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eprints@whiterose.ac.uk https://eprints.whiterose.ac.uk/ 1 Spatial and temporal variations in aquatic organic matter

2 composition in UK surface waters

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- 10

11 Abstract

- 12 Drinking water is becoming more difficult to treat, especially in the UK, due to changing
- concentration and composition of aquatic dissolved organic matter (DOM). The spatial and
 temporal variations in DOM composition are not well understood.
- 15 This study investigated how DOM composition varies along a north/south gradient in the
- 16 UK, over four years, and between headwaters and reservoirs.
- 17 There were trends in DOM composition metrics from north to south; carbohydrate and
- 18 peptide-like compounds were lower in northern sites, while lipid-like compounds were
- 19 lower further south, suggesting different sources of DOM in north/south catchments. DOM
- collected in Autumn 2021, after a Summer of low rainfall, was more aromatic, less
 oxidised, and more diverse than DOM collected in 2018-2020.
- 22 Decreased lipid content and increased oxy-aromatic content occurred in Autumn, at the
- 23 end of plant growing season, when increased rainfall re-wets catchments and mobilises
- 24 soil OM into surface waters. These seasonal changes in DOM composition coincide with
- 25 increased DOM concentrations in raw drinking water, leading to more challenges for
- 26 drinking water treatment, especially as climate change alters rainfall distribution in the UK. 27
- Keywords: FT-ICR MS, dissolved organic matter, elemental analysis, drinking watertreatment, carbon
- 30
- 31 Synopsis: Understanding natural variations in organic matter composition is important for
- 32 UK drinking water treatment. This study used four years of data to identify trends in
- 33 organic matter composition with latitude, climate, and with time of year.
- 34

- 35 Introduction
- 36 Decay of vegetation and peat leads to natural organic matter (OM) in waterways draining
- 37 from peatland sites that are rich in carbon-containing compounds; OM from peat can
- contain between 44 and 70% carbon (C) ^{1, 2}. Fluvial OM fluxes represent a significant C
- 39 loss from peatland habitats to downstream systems, and to the atmosphere 3, 4.
- 40 In temperate peatlands, OM inputs to aquatic systems vary seasonally due to climate-
- 41 driven changes in vegetation growth and decay, affecting both concentration and
- 42 composition of OM ⁵. OM concentrations in peatland waters are influenced by location,
- 43 climate, weather, vegetation and land use ⁶⁻⁸. Sea spray impacts peatland vegetation,
- 44 decomposition and soil OM, influencing terrestrial and aquatic OM near coastlines ^{9, 10}.
- 45 The UK's maritime climate is changing, with increasing summer temperatures and
- decreasing annual rainfall expected to alter peatland extent and OM concentrations ^{4, 11}.
- Additionally, rising sea levels around UK islands, and more frequent storms will likely
 increase sea spray ¹².
- 49 Variable OM compositions lead to complex issues for drinking water suppliers. In the UK,
- 50 up to 70% of drinking water is sourced from peatland and upland environments, and these
- 51 incoming waters contain high OM and organic C concentrations ^{13, 14}. Any residual OM
- 52 present after drinking water treatment (DWT) can form potentially carcinogenic disinfection
- 53 by-products (DBPs), and so water companies must minimise the residual OM
- 54 concentration in their water ¹⁵. Water companies know to expect seasonal variations in OM
- 55 concentration (e.g. high concentrations in Autumn, due to plant dieback after Summer
- 56 growing season), but seasonal changes in OM composition, and their impact on DWT 57 processes, are less well understood ¹⁶. Water entering DWT plants has become more
- 58 difficult to treat, with water companies reporting that OM concentrations have risked
- 59 exceeding the capacity of treatment works, especially in reservoirs on peat soils, and an
- 60 increase in DBPs in coastal and island reservoirs ^{17, 18}. To continue providing clean and
- 61 safe drinking water, water companies need to know more about OM composition in their
- raw water sources, how it varies over time in their supply area, and how to remove iteffectively and efficiently.
- 64 Dissolved organic matter (DOM, fraction smaller than 0.45μm) is comprised of thousands
- 65 of different compounds of various origins ¹⁹. In peatland headwater streams, compounds
- 66 are from biodegradation of vegetation, peat and photodegradation products, and from
- 67 physical erosion of peat, and contain aromatic compounds, lipids, carbohydrates, peptides,
- 68 amino acids and sugars ^{2, 20}. The relative contribution of these different compounds
- impacts bioavailability, and therefore is important in determining microbial productivity and
 reactivity ²¹, and its treatability during DWT ²².
- 71 Analytical methods have been used to understand more about aquatic DOM composition
- 72 (e.g. UV-Vis, fluorescence, elemental analysis and nuclear magnetic resonance ^{23, 24, 25}).
- 73 Techniques such as Fourier transform ion cyclotron resonance mass spectrometry (FT-
- 74 ICR MS) give much more detail of the molecular composition of complex mixtures ^{7, 17, 26,}
- 75 ²⁷⁻²⁹. Advances in compound libraries and analysis have made FT-ICR MS more
- 76 accessible, making it possible to analyse and interpret data from more samples in a short
- amount of time (e.g. Kitson, Kew, Ding and Bell 30).

