



# Whole-lake spatial variability of organic matter molecular composition and elemental

# inorganic properties in a small boreal Swedish lake

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#### 1 Abstract

2 The composition of organic matter (OM) exerts a strong control on biogeochemical processes 3 in lakes, such as for carbon, nutrients and trace metals. While between-lake spatial variability 4 of OM quality is increasingly investigated, we explored in this study how the molecular 5 composition of sediment OM varies spatially within a single lake, and related this variability 6 to physical parameters and elemental geochemistry. Surface sediment samples (0-10 cm) from 7 42 locations in Härsvatten – a small, boreal forest lake with a complex basin morphometry – 8 were analyzed for OM molecular composition using pyrolysis-gas chromatography-mass 9 spectrometry, and for the contents of twenty-three major/trace elements and biogenic silica. 10 160 organic compounds belonging to different biochemical classes (e.g., carbohydrates, 11 lignins, lipids) were identified. Close relationships were found between the spatial patterns of 12 sediment OM molecular composition and elemental geochemistry. Differences in the source 13 types of OM (i.e. terrestrial, aquatic plant and algal OM) were linked to the individual basin 14 morphometries and chemical status of the lake. The variability in OM molecular composition 15 was further driven by the degradation status of these different source-pools, which appeared 16 to be related to sedimentary physico-chemical parameters (e.g., redox conditions) and to the 17 molecular structure of the organic compounds. Given the high spatial variation in OM 18 molecular composition within Härsvatten and its close relationship with elemental 19 geochemistry, the potential for large spatial variability across lakes should be considered 20 when studying biogeochemical processes involved in the cycling of carbon, nutrients and 21 trace elements or when assessing lake budgets.

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### 23 Keywords

24 Lake sediment; spatial variability; organic matter; molecular composition; Py-GC-MS;

25 elemental geochemistry





## 26 1. Introduction

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28 In lake basins a wide range of factors are known to influence the transport and fate of 29 sedimentary material, such as the location of inlet streams, catchment topography, land-use 30 patterns, fetch, basin morphometry and sediment focusing. Sediment focusing results from a 31 combination of factors such as wind and wave action, basin slope and the settling velocity of 32 different particle sizes, which all contribute to the redistribution of light, fine-grained material rich 33 in clays, organic matter (OM) and associated trace elements from shallower to deeper waters (Blais 34 and Kalff, 1995; Ostrovsky and Yacobi, 1999). While sediment focusing is important, catchment 35 characteristics and lake morphometry can be complex and exert a primary influence on spatial 36 patterns in sediment geochemistry, such as in relation to land use in near-shore areas (Dunn et al., 37 2008; Vogel et al., 2010; Sarkar et al., 2014), complex lake/basin morphometries (Bindler et al., 38 2001; Rydberg et al., 2012) or river inflows (Kumke et al., 2005). The presence of macrophytes or 39 wind-induced water currents have also been shown to affect the spatial distribution of e.g., lead (Pb), phosphorus (P) and OM (Benoy and Kalff, 1999; Bindler et al. 2001). 40

41 Because trace metals and nutrients are primarily associated with - or are part of - OM, studies 42 focusing on the spatial patterns of metal or nutrient accumulation typically include an analysis of 43 the OM content. The two standard approaches to determine sediment OM content are the analysis 44 of loss-on-ignition (LOI; Ball, 1964; Santisteban et al., 2004) or the analysis of elemental carbon 45 (C), C being the main constituent of OM. However, either approach inherently treats OM as a 46 homogeneous sediment component. Recent studies interested in the role of sediments as a long-47 term C sink have likewise mainly treated OM and C as a homogeneous component (e.g., Sobek et 48 al., 2003; Tranvik et al., 2009; Heathcote et al., 2015). Even if this approach is rational from a 49 global perspective of calculating C budgets, treating OM as a homogeneous component is overly 50 simplistic from the perspective of developing insights into the biogeochemical behavior of OM and





51 its influence on C, nutrients and trace metals cycling, and does not take full advantage of the 52 information provided by differences in the OM quality.

53 In boreal lakes the sediment composition is often dominated by OM, typically ranging from 20 54 to 60 % on a dry weight basis, followed by biogenic silica (bSi), which may account for as much as 55 45 % of the sediment dry weight (Meyer-Jacob et al., 2014). The remaining sediment mainly 56 consists of detrital mineral matter and possibly authigenic minerals. Lake OM is an extremely 57 heterogeneous and complex mixture of molecules that are derived from plant, animal, fungal and 58 bacterial residues, and which are either transported into the lake from the surrounding catchment 59 (allochthonous) or produced within the lake (autochthonous). Furthermore, these organic 60 compounds may undergo transformations within the water column and the sediment through both 61 biotic and abiotic processes. Although there have been a few studies where the spatial complexity in 62 OM quality within a whole-lake basin has been assessed using infrared spectroscopy, which yields qualitative information on variations in OM quality (Korsman et al., 1999; Rydberg et al., 2012), or 63 64 using quantitative analyses of photopigments and lipids (Ostrovsky and Yacobi, 1999; Trolle et al., 65 2009; Vogel et al., 2010; Sarkar et al., 2014), little work has been done to detail the compositional 66 variability of the OM matrix as a whole.

67 In this study, we apply a newly optimized pyrolysis-gas chromatography-mass spectrometry 68 (Py-GC-MS) method to characterize the molecular composition of natural OM in surface sediments 69 (0-10 cm) from 42 locations within the lake basin of Härsvatten, a small boreal forest lake in 70 southwestern Sweden that was previously studied for the spatial distribution of Pb and OM contents 71 (Bindler et al., 2001). As an analytical tool to characterize OM composition, Py-GC-MS is a 72 compromise between the quantitative, molecular information obtained from wet chemical extractions associated with liquid chromatography (LC)-MS or GC-MS analyses, and the 73 74 qualitative, non-molecular information provided by high-throughput techniques such as visible-75 near-infrared spectroscopy or 'RockEval' pyrolysis. Beyond the rapidity in terms of analysis and 76 data treatment, our Py-GC-MS method yields semi-quantitative data on >100 organic compounds





77 belonging to different biochemical classes (e.g., lignins, lipids, chlorophylls, carbohydrates, 78 Nitrogen (N)-compounds), which makes it possible to explore the overall molecular composition of 79 OM (Tolu et al., 2015). Our objective here was to comprehensively investigate how the molecular 80 composition of sediment OM varies spatially across a lake with several basins. Our specific 81 research questions were: (i) what are the spatial patterns within a single lake for various organic 82 biochemical classes and compounds?; (ii) how does the spatial pattern of the OM molecular 83 composition relate to physical parameters (i.e., bulk density and water depth) and elemental, 84 inorganic geochemistry of the sediment material?; (iii) which factors or processes (e.g., origin, 85 transport way, decomposition) appear to explain the in-lake spatial variability of the OM molecular 86 composition?

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#### 88 2. Materials and Methods

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#### 90 2.1 Study site and samples

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92 Härsvatten is a boreal forest lake located in southwestern Sweden (58°02' N 12°03' E) in the 93 Svartedalen nature reserve. This acidified, clear-water, oligotrophic and fishless lake has been 94 intensively monitored since the 1980's (national database, Dept. of aquatic sciences and 95 assessment, Swedish university of agricultural sciences, Uppsala, Sweden; www.slu.se), during 96 which time the pH has ranged from 4.2-4.5 in 1983–1987 to 4.7-5.6 in 2010–2014. The lake is 97 dimictic with a thermal stratification between 10 and 15 m depth in the summer. Approximately 80 98 % of the lake bottom is within the epilimnion. The surface areas of the lake and its catchment are 99 0.186 and  $2.03 \text{ km}^2$ , respectively. The catchment is characterized by an uninhabited, coniferous-100 dominated forest (Picea abies Karst. and Pinus sylvestris L.), which extends to the rocky shoreline. 101 The bedrock consists of slow-weathering granites and gneisses, which are covered by thin and 102 poorly developed podsolic soils.





103 The basin of Härsvatten can be divided into four general areas (Bindler et al., 2001): 1) the 104 main south basin, which represents about half of the lake area (sample sites S1-24; maximum 105 depth, 24.3 m) and includes the lake's small outlet stream; 2) a north basin (sample sites N1-11; 106 maximum depth, 12 m), which includes a small inlet stream draining from the headwater lake 107 Måkevatten that enters Härsvatten through a small wetland; 3) an east basin, which has a maximum 108 depth of nearly 10 m (sample sites E1-6) and is separated from the main north-south axis of the 109 lake by a series of islands and shallow sills (<3 m water depth); and 4) a generally shallow (<3 m 110 water depth) central area separating the north/east and south basins (sample sites M1-6).

