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A 10,000 year record of sediment pore-water dissolved organic matter characteristics from Lake Peipsi as revealed by HPSEC

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In this study, high-performance size-exclusion chromatography (HPSEC) combined with diode-array detection (DAD) was applied for the investigation of dissolved organic matter (DOM) from sediment pore-water from Lake Peipsi, Estonia. The age of the 4 m long sediment core was estimated using the ¹⁴C dating method and suggested sediment accumulation for the past 10,000 years. Using the HPSEC approach it was possible to evaluate temporal changes in the content of DOM and its molecular weight characteristics during the Holocene period. The content of dissolved organic carbon (DOC) calculated from spectroscopic data was in good correlation with the total peak areas computed from HPSEC chromatograms. The results revealed that the content of detected DOC in the older samples [10,300 to 2,600 years before present (BP)] was twice as high as in the younger ones (from 2,400 years BP to present). Thus, HPSEC analysis with spectroscopic methods might provide useful information about temporal changes in DOM content and could be used in palaeolimnological research.

Keywords: pore-water dissolved organic matter; sediment; HPSEC; humic substances; palaeolimnology; Lake Peipsi

1. Introduction

Lake sediments represent archives that reflect past environmental conditions. Lacustrine sediments therefore provide an important time perspective on a range of natural processes, such as long- and short-term climatic changes, the development of lake ecosystems and the terrestrial catchment areas that drain into them, as well as prehistoric and modern human impacts on aquatic ecosystems. Lake sediments are generally rich in organic matter (OM), which consists of an extremely heterogeneous mixture of various biomolecules including proteins, carbohydrates, lipids and humic substances (HS), the products of partial breakdown of organic components [1]. The origin of lake sediment OM is different and diverse; it may have biogenic, biochemical and terrestrial, as well as human-induced origins. Roughly, sediment OM can be derived from two sources. Autochthonous OM is generated within the aquatic system as a result of degradation

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processes of organisms that have lived in the lake. Another type is allochthonous OM, which originates outside the lake basin, in the catchment of the lake, and these land-derived organic residues mainly enter the lake via inflowing rivers and streams. Even though the sediment OM is a diverse mixture of components from many sources and with variable degrees of preservation, the abundance and different components of lacustrine sedimentary OM provide evidence of the biota that have lived in the lake and its watershed area, and hence these proxies can be used to reconstruct palaeoenvironmental conditions [2].

Lake Peipsi is the largest transboundary lake in Europe, shared between Estonia and Russia. It is an important economic resource for Estonia and has been exposed to extensive human activity for a long time. The lake and its rivers are mainly used for fishing and water transport. The catchment area has been used for agricultural purposes for several millennia. On the northern side of the lake there are extensive mining areas and several electric power plants operating on oil shale. As a consequence, enhanced delivery of nutrients to Lake Peipsi has induced an increase in primary productivity within the lake and anthropogenic eutrophication during the last few decades [3].

Palaeolimnological studies for the assessment of the eutrophication history of Lake Peipsi are infrequent. A diatom composition study of short sediment core covering the last 130 years revealed that the man-made impact on Lake Peipsi started in the mid-1950s, and the eutrophication reached a maximum in the 1970s and 1980s and showed a slight decrease in the 1990s [4]. Research by Leeben et al. using fossil pigment analysis confirmed those results and also suggested that the contribution of autochthonous organic matter in the lake started to grow in the middle part of the last century [5]. Knowledge of the long-term post-glacial lake development and changing environmental conditions is even more sporadic, and mostly based on a poorly dated diatom and geochemical records with a low time-resolution [6].

However, without knowing the natural baseline conditions of the lake ecosystem it is hard to evaluate its current ecological state. Therefore, more adequate information about the natural development and changes of environmental conditions in Lake Peipsi are essentially needed to evaluate anthropogenic impact on the lake ecosystem. The studies of Leeben and co-authors have demonstrated the applicability of sedimentary pore-water dissolved organic matter (DOM) spectroscopic characteristics as proxies for understanding the origin and properties of OM, and consequently, temporal dynamics of past environmental changes in lakes [5,7–9]. The aim of this research was to investigate stratigraphic changes in the molecular size and quantity of sedimentary DOM from Lake Peipsi over the period of the last 10,000 years. For this purpose, high-performance size-exclusion chromatography (HPSEC) with diode-array detection (DAD) was applied to separate DOM from sediment pore-water. The HPSEC approach has demonstrated a great potential for pore-water DOM investigations [10–12], although it is not yet widely used for palaeolimnological investigations. However, HPSEC analysis may be a suitable approach because it is very simple and non-destructive, and requires minimum sample pre-treatment. In addition to HPSEC, the spectroscopic method was used to characterise pore-water DOM.

