Global Biogeochemical Cycles

Supporting Information for

Decreasing Photoreactivity and Concurrent Change in Dissolved Organic Matter Composition with Increasing Inland Water Residence Time

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Text S1. DOM photomineralization and photoreactivity values in the studied boreal inland waters

The photomineralization and wavelength-integrated apparent quantum yield (AQY) values were similar to values reported in the literature (Table S1, S5). Caution should however be used when comparing photomineralization and AQY values between laboratories, since methodologies continue to vary and develop.

Photoreactivity can be also reported as the dissolved organic carbon (DIC) gain per unit energy absorbed. To calculate the dissolved organic carbon (DIC) gain per unit energy absorbed, the DIC gain (in mg L^{-1}) was normalized by the E_{tot}, the radiation energy absorbed in J m^{-2} according to Bertilsson and Tranvik (2000) where $Abs_\lambda = a_{CDOM,\lambda} \times \frac{L}{\ln(10)}$:

$$E_{tot} = T \times \sum_{\lambda=280}^{\lambda=600} I_\lambda \times (1 - 10^{-Abs_\lambda})$$

As for Q_{tot}, E_{tot} was calculated using the average of $a_{CDOM,\lambda}$ obtained before and after irradiation. The dissolved organic carbon (DIC) gain per unit energy absorbed was 1 or 2 orders of magnitude lower than the values reported by Bertilsson and Tranvik (2000) and Panneer Selvam et al. (2019) who irradiated the water samples under UV sources. As short wavelengths have the highest photomineralization per unit energy or photon absorbed (Granéli et al., 1996; Koehler et al., 2016; Vachon et al., 2016), this likely explains the higher values of Bertilsson and Tranvik (2000) and Panneer Selvam et al. (2019) in comparison to our study. Furthermore, in these two studies, the DIC gain per unit energy absorbed was not normalized by the illuminated surface (the values are reported in mg L^{-1} kJ^{-1} m^2) but the vessels were exposed horizontally to light and thus had a higher illuminated surface than in our study.

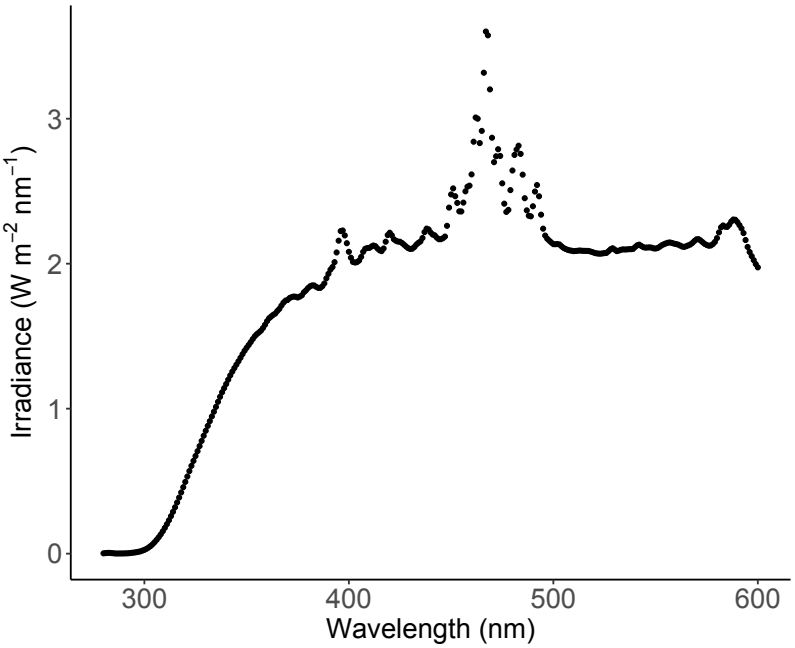


Figure S1. Irradiance spectrum of the solar simulator lamp used in this study (measured in November 2014).

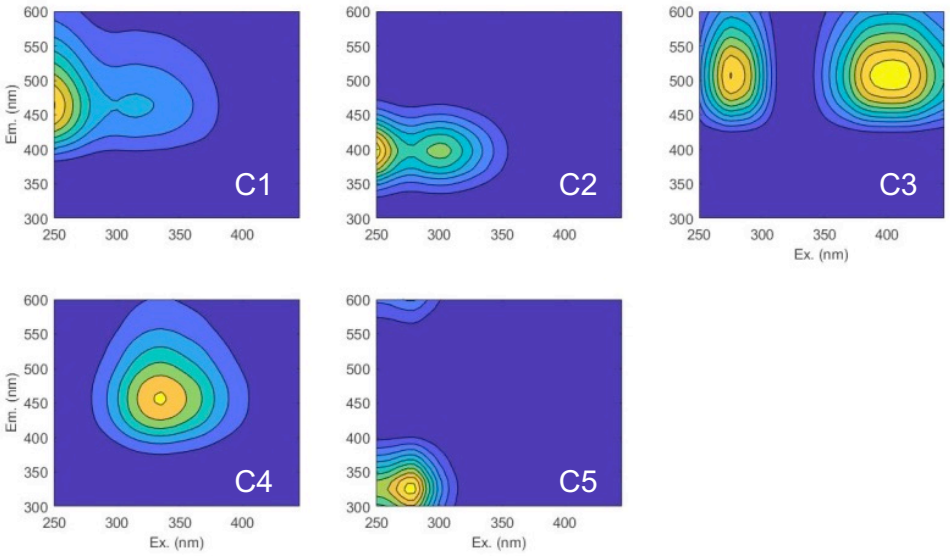


Figure S2. Excitation-emission plots of the fluorescence components identified from the PARAFAC model for samples before and after photoirradiation (n=512) from the 30 sites across the boreal continuum. See Table S2 for the values of the peak excitation and emission wavelengths.