In total, we analyzed 44 surface sediment (0–10 cm) samples that were collected in winter 112 1997–1998 (Fig. 1) for the study of Pb and SCP (Bindler et al., 2001). The freeze-dried samples 113 have been stored in plastic containers shielded from light and at room temperature. Before further 114 analysis in this study, the samples were finely ground at 30 Hz for 3 min using a stainless steel 115 Retsch ball mill.

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# 117 2.2 Major and trace elements concentrations

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The concentrations of major (Na, Mg, Al, Si, K, Ca, P, S, Mn, Fe) and trace elements (Sc, Ti, V, As, Br, Y, Zr, Ni, Cu, Zn, Sr, Pb) were determined using a wavelength dispersive X-ray fluorescence spectrometer (WD-XRF; Bruker S8 Tiger) and a measurement method developed for powdered sediment samples (Rydberg, 2014). Accuracy was assessed using sample replicates, which were within ±10 % for all elements.

Total mercury (Hg) concentrations were determined using thermal desorption atomic absorption spectrometry (Milestone DMA80) with the calibration curves based on analyses of different masses of four certified reference materials (CRMs). Analytical quality was controlled using an additional CRM and replicate samples included with about every ten samples. The CRM





- 128 was within the certified range, and replicate samples were within  $\pm 10\%$  for Hg concentrations <30
- 129  $\mu$ g kg<sup>-1</sup> and within ±5% for concentrations ≥30  $\mu$ g kg<sup>-1</sup>.
- 130 We also included the OM content (in % dry mass), determined as loss-on-ignition (LOI) after
- 131 heating dried samples at 550°C for 4 h in the earlier study of Bindler et al. (2001).
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- 133 2.3 Biogenic silica concentrations
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Biogenic silica (bSi) was determined by Fourier transform infrared (FTIR) spectroscopy following the approach described in Meyer-Jacob et al. (2014). In brief, sediment samples were mixed with potassium bromide (0.011 g sample and 0.5 g KBr) prior to analysis with a Bruker Vertex 70 equipped with a HTS-XT accessory unit (multisampler). The recorded FTIR spectral information were used to determine the bSi concentrations employing a PLSR calibration based on analyses of synthetic sediment mixtures with defined bSi content ranging from 0 to 100 %.

We calculated the mineral Si fraction (Si<sub>mineral</sub>) from the difference between the total Si
concentration determined by WD-XRF (Sect. 2.2) and the bSi concentration.

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144 2.4 Organic matter molecular composition

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The molecular composition of OM was determined by pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) following the method developed by Tolu et al. (2015). In brief,  $200 \pm$ 10 µg sediment was pyrolyzed in a FrontierLabs PY-2020iD oven (450 °C) connected to an Agilent 7890A-5975C GC/MS system. Peak integration was done using a data processing pipeline under the 'R' computational environment, and peak identification was made using the software 'NIST MS Search 2' containing the library 'NIST/EPA/NIH 2011' and additional spectra from published studies.





In Härsvatten, 160 Py-products were identified, and peak areas were normalized by setting the total identified peak area for each sample to 100 %. The 160 Py-products were reduced to 41 groups of compounds based on the similarities in their molecular structure and origin (Table S1 in supplementary information (SI)).

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158 2.5 Statistical analysis

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160 We performed all statistical analyses using SPSS software package PASW, version 22.0. Two 161 separate principal component analyses (PCA) were performed, one for the elemental geochemistry 162 (i.e., bulk density (B.D.) and contents of OM (LOI), major/trace elements and bSi) and the other for 163 the OM molecular composition. Prior to the PCA, all data were converted to Z-scores (average = 0, 164 variance = 1). Principal components (PCs) with eigenvalues > 1 were extracted using a Varimax 165 rotated solution. Factor loadings were calculated as regression coefficients, which is analogous to r166 in Pearson correlations. For convenience the loadings are reported as percentage of variance 167 explained, i.e., as squared loadings. For all PCs, variables with squared loadings <0.15 are not 168 discussed with respect to that PC. Others variables, e.g., water depth (W.D.) or ratios between 169 elements, were included passively in the PC-loadings plots by using bi-variate correlation 170 coefficients between these variables and the PC-scores of each PC. Hierarchical agglomerative 171 cluster analysis (CA) was performed for the elemental geochemistry and the OM molecular 172 composition datasets using Wards linkages (Ward, 1963) based on squared Euclidean distances. 173 The PC-scores from the PCAs were used instead of the original data in order to eliminate the effects 174 of autocorrelation in the dataset.





- 175 3. Results and discussion
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- 177 3.1. Sediment elemental geochemistry
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- 179 3.1.1 General description and trends
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181 Summary statistics of the elemental geochemical properties of the surface sediments from 182 Härsvatten are presented in Table 1 and the detailed data are given in Table S2 in SI. The sediments 183 from sites M4 and S15 are two outliers because they have a bulk density (B.D.), bSi, OM and 184 elemental contents (e.g., Na, Mg, Al, K) that deviated by more than four standard deviations from 185 the whole-lake average (Table 1). Because these sediment samples also contained too little OM for 186 Py-GC-MS analysis, they are excluded from the data analyses and discussion. Even when excluding 187 these two sites, the elemental geochemical parameters vary considerably across the lake basin, with 188 Hg, Fe, Co and Mn contents illustrating the greatest variabilities (i.e., coefficient of variation, CVs 189 >60 %) and Al, Br, K, Ti, V, Ni, Mg and Ca contents showing the lowest variabilities (CVs: 17-25 190 %; Table 1). For most of geochemical properties, the average to median ratios are approximatively 191 1.0, indicating no extreme values. Slightly higher values were, however, observed for P, Fe, As and 192 Co contents (average:median = 1.2-1.3), while Mn content is associated with extremely large values 193 outside the population distribution (average:median = 4.1).

The lowest B.D. is observed among the three deepest sampling locations (23.5-24.5 m) in the main south basin, where we also find the lowest bSi content and the highest contents in organically bound elements including S, Br, P and certain trace metals, i.e. Cu, Ni, Hg and Zn. These sediments have high OM content (>50 %), but the highest [OM] (57-58 %) are observed among isolated sites that are located close to the shoreline (N1-2, E3, S5, S23; 3.1-7.4 m) and which also include the lowest [Al], [P], [K], [Si<sub>inorganic</sub>], [V] and [Zr]. The highest B.D. and the lowest [OM], [S], [Br], [Cu], [Ni], [Hg] and [Zn] are observed among the shallow sites (1.8-2.5 m) located between the





201 north and east basins and between the larger north and south basins (i.e., sites N10, M1, M5-6), 202 which also contain the highest [bSi], [Sr], [Al], [Y], [Mn] and [Co]. The sediments located at 203 intermediate water depth (9-20 m) in the main south basin (S4, S9, S11, S13-14, S17, S19, S22) are 204 associated with the highest [Fe], [As], [K], [Mg], [Na], [Ti] and [Zr], while among the shallower 205 sites of the south basin we find the highest [Si<sub>inorganic</sub>]. The lowest [Fe], [As], [Co] and [Y] are 206 observed among the sediments of the east basin, and the sediments of the north basin include the 207 lowest [Mn], [Ca], [K], [Mg], [Na], [Sr] and [Zr]. To identify more accurately the most significant 208 relationships existing between the different elemental geochemical properties and to explore more 209 precisely their spatial distribution, the results of PCA and cluster analyses are further presented and 210 discussed.

