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QUALITY OF AGRICULTURAL SOILS IN SLOVAKIA

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Abstract. Risk elements distribution on agricultural soils in Slovakia is evaluated in this contribution. The measured results have been obtained on the basis of soil monitoring system in Slovakia which has been running consistently since 1993. Risk elements have been analysed in *aqua regia* extracts. The agricultural soils of Slovakia are not contaminated except some contaminated sites which are mostly situated in the industrial areas (anthropogenic impact) as well as in the areas situated under geogenic influence (mostly some mountainous regions). Their unfavourable state lasts often a long period and agricultural land use of those affected fields is not recommended.

Keywords: soil monitoring, soil contamination, heavy metals, Slovakia

INTRODUCTION

Governmental soil policy of Slovakia declares that the soil is and will be the basis of environmental, ecological, economic and social potential of Slovakia and, therefore, it must be carefully protected against damage. The new regulation concerning agricultural soils is the Act no. 220/2004 Z.z. on protection of agricultural soils and agricultural land use (MPSR 2004) and Act no. 59 of the Ministry of Agriculture and Rural Development of Slovakia from 11 March 2013 (MPRV SR 2013) in an attempt to increase quality and to integrate decision sphere concerning the protection of agricultural soils with the aim of their

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protection against degradation. For the better realization of this regulation in the praxis, it will be necessary to know the current state of soils and their development using the complex soil monitoring system in Slovakia which has been running consistently since 1993. Background soils contain native heavy metals concentrations plus an anthropogenic addition by the ubiquitous deposition resulting from diffuse heavy metal sources. However, there are some hot spots of severe heavy metals contamination in old mining areas or around heavy-industry facilities of the 20th century in Slovakia (Wilcke *et al*. 2005). The objective of this study was the evaluation of current quality of agricultural soils in Slovakia.

MATERIALS AND METHODS

The obtained results are evaluated on the basis of soil monitoring system in Slovakia. Soil monitoring network in Slovakia is constructed on ecological principles and includes the research data of all main soil types and subtypes, soil substrates, climatic regions, emission regions, contaminated and non-contaminated regions as well as various land use. There are 318 monitoring sites on agricultural (arable and grassland) and mountainous grassland (over 1,400 m above sea level) in Slovakia. All soil monitoring sites are localized using WGS 84 coordinates. The monitoring site represents the circular shape, with a radius of 10 m and an area of 314 m^2. The standard depths of 0–0.10 m, 0.20–0.30 m and 0.35–0.45 m on soils under grassland and 0–0.10 m and 0.35–0.45 m on arable land are sampled, but the depth is adjusted to characterize the main soil horizons. The soil monitoring in Slovakia is running in 5-year repetitions. The most important risk elements concerning soil contamination are included (Cd, Cr, Pb, Ni, Zn, Cu, Se, Co extracted with aqua regia and Hg – total content using AMA analyzer). Methodical and analytical procedures were realized according to the work of Kobza *et al*. (2011).

RESULTS AND DISCUSSION

The various impacts influencing the evaluation of soil contamination could be described as follows:

- anthropogenic influence (industry, agriculture, municipal waste materials, etc.);
- influence of geochemical anomalies (in the areas and monitoring sites of Slovakia based on geochemical prospection method – Petro 1991);
- mixed influence.

The human influence on contamination of soils in Slovakia (former Czechoslovakia) was the most significant after the Second World War and especially during the industrial period in the second half of the 20th century.

The geochemical anomalies occur especially in volcanic and crystalline rocks, mainly in mountainous regions, this process is manifested in agricultural land with less intensity. The most extended areas of geochemical anomalies appear in Štiavnické vrchy, Low Tatras and Slovenské Rudohorie mountains. These regions are often characterized by high to very high concentrations of some risk elements, especially in all soil profile (Cd, Pb, Cu, Zn, As).

The distribution of risk elements on agricultural soils (topsoil and subsoil) of Slovakia is given in Tables 1 and 2.