This study is an attempt to demonstrate that the changes in the content and structure of sedimentary pore-water DOM might be related to environmental and climatic changes in large aquatic ecosystems. Because the HPLC method has shown good results in investigations of small shallow lakes [8,13], it could probably be applied to the examination of larger lakes. However, in the case of small shallow lakes, especially with annually laminated sediments, diagenetic processes are supposed to be minimal, because little or no resuspension occurs and no bioturbation is present [1]. Processes occurring in larger lakes are more complicated because turbulence and bioturbation might affect the deposition of the original organic material.

2. Materials and methods

2.1. Study site

Lake Peipsi is the fourth largest lake in Europe by area (3,555 km², maximum length ~150 km, and width 42 km). It is a shallow (mean depth 7.1 m, maximum depth 15.3 m), unstratified and eutrophied lake. The lake system consists of two basins (Lake Peipsi *sensu stricto* and Lake Pihkva) which are joined by a narrow strait (Lake Lämmijärv). It has an outflow into the Gulf of Finland via the Narva River. The basin capacity is >25 km³, which is fed by more than 240 rivers, brooks and channels [14]. The average residence time of the water is ~2 years [15]. The water of Lake Peipsi has an average pH of 8.1 and a Secchi disk transparency of 1.6 m [16].

The formation of sediments in Lake Peipsi is controlled by hydro-meteorological processes such as waves, wind, water-level fluctuations, drift ice and currents [17]. The bottom topography of Lake Peipsi is monotonous and the composition of the sediments is more or less homogeneous. The shallower areas are mainly represented by sands, silts and late-glacial clays, whereas post-glacial organic-rich gyttja sediments are present in the areas with >9 m of water depth [18], reaching a thickness of 7 m [6].

2.2. Sediment coring and sample handling

In March 2007, a 4 m long sediment core was taken on the ice from the central part of the lake (58°47.213'N; 27°19.299'E), using a Russian-type peat corer at a water depth of 9.8 m. The recovered sediment core was immediately packed into 1 m plastic semi-tubes, wrapped in polyethylene film to avoid oxygen exposure and transported to the laboratory. During transportation and before slicing the wrapped core was stored at ~4 °C. The next day the core was sliced into continuous 1 cm thick sub-samples that were immediately packed into small plastic bags, again to maximally avoid oxygen exposure. The sub-samples were stored in the dark at 4 °C.

Additional information on the sample handling procedures can be found in supplementary text S1 (available online only).

2.3. High-performance size-exclusion chromatography and spectroscopic measurements

The sediment core was collected and processed with care to avoid oxygen exposure. However, some oxygen exposure might still have occurred during pore-water extraction at ambient atmosphere. That might have introduced some artefacts into the measurements of the abundance and molecular weight (MW) of the DOM. The samples were extracted directly before the HPSEC analysis (12 samples at a time). The sub-samples were centrifuged at 3500 rpm for 30 min and the pore-water obtained was filtered through a 0.45 µm Millipore filter. When they were not being analysed, the samples were stored in the dark at 4 °C to maximally avoid artefact introduction. The samples were measured with 5 cm intervals in the upper sediment layers (from 10.00 to 10.30 m) and further with 10 cm intervals.

Pore-water samples were analysed using a HPSEC system equipped with DAD. HPSEC measurements were carried out on a BioSep-SEC-S 2000 PEEK size-exclusion column filled with glycerol covered silica-based gel (300 × 7.50 mm, Phenomenex). The size of the particles was 5 µm and the size of the pores was 145 Å. The data obtained were analysed using Agilent Chem-Station software. The HPSEC system was equipped with a Knauer pump, Rheodyne injector, and Agilent Technologies 1200 Series diode-array detector.