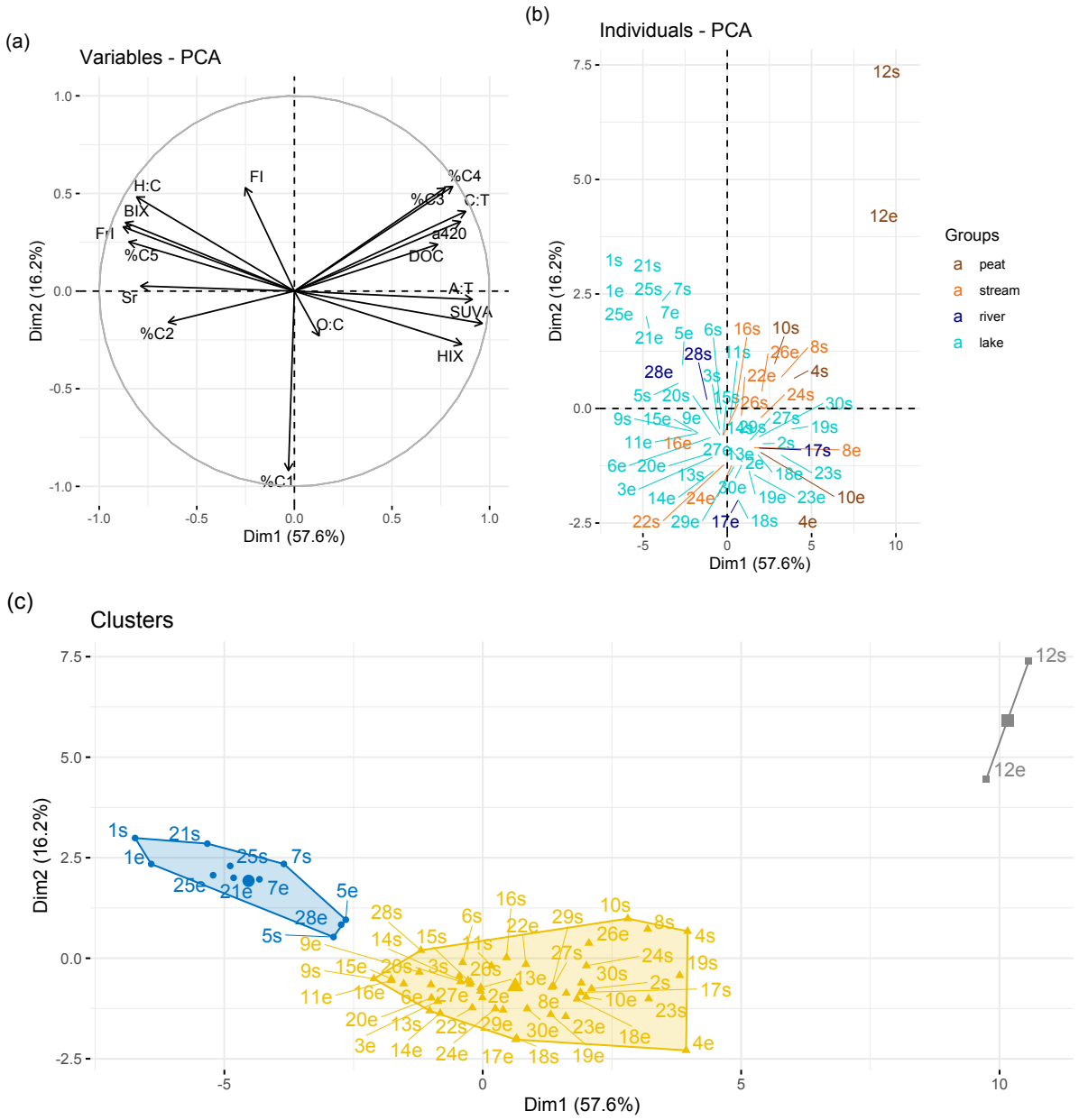


Figure S3. Principal component analysis of the 30 sites (sites numbered from 1 to 30 according to Table S1) before (s) and after (e) irradiation for DOC concentration and the variables describing DOM quality (listed in Table S2). Panel a) describes the variables, b) the individual sites grouped by category of inland water and c) the clustering between the individual sites. The cluster in blue correspond to sites with high WRT (sites 1, 5, 7, 21 and 25, WRT ≥4.3 yr; Table S1). The cluster in yellow corresponds to sites with low WRT (≤ 2.3 yr), at the exception of site 6 (WRT=10.7).

