



The Analysis of Sediments Contamination with Heavy Metals after Hydro-mechanical Treatment in the Southern Part of Lake Babrukas

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Abstract

Analytical method of X-ray fluorescence spectrometry and specifically Niton XL2 device for analysis of bottom sediments of lake Babrukas is analyzed in the article. The reliability of the method of X-ray fluorescence spectrometry for analysis of heavy metals is compared with atomic absorption spectrometry. Results of this method show a very impressive correlation of atomic absorption method. Quality parameters – concentrations of heavy metals in sediments are analyzed. Results of the analysis are overviewed and compared with concentrations of heavy metals in relevant legal documents in Lithuania. It is concluded that the X-ray method gives important and reliable information of anthropogenic impacts for lake ecosystems and human health. The assessment of heavy metals in bottom sediments with X-ray fluorescence method is much quicker and cheaper, thus it gives the opportunity to analyze more samples and more properly assess distribution of pollutants in the lake sediments.

The largest technogenic origins of heavy metals concentrations were determined. Geostatistical analysis shows the distribution of concentrations of heavy metals in surface and subsurface layer. The interpolated concentrations of heavy metals are given in maps using Golden Software Surfer computer program. It perfectly shows the distribution and concentrations of heavy metals in surface and subsurface layers after hydro-mechanical treatment. It appears that concentrations of heavy metals in surface layer are still much higher than in subsurface after the hydro-mechanical treatment.

After the detailed lake sediment studies the extent of anthropogenic impact which can be harmful to the lake ecosystem and human health is assessed. Most importantly it can give significant information about the centers of contamination and thus specify locations where hydro-mechanical treatment should be concentrated.

Keywords: X-ray fluorescence spectrometry; heavy metals; hydromechanical treatment.

Nomenclature

$\lambda\alpha(\underline{u})$	weight assigned to the measured concentration
$m(\underline{u})$	expected values of the random variables
$Zx(\underline{u})$	concentration to be estimated

1. Introduction

It is widely accepted that heavy metal contamination in sediment, soil and groundwater is one of the largest threats to environmental and human health. Sediments are the principle sinks for heavy metals in aquatic environments and can result in a secondary contamination source affecting the ecosystem. Analysis of heavy metal amounts in sediments and comparison with reference levels is a reliable indicator of ecosystem health, however understanding the distribution of pollutants is among most essential information for environmental research and critical for environmental management and decision-making. Environmental pollution studies are becoming increasingly important, not only to determine the cause and extent of pollution, but also to carry out effective environmental cleaning and targeted implementation of pollution prevention [1].

Heavy metals are considered serious pollutants not only because of their persistence and non-degradability in the environment but also because most of them have toxic effects on living organisms when they exceed a certain concentration [2], [3]. Additionally, aquatic organisms can bioaccumulate, biomagnificate or biotransfer certain metals to concentrations

high enough to bring about harmful effects, especially by the transfer of metals through the food chain [4]. Despite the differences in toxic effects of the metals, environmental conditions and the time of exposure, their concentrations are reliable indicators of ecosystem health [1].

One of the most common methods for assessing pollution levels and quantifying metal enrichment in bottom sediments is to compare identified concentrations with a background level or with a concentration posing serious environmental risks (e. g. maximum concentration defined in legal environmental regulations and guidelines). However, understanding distribution of pollutants is critical for the environmental management and decision-making [5], and spatial distribution of metals in sediments is among the most essential information for environmental research [6].

Partial (or full) sediment removal by the use of hydro-mechanical means is widely used to remove bottom sediments from water bodies. Adsorbed form of heavy metals prevailing during hydro-mechanical bottom sediments removal process can be very quickly desorbed into a free toxic form, this problem is in particular relevant when metals-contaminated bottom layer is exposed or bottom sediments lifted into water column because of sedimentation forming a new metals-contaminated surface layer.

A method combining both data on concentrations of sedimentary metals after hydro-mechanical treatment and simulation using algorithms of spatial interpolation and a geographic information system was applied to assess distribution of heavy metals in the southern part of Lake Babrukas.

