Trace elements in sediments of lakes in Latvia

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Abstract—Environmental pollution with trace elements is considered as one of the most important environmental problems. Analysis of trace element accumulation in sedimentary phases of waterbodies (lakes) may reflect the overall regional pollution level, but analysis of trace element accumulation patterns in sediment profiles can help to reconstruct history of anthropogenic impacts.

The aim of this study was to analyse trace element concentrations in the sediments in lakes of different origin in Latvia and analyze factors influencing their availability.

The metal concentrations in sediments of lakes in Latvia are at a background levels, especially of compared with metal concentrations in West European countries. However analysis of element concentration changes in sedimentary profiles gives information about trends of recent accumulation (within last 150 years) and balance between natural and human induced accumulation processes.

Keywords—Trace elements, pollution, lake sediments, accumulation.

I. Introduction

Trace elements, and especially the so called heavy metals, are among most common environmental pollutants and their occurrence in waters and biota indicate pollution sources [1]. The main natural sources of metals in waters are weathering of minerals. At the same time different industrial effluents and non-point pollution sources, as well as atmospheric precipitation [2] can be sources of increased concentrations of trace elements. Air masses supplying acidic pollutants also carry significant amounts of certain metals, which give rise to significant contamination of the terrestrial and aquatic environments in particular [3]. However, concentrations of metals and their actual impact can be greatly modified due to interaction with different natural water ingredients [4]. Therefore knowledge of the concentrations of trace elements is desirable for the estimation of pollution levels of waters and the determination of background values of metal concentrations in corresponding regions, their waters, sediments and biota as far as metals in biota are subjected to bioconcentration. As far as major burden of trace elements may be found in sediments, especially important is to analyze biota, which thus may serve as bioindicator of pollution. Trace element concentrations in waters and aquatic ecosystems have been extensively analyzed worldwide [5-8], but there are only few publications on their concentrations in waters and biota of the Latvia [9]. This question is especially important considering natural geochemical peculiarities in this country.

The aim of this study was to determine trace element concentrations in the sediments and macrophytes in lakes of different origin in Latvia and analyze factors influencing their availability.

II. Materials and Methods

The lakes investigated and the sampling sites used are shown in Figure 1. Water samples were taken from lakes in 2009, 2010 at a depth 0.5 m and basic aquatic chemistry were analysed (pH, conductivity, nutrients, major inorganic ions, total organic carbon) immediately on arrival of samples to the laboratory using standard methods for analysis of surface waters [10].

Surficial sediment layer were sampled by Ekman drag. Aditionally, sediment cores were taken from three different parts of the Lake Engure by using ordinary gravity corer with Plexiglas tube of diameter of 35 mm. Sediment cores were sliced into 1 cm thick layers. The dried and sieved (< 100 μm) samples (~ 1 g) were digested with 50 % HNO_3 and 30 % H_2O_2 on a hot plate at 70±5 °C [11]. Content of organic matter and carbonates in sediments was determined by loss-on-ignition analysis as described in [12].

Metal concentrations were measured by flame atomic absorption (Perkin Elmer 503). The reliability and accuracy of analytical results were checked using blank and reference (SLRSS-2 river water, BCSS- coastal marine sediments; Analytical Chemistry Standards NRC, Canada) samples. The results from the analysis of SRM were all within the 95 % confidence level of the SRMs.

Sediment dating of the upper 30 cm layers has been done using ^{210}Pb analysis by known methods [13, 14].

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III. Results and Discussion

The studied lakes (Fig. 1) are representative in general for lakes in Latvia and they represent different types of lake genesis. Laka Engure is a lagoon lake, but other studied lakes are of glacial origin.

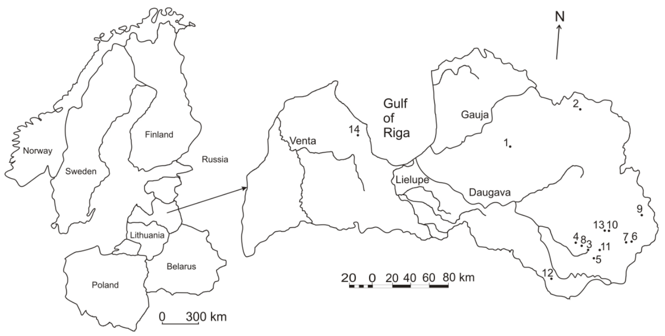

Fig. 1. Map of the sampling area (lake numbers are as in Tables 1, 2).