- 78 DOM composition metrics can be calculated from elemental content of carbon (C),
- 79 hydrogen (H), nitrogen (N) and oxygen (O), and molecular formula. C/N and oxidative
- $\,$ 80 $\,$ ratios give indicators about DOM treatability and oxidation state, and H/C and DBE $\,$
- 81 (double-bond equivalent) give indicators about DOM structure and reactivity ^{15, 16}.
- 82 Molecular formula allow 'molecular richness' diversity metrics to be calculated ³¹, and
- compounds classes to be assigned, including lipids, carbohydrates, peptides, amino
 sugars, oxy-aromatic phytochemicals and nucleotides ³².
- The aim of this study was to determine how DOM composition from peatland surface
 waters varies over space and time in the UK. Water and DOM samples were collected
- either monthly or yearly from sites within drinking water catchments in four geographical
 areas, and analysed to find their composition using elemental analysis and FT-ICR MS.
 Specifically, we hypothesized:
- DOM composition and molecular diversity would be different at geographic areas of
 the UK, related to mean annual temperatures, rainfall and marine influence (e.g. island
 and mainland locations) impacting on DOM source materials.
- 93 2. DOM composition and molecular diversity would vary over time, with inter-annual and
 94 intra-annual trends, due to inter-annual variations in climate, and intra-annual
 95 variations in vegetation cycles and seasonal weather.
- 96

97 Materials and Methods

98 <u>Study sites</u>

99 There were 192 water samples, from 41 individual sites in upland areas across the UK. Sites were visited up to 24 times between 2018 and 2021, and water samples were 100 101 collected and analysed from 28 catchments (some catchments contained more than one 102 site; Figure 1, Table 1). Water companies are keen to understand remote island drinking 103 water supplies, as they are particularly vulnerable to changes in DOM concentration and 104 composition, and so several sites on islands were included in this study. Locations were 105 chosen in four distinct groups with different mean annual temperatures (MAT) and rainfall 106 (MAR) to determine the impact of location, climate and distance to the sea on DOM (Table 107 1). Drinking water supplies from catchments with peat soils on Shetland Islands (Group 1, 108 highest latitude, coolest max MAT, close to the sea), the Inner and Outer Hebrides (Group 109 2, furthest west, close to the sea), Borders, and Argyll and Bute (Group 3, highest MAR), 110 Yorkshire Dales and Peak District (Group 4, highest MAT, lowest MAR, lowest latitude) 111 regions were included in the study. Water was collected from two or three sites within each 112 catchment, in collaboration with water company partners, and within access constraints. 113 Meta-data for each site, including catchment area, percentage peat cover, land use and 114 vegetation cover, and distance from the sea, was assigned based on observations at the 115 site, or derived from publicly available databases and maps. See Supplementary 116 Information for more detail.

- 117
- 118 Table 1. Groups, number of sites and number of samples in each group, frequency of
- 119 visits and site information. Elevation (m asl) = metres above sea level, Peat (%) =
- 120 proportion of the whole catchment covered in peat. Mean annual maximum and minimum

121 air temperatures and total rainfall (30-year averages, 1991-2020) from UK Met Office

122

Climate Data Portal, from met stations in each area.