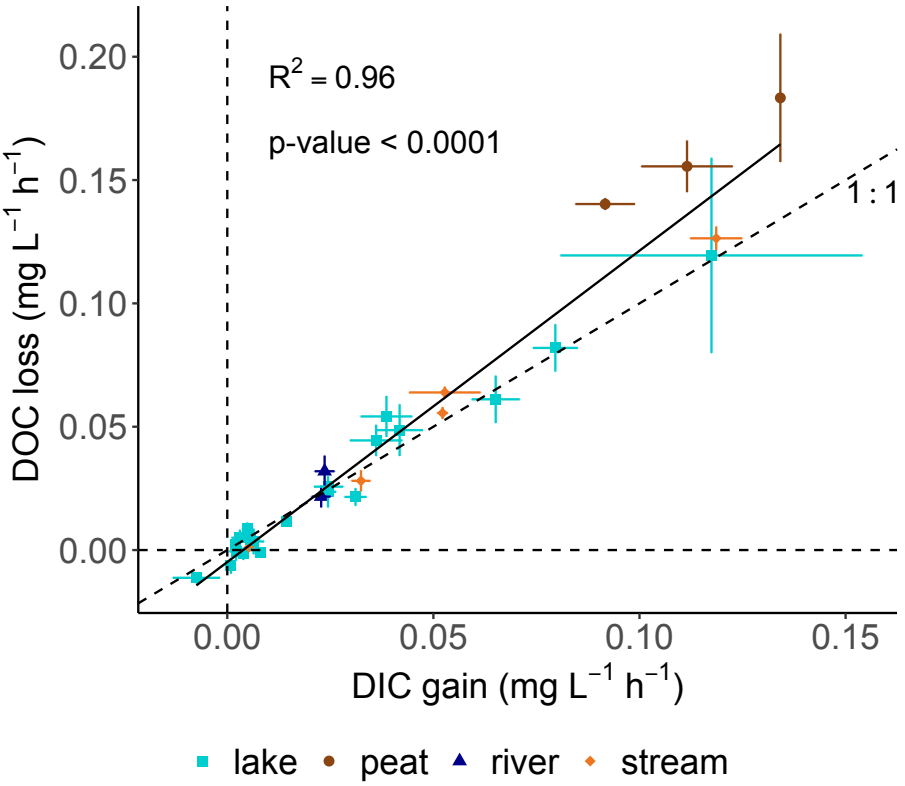


Figure S4. DOC loss versus DIC gain after irradiation for each of the 30 sites. Error bars show the average (n=3) ± SD. The dashed lines delimit DOC loss and DIC gain=0, and DOC loss=DIC gain (the 1:1 line). The slope of the regression is 1.26 ± 0.05 (SE). The solid line corresponds to the linear regression between DOC loss and DIC gain, the R^2 and the p-value of the regression are given directly on the figure.

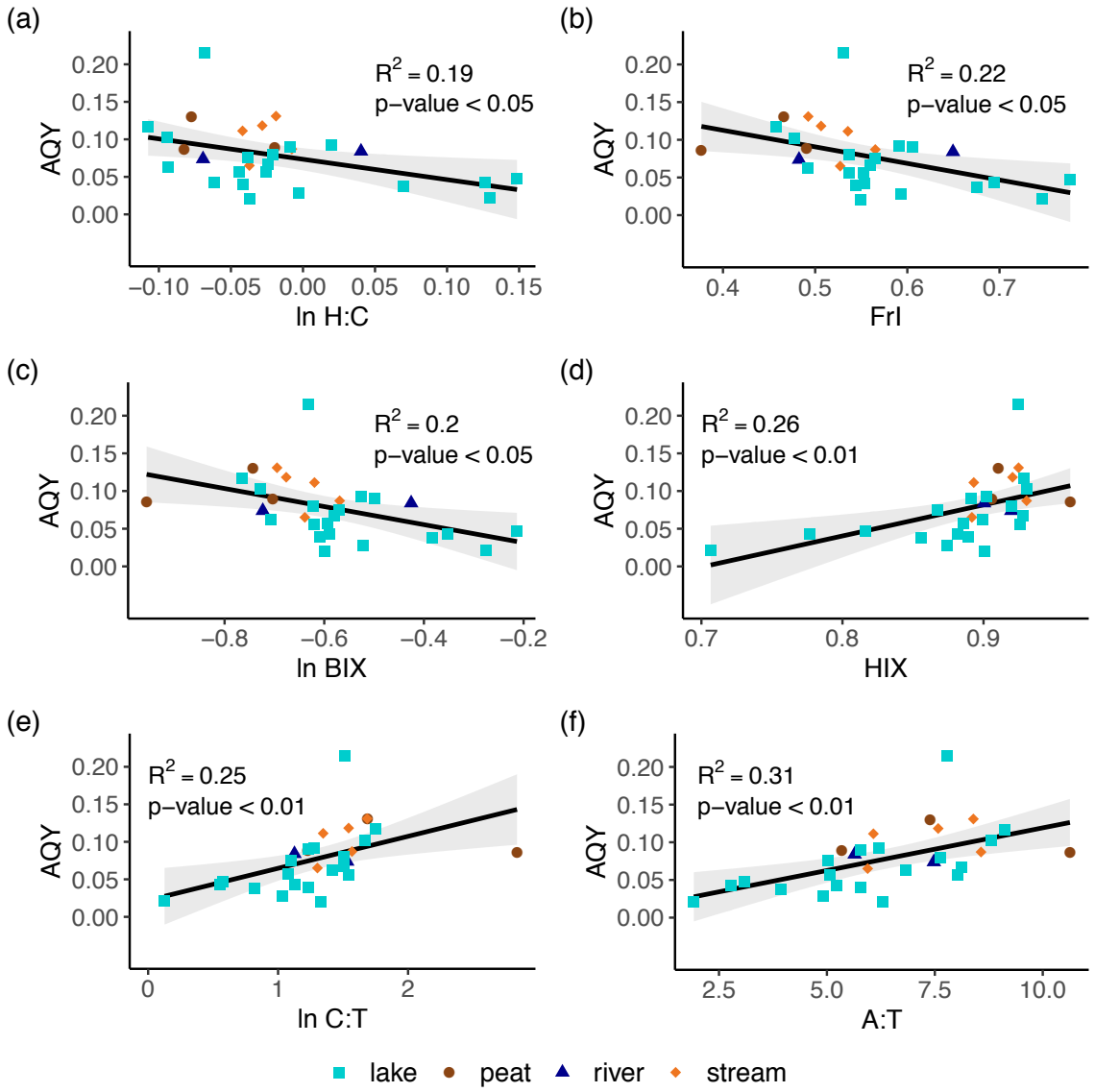


Figure S5. Linear regressions between the wavelength-integrated AQY (mmol DIC mol photon^{-1}) and DOM quality indices before irradiation: ln(H:C) (a), FrI (b), ln(BIX) (c), HIX (d), ln(C:T) (e) and A:T (f). The grey area represents the 95% confidence interval. The correlations between AQY, the O:C ratio and FI were not significant and are not presented here. The equations are given in Table S3 whereas the R^2 and p value are given in each panel.

