Geochemical composition of sapropel in lakes: reflections of paleoenvironmental conditions and anthropogenic influence

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Abstract

Geochemical and lithological parameters of sapropel in lakes, combined with pollen data and radiocarbon ^{14}C datings, contain a wide spectrum of environmental information. This includes records of fluctuations of water level and changes of conditions of sedimentation, accumulation of organic matter and chemical elements due to climate change, human impacts and other environmental changes. Four lakes with different trophic states and anthropogenic pressures were chosen for this study in Lithuania. Lake Balsys has a mesotrophic state while Lakes Didžiulis, Salotė and Gineitiškės have eutrophic states. X-ray fluorescence spectrometry was used to analyse concentrations of chemical elements, loss-on-ignition to determine organic, mineral and carbonate matter, pollen analysis and radiocarbon dating were applied for determination of paleoenvironmental conditions and age of sediments. Results of this study demonstrated rather different chemical compositions of sapropels in these lakes. Human impacts are evident in the upper layers of sapropel in all lakes, however very specific and complex geochemical composition was determined in deeper layers of sapropel in the different lakes. Higher concentrations of elements like Cr and Zn are expected in deeper layers of sapropel and are attributed to lithogenic association of trace elements. Pb and Cu were detected in upper layers of sapropel which indicates the impact of anthropogenic activity. Sapropel of eutrophic lakes (Salotė and Gineitiškės) is enriched by high concentrations of heavy metals (galbūt naudoti tiesiog chemical elements?) (Pb, Cr, Cu, Zn). Their main source was multidimensional anthropogenic pollution leading to a biogenic-anthropogenic association of elements. Sapropel with low concentrations of heavy metals exhibits a different inter-association matrix because most of the elements tend to form lithogenic-clastogenic associations.

Introduction

Lakes continuously accumulate sediments after the formation of their basins (kettle holes) and the time for development can last for several thousand years or even longer, dependent on paleoenvironmental conditions. These sediments are formed from biological remains originating in the lake and its catchment area as well as soil particles and other non-biological materials that were transported to the lake from the territory of the river basin and from atmosphere. One type of sediment that is commonly found in lakes in the North Temperate Zone is sapropel which is a type of fine organogenic sediment (Bradley 1999; Kurzo et al. 2004; Stankevica and Klavins 2013). According to the classification of lacustrine sediments used in Lithuania (Order ...2016), the sapropel is water laid very fine material containing more than 15% of organic matter and, depending on the amount of admixture, can be organic, carbonatic, sandy, silty or clayey.

Analysis of sapropel composition is important for determination of its quality as potential raw material, impact of anthropogenic activity and also paleoenvironmental conditions and dynamics of lake ecosystems. Sediments are formed under interaction of biological, chemical and physical processes that take place in the catchment area and lake itself. The intensity and combination of these processes are very variable depending on the different geological and geomorphological settings, hydrological regimes

and atmospheric conditions, as well as human activities (Bigler et al. 2002; Stankevica et al. 2015; Chondrogianni et al. 1996).

Hydroclimatic conditions essentially influence the manner and intensity of transport of lithogenic elements from the catchment area to the lake. Dry periods with sparse vegetation cover may cause an increase of physical weathering. During warm and wet periods, chemical weathering might be induced. Greater amounts of dust are transported during physical weathering which is more intense during cold periods with limited vegetation cover (deforestation, intensity of agriculture and etc.). Concentrations of trace metals are usually affected by anthropogenic atmospheric deposition. These different conditions influence changes of geochemistry in sediments (Brännvall et al. 2001; Koinig et al. 2003; Shotyk 1988). In addition to geochemical composition of sapropels, pollen analysis is very important as it provides information about vegetation cover in the catchment area of the lake, it allows reconstruct dynamics of past vegetation and provides climatostratigraphical data for determination of age of sediments (Gryguc et al. 2013; Rūtina et al. 2012; Heikkila and Seppa 2010).

Concentrations of heavy metals in sapropel layers can be very uneven. Most of dissolved heavy metals before settling to the bottom sediments are in colloidal or suspended phases in the aquatic systems of the lakes. Heavy metals in such environments can accumulate in high concentrations and become toxic for water organisms (Tylmann et al. 2011; de Boer et al. 2001; Ong et al. 2013; Moller et al. 2012). Heavy metals which enter aquatic environments typically bond with bottom sediments and, thus over time, can reach high concentrations. In these circumstances heavy metals can become a potential risk to human health through the food chain. Moreover, high concentrations of heavy metals pose a potential ecological hazard. Changes of hydrodynamic conditions, biological activities, and physical and chemical conditions can lead to secondary pollution. The cause of the high concentrations of heavy metals in sediments may also be due to natural environmental (lithological sources, erosion and etc.) conditions (Arnaboldi and Meyers 2007; Canavan et al. 2007; Zhu et al. 2005; Leonova et al. 2014; Lepane et al. 2007; Mimba et al. 2018).

