Response to the Associate Editor comments after reviewing process and marked-up versions of the revised manuscript and the supplementary information

Dear Editor,

We appreciate that you find our answer to the comments of the two reviewers thorough, and are thankful for your additional comments that helped to further improve our manuscript. We have made all the changes in the manuscript that we have indicated we would do in our answer to the reviewer's comments. We have also made additional changes with respect to your comments about these reviews. Please find, below, i) a point by point answer to your comments with a description of the corresponding modifications in the manuscript, and ii) the marked-up revised manuscript and supplementary information.

1. *"In reply to some of the comments of referee one you stated that a more extensive discussion on the Fe, Mn, and Al distributions in the lake falls outside the scope of this study. The scope of this study more or less defined as determining the spatial heterogeneity in the lake indicating that taking a single sample and scaling up to the entire surface area of the lake is not the way to go. I do agree that an extensive discussion is not warranted here, but you do suggest some mechanisms that might play a role and you specify these mechanisms. This makes the argument of the scope of the study invalid, I think, if something falls outside the scope of the work you could argue it should not be mentioned at all. It is not a very good excuse. Therefore I would like to ask you to either make the effort of writing a more extensive discussion on different possible mechanisms or you make it very clear that the mechanisms mentioned are just of few possibilities and that there might be others such as … (see review and reply)."*

We have now added a short discussion of the other possible factors and processes that could be involved in the spatial distribution of the redox elements (Fe, Mn) in the sub-section 3.3.2 (cf. lines 642-646 in the marked revised manuscript).

We have also changed the titles of the sub-section 3.3 to emphasize that the discussion of our data is mainly focused on the spatial distribution of the molecular composition of the sediment OM. The title "*3.3 Combined spatial patterns of elemental and organic biogeochemistry*" has been replaced by "*3.3 Factors and processes involved in the spatial distribution of OM molecular composition*" (cf. line 521 in the marked revised manuscript). The title "*3.3.1 Spatial variability in the sediment composition in the main south basin"* has been replaced by *"3.3.1 Spatial variability in the main south basin"* (cf. line 541 in the marked revised manuscript).

2. *"The other thing I noticed is that the "whole-lake" concept creates some response from both reviewers in different ways. As for the title I agree with the suggested changes. Throughout the manuscript, just realize that you did not analyze the whole lake. Rather than just the typical one sediment sample you analyzed more samples from different sites to get an idea of the heterogeneity.*

This is very interesting, and provides a much better picture than analyzing just one sample, but you did not analyze the whole lake or even the all the lake sediments."

We agree and have removed the term "whole-lake" everywhere in the revised manuscript (e.g., line 63 in the marked revised manuscript), except when we compare and discuss the average values of the different clusters with the average values of all analyzed sediment samples. We kept the term "whole lake average" for saying "averages of all analyzed sediment samples" because more convenient to read. However, we have clearly defined this term the first time we employ it in the revised manuscript (cf. lines 319-321 in the marked revised manuscript), as well as in Table 3 and in Tables S3 and S5 in the revised supplementary information.

3. *"One question I had is what about micro-heterogeneity did you analyze multiple "replicates" from the same sample to see how large the variation is within one sample? 200µg is a relatively small amount."*

200 µg is a very small amount, but all sediment samples were first very finely ground and could be easily mixed and weighted for Py-GC/MS analyses, except the sediments at sites M5 and S14, which were too coarse (for which we could not get Py-GC/MS data).

We did not measure replicates for the sediment samples in this study, but we have tested extensively the reproducibility for the different identified organic compounds when using only 200 µg of sediment in our methodological paper published in Analytica Chimica Acta. The reproducibility (i.e. relative standard deviation from triplicate analyses) we measured for the 233 identified compounds (including those that have been identified in Härsvatten sediment samples) was 5.5 ± 4.3%, with 90% of the RSD values within 10% and 98% within 15%.

4. *"You suggest that you looked at the whole matrix rather than only specific compounds or classes. And although I agree that pyrolysis might be one of the better tools to do this, the method still has biases and issues like all other analytical methods. If it doesn't fit in your analytical window you don't see it. The discussion about the pyrolysis temperature makes that quite clear, different temperatures show (slightly) different results, so please be careful in how you phrase what your pyrolysis results reflect. That brings me to a comment from referee two about other studies on OM composition studies. Other groups have investigated complex organic matter from lake and other sediments through a whole range of different techniques including pyrolysis (with and without TMAH), lipid extractions, GC and LC mass spectrometry etc etc. I think your approach of analyzing every samples the same way works fine for this manuscript, but I think it is good to put your own work in a larger, historical perspective by shortly mentioning other studies. Pyrolysis has been around for quite some time and it is good that this would be reflected in your reference list."*

We agree that saying we look at the whole OM matrix was not accurate enough. Therefore, we replaced the term "whole OM matrix" that was used in the introduction only. Please, see lines 66-68 and 127-128 in the marked revised manuscript.

We have also added an important paragraph in the introduction of the revised manuscript where the existing methods to characterize OM molecular composition are discussed in order to put our work and data provided by Py-GC/MS in a larger and historical perspectives (cf. lines 69-114 in the marked revised manuscript).

Moreover, few sentences in the material and method section have been added to explain that Py has been used previously for different environmental samples types and with different pyrolysis temperatures than the one we used in this study (cf. lines 207-226 in the marked revised manuscript). Thus, our reference list better reflects the literature (11 added references for Py-GC/MS applied to environmental samples).

Finally, we believe we have been extremely careful in interpreting and phrasing what our pyrolysis results reflect. Given the statistical approach we use and our experience in using Py-GC/MS, we think we have not over-interpreted our data in this manuscript. Notably, we are not concluding by claiming that our study provides how the molecular composition of OM is in the different areas of lake basin due to specific processes, but our conclusion is that OM molecular composition can vary significantly within a single lake system in relation to factors and processes that are common to lake ecosystems, and our main message for future research is that given these results, biogeochemical processes known to be influenced by OM composition such as C mineralization, Hg methylation and P desorption, should not only be studied by comparing between-lake variability using sediment of the deeper area as generally done, but the in-lake spatial variability should also be investigated.

5. *"As referee two mentions, be very careful with steroids and hopanoids, they come very different sources. Looks can be deceiving. Be very careful with assigning different classes and binning compounds together and using only or mainly the NIST database for compound identifications. Mistakes are easily made."*

We always seek to be very careful in i) assigning compounds to mass spectra from the NIST database; ii) classifying the different compounds into OM groups; and iii) discussing the origin of the different compounds; and we are very much aware about the mistakes that can be done when doing all these steps. To get accurate peak identification, organic compounds classification and interpretation about their origin and degradation status, we have carefully researched a large number of articles, i.e.,

i) almost all papers where Py-GC/MS was employed, and at least all papers on Py-GC/MS applied to environmental samples, i.e. soils, peat, plants and sediments for reaching different objectives, e.g. paleoreconstruction, variability in OM composition and identification of Py products from standards or specific OM fractions.

ii) a wide numbers of papers using other techniques and mainly mass spectrometry, such as specific extractions and LC-MS or GC-MS analyses for determination of specific biomarkers from the

different OM biochemical classes or Orbitrap-MS and FT-ICR-MS for the characterization of the whole OM matrix in liquid environmental samples.

This, we hope, is better reflect in the revised manuscript with the new paragraph in the introduction (cf. lines 69-115 in the marked revised manuscript and answer to comment 4 above), in the material and method (cf. lines 206-224 and text below) and the associated additional 25 references.

Our list of identified compounds is highly similar to the lists of identified Py-GC/MS organic compounds in soil, peat and sediment samples reported in published papers from other research groups, regarding both the organic compounds that are present and how these compounds are grouped into different OM families (i.e. carbohydrates, N-compounds, *n*-alkenes, chlorophyll, steroids, hopanoids…). This information has been added in the material and method section (cf. lines 206-224 in the marked revised manuscript). Our compound grouping into 41 groups is less common; and we have done this grouping for the sake of making the presentation of the data and the associated discussion more constrained and to avoid over-interpreting individual compounds. Given the comment 9 of the reviewer 2, we have now explained why and how the groupings of the 160 identified compounds into 41 groups have been done (cf. lines 344-367).

Regarding the specific comment on the steroids and hopanoids, we agree we have made a mistake by gathering them in Table 2 of the manuscript (this mistake has been now corrected; cf. Table 2 in the revised manuscript). But, we would like to point out that these compounds were neither grouped for the statistical analysis or in the detailed lists of identified organic compounds (Table S1 in SI). Moreover, in the text, we are clearly saying that the Py products of steroids in our samples mainly originate from algal production while hopanoids are well known to be of prokaryotes, especially bacteria, origin. Please see in the marked revised manuscript, lines 437-439 "*hopanoids, which are high-molecular weight pentacyclic compounds of prokaryotes, especially bacteria, origin (Meredith et al., 2008; Sessions et al., 2013).",* lines 452-453 "*and hopanoids of prokaryotes (mainly bacteria) origin (Meredith et al., 2008; Sessions et al., 2013)",* and lines 455-457 " *suggesting that the steroids released by Py in aquatic samples are mainly of algal origin*".

~~Whole-lake~~ Spatial variability of organic matter molecular composition and elemental ~~inorganic properties~~ geochemistry in surface sediments of a small boreal Swedish lake

J. Tolu[1*], J. Rydberg[1], C. Meyer-Jacob[1], L. Gerber[2] and R. Bindler[1]

[1] *Department of Ecology and Environmental Science, Umeå University, SE-901 87 Umeå, Sweden*

[2] *Umeå Plant Science Center, Swedish University of Agricultural Sciences, Department of Forest Genetics and Plant Physiology, SE-901 83 Umeå, Sweden*

* Corresponding author. julietolu@hotmail.com

Abstract.

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

Keywords.

Lake sediment; spatial variability; organic matter; molecular composition; Py-GC/MS; elemental geochemistry

1. Introduction

In lake basins a wide range of factors are known to influence the transport and fate of sedimentary material, such as the location of inlet streams, catchment topography, land-use patterns, fetch, basin morphometry and sediment focusing. Sediment focusing results from a combination of factors such as wind and wave action, basin slope and the settling velocity of different particle sizes, which all contribute to the redistribution of light, fine-grained material rich in clays, organic matter (OM) and associated trace elements from shallower to deeper waters (Blais and Kalff, 1995; Ostrovsky and Yacobi, 1999). While sediment focusing is important, catchment characteristics and lake morphometry can be complex and exert a primary influence on spatial patterns in sediment geochemistry, such as in relation to land use in near-shore areas (Dunn et al., 2008; Vogel et al., 2010; Sarkar et al., 2014), complex lake/basin morphometries (Bindler et al., 2001; Rydberg et al., 2012) or river inflows (Kumke et al., 2005). The presence of macrophytes or 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).

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

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

In boreal lakes the sediment composition is often dominated by OM, typically ranging from 20 to 60 % on a dry weight basis, followed by biogenic silica (bSi), which may account for as much as 45 % of the sediment dry weight (Meyer-Jacob et al., 2014). The remaining sediment mainly consists of detrital mineral matter and possibly authigenic minerals. Lake OM is an extremely heterogeneous and complex mixture of molecules that are derived from plant, animal, fungal and bacterial residues, and which are either transported into the lake from the surrounding catchment (allochthonous) or produced within the lake (autochthonous). Furthermore, these organic compounds may undergo transformations within the water column and the sediment through both biotic and abiotic processes. Although there have been a few studies where the spatial complexity in 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 using quantitative analyses of photopigments and lipids (Ostrovsky and Yacobi, 1999; Trolle et al., 2009; Vogel et al., 2010; Sarkar et al., 2014), little work has been done to detail how the molecular composition ~~compositional variability~~ of the sediment OM matrix, ~~as a whole~~ considering a large number of organic biochemical classes and compounds, varies spatially within a lake.

To characterize OM composition at the molecular level, the most commonly used methods are based on liquid or gas chromatography (LC or GC) coupled to fluorescence or mass spectrometry (MS) detection. These methods provide quantitative data on original organic compounds found in the analyzed samples, including highly specific biomarkers of, e.g., OM sources, and have been successfully employed to study OM composition and reactivity in environmental matrices as well as to reconstruct environmental changes (e.g., changes in vegetation, algal productivity) from peat or sediment cores. However, the associated sample preparation procedures, i.e. extraction/hydrolysis and derivatization, are fastidious and specific to the different biochemical classes of organic compounds such as carbohydrates, proteins/amino acids, lipids, chlorophylls and

lignins (e.g., Wakeham et al., 1997; Dauwe and Middelburg, 1998; Tesi et al., 2012). Moreover, sample masses > 10 mg are required. Hence, studies where different OM biochemical classes are targeted using these wet chemical extraction and GC/LC-MS methods are very scarce. However, efforts in characterizing the whole OM composition at the molecular level can bring important insights because the different biochemical classes of OM do not always include specific biomarkers for the different existing sources of OM (e.g., terrestrial plants, macrophytes, higher plants, mosses, algae, bacteria). For example, lignin compounds are only specific of higher plants (Meyer and Ishiwatari, 1997) and proteins/amino-acids mainly provide biomarkers for bacteria and planktonic production (Bianchi and Canuel, 2011). Moreover, the different biochemical classes of OM do not present the same reactivity; for example, proteins/amino-acids and neutral carbohydrates have been shown to be among the most reactive organic molecules (e.g., Fichez, 1991; Dauwe and Middelburg, 1998; Amon and Fitznar, 2001; Tesi et al., 2012). Advanced ultrahigh-resolution MS techniques, i.e. Fourier transformed-ion cyclotron resonance-mass spectrometry (FT-ICR-MS) or Linear trap Quadruple-Orbitrap-MS enable the determination of a large number of organic molecular formulas, belonging to the different biochemical classes of OM in liquid samples (> 1000; e.g., Hawkes et al., 2016). These method have been successfully used to link variability in the molecular composition of dissolved OM (DOM), also called DOM chemodiversity, with different factors and/or processes of environmental ecosystems, such as climate, hydrology and OM degradation in boreal lakes (Kellerman et al., 2014; Kellerman et al., 2015) or optical properties and DOM photo-chemical alterations in wetland and seawater (Stubbins and Dittmar, 2015; Wagner et al., 2015). But, in addition to the limited access to these advanced MS techniques due to instrumental costs, extraction/hydrolysis steps are required when studying solid samples, which make these methods also specific to the different biochemical classes of organic compounds.

To study the variability of OM composition in sediments, pyrolysis-gas chromatography – mass spectrometry (Py-GC/MS) is a good compromise between the quantitative LC/GC-MS or the high-resolution MS methods that target specific compounds and the qualitative, non-molecular

information provided by high-throughput techniques such as infrared spectroscopy or 'RockEval' pyrolysis. The sample preparation for Py-GC/MS analysis requires no complex sample preparation but yields semi-quantitative data on >100 organic compounds that are chemical fingerprints of the different OM biochemical classes, which include specific biomarkers for OM sources and OM degradation status (Faix et al., 1990; Faix et al., 1991; Peulvé et al., 1996; Nierop and Buurman, 1998; Schulten and Gleixner, 1999; Lehtonen et al., 2000; Nguyen et al., 2003; Page, 2003; Buurman et al., 2005; Fabbri et al., 2005; Kaal et al., 2007;Vancampenhout et al., 2008; Schellekens et al., 2009 ;Carr et al., 2010; Buurman and Roscoe, 2011; De La Rosa et al., 2011 ; Mcclymont et al., 2011; Micić et al., 2011; Stewart, 2012). Recently, we developed a method where Py-GC/MS is combined to a data processing pipeline in order to speed up the peak identification and integration that are otherwise very time-consuming (Tolu et al., 2015).

In the~~is~~ present study, we apply ~~a~~ our newly optimized ~~pyrolysis-gas chromatography-mass spectrometry (~~Py-GC/MS~~)~~ method to characterize the molecular composition of natural OM in surface sediments (0-10 cm) from 42 locations within the lake basin of Härsvatten, a small boreal forest lake in southwestern Sweden that was previously studied for the spatial distribution of Pb and OM contents (Bindler et al., 2001). ~~As an analytical tool to characterize OM composition, Py-GC/MS is a compromise between the quantitative, molecular information obtained from wet chemical extractions associated with liquid chromatography (LC)-MS or GC-MS analyses, and the qualitative, non-molecular information provided by high-throughput techniques such as visible-near-infrared spectroscopy or 'RockEval' pyrolysis. Beyond the rapidity in terms of analysis and data treatment, our Py-GC/MS method yields semi-quantitative data on >100 organic compounds belonging to different biochemical classes (e.g., lignins, lipids, chlorophylls, carbohydrates, Nitrogen (N)-compounds), which makes it possible to explore the overall molecular composition of OM (Tolu et al., 2015).~~ Our objective here was to comprehensively investigate how the molecular composition of sediment OM varies spatially across a lake with several basins. Our specific research questions were: (i) what are the spatial patterns within a single lake for various organic

biochemical classes and compounds?; (ii) how does the spatial pattern of the OM molecular composition relate to physical parameters (i.e., bulk density and water depth) and elemental, inorganic geochemistry of the sediment material?; (iii) which factors or processes (e.g., ~~origin~~ provenance, transport pathway, ~~decomposition~~ mineralization) appear to explain the in-lake spatial variability of the OM molecular composition?

2. Materials and Methods

2.1 Study site and samples

Härsvatten is a boreal forest lake located in southwestern Sweden (58°02' N 12°03' E) in the Svartedalen nature reserve. This culturally acidified, clear-water, oligotrophic and fishless lake has been intensively monitored since the 1980's (national database, Dept. of aquatic sciences and assessment, Swedish university of agricultural sciences, Uppsala, Sweden; www.slu.se), during 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 dimictic with a thermal stratification between 10 and 15 m depth in the summer. Approximately 80 % of the lake bottom is within the epilimnion. The surface areas of the lake and its catchment are 0.186 and 2.03 km^2, respectively. The catchment is characterized by an uninhabited, coniferous-dominated forest (*Picea abies* Karst. and *Pinus sylvestris* L.), which extends to the rocky shoreline. The bedrock consists of slow-weathering granites and gneisses ~~which~~ that are covered by thin and poorly developed podsolic soils.

The basin of Härsvatten can be divided into four general areas (Bindler et al., 2001): 1) the main south basin, which represents about half of the lake area (sample sites S1–24; maximum depth, 24.3 m) and includes the lake's small outlet stream; 2) a north basin (sample sites N1–11; maximum depth, 12 m), which includes a small inlet stream draining from the headwater lake Måkevatten that enters Härsvatten through a small wetland; 3) an east basin, which has a maximum

depth of nearly 10 m (sample sites E1–6) and is separated from the main north–south axis of the lake by a series of islands and shallow sills (<3 m water depth); and 4) a generally shallow (<3 m 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 1997–1998 (Fig. 1) for a study of Pb and SCP (Bindler et al., 2001). These samples were collected as follow: short sediment cores (0-25 cm) were taken with a gravity corer from the ice-covered lake in winter 1997 and 1998, and were sectioned into an upper sample (0-10 cm) and a lower sample (10-25 cm; not studied here) on-site. In the laboratory, the samples were weighed, freeze-dried, and reweighed to determine the water content and dry mass of the sediment. The freeze-dried samples have been stored in plastic containers within closed boxes shielded from light and at room temperature since winter 1997-1998. Before further analysis in this study, the samples were finely ground at 30 Hz for 3 min using a stainless steel Retsch ~~ball~~ swing mill.

2.2 Major and trace elements concentrations

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 was within the certified range, and replicate samples were within ±10% for Hg concentrations <30 μg kg^{-1} and within ±5% for concentrations ≥30 μg kg^{-1}.

We also included the OM content (in % dry mass), determined as loss-on-ignition (LOI) after heating dried samples at 550ºC for 4 h in the earlier study of Bindler et al. (2001).

2.3 Biogenic silica concentrations

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 ($Si_{mineral}$) from the difference between the total Si concentration determined by WD-XRF (Sect. 2.2) and the bSi concentration.

