Response to comments for the manuscript bg-2016-296 'Temporal changes in photoreactivity of dissolved organic carbon and implications for aquatic carbon fluxes from peatlands'

Amy E Pickard et al.

February, 2017

We thank the referees for their thorough reading of the manuscript. We address their points and those of the Associate Editor (shown in italics) below.

In addition to making the corrections advised by the two referees and associate editor, we have changed how photoreactivity is quantified in the Loch Katrine samples, where minimal net DOC changes upon irradiation were observed in the sample aliquots. Photoreactivity (mg C / mg DOC) is now expressed as the sum of gaseous photoproduction divided by the pre-irradiation DOC concentration (eq. 1). For example, in the Loch Katrine May 2014 sample:

$$\text{Photoreactivity} = \frac{\left(0.07 \text{ mg CO}_2\text{-C L}^{-1} + 0.02 \text{ mg CO-C L}^{-1}\right)}{5.05 \text{ mg DOC L}^{-1}} = 0.02 \text{ mg C /mg DOC} \quad \text{(eq. 1)}$$

This is in contrast to Black Burn water samples, where the sum of gaseous photoproduction is added to net DOC loss (expressed as a positive value) and divided by the pre-irradiation DOC concentration (eq. 2). For example in the Black Burn May 2014 sample:

$$\text{Photoreactivity} = \frac{\left(1.62 \text{ mg CO}_2\text{-C L}^{-1} + 0.13 \text{ mg CO-C L}^{-1} + 2.02 \text{ mg DOC L}^{-1}\right)}{50.9 \text{ mg DOC L}^{-1}}$$

$$= 0.07 \text{ mg C /mg DOC} \quad \text{(eq. 2)}$$

This method means that no negative photoreactivity values are produced for Loch Katrine (which may have been explained in large part by the limited resolution of the PPM LabTOC instrument at very low DOC concentrations). Photoreactivity data in figure 4b have been adjusted accordingly and text explaining the revised photoreactivity calculations has been added to the data analysis section 2.6 (lines 256-262). The revised method for calculating the photoreactivity of the Loch Katrine samples meant that the mean spring absorbance values shown in Figure 3b are now very similar to those for winter and autumn. Consequently the text referring to the previously apparent difference has been removed from Discussion section 4.1.

Associate Editor comments

> *Your manuscript has been reviewed by two referees. Both referees agreed that the manuscript represents a substantial contribution to scientific progress within the scope of this journal, and that the measurements discussed are novel and provide new insights on the chemical composition and photochemical reactivity of peatland DOM. At the same time, the reviewers recommended a number of improvements. Both referees were concerned about the choice of irradiation source, how relevant this study's findings are to photochemical transformation processes in natural waters and how comparable the results are, in quantitative terms, with those of other studies. The implications of the choice of irradiation source would need to be discussed in detail in the revised manuscript, also in the context of previous studies discussing the dependence of absorption and fluorescence photobleaching on the spectral quality of exposure.*

We thank the editor for their positive comments and for their suggestions to improve the manuscript. In alignment with these comments, we have added significant text to the discussion to highlight that the UV exposure used here allows only for relative differences over time and between our sites to be elucidated (lines 412-420). Furthermore we suggest that the spectral dependence of absorption may

mean that changes in for example the E4:E6 ratio may not be comparable to other studies and that its use in correlation analyses should be interpreted with caution (lines 439-448).

In addition to the discussion changes we have also added a spectral weighting function table to the methods section to compare the weighted exposure used in this study to standard weighting functions (Table 1).

> *In addition, the reviewers recommended to show additional parameters to get more insights on the composition and transformation of DOM in the study region. Additional information, from ancillary measurements or existing literature, on downstream water composition and light attenuation/optical depth could also help address the question raised by the reviewers regarding downstream DOC processing/turnover rates.*

We have added additional parameters that provide insights to DOM transformation to our paper, including changes to absorbance at 350 nm and the spectral slope of absorbance. These have been included in the correlation analyses shown in Table 3. In terms of additional parameters to estimate downstream DOC processing rates, we believe that without significant further data collection obtaining a reasonable estimate is beyond the scope of this study. Instead we have expanded the discussion of the uncertainties in downstream DOC processing and have suggested that future studies should focus attention on potential hotspots for DOC processing (lines 529-558), which include mixing zones of freshwaters with different pH, conductivity and metal concentrations as identified by Palmer et al. (2015) in their study of peatland headwaters.

> *As mentioned by Reviewer #2, filtration through 0.22 um does not completely remove bacteria from the sample. The authors should report in their revised manuscript whether during their experiments they observed any changes (with time) in CDOM or DOC in their "control" samples (0.22 um, not exposed to light). On line 286, the manuscript mentions that: "dark control samples showed a greater drop in absorbance upon irradiation than light exposed samples". More discussion is needed on these results.*

We thank the editor for highlighting this point. We have amended our text to make clear that the absorbance increases occurred in the irradiated samples relative to the initial absorbance values measured prior to the experiment (lines 305-306). Control samples showed no change relative to the initial samples. We have added a section to the discussion which reviews the potential effect of bacterial DOC production in the UV exposed samples in summer and suggest that carbon isotope data may help to resolve such uncertainties (lines 475-482).

Referee 1

> *Dissolved organic matter (DOM) has been sampled from Scottish peatlands, examining both the upper end stream drainage from a peat bog and from a lake as the lower end receiving basin. This material was experimentally exposed to UV radiation in order to understand DOM photoreactivity and address the hypotheses that photoreactivity is seasonally variable, linked to rainfall events and an important loss term of carbon from the peatland system. The report is a good contribution to on going efforts within the aquatic biogeochemistry community to better understand the significance of photoreactions to carbon and mineral flows. This is the first study addressing this topic for Scottish peatlands. The sampling and approaches have merit in regard to characterizing seasonality, response to rain events and comparing the systems. Clear patterns of response are resolved for the high DOM site at Black Burn with the interesting result of highest photoreactivity in early winter. On the other hand, DOM in Loch Katrine is much less photoreactive, and a seasonal pattern was not evident although resolution became an issue at the level of responses observed.*

We thank reviewer 1 for their positive comments. We believe the edits described below will significantly improve the original manuscript. In particular we have added more discussion about the potential influence of the irradiation source upon the measured results.

> *The authors have made an unusual choice as to irradiation source in the experimental exposures with consequences for the environmental relevance of the production rates and their relation to environmental factors. Unlike any other similar study that I am aware of, the authors chose to a primarily UVB (280-315 nm) emitting fluorescent lamp. This lamp has comparable UVB output as solar irradiance at noontime, on a summer solstice, clear day but much lower UVA (315-400 nm) and PAR (400-700 nm). Thus, most studies on this issue use Xe lamp based solar simulator (example stream study – Porcal et al. 2013) or lamps with primarily UVA output (example Lu et al. 2013). Spectral distribution is important because in most aquatic environments in situ, CDOM will absorb much more UVA than UVB. For relatively "fresh DOM" (using brackish tidal marsh CDOM as an example), about 90% of the absorbed irradiance at the surface is UVA and only 5% UVB (rest PAR). Thus the treatment described could substantially underestimate actual rates exhibited by a sample that experienced an equivalent period of full sun (the experimental 8 h exposure to 1.8 W m-2 is about the same as the cumulative incident UVB on a 14 h cloudless day at solstice, ca. 53 vs 49 kJ m-2 respectively). Potentially, some adjustment for comparability to other studies could be made for this by considering the general shape of the apparent quantum yield spectrum for CO and CO2 photoproduction from DOM comparing the lamp spectrum to solar irradiance (cf. the cited Stubbins et al. and Koehler et al. studies) and in addition by expressing results as a rate constant vs a simple change over the incubation period.*

The irradiation source was selected as UVB is the most effective source of radiation in producing photochemical effects (Häder et al., 2007; Zepp et al., 2007), however we agree with the reviewer that this choice makes comparison with both previous studies and natural photochemical responses more difficult. In order to allow clearer comparison with previous studies using UV lamp sources, we have now included in the manuscript the following table of weighted action spectra responses for commonly used spectral weighting functions including CH_4 from pectin (McLeod et al., 2008), plant growth function (Flint and Caldwell, 2003), general plant action spectrum (Green et al., 1974) and DNA damage (Setlow, 1974). We include this in the methods section where details of irradiance regime and output are stated (lines 154-160).

Table 1. Photosynthetically active radiation (PAR) and ultraviolet irradiances during 8 h exposures to Q-Panel 313 fluorescent lamps filtered with 125 µm cellulose diacetate.

Irradiance W m^{-2}							
Total UV (280-400 nm)	UV-A (315-400 nm)	UV-B (280-315 nm)	PAR (400-700 nm)	CH_4 [a]	GEN (G) [b]	PG [c]	DNA [d]
7.52	4.63	2.89	0.92	2.50	1.25	1.05	0.98

[a] CH_4, idealized spectral weighting function for CH_4 production (McLeod et al. 2008)
[b] weighted with a mathematical function of the general plant action spectrum (Green et al. 1974)
[c] weighted with the plant growth (PG) function (Flint & Caldwell 2003)
[d] weighted with the DNA damage action spectrum (Setlow 1974)

We have also added to the discussion a section on the potential influence of the UVB313 lamps on the results of the study and the potential implications the methodology may have for any upscaling attempts (lines 412-420).

> *However, there is a larger issue, which is that, as the authors state, due to the effects of bank shading and short transit time of water within the immediate catchment, light driven instream*

DOC processing is unlikely to be significant for the high DOM Black Burn. Instead, they suggest that the actual processing may occur considerably downstream, in unshaded streams or lentic systems. But the rates there will further depend on the residence time, transparency and optical depth of those systems which are basically unknown for this material. So in the end, I would be very cautious in making any estimate even of an upper bound in the carbon loss rates from these systems given the very substantial methodological bias and involvement of unknown factors. I do agree that given the demonstrated photoreactivity of fresh peatland DOM more work should be done to obtain such an estimate, in particular, if it could somehow be scaled up to a catchment or regional scale.

We agree with the reviewer's comment that there are significant uncertainties in downstream DOC turnover and have adopted more cautious wording in our discussion section 'Implications for photochemical turnover of DOC in aquatic systems'. We have also removed the potential evaded photochemical CO_2 estimate and instead suggest that given the significant volume of DOC produced by the catchment, in-stream photo-processing may be an important term in carbon budgets of peatland draining aquatic systems (lines 529-539).

The choices of irradiation source may also influence the correlation of photoreactivity with other factors, particularly optical characteristics. Several studies have demonstrated that the spectral dependence of absorption and fluorescence photobleaching depends on the spectral distribution of the irradiation source (Del Vecchio and Blough 2002, Tzortziou et al. 2007). UVB-313 fluorescent lamp-based exposure system could produce a distinctly different absorption difference spectrum than natural irradiance (incident or in water), however I do not know of any study that has made the comparison. The results could influence the correlation of photoreactivity and other variables with delta E4:E6, for example.

We thank the reviewer for highlighting this issue. We have added text to Discussion section 4.1 'Peatlands as a source of photochemically labile DOC' which evaluates the possible influence that the irradiation source (UV313 lamps) may have had on the optical characteristics of water samples and suggests that results should be interpreted with caution (lines 439-448). Correlations between delta E4:E6 values and other variables in Table 2 (now Table 3) remain in the manuscript as we assert that because all samples were exposed to the same irradiation conditions, the relative differences in the values can provide interesting information pertaining to factors influencing carbon budget changes.

Finally, the spectral distribution of the irradiance source could influence which chromophores are contributing to the mineralization processes for example, which lignin phenols are involved. I do not know whether this is the case, but it is something that should be kept in mind when relating photoreactions to DOM composition.

We agree that this would be an interesting line of enquiry. However, given the lack of literature on the topic we feel that it would be difficult to discuss the potential influence of spectral distribution of the irradiation source on preferential degradation of phenol groups. In our study lignin phenol analysis was not conducted on irradiated samples and hence we could not support such discussion with any evidence.

I made several minor comments on the mss which I have annotated directly on the pdf. On the figures, it would be helpful in visualizing the irradiance induced changes shown in Fig. 4 if independent scales were used for the Black Burn vs Loch Katrine samples. The point that the L. Katrine photoreactivity is much lower won't be lost if (like in the other figures), the difference in scale is called to the attention of the reader. A more important point, is the relative variation in time (or lack thereof) which is presently difficult to see for the L. Katrine results.

All the minor comments annotated directly on the pdf have been addressed. We have adjusted the y-axis scale in Fig. 4 for plots for the Loch Katrine samples, and noted the difference in scale in the figure caption. We have also adjusted the method for determining photoreactivity in Loch Katrine samples

where net DOC gains were observed upon irradiation, as explained on pp.1 of the author comment above.

