Understanding Dissolved Organic Matter Reactivity and Composition in Lakes and Streams Using Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)

Mike Peacock*[†], Dušan Materić[‡], Dolly N. Kothawala[§], Rupert Holzinger[‡], Martyn N. Futter[†].

[†]Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Lennart Hjelms väg 9, 756 51 Uppsala, Sweden

[‡]Institute for Marine and Atmospheric Research, Faculty of Science, Utrecht University, Princetonplein 5, 3584 CC, Utrecht, Netherlands.

[§]Department of Limnology, Evolutionary Biology Centre, Uppsala University, Norbyvägen 18D 752 36 Uppsala, Sweden.

*michael.peacock@slu.se

Abstract

Here, we present a novel approach for investigating dissolved organic matter (DOM) composition using thermal desorption proton-transfer-reaction mass spectrometry (PTR-MS); a technique that provides insight into the molecular composition of DOM <500 m/z (termed "PTR-DOC"). The applicability of PTR-MS for understanding the relationship between DOM composition and reactivity has yet to be explored. We present results from a synoptic sampling campaign of streams and lakes in a Swedish forest catchment where we measured DOM composition using PTR-MS and traditional optical methods, and conducted DOM biodegradability assays. PTR-DOC comprised up to 12% of the total DOC pool. We found significant relationships between PTR-DOC and DOM degradability; reduced chemodiversity and low concentrations of PTR-DOC were both associated with the total DOM pool being more susceptible to microbial degradation. Furthermore, molecular differences were apparent between headwater lakes, headwater streams, and lakes further down the catchment. Direct linkages between PTR-DOC and optical methods were observed. Using the quantitative data that PTR-MS generates, it could become possible to identify the fluorescing components of

DOM, and the method may be particularly informative in low-DOC waters such as marine environments where PTR-DOC may dominate the total DOM pool.

1. Introduction

The importance of inland waters in the global carbon cycle is well recognised[1]. Lakes process dissolved organic matter (DOM); either by complete degradation which results in emissions of carbon dioxide and methane, or partial degradation, which causes larger DOM molecules to be broken down into smaller molecules[2]. These processes therefore depend on, and can influence, the composition of DOM[3] which, in turn, is influenced by catchment land cover (e.g. forest, mire or agriculture), climate and water residence times[4,5]. As a result, the age of DOM varies throughout the aquatic continuum. In general, older DOM is less reactive and contains a greater proportion of autochthonous (internally produced) material[6].

DOM composition can be investigated using numerous methods of varying complexity. Simple methods including absorbance and fluorescence spectroscopy generate metrics such as specific ultraviolet absorbance (SUVA) and a suite of quality indices[7] which act as proxies for molecular structure and the degree of autochthonous DOM production[8,9]. More complex methods including thermochemolysis GC-MS and ^{13}C Nuclear magnetic resonance spectroscopy provide direct information on functional group composition[10] and DOM aromaticity[8]. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is widely used to identify individual DOM molecular constituents and provide new insights into DOM dynamics[11,12]. Similarly, Orbitrap MS has been suggested as a viable, more widely accessible alternative to FT-ICR MS[13].

Proton-transfer-reaction mass spectrometry (PTR-MS) is a novel method for molecular analysis of aquatic DOM[14]. PTR-MS has previously been used to measure gaseous volatile organic compounds and organic aerosol composition[15-17]. For instance, the method was able to identify differences in DOM composition between intact and degraded tropical peatlands[14]. The method is fast and the only pre-treatment required to analyse aquatic samples is evaporation/sublimation, leaving behind the residue or organic matter for analysis[14]. Unlike

Fourier transform-based methods, PTR-MS is quantitative (i.e. it provides actual concentrations of individual ions) and is unique in this respect amongst high-resolution MS methods. While it is optimised to target low molecular weight (LMW) (up to 500 m/z) DOM, and targets a small fraction of the total DOM pool, it remains unknown how this relates to DOM optical properties and reactivity. To address this knowledge gap, we collected samples from seven lakes and four streams in a boreal forest catchment and analysed them using PTR-MS. We also used traditional optical metrics of DOM composition and investigated DOM degradability with an incubation study.