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212 3.1.2. Principal components of the elemental geochemistry

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214 For the elemental geochemistry dataset, five principal components were extracted. We present 215 only the first four PCs, which together explain 74 % of the total variance (PC1-4<sub>geo</sub>; Fig. 2) because 216 no reasonable interpretation could be made for PC5<sub>geo</sub> (10 % of the total variance; Fig. S1 in SI). 217 PC1<sub>geo</sub> captures 25 % of the total variance and separates bSi and B.D. (negative loadings) from OM, 218 S, Cu, Hg, Ni, Zn and, to a lesser extent, As and Pb (positive loadings; Fig.2a). This means that bSi 219 and B.D. are significantly positively correlated, and both are significantly negatively correlated to 220 OM, S, Cu, Hg, Ni, Zn and, to a lesser extent, As and Pb. If those parameters do not have 221 significant loadings on PC2-5, it means there are not significantly correlated with the parameters 222 found on PC2-5, the PCs being orthogonal to each other. The negative loadings are interpreted as 223 reflecting a bSi-rich fraction, while positive loadings indicate an organic-rich fraction that is 224 enriched in organophilic trace metals (Lidman et al., 2014). For PC2geo, which captures 21 % of the 225 total variance, Si<sub>inorganic</sub>, K, Na, Mg, Zr and Ti have positive loadings, while no element is 226 significantly negatively correlated to PC2geo (Fig. 2a). High PC2geo scores likely represent samples





that are richer in silicate minerals such as quartz and clays (Koinig et al., 2003; Taboada et al.,

- 228 2006).
- 229 Positive loadings on PC3<sub>geo</sub>, which explains 16 % of the total variance, are found for Al and Fe 230 along with As, P and Y (Fig. 2b). This suggests a higher content of Fe and Al (oxy)hydroxides that 231 are known to bind both As and P (Mucci et al., 2000; Plant et al., 2005; Zhu et al., 2013). PC4<sub>eeo</sub> 232 captures 12 % of the total variance and separates Mn, Co, Pb and to a lesser extent Fe (positive 233 loadings) from OM and Br (negative loadings; Fig. 2b). The positive loadings are interpreted as 234 reflecting Mn (oxy)hydroxides, which bind Pb, especially when they contain cobalt (Co) (Yin et al., 235 2011). This interpretation is supported by the positive loadings on  $PC4_{geo}$  of the ratio Mn:Fe, often 236 used as a paleolimnological proxy for bottom water oxygenation (Naeher et al., 2013). The negative 237 loadings could indicate a terrestrial OM fraction that is rich in Br (Leri and Myneni, 2012).
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# 239 3.1.3 Cluster analysis of the elemental geochemistry

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For the cluster analysis of the elemental geochemistry dataset, we selected a solution of six clusters (cluster<sub>geo</sub> 1–6; Fig. 1c). The cluster averages and standard deviations of each physical and geochemical variable are given and compared to whole lake averages in Table S3 in SI, and Table 3 provides the cluster averages for a selection of geochemical parameters.

245 In the south basin, the sediments found at shallower water depth (cluster<sub>geo</sub> 6; n=10) have a 246 higher B.D., are richer in bSi (negative scores on PC1<sub>geo</sub>; Fig. 2a) and have lower than whole-lake 247 average trace metal concentrations (Table 1). In contrast, the sediments from the deeper sites 248 (clustergeo 5; n=3) have the lowest B.D. and lowest bSi content (Table 1), and are enriched in OM 249 and trace metals (positive scores on PC1geo; Fig. 2a). The sediments found at intermediate water 250 depths (cluster<sub>geo</sub> 2; n=8) have positive scores on PC2<sub>geo</sub> (Fig. 2a), and they have an OM content 251 within 10% of whole-lake average while trace metal concentrations are above 10% of whole-lake 252 averages (Table 1). The south basin as a whole has higher P concentrations than the northern,





- eastern and center areas, and in both intermediate and deeper sites, the sediments are rich in Fe and
- As (positive scores on  $PC3_{geo}$ ; Fig. 2b and Table 1).
- The sediments found at shallow water depth between the north and east basins and in the central area (cluster<sub>geo</sub> 3; n=4) have the highest B.D. and are the most enriched in both bSi (negative score on  $PC1_{geo}$ ; Fig. 2a) and Mn and Fe (oxy)hydroxides (positive score on  $PC4_{geo}$ ; Fig. 2b). A small number of shallow, near-shore sampling locations (cluster<sub>geo</sub> 4; n=4) have higher OM concentrations than the whole-lake average, and are enriched in S and trace metals (positive scores on  $PC1_{geo}$ ; Fig. 2a and Table 1).
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- 262 3.2 Sediment organic matter molecular composition
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- 264 3.2.1 General description and trends
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266 Summary statistics of sediment OM molecular composition of the surface sediments from 267 Härsvatten are presented in Table 2 and the detailed data are given in Table S4 in SI. The 268 coefficients of variation for the abundances of the different organic compound groups range from 269 15 to 106 % with an average of  $38 \pm 20$  %, showing a remarkable in-lake variability of OM 270 molecular composition (Table 2). For most of the organic compound groups, the average to median 271 ratios are approximatively 1.0, indicating no extreme values. However, slightly higher values (1.2-272 1.8) are observed for organic compounds derived from plants, i.e. levosugars, lignin oligomers 273 (syringols and guaiacols), *n*-alkanes C25-35, alkan-2-ones C23-31 and tocopherols.

Most of the N-compounds, which usually derive more from algae than from plant (Bianchi and Canuel, 2011), have the highest abundances among the three deepest sampling locations in the main south basin (S12, S18 and S24; 23.5-24.5 m) such as for the abundances of acetamino-sugars (pyrolytic products of micro-organisms exoskeletons; Gupta et al., 2007), phytadienes (i.e., pyrolytic products of chlorophylls; Nguyen et al., 2003), short-chain alkan-2-ones (2K C13-17) and





279 steroids. On the contrary, most of the carbohydrates, which usually derive mostly from plants 280 (Bianchi and Canuel, 2011), have the highest abundances among the sediments situated close to the 281 shoreline (N1-2, E3, S5, S23; 3-7 m) such as for the abundances of phenols, guaiacyl- and syringyl-282 lignin oligomers, long-chain *n*-alkenes (C27-28:1) and diketodipyrrole (N-compounds), all specific 283 of plant OM (Meyers and Ishiwatari, 1993; Schellekens et al., 2009). The highest abundances of 284 long-chain n-alkanes (C23-26:0 and C27-35:0) and mid-chain n-alkanes (C17-22:0) are, however, 285 observed for the shallower sites situated between the larger north and south basins (M5-6; <2 m). 286 Among the shallow sites located between the north and east basin (N10, M1; 2.5-3.0 m) and 287 the shallow and intermediate water depth sites of the south basin (S1-4, S6-11, S13-17, S19-22; 4-288 20 m), we find the highest abundances of degradation products of carbohydrates (i.e., furans and 289 big furans), of proteins and/or chlorophylls (i.e., pyridines o, (alkykl)pyrroles, pyrroles o, 290 maleimide, succinimide, pristenes) and of cell wall lipids (i.e., short-chain *n*-alkenes – C9-16:1 and 291 C13-16:0) as well as the highest abundances of (poly)aromatic compounds indicative of highly 292 degraded OM (Schellekens et al., 2009; Buurman and Roscoe, 2011). The lowest abundances of the 293 (poly)aromatic and certain aliphatic compounds (i.e. n-alkenes C17-22 and C27-28, n-alkanes C13-294 16 and alkan-2-oneds C13-17) are observed among the sediments located close to the shoreline 295 (N1-2, E3, S5, S23), while the two shallow sites situated between the larger north and south basins 296 (M5-6; <2 m) present the lowest abundances for all other organic compounds. To identify more 297 accurately the most significant relationships existing between the different organic compounds groups and to explore more precisely their spatial distribution, the results of PCA and cluster 298 299 analyses are further presented and discussed.

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#### 301 3.2.2 Principal components of OM molecular composition

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A detailed list of the 160 identified organic compounds and the reduced grouping into 41 compound groups is provided in the supplementary information (Table S1 in SI). For this dataset,

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305 six principal components (PC1-6<sub>OM</sub>) were extracted, which explain 85 % of the total variance (Fig. 306 3).  $PC1_{OM}$ , which captures 30 % of the total variance, separates organic compounds that are 307 produced during OM degradation (positive loadings), from molecules of plant origin including 308 those that are readily assimilated (negative loadings; Fig. 3a). Compounds with positive loadings 309 include i) (poly)aromatics (i.e., benzene, acetylbenzene, benzaldehyde, benzenes C2-9 and 310 polyaromatics); and ii) degradation products of carbohydrates ((alkyl)furans; Schellekens et al., 311 2009), proteins and/or chlorophylls (aromatic N, (alkyl)pyridines and (alkyl)pyrroles; Jokic et al., 312 2004; Sinninghe Damsté et al., 1992) and cell wall lipids (short-chain n-alkanes – C13-16:0 –, n-313 alkenes - C9-16:1 - and alkan-2-ones - 2K C13-17 -; Schellekens et al., 2009). The molecules of 314 plant origin with negative loadings are syringol and guaiacol lignin oligomers that are specific for 315 vascular plants, long-chain *n*-alkenes (C23-26:1 and C27-28:1) deriving from plant cell wall lipids 316 (Meyers and Ishiwatari, 1993) and long-chain alkan-2-ones (2K C23-31). Alkan-2-ones C23-31 317 may arise with degradative oxidation of n-alkanes/n-alkenes (Zheng et al., 2011) or are good 318 biomarkers for mosses such as Sphagnum (2K C23-25) and for aquatic plants (2K C27-31) (Baas et 319 al., 2000; Hernandez et al., 2001; Nichols and Huang, 2007). Furthermore, levosugars, Py-products 320 of fresh, high-molecular weight carbohydrates and cellulose from plants (never reported in Py-321 chromatograms of algae or arthropods; Marbot, 1997; Nguyen et al., 2003; Valdes et al., 2013), and 322 the ratio Levosugars:Furans, a proxy for plant OM freshness (Schellekens et al., 2009), have also 323 negative loadings on PC1<sub>OM</sub> (Fig. 3a). Thus, negative PC1<sub>OM</sub>-loadings likely reflect a fresh pool of 324 OM coming from in-lake vegetation.