Referee 2

> *This study investigates the seasonal and spatial variability in the photoreactivity of DOM from Scottish peatlands. Novel observations are presented on the chemical composition of peatland DOM, the influence of precipitation events on DOM mobilization and the significance of water residence time on DOM photodegradation and export. Peatland systems export high concentrations of photoreactive DOM, and this study demonstrates solar radiation can play an important role in carbon gas fluxes from these systems.*

We thank the reviewer for their positive comments and for their constructive criticism of the manuscript.

> *It is important to use lamps that provide a good simulation of sunlight (spectrum and intensity) when investigating photochemical alterations of natural organic matter in the environment. The UV-B 313 lamp used in this study emits short wavelength UV (below the 295 nm solar cutoff) that is particularly destructive of organic molecules. Therefore, while providing useful information about the relative photoreactivity of DOM among different seasons and locations, the results from this study should not be used to estimate rates of photodegradation in natural waters. In addition, comparisons of the results from this study with those of other studies should be of a qualitative, rather than quantitative, perspective.*

The UV313 lamps were covered with a film of 125 µm cellulose diacetate (CD), as described in the methods section of the original manuscript. However we made a typographical error when stating the transmission properties of the CD film. CD provides a cut-off point at 290 nm, below which no light is transmitted (e.g. McLeod et al., 2008; Fraser et al., 2015). This has now been corrected in the manuscript (lines 144-146 and 416-420) and should assure the reviewer that there are very limited photochemical effects generated as a function of short wavelength UV which is not present in the natural solar spectrum.

In alignment with this comment and similar comments provided by the first reviewer, we have removed the potential evaded photochemical CO_2 estimate and instead suggest that, given the significant volume of DOC produced by the catchment, in-stream processing may be an important term in carbon budgets of peatland draining aquatic systems (lines 529-539).

Comparisons of percentage DOC losses to other photodegradation studies cited in the discussion section 'Peatlands as a source of photochemically labile DOC' have been retained in the text. We believe that the inclusion in the manuscript of figures from other studies will give the reader confidence that although a UV-B irradiation source was used in this study, the magnitude of photochemically induced DOC losses are comparable to previous studies which used a solar simulator to output a natural irradiation spectrum.

> *A couple of additional optical parameters can provide insights about the source, composition and alteration of DOM. The following parameters should be included: spectral slope (S) 275-295 nm, and the absorption coefficient at 350 nm (a350). The S275-295 is an indicator of DOM molecular weight and extent of photochemical alteration, and the a350 has been used as in indicator of lignin phenol concentrations (Helms et al., 2008; Fichot and Benner 2012).*

Thanks for these suggestions. We have incorporated both parameters into Table 2 of the manuscript and have included a method description for the spectral slope calculation (lines 204-207).

Specific comments:

> *Line 48: include Miller and Zepp 1995*

Included (see line 46 and 718-720).

Lines 140-141: Filtration (0.22 um) does not exclude microbial activity, it reduces microbial activity (filtered samples contain some active bacteria)

Sentence corrected to: "…syringe driven pore size MCE filters 0.22 µm (Merck Millipore, UK) to reduce the effect of microbial activity" (lines 137-139).

Line 151 – report the wavelength range of light measured by the PMA2102 broad-band sensor

We have stated that the wavelength range covers both UVA and UVB and that the sensor is erythemally weighted which allows comparison with previous studies through use of spectral weighting functions (lines 148-160).

Lines 160-161 – estimation of the exposure time of DOM to solar irradiation needs to consider mixing processes and extinction coefficients for the solar spectrum

We believe that this information is more relevant in the discussion and have now explicitly alluded to difficulties in estimating DOM exposure due to mixing processes in the Discussion section 4.3 'Implications for photochemical turnover of DOC in aquatic systems' (lines 529-539 and 552-558).

Lines 180-182: provide information about the GC column and chromatographic conditions

We have added further information pertaining to GC analysis, including sample size, needle penetration depth and analytical run length (lines 179-190).

Line 186: concentrations of DIC were not measured

Corrected to "DOC and TC were measured…" (line 191)

Line 189: give the pathlength, not volume, of the quartz (?) cuvette

Pathlength information provided. We used disposable PLASTIBRAND® UV-Cuvettes for our analyses. This information has also been added to the method (line 194).

Line 216: provide information about the column and chromatographic conditions

We have added further information pertaining to the GC column and chromatographic conditions (lines 225-231).

Additional insights about lignin photodegradation can be found in Benner and Kaiser 2011 Biogeochem. and Lu et al. 2016 Frontiers Mar. Sci.

Thanks for these paper recommendations. We have referenced them in the text (lines 492, 504, 522, 595-597, 698-700).

The clarity of Figures 1, 3, 5, 6 and 7 would be improved by the use of different colors for different parameters

We have changed the figures and improved clarity by adopting a consistent colour palette.

Figure 3: present the change in absorbance as a percentage of the controls and only show the wavelengths starting at 250 nm

Adjusted as specified. We have chosen to show data from 250 – 400 nm in the revised figure, as percentage absorbance data became noisy for the Loch Katrine samples in the visible part of the spectrum (>400 nm).

Molar units are preferred for all chemical measurements

After consideration we have decided to retain the original units with concentrations expressed in $mg\,L^{-1}$ or $\mu g\,L^{-1}$, as this format allows comparison of results with both previous studies at the Auchencorth Moss catchment (Dinsmore et al., 2010, 2013) and other relevant research in the field of DOC processing (e.g. Moody et al., 2013; Palmer et al., 2015; Spencer et al., 2009).

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1 **Temporal changes in photoreactivity of dissolved organic carbon and implications for aquatic**

2 **carbon fluxes from peatlands**

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7 **Abstract**

8 Aquatic systems draining peatland catchments receive a high loading of dissolved organic carbon

9 (DOC) from the surrounding terrestrial environment. Whilst photo-processing is known to be an

10 important process in the transformation of aquatic DOC, the drivers of temporal variability in this

11 pathway are less well understood. In this study, 8 h laboratory irradiation experiments were

12 conducted on water samples collected from two contrasting peatland aquatic systems in Scotland; a

13 peatland stream and a reservoir in a catchment with high percentage peat cover. ~~The first system was~~

14 ~~a stream draining the Auchencorth Moss peatland with high DOC concentrations subject to strong~~

15 ~~seasonal and flow driven variability. The second was the low DOC reservoir, Loch Katrine, also~~

16 ~~situated in a catchment with a high percentage peat cover.~~ Samples were collected monthly at both

17 sites from May 2014 to May 2015 and from the stream system during two rainfall events. DOC

18 concentrations, absorbance properties and fluorescence characteristics were measured to investigate

19 characteristics of the photochemically labile fraction of DOC. CO_2 and CO produced by irradiation

20 were also measured to determine gaseous ~~total~~ photoproduction and intrinsic sample photoreactivity.

21 Significant variation was seen in the photoreactivity of DOC between the two systems, with total

22 irradiation induced changes typically two orders of magnitude greater at the high DOC stream site.

23 This is attributed to longer water residence times in the reservoir rendering a higher proportion of the

24 DOC recalcitrant to photo-processing. ~~Over the irradiation period~~During the experimental irradiation,

25 7% of DOC in the stream water samples was photochemically reactive and direct conversion to CO_2

26 accounted for 46% of the measured DOC loss. Rainfall events were identified as important in

27   replenishing photoreactive material in the stream, with lignin phenol data ~~(Ad:Al$_{v,s}$ and P:V)~~

28   indicating mobilisation of fresh DOC derived from woody vegetation in the upper catchment. ~~Using~~

29   ~~DOC-CO$_2$ conversion data from irradiation experiments, we estimate that the contribution of~~

30   ~~Auchencorth Moss catchment to photo-induced aquatic CO$_2$ production is up to 3.48 ± 2.02 kg CO$_2$~~

31   ~~yr^{-1}.~~ ~~We have shown~~ This study shows that peatland catchments produce significant volumes of

32   aromatic DOC and that photoreactivity of this DOC is greatest in ~~the~~ headwater streamss, however an

33   improved understanding of water residence times and DOC input-output along the source to sea

34   aquatic pathway is required to determine the fate of peatland carbon.

35   **Keywords:** Carbon budgets ▪ Rainfall events ▪ Lignin phenols

36   **1. Introduction**

37   DOC is transported from terrestrial environments to aquatic systems where it plays an important role

38   in carbon (C) cycling. Biogeochemical transformations of DOC via microbial and photochemical

39   pathways impact significantly on aquatic C cycles, with up to 55% of C exported as DOC to

40   freshwaters estimated to be lost to the atmosphere as CO_2 (Cole et al., 2007; Tranvik et al., 2009;

41   Cory et al., 2014). These estimates suggest that the C sink strength of the land surface globally has

42   been overestimated, as the role of freshwater systems in the biogeochemical processing of DOC and

43   the subsequent production of greenhouse gases had not been considered. Understanding of the rate of

44   turnover of DOC in aquatic systems remains incomplete and further efforts are required to quantify

45   the extent to which biogeochemical processes in aquatic systems are a source of C to the atmosphere.

46   Photochemical reactions in aquatic systems are induced by the absorption of solar radiation,

47   particularly in the UV region of the spectrum, and preferentially affect aromatic, high molecular

48   weight (HMW) molecules derived from allochthonous sources. Upon radiation, HMW DOC is

49   converted to microbially available low molecular weight (LMW) carbon substrates (Opsahl and

50   Benner, 1998; Sulzberger and Durisch-Kaiser, 2009). Photodegradation of DOC also results in the

51   production of C-based gases, primarily CO_2 and CO (Miller and Zepp, 1995; Stubbins et al., 2011).

52   Whilst it is understood that input of photochemically labile terrigenous DOC can regulate C cycling in

53 aquatic systems (Cory et al., 2014; Koehler et al., 2014), the significance of DOC photodegradation

54 processes in these cycles remains poorly constrained over time and space (Franke et al., 2012; Moody

55 et al., 2013). Due to low temperatures and short residence times limiting autochthonous (in situ) DOC

56 production in headwater systems of northern peatlands, photochemical processing may be a

57 proportionately more important process.

58 A key control on DOC concentrations in headwater systems is rainfall events which flush young, less

59 degraded plant material within the catchment into streams (Evans et al., 2007; Austnes et al., 2010).

60 Rainfall events have been shown to contribute significantly to annual C export from peatland

61 headwater streams (Clark et al., 2007), yet the degree to which they replenish photolabile material

62 within the aquatic environment is less certain. Stormflows in northern catchments have been

63 associated with increased contribution of humic like material (Fellman et al., 2009), suggesting that

64 DOC photoreactivity may also increase during these events. Several studies have explored seasonal

65 variation in intrinsic DOC photoreactivity in northern aquatic systems (Vachon et al., 2016; Franke et

66 al., 2012; Vachon et al., 2016) yet, to our knowledge, the contribution of rainfall events to the

67 seasonal cycle of photolabile material has not been previously investigated.

68 Further uncertainty remains in understanding the variation in DOC photolability at different positions

69 within a watershed (Franke et al., 2012). The increasing residence time of downstream aquatic

70 systems, as headwater streams drain into rivers, lacustrine and marine environments, may mean that

71 photo-processing becomes a more important control on overall C budgets with distance downstream.

72 Conversely, the extent to which the material has already been degraded in the upstream aquatic

73 environment may mean that further processing is limited (Catalán et al., 2016; Vähätalo and Wetzel,

74 2008; Catalán et al., 2016). Investigating the susceptibility of DOC to photo-processing in different

75 types of aquatic environments will allow the overall contribution of photochemical processes to C

76 cycling to be understood on a catchment scale.

77 The primary aim of this study was to assess temporal variation in the photochemical lability of DOC

78 from two contrasting aquatic systems draining peatlands and to understand how this variation may

79   impact aquatic C budgets. Controlled UV irradiation experiments were conducted on water samples

80   collected from the two contrasting aquatic systems, one a stream and the other a reservoir. Water from

81   both systems was sampled on a monthly basis over a 1-year period and also from the high DOC

82   stream system during two rainfall events to characterise short term variability in DOC concentration

83   and composition. After experimental exposure, optical, spectroscopic and biogeochemical analyses of

84   the water samples were conducted to explore DOC photoreactivity and the resultant production of C

85   based gases. The results were used to test the following hypotheses:

86   H1: Both aquatic systems will exhibit seasonality with regards to the supply of photochemically labile

87   DOC, with highest photolability detected in the winter due to limited processing in the aquatic

88   environment.

89   H2: Photochemical degradation of DOC will be a more significant loss term of C in the high DOC

90   aquatic system.

