SOIL CONTAMINATION BY HEAVY METALS FROM THE DUST DEPOSITION OF MAGNESIUM FACTORY JELŠAVA – LUBENÍK (SLOVAKIA)

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Abstract

Contamination of soil by heavy metals in immission field of the magnesium factory Jelšava – Lubeník (Slovakia) and their effect to the soil characteristics were determined. Soil samples were collected in the area Jelšava - Lubeník with specific alkaline pollutants, it is one of the most devastated regions of Slovakia and with the alarming degree of environmental damage. Production of clink accompanies the enormous emissions of dust particles of MgO into the air and the leakage of gaseous compounds, mainly SO_2 and NOx. The total content of heavy metals in soils (Cd, Pb, Zn, Cr, Mn, Mg) were determined in an accredited laboratory by atomic absorption spectrometry and X-ray fluorescence spectrometry. The assessed values of heavy metals in soils were compared to the limit values of Slovak soils. Soil reaction was determined in solution of 0.01 M $CaCl_2$. The research showed that the investigated sites are strongly alkaline. Based on the obtained results, it can be stated that the contents of Cd, Pb, Zn is below the level of toxicity but for Cr, Mn and Mg, it does not apply. Their significant exceedance points contamination in which we can take into account the harmfulness and toxicity.

Key words: *soil, heavy metals, pH, magnesium, manganese*

1. INTRODUCTION

One of the most significant environmental challenges of our time, which affects all components of the environment, is a global environmental contamination. The attention of researchers is focused primarily on hazardous substances (heavy metals) which are hardly degradable in the nature, with high persistence and often exhibit toxic effects in the environment (Fazekašová *et al.* 2014; Makovníková *et al.* 2006). The pollution of the biosphere with toxic heavy metal is a widespread ecological problem resulting from anthropogenic activities like fossil fuel burning, ore mining and smelting, industrial and municipal waste disposal and agricultural activities (Mahmood 2010; Adriano 2001). The soil samples represent an excellent medium to monitor heavy metal pollution because anthropogenic heavy metals are usually deposited in top soils (Singh *et al.* 2006). The result of economic activities of anthropogenic activities occurs in relation with nature to acidification, alkalization and metallization elements of the environment (Hronec *et al.* 2008). Soil alkalinity is conditioned by the presence of alkaline salts which are easily hydrolysed and allow formation of alkaline. The fundamental reason of soils alkalinity is exchangeable sodium and content of Na_2CO_3 or $NaHCO_3$ in soil solution and worsens some soil processes like soil acidity. Strong alkaline reaction of pH / KCl> 7.7 is inflicted by air alkaline pollutants from a magnesium factory currently located in the Jelšava and Lubeník. Magnesite air pollutants are a mixture of MgO and $MgCO_3$ due to which a soil reaction can move above pH 8 (Fazekašová *et al.* 2014; Hronec *et al.* 2008). The area Jelšava - Lubeník with specific alkaline pollutants, is one of the most devastated regions of Slovakia and with the alarming degree of environmental damage. The discovery of deposits of magnesite and its processing around Lubeník dates from 1897. The processing of magnesite raw materials began in the current Slovak Magnesite Works (SMZ) Jelšava in 1923 and Lubeník as early as 1903. Since then, both plants went through constant technological and volume-production alterations. The production of clink accompanies the enormous emissions of dust MgO particles into the air and the leakage of gaseous compounds, mainly SO_2 and NOx. The chemical compounds of MgO (75 %), CaO (2.3 %), Fe_2O_3 (6.9 %), SiO_2 (0.6 %), MnO (0.4 %), Al_2O_3 (0.3 %) were detected in the particles of toxic elements. The heavy metals are in the dust particles, in particular Cd, Pb, Zn, Mn, Cr. MgO emission of dust was rising with the volume of production; it was 44 t/yr in 1923, 4898 t/yr in the 1980. Since 1990, there has been a reduction in production, the technological discipline was improved, the volume of solid emissions decreased by

about 1/3. Even so, the pollution fallout remains enormous and devastating (Baluchová *et al.* 2011; Hronec *et al.* 2008).

The aim of the study was to assess the level of heavy metal pollution in soils from the dust deposition of the magnesium factory Jelšava – Lubeník (Slovakia).

