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SIGNIFICANT CORRELATIONS DEPENDENCE OF HIGH-RISK CHEMICAL ELEMENTS IN THE ENVIRONMENT

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With the development of industry, agriculture, exploitation of natural sources and with boom of settlement density, the environment is being affected by potentially toxic elements; the phenomenon is consequently reflected on human health. Cadmium is a high risk element for the whole environment. The aim of this research was to analyse and evaluate sediments of selected water reservoirs during the ten-year period in order to determine the concentrations of selected, potentially toxic elements. For statistical processing, the correlation coefficient by the Spearman method and the analysis of the index were used. Sediments are reliable indicators of environmental pollution. The analyses of the sediment samples were carried out by the flow electrochemistry and the atomic absorption spectrometry methods. The total concentration of Cd in sediments was up to 22.60 mg kg⁻¹ of dry matter. pH/KCl was marked in the range from 5.6 to 7.2. From statistical processing of sediments data by Spearman, we determined the dependencies between Cd and the following elements: As, Cu, Hg, Pb and Zn. The relations between Cd and the following elements: Pb, As and Cu were very highly positive.

Keywords: Analysis of the index, cadmium, correlation coefficient by Spearman, pH/KCl, sediment

Statistical methods are very important evaluation indicator of scientific observation. They represent an integral part of the results. The Spearman's rank correlation coefficient is a measure of dependence based on measurement of the correlation between rankings (Stehlíková, 1999). The indices analysis represents an analysis of phenomena and processes we want to assess from the perspective of their development dynamics, and compare the indicators in time, place and in light of their factual definition (Obtulovič, 2010). The potentially toxic elements are considered as elements – relatively widely present in the Earth's crust; they are being mined and exploited in average quantity; they constitute a content of materials people are coming into contact with; they have got toxic effects on organisms and they cause undesirable effects in biogeochemical cycle (Fergusson, 1990). Cadmium is a very important risk element for the whole environment. Cadmium is a second row transition metal belonging to the group 12 of the periodic table, along with Zn and Hg. The chemistry of cadmium is most similar to that of Zn. Cadmium is a low-abundance, chalcophile element that most commonly occurs as a substitute for Hg, Cu, Pb and Zn in sulphide minerals (Fergusson, 1990; Salminen et al., 2005; Resongles et al., 2014). Increased Cd values are generally indicative of sulphide mineralisation. Since Cd has strong chalcophile affinities, it may be used to validate a questionable Zn anomaly. In the surface environment, Cd is most mobile under oxidising conditions at pH levels below 8. Consequently, the mobility of Cd released from minerals is likely to be high, especially during conditions of increased flow, when pH is lower and Cd more readily leached (Khun et al., 2008). Mobility of cadmium and its bio accessibility has

the highest value of pH in an acidic medium of sediments as it was ranged from 4.5 to 5.5 (Makovníková et al., 2006). On the other hand, cadmium is less mobile in alkaline medium. It has a tendency to precipitate on the surface of clay minerals if its value of pH is in alkaline medium. Mobility of cadmium is controlled by solubility of CdCO₃ or Cd₃(PO₄)₂, if value of pH > 7.5. However, the sulphate and carbonate of Cd are less soluble than those of Zn, so Cd²⁺ mobility is more restricted in carbonate-rich sediments and soil (Salminen et al., 2005). Percentage level of cadmium loadings in sewage sludge represent problems from the perspective of their disposal and limitation or prevention of sludges being applied to land as fertilisers. Cadmium has no essential biological function, but it tends to accumulate in plants and aquatic biota, with consequent problems of toxicity. It is toxic to humans through the inhalation of dust, causing lung damage, and may cause cancer from long-term exposure (WHO); it is also teratogenic and embryocidal (Salminen et al., 2005; Khun et al., 2008). This study focuses on the analysis of sediments of selected water reservoirs of the Piargs group. Based on the results gained by chemical analysis we aim to predict possible adverse effects on the environment. Taking into account the environment, we also aim to determine correlation, the statistical significance of dependencies of analysed environmental parameters.