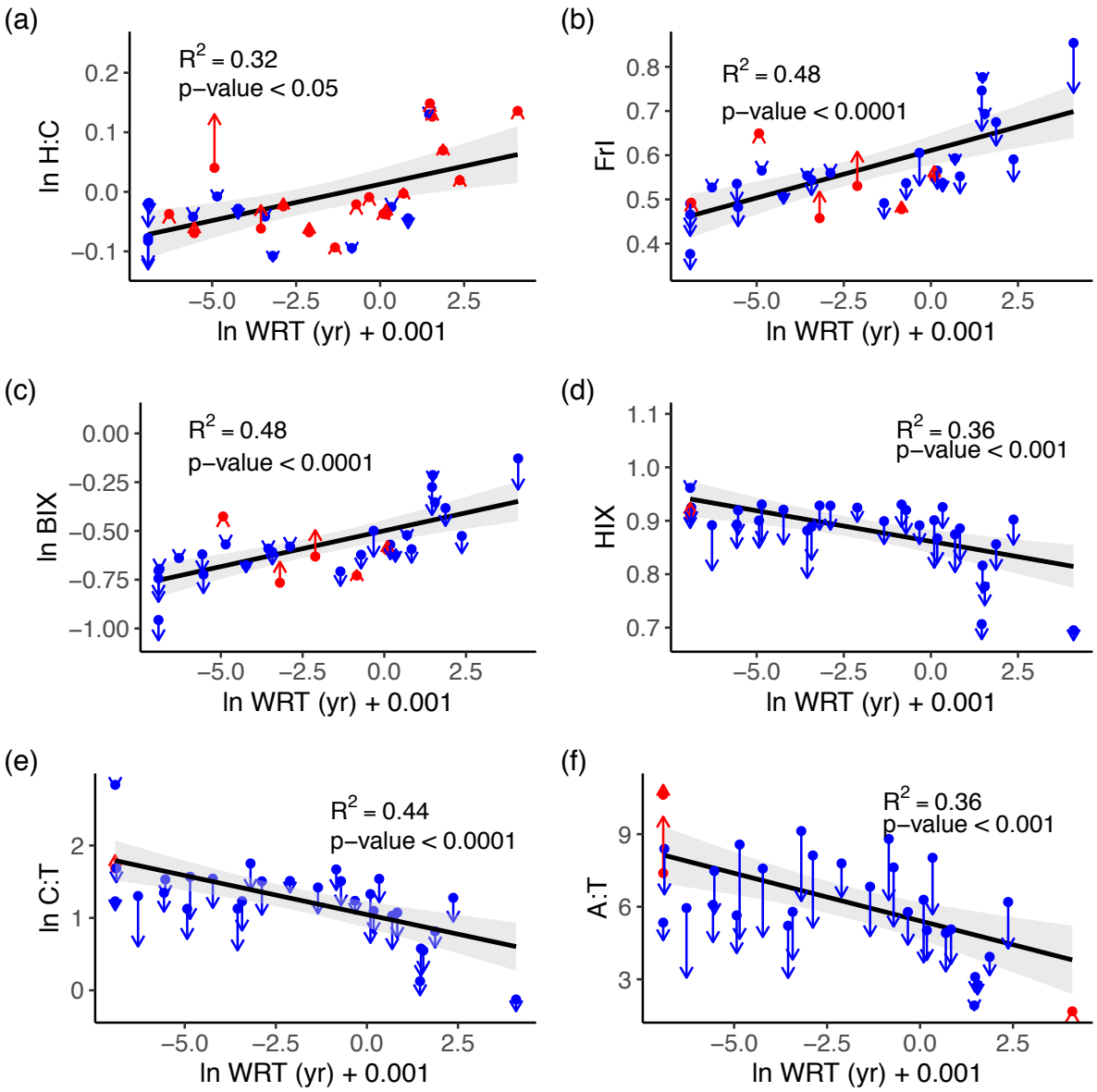
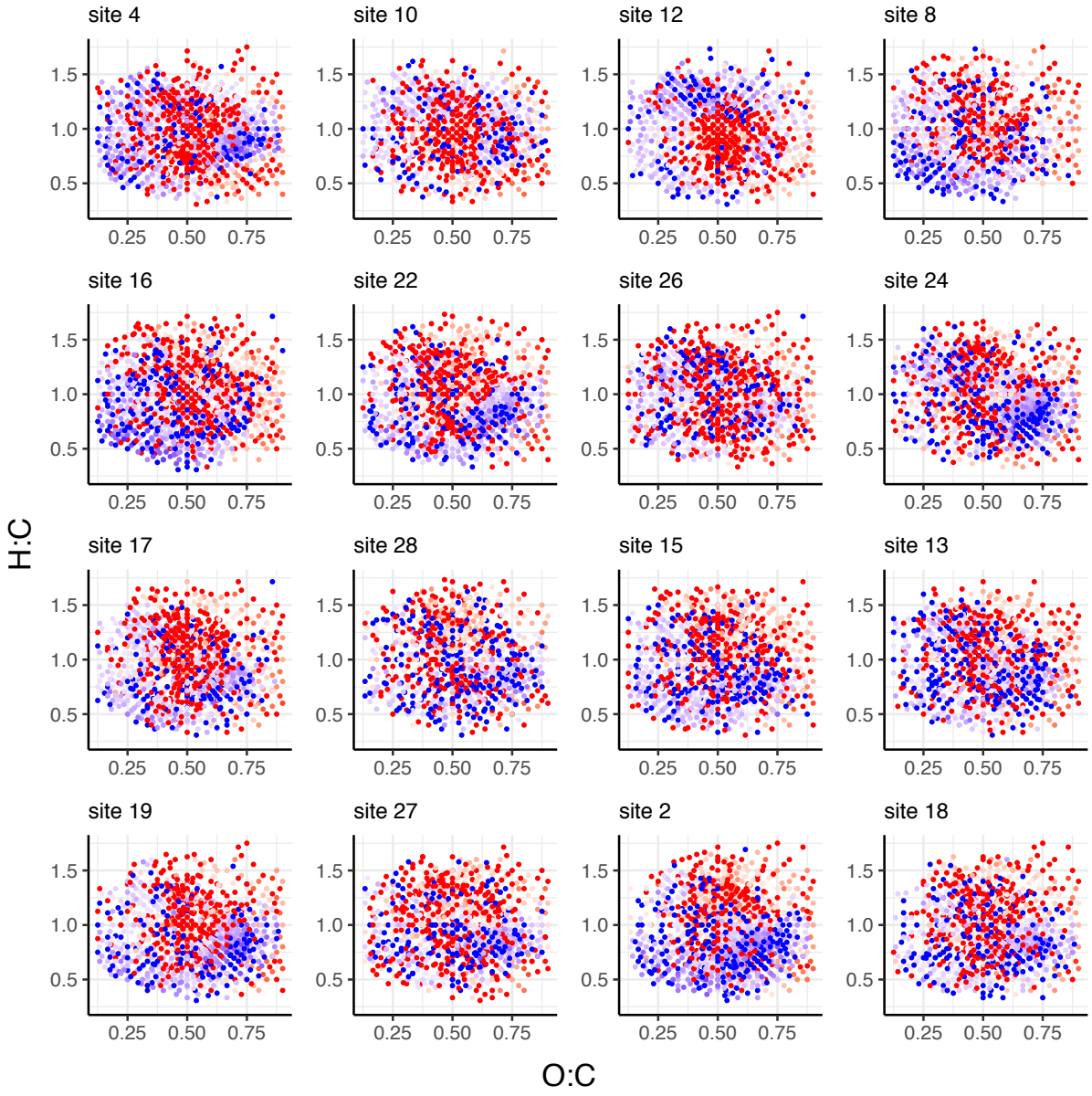


