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THE DISTRIBUTION OF HEAVY METALS IN SEDIMENTS IN THE LAKE TALKSA OF LITHUANIA

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Abstract. The intensification and development of industrial processes has harmful effects of human activities on nature and entire environment. Having performed the assessment of contamination of environmental components, especially geological environment (soil, sediments from bottoms of water bodies, including sapropel), it is possible to make a quantitative evaluation of the scope of anthropogenic influence and often the hazardousness of such influence on biota and people. Heavy metals enter water reservoirs and, at the same time, sapropel from atmosphere and with surface-water and underwater. Part of heavy metals, which are found in deeper deposits of sapropel, have built up naturally in the course of complex hydro-chemical and hydro-biological processes, which formed over thousands of years when the atmosphere and waters were not as polluted as they are today.

A large number of sediment samples representing most of the active accumulation areas in Lake Talksa of Lithuania were studied for total copper (Cu), zinc (Zn), chromium (Cr), nickel (Ni), lead (Pb) and manganese (Mn). Quantities of most heavy metals in sapropel decline noticeably with depth, if compared to the surface layer. The lowest concentrations of heavy metals are discovered at a depth of 200–250 cm. The trend of declining concentration of heavy metals in sapropel layers with depth is obvious throughout the section.

Keywords: lake sediments, sapropel, heavy metals, distribution.

1. Introduction

Lakes are important and significant bodies in preserving freshwater and replenishing underwater. Lithuania has about 2850 lakes each covering over 0.5 hectare and around 3150 lakes of under 0.5 hectare each. In total, they cover the territory of 91360 hectares (Kilkus 2005). Eutrophication makes lakes decline, and they accumulate sludge, lakeshores get covered with excess vegetation and, consequently, all this entails a serious ecological problem. The process of declining lakes may also be natural, yet anthropogenic contamination adds to a fast-paced silting up of lakes (Bakšienė and Ciūnys 2007; Žvironaitė *et al.* 2002; Alkan *et al.* 2009).

According to many scientists, sapropel or lake silt, which has accumulated in natural environment, is unique and valuable sediment (Rohling *et al.* 2004; Knicker and Hatcher 2001). It is a complex matter of organic and mineral origin and it mostly consists of the remains of plankton, benthos, algae and other hydrophytes that have stratified with particles of sand, clay and limestone (Menzell *et al.* 2003; Capozzi and Picotti 2003).

Sapropel is found in Lithuania at the bottoms of lakes and swamps. According to the data by Katkevičius and other researchers (1998), Lithuanian lakes and swamps store approximately 10 billion m^3 of sapropel of 7–15 m-thick deposits, which have built up over thousands of years and preserve naturally balanced minerals (Ciūnys *et al.* 1994).

According to its origin, sapropel may be organic or mineral–carbonaceous with pH 6.0–7.5 (Bakšienė and Janušienė 2005; Katkevičius *et al.* 1998). Its dry matter may include 79.8–90.8 % of organic substances, 2.27–3.56 % of nitrogen, 0.56–1.18 % of calcium, 0.9–0.15 % of P_2O_5, and 0.055–0.2 % of K_2O.

Sapropel may include microelements and metals such as Al, Ca, Co, Cu, Fe, K, Mo, Zn, Se, C, J, N, P, S, Si and many more. The organic part of lake sludge is rich in biologically active substances and vitamins, especially those of B group, also enzymes, indispensable amino acids, antibiotics, carbohydrates, estrogens, humic acids, growth stimulators for lipid fractions and other biostimulators and probiotics (Katkevičius *et al.* 1998).

Sapropel may be of different colors: its color is very important as it discloses the quantities of organic and non-organic matters. Jade color shows that sapropel includes chlorophyll, pink means sapropel has carotene, blue color reveals that sapropel includes vivianite, grey means lime addition and black color or a quickly darkening shade means sapropel includes iron. After being pumped out of a lake, sapropel undergoes fast oxidation and loses its natural shade (Žvironaitė *et al.* 2002; Katkevičius *et al.* 1998; Bakšienė and Janušienė 2005; Косов 2007).