| Variable | Longitude (°W) | Latitude (°N) | Elevation (m asl) | Catchment area (km²) | Peat (%) | Distance to the sea (km) | Mean annual air temp (°C) | Mean annual rainfall (mm) | | | |
|----------------------------------------------------------------------------------------------------|-------------------|------------------|----------------------|-------------------------|-------------|-----------------------------|------------------------------|------------------------------------|--|--|--|
| N | 41 | 41 | 41 | 41 | 41 | 41 | | | | | |
| Min. | -7.45 | 53.43 | -0.76 | 0.03 | 52.3 | 0.10 | 5.53 | | | | |
| Max. | -0.90 | 60.82 | 401.00 | 47.13 | 100 | 70.5 | 12.79 | | | | |
| Mean | -3.30 | 57.88 | 131.94 | 5.88 | 90.3 | 11.23 | | 1162.93 | | | |
| Std. Er. | 0.38 | 0.38 | 19.30 | 1.54 | 1.5 | 3.04 | | | | | |
| Group 1, Shetland Islands n = 18, visited yearly, 55 DOM samples | | | | | | | | | | | |
| Mean | -1.21 | 60.32 | 61.76 | 3.29 | 92.4 | 2.04 | Min:5.60 | 1252.34 | | | |
| Std. Er. | 0.04 | 0.04 | 12.57 | 1.02 | 2.7 | 0.35 | Max:9.80 | (Lerwick) | | | |
| Group 2, Outer and Inner Hebrides n = 10, visited yearly, 30 DOM samples | | | | | | | | | | | |
| Mean | -6.90 | 57.33 | 62.78 | 1.42 | 89.6 | 1.78 | Min:6.17 | 1235.52 | | | |
| Std. Er. | 0.19 | 0.11 | 17.54 | 0.53 | 3.0 | 0.30 | Max:11.50 | (Stornoway) | | | |
| Group 3, S. Scotland (Borders, Argyll and Bute) n = 9, visited yearly, 36 DOM samples | | | | | | | | | | | |
| Mean | -4.16 | 55.48 | 267.78 | 16.95 | 86.3 | 21.12 | Min: 4.07 | 1827.17 | | | |
| Std. Er. | 0.37 | 0.07 | 32.61 | 5.27 | 2.3 | 4.31 | Max: 11.40 | (Eskdalemuir) | | | |
| Group 4, N. England (N. Yorkshire, Peak District) n = 4, visited quarterly/monthly, 71 DOM samples | | | | | | | | | | | |
| Mean | -1.79 | 53.66 | 315.05 | 3.78 | 91.8 | 68.27 | Min:6.92 | 831.55 | | | |
| Std. Er. | 0.10 | 0.13 | 42.42 | 2.83 | 4.6 | 1.40 | Max:13.71 | (Sheffield) | | | |

123

124 Sampling frequency

125 The sites were re-visited between 2018 and 2021, yearly, quarterly (every 3 months) or 126 monthly (

127 Table 1) and were therefore subject to different weather and flow conditions. Underlying

128 geology has been shown to impact groundwater contributions to peat streams and rivers at

129 baseflow conditions ³⁴; the annual samples were collected during Autumn when flows were

130 high, therefore the impact of underlying geology on annual samples was considered

131 minimal. Flow conditions varied during quarterly and monthly sampling in Group 4 sites.

132 Sampling was disrupted by the covid-19 pandemic lock down in Spring/Summer 2020,

133 during which only sites local to the authors could be sampled. Due to variable reservoir

and lake surface water levels, the exact sampling location varied by up to 5 m (up/downslope).

135 136



Figure 1. Locations of sites used in this study. Some symbols represent more than one site, as they were too close to separate at this scale. The number of sites in each group are in Table 1.

137

138 Sample collection and water chemistry

- 139 Water pH, electrical conductivity, dissolved oxygen and temperature (Hach MM156
- 140 portable multi-parameter meter), and air temperature, pressure and humidity were
- 141 recorded at time of water sample collection. Two water samples were collected at each
- 142 site. A small sample (50mL) was immediately filtered (0.45 μ m), stored in a cool box (in the
- 143 dark) and later analysed for DOC, total nitrogen, total phosphorous, dissolved nutrients,
- 144 metals and ions concentrations, and absorbance. A large sample (approx. 5L) was filtered
- 145 $(0.7\mu m)$ and particulate organic matter (POM) collected, and rotary evaporated and DOM
- 146 collected (using the method from Moody ²⁵). For all analysis methods, a sub-set of
- 147 samples were analysed in replicate, and certified reference materials were used to
- 148 calibrate equipment.
- 149
- 150 DOM analysis
- 151 Solid DOM samples (n=192), extracted from filtered water using low temperature rotary
- 152 evaporation (<60°C), were analysed by elemental analysis (EA) for their carbon, hydrogen
- 153 (H), nitrogen (N), oxygen (O) and organic C (Corg) content (Elementar Vario MICRO cube).
- 154 10% of samples were analysed in replicate, and re-analysed if the root mean square error
- 155 of the replicates was less than 95%.