PC2<sub>OM</sub> captures 14 % of the total variance and positive loadings are associated with (i) midchain *n*-alkanes/*n*-alkenes doublets that are Py-products of resistant biomacromolecules such as cutin, suberin and algaenan (Buurman and Roscoe, 2011); (ii) pristenes, resistant degradation products of chlorophylls (Nguyen et al., 2003); and (iii) hopanoids, which are high-molecular weight pentacyclic compounds of prokaryotes, especially bacteria, origin (Meredith et al., 2008; Sessions et al., 2013). No compounds are significantly negatively correlated to PC2<sub>OM</sub> (Fig. 3a).





High  $PC2_{OM}$  scores thus represent samples rich in organic molecules that are resistant upon degradation.

PC3<sub>OM</sub> explains 13 % of the total variance and separates carbohydrates and N-compounds derived from proteins, chlorophylls and chitin, i.e., pyridines or maleimide-succinimide, acetamidosugars (positive loadings), from aliphatic long-chain *n*-alkanes (C23-26:0 and C27-35:0) coming from plant cell wall lipids (negative loadings; Fig. 3b).

337 On PC4<sub>OM</sub>, which explains 13 % of the total variance, positive loadings are found for proteins, 338 alkylamides and chlorophyll-derived phytadienes that indicate fresh algal organic residues (Peulvé 339 et al., 1996; Nguyen et al., 2003; Fabbri et al., 2005; Micić et al., 2010) as well as acetamido-340 sugars, which derive from the chitin of micro-organisms exoskeletons (Gupta et al., 2007), and 341 hopanoids (bacterial steroids; Meredith et al., 2008; Sessions et al., 2013). No compounds are 342 significantly negatively correlated to PC4<sub>OM</sub> (Fig. 3b). Therefore, PC4<sub>OM</sub> reflects OM input from in-343 lake algae and micro-organisms (e.g., zooplankton). Steroids, which have not yet been reported by 344 Py-GC-MS in aquatic matrices, have positive loadings on this PC4<sub>OM</sub> suggesting that the steroids 345 released by Py in aquatic samples are mainly of algal origin.

346 For PC5<sub>OM</sub>, capturing 8 % of the total variance, positive loadings are related to lignin 347 oligomers, which are specific for vascular plants (Meyers and Ishiwatari, 1993), and 348 diketodipyrrole, a N-compound often reported in soil pyrolysates (Schellekens et al., 2009; 349 Buurman and Roscoe, 2011). No compounds are associated with negative loadings on  $PC5_{OM}$  (Fig. 350 3c). Interestingly, the long-chain *n*-alkanes from plant cell wall lipids do not have positive loadings 351 on PC5<sub>OM</sub>. We therefore interpret PC5<sub>OM</sub> to relate to OM inputs from the forested catchment, which 352 is dominated by coniferous species. Coniferous trees generally have higher lignin contents as 353 compared to other vascular plants (Campbell and Sederof, 1996), while they contain much lower 354 amounts of *n*-alkanes than other plant species (Bush and Mcinerney, 2013).

355  $PC6_{OM}$  captures 7 % of the total variance and has four compounds with significant positive 356 loadings, i.e., benzene, two benzenes with oxidized side-chain and furans with long side-chains





- (big\_furans; Fig. 3c). PC6<sub>OM</sub> may represent an intermediate degradation status of plant residues,
  between the lignin oligomers or levosugars (fresh) and the degraded polyaromatics and benzenes
  C2-9 or furans with short side-chain (i.e. (alkyl)furans).
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- 361 3.2.3 Cluster analysis of OM composition
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As with the elemental geochemistry dataset, a solution of six clusters (cluster<sub>OM</sub> 1–6) was relevant to represent the data on the spatial heterogeneity of OM molecular composition (Fig. 1d). Each cluster is associated with one or a few of the OM types that were identified by the PC1-6<sub>OM</sub> (Fig. 3; Sect. 3.2.1). The cluster averages and standard deviations of each organic compound are given and compared to whole-lake averages in Table S5 in SI. Table 3 provides the cluster averages for ratios indicative of OM source types and their degradation status based on literature data and on the distribution of the organic compounds on PC1-6<sub>OM</sub>.

370 In the south basin, the majority of sites found at shallower and intermediate water depths group 371 in cluster<sub>OM</sub> 3 (n=14) and are enriched in degraded, resistant and bacterial OM (positive scores on 372 PC1<sub>OM</sub>; Fig. 3a). The deep basin sites (cluster<sub>OM</sub> 2; n=3) are enriched in fresh algal and 373 zooplanktonic OM (positive scores on PC4<sub>OM</sub>; Fig. 3b). Accordingly, the values for the ratios 374 indicative of higher proportions of fresh, labile algal OM, based on N-compound or chlorophyll 375 composition, are higher in the deeper sites as compared to whole-lake averages, while the values 376 are below or within  $\pm 10$  % of whole-lake averages in the sediments found at shallower and 377 intermediate water depths (Table 1). In contrast, these two types of south basin sites have similar 378 values, and lower as compared to whole-lake averages, for the ratios indicative of plant OM 379 freshness based on carbohydrate or lignin composition. Furthermore, the clusters<sub>OM</sub> 2 and 3 are 380 characterized by higher values for the ratios specific of algal versus plant OM based on the 381 proportions of N-compounds versus carbohydrates and chlorophylls versus lignin and long-chain n-





382 alkanes and alkan-2-ones (Table 1). The rest of the south basin sites, fall within cluster<sub>OM</sub> 1 (n=1), 5

383 (n=2) or 4 (n=1), which are described below.

The majority of sites in the northern half of the lake group within cluster<sub>OM</sub> 1 (n=15) with isolated shallower sites falling within clusters<sub>OM</sub> 3 (n=1), 4 (n=2) and 5 (n=2). The sediments of cluster<sub>OM</sub> 1 are rich in fresh plant OM coming from in-lake productivity (negative scores on PC1<sub>OM</sub>; Fig. 3a) and have higher values than whole-lake averages for the ratios specific of in-lake vs terrestrial plant OM and of plant OM freshness (Table 1). In contrast, the values for these ratios are below 10% of whole-lake averages for the south basin sites, indicating that terrestrial input is the main source of plant OM to the sediments of the main basin of Härsvatten.

391 The cluster<sub>OM</sub> 5 represents some near-shore locations (n=4), which are enriched in OM derived 392 from the coniferous-forested catchment (positive scores on  $PC5_{OM}$ ; Fig. 3c). The cluster<sub>OM</sub> 4 (n=4), 393 which groups shallow sites located close to the lake outlet (south basin, S16) and between the north 394 and east basins (N10 and M1), is characterized by high proportions of degraded, resistant and 395 bacterial OM (positive scores on PC5<sub>OM</sub>; Fig. 3a). Two shallow sites of the central area (cluster<sub>OM</sub>) 396 6; n=2) show an enrichment in aliphatic molecules derived from plant cell wall lipids (negative 397 loadings on PC3<sub>OM</sub>; Fig. 3b). Both clusters<sub>OM</sub> 4 and 6 have values for the ratio indicative of in-398 lake:terrestrial plant OM above 10% of the whole-lake average, while the values for the ratios 399 specific of algal vs plant OM and of algal and plant OM freshness based on N-compounds and 400 carbohydrates composition are below 10% of whole-lake averages (Table 1). Cluster<sub>OM</sub> 6 differs 401 from cluster<sub>OM</sub> 4 by its higher values for the ratios specific of algal and plant OM freshness based 402 on chlorophyll and lignin composition.

403

#### 404 3.3 Combined spatial patterns of elemental and organic biogeochemistry

405

406 The surface sediments used in this study comprise the uppermost 10 cm. Given the inherent 407 variation in sedimentation rates across a lake basin, each bulk sample represents material deposited





408 over different timescales. We know from the developmental work for our Py-GC-MS method using 409 annually laminated sediments that there are transformations in OM composition within the 410 uppermost few cm, i.e., the first few years following deposition (Tolu et al. 2015). Thus these bulk 411 sediment samples provide initial insights into the spatial variability in molecular OM composition 412 within a lake basin resulting from longer-term sedimentation processes (including those within the 413 sediment) reflecting years to decades.

