

# Accumulation of Metals in Sapropel

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**Abstract:** Concentrations of 13 metallic elements were determined in organic rich lake sediment profiles from three lakes – Padēlis, Pilcenes and Pilveļu (Latvia). Concentrations of metallic elements are related to the basic chemical properties of sapropel– moisture, organic matter, carbonate content and elemental composition. Sapropel from the studied lakes is not polluted by industrial sources and can be considered as prospective material for agricultural and other applications. The heavy metal concentration depends on the organic matter content of the sediment and the geochemical properties (composition of minerals, rate of their weathering, hydrological and climatological conditions) of the lakes' catchment areas. Increased concentrations of Pb and Cd are found in upper layers of sediments from anthropogenic pollution.

**Keywords:** sapropel, organic-rich sediments, metal, pollution

## I INTRODUCTION

Studies of lake sediment composition not only might reveal changes in lake formation conditions, but also reflect human impacts [1, 2]. This study aims to reconstruct the evolution of aquatic ecosystem of lakes in Latvia in the past, to determine the anthropogenic stress in the upper sediment layers [3, 4], as well as get an insight about natural accumulation of metals in lakes.

Another reason of the importance of organic rich lake sediments studies can be related to their application possibilities since sedimentary deposits of eutrophic lakes generally have a high organic matter content (above 15%) [5], and they can be used as equivalent to peat in different fields – balneology, agriculture, livestock farming and building. These sediments are called sapropel. Sapropel deposits, formed on the lake's bottom from water plants, plankton and benthic organism remains, were transformed under influence of bacteria and mixed with mineral components. Sapropel has finely dispersed and plastic structure; the colour – from light pink to dark brown [6]. Sapropel in natural state with high content of phosphorus has dark blue colour; after drying it becomes bright blue.

The distribution of metallic elements across the sapropel layer can be effective in evaluating potential opportunities for the usage of these sediments; as in the hydro environment less than 0.1%, but more than 99.9% of the dissolved metals in water are accumulated in the bottom deposit in colloidal or suspended phase [7]. Thus, depending on metal concentration during sapropel formation in water bodies and peculiarities of sapropel formation, the concentration of metallic elements can be distributed unevenly across the sapropel layer.

Enhanced metal concentration in the upper layer of sapropel deposits can affect the benthic organisms and become a contamination source for higher plants and animals [1, 8]. High metal concentration in the upper layers of sapropel can affect its usage potential as raw material for various products

(medicine mud, animal feed additives and fertilizers); furthermore the element concentration unevenness in sediments may decrease product quality.

The main sources of metals in the aquatic environment are the weathering processes of rocks, but in recent years a significant source is industrial wastes, diffuse pollution source and atmospheric deposition [9]. Metal distribution data throughout the sapropel layer will assess the impact of anthropogenic stress on the lake's ecosystem and determine the contamination of organic sediments with heavy metals, as well as define the concentration of metals in sapropel layer.

The aim of this study is to determine the metal concentration across the thickness of the sediments of three lakes in Latvia.

## II MATERIALS AND METHODS

### A. Site location

Full sediment profiles from three lakes in Latvia were used in this study. The lakes– Padēlis, Pilcenes and Pilveļu – are located in Rēzekne district, Latgale region (Fig.1).

All the lakes are inter-hilly water bodies and in origin belong to the glacial type. The water surface area of each lake does not exceed 10 hectares, and the sediment fills the lakes' trench for more than 80%.

Sampling points were selected by the lakes' characteristics and preliminary data for sapropel layers in the given location.

After sampling the specimens were cut into 10 cm layers and stored in frozen condition at -20°C before analyses.

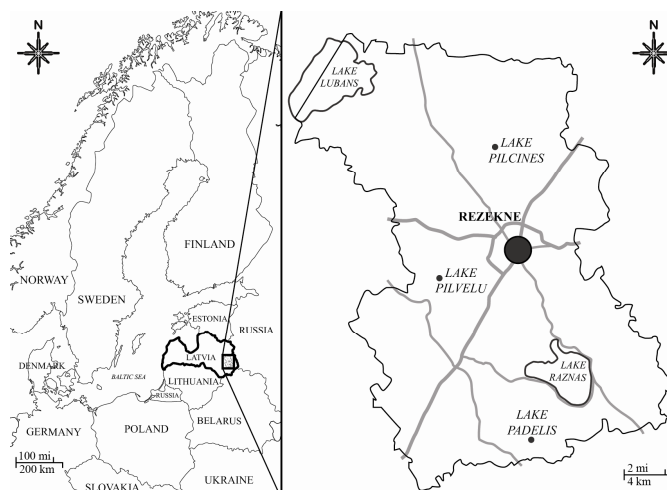


Fig. 1. Map of the sampling area

### B. Methods

Loss on ignition (LOI) method was applied in order to estimate moisture, organic matter and carbonate matter content in the sediments [10]. At first, the moisture of sediments was determined after drying at 105°C. The content

of organic and carbonate matter was analyzed by ashing samples sequentially at 550°C for 4 h and at 900°C for 2 h.