2. Methodology

The location of sampling sites was influenced by two major assumptions: to provide uniform spatial coverage of the southern bay of the lake Babrukas, and to allow assessment of sediment quality through the surface (0–0.6 m) and subsurface (0.6–1.2 m) layers of bottom sediments. For this purpose, the area of the southern part of the lake was covered with a grid, consisting of equilateral blocks with a border length of 10 m, forming 47 sampling sites in the intersection points of the gridlines. The coordinates of intersection points of the grid, were set with Garmin GPS „eTrex Venture“. The grid was then overlaid on the sediment distribution map and the points lacking sufficient sediment layer were screened out, resulting in 31 final sampling sites (Fig. 1). Samples from each of the two layers of bottom sediments were collected in the 31 sites constituting a total batch of 62 samples.

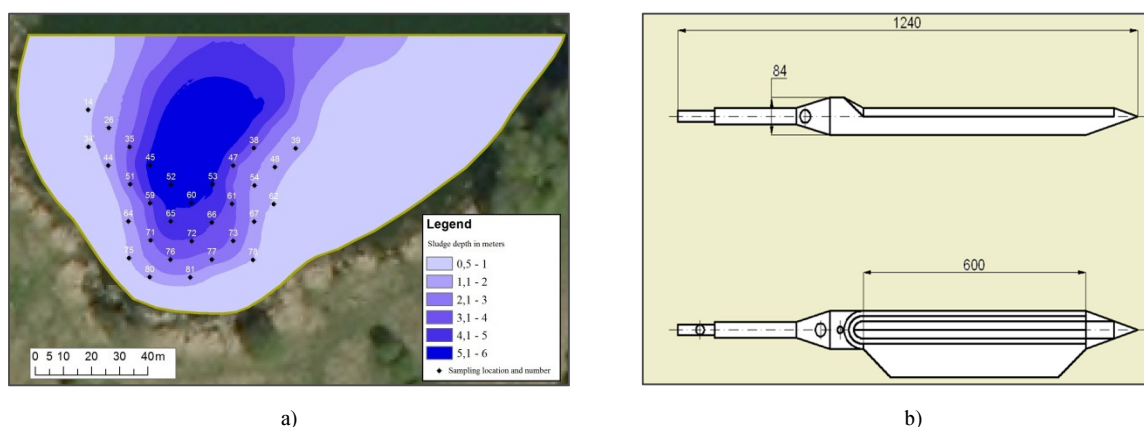


Fig. 1. Sampling sites (a) overlaid on the sediment distribution map and corer (b) with protective valve

Sampling was performed on the ice, drilling holes, and taking sediment samples using a stainless steel sediment corer with a protective valve (Fig. 1) to ensure isolation of the core from surrounding sediment and water.

In each of 31 sampling sites, sediment core samples were taken from the surface (0–0.6 m) and subsurface (0.6–1.2 m) layers of lake bottom sediments. The length and diameter of a sampled sediment core amounted up to 60 cm and 8 cm, respectively. Each sediment core sample was placed in a sealed polyethylene bag and transported to the laboratory.

Each sediment core sample was homogenized to create a uniform batch, and a combined sample from each batch was taken and placed in a Petri dish to promote uniform air drying. Samples were dried for 11 hours at the temperature of 110 °C and ground using a porcelain pestle and mortar. Grounded samples were sieved through a 2.0 mm and 250 µm stainless steel sieves, as required for X-Ray Fluorescence analysis [7]. Sieved samples were analyzed using a Thermo Scientific Niton® XL2 X-Ray fluorescence spectrometer.

2.1. Hydro-mechanical treatment

Hydro-mechanical removal of bottom sediments from the lakes is based on destruction of sedimentation layers and their mixture with water. This process causes destruction of relatively stable compounds and complexes, vertical and horizontal migration of various materials and resuspension processes. Though interrelation between the water body bottom sediments removal and water pollution is universally recognised, there is surprisingly limited amount of information about behaviour of pollutants and their potential hazard to environment during the execution of works and upon their completion. This

shortage of information usually is explained by rapid physical and chemical changes in water and bottom media and their variability in time and space [8]. Though the bottom disruption itself and its caused redistribution of sediment particles affects 50–100 m wide zone at a time and lasts only from a few to under twenty hours [9], but big and uneven gradients of sediment particles concentrations, processes of sedimentation and secondary pollution redistribution are very complex and not thoroughly researched [1], [10], [11].