Material and methods

The status of the monitored areas was assessed based on the observation and chemical analysis of sediments from

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the selected water reservoirs called the Piargs group. The statistical analysis was performed by Spearman's rank correlation coefficient (Stehlíková, 1999) and indices analysis (Obtulovič, 2010). The Spearman's rank correlation coefficient (ρ_s) is a measure of dependence based on measurement of the correlation between rankings:

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

The coefficient indicates the interdependence between two elements, e.g. interdependence between the concentration of two specific elements. $\sum d_i$ ($i = 1, 2, \dots, n$) means the sum of the differences between ranking, n represents the number (eg. number of monitored community). The indices analysis represents an analysis of phenomena and processes we want to assess from the perspective of their development dynamics, and compare the indicators in time, place and in light of their factual definition (Obtulovič, 2010). Sediment samples were taken once a year in autumn from the selected water reservoirs. The samples were taken mainly with a hand sampler from a part of the bank. The weight of all samples was up to 5 kg. The samplings were extracted from a dam sediment and from the settled sediment located opposite the dam. One analysed sample represents five samplings from one sampling location, while the sample material was mixed in clean polyethylene

containers. The sediment samples were homogenised and dried at 40 °C under bulbs during the period of 48 hours. The samples were subsequently grounded into fine-textured soil by a soil mill (VEB Thurm ZG 1). To determine the content of analysed element Cd, the sedimental fractionation with the texture under 0.125 mm was used. The analysis of samples in leachate was carried out according to existing legislative measures. The flow electrochemical method and the atomic absorption spectrometric method were used to analyse chemical elements in leachate. The analysis of samples in leachate to find out values of exchange reactions in soil was carried out by the machine "pH meter- JENWAY 3510". It was calibrated on 3 point pH calibration (buffer) (pH 4, 7, 9). The values of exchange reaction in soil were determined by potentiometry in aqueous suspension and in 1 mol dm⁻³ from the solution KCl according to the methodology by Fiala et al. (1999) in Urminská (2011).

Results and discussion

The monitored area is situated in the region of hydrothermally converted volcanic rocks and in the region with anthropogenic activities. In the study area of the selected water reservoirs in the Banská Štiavnica region, the samples were collected from 2001 to 2010, and we found the following concentrations of cadmium to 22.60 mg kg⁻¹ Cd of dry matter, As to 0.481 mg kg⁻¹ As of dry matter, Cu to 14.0 mg kg⁻¹ Cu of dry matter,

Figure 1 Value indices of cadmium in Počúvadlo Lake

Figure 3 Value indices of cadmium in Great Richňava Lake

Figure 2 Value indices of cadmium in Little Richňava Lake

Figure 4 Value indices of Cd in Windsachta Lake

Note for Figs 1–4: dam sampling points, opposite to dam sampling points

A – 2002/2001, B – 2003/2002, C – 2004/2003, D – 2005/2004, E – 2006/2005, F – 2007/2006, G – 2008/2007, H – 2009/2008, I – 2010/2009

Table 1 The Spearman coefficients – relationship between Cd and selected elements and pH/KCl for years 2001 to 2010