Metal concentrations were measured by flame atomic absorption (Perkin Elmer 503). The reliability and accuracy of the analytical results were checked using blank and reference samples (ISE 1998.3-921 (Wageningen Evaluating Programmes for Analytical Laboratories), SLRSS-2 river water, BCSS- coastal marine sediments; Analytical Chemistry Standards NRC, Canada). The results from the analysis of SRM were all within the 95 % confidence level of the SRMs. The average recovery varied from 82 % for Zn to 99 % for Cr (mean recovery for nine metals was 93 %).

Carbon, hydrogen, nitrogen and sulphur concentrations in sapropel samples (elemental analysis of C, H, N, S) were carried out using an Elemental Analyzer Model EA-1108 (Carlo Erba Instruments) by combustion-gas chromatography technique. The instrument was calibrated using cystine (Sigma – Aldrich Inc.), and all the sapropel samples were analyzed in duplicate. Ash content was measured after heating 50 mg of each sapropel sample at 750°C for 8 h. Elemental composition was corrected considering the ash content, but the oxygen amount was calculated as a difference.

III RESULTS AND DISCUSSION

Sapropel is a fresh water sediment material with organic matter content of more than 15%. This parameter determines sapropel value and application potential – the more is the organic matter in the sapropel, the more valuable it is and the better are the possibilities for its use. Combustion at different temperatures provides information on mass losses – moisture, organic matter and carbonate content. Sapropel with a high content of organic matter is in Pilveļu Lake at a depth of 0.0 to 3.8 m, the ash content is below 35% (Table 1). An increasing carbonate and ash content is observed in the sapropel of Pilveļu Lake in the layer of 1.4 to 2.0 m, where the organic matter is decreased up to 62%, but carbonate content is 1.2% on average. The average carbonate amount is 2.2% at a depth of 2.5 to 2.8 m that may indicate the hydrological regime changes in the lake. In Pilveļu and Padēlis Lakes the quantity

of organic matter decreases with sediment depth likely due to organic matter mineralization. The lowest organic matter content is in the sapropel of Padēlis Lake (Table 1) – 41% on average, but the high carbonate content – up to 38% – indicates that there is carbonatic sapropel in this lake. In the sapropel of Pilcenes Lake the organic matter content is 55% on average, moisture range is from 81% to 91%, carbonate content is 2% on average. Correlation between quantity of organic matter and its moisture is observed in the sediments of all the three lakes – if organic matter content increases so does the sapropel moisture. This is due to colloidal structure of sapropel organic matter and the ability of organic matter to bind water [11].

1. TABLE

THE CHARACTERISTICS OF MOISTURE, ORGANIC MATTER AND CARBONATES CONTENT IN STUDIED SAPROPEL (MIN – MAX (AVERAGE))

Lake	Moisture, %	Organic matter, %	Carbonates, %
Padēlis	74 – 94 (83)	15 – 94 (41)	1 – 38 (26)
Pilcenes	81 – 91 (89)	28 – 68 (55)	0.76 – 6.91 (2)
Pilveļu	71 – 95 (93)	16 – 94 (83)	0.25 – 1.8 (0.85)

The percentage of the carbonate, hydrogen, nitrogen and sulphur content has been analysed in the elemental composition of sapropel of the lakes.

The elemental composition analysis of sapropel provides information about distribution of elements (C, H, N, O, S) in organic material, as well as gives indirect evidences of sedimentary materials origin and its characteristics.

It is known that the composition of phyto- and zooplankton, as well as the benthic organisms have protein content with a large amount of nitrogen, but macrophytes are mainly composed of carbohydrates. It is assumed that plankton and benthic organisms form nitrogen rich sediments and sediments with low nitrogen content were formed by highest coastal plants, algae and, in part, by the humic substances from the catchment areas [9].

