Monitoring of Risky Elements in Zone of Pollution Strážske Area

J. TOMÁŠ, J. ČÉRY, S. MELICHÁČOVÁ, J. ÁRVAY and P. LAZOR*

*Department of Chemistry, Faculty of Biotechnology an Food Sciences, Slovak University of Agriculture in Nitra, 949 76 Nitra, Slovak Republic, *E-mail: jan.tomas@uniag.sk*

Abstract: The work aimed to evaluate the state of agricultural soil contamination what is important for the gaining of information needed for growing of hygienic safe raw materials and foodstuffs. Metallic pollution of soil in Zemplínska polluted area has begins by accumulation of heavy metals in soil, mainly resulting from location in vicinity of chemical and industrial factories, as well as from many others sources. The pH value development indicates gradual trend of soils acidification, except of alkalic ones reaching up to 20% from total arable soils in Slovakia. Acidification is process, where acidity of abiotic compounds has been increased. Soil reaction is a significant agrochemical property markedly affecting growing and developing of plants, and has directly effect on soil fertility, influencing the ecological conditions for plants and soil microorganisms. The site had been localised with GPS and 5 sampling places had been fixed. From these sites the soil samples were taken from 1 depth, A horizon (0–0,2 m) and then processed and managed according to particular ISO norms. The soil reaction and the heavy metals contents in solution of *aqua regia* and HNO_3 in soil samples were assessed. Afterwards the gained results had been compared with limit values from legislative documents.

Keywords: heavy metals; agricultural; soil hygiene; Strážske area

INTRODUCTION

Soil contaminated with heavy metals is a salient example of environmental risk. The level of contamination varies with the distance from the source of the contamination, a metal processing plant, etc. One of the consequences could be the consumption of crops cultivated in contaminated soil negatively affecting human health. The potential mobilisation of metals is a concern in the risk assessment of metal-polluted soils. Metal mobilisation depends on soil characteristics and is controlled by the soil matrix and the composition of the soil solution (Tóth *et al*. 2006). The environmental persistence of heavy metals associated with their intensive use by modern society has, over the years, caused metal accumulation in the biosphere (Kakkar & Jaffery 2005), and may induce adverse effects on food quality, soil health and the environment. In response to these negative effects, there has been ongoing development of a variety of technologies to treat the soils contaminated by heavy metals (Gray *et al*. 2006). Soil quality is a complex characteristic determined by physical, chemical and biological components of the soil (Jomová *et al*. 2002). Soil system is very specific component and can effectively detoxify various foreign substances. Soil is not passive acceptor of heavy metals, because it could be the source for food chain (Vollmannová *et al*. 2006; Tobiášová *et al*. 2008). Heavy metals belong among most risky foreign substances in soil. The assessment of environmental risk due to soil pollution is obviously important for agricultural area, because heavy metals which are potentially harmful for human health can be persistent in soil for a long period. And thus, as the consequence, heavy metals can enter into food chain in abundant amounts (Tóth *et al*. 2006). The aim of the work was to evaluate the level of contamination of agricultural soil, which is important for gaining of information needed for cultivation of hygienic safe foodstuffs. This way of evaluation is relatively precise and enables the using of results in exact agriculture.