It is advisable to use sapropel as a fertilizer, as forage additive, in chemical industry, medicine and in the energy sector because of the matter's chemical and physical properties.

2. Methods and Technologies of Extracting Sapropel

Deposits of sapropel may be extracted by applying hydraulic or mechanical methods, also a complex method when both suction dredges and excavators are used (Katkevičius *et al.* 1998).

Suction dredge includes pontoons, soil pump, tail pipe, slurry pipe, equipment for moving: winches with hawsers and poles. With all equipment for pumping sapropel, lake clearing and sapropel extraction works may successfully be implemented. A lake is relatively divided into individual sectors, and the succession of cleaning the sectors is established. Suction dredge is secured on the digging site and consistently pumps out sapropel in the designated zone. Sapropel is excavated layer by layer until the bottom or the desired depth is reached.

There are two cases of mechanical purification of lakes: when a silted up lake is not fully waterlogged or when a lake has turned out into a marsh. When a lake has deteriorated into a bog, 1–3 m-thick deposit of turf has formed above the layer of sapropel. If the turf is not bulldozed, standard machinery may be driven over the surface after it is drained. Excavators are used to dig sapropel together with turf, and then it is loaded into self-dumping metal hitches pulled by tractors.

The aim of this article is to survey the concentration of heavy metals in sapropel in Lithuanian lakes and determine whether or not sapropel of such consist qualifies as an agricultural fertilizer.

3. Methods of Taking Samples and Their Analysis

Sapropel samples have been taken from Lithuanian the Lake Talkša. The samples of lake sediments were taken in winter with a 50 cm-thick ice cover.

Having drilled the ice cover to different depths of bottom sediment samples were taken by peat type drills (Fig 1).

In order to examine the concentration of heavy metals in samples and to find out other parameters of sludge, the analysis of samples is carried out. Contamination of lake mud in Lithuania is usually determined based on LAND 20-2005: Requirements for Sewage Sludge Application in Fertilization and Recultivation (Table 1).

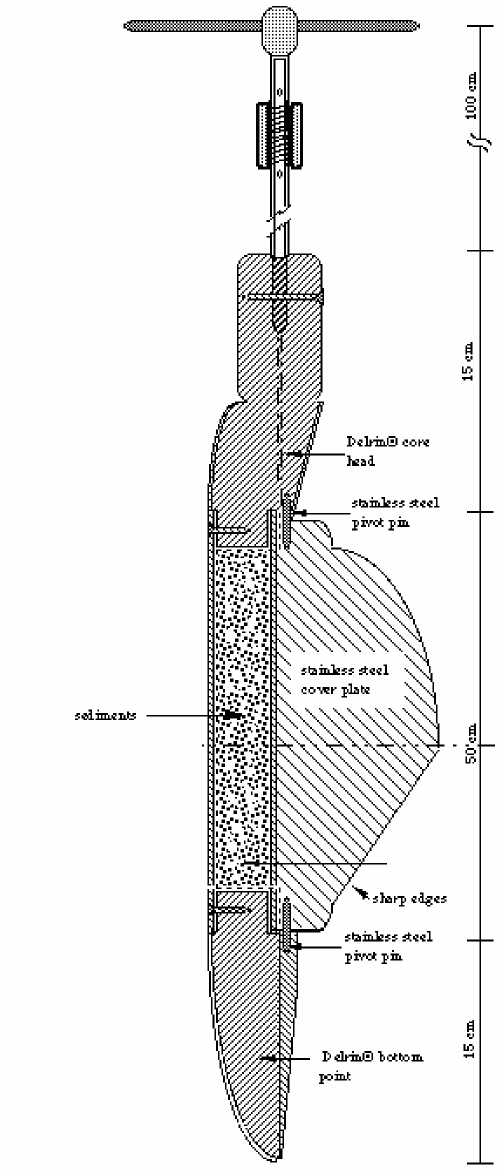

Fig 1. Peat type drill method to obtain the examples of the lake bottom sediments

1st category sludge includes mud that may be used for fertilization and pit recultivation. It is prohibited to use 2nd category sludge to fertilize the areas intended for vegetables and fruit trees, but crops may be grown after 1 year after spreading sludge over the cultivated area. When planning to fertilize soil with 2nd category sludge for the first time, it is required to determine soil quality: heavy metal quantities (Pb, Cd, Cr, Cu, Ni, Zn and Hg), granulometric composition and pH.

