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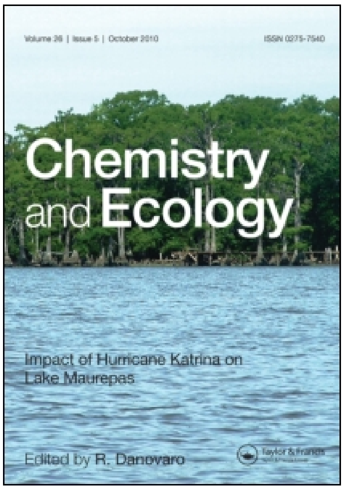

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Partitioning of metals between operational fractions in the sediment record from Lake Peipsi

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A sequential extraction procedure was used to study the partitioning of metals (Ca, Mn, Fe, Cu, Zn and Cd) between operationally defined fractions in the interval covering the last 150 years of the sediment record from Lake Peipsi, Estonia. The results indicated decreased total and bioavailable Cu and Zn levels from the 1980s to the present, and increased Cd. The variability in Mn and Fe concentrations was possibly induced by changes in redox conditions at the bottom of the lake. The dissolved organic fraction of the sediment core was characterised by high-performance size-exclusion chromatography and spectroscopy. The dissolved organic matter pool was comprised mainly of humic substances and of a very small high molecular weight fraction. This study revealed increasing trends for general sediment characteristics (organic matter, dissolved organic carbon and absorbance ratio) since the 1960s, together with some molecular characteristics (peak areas of humic and high molecular weight fractions). Statistical cluster analysis revealed that metal concentration data in combination with some chromatographic and spectrometric parameters can be used to reveal periods with similar characteristics in Lake Peipsi sediments.

Keywords: metals; sequential extraction; dissolved organic matter; lake sediment; HPSEC; AAS

1. Introduction

Organic constituents in aquatic ecosystems are considered to be a complex mixture of lipids, carbohydrates, proteins and other biochemicals that are contained in the tissues of living microorganisms and are derived from the detritus of organisms formerly living in the lake and its watershed. Humic substances (HS) are diagenetically formed from these biochemical starting materials and constitute the majority of the complex mixture of organic matter [1–3]. A modern structural description regards HS as supramolecular associations of relatively small molecules with an amphiphilic nature (with a molecular mass <1000 Da) that are able to aggregate, polymerise and form micelles. Because of the formation of aggregates of different sizes and shapes, HS show a wide range of reactions with other materials under environmental conditions [4]. The different types of biota populating a lake and its watershed produce organic matter with a distinctive biochemical composition. However, the composition and characteristics of deposited organic matter may be subject to post-depositional changes due to microbial activity and geochemical processes.

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The stratigraphy of organic constituents in lake sediments holds important information about environmental conditions in the lake and its catchment and their changes over time, and together with metal analyses, makes it possible to reveal the contamination of aquatic ecosystems [5]. Studies based on sediment analysis permit the historical monitoring of the content of heavy metals in the environment and establishment of the share of their anthropogenic input [6–8]. However, post-deposition redox conditions, mobilisation and diagenesis [9] complicate the distribution of heavy metals in the sediment sequence and must be considered when past metal contamination trends are reconstructed from lake sediment profiles. Changes in environmental conditions (acid rain, anoxic conditions during winter) might cause the metals accumulated in sediments to dissolve back into the water, to the detriment of the aquatic system.

The pollution levels in a lake can be estimated by the total metal concentrations in the sediment. However, knowledge of the chemical forms of metals in sediments is essential for estimating their toxicity and bioavailability. In order to determine the chemical forms of metals in sediments, several sequential extraction procedures that selectively mobilise metals bound to operationally defined sediment fractions have been used [10–16]. Many of these methods are based on the five-step procedure of Tessier et al. [17]. However, the lack of suitable reference materials and operational differences between different extraction methods has led to significantly different results. To overcome such problems, the modified sequential extraction procedure for trace metal speciation was developed by the European Community Bureau of Reference (BCR) [18–28]. The application of the BCR method to sediment core samples has so far been limited because of poor recoveries. Normally the quantity of sample required for sequential extraction is 1 g, but the quantity of sub-samples obtained from geological sediment cores is only a few hundred milligrams. Thus a revised and validated BCR procedure has recently been developed [29]. The aim of this study was to speciate the particulate metals from a Lake Peipsi sediment core by a sequential extraction procedure, involving chemical extractions of metals into five fractions. The Tessier method was chosen as an example of a classical fractionation method, although it is more time-consuming and more complicated than the alternative newer BCR extraction procedure.

The sediment dissolved organic matter (DOM) was further analysed by high-performance size-exclusion chromatography (HPSEC) coupled with diode-array detection (DAD) to obtain the molecular characteristics of DOM including the molecular masses, spectra of molecular fractions, the polydispersity and peak areas. The method used was applied to pore-water analysis in earlier studies [30–33]. The dataset obtained was statistically analysed to reveal similarities or differences between the sediment layers. An attempt was made to relate the results obtained to environmental changes.