414 The distribution of both clusters<sub>geo</sub> and clusters<sub>OM</sub> within Härsvatten shows a similar general 415 pattern (Fig. 1c and 1d) where a main feature is the separation of most of the sample locations from 416 the north and east basins (clustergeo 1 and cluster<sub>OM</sub> 1) from those in the main south basin 417 (clusters<sub>geo</sub> 2, 5, 6 and clusters<sub>OM</sub> 2, 3). The other similarities are i) the separation of the sediments 418 within the main, south basin according to water depth, with cluster<sub>geo</sub> 5 and cluster<sub>OM</sub> 2 grouping 419 the deeper sites and clusters<sub>geo</sub> 2, 6 and cluster<sub>OM</sub> 3 grouping the shallow and intermediate depth 420 sites; and ii) the separation of the shallower sites that are located close to the shore (cluster<sub>geo</sub> 4 and 421 cluster<sub>OM</sub> 5) from the ones that are found between the north and east basins and between the central 422 area and the south basins (cluster $_{geo}$  3 and clusters<sub>OM</sub> 4 and 6).

423

424 3.3.1 Spatial variability in the sediment composition in the main south basin

425

426 As shown previously for OM (as % LOI) and Pb (Bindler et al. 2001), there is a physical and 427 inorganic geochemical gradient from shallower to deeper waters reflecting sediment focusing in the 428 south basin of Härsvatten. B.D. and bSi decrease from shallower (cluster<sub>geo</sub>6) to intermediate 429 (cluster<sub>geo</sub>2) to deeper areas (cluster<sub>geo</sub>5), whereas there is a progressive enrichment in organic 430 matter and trace elements with increasing water depth (Fig. 1c; Table 1). For example, B.D. decreases from ~0.07 to 0.03 g cm<sup>-3</sup> while OM and Hg increase from ~34 to 52 % and from ~230 to 431 920 ng g<sup>-1</sup>, respectively, in shallower versus the deepest locations. At intermediate depths 432 433 (clustergeo2), OM, B.D., bSi and most trace metals (i.e., Cu, Ni, Hg, Zn) are between those of





434 shallow and deep locations. Sediment focusing is thus an important process for sediment 435 geochemistry in the large, deep basin of Härsvatten, which presents a relatively simple 436 morphometry. The sediments found at shallower (<11 m; cluster<sub>geo</sub> 6), intermediate (11-21 m; 437 cluster<sub>geo</sub> 4) and deeper water depths (>23 m; cluster<sub>geo</sub> 5) would correspond approximatively to 438 erosion, transportation and accumulation bottoms, respectively (Håkanson, 1977). The bSi decline, 439 from ~15 to 4 %, would reflect the fact that the diatom assemblage in many acidified lakes, such as 440 the lakes in Svartedalen, has been shown to be dominated almost exclusively by benthic diatoms, 441 with a near absence of planktonic diatoms (e.g., Andersson, 1985; Anderson and Renberg, 1992).

442 In this main basin of Härsvatten, OM originates from a combination of autochthonous algal 443 production and allochthonous input (Sect. 3.2.2). The dominance of benthic diatoms in acidified 444 lakes and the declining bSi content with depth would indicate the algal material in deeper areas of 445 the basin should derive from resuspended benthic algal production. However, this benthic algal 446 production is not reflected in the OM molecular composition. The sediments from shallow and 447 intermediate water depths (cluster<sub>OM</sub> 3) are mainly composed of degraded, resistant and bacterial 448 OM, while the sediments from deeper sites (cluster<sub>OM</sub> 2) are enriched in fresh algal OM (Fig. 1d; 449 Sect. 3.2.2). Although our results are based on the top 10 cm of sediment and thus account for 450 different sediment ages, we suggest that the higher proportions of decomposed algal material, based 451 on N-compound and chlorophyll composition (Table 1), at shallower and intermediate water depths 452 (<21m) than at the deepest sites (23.5–24.5 m) reflect higher mineralization rates of OM in 453 shallow/intermediate areas, most probably due to more oxic conditions. Oxic conditions are known 454 to prevail in epilimnitic and metalimnitic sediments (Ostovsky and Yacobi, 1999): the epilimnion in 455 Härsvatten has been assessed to extend to 10-15 m water depth. Moreover, the elemental 456 geochemistry indicates that the sites found at intermediate water depths (clustergeo 6; 11-21 m) 457 correspond in the sediment-focusing model to transportation bottoms, which experience recurrent 458 resuspension events that favor gas exchanges and mineralization of OM (Ståhlberg et al., 2006). 459 Occurrence of oxic conditions at intermediate depths in the south basin are supported by the higher





460 concentrations of Fe, Mn, As, Co and P and the high Fe:Al values, this combination of parameters 461 being often indicative of Fe and Mn (oxy)hydroxides (Table 1; Sect. 3.1.1). In line with our 462 hypothesis, higher OM mineralization rates in oxic versus anoxic sediments have previously been 463 reported (Bastviken et al., 2004; Isidorova et al., 2016). However, in contrast to the more algal-464 derived OM, we do not observe significant differences between the sediments of 465 shallower/intermediate water depth and the deepest sites for ratios indicative of plant OM freshness 466 (Table 1). Because plant OM is mainly of allochthonous origin in this basin, our results indicate 467 that primarily autochthonous algal OM is mineralized in the epilimnitic and metalimnitic sediments 468 of this deeper, steeper-sloped, basin of Härsvatten. This is consistent with the suggestion that 469 allochthonous OM is recalcitrant to sediment mineralization after its degradation in the catchment 470 and within the water column (Gudasz et al., 2012).

471 Overall, our molecular characterization of OM in the south basin suggests an enrichment in 472 algal versus allochthonous OM (e.g., higher N-compounds:carbohydrates) in the deeper areas of a 473 deep, simple lake basin, in line with previously reported sediment C:N ratios along lake-basin 474 transects (Kumke et al., 2005; Dunn et al., 2008; Bruesewitz et al., 2012). Given our data on the 475 degradation status of the different OM source-pools, we believe that this trend in OM quality results 476 from preferential degradation of algal versus allochthonous OM in sediments at 477 shallower/intermediate water depth in addition to the known focusing of living, and residues of, 478 authochthonous OM towards deeper sites (Ostrovsky and Yacobi, 1999).

479

480 3.3.2 Spatial variability in the central, north and east basins and near-shore locations

481

In the northern half of the lake, 11 of 19 locations fall within cluster<sub>geo</sub>1 (Fig. 1c), which distinguishes itself geochemically only by somewhat lower than average concentrations of elements often associated with (oxy)hydroxides (i.e., Fe, Mn, As, P and Co; Table 1 and Sect. 3.1.2). Sediments from the shallowest locations can potentially fall in one of four different clusters





486 (clusters  $_{geo}1$ , 3, 4 or 6). Thus, for the northern half of the lake there is no evidence of sediment 487 focusing. The effect is either limited by the more gentle slopes of the north and east basins (Blais 488 and Kalff, 1995), modified by the water circulation resulting from the prevailing winds towards the 489 north-east (Bindler et al. 2001, Abril et al., 2004), and/or interrupted by aquatic vegetation that acts 490 as a sediment trap (Benoy and Kalff, 1999). Indeed, aquatic vegetation represents a major source of 491 OM to the sediments of the northern, eastern and central basins (clusters<sub>OM</sub> 1, 4 and 6; Fig. 1d; 492 Table 1 and Sect. 3.2.2). The enrichment of aquatic plant OM in these sediments is consistent with 493 field observations during the original sediment coring in winter 1997, where mosses and *Isoetes* (a 494 vascular angiosperm plant) were observed in some parts of the lake to a depth of at least 10 m 495 (Bindler et al., 2001). The presence of such submerged vegetation in Härsvatten is favored by its 496 acidic, clear water (i.e., deeper light penetration), as previously observed for other acidified boreal 497 Swedish lakes, such as the nearby lake Gårdsjon (Andersson, 1985; Grahn, 1985). Benthic aquatic 498 vegetation is also favored in the northern half of Härsvatten by the more gentle slopes, 499 comparatively shallow water depth and thus greater availability of light than in the deep, steeper-500 sloped south basin where allochthonous input appears as the main source of plant OM (Sect. 3.2.2; 501 Table 1).

