Magnesium Contamination in Soil at a Magnesite Mining Area of Jelšava-Lubeník (Slovakia)

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Abstract. Magnesium contamination in soil at a magnesite mining area of 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. Magnesite air pollutants are a mixture of MgO and MgCO₃ due to which a soil reaction can move above pH 8. Production of clink accompanies the enormous emissions of dust particles of MgO into the air and the leakage of gaseous compounds, mainly SO₂ and NOx. The total content of heavy metals in soils (Pb, Zn, Cr, Mn, Mg) were determined by atomic absorption spectrometry and X-ray fluorescence spectrometry. Soil reaction was determined in solution of 0.01 M CaCl₂. The research showed that the investigated sites are mostly strongly alkaline. Based on the obtained results, it can be stated that the contents of 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.

1. Introduction

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 [1,2]. The soil samples represent an excellent medium to monitor heavy metal pollution because anthropogenic heavy metals are usually deposited in top soils [3]. The result of economic activities of anthropogenic activities occurs in relation with nature to acidification, alkalinization and metallization elements of the environment [4]. 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 Na₂CO₃ or NaHCO₃ 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 MgCO₃ due to which a soil reaction can move above pH 8 [4,5,6]. 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 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

2.1. Study area
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 [7]. Geologically, the area belongs to the Central Western Carpathians. Twelve research sites in the country agrarian of the problem area Jelšava and Lubeník were monitored (figure 1). 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. Location of research sites in investigated areas Jelšava and Lubeník (Slovakia).](image)

2.2. Soil assays
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 Pb, Zn, Cr, Mn and Mg was determined by X-Ray fluorescence spectrometry following the methodology as devised by Fiala [8]. The assessed values of heavy metals in soils were compared to the limit values of Slovak soils (Act No. 220/2004).

2.3. Statistical analysis
STATISTICA 13 software was used for all data analyses. The significance level between the heavy metals and other soil properties was calculated by Spearman's correlation coefficient.

3. Results and discussion

3.1. Soil reaction
The values of soil reaction measured on the Jelšava–Lubeník area are listed in table 1. The research showed that the investigated sites are slightly acidic (pH 6.23-6.36), neutral (pH 6.66–6.68) and strongly alkaline (pH 7.7 to 8.8). The highest values pH were found at the post Lub9, 10 and Jel 4, 11, 12, 13 and 14 (figure 2). 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 [9].
Figure 2. Values of soil reaction and heavy metal content measured of investigated areas in Jelšava and Lubeník (Slovakia).

3.2. Heavy metal pollution

The content of heavy metals (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 2). The median level of chromium in the soil of Slovakia was 85 mg kg\(^{-1}\) to A-horizon [10]. However, data presented by Čurlík and Šefčík [11] 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 [12]. Hexavalent chromium (Cr\(^{+6}\)) is classified as one of the most important environmental contaminants [13]. Readily soluble Cr\(^{6+}\) 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 [14].

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 [15]. On the studied area, we found significant contamination of soil by magnesium and its values were within the range from 7000 to 197000 mg kg\(^{-1}\), which is on average 18 to 493 times exceeded. The highest values were found at the post Jel 12 (figure 2).

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 2). 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 [14] 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 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.

| Table 1. Variance analyses of heavy metals [mg kg\(^{-1}\)] and soil reaction of investigated areas in Jelšava and Lubeník (Slovakia). |
|-------------------------------------------------------------|
| pH/CaCl\(_2\) | Pb | Zn | Cr  | Mn | Mg          |
| Mean           | 7.63 | 32.42 | 88.33 | 231.08 | 1575.00 | 49841.67 |
| Minimum        | 6.23 | 17.00 | 48.00 | 83.00 | 800.00 | 7000.00 |
| Maximum        | 8.80 | 45.00 | 108.00 | 1055.00 | 2300.00 | 197000.00 |
| Standard deviation | 1.03 | 8.16  | 15.17 | 279.49 | 517.20 | 59039.25 |
| *Limit value   | 70   | 150  | 70    | -     | -      |

*Act No. 220/2004 Coll. of Laws

Relationships between heavy metals are listed in table 2. Spearman’s correlation coefficients confirmed negative correlation between Pb–Mg and but only Zn–Mg were significant. A significant positive correlation (p<0.05) between soil pH – Mnand pH –Mg was determined in this 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). |
|-------------------------------------------------------------|
| pH/CaCl\(_2\) | Pb | Zn | Cr  | Mn | Mg          |
|-------------------------------------------------------------|
| Pb | 0.409 | 0.239 | 0.211 | 0.718* | 0.696* |
| Zn | 0.723* | 0.210 | 0.154 | 0.066* | -0.519* |
| Cr | 0.411 | 0.154 | 0.004 |
| Mn | 0.417 | 0.004 |

p<0.05*
4. Conclusion
In this paper we presented the results of the study carried out in former mining area of 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 research showed that the investigated sites are mostly strongly alkaline. Based on the obtained results it can be stated that the contents of 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.

Acknowledgments
The study was supported by VEGA 1/0127/16 and KEGA 011PU-4/2016.

References
[1] Mahmood T 2010 Review Phytoextraction of heavy metals – the process and scope for remediation of contaminated soils Soil & Environ. 29 pp 91-109
[2] Adriano D C 2001 Trace elements in the Terrestrial Environment (New York: Springer) p 867
[3] Singh R Chavan S L and Sakale P H 2006 Heavy metal concentration in water, sediments and body tissues of Red Worm (tubifex SPP) collected from Natural Habitats in Mumbai, India Environ. Monit. Assess. 129 pp 471–481
[4] Hronec O et al. 2008 Heavy metals in soils and plants in Rudniansko-Gelnická loaded area Acta regionalia et environmentalica 1 p 24-28
[5] Fazekašová D Barančíková G Torma S Ivanová M and Manko P 2014 Chemical and environmental aspect of the component of the environment and landscape (Prešov: University of Prešov in Prešov, Faculty of Management) p 257
[6] Wang L Tai P Jia Ch Li X Li P and Xiong X 2015 Magnesium Contamination in Soil at a Magnesite Mining Region of Liaoning Province, China Bull. Environ. Contam. Toxicol. 95 p 90–96
[7] Mazúr E and Lukniš M 1980 Regional division SSR (Bratislava: Institute of Geography)
[8] Fiala K et al. 1999 Partial monitoring system – soil, binding methods (Bratislava:Research Institute of Soil Science and Conservation)
[9] Baluchová B Bačík P Fejdi P and Čaplovičová M 2011 Mineralogical research of the mineral dust fallout from the years 2006–2008 in the area of Jelšava (Slovak Republic) Mineralia Slovaca 43 pp 327-334
[10] Ševčík P Pramuka S and Gluch A 2008 Assessment of soil contamination in Slovakia according index of geoaccumulation Agriculture 54 pp 119-130
[11] Čurlík J and Šefčík P 1999 Geochemical Atlas of the Slovak Republic (Bratislava: MŽP SR) p 99
[12] Takáč P Kozáková L Vaľková M and Zeleňák F 2008 Heavy metals in soils in the middle Spiš Acta Montanistica Slovaca 13 pp 82–86
[13] Kafka Z and Punčochářová J 2002 Toxicity of heavy metals in nature Chem. Listy 96 pp 611-617
[14] Kabata–Pendias A 2011 Trace Elements in Soil and Plants (London: CRC Press) p 505
[15] Kobza J Barančíková G Dodok R Hrivňáková K Makovníková J Mališ J Pálka B Styk J and Širáň M 2010 Soil monitoring of Slovakia (Bratislava: Research Institute of Soil Science and Conservation) p 38