91   H3: Rainfall events in the high DOC system will replenish the supply of photolabile material.

92   **2. Methods**

93   **2.1 Study sites**

94   Water samples for the irradiation experiments were collected from two aquatic systems located in

95   peatland catchments. The Black Burn (55°47'34″ N; 3°14'35″ W; 254 m a.s.l.) is a small headwater

96   stream draining Auchencorth Moss, an ombrotrophic peatland located in central Scotland covering

97   3.35 km^2 (Billett et al., 2010). The stream is fed by a number of small tributaries from the surrounding

98   peatland, part of which is used for peat extraction. Low density sheep grazing is the primary land use

99   within the catchment and vegetation comprises a *Sphagnum* base layer and hummocks of

100   *Deschampsia flexuosa* and *Eriophorum vaginatum*, or *Juncus effusus*. In the upper catchment shrubs

101   are present, including *Calluna vulgaris*, *Erica tetralix* and *Vaccinium myrtillus* (Dinsmore et al., 2010;

102   Drewer et al., 2010).

4

103 The Black Burn stream hydrographic record is characterised by a steady base flow and rapid ('flashy')

104 response to rainfall events which typically produce high flow accompanied by elevated DOC

105 concentrations. Annual mean stream water DOC concentrations determined by weekly sampling over

106 a 2-year period were high, at 28.4 ± 1.07 mg L^{-1} (Dinsmore et al., 2013), with a marked seasonal

107 pattern, characterised by low DOC in winter and high concentrations in summer. In this study, water

108 samples were collected from an established sampling site where DOC concentrations have been

109 recorded for >9 years as part of the Centre for Ecology & Hydrology (CEH) Carbon Catchments

110 project (https://www.ceh.ac.uk/our-science/projects/ceh-carbon-catchments).

111 The other sampling site was Loch Katrine (56°25'25″ N; 4°45'48″ W; 118 m a.s.l.) in the Loch

112 Lomond and Trossachs National Park, Scotland. Loch Katrine has a surface area of 8.9 km^2 and is fed

113 by >~808 tributaries which predominantly drain a catchment of upland blanket bog. (SNH, 2005).

114 Loch water DOC concentrations have been recorded by the Scottish Environment Protection Agency

115 (SEPA) at Ruinn Dubh Aird, a peninsula located at the south eastern end of the loch, which was also

116 selected as the sampling point for this study. DOC concentrations measured approximately six times a

117 year from 2009−2014 were low at 3.68 ± 0.56 mg L^{-1} (SEPA, personal communication).

118 **2.2 Sample collection**

119 Water was sampled monthly from both sites from May 2014 to May 2015 inclusive (13 samples over

120 the study duration) to characterise seasonal variation in DOC concentration and composition. Samples

121 were collected at 20 cm below the surface of the water in a screw top sterile clear glass bottle. Upon

122 return to the laboratory, samples were stored in the dark at 4°C and exposed to experimental

123 conditions within a week of collection. Additional water sampling to characterise the effect of rainfall

124 events focused on the Black Burn head water system. Intensive stream water sampling was conducted

125 during two rainfall events, one in winter (defined as 1 October to 31 March) and the other during the

126 summer (1 April to 30 September) (Gordon et al., 2004). An automatic water sampler (Teledyne Isco,

127 USA) was programmed to collect a composite 1 L sample of water from the Black Burn into separate

128 polypropylene bottles every 60 minutesmin (comprising two 500 mL samples collected each 30

129 minutesmin) throughout the rainfall events. Stream water sampling in the winter rainfall event was

130 conducted from 11:00 on 9 December to 17:00 GMT on 10 December 2014, resulting in 31 samples

131 across the event. Stream water sampling in the summer rainfall event started at 14:30 on 1 September

132 and finished at 06:30 GMT on 2 September 2015, resulting in 17 samples. Water samples were

133 transferred into glass bottles from the automatic water sampler for transport to the laboratory and

134 irradiated within 5 days of collection.

135 Throughout the year of sampling, the Black Burn water depth was measured at 15 minute intervals

136 approximately 2 km downstream from the sampling site using a Level Troll pressure transducer (In

137 Situ Inc., USA) with atmospheric correction from a BaroTroll sensor (In situ Inc., USA) located

138 above the water surface. Water depth readings from the pressure transducer were converted to

139 discharge at the sampling site using rating curves ($R^2 > 0.90$) based on flows measured by dilution

140 gauging (Dinsmore et al., 2013). Equivalent hydrological data were not available for Loch Katrine.

141 **2.3 Sample preparation**

142 Prior to experiments, water samples were degassed under a vacuum pressure system for 20

143 minutesmin to remove dissolved gas from the water and then filtered using syringe driven pore size

144 filters 0.22 μm MCE filters (Merck Millipore, UK) to reduce the effect of microbial activity. 15 mL of

145 filtered sample was immediately transferred into 21 mL quartz vials (Robson Scientific, UK) which

146 were sealed with aluminium crimp tops and rubber butyl plugs (Speck and BurkeChromacoal, UK).

147 All samples were prepared at room temperature in oxygenated conditions.

148 **2.4 Irradiation experiments**

149 Experiments providing both UV-A and UV-B irradiation were conducted using UV313 lamps (Q-

150 Panel Company, USA) covered with 125 μm cellulose diacetate (A. Warne, UK) to exclude UV-C

151 (<280 nm) and short wavelength UV-B (<290 nm).Irradiation experiments were conducted using UV-

152 B 313 lamps (Q-Panel Company, USA) covered with 125 μm cellulose diacetate (A. Warne, UK) to

153 exclude UV-C (<280 nm) and short wavelength UV-B (<2980 nm), and providing both UV-A (400-

154 315 nm) and UV-B (315-2980 nm) exposure. Lamps were mounted inside quartz tubing (Robson

155 Scientific, UK) beneath the water surface in a water bath maintained at 16°C and vials were irradiated

156 sideways while submerged. UV irradiance of the samples was modulated to remain constant

157 throughout the 8-h exposure by measurement with an erythemally weighted UV-B broad-band sensor

158 with a dimmer (Model PMA2102; Solar Light Inc., USA). The sensor was held beneath the water

159 surface behind a quartz window of the same thickness as the vials. The UV exposure~~sensor~~ was

160 calibrated with a double monochromator scanning spectroradiometer (Irradian™, UK), itself

161 calibrated against a ~~secondary deuterium lamp~~ quartz halogen standard (FEL Lamp, F-1297) operated

162 by the NERC Field Spectroscopy Facility, Edinburgh (http://fsf.nerc.ac.uk/). Total unweighted

163 irradiance was 2.89 ~~1.81~~ W m^{-2} in the UV-B, 4.63 W m^{-2} in the UV-A, and photosynthetically active

164 radiation (PAR) was 0.92 W m^{-2} (Table 1; Supplementary Information Figure S1). These conditions

165 reflect twice the ~~a~~ UV-B irradiance that could be expected over a~~over two~~ cloudless summer day~~s~~ in

166 the UK and a significant underestimation of summer time daily ambient UV-A and PAR radiation.

167 Weighting functions derived for a range of photochemical processes were applied to the spectral

168 output (Table 1) and were determined to be within the range of global irradiance values~~within~~

169 ~~globally realistic values (Table 1).~~ The time duration of the experiment (8 h) was selected to

170 represent a conservative estimate of the exposure time of surface water during transit through a

171 headwater peatland catchment to a marine outlet. Water temperatures of ~16°C were measured in both

172 field sites in May 2014 prior to commencement of the year-long sampling programme and was

173 employed in the experiments to represent summer time conditions. Controls comprising quartz vials

174 containing water samples and wrapped in aluminium foil to exclude radiation were kept in the water

175 bath for the experiment duration, with four replicates of each of the UV-exposed and control samples.

176 To select water samples from the Black Burn for irradiation experiments, POC concentrations, A~~a~~$_{254}$

177 values and E4:E6 ratios were measured within 24 h in all samples (using the methods described

178 below) and, from these results, eight stream water samples were selected from each rainfall event

179 which represented the minimum, maximum and median values of these parameters (Supplementary

180 Information Table S1).

181 **2.5 Analytical methods**

182 On each monthly sampling occasion the water dissolved oxygen (DO), conductivity, pH and

183 temperature were measured on site with a handheld Hach HQd multimeter (Hach, USA). Measured

184 volumes of water samples were filtered within 24 h of collection through pre-ashed (8 h at 450°C),

185 pre-weighed Whatman GF/F (0.7 μm pore size) filter papers. POC was determined using loss-on-

186 ignition, following the method of Ball (1964).

187 Following irradiation, partitioning of dissolved C gases from the liquid into the vial headspace was

188 encouraged through use of a wrist action shaker for 30 ~~seconds~~. An Agilent gas chromatography (GC)

189 system (Hewlett Packard 6890; Agilent Technologies, USA) equipped with an autosampler (HTA,

190 Italy) and a flame ionisation detector (FID) held at 250°C was used to analyse samples for headspace

191 CO_2, CO and CH_4 ~~CH_4~~ concentration within 8 h of irradiation. Needle penetration depth was set to a

192 standard depth and 1.5 mL of headspace sample was automatically injected i~~o~~nto the sample loop.

193 Analytical runs lasted for 10.5 min~~s~~ and the column carrier gas was N_2 at a constant flow rate of 45

194 mL min^{-1}. CO_2 and CO measurements were made possible by a methaniser fitted between the column

195 and FID. ~~One~~A standard 7-gas mixture (BOC Special Gases, UK) was used for daily detector

196 calibration prior to sample analysis (detection limits: CO_2 78 ppm; CO 1.6 ppm; CH_4 0.8 ppm).

197 Dilutions of 50 and 75% were made from this standard using Zero Grade N_2 to produce a 3-point

198 calibration ~~series~~ for each gas. Post-run peak analysis and integration were performed using Clarity

199 software (DataApex, Czech Republic).

200 DOC and total carbon (TC) concentrations were measured using a PPM LABTOC Analyser

201 (Pollution and Process Monitoring Ltd., UK) in UV treatment and control samples after exposure.

202 Dissolved inorganic carbon (DIC) was calculated as the difference between ~~total carbon (~~TC~~)~~ and

203 DOC. UV-visible absorbance of UV treatment and control samples contained in 3.5 mL

204 PLASTIBRAND® UV-Cuvettes with a path length of 10 mm was measured at room temperature

205 between 200 and 800 nm at increments of 1 nm using a Jenway spectrophotometer (Model 7315;

206 Bibby Scientific, UK). Deionised water controls were used between each sample. Absorption

207 coefficients a_λ were calculated as:

208
$$a_\lambda = 2.303 \, x \left(\frac{A\lambda}{L}\right) \tag{1}$$

209 where A is the absorbance at each wavelength and L is the path length (m) of the cuvette (Green and

210 Blough, 1994). Specific UV absorbance (SUVA$_{254}$) values, a measure of DOC aromaticity, were

211 determined by dividing the UV absorbance measured at $\lambda = 254$ nm by the DOC concentration

212 (Weishaar et al., 2003). E4:E6 ratios were estimated using the absorbance values at 465 and 665 nm,

213 respectively (Peacock et al., 2014). Spectral slope (S) was calculated using a nonlinear fit of an

214 exponential function to the absorption spectrum in the ranges of 275–295 and 350–400 nm, where S is

215 the slope fitting parameter. The spectral slope ratio (S$_R$) was calculated as the ratio of S-275––295 to

216 S350––400 (Helms et al., 2008; Spencer et al., 2009).

217 Fluorescence intensity in water samples filtered to 0.2 µm was measured using a FluroMax-4

218 spectrofluorometer (Horiba Jobin Yvon Ltd., Japan). The instrument was programmed to scan across

219 excitation wavelengths 200-400 nm (5 nm increments) and emission wavelengths 250-500 nm (2 nm

220 increments) with a 1 cnm path interval. Data were obtained at room temperature and were blank

221 corrected using deionised water. Intensity ratios derived using these data allow discrimination

222 between different sources of DOC. Here, the fluorescence index (FI), f_{450}/f_{500}, the ratio of fluorescence

223 intensity at the emission wavelength 450 nm to that at 500 nm at excitation wavelength 370 nm, was

224 calculated to help identify dissolved organic matter (DOM) source material. Values around 1.8

225 suggest autochthonous organic material, whereas values around 1.2 indicate terrestrially derived

226 material (Cory and McKnight, 2005).