2. Materials and Methods

Sampling was undertaken on August 19th 2017 in the Gårdsjön research catchment, southwest Sweden (Table S1, Figure S1). The climate is temperate and annual precipitation is 700-1200 mm. Altitude is 100-170 m above sea level[18]. The catchment is predominantly forest covered with *Picea abies* and *Pinus sylvestris* and small areas (10%) of mire. Soils are mainly thin podzols, with bedrock outcrops[18]. Sampling included eleven sites: three headwater lakes, the inflow and outflow of Gårdsjön, three headwater streams draining wholly terrestrial catchments, and one stream draining a headwater lake. Additionally, we sampled two nearby brownwater lakes that had much larger catchments.

Samples for DOM degradability analyses were filtered in-situ with pre-rinsed cellulose acetate 1.2 µm filters and collected in pre-combusted 40 ml glass vials. Samples were stored overnight in the dark at 20°C and transported to the laboratory (six hour journey) where they were stored in a dark incubator at 20°C. These samples were used to measure oxygen (O_2) concentration as a proxy for bacterial respiration[19]. A PreSens O_2 sensor spot (PreSens GmbH, Regensburg, Germany) placed on the inner wall of each vial allowed for measurement of O_2 concentrations non-invasively with a PreSens Fibox 3. The first O_2 reading was taken after all samples had been collected and allowed to adjust to the ambient temperature. Measurements were made twice a day for the first four days, then once a day for three days (seven day incubation). We plotted

89 log-transformed oxygen concentrations against time and calculated slopes for each sample,
90 representing first-order oxygen decay rate constants (kO_2).
91
92 Samples for DOM composition using optical analysis were collected in 100 ml glass bottles and
93 filtered in-situ with pre-rinsed 0.45 µm cellulose nitrate filters, then stored in the dark at 4°C.
94 They were transported on ice the following day to the laboratory. Dissolved organic carbon
95 (DOC) concentrations were measured as non-purgeable organic carbon on a Shimadzu TOC-V_{CPH}
96 (Shimadzu, Kyoto, Japan). Fluorescence and absorbance were measured on an Aqualog
97 spectrofluorometer (Horiba, Kyoto, Japan), and from this we calculated the fluorescence
98 index[20], freshness index[9], humification index[21], SUVA[8] and fluorescence peaks[22] (detailed in SI).
99
100 To prepare samples for PTR-MS analysis[14], a low-pressure evaporation/sublimation system
101 removed water from the samples, leaving residues of semi-volatile and non-volatile OM. The
102 samples were then thermally desorbed at 250°C and measured using a PTR-TOF 8000 (IONICON
103 Analytik, Innsbruck, Austria). Five of the samples were analysed in duplicate, and
104 reproducibility was comparable to other MS methods (Bray Curtis dissimilarity = 5.24%). Peak
105 identification and integration was performed using PTRwid[23]. Chemical formulae were assigned
106 using PTRwid and mMass[24] and classified into structural groupings (e.g. aliphatic)[25]. We term
107 the output of this analysis "PTR-DOC". The PTR-DOC metrics O/C, H/C, mean oxidative state of
108 carbon (OSC), and mean number of carbon (nC) atoms per molecule were calculated for each
109 sample. Percent PTR-DOC was calculated as the sum of individual ion concentrations multiplied
110 by the ion-specific C mass fraction obtained from the chemical formulae, and expressed as a
111 percentage of the DOC concentration from the Shimadzu. We used Shannon's index of
112 diversity[26] as a measure of chemodiversity (refer to SI for further PTR-MS information).
113
114 We conducted principal component analysis (PCA) using Canoco 5.0, with pH, DOC
115 concentration PTR-DOC metrics (listed above), and fluorescence/absorbance metrics to
116 investigate differences in DOM quality. We used Pearson's correlation coefficient to test for
117 relationships between individual ions and DOM fluorescence/absorbance metrics[27]. For these

tests, we only included ions that were detected in all samples. Additionally, we performed Pearson correlation analyses using the PTR-DOC metrics. Correlations analyses were performed using SPSS Statistics 24, with a significance level set at $p < 0.05$.