Conductivity of lake waters are in range 170 – 300 µS/cm. In most of the lakes hydrogencarbonates are dominating anions (average concentrations around 150 mg/l), in lagoon type Lake Engure chlorides are found in higher concentrations because of inflow of sea waters through canal. Dominating cations are Ca^{2+} and Mg^{2+} (Table 1). Most of the selected water bodies have been subjected to anthropogenic pollution, at first due to agricultural activities. According to trophic status lakes can be characterized as slightly eutrophic and eutrophic. L.Engure belongs to polytrophic type.

Table 1. Aquatic chemistry of the studied lakes.

No	Lake	N_{inorg} mg/l	Color ^{0}Pt/Co	Cond. µS/cm	pH	Cl^- mg/l	HCO_3^- mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l	Na^+ mg/l
1	Alauksts	0.20	26.0	186.7	9.12	20.52	117.1	25.85	8.39	3.1
2	Alūksnes	0.16	16.5	178.4	9.22	22.15	115.9	20.94	10.28	7.3
3	Ārdavs	0.23	21.0	224.0	8.48	17.92	153.7	31.80	12.69	3.7
4	Bešons	0.36	41.0	259.0	8.88	16.29	187.9	39.08	15.50	3.4
5	Drīdzis	0.23	23.0	234.0	8.96	15.31	158.6	30.36	15.50	4.2
6	Ežezers	0.36	37.5	265.0	8.82	15.96	195.2	41.88	15.32	4.5
7	Galšūns	0.35	35.0	276.0	8.35	17.26	203.7	39.48	18.00	4.6
8	Lejas	0.35	34.5	228.0	8.89	17.92	159.8	33.87	13.50	3.6
9	Nirzas	0.18	23.0	250.0	8.90	19.87	175.7	29.36	18.54	4.5
10	Rāzna 5	0.28	15.3	221.3	9.10	16.29	137.9	26.05	12.16	4.4
10	Rāzna 11	0.20	16.0	223.0	9.09	17.59	137.9	21.24	15.02	4.0
11	Sīvers	0.24	25.5	202.8	8.85	16.61	137.9	27.92	12.36	3.1
12	Sventes	0.24	13.0	212.1	8.92	14.01	137.9	25.45	11.61	
13	Zosna	0.39	36.0	303.0	8.62	15.31	200.7	41.55	15.34	3.5
14	Engure	0.50	55.2	248.7	8.56	11.94	163.5	33.8	15.3	6.7

Loss-on ignition analysis show that content of organic matter in lake sediments vary from 3 – 46 %. Sediment bulk chemistry in most of the studied sampling stations indicate that with exception of several sampling sites, a significant sediment ingredient is organic matter which may form up to 46 % of the sedimentary phase. As good pollution and eutrophication indicator may serve also increased concentrations of nitrate and phosphorous compounds, appreciable amounts of which are accumulated in lake sediments (Table 2).

Table 2. Characteristics of the sampled sediments

No	Lakes	OM, %	Carbonates, %	P_{tot} mg/kg	N_{inorg} mg/kg
1	Alauksts	38.50	2.22	807.5	910.2
2	Alūksnes	2.97	0.26	172.3	627.9
3	Ārdavs	39.64	1.68	554.1	903.2
4	Bešons	18.48	2.19	753.4	930.2
5	Drīdzis	11.05	2.02	608.1	690.6
6	Ežezers	29.82	3.05	601.4	988.1
7	Galšūns	20.77	3.92	1601.5	1112.8
8	Lejas	12.46	1.78	767.0	642.4
9	Nirza	19.81	2.17	763.6	919.6
10	Rāzna 11	24.74	2.06	966.3	1166.9
10	Rāzna 5	5.00	1.95	342.9	768.8
11	Sīvers	34.96	1.57	500.0	973.8
12	Svente	17.92	2.40	594.6	864.7
13	Zosna	46.24	3.99	780.5	1193.7
14	Engure	35.27	13.30		

The concentrations of metals in the upper layer (0-5 cm) of the studied lake sediments vary greatly (Table 3). The studied lakes are not directly influenced by pollution from industrial sources. Concentration of heavy metals is rather dependent on content of organic matter in sediments or geochemical peculiarities of catchment area. Amongst the studied lakes no one is influenced by human activities and thus the obtained metal concentration values can be considered as low. According to Swedish environmental quality criteria [15], concentrations of Cr and Ni are moderate to low, Cu – low to very low, but Zn, Cd and Pb – very low.

