Selection of investigation methods for heavy metal pollution on soil and sediments of water basins and river bottoms: a review

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Most heavy metals have a negative impact on humans and the environment. Thus, evaluation of toxin concentration in the environment allows taking measures to improve the quality of life and the environmental conditions. In order to accomplish the research, more accurate methods to reflect the real research object data, are required. Various pedogeochemical researches on pollution with heavy metals in Lithuania started in the 6th decade of this century and since then a lot of large-scale studies have been done. The methods used in these studies have become a methodical basis for other researchers. All these research methods have a sequence, accurate order of coherent field work planning and its uimplementation. Furthermore, these researches require accurate laboratory studies, hitech and the newest analysis methods. This work describes the most commonly examined and applied research methods, focusing on practice, which often raises research objectives. Besides, the paper presents the sequence of research works from sampling up to the methods and tools for analysis of results.

Key words: heavy metal, soil, bottom sediments, methods, sampling, analysis, extraction

INTRODUCTION

Heavy metals (HM) get into the environment in different ways: with industrial, agricultural and household wastewaters, atmospheric deposits, or in the process of extraction of natural resources. The major part of heavy metal accumulates on the surface of soil and in the upper layers of bottom sediments of water basins. Heavy metals mix with the substances existing in such upper layers and change their characteristics. Soil reaction (pH) conditions a mobile form of HM amounts and organic substances in sediments acting like a buffer and storing these materials for a long time (Budavičius, Kadūnas, 1999; Crusberg et al., 2004; Hullebusch et al., 2005; Smolders et al., 2007; Liu et al., 2009).

The degree of the HM accumulation in surface sediments depends on different emission sources and the distance between them. As per data of investigations of other authors, the HM amounts in soil, river and lake bottom sediments depend on what human settlements and industrial objects are in the neighbourhood (Grčman et al., 2001; Salati, Moore, 2009; Liu et al., 2009; Martin-Puertas et al., 2009; Jernström et al., 2010).

High HM concentrations in the surface layers of soil have an adverse effect on soil organisms as well as on humans. The researchers, who studied Lithuanian soils, found that the sickness rate of adults and teenagers with diseases caused by heavy metals was as much as 1.4–4.5 times and that of children under14 as much as 1.5–3.9 times higher in the areas contaminated with these toxins, in comparison with the average sickness rate with such diseases in the country (Smolders et al., 2007; Juozulynas et al., 2008). Similar assumptions can be made regarding the HM accumulation in bottom sediments of water bodies.

In order to evaluate the ecological status of surface sediments and their impact on biota and man, it is important to measure the HM amounts. A great variety of surface sediments, various HM mobility forms, different levels and sources of contamination require different methods of investigation to measure the concentrations of these toxins.

The methods for geological investigation of the environment (ecogeological conditions, geological potential) have been in the constant process of development for over twenty years and are based on the experience of concrete investigations (Baltrūnas et al., 1998).

Over the last twenty years, many large-scope investigations have been conducted in Lithuania and the methods

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applied have become the reference ones for other researchers. Such methods are in compliance with the globally used techniques, applicable to similar investigations.

The course and methods of investigation, used in geochemical mapping of Lithuanian towns, have become the key ones for measuring urban geochemical pollution (Gregorauskienė, 2006).

The techniques used in the geochemical mapping of the territory of Lithuania have become the reference methods for the assessment of geochemical pollution of non-urban areas. Further, the geochemical mapping of the territory of Lithuania was the basis for the development of methodology to investigate the bottom sediments (Kadūnas et al., 1999).

The methods, used for the assessment of the microelement pollution level in Vilnius residential districts and for geochemical mapping of the territory of Lithuania, served as the basis for methodology used in investigating the HM concentration in surface soils around the sources of pollution of anthropogenic origin (factories, boiler-houses, other plants) (Kadūnas et al., 1999; Taraškevičius, 2000).