3. Results and Discussion

The PTR-MS detected a total of 314 unique ions across the dataset ranging from 27.023 m/z to 395.374 m/z (Figure S2, S3), which corresponded to a mean of 5.5% of the measured DOC pool (%PTR-DOC in Table 1). Aliphatic ions were most numerous (72), followed by condensed aromatics (63), aromatics (60), and peptides (63). 246 of the ions were found in all samples. Mean ion concentrations ranged over multiple orders of magnitude, and generally declined with increasing m/z. Two of the three streams had low numbers of ions and low chemodiversity, as did two downstream lakes (Bjurevatten and Västersjön). In contrast, the three headwater lakes had the highest chemodiversity (Table 1). The percent of total DOC detected by PTR-MS (%PTR-DOC) was lowest in the headwater streams and for all samples was inversely related to log-transformed DOC concentration (Figure S4, $r^2 = 0.62$, $p = 0.004$). PCA showed that headwater streams grouped distinctly from lakes and the stream with an upstream lake (Figure 1). Specifically, streams were defined by high values for DOC, SUVA, humification and fluorescence indices, and fluorescence peaks A and M. Upstream lakes were defined by higher values for chemodiversity, %PTR-DOC, freshness index, and total number of ions detected. The two lakes farthest downstream, Bjurevatten and Västersjön, were defined by higher values for O/C and H/C. Running a PCA using only the concentrations of ions detected resulted in similar groupings being detected between sites (Figure S5). Notably, the headwater streams clustered separately from the lakes on both analyses, and the two downstream lakes were sited close to one another.

Table 1. Details of sampling sites showing waterbody type (HWL = headwater lake, DSL = downstream lake, HWS = headwater stream, S = stream draining a lake), lake area and lake mean depth, water pH and dissolved organic carbon (DOC) concentration. Then follow PTR-DOC metrics: ratio of hydrogen to carbon atoms (H/C), ratio of oxygen to carbon atoms (O/C), concentration of DOC measured by proton-transfer-reaction mass spectrometry (PTR-MS) normalised against DOC concentration (%PTR-DOC), mean oxidative state of carbon (OSC), mean number of carbon atoms per molecule (nC), molecular chemodiversity and number of ions. kO_2 is the first-order oxygen decay rate. Values for all analytical replicates are in Table S2.

	Waterbody type	pH	DOC (mg l^{-1})	H/C	O/C	% PTR-DOC	OSC	nC	Chemodiversity	Number of ions	kO_2 (d^{-1})
Gaffeln	HWL	6.2	4.80	1.51	0.42	11.8	-0.62	3.81	4.07	301	0.001
Gaffeln Stream	S	6.0	9.24	1.50	0.46	3.9	-0.52	3.49	3.89	300	0.012
Stora Hästevatten North	HWL	6.5	3.43	1.42	0.36	9.4	-0.64	4.52	4.08	294	0.077
Stora Hästevatten South	HWL	6.5	4.06	1.47	0.39	10.2	-0.64	4.11	4.07	301	0.037
Gårdsjön inflow	DSL	6.7	7.33	1.50	0.41	11.3	-0.63	3.94	4.06	302	0.023
F1 stream	HWS	4.6	14.56	1.39	0.51	0.8	-0.31	3.03	3.46	260	0.325
F2 stream	HWS	4.8	43.29	1.46	0.49	0.4	-0.43	3.15	3.67	289	0.277
F3 stream	HWS	4.9	16.25	1.34	0.34	1.8	-0.63	4.90	3.83	294	0.107
Gårdsjön outflow	DSL	6.9	6.19	1.47	0.40	5.5	-0.62	4.09	4.01	299	0.029
Stora Bjurevatten	DSL	7.0	9.68	1.49	0.48	3.3	-0.47	3.40	3.80	292	0.165
Västersjön	DSL	7.2	8.68	1.52	0.47	1.6	-0.53	3.43	3.78	266	0.037