2. Materials and methods

2.1. *Study area*

Lake Peipsi is situated on the border between Estonia and Russia. It is the fourth biggest lake in Europe. Its surface area is 3,500 km^2 with an average depth of 7 m. The maximum depth is only 15 m. Lake Peipsi is connected to the Gulf of Finland by the River Narva. The Lake Peipsi catchment area is made up of 4,500 lakes, of which the largest is Lake Võrtsjärv (270 km^2). The catchment area covers $>$47,000 km^2 and is mostly agricultural land. The lake has more than 240 inflows and only one outflow – the River Narva. Thus 84% of the water input to the lake comes from rivers and 16% from atmospheric precipitation [34]. Today the lake is classified as eutrophic. The northern part of the basin is the most industrialised, because this area is rich in oil shale, which is used in five thermal power plants in Estonia and one in Russia [35]. Thermal power plants and chemical industries are the source of the atmospheric pollution in the lake. The lake is considered as the main water resource for north-eastern Estonia and in particular for the capital Tallinn. The wastewaters and gaseous emissions of toxic sulphur and nitrogen oxides, hydrogen chloride and carcinogenic compounds from power stations operating on pulverised oil shale have a considerable impact on the chemical composition of the water in Lake Peipsi.

2.2. *Sampling and dating*

A 43 cm long sediment core was collected from Lake Peipsi in March 2007 from location 58°47′13″N and 27°19′18″E. This sampling point was located in the middle of the lake at the same location as in previous studies in order to allow comparisons [35–37]. The water depth at the sampling site was 9.8 m. Sediment samples were taken using a Willner corer. The core was cut into 1 cm thick subsamples, packed into plastic bags and transported to the laboratory. The chronology of the core was established via correlation of its loss-on-ignition curve with that of the 2002 year core, which was previously dated by the ^{210}Pb radiometric method using gamma spectrometry [38]. For calculations of the ^{210}Pb dates the constant rate of supply model [38] was applied and the results were compared with two other independent dating approaches – the sediment distribution of artificial radionuclide ^{137}Cs and spheroidal fly-ash particles [39]. The methodology and the results of all these dating methods and the reliability of the chronology are explained in detail in Heinsalu et al. [37].

Pore-water samples for analysis were obtained by extraction of unfrozen sediments by centrifugation at 3,500 rpm for 30 min and filtration through 0.45 μm filters (Millex, Millipore). Samples were stored at 4 °C in the dark.

2.3. *Chemical analyses*

2.3.1. *Sequential extraction of metals*

The sequential extraction of metals from sediments was carried out using a procedure decribed in detail by Tessier et al. [17]. Additional information on the method used can be found in supplementary text S1 (available online only). To obtain the total metal concentrations, five successive extractions of each sediment sample were performed and the results were summed.

2.3.2. *Atomic absorption spectrometric analysis*

The flame atomic absorption spectrometer (FAAS) Varian Spectra AA 220 FS (Mulgrave, Australia) was used to analyse Cu, Ca, Mn, Zn and Fe in each leachate obtained from sediment samples by sequential extraction. The conventional parameters of acetylene–air FAAS were applied [40]. Cd was analysed with the furnace atomic absorption spectrometer Varian Spectra AA 220Z (Mulgrave, Australia) with an end-heated GTA-110Z graphite atomiser, Zeeman-effect background correction and integrated autosampler. Graphite tubes with a pyrolytic graphite coating were used throughout the work. Argon of 99.998% purity (AGA, Helsinki, Finland) was used as the purge gas. The instrumental parameters and temperature programs for Cd measurements are reported in Viitak and Volynsky [41].

The standards of Cu, Ca, Mn, Zn, Fe and Cd were prepared by dilution of certified standard solutions (1000 $\mathrm{mg \cdot mL^{-1}}$, Trace CERT, Fluka, Buchs, Switzerland) of the respective metal ions. High-purity deionised water obtained using a MilliQ water purification system, Millipore (Bedford, USA), was used to prepare the dilutions. Multielement Quality Control Standard 26 (High-Purity Standards, Charleston, SC, USA) and certified reference material river sediment (LGC6187) were used to check the accuracy of the method. At least two replicates were measured for each solution. As a rule, the reproducibility of the measurements was better than 10%. The detection limits (LOD), quantitation limits (LOQ) and optimal concentration range of the analytes were as follows ($\text{mg} \cdot \text{L}^{-1}$): Ca 0.01, 0.023, 0.03–3.0; Cu 0.005, 0.011, 0.03–10.0; Zn 0.003, 0.007, 0.01–2.0; Mn 0.003, 0.010, 0.02–5.0; Fe 0.018, 0.074, 0.08–15; and Cd ($\text{ng} \cdot \text{mL}^{-1}$) 0.024, 0.057, 0.06–5.0.

2.3.3. *General parameter analyses*

The organic matter content was determined as loss on ignition (LOI) at 550 °C for 4 h and the carbonate content at 950 °C for 2 h according to standard procedures [42]. Absorbance spectra of the pore-water samples were collected using the Jasco V-530 UV/vis spectrophotometer (Japan), with 1 cm pathlength fused silica cells and ultrapure water as the blank. Spectra were measured over the range of 200–500 nm with a 2.0 nm bandwidth. The dissolved organic carbon (DOC) concentration in pore waters was calculated from absorption spectra using the equation given by Højerslev [43]. The absorbance ratio at 250 and 360 nm ($A_{250/360}$) was calculated from the spectra.

2.3.4. *Chromatographic analyses*

The molecular characteristics of DOM in sediments were determined using an HPLC system. The chromatograms were recorded and processed by Agilent ChemStation software. The full details of the method are available elsewhere [30] and reported in supplementary text S2 (available online only).