227 Lignin phenol concentrations in unirradiated Black Burn water samples were measured using the CuO

228 oxidation method (Benner et al., 2005; Spencer et al., 2008). After filtration to 0.2 µm, 45 mL of

229 water sample was freeze dried to produce lyophilised DOM which was transferred to stainless steel

230 pressure bombs with 1 g of CuO and 100 mg of $Fe(NH_4)_2(SO_4)_2H_2O$ $Fe(NH_4)_2(SO_4)_2H_2O$. Under

231 anaerobic conditions, 8 mL of NaOH was added to the bombs before they were sealed. Samples were

232 then oxidised at 155°C for 3 h. Following oxidation, samples were acidified to pH 1 with H_2SO_4,

233 H_2SO_4, extracted with ethyl acetate three times, and then passed through Na_2SO_4 Na_2SO_4 drying

columns. Samples were dried using a flow of N_2 and kept frozen prior to GC analysis. After

redissolution in ~200 μL pyridine, lignin phenols were derivatised with bis-trimethylsilyltri-

fluoromethylacetamide (BSTFA) at 60ºC for 30 ~~minutes~~min and quantified on a GC (Agilent 5890

MkII with twin FID). Specifically, a twin-column split-injection method was used with Agilent DB1

and DB1701~~1~~ (both 30 m x 0.25 mm diameter x 0.25 μm film thickness) flow being split in the

injection liner with a twin-hole ferrule. Column flow was 1 mL/ min~~ute~~$^{-1}$ with a split ratio of 20:1.

The chromatographic conditions were 100ºC ~~at T=0~~held for 1.25 min~~utes~~, followed by a heating rate

of 4ºC/ min^{-1} until 270ºC, then ~~holding~~held for 15 min~~utes~~.

Eleven lignin phenols were measured, including three p-hydroxybenzene phenols (P): p-

hydroxybenzaldehyde, p hydroxyacetophenone, p-hydroxybenzoic acid; three vanillyl phenols (V):

vanillin, acetovanillone, vanillic acid; three syringyl phenols (S): syringaldehyde, acetosyringone,

syringic acid; and two cinnamyl phenols (C): p-coumaric acid and ferulic acid. Blank controls, taken

through the method from CuO oxidation onwards, were quantified and subtracted from sample

concentrations. Quantification was achieved through use of cinnamic acid as an internal standard. In

addition to total concentration of lignin phenols (Σ_{11}) and carbon normalised yields (Λ_{11}), the ratio of

syringyl to vanillyl phenols (S/V), the ratio of cinnamyl to vanillyl (C/V) phenols, the ratio of p-

hydroxybenzenes to vanillyl phenols (P/V) and the ratio of acids to aldehydes ($Ad/Al_{v,s}$) were

calculated to aid interpretation of the data. Lignin phenols for Loch Katrine samples were not

measured due to insufficient production of lyophilised material using the stated method.

2.6 Data analysis

Data collected in the irradiation experiments were tested for normality using the Shapiro-Wilks test

and were found to be normally distributed. Unpaired t-tests were conducted between irradiated and

unirradiated samples to assess differences in spectral properties, DOC and DIC concentrations, lignin

phenol concentration and gaseous production. Pearson correlation coefficients were used to test the

potential role of DOC composition and site conditions in regulating photochemical lability, measured

as total DOC loss, production of DIC and C gases (CO and CO_2) and change to a_{254} and E4:E6 ratios.

10

260 Carbon species DOC, ~~DIC,~~ CO_2 and CO measured each month at the Black Burn and Loch Katrine

261 were included in C mass budgets calculated for irradiated and unirradiated samples. By converting all

262 data to mg L^{-1}, the difference in C budget between treatment and control samples could be determined

263 (see Supplementary Information Table S2 for example calculations). To obtain a standard error value

264 for differences between irradiated and control samples, the mean control value was determined and

265 subtracted from each of the irradiated replicates.

266 Photoreactivity (mg C / mg DOC) was determined as total change to C species (DOC, CO_2 and CO)

267 upon irradiation normalised for initial DOC concentration. For the Loch Katrine samples, where

268 minimal net DOC changes upon irradiation were observed in the sample aliquots, photoreactivity (mg

269 C / mg DOC) is expressed as the sum of gaseous photoproduction (CO_2 and CO only) divided by the

270 initial DOC concentration. This is to avoid production of negative photoreactivity values for Loch

271 Katrine which may have been explained in large part by the limited resolution of the PPM LabTOC

272 instrument at very low DOC concentrations.

273 Correlation coefficients were ~~also~~ calculated between intrinsic sample photoreactivity ~~y, measured as~~

274 ~~total change to C species upon irradiation normalised for initial DOC concentration,~~ and lignin phenol

275 data. The Durbin-Watson statistic was used to test for the presence of autocorrelation in residuals of

276 lignin phenol analyses of stream water samples collected during rainfall events and showed no

277 correlation between the samples. Minitab v.16 (Minitab Inc., USA) was used for all statistical

278 analyses.

3. Results

3.1 Climate and water chemistry conditions at time of sampling

281 Total rainfall measured at the European Monitoring and Evaluation Programme (EMEP) supersite at

282 Auchencorth Moss (Torseth et al., 2012) for the 13 month sampling period was 1015 mm. It varied

283 from lowest monthly values in September and April to the highest in October (Figure 1a). The mean

284 air temperature of the study period was 7.7°C, similar to the 8 year average of 7.6°C, and reached a

285 maximum of 27.6°C in July 2014 and a minimum of -7.9°C in January 2015.

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286   At Comer meteorological station, located 10 km from the Loch Katrine sampling site, rainfall was

287   considerably higher, totalling 2368 mm over the sampling period (Figure 1b) (Met Office, 2012).

288   Seasonal variation in rainfall was clear, with >40 % of rainfall falling from December to February.

289   Air temperatures were higher than at the Black Burn, with a mean of 10.2°C.

290   Water chemistry differed considerably between the two aquatic systems over the year-long sampling

291   (Table 2$\underline{2}$1). The water temperatures reflected the difference in air temperature between the sites, with

292   higher mean values at Loch Katrine than at the Black Burn. Mean pH at the Black Burn was 5.4,

293   compared to 6.7 at Loch Katrine. Conductivity was more variable at the Black Burn and was on

294   average 53 μS cm^{-1} higher than at Loch Katrine, although values at both sites were low. POC

295   concentrations at the Black Burn were over double those at Loch Katrine. FI values were slightly

296   higher at the Black Burn, but at both sites were low and stable, indicative of terrestrially derived DOC

297   material (Cory and McKnight, 2005)

298   DOC concentrations at the Black Burn ranged from 14.2 to 50.9 mg L^{-1} (Figure 2) and showed a

299   similar seasonal pattern as described in Dinsmore et al. (2013). Concentrations were lowest in late

300   winter and highest in autumn; the latter consistent with increased organic matter inputs to the stream

301   from flushing of soils during autumn rainfall events.

302   At Loch Katrine, DOC concentrations were low and consistent, ranging from 3.1θ to 5.8$\underline{2}$ mg L^{-1}.

303   Concentrations were lowest in spring and highest in summer. SUVA$_{254}$ values at the Black Burn were

304   higher than at Loch Katrine, suggesting that the DOC pool was comprised of a greater percentage of

305   aromatic material (Weishaar et al., 2003). The E4:E6 ratio at the Black Burn varied considerably over

306   the sampling period, ranging from 1.0 to 10.2. At Loch Katrine, the E4:E6 ratios were lower and less

307   variable, but are a less meaningful parameter in the low DOC concentration Loch Katrine samples due

308   to minimal absorbance in wavelengths greater than 400 nm.

309   **3.2 Optical changes in water samples upon irradiation**

310   Absorbance coefficients typically decreased upon irradiation of water samples relative to dark

311   controls, with the strongest decrease occurring in the UV part of the spectrum at ~225 nm, and a

312 smaller inflection at ~300 nm (Figure 3). PThe maximum change in ercentage loss of absorbance

313 upon irradiation was 5% a factor of 4 higher greater in water samples from the Black Burn than

314 fromcompared to Loch Katrine samples when averaged across wavelengths 250-400 nm. In the Black

315 Burn, decreases in absorbance were greater in the summer and autumnst in the summer, whereas at

316 Loch Katrine the decreases in absorbance were greater in the winter and spring.

317 Positive valuesPercentage values consistently >100% (where dark controlUV exposed samples

318 showed an increase in greater drop in absorbance upon irradiation than relative to dark controllight

319 exposed samples) were recorded for summer water samples from Loch Katrine. E4:E6 ratios

320 decreased by a mean of 1.52 in irradiated Black Burn water samples, indicating accumulation of

321 increasingly humic material in the remaining DOC pool during light UV exposure. At Loch Katrine,

322 E4:E6 ratios decreased by a mean of 0.21 upon irradiation.

323 **3.3 Carbon budget changes upon irradiation**

324 Typically, DOC concentrations in Black Burn water samples decreased after light exposure compared

325 to unirradiated controls (Figure 4a). Mean change in DOC in irradiated samples from the Black Burn

326 for the whole sampling period was -2.14 mg C L^{-1} (ranging from 0.06 to -4.35 mg C L^{-1} for individual

327 months). DOC decreased after irradiation in all Black Burn samples with the exception of September

328 2014, indicating a photolabile DOC pool for most of the year. In contrast, in water samples from Loch

329 Katrine irradiation induced DOC losses occurred in 56 of 13 samples and small gains were observed

330 in 87 of 13 samples (Figure 4b). Whilst these results should be interpreted with caution as small

331 differences in DOC concentrations (<0.5 mg C L^{-1}) are below the instrument detection limit, they

332 suggest that the DOC pool in Loch Katrine was largely recalcitrant to photochemical degradation.

333 Irradiation resulted in notable photoproduction of DIC, CO_2 and CO from Black Burn samples. DIC

334 concentration increased by a mean of 0.77 mg C L^{-1} for the whole sampling period, although

335 production across the samples was highly variable between months. CO_2 was the most abundant

336 photoproduct and was produced at a mean rate of 1.2 mg C L^{-1} across all monthly samples. At Loch

337 Katrine, CO_2 production was two orders of magnitude lower than in the Black Burn, produced at a

338 mean rate of 0.06 mg C L^{-1}. In all monthly water samples from both sites CO concentrations increased

339 in the irradiation experiments, with mean production rates of 0.07 and 0.01 mg C L^{-1} observed for

340 Black Burn and Loch Katrine samples, respectively.

341 Carbon mass budgets for DOC loss and photoproduct accumulation (DIC, CO_2 and CO) in water

342 samples were calculated for all the irradiation experiments. Budgets for all monthly water samples

343 from the Black Burn were balanced to within ± 5.1% of the total measured C concentration. For Loch

344 Katrine water samples, budgets were balanced to within ± 11%. The lower accuracy of budget closure

345 in the Loch Katrine samples is likely due to lower overall C concentrations, which are more

346 susceptible to measurement error. CH_4 was detected in all samples at very low levels, with mean

347 concentrations of 0.63 and 0.57 $\mu g \ L^{-1}$ detected at the Black Burn and Loch Katrine, respectively, and

348 thus were not included in the mass calculations.

349 Intrinsic photoreactivity of C in the Black Burn ranged from 0.02 to 0.15 mg C/mg DOC L^{-1} and was

350 highest in August (Figure 4a). Photoreactivity peaked again in November and remained elevated until

351 January. Lowest sample photoreactivity was detected in September. At Loch Katrine, mean C

352 photoreactivity was 0.017~~04~~ mg C/mg DOC L^{-1}, with a maximum of 0.025~~9~~ mg C/mg DOC L^{-1}

353 detected in ~~July~~November.

3.4 Factors influencing carbon budget changes

355 Factors influencing irradiation induced changes to C species and spectral properties in Black Burn

356 water samples were investigated using Pearson correlations (Table 3~~2~~). Loss of DOC, absorbance at

357 254 nm and production of both CO_2 and CO were significantly positively correlated with initial DOC

358 concentration. Initial E4:E6 ratios had positive coefficient values with all light induced changes to the

359 DOM pool, whilst FI values were all negative, although most of these correlations were not

360 significant.

361 Of the meteorological and discharge variables investigated, air temperature and PAR were

362 significantly negatively correlated with changes to E4:E6 ratios. Total monthly rainfall had positive

363 coefficient values with irradiation induced changes to the DOM pool. Correlations between C species

364 changes and discharge were less consistent, although mean monthly discharge was significantly

365 positively correlated with changes to E4:E6 ratios.

15

3.5 Effect of rainfall events on carbon photo-processing in Black Burn water samples

The Black Burn was sampled hourly during a winter rainfall event, with collection commencing 6 h before peak rainfall (Figure 5a). Total rainfall during the event, which we define here as the water sampling period, was 19.6 mm, with an hourly maximum of 3.3 mm and rainfall recorded in 22 of the 31 sampling hours. Stream discharge peaked at 391 L s^{-1} although a separate smaller peak of 266 L s^{-1} also occurred during the sampling period.