The Regulation of Ecological Investigations establishes sampling and sample analysis methods to be applied in territories, contaminated with chemical substances (Lithuanian Geological Service... 2008).

Examination of microelement composition of technogenically polluted lake bottom sediments defines the methods for evaluating their geochemical pollution (Radzevičius, 2001).

Investigations of microelement composition of other environmental components, e. g. arable lands, or lands fertilized with sewage sludge, are carried out applying the methods regulated by the legal acts and different standards.

This paper presents a summary of the major methods and procedures, field and laboratory works, including the order of priority, applied for the investigations of surface sediments.

MATERIALS AND METHODS

Selection of sampling sites

The first step in any investigation is to formulate clearly and precisely the purpose and define the appropriate field works: in order to get a result reflecting a concrete process or object, it is necessary to precisely determine the position of each sampling site; each site must give a separate representative result. Generalising data can be obtained if we select obviously similar objects, the size of which complies with the scale requirements and the degree of the parameter change, which in the area should be minimal. Besides, it is necessary to collect a statistically adequate number of subsamples from a representative area so that the real error of the mean result of subsamples would not be higher than the error of the analysis method (Taraškevičius, 1998).

For soil sampling around local pollution sources, a sampling grid is formed depending on the conditions and purpose of investigation. If pollution is predicted to be spread evenly, samples are collected at regular distances from each other. If pollution is predicted to be spread unevenly, the distances between samples depend on the distance from the source of pollution (the nearer the source of pollution the denser the sampling grid) and other factors influencing the spread of pollution (wind direction, soil gradient) (Baltrėnas et al., 2003; Skoulikidis et al., 2008).

When mapping the HM contamination in urban soils, the sampling grid should be irregular, depending upon the technogenic load. In residential districts without potential sources of pollution, soil is mapped by a 250×250 m grid; and in sanitary zones of enterprises, by a 100×100 m grid. Within the territories of enterprises and other sources of pollution, the sampling grid is made even denser by separating pollution sources and their outwash areas. In a pollution source itself, the sampling grid formation methods, designed for territories of local pollution sources, are applied (Gregorauskienė, 2006).

For the investigation of larger soil areas, e. g. territories of separate districts or countries, the sampling grid with a 10×10 km mesh size is applied. The sampling sites within a grid mesh should represent 4 soil types of different mechanical composition, namely clay-loam, sand, sandy loam and peat. Each sample should represent one fourth of the grid mesh. In the absence of any soil type, an additional sample of a prevailing soil type is taken. Such methods enable drawing monoelemental (pollution) maps of separate soil types according to the mechanical composition. Upon calculation of the spread of separate soil types in each mesh, it is possible to make monoelemental (pollution) maps of mean values (geochemical field) (Kadūnas et al., 1999).

The Regulation of Ecological Investigations indicates that a territory, in which the activities listed in Annex I of the order have been pursued, has to be divided into parts (blocks) of the same size. The number of blocks and amount of collected soil or ground samples depends on the area of the territory (Lithuanian Geological Service..., 2008).

It is rather complicated to make a sampling grid for investigation of river bottom sediments (except for very large rivers) because rivers are linear-type objects. When investigating the effects of local pollution sources on river bottom sediments, the sampling sites, closer to the pollution source, have to be denser and the samples should be taken from the fairway in order to avoid bottom sediment folding differences related to seasonal fluctuation of river water.

When investigating the sediments of rivers in large areas (territories of separate districts or countries), the samples are taken from the segment of the river which falls within a 10×10 km grid mesh. If several rivers fall within the mesh, samples are taken from the river in the region of the basin, which occupies the greatest area of the mesh (Kadūnas et al., 1999).