The HPSEC system was calibrated with four protein standards purchased from Phenomenex: bovine thyroglobulin (MW, 670,000), human gamma globulin IgG (MW, 150,000), ovalbumin

(MW, 44,000) and myoglobin (MW, 17,000); also, uridine (MW, 244), Phenomenex, was used to obtain a low molecular range calibration. For the calibration curve standards, elution times were plotted against the logarithm of their molecular weights.

According to the obtained chromatograms total peak areas and areas of separated peaks were calculated. Total peak areas represented the whole amount of ultraviolet (UV)-absorbing biomolecules in pore-water DOM. Also, according to the results, number- and weight-average molecular weights (M_n and M_w , respectively) and their ratios were calculated. For additional information, see supplementary text S2 (available online only).

We used mostly HPSEC peak areas (the total peak area and the HS fraction area) for the evaluation of DOM content in pore-waters, but the DOC concentrations were used to show precise concentrations.

3. Results

The studied sediment core (the core-depth of 13.5 to 9.8 m from the water surface) consisted of greenish grey homogeneous gyttja, whereas the topmost 25 cm of the sequence contained dark coloured gyttja. The age model for the studied Lake Peipsi sediment core showed that the onset of gyttja accumulation at the profile base was dated to 10,400 cal BP (cal BP = calibrated years before present; ^{14}C dates calibrated to calendar years before present, the time scale used with radiocarbon dating in archeology, geology, etc. As the zero point of the age scale, 1 January 1950 is used; e.g. 1500 BP means 1500 years before 1950, that is 450 AD). The age of the upper part of the sediment record was estimated by the correlation of particulate OM content with a core taken in 2002 that was subjected to detailed ^{210}Pb dating [4]. The core depth of 10.0 m was estimated to correspond to approximately AD 1950.

Temporal changes in the content of sediment particulate OM could be roughly divided into three periods: 10,300 to 7,600 cal BP; 7,600 to 2,600 cal BP; and 2,600 cal BP to present (Figure 1). The content of particulate OM in the oldest samples exhibited a distinctly increasing trend. After 7,500 cal BP it became relatively stable. A period of slight increase was observed in 2,600 to 1,000 cal BP, and thereafter the content of particulate OM showed a certain decrease.

The DOM from all pore-water samples was resolved by HPSEC into two main fractions. The first fraction contained compounds with very high MW values (first peak on HPSEC chromatograms, Figure 2). The components of the second fraction (second peak on HPSEC chromatograms, Figure 2) was eluted from the chromatographic column as a broad distribution, sometimes with partially resolved sub-shoulders. The peak of the first fraction was much smaller than the peak of the second fraction. The DAD spectrum of the first fraction revealed that it was typical of proteinaceous material, whereas the second fraction spectrum was characteristic of HS. The position and shape of the first fraction peak were mostly quite stable in almost all samples. By contrast, the shape of the second fraction peak varied temporally (Figure 2), although the retention times remained more or less stable. Poorly resolved sub-shoulders appeared in pore-water samples from older sediment layers. In some samples, the third fraction (third peak) with very low MW appeared (Figure 2(c)), but this appearance did not seem to be regular.

According to the obtained results, temporal trends in the contents of DOC, UV-absorbing DOM (calculated as total peak area), and HS fraction were constructed (Figure 3). In addition, chronological changes of the ratio $A_{250/360}$, indicating aromaticity, and the M_n , M_w and their ratios were constructed (Figure 4).

Unlike the HS fraction, the high MW material eluted from the chromatographic column mostly before the calibrated range ($>670,000$ Da), and thus it was not possible to estimate its MW distribution adequately. Besides, the amount of the detected high MW fraction was negligible ($\sim 5\text{--}6\%$ of the total area of all detected DOM). The MW distribution for the HS fraction was