2.4 Organic matter molecular composition

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 ± 10 µg sediment was pyrolyzed in a FrontierLabs PY-2020iD oven (450 ºC) 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 the sediments of Härsvatten, ~~160~~ 162 Py-products were identified, and peak areas were normalized by setting the total identified peak area for each sample to 100 %. A detailed list of the 160 identified organic compounds with information on their molecular mass and structure and on

their reference mass spectra and calculated or reference retention index values is provided in the supplementary information (Table S1). Although the pyrolysis temperature we employed, i.e. 450°C as used in plant science (e.g., Faix et al., 1990; Faix et al., 1991), is different from the pyrolysis temperature most commonly used in previous studies analyzing soils, sediments and peat records (i.e. >600°C), our list is highly similar to published lists of identified pyrolytic organic compounds both in terms of the organic compounds and of their classification into 13 OM classes (Faix et al., 1990; Faix et al., 1991; Peulvé et al., 1996; Nierop and Buurman, 1998; Schulten and Gleixner, 1999; Lehtonen et al., 2000; Nguyen et al., 2003; Page, 2003; Buurman et al., 2005; Fabbri et al., 2005; Kaal et al., 2007;Vancampenhout et al., 2008; Schellekens et al., 2009 ;Carr et al., 2010; Buurman and Roscoe, 2011; De La Rosa et al., 2011 ; Mcclymont et al., 2011; Micić et al., 2011; Stewart, 2012). ~~The 160 Py-products were then reduced to 41 groups of compounds based on the similarities in their molecular structure and origin as detailed in Table S1 in supplementary information (SI).~~. We used a pyrolysis temperature of 450°C because during our methodological development for lake sediments, we showed that, when using sub-mg sample mass, a pyrolysis performed at this temperature enable to avoid complete degradation of some specific biomarkers of OM sources and/or degradation status (e.g., syringol lignin oligomers, Py products of polysaccharides and/or cellulose) as compared to 650 °C (Tolu et al., 2015).

2.5 Statistical analysis

We performed all statistical analyses using SPSS software package PASW, version 22.0. Two separate principal component analyses (PCA) were performed, one for the elemental geochemistry (i.e., dry bulk density (B.D.) and contents of OM (LOI), major/trace elements and bSi) and the other for the OM molecular composition. Prior to the PCA, all data were converted to Z-scores (average = 0, variance = 1). Principal components (PCs) with eigenvalues > 1 were extracted using a Varimax rotated solution. Factor loadings were calculated as regression coefficients, which is

analogous to *r* in Pearson correlations. For convenience the loadings are reported as percentage of variance explained, i.e., as squared loadings. For all PCs, variables with squared loadings <0.15 are not discussed with respect to that PC. Others variables, e.g., water depth (W.D.) or ratios between elements, were included passively in the PC-loadings plots by using bi-variate correlation coefficients between these variables and the PC-scores of each PC. Hierarchical agglomerative cluster analysis (CA) was performed for the elemental geochemistry and the OM molecular composition datasets using Wards linkages (Ward, 1963) based on squared Euclidean distances. The PC-scores from the PCAs were used instead of the original data in order to eliminate the effects of autocorrelation in the dataset.

3. Results and discussion

3.1. Sediment elemental geochemistry

3.1.1 General description and trends

Summary statistics of the elemental geochemical properties of the surface sediments from Härsvatten are presented in Table 1 and the detailed data are given in Table S2 in SI. The sediments from sites M4 and S15 are two outliers because they have a B.D., bSi, OM and elemental contents (e.g., Na, Mg, Al, K) that deviated by more than four standard deviations from the ~~whole-lake~~ average values of all analyzed sediment samples (Table 1). Because these sediment samples are too coarse (predominantly sand) ~~also contained too little OM~~ for Py-GC/MS analysis according to our method based on 200 ± 20 µg analyzed sample mass, they are excluded from the ~~data~~ statistical analyses and discussion. Even when excluding these two sites, the elemental geochemical parameters vary considerably across the lake basin, with Hg, Fe, Co and Mn contents illustrating the greatest variabilities (i.e., coefficient of variation, CVs >60%) and Al, Br, K, Ti, V, Ni, Mg and

Ca contents showing the lowest variabilities (CVs: 17-25%; Table 1). For most of geochemical properties, the average to median ratios are approximatively 1.0, indicating no extreme values. Slightly higher values were, however, observed for P, Fe, As and Co contents (1.2-1.3), and Mn content is associated with extremely large values 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) and which also include the lowest [Al], [P], [K], [$Si_{inorganic}$], [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 north and east basins and between the larger north and south basins (i.e., sites N10, M1, M5-6), which also contain the highest [bSi], [Sr], [Al], [Y], [Mn] and [Co]. The sediments located at intermediate water depth (9-20 m) in the main south basin (S4, S9, S11, S13-14, S17, S19, S22) are associated with the highest [Fe], [As], [K], [Mg], [Na], [Ti] and [Zr], while among the shallower sites of the south basin we find the highest [$Si_{inorganic}$]. The lowest [Fe], [As], [Co] and [Y] are observed among the sediments of the east basin, and the sediments of the north basin include the lowest [Mn], [Ca], [K], [Mg], [Na], [Sr] and [Zr]. To identify more accurately the most significant relationships existing between the different elemental geochemical properties and o explore more precisely their spatial distribution, the results of PCA and cluster analyses are further presented and discussed.

3.1.2. Principal components of the elemental geochemistry

For the elemental geochemistry dataset, five principal components were extracted. We present only the first four PCs, which together explain 74 % of the total variance (PC1-4$_{geo}$; Fig. 2) because no reasonable interpretation could be made for PC5$_{geo}$ (10 % of the total variance; Fig. S1 in SI). PC1$_{geo}$ captures 25 % of the total variance and separates bSi and B.D. (negative loadings) from OM, S, Cu, Hg, Ni, Zn and, to a lesser extent, As and Pb (positive loadings; Fig.2a). This means that bSi and B.D. are significantly positively correlated, and both are significantly negatively correlated to OM, S, Cu, Hg, Ni, Zn and, to a lesser extent, As and Pb. If those parameters do not have significant loadings on PC2-5, it means there are not significantly correlated with the parameters found on PC2-5, the PCs being orthogonal to each other. The negative loadings are interpreted as reflecting a bSi-rich fraction, while positive loadings indicate an organic-rich fraction that is enriched in organophilic trace metals (Lidman et al., 2014). For PC2$_{geo}$, which captures 21 % of the total variance, Si$_{inorganic}$, K, Na, Mg, Zr and Ti have positive loadings, while no element is significantly negatively correlated to PC2$_{geo}$ (Fig. 2a). High PC2$_{geo}$ scores likely represent samples that are richer in silicate minerals such as quartz and clays (Koinig et al., 2003; Taboada et al., 2006).

Positive loadings on PC3$_{geo}$, which explains 16 % of the total variance, are found for Al and Fe along with As, P and Y (Fig. 2b). Compared to elements such as Mg, Na and K that are mostly confined to the silicate fraction of sediments, Fe and Al may reflect both detrital material and dissolved or amorphous phases. However, the fact that As and P contents as well as the Fe:Al ratio plot together with Fe and Al contents on the positive side of PC3$_{geo}$, but not with the S content, strongly suggest that sediments with high PC3$_{geo}$ scores are associated with ~~This suggests a~~ higher contents of Fe and Al (oxy)hydroxides, which are ~~that are~~ known to strongly bind both As and P (Mucci et al., 2000; Plant et al., 2005; Zhu et al., 2013). PC4$_{geo}$ captures 12 % of the total variance and separates Mn, Co, Pb and to a lesser extent Fe (positive loadings) from OM and Br (negative loadings; Fig. 2b).

Although Mn, like Fe and Al, is not confined to a specific mineral phases and can reflect both detrital or dissolved and amorphous phases, the positive loadings are interpreted as reflecting Mn (oxy)hydroxides, which bind Pb, especially when they contain cobalt (Co) (Yin et al., 2011). This interpretation is supported by the positive loadings on $PC4_{geo}$ of the ratio Mn:Fe, often used as a paleolimnological proxy for bottom water oxygenation (Naeher et al., 2013). The negative loadings could indicate a terrestrial OM fraction that is rich in Br (Leri and Myneni, 2012).

3.1.3 Cluster analysis of the elemental geochemistry

For the cluster analysis of the elemental geochemistry dataset, we selected a solution of six clusters ($cluster_{geo}$ 1–6; Fig. 1c). The cluster averages and standard deviations of each physical and geochemical variable are given in Table S3 in SI ~~and~~ where they are compared to ~~whole-lake~~ the average~~s~~ values of all analyzed sediment samples, which are referred to hereafter as 'whole-lake average'~~, in Table S3 in SI~~, and Table 3 provides the cluster averages for a selection of geochemical parameters.

In the south basin, the sediments found at shallower water depth ($cluster_{geo}$ 6; n=10) have a higher B.D., are richer in bSi (negative scores on $PC1_{geo}$; Fig. 2a) and have lower than whole-lake average trace metal concentrations (Table 1). In contrast, the sediments from the deeper sites ($cluster_{geo}$ 5; n=3) have the lowest B.D. and lowest bSi content (Table 1), and are enriched in OM and trace metals (positive scores on $PC1_{geo}$; Fig. 2a). The sediments found at intermediate water depths ($cluster_{geo}$ 2; n=8) have positive scores on $PC2_{geo}$ (Fig. 2a), and they have an OM content within 10% of whole-lake average while trace metal concentrations are above 10% of whole-lake 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 ($cluster_{geo}$ 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 ($cluster_{geo}$ 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).

3.2 Sediment organic matter molecular composition

3.2.1 General description and trends

The Py-products identified in the surface sediments of Härsvatten were classified into 13 OM classes, i.e., carbohydrates, N-compounds, chitin-derived Py products, phenols, lignins, chlorophylls, *n*-alkenes, *n*-alkanes, alkan-2-ones, steroids, tocopherol, hopanoids, and (poly)aromatics, in agreement with previous studies using Py-GC/MS for different environmental matrices such as soil, sediment, peat cores, plants or algae (Faix et al., 1990; Faix et al., 1991; Peulvé et al., 1996; Nierop and Buurman, 1998; Schulten and Gleixner, 1999; Lehtonen et al., 2000; Nguyen et al., 2003; Page, 2003; Buurman et al., 2005; Fabbri et al., 2005; Kaal et al., 2007;Vancampenhout et al., 2008; Schellekens et al., 2009 ;Carr et al., 2010; Buurman and Roscoe, 2011; De La Rosa et al., 2011 ; Mcclymont et al., 2011; Micić et al., 2011; Stewart, 2012). For the sake of making the presentation of the data and the associated discussion more constrained (and avoid over-interpreting individual compounds), the 160 identified organic compounds were reduced to 41 groups of compounds as described in Table 2. This grouping is based on the similarities in the molecular structure within the OM classes, and preliminary principal components analyses have shown that the compounds within each of our 41 groups are highly positively correlated and thus present the same trends in this study (data not shown). As an example, the 20 identified

carbohydrate compounds, previously demonstrated to derive from pyrolysis of polysaccharides (Faix et al., 1991), have been separated into 6 groups based on the number of C in the heterocycles of these compounds and on their side-chain functional groups. Thus, the heterocycle of "furan" and "furanone" compounds contains 4 C and 1 oxygen (O) atoms, and the side-chain are either aliphatic ((alkyl)furans and (alkyl)furanones) or contains an oxygenated functional group (hydroxy- or carboxy-furans and furanones). While the heterocycle of "pyran" compounds has 5 C and 1 O, the one of dianhydrohamnose, levoglucosenone and levosugars consists in 6 C and 1 O, but the levosugars contain three hydroxyl functional groups whereas dianhydrorhamnose contains 2 hydroxyl groups and levoglucosenone have a carbonyl group.

Summary statistics of these 41 groups of organic compounds ~~sediment OM molecular composition of the surface sediments from Härsvatten~~ are presented in Table 2 and the detailed data are given in Table S4 in SI. The coefficients of variation for the abundances of the different organic compound groups range from 15 to 106 % with an average of 38 ± 20 %, showing a remarkable in-lake variability of OM molecular composition (Table 2). For most of the organic compound groups, the average to median ratios are approximatively 1.0, indicating no extreme values. However, slightly higher values (1.2-1.8) are observed for organic compounds derived from higher plants and mosses, i.e. levosugars, lignin oligomers (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 higher plants and mosses (Bianchi and Canuel, 2011), have the highest abundances among the three deepest sampling locations (23.5-24.5 m) in the main south basin (S12, S18 and S24). ~~such as for the abundances of~~ Pyrolytic compounds containing an acetamide functional group previously shown to be a good indicator of the presence of chitin from micro-organisms exoskeletons in biological and geological samples (~~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 steroids present also the highest abundances among the three deepest sampling locations. ~~On the~~

~~contrary~~ In contrast, most of the carbohydrates, which usually derive mostly from higher plants and mosses (Bianchi and Canuel, 2011), have the highest abundances among the sediments situated close to the shoreline (N1-2, E3, S5, S23) such as for the abundances of phenols, guaiacyl- and syringyl-lignin oligomers, long-chain *n*-alkenes (C27-28:1) and diketodipyrrole (N-compounds), all specific of higher plants and/or mosses OM (Meyers and Ishiwatari, 1993; Schellekens et al., 2009). The highest abundances of long-chain *n*-alkanes (C23-26:0 and C27-35:0) and mid-chain *n*-alkanes (C17-22:0) are, however, observed for the shallower sites (<2 m) situated between the larger north and south basins (sites M5-6).

Among the shallow sites (2.5-3.0 m) located between the north and east basin (N10, M1) and the shallow and intermediate water depth (4-20 m) sites of the south basin (S1-4, S6-11, S13-17, S19-22), we find the highest abundances of degradation products of carbohydrates (i.e., (alkyl)furans & furanones and hydroxyl- or carboxy-furans & furanones ~~big_furans~~), of proteins, amino-acids and/or chlorophylls (i.e., pyridines_O, (alkykl)pyrroles, pyrroles_O, pyrroledione & pyrrolidinedione ~~maleimide, succinimide~~, pristenes) and of cell wall lipids (i.e., short-chain *n*-alkenes and *n*-alkanes – C9-16:1 and C13-16:0) as well as the highest abundances of (poly)aromatic compounds indicative of highly degraded OM (Schellekens et al., 2009; Buurman and Roscoe, 2011). The lowest abundances of the (poly)aromatic and certain aliphatic compounds (i.e. *n*-alkenes C17-22 and C27-28, *n*-alkanes C13-16 and alkan-2-ones C13-17) are observed among the sediments located close to the shoreline (N1-2, E3, S5, S23), while the two shallow sites situated between the larger north and south basins (M5-6) present the lowest abundances for all other organic compounds. To identify more 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 analyses are further presented and discussed.

3.2.2 Principal components of OM molecular composition

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

$PC2_{OM}$ captures 14 % of the total variance and positive loadings are associated with (i) mid-chain *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 $PC2_{OM}$ (Fig. 3a). High $PC2_{OM}$ scores thus represent samples rich in organic molecules that are resistant ~~upon~~ to degradation.

$PC3_{OM}$ explains 13 % of the total variance and separates carbohydrates and N-compounds ~~derived from~~ that are Py or degradation products of proteins, amino acids and/or chlorophylls (i.e., pyridines, ~~or maleimide-succinimide~~, pyrroledione & pyrrolidinedione) and of chitin (positive loadings), from aliphatic long-chain *n*-alkanes (C23-26:0 and C27-35:0) coming from ~~plant~~ cell wall lipids of higher plants or mosses (negative loadings; Fig. 3b).

On $PC4_{OM}$, which explains 13 % of the total variance, positive loadings are found for the diketopiperazines, i.e. specific Py products of proteins or amino acids, the alkylamides and the chlorophyll-derived phytadienes, ~~that~~ which altogether indicate fresh algal organic residues (Peulvé et al., 1996; Nguyen et al., 2003; Fabbri et al., 2005; Micić et al., 2010). ~~as well as acetamido-sugars, which derive from~~ Py products of chitin ~~of micro-organisms exoskeletons~~ (Gupta et al., 2007), and hopanoids that are of prokaryotes, mainly bacteria, origin (Meredith et al., 2008; Sessions et al., 2013) also have positive loadings on $PC4_{OM}$, while no compounds are significantly negatively correlated to $PC4_{OM}$ (Fig. 3b). Therefore, $PC4_{OM}$ reflects OM input from in-lake algae and micro-organisms (e.g., zooplankton). Steroids, which have not yet been reported by Py-GC/MS in aquatic matrices, have positive loadings on this $PC4_{OM}$ suggesting that the steroids released by Py in aquatic samples are mainly of algal origin.

For $PC5_{OM}$, capturing 8 % of the total variance, positive loadings are related to lignin oligomers, which are specific for vascular plants (Meyers and Ishiwatari, 1993), and

diketodipyrrole, a N-compound often reported in soil pyrolysates (e.g., Schellekens et al., 2009; Buurman and Roscoe, 2011). No compounds are associated with negative loadings on $PC5_{OM}$ (Fig. 3c). Interestingly, the long-chain *n*-alkanes from ~~plant~~ cell wall lipids of higher plants or mosses do not have positive loadings on $PC5_{OM}$. We therefore interpret $PC5_{OM}$ to relate to OM inputs from the forested catchment, which is dominated by coniferous species. Coniferous trees generally have higher lignin contents as compared to other vascular plants (Campbell and Sederof, 1996), while they contain much lower amounts of *n*-alkanes than other plant species (Bush and Mcinerney, 2013).

$PC6_{OM}$ captures 7 % of the total variance and has four compounds with significant positive loadings, i.e., benzene, two benzenes with oxidized side-chain and carboxy- or hydroxy-furans and furanones, i.e. furan and furanone heterocycles with an oxygen atom in the side-chain~~with long side-chains (big_furans; ~~(Fig. 3c). $PC6_{OM}$ may represent an intermediate degradation status of higher plants and/or mosses residues, between the lignin oligomers or ahnhydrosugars (fresh) and the degraded polyaromatics and benzenes C2-9 or (alkyl)furans and furanones ~~with short side-chain~~ (i.e. furan and furanone heterocycles with an aliphatic side-chain~~(alkyl)furans~~).

3.2.3 Cluster analysis of OM composition

As with the elemental geochemistry dataset, a solution of six clusters ($cluster_{OM}$ 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 $PC1\text{-}6_{OM}$ (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 $PC1\text{-}6_{OM}$.

In the south basin, the majority of sites found at shallower and intermediate water depths group in $cluster_{OM}$ 3 (n=14) and are enriched in degraded, resistant and bacterial OM (positive scores on $PC1_{OM}$; Fig. 3a). The deep basin sites ($cluster_{OM}$ 2; n=3) are enriched in fresh algal and zooplanktonic OM (positive scores on $PC4_{OM}$; Fig. 3b). Accordingly, the values for the ratios indicative of higher proportions of fresh, labile algal OM, based on N-compound or chlorophyll composition, are higher in the deeper sites as compared to whole-lake averages, while the values are below or within ±10 % of whole-lake averages in the sediments found at shallower and intermediate water depths (Table 1). In contrast, these two types of south basin sites have similar values, and lower as compared to whole-lake averages, for the ratios indicative of higher plant and moss OM freshness based on carbohydrate or lignin composition. Furthermore, the $clusters_{OM}$ 2 and 3 are characterized by higher values for the ratios specific of algal versus higher plant and moss OM based on the proportions of N-compounds versus carbohydrates or chlorophylls versus lignin and long-chain *n*-alkanes and alkan-2-ones (Table 1). The rest of the south basin sites, fall within $cluster_{OM}$ 1 (n=1), 5 (n=2) or 4 (n=1), which are described below.

The majority of sites in the northern half of the lake group within $cluster_{OM}$ 1 (n=15) with isolated shallower sites falling within $clusters_{OM}$ 3 (n=1), 4 (n=2) and 5 (n=2). The sediments of $cluster_{OM}$ 1 are rich in fresh plant (higher plants or mosses) OM coming from in-lake productivity (negative scores on $PC1_{OM}$; Fig. 3a) and have higher values than whole-lake averages for the ratios specific of in-lake vs terrestrial plant OM and of higher plant and moss 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.