Bottom sediment sampling from standing water bodies and lakes is based on several factors, influencing accumulation of heavy metals in bottom sediments. The HM accumulation is influenced by prevailing currents, waves, a littoral

zone and the like. In particular, sampling should be avoided in the littoral zone of lakes or ponds, because in this part the folding of sediments is mostly affected by waves. Besides, littoral zones exhibit a specific accumulation of organic substance, which is conditioned by the peculiarities of a concrete littoral (Kilkus, 2005).

An investigation of HM concentration in bottom sediments of water bodies is started with exploration drilling through the cross-section of sediments in order to study the peculiarities of sediment composition (granulometric content, amounts of organic matter, etc.), which influences the distribution of microelements. In lakes and other water basins, samples are taken in profiles oriented according to the vertical axis of the lake by crossing the deepest depressions of the lake. Such sampling sites are positioned by using bathymetric plans of the lake. Occasionally, sampling is done by dividing the area of the lake based on the grid principle. After the sampling sites are positioned, they are linked to geographical objects or a satellite GPS (*Global Positioning System*) is used for the detection of such sites (Larsen, 2000; Mecray et al., 2001; Kadūnas, Radzevičius, 2003; Skoulikidis et al., 2008).

Principles of sampling and subsampling

Soil sampling is most often accomplished by selecting, according to the "envelope" principle, i. e. 5 subsampling sites within the representative area of the single sampling. Subsampling sites are selected at a distance of 1–5 m from each other, and the subsamples collected are put into one representative sample (Kadūnas et al., 1999; Baltrėnas et al., 2003).

Soil sampling in fields, used for agricultural needs, is recommended to possibly represent the whole field. If a field is composed of several soil types, the subsamples are taken from each type of soil (LST ISO 10381-2 : 2005).

In agricultural lands fertilised with sewage sludge, 25 samples per 5 ha area have to be taken (The Council of..., 1986).

No data are available on the number of subsamples when investigating the microelement composition of bottom sediments of lakes, probably because of complicated collection procedures of such samples. Most frequently, a single sample is taken from bottom sediments of the lake to represent the whole area (Budavičius, 2003).

To investigate river bottom sediments in large territories, 3–5 subsamples at a distance of 20–50 m apart are collected to form a representative sample (Kadūnas et al., 1999).

When investigating contamination of river bottom sediments with heavy metals around local sources of pollution and when sampling in the river fairway, it is recommended to collect 3–5 subsamples to achieve the greatest preciseness of the representative data and to avoid different anomalies. However, such multiple sampling often encounters difficulties; therefore, researchers most often confine to a single sample from a selected river section.

Selection of sampling depth

The depth of sampling from surface sediments depends upon the purpose of investigation. For the most precise examination of soil contamination with heavy metals, which fall onto soil from air, samples should be collected from the top surface layer of soil at a depth of 0–6 cm (Taraškevičius et al., 1999; Baltrėnas et al., 2003). However, in practice samples are also collected from deeper, 0–10 cm or 10–20 cm soil layers (Baltrėnas et al., 2003; Zinkutė et al., 2007).

Samples for ecological investigations should be collected at a depth of 10–25 cm (Lithuanian Geological Service..., 2008); however, in other similar investigations samples are taken from deeper layers of soil (0–30 cm) (Grčman et al., 2001). Samples for studying the HM migration forms in soil are collected at a depth of 0–10, 20–30 and 30–40 cm (Kadūnas, Budavičius, 2001). Samples for geochemical mapping of soil are collected at a depth of 10 cm (Kadūnas et al., 1999). However, any of the above-mentioned depth selections might lack precision due to outwash of clay fractures. Physical clay soil fractures condition the HM spread in deeper (20–40 and 40–60 cm) layers, too. In Lithuanian moderate soils and soils of heavier granulometric composition, physical clay fractures are rather often washed from upper layers into the B horizon (40–60 cm) layer. For this reason, the greatest concentrations of Cr, Ni, Zn and Cu are in this layer (Mažvila, Adomaitis, 2001). Samples for analysis of surface sediments of water bodies are taken at a depth of 20–30 cm (Budavičius, Kadūnas, 1999; Kadūnas, Radzevičius, 2001).