2. MATERIAL AND METHODS

Jelšava and Lubeník lie in the south-central part of the Slovak Ore Mountains, in the valley Muran, in the district called Jelšava podolie. Jelšava podolie geomorphologically belongs to Revúca Highlands (Mazúr & Lukniš 1980). Geologically, the area belongs to the Central Western Carpathians. The area is built mainly by rocks of Paleozoic and Mesozoic. Paleozoic rocks are found in a wide belt between Jelšava and Lubeník and consist of phyllites, sandstones, shales, limestones and conglomerates. The soil type of Cambisol was evolved on this bedrock, it is lightly skeletal, mostly medium depth (60-120 cm), the steeper slopes are prone to erosion. The original reaction soil pH of about 5 was due to contamination of magnesite dust changed to a pH of about 7.2 to 8.5. Second largest group of rock consists of limestone, dolomite and slate limestone which we assign to the Mesozoic rocks. The developed soils are mostly shallow (15-20 cm), loam to loamy clay, predominantly strongly skeletal, classified as Rendzinas. The third group consists of rocks of upper Pliocene sediments, they are the clays, sands and gravels with overlays quaternary clays, in which there were developed Luvisols. Fluvisols and their various subtypes are developed in the alluvium of the river Muran (Hronec *et al.* 2008; Čaboun & Priwitzer 2004).

The Jelšava and Lubeník belong to a warm climate region with 50 and more summer days (a summer day has a daily maximum air temperature of 25° C). The climate is warm, moderately humid with cold winter. The average temperature in January is -3°C to -5°C and in July 14.5°C to 16.5°C. The annual precipitation is 600-800 mm (Climate Atlas of Slovakia 2015; Lapin *et al.* 2002).

Seven research sites in the country agrarian of the problem area Jelšava and Lubeník were monitored - 1 (Lub 9), 2 (Lub 10), 3 (Jel 4), 4 (Jel 11), 5 (Jel 12), 6 (Jel 13), 7 (Jel 14). Soil samples were sampled on permanent research sites, which are used as permanent grasslands and are in the immission field of the magnesium factory Jelšava-Lubeník (Slovakia), from A horizons the depth of 0.05 m to 0.15 m (Figure 1).

