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Original Paper

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Mercury as a potentially toxic element in sediments in the region markedly affected by anthropogenically activity

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The environment is threatened by potentially toxic elements. Transport mediums of potentially toxic elements are water and air flow in individual components of environment. The aim of this paper was to analyze and evaluate the sediment of selected water reservoirs Počúvadlo, Malá Richňava, Veľká Richňava, Windšachta, to determine the concentrations of mercury in monitored water reservoirs in the Banská Štiavnica region. The analyses of the sediment samples were carried out by the flow electrochemistry and the atomic absorption spectrometry. In the study area samples collected from 2001 to 2010, we found the following concentrations of mercury in the range from 0.018 to 0.49 mg kg^{-1} Hg of dry matter. Based on the calculated dependency index, it is possible to assess the development of changes in concentrations over the years as highly dynamic, the natural environment unsatisfactory. From statistical processing by Spearman of sediments data we had ascertained, that dependencies of Hg : As, Cd, Cu, Pb and Zn.

Keywords: mercury, sediment, statistical processing, water reservoirs

1. Introduction

Potentially toxic elements is a concept currently used as a suitable alternative for term of groups of metals and metalloid with specific characteristics affecting the environment. If the concentration of these elements increases over tolerated limit, it may adversely affect human health or crop and livestock production. If we talk about potentially toxic trace elements, we do not preclude that their low concentrations may also act stimulatingly (Khun et al., 2008). Water reservoirs have a significant function for landscapes and act as an important component of watermanagment system. Silting of reservoirs is a process which affects not only the capacity and lifetime of water facilities, but also the way of their use. This process brings a lot of problems (Pariláková et al., 2005). The regions affected by mining activity are considered as risky regions, where an increased content of potentially toxic elements in soil sediments could be found. Due to aeration and oxidation of minerals in these areas there are risky elements released into solutions. One of the problem is that elements are released and mobilized into the environment. Therefore streams, which are located nearby the territory or within the territory of workings and spoil heaps, are considered to be a significant source of pollution. Contaminated water can be brought by these streams and thus highly contaminated sediments, captured as sediments in the waterworks can be delivered after precipitation of risk elements (Šutriepka, 2006). Potentially toxic elements can be significantly toxic even at low concentrations and a large part of them can be accumulated in living organisms. Their presence in sediments can pose a risk of negative changes in the environmental quality. One of the high risk elements is mercury. Mercury has one of the highest accumulation coefficient (Alloway, 1990). It can be considered as a chemical element, which contaminates the environment on a large scale primarily from anthropogenic sources. Its concentration goes up to the range of 0.3 mg kg^{-1} in almost 90 % of all values. Bed load sediments are an important and prior reservoir of pollutants in the contaminated areas of the environment. Bed load sediments indicate reliably the state of environmental pollution (Potančok, 1997). The highest concentrations of mercury are indicated by the sediments from source areas in the Spišsko-gemerské rudohorie and the surroundings of Banská Bystrica (Bodiš and Rapant, 1999). In the sedimental environment mercury poses a high risk especially for sensitive organisms. It is an accompanying element in the complex of siderite-sulphide ores. An increased mercury content in the external flysch zone corresponds with lithology, while the average content of Hg in the claystones is 0.185 mg kg^{-1} and the average content of Hg in the sandstones is 0.137 mg kg^{-1}. The zones containing mercury were identified in industrial areas (Bodiš and Rapant, 1999). The high concentrations of Hg in sediments (>0.09 mg kg^{-1}) are associated with Pb-Zn-Cu, Au-As, Zn-Pb-pyrite, F-Pb-Ba mineralization,