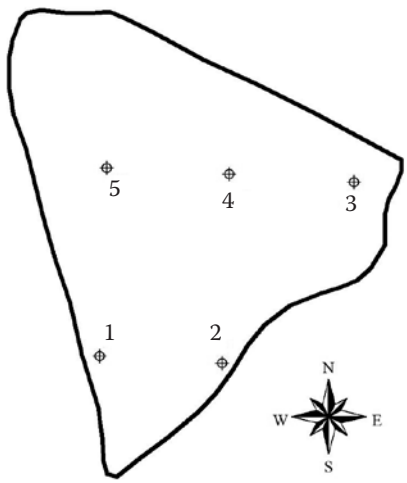

Figure 1. Graphical evaluation of pH/KCl

MATERIAL AND METHODS

This area which is evaluated in the work, lies in Strážske location (Figure 1), has coordinates: 48°52.208' of northern latitude (ϕ) and 21°46.946' of eastern longitude (λ). Its acreage is 6.9 ha. Five sampling sites were gained on this area. Bonited soil-ecological unit (BPEJ) of this area is 0669402. Soil type is KA – cambisoil, middle-heavy, clay-loam. Soil type was assessed on the basis of granulation soil composition by densitometry method by Cassagrande. Above sea level was in range of 150–178 m.s.l. The tested soil was sampled from the depth 0–0.2 m, (A horizon) using the methods of instructions for soil monitoring of Slovakia. Localisation of the area and of sampling sites was managed by GPS navigation. Soil samples from 5 sampling sites were taken. Graphical processing and formation of content maps were carried out by ArcView 3.2. The values of risky elements contents were determined in *aqua regia* solution and in nitric acid solution (c = 2 mol/dm^3). Changeable soil reaction pH/KCl and the humus content as important factors influencing behaviour and fate of risky elements in the system soil-plant were assessed for the evaluation of the risk resulting from mobility and transfer of risky elements. Contents of risky elements were determined by flame-AAS method.

RESULTS AND DISCUSSION

Soil reaction is important for the mobility and acceptability of risky elements by the plant. The value of pH_{KCl} was assessed on key parcels. The soil reaction in soil samples in the area of Vranov had the average value 5.67 with standard deviation ±0.44, whereas in larger part of key site the value pH/KCl ranged from 5.01 to 5.77. Statistically the range of pH/KCl and pH/H_2O is evaluated in Figure 2. The obtained results could be characterised as extremely acid and weakly acid, what has the influence on its quality and biotic traits, as well as on grown plant production. *Aqua regia* is an extraction agent. The content of heavy metals in soil solution of *aqua regia* presents pseudototal content of heavy metals. *Aqua regia* has not ability to decompose all silicate and alumosilicate lattice of soil particles and therefore metals that are involved in these structures will not be digested. The content of Cd, Pb, Ni, Zn, Cu, Cr, Co in our soil samples was determined.