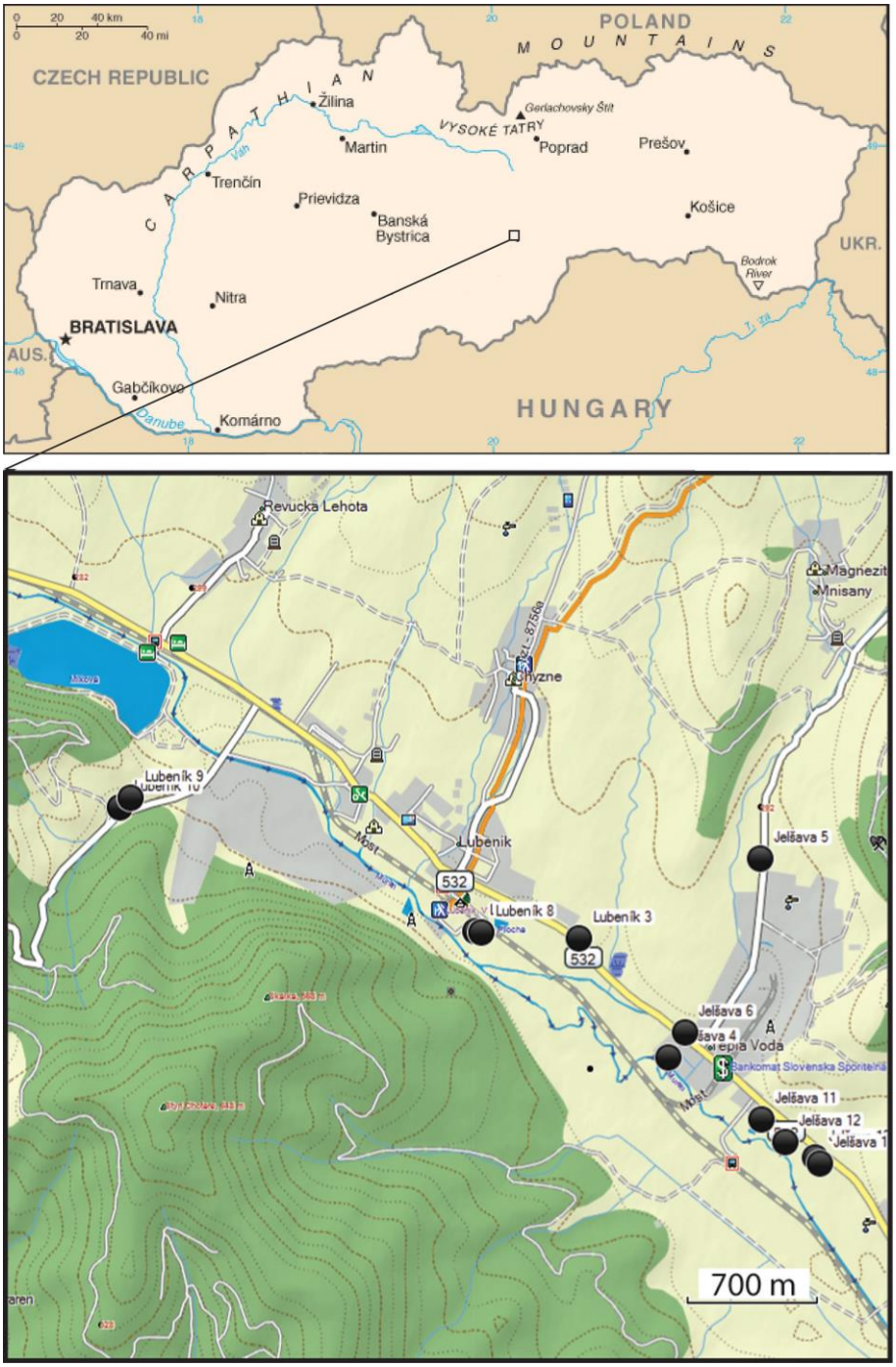


Fig. 1. Location of investigated areas in Jelšava and Lubeník (Slovakia).

After homogenization, the soil samples were manually crumbled, dried at a room temperature, sieved (<2 mm) and stored in polyethylene bags until the analysis. We studied and evaluated the soil reaction in 1N solution $CaCl_2$ (5 g of soil mixed with 25 ml of 0.01M $CaCl_2$) using a pH meter Mettler Toledo. The total content of cadmium was determined by atomic absorption spectrometry (AAS) and the total content of Pb, Zn, Cr, Mn and Mg was determined by X-Ray fluorescence spectrometry following the methodology as devised by Fiala *et al.* (1999). The assessed values of heavy metals in soils were compared to the limit values of Slovak soils (Act No. 220/2004) and Decree number 151/2016 Collection of Laws. STATISTICA 13 software was used for all data analyses. The level of significance between soil properties was calculated using a Spearman's correlation coefficient.

3. RESULTS AND DISCUSSION

The major component of environmental pollution in Jelšava - Lubeník is magnesite powder belonging to aerosol particles which is crucial for the deposition process of gravitational sedimentation. The dominant mineral phases of dust are carbonates, particularly magnesite and periclase. Most of the free magnesium oxide is in the finest dust fraction. These particles are highly active and are capable of a chemical reaction with substances in the soil on the surface of plants and plant tissues. Considering the low wind speed, dust particles disposed in a relatively small area (Čaboun & Priwitzer 2004; Hančulák 2000). The flue dust particle strongly influenced the dynamic properties of soils, especially pH. The continuous magnesite crust covers a part of the soil; the vegetation cover is considerably eliminated and reduces a landscaping and environmental aesthetic function (Figure 2) and has affected ecologically important soil functions.



Fig. 2. Soil covered with continuous magnesite crust and damaged by accelerated soil reaction in investigated areas in Jelšava and Lubeník (Slovakia).

The research showed that the investigated sites are strongly alkaline (pH 7.7 to 8.8), (Table 1). Mg flings with significant reactive caustic magnesite are aggressive in natural environments, already in small quantities, in contact with the soil and crop moisture, form saturated solutions with a high alkaline pH value (Baluchová *et al*. 2011). The content of heavy metals (Cd, Pb, Zn) on the studied area was not exceeding those set out by law (Act No. 220/2004). The chromium contents in the soil on the studied area were within the range 83 -1055 mg kg^{-1} (Table 1), the highest values were found at the post Lub 10 (Figure 1). The median level of chromium in the soil of Slovakia was 85 mg kg^{-1} to A-horizon (Šefčík *et al.* 2008). However, data presented by Čurlík & Šefčik (1999) indicate that high Cr levels (up to 6096 mg kg^{-1}) are in both, A and C horizons of soils from Outer Carpathians. Chromium along with cobalt and nickel are considered as metals that come from geogenic load (Takač *et al.* 2008). Hexavalent chromium (Cr^{+6}) is classified as one of the most important environmental contaminants (Kafka & Punčochářová 2002). Readily soluble $Cr6^{+}$ in soils is toxic to plants and animals. Therefore, the variability in the oxidation states of Cr in soils is of a great environmental concern (Kabata-Pendias 2011).