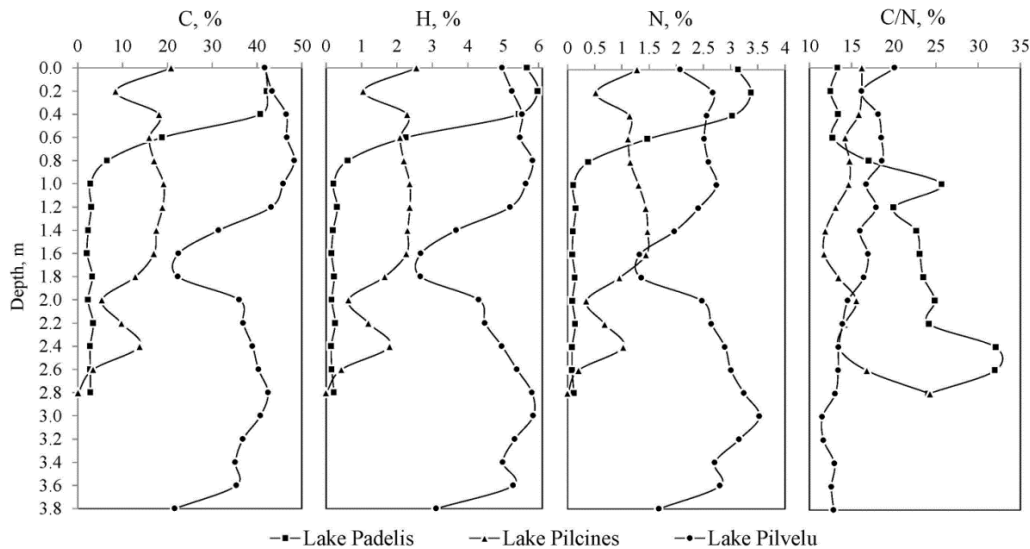


Fig.2. Elemental composition in the sapropel samples of studied lakes (%)

As can be seen from the graphs (Fig. 2), nitrogen content in various organic sediments of the lakes is in the range of 0.1-0.4% in the high-ash and carbonate sediments, 0.2-1.5% in the medium-ash sapropel (ash content of 35-50%) and 1.3-3.5% in low ash sapropel (ash content less than 35%). Hydrogen is in the high-ash sediment in the range of 0.1-1.1%, in the medium-ash – 1.7-2.3%, in the low-ash – 3.1-5.9%. The concentration of carbon in the carbonate sapropel varies in the range of 2.1-6.6%, in the medium-ash – 8.4-19.2% and in the organic sapropel – 31.5-48.3%.

In the studied samples the sulphur concentration does not exceed 0.47%; this higher concentration is observed in organic sapropel.

The carbon and nitrogen ratio is commonly used for material characterization of sapropel origin (Fig. 2). In assessing ratio of numerical values it is possible to discuss the origin of organic material: C/N ratio 7-11 is common for macrophytes, while C/N ratio >20 is common for terrestrial vegetation [12, 13].

Pilveļu, Pilcenes and Padēlis Lakes profiles are characterized by different changes of C/N ratio. The ratio of the sapropel of Padēlis Lake has tendency to increase with depth, in Pilveļu – to decrease, and in Pilcenes Lake to decrease in the first 1.5 m, but in the ratio of the lower layers – to increase.