- 156 A sub-set of DOM samples (n=77) were analysed by negative-mode electron spray
- 157 ionisation (ESI) Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR
- MS). 24 monthly DOM samples from Group 4 reservoir and headwater paired sites, 32
- 159 from four catchments in Group 3, 15 from two catchments in Group 2 and six from Group 1
- 160 catchment were included in this analysis. Samples were chosen based on sampling
- 161 frequency and site, and enough material available for analysis, to give more information 162 about annual and seasonal variation in DOM composition.
- 163 0.5mL of each sample was added to 0.5mL of LC-MS grade methanol and centrifuged at
- 164 10,000rpm for 5 minutes. 200µL of the supernatant was then drawn into an analytical
- 165 syringe and injected directly into the ESI source. The FT-ICR MS analysis was conducted
- 166 on a 12T Bruker Solarix at the University of Edinburgh, SIRCAMS facility. The following
- 167 tuning parameters were used: flow rate 120μ Lh⁻¹, capillary voltage 4500V, low mass cut 168 off 100m/z, high mass cut off 3000m/z, ion accumulation time 0.2s and time of flight
- 169 0.7ms. In each case 200 scans at 8MW were summed.
- 170 The FT-ICR MS output data were processed using the CoreMS Python library (Corilo, Kew
- 171 and McCue ³⁵; <u>https://github.com/EMSL-Computing/CoreMS</u>). Briefly, raw spectra were
- 172 peak-picked in the range 100 to 700m/z after applying a noise-threshold based on the log-
- 173 intensity distribution of each spectrum ³⁶ and a minimum peak prominence filter of 0.01%.
- 174 Next, internal calibration was performed with a second-degree polynomial fit against a
- 175 reference peak list of CHO containing formula with double bond equivalent (DBE) of -1, 0
- and 1, shown to be highly abundant in DOM ^{28, 37}. The ppm error thresholds for peak
- 177 matching during internal calibration were pre-determined by performing an unconstrained
- assignment of CHO containing formula to each spectra and visualising the intrinsic error
- 179 distribution (i.e. the relationship between m/z error and m/z). Following internal calibration,
- 180 constrained formula assignment was performed using the following elemental constraints:
- 181 C 1–90, H 4–200, O 1–26, N 0–2, S 0–1 and an m/z error tolerance of ± 0.5 ppm.
- 182 Phosphorous was not included in elemental constraints as the ionisation efficiency of P
- 183 molecules during FT-ICR MS is very limited, and adding P to formulae assignments
- 184 increases the number of false assignments. Finally, formula detected in blank methanol
- 185 samples with a prominence of more than 20% were removed from samples acquired on
- 186 the same day as the blank. Assigned peak lists were then imported into the PyKrev Python
- 187 library for analysis ³⁰.
- 188

189 Data and statistical analysis

- 190 CHNO and organic C molar concentrations (from elemental analysis and FT-ICR MS)
- 191 were used to calculate derived metrics: %Corg (organic C portion of total C), DBE/C
- 192 (double bond equivalent per carbon, SI Eq. 1), Cox (carbon oxidation state, SI Eq. 2), OR
- 193 (oxidative ratio, SI Eq. 3), NOSC (nominal oxidation state of carbon, SI Eq. 4), C/N, H/C,
- 194 O/C, and AI (aromaticity index, SI Eq. 5) ^{27, 38, 39}. NOSC, Cox and OR indicate oxidation
- 195 state, with negative NOSC and C_{ox} values representing reduced compounds ⁴⁰. DBE/C
- and AI reflect aromaticity while %C_{org} estimates organic soil contribution. Molar ratios help
- 197 classify compounds and determine degradation state ²⁴. FT-ICR MS data were also used
- 198 to assign molecules to compound classes (lipids, carbohydrates, peptides, amino sugars,

- 199 oxy-aromatic phytochemicals and nucleotides) based on stoichiometry ³² and calculate
- 200 molecular richness ³¹. See the Supplementary Information for details.
- 201 DOM composition metrics were analysed in a general linear model (GLM). Samples
- 202 collected in Autumn (Sep, Oct and Nov), at all sites and groups and across all four years,
- were included (Table S1). Results are reported as significant if p value less than 0.05.
- 204 Post-hoc Waller-Duncan k-Ratio t-tests showed differences within significant groups and
- 205 years. Linear regressions were used to find relationships between DOM composition
- metrics and possible explanatory factors, including air and water temperatures, distance to
 sea and latitude. Results are reported as adjusted R² (adj. R²) values.
- The seasonal cycle of DOM composition metrics was investigated using Group 4 DOM samples, in each calendar month (Jan=1, Dec=12), and in each UK season (Winter=Dec,
- Jan, Feb; Spring=Mar, Apr, May; Summer=Jun, Jul, Aug; Autumn=Sep, Oct, Nov), using a
- 211 repeated measures GLM. To investigate seasonal and within-catchment differences in
- diversity, the molecular formulae data for two Group 4 sites (a headwater stream and
- 213 reservoir surface water within the same catchment, visited monthly for a year) were
- compared. Compounds unique to either site (headwater or reservoir) or sampling month
 (Jan to Dec) were identified. This provides an estimate of diversity, by identifying how
- (Jan to Dec) were identified. This provides an estimate of diversity, by identifying how'unique' each DOM sample is.
- 217
- 218 Results and Discussion
- 219 Spatial analysis
- Most DOM composition metrics differed significantly between groups, but group differences only explained 1-28% of the variation (GLM, partial R²). No metric was
- significantly different across all four groups, though there were some spatial trends. Group
- 1 DOM had higher H/C and DBE/C but lower carbohydrate content (Figure 2). Group 2
- and 3 DOM had intermediate values, differing significantly in H/C and carbohydrate
- content. Group 4 DOM had higher %C_{org} and NOSC but lower in lipid content, C/N and DBE/C. Overall, DOM from island sites (Groups 1 and 2) had lower carbohydrates and
- NOSC but higher lipid content than mainland sites (Groups 3 and 4).
- Latitude and air or water temperature explained 4-23% of variation in DOM composition and molecular diversity (linear regression, p<0.05). Gini-Simpson diversity decreased with
- increasing air temperature (adj. R²=13%, p=0.0114), but Shannon-Wiener values showed
- no significant relationship with temperature or latitude. C/N, oxygen state (O/C, Cox, OR)
- and peptide content were significantly related to distance from the sea (lake and reservoir
- DOM, linear regression, adj. R²=11-49%). However, across all annual samples, distance to
- the sea explained at most 9% of variation, and showed no significant relationship with
- DOC concentration. Models including six physical location parameters explained up to 236 29% of DOM composition variation (Table S2).
- 237 Spatial variation in DOM composition differed significantly between northern and southern
- 238 UK sites, supporting the hypothesis of spatial differences. However, these were not solely
- explained by location (island vs mainland) or strongly linked to latitude, distance to sea or
- temperature, despite their relevance to DOM decomposition and plant growth ^{9, 41}.
- Northern sites had lower carbohydrate, oxy-aromatic and peptide compounds, while lipid