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and mainly with Zn-Pb-Ag-Au-Hg (Salminen et al., 2005). Mercury in sediments shows a good correlation with Cu, Cd ($P > 0.4$) and a low correlation with Zn and P_2O_5. There is an influence of geochemical differences in geological bedrock and mineralized areas on the distribution of mercury in the sediments. This fact indicates the mineralization process (Cu, Zn, Cd). The organic matter plays a key role in a solid binding between mercury and the environment, thus it contributes to a reduced migration of Hg in the environment. Inorganic mercury is more bound to the organic matter, whereas organic mercury has a low degree of dissociation and adsorption. Mobility of mercury is increased by the influence of decomposition of its organic complexes and there starts up the formation of solid complexes with fulvic and humic acids. Mercury sorbs to humus if the pH is acidic, in an alkaline medium it sorbs to clayey minerals, oxides and hydroxides of other metals (Kabata-Pendias and Pendias, 1984; Urminská, 2011). Microorganisms have a significant impact on the occurrence and migration of mercury in soils, and mercury can be methylated and reduced by microorganisms (Urminská, 2011). The pollution is also affected by other anthropogenic activities, eg. poor quality application of phosphate fertilizers or burning of fossil fuels (Salminen et al., 2005).

The aim of this work is to analyze sediments in the selected water reservoirs of Piargs group (Počúvadlo, Malá Richňava, Veľká Richňava, Windšachta) and to determine the concentrations of mercury in these sediments. Moreover, results gained by chemical analysis and with emphasis on the environment the study focuses on the prediction of potentially negative effects of mercury contained in sediments on organisms. Furthermore, our target is to determine the correlation relationships and the statistical significance of dependencies of analyzed environmental parameters.

2. Material and methods

The status of the monitored areas has been assessed based on the observation and chemical analysis of sediments from selected water reservoirs in Banská Štiavnica territory. A statistical analysis was performed by "Indices Analysis" (Obtulovič, 2010) and "Spearman's rank correlation coefficient" (Stehlíková, 1999). The Spearman's rank correlation coefficient (ρ_s) is a measure of dependence based on measurement of the correlation between rankings. The calculation of Spearman's correlation coefficient (Stehlíková, 1999 in Urminská, 2002):

$$\rho_s = 1 - \frac{6\sum_{i=1}^{n} d_i^2}{n \cdot (n^2 - 1)}$$

The coefficient indicates the interdependence between two elements, e.g. interdependence between the concentration of two specific elements. $\Sigma\, d_i$ ($i = 1, 2, ..., n$) means the sum of the differences between ranking, n represents the number (eg. number of monitored community). "Indices Analysis" represents an analysis of phenomena and processes of which we would like to assess in aspect of their development dynamics, time, place and matter-of-fact define (Obtulovič, 2010).

Sediment samples were taken once a year in autumn from the selected water reservoirs. Samples were taken mainly with a hand sampler from a part of the bank. The weight of all samples was up to 5 kg. Samplings were carried out from a dam sediment and from the settled sediment located opposite the dam. In 2002 the samplings from the water reservoirs Počúvadlo, Malá a Veľká Richňava were taken from the depth of 3.0 m, 5.0 m and 8.0 meters using a submersible digger launched from a boat. The Windšachta sediment was taken from a bottom of the reservoir using a sink-hole technique. One analysed sample represents five samplings from one sampling location, while the sample material was mixed in a clean polyethylene containers. To determine the content of analyzed element a sedimental fractionation with the texture under 0.125 mm has been used. Two different methods such as a flow electrochemical method and an atomic absorption spectrometric method have been used to analyze chemical elements in the leachate.

3. Results and discussion

The concentration of mercury in sediments was ranged from 0.018 mg kg^{-1} to 0.49 mg kg^{-1} in dry matter during the period from 2001 to 2010. In accordance with the assessment presented in The Methodological Instruction of the Ministry of Environment of the Slovak Republic no. 549/98-2 findings show that mercury concentration most exceeded the limit (0.3 mg kg^{-1}) by 63.3 % in Windšachta sampling location. And according to the Law no. 220/2004 on the conservation and use of agricultural land. Mercury concentration not exceeded the limit for this Act (0.75 mg kg^{-1}) and reached only 65.3 %. In accordance with the assessment presented in the Law no. 203/2009 – Attachment 8 – Part 3 supplementing Law no. 188/2003 Application of sewage sludge and bottom sediments in the soil. Mercury concentration not exceeded the limit (10.0 mg kg^{-1}) and reached only 4.9 % of the sampling sites Windšachta.