Bottom sediment samples, for investigation of microelemental concentrations and change in their associations during time, are collected from the surface (50 cm) layer to a 12 m depth layer (Mecray et al., 2001; Budavičius, 2003; Skoulikidis et al., 2008; Dong et al., 2009). River sediment samples for the mapping of large territories are collected like soil, from a 0–10 cm surface layer (Kadūnas et al., 1999; Liu et al., 2009).

Sample weight and sampling techniques

The weight of a sample collected, after all stages of treatment and ready for analysis, has to be about 1 gram (Taraškevičius, 1998).

Having evaluated the sample's moisture (which is dried before analysis), the amount of organic matter (which is burned before analysis; heating losses can reach 63% and above) and the portion of a coarse fraction in the sample (which is sieved out), the weight of the sample collected has to be 20–50 g (Taraškevičius 1998; Kadūnas, Radzevičius, 2003). It is advisable to take duplicate samples from another site of the same representative area (Kadūnas et al., 1999).

The choice of sampling techniques depends on the purpose of investigation. Surface soil samples are collected by a spade, and river mud samples are taken with hands or by a shovel (Kadūnas et al., 1999; Baltrėnas et al., 2003).

Sampling from soil layers deeper than 0–10 cm requires a more sophisticated equipment, e. g. soil drills. Samples from surface bottom sediments of lakes are collected by a Van-Veen type shovel. Samples from deeper sediment layers (up to 50 cm) are taken by a Niemist type gravity tube. Sampling in very deep layers is carried out by peat type drills (Kadūnas, Radzevičius, 2003; Budavičius, 2003).

The sampling tool recommended, must be covered with non-metal resistant material or made from stainless steel. Collected samples are poured into plastic or canvas bags (Baltrėnas et al., 2003; Löser et al., 2006; Salati, Moore, 2009).

Samples of soil and river bottom sediments from places of mud deposits are collected in summer (Kadūnas et al., 1999).

Lake bottom sediments, depending on the possibilities and methods applied, can be collected both in a warm period of the year and in winter from ice. The shovels and Niemist type gravity tubes are used for sampling from a boat (Budavičius, 2003).

The sampling with peat type drills requires a strong base; therefore, sampling is done from ice or a pontoon ferry (Kadūnas et al., 1999; Šeirienė et al., 2008).

Sample preparation for analysis
The collected samples are taken to the laboratory, then dried at room temperature and sieved to remove large fractions. Soil is sieved with a 1×1 mm sieve; and bottom sediments with a 0.2×0.2 mm sieve and occasionally a 1×1 mm nylon sieve (Taraškevičius, 1998; Baltrėnas et al., 2003; Budavičius, 2003; Choe et al., 2009). Sometimes, to save time, samples are dried at 105 °C (Sandor et al., 2001; Rippey et al., 2008).

A sieved sample, in particular bottom sediments, contains a lot of organic compounds. Prior to mineralization of samples, the organic compounds should be oxidised to increase the efficiency of acid digestion. It is done by heating samples at 450 °C in a muffle furnace (Kadūnas, Budavičius, 2001; Budavičius 2003; Zinkutė et al., 2007; Lithuanian Geological Service…, 2008).

Ash is treated with royal water (a mixture of nitric acid and hydrochloric acid in a ratio 1 : 3, respectively) or with 20% nitric acid by heating for 15 min. Then, the mixture of the sample and acid is filtered through glass filters (Baltrėnas et al., 2003; LST EN 13650 : 2006; Lithuanian Geological Society…, 2008; Choe et al., 2009).

Royal water is very aggressive, and the hydrochloric acid steam, released during heating, is very strong and dangerous. Therefore, acid is often digested in 65% of HNO_3 and 30% of H_2O_2 using a microwave technique (Tekin-Özan, Kir, 2005; Ciszewski, Turner, 2009).