502 The sediments found across the north and east basins and at the deeper sampling site of the central area (clusters<sub>OM</sub> 1; Fig. 1d) have the highest proportions of fresh, labile plant OM 503 504 considering the whole lake (Sect. 3.2.2; Table 1). Also, the proportions of fresh, labile algal OM is 505 as high as in the deeper anoxic sediments of the main south basin and two times higher than in the 506 sediments found at shallow water depth in the south basin and central areas, although these sites 507 span the same depth range (3-11 m) and have relatively similar bSi contents (Table 1). These 508 results indicate the accumulation of fresh autochthonous, both plant and algal, OM in sediments 509 associated with in-lake vegetation even if they are below or within the epilimnion (i.e., supposed 510 oxic conditions). A possible explanation is that the input of labile, decomposing in-lake plant OM 511 consumes oxygen and results in locally anoxic conditions in the sediment, which in turn lower OM





mineralization rates (Bastviken et al., 2004; Isidorova et al., 2016). This hypothesis may explain the lower than whole-lake average concentrations of elements or elemental ratios often associated with (oxy)hydroxides (i.e., Fe, Mn, As, Co, P contents and Fe:Al) in these epilimnitic/metaliminitic sediments (cluster<sub>geo</sub> 1; Table 1). Our interpretation is consistent with laboratory experiments, where, for example, Kleeberg, 2013 had shown that inputs of macrophyte residues to sediments results in oxygen depletion and microbially mediated reduction of Fe and Mn oxides.

518 The shallow sites located between the north and east basins and between the central area and 519 the south basin (i.e., cluster<sub>geo</sub> 3 and clusters<sub>OM</sub> 4 and 6; Fig. 1c and 1d) have higher than whole-lake 520 averages bSi contents and values for the ratio in-lake:terrestrial plant OM, suggesting that these 521 sediments receive plant OM from in-lake vegetation and algal OM from benthic production (Table 522 1). However, the proportions of fresh, labile plant and algal OM based on N-compound and 523 carbohydrate composition in these central sediments are much lower than in the sediments found 524 across the north and east basins (Table 1). Probably, these central areas are not sites for aquatic 525 vegetation growth, but receive in-lake plant OM produced within the north and east basins that has 526 been degraded during transport and/or is degraded at these shallow central sites due to more oxic 527 conditions as suggested by a higher occurrence of Fe and Mn (oxy)hydroxides (Fe, Mn, As, Co, and 528 P contents, Fe:Al and Mn:Fe above 10% of whole-lake averages; Table 1). Among these shallow 529 central sites, two locations (cluster<sub>OM</sub> 6) are specifically rich in plant lipids (i.e., C23-35:0; Table S3 530 in SI) and have high proportions of fresh plant OM based on lignin composition (Table 1). This 531 suggests preservation of plant cell-wall lipids and lignin with respect to carbohydrates at these two 532 shallow sites, in agreement with the known faster assimilation of carbohydrates versus lipid and 533 lignin structures (Bianchi and Canuel, 2011). However, no reasonable hypothesis could be given to 534 explain this difference in OM molecular composition between the sediments at sites M5-6 and the 535 ones at sites N10 and M1 given their similar water depth and elemental geochemistry.

536 The sediments found in a small number of near-shore locations (cluster<sub>geo</sub> 4 and cluster<sub>OM</sub> 5) 537 predominantly accumulate OM derived from the coniferous-forested catchment and have high





- concentrations of S and trace metals (i.e., Hg, Pb and Zn; Table 1), which are known to accumulate
  in organic soils due to pollutant deposition (Lidman et al., 2014). Three of the sediments sites are in
  two more-sheltered bays at the northwestern corner and the southern end of the lake, which would
  be more protected from wind circulation (Bindler et al. 2001, Abril et al. 2004).
- 543 3.3.3 Implication for in-lake and/or global elemental (e.g., C, nutrients, trace metals) cycling
- 544

545 The molecular composition of natural OM has been shown to exert a strong influence on key 546 biogeochemical reactions involved in in-lake and global cycling of C, nutrients and trace metals, 547 such as C mineralization or nutrients/trace metals sorption and transformations into mobile and 548 bioavailable species (Drott A et al., 2007; Sobek et al., 2011; Gudasz et al., 2012; Tjerngren et al., 549 2012; Kleeberg, 2013). Our work demonstrates that OM molecular composition can vary 550 significantly within a single lake system in relation to basin morphometry, lake chemical and 551 biological status (e.g., presence of macrophytes, which is influenced by, e.g., acidification) and the 552 molecular structure/properties of the different OM compounds (e.g., higher resistant of 553 allochthonous versus autochthonous OM upon degradation). Our results further show that it may be 554 problematic to extrapolate data on OM composition from only a few sites or one basin when scaling 555 up to a whole lake. Thus, investigating sedimentary processes and the resulting fate of C and trace 556 elements using sampling strategies focused on the deepest area of a lake or on single transects from 557 shallower to deeper sites, may not fully capture the variation in either elemental geochemistry or 558 OM composition.

559 Overall, this study underlines that the OM molecular composition and its spatial heterogeneity 560 across lake are two factors that should be considered to better constrain processes involved in the 561 fate of C, nutrients and trace metals in lake ecosystems, to improve whole-lake budgets for these 562 elements and to better assess pollution risks and the role of lakes in global elemental cycles.

563





#### 564 Author contribution.

- 565 J. Tolu and R. Bindler designed research. J. Tolu performed Py-GC-MS analyses with help from L.
- 566 Gerber and did the data treatment with the data processing pipeline of L. Gerber. J. Tolu and J.
- 567 Rydberg performed XRF and mercury analyses. J. Tolu and C. Meyer-Jacob performed FTIR
- 568 measurements and C. Meyer-Jacob determined the inferred bSi. J. Tolu, J. Rydberg, C. Meyer-
- 569 Jacob and R. Bindler interpreted the data. J. Tolu prepared the manuscript with consistent
- 570 contributions from J. Rydberg, R. Bindler and C. Meyer-Jacob.

571

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# Tables

Table 1. Su	ımmary stati	stics for the sedi	iment e	lemental ge	eochemistry	7				
		Whole sample c	ollectio	on except t	he two out	liers	0	Outliers (	(M4, S15)	
	Unit	$Av.^{a} \pm sd^{b}$	CV <sup>c</sup>	Median	A:M <sup>d</sup>	Min <sup>e</sup> -Max <sup>f</sup>	Av. $\pm$ sd	CV <sup>c</sup>	Median	Min-Max
W.D.	m	<b>9</b> ± 7	74	7	1.23	2-25	$3.4 \pm 0.6$	19	3	2.9-3.8
B.D.	g cm <sup>-3</sup>	$\textbf{0.06} \pm 0.02$	38	0.06	1.05	0.02-0.13	$\textbf{0.67} \pm 0.09$	14	0.06	0.61-0.74
bSi	%	$13 \pm 6$	48	12	1.05	4-25	$\textbf{1.9} \pm 0.2$	0	12	1.7-2.0
LOI	%	$38 \pm 10$	26	37	1.01	10-58	$\textbf{3.6} \pm 0.8$	20	37	3.0-4.1
[S]	mg kg <sup>-1</sup>	$\textbf{11876} \pm 5920$	50	11305	1.05	4685-29190	$\textbf{2570} \pm 552$	21	10610	2180-2960
[Br]	mg kg⁻¹	$149\pm35$	23	152	0.99	71-225	$16 \pm 7$	44	148	11-21
[Cu]	mg kg <sup>-1</sup>	<b>34</b> ± 13	37	32	1.07	12-75	<b>9</b> ± 3	31	31	7-11
[Ni]	mg kg <sup>-1</sup>	$19 \pm 4$	24	19	0.99	10-27	$12 \pm 4$	35	19	9-15
[Hg]	µg kg <sup>-1</sup>	$\textbf{337} \pm 202$	60	286	1.18	117-1152	$28 \pm 9$	33	274	21-34
[Pb]	mg kg <sup>-1</sup>	$192 \pm 74$	39	184	1.05	58-422	$22 \pm 16$	76	178	10-33
[Zn]	mg kg <sup>-1</sup>	$\textbf{219} \pm 108$	49	207	1.06	43-445	$50 \pm 16$	31	200	39-61
[Al]	%	$3 \pm 1$	17	3	1.06	2-4	$\textbf{5.67} \pm 0.01$	0.1	3	5.66-5.67
[Y]	mg kg <sup>-1</sup>	$25\pm 8$	32	25	1.01	7-43	$20 \pm 4$	18	25	17-22
[Fe]	%	<b>5</b> ± 3	65	4	1.26	1-12	$3.4 \pm 0.1$	4	4	3.3-3.5
[As]	mg kg <sup>-1</sup>	$35 \pm 20$	56	28	1.26	5-73	<dl< td=""><td></td><td>27</td><td>0-0</td></dl<>		27	0-0
[ <b>P</b> ]	mg kg <sup>-1</sup>	$\textbf{1624} \pm 741$	46	1401	1.16	655-3769	$\textbf{949} \pm 57$	6	1389	908-989
[Mn]	mg kg <sup>-1</sup>	<b>729</b> ± 1690	232	180	4.06	94-7981	$\textbf{1060} \pm 845$	80	184	462-1657
[Co]	mg kg <sup>-1</sup>	$19 \pm 15$	77	14	1.39	5-76	$17 \pm 9$	56	14	10-23
[Ca]	mg kg <sup>-1</sup>	$\textbf{5261} \pm 1306$	25	5213	1.01	2860-9300	$\textbf{26540} \pm 7566$	29	5283	21190-31890
[K]	mg kg <sup>-1</sup>	$\textbf{4426} \pm 1020$	23	4485	0.99	2420-6140	$\textbf{10510} \pm 2616$	25	4580	8660-12360
[Mg]	mg kg <sup>-1</sup>	$\textbf{1488} \pm 354$	24	1500	0.99	870-2130	$\textbf{7495} \pm 3599$	48	1515	4950-10040
[Na]	mg kg <sup>-1</sup>	$\textbf{1795} \pm 659$	37	1743	1.03	440-3380	$\textbf{10695} \pm 587$	5	1783	10280-11110
[Si <sub>inorganic</sub> ]	%	$11 \pm 4$	33	11	1.06	4-21	$23 \pm 1$	3	11	22-23
[Sr]	mg kg <sup>-1</sup>	<b>55</b> ± 16	29	55	1.01	27-116	<b>235</b> ± 24	10	55	218-252
[Ti]	mg kg <sup>-1</sup>	$\textbf{2115} \pm 495$	23	2200	0.96	997-2870	$4357 \pm 2348$	54	2215	2697-6017
[V]	mg kg <sup>-1</sup>	<b>63</b> ± 15	23	60	1.05	36-101	<b>75</b> ± 23	31	60	58-91
[Zr]	mg kg <sup>-1</sup>	$\textbf{101} \pm 31$	31	100	1.01	39-160	$158 \pm 6$	4	103	153-162
<sup>a</sup> Av.: avera	ıge; <sup>b</sup> sd: star	idard deviation;	<sup>c</sup> CV: c	oefficient o	of variation	calculated as re-	lative standard de	viation in	n %; <sup>d</sup> A:M	: ratio between
average and	i median Mi	n · minimal valu	es <sup>, e</sup> M:	ax · maxim	al value					