The $cluster_{OM}$ 5 represents some near-shore locations (n=4), which are enriched in OM derived from the coniferous-forested catchment (positive scores on $PC5_{OM}$; Fig. 3c). The $cluster_{OM}$ 4 (n=4), which groups shallow sites located close to the lake outlet (south basin, S16) and between the north and east basins (N10 and M1), is characterized by high proportions of degraded, resistant and

bacterial OM (positive scores on $PC5_{OM}$; Fig. 3a). Two shallow sites of the central area ($cluster_{OM}$ 6; n=2) show an enrichment in aliphatic molecules derived from higher plant and moss cell wall lipids (negative loadings on $PC3_{OM}$; Fig. 3b). Both $clusters_{OM}$ 4 and 6 have values for the ratio indicative of in-lake:terrestrial plant OM above 10% of the whole-lake average, while the values for the ratios specific of algal vs higher plant and moss OM and of algal and plant OM freshness based on N-compounds and carbohydrates composition are below 10% of whole-lake averages (Table 1). $Cluster_{OM}$ 6 differs from $cluster_{OM}$ 4 by its higher values for the ratios specific of algal and higher plant OM freshness based on chlorophyll and lignin composition.

~~3.3 Combined spatial patterns of elemental and organic biogeochemistry~~

3.3 Factors and processes involved in the spatial distribution of OM molecular composition

The surface sediments used in this study comprise the uppermost 10 cm. Given the inherent variation in sedimentation rates across a lake basin, each bulk sample represents material deposited over different timescales. We know from the developmental work for our Py-GC/MS method using annually laminated sediments that there are transformations in OM composition within the uppermost few cm, i.e., the first few years following deposition (Tolu et al. 2015). Thus these bulk sediment samples provide initial insights into the spatial variability in molecular OM composition within a lake basin resulting from longer-term sedimentation processes (including those within the sediment) reflecting years to decades.

The distribution of both $clusters_{geo}$ and $clusters_{OM}$ within Härsvatten shows a similar general pattern (Fig. 1c and 1d) where a main feature is the separation of most of the sample locations from the north and east basins ($cluster_{geo}$ 1 and $cluster_{OM}$ 1) from those in the main south basin ($clusters_{geo}$ 2, 5, 6 and $clusters_{OM}$ 2, 3). The other similarities are i) the separation of the sediments within the main, south basin according to water depth, with $cluster_{geo}$ 5 and $cluster_{OM}$ 2 grouping the deeper sites and $clusters_{geo}$ 2, 6 and $cluster_{OM}$ 3 grouping the shallow and intermediate depth

sites; and ii) the separation of the shallower sites that are located close to the shore ($cluster_{geo}$ 4 and $cluster_{OM}$ 5) from the ones that are found between the north and east basins and between the central area and the south basins ($cluster_{geo}$ 3 and $clusters_{OM}$ 4 and 6).

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

As shown previously for OM (as % LOI) and Pb (Bindler et al. 2001), there is a physical and inorganic geochemical gradient from shallower to deeper waters reflecting sediment focusing in the south basin of Härsvatten. B.D. and bSi decrease from shallower ($cluster_{geo}$6) to intermediate ($cluster_{geo}$2) to deeper areas ($cluster_{geo}$5), whereas there is a progressive enrichment in organic matter and trace elements with increasing water depth (Fig. 1c; Table 1). For example, B.D. decreases from ~0.07 to 0.03 g cm^{-3} while OM and Hg increase from ~34 to 52 % and from ~230 to 920 ng g^{-1}, respectively, in shallower versus the deepest locations. At intermediate depths ($cluster_{geo}$2), OM, B.D., bSi and most trace metals (i.e., Cu, Ni, Hg, Zn) are between those of shallow and deep locations. Sediment focusing is thus an important process for sediment geochemistry in the large, deep basin of Härsvatten, which presents a relatively simple morphometry. The sediments found at shallower (<11 m; $cluster_{geo}$ 6), intermediate (11-21 m; $cluster_{geo}$ 4) and deeper water depths (>23 m; $cluster_{geo}$ 5) would correspond approximatively to erosion, transportation and accumulation bottoms, respectively (Håkanson, 1977). The bSi decline, from ~15 to 4 %, ~~would reflect~~ indicates a decrease of diatom production with depth due to increasing light attenuation, and thus suggests ~~the fact~~ that the diatom assemblage is dominated by benthic diatoms~~, such~~ as ~~in~~ shown for many acidified lakes, such as ~~the~~ surrounding lakes in the Svartedalen nature reserve~~, has been shown to be dominated almost exclusively by benthic diatoms, with a near absence of planktonic diatoms~~ (e.g., Andersson, 1985; Anderson and Renberg, 1992).

In this main basin of Härsvatten, OM originates from a combination of autochthonous algal production and allochthonous input (Sect. 3.2.2). The dominance of benthic diatoms in acidified

lakes and the declining bSi content with depth would indicate that the algal material in deeper areas of the basin should derive from resuspended benthic algal production. However, this benthic algal production is not reflected in the OM molecular composition. The sediments from shallow and intermediate water depths ($cluster_{OM}$ 3) are mainly composed of degraded, resistant and bacterial OM, while the sediments from deeper sites ($cluster_{OM}$ 2) are enriched in fresh algal OM (Fig. 1d; Sect. 3.2.2). Although our results are based on the top 10 cm of sediment and thus account for different sediment ages, we suggest that the higher proportions of decomposed algal material, based on N-compound and chlorophyll composition (Table 1), at shallower and intermediate water depths (<21m) than at the deepest sites (23.5–24.5 m) reflect higher mineralization rates of OM in shallow/intermediate areas. Higher OM mineralization rates in shallow/intermediate areas are most probably due to more oxic conditions, which ~~. Oxic conditions~~ are known to prevail in epilimnitic and metalimnitic sediments (Ostovsky and Yacobi, 1999); the epilimnion in Härsvatten has been assessed to extend to 10–15 m water depth. Higher OM preservation in the deeper area may also be favored by higher accumulation rates as compared to shallow/intermediate areas (as consequence of sediment focusing), but the sedimentation rates in the deeper areas of Härsvatten are nonetheless very low, with the uppermost 30 cm being deposited during the last c. 500 year (Bindler et al., 2001). Moreover, the elemental geochemistry indicates that the sites found at intermediate water depths ($cluster_{geo}$ 6; 11–21 m) correspond in the sediment-focusing model to transportation ~~bottoms~~ zones, which experience recurrent resuspension events that favor gas exchanges and mineralization of OM (Ståhlberg et al., 2006). Occurrence of oxic conditions at intermediate depths in the south basin ~~are~~ is supported by the higher concentrations of Fe, Mn, As, Co and P and the high Fe:Al values, this combination of parameters being often indicative of Fe and Mn (oxy)hydroxides (Table 1; Sect. 3.1.1). In line with our hypothesis, higher OM mineralization rates in oxic versus anoxic sediments have previously been reported (Bastviken et al., 2004; Isidorova et al., 2016). However, in contrast to the more algal-derived OM, we do not observe significant differences between the sediments of shallower/intermediate water depth and the deepest sites for ratios indicative of higher

plant and moss OM freshness (Table 1). Because higher plant and moss OM is mainly of allochthonous origin in this basin, our results indicate that primarily autochthonous algal OM is mineralized in the epilimnitic and metalimnitic sediments of this deeper, steeper-sloped, basin of Härsvatten. This is consistent with the suggestion that allochthonous OM is recalcitrant to sediment mineralization after its degradation in the catchment and within the water column (Gudasz et al., 2012).

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

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

In the northern half of the lake, 11 of 19 locations fall within $cluster_{geo}1$ (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 ($clusters_{geo}1$, 3, 4 or 6). Thus, for the northern half of the lake there is no evidence of sediment focusing. The effect is either limited by the more gentle slopes of the north and east basins (Blais and Kalff, 1995), modified by the water circulation resulting from the prevailing winds towards the north-east (Bindler et al. 2001, Abril et al., 2004), and/or interrupted by aquatic vegetation that acts as a sediment trap (Benoy and Kalff, 1999). Indeed, aquatic vegetation represents a major source of

OM to the sediments of the northern, eastern and central basins (clusters$_{OM}$ 1, 4 and 6; Fig. 1d; Table 1 and Sect. 3.2.2). The enrichment of aquatic higher plant or moss OM in these sediments is consistent with field observations during the original sediment coring in winter 1997, where mosses and *Isoetes* (a vascular angiosperm plant) were observed in some parts of the lake to a depth of at least 10 m (Bindler et al., 2001). The presence of such submerged vegetation in Härsvatten is favored by its acidic, clear water (i.e., deeper light penetration), as previously observed for other acidified boreal Swedish lakes, such as the nearby lake Gårdsjön (Andersson, 1985; Grahn, 1985). Benthic aquatic vegetation is also favored in the northern half of Härsvatten by the more gentle slopes, comparatively shallow water depth and thus greater availability of light than in the deep, steeper-sloped south basin where allochthonous input appears as the main source of higher plant and moss OM (Sect. 3.2.2; Table 1).

The sediments found across the north and east basins and at the deeper sampling site of the central area (clusters$_{OM}$ 1; Fig. 1d) have the highest proportions of fresh, labile higher plant and moss OM ~~considering the whole lake~~ (Sect. 3.2.2; Table 1). Also, the proportions of fresh, labile algal OM is as high as in the deeper anoxic sediments of the main south basin and two times higher than in the sediments found at shallow water depth in the south basin and central areas, although these sites span the same depth range (3–11 m) and have relatively similar bSi contents (Table 1). These results indicate the accumulation of fresh autochthonous, both plant and algal, OM in sediments associated with in-lake vegetation even if they are below or within the epilimnion (i.e., supposed oxic conditions). A possible explanation is that the input of labile, decomposing in-lake higher plant and moss OM 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$_{geo}$ 1; Table 1). ~~Our~~ This 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. However, the lower concentrations of Fe, Mn and other elements known to be associated with Fe and Mn (oxy)hydroxides in these sediments of the north and south basins as compared to the sediments of the south basin and to the whole-lake averages may also be related to shallow groundwater discharges that are rich in (oxy)hydroxides or diagenetic processes that lead to Fe enrichment in the sediments of the south basin.

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

Among the sediments found in a small number of near-shore locations ($cluster_{geo}$ 4 and $cluster_{OM}$ 5; n=4), three are located in two more-sheltered bays at the northwestern corner and the southern end of the lake that are more protected from wind circulation (Bindler et al. 2001, Abril et al. 2004). The sediments of these three locations predominantly accumulate terrestrial OM ~~derived from the coniferous-forested catchment and~~ ~~have~~ as indicated by the abundance in lignin oligomers and the ratio indicative of in-lake:terrestrial plant OM that are respectively above and below 10% of the whole-lake averages (Table 3). Accumulation of OM coming from the coniferous-forested catchment most probably explained the high OM content (i.e. 52-58% , which is as high as in the deeper sediments of the main south basin) as well as the high concentrations of S and trace metals (i.e., Hg, Pb and Zn~~; Table 1~~) in these near-shore sediments (Table 1)~~which are known to accumulate in organic soils due to pollutant deposition (Lidman et al., 2014)~~. Boreal forest soils are known to be enriched in S and trace metals because their organic fraction retains atmospheric S and trace metals deposited over the industrial era (Johansson and Tyler, 2001). Also, there is evidence that the transport of terrestrial OM to boreal aquatic ecosystems is associated with significant inputs of trace metals (Grigal, 2002; Rydberg et al., 2008). ~~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).~~ Alternatively, high S and trace metal contents could be due to accumulation of metal sulfides due to near-shore groundwater gradients and/or anoxic conditions, or to redox cycling related to the important input of terrestrial OM.

3.3.3 Implication for in-lake and/or global elemental (e.g., C, nutrients, trace metals) cycling

The molecular composition of natural OM has been shown to exert a strong influence on key biogeochemical reactions involved in in-lake and global cycling of C, nutrients and trace metals, such as C mineralization or nutrients/trace metals sorption and transformations into mobile and

bioavailable species (Drott A et al., 2007; Sobek et al., 2011; Gudasz et al., 2012; Tjerngren et al., 2012; Kleeberg, 2013; Bravo et al., 2017). Our work demonstrates that OM molecular composition can vary significantly within a single lake system in relation to basin morphometry, lake chemical and biological status (e.g., presence of macrophytes, which is influenced by, e.g., acidification) and the molecular structure/properties of the different OM compounds (e.g., higher resistant of allochthonous versus autochthonous OM upon degradation). Our results further show that it may be problematic to extrapolate data on OM composition from only a few sites or one basin when scaling up to a whole lake. Thus, investigating sedimentary processes and the resulting fate of C and trace elements using sampling strategies focused on the deepest area of a lake or on single transects from shallower to deeper sites, may not fully capture the variation in either elemental geochemistry or OM composition.

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

Author contribution.

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

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Tables

Table 1. Summary statistics for sediment elemental geochemistry

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

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

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

		Av.[a] ± sd[b]	CV[c]	Median	A:M[d]	Min[d]-Max[e]
Carbohydrates	Furans	**15** ± 4	30	*14*	**1.06**	8-28
	Big_furans	**4.1** ± 1.2	29	*4.0*	1.03	0.8-7.5
	Pyrans	**3.4** ± 1	30	*3.2*	1.06	1.2-5.3
	Dianhydrorhamnose	**1.6** ± 0.5	28	*1.7*	0.99	0.3-2.7
	Levoglucosenone	**2.2** ± 0.4	20	*2.2*	1.00	1.3-3.1
	Levosugars	**3.7** ± 2.6	71	*2.5*	1.46	0.8-19
Chitin	Acetamidosugars	**2.5** ± 1	40	*2.6*	0.98	0.2-4.2
N-compounds	(alkyl)pyridines	**0.3** ± 0.1	34	*0.3*	0.95	0.1-0.5
	Pyridines_o	**0.7** ± 0.1	18	*0.7*	1.00	0.2-0.9
	(alkyl)pyrroles	**2.4** ± 0.5	22	*2.4*	1.01	1.7-3.5
	Pyrroles_o	**1.0** ± 0.2	25	*0.9*	1.04	0.5-1.4
	Maleimic & succinimide	**1.2** ± 0.3	29	*1.2*	0.98	0.2-1.7
	Aromatic N	**0.8** ± 0.3	36	*0.8*	1.03	0.3-1.4
	Indoles	**1.5** ± 0.4	24	*1.5*	1.03	0.5-3.1
	Diketodipyrrole	**0.8** ± 0.2	22	*0.8*	1.01	0.4-1.9
	Proteins	**1.5** ± 0.4	30	*1.5*	1.02	0.3-2.6
	Alkylamides	**0.6** ± 0.3	51	*0.6*	1.06	0.1-1.9
Phenols and Lignins	Phenols	**8** ± 1	15	*8*	1.02	4.4-11.4
	Syringols	**0.5** ± 0.4	83	*0.4*	1.32	0.1-1.9
	Guaiacols	**3.6** ± 2.3	65	*2.9*	1.24	1.1-13.5
Chlorophylls	Pristenes	**2.7** ± 0.8	28	*2.8*	0.97	0.4-4.6
	Phytadienes	**1.9** ± 0.7	35	*1.8*	1.04	0.2-3.6
Lipids	C9-16:1	**3.5** ± 0.8	23	*3.6*	0.98	1.8-5.1
	C17-C22:1	**6** ± 1	17	*6.2*	0.97	3.5-8.9
	C23-26_1	**2.9** ± 0.9	32	*2.7*	1.09	0.6-5.4
	C27-28:1	**0.8** ± 0.4	47	*0.7*	1.10	0.1-1.4
	C13-16:0	**2.5** ± 0.6	23	*2.5*	1.03	1.3-4.1
	C17-22:0	**3.9** ± 0.8	21	*4.0*	0.98	1.6-5.4
	C23-26:0	**2.8** ± 1.4	49	*2.7*	1.07	1.4-8.8
	C27-35:0	**4.3** ± 3.5	80	*3.6*	1.20	1.1-21.3
	2K C13-17	**1.3** ± 0.4	33	*1.4*	0.96	0.6-2.2
	2K C19-22	**0.3** ± 0.1	45	*0.3*	0.97	0-0.8
	2K C23-31	**1.3** ± 0.8	62	*1.1*	1.24	0.1-3.3
High molecular mass compounds	Steroids	**1.2** ± 0.9	70	*1.1*	1.10	0-4.3
	Tocopherols	**0.3** ± 0.3	106	*0.2*	1.75	0-1.5
	Hopanoids	**1.3** ± 0.4	31	*1.4*	0.94	0.2-1.9
(poly)aromatics	Benzene	**0.9** ± 0.4	43	*0.8*	1.14	0.4-2.5
	Benzaldehyde	**0.6** ± 0.3	41	*0.6*	1.08	0.3-1.5
	Acetylbenzene	**1.1** ± 0.4	39	*1.0*	1.10	0.6-2.3
	Alkylbenzenes C3-9	**1.9** ± 0.5	23	*1.8*	1.07	1.4-3.5
	Polyaromatics	**1.4** ± 0.4	27	*1.3*	1.04	0.8-2.1

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

Table 2. Summary statistics for the molecular composition of sediment OM given as relative abundances (expressed in %) of the 41 groups of Py organic compounds, which belong to 13 classes of OM that are indicated by the grey shading *(to be continued)*

	Compounds included	Av[a] ± sd	CV	Median	A:M	Min-Max
Carbohydrates						
(Alkyl)-furans &furanones	3-furaldehyde, 2-furaldehyde, 2-acetyl-furan, Methyl-3-furaldehyde, 2(5H)-furanone, Methyl-2-furaldehyde, Dihydro-methyl-furanone, Methyl-2(5H)-furanone, Methyl-2-furaldehyde	**15** ± 4	30	*14*	1.06	8-28
Hydroxy- or carboxy-furans & furanones	2-Furancarboxylic acid, methyl ester; 2,5-Dimethyl-4-hydroxy-3(2H)-furanone; 5-(hydroxymethyl)-2-furaldehyde	**4.1** ± 1.2	29	*4.0*	1.03	0.8-7.5
Pyrans	5,6-dihydro-pyran-2-one, 4-hydroxy-5,6-dihydro-pyran-2-one	**3.4** ± 1	30	*3.2*	1.06	1.2-5.3
Dianhydrorhamnose	Dianhydrorhamnose	**1.6** ± 0.5	28	*1.7*	0.99	0.3-2.7
Levoglucosenone	Levoglucosenone	**2.2** ± 0.4	20	*2.2*	1.00	1.3-3.1
Anhydrosugars	Anhydrohexose, Levogalactosan, Levomannosan, Levoglucosan	**3.7** ± 2.6	71	*2.5*	1.46	0.8-11
Chitin derived compounds						
Chitin-derived compounds	Acetamide, 3-acetamido-furan, 3-acetamido-4-pyrone, Oxazoline	**2.5** ± 1	40	*2.6*	0.98	0.2-4.2
N-compounds						
(Alkyl)pyridines	Pyridine, 2-methyl-pyridine, 3/4-methyl-pyridine	**0.3** ± 0.1	34	*0.3*	0.95	0.1-0.5
Pyridines_O, i.e. pyridines with side chain containing a ”C=O” function	2-acetylpyridine, 3-acetylpyridine, 2-Methyl-5-acetoxypyridine	**0.7** ± 0.1	18	*0.7*	1.00	0.2-0.9
(Alkyl)pyrroles	Pyrrole, Methyl-pyrrole	**2.4** ± 0.5	22	*2.4*	1.01	1.7-3.5
Pyrroles_O , i.e. pyrroles with side chain containing a ”C=O” function	2-formyl-pyrrole, 2-acetyl-pyrrole, 2-formyl-1-methylpyrrole	**1.0** ± 0.2	25	*0.9*	1.04	0.5-1.4
Pyrroledione & pyrrolidinedione	2,5-pyrroledione, 2,5-pyrrolidinedione	**1.2** ± 0.3	29	*1.2*	0.98	0.2-1.7
Aromatic N- compounds	Benzeneacetonitrile, Benzenepropanenitrile	**0.8** ± 0.3	36	*0.8*	1.03	0.3-1.4
Indoles	Indole, Methyl-indole	**1.5** ± 0.4	24	*1.5*	1.03	0.5-3.1
Diketodipyrrole	Diketodipyrrole	**0.8** ± 0.2	22	*0.8*	1.01	0.4-1.2
Diketopiperazines	Pro-Ala, Pro-Val, Pro-Val, Cyclo-Leu-Pro, Pro-Pro, Pro-Phe	**1.5** ± 0.4	30	*1.5*	1.02	0.3-2.6
Alkylamides	6 alkylamides	**0.6** ± 0.3	51	*0.6*	1.06	0.1-1.7
Phenols						
Phenols	Phenol, 2-methyl-phenol, 3/4- methyl-phenol, dimethyl-phenol, Ethyl-phenol, Propenyl-phenol	**8** ± 1	15	*8*	1.02	4.4-11.4
Lignins						
Syringols	Syringol, 4-vinyl-syringol, 4-formyl-syringol, 4-allenesyringol, Acetosyringone	**0.5** ± 0.4	83	*0.4*	1.32	0.1-1.9
Guaiacols	Guaiacol, Ethyl-guaiacol, 4-vinyl-guaiacol, 4-propenyl-guaiacol, Vanillin, 4-alleneguaiacol, Acetovanillone, Vanillic acid, methyl ester, Guaiacylacetone	**3.6** ± 2.3	65	*2.9*	1.24	1.1-13.5