Sapropel can be used in agriculture, livestock farming, medicine and construction industry etc. Recently the extraction and use of sapropel has increased, thus it is of great importance to carry out detailed researches on the geochemical composition of sapropel but there is currently a lack of detailed studies of geochemical composition of these deposits, especially in Lithuania. Research is required to both provide the information about conditions of the formation of sapropel, but also detailed composition in terms of chemical elements. This is important as sapropel is extracted from the top-most layers to the deeper layers. The aim of this study to analyse and evaluate processes that took place during the formation of sapropel in lakes in Lithuania and geochemical composition that is influenced and determined by those processes.

Materials And Methods

Study area

Four lakes with different trophic levels and anthropogenic pressures were selected for this study (Fig. 1, Table 2). All lakes are situated within the area of Late Weichselian Glaciation in the eastern part of Lithuania (Guobytė and Satkūnas 2011) and sedimentation history in their basins span from Late Glacial through Holocene until modern times.

Lake Balsys covers 0.55 km² area with average depth of 15.2 m. This lake is a typical deep glaciokarstic tunnel valley originating after melting of an ice block buried under glaciofluvial sediments. The surroundings of the lake are formed by sandy hills dissected by numbers of ravines. This lake is situated in Verkiai Regional Park. Its catchment area is forested, semi-natural with minimal load of anthropogenic activity. The lake has one outflow and inflow but is mainly groundwater-fed complemented by rainfall and surface runoff. Hydrochemical characteristics of Lake Balsys are: average dissolved oxygen concentration – 8.1 mg/L O₂, pH – 8.5, clarity – 3.5 m, suspended particles – 1.9 mg/L, electric conductivity – 347.5 μS/cm.

Lake Didžiulis covers 0.87 km² area with average depth of 6.5 m. The kettle hole of the lake was formed when block of inactive ice was left by a melting glacier of the Late Weichselian glaciation. The lake is surrounded by high morainic hills. The catchment area of this lake is occupied mostly by agricultural land in which there are several small settlements and farmsteads. The Vilnius-Kaunas highway passes close to the southern shore of the lake. The lake is popular for fishing, especially in winter time. It has three inflows and one outflow. It is mostly groundwater-fed complemented by rainfall and surface runoff. The hydrochemical characteristics of Lake Didžiulis are: average dissolved oxygen concentration – 9.1 mg/L O₂, pH – 8.4, clarity – 1.2 m, suspended particles – 4.8 mg/L, electric conductivity – 432 μS/cm.

Lake Salotė covers 0.13 km² area with average depth of 1.8 m. The origin of the kettle hole is complex – glacial-glaciofluvial and surrounded by slightly undulating relief composed of sandy sediments and glacial clayey loam (to the eastern side of the lake). The catchment area had been recently urbanized (a suburb of Vilnius City). The lake is very popular for bathing in summer time. It has one inflow and one outflow. Mostly this lake is fed by rainfall, surface runoff and groundwater. The hydrochemical characteristics of Lake Salotė had not then been observed.

Lake Gineitiškės covers 0.13 km² area with average depth of 1.8 m. The basin is of glacial origin. The relief north of the lake is composed of glacial loam (till) and on the other sides by sandy glaciofluvial formations. The lake is situated in the centre of Gineitiškės village, which is now a western suburb of Vilnius City. The lake has one inflow and one outflow. It is mostly fed by rainfall, surface runoff and groundwater. The hydrochemical characteristics of Lake Gineitiškės had not yet been observed.

All of these lakes are situated in a fairly small area so there is no difference in climatic conditions that could influence conditions of sapropel accumulation. However, deposition is dependent on the topography and lithological composition of surroundings of the lake, the hydrological regime, soils and vegetation types.

The depth of shallow (unconfined) groundwater in the vicinities of all of these lakes varies from 5 to 1 meter and depends on morphology of the kettle hole (Groundwater of Lithuania, 2018) thus stable alimentation by groundwater is provided for the hydrological regime of the lakes. The average annual pH values of lakes that are <4 m in depth are 8.07, maximum – 9.5 and minimum – 4.52. The average annual pH values of lakes that are >4 m in depth are 8.1, maximum – 9.8 and minimum – 6.32. There are no anomalies of geochemical contamination recorded (Kadūnas et al. 1999). There are few potential pollution sources in the catchment areas of Lakes Gineitiškės, Salotė and Didžiulis. Mostly these are industrial yards, garages or former farms, but there is no heavy industry (plants, factories, etc.). Such potential pollution sources cause the intensified migration of chemical elements from catchment area and thus enrichment of lake sediments with heavy metals (Zn, Cu, Cr, Pb) as well as lithogenic elements (Zr, Sr, Rb).

Coring and sampling

The lakes are open systems, the physicochemical characteristics and dynamics of which are determined by interrelated factors: the morphometrical features (the depth, the area, the water volume), the slope and bottom morphology, the trophic state, the catchment size, the groundwater interactions, the climatic conditions and the flow input (Schnurrenberger, 2003). The most important factor for securing appropriate and representative samples of sapropel is the bottom morphology. Sampling points were selected in flat parts of lake depressions to ensure even sedimentation conditions and processes. For this purpose, available bathymetry plans were digitized using “ArcMap” software and used for precise selection of sampling points.