Table 2. Summary statistics for the molecular composition of sediment OM (expresse	d as
relative abundance, %)	

		$\mathbf{Av.}^{\mathbf{a}} \pm sd^{b}$	CV <sup>c</sup>	Median	A:M <sup>d</sup>	Min <sup>d</sup> -Max <sup>e</sup>
	Furans	$15\pm4$	30	14	1.06	8-28
	<b>Big_furans</b>	<b>4.1</b> ± 1.2	29	4.0	1.03	0.8-7.5
Carbabydratas	Pyrans	<b>3.4</b> ± 1	30	3.2	1.06	1.2-5.3
Carbonyurates	Dianhydrorhamnose	$\pmb{1.6} \pm 0.5$	28	1.7	0.99	0.3-2.7
	Levoglucosenone	$\textbf{2.2} \pm 0.4$	20	2.2	1.00	1.3-3.1
	Levosugars	$\textbf{3.7} \pm 2.6$	71	2.5	1.46	0.8-11
Chitin	Acetamidosugars	$\textbf{2.5}\pm 1$	40	2.6	0.98	0.2-4.2
	(alkyl)pyridines	$\textbf{0.3} \pm 0.1$	34	0.3	0.95	0.1-0.5
	Pyridines_0	$\textbf{0.7} \pm 0.1$	18	0.7	1.00	0.2-0.9
	(alkyl)pyrroles	$\textbf{2.4} \pm 0.5$	22	2.4	1.01	1.7-3.5
	Pyrroles_o	$\pmb{1.0} \pm 0.2$	25	0.9	1.04	0.5-1.4
N-compounds	Maleimie & succinimide	$\pmb{1.2} \pm 0.3$	29	1.2	0.98	0.2-1.7
recompounds	Aromatic N	$\textbf{0.8} \pm 0.3$	36	0.8	1.03	0.3-1.4
	Indoles	$\textbf{1.5}\pm0.4$	24	1.5	1.03	0.5-3.1
	Diketodipyrrole	$\textbf{0.8} \pm 0.2$	22	0.8	1.01	0.4-1.2
	Proteins	$\textbf{1.5}\pm0.4$	30	1.5	1.02	0.3-2.6
	Alkylamides	$\textbf{0.6} \pm 0.3$	51	0.6	1.06	0.1-1.7
Phonols and	Phenols	${\bf 8}\pm 1$	15	8	1.02	4.4-11.4
Lignins	Syringols	$\textbf{0.5} \pm 0.4$	83	0.4	1.32	0.1-1.9
	Guaiacols	$\textbf{3.6} \pm 2.3$	65	2.9	1.24	1.1-13.5
Chlorophylls	Pristenes	$\textbf{2.7} \pm 0.8$	28	2.8	0.97	0.4-4.6
	Phytadienes	$\pmb{1.9} \pm 0.7$	35	1.8	1.04	0.2-3.6
	C9-16:1	$\textbf{3.5} \pm 0.8$	23	3.6	0.98	1.8-5.1
	C17-C22:1	<b>6</b> ± 1	17	6.2	0.97	3.5-8.9
	C23-26_1	$\textbf{2.9} \pm 0.9$	32	2.7	1.09	0.6-5.4
	C27-28:1	$\textbf{0.8} \pm 0.4$	47	0.7	1.10	0.1-1.4
	C13-16:0	$\textbf{2.5} \pm 0.6$	23	2.5	1.03	1.3-4.1
Lipids	C17-22:0	$\textbf{3.9} \pm 0.8$	21	4.0	0.98	1.6-5.4
	C23-26:0	$\textbf{2.8} \pm 1.4$	49	2.7	1.07	1.4-8.8
	C27-35:0	$\textbf{4.3} \pm 3.5$	80	3.6	1.20	1.1-21.3
	2K C13-17	$\textbf{1.3}\pm0.4$	33	1.4	0.96	0.6-2.2
	2K C19-22	$\textbf{0.3} \pm 0.1$	45	0.3	0.97	0-0.8
	2K C23-31	$\pmb{1.3} \pm 0.8$	62	1.1	1.24	0.1-3.3
High molecular	Steroids	$\pmb{1.2} \pm 0.9$	70	1.1	1.10	0-4.3
mass compounds	Tocopherols	$\textbf{0.3} \pm 0.3$	106	0.2	1.75	0-1.5
<u> </u>	Hopanoids	$\textbf{1.3}\pm0.4$	31	1.4	0.94	0.2-1.9
	Benzene	$\textbf{0.9}\pm0.4$	43	0.8	1.14	0.4-2.5
	Benzaldehyde	$\textbf{0.6} \pm 0.3$	41	0.6	1.08	0.3-1.5
(poly)aromatics	Acetylbenzene	$\textbf{1.1}\pm0.4$	39	1.0	1.10	0.6-2.3
	Alkylbenzenes C3-9	$\pmb{1.9} \pm 0.5$	23	1.8	1.07	1.4-3.5
	Polyaromatics	$1.4 \pm 0.4$	27	1.3	1.04	0.8-2.1

<sup>a</sup> Av.: average; <sup>b</sup>sd: standard deviation; <sup>c</sup>CV: coefficient of variation calculated as relative standard deviation in %; <sup>d</sup>A:M: ratio between average and median Min.: minimal values; <sup>e</sup>Max.: maximal value



Table 3. Whole-lake and clusters average for a selection of elemental geochemical parameters and of ratios indicative of OM source types and their degradation status