As a semi-quantitative DOM characteristic, the total chromatogram peak areas, representing the total UV-absorbing fraction of the specific molecular size fraction of DOM in each sample, were used in the data analysis. The total chromatogram peak areas obtained with DAD actually represent the variations in optical intensities of DOM fractions at the chosen wavelength of 280 nm. The detector response (the height of the chromatogram at the i-th elution volume) refers to the amount of DOM in a specific molecular size fraction. The sum of all peak heights represents the total amount of DOM capable of UV adsorption in the sample [44–46]. Peak areas as a semi-quantitative characteristic were used to present age-related variations in the DOM fractions. To obtain qualitative DOM characteristics the chromatograms were divided into two molecular size fractions: (1) HS, with molecular masses between 700 and 3700 Da; and (2) high molecular weight (HMW), with molecular masses between 200 and 270 kDa. Weight-average and number-average molecular masses of DOM (M_w and M_n, respectively) were determined using the formulae reported in supplementary text S2 [47]. The polydispersity M_w/M_n, describing the homogeneity or heterogeneity of organic matter, was calculated from the data obtained. Three to four replicate runs were performed for each sample. In general, the relative standard deviations for the replicated measurements did not exceed 5% (obtained by comparison of total peak areas).

2.4. ***Statistical analyses***

Cluster analysis using the Ward method was applied to reveal age-related periods in the analysed samples [48]. The analysis was performed on the chromatographic-, metal- and sediment solid-phase data (LOI, carbonates). As descriptors of the DOM, all of the separated peak areas and total chromatogram areas, molecular masses and their ratios, DOC and $A_{250/360}$ for all samples were included in the analysis. The Euclidean distance was used as a measure of the similarity–dissimilarity of the samples.

The statistical analyses were carried out using WinSTAT for Excel software (R. Fitch Software, Germany).

3. Results and discussion

3.1. *Characteristics of analysed sediments*

The 43 cm long sediment core from Lake Peipsi covered the period 1852–2006. The sediment particulate phase composition (Figure 1) was characterised by the organic matter (LOI) and carbonate contents. The carbonate levels were stable during the analysed period. The values for organic matter varied between 23 and 25% for the period 1860–1950 and showed an increasing trend up to 27% after the 1950s. A similar pattern was obtained for DOC, for which the levels started to increase from the 1960s, indicating degradation of organic matter. The increase in DOC has been explained by the accumulation of organic matter in anoxic sediment layers, the formation of humic substances by polymerisation of low molecular mass organic compounds or by anaerobic degradation [32,49]. Moreover, the organic matter adsorbed to Fe–Mn oxides is soluble in an anoxic environment and might dissolve into the pore water [50]. The ratio of Fe/Mn as an indicator of redox changes in sediments fluctuated widely during the period 1940–1990. Changes were interpreted in terms of anoxic conditions during some winters when the lake was iced over. Under reducing conditions Mn is released from sediments earlier than Fe, resulting in an increased Fe/Mn ratio. However the Fe/Mn ratio has been considered not only as an indicator of palaeoredox changes in the lake catchment, but also as an indicator of sediment sources [51].

The sediment DOM was characterised by pore-water sample analysis using HPSEC with DAD. The analysis conditions were determined previously and used in this study with slight modifications [30]. In order to decrease the noise in the chromatograms, the potassium salts used for preparation of the eluent buffer were replaced by ammonium salts. The detection wavelength for the calibration and comparison of characteristics was 280 nm. All chromatograms were very similar, consisting of two main peaks representing different size fractions. As spectroscopic DAD was used, the HPSEC peak areas of separated fractions served as rough semi-quantitative estimates of DOC, but only of the UV-absorbing fraction. Several characteristic variables [areas of the separated peaks; weight (M_w) – and number (M_n) – average molecular masses and their ratios (M_w/M_n)] were computed from the chromatographic data (Figure 2). The area of the first HMW fraction was always smaller ($\sim$3% of the total area) than the second HS fraction with an area of $\sim$97%. The calculated molecular masses for the HMW fraction varied between 200 and 270 kDa. The HMW fraction was not separated in samples dating from the 1990s and in older samples from the nineteenth century. The quantity of this fraction remained more or less constant during the twentieth century. The largest DOM fraction was HS, with calculated molecular masses between 700 and 3,700 Da, and an average value of 1,500 Da for M_w. The depth profiles shown in Figure 2 indicated similar changes in both molecular mass values. The results correlate well with the results of other studies [52,53]. Both down-core profiles of the chromatogram total areas and HS fraction areas were similar and exactly followed the changes in DOC (Figure 1). The polydispersity (M_w/M_n) is an indicator of the homogeneity or heterogeneity of the organic matter. The mean value for sediment profile HS was 2.0 (values between 1.9 and 3.0), which indicated a relatively homogeneous HS fraction. Large variation was detected between 1880 and 1920 (Figure 2) and was attributed to organic molecules with different structures.