	As	Cu	Hg	Pb	Zn	pH/KCl
Cd	0.30720*	0.68832	0.34844	0.63556	0.10185	0.94161
2001	0.4592**	0.0591	0.3976	0.0903	0.8103	0.0584
Cd	0.44298	0.5385	0.33246	0.16393	0.60269	0.01507
2002	0.0982	0.0384	0.2260	0.5594	0.0174	0.9670
Cd	0.95589	0.73898	0.63585	0.61677	-0.05746	-0.72102
2003	0.0062	0.0362	0.0901	0.1034	0.8925	0.2790
Cd	0.15579	0.43189	0.58941	0.96436	0.17063	0.42835
2004	0.7126	0.2853	0.1241	0.0001	0.6862	0.5716
Cd	0.86091	0.85698	0.73126	0.91483	0.77906	0.08595
2005	0.0060	0.0066	0.0393	0.0014	0.0227	0.9141
Cd	-0.32644	0.28546	0.31187	0.04819	0.68000	-0.11725
2006	0.4300	0.4931	0.4520	0.9098	0.0635	0.8828
Cd	0.04012	0.09093	0.47651	0.16492	-0.09089	-0.29662
2007	0.9249	0.8304	0.2326	0.6963	0.8305	0.7034
Cd	0.8397	0.73988	0.61688	0.58665	0.80806	0.71974
2008	0.0091	0.0359	0.1033	0.1263	0.0152	0.2803
Cd	0.90936	0.92409	0.18673	0.49515	0.71726	0.79829
2009	0.0017	0.0010	0.6579	0.2122	0.0452	0.2017
Cd	0.79313	0.10374	0.60748	0.91645	0.66909	0.39927
2010	0.0188	0.8069	0.1102	0.0014	0.0696	0.6007

* the Spearman coefficient, ** level of significance

Hg to 0.49 mg kg⁻¹ Hg of dry matter, Pb to 59.04 mg kg⁻¹ Pb of dry matter and Zn to 98.0 mg kg⁻¹ Zn of dry matter. pH/KCl in the range from 5.6 to 7.2 (Urminská, 2011). pH is a very interesting key parameter in the evaluation of mobility and bio accessibility of elements in the environment (Barančíková, 1998; Makovniková et al., 2006). Most of the risk elements intensely migrate in the environment, when pH is under 7 (Khun et al., 2008). These sediments showed higher amounts of cadmium as a high risk factor in the environment. According to the index analysis observation, the monitored period from 2001 to 2010 showed the values of moderate dynamics (Figs 1–4).

The most significant index values were found in the water reservoir Počúvadlo in 2006. They were decreased by 75.64% compared to year 2005 and index values were increased by 666.15% in 2010 compared to 2009. For the location Malá Richňava, the index values were decreased by 83.63% in 2007 compared to 2006, the index values were increased by 725.24% in 2009 compared to 2008. In addition, significant index values were found in the water reservoir Velká Richňava in 2008. They were decreased by 86.64% compared to year 2007 and index values were increased by 1661.01% in 2009 compared to 2008. Moreover, index values with the decrease of 83.85% in 2006 compared to 2005 and index values with the increase of 1180.76% in 2009 compared to 2008 were observed in the water reservoir Windschta. The development is highly dynamic and reflective to the environment, because water reservoirs are affected by chemical and physical factors.

The Spearman coefficients – correlation between Cd and selected elements and pH/KCl for years 2001 to 2010 are shown in table 1.

The most significant correlation between Cd and Cu was shown in 2002. The value of the Spearman's rank correlation coefficient for concentration of dependencies between Cd and Cu was 0.53850. The Spearman's coefficient was highly significant at the 0.05 alpha level ($p_{\text{value}} 0.0384 < 0.05$). The dependence was a positive one, which means there was the increased concentration of Cd in the environment with increased concentration of Cu. Similarly, the value of Spearman's rank correlation coefficient for concentration of dependencies between Cd and Zn was 0.60269. The Spearman's coefficient was highly significant at the 0.05 alpha level ($p_{\text{value}} 0.0174 < 0.05$). The given dependence was a positive one, which means there was the increased concentration of Cd in the environment with increased concentration of Zn. In the next year, in 2003, the value of the Spearman's rank correlation coefficient for the concentration of dependencies between Cd and As was 0.95589. The Spearman's coefficient was highly significant at the 0.05 alpha level ($p_{\text{value}} 0.0002 < 0.05$). The given dependence was a positive one, which means there was the increased concentration of Cd in the environment with increased concentration of As. Similarly, year 2003 was very interesting, same as in 2002, for the correlation Cd and Cu. The most significant correlation between Cd and Pb was shown in 2004. The value of the Spearman's rank correlation coefficient for the concentration of dependencies between Cd and Pb was 0.96436. The Spearman's coefficient was highly significant at the 0.05 alpha level ($p_{\text{value}} 0.0001 < 0.05$). The given dependence was a positive one, which means there was the increased concentration of Cd in the environment with increased