The above-mentioned processes of heating and acid digestion are necessary when estimating the HM amounts by the methods of atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectroscopy (ICP-MS).

The HM migration forms in samples are determined by a gradual extraction method: a mobile migration form I, i. e. a part of the metal soluble in water and of ion exchange type, is extracted from the sample with ammonium acetate solution (1N NH_4COOCH_3), pH = 7. Then the sample is treated with ammonium acetate solution, pH = 4.8, and in such a way a mobile form II is extracted, which is sorbed by clay minerals, carbons and hydroxides as well as organic components. The migrating or inert form III of microelements is determined by subtracting the data of both analyses from the total microelement amount. The HM in the extract is determined by AAS method (Lubytė, 2001; Kadūnas, Radzevičius, 200).

Sample analysis
Further analysis of samples is carried out using AAS (Atomic Absorption Spectroscopy), ICP-AAS (Inductively Coupled Plasma Atomic Absorption Spectroscopy) and DC Arc ES (Direct current electrical breakdown of a gas atomic emission spectroscopy) atomic emission spectral change analyzers, the essence of which is the registration of intensive atomic emission radiation. ICP-AAS and DC Arc ES procedures register the spectra of direct atomic emission. The above-mentioned techniques differ in the way the atoms in the sample are excited: in ICP-AAS atoms are excited in the inductively excited high frequency plasma, while in the DC Arc ES it occurs in the electric field plasma. The AAS registers the size of the absorption signal of atomic emission spectrum. All these techniques rely on the substance of known composition, i. e. reference substance samples, on which, as a rule, the quality of analysis depends (Taraškevičius, 1998; Lubytė, 2001; Marcovecchio et al., 2006; Fenton, 2002).

AAS is approved in Lithuania, like in other countries, as a national method. The highest permissive concentrations, the methods of analysis and the HM extraction from samples for the AAS are established (Lubytė, 2001; LST EN 13650 : 2006).

Currently, inductively coupled plasma mass spectroscopy and laser ablation inductively coupled plasma mass spectroscopy (ICP-MS; LA-ICP-MS) are often used. These methods are widely applied in different investigations, including soil and bottom sediment analysis (Salati, Moore, 2009; Martin-Puertas et al., 2009; Jernström et al., 2010). These methods are based on extraction of microplasma from the sample. In microplasma, chemical links are interrupted and excited atoms and ions prevail, which are later analysed by mass spectroscopy. ICP-MS and LA-ICP-MS differ as follows: the essence of ICP-MS is that microplasma is extracted from the sample when the sample is introduced into argon plasma (8 000 °C). The essence of LA-ICP-MS is that microplasma is extracted from the sample by a powerful laser beam, which converts the sample into microplasma through evaporation, while further procedures are the same as in ICP-MS (Fenton, 2002; Marcovecchio et al., 2006; Evans Analytical Group…, 2011a).

Another way to determine the microelement composition of samples is to use X-ray fluorescence analyzers (XRF and EDXRF). The work of these techniques is based on the measurement of fluorescence and dispersion of chemical elements excited by X-ray. When analysing samples the concentrations of chemical elements are determined by basic physical identification characteristics (Taraškevičius, 1998; Löser et al., 2006). The above-mentioned methods differ not only in the technique, but also in the preparation of samples for testing. As already mentioned, all sample preparation procedures are required when analysing samples by standardised AAS and ICP-MS methods. These techniques are widely used when analysing the HM pollution in soil and bottom sediments of water basins (Evans Analytical Group..., 2011b). The LA-ICP-MS method is simpler, because sample analysis does not require chemical extraction of microelements. The method itself allows determining the microelement composition even in very small sample amounts (Evans Analytical Group..., 2011a).

For analysis with XRF and EDXRF techniques, the samples need to be finely ground. No additional chemical treatment is required, as in case with LA-ICP-MS (Taraškevičius, 1998).