TABLE 1. CONTENT OF RISK ELEMENTS ($mg \cdot kg^{-1}$) EXTRACTED WITH *AQUA REGIA* IN AGRICULTURAL SOILS (DEPTH 0–10 CM) OF SLOVAKIA

Elements Statistics	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Se	Hg[1]
x	10.1	0.38	8.8	42	24.5	29.4	26.4	80.9	0.25	0.09
median	8.91	0.27	8.04	41.6	20.2	26.8	19.3	70.9	0.19	0.07
X_{min}	1	0.07	1	0.99	0.39	0.24	3.45	19.8	0.04	0.01
X_{max}	223	9.9	28.6	141	155.3	136.1	1238	1191.00	0.72	0.8
Sd	7.14	0.39	4.15	19.4	14.9	14.2	37.8	46.3	0.11	0.06
Vc (%)	61.3	83.3	49.1	48.9	59.3	48.6	100.4	48.5	50.1	66.5
n	318	318	318	318	318	318	318	318	318	318

Explanations: x – arithmetic mean, X_{min} – minimum value, X_{max} – maximum value, Sd – standard deviation, Vc – coefficient of variability, n – frequency, Hg[1] – total content (AMA analyzer)

TABLE 2. CONTENT OF RISK ELEMENTS ($mg \cdot kg^{-1}$) EXTRACTED WITH *AQUA REGIA* IN AGRICULTURAL SOILS (DEPTH 35–45 CM) OF SLOVAKIA

Elements Statistics	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Se	Hg[1]
x	9.55	0.41	10	42.9	23.1	32.1	22.7	71.2	0.21	0.05
median	8.6	0.21	8.85	40.3	19.1	29	14.7	62.9	0.13	0.04
X_{min}	0.77	0.01	1	1.99	1.33	0.29	4.1	3.8	0.02	0.01
X_{max}	100	89	215.7	135	137	141	1941	1340	0.62	0.55
Sd	6.4	1.57	7.36	21.5	14.9	16.6	45.4	44.2	0.1	0.04
Vc (%)	65.2	191.7	66,9	56.6	60.8	56	121.4	53.8	43.9	69.8
n	318	318	318	318	318	318	318	318	318	318

Explanations: x – arithmetic mean, X_{min} – minimum value, X_{max} – maximum value, Sd – standard deviation, Vc – coefficient of variability, n – frequency, Hg[1] – total content (AMA analyzer)

Arsenic (As)

Arsenic is an important component of arsenopyrite (FeAsS), which is the most extended arsenic mineral in Slovakia. Its migration in soil is limited (sorption with clay, hydroxides, oxides and with soil organic matter – Čurlík and Šefčík 1999). Leaching of arsenic into the groundwater is relatively low as well as its bioavailability (Kobza *et. al*. 2007). Occurrence of arsenic is often located in the mostly mountainous regions with existence of geochemical anomalies from which can be transported by water recipients (creeks and rivers) to the lowland (sporadically higher concentration of arsenic on alluvial deposits).

On the basis of obtained results the content of arsenic in agricultural soils of Slovakia is rather variable (Vc>50%). The highest values of arsenic content occur in Cambisols especially with existence of geochemical anomalies (mostly Cambisols on granitic, methamorphic and volcanic rocks).

Average value of arsenic content is lower than the threshold for Slovakia in topsoil and subsoil, as well (Tables 1 and 2). Its content in subsoil is slightly lower in comparison to topsoil. In general, it may be said that anthropogenic input concerning arsenic in agricultural soils of Slovakia seems to be low.

Cadmium (Cd)

Cadmium is a trace element whose content in rocks is negligible. Natural content of cadmium is running between 0.01–0.07 $mg \cdot kg^{-1}$ (Bolt and Bruggenwert 1978). Cadmium mostly occurs in sulphide minerals (e.g. sphalerite, wurtzite) of which the first one is very common in Slovakia. Its mobility in soil is influenced by pH value, content of humus as well as by composition of soil solution and sorption complex. Availability of cadmium increases with decreasing of pH value.

Average content of cadmium in agricultural soils of Slovakia is lower than the threshold (MPRV SR 2013). Its average values in topsoil and subsoil are very similar (Tables 1 and 2), but the variability of cadmium in subsoil is much higher in comparison to topsoil. It mostly refers to natural geogenic origin of cadmium occurrence in agricultural soils of Slovakia. The highest heterogeneity of cadmium was observed in Fluvisols (Kobza *et al*. 2014). It is a result of transporting of soil – sedimentary material by water recipients from variously mineralized zones differently enriched in cadmium.

Cobalt (Co)

The average content of cobalt in world soils is 26.6 $mg \cdot kg^{-1}$ (Rudnick and Gao 2003). Cobalt is mostly concentrated in ultrabasic and basic rocks (100–220 $mg \cdot kg^{-1}$) (Čurlík 2011). The average content of cobalt in soils of the Czech Republic is 14 mg·kg^{-1} (Poláková *et al*. 2010). The Co content in soils is inherited from parent rocks, and partly caused by pedogenesis (Čurlík and Šefčík 1999).