Table 2. Summary statistics for the molecular composition of sediment OM given as the relative abundances (expressed in %) of the 41 groups of Py organic compounds, which belong to 13 classes of OM that are indicated by the grey shading *(following part)*

Chlorophylls						
Pristenes	Prist-1-ene, Prist-2-ene	**2.7** ± 0.8	28	*2.8*	0.97	0.4-4.6
Phytadienes	Phytadiene 1, Phytadiene 2	**1.9** ± 0.7	35	*1.8*	1.04	0.2-3.6
***n*-alkenes**						
C9-16:1	*n*-alkenes C9, C13, C14, C16	**3.5** ± 0.8	23	*3.6*	0.98	1.8-5.1
C17-C22:1	*n*-alkenes C17, C18, C19, C20, C21, C22	**6** ± 1	17	*6.2*	0.97	3.5-8.9
C23-26_1	*n*-alkenes C23, C24, C25, C26	**2.9** ± 0.9	32	*2.7*	1.09	0.6-5.4
C27-28:1	*n*-alkenes C27, C28	**0.8** ± 0.4	47	*0.7*	1.10	0.1-1.4
***n*-alkanes**						
C10-16:0	*n*-alkanes C10, C11, C12, C13, C14, C15, C16	**2.5** ± 0.6	23	*2.5*	1.03	1.3-4.1
C17-22:0	*n*-alkanes C17, C18, C19, C20, C21, C22	**3.9** ± 0.8	21	*4.0*	0.98	1.6-5.4
C23-26:0	*n*-alkanes C23, C24, C25, C26	**2.8** ± 1.4	49	*2.7*	1.07	1.4-8.8
C27-35:0	*n*-alkanes C27, C28, C29, C30, C31, C32, C33, C35	**4.3** ± 3.5	80	*3.6*	1.20	1.1-21.3
Alkan-2-ones						
2K C13-17	Alkan-2-ones C13, 16, 17	**1.3** ± 0.4	33	*1.4*	0.96	0.6-2.2
2K C19-21	Alkan-2-ones C19, 20, 21	**0.3** ± 0.1	45	*0.3*	0.97	0-0.8
2K C23-31	Alkan-2-ones C23, 14, 25, 26, 27, 28, 29, 31	**1.3** ± 0.8	62	*1.1*	1.24	0.1-3.3
Steroids						
Steroids	Cholest-2-ene, Cholesta-3,5-diene, Stigmasta-5,22-dien-3-ol, acetate, Sitosterol, Cholesta-3,5-dien-7-one, Stigmasta-3,5-dien-7-one	**1.2** ± 0.9	70	*1.1*	1.10	0-4.3
Tocopherols						
Tocopherols	γ-Tocopherol, α-Tocopherol	**0.3** ± 0.3	106	*0.2*	1.75	0-1.5
Hopanoids						
Hopanoids	Trinosphopane, Norhopene, 22,29,30-trisnorhop-17(21)-ene, 22,29,30-trisnorhop-16(17)-ene, Norhopane, 25-norhopene	**1.3** ± 0.4	31	*1.4*	0.94	0.2-1.9
(Poly)aromatics						
Benzene	Benzene	**0.9** ± 0.4	43	*0.8*	1.14	0.4-2.5
Benzaldehyde	Benzaldehyde	**0.6** ± 0.3	41	*0.6*	1.08	0.3-1.5
Acetylbenzene	Acetyl-benzene	**1.1** ± 0.4	39	*1.0*	1.10	0.6-2.3
Alkylbenzenes C3-9	Ethyl-methyl-benzene, Benzene C7, Benzene C9,	**1.9** ± 0.5	23	*1.8*	1.07	1.4-3.5
Polyaromatics	Styrene, Indene, 1,2-dihydro-naphthalene, 2,3-dihydro-inden-1-one, 1-methyl-napthalene, 2methyl-napthalene, Biphenyl, Fluorene, Anthracene	**1.4** ± 0.4	27	*1.3*	1.04	0.8-2.1

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 FEATURES IN GEOCHEMISTRY

	Whole-lake[a]	Near-shore sites	North/East basins	South basin *Shallower*	South basin *Intermediate depth*	South basin *Deeper*	Shallow central areas
		Cluster$_{geo}$ 4	*Cluster$_{geo}$ 1*	*Cluster$_{geo}$ 6*	*Cluster$_{geo}$ 2*	*Cluster$_{geo}$ 5*	*Cluster$_{geo}$ 3*
	(n[b]=42)	*(n=4)*	*(n=13)*	*(n=10)*	*(n=8)*	*(n=3)*	*(n=4)*
Water depth (m)	**9** ± 7 *(78%)*[c]	**4** ± 2	**5** ± 3	**8** ± 3	**15** ± 4	**24** ± 1	**2** ± 1
Bulk density (g cm^{-3})	**0.06** ± 0.02 *(33%)*	**0.06** ± 0.03	**0.07** ± 0.02	**0.07** ± 0.02	**0.05** ± 0.01	**0.026** ± 0.009	**0.10** ± 0.02
[bSi] (%)	**13** ± 6 *(46%)*	**12** ± 6	**13** ± 3	**15** ± 7	**7** ± 3	**4.2** ± 0.3	**21** ± 4
LOI] (%)	**38** ± 10 *(26%)*	**50** ± 12	**39** ± 5	**34** ± 7	**37** ± 4	**52** ± 2	**20** ± 8
[S] (mg kg^{-1})	**11876** ± 5920 *(50%)*	**17510** ± 833	**11683** ± 3440	**7550** ± 1900	**12896** ± 3315	**26227** ± 4833	**4879** ± 148
[Br] (mg kg^{-1})	**149** ± 35 *(23%)*	**130** ± 6	**153** ± 36	**145** ± 35	**154** ± 19	**204** ± 26	**116** ± 32
[Cu] (mg kg^{-1})	**34** ± 13 *(38%)*	**36** ± 5	**28** ± 6	**30** ± 7	**42** ± 6	**65** ± 10	**24** ± 13
[Ni] (mg kg^{-1})	**19** ± 5 *(25%)*	**21** ± 1	**18** ± 4	**17** ± 2	**21** ± 4	**27** ± 1	**12** ± 4
[Hg] (µg kg^{-1})	**337** ± 202 *(60%)*	**407** ± 141	**251** ± 47	**230** ± 69	**427** ± 94	**917** ± 212	**203** ± 87
[Zn] (mg kg^{-1})	**219** ± 108 *(49%)*	**279** ± 31	**212** ± 68	**139** ± 42	**305** ± 86	**417** ± 33	**63** ± 16
[Fe] (%)	**5** ± 3 *(60%)*	**3.1** ± 2.1	**2.7** ± 1.7	**3.6** ± 1.5	**9.1** ± 2.4	**4.3** ± 2.2	**5.5** ± 1.7
Fe:Al	**1.5** ± 0.8 *(53%)*	**1.0** ± 0.5	**1.0** ± 0.6	**1.1** ± 0.3	***2.5*** ± *0.9*	***1.3*** ± *0.6*	***1.9*** ± *0.3*
[As] (mg kg^{-1})	**35** ± 20 *(57%)*	**27** ± 17	**26** ± 16	**25** ± 11	**64** ± 11	**48** ± 14	**29** ± 9
[P] (mg kg^{-1})	**1624** ± 741 *(46%)*	**927** ± 240	**1065** ± 295	**2088** ± 730	**2074** ± 275	**2766** ± 869	**1224** ± 216
[Mn] (mg kg^{-1})	**729** ± 1690 *(231%)*	**162** ± 53	**182** ± 67	**184** ± 50	**305** ± 93	**171** ± 13	**5700** ± 1597
Mn:Fe	**0.02** ± 0.03 *(150%)*	**0.007** ± 0.002	**0.008** ± 0.003	**0.006** ± 0.002	**0.004** ± 0.001	**0.005** ± 0.002	**0.111** ± 0.051
[Co] (mg kg^{-1})	**19** ± 15 *(79%)*	**15** ± 8	**12** ± 6	**13** ± 5	26 ± 11	**14** ± 2	**49** ± 24
[Pb] (mg kg^{-1})	**192** ± 90 *(47%)*	**199** ± 58	***132*** ± *53*	**115** ± 42	**300** ± 59	**315** ± 7	**182** ± 96

SPECIFIC FEATURES IN OM COMPOSITION

		Whole-lake	Near-shore sites	North/East basins	South basin *Shallower/intermediate depth*	South basin *Deeper*	Shallow central areas	
			Cluster$_{OM}$ 5	*Cluster$_{OM}$ 1*	*Cluster$_{OM}$ 3*	*Cluster_$_{OM}$ 2*	*Cluster$_{OM}$ 4*	*Cluster$_{OM}$ 6*
		(n=42)	*(n=4)*	*(n=16)*	*(n=14)*	*(n=3)*	*(n=3)*	*(n=2)*
Water depth (W.D.)		**9** ± 7 *(78%)*	**4** ± 2	**7** ± 5	**11** ± 5	**24.1** ± 0.5	**3.2** ± 0.9	**1.8** ± 0.1
LOI (%)		**38** ± 10 *(26%)*	**50** ± 12	**39** ± 4	**36** ± 5	**52** ± 2	**24** ± 4	**14** ± 6
(C23-35:0+2K C23-31): Lignins[d]	In-lake:Terrestrial plant OM	**2** ± 1 *(50%)*	**0.8** ± 0.5	**3** ± 1	**1.7** ± 0.4	**1.8** ± 0.6	**3** ± 1	**19** ± 11
N-compounds : Carbohydrates	Algal:Plant OM	**0.37** ± 0.09 *(24%)*	**0.32** ± 0.08	**0.35** ± 0.04	**0**.39 ± 0.05	**0.6** ± 0.1	**0.29** ± 0.02	**0.23** ± 0.05
Chlorophylls : Plant lipids+lignins	Algal:Plant OM	**0.18** ± 0.09 *(50%)*	**0.10** ± 0.05	**0.13** ± 0.06	**0.24** ± 0.08	**0.31** ± 0.07	**0.18** ± 0.05	**0.03** ± 0.03
Proteins:(alkyl)pyrroles+ (alkyl)pyridines+Aromatic N	Algal OM (N-compounds) freshness	**0.3** ± 0.1 *(33%)*	**0.39** ± 0.09	**0.36** ± 0.05	**0.22** ± 0.06	**0.42** ± 0.06	**0.20** ± 0.08	**0.13** ± 0.08
Phytadienes:pristenes[c]	Algal OM (chlorophylls) freshness	**0.4** ± 0.1 *(25%)*	**0.4** ± 0.1	**0.37** ± 0.09	**0.40** ± 0.06	**0.56** ± 0.05	**0.42** ± 0.07	**0.5** ± 0.2
Anhydrosugars:(alkyl)furans & furanones	Plant OM (carbohydrates) freshness	**0.2** ± 0.2 *(100%)*	**0.4** ± 0.2	**0.3** ± 0.2	**0.12** ± 0.11	**0.14** ± 0.04	**0.08** ± 0.01	**0.042** ± 0.002
Guaiacyl-acid:Guaiacyl-aldehyde[e]	Plant OM (lignin) freshness	**0.07** ± 0.03 *(43%)*	**0.13** ± 0.02	**0.07** ± 0.03	**0.05** ± 0.02	**0.04** ± 0.01	**0.04** ± 0.03	**0.10** ± 0.06
Guaiacyl -2C: Guaiacyl -1C[e]	Plant OM (lignin) freshness	**0.8** ± 0.3 *(38%)*	**1.23** ± 0.07	**1.0** ± 0.2	**0.5** ± 0.2	**0.6** ± 0.2	**0.5** ± 0.1	**1.1** ± 0.2
Syringyl-2C:Syringyl-1C[e]	Plant OM (lignin) freshness	**1.0** ± 0.8 *(80%)*	**2.4** ± 0.3	**1.1** ± 0.6	**0.5** ± 0.2	**0.6** ± 0.1	**0.3** ± 0.3	**1.4** ± 0.8

[a] whole-lake: averages of all analyzed sediment samples ~~are calculated without the~~ excluding the two outlier samples (sites M4, S15; cf. Sect. ~~2.5~~3.1.1); [b] n: number of samples; [c] the data are presented as follow: **average** ± standard deviation *(relative standard deviation)*; [d] the compounds included in the ratios are given in detail in Table S1 in the supplementary information.
Light grey background denotes average values below whole-lake average (<10%); No background denotes values close to whole-lake average (±10%); Dark grey background are values above whole-lake average (>10%).

1000

Figures

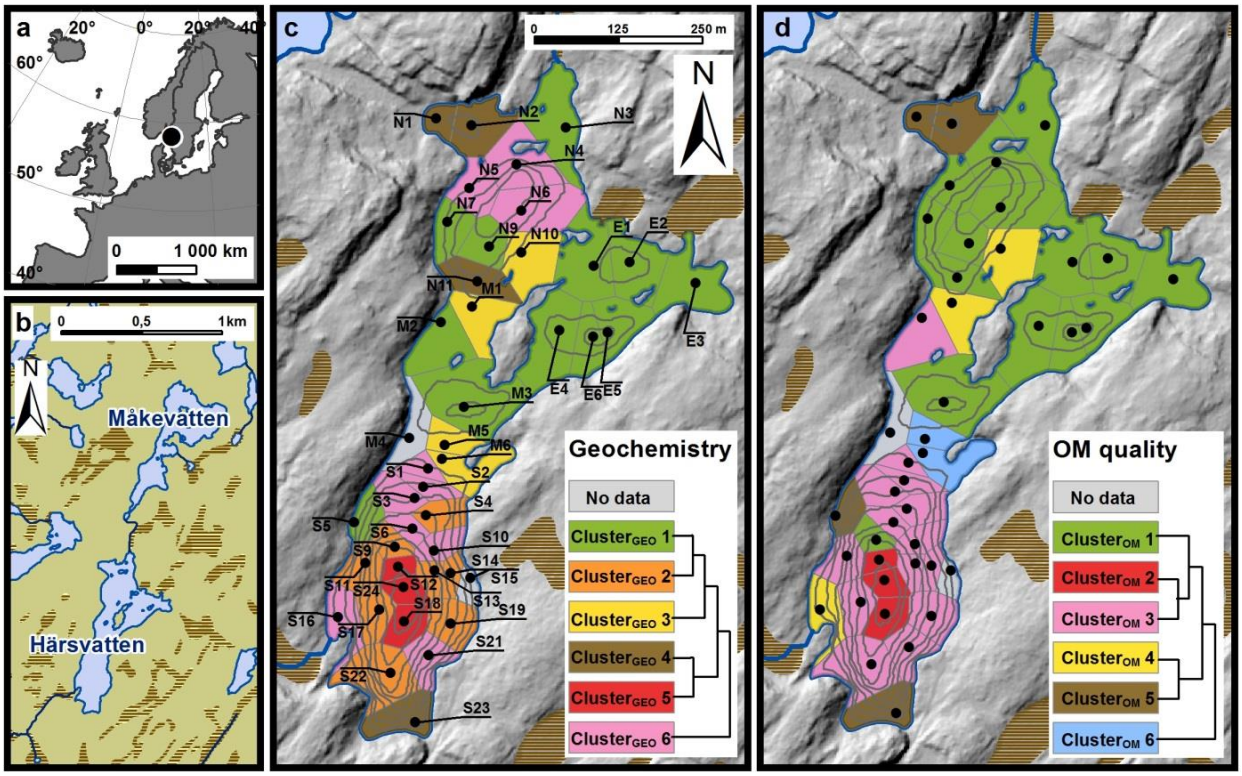

Fig. 1 Maps of Härsvatten showing (a) its location in Europe; (b) its catchment with lakes, mires and larger streams; and (c, d) its bathymetry along with the spatial distribution of the 44 sampling sites and the six selected clusters based on sediment elemental geochemistry (c) and sediment OM molecular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

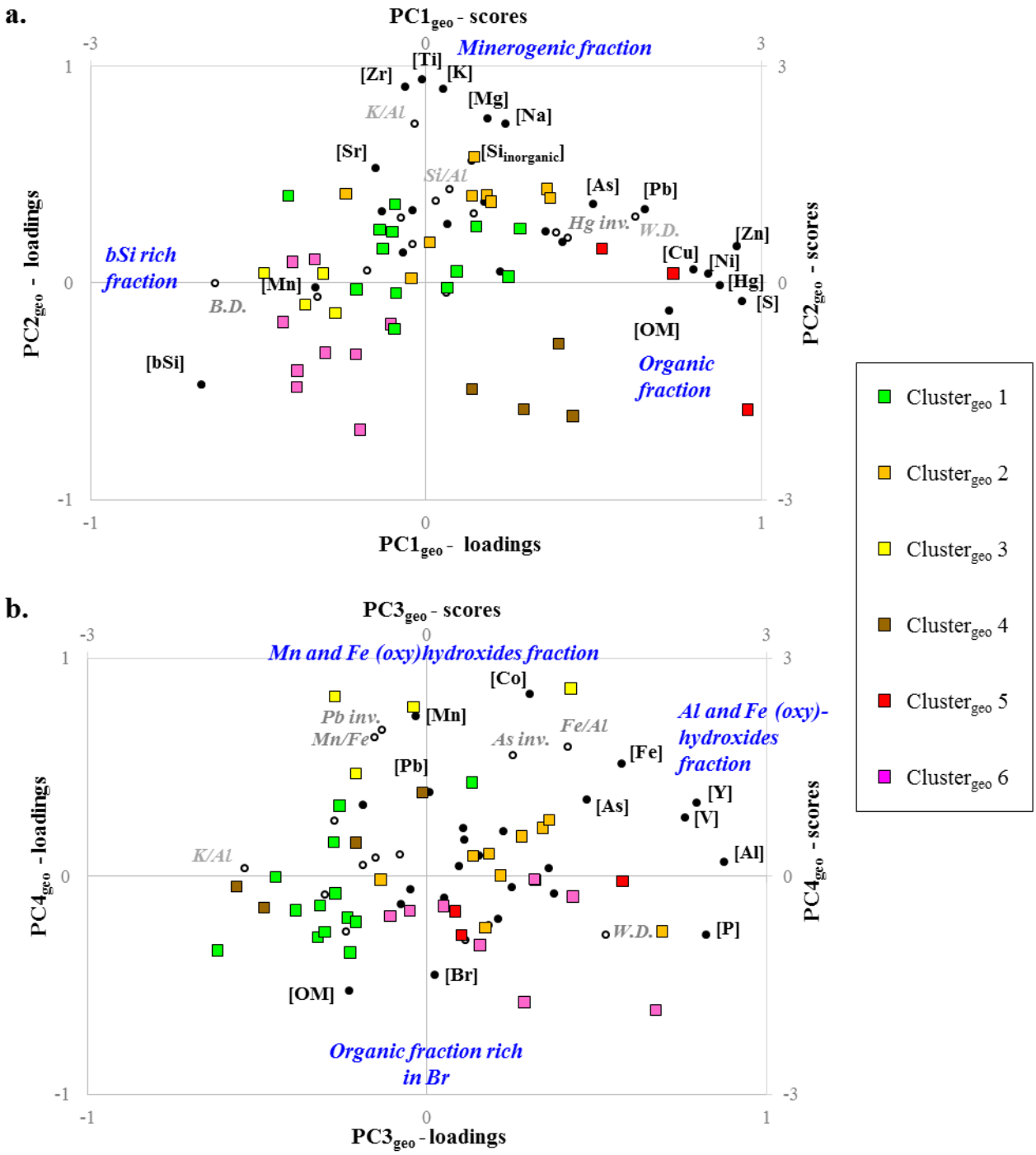

Fig. 2 Combined loading- and score-plots for PCs 1-4 of the elemental geochemistry dataset. For the PC-loadings, filled circles correspond to active variables. Others variables (empty circle and italics letter) were added passively. Sediment samples are colored according to the results of the cluster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