During the event, an initial dilution of stream DOC concentrations was followed by recovery to pre-event levels (Figure 5a). DOC was most photoreactive at 06:00, with DOC concentration reduced after irradiation by 6.72 mg L^{-1}. DOC loss in this sample was greater than at any time through the year-long study (Figure 4a), even though the DOC concentration (44.4 mg L^{-1}) was within the range of measured monthly concentrations. The greatest irradiation induced increase in CO_2 concentration (2.25 mg L^{-1}) occurred in the first event sample at 11:00, collected prior to rainfall input. Photoreactivity was lowest at 12:00, and was similarly low in the sample collected at 17:00, which coincided with peak rainfall.

In the late summer rainfall event occurring at the end of an extended period of base flow in the Black Burn (Supplementary Information Figure S2), 3.2 mm of rainfall was recorded with a maximum hourly total of 2.2 mm. Samples were collected from 14:30 to 06:30, with rainfall only occurring between 16:30 and 18:30. Discharge remained low and relatively stable throughout the event, with a mean flow of 6.14 L s^{-1}. Rainfall marginally diluted the stream DOC concentrations (Figure 5b). Photo-induced changes were much smaller than in the winter event and maximum DOC losses were a factor of 2.5 lower than the mean DOC reduction observed in the Black Burn monthly water sample experiments (Figure 4a). Photoreactivity was lowest in the initial sample collected at 14:30 prior to rainfall and coinciding with the highest discharge during the sampling period. Photoreactivity was highest in the 19:30 sample collected 3 h after peak rainfall.

16

3.6 Lignin phenol composition of Black Burn water samples

390 **3.6 Lignin phenol composition of Black Burn water samples**

391 To understand the effect of DOM composition on photolability, lignin phenols were measured in all

392 the Black Burn monthly and rainfall events water samples prior to the irradiation experiments.

393 Dissolved lignin concentrations ranged from 15.3 to 108 µg L^{-1} (mean = 52.8; n = 28) and were

394 significantly positively correlated with sample DOC concentration (Pearson = 0.831; $p < 0.01$)

395 (Supplementary Information Figure S3). Carbon normalised yields were between 0.71 and 2.66 mg

396 (100 mg OC)$^{-1}$. The contribution of individual phenol groups to the lignin signature varied between

397 monthly samples of the year-long study and the rainfall events (Figure 6). In the monthly samples, the

398 P phenols were most abundant, followed by V phenols (Figure 6a). Samples in the winter rainfall

399 event contained higher and more variable mean yields for each phenol group, with S phenols most

400 abundant, followed by V phenols and P phenols.

401 Overall yields were significantly lower (1-way ANOVA, $p < 0.01$) during the summer rainfall event.

402 As in the year-long samples, P phenols were the most abundant, followed by S phenols and V

403 phenols. Across all three sampling regimes, the contribution of C phenols to the overall lignin

404 signature was smallest.

405 P:V ratios, an indication of *Sphagnum* derived DOC (see section 4.2), ranged from 0.83 to 1.69 across

406 all samples, indicating significant temporal variability in DOM source material. Photoreactivity was

407 significantly negatively correlated with P:V ratios when all samples were combined in a correlation

408 analysis (-0.523; $p < 0.01$) (Figure 7a). This suggests that the relative abundance of P versus V

409 phenols contributed considerably to sample photoreactivity. The lowest P:V ratios were in winter

410 rainfall event samples, where photoreactivity was highest.

411 Ad:Al$_{v,s}$ ratios, which are an indicator of sample degradation, ranged from 0.58 to 1.26, towards the

412 lower end of reported values in the literature (Winterfeld et al., 2015). Photoreactivity was also

413 significantly negatively correlated with Ad:Al ratios (-0.492; $p < 0.01$) (Figure 7b) and again lower

414 ratios typically occurred in winter rainfall event samples.

17

4. Discussion

4.1 Peatlands as a source of photochemically labile DOC

Photo-processing resulted in considerable DOC loss from water samples from the Black Burn. Mean DOC loss in the 8-h irradiation experiments conducted on the monthly water samples was 7~~6~~% relative to initial concentrations. Percentage DOC losses determined here are similar to those reported from irradiation experiments conducted over similar timescales using stream water draining a boreal watershed (3–10 % DOC loss over 10 h; Franke et al., 2012 and 11% TOC loss over 19 h; Köhler et al., 2002). ~~It should be noted that percentage loss rates reported in this study are not directly comparable to these~~~~the reported other studies due to the use of UV-B 313 lamps. These lamps emit short wavelength UV~~~~, that is particularly destructive of organic molecules so possible that the magnitude of photo-processing may have been over-estimated?~~~~. Use of a cellulose diacetate filter ensured that no wavelengths below 290 nm were emitted, however the lamp output is not comparable to a solar spectrum.~~

However, photochemical processes are dependent on the spectral composition of irradiation sources and direct comparison of percentage loss rates in this study with those of other experimental studies using different lamp types or ambient sunlight is not possible.

 The irradiation source used in this study was selected as UV is the most effective source of radiation in producing photochemical effects (Häder et al., 2007; Zepp et al., 2007). The UV313 lamps ~~used in this study~~ provided both UVB and UVA exposures (2.89 and 4.63 W m^{-2} respectively) which w~~ere~~as an appropriate UVB exposure but a lower proportion of UVA and visible wavelengths than ambient sunlight. Cellulose diacetate filters ~~were used in this study to~~ removed wavelengths <290 nm (which are absent in sunlight.)but lamp outputs used in the irradiation experiments are not directly comparable to the solar spectrum. Consequently, the magnitude of photo-processing determined in this study allows relative comparison of temporal changes and ~~and~~ between our sites but do not provide an accurate value of ambient photo-processing.

441   Photochemical transformations were low in the Loch Katrine samples, with minimal losses to the

442   DOC pool (-0.4303%; mean from year-long study). Whilst our sites were not located within the same

443   watershed, it seems likely that position within the catchment plays a role in determining the

444   photolability of DOC. The Black Burn headwater stream at Auchencorth Moss receives fresh inputs

445   of DOC from the surrounding peatland catchment and material has less time for light solar irradiation

446   exposure in the water column relative to the DOC in the reservoir system. DOC losses may occur in

447   Loch Katrine soon after water entry into the loch but, due to long water residence times, DOC may

448   have become recalcitrant to photo-processing by the time of sample collection. Catalán et al. (2016)

449   observed a negative relationship between organic carbon decay and water retention time, resulting in

450   decreased organic carbon reactivity along the continuum of inland waters. $SUVA_{254}$ data suggest that

451   DOC in Loch Katrine samples was less aromatic than in the Black Burn (Table 21), with values

452   indicating an approximate humic content of 30% based on the findings of Weishaar et al. (2003). As

453   humic molecules are more labile to photo-processing, irradiation had a greater effect on the stream

454   samples relative to the reservoir samples.

455   Strong seasonal fluctuations in DOC concentration and composition occurred in the Black Burn, in

456   agreement with patterns observed in the same system by Dinsmore et al. (2013). DOC concentrations

457   were highest in the late autumn, consistent with a flushing effect whereby soil organic material

458   produced over the summer is mobilised and delivered to aquatic environments by more intense

459   rainfall after a prolonged, relatively dry period (Fenner et al., 2005). Positive correlation between the

460   irradiation induced change in the E4:E6 ratio and mean monthly discharge suggest that hydrological

461   conditions in the month prior to sampling significantly influence the reactivity of the sample, with

462   high flow delivering more reactive carbon to the stream. Change in the E4:E6 ratio correlated

463   significantly with several other variables, however spectral dependence of absorption photobleaching

464   depends on the spectral distribution of the irradiation source (Del Vecchio and Blough 2002,

465   Tzortziou et al. 2007). UVB-313 exposure may have produced a distinctly different absorption

466   difference spectrum than ambient irradiance, though there is a lack of literature to test this assertion.

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467　Hence, whilst the correlations are significant and can be explained theoretically, they should be

468　interpreted with caution.

469　Overall the magnitude of photo-induced C losses was significantly positively correlated with DOC

470　concentration in the year-long Black Burn dataset. However, despite low DOC concentrations,

471　photoreactivity remained elevated in January. This suggests that even when lower DOC

472　concentrations are detected in aquatic systems, the DOC may be intrinsically more photoreactive due

473　to its aromatic content and minimal light exposure history.

474　Lowest DOC concentrations were observed in the late winter and early spring, due to depletion of soil

475　organic C within the catchment by autumn and winter rainfall events. Low rainfall inputs limit the

476　recharge of fresh, photolabile material to the stream and may account for the reduction in DOC

477　photoreactivity detected in September. Furthermore, due to longer residence time in the water column,

478　these samples may have already been degraded by natural light. A previous study at the Black Burn

479　reported ^{13}C enrichment of stream water DOC in September, consistent with increased in-stream

480　processing at this time of year (Leith et al., 2014). Reductions in intrinsic DOC photolability during

481　summer have similarly been reported in northern lakes (Vachon et al., 2016) and a boreal watershed

482　(Franke et al., 2012). Another minimum in photoreactivity occurred in April, where SUVA$_{254}$ data

483　indicate decreased contribution of aromatic material to C within the stream. Although algal abundance

484　was not measured during this study, production of DOC from such sources would account for the

485　reduction in photolability (Nyugen et al., 2005).

486　Whilst DOC losses from Loch Katrine water samples were minimal, the peak in photolability,

487　indicated by the greatest absorbance reduction in the light exposure experiments, occurred in spring.

488　Similar seasonal photolability peaks have been observed in northern lakes (Vachon et al., 2016) and

489　boreal streams (Porcal et al., 2013) and are partly attributed to mobilisation of terrigenous material

490　with high flows associated with spring snow melt. The magnitude of melt in the Loch Katrine

491　catchment will be considerably less than in snow dominated northern catchments (e.g. Laudon et al.,

492 2013), although increased flow and stream water chemistry changes with spring snow melt have been

493 reported in upland Scottish catchments (Abrahams et al., 1989; Gilvear et al., 2002).

494 Absorbance increased during irradiation of Loch Katrine samples in summer. Absorbance increased in

495 light exposed samples during irradiation in summer Loch Katrine samples, indicating production of

496 DOC. Prior filtration of samples to 0.22 µm means that this effect is unlikely to be the result of

497 microbial DOC production. A possible explanation for increased absorbance in the irradiated water

498 samples is the formation of an iron (Fe)-DOC complex, since the reaction kinetics of Fe-DOC

499 complexes are directly affected by light exposure (Maranger and Pullin, 2003). Whilst Fe

500 concentrations were not measured in this study, in in a long term SEPA bimonthly measurement

501 campaign (2009-2013) at Loch Katrine , peak Fe concentrations in August of up to 0.50 mg L^{-1} were

502 detected, corresponding to the time of year when we found increased absorbance in irradiated water

503 samples. As the data set does not cover the sampling period, the role of Fe-DOC complexes in

504 producing the observed effect cannot be directly determined; however the role of micronutrients in

505 peatland aquatic C cycling should be further investigated.

506 Prior filtration of samples to 0.22 µm means that the anomalous absorbance increases are unlikely to

507 be the result of microbial DOC production. However, this cannot be entirely discounted as some

508 bacteria can pass through 0.22 µm filters and lacustrine freshwater bacteria colonies are seasonally

509 variable, which may explain why the effect was only observed in summer (Kent et al., 2004;

510 Fortunato et al., 2012). In order to determine microbial effects in the samples, stable C isotope (δ^{13}C)

511 data could be used as it can distinguish microbial activity from photochemical effects due to

512 preferential fractionation of DOC fractions of different molecular weights for each respective process

513 (Opsahl and Zepp, 2001).

514 **4.2 Importance of rainfall events in mobilising photolabile material**

515 Dissolved lignin phenol composition indicates that different sources of plant material were mobilised

516 as a result of rainfall in the Auchencorth Moss catchment. High P:V ratios have been used as an

517 indicator of peatland inputs to aquatic systems, as *Sphagnum*-derived organic acids *Sphagnum* acid

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518 typical of peatlands ~~is~~ are converted into P phenols during lignin extraction (~~Fichot et al., 2016;~~

519 Winterfeld et al., 2015; Fichot et al., 2016). Typically P phenols constituted the largest contribution to

520 the total lignin concentration of the measured phenols, consistent with *Sphagnum* inputs. However,

521 during the winter rainfall event where stream discharge was considerably higher than the year-long

522 mean value, the largest contribution to total lignin concentration was from S and V phenols (Figure

523 6). The former are reported to be the most photolabile phenol (Opsahl and Benner, 1998; ~~(~~Benner and

524 Kaiser, 2011)~~)~~ and are unique to woody angiosperms. This suggests that hydrological pathways within

525 the catchment were activated upon rainfall, causing DOC release from soil profiles associated with

526 angiosperm plant material. Potential sources within the Auchencorth upper catchment are *Calluna*

527 *vulgaris*, *Erica tetralix* and *Vaccinium myrtillus.* Further evidence of the operation of variable source

528 areas in the catchment was the observation of delayed input of water, containing high CO_2

529 concentrations, from the deep peat area in the upper catchment at Auchencorth Moss during a storm

530 event (Dinsmore and Billett, 2008). Low P:V values and high lignin concentrations have been

531 reported during peak flow in Arctic rivers, and the reverse during base flow (Amon et al., 2012). As

532 samples with low P:V values were typically more photoreactive (Figure 7a), our data indicate that

533 rainfall events are important in mobilising photolabile material from this catchment.