All kettle holes of lakes are located in Quaternary glacial formations the general thickness of which is 80-100 metres (dependent on the elevation of topography). Pre-Quaternary bedrock occurs under the Quaternary cover but the bottoms of kettle holes do not reach it. The base of lacustrine sediments was penetrated by borings only in Lake Salotė.

Coring was done from ice at selected drilling points. Sediment coring was carried out using a 10 cm diameter sampler with a 0.5 m long camera. The cored sediment thickness reached 2.6 m in Lake Salotė, 3.0 m in Lake Balsys, 3.0 m in Lake Didžiulis and 9.1 m in Lake Gineitiškės. The thicknesses of sediment cores vary due to technical possibilities (length of borer and water column). In each case, three parallel overlapping sediment cores were documented according to the requirements (Domaševičius et al. 1999) and packed into plastic bags and transported to the laboratory for physical, chemical and pollen analyses.

The thickness of the sediments in the lakes, depth and rate of contamination were not known before the beginning of investigations. Therefore it was not possible to foresee the total number of samples at the outset. Following the logging recommendations for environmental investigations (Domaševičius et al. 1999) it was decided to take samples with an optimal spacing of 10 cm assuming that this frequency would be adequate enough to determine stratigraphy of the sections and detect traces of possible

anthropogenic contamination. Accordingly, sapropel cores were sampled with at intervals of 10 cm and 356 samples were analysed in total.

X-ray fluorescence spectrometry

Samples were dried at 105 °C to a constant mass, then the particles of <125 µm size were separated and concentrations of heavy metals were analysed using an X-ray fluorescence spectrometer Niton XL2 Analyzer (2009). The total relative analytical error was within 5%. The device was used only in a stand at laboratory and 600 seconds of analysis time was selected to achieve the highest accuracy that could be achieved. The overall accuracy of analysis of chemical elements varies from 10% (Cr, Cu, Zn, Zr, Sr, Rb, Mn, Fe) to 20% (As, Pb, Cd, Hg). Furthermore, this device was inter-calibrated with an atomic absorption spectrometer and results were found to be up to 20% of significant systematic difference.

Loss-on-ignition (LOI)

This method was applied in order to determine the content of moisture, organic matter and mineral matter. A 5% solution of HCl was used to estimate the content of carbonates. The moisture content in sediment samples was determined after drying at 105 °C to a constant mass. The content of the organic and carbonate matter was analysed by incinerating the samples at 550 °C for 4 h and then using 5% HCl solution sequentially.

Pollen analysis

The pollen analysis was undertaken to identify stratigraphical subdivisions of the sections of lake sediments and thus to determine the ages of sapropel layers. The samples for pollen analysis were prepared in the laboratory of the Nature Research Centre in Vilnius according standardized procedures. 500-1000 of pollen grains were counted per sample (except aquatic plant pollen and spores). The basic sum (100%) for pollen percentage calculations was based on the sum of all pollen, except the aquatic plant pollen. For processing of pollen data, Tilia 2.0.41 software was used. Comparison of all of the cores of different depth is based on the stratigraphic correlation of sediments subdivided by pollen analyses.

Radiocarbon (¹⁴C) dating

The absolute age of sediments was determined by radioactive carbon (¹⁴C) dating at the Laboratory of Nuclear Geophysics and Radioecology of the Nature Research Centre in Vilnius. 8 samples were dated (Table 1) in total from all boreholes. The results were combined with pollen data and to determine chronozones of sediments.

Table 1 Details of lakes sediment samples that were dated

No.	Lake and description of sample	Material analysed	Amount of Benzen, g	¹⁴ C activity. pMC (±1s)	Age according ¹⁴ C	Error, years (±1s)	Calibrated age*, years for 1s and 2s intervals (for 68.2% and 95.4% probability)
					years (BP)		(cal. BP or BC/AD)
1	Lake Gineitiškės. Sapropel. 0.4-0.6 m	TOC	0.55505	87.38±0.81	1085	75	68.2% probability
							1170 - 1160 BP (1.6%)
							1075 - 925 BP (66.6%)
							95.4% probability
							1225 - 1210 BP (0.6%)
							1185 - 900 BP (90.1%)
							870 - 820 BP (3.6%)
							815 - 795 BP (1.1%)
2	Lake Gineitiškės. Sapropel. 2.2-2.4 m	TOC	192.824	85.13±0.41	1295	40	68.2% probability
							1285 - 1230 BP (45.4%)
							1210 - 1180 BP (22.8%)
							95.4% probability
							1300 - 1170 BP (93.5%)
							1160 - 1145 BP (0.9%)
							1110 - 1090 BP (1.0%)
3	Lake Gineitiškės. Sapropel. 4.2-4.4 m	TOC	0.85397	66.80±0.56	3240	70	68.2% probability
							3560 - 3525 BP (12.9%)
							3515 - 3390 BP (54.3%)
							95.4% probability
							3640 - 3340 BP (94.6%)
							3285 - 3270 BP (0.8%)
							7930 - 7890