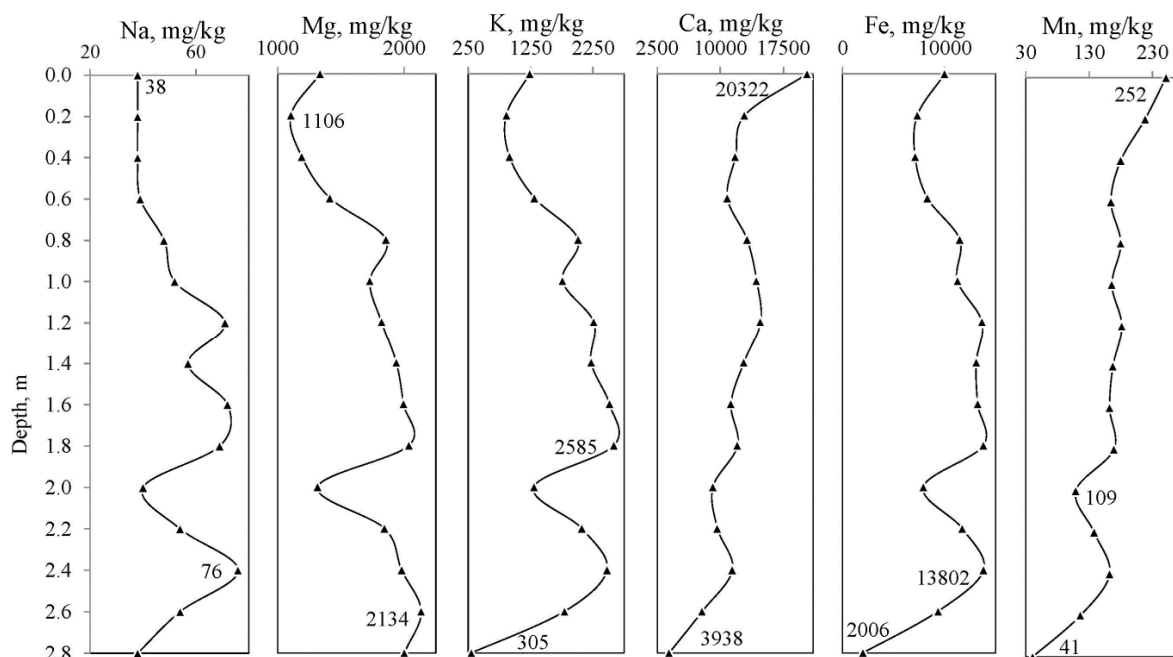


Fig.3. The distribution pattern of major elements in sapropel from Padēlis Lake

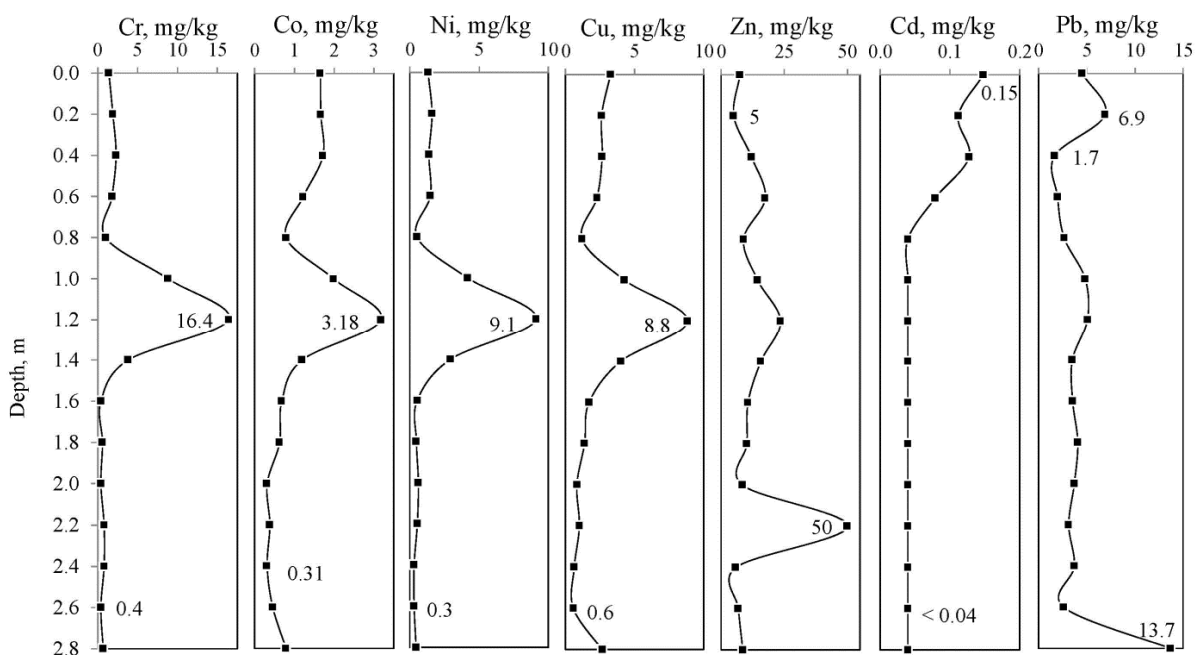


Fig.4. The distribution pattern of heavy metals in sapropel from Padēlis Lake

The decrease of metal concentrations in the deepest layers of Pilcenes Lake might be explained by the contribution of undecomposed coastal plants in the formation of the sapropel mass. However, in the organic matter of Padēlis Lake the impacts of macrophytes can be observed only in the first meter of the surface sediments, where the character of changes can indicate the eutrophication process. A tendency of increasing C/N ratio with depth can be observed in Pilveļu Lake

indicating that the origin of humic substances are from emerged and floating macrophytes and terrestrial plants.

The analysis of metal contents in the sediments provides information on natural and anthropogenic origin of the metal flow in the lake's ecosystem, drainage conditions, changes in

land use in the catchment area, and the influence on sapropel application in medicine and agriculture [9].

Metal concentrations (Fig. 3 to 7) for all the three lakes' sediments vary over a wide range, indicating that sediments formation took place at different environmental conditions varying not only among the lakes, but also in the same water body at different times.