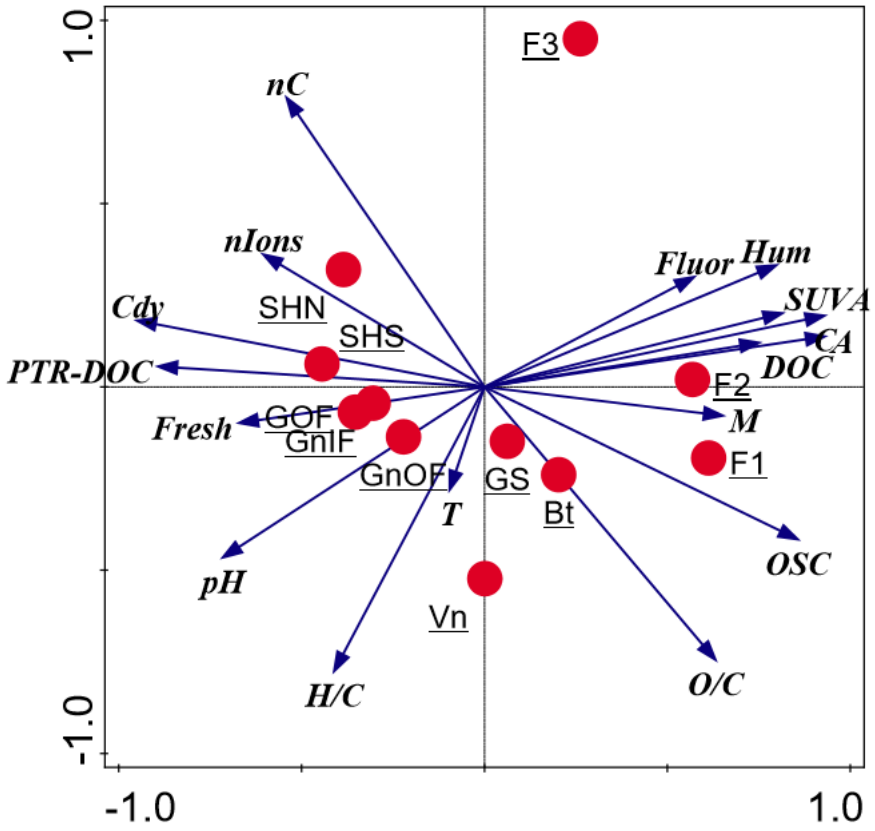
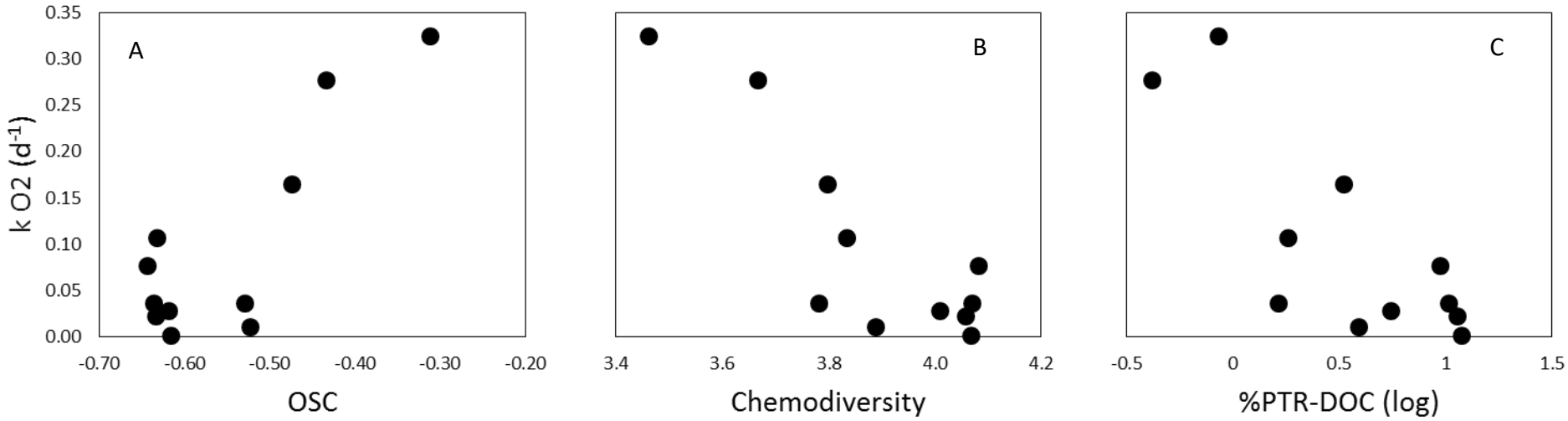