The absorbance ratio $A_{250/360}$ reflects the aromaticity of the DOM. The ratio was constant until the 1960s, with an average value close to 4.0. Thereafter, up to the present, it increased to 6.5, meaning that the origin of organic matter changed to autochthonous. To conclude, according to the

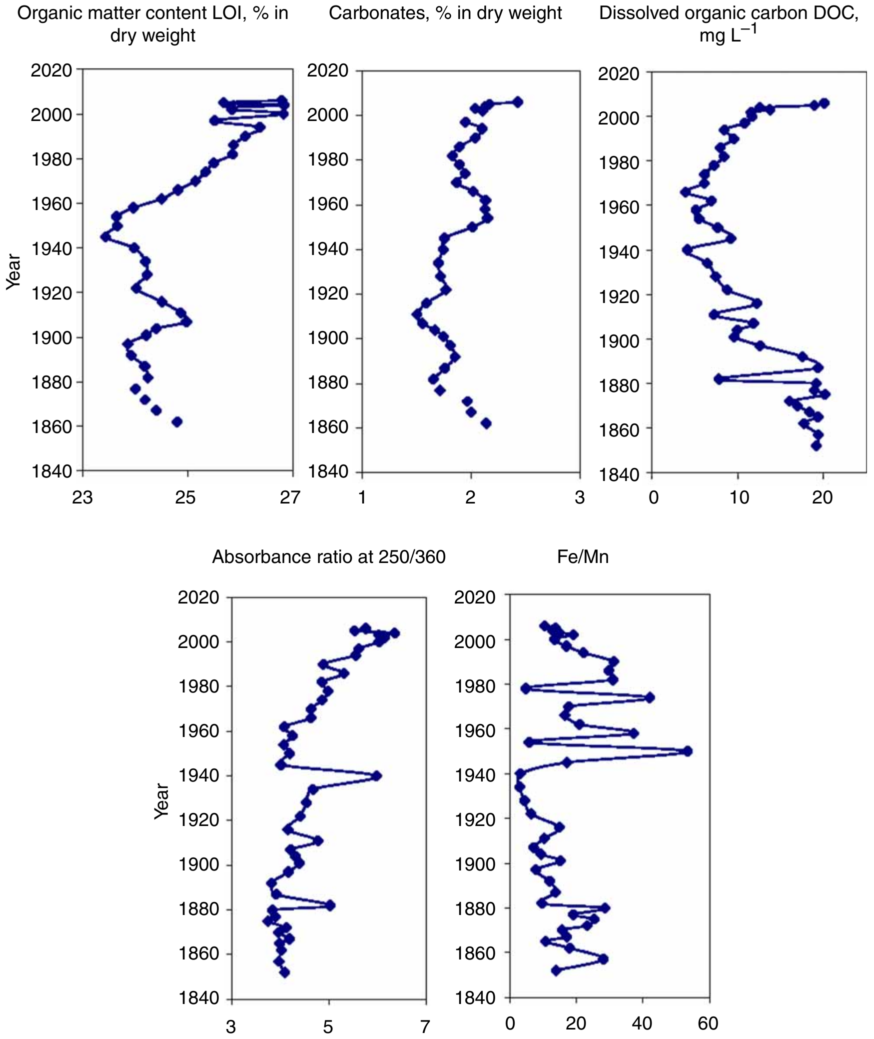

Figure 1. Profiles of general chemical characteristics of analysed Lake Peipsi sediments and sediment pore-waters. Year denotes year of sediment deposition.

sediment DOM analysis from Lake Peipsi, the core can be divided into two periods: (1) 1850–1960, decreasing aromaticity and DOC; and (2) 1960–2006, increasing aromaticity and DOC.

3.2. *Temporal changes in total metals in sediment record*

The total metal concentration profiles for the Lake Peipsi sediments are shown in Figure 3. The mean metal concentrations together with concentration ranges were as follows (Table 1): 23.6 (15.7–47.7) for Cu ($\mu g \cdot g^{-1}$), 65.8 (48.2–109.2) for Zn ($\mu g \cdot g^{-1}$), 0.72 (0.26–1.08) for Cd ($\mu g \cdot g^{-1}$), 12.6 (4.5–54.7) for Ca ($mg \cdot g^{-1}$), 2.8 (0.3–15.8) for Mn ($mg \cdot g^{-1}$) and 31.2 (5.2–63.7) for Fe ($mg \cdot g^{-1}$). The results indicate decreased total Cu and Zn contents from the 1980s to the present, in comparison with older sediment layers. As the source of Cu and Zn pollution in Lake Peipsi is industrial activity (oil shale mining and operation of electrical power plants), it can be concluded that the state of the environment has improved. The concentrations of those