In the sapropel of all the three lakes the highest metal concentrations have natural origin: magnesium, calcium and iron (Fig. 3, 5, 7). High concentrations of Mg up to 5752 mg/kg and Ca up to 34986 mg/kg are observed in Padēlis Lake's carbonate sapropel.

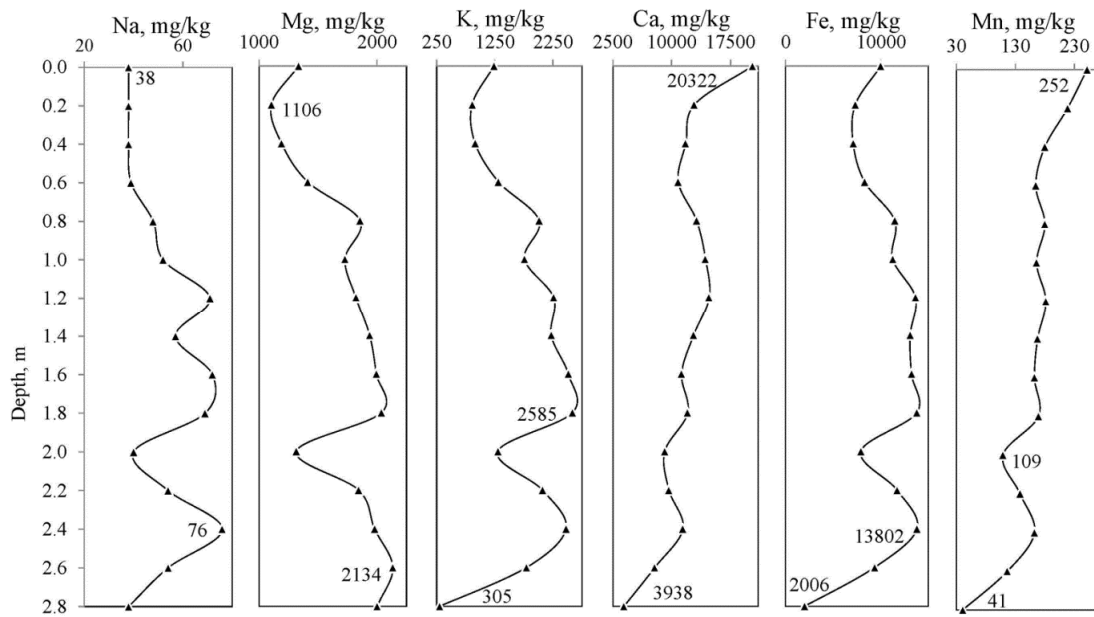


Fig.5. The distribution pattern of major elements in sapropel from Pilcenes Lake

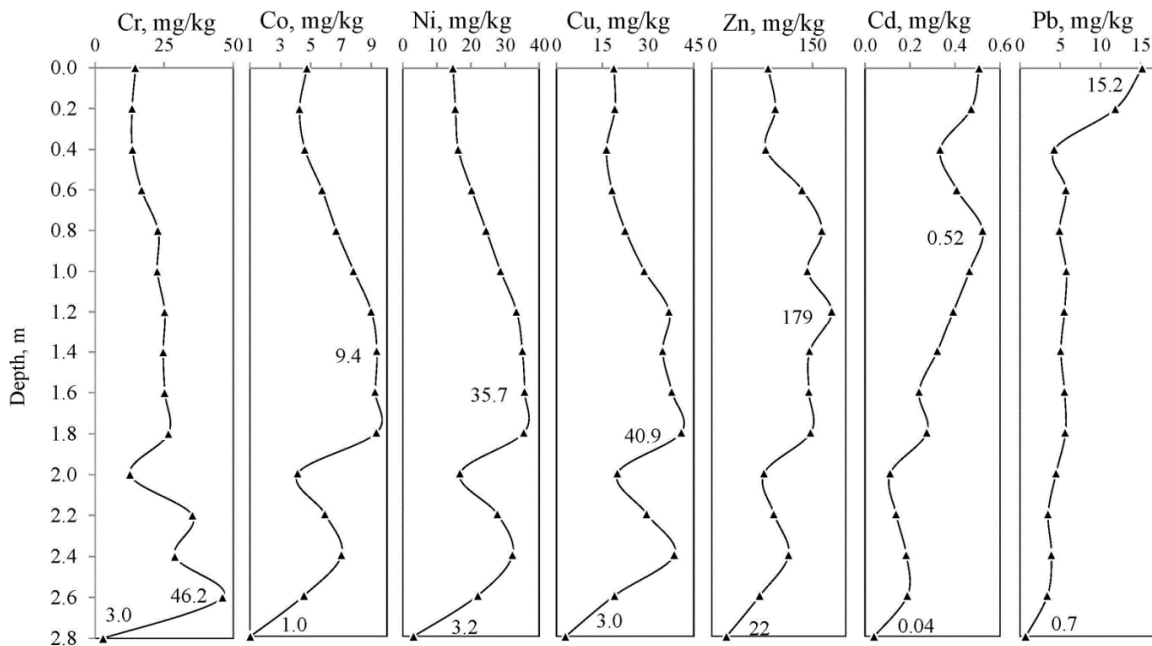


Fig.6. The distribution pattern of heavy metals in sapropel from Pilcenes Lake

Correlation of metal elements in all the lakes in the full profile of sediment showed that metals of natural origin such as Fe and Mg are associated with K, and Ca – with Mg [14]. This is because these elements in sediments are mainly retained with runoff from the catchment basin, as well as from groundwater, where their source are rock weathering (such as calcium and magnesium) due to erosion of the dolomites ( $\text{CaMg}(\text{CO}_3)_2$ ); however, if Ca and Mg is not related, the source of calcium most likely is calcite ( $\text{CaCO}_3$ ). Potassium in water and sediments mainly comes from the weathering of orthoclase, biotite, feldspar and silvinit, though only biotite ( $\text{K}(\text{Mg}, \text{Fe})_3[\text{Si}_2\text{AlO}_{10}](\text{OH}, \text{F})_2$ ) of these minerals contain Fe, Mg and K. In the sediment of Padēlis Lake at a depth of 0.75 to 1.5 m the amount of Mg, Fe, K, Cr, Co, Ni, Pb and Zn is increased. As in the example of Pilcenes Lake the rapid changes in metal concentration in two meter deep layer can be explained by the drastic environmental condition changes. The

ash increases till 68.20%, but metallic elements and carbonates content are low. The sample ash visual inspection shows high silicate admixture and thus might be associated with increased loadings from lake basin.

In Pilveļu Lake sediment profile the metals Mg, Fe, K, Cr, Co, Ni, Cu in the deeper layer are characterized by higher concentrations of sapropel deposition, while at 3.75 m to 3.50 m they are decreased rapidly (Fig. 7, 8). It indicates the increasing input of metals in the sediments by natural conditions (weathering, runoff from the catchment area, groundwater flow). The largest fluctuations are in the Na, Cu and Ca concentrations. Lead concentration growth is observed at 0.50 m depth, but at 0.10 m depth it is reduced. This can be attributed to anthropogenic pollution [15], but calcium and manganese concentrations increase in the upper sapropel layers and can be related to natural processes.