534 Elevated $Ad:Al_{v,s}$ ratios have previously been interpreted as indicators of decomposition of organic

535 matter resulting from preferential degradation of aldehydes relative to acids (Spencer et al., 2009; Lu

536 et al., 2016; ~~(Spencer et al., 2009~~). In the Black Burn water samples, lowest ratios were measured in

537 the winter rainfall event. This implies that DOC mobilised during rainfall is less degraded relative to

538 base flow DOC, in agreement with previous studies of peatland high flow events which detected

539 increased contribution of near surface flow and younger DOC (Clark et al., 2008). The form of the

540 degradation, either microbial or photochemical, cannot be distinguished using these data. However,

541 based on the higher measured photoreactivity of samples with lower ratios (Figure 7b), light exposure

542 history may be one of the key moderators of $Ad:Al_{v,s}$ ratios in the Black Burn. High flow events

543 release fresh DOC from soils derived from recent plant material (Evans et al., 2007) and may have

544 significant implications for C processing rates in streams as they are recharged with labile material

545 (Lapierre et al., 2013).

546 Whilst the samples collected during the winter rainfall event were clearly distinct in composition

547 relative to samples from the year-long study, the summer rainfall event samples had similar P:V and

548 Ad:Al$_{v,s}$ ratios, but significantly lower photoreactivity and overall lignin yields (Figures 5b, 6c, 7).

549 This could be attributed to the timing of sample collection in early September at the end of summer,

550 where considerable degradation may have already occurred across all phenol groups so that the DOC

551 pool remaining was more recalcitrant to further photo-processing. Discharge data indicate that there

552 was no discernible flushing effect during the summer rainfall event, with slight decreases in DOC

553 concentration attributed to dilution of the stream water by direct rainfall inputs or overland flow. The

554 abundance of P phenols, which have been determined as the least photoreactive phenol (Benner and

555 Kaiser, 2011), within the samples suggest that passive transfer of DOC from the riparian zone, which

556 is dominated by *Sphagnum* and *Juncus* vegetation, to the stream was the dominant mode of stream

557 DOC recharge at this time of year (Jeanneau et al., 2015). The summer rainfall event samples were

558 notably depleted in V phenols, suggesting that these phenols exert an important control on sample

559 photoreactivity in addition to S phenols.

560 **4.3 Implications for photochemical turnover of DOC in aquatic systems**

561 Our 8--h irradiation experiments found 7% of DOC to be labile to photo-processing, with and

562 conversion to CO_2 was the main loss pathway, DOC loss from samples upon irradiation resulted in

563 significant production of CO_2. MThe mass budget calculations for Black Burn water samples show

564 that a mean of ~46% of DOC loss in the irradiation experiments was accounted for by production of

565 CO_2. Dinsmore et al. (2010) estimate that 108 ± 62.7 kg DOC yr^{-1} is exported to the Black Burn from

566 the Auchencorth Moss catchment. Based on our finding that 7% of DOC is removed via photo-

567 processing, and assuming that 46% of this loss is converted to CO_2 and also that UV-B irradiance was

568 comparable to a clear sky summer day, we estimate a potential evasion loss of 3.48 ± 2.02 kg CO_2 yr^{-1}

569 to the atmosphere. Whilst this calculation makes significant assumptions in upscaling from 8 h

570 exposure experiments, it highlights the potential importance of photo-processing in the turnover of

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571 ~~aquatic C and the need for more in situ studies.~~ Given the significant volume of DOC produced by the

572 catchment, in-stream photo-processing may be an important term in carbon budgets of peatland

573 draining aquatic systems~~Clearly headwater peatland streams are important sources of photoreactive~~

574 ~~material to the freshwater aquatic continuum~~ and may contribute to the high CO_2 efflux reported from

575 these systems (Billett et al., 2015). However, determining the volume of material photo-processed

576 both in the stream and in downstream environments relies upon a range of un~~known~~quantified factors,

577 including optical depth and mixing processes in downstream aquatic environments which are

578 generally poorly understood in relation to photochemical DOC processing.

579 Due to the effects of bank shading and short transit time of water within the immediate catchment,

580 light driven instream DOC processing is unlikely to be significant. The river continuum concept

581 suggests that increased DOC processing will occur further downstream, where the channel widens

582 (Vannote et al., 1980), and will be partly controlled by the stream water mean transit time (McGuire

583 and McDonnell, 2006; McDonnell et al., 2010~~; McGuire and McDonnell, 2006~~). Based on mean

584 velocity (~0.58 m s^{-1}) of a larger nearby river (~~-~~Ledger, 1981), we estimate a mean water transit time

585 of ~19 h from the Black Burn at Auchencorth Moss to its coastal outlet ~~in the River Esk~~ 34 km

586 downstream, considerably longer than the exposure time in our experiments. However, in a study of

587 1st to 4th order streams in Sweden no significant change to DOM composition as stream order

588 increased was detected and this was partly attributed to short transit times (<2 days) restricting DOC

589 processing (Kothawala et al.~~,~~. 2015). Peatland derived C ~~carbon~~ in this study is clearly photoreactive,

590 but limited time for in-stream processing may render photo-processing unimportant in the C budgets

591 of some freshwater systems.~~freshwater aquatic C budgets.~~

592 Recent studies have determined hotspots of DOC processing within peatland draining systems, which

593 include mixing zones of freshwaters with different pH, conductivity and metal concentrations (Palmer

594 et al., 2015; Jones et al., 2016). In the context of this study, measuring DOC processing at the

595 confluence of the Black Burn, which largely drains peatland, and the River North Esk, which drains a

596 catchment of mixed land use including natural and plantation forestry, 4 km downstream of the point

597 from which our samples were collected would provide a logical starting point for quantifying in situ

598 DOC turnover. ~~The optical depth and mixing processes in downstream aquatic environments are~~

599 ~~generally poorly understood in relation to photochemical DOC processing and further work is needed~~

600 ~~to reduce uncertainties of their influence.~~

601 Determining the C cycling implications of this study is further complicated as the most photoreactive

602 material was recorded during a heavy winter rainfall event. The potential for photochemical

603 transformation of DOC within the freshwater aquatic environment would have been limited due to

604 low light availability, extensive cloud cover and ~~increased~~ decreased stream water transit times

605 associated with the event. During the year-long study period, 12 rainfall events occurred which

606 resulted in similar flow conditions in the Black Burn (stream discharge exceeding 250 L s^{-1}), with a

607 maximum discharge of 2059 L s^{-1} in a late winter storm. Of these high flow events, 11 occurred

608 during winter and one in summer and hence, whilst large quantities of photoreactive material may

609 have been mobilised during heavy rainfall, the likelihood of in-stream processing would remain small.

610 Increases in precipitation, with more frequent and intense rainfall events, are expected with climate

611 change (Capell et al., 2013; Edenhofer et al., 2014) with heavier summer downpours predicted in the

612 UK (Kendon et al., 2014). Thus, although the contribution of rainfall events to ~~freshwater~~

613 ~~aquatic~~photochemically induced C cycling in this study is likely to be minimal, they could become

614 more significant if heavy rainfall events occur more frequently in summer.

615 **Author Contributions**

616 AEP collected field samples and undertook laboratory experiments, ~~analyses. Dd~~ata analysis and

617 writing of the paper. ~~were also carried out by AEP.~~ KVH, ARM and KJD provided guidance on the

618 scope and design of the project, and contributed to the editing of the manuscript.

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624 phenol analyses and Andrew Addison for his contribution to fieldwork. We also thank Tony

625 Dickinson and Jim Donnelly at the University of Central Lancashire for use of a Horiba FluroMax-4

626 spectrofluorometer.

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Table 1. Photosynthetically active radiation (PAR) and ultraviolet irradiances during 8 h exposures to Q -Panel UV313 fluorescent lamps filtered with 125 µm cellulose diacetate.

Irradiance W m^{-2}

Total UV (280-400 nm)	UV-A (315-400 nm)	UV-B (280-315 nm)	PAR (400-700 nm)	CH$_4$[a]	GEN (G)[b]	PG[c]	DNA[d]
7.52	4.63	2.89	0.92	2.50	1.25	1.05	0.98

[a] CH$_4$, idealized spectral weighting function for CH$_4$ production (McLeod et al., 2008)
[b] weighted with a mathematical function of the general plant action spectrum (GEN G) (Green et al., 1974)
[c] weighted with the plant growth (PG) function (Flint and Caldwell, 2003)
[d] weighted with the DNA damage action spectrum (Setlow, 1974)

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Table 21. Mean (n=13 ± 1 standard deviation) water temperature and chemistry parameters including pH, conductivity, POC concentrations, and fluorescence index FI values at the Black Burn and Loch Katrine. (n=13 ± 1 standard deviation).

	Black Burn	**Loch Katrine**
Water temperature °C	8.3~~26~~ ± 4.5~~3~~	10.9 ± 5.1~~07~~
pH	5.4~~38~~ ± 0.9~~85~~	6.7~~4~~ ± 0.3~~2~~
Conductivity μS cm^{-1}	78.2 ± 30.7	25.2 ± 4.0~~1~~
POC mg L^{-1}	5.7~~8~~ ± 2.7~~8~~	3.02~~2.96~~ ± 0.6~~3~~
FI value	1.2~~15~~ ± 0.1~~3~~	1.1~~08~~ ± 0.2~~18~~

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900 **Table 32.** Pearson correlation coefficients between irradiation induced changes to aqueous carbon species and
901 spectral properties, and water chemistry of Black Burn water samples from the year-long sampling campaign
902 prior to irradiation and site conditions at Auchencorth Moss (n=13).

	ΔDOC	ΔDIC	ΔCO$_2$	ΔCO	Δa$_{254}$	Δa$_{350}$ ΔE4:E6	ΔE4:E6	ΔS$_R$
DOC	**0.708****	-0.074	**0.773****	**0.824****	**0.766****	0.168 -0.095	0.095	-0.547
E4:E6	0.366	0.049	0.463	0.434	0.183	-**0.579*** 0.770**	**0.770****	-0.157
SUVA$_{254}$	0.228	0.460	0.232	0.129	0.231	0.157 -0.098	-0.098	-0.059
FI	-0.438	-0.161	-0.318	-0.238	-0.115	0.492 -0.485	-0.485	-0.186
Air temperature[a]	-0.032	-0.379	-0.029	-0.052	0.220	0.402 -0.571*	**-0.571***	-0.405
Rainfall[b]	**0.603***	0.061	0.537	0.445	0.365	-0.389 0.492	0.492	-0.226
PAR[c]	-0.161	-0.459	-0.380	-0.267	-0.224	0.054 -0.662*	**-0.662***	-0.489
Discharge[d]	0.132	0.237	0.123	0.088	-0.139	-0.435 0.767**	**0.767****	-0.072

* p < 0.05
** p < 0.01
[a] Mean monthly air temperature
[b] Total monthly rainfall (mm)
[c] Mean monthly PAR (μmol m^{-1} s^{-1})
[d] Mean monthly discharge (L s^{-1})

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913 **Figure 1.** Mean monthly air temperature, total rainfall and mean discharge from May 2014 to May 2015 are

914 shown for a) Auchencorth Moss, with discharge of the Black Burn shown on the left hand offset axis. Mean

915 monthly air temperature and total rainfall are shown for the same period for Comer meteorological station, near

916 b) Loch Katrine. Note inverted right hand y axes.