Magnesium is considered the fifth major nutrient in plant nutrition. They are located in several primary and the secondary minerals. Content values of the available magnesium are in the topsoil of agricultural land in Slovakia in the range 200-400 mg kg^{-1}Mg high content of this element in the soil (Kobza *et al.* 2010). On the studied area, we found significant contamination of soil by magnesium and its values were within the range from 12100 to 197000 mg kg^{-1}, which is on average 30 to 493 times exceeded. The highest values were found at the post Jel 12 (Figure 1).

The measured levels of manganese have a similar pattern and contents in the range 800-2300 mg kg^{-1} (Table 1) were found, the highest values were found at the post Jel 12 (Figure 1). The average content of manganese in the soil of the Slovak Republic is in the range of 0.85 to 112.90 mg kg^{-1}, indicating a

significant spatial heterogeneity of the elements, however the dominates medium supply of this element in soils. Kabata-Pendias & Pendias (2001) referred to the value of 1500 mg kg^{-1}, which show symptoms of the toxicity of manganese. Based on the obtained results, it can be stated that the contents of Cd, Pb, Zn is below the level of toxicity but for Cr, Mn and Mg, it does not apply. Their significant exceedance points contamination in which we can take into account the harmfulness and toxicity.

Significant soil contamination was also reflected in the stability of ecosystems and stability and there was a total destruction and a disposal of natural and forest ecosystems in the contested zone. The studied ecosystems had disturbed stability and there was a total destruction and the disposal of natural and forest ecosystems in the contested zone (Fazekašová *et al.* 2016; Michaeli *et al*. 2015). Permanent grasslands were represented by competitively strong species Elytrigia repens and Phragmites australis which generate up to monoculture (sites Jelsava 11, 12, 13, 14) (Figure 1).

Similar results have been found in the magnesite mining areas of Liaoning Province in China. The dust emissions from mining enterprises are enormous, with some of the mining entities completely ignoring environmental protection, thus bringing about significant destruction to the vegetation, landscape and water bodies (Wang *et al*. 2015).

Table 1. Variance analyses of heavy metals (mg kg^{-1}) and soil reaction (pH/$CaCl_2$) of investigated areas in Jelšava and Lubeník (Slovakia).

Parameter	Average	Min.	Max.	Standard deviation	Limit value*
pH/$CaCl_2$	8.414	7.7	8.8	0.3976	-
Cd	0.5	0.5	0.5	0	0.7
Pb	29.43	17	37	6.9	70
Zn	86.57	48	108	18.42	150
Cr	453.43	83	1180	473.87	70
Mn	1814.29	800	2300	508.03	-
Mg	76742.86	12100	197000	65952.3	-

*Act No. 220/2004 Coll. of Laws

Spearman's correlation coefficients confirmed negative correlation between soil pH and Cr and but only Mg and Cr were significant. A significant positive correlation ($p<0.05$) between soil pH and Mg was determined in this study. At the same, significant positive correlations between Pb – Zn, Pb – Cr and Zn - Cr were found in our study. Positive correlations were detected between Mn and Mg (Table 2).

Table 2. Correlations between heavy metals and soil reaction (pH) of investigated areas in Jelšava and Lubeník (Slovakia).

	Pb	Zn	Cr	Mn	Mg
pH/$CaCl_2$	-0.273	-0.343	-0.709*	0.437	0.873*
Pb		0.861*	0.714*	0.107	-0.286
Zn			0.805*	-0.112	-0.318
Cr				-0.322	-0.679*
Mn					0.750*

$p<0.5$*

4. CONCLUSIONS

A strong alkaline reaction of pH/KCl> 7.7 is inflicted by air alkaline pollutants from a magnesium factory currently located in the Jelšava and Lubeník. Magnesite air pollutants are a mixture of MgO and $MgCO_3$ due to which a soil reaction can move above pH 8. The area Jelšava - Lubeník with specific alkaline pollutants, is one of the most devastated regions of Slovakia and with the alarming degree of environmental damage. The major component of environmental pollution in Jelšava - Lubeník is magnesite powder belonging to aerosol particles which is crucial for the deposition process of gravitational sedimentation. The continuous magnesite crust covers a part of the soil; the vegetation cover is considerably eliminated and reduces a landscaping and environmental aesthetic function and has affected ecologically important soil functions. The research showed that the investigated sites are strongly alkaline. Based on the obtained results, it can be stated that the contents of Cd, Pb, Zn is below the level of toxicity but for Cr, Mn and Mg, it does not apply. Their significant exceedance points the contamination in which we can take into account the harmfulness and toxicity.

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