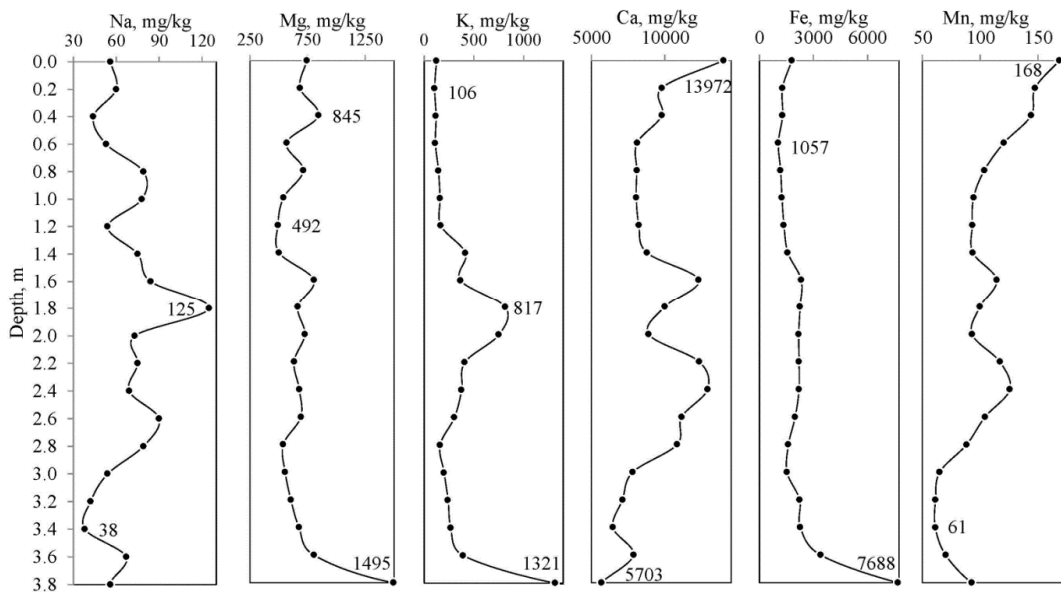


Fig.7. The distribution pattern of major elements in sapropel from Pilveļu Lake

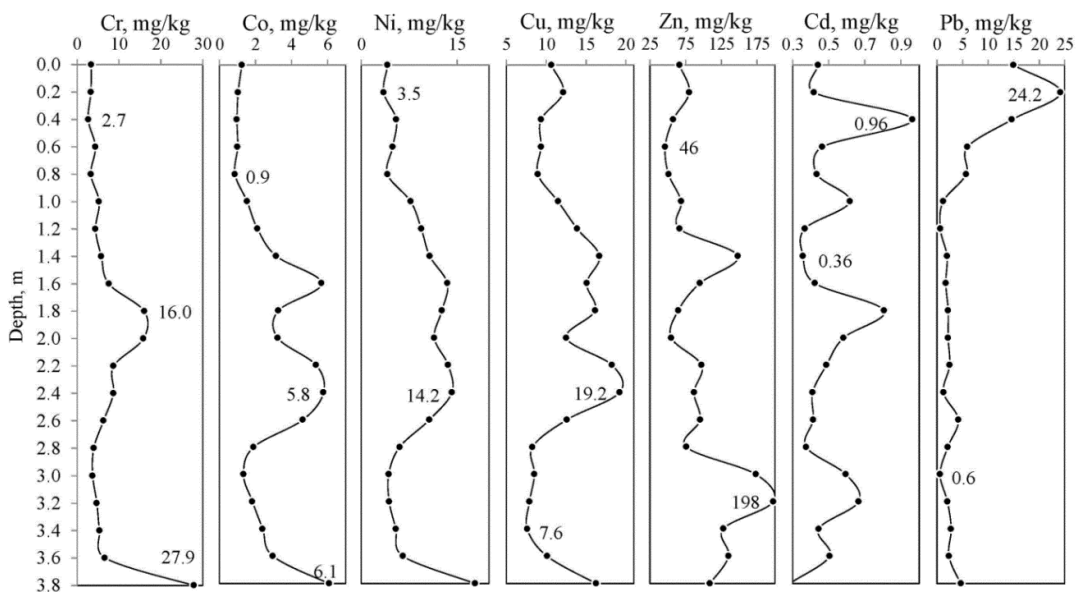


Fig.8. The distribution pattern of heavy metals in sapropel from Pilveļu Lake

At approximately 2 m depth of sapropel of Pilcenes Lake sediment profile the amount of Na, Mg, Fe, K, Mn, Cr, Ni, Cu and Zn is increased (Fig. 5, 6). Rapid changes in metal concentrations may be associated with the lake water level fluctuations and recycling of nutrients [15].

Anthropogenic metals as Cr, Cu, Co, as well as Fe and Ca – of natural origin – are correlated with Ni; it can be explained by the fact that Ni can have both natural and anthropogenic origin.

To assess the ecological condition of sediments, these heavy metals – Cr, Co, Ni, Cu, Zn, Cd and Pb – were compared with the allowed maximum concentration of heavy metals in the soil [16]. Cr, Co, Pb, Cd concentration does not exceed the maximum allowed limits; however, Cd and Pb are increased in the upper layers of sediment, indicating their anthropogenic origin. Cd, Pb and their compounds present in the exhaust gases of internal combustion engine makes one of the main indicators of human impact on lake ecosystems. Increased Ni values – up to 35.7 mg/kg (permissible soil concentration is 30 mg/kg) – were observed in Pilcenes Lake sediments at a depth of 1.2 to 2.4 m. Ni concentrations in the upper layers of sediments of all the three lakes are below the maximum permit limits and less than in lower layers, indicating the natural origin of Ni in the sediments. Slightly increased concentrations of Zn – 179 mg/kg (permissible concentration in soils is 150 mg/kg) – were found in Pilcenes Lake at a depth of 1 m of sediment layer, and in Pilveļu Lake at a depth of 3 m – 198 mg/kg. Zn concentrations range from 7 mg/kg to 95 mg/kg in the upper layers of the lakes sediment, which is the maximum allowable concentration, indicating that similarly Ni and Zn are of natural origin.

#### IV. CONCLUSION

The sapropel elemental analysis of the entire sediment layer showed that lake sediments in comparison with peat have a higher N concentration, which can be explained by the chemical differences among sapropel-forming and peat-forming organisms.