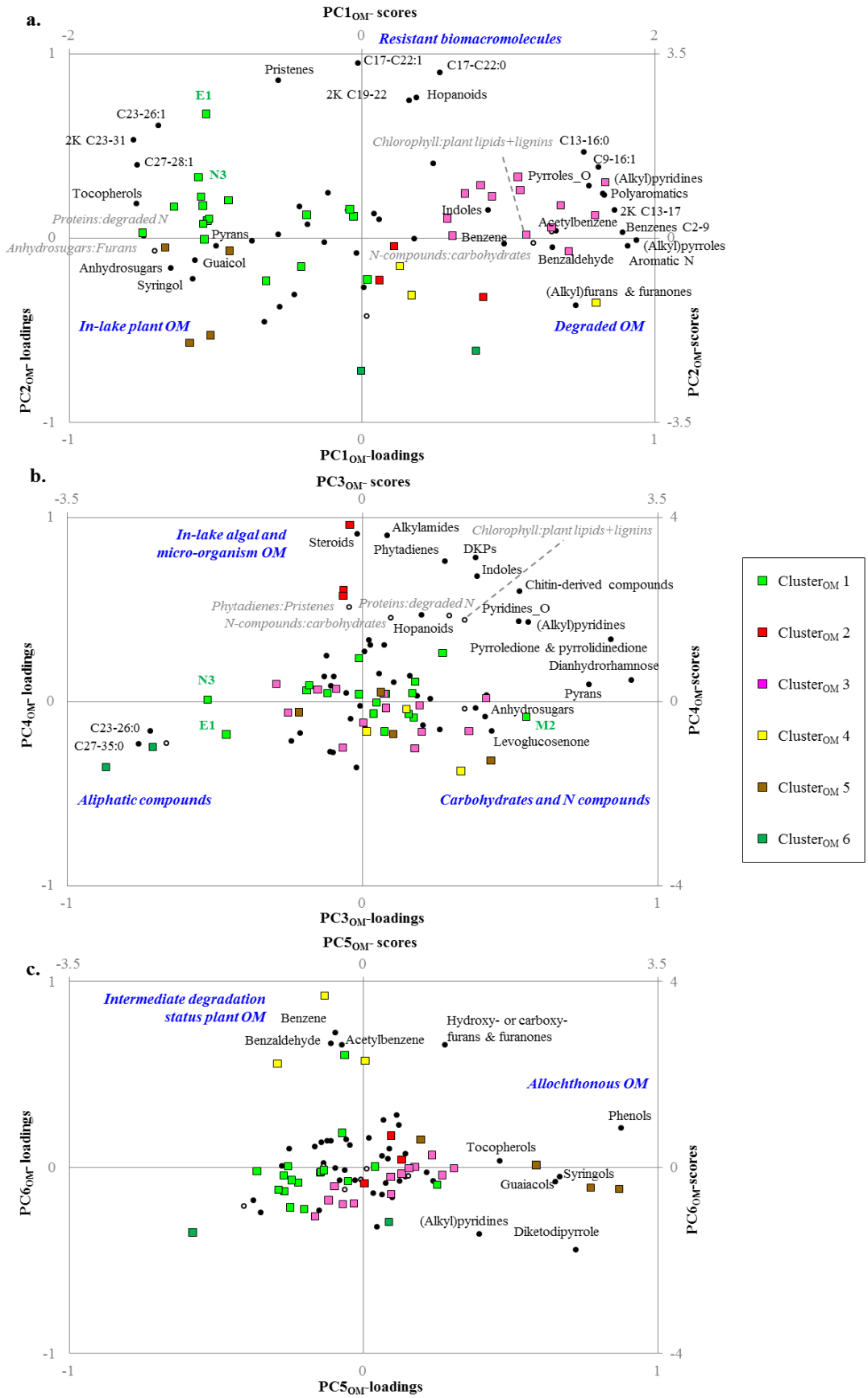

Fig. 3 Combined loading- and score-plots for PCs 1-6 (a, b and c) of the OM molecular composition dataset (i.e. the 41 groups of organic compounds as defined in Table 2). For the PC-loadings, filled circles correspond to active variables. Others variables (empty circle and italics letter) were added passively. Sediment samples are colored according to the results of the cluster analysis.

Supplementary information

Table S1. Identified organic compounds by Py-GC-MS along with their formula, molecular mass (M)~~, specific mass fragments~~,, retention time (RT), calculated and reference retention index (Kovats retention index, RI[a]), references for the mass spectra (REF) and how ~~they~~ the individual organic compounds have been grouped for the statistical analyses

Name	Formula	M	RT	$RI_{this\ study}$	reference RI[b] $RI_{estimated}$	$RI_{experimental}$	REF	Compounds groups
Carbohydrates								
3-furaldehyde	C5H4O2	96	189.5	N.D.[c]			NIST, [1]	~~Furans~~ (Alkyl)furans & furanones
2-furaldehyde	C5H4O2	96	204.1	N.D.			NIST, [1]	
2-acetyl-furan	C6H6O2	110	267.2	N.D.			NIST, [1]	
Methyl-3-furaldehyde	C6H6O2	110	269.8	N.D.			NIST, [1]	
2(5H)-furanone	C4H4O2	84	270.5	N.D.			NIST, [1]	
Methyl-2-furaldehyde	C6H6O2	110	276.9	N.D.			NIST, [1]	
Dihydro-methyl-furanone	C5H6O	98	277.8	N.D.			[1]	
5-methyl-2(5H)-Furanone	C5H6O2	98	292.5	907	868	914-917	NIST, [1]	
Methyl-2-furaldehyde	C6H6O2	110	312.8	920	920	924-987	NIST, [1]	
2-Furancarboxylic acid, methyl ester	C6H6O3	126	422.7		909		NIST, [1]	~~Big_furans~~ Hydroxyl or carboxy-furans & furanones
2,5-Dimethyl-4-hydroxy-3(2H)-furanone	C6H8O3	128	424.6	1088	1022	1023-1097	NIST	
5-(hydroxymethyl)-2-Furaldehyde	C6H6O3	126	551.9	1236	1163	1176-1236	NIST, [1]	
5,6-dihydro-2H-Pyran-2-one	C5H6O2	98	278.7	N.D.			NIST	Pyrans
4-hydroxy-5,6-dihydro(2H)-pyran-2-one	C5H6O3	114	344.2	941	N.R.[d]	N.R.	[1]	
Dianhydrorhamnose	$C_6H_8O_3$	128	383.4	1041	N.R.	N.R.	[2]	Dianhydrorhamnose
Levoglucosenone	C6H6O3	126	450.1	1119	N.R.	1070	NIST	Levoglucosenone
Levosugars (Levogalactosan)	C6H10O5	162	535.7	1375	N.R.	N.R.	[1]	Anhydrosugars
Ahydrohexose	Unknown		729.0	1450	N.R.	N.R.	[1]	
Levosugars(Levomannosan)	C6H10O5	162	761.5	1447	N.R.	N.R.	[1]	
Levosugars (Levoglucosan)	C6H10O5	162	771.4	1493	1404	1486-1491	[1]	
~~Acetamido-sugars~~ Chitin derived compounds								
Acetamide	C2H5NO	59	166.3	N.D.			NIST	Chitin derived compounds
3-acetamido-furan	C6H7NO2	125	555.4	1239	N.R.	N.R.	NIST	
3-acetamido-4-pyrone	Unknown	153	656.4	1353	N.R.	N.R.	[3]	
Oxazoline	Unknown		801.9	1548	N.R.	N.R.	[3]	
N-compounds								
Pyridine	C5H5N	79	151.9	N.D.			NIST	(Alkyl)pyridines
2-methyl-pyridine	C6H7N	93	197.6	N.D.			NIST	
3/4-methyl-pyridine	C6H7N	93	234.6	N.D.			NIST	
2-Acetylpyridine	C7H7NO	121	377.2	1034	N.R.	N.R.	NIST	Pyridines_O
3-Acetylpyridine	C7H7NO	121	404.0	1065	N.R.	N.R.	NIST	
2-Methyl-5-acetoxypyridine	C8H9NO2	151	734.1	1457	N.R.	N.R.	NIST	
Pyrrole	C4H5N	67	154.2	N.D.			NIST	(Alkyl)pyrroles
Methyl-pyrrole	C5H7N	81	216.2	N.D.			NIST	
2-formyl-pyrrole	C5H5NO	95	354.2	1008	988	1005-1030	NIST	Pyrroles_O
2-acetyl-pyrrole	C6H7NO	109	402.0	1062	1035	1026-1064	NIST	
2-Formyl-1-methylpyrrole	C6H7NO		459.9	1129	1077	1092-1105	NIST	
~~Maleimide~~ 2,5-pyrroledione	C4H3NO2	97	335.9	935	N.R.	N.R.	NIST	Pyrroledione & pyrrolidinedione
~~Succinimide~~ 2,5-pyrrolidinedione	C4H5NO2	99	462.1	1131	934	N.R.	NIST	
Benzeneacetonitrile	C8H7N	117	474.2	1147	1138	1089-1143	NIST	Aromatic N
Benzenepropanenitrile	C9H9N	131	563.9	1248	1238	1186-1242	NIST	
Indole	C8H7N	117	609.9	1293	1174	1260-1303	NIST	Indoles
Methyl-indole	C9H9N	131	686.1	1394	1288	1380-1410	NIST	
Diketodipyrrole	Unknown	186	922.7	1722	N.R.	N.R.	[4]	Diketodipyrrole
Diketopiperazine Pro-Ala	C8H12N2O2	168	938.0	1746	N.R.	N.R.	[5, 6]	Diketopiperazines
Diketopiperazine Pro-Val	C10H16N2O2	196	989.4	1826	N.R.	N.R.	[5, 6]	
Diketopiperazine Pro-Val	C10H16N2O2	196	1005.9	1852	N.R.	N.R.		
Diketopiperazine Cyclo-Leu-Pro	C11H18N2O2	210	1049.0	1922	N.R.	N.R.	NIST	
Diketopiperazine Pro-Pro	C10H14N2O2	194	1067.0	1953	N.R.	N.R.	[5, 6]	
Diketopiperazine Pro-Phe	C14H16N2O2	244	1284.3	2352	N.R.	N.R.	[5, 6]	
Alkylamide1	Unknown		986.8	1821	N.R.	N.R.	NIST	Alkylamides
Alkylamide2	Unknown		1081.1	1977	N.R.	N.R.	NIST	
Alkylamide3	Unknown		1197.6	2185	N.R.	N.R.	NIST	
Alkylamide4	Unknown		1237.3	2260	N.R.	N.R.	NIST	
Alkylamide5	Unknown		1304.2	2392	N.R.	N.R.	NIST	
Alkylamide6	Unknown		1579.6	3020	N.R.	N.R.	NIST	

***n*-alkenes**								
n-C9:1	C9H18	126					NIST	C9-16:1
n-C13:1	C13H26	182	603.4	1286	1204	1187-1289	NIST	
n-C14:1	C14H28	196	684.6	1392	1421	1389-1396	NIST	
n-C16:1	C16H32	224	834.4	1593	1602	1590-1593	NIST	
n-C17:1	C17H34	238	903.6	1693	N.R.	1692-1703	NIST	C17-22:1
n-C18:1	C18H36	252	969.2	1794	1801	1788-1793	NIST	
n-C19:1	C19H38	266	1031.8	1894	1900	1883-1899	NIST	
n-C20:1	C20H40	280	1091.5	1994	N.R.	1889-1994	NIST	
n-C21:1	C21H42	294	1148.5	2096	2117	2060	NIST	
n-C22:1	C22H44	308	1203.2	2195	2198	2192-2195	NIST	
n-C23:1	C23H46	322	1255.5	2295	N.R.	2288-2295	NIST	C23-26:1
n-C24:1	C24H48	336	1305.7	2395	N.R.	2394-2396	NIST	
n-C25:1	C25H50	350	1352.9	2498	N.R.	2483-2496	NIST	
n-C26:1	C26H52	364	1400.5	2596	N.R.	2593-2596	NIST	
n-C27:1	C27H54	350	1445.6	2697	N.R.	2688-2694	NIST	C27-28:1
n-C28:1	C28H56	364	1488.5	2796	N.R.	2794-2797	NIST	
***n*-alkanes**								
n-C10:0	C10H22	142	347.4				NIST	C10-16:0
n-C11:0	C11H24	156	435.0				NIST	
n-C12:0	C12H26	170	515.5				NIST	
n-C13:0	C13H28	184	617.3				NIST	
n-C14:0	C14H30	198	690.7				NIST	
n-C15:0	C15H32	212	767.1				NIST	
n-C16:0	C16H34	226	839.5				NIST	
n-C17:0	C17H36	240	908.1				NIST	C17-22:0
n-C18:0	C18H38	254	973.5				NIST	
n-C19:0	C19H40	268	1035.7				NIST	
n-C20:0	C20H42	282	1095.0				NIST	
n-C21:0	C21H44	296	1150.7				NIST	
n-C22:0	C22H46	310	1206.1				NIST	
n-C23:0	C23H48	324	1258.1				NIST	C23-26:0
n-C24:0	C24H50	338	1308.1				NIST	
n-C25:0	C25H52	352	1355.1				NIST	
n-C26:0	C26H54	366	1402.4				NIST	
n-C27:0	C27H56	380	1447.1				NIST	C27-35:0
n-C28:0	C28H58	394	1490.2				NIST	
n-C29:0	C29H60	408	1530.3				NIST	
n-C30:0	C30H62	422	1571.8				NIST	
n-C31:0	C31H64	436	1610.9				NIST	
n-C32:0	C32H66	450	1648.6				NIST	
n-C33:0	C33H68	464	1685.0				NIST	
n-C35:0	C35H72	492	1723.9				[7]	
Alkan-2-ones								
2-K C13	C13H26O	198	765.4	1498	1449	1476-1498	NIST	2K C13-17
2-K C16	C16H32O	240	975.0	1803	1748	1780-1805	NIST	
2-K C17	C17H34O	254	1038.2	1904	1847	1875-1890	NIST	
2-K C19	C19H38O	282	1155.9	2109	2046	2087-2106	NIST	2K C19-22
2-K C20	C20H40O	396	1210.9	2209	2206	N.R.	NIST	
2-K C21	C21H42O	310	1263.7	2311	2309	N.R.	NIST	
2-K C23	C23H46O	338	1363.0	2517	2513	N.R.	NIST	2K C23-31
2-K C24	C24H48O	352	1410.0	2617	N.R.	N.R.	NIST	
2-K C25	C25H50O	366	1455.1	2719	N.R.	N.R.	NIST	
2-K C26	C26H52O	380	1498.6	2821	N.R.	N.R.	NIST	
2-K C27	C27H54O	394	1540.6	2925	N.R.	N.R.	[7]	
2-K C28	C28H56O	408	1581.3	3024	N.R.	N.R.	[7]	
2-K C29	C29H58O	422	1620.7	3126	N.R.	N.R.	[7]	
2-K C31	C31H62O	450	1696.0	3328	N.R.	N.R.	[7]	
Phenols								
Phenol	C6H6O	94	329.2	931	901	952-1004	NIST	Phenols
2- methyl-phenol	C7H8O	108	396.2	1056	1014	1029-1039	NIST	
3/4- methyl-phenol	C7H8O	108	414.9	1077	1014	1051-1063	NIST	
Dimethyl-phenol	C7H8O	122	418.4	1156	1127	1077-1130	NIST	
Ethyl- phenol	C8H70O	122	497.3	1177	1114	1106-1162	NIST	
Propenyl-phenol	C9H10O	134	646.7	1340	1203	1232-1258	NIST	
Lignins								
Guaiacol **(G)**	C7H8O2	124	428.7	1093	1090	1052-1090	NIST	Guaiacols
Ethyl-guaiacol **(guaiacyl-2C)**	C9H12O2	152	596.2	1279	1303	1243-1287	NIST	

4-vinyl-guaiacol **(guaiacyl -2C)**	C9H10O2	150	625.6	1311	1293	1272-1295	NIST	
4-propenyl-guaiacol **(guaiacyl -3C)**	C10H12O2	164	660.9	1359	1392	1339-1452	NIST	
Vanillin **(guaiacyl -1C or -aldehyde)**	C8H8O3	152	695.9	1407	1392	1350-1447	NIST	
4-alleneguaiacol **(guaiacyl -3C)**	C10H10O2	162	741.0	1466	N.R.	N.R.	[8]	
Acetovanillone **(guaiacyl -2Cor aldehyde)**	C9H10O3	166	763.1	1495	1439	1447-1503	NIST	
Vanillic acid, methyl ester (**guaiacyl -1C or -acid)**	C9H10O4	182	785.5	1525	1470	1463-1525	NIST	
Guaiacylacetone **(guaiacyl -3Cor -aldehyde)**	C10H12O3	180	796.0	1540	1538	1488-1531	NIST	
Syringol **(syringyl)**	C8H10O3	154	655.4	1352	1279	1349-1367	NIST	Syringols
4-vinyl-syringol **(syringy-2C)**	C11H14O4	210	819.5	1572	N.R.	1517-1573	NIST	
4-formyl-syringol **(syringy-1C)**	C9H10O4	182	887.6	1670	1581	1617-1670	NIST	
4-allenesyringol **(syringy-3C)**	C11H12O3	192	901.0	1690	N.R.	N.R.	[8]	
Acetosyringone **(syringy-2C)**	C10H12O4	196	961.1	1781	1628	1740-1744	NIST	
Chlorophylls								
Prist-1-ene	C19H38	266	929.0	1732	N.R.	N.R.	[9]	Pristenes
Prist-2-ene	C19H38	266	936.3	1743	N.R.	N.R.	[9]	
Phytadiene 1	C20H38	278	999.1	1841	N.R.	N.R.	[9]	Phytadienes
Phytadiene 2	C20H38	278	1026.0	1884	N.R.	N.R.	[9]	
Steroids								
Cholest-2-ene	$C_{27}H_{46}$	370	1522.1	2880	2380	N.R.	NIST	Steroids
Cholesta-3,5-diene	$C_{27}H_{44}$	368	1543.4	2932	N.R.	N.R.	NIST	
Stigmasta-5,22-dien-3-ol, acetate	$C_{31}H_{50}O_2$	454	1601.1	3075	2879	N.R.	NIST	
Sitosterol	$C_{29}H_{50}O$	414	1623.4	3133	2731	3173-3220	NIST	
Cholesta-3,5-dien-7-one	$C_{27}H_{42}O$	382	1668.7	3255	2562	N.R.	NIST	
Stigmasta-3,5-dien-7-one	C28H46O	410	1750.1	3462	2696	N.R.	NIST	
Tocopherols								
γ-Tocopherol	C28H48O2	416	1594.1	3057	3036	3055	NIST	Tocopherols
α-Tocopherol	C29H50O2	430	1632.2	3157	3149	3111	NIST	
Hopanoids								
Trinosphopane	unknown		1526.4	2890	N.R.	N.R.	[10]	Hopanoids
Norhopene (triterpene C29)	unknown		1548.9	2945	N.R.	N.R.	[10]	
22,29,30-trisnorhop-17(21)-ene	$C_{27}H_{44}$	368	1553.8	2957	N.R.	N.R.	[11]	
22,29,30-trisnorhop-16(17)-ene	$C_{27}H_{44}$	368	1567.1	2989	N.R.	N.R.	[11]	
Norhopane (C30/C31?)	unknown		1630.7	3153	N.R.	N.R.	[10]	
25-norhopene (C30/C31?)	unknown		1659.0	3229	N.R.	N.R.	[10]	
(Poly)aromatics								
Benzene	C_6H_6	78	113.9	N.D.			NIST	Benzene
Benzaldehyde	C_7H_6O	106	311.2	919	982	925-966	NIST	Benzaldehyde
Acetyl-benzene	C8H8O	120	408.1	1069	1029	1041-1078	NIST	Acetyl-benzene
Styrene	C8H8	104	254.2	N.D.			NIST	Benzenes C2-9
Ethyl-methyl-benzene	C9H12	120	368.2	1024	N.R.	945-973	NIST	
Indene	C9H8	120	389.7	1048	1014	1029-1051	NIST	
Benzene C7	C13H20	176	664.9	1365	1390	1337-1350	NIST	
Benzene C9	C15H24	204	822.1	1576	1555	1552-1586	NIST	
1,2-dihydro-naphthalene	C10H10	130	484.9	1160	1149	1137-1166	NIST	(Poly)aromatics
2,3-dihydro-inden-1-one	C9H8O	132	599.8	1283	1218	1218-1320	NIST	
1/~~2~~-methyl-napthalene	C11H10	142	612.1	1295	1345	1263-1298	NIST	
2/~~1~~methyl-napthalene	C11H10	142	626.7	1313	1345	1267-1298	NIST	
Biphenyl	C12H10	154	680.8	1386	1367	1338-1392	NIST	
Fluorene	C13H10	166	836.9	1596	1494	1549-1611	NIST	
Anthracene	C14H10	178	972.2	1798	1782	1740-1800	NIST	

[a] Kovats retention index (RI) is used to convert retention times into system-independent constants. The RI of a certain chemical compound is its retention time normalized to the retention times of adjacently eluting *n*-alkanes and is determined as follow:

$$\mathrm{RI} = 100 \text{ x } [\mathrm{n} + \frac{\log(RT\ unknown) - \log(RT\ n)}{\log(RT\ N) - \log(RT\ n)}$$

With, n is the number of carbon in the adjacently eluting smaller *n*-alkane; RT unknown is the retention time of the compound to identify, RT n is the retention time of the adjacently elution smaller *n*-alkane, and RT N is the retention time of the adjacently eluting larger *n*-alkane.