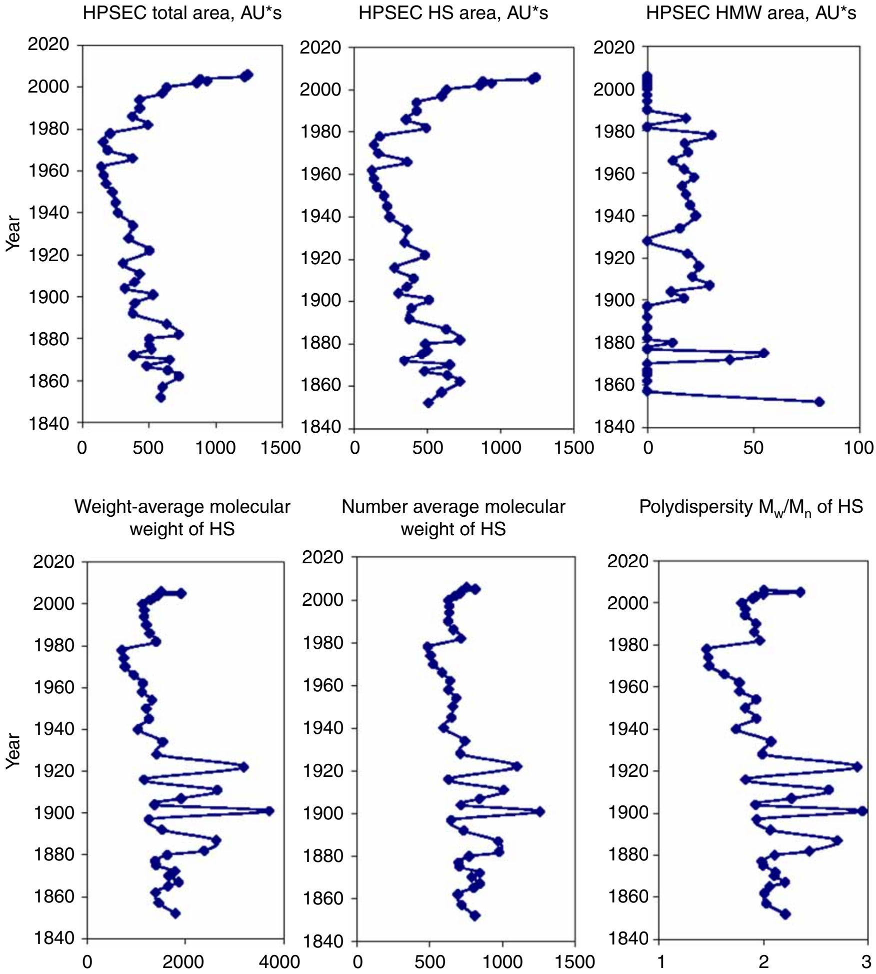

Figure 2. Profiles of characteristic variables of Lake Peipsi sediment pore waters by HPSEC.

metals were similar to values reported for natural non-polluted areas, 20 and 50 $\mu g \cdot g^{-1}$ for Cu and Zn, respectively [54]. The Cd concentration profile was opposite to that of Cu and Zn. The increased Cd content in the environment has mainly been caused by anthropogenic activities, like wastewater input or other industrial or agricultural activities. Despite the increased concentrations, the Cd content in Lake Peipsi sediments is also within the range of the natural background level ($1.5\,\mu g \cdot g^{-1}$).

During the 1940s certain changes in environmental conditions took place as indicated by the decrease in Fe and occasional increase in Mn in sediment layers. Both elements are mobilised from sediments by changes in redox potential. Fe becomes mobile at a lower redox potential than Mn but it is released from the sediment and likely precipitated again as hydroxides, oxyhydroxides, carbonates, silicates or phosphates, which are insoluble and thus do not interfere with diffuse transport processes in the sediment profile. Because calcareous soils dominate in the lake catchment area we assume that reduction of Fe leads to the formation of ferrous carbonate of low solubility.

Table 1. Partitioning of metals between operational fractions.

	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Total
[Cd], $\mu g\, g^{-1}$						
Valid cases	6	6	6	6	6	6
Mean	0.02	0.21	0.38	0.09	0.02	0.72
Std. error of mean	0.01	0.06	0.07	0.02	0.01	0.14
Std. deviation	0.01	0.15	0.16	0.06	0.02	0.34
Minimum	0.01	0.05	0.17	0.02	0.01	0.26
Maximum	0.04	0.47	0.53	0.17	0.05	1.08
% of total	3	29	53	12	3	100
[Cu], $\mu g\, g^{-1}$						
Valid cases	43	43	43	39	39	39
Mean	0.86	0.17	0.26	7.03	15.3	23.6
Std. error of mean	0.10	0.01	0.02	0.53	0.85	1.04
Std. deviation	0.66	0.09	0.12	3.34	5.31	6.50
Minimum	0.13	0.02	0.06	1.45	7.25	15.7
Maximum	2.00	0.39	0.48	17.4	29.4	47.7
% of total	4	1	1	30	65	100
[Zn], $\mu g\, g^{-1}$						
Valid cases	43	43	43	39	39	39
Mean	0.02	2.97	4.02	10.3	48.0	65.8
Std. error of mean	0.01	0.36	0.80	0.88	2.32	2.03
Std. deviation	0.07	2.37	5.26	5.52	14.5	12.7
Minimum	0	0.12	0.40	4.79	23.8	48.2
Maximum	0.37	15.8	20.4	29.3	81.7	109.2
% of total	0	5	6	16	73	100
[Ca], $mg\, g^{-1}$						
Valid cases	42	43	42	39	39	43
Mean	7.0	4.1	1.5	0.055	0.12	12.6
Std. error of mean	1.0	0.4	0.2	0.014	0.02	1.3
Std. deviation	6.6	2.4	1.2	0.087	0.11	8.2
Minimum	0.4	1.6	0.5	0.001	0.01	4.5
Maximum	42.2	14.0	3.9	0.324	0.34	54.7
% of total	55	33	12	0	1	100
[Mn], $mg\, g^{-1}$						
Valid cases	41	43	43	37	39	43
Mean	0.31	0.40	0.45	1.66	0.22	2.83
Std. error of mean	0.05	0.05	0.06	0.60	0.01	0.52
Std. deviation	0.30	0.34	0.41	3.64	0.08	3.42
Minimum	0.03	0.08	0.06	0.02	0.08	0.31
Maximum	1.33	1.43	2.10	15.0	0.36	15.8
% of total	11	14	16	59	8	100
[Fe], $mg\, g^{-1}$						
Valid cases	41	43	43	39	39	43
Mean	0.021	0.028	6.21	7.32	20.2	31.2
Std. error of mean	0.003	0.003	0.21	0.47	2.33	2.40
Std. deviation	0.021	0.022	1.37	2.91	14.5	15.8
Minimum	0.002	0.002	4.44	2.60	3.47	5.24
Maximum	0.077	0.100	13.8	16.0	41.7	63.7
% of total	0	0	20	23	65	100