242 content was lower further south, indicating different DOM sources. Low-lipid samples likely

243 originate from terrestrial (plant and peat) sources, whereas high-lipid samples suggest

- 244 microbial origins ⁴². DOM in northern sites was more oxidised and had fewer double bonds 245 per C (more saturated) than further south, suggesting it would degrade more readily at 246 northern sites (Moody and Worrall 2017; Leifield et al 2020).
- 247 Vegetation cover differed between island and mainland sites, with no trees on the islands.
- As a key source of terrestrial DOM, vegetation influences DOM composition ⁵. Removing
- As a key source of terrestrial DOM, vegetation influences DOM composition ⁵. Removing vascular plants from peatlands increased humic to lignin ratios and decreased aliphatic to
- 250 polysaccharide ratios, due to changes in root exudates ⁴³, and planting trees reduced soil
- 251 organic C in moorland soils ⁴⁴. However, in this study, vegetation cover explained only 14-
- 17% of variation in a few DOM composition metrics (Table S2). Site land, which correlated
 with vegetation cover, was significant for C/N, H/C and AI, explaining 15-23% of variation
 (Table S2).
- 255 Soil is a major source of aquatic DOM, and all study sites had at least 50% peat cover.
- 256 Group 4 sites (low lipid content) were likely dominated by terrestrial inputs, with 81-100%
- peat cover. Some Group 1 sites had nearly 50% freshwater cover, where microbial activity
 could increase DOM lipid content ^{20, 42}. However, lipid content was not significantly related
 to peat cover, indicating a more complex DOM-peat relationship.
- 260 Studies by Roth, Dittmar, Gaupp and Gleixner ^{41,} Zhu, Zhao, Bai, Zhou, Chen and Wei ^{45,}
- 261 Verbeke, Lamit, Lilleskov, Hodgkins, Basiliko, Kane, Andersen, Artz, Benavides and
- 262 Benscoter ⁴⁶ found significant DOM differences across latitudes (79°N 65°S), and
- attributed these to temperature, vegetation cover, and DOM degradability, with
- 264 implications for drinking water treatment. The differences in DOM composition across
- latitude, vegetation cover and land use show the challenge facing water companies,
- especially those with large catchments, to treat incoming raw water with highly variableDOM compositions and concentrations. However, the differences in DOM compositions in
- this study explained by Group, latitude, distance to sea and temperature, was at most
- 269 28%, highlighting the need to consider other factors, such as the impact of riparian zone
- peat and vegetation cover. For example, in large reservoir catchments, the vegetation
- cover of a distant part of the catchment may have minimal impact on the in-reservoir DOM
- composition, compared to vegetation in the reservoir riparian zone. Small streams may
- 273 have 100% peat in their riparian zone but have lower % peat cover across the whole
- catchment, leading to lower explanatory power of peat cover in models.
- 275



278 279

280 Figure 2. Box plots of DOM composition metrics for groups 1-4. Groups: 1=Shetland, 281 2=Hebrides, 3=South Scotland, 4=North England. Letters indicate significant differences.

282

283 Temporal analysis - annual

284 Annual comparisons of Autumn DOM samples showed significant interannual differences 285 in most composition metrics (GLM, partial R² 1-44%, Table S1), though no metric differed 286 across all four years. Shannon-Wiener diversity, oxy-aromatic content and C/N ratios 287 remained stable. Notably, 2021 samples were more aromatic, less oxidised, and more 288 diverse, with high amino sugars and peptide content, but lower lipid content than 2018-289 2020 samples (Figure 3).

290 Shatilla and Carey ⁴⁷ linked interannual DOM variation to rainfall and temperature, where

291 high rainfall led to high stream discharge and high DOC concentrations, but inversely

292 affected SUVA and fluorescence indices. Verbeke, Lamit, Lilleskov, Hodgkins, Basiliko,

293 Kane, Andersen, Artz, Benavides and Benscoter⁴⁶ found MAT influenced carbohydrate 294 and aromatic content in DOM, alongside latitude and altitude.