[b] reference RI: the reference RI values were found on the website "NIST Chemistry Webbook" (http://webbook.nist.gov/chemistry/) and/or in the 'NIST/EPA/NIH 2011' library included in the software "NIST MS Search v.2.0"; the reference RI values reported in this table have been either assessed or determined experimentally for non-polar GC column and temperature gradient GC program.;

[c] N.D.: the RI value could not be determined in this study because the adjacently eluting *n*-alkanes needed to calculate the RI could not be identified.

[d] N.R.: no reference RI values were found in the NIST Webbook or library.

[1] Faix et al. (1991) *Holz als Roh- und Werkstoff*, 49: 213-219; [2] Schellenkens et al. (2009) *Organic geochemistry* 40: 678-691; [3] Gupta and Cody (2011), *in N.S. Gupta (ed.), Chitin, Topics in Geobiology* 34, Springer Science+Busines Media ; [4] Schellenkens et al. (2014) *Organic Geochemistry* 77: 32-42; [5] Chen et al., (2009) *Journal of Food Science*, 74: 100-105; [6] Fabbri et al., (2012) *Journal of Analytical and Applied Pyrolysis*, 95: 145-155; [7] For these long-chain *n*-alkanes and alkan-2-ones, the number of C in the molecule has been determined based on the highest *m/z* present in the mass spectra that corresponds to the molecular mass and on the order of elution; [8] Faix et al. (1990) *Holz als Roh- und Werkstoff*, 48: 281-285; [9] Nguyen et al. (2005) *Organic Geochemistry*, 34: 483-497; [10] Gill (1997) Chapter 16. Analytical techniques in organic chemistry; in: Modern analytical Geochemistry; Taylor & Francis, New York (USA), pp. 243-272; [11] Meredith et al. (2008) *Organic Geochemistry*, 39: 1243-1248

~~For long-chain *n*-alkanes and alkan-2-ones indicated by * in the 'ref spectra' column, the number of C in the molecule has been determined based on the highest *m/z* present in the mass spectra that corresponds to the molecular mass and on the order of elution~~

Table S2. Sediment elemental geochemistry variables for the 44 studied sediment samples *(to be continued)*

	WD	BD	bSi	LOI	[S]	[Br]	[Cu]	[Ni]	[Hg]	[Pb]	[Zn]
unit	m	g cm^{-3}	%	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	µg kg^{-1}	mg kg^{-1}	mg kg^{-1}
N1	3.1	0.057	15	**57**	16620	134	29	**21**	283	151	285
N2	7.4	0.088	6	**58**	18050	127	39	**23**	510	168	320
N3	**1.6**	0.078	14	34	**5570**	**216**	34	**10**	261	170	**43**
N4	7.4	0.056	**22**	37	9700	138	33	17	288	120	121
N5	4	0.073	19	36	9740	174	26	18	187	114	195
N6	7.1	0.061	14	40	9770	176	27	18	291	208	199
N7	4	0.063	11	40	16240	168	34	23	309	236	332
N8	5.3	0.064	15	40	9960	138	28	17	224	175	218
N9	7.7	0.054	11	48	14570	**214**	34	20	288	187	248
N10	2.5	0.080	**21**	27	**4990**	129	37	**10**	290	261	50
N11	3.9	0.068	19	32	17000	134	36	**21**	288	226	254
E1	2	0.061	15	36	15440	119	28	19	235	208	188
E2	6.7	0.087	11	36	11510	129	26	19	242	118	195
E3	3.5	0.075	14	45	8240	177	19	16	198	109	213
E4	6	0.086	13	39	11600	158	27	19	235	152	228
E5	9.4	0.092	9	41	11260	145	29	19	265	138	200
E6	10	0.035	13	42	11350	150	30	20	309	**422**	222
M1	3	0.084	**25**	25	**4840**	146	33	**10**	264	235	49
M2	3.7	0.075	**20**	35	9640	167	22	20	193	120	239
M3	7.9	0.083	8	35	17560	120	36	22	326	206	279
M4	*3.8*	***0.608***	***2***	***3***	***2960***	***11***	***7***	***9***	***34***	***33***	***61***
M5	1.9	**0.127**	**23**	**18**	**5000**	120	**13**	**10**	**117**	135	74
M6	1.8	0.104	16	**10**	**4685**	**71**	**12**	18	141	175	80
S1	5.7	0.083	17	30	6640	104	27	19	181	103	144
S2	6.5	0.091	**23**	27	6600	101	25	14	177	97	111
S3	9.5	0.047	12	35	7410	157	31	14	263	145	104
S4	14	0.035	10	32	6295	133	29	13	242	180	173
S5	3.7	0.101	11	32	8940	91	15	12	177	105	146
S6	12.5	0.043	15	42	6040	172	31	18	196	**58**	104
S9	21	0.040	6	45	12650	175	44	**23**	507	244	299
S10	12.8	0.053	7	40	9230	**187**	49	**21**	370	188	196
S11	14.8	0.058	6	37	12460	159	41	**21**	428	256	308
S12	23.5	0.033	**4**	**50**	20650	**225**	56	**26**	740	279	380
S13	16.5	0.048	12	38	11780	160	45	**22**	491	258	303
S14	9.1	0.046	6	32	18260	119	43	20	385	279	336
S15	*2.9*	***0.737***	***2***	***4***	***2180***	***21***	***11***	***15***	***21***	***10***	***39***
S16	4.2	0.097	**23**	20	5420	90	24	18	162	120	100
S17	18.2	0.047	**4**	41	13980	170	48	25	461	295	**404**
S18	24.5	0.027	5	**51**	**29190**	**212**	**64**	**27**	858	277	**425**
S19	9.5	0.036	9	34	13790	153	39	18	368	224	199
S21	11	0.060	**5**	34	**4950**	153	28	15	187	112	118
S22	19.8	0.057	**5**	40	13950	164	48	**24**	533	299	**415**
S23	3.6	0.024	10	**52**	18370	123	39	20	547	243	255
S24	**24.3**	**0.016**	**4**	**54**	**28840**	175	**75**	**27**	**1152**	273	**445**

The font colors of the sample ID cells correspond to the six clusters identified by the cluster analysis on the elemental geochemistry dataset

The bold and underlined numbers corresponds to the minimal and maximal value, and the value in bold corresponds to the values that are below or above 20 % of the maximal and minimal values respectively.

Table S2. *Continuation* Sediment elemental geochemistry variables for the 44 studied sediment samples

	Al	Y	Fe	Fe:Al	Fe:S	[As]	As_{inv}	[P]	[Mn]	Mn:Fe	[Co]	[Ca]	[K]	[Mg]	[Na]	$Si_{inorganic}$	[Sr]	[Ti]	[V]	[Zr]
	%	mg kg^{-1}				mg kg^{-1}	$\mu g\ cm^{-2}$	mg kg^{-1}					mg kg^{-1}			%		mg kg^{-1}		
N1	**2.1**	**9**	1.5	0.7	**0.9**	15	9	**760**	149	0.010	11	6230	**2740**	1060	1190	**4**	41	1293	**38**	**44**
N2	**2.2**	15	1.3	0.6	**0.7**	14	13	1230	125	0.010	12	4800	3610	1050	1910	10	45	1648	**36**	70
N3	2.8	25	4.5	1.6	8.1	22	17	1288	397	0.009	8	4530	5490	**990**	2220	9	56	2262	45	**152**
N4	2.6	19	1.8	0.7	1.8	23	13	1839	**94**	0.005	7	**2860**	**2420**	**870**	**440**	7	**27**	1228	51	**39**
N5	2.8	25	2.5	0.9	2.5	19	14	1133	163	0.007	12	3870	3110	**1020**	940	10	39	1676	54	69
N6	2.8	24	2.5	0.9	2.6	20	12	1149	169	0.007	11	3950	3160	1060	860	15	39	1714	54	68
N7	2.7	24	3.6	1.3	2.2	56	36	933	202	0.006	26	4650	4150	1220	1620	13	51	2009	55	105
N8	2.6	20	2.3	0.9	2.3	26	17	1081	175	0.008	13	4850	4110	1240	1360	11	48	2118	53	89
N9	2.7	22	2.5	0.9	1.7	37	20	1285	148	0.006	11	4930	4100	1270	1720	10	51	2219	59	91
N10	**2.3**	25	4.3	1.9	8.7	39	31	1423	**7981**	**0.184**	35	**3050**	3860	1100	1230	9	36	1965	54	76
N11	2.8	28	5.8	2.1	3.4	51	34	1005	240	0.004	27	**3080**	**2670**	**920**	800	9	34	1267	62	81
E1	2.6	26	7.3	2.9	4.7	49	30	**712**	185	0.003	23	5700	3620	1250	1890	10	65	1963	55	129
E2	**2.4**	19	1.8	0.7	1.6	22	19	1183	149	0.008	9	6030	4880	1600	1660	16	61	**2453**	48	119
E3	**2.3**	**7**	**0.9**	**0.4**	1.1	**5**	**3**	**672**	144	0.016	**5**	**7460**	**5070**	1540	1800	7	57	**2357**	**43**	101
E4	2.6	19	1.8	0.7	1.5	22	19	1190	141	0.008	9	5310	4820	1600	1640	14	56	**2541**	54	112
E5	2.9	18	2.0	0.7	1.8	18	17	1396	160	0.008	9	6590	**5370**	**1910**	2180	14	63	**2852**	57	119
E6	2.8	17	1.8	0.6	1.6	14	5	1405	158	0.009	10	6810	**4970**	**1780**	1765	10	60	**2659**	55	99
M1	**2.5**	21	4.0	1.6	8.2	32	27	1381	4288	0.108	22	**3410**	4070	1260	1150	6	38	2188	56	82
M2	**2.5**	17	1.8	0.7	1.9	19	14	688	164	0.009	9	6230	3830	1450	1200	8	53	1679	50	78
M3	3.0	26	3.5	1.2	2.0	48	40	1362	173	0.005	14	5610	**5850**	**1820**	2380	16	69	**2524**	68	**152**
M4	***5.7***	*17*	*3.5*	*0.6*	*11.8*	***<DL***	***<DL***	*989*	*462*	*0.013*	*10*	***31890***	***8660***	***10040***	***11110***	***22***	***218***	***6017***	***91***	***153***
M5	2.8	34	6.5	2.3	12.9	27	**34**	1128	5463	0.085	**62**	5710	4230	**1770**	1710	8	73	**2461**	64	117
M6	**4.3**	**43**	7.4	1.7	**15.8**	18	18	965	5067	0.068	**76**	**8105**	**6140**	**1920**	**3380**	12	**116**	2211	**90**	109
S1	**3.5**	30	3.7	1.0	5.5	29	24	2042	221	0.006	19	4310	4540	1250	1210	11	55	1646	78	89
S2	**3.4**	24	4.5	1.3	6.9	29	26	2001	222	0.005	16	4650	3260	1220	1080	6	41	1642	64	76
S3	2.9	27	3.4	1.2	4.6	27	13	2216	143	0.004	8	4170	4380	1620	1550	13	51	2236	64	104
S4	3.3	29	**11.5**	**3.5**	**18.3**	**57**	20	2013	345	0.003	17	5065	**5560**	**1735**	2695	9	60	**2730**	68	**147**
S5	2.7	16	1.5	0.6	1.7	**7**	7	**655**	176	0.011	7	**9300**	4660	1340	2570	11	**101**	1524	**42**	109
S6	**3.6**	**35**	3.7	1.0	6.1	20	9	**3503**	177	0.005	8	6260	3170	1440	1320	8	46	1677	57	62
S9	**3.5**	28	4.3	1.2	3.4	43	17	2228	195	0.005	13	5300	**5900**	**2030**	2410	14	59	**2844**	79	122
S10	**3.8**	**42**	7.3	1.9	7.9	53	28	2907	208	0.003	18	5160	4430	**1720**	1920	13	56	2079	79	98
S11	**3.7**	33	8.1	2.2	6.5	**69**	**40**	2001	252	0.003	18	6420	**6090**	**2090**	**2920**	14	69	**2870**	77	**160**
S12	**3.4**	25	2.7	0.8	1.3	39	13	2226	182	0.007	12	4960	5130	**1820**	2120	14	53	**2344**	76	92
S13	**3.7**	**36**	**10.2**	2.7	8.6	**71**	**34**	2255	262	0.003	24	6020	**5970**	**2040**	**3030**	6	65	**2859**	**85**	**152**
S14	3.2	32	**11.3**	**3.5**	6.2	**71**	**33**	1744	308	0.003	39	4610	**4980**	1590	2230	**17**	55	**2386**	75	**131**
S15	***5.7***	*22*	*3.3*	*0.6*	*15.1*	***<DL***	***<DL***	*908*	*1657*	*0.050*	*23*	***21190***	***12360***	***4950***	***10280***	***23***	***252***	***2697***	*58*	***162***
S16	**4.0**	30	3.2	0.8	6.0	17	16	1705	275	0.008	22	6150	4710	1490	1810	8	61	2135	59	109
S17	**3.7**	**35**	**9.1**	2.4	6.5	**73**	**34**	2133	389	0.004	35	5380	**5510**	**1990**	**2790**	15	61	**2671**	**80**	**145**
S18	3.3	24	3.4	1.0	1.1	42	11	2303	175	0.005	14	4900	**4930**	**1820**	2040	14	51	2255	77	91
S19	3.0	31	7.4	2.5	5.3	55	20	1690	216	0.003	20	4360	4620	1520	1680	14	54	**2344**	78	126
S21	3.2	26	3.1	1.0	6.2	20	12	2386	170	0.006	10	5420	3810	1510	1230	**21**	53	2109	61	90
S22	**3.6**	**38**	**10.7**	**2.9**	7.7	**73**	**42**	2525	471	0.004	41	5590	**5590**	**2130**	2650	14	64	**2695**	79	**137**
S23	2.7	14	3.6	1.3	2.0	27	7	**711**	134	0.004	10	3920	2970	1110	1270	7	33	**997**	77	48
S24	**3.5**	20	6.9	2.0	2.4	**64**	10	**3769**	157	**0.002**	16	5265	3410	1330	1800	9	44	1491	**101**	53

The font colors of the sample ID cells correspond to the six clusters identified by the cluster analysis on the elemental geochemistry dataset

The bold and underlined numbers corresponds to the minimal and maximal value, and the value in bold corresponds to the values that are below or above 20 % of the maximal and minimal values respectively.