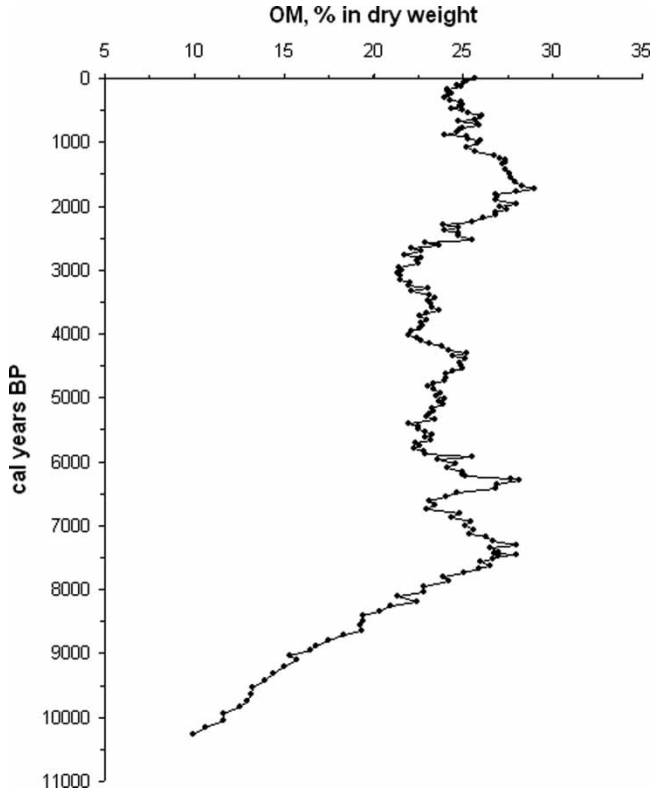


Figure 1. Age-related changes in particulate organic matter content in sediments from Lake Peipsi; cal years BP: calibrated years before present; 0 cal BP = 1950 AD.

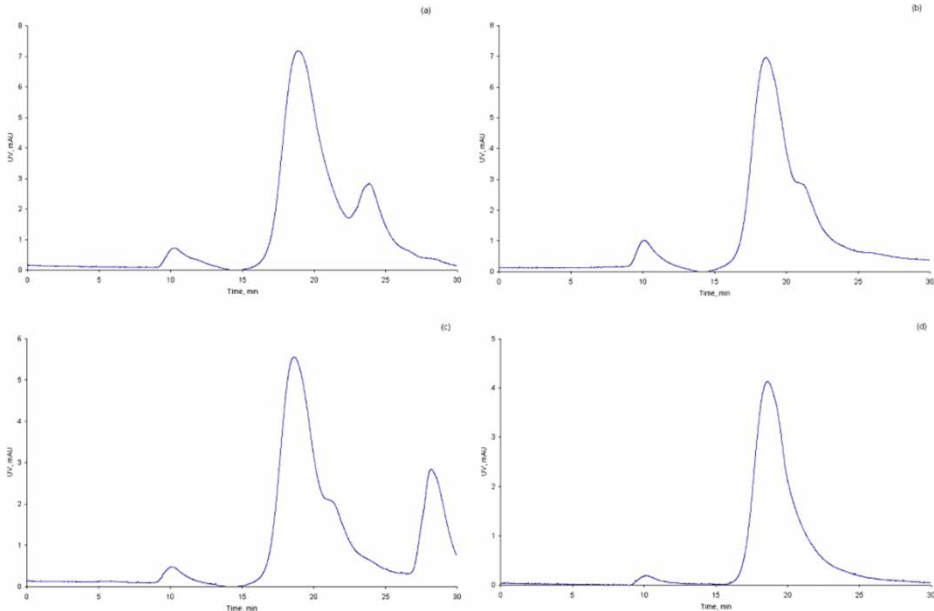


Figure 2. HPSEC chromatograms of pore-waters dated to: (a) 7,200 cal BP; (b) 5,500 cal BP; (c) 4,300 cal BP; (d) 800 cal BP. HPSEC conditions: mobile phase – 100 mM phosphate buffer (pH 6.8) at $0.5 \text{ mL} \cdot \text{min}^{-1}$, sample volume $20 \mu\text{L}$, detection wavelength 280 nm.

