REGULAR ARTICLE

CONTENT OF HEAVY METALS IN SOIL AND CROP FROM MIDDLE SPIŠ AREA

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ABSTRACT

The aim of this work is to show the importance of monitoring and soil hygienic quality evaluation in the eastern Slovakia area. In the past, when no emphasis was put on ecology, as it is nowadays, there was an uncontrolled emission of pollutants from different fields of anthropogenic activities. The consequences are manifested also nowadays, but immediate and expensive solutions are needed. In this work the results of the research of soil heavy metals contamination degree as well as their plant availability depended on soil reaction in the area of "middle Spiš" have been presented. The choice of this area is related to specific of mentioned the areas above are characteristic by anthropogenic (emission), but also natural (geochemical) contamination and intensive agricultural activity, too.

Keywords: (soil, mercury, emission, contamination)

INTRODUCTION

Heavy metals are ubiquitous part of the environment as a result of mutual natural and anthropogenic activities causing increased exposure of human populations to their effects through various channels **(Wilson - Pyatt, 2007, Poty *et al.*, 2012)**. Increasing concentrations of certain trace elements, especially their mobile forms can cause serious environmental concern about contamination and accumulation in soil, vegetation, animals, respectively, surface and ground waters **(Chopin - Alloway, 2007)**.

The primary source of environmental contamination is mainly metals, whose main part is particularly lead, zinc or copper, in addition, antimony, arsenic, mercury, cadmium, thallium, gallium, and others. In addition to the production of metals is a very important source of environmental contamination by metals and burning of fossil fuels, especially coal. Fly ash from the incineration of atmospheric leakage through contaminated soil. Increasingly important source of environmental pollution with heavy metals is becoming a burning municipal waste streams and pollution effluents containing elevated levels of toxic metals **(Bencko *et al.,* 1995)**.

Soil as a conglomerate of mineral components, organic matter - humus, living organisms, air and water is vital for a healthy and viable population. In today's urban areas, the soil is shaken. Most affected are roads and adjacent areas, industrially used areas and regions that are affected by emissions from metalworking companies. Anthropogenic material (exhaust, oil residue, particles of tire components weathered surfaces of roads) together with the natural biogenic material (fallen leaves and other plant material) can be adsorbed on its surface dust and thus represent a potential vector contamination larger area **(Omar *et al.* 2007)**.

Atmospheric deposition is related to the clearing of the atmosphere by dry or wet. It is one of the most important sources of soil contamination. The territory of Slovakia has the disadvantage that the air masses bring emissions from Western Europe and most particularly through wet deposition increase the level of soil contamination. Atmospheric deposition of contaminants (heavy metals) derived from the atmosphere accumulates and is concentrated mainly in the upper soil layer **(Stein *et al*., 2005; Hovmand *et al.,* 2008)**. It is very difficult to discern the amount of heavy metals taken root system and leaf area, especially for lead **(Hovmand *et al.,* 2008)**.

Emissions of heavy metals (Pb, As, Cd, Cr, Cu, Hg, Ni, Se, Zn) since 1990 in the Slovak Republic downward trend. In the same year amounted to emissions of heavy metals, the value of 675.44 tons, in 2006 it was 287.77 tons, a decrease compared to 1990 by 57%. In addition, closure of some inefficient outdated technology trend influenced by extensive reconstruction of separation equipment, change of raw materials and in particular the transition to the use of unleaded petrol types. Since 2003 there has been an increase in Pb emissions due to increasing production in the sintering ore and copper production. Area of interest for tracking distribution of heavy metals in the soil - plant an area which was previously loaded by emissions from the Iron Ore mine Rudňany. This is the area of some 100 km^2. The most serious contaminants from this source was mercury and accompanying contaminants were Cd, Cu, Zn and SO2. Fumes from this company burdened emission area of 1922. In 1985 mercury plant issued annually from 4.64 to 6.5 t Hg. Mercury plant was shut down in 1993, but the impact of its operations on the register now, and this is reflected in the quality of soil and plants but also to the health of the population **(Vilček *et al.*, 2012)**.

MATERIAL AND METHODS

In the present work, we focused on monitoring the level of contamination of agricultural products grown in the central file - districts Spišská Nová Ves, Gelnica, Rožňava and Levoča. In 2012, we monitored levels of selected risk metals in soil and production parts of wheat, barley, canola and corn. Delivery points are precisely defined by GPS coordinates. Table 1 shows the basic soil conditions soil samples taken, which have a significant impact on the behavior of the risk elements. The identical place, we sampled soil depth from 0.0 to 0.20 m A samples of plant material (production of cultivated crops). The samples (n = 12), we performed basic soil agrochemical analysis: pH - H_2O (ISO 10390), pH - $CaCl_2$ (ISO 10390) and humus, which have a significant effect on the distribution of heavy metals in the soil - plant. Furthermore, we all soil samples investigated the overall levels of risk elements studied: Total mercury - THG on dedicated spectrometry AMA - 254 (fy. Altech - Czech Republic) (Fig. 1), the contents of Cd, Pb and Cu in aqua regia extract (STN ISO 11466) and mobile forms of NH_4NO_3 extract (1 $mol.dm^{-3}$) - (ISO 11047). To assess the risk of the reference area because of the possibility of heavy transition metals are of identical sampling sites sampled parts of the production of cultivated crops.