Average concentrations of mercury in our sampling locations showed moderate-to-high dynamics during the period from 2001 to 2010 (Fig. 1–4). This phenomenon could be caused by local hydrometeorological conditions, by changing thermodynamic conditions and by anthropogenic activities (Urminská, 2011).

The most significant high-to-extreme high index values have been found in the dam sampling location of the water tank Počúvadlo in 2003. It was decreased by 86.96 % compared to year 2002. The index values

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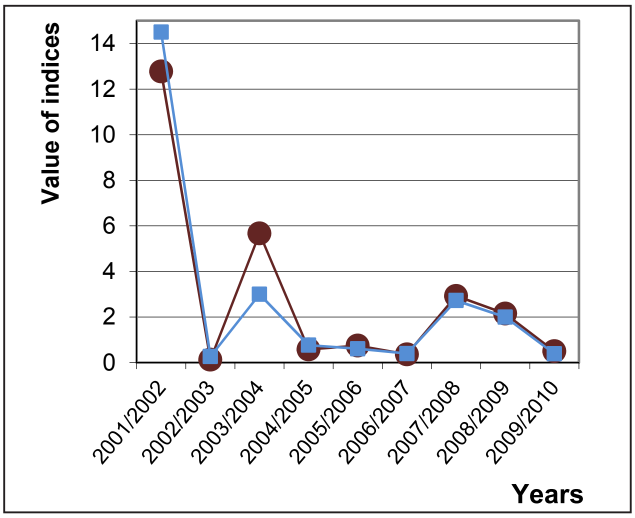

Figure 1 Value of indices for mercury in Počúvadlo
dam sampling points, opposite the dam sampling points

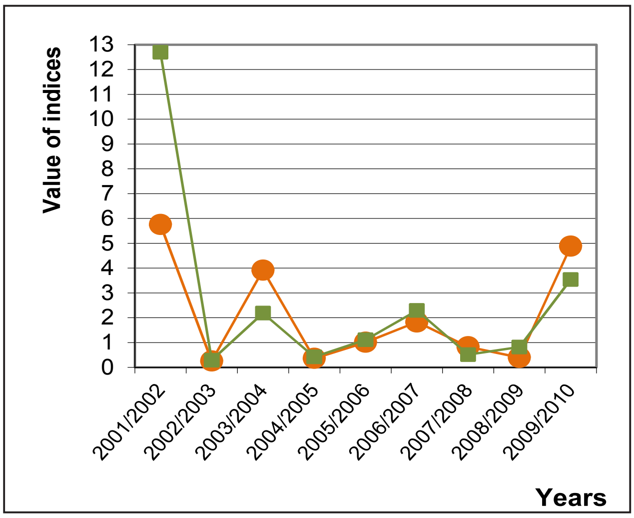

Figure 3 Value of indices for mercury in V. Richňava
dam sampling points, opposite to dam sampling points

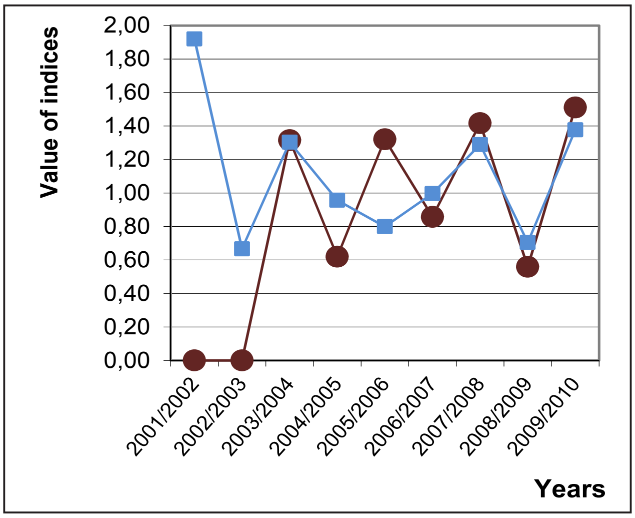

Figure 2 Value of indices for mercury in Malá Richňava
dam sampling points, opposite the dam sampling points