Table 1. Maximum limit values for concentration in sludge

Sludge Category	Quantities of Heavy Metal, mg/kg				
	Pb	Ni	Cr	Zn	Cu
1st	≤60	≤45	≤60	≤200	≤60
2nd	61-165	45-100	61-130	201-660	61-200

Micro-quantities of sapropel heavy metals were analyzed in lined-up solutions from sapropel (extracts) by Atomic Absorption Spectroscopy with the use of Atomic Absorption Spectrophotometer Buck Scientific 210 VGP with acetylene–air flame.

0.5 g of each sapropel sample were digested with a mixture of HNO_3 (65 %) and H_2O_2 (37 %) at the microwave digester *Milestone ETHOS*. The solution was poured in flasks of 50 ml and diluted with deionised water to the mark of 50 ml.

4. Results of the Analysis

Most chemical elements released into environment accumulate in soil and in bottom deposits of water reservoirs (Baltrėnas *et al.* 2009; Buinevičius and Puida 2005). Heavy metals enter water reservoirs and, at the same time, sapropel from atmosphere and with surface-water and underwater. Part of heavy metals, which are found in deeper deposits of sapropel, have built up naturally in the course of complex hydro-chemical and hydro-biological processes, which formed over thousands of years when the atmosphere and waters were not as polluted as they are today. The chemical and biogenic consists of the built up sapropel differ depending on lake background and the type of eutrophication. Mineral consist of sapropel determines its use.

Lake Talkša is located 1 km from the center of Šiauliai town. The lake covers 56.2 hectares, it is 2 km long, and its maximum width reaches 550 m. The northern part of Lake Talkša is connected with Lake Ginkūnai covering 16 hectares via 150 m-long and 5 m-wide Kulpė canal covered with reed. Overgrowth of vegetation covers almost all shores of the lake.

Rather considerable amounts of Cr and Ni have been found in deposits of Lake Talkša (Fig 2). Pb and Zn evidently dominate in most deposits of Lithuanian lakes and this shows relationship with prevailing contamination of urbanized areas, therefore the said elements mostly precipitate in bottom deposits. Deposits of lake bottoms rich in organic matter have superior sorption qualities, thus they attract higher quantities of elements and pollutants than the soil of urbanized areas. This is clearly evident when comparing amounts of heavy metals in soils located near water reservoirs.

Deposits of Lake Talkša have accumulated Zn, Cr and Ni for the most part. The highest concentration of the said elements is found in surface sediments (up to 50 cm), and the concentration of all heavy metals gradually decreases with depth. Surface sediments located at the bottoms of lakes shall not be attributed to 1st category of sludge, which is used for fertilization and pit recultivation because Zn, Cr and Ni concentrations exceed their limit values, but they can be assigned to 2nd category of sludge as higher concentrations of heavy metals are allowed here. Concentration of Zn in the surface layer of sludge reaches 201.3 mg/kg, Cr – 63.8 mg/kg, and Ni – 51.2 mg/kg, accordingly, and this conforms to the requirements for 2nd category sludge.

Quantities of most heavy metals in sapropel decline noticeably with depth, if compared to the surface layer. The lowest concentrations of heavy metals are discovered at a depth of 200–250 cm. The trend of declining concentration of heavy metals in sapropel layers with depth is obvious throughout the section. At a depth of 200–250 cm, the concentration of Zn, Cu and Ni is two times less: Zn – 84.3 mg/kg, Cu – 17.8 mg/kg, Ni – 17.3 mg/kg. The concentration levels of heavy metals at a depth of 50–250 cm do not exceed maximum limit values for sludge contamination and correspond to 1st category sludge; therefore it may amply be used in agriculture for production of bio-compost, fertilizers or as a growth stimulator for plants.

The variation of the amount of chemical elements discloses that they are of natural origin in deeper layers of sapropel and they depend on the mineral consist of lake reservoir residues as well as the peculiarities of sedimentation processes.