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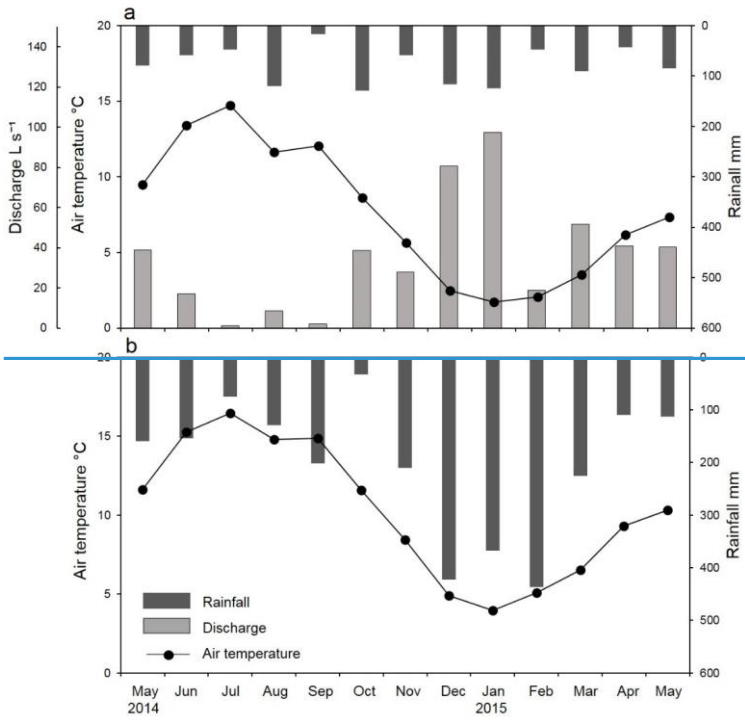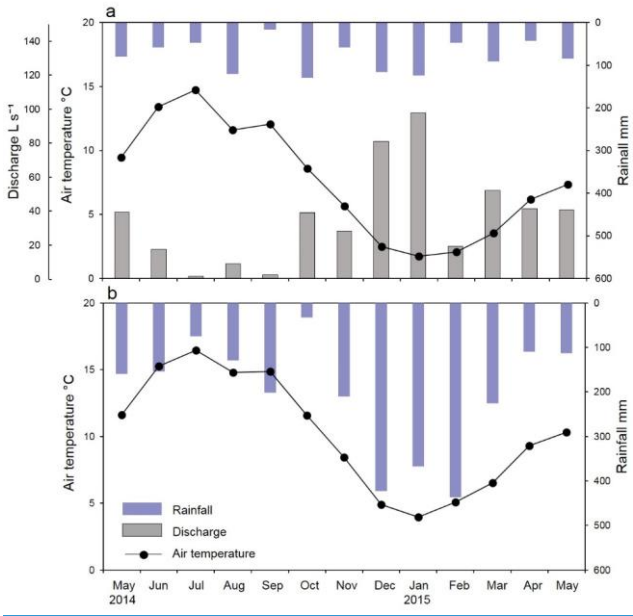
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927   **Figure 2**. Time series at a) the Black Burn and b) Loch Katrine of DOC concentration and parameters for DOC

928   quality: SUVA$_{254}$ and E4:E6 from May 2014 to May 2015. Note different y axis scales for DOC data.
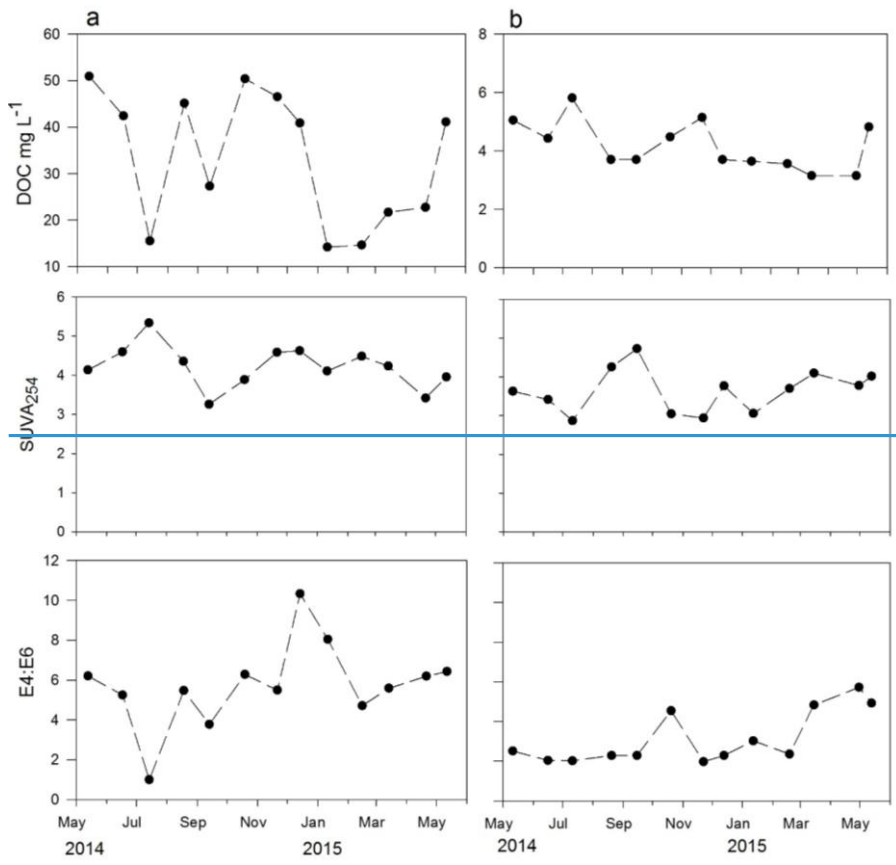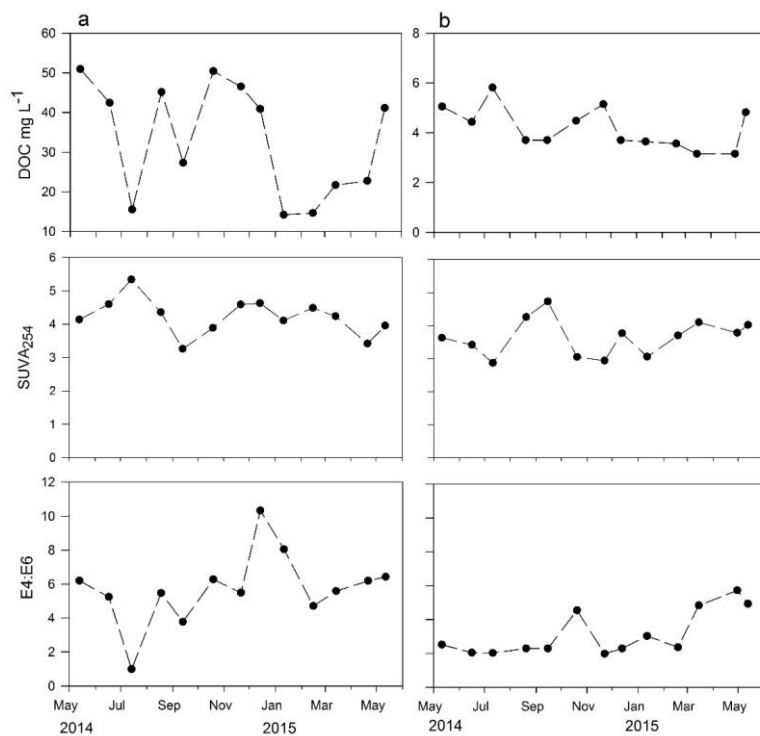
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940 **Figure 3.** Change in absorbance upon irradiation expressed as a percentage of the unirradiated control samples
941 from 250 - 400 nm at a) Black Burn and b) Loch Katrine. Summer is the mean of June, July and August values,
942 autumn is the mean of September, October and November values, winter is the mean of December, January and

943 February values, and spring is the mean of March, April and the combined mean of May '14 and May '15
944 values. Note different y axis scales.
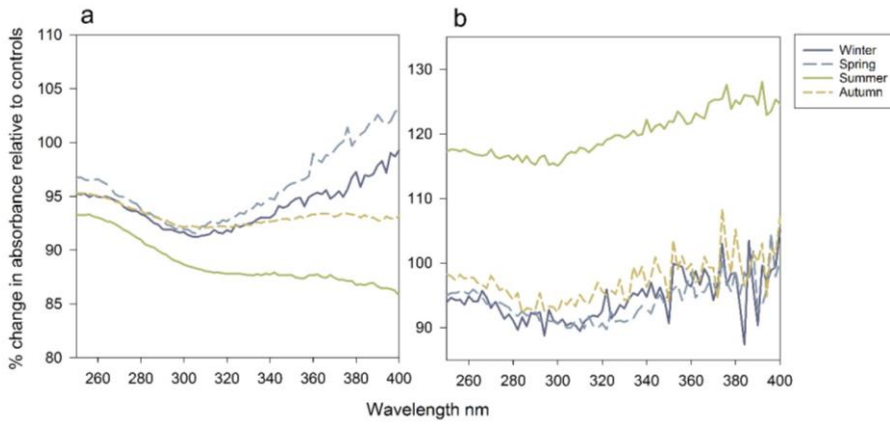
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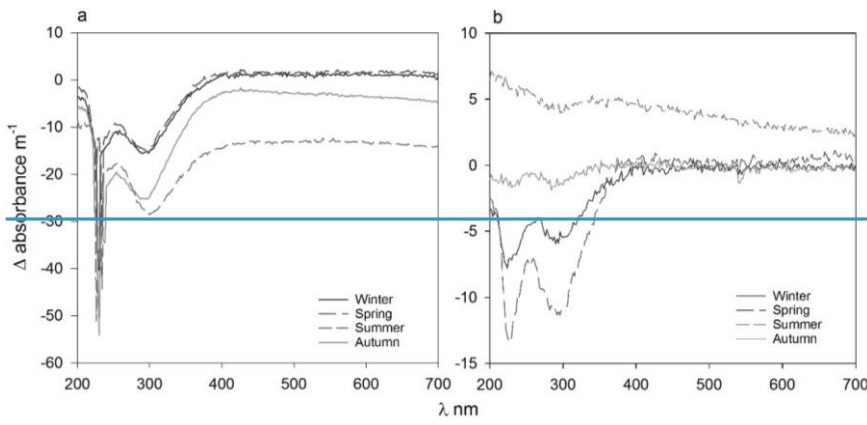
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959   **Figure 4.** Irradiation induced changes to carbon species DOC, DIC, CO_2 and CO in monthly water samples from

960   panel Black Burn (panel a) and Loch Katrine (panel b). DOC normalised changes to all C species changes

961   (photoreactivity, quantified as explained in the text) are shown on the bottom row. Data represent the difference

962   between the mean of irradiated and unirradiated control samples. Error bars show the standard error of the mean