Table 3. Content of heavy metals (mg/kg) in upper layers of lake sediments.

Lakes	Cr	Co	Ni	Cu	Zn	Cd	Pb
Alauksts	32.8	9.6	23.4	22.0	121.7	1.02	61.6
Alūksnes	2.9	1.7	2.1	2.4	10.2	0.12	2.2
Ārdavs	26.3	7.2	20.5	19.6	70.1	0.12	23.6
Bešons	38.2	11.8	26.5	22.6	102.5	0.35	30.7
Drīdzis	33.5	12.7	25.8	24.6	74.3	<0.03	19.4
Ežezers	33.9	9.3	24.0	24.5	115.6	0.58	35.2
Galšūns	23.5	9.0	16.0	22.1	88.1	0.22	28.8
Lejas	27.4	9.7	19.9	19.0	75.5	0.06	15.4
Nirza	25.2	9.8	18.5	22.8	84.6	0.40	24.9
Rāzna 11	25.2	7.0	19.0	19.7	103.3	0.73	49.2
Rāzna 5	6.1	2.0	2.9	3.7	21.7	0.12	6.8
Sīvers	20.0	6.6	16.1	19.0	64.2	0.57	24.8
Svente	42.3	9.3	28.9	18.4	77.6	0.33	28.9
Zosna	15.6	7.1	11.5	10.7	128.4	0.33	13.1
Engure	6.3	2.2	6.7	8.8	40.1	0.30	15.0

The mean concentrations of metals in sediments of lakes of Latvia in general are substantially lower than the estimated world averages, metal concentrations in other regions of world and thus can be assumed as metal background concentrations

[1, 16] determined for industrially developed countries in lake sediments. Observed concentrations of heavy metals seem not to be alarmingly high from a toxicological point of view [16]. Nearly all of the observed elemental concentrations may be explained by natural sources and processes. However in vicinity of biggest cities it is possible to observe increase of metal concentrations in sediments. In all cases, when increased metal concentrations are found, presence of pollution sources (introduction of domestic or industrial wastewaters, dumping of solid wastes) is evident.

Dating of the sedimentary profiles using ^{210}Pb shows that upper 30 cm of the sedimentary layers roughly corresponds to last 300 years of the lake history. To identify impacts of changes on the lake development in-depth study was run on example of Lake Engures (sampling station 1 in Fig. 1) and sediment profile composition as well as major and trace element concentrations in a full lake sediment profile were studied.

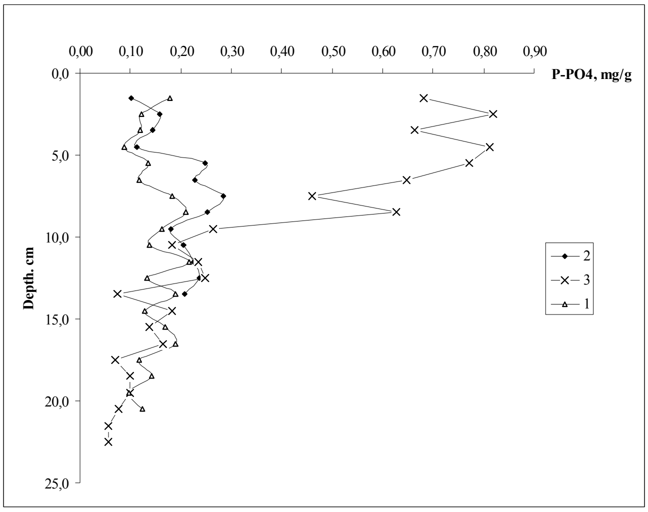

Fig. 2. Concentration of phosphorus in the upper layers of Lake Engures sediment profiles (Sampling sites in the lake body (1- northern part; 2, southern part – 3 centre of the lake)

The Lake Engure is located in the western part of coastal lowland of Latvia and is separated from the Gulf of Rīga by 1.5 to 2 km wide dune zone. According to the origin the lake belongs to the lagoon lakes. Partly due to its origin the Lake Engure is very shallow, the average depth is 0.4 m, the deepest place 2.1 is located in northeastern part of the lake, but a significant lowering of water level happed when in 1842 a canal were built connecting the lake with the Gulf of Rīga. Lake Engure is the largest shallow coastal lake remaining in the territory of Latvia from the age of the Littorina Sea, and have a high biodiversity. Since 1995 the lake was included in the list of Ramsar sites, and in 1998 Lake Engure Nature Park was established. For the management of the lake thus is of importance to understand the interaction between physical, chemical and biological processes in the lake basin, study the character of natural and human induced pressures and the reaction that could help to understand the character of processes in lake itself, its basin and support development of lake management strategies and action plans.