On the basis of our results (Tables 1 and 2), the average content of cobalt in agricultural soils of Slovakia is 8.8 mg·kg^{-1}, what is lower value than threshold for Slovakia (MPRV SR 2013). The average content of cobalt in subsoil (10 mg·kg^{-1}) is little higher what is mostly caused by parent material. The variability of cobalt in the subsoil is also higher in comparison to the topsoil. Finally, it may be said that anthropogenic input of cobalt in soils of Slovakia is not significant.

Chromium (Cr)

Chromium, just like cobalt, is characterised by higher concentration in basic and ultrabasic rocks (mainly serpentinites), in bauxites and in coal (Vostál and Penk 1989). The average content of chromium in world soils is about 80 mg·kg^{-1} (Koljonen 1992), in soils of Poland – 20 mg·kg^{-1} (Kabata-Pendias and Pendias 2001), in soils of England – 40 mg·kg^{-1} (McGrath and Loveland 1992). For the soils of Northern Europe, the average content of chromium is calculated 60 mg·kg^{-1} (Reimann *et al.* 2003). On the basis of of soil monitoring system in the Czech Republic the average value of Cr content in those soils is 36.5 mg·kg^{-1} (Poláková *et al*. 2010). Individual soil types are characteristic in terms of significant variability of Cr content range from 7 to 150 mg·kg^{-1} (Čurlík 2011), which was confirmed also in our soil monitoring system in Slovakia (0.99–141 mg·kg^{-1}).

Reffering to our results, the average content of chromium in agricultural soils of Slovakia is 42 mg·kg^{-1}. The difference between topsoil and subsoil is very low. It means the content of chromium in soil profiles is even-tempered and reflects mostly the natural distribution of chromium in soils of Slovakia. The average values of Cr content in topsoil and subsoil of agricultural soils of Slovakia are lower than threshold (MPRV SR 2013).

Copper (Cu)

In the earth crust, Cu is most abundant in mafic to intermediate rocks, with the lowest concentrations in acid igneous and carbonate rocks, Cu is mostly concentrated in sulphides (chalcopyrite, pyrite, tetraedrite, chalkosine – Čurlík and Šefčík 1999).

According to Alloway (1990), the content of copper in natural soils reflects parent rocks and soil forming processes. Characteristic feature of Cu distribution is its accumulation in humus horizons (Čurlík 2011). Toxicity of copper increases with its higher concentrations in soil, at low concentration it is an important microelement. Anthropogenic input of Cu can be caused by application of some fertilizers, agricultural and municipal waste materials, from the sources of industrial contamination as well as the pesticides used in agriculture (e.g. chemical preparation Kuprikol, bluestone) mainly in vineyards where it is possible to determine higher concentration of copper in soil.

On the basis of the results the average content of copper in agricultural soils of Slovakia is 24.4 $mg \cdot kg^{-1}$. In subsoil the average Cu content is little lower (23.1 $mg \cdot kg^{-1}$) – Tables 1 and 2. The variability of copper is rather high (Vc>50%) where the values of coefficient variability are very similar. The highest concentrations of copper were determined in some Cambisols and Fluvisols (the areas with geochemical anomalies occurrence and alluvial deposits with accumulated soil-sedimentary material from those areas).

Nickel (Ni)

Nickel is a siderophile element that accompanies Fe in dark minerals. In sedimentary rocks Ni occurs also in sulphidic phases. Sometimes it also enters phosphates, carbonates and some silicates (Kabata-Pendias 1993). The highest content of Ni occurs in ultrabasic rocks (near to 2,000 $mg \cdot kg^{-1}$) and the lowest content of Ni is characteristic for acid granite rocks (5–15 $mg \cdot kg^{-1}$) (Čurlík and Šefčík 1999).

From among the anthropogenic inputs, metallurgy and fossil fuels are significant. In addition, on agricultural land, the application of fertilizers and some sewage sludge could be also important.

On the basis of our results, the average content of nickel in agricultural soils of Slovakia is 29.4 $mg \cdot kg^{-1}$ what is lower value than the threshold for Slovakia (MPRV SR 2013). In addition, the average content of Ni in subsoil is little higher (32.1 $mg \cdot kg^{-1}$) what probably indicates mostly geogenic influence. Variability of Ni content is also little higher in subsoil in comparison to topsoil (Tables 1 and 2) which depends on various parent rocks.