963   (n=4). Note different y axis scales for Black Burn and Loch Katrine water samples.
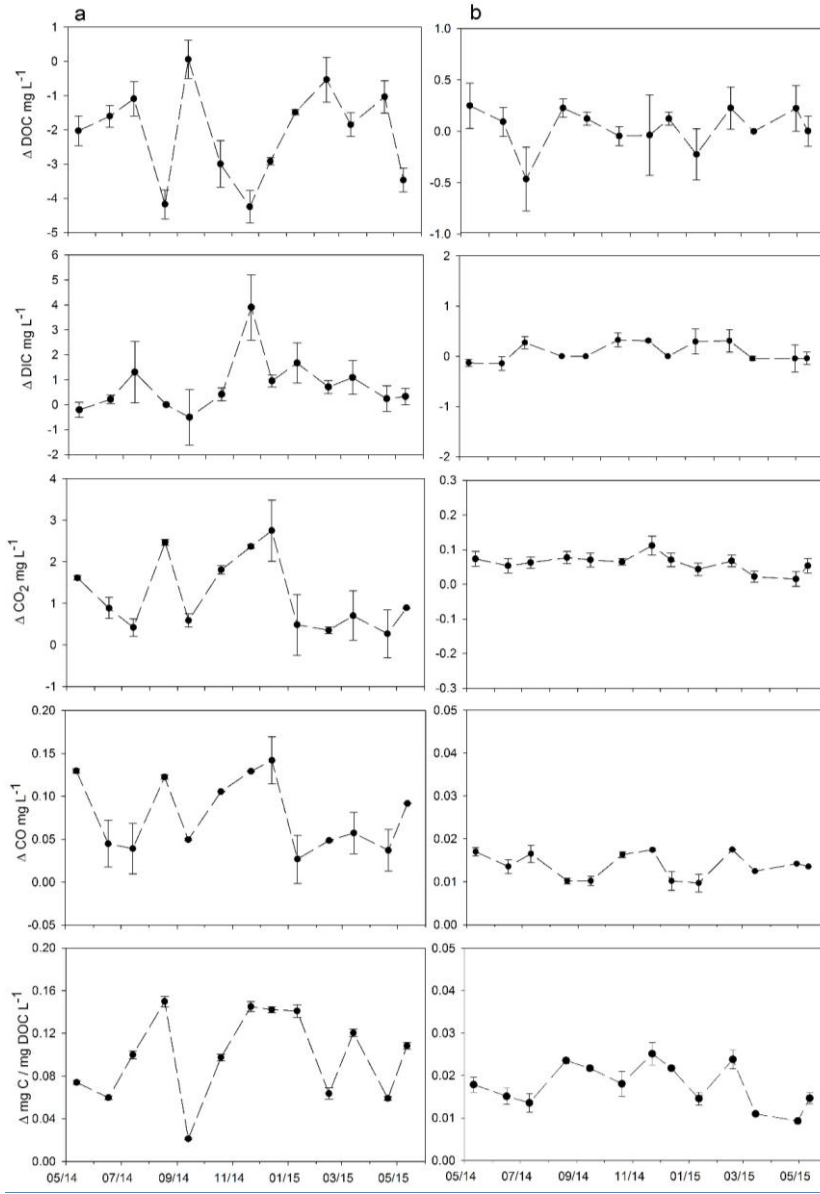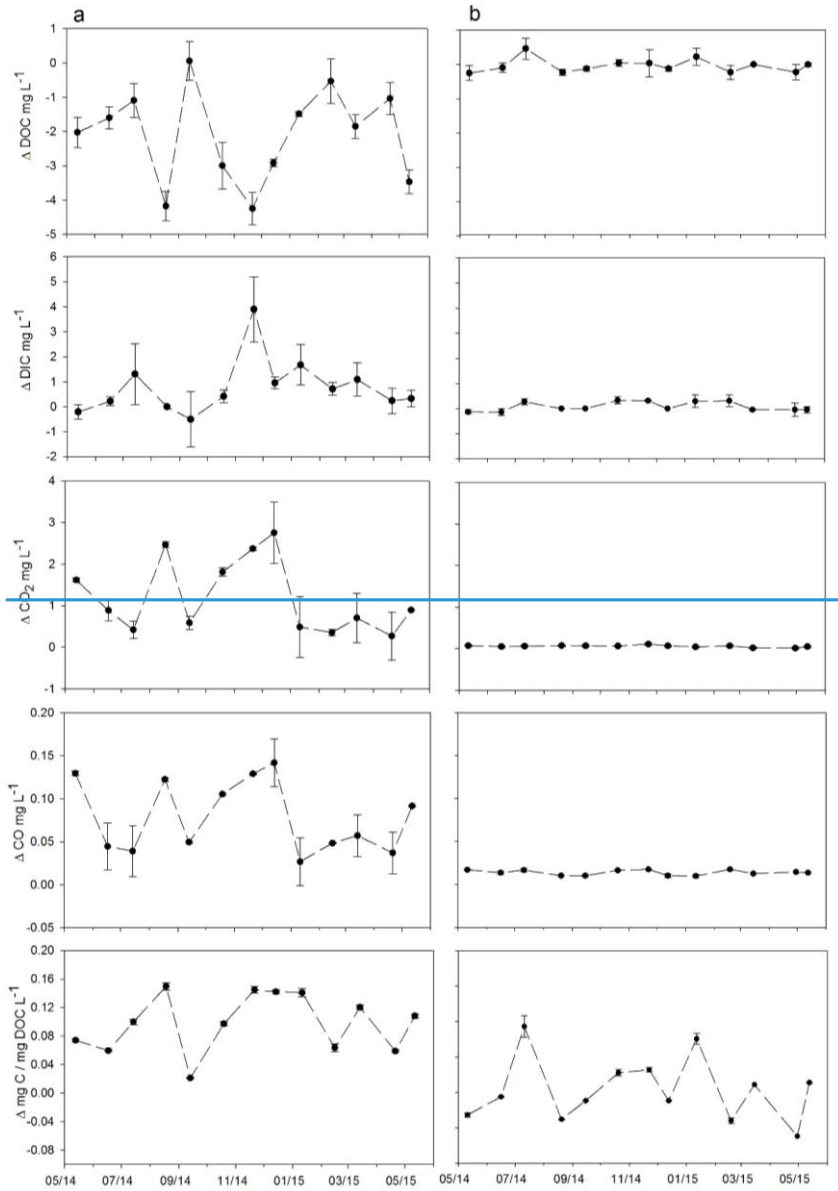
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967 **Figure 5.** Rainfall events sampled on 9-10 December 2014 (panel a) and on 1-2 September 2015 (panel b). Row
968 one shows a time series of hourly rainfall, discharge and DOC concentrations for each event. Row two shows
969 photo-induced C pool changes of irradiated samples expressed as a total change value per C species in vertical

970   bars (left y axis) and as a DOC normalised value in dots (right y axis). Data represent the difference between the

971   mean of irradiated and unirradiated control samples (n=4). Note different x- and y-axis scales.

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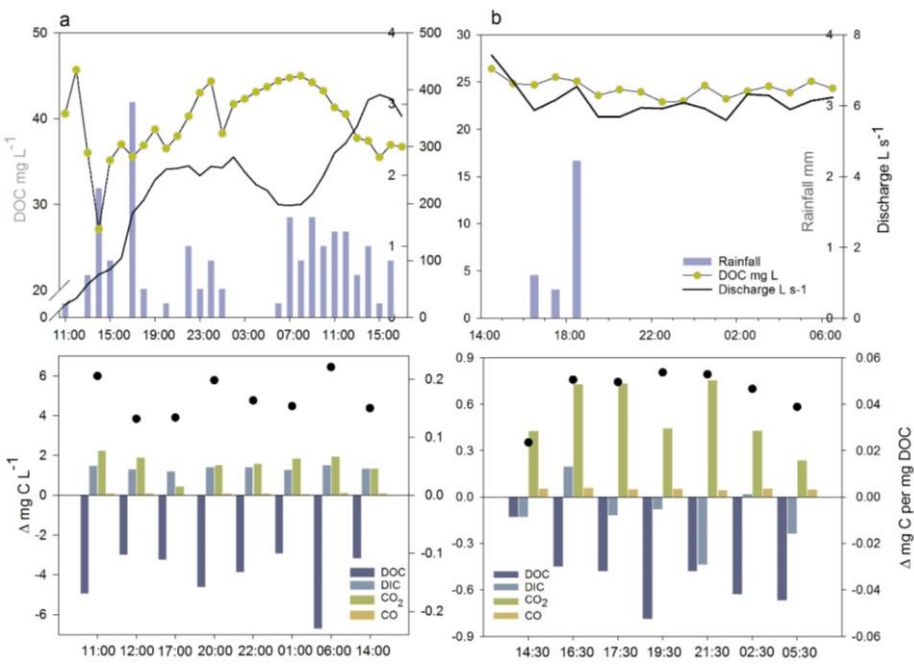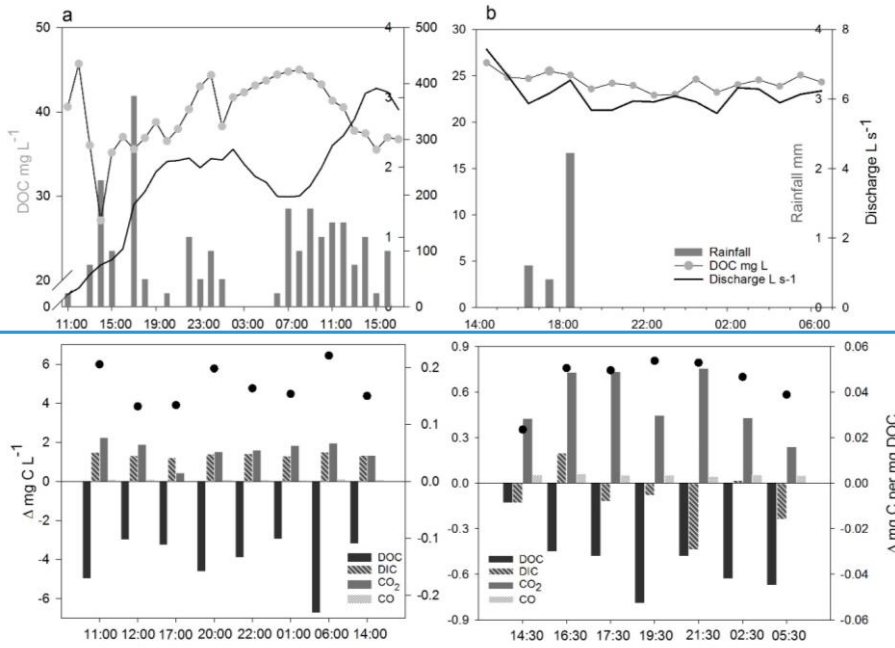
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Figure 6. Boxplots of carbon-normalised yields of phenols groups for Black Burn water samples collected a) monthly in the year-long study (n=13), b) during the winter rainfall event (n=8) and c) during the summer rainfall event (n=7). P = p hydroxyl, V = vanillyl, S = syringyl and C = cinnamyl. The box spans from the first quartile to the third quartile, with the line showing the median value. Whiskers show the minimum and maximum values, with dots representing outlying values.
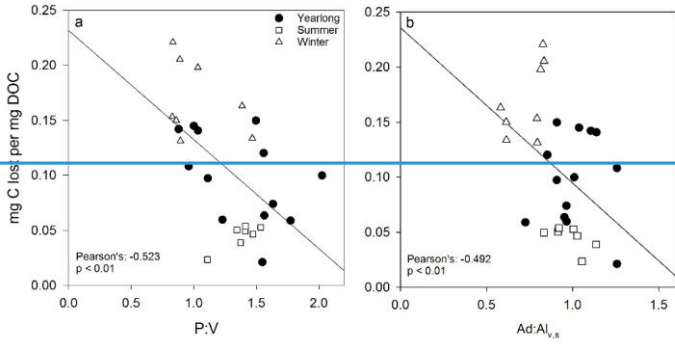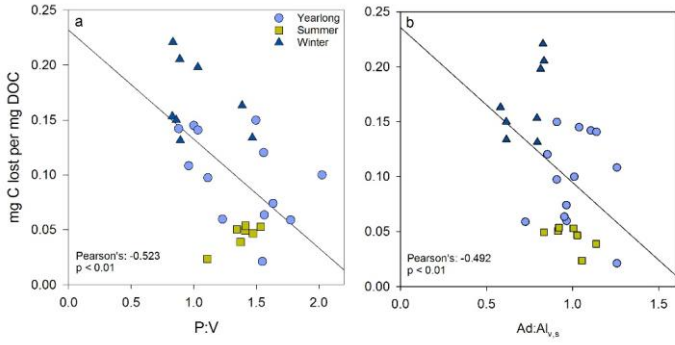
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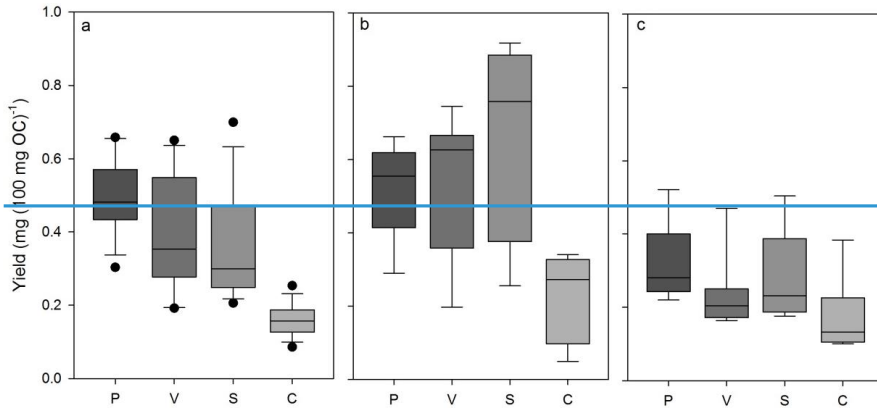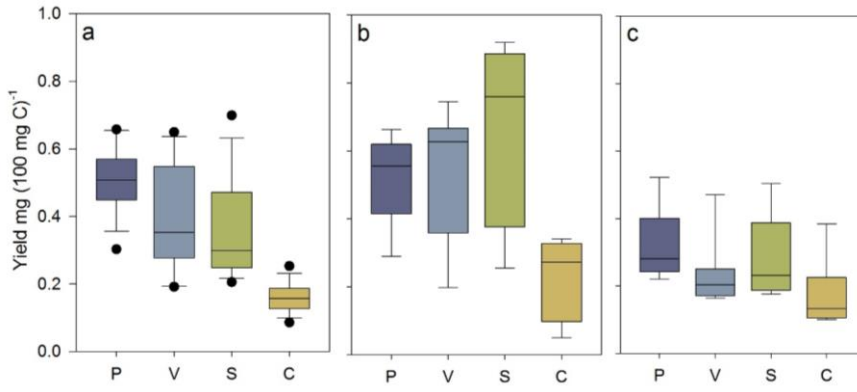
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1004 **Figure 7.** Pearson correlation between mg DOC lost upon irradiation per mg DOC and a) P:V ratios and b)
1005 Ad:Al$_{v,s}$ (derived from acids and aldehydes from vanillyl and syringyl phenol groups) ratios in all Black Burn
1006 water samples analysed (n=28). Lines of best fit for all water samples are also shown. The monthly samples in
1007 the year-long study and the winter and summer rainfall event samples are indicated.

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