concentration of Pb. Again, in 2005 it was very interesting for As, Cu, Pb and Hg, Zn. The value of Spearman's rank correlation coefficient for concentration of dependencies between Cd and Hg was 0.73126. The Spearman's coefficient was highly significant at the 0.05 alpha level ($p_{\text{value}} = 0.0393 < 0.05$). The given dependence was a positive one, which means there was the increased concentration of Cd in the environment with increased concentration of Hg. Similarly, the value of the Spearman's rank correlation coefficient for the concentration of dependencies between Cd and Zn was 0.77906. The Spearman's coefficient was highly significant at the 0.05 alpha level ($p_{\text{value}} = 0.0227 < 0.05$). The given dependence was a positive one, which means there was the increased concentration of Cd in the environment with increased concentration of Zn. Again in 2008 and 2009, there were found positive dependencies between Cd and As, Cu and Zn, where the Spearman's coefficient was significant at the 0.05 alpha level. These findings showed that the increase of Cd concentration in the environment was associated with the increased level of As, Cu, Zn. The most significant correlation between Cd and As, Pb was shown in 2010. The Spearman's coefficient was highly significant at the 0.05 alpha level. The given dependence was a positive one, which means there was the increased concentration of Cd in the environment with increased concentration of As and Pb. Cadmium 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 elements, including cadmium. Salminen et al. (2005) states that the detected concentration of Cd is associated with many chemical elements and shows strong positive correlations with Zn, Pb and Cu. However, it shows a weak correlation with As, Hg. It points to the combined impact of mineralization, anthropogenic activities, mining, metallurgy and the impact of effluents from the urban agglomerations as well. Industry and mining of non-renewable resources form significant sources of toxic contamination of surface water, sediments and groundwater (Urminská, 2011; Resongles et al., 2014). Industrial and mining contamination may enter to the aquatic environment by atmospherically transported emissions which are subsequently deposited directly by dry or wet deposition into surface waters or may also be deposited indirectly by flush and leaching of soil deposits (Enfeng et al., 2010). Cadmium is an element accompanying lead in all environments and showing geochemical significance in relation to lead. Cd shows a similar pattern with Cu and Hg in the hypo-, meso- and epithermal deposits. Evidential significances were in relation to Pb and Zn, as the elements are extensively bound to the sulphide minerals. The similar observations of heavy metals pollution of the environment and the correlation relationships between the chemical elements were reported by papers of Salminen et al. (2005), Kamala-Kannan et al. (2008), Andráš et al. (2013), Resongles et al. (2014). From the statistical processing of sediments data by the Spearman determined the dependencies between Cd and the following elements: As, Cu, Hg, Pb and Zn. The relations between Cd and the following elements: Pb, As and Cu were very highly positive. Cadmium is a high risk factor in the environment. In industrialised countries there is

a concern over anthropogenic accumulations of Cd in the environment, and it is classified as a potentially harmful element with respect to soil biological activity, plant metabolism and the health of humans and animals (Kabata-Pendias and Pendias, 1992; Nguyen et al., 2005; Hegedúsová, et al., 2006; Khun et al., 2008; Resongles et al., 2014).