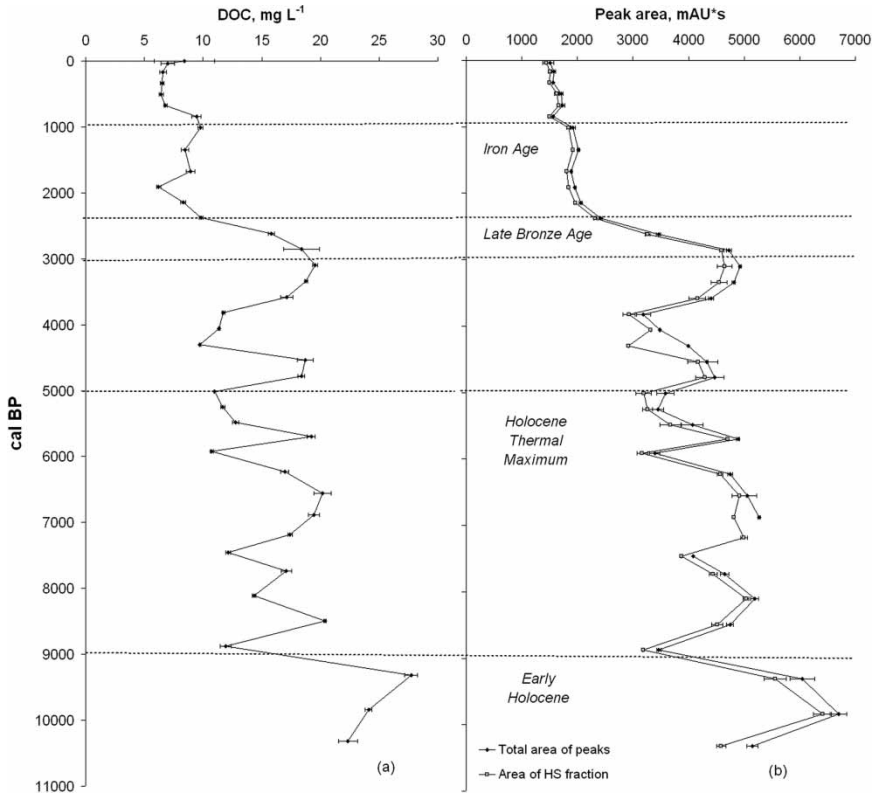


Figure 3. Age-related profiles of: (a) DOC content; (b) total peak area and area of HS fraction.

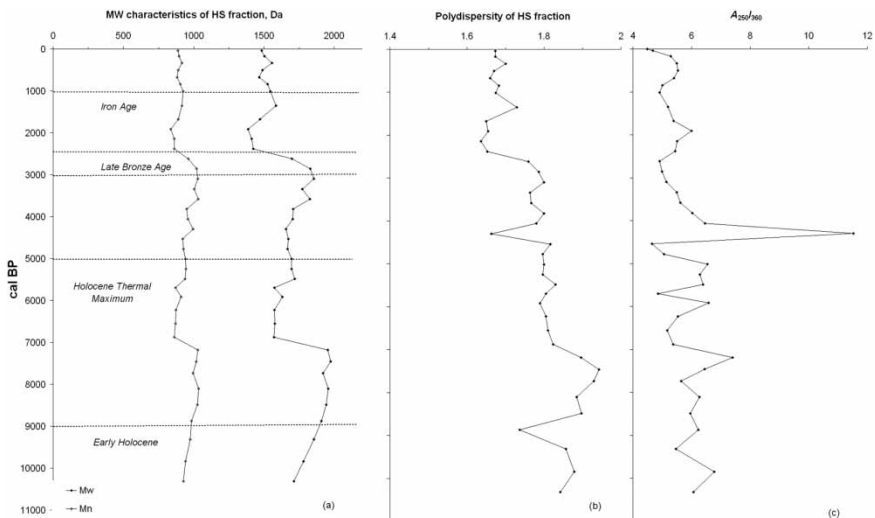


Figure 4. Age-resolved profiles of (a,b) MW characteristics and (c) absorbance ratio $A_{250/360}$ of pore-water DOM.

calculated only for the calibrated range (up to 244 Da). Thus, the MW distribution of HS are probably slightly overestimated. The MW values of the third peak were not calculated, because the peak eluted below the calibrated range.

Temporal distributions of the DOC content, the total area of the peaks (UV-absorbing DOM), and the area of the HS fraction showed similar trends (Figure 3).

Generally, the DOM content in the pore-water decreased over the last 10,000 years – older samples contained amounts of DOM almost twice as high as the ones accumulated recently. According to the characteristics reflecting DOM content (DOC concentration, the total peak area and the HS fraction area), the temporal changes could be roughly divided into two periods:

1. 10,300 to 2,400 cal BP. During that period the content of DOM in pore-water varied greatly with the average DOC content being 16.4 mg L^{-1} ;
2. 2,400 cal BP to the present. After 2,400 cal BP the content of DOM decreased drastically more than two-fold (average DOC 7.7 mg L^{-1}).