							BP (9.4%)
							7880 - 7670 BP (58.8%)
							95.4% probability
							8025 - 7565 BP (95.4%)
4	Lake Salotė. Sapropel. 1.4-1.6 m	TOC	232.999	51.68±0.31	5305	50	68.2% probability
							6180 - 6145 BP (14.4%)
							6125 - 6000 BP (53.8%)
							95.4% probability
							6265 - 6245 BP (1.5%)
							6215 - 5980 BP (88.6%)
							5975 - 5940 BP (5.3%)
5	Lake Salotė. Peat. 2.2-2.4 m	TOC	0.53591	37.22±0.64	7940	140	68.2% probability
							8995 - 8625 BP (68.2%)
							95.4% probability
							9235 - 9225 BP (0.1%)
							9200 - 9180 BP (0.5%)
							9140 - 8425 BP (94.7%)
6	Lake Balsys. Sapropel. 2.4-2.6 m	TOC	0.53797	54.74±0.79	4840	115	68.2% probability
							5715 - 5465 BP (65.8%)
							5350 - 5330 BP (2.4%)
							95.4% probability
							5890 - 5805 BP (5.6%)
							5765 - 5315 BP (89.8%)
7	Lake Didžiulis. Sapropel. 1.2-1.4 m	TOC	0.96803	91.92±0.60	675	55	68.2% probability
							680 - 635 BP (38.5%)
							595 - 560 BP (29.7%)
							95.4%

							probability
							695 – 540 BP (95.4%)
8	Lake Didžiulis. Sapropel. 3.7-3.9 m	Carbonates	0.44382	33.26±0.70	8845	145	68.2% probability
							10160 – 9735 BP (67.5%)
							9715 – 9710 BP (0.7%)
							95.4% probability
							10230 – 9550 BP (95.4%)

* Program for calibration – OxCal 4.2 (Bronk Ramsey C., 2013).

* Curve for calibration – IntCal2013 (Reimer P.J. et al., RADIOCARBON, Vol 55, No. 4, 2013, p 1869–1887).

Statistical methods

Data on concentrations of heavy metals were analysed using an XLSTAT statistical package. Agglomerative Hierarchical Clustering (AHC) was used as the clustering (or classification) method which determines dissimilarities between the objects to be grouped together. As a statistical method, a Spearman correlation model was used as it is a non-parametric method which is the most suitable for environmental sciences. As a result, chemical elements were visualized as dendrograms which show the progressive grouping of the data. It makes possible to gain an idea of a suitable number of classes into which the data can be grouped.

Results

Results of the analyses are presented in order according to the anthropogenic conditions of locations of the catchments of lakes:

First group: Lakes Balsys and Didžiulis are situated in semi-natural environments with minimum pressure of anthropogenic activities.

Second group: Lakes Salotė and Gineitiškės are situated in environments with moderate and intense anthropogenic activity depending on the degree of urbanisation of surroundings. The anthropogenic influence is demonstrated by elements such as Cr for which a concentration up to 1.7 times exceeds the maximum allowable concentration (MAC) (LME 2014) in modern sediments of Salotė and up to 3.17 times in Gineitiškės (Table 2). Furthermore, Zn concentrations up to 1.5 times exceed the MAC in Salotė. High Cr concentrations in most of cases are distributed in upper layers of sediments due to anthropogenic activity (sewage and rain water inflow, leaks from garages, intensive traffic and etc.).

However, deeper layers can also be enriched with Cr due to formation of acidic environments which mostly form in shallow lakes during warm and dry periods.

Table 2 The comparison of minimum, average and maximum values of Pb, Cr, Cu and Zn (mg.kg^{-1}) with maximum allowable concentrations (MAC) in bottom sediments of surface water bodies (LME 2014).

LOD – level of detection

			Metals			
			Pb	Cr	Cu	Zn
MAC in mg.kg ⁻¹			140	140	75	300
Lake	Trophic state					
Balsys	Mesotrophic	Min.	< LOD	< LOD	< LOD	6.18 ± 7
		Avg.	< LOD	< LOD	< LOD	26.94 ± 7
		Max.	< LOD	< LOD	< LOD	54.55 ± 7
Didžiulis	Eutrophic	Min.	< LOD	< LOD	< LOD	10.81 ± 7
		Avg.	< LOD	< LOD	< LOD	27.69 ± 7
		Max.	< LOD	< LOD	< LOD	114.80 ± 7
Salotė	Eutrophic	Min.	5.49 ± 4	18.00 ± 8	4.89 ± 8	33.31 ± 7
		Avg.	13.68 ± 4	85.43 ± 8	14.67 ± 8	139.02 ± 7
		Max.	19.17 ± 4	241.04 ± 8	28.85 ± 8	446.87 ± 7
Gineitiškės	Eutrophic	Min.	3.20 ± 4	22.48 ± 8	6.51 ± 8	84.71 ± 7
		Avg.	12.41 ± 4	107.48 ± 8	18.52 ± 8	161.52 ± 7
		Max.	38.54 ± 4	445.21 ± 8	29.78 ± 8	266.97 ± 7
			LOD = 3	LOD = 7	LOD = 4	LOD = 5