295 Despite interannual variations in UK temperature and rainfall ^{48, 49}, 2021's annual values

296 were not extreme (Figure S1A, S1B). Scotland's Autumn (Sep-Nov) rainfall quantities were 297 consistent across 2018-2021 (382-527mm; Figure S1C). However, Summer rainfall varied 298 widely, from 197mm in 2021, to 436mm in 2019 (Figure S1C), with 2021 also experiencing 299 the driest September (Figure S1D). Drought alters plant root exudates, influencing soil C 300 cycling and decomposition ^{8, 14, 50}. In UK peatlands, late-Summer rainfall mobilises soil OM 301 into surface waters ⁵; therefore dry summers, such as the Summer of 2021, may yield 302 distinctly different aquatic DOM.





307

308 Figure 3. Boxplots of DOM composition metrics for years 2018-2021. Letters indicate 309 significant differences.

310

311 Temporal analysis - seasonal

312 Monthly analysis of Group 4 DOM samples showed significant seasonal shifts in

313 composition (DBE/C, NOSC, Shannon-Wiener diversity, %lipid, %amino and %oxy-

314 aromatic content). Most change occurred in late Summer and Autumn (Figure 4, Figure

315 S2). Oxy-aromatic content remained stable (~70%) from January to August, then

decreased to 55% in Autumn, before recovering in December. Lipid content showed an 316

317 inverse trend, rising from ~20-25% (January to August) to 34-42% in Autumn. Al varied but 318 was stayed low during Autumn. The C/N ratio increased from 25 in Spring to 41 in Autumn 319 before slightly decreasing in Winter. Cox peaked in Spring (April=1.97) and Summer 320 (August=1.48), while OR showed an inverse pattern. Amino sugar content followed a 321 similar trend to Cox, peaking in May and August. Molecular diversity, NOSC and DBE/C 322 also decreased in Autumn.

323





- 330
- 331 The Shannon-Wiener diversity reduction coincides with an increase in lipid-like
- 332 compounds, suggesting a shift in DOM composition. Autumn increased rainfall flushes
- 333 freshly leached plant-derived DOM from plant senescence and decomposition ⁵¹. The H/C
- 334 and O/C values indicate a greater contribution of lignin-derived compounds, while the
- 335 reduced NOSC and decline in oxy-aromatic compounds support the interpretation that the
- 336 DOM is less degraded and freshly mobilised from the soil. Additionally, towards the end of

the growing season, microbial activity in the peat declines, leading to reduced degradation
 and oxidation of DOM ⁵².

- 339 Wilske, Herzsprung, Lechtenfeld, Kamjunke, Einax and von Tümpling ⁵³ showed monthly
- 340 changes in molecular formula intensities in reservoirs in Germany. They discovered
- 341 significant changes in DOM composition, such as aliphatic compounds with low molecular
- 342 weights were more intensive when the reservoir was stratified, and were generally found at
- the surface, and during Summer, aromatic compounds with high molecular weight and
 high O content decreased. These changes impacted on DWT, as highly unsaturated and
- 345 O-rich compounds can be removed by coagulation with Fe or AI, whereas smaller products
- of photo-degradation were precursors of DBPs. Wilske, Herzsprung, Lechtenfeld,
- Kamjunke, Einax and von Tümpling ⁵³ and Chen, Uzun, Tolić, Chu, Karanfil and Chow ⁴⁰
 show that proxies for H/C ratios, and DOM molecular weight, could be useful for water
 companies to determine DOM removal efficiency, particularly via coagulation treatment.
- 350

351 Spatial and temporal analysis within a catchment

352 Headwater DOM had more individual compounds (average=6,554) than reservoir DOM 353 (average=5,453; Figure S2) in the same catchment, suggesting higher DOM composition 354 diversity in the headwater. Across both Group 4 sites, 7,388 compounds appeared only 355 once in a single sample (Figure 5). Headwater DOM had more unique compounds 356 (average=493, 8% of total) than the reservoir (average=123, 2.4% of total). Unique 357 compounds in headwater DOM peaked in Summer, while reservoir DOM had the most in 358 Spring. The high number of unique compounds in headwater DOM coincided with warmer 359 temperatures and lower rainfall; though relationships were not significant. Increased 360 Summer headwater DOM diversity could indicate a higher input of groundwater during 361 baseflow conditions ³⁴.

362



363

Figure 5. The number of unique compounds from the headwater (white) and reservoir(grey) A) on each sampling occasion; with B) mean N content of DOM.