Table S3. Average of the sediment elemental geochemistry variables for the whole-lake, the six clusters and the two outliers

Variables (unit)	Whole-lake[a] (n[b]=42)	Near-shore sites	North/East basins	South basin			Shallow central areas	Outliers (M4, S15)
		$Cluster_{geo}$ 4 (n=4)	$Cluster_{geo}$ 1 (n=13)	$Cluster_{geo}$ 6 (n=10)	$Cluster_{geo}$ 2 (n=8)	*$Cluster_{geo}$ 5 (n=3)*	$Cluster_{geo}$ 3 (n=4)	
W.D. (m)	*9 ± 7 (74%)*[c]	*4 ± 2*	*5 ± 3*	*8 ± 3*	*15 ± 4*	*3 ± 1*	*2 ± 1*	*3 ± 1*
B.D. (g cm^{-3})	0.06 ± 0.02 *(38%)*	0.06 ± 0.03	0.07 ± 0.02	0.07 ± 0.02	0.05 ± 0.01	0.67 ± 0.09	0.100 ± 0.02	0.67 ± 0.09
bSi (%)	12 ± 6 *(31%)*	12 ± 6	13 ± 3	15 ± 7	7 ± 3	1.8 ± 0.2	21 ± 4	1.8 ± 0.2
OM and organophilic trace elements								
LOI (%)	38 ± 10 *(27%)*	50 ± 12	39 ± 5	34 ± 7	37 ± 4	52 ± 2	20 ± 8	4 ± 1
S (mg kg^{-1})	11876 ± 5920 *(50%)*	17510 ± 833	11683 ± 3440	7550 ± 1900	12896 ± 3315	26227 ± 4833	4879 ± 148	2570 ± 552
Br (mg kg^{-1})	149 ± 35 *(23%)*	130 ± 6	153 ± 36	145 ± 35	154 ± 19	204 ± 26	116 ± 32	16 ± 7
Cu (mg kg^{-1})	34 ± 13 *(37%)*	36 ± 5	28 ± 6	30 ± 7	42 ± 6	65 ± 10	24 ± 13	9 ± 3
Ni (mg kg^{-1})	19 ± 5 *(23%)*	21 ± 1	18 ± 4	17 ± 2	21 ± 4	27 ± 1	12 ± 4	12 ± 4
Hg (µg kg^{-1})	337 ± 202 *(60%)*	407 ± 141	251 ± 47	230 ± 69	427 ± 94	917 ± 212	203 ± 87	28 ± 9
Pb (mg kg^{-1})	192 ± 74 *(39%)*	199 ± 58	156 ± 58	115 ± 42	300 ± 59	315 ± 7	182 ± 96	24 ± 7
Zn (mg kg^{-1})	219 ± 108 *(49%)*	279 ± 31	212 ± 68	139 ± 42	305 ± 86	417 ± 33	63 ± 16	50 ± 16
Cu (µg cm^{-2})	*20 ± 6 (30%)*	*21 ± 11*	*20 ± 6*	19 ± 4	*20 ± 6*	*16 ± 4*	*22 ± 8*	*62 ± 27*
Ni (µg cm^{-2})	*12 ± 4 (35%)*	*13 ± 6*	*13 ± 4*	11 ± 3	*10 ± 3*	*7 ± 2*	*12 ± 5*	*83 ± 39*
Hg (ng cm^{-2})	*185 ± 65 (35%)*	*234 ± 146*	*180 ± 45*	146 ± 32	*201 ± 69*	*222 ± 33*	*187 ± 46*	*181 ± 36*
Pb (µg cm^{-2})	*123 ± 60 (48%)*	*111 ± 46*	*132 ± 53*	83 ± 29	*126 ± 29*	*84 ± 9*	*234 ± 84*	*138 ± 90*
Zn (µg cm^{-2})	*126 ± 60 (47%)*	*170 ± 90*	*152 ± 54*	92 ± 33	*145 ± 60*	*105 ± 30*	*64 ± 28*	*329 ± 59*
Elements that can be part of or be associated with clays and (oxy)hydroxides								
Al (%)	3.0 ± 0.5 *(18%)*	2.4 ± 0.3	2.7 ± 0.2	3.3 ± 0.5	3.5 ± 0.3	3.4 ± 0.1	3.0 ± 0.9	5.7 ± 0
Y (mg kg^{-1})	25 ± 8 *(32%)*	16 ± 8	20 ± 5	28 ± 6	33 ± 3	23 ± 3	31 ± 10	20 ± 3
Fe (%)	4.5 ± 3.0 *(65%)*	3.1 ± 2.1	2.7 ± 1.7	3.6 ± 1.5	9.1 ± 2.4	4.3 ± 2.2	5.5 ± 1.7	3.4 ± 0.2
Fe:Al	*1.5 ± 0.8 (57%)*	*1.0 ± 0.5*	*1.0 ± 0.6*	1.1 ± 0.3	*2.5 ± 0.9*	*1.3 ± 0.6*	*1.9 ± 0.3*	*2.0 ± 0.4*
Fe:S	*5.2 ± 4.3 (86%)*	*1.7 ± 1.2*	*2.5 ± 1.9*	*5.0 ± 0.9*	*8 ± 4*	*1.6 ± 0.7*	*11 ± 4*	*13 ± 2*
As (mg kg^{-1})	35 ± 20 *(56%)*	27 ± 17	26 ± 16	25 ± 11	64 ± 11	48 ± 14	29 ± 9	< D.L.[d]
As (µg cm^{-2})	*20 ± 11 (52%)*	*15 ± 13*	*19 ± 11*	17 ± 7	*30 ± 10*	*12 ± 1*	*28 ± 7*	*< D.L.*
P (mg kg^{-1})	1624 ± 741 *(46%)*	927 ± 240	1065 ± 295	2088 ± 730	2074 ± 275	2766 ± 869	1224 ± 216	949 ± 57
Mn (mg kg^{-1})	729 ± 1690 *(232%)*	162 ± 53	182 ± 67	184 ± 50	305 ± 93	171 ± 13	5700 ± 1597	1060 ± 845
Mn:Fe	*0.016 ± 0.034 (214%)*	*0.007 ± 0.002*	*0.008 ± 0.003*	0.006 ± 0.002	*0.004 ± 0.001*	*0.005 ± 0.002*	*0.111 ± 0.051*	*0.08 ± 0.01*
Co(mg kg^{-1})	19 ± 14 *(77%)*	15 ± 8	12 ± 6	13 ± 5	26 ± 11	14 ± 2	49 ± 24	17 ± 9
Others minerogenic elements								
Ca (mg kg^{-1})	5261 ± 1306 *(25%)*	4508 ± 1346	6000 ± 1331	4680 ± 1072	5343 ± 683	5042 ± 196	5069 ± 2342	26540 ± 7566
K (mg kg^{-1})	4426 ± 1020 *(23%)*	2998 ± 428	4686 ± 682	3699 ± 781	5528 ± 504	4490 ± 941	4575 ± 1054	10510 ± 2616
Mg (mg kg^{-1})	1488 ± 354 *(24%)*	1035 ± 81	1462 ± 274	1320 ± 280	1891 ± 239	1657 ± 283	1513 ± 394	7495 ± 3599
Na (mg kg^{-1})	1794 ± 659 *(37%)*	1293 ± 460	1847 ± 395	1236 ± 446	2551 ± 437	1987 ± 167	1868 ± 1038	10695 ± 587
$Si_{inorganic}$ (%)	12 ± 4 *(33%)*	8 ± 3	11 ± 3	11 ± 5	13 ± 3	12 ± 3	9 ± 2	23 ± 1
Sr (mg kg^{-1})	55 ± 16 *(30%)*	38 ± 6	61 ± 13	47 ± 10	61 ± 5	49 ± 5	66 ± 38	235 ± 24
Ti (mg kg^{-1})	2115 ± 495 *(23%)*	1301 ± 267	2243 ± 382	1814 ± 314	2675 ± 206	2030 ± 469	2206 ± 203	4357 ± 2348
V (mg kg^{-1})	63 ± 15 *(23%)*	53 ± 20	53 ± 7	62 ± 10	78 ± 5	85 ± 14	66 ± 16	75 ± 23
Zr (mg kg^{-1})	101 ± 32 *(31%)*	61 ± 18	112 ± 22	80 ± 22	140 ± 13	79 ± 23	96 ± 20	158 ± 6

[a]whole-lake: averages of all analyzed sediment samples excluding the two outlier samples (sites M4, S15); [b]n: number of sample; [c]the values in parentheses correspond to the relative standard deviation; [d]D.L.: detection limit; The six clusters are presented in Fig. 1b in the manuscript.

Light grey background denotes average values below 10 % of whole-lake average; No background denotes average values close to whole-lake average (±10 %). Dark grey background denotes average values above 10 % of whole-lake average. The variables *in italic* are passive variables in the PCA and cluster analyses.

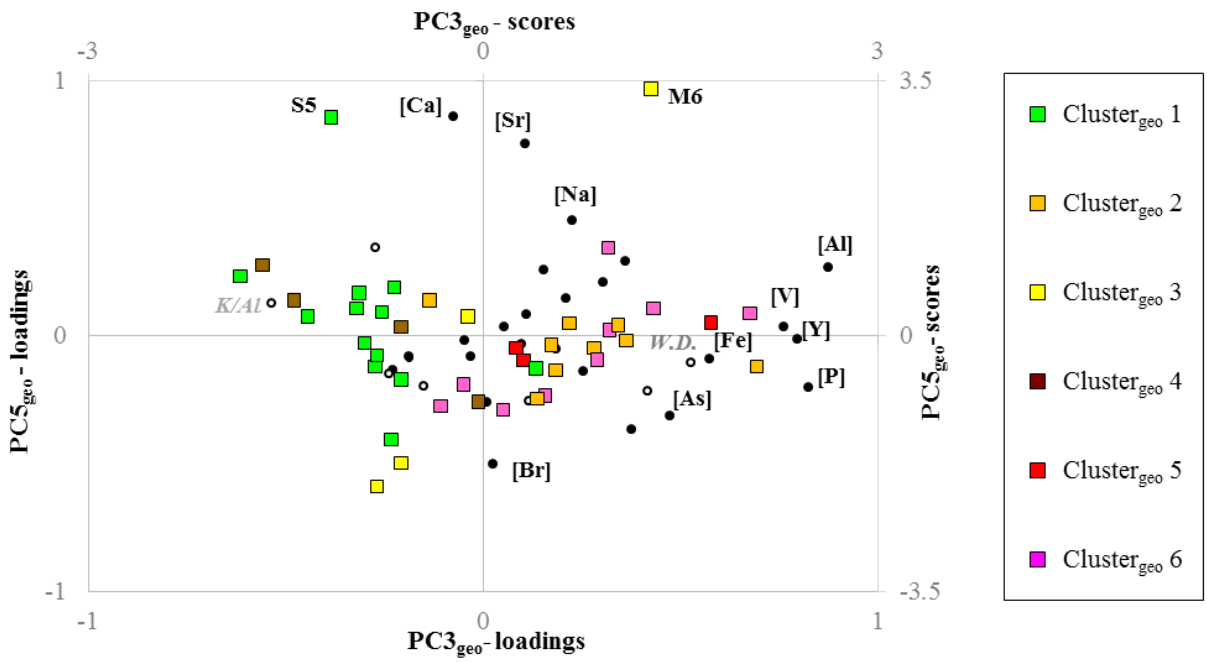

Fig. S1 Combined loading- and score-plots for PCs 3-5 of the elemental geochemistry dataset. For the PC-loadings, filled circles correspond to active variables, and others variables (empty circle and italics letter) were added passively. Sediment samples are colored according to the results of the cluster analysis.

This figure shows that $PC5_{geo}$ (10 % of total variance) separates Ca, Na and Sr on the positive side from Br on the negative side. No reasonable interpretation could be made for this $PC5_{geo}$, which appears to be driven by only two samples which are split into two different clusters by the cluster analysis.

Table S4. Sediment OM molecular composition variables for the 42 studied sediment samples *(to be continued)*

	Carbohydrates						Chitin-derived compounds	N-compounds									
	(Alkyl)-furans & furanones	Hydroxy- or carboxy-furans & furanones	Pyrans	Dianhydro-rhamnose	Levoglu-cosenone	Anhydro-sugars		(Alkyl)-pyridines	Pyridines_O	(Alkyl)-pyrroles	Pyrroles_O	Pyrroledione & pyrrolidinedione	Aromatic N	Indoles	Diketodi-pyrrole	Diketopi-perazines	Alkyl-amides
N1	**10**	5.1	**4.5**	2.0	2.2	3.1	2.9	**0.42**	0.68	2.1	0.61	1.20	**0.40**	1.40	**1.10**	1.90	0.46
N2	**8**	5.1	3.6	1.3	2.3	3.1	**3.3**	**0.37**	0.69	**2.0**	0.66	1.10	**0.40**	1.40	**1.20**	1.20	0.47
N3	11	5.9	1.7	0.8	**1.5**	2.5	1.2	0.11	0.62	**1.8**	0.86	0.60	0.60	1.20	**0.50**	1.30	0.74
N4	17	4.2	**4.7**	**2.2**	3.1	2.9	**4.0**	**0.40**	**0.91**	2.5	**1.13**	**1.50**	0.60	1.70	0.80	1.80	0.83
N5	13	4.0	3.7	1.7	2.2	6.4	2.9	0.34	0.65	2.2	1.00	**1.40**	0.70	1.40	0.70	1.50	0.61
N6	12	4.1	3.8	1.6	**2.8**	**8.1**	2.2	0.28	0.69	**1.8**	0.79	1.30	0.50	1.30	0.60	1.50	0.70
N7	13	4.0	3.8	1.8	2.3	4.3	2.7	0.31	0.71	**2.0**	0.81	1.20	0.60	1.40	0.70	1.50	0.73
N8	12	4.0	4.1	2.0	2.3	**8.1**	2.7	0.32	0.69	**1.8**	0.82	1.20	0.50	1.30	0.70	1.60	0.63
N9	13	4.6	**4.3**	1.6	**2.6**	2.3	2.5	0.30	0.65	**1.9**	0.75	1.10	0.50	1.30	0.80	1.60	0.74
N10	19	**7.0**	4.1	1.8	**2.7**	2.2	2.5	0.20	**0.85**	2.4	**1.33**	**1.50**	0.80	1.50	0.70	1.50	0.49
N11	16	3.2	2.6	1.5	2.2	2.2	1.9	0.20	**0.73**	2.4	0.96	1.20	0.80	1.50	0.70	1.30	0.69
E1	**10**	3.2	2.2	1.2	1.7	2.0	1.1	0.11	0.57	**1.8**	0.74	0.90	0.70	1.30	0.60	1.10	0.46
E2	**10**	4.2	3.8	1.8	2.3	**8.1**	2.6	0.27	0.70	**1.9**	0.75	1.10	**0.40**	1.30	0.60	1.50	0.73
E3	**9**	5.1	**5.0**	2.1	2.0	4.0	2.5	0.31	0.69	**1.7**	0.67	1.20	**0.30**	1.30	0.80	1.30	0.56
E4	11	4.3	**4.6**	2.0	2.3	6.2	3.2	0.34	**0.81**	2.1	0.82	1.30	0.50	1.40	0.70	1.70	0.74
E5	**10**	4.0	4.0	1.9	2.3	5.6	3.2	0.30	0.70	**2.0**	0.79	**1.40**	0.50	1.40	0.70	1.80	0.80
E6	**10**	4.4	3.8	2.0	1.9	6.8	**3.6**	0.32	0.72	**1.8**	0.87	**1.50**	0.50	1.70	0.70	1.90	0.79
M1	18	**7.5**	3.2	1.3	2.6	2.2	1.4	0.20	0.68	2.6	**1.19**	1.30	0.80	1.40	**0.40**	1.20	0.31
M2	14	4.5	**5.2**	**2.7**	2.2	**8.9**	3.2	0.36	**0.77**	**1.9**	0.91	**1.70**	0.60	1.60	0.70	1.70	0.54
M3	11	3.3	2.6	1.2	2.0	6.2	2.6	0.29	0.71	2.1	0.83	1.10	0.60	1.50	0.80	1.60	0.49
M5	21	**0.8**	**1.2**	**0.3**	**1.5**	**1.0**	**0.2**	**0.06**	**0.17**	2.1	**0.51**	**0.20**	0.60	**0.50**	**0.40**	**0.30**	**0.15**
M6	24	1.6	1.7	0.6	2.3	**1.1**	**0.3**	**0.07**	0.50	2.7	0.77	**0.30**	**1.10**	0.90	1.00	1.00	**0.06**
S1	20	3.2	3.2	1.5	2.5	2.1	2.3	**0.40**	**0.76**	**3.0**	**1.27**	**1.40**	1.00	1.80	0.70	1.20	0.46
S2	**22**	3.2	2.5	1.7	2.1	1.6	1.7	0.33	**0.74**	**3.2**	**1.27**	1.00	**1.10**	1.90	0.60	0.90	0.24
S3	18	4.8	**4.9**	**2.3**	**2.7**	**0.8**	**3.8**	**0.45**	**0.86**	2.7	**1.28**	**1.60**	0.80	1.70	0.80	1.80	0.64
S4	17	3.1	2.2	1.3	1.7	1.8	1.6	0.36	**0.76**	**3.4**	**1.16**	0.80	1.30	1.80	0.70	0.90	0.27
S5	11	5.4	**4.4**	1.9	1.9	**11.0**	1.7	0.34	0.59	**1.7**	0.69	1.30	0.50	1.30	0.90	1.80	0.34
S6	15	3.6	2.9	1.7	1.8	2.5	4.0	0.17	**0.85**	2.7	**1.33**	**1.40**	0.80	1.80	0.80	1.40	0.65
S9	13	4.1	3.2	1.8	1.9	3.2	**3.6**	**0.37**	**0.80**	2.4	0.96	1.10	0.70	1.60	0.90	2.00	0.91
S10	16	3.7	2.5	1.5	2.0	2.7	**3.4**	**0.40**	**0.89**	**3.4**	**1.37**	1.10	0.90	1.70	0.90	1.40	0.58
S11	16	3.7	3.0	1.7	2.5	2.2	2.3	0.31	**0.79**	2.5	**1.19**	0.90	1.00	1.60	0.80	1.20	0.44
S12	12	3.7	3.2	1.5	2.2	1.7	**4.2**	**0.46**	**0.75**	**2.8**	0.90	**1.50**	0.80	1.90	**1.00**	**2.60**	**1.17**
S13	14	3.7	2.3	1.0	1.7	2.0	2.0	0.32	0.65	**2.8**	**1.07**	0.80	1.00	1.60	0.80	1.40	1.08
S14	20	3.6	3.0	1.5	2.6	2.1	1.7	**0.37**	**0.79**	**3.4**	**1.10**	0.90	**1.30**	1.70	0.80	1.30	0.33
S16	**28**	3.9	2.6	2.0	**3.1**	2.2	0.9	0.08	0.48	**3.5**	**1.20**	**1.70**	**1.30**	1.70	0.40	0.80	0.09
S17	14	3.8	2.8	1.5	1.7	2.2	2.6	0.30	**0.81**	2.6	**1.07**	0.80	1.00	1.60	0.80	1.50	0.47
S18	13	3.6	3.2	1.5	2.1	2.9	**3.7**	**0.40**	0.69	**2.8**	0.94	1.30	0.80	1.90	0.90	**2.60**	**1.12**
S19	21	3.8	3.5	1.6	**2.7**	0.9	2.5	0.32	**0.85**	**2.9**	**1.27**	1.30	1.00	1.60	0.70	1.30	0.39
S21	18	3.6	**4.3**	**2.3**	2.1	2.6	**3.4**	**0.37**	**0.85**	2.5	**1.37**	**1.50**	0.90	1.50	0.70	1.40	0.49
S22	14	3.3	2.0	1.3	1.7	1.8	2.1	0.36	0.72	2.7	**1.09**	0.70	1.00	1.60	0.90	1.20	0.38
S23	17	**6.0**	**5.3**	1.6	**2.9**	**8.2**	1.3	0.35	0.57	**1.9**	0.55	1.20	0.70	1.50	0.90	1.40	0.56
S24	11	3.6	2.7	1.8	**1.3**	1.9	**3.4**	**0.37**	**0.86**	**3.1**	0.85	**1.60**	**1.40**	**3.10**	0.90	**2.30**	**1.66**

The font colors of the sample ID cells correspond to the six clusters identified by the cluster analysis on the OM molecular composition dataset

The bold and underlined numbers corresponds to the minimal and maximal value, and the value in bold corresponds to the values that are below or above 20 % of the maximal and minimal values respectively.