2.2. X-ray fluorescence spectrometry

XRF spectroscopy is an analytical technique that exposes a solid sample to an x-ray source. The x-rays from the source have the appropriate excitation energy that causes elements in the sample to emit characteristic x-rays. A qualitative elemental analysis is possible from the characteristic energy, or wavelength, of the fluorescent x-rays emitted. A quantitative elemental analysis is possible by counting the number (intensity) of x-rays at a given wavelength [12].

Fully prepared XRF samples showed excellent correlation with laboratory AAS for material split after the final grinding, sieving, and homogenization. A set of 20 fully prepared XRF samples (oven dried, ground to 0.125 mm), including 11 bridge site samples, 6 residential lead samples, and 3 NIST SRM soils, gave a linear regression slope of 1.004 and an R² of 0.995. For the 17 samples with lead concentrations above 100 ppm, the mean recovery of the XRF relative to AAS was 0.952 and the standard deviation of the recovery was 0.068, for an RSD of 7.1 percent [13].

2.3. Spatial interpolation

The kriging interpolation technique was used to demonstrate spatial distribution patterns of heavy metals in the two layers of sediments in the northern part of Lake Babrukas. Kriging is a method of interpolation, which predicts unknown values from data observed at known locations.

This method uses a variogram to express spatial variation, and minimizes the error of predicted values which are estimated by spatial distribution [14]. In a geostatistics context, kriging can be defined as a generalized linear regression technique used with a variogram model for spatial data interpolation. In this study, the spatial data are the measured concentrations of metals in sediment. The linear regression estimator $Z(\underline{u})$ is the unknown concentration to be estimated by kriging, Eqn. (1).

$$Z(\underline{u}) - m(\underline{u}) = \sum_{\alpha=1}^{N(h)} \lambda_{\alpha} [Z(\underline{u}_{\alpha}) - m(\underline{u}_{\alpha})], \quad (1)$$

$\lambda_{\alpha}(\underline{u})$ is the weight assigned to the measured concentration $Z(\underline{u}_{\alpha})$, which is interpreted as a realization of the random variable $Z(\underline{u}_{\alpha})$. The means $m(\underline{u})$ and $m(\underline{u}_{\alpha})$ are the expected values of the random variables, $Z(\underline{u})$ and $Z(\underline{u}_{\alpha})$. The mean $m(\underline{u})$ is used to represent the large scale variation (trend) in the data [15]. Spatial interpolation in this study was performed by using ordinary kriging, where the mean $m(\underline{u})$ is unknown and allowable to fluctuate globally, but assumed constant within the local neighbourhood. It is assumed that kriging provides statistically optimal and unbiased prediction [16–18]. Kriging procedures were performed and spatial distribution contour maps were prepared using Golden Software Surfer 9.0 software package.

3. Results

3.1. Comparison of results with normative documents

Results of the heavy metals X-Ray Fluorescence analysis are presented in Table 1, along with maximum allowable concentrations for the sludge of I-III category (LAND 20-2005), because Lithuanian legislation does not provide requirements (or permissible values) for heavy metals concentrations in sediments of natural water bodies. Almost all average values of heavy metals in surface (0–0.6 m) sediment layer do not exceed the concentrations that are determined for the I sludge category. Only Cd (8.6 times) and Hg (6.8 times) exceeds the requirements for I sludge category. Surface layer sediments are attributed to the II category sludge which means that sediments are slightly polluted with heavy metals and can be used with restrictions that are specified in Lithuanian environmental normative document (LAND 20-2005). Subsurface (0.6–1.2 m) layer sediments are not contaminated with heavy metals and all concentrations are significantly lower than surface layer sediments. Pb, Cd, Ni, Hg concentrations are below the level of detection.

Table 1. Concentrations in sediments and sludge

Sludge category	Heavy metals concentrations, mg/kg						
	Pb	Cd	Cr	Cu	Ni	Zn	Hg
I	< 140	< 1.5	< 140	< 75	< 50	< 300	< 1.0
II	140–750	1.5–20	140–400	75–1000	50–300	300–2500	1.0–8.0
III	> 750	> 20	> 400	> 1000	> 300	> 2500	> 8.0
Babrukas lake 0–0.6 m deep layer	32.65	12.97	61.62	20.85	39.05	37.91	6.87
Babrukas lake 0.6–1.2 m deep layer	<LOD*	<LOD	23.75	21.39	<LOD	22.33	<LOD

*LOD – level of detection

3.2. Results of spatial interpolation

The results of spatial interpolation for these metals (As, Cr, Cu and Zn) are presented in Figs. 2–4. Cu was detected in 13 samples of the surface layer of bottom sediments and in 7 samples of the subsurface layer. Cu concentrations in surface layer are visually situated in four centres. Moving away from these centres concentrations fastly decrease (Fig. 2). Concentrations in subsurface layer are much lower. Comparing Cu concentrations in surface and subsurface layers, it is obvious that Cu concentrations are much higher in surface layer, thus it shows anthropogenic influence for lake ecosystem.