Figure 1. Principle components analysis (PCA) of pH and dissolved organic matter (DOM) composition. Circles indicate sampling sites, whilst DOM metrics are in bold. Site codes are underlined: Gaffeln (GOF), Gaffeln Stream (GS), Stora Hästevatten North (SHN), Stora Hästevatten South (SHS), Gårdsjön inflow (GnIF), F1 stream (F1), F2 stream (F2), F3 stream (F3), Gårdsjön outflow (GnOF), Stora Bjurevatten (Bt), Västersjön (Vn). PTR-DOC metrics: ratio of hydrogen to carbon atoms (H/C), ratio of oxygen to carbon atoms (O/C), concentration of DOC measured by proton-transfer-reaction mass spectrometry (PTR-MS) normalised against DOC concentration (PTR-DOC), mean oxidative state of carbon (OSC), mean number of carbon atoms per molecule (nC), molecular chemodiversity (Cdv) and number of ions (nIons). DOM metrics from fluorescence/absorbance: fluorescence index, freshness index, humification index, SUVA, fluorescence peaks C, A, M, T. 53% of the variation is explained on the x axis and 16% on the y axis.

First-order oxygen consumption rate constants (kO_2) varied considerably, from 0.001 to 0.325 d^{-1}. Significant correlations were found between kO_2 and three PTR-DOC metrics: OSC (r = 0.84), chemodiversity (r = 0.86) and %PTR-DOC (r = - 0.80) (Figure 2). Furthermore, significant correlations were detected between kO_2 and 70 individual ions; meaning 28.5% of ions significantly correlated (mean absolute r = 0.64, mean p = 0.036) (Table S3). Out of these correlations, 67 were negative and only three were positive. The majority of correlated ions were peptides (21), aromatics (13) and condensed aromatics (19).



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173 Figure 2. Scatter plots between first-order oxygen decay rates (kO_2) and A) mean oxidative state of carbon (OSC) (r = 0.84, p = 0.001), B) molecular

174 chemodiversity (r = -0.86, p = 0.001) and C) total concentration of DOC measured by proton-transfer-reaction mass spectrometry (PTR-MS) normalised against

175 DOC concentration (log-transformed) (%PTR-DOC) (r = -0.80, p = 0.003).

Three PTR-DOC metrics, %PTR-DOC, OSC and chemodiversity, showed significant correlations with fluorescence/absorbance measures of DOM composition (mean absolute r = 0.73, mean p = 0.017) (Table 2). Additionally, we found 21 ions which had significant correlations with optical measures of DOM composition (mean absolute r = 0.64, mean p = 0.032, Table S4). For this analysis we only included ions that were detected in all samples, giving a total of 246. Thus, 8.5% of ions had nominally significant correlations.

Table 2. Pearson r values and nominal p values (in parenthesis) for significant ($p < 0.05$) correlations between PTR-DOC metrics and fluorescence/absorbance metrics. PTR-DOC metrics are: total concentration of DOC measured by proton-transfer-reaction mass spectrometry (PTR-MS) normalised against DOC concentration (%PTR-DOC), mean oxidative state of carbon (OSC), and molecular chemodiversity.

	%PTR-DOC	OSC	Chemodiversity
SUVA	-0.73 (0.01)		-0.73 (0.012)
Freshness	0.62 (0.044)		
Humification	-0.66 (0.028)		-0.62 (0.041)
Peak A	-0.85 (0.001)	0.68 (0.02)	-0.82 (0.002)
Peak C	-0.82 (0.002)	0.68 (0.021)	-0.81 (0.003)
Peak M	-0.70 (0.017)		

PTR-MS detected proportionally less of the total DOC pool in headwater streams. These streams drain highly organic peat soils[28] which typically have humic, HMW DOM that is less likely to be detected by PTR-MS, which, in this study, principally targets DOM < 500 m/z. Our findings show that headwater streams (i.e. "new" water) generally have fewer ions and lower chemodiversity of PTR-DOC. Other work in boreal forests has shown that extensive degradation of LMW DOM occurs at the soil-stream interface[29] which could explain the observed lack of chemodiversity in our headwater streams, when compared to lakes. The small sample size makes robust statistical analysis unwise, but these data suggest that DOM composition in streams draining small, terrestrially-dominated catchments can vary considerably across small spatial scales.