The shapes of the HPSEC chromatograms of the analysed samples varied significantly. The chromatograms of the first period varied greatly in comparison with the second period. The pore-water samples from 10,300–3,800 cal BP were mostly separated into two peaks, one with high MW and the second as a HS peak, usually with a partially resolved low MW sub-shoulder (Figure 2(a),(b)). The major part of this sub-shoulder was usually below the calibrated range (<244 Da). In a few samples, the third peak eluted at longer retention times reflecting extremely low MW compounds (Figure 2(c)).

The components of the high MW fraction were very unstable in the oldest samples (10,300–6,600 cal BP) as the peak varied greatly in height and shape. After 6,200 cal BP the shape of this peak did not change.

The chromatograms of the samples from 3,600 cal BP to the present were all invariant. Components were eluted as two peaks, high MW components and a smooth HS fraction without any sub-shoulder (Figure 2(d)).

According to the protein calibration, the M_w from the HS fraction did not exceed 2,000 Da, varying from 1,400 to 1,900 Da, and the M_n was mostly between 900 and 1,000 Da (Figure 4(a)). In general, both trends were very similar and they did not exhibit any drastic changes. However, several characteristic periods could be distinguished. In the oldest samples (10,300–7,200 cal BP), average MW values increased slightly until 7,200 cal BP. M_w and M_n were $\sim 1,890$ and 990 Da, respectively. The changes occurred around 7,200 cal BP when average MW values decreased. After 2,400 cal BP, M_w and M_n decreased even more (1,490 and 890 Da, respectively).

Polydispersities calculated for the humic-type fraction did not take into consideration components that were below 244 Da. This way, polydispersity values varied between approximately 1.6 and 2.0 and should, in fact, have been higher (Figure 4(b)).

Figure 4(c) shows the temporal changes in pore-water absorbance ratios at 250 and 360 nm. The aromaticity values of the analysed samples varied around ~ 4.5 – 6.5 without any sharp changes. Only one sample, dated to 4,300 cal BP, was differentiated with an extremely high value of 11.52, which might be occasional.

4. Discussion

4.1. HPSEC analysis of Lake Peipsi pore-water DOM

The choice of calibration standards for pore-water DOM is crucial in HPSEC. To obtain reliable and adequate results using HPSEC, calibration standards should match the molecular structure of the analysed components as closely as possible [19]. The components of lacustrine pore-water

DOC are very diverse and it is a rather difficult task to find standards which would represent all the compounds. However, according to the literature [12,20,21], HS comprise the main part of the lacustrine DOC. Indeed, in this study, HPSEC analysis also revealed that the dominant components of DOC in Lake Peipsi sediment pore-waters were HS. Also, some compounds of proteinaceous origin were detected. It is not simple to choose appropriate calibration standards for humics because of their unique structure. There is a general agreement that random coil standards such as polystyrene sulphonates should be used for humics MW distribution determination [21]. Globular protein standards could also be used but they were reported to overestimate the MW values of humics by a factor of five or more [21]. In this study, the HPSEC column was calibrated with globular proteins. Despite the statement of caution [21], M_w and M_n values for Lake Peipsi pore-water DOM were in good agreement with MW distributions reported for aquatic fulvic acids [10,12,22] and for freshwater sediment pore-waters [21]. Thus, in our study, the calibration with globular proteins did not lead to over-prediction of HS MW values and might be used for estimation of MW distribution of pore-water DOM.

The presence of proteinaceous matter in pore-water DOM might be caused by the association of undecomposed proteins and humic material into large aggregates. Humic-type molecules could probably encapsulate protein molecules, making them unavailable for bacterial degradation [23].

Light absorbance has usually been used to estimate DOC concentrations in sediment pore-water. However, the exclusive use of UV-absorption for DOC and its MW measurement has a considerable disadvantage because it detects only UV-absorbing molecules. Estimating DOC concentrations by UV-absorbance provides a bias in favour of molecules that contain chromophores and absorb light at the chosen wavelength(s). Components that absorb UV weakly (e.g. polysaccharides) will not be represented properly. Thus, measurements based on UV-absorption may underestimate DOC concentrations. To avoid this, one should use another approach for measuring pore-water DOC concentration (e.g. a combustion-based TOC analyser). Unfortunately, in this study there was no possibility of using a TOC analyser and all DOC contents could be to some extent underestimated. The same applies to the HPSEC analysis with the UV-absorbance detector. As UV-nonabsorbing components are not properly represented, this could also affect MW calculations and introduce a bias in the results. Thus, we should point out that the obtained results concern only UV-absorbing DOM and are discussed in these terms.