366

- 367 There were several significant relationships between the number of unique compounds on
- 368 each sampling occasion and other metrics (DOM composition and water chemistry),
- explaining 16-88% of the variation (Table 2). DOM samples with high numbers of unique
- 370 compounds had low lipid, peptide and H content, low H/C, O/C and Cox values, and low pH
- and cation (Ca, K, Mg and Na) concentrations. This indicates that the increase in unique
- 372 compounds during Summer (e.g. baseflow conditions) is not due to groundwater input, as
- 373 groundwater has higher cation concentration (specifically Ca, Na and Mg), electrical
- 374 conductivity and higher pH than peat stream water ³⁴.
- 375 DOM samples with high numbers of unique compounds had high DOC concentration; this
- 376 shows that water with high DOC concentrations is more likely to have more unique
- 377 compounds. These DOM samples also had high C, O, N (Figure 5B), carbohydrate, amino
- 378 sugar and oxy-aromatic content, and high C/N and OR. Water with high heavy metal and
- 379 DON concentrations, and a high proportion of organic N (%DON) also had DOM with a
- high number of unique compounds. These higher values also coincide with the end of
- 381 growing season, and a change in weather (the Summer of 2021 had lower than average
- rainfall in the UK ⁴⁹), when compounds that have built up in the soil over dry Summer will be mobilised into the water as the catchments re-wet ⁵⁴.
- 384

Table 2. Relationship between number of unique compounds in all 24 samples with DOM
 metrics and water chemistry metrics. Alkali and alkaline earth metals (AEM) = Ca, K, Mg

| | Variable (y) | n | adj R ² | р | Intercept | Count of unique compounds |
|-------|----------------|----|--------------------|--------|-----------|---------------------------|
| | | | | | | parameter estimate (x) |
| EA | C/N | 24 | 0.43 | 0.0003 | 14.38 | 0.03527 |
| EA | Cox | 23 | 0.20 | 0.0174 | 1.78 | -0.00121 |
| EA | H/C | 22 | 0.33 | 0.0029 | 2.50 | -0.00146 |
| EA | O/C | 15 | 0.43 | 0.0050 | 1.57 | -0.00079 |
| EA | OR | 23 | 0.16 | 0.0355 | 0.61 | 0.00025 |
| MS | %amino | 24 | 0.49 | 0.0001 | 0.68 | 0.00097 |
| MS | %carb | 24 | 0.22 | 0.0116 | 0.50 | 0.00031 |
| MS | %lipid | 24 | 0.52 | 0.0001 | 30.10 | -0.01899 |
| MS | %oxy-aro. | 24 | 0.46 | 0.0002 | 63.00 | 0.01758 |
| MS | %peptide | 24 | 0.46 | 0.0002 | 1.93 | -0.00142 |
| MS | Mean Al | 24 | 0.34 | 0.0016 | 0.06 | 0.0008 |
| MS | Mean C | 24 | 0.60 | 0.0001 | 21.28 | 0.00334 |
| MS | Mean H | 24 | 0.38 | 0.0008 | 24.68 | -0.00253 |
| MS | Mean m/z | 24 | 0.61 | 0.0001 | 411.46 | 0.06774 |
| MS | Mean N | 24 | 0.88 | 0.0001 | 0.37 | 0.00025 |
| MS | Mean NOSC | 24 | 0.56 | 0.0001 | -0.30 | 0.00030 |
| MS | Mean O | 24 | 0.37 | 0.0009 | 7.56 | 0.00132 |
| MS | DBE/C | 24 | 0.53 | 0.0001 | 0.48 | 0.00013 |
| Water | %DON | 22 | 0.39 | 0.0010 | 32.73 | 0.05446 |
| Water | DOC | 24 | 0.63 | 0.0001 | 4.80 | 0.04634 |
| Water | DON | 22 | 0.61 | 0.0001 | 0.18 | 0.00092 |
| Water | Alkali and AEM | 24 | 0.31 | 0.0027 | 17.95 | -0.01502 |
| Water | Heavy metals | 24 | 0.42 | 0.0004 | 0.44 | 0.00153 |
| Water | рН | 20 | 0.48 | 0.0004 | 6.45 | -0.00294 |

and Na; Heavy metals = Al, Fe, Pb, Co, Cu and Zn.

389 Using the molecular composition data showed the number and complexity of DOM 390 compounds (similar to Liu, Tan, Fang, Chen, Tang, Liu and Yu⁵⁵ and Cooper, Chanton, 391 D'Andrilli, Hodgkins, Podgorski, Stenson, Tfaily and Wilson²⁹) found in reservoir water that 392 are not present in headwaters, to show how much in-stream processing occurs in streams. 393 The results also show that the number of unique compounds in a water can be directly 394 related to water chemistry variables, with important implications for carbon cycling and 395 DWT. Water chemistry and DOM metrics can give indications about how many unique 396 compounds are likely to be in a water body, which can be used as a proxy for turnover of 397 DOM – a water body with a high number of unique compounds, with high m/z will have 398 high DOC concentration and therefore lots of DOM available for photo and bio degradation 399 and will therefore have a high turnover. Water with a low number of unique compounds 400 has a more 'stable' and less varied composition, with low m/z and low DOC, and therefore is likely to be more refractory and have lower DOM turnover ^{39, 55}. 401