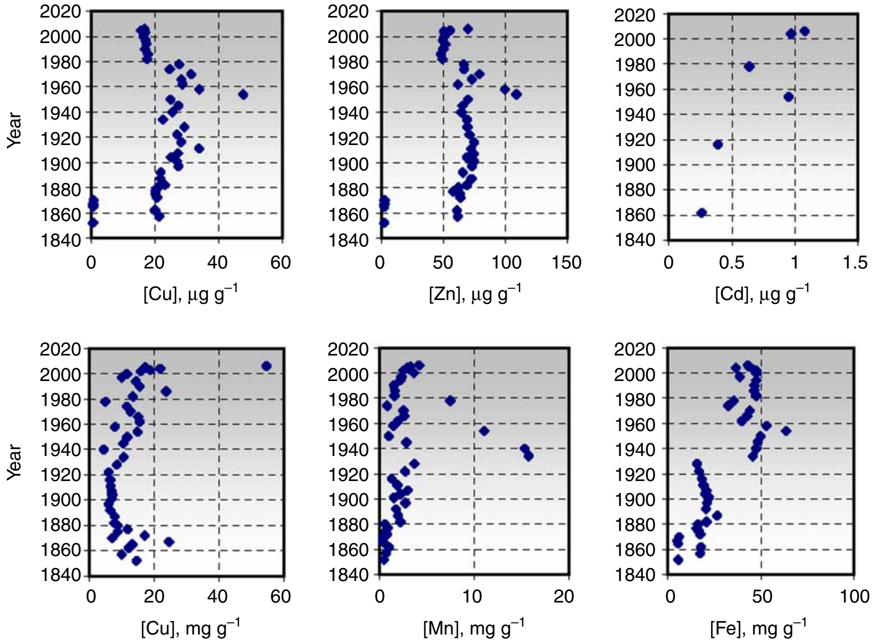

Figure 3. Down-core profiles of total metal (sum of five fractions) concentrations in Lake Peipsi sediments.

Ca concentrations have changed relatively little during the last 150 years. Because the concentrations of Ca, Fe and Mn are naturally high in sediments, they may be less influenced by anthropogenic activities than the trace metals Cu, Zn and Cd. With regards the total metal concentration data, it was not possible to clearly differentiate between natural background concentrations and anthropogenic levels. However, the metal concentrations in the upper sediment layers reflect not only the pollution history, but are also dependent on sediment clay and organic matter content. Therefore by normalising the total metal concentration data to the sedimentation rate it is possible to account for the influence of sediment texture as well. The metal accumulation rate profiles (data not shown) correlated well with the concentration curves shown in Figure 3, with the exception of the top sediment layer, in which the metal accumulation rates showed increased values.

3.3. *Metal partitioning between operational fractions*

Metal partitioning between operationally defined sediment fractions was quantified by the sequential extraction procedure. By applying the Tessier fractionation scheme it was not possible to distinguish between the organic matter and sulphide fractions. Figure 4 shows the depth profiles of speciated metals (Cu, Zn, Ca, Mn and Fe). The profile data for Cd are not shown because this metal was only analysed in a few sediment layers. Table 1 depicts the partitioning of analysed metals between different fractions in the Lake Peipsi sediment core. Nearly 90% of Ca was found in the sediments as ion-exchangeable compounds (fraction 1) and carbonates (fraction 2). However, increased Ca concentrations in the Fe and Mn oxide fractions (fraction 3) and both organic (4 and 5) fractions have occurred since the 1980s.

The environmental conditions of the lake have improved according to the decrease in the total Cu concentrations in the sediments between 1980 and the present. The majority of Cu (95%) and Zn (89%) are bound to organic and sulphide fractions (fractions 4 and 5, respectively): weak organic Cu complexes (fraction 4) account for 30%, and Zn complexes for 16% of the total