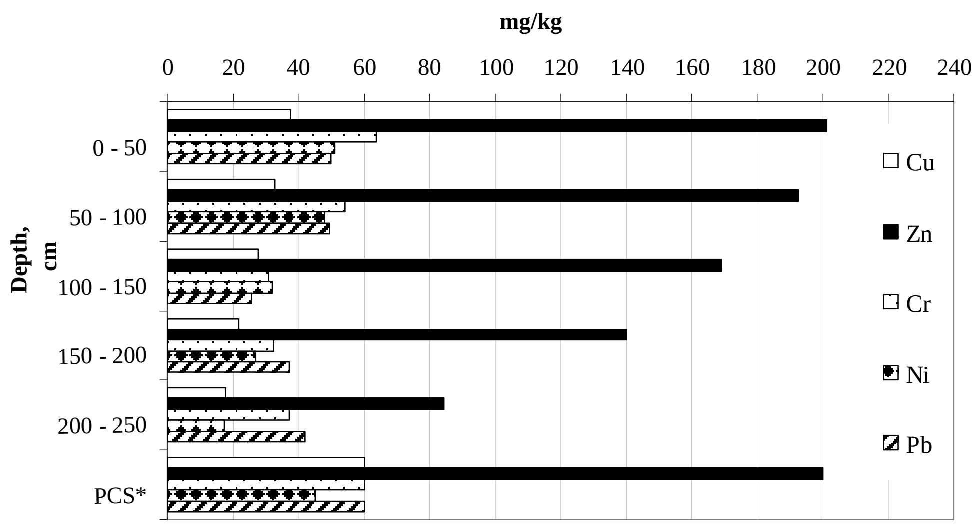

Fig 2. Variations of heavy metal concentration in the sapropel of Lake Talksa (in vertical profile)
*PCS – Permissible concentration in sludge

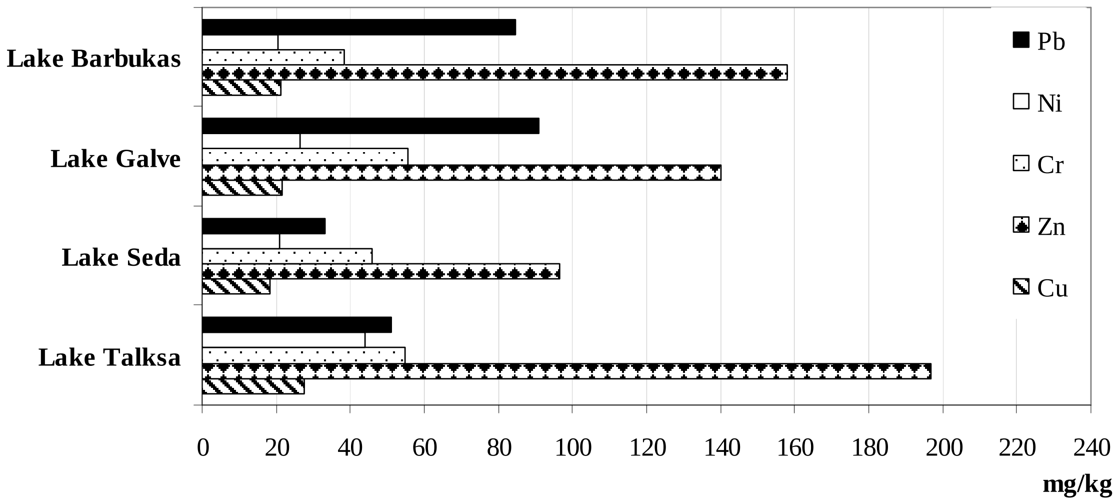

Fig 3. Variations of heavy metal concentration mean values in the sapropel of different Lakes

The established concentration of elements that represent a hazard to human health or to the environment (Cr, Cu, Ni and Zn) in two lakes in Lithuania do not exceed limit values, except for the surface layer in Lake Talkša (up to 50 cm), and therefore they are not hazardous to the environment or animal health and may abundantly be used in agriculture, for additives to combined forage and for fertilizing.