Lead (Pb)

Lead is a chalcophile element with a tendency of increased concentration in hydrothermal processes, with major sulphidic mineral – galenite (PbS). The average content of Pb in soils is running in the range from 10 to 62 $mg \cdot kg^{-1}$ (Kabata-Pendias and Pendias 2001). The natural sources of lead are mainly ore minerals. Sulphophile character of Pb causes its low solubility (Polanski and Smulikowski 1978).

Average Pb content in earth crust ranges between 6 and 15 $mg \cdot kg^{-1}$ (Alloway 1999, Adriano 2001). In addition, the average Pb content in soils of Europe is 22.6 $mg \cdot kg^{-1}$, in subsoil – 17.2 $mg \cdot kg^{-1}$ (de Vos and Tarvainen 2006).

According to our results, the average content of lead in agricultural soils of Slovakia is 26.4 $mg \cdot kg^{-1}$, in subsoil – 22.7 $mg \cdot kg^{-1}$ (Tables 1 and 2). Variability of Pb is rather high in topsoil (100.46%) and still higher in subsoil (121.4%) – Tables 1 and 2. The highest values of lead were determined in Fluvisols where Pb was often accumulated on alluvial deposits in down part of rivers.

Zinc (Zn)

Zinc is a chalcophile element that is concentrated in simple sulphides (ZnS). The average content of zinc in world soils is 64 $mg \cdot kg^{-1}$ and it ranges from 10 to 300 $mg \cdot kg^{-1}$ (Kabata-Pendias and Mukherjee 2007). In addition, the average content of zinc in soils of Europe in topsoil is 52 $mg \cdot kg^{-1}$ and in the subsoil – 47 $mg \cdot kg^{-1}$ (de Vos and Tarvainen 2006). Zinc can be toxic in high concentration in soil, in low concentration it is an important microelement.

Zinc in conditions of Slovakia is common especially in areas with geochemical anomalies occurrence as well as in some alluvial deposits. On the basis of our results (Tables 1 and 2), the average content of zinc in agricultural soils of Slovakia is 80.9 $mg \cdot kg^{-1}$. In the subsoil the average Zn content is lower (71.2 $mg \cdot kg^{-1}$). The highest content of zinc was determined in Fluvisols – especially on alluvial deposits in down part of rivers. The variability of zinc in topsoil and subsoil is similar (about 50%) which is in correspondence with Čurlík and Šefčík (1999), that zinc is one of the most evenly distributed elements in soils.

Selenium (Se)

Selenium belongs to very dispersed elements in earth crust and it can be concentrated in some sulphidic minerals. Se is often an accompanying element of sulphur. Most of soils contain Se in the range from 0.01 to 2 $mg \cdot kg^{-1}$ (Čurlík and Šefčík 1999). According to Kabata-Pendias and Pendias (2001), the surface horizons of world soils contain mainly 0.33 $mg \cdot kg^{-1}$ of Se. In addition, the average content of Se in soils of England was calculated on 0.5 $mg \cdot kg^{-1}$ (Archer and Hodgson 1987). In individual soil types, there exist evident differences in content of Se, while it is indicated a narrow relationship between soil forming substrates rich in Se and its content in soils (Čurlík 2011).

On the basis of our results, the average content of Se in agricultural soils of Slovakia is 0.25 $mg \cdot kg^{-1}$ (Table 1). Similar average content of Se is also in subsoil (0.21 $mg \cdot kg^{-1}$) – Table 2 which means that these contents are lower than the threshold for Slovakia (MPRV SR 2013). Se is characterised by irregular distribution and low to high content in soils of Slovakia. Its occurrence is often common in soils on volcanic rocks. The variability of Se is higher in topsoil (50.1%) in comparison to subsoil (43.9%) – Tables 1 and 2. Probably, it could be caused by input of soil-sedimentary material from environment rich in Se on the surface of soils.

Mercury (Hg)

Content of Hg in rocks and soils is relatively low. Hg level in soils depends on parent material and on technogene contamination. Higher concentrations are reported for clays and organic deposits, where concentrations reach up to 0.04 $mg \cdot kg^{-1}$ (Čurlík and Šefčík 1999). Hg content in natural soils is mostly inherited from parent material, but regarding to its volatility, it can be accumulated in surface soil horizons. The average content of Hg in surface soil horizons (topsoil) in Europe is 0.04 $mg \cdot kg^{-1}$ and in subsoil – 0.02 $mg \cdot kg^{-1}$ (de Vos and Tarvainen 2006).