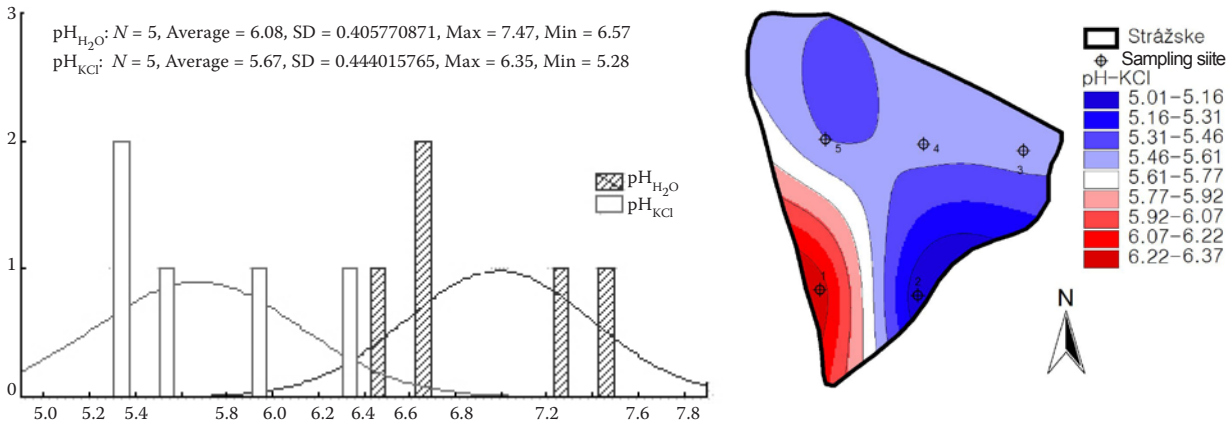

Figure 2. Measured values pH_{KCl} and pH_{H_2O} site of Strážske

Table 1. Contents of risky elements (mg/kg) in *aqua regia* solution

	Cd	Pb	Ni	Zn	Cu	Cr	Co
1	0.34	16.0	15.2	33.8	8.2	17.6	9.6
2	0.40	15.2	23.2	42.2	7.4	23.4	13.0
3	0.38	17.0	11.6	28.8	3.6	15.6	11.8
4	0.38	15.6	12.6	31.6	3.9	15.8	10.8
5	0.34	13.6	16.6	29.6	4.0	14.6	11.8
LV	**1.0**	**11.5**	**60.0**	**200.0**	**70.0**	**90.0**	**20.0**

LV – limit value

Table 2. Contents of risky elements (mg/kg) in solution of 2 mol/dm^3 HNO_3 (mg/kg)

	Cd	Pb	Ni	Zn	Cu	Cr	Co
1	***0.6***	27.0	***10.8***	28.0	17.9	8.4	6.5
2	***0.5***	26.2	6.9	29.9	22.8	8.7	9.4
3	***0.7***	28.2	9.7	21.2	13.2	4.9	7.8
4	***0.6***	23.3	9.9	29.8	15.3	6.0	6.8
5	***0.7***	26.4	***12.8***	35.5	15.7	3.9	6.5
A_1	**0.3**	**30.0**	**10.0**	**40.0**	**20.0**	**10.0**	–

A_1 – reference value

Our results were evaluated by law 220/2004 law digest about protection and using of agricultural soil (Table 1).

Our measured values of risky elements did not exceed the limit value. Values of Cd were in the range from 0.40–0.34 mg/kg soil. The average value of total content in Slovakia is in the range of level 0,285 mg/kg Cd soil. Enhancement of the value is almost 2-times higher as the average value. Values of Pb and Ni contents ranged from (Pb 13.6–17.0), (Ni 11.6–23.2) mg/kg soil, respectively. Average values of the total content were 24.850 mg/kg Pb in soil, 12.790 mg/kg Ni, respectively. Assessed Ni contents on key site did not reach average value of observed risky element in Slovakia.

Content of heavy metals in solution of 2 mol/dm^3 HNO_3 marked as potential releasable content, includes various fractions of elements from the point of view of their solubility. This solution enables with sufficient sensitivity find out minimal, also maximal contents by all elements in soils. The results were evaluated by law "Decision of Ministry of Agriculture SR No. 531/1994-540 about the highest acceptable values of risky elements in soil" (Table 2).

Reference value A_1 presents background content of exact element in soil, assessed in solution of HNO_3 (c = 2 mol/dm^3). Although, its enhancement does not mean the soil contamination, it indicates potential risk toxic influence of heavy metal. Content of heavy metals in solution of 2 mol/dm^3 nitric acid on the site Strážske does not correlate with their content in the *aqua regia* solution. In depth 0–0.20 m the reference values were exceeded in the case of Cd and Ni. By cadmium these values were enhanced in all sampling points. Range of values was from 0.5–0.7 mg Cd/kg. The highest value 0.7 mg Cd/kg presented the enhancement by 133% to reference value. The lowest value of Cd presented 0.5 mg Cd/kg soil, which enhanced 1.4-times the reference value. The highest value was enhanced by 4.14-times in comparison with average value (0.169 mg/kg). Measured contents of Ni enhanced the reference value A_1 in two sampling site. The range of values was from