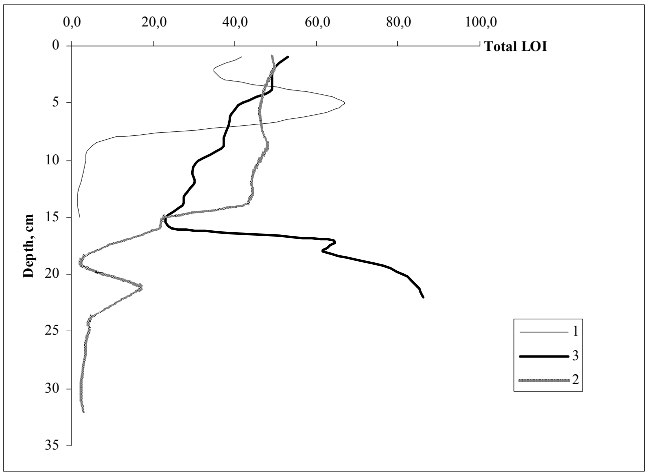

Fig. 3. Concentration of organic matter (estimated as loss on ignition (LOI) in the upper layers of Lake Engures sediment profiles (Sampling sites in the lake body (1- northern part; 2, southern part – 3 centre of the lake)

Analysis of phosphorus and LOI values in the upper layers of the sedimentary phases (Fig. 2, 3)indicate a significant differences in the accumulation processes in the lake water body, but at the same time intensification of accumulation processes within last decades.

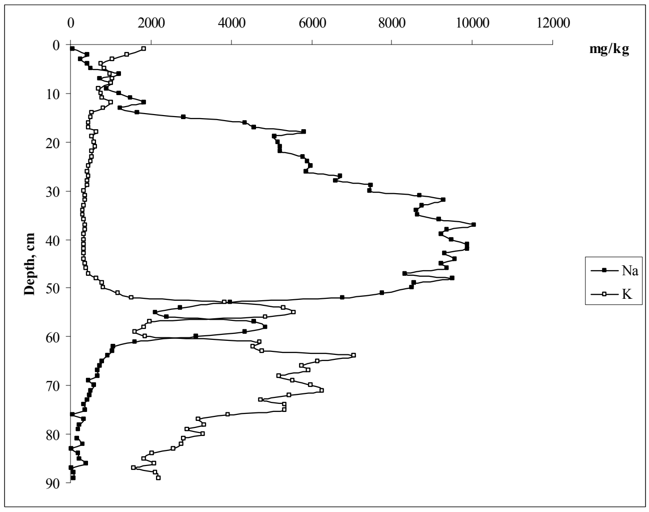

Fig. 4. Changes of Na and K concentrations in a profile of Lake Engure sediments (central part of the lake).

To identify impacts of the major and trace element accumulation a metal accumulation character in a full profile of lake sediments has been done (Fig. 4-7). As it can be seen on example of Na and K concentration distribution in a sediment profile pattern of K and Na concentration changes have an opposite character – when Na concentrations are increasing (after building of Mersrags channel in 1842) and inflow of brackish waters from Gulf of Riga takes place, K concentrations decreases. Historically K concentrations have been elevated probably considering biogenic origin of K in the aquatic environment.

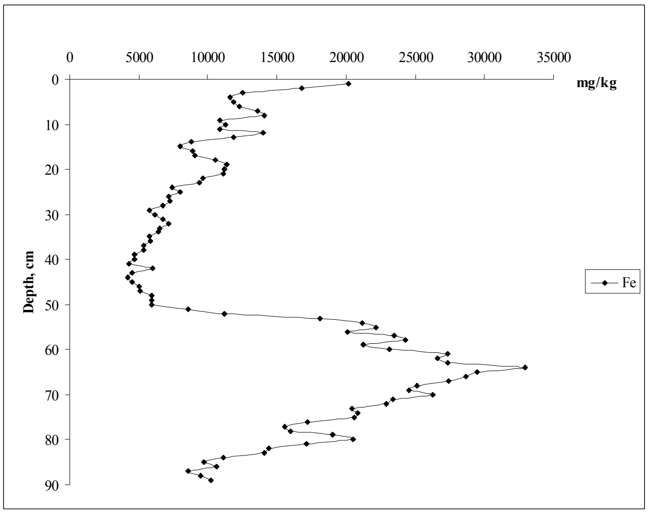

Fig. 5. Changes of Fe concentrations in a profile of Lake Engure sediments (central part of the lake).