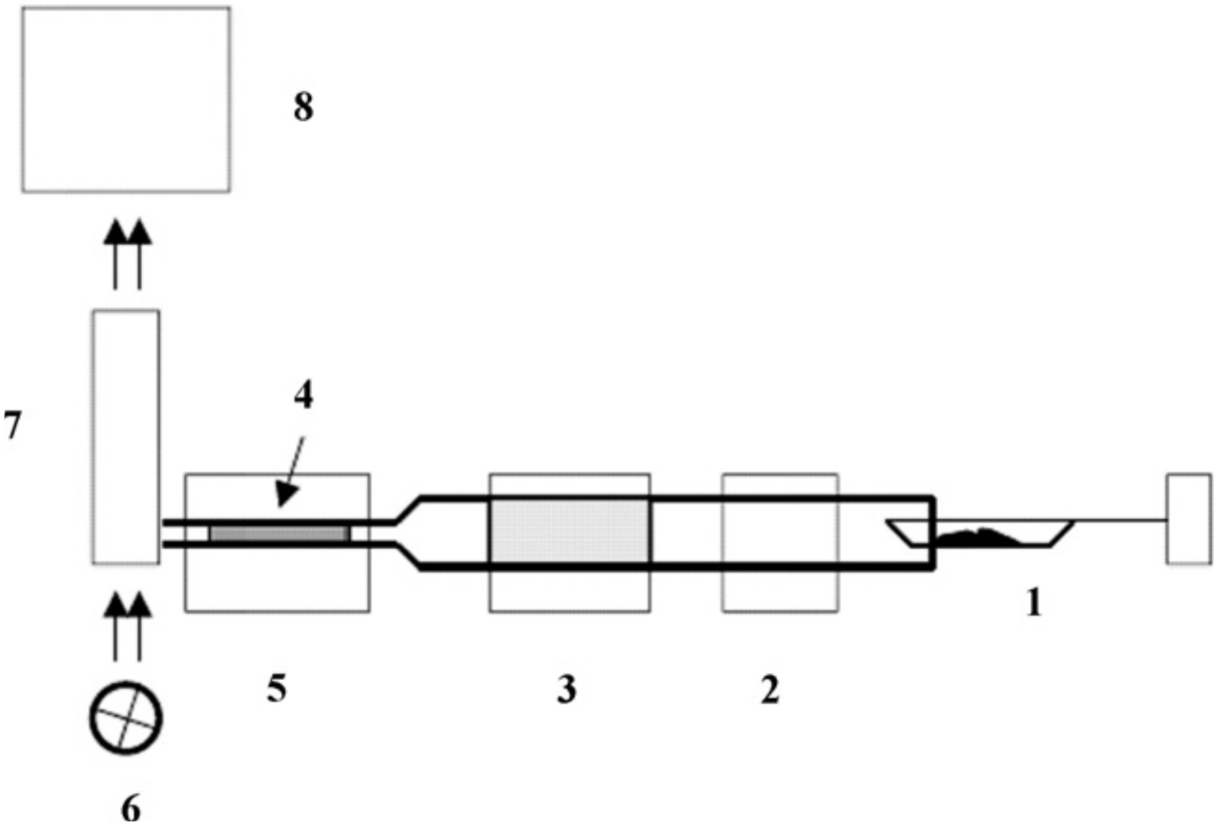

Figure 1 Scheme of the AMA 254 spectrometer. (1) Sampling boat, (2) decomposition furnace, (3) catalytic column, (4) gold amalgamator, (5) releasing furnace, (6) mercury cathode lamp, (7) optical cell system, and (8) detector (**Spěváčková *et al.*, 2004**).

RESULTS AND DISCUSSION

The main task of the present study was to evaluate and then draw conclusions on whether the monitored area middle Spiš a health risk cultivation of agricultural crops for food, respectively, forage utilization. In this research work we focus on monitoring the level of contamination of agricultural land and crops grown on it. In all soil samples analysis was performed to determine the basic agrochemical properties.

The most significant effect on the translocation of heavy metals in the system of solid - liquid phase has a plant. The studied sites are active at pH varied averaging 7.46 ± 0.73 (median ± standard deviation) and exchange activity 6.88 ± 0.83.