References

- ANDRÁŠ, P. – KRŇÁČ, J. – KHARBISH, S. – DIRNER, V. 2013. Distribúcia vybraných ťažkých kovov na haldových poliach Cu ložiska Ľubietová. In *Mineralia Slovaca*, 2013, no. 45, 213–224. ISSN 0369-2086
- BARANČÍKOVÁ, G. 1998. Návrh účelovej kategorizácie poľnohospodárskych pôd Slovenska z hľadiska ich citlivosti k znečisteniu ťažkými kovmi. In *Rostlinná výroba*, vol. 44, 1998, no. 3, pp. 117–122.
- ENFENG, L. – JI, S. – LIYUAN, Y. – ENLOU, Z. – XIANGHUA, M. – JIANJUN, W. 2010. Assessment of heavy metals contamination in the sediments of Nansihu Lake catchment, China. In *Env. Monit & Assess.*, 2010, no. 161, pp. 217–227.
- FERGUSON, J. E. 1990. *The Heavy Elements, Chemistry, Environmental Impact and Health Effects*. New Zeland : Pergamon Press, 1990, 614 p.
- FIALA, K. 1999. Závazné metódy rozborov pôd. Čiastkový monitorovací systém – pôda. Bratislava : VÚPOP, 1999, 142 p.
- HEGEDÚSOVÁ, A. – HEGEDŮS, O. – MUSILOVÁ, J. 2006. Riziká kontaminácie pôd kadmium. Nitra : UKF, ed. *Príroda*, 2006, 89 p.
- KABATA – PENDIAS, A. – PENDIAS, H. 1992. *Trace Elements in Soils and Plants*. Florida : CRC Press, 1992, 365 p.
- KAMALA-KANNAN, S. – PRABHU DASS BATVARI, B. – LEE, K. J. – KANNAN, N. – KRISHNAMOORTHY, R. – SHANTHI, K. – JAYAPRAKASH, M. 2008. Assessment of heavy metals (Cd, Cr and Pb) in water, sediment and seaweed (*Ulva lactuca*) in the Pulicat Lake, South East India. In *Chemosphere*, vol. 71, 2008, no. 7, pp. 1233–1240.
- KHUN, M. – ĐURŽA, O. – MILIČKA, J. – DLAPA, P. 2008. *Environmentálna geochémia*. Bratislava : Geo-grafika, 2008, 278 p.
- MAKOVNÍKOVÁ, J. – BARANČÍKOVÁ, G. – DLAPA, P. – DERCOVÁ, K. 2006. Anorganické kontaminanty v pôdnom ekosystéme. In *Chemické lity*, 2006, no. 100, pp. 424–432.
- NGUYEN, H. L. – LEERMAKERS, M. – OSÁN, J. – TÖRÖK, S. – BAEYENS, W. 2005. Heavy metals in lake Balaton: water column, suspended matter, sediment and biota. In *Sc. of the Tot Environ.*, 2005, no. 340, pp. 213–230.
- OBTULOVÍČ, P. 2010. *Bioštatistika*. Nitra : SPU, 2010, pp. 139–141.
- RESONGLES, E. – CASIOT, C. – FREUDIER, R. – DEZILEAU, L. – VIERS, J. – ELBAZ-PULICHET, F. 2014. Persisting impact of historical mining activity to metal (Pb, Zn, Cd, Tl, Hg) and metalloid (As, Sb) enrichment in sediments of the Gordon river, Southern France. In *Science of the total environment*, vol. 481, 2014, pp. 509–521. DOI: 10.1016/j.scitotenv.2014.02.078
- SALMINEN, R. – BATISTA, M. J. – BIDOVEC, M. – DEMETRIADES, A. – DE VIVO, B. et al. 2005. *Geochemical Atlas of Europe. Part 1 – Background Information, Methodology and Maps*. Brussels : EuroGeoSurveys Belgium, 2005, 525 p.
- STEHLÍKOVÁ, B. 1999. *Biometrika (Terminologický slovník)*. Nitra : SPU, 1999, 95 p.
- ŠUTRIEPA, M. 2006. <http://www.banskeodpady.sk/files/Michal%20C5%A0utriepeka.pdf>
- URMINSKÁ, J. 2011. *Riziko vplyvu vybraných ťažkých kovov v sedimentoch sledovaných bansko-štiavnických vodných nádrží na životné prostredie*. Habilitation thesis, Nitra : SPU, 2011, 177 p.