Lake Balsys was drilled in a bay with a flat bottom. Analysis of concentrations of heavy metals in sediment cores shows that this part of lake was influenced by significant changes in catchment area as well of water regime. Four stages of different sedimentation conditions are observed as the ratio of organic and mineral matter changes considerably (Fig 2). Concentrations of Sr are strongly positively correlated with the amount of mineral matter and negatively with the amount of organic matter. Higher concentrations of Sr most likely reflect the intensity of soil erosion in the catchment area. Zn concentrations do not reach the MAC. Changes in Zn are related with the higher amount of organic matter in deeper layers of sediments, as correlation coefficient r is 0.84, $p < 0.05$ (Fig 10). Most of the determined chemical elements in sediments are strongly associated with amount of organic matter (Fig. 2) with the one exception of the top layer, where is a low proportion of organic matter and significant increase of concentrations of Zn. This increase might suggest an anthropogenic source. It could be mostly due to airborne dust particles and direct input from surrounding areas with higher intensity of human activity. Pb, Cu, Cr, Cd were not detected as concentrations were lower than detection limit.

Mn/Fe ratios are slightly variable, suggesting changes in the hydrological regime of the lake with phases of formation of standing anoxic bottom water as the fluctuations of Mn/Fe ratio are well correlated with

oxygen concentrations in lakes (Naeher et al. 2014). The Mn/Fe ratio decrease indicates that deeper layers are formed in anoxic conditions while upper layers are formed in water which was slightly more enriched with oxygen. Such results of chemical elements analysis indicate specific conditions in this part of the lake. This could be influenced by this bay of the lake in some periods (sediment layer from 3.0 to 2.4 meters) forming separately from remainder of the lake sediments due to lower water levels, thus the oxygen saturation was much lower.

The pollen analysis (Fig. 3) shows five local pollen assemblage zones (LPAZ): *Pinus-Ulmus*, *Picea*, *Pinus-Betula-Alnus* and *Quercus*-NAP. These zones indicate major changes in vegetation structure in catchment area of Lake Balsys during the formation of sapropel. Sedimentation of deeper layers was less influenced by erosion and surface runoff as vegetation cover was mostly composed by coniferous trees (pine, fir) with admixture of alder, birch, however with weak grass cover. Such pollen structure indicates that sapropel in the interval from 3.0 - 0.2 m was formed during the Late Atlantic, Subboreal and Subatlantic climatic periods (Kabailiene, 2006).

The radiocarbon C^{14} dating of the sample from the depth 2.6 m yield an age of 5715-5465 cal yr BP and this result supports the chronostratigraphical interpretation of the pollen diagram.

The data show that Lake Didžiulis was not influenced by such significant sedimentation changes as Lake Balsys since the ratio of organic and mineral matter remains constant along all of the sediment core (Fig. 4). The values of chemical elements such as Zr, Sr and Rb reveal slight changes. Only the top-most layer is slightly enriched with Zn which reaches 114.8 mg.kg^{-1} but do not exceed the MAC. Other heavy metals were not detected as concentrations were lower than the detection limit. Most of the chemical elements in sediment core are strongly associated (Fig. 10) with organic matter (r values varies from 0.75 to 0.98, $p < 0.05$). The reduced form of Fe is less stable in the water column than that of Mn and consequently Mn/Fe ratios in the sediments are low when the sediment becomes anoxic (Davison 1993; Stumm and Morgan 1996; Granina et al. 2004). In this lake, the ratio of Mn/Fe is rather constant showing that sediments were formed in similar redox conditions with a trend towards lowering of oxygen concentrations, which could be due to eutrophication and changes in water level during recent decades. Only the upper layers have a higher ratio of Mn/Fe, which could be because this lake was dammed raising the water level thus giving a higher saturation of oxygen.

The four LPAZ (Fig. 5) were distinguished in the pollen diagram (from the bottom of the section): *Alnus-Corylus*, *Pinus-Betula*, *Picea*, *Pinus*-NAP. The vegetation of the first LPAZ (depth of the core 4.1-3.6 m), especially *Alnus*, is characteristic of the beginning of the Atlantic chronozone (Kabailiene 2006). However, the radiocarbon ^{14}C dating of the sample from the depth interval 3.9-3.7 m yielded the age of 10160-9735 cal yr BP which is evidently too old for the Atlantic chronozone (boundaries of this chronozone are calibrated at 8590-5731 yr) (Damušytė, 2011). This discrepancy could explained by admixture of older sediments due to re-deposition as is indicated by presence of herbs and in particular *Artemisia* and fragments of charcoal in the sediments of the interval under discussion. According to the characteristic

pollen spectra the second LPAZ (depth 3.6-1.9 m) is attributed to the Subboreal, and the upper two LPAZ (depth 1.9-0.2 m) - to the Subatlantic chronozones.