Figure S6. Change in DOM quality indices, ln(H:C) (a), FrI (b), ln(BIX) (c), HIX (d), ln(C:T) (e) and A:T (f) after irradiation, and linear regression with ln WRT + 0.001. All linear regressions are tested between the variable measured before irradiation and WRT. The regressions between the O:C ratio, FI and WRT were not significant and are not presented here. The change between the start (start of the arrow) and the end (head of the arrow) of the irradiation was significant for all variables except the H:C ratio (Table S2). Red arrows depict an increase of the variable with irradiation while blue arrows depict a decrease. The grey area represents the 95% confidence interval. Note that the variables describing autochthonous production (FrI and BIX) are decreasing after irradiation but are positively correlated to WRT. The equations are given in Table S3 whereas the R^2 and p value are given in each panel.


site 4
site 10
site 12
site 8
site 16
site 22
site 26
site 24
site 17
site 28
site 15
site 13
site 19
site 27
site 2
site 18
H:C
O:C
1.5
1.0
0.5
0.25
0.50
0.75

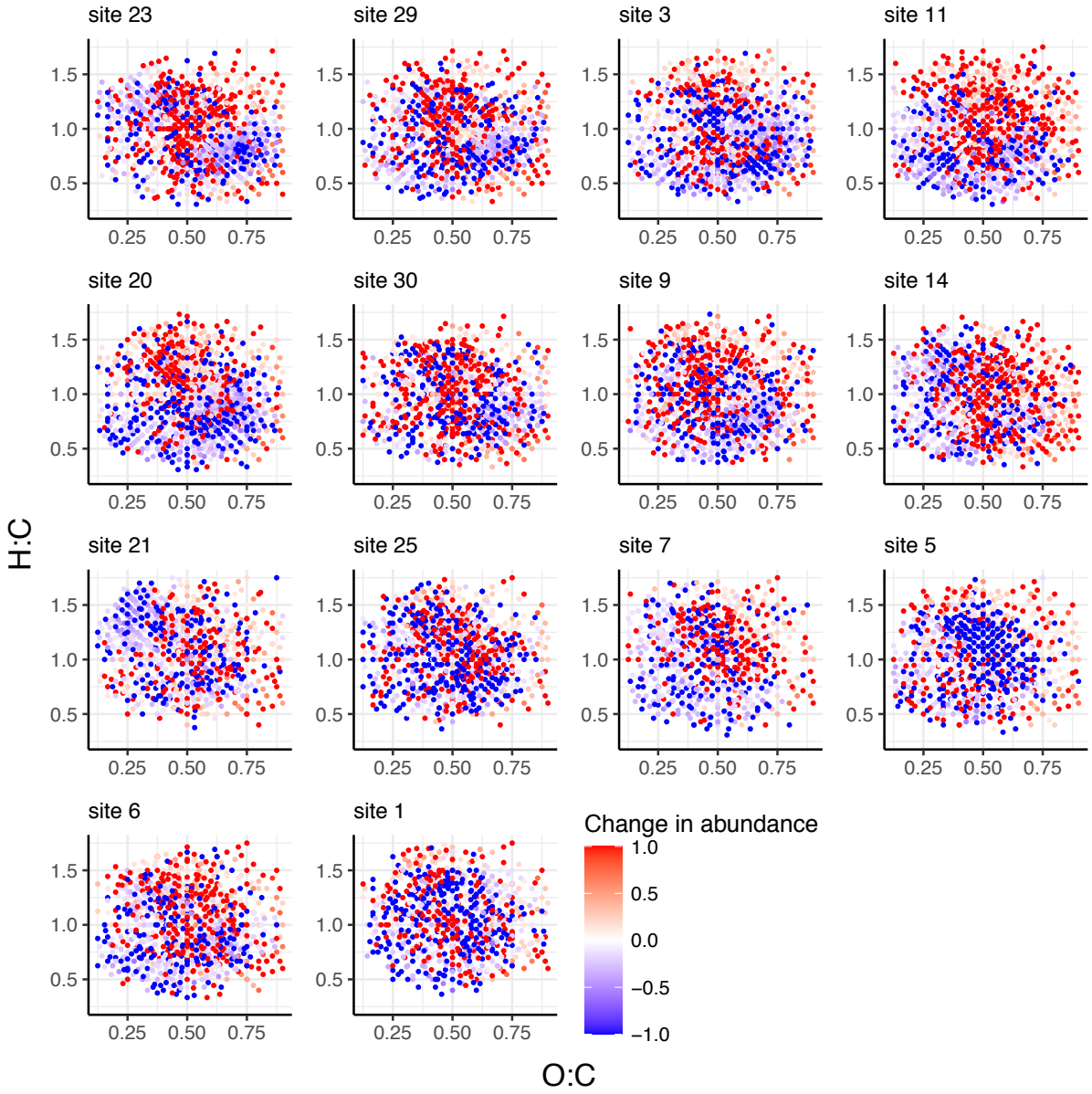


Figure S7. Change in the abundance of individual molecules after irradiation for each site. The sites are ordered by category of inland water and by increasing WRT (Table S1), sites 4 to 12 are peatlands, sites 