Sapropel may well be used for growing not only agricultural produce (vegetables and fruit trees), but also gramineous plants for energy production. After proper preparation, the plants may be used to produce heat in boiler houses. In order to guarantee fine and fast growth of such plants, it is advisable to fertilize them with sapropel. According to scientists, sapropel is an ecological fertilizer for all agricultural crops. Agrochemical research of fertilization with sapropel reveals that it is highly effective in increasing and quickening the harvest of vegetation.

Sapropel may differ greatly in individual lakes and even in different zones of the same lake. Thus the average concentration levels of heavy metals are compared with the levels of heavy metal concentrations in Lithuanian lakes Galvė and Barbukas (the Trakai Region) as established by Lithuanian authors (Kadūnas *et al.* 2001) (Fig. 3).

Chemical consist and the level of contamination of sapropel depend on various factors. Water reservoirs and sediments at their bottoms are more contaminated in urban areas than those located further away from towns and cities. Figure 3 clearly demonstrates that lakes in Lithuania have accumulated sapropel of different consist and sometimes the levels of sapropel contamination with heavy metals are higher, sometimes they are lower.

The highest quantities of heavy metals have been found in sapropel in Lake Talkša: Zn concentration level reaches 196.9 mg/kg, Cr – 54.6 mg/kg, Ni – 43.9 mg/kg, Pb – 51.1 mg/kg, Cu – 27.5 mg/kg, respectively. Slightly lower concentration levels of heavy metals are in Lake Barbukas (the Trakai Region). Analysis carried out by scientist Kadūnas (2001) reveal that the concentration of Zn in Lake Barbukas is 158.0 mg/kg. Zn concentration level in Lake Galvė reaches 140 mg/kg and is similar to the concentration level of Zn in Lake Barbukas.

Higher concentration levels of heavy metals are recorded in Lake Galvė, just as in Lake Talkša and Lake Barbukas. Pb concentration level in Lake Galvė, especially its southwestern shore are abnormal – Pb – 90.8 mg/kg – and reveal greater contamination with this element. Most microelements, a part of which is of technogenic origin, make a single association (Pb-Cu-Zn), which is a further factor of pollution influence.

Lakes Talkša, Barbukas and Galvė are located close to towns; therefore concentration levels of heavy metals in sapropels are higher. The reason behind an increase in heavy metal concentration in the sapropel of Lake Talkša is industry. As Lake Talkša interconnects with Kulpė watercourse (Kulpė canal), sewage from a former nearby tannery and shoe factory contaminated the lake. In the beginning of the 20th century, little attention was paid to environment protection, and non-purified sewage went to water reservoirs and soil. The contamination is evidenced in surface layers of sapropel near the canal of Kulpė. Although the levels of heavy metal concentration in the sapropel of Lake Talkša are higher, they do not represent hazard.

5. Conclusions

1. Researches of heavy metal concentration levels in lakes in Lithuania have revealed that the consist of sapropel is different in individual cases; and in order to start an expansive use of sapropel it is indispensable to carry out thorough analysis of the matter. High sorption properties are characteristic of sapropel; therefore the highest levels of heavy metal concentration in both lakes are recorded in surface layers, whereas the levels of concentration of heavy metals gradually decrease with depth.
2. Levels of heavy metal concentration in the sapropels of Lake Talkša do not exceed the maximum limit values

for contamination of sludge, used for soil fertilization and pit recultivation, as provided for in LAND 20-2005 normative. The amount of heavy metals in the sapropels of Lake Talkša meets the requirements for 1st category sludge and may be used without restrictions. Higher amounts of Zn (≤200 mg/kg), Cr (≤60 mg/kg) and Ni (≤45 mg/kg) have been found in some samples from the upper part of sapropel layer in Lake Talkša, but his has no influence on their amounts in the entire deposit of sapropel.

3. The analyses of sapropel has disclosed that the sapropel from lakes in Lithuania may extensively be used in agriculture (as bio-compost, growth stimulator for vegetation, fertilizer and forage additive), in industry (for diluents, binders in panel production) and in medicine (as curative mud, bio-preparations and masks), but it is indispensable to carry out extensive analysis of sapropel before starting to use it.

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