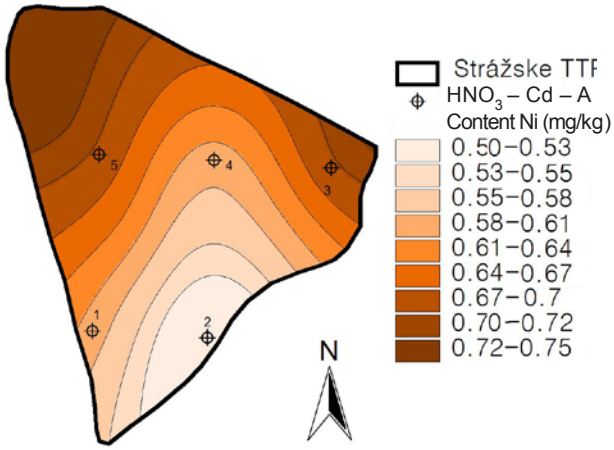

Figure 3. Graphical evaluation of Cd (mg/kg) in solution of HNO_3 (c = 2 mol/dm^3)

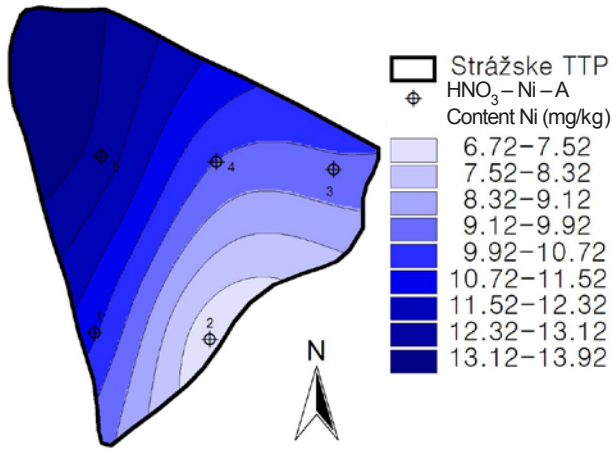

Figure 4. Graphical evaluation of Ni (mg/kg) in solution of HNO_3 (c = 2 mol/dm^3)

6.9 to 12.8 mg/kg soil. The highest value 12.8 mg/kg meant the enhancement by 28% in comparison with reference value A_1 (Figures 3 and 4).

CONCLUSION

Soil is the dynamic system affected by various factors, not only by natural, but also by anthropogenic ones, which cause its contamination. The changes in soil can modify bioavailability of metals that can enrich the soil with other elements, which are biological active or in contrary can affect the soil in negative way and it becomes unsuitable for growing of agricultural crops. At monitored site the soil contamination by Cd and Ni was assessed. Enhanced Ni contents were determined in two sampling sites of monitored area in comparison with their background soil content, what can affect the food chain. Key area requires the application of remediation amendments.

Acknowledgements: The work was supported by the Scientific Grant Agency (VEGA) of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences (Grants No. VEGA 1/2428/05 and KEGA No. 3/5081/07).

References

Gray C.W., Dunham S.J., Dennis P.G., Zhao F.J., McGrath S.P. (2006): Field evaluation of *in situ* remediation of a heavy metal contaminated soil using lime and red mud. Environmental Pollution, **142**: 530–539.

Jomová K., Hegedusová A., Vollmannová A., Tóth T. (2002): Vplyv imobilizačných zásahov na obsah zinku a medi v nadzemnej biomase a v zrne cícera baranieho (*Cicer arietinum* L.). Chemické listy, **96**: 512.

Kakkar P., Jaffery F.N. (2005): Biological markers for metal toxicity. Environmental Toxicology and Pharmacology, **19**: 335–349.

Tobiášová E., Tóth T., Šimanský V. (2008): Determination of changes in soil organic matter content through carbon and nitrogen labile fractions. Chemické listy, **100**: 491–492.

Tóth T., Vollmannová A., Musilová J., Bystrická J., Hegedusová A., Jomová K. (2006): Rizikové prvky antropogénneho pôvodu v pôdach stredného Spiša. Chemické listy, **100**: 701–702.

Vollmannová A., Tóth T., Lahučký L., Musilová J., Jomová K. (2006): Kumulácia medi a kadmia alternatívnymi plodinami. Chemické listy, **100**: 720–721.