrient additions, is that the photo-mineralisation of DOC to CO$_2$ simultaneously converted organic N and P to inorganic forms (Zepp 2005), and thus enhanced the production of new DOM.

Implications for the in-stream headwater DOM with three end-members

The spatial organization of fluvial networks controls the dynamics of aquatic carbon from upstream to downstream via a combination of heterotrophic, autotrophic and abiotic processes (Battin et al. 2008; Cory et al. 2014). General understanding suggests that oligotrophic headwaters are dominated by heterotrophic organisms able to use terrestrial DOM, whereas autotrophic production of DOM becomes prevalent downstream as light exposure and nutrient levels increase, and water residence times become longer (Raymond et al. 2016; Creed et al. 2015; Evans et al. 2017). The complexity of microbial communities allows them to adapt their metabolic processes to the nature, quantity and stoichiometric ratios of DOM and the nutrients present (Berggren and del Giorgio 2015; Stutter et al. 2018). Observed DOM dynamics at our two study sites appear broadly consistent with the concept of functionally distinct DOM 'end-member' pools within natural waters. Our results suggest the presence of three end members. Two of these derive from the terrestrial ecosystem, and comprise (i) a coloured, aromatic, photo-reactive and bio-recalcitrant pool, and (ii) a more transparent, aliphatic, photo-unreactive and bio-available pool, as has been suggested previously based on experimental and compositional studies (Benner and Kaiser 2011; Berggren et al. 2018; Weishaar et al. 2003). The first end-member appears to derive primarily from organic soils or surface organic horizons. The second end-member is more associated with mineral soils, although it may include other allochthonous sources such as fresh plant or animal material. A third

aquatic DOM component is produced within the aquatic system through algal growth, exudation and cell death. Our results suggest that this production is largely autotrophic, although some heterotrophic production is also possible via bacterial processing of particulate or dissolved organic matter derived from catchment sources. Therefore, human activities such as land use changes or agricultural fertilization are likely to change the way carbon is processed in headwaters (Biddanda 2017). This processing of carbon has direct impacts on the headwater ecosystems via its metabolism, but can also have indirect ecological impacts such as the increase of UV penetration depths when coloured DOM decreases (Gorham 1996).

Our conceptual framework allows inferences to be made about biological activity in the water column, but does not take account of benthic processes. Previous experiments using a similar experimental setup and source waters (Jones et al. 2016) did include biofilms as a treatment. They found that the presence of biofilms did not significantly alter the rate of DOC processing, or fate of a ^{14}C-labelled DOC tracer, in experiments based on water from single sources, but did increase DOM removal to some extent when water from different sources was mixed. Thus, benthic activity is likely to contribute considerably to further in-stream processing of OM, especially following storm events associated with pulses of suspended sediments and POM as emphasized by Aspray et al. (2017) in similar blanket peatland contexts.

We conceptualise these three end-member DOM pools and key transformation processes in Fig. 4. This conceptualisation also forms the basis of recent attempts to model DOM transport and transformation within aquatic systems (Anderson et al. 2019). New insights demonstrated by our results are that: (i) DOM derived from different terrestrial sources has strongly varying susceptibility to photo- and biodegradation; (ii) catchment nutrient exports have the potential to strongly modify DOM quantity and quality in aquatic ecosystems by stimulating autochthonous DOM production; and iii) DOM processing rates in samples collected from headwater streams, under environmentally realistic conditions, are sufficient to modify DOM concentrations on a timescale of hours to days, consistent with previous studies suggesting high reactivity of 'fresh' DOM (Köhler et al. 2002; Moody et al. 2013; Cory et al. 2014; Jones et al. 2016; Catalán et al. 2016; Evans et al. 2017). This production of a more bio-reactive pool is consistent with the observed increase of DOC bio-reactivity through the inland water continuum despite the decrease of its amount (e.g. Soares et al. 2019). Overall, our findings are highly consistent with the 'active pipe' conceptualisation of aquatic C transport (Cole et al. 2007; Tranvik et al. 2009) and suggest that headwater streams may be major, but currently under-represented, hotspots of biogeochemical processing at a landscape scale.
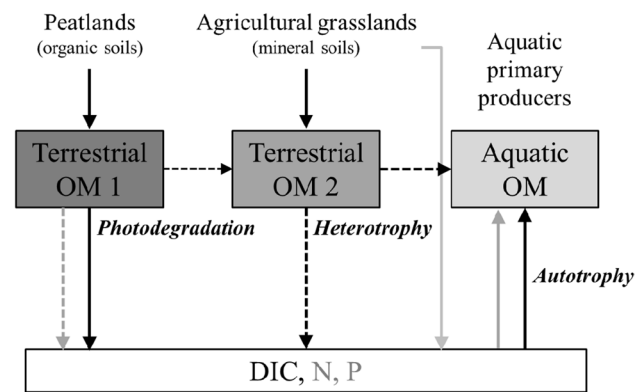

Fig. 4 Conceptual framework of DOM dynamics in headwaters. Three conceptual DOM pools are distinguished based on their sensitivity to photo or biodegradation: "terrestrial OM 1" is highly aromatic, represents largely unmodified material leached from organic soils, "terrestrial OM 2" is less aromatic, exported from mineral soils or produced in the aquatic system via oxidation of terrestrial OM 1; and "aquatic OM" has lowest aromaticity and is generated by in-stream biomass production. Nutrients can be partly released when the terrestrial OM pool is photo-oxidized but mainly originate from agricultural headwater catchments

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