The headwater lakes had high chemodiversity and proportionally more PTR-DOC. These are clear, low-DOC lakes, so it is likely that autochthonous and photochemical production result in

more PTR-DOC in these systems[30]. As water moves through the catchment, highly humic autochthonous DOM enters the system from wetlands and headwater streams. In downstream, brownwater lakes, microbial processes should lead to decreases in LMW DOM[31]. Our analysis shows some indication of this, with increased DOM oxidation, lower number of C atoms per molecule, and less PTR-DOC as a percentage of total DOC in downstream waters. All of these can be considered signatures of DOM processing[14]. Indeed, the proportion of PTR-DOC to total DOC approximately halves between the inflow and outflow of Gårdsjön, and declines again in the next lake down the catchment, presumably as a result of DOM processing and also due to the input of DOM from headwater streams. Furthermore, of all the lakes sampled, chemodiversity and total number of ions were lowest in Bjurevatten and Västersjön. These brownwater lakes have large catchments and will receive older water with highly-processed DOM from upstream lakes and streams. This is consistent with other studies reporting molecular alterations related to the ageing and reworking of DOM[27,32].

Both the bulk molecular signal and individual ions detected by PTR-MS were significantly related to DOM degradability, as measured by optode experiments. Such experiments can be informative measures of bacterial respiration and carbon processing[19,33,34]. Correlation analyses produced statistically significant relationships between O_2 losses and both DOM chemodiversity and the oxidation state of carbon. Specifically, the lower the chemodiversity and the more oxidised the PTR-DOC, the more susceptible the total DOM pool appears to be to rapid microbial consumption. Furthermore, our findings show that as the amount of PTR-DOC increases (either as a proportion of the total DOC concentration or as individual ions), DOM degradability decreases, suggesting that a higher concentration of PTR-DOC is associated with a recalcitrant bulk DOM pool. This contrasts with research showing that LMW compounds such as dissolved free carboxylic acids can be important microbial substrates[35], although we observed few of these compounds in our samples, presumably due to their high volatility. It could be that HMW compounds are more bioavailable[36], or that chemical structure (OSC, chemodiversity) is a more informative indicator of DOM reactivity[37], but it is also important to

231 consider that some PTR-DOC is likely to be generated during analysis, by fragmentation of
232 larger ions (see SI).
233
234 This is the first use of PTR-MS to characterise DOM across the aquatic continuum. Despite our
235 relatively small sample size, we observed several statistically significant correlations between
236 PTR-DOC and optical analyses. Furthermore, PCA found similar groupings of sample sites when
237 performed on either the optical data, or the molecular data. Relationships have been found
238 between molecular formulae generated by FTICR-MS and optical indices for DOM from rivers,
239 wetlands and seas[25,27,38], but our data provide evidence PTR-DOC behaves in a similar way to
240 the bulk DOM pool measured by absorbance and fluorescence.
241
242 In conclusion, PTR-MS is a useful tool for understanding DOM. It provides detailed molecular
243 information on DOM composition and appears to act as a proxy for the bulk DOM pool.
244 Furthermore, PTR-DOC can comprise a significant portion of total DOC, and significantly relates
245 to the degradability of the total DOM pool. Future studies with PTR-MS analysis before and
246 after incubation would elucidate whether PTR-DOC is an accessible substrate for microbial
247 respiration. If combined with optical analyses, PTR-MS would enrich understanding of DOM
248 dynamics by giving detailed molecular metrics (chemodiversity, oxidation state) alongside the
249 LMW/HMW, autochthonous/allochthonous, humic/non-humic data provided by
250 fluorescence/absorbance. The fact that the method is quantitative also potentially paves the
251 way to understanding what portions of DOM are responsible for fluorescence properties.
252 Additionally, as PTR-DOC increases proportionally with decreasing DOC, it could be that PTR-MS
253 would be a particularly useful tool in understanding marine and coastal DOM.
254
255 **Supporting Information Available**
256 Supporting information includes: location map of sampling sites, depths and areas of sampled
257 lakes, several additional figures displaying PTR-MS data, two tables of statistical results, and
258 detailed information concerning methods. This information is available free of charge on the

ACS Publications website. Additionally, the full PTR-MS data is available at Figshare: https://figshare.com/s/53ab73e8f7f7a5084ee9.

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Mike Peacock, Dušan Materić, Dolly N. Kothawala, Rupert Holzinger, Martyn N. Futter.