The radiocarbon ^{14}C dating of the sample from the depth 1.2 m yielded an age of 680-635 cal yr BP, a date that supports this interpretation. Therefore, the section of sediments of Lake Didžiulis differs from that of Lake Balsys, as in Didžiulis there is much thicker layer of younger sediments. Local pollen assemblage zones of these sediments indicate a colder and dryer climate with an increase of herbs (especially in the uppermost LPAZ, from 1.1m depth upwards) in environs of the lake that in turn could have result in an increase of soil erosion. However changes in ratio of organic and mineral matter of these sediments are minor.

Lakes Salotė and Gineitiškės are situated in urbanized areas, thus the variety of heavy metals is higher with the presence of Pb, Cr, Cu. These elements were not detected in Lakes Balsys and Didžiulis. The highest Zn concentrations were detected in sapropel layers at depths of 1.7-2.0 m. and values of Zn reach $446.87 \text{ mg.kg}^{-1}$, which exceed the MAC. Such high concentrations in deeper natural layers could be explained by influence of clay material that occurs just below the sapropel (Fig 7). Sapropel is a receptive sorbtion material so it could sorb Zn from clay minerals. It can be assumed that variations of concentrations of Rb, Ti, Zr, Fe, As, and Pb are closely related to respective concentrations of quartz and clay minerals. They are thus considered to represent the silicate fraction which shows an increase from the oldest to the youngest core section (Koinig 2003; Gehrke et al. 2009). In Lake Salotė a layer of such clay is beneath 2.0 m of sapropel and peaty sapropel. Nevertheless, sapropel in Salotė is rich with organic matter and the main associations of chemical elements are formed by lithogenic elements as correlation coefficients vary from 0.74 to 0.98 ($p < 0.05$) for the most of the elements (Fig. 11).

Concentrations of Pb and Cu are only detected in upper layers of sapropel, thus it clearly shows the impact of human activity. Cr concentrations up to 1.7 times exceed the MAC in upper and bottom layers of sapropel. High concentrations of Cr in the upper layer are evident as an impact of urban factors while bottom layers are enriched through natural processes linked to the underlying clay formation.

Significant changes of concentrations of chemical elements were also influenced by high variety of redox conditions as shown by the ratio of Mn/Fe which changes from bottom to the top of the sediment layers (Fig. 6). The deepest layers were formed with a highly oxygen saturated water column as, after glacial melting the lake was filled with water highly saturated with oxygen. Consequently, it promoted the growth of water vegetation which first produced oxygen. However, due to the shallow depth of the lake it began to overgrow and eventually consumed more oxygen than produced, hence the significant drop of Mn/Fe ratio which is evident at the depth of 1.4-1.5 meters of sapropel layers.

Seven pollen zones (*Artemisia*, *Betula*, *Pinus*, *Ulmus-Tilia*, *Alnus Betula*, *Picea-Pinus* and *Pinus-Betula-NAP*) are distinguished in the pollen diagram (Fig. 7). The base layers (depth 2.3-2.6m) of this lake were accumulating when the climate was cold and dry (*Artemisia*, *Betula* LPAZ, Younger Dryas-Borealis

chronozones (Fig. 7). These conditions were favourable for physical weathering and accumulation of more mineral matter.

Layers at depths of 0.8-2.0 were forming during the Atlantic to Subboreal chronozones and these sediments are characterized by higher amounts of organic matter (Fig. 6). Sediments of the uppermost at the bottom of the lake to a depth 0.8 m are attributed to modern times and therefore are enriched by heavy metals as explained above.

Lake Gineitiškės is also situated in the urbanized area and has received an anthropogenic load. The sediments of the lake were cored to a depth of 9.1 m. The amounts of organic matter are slightly higher in deeper layers than the upper. Concentrations of Zn are quite high (Fig. 8) in all layers of sapropel, but do not exceed the MAC. Higher concentrations of Zn are related directly to higher amounts of organic matter ($r = 0.76$, $p < 0.05$).

Concentrations of Pb and Cu were detected in all core samples with higher concentrations in the upper sapropel layers. It clearly shows the impact of anthropogenic inputs. Cr concentrations exceed the MAC by 3.17 times. The high concentrations were determined in the layer of sapropel from the lake bottom down to the depth of 1.0 meter. These concentrations might be due to migration of chemical elements since the sapropel contains up to 95% of water.