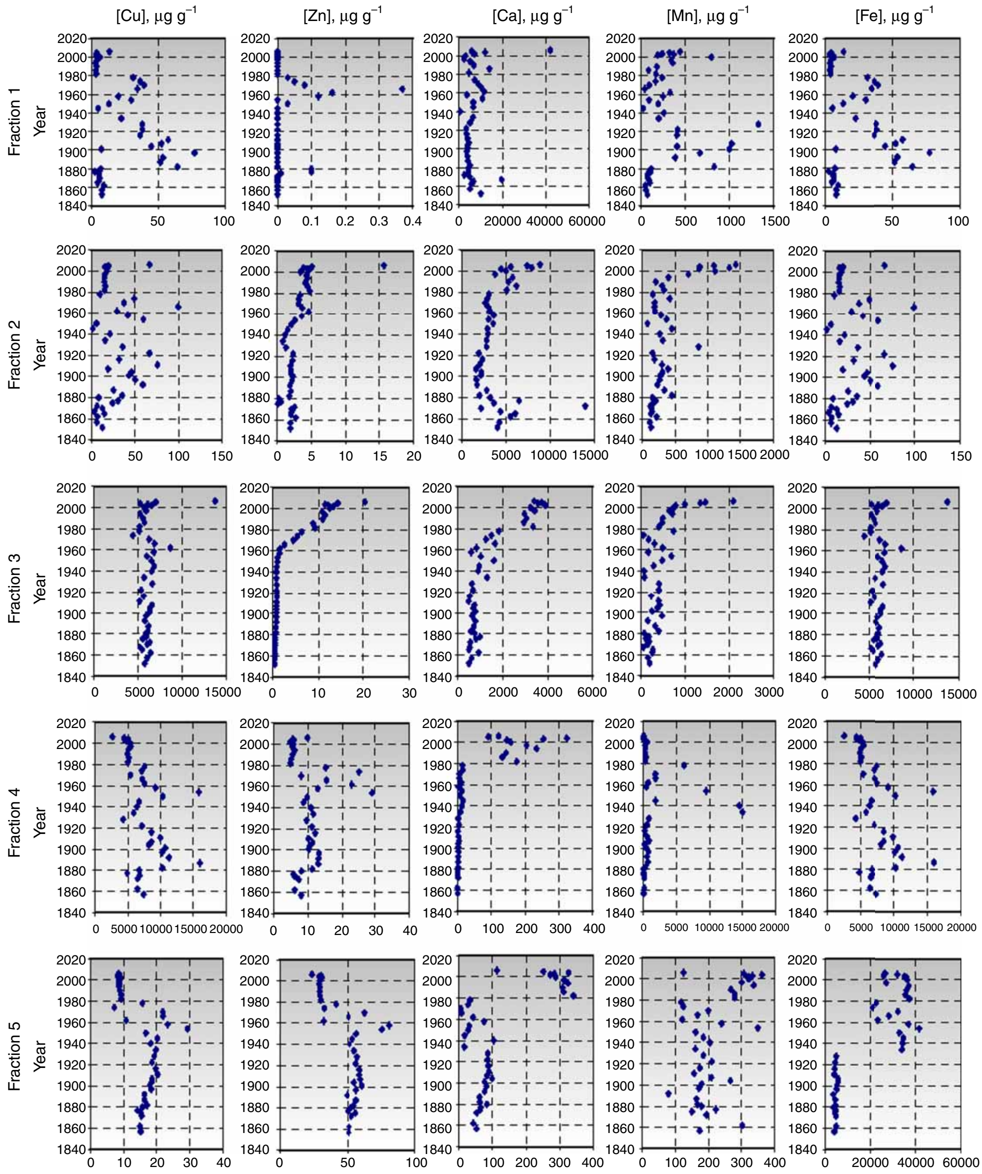

Figure 4. Partitioning of Cu, Zn, Ca, Mn and Fe between operationally defined fractions in sediment profiles from Lake Peipsi.

metal in sediments. Sixty-five per cent of Cu and 73% of Zn were associated with strong organic complexes and sulphides (fraction 5). From the environmental point of view the most important finding was that Cu concentrations have decreased in the exchangeable and carbonate fractions since the 1960s. Cu in the first two fractions would be potentially bioavailable and toxic to the aquatic environment. Zn was not present in the exchangeable fraction except during the period 1960 to 1980. The behaviour of Zn in the organic and sulphide fractions (4 and 5) was similar to Cu, showing increasing concentrations down the core. Since the 1960s, the Zn content has increased in the Fe–Mn oxides fraction. This might indicate a change in the Zn source or changes in the redox conditions at the lake bottom (variations in Fe/Mn ratio, see Figure 1). This metal