Another important parameter, is the sensitivity of methods. Sensitivity limits of AAS, ICP-MS and LA-ICP-MS are around 1 ppm, whereas the sensitivity of XRF and EDXRF is about 10 ppm (Marcovecchio et al., 2006; Galbraith Laboratories..., 2009). Updated ICP-MS and LA-ICP-MS analysers reach higher sensitivity limits and can even detect 0.001 ppm metal concentration in a sample (Marcovecchio et al., 2006).

As already mentioned, atomic emission spectrum change analysers are based on reference solvents and concentrations of microelements in them, which is essential for analysis of the prepared samples.

The international reference samples OOKO 151, 152 and 153, SRM 2709 and 2 711 are recommended for soil, and OOKO 301, 302 and 303, OOPE 101, 201 and 401 – for bottom sediments (Kadūnas et al., 1999).

OKOO 152 is used for humus soil, OKOO 153 – for sensitive soil, OKOO 301 – for terrigenous background bottom sediments, OKOO 302 – for anomalous bottom sediments and OKOO 303 – for carbonaceous background bottom sediments (Taraškevičius, 1998). The results of emission spectroscopy are recalculated for air-dry material (Kadūnas et al., 1999).

RESULTS AND DISCUSSION

Calculations and evaluation of the sample analysis results
Having analysed samples and detected amounts of heavy metals and other microelements, a question arises how to interpret the results obtained. The amounts of certain elements in soil can be directly assessed according to the highest permissive concentrations indicated in the hygiene norms (HN 60 : 2004).

A comparison and interpretation of the results of analysis on river or water basin bottom sediments, is rather complicated, because the highest permissive concentrations for such sediments are not specified. Often, the results of such investigations are compared with the requirements for the use of sewage sludge for fertilization and recultivation, seeking a possibly better protection of the environment, when such type matter is used in agriculture (Baubinas, 2003; LAND 20-2005).

Until permissive concentrations of heavy metals and other contaminants in river and water basin bottom sediments are not established, the HM amounts in such sediments may be evaluated according to the permissive values established for technical compost, provided in the technical compost use programme. The programme was prepared on 14 06 2010. It indicates (Annex 2) that the environmental requirements for technical compost use (norms, permissive HM amount in soil, etc.) will be prepared until the year 2012 (Ministry of Environment of the Republic of Lithuania.., 2010).

The degree of contamination with HM or other microelements is most precisely described by the total soil contamination index (Zd), which might also be applied to interpret the data on river and water basin bottom sediments (Budavičius, 2003; Kadūnas et al., 1999; Taraškevičius, Gregorauskas, 1993):

$$Zd = \sum_{i=1}^{n} Kk_i - (n-1) \text{ , where } Kk_i = \frac{C_i}{C_f} , \qquad (1)$$

where C_i: chemical element concentration in the soil sample, C_f: background amount of chemical element in contaminated soil, n: number of chemical elements (Kadūnas et al., 1999; HN 60 : 2004).

Table 1. **Soil contamination degree according to the total contamination index Zd (Kadūnas et al., 1999; HN 60 : 2004)**

Contamination category, degree	*Zd*	Change of public health indices in contamination sources
I. Permissive	<16	Children's lowest sickness rate and a minimal frequency of functional disorder
II. Moderate hazard	16–32	General increase of sickness rate
III. Hazardous	32–128	General increase of sickness rate, increase in the number of frequently sick children and children ill with chronic diseases, having heart and blood vessel functional disorders
IV. Highly hazardous	>128	Increase of children sickness rate, disorder of women reproductive function (increase of the number of pregnancy intoxications, premature babies and dead newborns, and increase of newborn hypotrophy)

The hazard of contamination according to the values of this index is defined in the hygiene norm (HN 60 : 2004), and the effects of the values of this index on human health are presented in the Lithuanian Geochemical Atlas (Table 1) (Kadūnas et al., 1999).

