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REGULAR ARTICLE

THE CONTENT OF HEAVY METALS IN PASTURES 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

Persistence and accumulation of heavy metals in the environment is closely related to their intensive use in modern society, while continuing to contribute to the amount of content in the biosphere, which will be automatically reflected adversely on all levels of the food chain, soil quality and the environment.

Environmental Policy of the European Union in recent years has changed significantly in the direction of improving access to soil contamination and pollution sources. 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. 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)**.

Since the beginning of the industrial revolution there has been a dramatic increase in the level of contamination of the biosphere by heavy metals. With the amount of resources among the hardest soil contamination contributes to the metallurgical industry. In most developed countries, is now the primary task of caring for contaminated soil due to persistence of heavy metals in the environment and the negative effects on environment and human health **(Cui *et al.*, 2005)**.

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. **(Alloway, *et al.*, 1997).** Atmospheric deposition of contaminants (heavy metals) derived from the atmosphere accumulates and is concentrated mainly in the upper soil layer. It is very difficult to discern the amount of heavy metals taken root system and leaf area, especially for lead **(Hovmand *et al.*, 2008)**.

Transport of hazardous elements in plant nutrition when it becomes limiting the quantity but also the quality of production, which is decisive for the composition of foods. This fact should be appropriately evaluated to, have it under control and it will inevitably be associated with the health of the population. **(Zhenli, *et al.*, 2005)**

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, Poti *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 are mainly metals, which main part is particularly lead, zinc or copper, in addition, antimony, arsenic, mercury, cadmium, thallium, gallium, and others **(Cardoso, *et al.* 2001)**. In addition to the production of metals is a very important source of environmental contamination by metals and burning of fossil fuels, especially coal. 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)**.

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 were mercury and accompanying contaminants were Cd, Cu, Zn and SO_2. Fumes from this company burdened emissions area of 1922. In 1985 mercury smelter issued annually from 4.64 to 6.5 t Hg. Mercury smelter 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.

MATERIAL AND METHODS

In the present work, we focused on monitoring the level of contamination of permanent grassland (PG) in the middle Spiš area - districts Spišská Nová Ves, Gelnica, Rožňava and Levoča. In 2012, we monitored levels of selected risk metals in soil and PG. Delivery points are precisely defined by GPS coordinates. Table 1 shows the basic soil conditions of the soil samples chosen, which have a significant impact on the behaviour of the risk elements. The identical sites, we sampled soil depth from 0.0 to 0.20 m PG samples. In the samples (n = 17) 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 investigated the overall levels of risk elements in all soil samples studied: Total mercury content - THG on dedicated spectrometry AMA - 254 (fy. Altech - Czech Republic) (Fig. 1) and the contents of Cd, Pb and Cu in aqua regia extract (STN ISO 11466). To assess the risk of the reference area because of the possibility of heavy transition metals were sampled identical sampling sites of PG.