In our study, we observed that the temporal distributions of the DOC content, total area of the peaks (UV-absorbing DOM), and the area of the HS fraction showed similar periods which had a good correlation between themselves (the correlations between DOC concentration and total peak area and between DOC concentration and HS fraction area were both $R^2 = 0.86$). Thus, the total peak area calculated from HPSEC chromatograms may be a good predictor for DOC concentrations in sediment pore-waters.

4.2. Temporal changes of sediment pore-water DOM characteristics

In this study, sediment pore-water DOM variables from Lake Peipsi were employed to track changes in a sediment core representing $\sim 10,400$ years of accumulation. HPSEC analysis of pore-water samples revealed several periods of structural and quantitative DOM changes. These changes were probably dependent on post-glacial changes of lake environmental conditions. However, OM diagenesis might also have affected the nature and distribution of DOM in the upper sediment layers.

Several earlier investigations indicate that the beginning of the Holocene coincided with the shallow water level of Lake Peipsi. According to Hang et al. [24], at the onset of the Holocene a low-level period occurred during which 'Small Lake Peipsi', with a water level 8 m lower than today, existed. In addition, the presence of lake lime layers in between late glacial clays and gyttja

beds in several locations of the basin has been associated with an early Holocene lake level low stand [6,25,26].

Therefore, we attribute the up-core transition from low to high sediment particulate OM content to a progressively deepening water body. A shallower water depth likely induced fine-grained mineral sediment redistribution through wave turbulence and deposition of sediment with low OM content, whereas deeper conditions allowed accumulation of OM-rich gyttja. Also different sediment pore-water DOM variables indicate variations that might be related to changing environmental conditions in Lake Peipsi. The content of DOM in pore-waters was highest during that period. In addition, the shapes of the pore-water DOM chromatograms varied. The variation occurred in the area of high MW fraction, probably due to the diverse aggregation of proteinaceous matter with HS. The elution profile of the HS fraction also varied greatly in that period, resulting in partially resolved compounds with different degrees of resolution. These variations during that period might reflect the fact that they contained a very complex mixture of components of different origin. The sources of the OM could be different, being the increased inflow of terrestrial OM and elevated lake biological productivity. The relatively higher polydispersity of the HS fraction in these samples was in agreement with this assumption (Figure 4(c)). This evidence might suggest that as the lake level rose rapidly, forcing the coastline to retreat, large areas of coastal soils, terrestrial plants and marginal peatlands were eventually flooded, abraded and transported to the basin, and thus land-derived material may have provided a source of sediment OM. However, the increased release of nutrients from intensively abraded and drowned shoreline, combined with increased run-off to the lake, possibly brought abundant dissolved nutrients to the lake and stimulated higher rates of primary in-lake production.

However, the real sources of OM could be difficult to identify. The absorbance ratio $A_{250/360}$ did not vary drastically, and thus it did not allow the dominance of allochthonous or autochthonous OM to be differentiated. Probably both sources (in-lake bioproductivity and land-derived influx) were responsible for formation of the sediment OM. As average MW values were slightly higher compared with the younger samples (M_w was $\sim 1,900$ Da and M_n was $\sim 1,000$ Da), it might be possible that OM derived from terrigenous sources could even dominate during the early Holocene. Although the changes in average MW values were not great, it is possible that they were also related to temporal changes in DOM content and structure. The polydispersity of the samples was 1.80–1.90, suggesting relatively homogeneous OM.

In the early stages of Lake Peipsi's development (10,300–7,600 cal BP), when the water level was low, OM in the upper sediment layers could also have been slightly resuspended by turbulence events. When the water level rose, turbulence no longer caused OM resuspension as waves could not reach the lake bottom.