Table S4. *Continuation* Sediment OM molecular composition variables for the 42 studied sediment samples *(to be continued)*

	Lignins			Chlorophylls		*n*-alkenes				*n*-alkanes				Alkan-2-ones		
	Phenols	**Syringols**	**Guaiacols**	**Pristenes**	**Phytadienes**	**C9-16:1**	**C17-22:1**	**C23-26:1**	**C27-28:1**	**C13-16:0**	**C17-22:0**	**C23-26:0**	**C27-35:0**	**2K C13-17**	**2K C19-22**	**2K C23-31**
N1	**10.6**	**1.9**	**10.6**	3.7	1.6	**2.0**	5.2	3.9	**1.2**	1.7	3.1	**1.9**	2.3	**0.6**	0.24	1.7
N2	**11.4**	**1.4**	7.7	3.0	1.7	2.3	5.8	3.0	0.9	1.9	3.2	3.2	6.3	**0.6**	0.21	1.5
N3	9.0	0.6	3.6	2.8	1.3	3.8	**7.1**	**4.8**	**1.3**	2.7	4.5	4.1	6.1	1.0	0.40	**3.2**
N4	7.6	0.3	2.3	2.3	**3.5**	2.8	5.1	2.1	0.6	1.9	3.4	2.4	4.1	1.4	0.24	1.0
N5	7.3	0.4	3.0	3.2	1.7	3.5	6.7	3.0	1.0	2.6	4.2	2.7	3.9	1.3	0.35	1.5
N6	7.3	0.4	3.8	3.2	1.9	2.8	6.2	3.4	0.8	1.9	3.5	3.1	6.1	1.1	0.28	1.9
N7	7.6	0.5	3.8	3.2	1.9	3.1	6.5	4.1	**1.2**	2.1	4.0	2.8	4.3	1.1	0.34	**2.6**
N8	7.2	0.4	3.6	3.2	1.6	3.1	6.6	3.4	**1.1**	2.3	3.9	3.0	4.9	1.1	0.33	2.0
N9	8.7	0.6	4.1	3.7	2.0	2.9	6.6	4.0	**1.2**	2.3	4.0	2.8	4.3	0.8	0.36	2.5
N10	9.5	0.2	1.8	1.5	1.5	3.0	5.2	2.1	0.4	2.4	3.1	2.7	3.5	1.0	0.19	0.6
N11	6.6	0.2	2.1	2.5	2.3	3.9	6.7	3.5	**1.4**	2.6	**4.4**	**4.8**	6.6	1.4	0.30	1.0
E1	8.1	0.3	3.5	**4.6**	1.4	**4.0**	**8.9**	**5.4**	**1.3**	2.7	**5.1**	3.9	5.6	1.0	0.35	**3.3**
E2	7.4	0.5	3.7	3.4	1.5	3.1	**7.1**	3.6	**1.2**	2.2	4.1	3.4	5.4	0.9	0.30	2.3
E3	8.8	**1.4**	7.5	3.2	1.5	2.5	6.1	3.8	1.0	1.7	3.5	3.2	6.2	0.6	0.31	2.3
E4	7.3	0.5	3.7	3.2	1.9	2.9	6.6	3.6	1.0	2.0	3.9	2.6	4.8	1.1	0.31	2.3
E5	7.9	0.6	4.1	3.5	1.5	3.0	6.6	3.8	1.0	2.3	4.1	2.8	4.7	1.0	0.36	2.3
E6	8.0	0.7	4.6	3.1	1.8	2.9	6.2	3.6	**1.1**	2.4	3.8	2.4	4.3	1.0	0.40	2.1
M1	8.0	0.2	1.9	2.1	1.3	3.8	6.2	3.0	0.5	2.6	3.5	2.7	3.6	0.9	0.15	0.8
M2	7.0	0.7	4.0	2.2	1.9	2.8	5.4	2.6	0.8	2.1	3.3	2.5	3.5	1.1	0.27	1.2
M3	6.9	0.3	3.3	2.3	2.0	3.1	5.6	2.6	0.6	2.2	3.5	**4.5**	10.1	1.2	0.23	1.3
M5	**4.4**	**0.1**	**1.1**	**0.4**	**0.2**	**4.1**	**3.8**	**0.6**	0.1	2.3	**1.6**	**8.8**	**21.3**	1.6	**0.02**	**0.1**
M6	7.7	0.2	1.5	0.6	1.0	3.8	**4.0**	1.5	0.1	2.4	2.1	**6.7**	11.8	1.6	**0.03**	0.3
S1	8.0	0.3	2.4	2.5	1.8	**4.6**	6.4	2.2	0.3	3.2	**4.6**	2.2	1.9	**1.8**	0.34	0.4
S2	6.9	0.2	2.1	2.7	2.2	**5.1**	6.9	2.1	0.3	**3.7**	**4.6**	2.0	1.4	**1.9**	0.31	0.3
S3	7.8	0.4	2.8	2.6	2.1	3.7	5.8	2.2	0.7	2.8	4.1	**1.5**	1.6	1.6	0.44	0.7
S4	**9.1**	0.3	2.9	3.4	1.5	**4.8**	6.7	2.5	0.4	**4.1**	**4.7**	1.8	1.8	**1.9**	0.38	0.8
S5	**9.6**	**1.8**	**13.5**	2.2	1.2	**2.1**	4.4	2.6	0.7	1.7	2.5	**1.4**	1.4	**0.7**	0.15	0.7
S6	7.9	0.4	2.8	2.9	1.9	**4.6**	6.9	2.5	0.5	**3.7**	**5.4**	**1.8**	1.7	**1.8**	0.53	0.9
S9	8.4	0.4	2.9	2.8	1.9	3.7	6.3	3.1	1.0	2.7	**4.6**	2.5	3.5	1.5	0.44	1.6
S10	8.0	0.3	2.3	2.6	2.1	**4.4**	6.6	2.1	0.6	3.2	**4.6**	**1.6**	1.7	**2.0**	0.47	0.7
S11	8.8	0.3	2.9	3.2	1.6	**4.3**	6.8	2.6	0.7	2.9	**4.5**	**1.9**	2.3	**1.8**	0.40	0.9
S12	8.6	0.4	2.5	2.6	**2.8**	3.4	5.8	2.7	1.0	2.6	4.1	2.2	3.6	1.6	0.34	1.2
S13	9.0	0.3	2.6	2.8	1.4	**4.5**	6.6	2.3	0.6	3.1	4.2	2.9	3.9	**2.0**	**0.82**	1.1
S14	8.5	0.2	2.2	2.9	**3.3**	**4.0**	5.6	2.2	0.4	2.3	3.2	**1.6**	2.4	1.7	0.28	0.6
S16	6.4	0.2	2.1	2.0	1.3	**4.5**	5.8	1.5	**0.1**	3.0	3.4	**1.7**	**1.1**	1.4	0.05	0.1
S17	9.0	0.3	2.7	3.0	2.0	**4.1**	6.6	3.2	0.7	2.8	**4.6**	2.4	3.0	**1.8**	0.44	1.1
S18	8.7	1.2	3.8	2.4	**2.9**	3.1	5.1	2.6	0.9	2.4	3.7	2.2	3.3	1.4	0.30	1.0
S19	8.7	0.2	2.3	2.8	2.4	3.9	5.7	2.3	0.5	2.5	3.9	**1.7**	2.1	1.5	0.27	0.6
S21	7.0	0.4	2.9	2.7	1.5	**4.0**	6.2	2.4	0.5	2.9	**4.7**	2.7	1.9	1.6	0.33	0.7
S22	**9.1**	0.3	2.7	3.1	1.6	**4.5**	7.0	3.3	0.7	3.0	**5.0**	2.9	3.4	**1.9**	0.39	1.0
S23	8.5	1.3	4.6	1.6	2.5	**1.8**	**3.5**	3.5	**1.4**	**1.3**	2.3	3.0	3.6	**0.7**	0.10	1.4
S24	**10.3**	0.5	3.0	2.2	**3.6**	3.4	4.3	2.0	0.6	2.6	3.7	**1.9**	2.7	**2.2**	0.35	1.0

The font colors of the sample ID cells correspond to the six clusters identified by the cluster analysis on the OM molecular composition dataset

The bold and underlined numbers corresponds to the minimal and maximal value, and the value in bold corresponds to the values that are below or above 20 % of the maximal and minimal values respectively.

Table S4. *Continuation* Sediment OM molecular composition variables for the 42 studied sediment samples

	Steroids	Tocopherols	Hopanoids	(Poly)aromatics				
				Benzene	Benzaldehyde	Acetophenone	alkylbenzene C3-9	Polyaromatics
N1	0.91	**1.45**	1.1	**0.4**	**0.31**	**0.57**	**1.4**	**0.9**
N2	1.49	1.00	1.0	0.8	**0.36**	**0.72**	**1.6**	**1.0**
N3	0.99	0.57	1.3	0.9	0.96	1.51	**1.6**	1.4
N4	1.27	0.16	1.2	0.8	0.44	0.76	**1.7**	**1.0**
N5	0.63	0.30	1.4	0.8	0.52	0.94	**1.7**	1.2
N6	1.23	0.42	1.4	0.7	0.42	0.72	**1.5**	**1.0**
N7	1.04	0.42	**1.6**	0.7	0.44	0.82	**1.7**	1.1
N8	0.96	0.42	1.4	0.5	0.43	0.74	1.6	**0.8**
N9	1.50	0.60	1.5	0.7	**0.40**	0.72	1.6	**1.0**
N10	0.32	0.15	0.7	1.8	1.08	**1.98**	1.9	1.6
N11	0.67	0.09	1.3	1.0	0.56	1.01	1.9	1.4
E1	0.90	0.75	**1.5**	0.8	0.61	1.06	1.8	1.5
E2	0.82	0.47	1.3	0.8	0.41	0.75	**1.5**	**1.0**
E3	0.92	0.78	1.3	0.5	**0.35**	0.61	**1.4**	**0.8**
E4	1.03	0.42	1.4	0.8	**0.40**	**0.72**	**1.5**	**1.0**
E5	1.37	0.57	**1.6**	0.8	0.42	0.74	**1.5**	**1.0**
E6	1.39	0.52	**1.5**	0.7	**0.40**	**0.71**	**1.5**	**1.0**
M1	0.28	0.19	0.8	**2.5**	1.33	**2.30**	2.1	1.7
M2	0.47	0.26	1.2	0.7	0.46	0.78	1.8	**1.0**
M3	1.22	0.18	1.3	0.7	**0.40**	0.73	1.8	1.1
M5	**0.03**	**<DL**	**0.2**	0.7	0.64	1.02	1.7	1.5
M6	0.09	**0.01**	**0.2**	0.6	0.78	1.19	1.8	1.3
S1	0.54	0.04	1.3	0.9	0.67	1.16	2.1	**1.7**
S2	0.51	**<DL**	1.4	1.1	0.83	1.41	2.3	**1.7**
S3	1.16	0.09	1.4	0.7	0.63	1.05	2.0	1.3
S4	0.79	0.13	**1.8**	1.1	0.95	1.62	2.7	2.1
S5	0.93	0.48	0.7	**0.5**	0.44	0.68	**1.4**	1.1
S6	1.32	0.12	**1.5**	0.7	0.60	1.05	2.1	1.4
S9	2.14	0.21	**1.6**	0.9	0.53	0.94	1.8	1.3
S10	1.62	0.06	**1.6**	1.1	0.77	1.36	2.2	**1.7**
S11	1.48	0.12	**1.5**	1.1	0.76	1.37	2.4	**1.8**
S12	**3.30**	0.12	**1.6**	1.0	0.43	0.80	2.2	1.2
S13	1.49	0.09	**1.6**	0.9	0.75	1.44	**3.5**	2.0
S14	1.38	0.04	1.4	1.6	0.84	1.45	**2.8**	**1.9**
S16	0.14	**0.01**	0.9	1.7	**1.47**	**2.15**	2.4	**1.8**
S17	2.02	0.08	**1.8**	0.9	0.76	1.35	2.2	**1.8**
S18	**3.53**	0.08	**1.6**	1.2	0.42	0.77	2.1	1.2
S19	1.21	0.03	**1.6**	1.0	0.71	1.29	2.6	**1.7**
S21	0.92	0.09	**1.8**	0.7	0.61	1.03	1.8	1.4
S22	1.51	0.09	**1.8**	1.1	0.76	1.45	2.5	**2.1**
S23	1.18	0.33	0.5	0.6	0.47	0.79	**1.4**	1.0
S24	**4.28**	0.17	**1.9**	0.7	0.67	0.93	2.1	1.2

The font colors of the sample ID cells correspond to the six clusters identified by the cluster analysis on the OM molecular composition dataset

The bold and underlined numbers corresponds to the minimal and maximal value, and the value in bold corresponds to the values that are below or above 20 % of the maximal and minimal values respectively.

Table S5. Average of the OM molecular composition variables for the whole-lake and the six clusters

		Near-shore sites	North/East basins	South basins		Shallow central areas	
Variables (unit)	**Whole-lake[a] (n[b]=42)**	$Cluster_{OM}$ 5 (n=4)	$Cluster_{OM}$ 1 (n=16)	$Cluster_{OM}$ 3 (n=14)	$Cluster_{OM}$ 2 (n=3)	$Cluster_{OM}$ 4 (n=3)	$Cluster_{OM}$ 6 (n=2)
Carbohydrates							
(Alkyl)-furans & furanones	15 ± 5	12 ± 4	12 ± 2	17 ± 3	11.9 ± 0.7	22 ± 5	23 ± 2
Hydroxy- or carboxy-furans & furanones	4 ± 1	5.4 ± 0.4	4.2 ± 0.7	3.7 ± 0.5	3.7 ± 0.1	6.1 ± 1.9	1.2 ± 0.6
Pyrans	3 ± 1	4.7 ± 0.7	3.6 ± 0.9	3 ± 1	3.0 ± 0.3	3.3 ± 0.8	1.4 ± 0.4
Dianhydrorhamnose	1.6 ± 0.5	1.7 ± 0.3	1.7 ± 0.4	1.7 ± 0.5	1.6 ± 0.2	1.7 ± 0.3	0.5 ± 0.2
Levoglucosenone	2.2 ± 0.4	2.3 ± 0.4	2.2 ± 0.4	2.2 ± 0.4	1.9 ± 0.5	2.8 ± 0.3	1.9 ± 0.5
Anhydrosugars	4 ± 3	6.4 ± 3.9	4.9 ± 2.3	2.4 ± 1.9	2.2 ± 0.6	2.19 ± 0.03	1.02 ± 0.06
Chitin-derived compounds							
Chitin-derived compounds	3 ± 1	2.3 ± 0.9	2.7 ± 0.8	2.6 ± 0.8	3.8 ± 0.4	1.6 ± 0.8	0.23 ± 0.1
N-compounds							
(alkyl)pyridines	0.3 ± 0.1	0.37 ± 0.03	0.28 ± 0.08	0.35 ± 0.06	0.41 ± 0.04	0.16 ± 0.07	0.06 ± 0.01
Pyridines_O	0.7 ± 0.1	0.63 ± 0.06	0.71 ± 0.08	0.79 ± 0.06	0.77 ± 0.09	0.7 ± 0.2	0.3 ± 0.2
(alkyl)pyrroles	2.4 ± 0.5	1.9 ± 0.1	2.0 ± 0.3	2.8 ± 0.4	2.9 ± 0.2	2.8 ± 0.6	2.4 ± 0.4
Pyrroles_O	1.0 ± 0.2	0.63 ± 0.06	0.9 ± 0.1	1.2 ± 0.1	0.90 ± 0.04	1.24 ± 0.08	0.6 ± 0.2
Pyrroledione/ pyrrolidinedione	1.2 ± 0.3	1.2 ± 0.08	1.2 ± 0.2	1.1 ± 0.3	1.5 ± 0.2	1.5 ± 0.2	0.2 ± 0.1
Aromatic N	0.8 ± 0.3	0.5 ± 0.1	0.6 ± 0.1	1.0 ± 0.2	1.0 ± 0.4	1.0 ± 0.3	0.9 ± 0.3
Indoles	1.5 ± 0.4	1.39 ± 0.08	1.4 ± 0.2	1.7 ± 0.1	2.3 ± 0.7	1.5 ± 0.2	0.7 ± 0.3
Diketodipyrrole	0.8 ± 0.2	1.0 ± 0.2	0.7 ± 0.1	0.78 ± 0.08	0.92 ± 0.07	0.5 ± 0.2	0.7 ± 0.4
Proteins	1.5 ± 0.4	1.6 ± 0.3	1.6 ± 0.2	1.3 ± 0.3	2.5 ± 0.2	1.2 ± 0.4	0.6 ± 0.5
Alkylamides	0.6 ± 0.3	0.46 ± 0.09	0.7 ± 0.1	0.5 ± 0.2	1.3 ± 0.3	0.3 ± 0.2	0.11 ± 0.06
Phenols and Lignins							
Phenols	8.2 ± 1.2	10 ± 1	7.7 ± 0.7	8.2 ± 0.8	9.2 ± 0.9	8 ± 1	6 ± 2
Guaiacols	4 ± 2	9 ± 4	4 ± 1	2.7 ± 0.5	3.1 ± 0.7	1.9 ± 0.1	1.3 ± 0.3
Syringols	0.5 ± 0.4	1.6 ± 0.3	0.5 ± 0.3	0.3 ± 0.1	0.7 ± 0.4	0.21 ± 0.01	0.1 ± 0.1
Chlorophylls							
Pristenes	2.7 ± 0.8	2.6 ± 0.9	3.1 ± 0.6	2.8 ± 0.3	2.4 ± 0.2	1.9 ± 0.3	0.5 ± 0.1
Phytadienes	1.9 ± 0.6	1.7 ± 0.6	1.8 ± 0.5	1.9 ± 0.5	3.1 ± 0.4	1.3 ± 0.2	0.6 ± 0.6
***n*-alkenes (Cn:1)**							
C9-16:1	3.5 ± 0.8	2.1 ± 0.2	3.2 ± 0.4	4.2 ± 0.6	3.3 ± 0.2	3.7 ± 0.7	3.9 ± 0.3
C17-C22:1	6 ± 1	5 ± 1	6.6 ± 0.8	6.4 ± 0.5	5.1 ± 0.7	5.7 ± 0.5	3.9 ± 0.2
C23-26_1	2.9 ± 0.9	3.3 ± 0.6	3.6 ± 0.8	2.5 ± 0.4	2.4 ± 0.4	2.2 ± 0.7	1.0 ± 0.6
C27-28:1	0.8 ± 0.4	1.1 ± 0.3	1.1 ± 0.2	0.6 ± 0.1	0.9 ± 0.2	0.3 ± 0.2	0.12 ± 0.02
***n*-alkanes (Cn:0)**							
C13-16:0	2.5 ± 0.6	1.7 ± 0.3	2.3 ± 0.3	3.0 ± 0.5	2.6 ± 0.1	2.7 ± 0.3	2.4 ± 0.1
C17-22:0	3.9 ± 0.8	2.8 ± 0.4	4.0 ± 0.5	4.4 ± 0.6	3.9 ± 0.2	3.3 ± 0.2	1.9 ± 0.4
C23-26:0	3 ± 1	2.4 ± 0.9	3.2 ± 0.8	2.1 ± 0.5	2.1 ± 0.1	2.4 ± 0.6	8 ± 1
C27-35:0	4 ± 4	3 ± 2	5 ± 1	2.3 ± 0.8	3.2 ± 0.4	2.8 ± 1.4	17 ± 7
Alkan-2-ones (2K)							
2K C13-17	1.3 ± 0.4	0.7 ± 0.1	1.1 ± 0.2	1.8 ± 0.2	1.7 ± 0.4	1.1 ± 0.3	1.60 ± 0.02
2K C19-22	0.3 ± 0.1	0.18 ± 0.06	0.33 ± 0.06	0.4 ± 0.1	0.33 ± 0.03	0.13 ± 0.07	0.03 ± 0.01
2K C23-31	1.3 ± 0.8	1.3 ± 0.4	2.1 ± 0.7	0.8 ± 0.3	1.1 ± 0.1	0.5 ± 0.4	0.2 ± 0.2
Steroids							
Steroids	1.2 ± 0.9	1.1 ± 0.3	1.1 ± 0.4	1.2 ± 0.5	3.7 ± 0.5	0.25 ± 0.09	0.06 ± 0.04
Tocopherols							
Tocopherols	0.3 ± 0.3	0.8 ± 0.5	0.4 ± 0.2	0.09 ± 0.06	0.12 ± 0.04	0.11 ± 0.09	0.01 ± 0.01
Hopanoids							
Hopanoids	1.3 ± 0.4	0.8 ± 0.3	1.4 ± 0.1	1.6 ± 0.2	1.7 ± 0.2	0.78 ± 0.09	0.17 ± 0.01
(Poly)aromatics							
Benzene	0.9 ± 0.4	0.6 ± 0.2	0.8 ± 0.1	1.0 ± 0.3	1.0 ± 0.3	2.0 ± 0.4	0.67 ± 0.06
Benzaldehyde	0.6 ± 0.3	0.39 ± 0.07	0.5 ± 0.1	0.7 ± 0.1	0.5 ± 0.1	1.3 ± 0.2	0.71 ± 0.09
Acetylbenzene	1.1 ± 0.4	0.7 ± 0.1	0.8 ± 0.2	1.3 ± 0.2	0.84 ± 0.09	2.2 ± 0.2	1.1 ± 0.1
Alkylbenzenes C3-9	1.9 ± 0.5	1.44 ± 0.09	1.6 ± 0.2	2.4 ± 0.4	2.10 ± 0.04	2.1 ± 0.2	1.71 ± 0.07
Polyaromatics	1.4 ± 0.4	1.01 ± 0.07	1.1 ± 0.2	1.7 ± 0.3	1.21 ± 0.03	1.7 ± 0.1	1.4 ± 0.1

[a]whole-lake: averages of all analyzed sediment samples excluding the two outlier samples (sites M4, S15); [b]n: number of sample; The six clusters are presented in Fig. 1d in the manuscript.

Light grey background denotes average values below 10 % of whole-lake average. No background denotes values close to whole-lake average (±10 %). Dark grey background denotes average values above 10 % of whole-lake average.