402

403 Implications for drinking water treatment

404 Water companies need to know the DOM composition in their incoming water supplies, so combining these results with findings from other studies (e.g. Moody ⁵⁶ will allow water 405 406 companies to predict their composition envelopes and build treatment plans to manage 407 with the variations likely to occur. This study showed significant changes in molecular-level 408 DOM composition over time and space. However, smaller molecules, (below the low mass 409 cut off for FT-ICR MS 100m/z) such as short-chain organic acids, and amino acids, small 410 peptides, sugars and phenol from plant decomposition and microbial metabolism, were not 411 included in this analysis ⁵⁷. Including metrics derived from elemental analysis ensured 412 these compounds were included in measures of DBE/C, Cox etc, and show the benefit of 413 analysing DOM by more than one method.

414 In the UK, water companies use water colour and SUVA₂₅₄ to determine the best methods 415 for treating drinking water 'envelopes'. SUVA254 is a good predictor of precursors of DBPs in water treatment ⁵⁸. DBP-precursors with high SUVA₂₅₄, C/N and C/O values resulted 416 417 from C-rich DOM with high molecular weight and aromatic structures. DOM that was rich in 418 N or O, and lower C, resulted in DBP-precursors with low SUVA₂₅₄ values. Only extremely 419 low SUVA₂₅₄ values resulted in low yields of DBPs. Hua, Chao, Huang and Huang ⁵⁸ 420 conclude that SUVA₂₅₄ is a useful parameter for water companies, but it should be used in 421 combination with other indicators, especially when SUVA₂₅₄ is low, as it is not necessarily 422 co-linear with DOM composition or DOC concentration in water from varied locations, as it 423 overlooks UV-inactive DOM components ⁵⁹. Combining SUVA₂₅₄ measurements with high 424 resolution techniques such as NMR or FT-ICR MS will allow water companies understand 425 and treat their incoming DOM more efficiently.

- 426 The seasonal fluctuations in DOM composition found in reservoirs (such as changes in
- 427 DBE/C, molecular diversity and C/N) in this study would likely result in changes to the
- 428 DBP-precursors and could lead to issues for DWT capabilities, especially when further
- 429 enhanced by increased DOC concentrations during late Summer/early Autumn. DOM
- 430 seasonal changes (and their impact on DWT) have been reported in countries with wet/dry
- 431 seasons (e.g. Australia ⁶⁰ and Bangladesh ⁶¹), and snowmelt (e.g. USA ⁶². Autumn leaf fall

- 432 was a significant component in changing DOM composition in forested catchments in
- 433 Maryland, USA ⁶³.
- 434 Shi, Zhuang, Hur and Yang ¹⁵ show how each DOM metric can give information about
- 435 potential DWT efficiency e.g. compounds with high DBE and NOSC are adsorbed by
- 436 ferrihydrite, whereas DOM with more lipid-like compounds were degraded by RuO₂/Ti
- 437 electrolysis. Smith, Moore, Semiao and Uhrín ⁶⁴ used FT-ICR MS to show that ceramic
- 438 membrane filtration significantly decreased aromatic and highly-oxygenated DOM
- 439 compounds (most likely to form DBPs), using unique compound analysis to determine the
- differences between raw and treated water. These studies demonstrate that with enough
- information about the DOM composition, treatment processes can be targeted at specific
- types of DOM, resulting in lower DBPs and more efficient drinking water treatment.
- 443
- 444 Conclusion

445 The results of this study show DOM composition varied spatially across 8° latitude, 446 between the north of Scotland and mid-England in the UK, and temporally, between 2018 447 and 2021, both inter- and intra-annually. These differences were likely related to differences in Summer and Autumn rainfall trends, and plant senescence at the end of the 448 449 growing season. During 2021, when there was lower Summer rainfall, DOM was more 450 aromatic, less saturated and more diverse; these compounds could be absorbed by 451 hematite nanocrystal adsorbent or coagulation during drinking water treatment (Shi et al 452 2021). Higher rainfall (e.g. 2019 and 2020) resulted in DOM with lower diversity and 453 peptide content, low H/C and higher lipid content, and lower NOSC. These samples were 454 more reduced, and would be removed via sand filtration. This study also showed no simple 455 model could explain or predict fluctuations of spatial and temporal DOM, highlighting the 456 need to further investigate the drivers of the identified differences. As water companies are 457 finding it more difficult to supply consistently high quality and quantity of water as the 458 climate changes, these results can help determine future trends in DOM composition and 459 steer water treatment priorities and requirements.

460

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- 472 results (spatial analysis, and temporal analysis), is available online.
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- 474

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