On the basis of our results (Tables 1 and 2), the average content of Hg in agricultural soils of Slovakia is 0.09 $mg \cdot kg^{-1}$ (topsoil) and in subsoil – 0.05 $mg \cdot kg^{-1}$ which means that these values are lower than the threshold in Slovakia (MPRV SR 2013). The high variability of Hg in evaluated soils of Slovakia is characteristic for this element (>60%) in topsoil and subsoil, as well (Tables 1 and 2) caused by volatility of elemental Hg.

Fluorine (F)

Fluorine is a typical litophile element that is concentrated in intermediary to acid igneous rocks. It may be said that fluorine occurs mostly in acid granite rocks in comparison with alkaline rocks. According to Rösler and Lange (1972), the average content of fluorine is in acid rocks – 850 $mg \cdot kg^{-1}$, in diorites – 500 $mg \cdot kg^{-1}$, in basaltes – 370 $mg \cdot kg^{-1}$ and in ultraalkalic rocks only about 100 $mg \cdot kg^{-1}$. Average contents of fluorine in soil cover range from 0.02 to 0.1% (Garber 1967). Among the anthropogenic inputs, there are F emissions coming from industrial sources, predominantly from alumina works, from power stations, phosphate fertilizers factories, glass and china works can contribute to the soil pollution (Čurlík and Šefčík 1999).

Fluorine in conditions of Slovakia is not very common in soils of Slovakia (few mineral sources rich in fluorine). As for F pollution, only surroundings of the area of aluminium smelter in central Slovakia is worth paying attention to. Because the total content of fluorine does not offer review on mobile fluorine forms, soils polluted with fluorine are tested for watersoluble fluorine (Linkeš *et al*. 1997).

Development of watersoluble fluorine (Fw) in topsoil of Planosol in the surroundings of aluminium smelter as well as the concentration development of fluorine in the air (F – emissions) are represented in Fig. 1.

Fluorine was emitted from aluminium smelter in the past, especially in the second half of the 20th century. Nowadays, concerning new technology of Al production, the concentration of fluorine in the air is sufficient already. In contrast, the content of watersoluble fluorine in soil is only slightly decreasing, but its con-

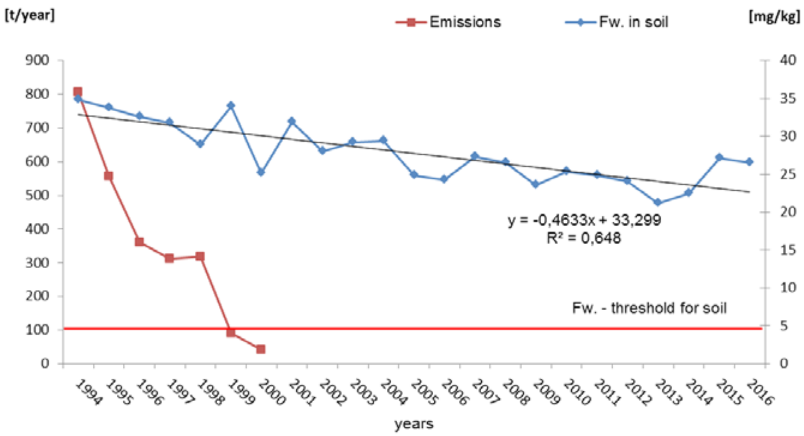

Fig. 1. Development of fluorine in the surroundings (on Planosol) of aluminium smelter in Žiarska kotlina (depression)

centration in soil (Planosol) is about 5 times over the threshold for Slovakia at present (MPRV SR 2013). It means that soil pollution in contrast of air pollution is a long-term problem and, therefore, it is necessary to monitor it also in the future.

CONCLUSIONS

In general, on the basis of our results it may be said that the hygienic state of agricultural soils in Slovakia is practically good except for some contaminated sites which are mostly situated in the industrial areas (anthropogenic impact) and in the areas influenced by geogenic impact – occurrence of geochemical anomalies (mostly mountainous areas). The area of slightly to strongly contaminated agricultural soils is less than 1% of total area of agricultural soils (less than 20 thous. ha) in Slovakia. The unfavourable state of these contaminated sites often lasts long period, without any significant change noticed during soil monitoring period since 1993 and, therefore, it is necessary to monitor them also in the future.

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