Of particular importance for such evaluation are the microelement background amounts as indicators of both natural and technogenic-geochemical processes (Baltrū-nas et al., 1998).

The background amounts of microelements were established based on long-term geochemical data of different components of the Lithuanian natural environment (soils, river and lake bottom sediments), which are compiled in the data bases of the Institute of Geology and Geography and Lithuanian Geological Society (Kadūnas, Radzevičius, 2003).

A potential ecological risk can be assessed by using the Hakanson index, which was used as a diagnostic tool for water pollution control purposes, i. e. to sort out which lakes or basins and substances should be given a special attention to (Hakanson 1980). The methodology is based on the assumption that the sensitivity of the aquatic system depends on its productivity. The potential ecological risk assessment system is based on the element abundance and several preconditions: (1) concentration – the RI will increase with the aggravated metal pollution degree in sediments; (2) species number – the metals in sediment express the additive effect, namely a potential ecological risk is larger with multiple metals. The metals As, Hg, Cr, Cd, Pb, Cu and Zn are prior considered objects; (3) toxic-response – heavy biological-toxicity metals have larger evidence for RI and magnitude for abundance correction; (4) sensitivity – based on the biological production index (BPI), namely sensitivity was different in different water quality systems (Liu et al., 2009).

The potential ecological risk of a given contaminant is defined (Table 2), as:

$$E_r^i = T_r^i \times C_f^i; \left(C_f^i = C_D^i / C_R^i; C_d = \sum_{i=1}^{m} C_f^i, \right) \quad (2)$$

where E_r^i : the toxic-response factor for a given substance; C_f^i : the contamination factor (a ration between reference records and present concentration values in sediments); Cd : contamination degree of multiple metals; C_D^i : measured concentrations of samples; C_R^i : reference records (Liu et al., 2009).

The sum of the individual potential risks (RI) is the potential risk for the water body (Table 2) (Liu et al., 2009):

$$RI = \sum_{i=0}^{m} E_r^i \quad . \quad (3)$$

The background values for these calculations can be determined by collecting representative samples from zones adjacent to the study areas, which were the least affected by contamination and in which natural processes were taking place. The summary values of the background composition of microelements in soil and river bottom sediments are presented in the Lithuanian Geochemical Atlas (Kadūnas et al., 1999).

The background amounts of microelements in the lake bottom sediments were determined after relevant investigations in Lithuanian lakes (Budavičius, 2003).

One more way to assess the contamination degree with heavy metals is the calculation of the geo-accumulation index (Vinod et al., 2005; Sayadi et al., 2009).

I_{geo} index (geo-accumulation index) can be calculated with the following formula (4), given by Muller (1979):

$$I_{geo} = \log_2 C_n / 1.5 B_n \quad , \quad (4)$$

where C_n is the concentration of the element 'n' in the fraction <63 μm and C_n is the background value for this element in the same fraction. The factor 1.5 is used to take into account possible variations in the background data. I_{geo} classes for the heavy metals Co, Cd and Pb from the sediment samples of ten sampling sites are presented in Table 2. The I_{geo} class 0 indicates the absence of contamination while the I_{geo} class 6 represents its upper limit (Table 3) (Vinod et al., 2005; Sayadi et al., 2009). Statistical evaluation of data obtained was carried out with the statistical package STATISTICA or SPSS (Kadūnas et al., 1999; Kadūnas, Radzevičius, 2001; Skoulikidis et al., 2008).