8 to 24 are streams, sites 17 and 28 are rivers and sites 15 to 1 are lakes (reading from left to right and top to bottom). The difference is calculated as the relative intensity of the molecule before irradiation minus the relative intensity after irradiation and divided by the sum of the relative intensity before and after irradiation. The color scale indicates the change in the abundance of molecules after irradiation, red dots indicate molecules increasing in abundance with irradiation while blue dots indicate a decrease. Only one out of the three replicates measured after irradiation was used to calculate the change in molecule abundance but using the two other end replicates for the calculations produces similar figures. The average difference for all sites pooled with WRT < 3 yr and > 3 yr are represented in Figures 5b and 5c, respectively.

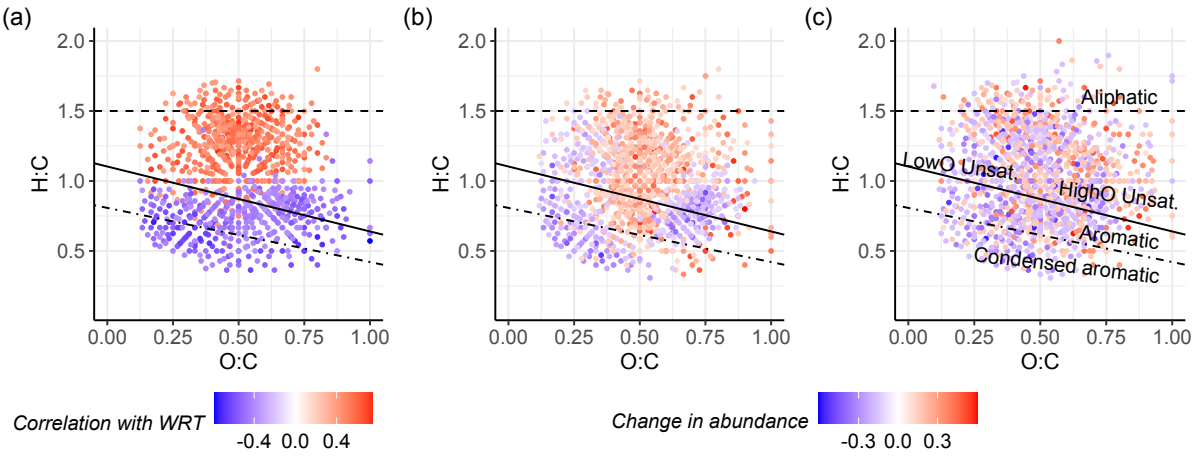


Figure S8. Van Krevelen plots of the change in the abundance of individual molecules along the WRT gradient (a) and after irradiation for waters with WRT < 3 yr (b) and WRT > 3 yr (c). The average change in abundance for all sites pooled with WRT < 3 (b) yr and > 3 yr (c) is calculated using the second end replicate while the first end replicate is used for Figure 5b and 5c. For more details, see the legend of Figure 5.