In case of changes of Fe concentrations in Lake Engures sediment profiles a pattern can be observed indicating major changes in the sedimentation profiles caused by building of channel connecting lake with the Gulf of Riga in 1842. In this case an abrupt decrease of the Fe sedimentation happened. Changes in the Fe accumulation also can be related to changes in the oxygen conditions as far as only Fe (III) is tending to form stable sedimentary phases, but if anoxic events becomes frequent Fe (III) can be reduced to soluble forms of Fe (II) and the iron accumulation reduces. In recent decades Fe accumulation again is increasing.

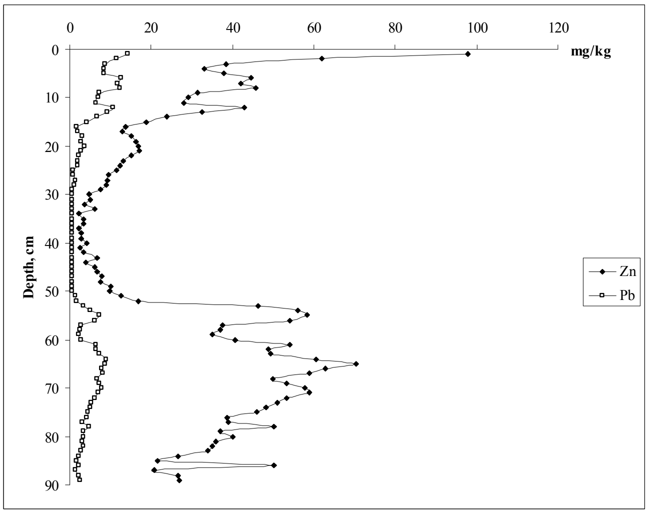

Fig. 6. Changes of Zn and Pb concentrations in a profile of Lake Engure sediments (central part of the lake).

Concentrations of trace elements like Pb, Co, Ni, Cu and elements which presence might be associated with human activities (as Zn) may help to identify human caused pollution and help to follow human induced changes in the pollution loading (Fig. 6, 7).

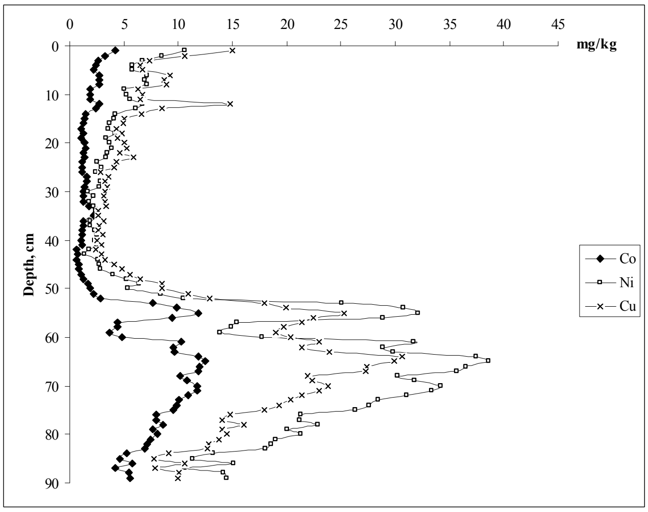

Fig. 7. Changes of Co, Ni and Cu concentrations in a profile of Lake Engure sediments (central part of the lake).

Influences of geochemical processes are evident, if analyzing differences in metal concentrations, especially in case of Zn and lead. Zn values in lakes of Latvia are at the same level as background levels in Sweden (in oligotrophic-humic lakes in northernmost Sweden which hitherto have been relatively spared acidification and atmospheric deposition of metals). In relation to the geochemically associated element zinc, the cadmium values in Latvian waters seem surprisingly high. The Zn/Cd ratios of 400-600 has been reported for common types of igneous and sedimentary rocks [17] while a ratio 150 was typical for lakes of Latvia. The substantial difference might indicate that processes other than the weathering of rocks, such as atmospheric precipitation [18] and nonpoint sources contribute to the supply of these elements to the lakes. Similarly the concentrations of lead are somewhat increased in comparison with those of other elements.