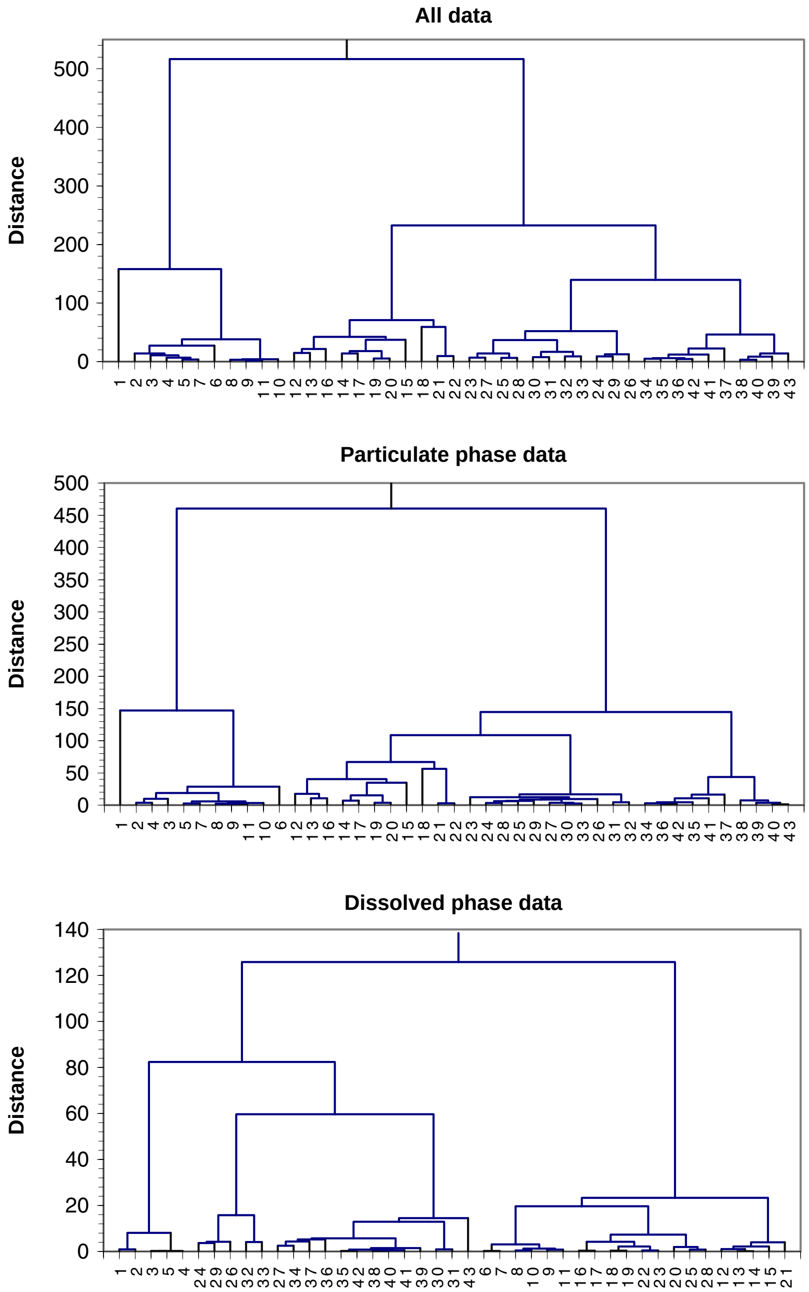

Figure 5. Cluster analysis (Ward method) of Lake Peipsi sediment samples from different depths (numbers indicate sediment depth in cm; particulate phase data – metal concentrations of five fractions and of total metal, LOI, carbonates; dissolved phase data – DOC, A250/360, HPSEC peak areas for separated HMW and HS fractions and total peak areas, molecular masses M_w and M_n, M_w/M_n).

fraction becomes bioavailable in cases of anoxia during the winter (lake covered with ice). Eighty-five per cent of Cd was bound to inorganic fractions, mostly Fe–Mn oxides (53%) and carbonates (29%). The results for this metal indicated that one third of Cd that has been deposited in the Lake Peipsi sediments is bioavailable. Eighty per cent of Fe and 59% of Mn in sediments were connected with the organic fractions and sulphides. A decreasing down-core trend was detected for Mn in the carbonate fractions. The behaviour of these metals differed in fraction 5 (increased Fe concentrations in sediments from the 1930s to the present). The variability in Mn and Fe concentrations was possibly induced by changes in the redox conditions at the bottom of the lake. Changes in the redox conditions are caused mainly by varying weather and temperature conditions that influence the bioproductivity and oxidation of organic matter.

3.4. *Relationships between dissolved organic matter characteristics and metals*

The statistical analysis of data was performed to reveal periods with similar characteristics in the Lake Peipsi sediments. The dendrograms are shown in Figure 5. Cluster analysis identified homogeneous subgroups within the dataset. Based on cluster analysis including all variables, the sediment core was operationally grouped into two main depth/age periods: the uppermost 0–11 cm, corresponding to years 1980–2006; and 12–43 cm, corresponding to years 1850–1980. The second group was further divided into two groups: 12–22 cm (1930–1980) and 23–43 cm (1850–1930). The sediment DOM data allowed grouping of the layers into two main periods. According to the results, the DOM from 2000–2006 formed a homogeneous group that was in the same cluster as samples dating from 1850–1910 (24–43 cm). The second cluster included samples dating from the period 1915–2000 (6–25 cm). The metal data resulted in a similar surface layer group as the DOM data (2000–2006). The rest of the sediment layers were mixed in terms of the grouping based on metal data.

To conclude, the statistical analyses revealed that metal concentration data can be used in combination with some chromatographic and spectrometric parameters to differentiate between sediment layers.

4. Conclusions

The total metal concentration profiles of the major elements Ca, Mn, Fe and trace elements Cu, Zn and Cd were determined in the Lake Peipsi sediments. The results indicate decreased total and bioavailable Cu and Zn levels from the 1980s to the present, and increased Cd. The concentrations were characteristic of natural non-polluted areas despite the increases in recent sediment layers. The variability in Mn and Fe concentrations may have been induced by changes in redox conditions at the bottom of the lake. Almost 90% of Ca and 30% of Cd were found in sediments as ion-exchangeable compounds and carbonates. The majority of Cu (95%), Zn (89%) and Fe (80%) was bound to organic and sulphide fractions.

The sediment core DOM, characterised by high-performance size-exclusion chromatography and spectroscopy, was comprised mainly of HS (97%) and of a very small HMW fraction (3%). The molecular masses for the HMW fraction varied between 200 and 270 kDa, and for HS between 700 and 3700 Da, with an average value of 1500 Da. According to the sediment DOM analysis the Lake Peipsi core can be divided into two periods: (1) 1850–1960, decreasing aromaticity and DOC; and (2) 1960–2006, increasing aromaticity and DOC.

Based on statistical cluster analysis, the sediment core was operationally grouped into two main depth/age periods: the uppermost 0–11 cm, corresponding to years 1980–2006; and 12–43 cm, corresponding to years 1850–1980.

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