Table 1 Basic characteristics of the soil samples and the types of crops grown on the land interest

Sampling point	Distance (km)	Soil - plots					Crop
		LPIS	BPEJ	Cadaster	Soil type	Soil kind	
Spiš 07	1	7701/1	0870343	Markušovce	KMg	Medium	Spring Barley
Spiš 08	1	6614/1	0877302	Markušovce	KM	Medium	Spring Barley
Spiš 17	3	5402/2	0869312	Odorín	KMg	Medium	Oil rape
Spiš 25	4	5302/1	0869312	Odorín	KMg	Medium	Wheat
Spiš 32	4	8403/1	0711002	Markušovce	FMG	Medium	Spring Barley
Spiš 33	5	6102/2	0870213	Jamník	KMg	Heavy	Oil rape
Spiš 40	5	8403/1	0711002	Lieskovany	FMG	Medium	Oil rape
Spiš 48	6	0301/2	0729202	Spiš. N. Ves	ČAm	Medium	Wheat
Spiš 57	10	5703/1	0863245	Spiš. Hrhov	KMm	Medium	Spring Barley
Spiš 66	12	7802/1	0829402	Spiš. Podhr.	ČAm	Medium	Oil rape
Spiš 74	14	5701/1	0829203	Žehra	ČAm	Medium	Oil rape
Spiš 82	16	4501/1	intravilan	Biacovce	--	--	Corn

The data obtained show a weak acid, respectively, neutral soil reaction, which has a positive impact on the mobility of hazardous elements in relation to the contamination of agricultural production. The content of humic substances, which are characterized by high sorption capacity, and thus have a greater effect on the mobility of heavy metals fluctuated mean 2.47 ± 0.84% of the land area classified as a medium to high humus. THg content in the upper horizon, which was long the greatest extent influenced by emissions from the emission source. Content of total mercury in the monitored sites stood at the mean value in the interval 0.42 ± 1.00 $mg.kg^{-1}$, the maximum content of 3.0789 $mg.kg^{-1}$ was recorded at the sampling point "Spiš 07", which is located 1000 m from the emission source, oriented westward. The record also indicates a clear negative correlation between the distance from the point of consumption and emission source THg content in the sample. Compared to other ways to define the prevailing wind directions, we observed significantly higher levels of mercury (southeast, south), but these data are not included in this work. Total contents of other elements observed in the upper soil horizon were in the following intervals: Cd - 2.33 ± 0.70 $mg.kg^{-1}$, Pb - 35.5 ± 10.06 $mg.kg^{-1}$ and Cu - 24.75 ± 16.06 $mg.kg^{-1}$. Exceeding the limit values defined by the law 220/2004 was recorded in cadmium (0.70 mg.kg-1) in all cases, the maximum overshoot was recorded at the point of delivery "Spiš 07" and up to 450%. At other sampling sites were below the excess. In the case of copper we had exceeded the limit of 60 $mg.kg^{-1}$ at only one point of delivery "Spiš 74", but found us content exceeded the limit value of only 23%. For lead, we exceeded the limit of 70 $mg.kg^{-1}$ recorded.

Table 2 The resulting values of basic agrochemical indicators, total mercury and total contents of the other monitored heavy metals in aqua regia extracts of soil

Sampling point	$pH-H_2O$	$pH-CaCl_2$	Humus (%)	THg ($mg.kg^{-1}$)	Aqua regia ($mg.kg^{-1}$)		
					Cd	Pb	Cu
Spiš 07	8.02	7.16	1.57	3.0789	3.85	64.0	48.2
Spiš 08	8.13	7.32	1.33	2.7438	3.01	45.3	38.2
Spiš 17	7.62	6.77	2.00	1.0284	2.70	41.0	29.7
Spiš 25	6.57	5.36	2.18	0.6441	1.79	33.4	21.2
Spiš 32	8.13	7.16	3.27	0.6896	1.80	25.9	18.9
Spiš 33	6.77	5.99	3.69	0.5224	1.94	36.4	23.5
Spiš 40	8.11	6.99	2.36	0.2161	2.19	37.9	25.9
Spiš 48	6.49	5.64	2.75	0.3181	2.85	34.1	27.1
Spiš 57	7.30	7.18	2.09	0.1343	3.57	28.4	17.7
Spiš 66	6.48	6.03	3.00	0.3156	1.89	29.9	23.6
Spiš 74	8.11	7.21	4.15	0.3127	2.47	42.6	74.0
Spiš 82	6.65	5.75	2.57	0.1874	2.08	34.6	22.8