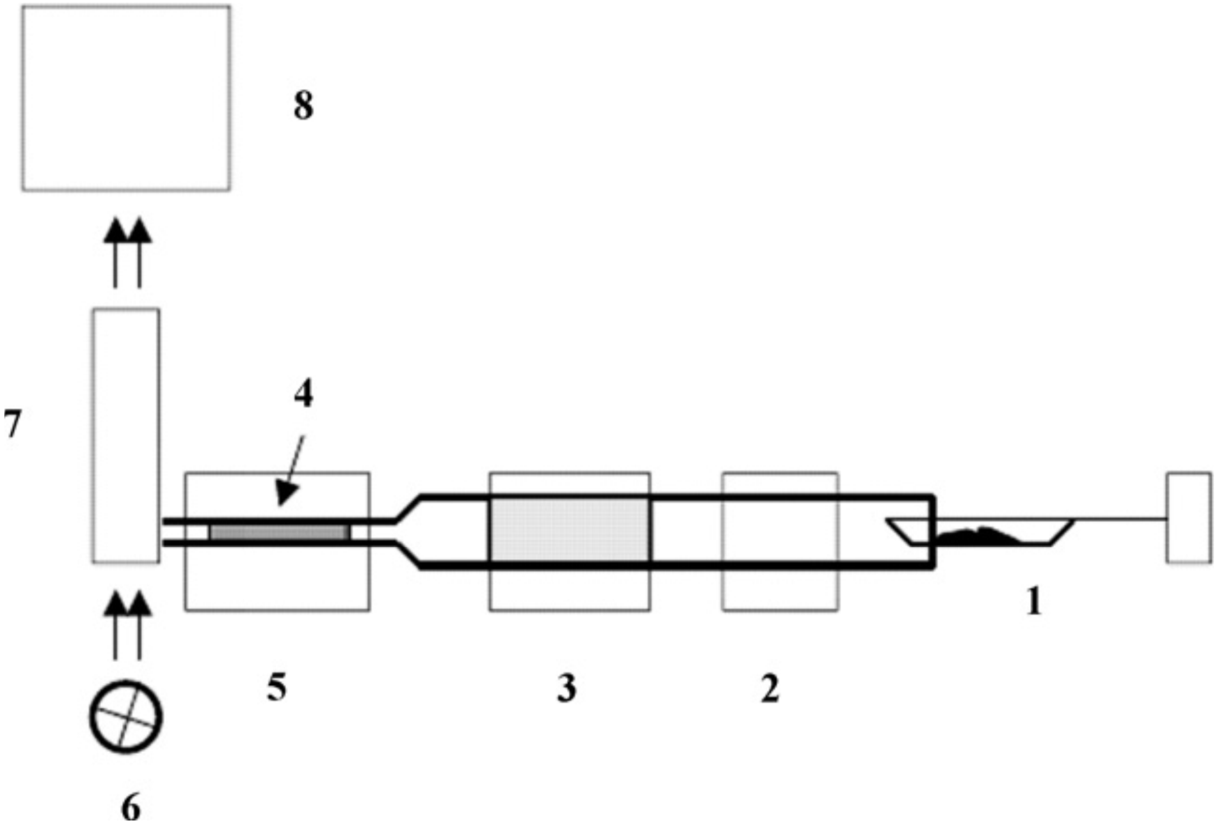

Figure 1 Scheme of the AMA 254 spectrometer. (1) Sampling boat, (2) decomposition furnace, (3) catalytic column, (4) gold amalgamator, (5) releasing furnace, (6) mercury cathode lamp, (7) optical cell system, and (8) detector (**Spěváčková *et al.*, 2004**).

RESULTS AND DISCUSSION

The main task of the present study was to evaluate results and then draw conclusions on whether the secondary file of monitored area is a health hazard cultivation of agricultural crops for food, respectively, forage utilization. In this research we focus on monitoring the level of contamination of agricultural land and crops grown on it. In all soil samples analyses the basic agrochemical properties were determined.

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

Sampling point	Distance by ES (km)	Basic soil properties					Crop
		LPIS	BPEJ	Cadaster	Soil type	Soil kind	
Spiš 01	1	6602/7	0760542	Markušovce	KMm[a]	medium	PG
Spiš 02	1	5602/1	0869445	Markušovce	KMg	medium	PG
Spiš 16	2	Int.	0702005	Markušovce	FMm[c]	medium	PG
Spiš 22	3	8903/1	1066442	Závadka	KMm[a]	medium	PG
Spiš 23	3	8706/1	0871542	Markušovce	KMg	medium	PG
Spiš 24	3	8501/1	0711002	Markušovce	FMG	medium	PG
Spiš 30	4	8003/1	1000992	Závadka	>25 °	heavy	PG
Spiš 31	4	0702/1	0876562	Teplička	KM	medium	PG
Spiš 38	5	F	F	Závadka	--	--	PG
Spiš 39	5	1701/2	0976562	Jamník	KM	medium	PG
Spiš 41	6	6003/1	0889512	Závadka	PGm	medium	PG
Spiš 46	6	0103/1	1076462	Lieskovany	KM	medium	PG
Spiš 64	10	3001/1	0875243	Spiš. N. Ves	KM	medium	PG
Spiš 65	12	6501/2	0978265	Spiš. Hrhov	KM	medium	PG
Spiš 72	12	4802/2	0992682	Iliášovce	RAm	medium	PG
Spiš 80	14	5702/1	0963535	Iliášovce	KMm	medium	PG
Spiš 88	16	6505/1	0970243	Sp. Štvrtok	KMg	heavy	PG

The most significant effect on the translocation of heavy metals in the system of solid phase - liquid phase has a pH. The studied sites are active at pH varied averaging 6.58 ± 1.03 (median ± standard deviation) and exchange activity 5.41 ± 0.96. The obtained data showed 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 2.72 ± 1.34%, the soil of this area belongs to the moderate to high humus. Total Hg 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 0.70 ± 3.37 $mg.kg^{-1}$, the maximum content of 10.6649 $mg.kg^{-1}$ was recorded at the point of delivery "Spiš 38", which is located 5 km far from the emission source, facing southwest. The record also indicates a clear negative correlation between the distance from the point of consumption and emission source THg content in the sample. Total contents of other elements observed in the upper soil horizon were in the following intervals: Cd - 3.00±1.32 mg.kg^{-1}, Pb - 37.2±8.73 mg.kg^{-1} and Cu - 25.80 ± 34.20 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 38" and up to 767%. At other sampling sites were below the excess. In the case of copper we had exceeded the limit of 60 mg.kg^{-1} for the two sampling locations and the point of delivery "Spiš 16", where the measured value exceeds the limit of 75% and at the point of delivery "Spiš 38", where the value was exceeded increased by 142%. For lead, we exceeded the limit of 70 mg.kg^{-1} recorded.