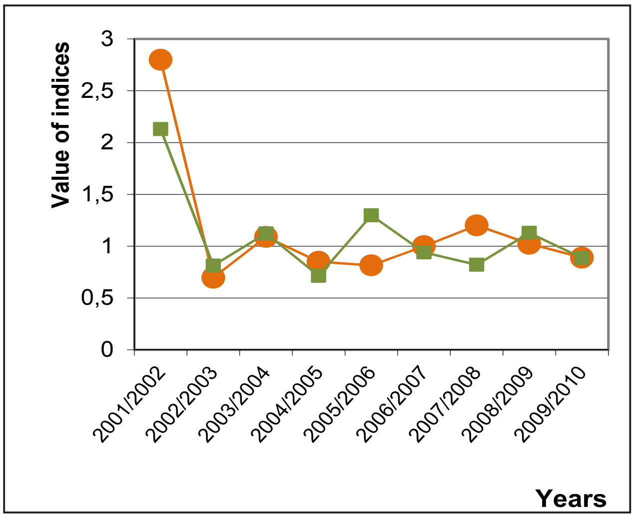

Figure 4 Value of indices for mercury in Windšachta
dam sampling points, opposite to dam sampling points

of settled sampling situated opposite the dam was increased by 1350.0 % in 2002 compared to year 2001.

For the location Malá Richňava the index values of dam sampling location were decreased by 44.12 % in 2009 compared to 2008, the index values of settled sampling across the dam were increased by 92 % in 2002 compared to 2001. There was found a decrease of the extreme index values from a dam sampling location of 74.2 1% (2003) in the location Veľká Richňava compared to 2002. On the other hand the index values from settled sampling were increased by 1169.23 % in 2002 compared to 2001. Higher index values with a decrease of 30.48 % were observed in the dam sampling location in the water tank Windšachta in 2003 compared to index values found in 2002 and index values with an increase of 180.0 % in the settled sampling situated across the dam in 2002 compared to 2001. According to the calculated indices of dependencies the development of mercury values can be evaluated as highly dynamic and non-compliant for the environment due to an insignificant increase or decrease in percentage of values in all observed sampling locations during the monitored period.

Dependencies between Hg and selected chemical elements for the period from 2001 to 2010 are presented in Table 1. The most significant correlation between Hg and As was shown in 2002. The value of Spearman's rank correlation coefficient for concentration of dependencies between Hg and As is 0.65352. Spearman's coefficient is highly significant at the 0.05 alpha level (pvalue 0.0082<0.05). A given dependence is a positive dependence, which means there is an increased concentration of Hg in the environment with increased concentration of As. The

Table 1 The Spearman's coefficients – relationship between mercury and selected elements in years from 2001 to 2010

	As	Cd	Cu	Pb	Zn
Hg 2001	0.61959 (1)	0.34844	0.43641	0.71534	0.86150
	0.1013 (2)	0.3976	0.2797	**0.0461**	**0.0060**
Hg 2002	0.65352	0.33246	0.65463	0.75573	0.72950
	0.0082	0.2260	**0.0081**	**0.0011**	**0.0020**
Hg 2003	0.60910	0.63585	0.2137	0.94677	0.66803
	0.1090	0.0901	0.6136	0.0004	0.0702
Hg 2004	-0.17535	0.58941	0.18099	0.73220	0.84024
	0.6779	0.1241	0.6680	**0.0389**	**0.0090**
Hg 2005	0.65704	0.73126	0.57401	0.60911	0.82712
	0.0767	**0.0393**	0.1368	0.1090	0.0113
Hg 2006	0.53418	0.31187	0.79977	0.78884	0.81591
	0.1726	0.4520	**0.0172**	**0.0200**	**0.0135**
Hg 2007	0.49828	0.47651	0.61078	0.65896	0.76514
	0.2088	0.2326	0.1077	0.0755	**0.0270**
Hg 2008	0.35553	0.61688	0.25709	0.90467	0.72333
	0.3874	0.1033	0.5388	**0.0020**	**0.0426**
Hg 2009	0.45107	0.18673	0.49736	0.84127	0.45961
	0.2620	0.6579	0.2098	**0.0088**	0.2519
Hg 2010	0.33328	0.60748	-0.06805	0.50985	0.71588
	0.4198	0.1102	0.8728	0.1968	**0.0458**