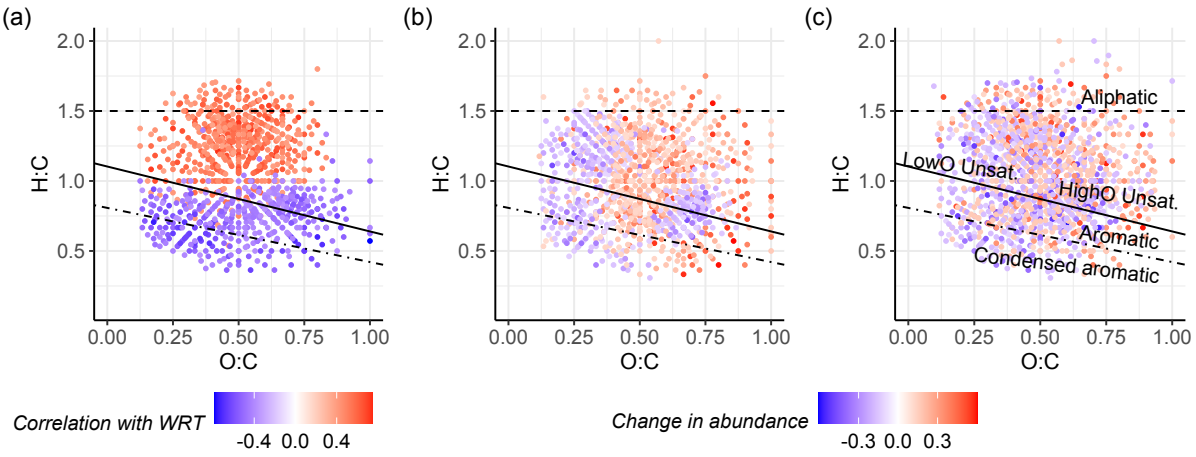


Figure S9. Comparison between the change in the abundance of individual molecules along the WRT gradient (a) and after irradiation for waters with WRT < 3 yr (b) and WRT > 3 yr (c) with Van Krevelen diagrams. The average change in abundance for all sites pooled with WRT < 3 yr (b) and > 3 yr (c) is calculated using the third end replicate while the first end replicate is used for Figure 5b and 5c. For more details, see the legend of Figure 5.

Table S1. Sampling sites and information on the inland water type, sampling region in Sweden, water residence time (WRT) and wavelength integrated AQY. See Groeneveld et al. (2020) and Attermeyer et al. (2018) for more information on the physico-chemical characteristics of the different sites.

Site number	Name	Region	Type	WRT (year)	Weather day of the sampling	AQY (mmol DIC mol photon^{-1})
1	Vättern	Småland	lake	60	rainy	-0.31 ± 0.24
2	Skärshultsjön	Småland	lake	0.12	rainy	0.22 ± 0.07
3	Förhultasjön	Småland	lake	0.72	rainy	0.09 ± 0.01
4	Aneboda	Småland	peat	0	rainy	0.13 ± 0
5	Fiolen	Småland	lake	6.5	windy	0.04 ± 0.01
6	Stråken	Småland	lake	10.7	windy	0.09 ± 0.01
7	Klintsjön	Småland	lake	4.7	windy	0.04 ± 0.03
8	Hisshult	Småland	stream	3.1×10^{-5}	windy	0.13 ± 0.01
9	Storsjön	Jämtland	lake	2.0	cloudy	0.03 ± 0.02
10	Rismyren	Jämtland	peat	0	cloudy	0.09 ± 0.01
11	Ånnsjön	Jämtland	lake	1.1	rainy	0.02 ± 0
12	Duved	Jämtland	peat	0	rainy	0.09 ± 0.01
13	Häggsjön	Jämtland	lake	3.2×10^{-2}	rainy	0.04 ± 0.02
14	Kallsjön	Jämtland	lake	2.3	cloudy	0.06 ± 0.01
15	Åresjön	Jämtland	lake	2.8×10^{-2}	rainy	0.04 ± 0.01
16	Linan	Jämtland	stream	8.7×10^{-4}	rainy	0.07 ± 0.01
17	Ljusnan	Jämtland	river	3.0×10^{-3}	rainy	0.07 ± 0.01
18	Gäddtjärn	Bergslagen	lake	0.26	cloudy	0.06 ± 0.01
19	Svarttjärn	Bergslagen	lake	4.0×10^{-2}	cloudy	0.12 ± 0.01
20	Lilla Sångaren	Bergslagen	lake	1.2	cloudy	0.08 ± 0.01
21	Ljustjärn	Bergslagen	lake	4.3	cloudy	0.02 ± 0.02
22	Hedströmmen	Bergslagen	stream	2.8×10^{-3}	cloudy	0.11 ± 0.01
23	Oppsveten	Bergslagen	lake	0.43	cloudy	0.1 ± 0.01
24	Bjursjöbacken	Bergslagen	stream	1.4×10^{-2}	cloudy	0.12 ± 0
25	Lötsjön	Uppland	lake	4.4	sunny	0.05 ± 0.02
26	Sävjaån	Uppland	stream	6.8×10^{-3}	sunny	0.09 ± 0.02
27	Stensjön	Uppland	lake	5.5×10^{-2}	sunny	0.07 ± 0.01
28	Fyrisån	Uppland	river	6.2×10^{-3}	sunny	0.08 ± 0.01
29	Siggeforasjön	Uppland	lake	0.49	sunny	0.08 ± 0.01
30	Ramsjön	Uppland	lake	1.4	sunny	0.06 ± 0.01

The wavelength integrated AQY is given as mean ± SD (n=3).

Table S2. Variables included in the PCA and change between the start and the end of the irradiation, tested with a Wilcoxon test for paired samples. See Table 1 in Hansen et al. (2016) for references.

Index	Description	Interpretation	change after irradiation* (p value)
DOC			- (<0.0001)
$SUVA_{254}$	Absorption coefficient at 254 nm/DOC	DOM aromaticity	- (<0.0001)
α_{420}	Absorption coefficient at 420 nm	DOM aromaticity/color	- (<0.0001)
Sr	Spectral slope ratio, the slope of the absorbance between 275-295 nm / slope of the absorbance between 350-400 nm	DOM molecular weight	+ (<0.0001)
A:T	The ratio of peak A (ex260/em450) to peak T (ex275/em304)	Amount of humic-like vs. fresh-like compounds	- (<0.0001)
C:T	The ratio of peak C (ex350/em452) to peak T (ex275/em304)	Amount of humic-like vs. fresh-like compounds	- (<0.0001)
FI	Fluorescence index, the ratio of em 470 to 520 nm at ex 370 nm	Contribution of terrestrial vs microbial sources	- (<0.0001)
FrI	Freshness index, the ratio of the em 380 nm to the maximum intensity found between em 420–435 nm at ex 310 nm	DOM freshness	- (<0.01)
BIX	Biological index, the ratio of the intensity at em 380 nm to the maximum intensity between em 420 nm and em 435 nm at ex 310 nm.	Autotrophic productivity	- (<0.001)
HIX	Humification index, calculated at ex 254 nm, as the area of peak under em 435–480 nm divided by peak area under em 300–345 nm	Degree of humification	- (<0.0001)
$\%C_1$	Projection on PARAFAC C_1/C_{total} Peak at ex 250 nm, em 464 nm	Humic-like compounds	ns
$\%C_2$	Projection on PARAFAC C_2/C_{total} Peak at ex 250 nm, em 396 nm		ns
$\%C_3$	Projection on PARAFAC C_3/C_{total} Peak at ex 275/405 nm, em 508		- (<0.01)
$\%C_4$	Projection on PARAFAC C_4/C_{total} Peak at ex 335 nm, em 456 nm		- (<0.0001)