Concentrations of heavy metals were also influenced by very variable redox conditions since the ratio of Mn/Fe changes from bottom to the top of the sediment layers in a wide range (Fig. 8). Oxygen concentrations were increasing from the bottom layers of sapropel to 2.5 meters, but then drastically dropped and then remained low until the present. This clearly shows the changes of anthropogenic activity in the catchment area of the lake. The lake became shallow and overgrown with low clarity of the water and with no possibility of enriching the water column with oxygen. The association matrix shows the similar correlations to those at Lake Salotė (Fig. 11). The main associations ($r = 0.76-0.96$, $p < 0.05$) of chemical elements were formed by mineral matter (with exception of Zn). This proves that eutrophic lakes when under the influence of anthropogenic loads are characterized by similar chemical compositions and widely fluctuating changes through the whole sediment core.

The sampled section for pollen was 4.4 m deep and in that interval three local pollen assemblage zones (*Alnus-Quercus-Corylus*, *Betula-Pinus*, *Pinus-NAP*) have been distinguished. However this section is characterized by minor changes in pollen data (Fig. 9). Pollen data of the depth interval of the core 3.7-4.4 m (*Alnus-Quercus-Corylus* LPAZ) shows a quite warm climate and favourable conditions for accumulation of organic matter so this layer is attributed to the Subboreal chronozone. In the depth interval 1.2 – 3.7 m. a decrease of broad leaved trees and increase of grass coverage are observed so this section is attributed to the Subatlantic chronozone. The uppermost section (up to depth 1.2 m) is characterized by a significant increase of grass coverage (*Pinus-NAP* LPAZ) that was influenced by climate conditions as well as by changes of land use and increased agriculture. The radiocarbon ^{14}C date of the sample from the depth 0.4-0.6 m is 1075-925 cal yr BP which suggests that human activities were

present around Lake Gineitiškės a thousand years ago. The geochemical traces of anthropogenic activity are evident in the sapropel section up to 1 m depth as discussed above.

In natural lakes that were later affected by human activities, the main association of chemical elements in sapropels is formed by biophylic elements (Fig. 10) Fe, Mn, Zn, K, Ca which are associated with the strongest correlation ($r = 0.75-0.98$, $p < 0.05$) together with minerogenic elements Sr and Rb. The clastogenic elements Ti, Rb, Zr together with the biophylic elements Zn, K, Mn, Fe ($r = 0.67-0.97$, $p < 0.05$) form the main association of sapropel chemical elements in the different paleo-environmental conditions. The concentration of Zn is determined by the accumulation of organic matter ($r = 0.84$, $p < 0.05$). Thus, the associations and distribution of the chemical elements in sapropel of lakes that are influenced by anthropogenic activity (Fig. 11) depend on the changes of the amount of mineral matter and land use and industrial patterns. Mobile elements such as Pb, Cr, Cu, together with lithogenic elements (Ti, Rb, Sr, Zr) show the strongest correlations ($r = 0.62-0.97$, $p < 0.05$).

Discussion

The geochemistry of sapropels in lakes studied in Lithuania was analysed. Results demonstrated a high natural variability of all elements but with significant impacts of anthropogenic activities that are evident in upper layers formed in recent times. Changes in the structure of catchment vegetation strongly affected the proportion of organic and mineral matter as well as geochemistry of lake sediments (c.f. Giguet-Covex et al. 2011; Haas et al. 1998). A multiproxy approach in analysis of lake sediments allows not only the reconstruction of climatic and water level changes in lakes, but also reveals changes in weathering and erosion patterns in the associated catchment areas. These processes determine the geochemistry and physical composition of lake sediments as well as sedimentation rates (c.f. Kurzo et al. 2004; Canavan et al. 2007).

The sapropel of eutrophic lakes (Salotė and Gineitiškės) is shown to be enriched with heavy metals (Pb, Cr, Cu, Zn). Two main elements Cr (from 1.7 to 3.17 times) and Zn (up to 1.48 times) exceed the MAC in various, mostly the upper, layers of the sapropel. Due to the adjacent presence of clay minerals sapropel can be enriched by heavy metals (Cr, Zn) in deeper layers as well. In previous studies, authors have stated that the enrichment of sediments with heavy metals is not only related to anthropogenic activity, but it also depends on the nature of geological layers that occur in different regions (Petersen et al. 1997; Wang et al. 2012). Nevertheless, interrelations of heavy metals and associations with organic and mineral matter can depend on vegetation, anthropogenic load, depth and bottom relief of lakes as well as the nature of geological layers and geomorphology of the catchment area of the lake.

The observed main correlations of chemical elements identified two different compositions of sapropel in contaminated and relatively clean lakes. Sapropel with high concentrations of heavy metals forms lithogenic association of chemical elements - mineral matter, As, Fe, Cr, Pb, Ti, K, Zr, Sr, Rb - with $r = 0.76$ to 0.96 , $p < 0.05$. The other association with organic matter - Zn, Mn, Sc, Ca - varies from $r = 0.36$ to 0.76 , $p < 0.05$. Sapropel with low concentrations of heavy metals has a different “mixed-association” matrix.