Table 2. **Indices and grades of potential ecological risk assessment (Liu et al., 2009)**

Potential ecological risk factor E_r^i	Critical range for *i* th heavy metal	Grade for ecological risk factor
	$E_r^i < 40$	Low
	$40 \le E_r^i < 80$	Moderate
	$80 \le E_r^i < 160$	Considerable
	$160 \le E_r^i < 320$	High
	$E_r^i \ge 320$	Very high
Potential ecological risk index	**Critical range for six heavy metals**	**Grade for ecological risk index**
	RI < 110	Low – A
	$110 \le RI < 220$	Moderate – B
	$220 \le RI < 440$	High – C
	$RI \ge 440$	Very high – D

Table 3. I_{geo} classes according to sediment quality (Muller, 1979)

I_{geo}	I_{geo} class	Sediment quality
0–0	0	Unpolluted
0–1	1	Unpolluted to moderately polluted
1–2	2	Moderately polluted
2–3	3	Moderately to highly polluted
3–4	4	Highly polluted
4–5	5	Highly to very highly polluted
5–6	>5	Very highly polluted

Upon performance of statistical calculations and determination of Pearson correlation coefficients "R" between the amounts of microelements, cluster analyses by Ward are often conducted (Budavičius, 2003; Radzevičius, Kadūnas, 2006).

CONCLUSIONS

Collection of soil and, in part, of river bottom sediment samples is mostly accomplished using sampling grids; while subsamples are collected by applying an "envelope" principle. The sampling of water basin bottom sediments is rarer accomplished by sampling grids; instead, the sampling lines are oriented according to the vertical axis of the water basin by crossing the deepest depressions. Soil sampling depth fluctuates from 0 to 60 cm. The samples of water basin bottom sediments are collected at a depth of 0–12 m.

Different sampling techniques are used. Soil samples are most often collected by spades or soil drills. The samples of water basin bottom sediments are collected by shovels, gravity tubes or peat drills. Sampling instruments should not be metal, or they should be covered with resistant non-metal material.

Soil samples can be analysed by applying two analytical methods: AES (atomic emission spectroscopy), ICP-MS (inductively coupled plasma mass spectroscopy). The samples for the most frequently used atomic emission spectroscopy methods are prepared by treating them thermally and mechanically and by conducting the microelement extraction in one or several steps. Any tool should be calibrated by reference samples. However, for investigation of soil and water basin bottom sediments, more suitable are the techniques which do not require chemical treatment of a sample. This saves time and enables avoiding errors, contaminations and other factors which could influence the accuracy of the final result. Therefore, soil and water basin bottom sediment samples are recommended to be analysed by LA-ICP-MS (laser ablation coupled plasma mass spectroscopy); XRF (X-ray fluorescence spectroscopy).

The results of investigations carried out in Lithuania are most often compared to the highest permissive concentrations established by legal acts and to the total soil contamination index (*Zd*).

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DIRVOŽEMIO, UPIŲ BEI VANDENS BASEINŲ NUOSĖDŲ UŽTERŠTUMO SUNKIAISIAIS METALAIS TYRIMO METODŲ ATRANKA

Santrauka

Dauguma sunkiųjų metalų (SM) pasižymi neigiamu poveikiu žmogui ir aplinkai. SM koncentracijų, viršijančių leistinas normas, nustatymas aplinkoje įpareigoja imtis priemonių, kurios pagerintų žmonių gyvenimo kokybę ir aplinkos būklę. Šiems tyrimams atlikti reikalingi metodai, kurie tiksliai atspindėtų realius tiriamo objekto duomenis. Įvairūs pedogeocheminiai užterštumo SM tyrimai Lietuvoje buvo pradėti praeito amžiaus 6-ajame dešimtmetyje. Nuo to laiko buvo atlikta daug platus masto tyrimų, kuriuose taikomi metodai tapo pamatiniais kitiems tyrėjams. Tyrimų metodai pasižymi eiliškumu, nuosekliu lauko darbų suplanavimu ir atlikimu, laboratorinių tyrimų ir naujausių technologijų bei analizių taikymu. Straipsnyje aprašyti dažniausi tyrimų metodai, kurie parenkami atsižvelgiant į keliamus tyrimų tikslus.

Raktažodžiai: sunkieji metalai, dirvožemis, metodai, analizė, dugno nuosėdos