Table 2 The resulting value of the underlying agrochemical indicators, total mercury and total other watched 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 01	6,58	5,16	2,06	9,1284	1,695	33,2	40,6
Spiš 02	6,01	5,21	1,45	7,0314	1,56	26,4	29,5
Spiš 16	7,94	7,19	2,72	0,7016	3,17	47,70	105,1
Spiš 22	5,56	4,60	4,42	1,3444	4,78	45,7	21,5
Spiš 23	6,17	5,41	4,05	1,2642	3,00	56,2	26,9
Spiš 24	7,94	7,27	1,57	0,7149	1,68	25,6	24,0
Spiš 30	5,60	5,00	4,60	0,1335	4,72	37,2	13,7
Spiš 31	5,81	4,93	3,27	0,7491	2,96	43,0	22,5
Spiš 38	5,48	4,63	6,60	10,6649	6,07	39,7	145,2
Spiš 39	5,92	5,34	2,06	0,2633	3,33	40,1	22,2
Spiš 41	7,47	5,98	2,15	0,3426	2,75	28,6	23,5
Spiš 46	5,89	5,35	4,05	0,5953	3,03	46,5	45,9
Spiš 64	8,38	7,36	2,33	0,1951	5,22	39,9	29,4
Spiš 65	7,23	6,30	2,57	0,1867	4,20	33,0	25,8
Spiš 72	8,50	7,29	2,63	0,1690	2,42	28,3	25,5
Spiš 80	6,73	6,01	2,81	0,1831	2,34	30,0	24,7
Spiš 88	6,82	6,20	4,27	0,1811	2,22	30,5	26,1

Table 3 The resulting values of the monitored content of risk elements in PG

Sample point	**Plant material (mg.kg^{-1})**			
	Hg	Cd	Pb	Cu
Spiš 01	0,2170	0,11	0,67	6,07
Spiš 02	0,0937	0,61	0,49	7,23
Spiš 16	0,0557	0,39	1,29	5,26
Spiš 22	0,0888	0,29	0,70	5,00
Spiš 23	0,0277	0,30	0,10	4,00
Spiš 24	0,0236	0,51	0,79	5,12
Spiš 30	0,0401	0,33	0,00	5,40
Spiš 31	0,3166	0,30	0,90	11,30
Spiš 38	0,1364	0,42	0,50	7,70
Spiš 39	0,0638	0,20	1,70	7,30
Spiš 41	0,0325	0,38	2,06	5,41
Spiš 46	0,0281	0,06	0,00	4,30
Spiš 64	0,0625	0,26	0,80	4,89
Spiš 65	0,0572	0,33	0,60	3,79
Spiš 72	0,0411	0,14	0,99	4,05
Spiš 80	0,0267	0,23	0,99	5,25
Spiš 88	0,0528	0,47	1,70	10,20

To assess the level of contamination of the food chain are identical sampling points collected plant material. Since they were grassy vegetation, plant material was instantiated. In all cases, we performed analyzes to ascertain the risk elements observed in the aboveground biomass, which is an objective indicator of the level of contamination of air pollutants affected areas. **(Takáč, *et al.*, 2009).** Mercury content in the monitored aboveground biomass fluctuated within a relatively wide range. We found concentrations which were in the range of 0.0557 ± 0.0780 mg.kg^{-1}. A high standard deviation indicates a wide interval, which is confirmed by the measured minimum and maximum values (from 0.0236 to 0.3166 mg.kg^{-1}). The maximum amount of THg for compound feed (0.1 mg.kg^{-1}) (also MLA), which determines the Act 438/2006 Coll - Government Decree on undesirable substances in animal feed, and other indicators of safety and usability of feed was exceeded at two sampling sites "Spiš 31" - 0.3166 mg.kg^{-1} and "Spiš 38" - 0.1364 mg.kg^{-1}. In other cases, we recorded excess

NPM. The cadmium and lead are exceeded or NPM recorded at one sampling site. The maximum amount of copper Act 438/2006 Coll mentioned.

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 to the west and southwest. We gained contents of heavy metals in the soil which are closely correlated with the contents of the PG, where in the case of mercury was recorded exceeding the MLA. 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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