%C_5	Projection on PARAFAC C_5/C_{total} Peak at ex 275 nm, em 324 nm	Protein-like compounds	+ (<0.0001)
O:C	Weighted average O:C ratio	Oxidized compounds	+ (<0.0001)
H:C	Weighted average H:C ratio	Aliphatic compounds	ns

* "-" corresponds to a decrease in the value of the index after irradiation while "+" corresponds to an increase. The variables in bold correlated well to PC1 (Fig S2) and were selected to test the relationships between AQY, DOC concentration and DOM quality. The abbreviations "em" and "ex" mean emission and excitation, respectively.

Table S3. Equations of the models between AQY, DOM quality indices and WRT. AQY is given in mmol DIC mol photon^{-1}, DOC in mg L^{-1}, $SUVA_{254}$ in L mg^{-1} m^{-1}, α_{420} in m^{-1} and WRT in year.

y	x	Equation
AQY	ln DOC	y= 0.03x + 0.01
AQY	$SUVA_{254}$	y= 0.03x -0.01
AQY	ln α_{420}	y= 0.02x + 0.06
AQY	ln Sr	y= -0.15x + 0.05
AQY	logit $\%C_3$	y= 0.046x + 0.20
AQY	$\%C_5$	y= -0.5x + 0.11
AQY	ln H:C	y= -0.27x + 0.07
AQY	FrI	y= -0.22x + 0.2
AQY	ln BIX	y= -0.12x + 0.01
AQY	HIX	y= 0.41x -0.29
AQY	ln C:T	y= 0.04x + 0.02
AQY	A:T	y= 0.01x + 0.01
AQY	ln WRT + 0.001	y= -0.006x + 0.07
ln DOC	ln WRT + 0.001	y= -0.12x + 1.97
$SUVA_{254}$	ln WRT + 0.001	y= -0.18x + 2.86
ln α_{420}	ln WRT + 0.001	y= -0.24x + 0.19
ln Sr	ln WRT + 0.001	y= 0.04x + -0.05
logit $\%C_3$	ln WRT + 0.001	y= -2.72x -0.08
$\%C_5$	ln WRT + 0.001	y = 0.03*exp(0.47x)+0.05
ln H:C	ln WRT + 0.001	y= 0.01x + 0.01
FrI	ln WRT + 0.001	y= 0.02x + 0.61
ln BIX	ln WRT + 0.001	y= 0.04x -0.5
HIX	ln WRT + 0.001	y= -0.01x -0.15
ln C:T	ln WRT + 0.001	y= -0.11x + 1.05
A:T	ln WRT + 0.001	y= -0.39x + 5.41

Table S4. Information on the compounds present only before irradiation (i.e., photolabile), only after irradiation (i.e., photoproduced) or both before and after irradiation (i.e., photoresistant). All information is given as the average for each site (n=30) ± SD.

	Average number of molecules	Average abundance (%)*	Average mass (m/z, unitless)	Average O:C	Average H:C
Photolabile compounds	193 ± 38	2.0 ± 0.5	453 ± 18	0.49 ± 0.03	0.95 ± 0.06
Photoresistant compounds	1106 ± 102	_	389 ± 13	0.52 ± 0.02	0.99 ± 0.06
Photoproduced compounds	304 ± 68	2.4 ± 1.1	424 ± 13	0.53 ± 0.02	1.02 ± 0.04

*Relative abundance pre-irradiation or post-irradiation. The total abundance of photolabile + photoresistant compounds pre-irradiation is 100%, and the total abundance of photoproduced + photoresistant compounds post-irradiation is 100%.

Table S5. Comparison of photomineralization and AQY values with other studies

Study	Category of inland water	Light source (incubation time)	DIC produced (mg L^{-1} h^{-1})	Wavelength integrated AQY (mmol DIC mol photon^{-1})	DIC gain per unit energy absorbed (mg L^{-1} kJ^{-1} m^2)
This study	Peatlands, rivers, streams and lakes	Solar simulator (24h)	0.04 (0 - 0.13)	0.08 (0.02 - 0.22)	0.0001 (0 - 0.0002)
Bertilsson and Tranvik (2000)	Boreal lakes	UV-A irradiation (peak at 340 nm) (8h)	0.05 (0.001 - 0.16)	_	0.0011 (0 - 0.0022)
Groeneveld et al. (2016)	Humic boreal lake	Solar simulator (5h)	0.23 (0.09 - 0.41)	0.23 (0.09 – 0.38)	_
Koehler et al. (2016)	Lakes	Solar simulator (5-88h depending on sample absorbance)	0.09 (0 - 0.49)	0.24 (0.05 - 0.61)	_
Panneer Selvam et al. (2019)	Peatlands, rivers, streams and lakes	UV irradiation (UV-A, UV-B) (48h)	_	_	0.005 - 0.019
Vachon et al. (2016)	Lakes	Solar simulator (24h)	0.02 (0.003 - 0.05)	0.26 (0.1 - 1)	_

Values are given as mean (min - max).