Higher concentrations in organic lake sediments are common for metals of natural origin – Ca, Fe and Mg, which is discharged into water bodies as a result of rock weathering in the lake catchment area. Heavy metal concentrations compared to its maximum permissible concentrations in soil showed that the sapropelic sediments are not contaminated. In some layers the slightly increased Zn and Ni concentrations are associated with the impact of natural rock weathering. Pb and Cd increase in the upper layers of sediments indicate anthropogenic impacts growth on lake ecosystem, likewise the metal concentration is low and does not cause adverse effects to aquatic organisms in the lakes

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#### **Karina Stankeviča, Māris Kļaviņš, Līga Rūtiņa. Metālu akumulācija sapropelā sastāvā**

Metālu koncentrācijas ezeru nogulumos dod iespēju rekonstruēt ūdens ekosistēmas attīstības gaitu pagātnē, noteikt antropogēnas slodzes izraisīto piesārņojumu virsējo nogulumu slāņos, veidot ģeokīmisku apskatu dziļāko slāņu nogulumiem, iegūstot informāciju par metālu dabisku akumulāciju ūdens baseinos, kā arī priekšstatu par nogulumu iespējamo izmantošanu. Dotajā pētījumā tika analizētas 13 metālisko elementu koncentrācijas trijos Latgales ezeru organogēno nogulumu profilos. Papildus nogulumiem tika veikta karsēšanas zuduma analīze, kas parāda nogulumu mitrumu, pelnu un karbonātu saturu, kā arī elementsastāva analīze, kas sniedz informāciju par sapropelā organisko materiālu veidojošo elementu procentuālo sadalījumu, kā arī netieši liecina par nogulumu izcelsmes materiālu un tā īpašībām. Rezultāti uzrādīja, ka lielākas koncentrācijas ir dabīgas izcelsmes metāliem – Ca, Fe, un Mg, kas ezerā nokļuvuši iežu dēdēšanas rezultātā no ezera sateces baseina teritorijām. Smago metālu koncentrācijas, salīdzinot ar pieļaujamo smago metālu koncentrāciju augsnēs, uzrādīja, ka sapropelā nogulumi nav piesārņoti ar smagajiem metāliem. Dažos nogulumu slāņos konstatēta paaugstināta Zn un Ni koncentrācija, kas skaidrojams ar iežu dēdēšanu, kas satur šos metālus. Cd un Pb augstākās koncentrācijas nogulumu virsējos slāņos liecina par pēdējā 100 gadu laikā cilvēku radīto ietekmi uz ezeru ekosistēmu. Tomēr šo metālu koncentrācijas nepārsniedz pieļaujamo maksimumu un nerada nelabvēlīgas sekas ezerā dzīvojošiem organismiem. Sapropelā elementsastāvs uzrādīja, ka sapropelī, salīdzinot ar kūdru, ir augstāka slāpekļa koncentrācija. Tas skaidrojams ar sapropelā un kūdras veidojošo organismu ķīmiskā sastāva atšķirībām.

#### **Карина Станкевича, Марис Клявиньш, Лига Рутиня. Аккумуляция металлов в составе сапропеля**

Изучение концентрации металлов в отложениях пресноводных водоемов делает возможным реконструкцию развития водной экосистемы в прошлом, установление антропогенного влияния на верхние слои отложений, создание геохимического обзора более глубоких слоев донных отложений, а так же дает представление о возможных путях использования этих отложений. В данном исследовании были установлены концентрации 13 металлов по всему профилю органических донных отложениях трех Латгальских озер. Дополнительно была установлена естественная влажность, зольность и количество карбонатов, а так же элементарный состав сапропеля, который дает представления о процентильном соотношении элементного состава органической части отложений и косвенно свидетельствует о происхождении сапропеля и его свойствах. Результаты показали, что в сапропеле самые большие концентрации занимают металлы – Ca, Fe, и Mg – природного происхождения, которые попадают в озеро при выветривании горных пород в водосборных бассейнах озер. Концентрации тяжелых металлов по сравнению с предельно допустимыми концентрациями в почвах показали, что сапропелевые отложения не загрязнены тяжелыми металлами. В некоторых слоях донных отложений несколько увеличены концентрации Zn и Ni, что объясняется выветриванием горных пород содержащих эти металлы. Более высокие концентрации Cd и Pb в верхних слоях донных отложениях указывают на влияние человека на экосистему озер в последние 100 лет. Однако концентрации этих тяжелых металлов не превышают допустимого максимума и не опасны для живых организмов, живущих в озерах. Элементарный анализ донных отложений показал, что в сапропеле по сравнению с торфом более высокая концентрация азота. Это объясняется различием химического состава организмов, формирующих сапропель и торф.