To assess the level of risk elements translocation system soil - plant we all carry out analyzes of soil samples to determine the cellular content, respectively, potentially biologically hazardous forms of risk elements studied. In this paper, we focus on the detection of mobile forms of cadmium, lead and copper. To assess the biological risk of mercury would be found to contain organic forms of Hg (MetHg respectively EtHg), but our analysis capabilities such analyzes do not allow us. The content of mobile forms of cadmium in the soil samples studied was around the mean value in the range 0.038 ± 0.013 mg.kg-1, and in any case we did not exceed the critical value defined by Law 220/2004 (0.1 $mg.kg^{-1}$). The highest content of mobile forms of Cd was recorded at the point of delivery "Spiš 08" (0.060 $mg.kg^{-1}$). For lead, the situation was critical. Mobile content of lead exceeded the critical value of 0.1 $mg.kg^{-1}$ in 10 soil samples, with the highest concentrations were on the point of delivery "Spiš 74". Cellular copper content did not exceed the critical value in either case. Similar concentrations of hazardous elements were also found **Vilček et al., 2012**, which also monitored the level of load reporting area.

Table 3 The resulting values of the monitored content of risk elements in the NH_4NO_3 leachate (soil) and used parts of crops

Sampling point	NH_4NO_3 (1 mol.dm^{-3})			Plant materials (mg.kg^{-1})			
	Cd	Pb	Cu	Hg	Cd	Pb	Cu
Spiš 07	0.050	0.200	0.145	0.2006	0.17	0.49	5.08
Spiš 08	0.060	0.250	0.160	0.1149	0.14	0.49	4.52
Spiš 17	0.040	0.180	0.145	0.0358	0.83	1.19	3.66
Spiš 25	0.055	0.220	0.075	0.0251	0.03	0.10	3.75
Spiš 32	0.035	0.190	0.105	0.0332	0.05	0.59	5.84
Spiš 33	0.035	0.155	0.055	0.0412	0.53	1.47	3.52
Spiš 40	0.025	0.215	0.055	0.0359	0.54	0.99	3.55
Spiš 48	0.020	0.065	0.030	0.0239	0.04	0.20	3.88
Spiš 57	0.025	0.100	0.080	0.0258	0.24	0.98	3.92
Spiš 66	0.045	0.190	0.075	0.0352	0.07	1.00	4.58
Spiš 74	0.050	0.260	0.130	0.0482	0.68	1.78	3.56
Spiš 82	0.030	0.145	0.045	0.0401	0.20	0.70	5.59

To assess the level of contamination of the food chain are identical sampling points collected used cultivated food crops. It was the 4 samples of spring barley (*Hordeum sativum*, L.), 5 samples of oil rape (*Brassica napus subsp. Oleifera*, L.), 2 samples of winter wheat f. winter (*Triticum aestivum,* L.) and 1 sample of maize (*Zea mays,* L.). In all cases, we performed analyzes to ascertain the risk elements observed in the grain, respectively seed, which is an objective indicator of the level of contamination of air pollutants affected areas **(Tomáš *et al.*, 2012)**. Mercury content in the studied crops fluctuated within a relatively wide range. Our found concentrations were in the range of 0.0358 ± 0.0518 mg.kg^{-1}. A high standard deviation indicates a wide interval, which is confirmed by the measured minimum and maximum values (0.2006 to 0.0251 mg.kg^{-1}). The maximum limits amount (the MLA), which determines the Codex Alimentarius of the Slovak Republic was exceeded at two sampling sites "Spiš 07" - 0.2006 mg.kg^{-1} and "Spiš 08" - 0.1149 mg.kg^{-1}. In other cases, we recorded excess MLA. For cadmium, the situation was different. Exceeding the MLA for "other foods" (0.1 mg.kg^{-1}) was recorded at eight sites. The highest value was recorded at the point of delivery "Spiš 17", where the cabbage seed rape - true, we measured 0.83 mg.kg^{-1}, which represents a 7.3-fold excess MLA. For lead, the situation was similar. Exceeding the NPM for "other food" was recorded at 10 sampling sites, with the highest concentrations were on the point of delivery "Spiš 74" (1.78 mg.kg^{-1}), which represents a 7.9-fold excess MLA.

CONCLUSION

In the present work we aimed to determine the level of contamination of the top soil layer, intended for production of food ingredients. Total contents of risk elements studied show increased concentration in the extract aqua regia, which generally evaluates the monitored area as risky. High-risk area is located mainly within 5 km from the emission source in the south, east and southeast. These findings confirm the results of the mobile fraction of monitored content of risk elements, especially in the case of lead, where we had exceeded the statutory critical values in 10 samples. Our gained contents of heavy metals in the soil were closely correlated with the contents of the harvested agricultural production, which in the case of cadmium and lead exceeded NPM was recorded in most samples. For a more thorough assessment of the level of risk of the reference area should be thorough and long-term monitoring of all factors that greatly contribute to reducing the quality level of the ecosystem, which is even longer (19 year) idle source of contamination, high hit.

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