Most of the elements tend to form mixed complexes in organic parts of sediments (organic matter, Zn, Fe, Zr, Ti, Rb, K with $r = 0.69$ to 0.98 , $p < 0.05$), whereas elemental associations of mineral matter are associated with As, Mn, Sr, Ca and correlation values vary from $r = 0.47$ to 0.89 , $p < 0.05$. Similar distribution and relation patterns of lake sediment geochemistry have been identified by other authors (Moberly et al. 2016; Javed et al. 2018).

It is noteworthy that variations of concentrations of heavy metals are influenced not only by anthropogenic activity, but also geochemical processes. Complex analysis reveals the sensitive relations of chemical elements which are bound into sediments which reflect both the anthropogenic load and the natural evolution of lake environments. The results of chemical analysis in lake sediment core samples also showed the influence of different lake parameters (depth, surrounding catchment area, sedimentation rate, etc.) to migration of chemical elements, which create the different correlation matrixes and bonding components in organic and mineral matter. Concentrations of heavy metals together with lithogenic elements clearly demonstrate changes in water level, changes in redox potential and development of surroundings in catchment area.

The pollen analysis revealed that sapropel in these lakes was formed mainly in Subboreal and Subatlantic chronozones of the Holocene (Fig. 12). DR3 - Younger Dryas, BO – Boreal, AT – Atlantic, SB – Subboreal, SA – Subatlantic, Mo T – modern times. Changes in vegetation structure during alternating warm, cold, wet and dry climates influenced the different conditions mainly physical and chemical weathering intensities (Schnurrenberger et al. 2003; Rūtina et al. 2012). These processes directly influenced the sedimentation changes in lakes and the resulting chemical composition of sapropels.

Investigation of the formation of sediments in selected lake ecosystems in Lithuania provides records of natural changes as well as anthropogenic impacts on the environment and provides perspectives for better management of lacustrine natural resources. While anthropogenic effects are significant it should be recognised that natural environment conditions can also cause increased concentrations of heavy metals and other chemical elements. All of the lakes are located in the same geographical region and have experienced similar paleoclimate conditions however their pollen assemblage zones slightly differ due to local biogeographic conditions, lithology and soils, hydrography, catchment area and other factors. Due to these local conditions different rates of accumulation of sediments have existed and this is demonstrated by different thickness of the layers belonging to the same chronozone (Fig. 12).

The anthropogenic impacts can still be traced despite the absence of any heavy industry and mainly due to household and transport activities e.g. at Lake Gineitiškės. The contaminated layers in further investigation have to be examined in more detail, applying much shorter intervals of sampling and applying precise chronology (e.g. ^{210}Pb dating).

All lakes are located in the same geographical region and they did pass actually through similar paleoclimate conditions, however their pollen assemblage zones slightly differ due to local biogeographic conditions, lithology and soils, hydrography, catchment area and other factors. Due to these local

conditions different rates of accumulation of sediments have existed and this is evidenced by different thickness of the layers belonging to the same chronozone (Fig. 12).

Declarations

Ethics approval and consent to participate

Authors have no conflicts on ethics approval and give the consent to participate.

Consent to publication

Authors give the consent to publication.

Availability of data and material

Authors ensure the availability of data and material.

Competing interests

Authors have no competing interests.

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Authors' contributions

Jonas Satkūnas – managed all the process of the methodological approach. Made analysis and discussion on geological and paleoenvironment perspective in regard of radiocarbon dating.

Vaidotas Valskys – made analysis of concentrations of heavy metals as well as discussion on geochemical interactions on anthropogenic induced changes and paleoenvironment influence.

Gytautas Ignatavičius – made analysis of the data on environmental impact. Contributed in making insights of interactions of pollution and potential sources.

Alma Grigienė – made palynological analysis and discussion on changes of paleoenvironment.

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Figures

Figure 1

Location of investigated lakes: 1 – Balsys, 2 – Didžiulis, 3 – Salotė, 4 – Gineitiškės

Figure 2

Concentrations of heavy metals in sediments of the lake Balsys

Figure 3

Percentage pollen diagram of the core of lake Balsys

Figure 4

Concentrations of heavy metals in sediments of lake Didžiulis

Figure 5

Percentage pollen diagram of the core of lake Didžiulis

Figure 6

Concentrations of heavy metals in sediments of lake Salotė

Figure 7

Percentage pollen diagram of the core of lake Salotė

Figure 8

Concentrations of heavy metals in sediments of lake Gineitiškės

Figure 9

Percentage pollen diagram of the core of lake Gineitiškės

Figure 10

Cluster analysis (Spearman correlation matrix, $p < 0.05$) of data from Lakes Balsys and Didžiulis

Figure 11

Cluster analysis (Spearman correlation matrix, $p < 0.05$) of data from Lakes Salotė and Gineitiškės

Figure 12

Correlation of chronozones of the sediments of the investigated lakes on the basis of pollen data and radiocarbon C14 datings. The boundaries of chronozones are given in calibrated years BP (Damušytė, 2011).