Vertical distribution of elements in the sedimentary profiles indicate a significant very recent increase (last few decades), However increasing intensity of sedimentation processes can be related to time span for a period 1950 – 1980 characteristic with an intensive industrialization of the country. Remarkable changes in the sedimentation processes happened after the building of channel connecting lake with the Gulf of Riga in 1842 dramatically changing intensity of accumulation of many trace elements. These changes take place at conditions when traditional low-intensity agricultural activities in the lake basin was common (actually the lake basin is relatively sparsely settled and forests and natural meadows dominates). Thus the sedimentary records of their elemental composition can allow to follow the changes of human induced and natural loading coming from lake basin.

IV. Conclusion

The metal concentrations in sediments of lakes in Latvia are at a background levels. This may be explained with a geochemical factors and abundance of sedimentary deposits in the drainage basins, as well as minimal anthropogenic load. In the same time in several places direct anthropogenic impacts are evident; regarding influences of point sources both transboundary transport impacts. Analysis of elemental composition of sediment profiles can provide information about the changes of human induced and natural loading within the lake basin.

REFERENCES

[1] W. Solomons, U. Förstner, *"Metals in the hydrocycle"*, Berlin: Springer Verlag, 1984.

[2] U. Förstner, G.T.W. Wittman, *"Metal pollution in the aquatic environment"*, Berlin: Springer Verlag, 1979.

[3] E. Steinnes, "Lead, cadmium and other metals in Scandinavian surface waters, with emphasis on acidification and atmospheric deposition", *Sci.Total Environ.*, vol. 9, pp. 825-831, 1990.

[4] C. Pettersen, K. Hakanson, S. Karlson, B. Allard, "Metal speciation in a humic surface water system polluted by acidic leachates from a mine deposit in Sweden", *Water Res.*, vol. 27, pp. 863-871, 1993.

[5] K. Lenvik, E. Steinnes, A.C. Pappas, "Contents of some heavy metals in Norvegian rivers", *Nordic Hydrol.*, vol. 9, pp. 197-206, 1978.

[6] Anonymous, "Environmental problems of River Rhine", *The council of experts on environmental affairs (FRG),* Stuttgart: Kohlhammer, 1976.

[7] H. Borg, K. Johansson, "Metal fluxes to Swedish forest lakes", *Water, Air and Soil Pollut.*, vol. 47, pp. 427-440, 1989.

[8] D.C. Runnels, T.A. Shepherd, E.A. Angino, "Metals in water: Determining natural background concentrations in mineralized areas". *Environ. Sci. Technol.*, vol. 26, pp. 2316-2323, 1992.

[9] *Water analysis*. (Ed.W.Fresenius, W.Schneider). Berlin: Springer Verlag, 1988.

[10] *Standard methods for the examination of water and wastewater*, Washington: APHA, 1989.

[11] *HACH water analysis handbook,* 2nd ed. Loveland: HACH, 1992.

[12] M. Csuros, C. Csuros, "*Environmental Sampling and analysis for metals*", Boca Raton: CRC Press, 2002.

[13] O. Heiri, A.F. Lotter, G. Lemcke, "Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results", *J.Paleolimnol.*, vol. 25, pp.101-110, 2001.

[14] F. Schönhofer, G. Wallner, "Very rapid determination of ^{226}Ra, ^{228}Ra and ^{210}Pb by selective adsorption and liquid scintillation counting", *Radioactiv. Radiochem.*, vol. 12, pp. 33-38, 2001.

[15] Y.Y. Ebaid, E.M. Khater, „Determination of ^{210}Pb in environmental samples", *J. Radioanal. Nucl. Chem.* vol. 270, pp 609–619, 2007.

[16] *Environmental quality criteria.* Lakes Watercourses. Report 5050, Stockholm: Swedish EPA, 2000.

[17] K.K.Turekian, "*The oceans, streams and atmosphere*", Berlin: Springer Verlag, 1969.

[18] G. Lithner, "Some fundamental relationships between metal toxicity in freshwater, physicochemical properties and background levels", *Sci. Total Environ.*, vol. 87/88, pp. 365-380, 1989.