(1) the Spearman's coefficients, (2) level of significance

significant correlation between Hg and Cd was shown in 2005. The value of Spearman's coefficient for relationship of Hg and Cd concentrations is 0.73126. Spearman's coefficient is highly significant at the 0.05 alpha level (p_{value} 0.0393<0.05). It means a positive dependence, where there is a growth of content of the reference element in the environment with an increased concentration of Cd. There were important findings observed about relationship between Hg and Cu in 2002. The value of Spearman's coefficient for dependence between Hg and Cu is 0.65463. There is a significant Spearman's correlation at the 0.05 alpha level (p_{value} 0.0081<0.05). It is a positive dependence which indicates an increasing concentration of Cu in the environment and it could be associated with an increase of Hg content. Relationship between Hg and Pb in 2002, 2003 and 2008. In 2002 the value of Spearman's coefficient for dependence between Hg and Pb was 0.75573, Spearman's coefficient is highly statistically significant at the 0.05 alpha level (p_{value} 0.0011<0.05). In 2003 the value of Spearman's coefficient was 0.94677 with a highly statistically significant correlation at the 0.05 alpha level (p_{value} 0.0004<0.05).

Again in 2008 there was found a positive dependence between Hg and Pb, where the Spearman's coefficient was significant at the 0.05 alpha level (Spearman's coefficient = 0.90467; p_{value} 0.0020<0.05). These findings showed that an increase of Hg concentration in the environment is associated with an increased level of Pb. The significant correlation between Hg and Zn was shown in 2001 and 2002. In 2001 the value of Spearman's coefficient was 0.8615. The Spearman's coefficient is highly significant at the 0.05 alpha level (p_{value} 0.0060<0.05). In 2002 the value of Spearman's coefficient was 0.72950. It means that the Spearman's coefficient is highly significant at the 0.05 alpha level (p_{value} 0.0020<0.05). It is a positive dependence which indicates an increasing concentration of Hg in the environment and it could be associated with an increase of Zn content. Hg is an interesting chemical element which is characterized by its dynamics, varied state in the environment and also its geochemical condition. Because of variations of geochemical background it is necessary to deal with a riskiness of increased content of various chemical element, including mercury. Several authors (Khun et al., 2008; Liu et al., 2008; Tang et al., 2008; Wei et al., 2010) claim that diverse anthropogenic acitivities contribute to an environmental degradation. Mishra et al. (2008) found that increased concentrations of Hg in sediment significantly influenced the whole aquatic ecosystem. Similar findings were observed by Hiller et al. (2010). Environmental monitoring indicates that

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sediments in different parts of the world, especially in industrial areas, contain irregularly risky concentrations of potentially toxic elements.

4. Conclusions

Chemical elements influence the environment all over the world because of industrial and agricultural development, exploitation of natural resources and soaring population density and it is reflected one health of all organisms. According to the assessment presented in The Methodological Instruction of the Ministry of Environment of the Slovak Republic no. 549/98-2 the analysed sedimental samples from studied area of the water tanks near Banská Štiavnica show that the Hg content most exceeded the limited concentration (0.3 mg kg^{-1}) by 63.3 % in the sampling location Windšachta. And according to the Law no. 220/2004 on the conservation and use of agricultural land and the Law no. 203/2009 – Attachment 8 – Part 3 supplementing Law no. 188/2003 Application of sewage sludge and bottom sediments in the soil. Mercury concentration not exceeded the limit for these "Acts". Based on the calculated indices of dependencies we can assess that the development has medium-to-high dynamic and negative effect on the environment. There was manifested a highly statistical significance (based on Spearman's rank correlation coefficient) in relationship of mercury with arsenic, copper, cadmium, lead and zinc. With increased concentrations of mercury in the environment there is also an increase of above mentioned chemical elements observed and this fact means a very high risk for the environment.

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