The content of particulate OM showed steady values at 7,600 cal BP, suggesting that the lake-level of Lake Peipsi may have stabilised. Thereafter, variations in the data were mostly minor gradual oscillations, additionally indicating relatively uniform environmental conditions. This possibly implies that by approximately 7,000 cal BP, Lake Peipsi had attained a size and morphology comparable with that of today. However, the content and structure of DOM were still not stable. Chromatographic elution profiles of HS components dissolved in pore-water were still variable until 3,800 BP. Mostly compounds with MW values < 800 Da varied. As the lake system and its water level were stable by that time, the changes in DOM content and structure were probably related to the lake inner processes like changing bioproduction. In addition, climatic change might have influenced the accumulation of OM in the lake. The period in Estonia between 9,000 and 5,000 cal BP, the Holocene thermal maximum, had an annual mean temperature 2.5°C higher than today [27]. This may have affected the higher DOM content several thousand years ago compared with the present time.

Chromatograms of the DOM accumulated after 3,600 cal BP were very similar. Thus, the composition of OM in Lake Peipsi was probably more or less stable during the last 3,600 years.

In addition, after 2,400 cal BP a sharp decrease in the DOM content of pore-water was observed. As could be seen from the results, the content of DOM including HS in the early Holocene was almost twice as high as during the late Holocene. At the same time, the proportion of particulate OM increased. These changes temporally coincided with the beginning of human activity in the area around Lake Peipsi. The earliest traces of the adoption of cereal farming in Lake Peipsi catchment area, defined as the start of continuous cereal pollen grains in sediment pollen curves, are dated to the Late Bronze Age at 3,000 to 2,500 cal BP, whereas the overall adoption of cereal cultivation and onset of the formation of an agrarian landscape throughout Estonia took place during the Iron Age from 2,500 cal BP [28]. Extensive agricultural land use would lead to deforestation. The opening up of catchment essentially might lead to topsoil disturbances and increased intensities of erosion, and could produce an outbreak of soil-derived nutrients to the basin, subsequently stimulating the increase in productivity of the lake. However, pore-water DOM variables indicate decreasing trends. The possible explanation for this might be due to the changes in the nature of DOM in the sediments from 2,400 cal BP to the present, because during this period OM content increased in the particulate phase, but decreased in the dissolved phase (Figures 1 and 3). Leebein et al. [5] reported that Lake Peipsi had become eutrophic in the past few decades. This might have led to a greater input of microbially derived OM. Microbially derived OM has a more aliphatic character because of large amounts of lipids and polysaccharides which do not absorb UV light. Thus, this part of DOM is likely to have remained undetected by UV detection. According to Meyers and Ishiwatari [1], OM buried in the deeper sediment layers undergoes anaerobic degradation. Material derived from aquatic sources is generally more sensitive to biodegradation than the OM derived from terrestrial sources. Thus, land-derived OM (HS and lipids) becomes dominant as the components from aquatic sources are converted by microbial activity (carbohydrates, amino acids). Owing to diagenesis, only the most resistant components of original organic material remain. Microbially reprocessed OM also contributes to the sediment material. Thus, the amount and structure of OM buried in the sediments might be different to a certain extent from the original deposited OM. So, on the one hand, the higher DOC concentrations in the older pore-water samples from Lake Peipsi (10,300 to 2,600 cal BP) might to some degree reflect a typical OM diagenesis, leading to more humic-like DOC which would be detected by UV absorption-based techniques. But on the other hand, because during the water level rise in the lake, land-derived humic material would have been dominant, the higher DOC concentrations would more likely correspond with the depositional history.

5. Conclusions

The HPSEC method combined with spectroscopic data provides valuable information about DOM properties in lacustrine sediment pore-water.

In this study, DOC concentrations calculated from absorbance spectra correlated very well with the total areas of the peaks and HS fraction areas computed from the HPSEC chromatograms. Thus, HPSEC analysis allows the DOM content in sediment pore-waters to be evaluated and might be useful as an alternative method when there is no possibility of measuring DOC concentration. Also, HPSEC analysis combined with spectroscopic methods might provide general information about temporal changes in lacustrine sediment DOM characteristics. This approach could be used in palaeolimnological research, especially in research on small shallow lakes. Processes in the sediments of large lakes are diverse and the interpretation of the results might be more sophisticated.

The advantages of the HPSEC method used with UV detection were its simplicity and minimal sample pretreatment. However, the potential disadvantage of UV absorption-based techniques

was that the UV-nonabsorbing fraction remained unrepresented and a part of the potential DOM was underestimated.

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