		SPECIFIC FEA	<b>TURES IN CEO</b>	CHEMISTRY					
		Whole-lake <sup>*</sup>	Near-shore	North/East		South basin	-	Shallow cent	ral areas
			sites	basins	Shallower	Intermediate depth	Deeper		
			Cluster geo 4	Cluster geo I	Cluster goo 6	Cluster geo 2	Cluster geo 5	Cluster,	<sub>500</sub> 3
		$(n^{b}=42)$	(n=4)	(n=13)	(n=10)	(n=8)	(n=3)	(m=4	
Water dep	oth (m)	9±7 (78%)°	4±2	5±3	8±3	15±4	24±1	2±1	
Bulk density	r (g cm <sup>-3</sup> )	$0.06 \pm 0.02$ (33%)	$0.06 \pm 0.03$	$0.07 \pm 0.02$	$0.07 \pm 0.02$	$0.05 \pm 0.01$	$0.026 \pm 0.009$	$0.10 \pm 0$	0.02
[lssi] (	(%)	$13 \pm 6 (46\%)$	12±6	<b>13±3</b>	$15 \pm 7$	7±3	$4.2 \pm 0.3$	21±	4
[IO]	(%)	$38 \pm 10 \ (26\%)$	$50 \pm 12$	$39 \pm 5$	34±7	37±4	$52 \pm 2$	20±	8
[S] (mg	(i)	$11876 \pm 5920$ (50%)	$17510 \pm 833$	$11683 \pm 3440$	$7550 \pm 1900$	$12896 \pm 3315$	$26227 \pm 4833$	4879 ±	148
[Br] (mg		$149 \pm 35 (23\%)$	$130 \pm 6$	$153 \pm 36$	145 ± 35	<b>I</b> 54± I9	$204 \pm 26$	116±	32
[Cu] (mg	(rg)	$34 \pm 13 (38\%)$	36±5	28±6	30±7	42±6	$65 \pm 10$	[ <b>∓</b> };	<u> </u>
[N] (mg		$19 \pm 5 (2)\%$	21±1	18±4	17±2	21±4	27±1	# 13	4
[Hg] (ng	(kg')	$337 \pm 202 \ (60\%)$	$407 \pm 141$	$251 \pm 47$	$230 \pm 69$	$427 \pm 94$	$917 \pm 212$	203 ±	87
[Zu] [m2]	(i, 21)	$219 \pm 108 (49\%)$	279 ± 31	212 ± 68	$139 \pm 42$	305±86	417±33	63±1	9
[re]	(0)	00.00) 5 ± 6	17 1 1 2		C1 ≠ 0.5	9.1 ± 2.4	$4.5 \pm 2.2$	1 C C	
Fe:A	4	$1.5 \pm 0.8 (53\%)$	$1.0 \pm 0.5$	$1.0 \pm 0.6$	$1.1 \pm 0.3$	$2.5 \pm 0.9$	$1.3 \pm 0.0$	19±(	13
[As] (mg	(, SH	$35 \pm 20$ (2/%)	11 = 17	26 ± 16	25±11	64±11	48 ± 14	<b>#67</b>	4
[P] (mg	[rg.])	$1624 \pm 741$ (46%)	$927 \pm 240$	$1065 \pm 295$	$2088 \pm 730$	$2074 \pm 275$	$2766 \pm 869$	1224 ±	216
[Min] (mg	g ltg. <sup>1</sup> )	$729 \pm 1690 (231\%)$	$162 \pm 53$	$182 \pm 67$	$184 \pm 50$	$305 \pm 93$	171±13	5700±	597
Mn:1		$0.02 \pm 0.03$ (150%)	$0.007 \pm 0.002$	$0.008 \pm 0.003$	$0.006 \pm 0.002$	$0.004 \pm 0.001$	$0.005 \pm 0.002$	$0.111 \pm 0$	0.051
[Co] (mg		$19 \pm 15$ (79%)	$15 \pm 8$	$12 \pm 6$	<b>13±5</b>	$26 \pm 11$	<b>14±2</b>	49 ± 2	14
[Pb] (mg	[kg <sup>-1</sup> ]	$192 \pm 90 (47\%)$	$199 \pm 58$	$132 \pm 53$	$115 \pm 42$	300±59	$315 \pm 7$	182 ±	96
		SPECIFIC FEAT	TURES IN OM C	OMPOSITION					
			Near-shore	North/East		South basin		Shallow cent	ral areas
		Whole-lake	sites	basins	Shallower/inte	rmediate depth	Deeper		
			Cluster on 5	Cluster on I	Cluste	er our 3	Cluster_om 2	Cluster on 4	Cluster on 6
		(n=42)	(n=4)	(n=16)	(n=	14)	(n=3)	(n=3)	(n=2)
Water dept	h (W.D.)	$9 \pm 7 (78\%)$	4±2	7±5	Ħ	₹Ş	$24.1 \pm 0.5$	$3.2 \pm 0.9$	$1.8 \pm 0.1$
) IOT	(9/6)	$38 \pm 10 (26\%)$	$50 \pm 12$	39±4	36.	ŧS	$52 \pm 2$	24±4	14±6
(C23-35:0+2K C23-31): Lignins"	In-lake:Terrestrial plant OM	$2 \pm 1$ (50%)	$0.8 \pm 0.5$	3±1	1.7±	± 0.4	$1.8 \pm 0.6$	3±1	19±11
N-compounds : Carbohydrates	Algal: Plant OM	$0.37 \pm 0.09 \ (24\%)$	$0.32 \pm 0.08$	$0.35 \pm 0.04$	e.39 ±	± 0.05	$0.6 \pm 0.1$	$0.29 \pm 0.02$	$0.23 \pm 0.05$
Chlorophylls : Plant lipids+lignins	Algal: Plant OM	$0.18 \pm 0.09 \ (50\%)$	$0.10 \pm 0.05$	$0.13 \pm 0.06$	0.24 ±	± 0.08	$0.31 \pm 0.07$	$0.18 \pm 0.05$	$0.03 \pm 0.03$
Proteins:(alkyl)pyrroles+ (alkyl)myridines+Arometic N	Algal OM (N-compounds) freshness	$0.3 \pm 0.1$ (33%)	$0.39 \pm 0.09$	$0.36 \pm 0.05$	0.22 ±	± 0.06	$0.42 \pm 0.06$	$0.20 \pm 0.08$	$0.13 \pm 0.08$
Phytadienes: pristenes <sup>6</sup>	Algal OM (chlorophylls) freshness	$0.4 \pm 0.1$ (25%)	$0.4 \pm 0.1$	$0.37 \pm 0.09$	÷0+0	+ 0.06	$0.56 \pm 0.05$	$0.42 \pm 0.07$	$0.5 \pm 0.2$
Levosus ars: Furans	Plant OM (carbohvdrates) freshness	$0.2 \pm 0.2$ (100%)	$0.4 \pm 0.2$	$0.3 \pm 0.2$	0.12±	+ 0.11	$0.14 \pm 0.04$	0.08 ± 0.01 0	$0.042 \pm 0.002$
Guaiacyl-acid:Guaiacyl-aldehyde <sup>e</sup>	Plant OM (lignin) freshness	$0.07 \pm 0.03$ (43%)	$0.13 \pm 0.02$	$0.07 \pm 0.03$	0.05 ±	± 0.02	$0.04 \pm 0.01$	$0.04 \pm 0.03$	$0.10 \pm 0.06$
Guaiacyl -2C: Guaiacyl -1C <sup>e</sup>	Plant OM (lignin) freshness	$0.8 \pm 0.3 (38\%)$	$1.23 \pm 0.07$	$1.0 \pm 0.2$	0.5 ±	± 0.2	$0.6 \pm 0.2$	$0.5 \pm 0.1$	$1.1 \pm 0.2$
Syringyl-2C:Syringyl-1C*	Plant OM (lignin) freshness	$1.0 \pm 0.8 \ (80\%)$	$2.4 \pm 0.3$	$1.1 \pm 0.6$	0.5±	± 0.2	$0.6 \pm 0.1$	$0.3 \pm 0.3$	$1.4 \pm 0.8$
* whole-lake averages are calculated with the second se	ithout the outlier samples (sites M4, S	515; Sect. 2.5); <sup>b</sup> n: nun	aber of samples; <sup>e</sup>	the data are pre	sented as follow:	average ± standa	rd deviation (reli	ative standard den	iation); <sup>d</sup> the
compounds included in the ratios are giv	en in detail in Table S1 in the supplem	entary information.							









## Figures



**Fig. 1** Maps of Härsvatten showing (a) its location in Europe; (b) its catchment with lakes, mires and larger streams; and (c, d) its bathymetry along with the spatial distribution of the 44 sampling sites and the six selected clusters based on sediment elemental geochemistry (c) and sediment OM molecular composition (d). In the panel c) and d), the dendrogram shows the relationship between the six identified clusters.







Fig. 2 Combined loading- and score-plots for PCs 1-4 of the elemental geochemistry dataset. For the PC-loadings, filled circles correspond to active variables. Others variables (empty circle and italics letter) were added passively. Sediment samples are colored according to the results of the cluster analysis.







Fig. 3 Combined loading- and score-plots for PCs 1-6 (a, b and c) of the OM molecular composition dataset. For the PC-loadings, filled circles correspond to active variables. Others variables (empty circle and italics letter) were added passively. Sediment samples are colored according to the results of the cluster analysis.