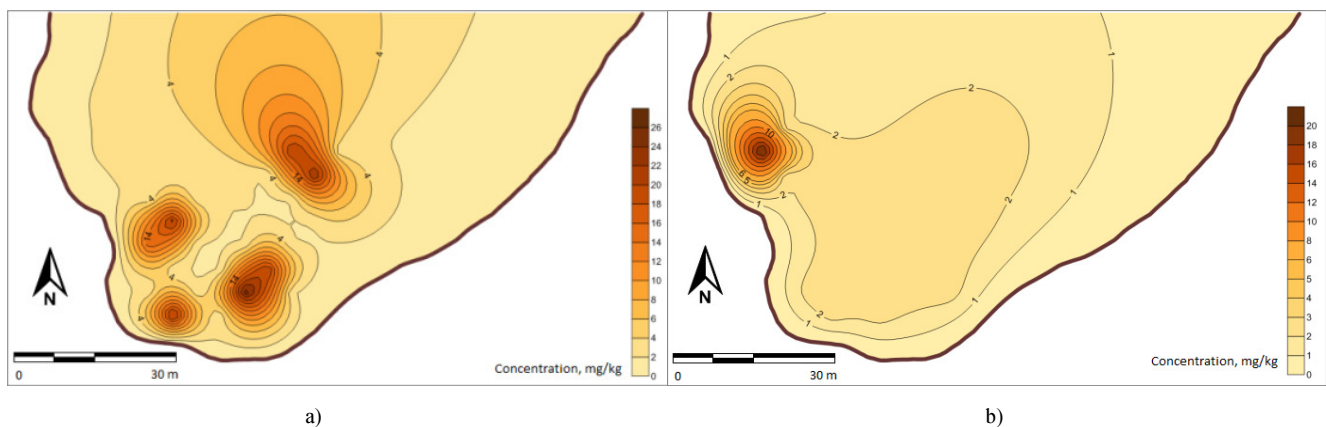


Fig. 2. Cu concentrations in surface (a) and subsurface (b) layers

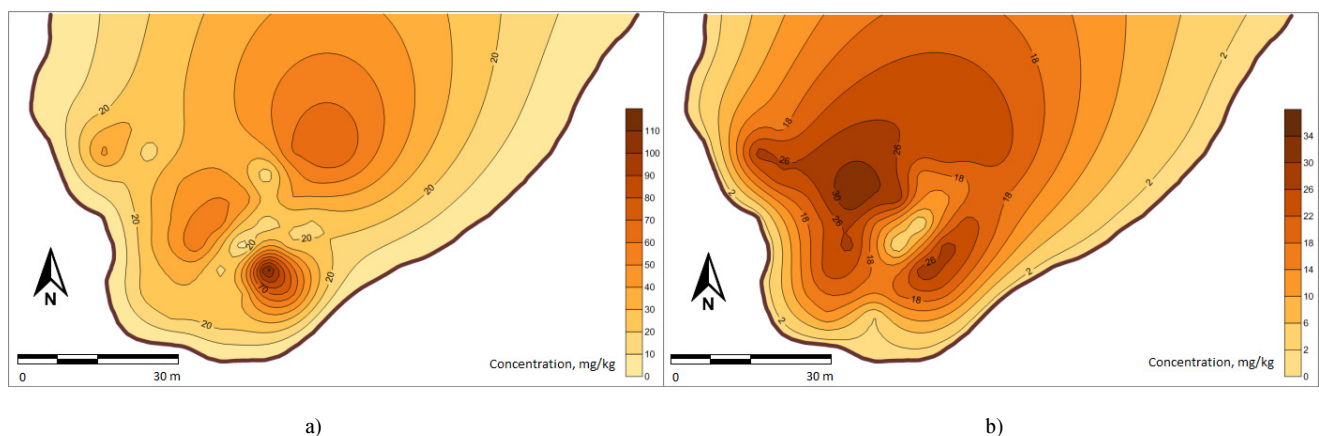


Fig. 3. Zn concentrations in surface (a) and subsurface (b) layers

Zn was found in 15 and 12 samples of the surface and subsurface layers, respectively. Zn concentrations show that there are two certain centres in surface layer. These concentrations are much higher than in subsurface layer. Quite low and equivalent concentrations are observed in subsurface layer (Fig. 3). It also shows that this pollution can be caused by anthropogenic activity. The hydro-mechanical treatment was not effective enough as we can see the surface layer sediments are slightly polluted with Zn. Hydro-mechanical treatment did not reach enough deep to remove the layer which is significantly polluted with such heavy metals.

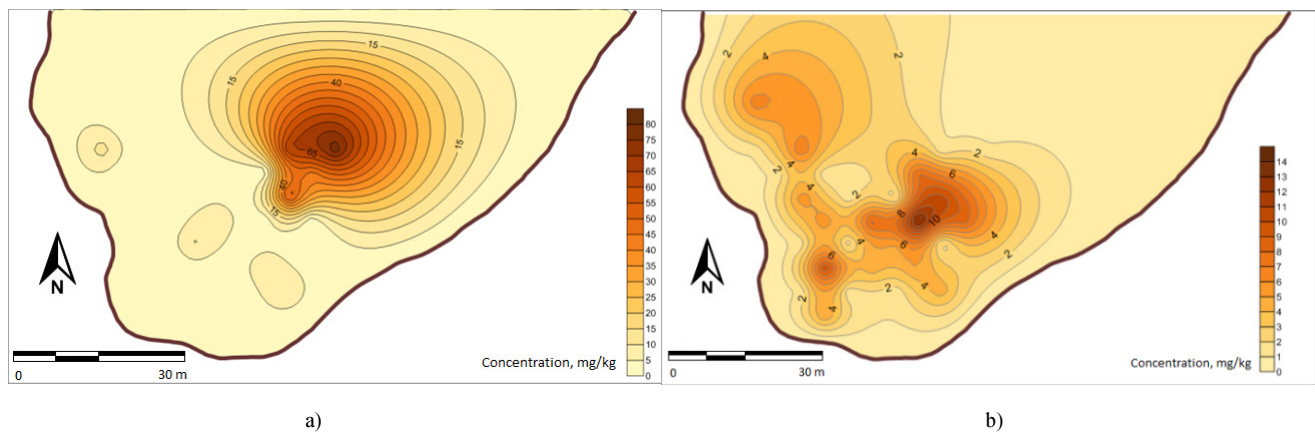


Fig. 4. Pb concentrations in surface (a) layer and As concentrations in surface (b) layer

Pb was found in 4 samples of the surface layer only. Concentrations show that there is one centre of this metal which is situated in the eastern side of the area. As was found in 7 samples of the surface layer only and the highest concentrations are also situated in the eastern, south eastern part of the analysed area (Fig. 4). A comparison of heavy metal amounts and spatial distribution patterns in the two layers of sediments reveals higher pollution levels in the surface (0–0.6 m) than subsurface (0.6–1.2 m) layer by most metals, namely Cu, Zn, As, Pb and others.

Although distribution of metals in aquatic environments is determined by many physical and chemical processes, the general trend of high concentration anomalies stretching through the southern part of the lake towards its centre point may be explained by former discharges of wastewater into the littoral zone of the southern shoreline. Taking into account the distribution of heavy metals concentrations the hydro-mechanical treatment should be carried not only in the coastal areas but also in such locations where concentrations of heavy metals distribute.

4. Conclusions

1. The comparison of heavy metals concentrations in surface layer with normative documents showed that Cd 8,6 times and Hg 6,8 times exceeds the requirements for I sludge category (LAND 20-2005);
2. The concentrations in subsurface sediments layer are much lower and do not exceed the requirements for I sludge category;
3. Spatial interpolation in surface layer showed that the concentrations of heavy metals are mostly situated in the south and south-eastern part of the analysed area;
4. The interpolated concentrations of subsurface sediments layer showed that concentrations are much lower and situated in one or few centres that do not exceed requirements for the I sludge category;
5. Measured concentrations and spatial distribution showed that hydro-mechanical treatment should not be only concentrated on the coastal area but also situated to the pollution centres.

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