

# THE DISTRIBUTION AND MOBILITY OF HEAVY METALS IN THE SOILS FROM DRAHANY UPLAND

VOROS DOMINIK<sup>1</sup>, GERSLOVA EVA<sup>1</sup>, GERSL MILAN<sup>2</sup>, ZEMAN JOSEF<sup>1</sup>

<sup>1</sup>Department of Geological Sciences

Masaryk University

Kotlarska 2, 611 37 Brno

<sup>2</sup>Department of Agricultural, Food and Environmental Engineering (FA)

Mendel University in Brno

Zemedelska 1, 613 00 Brno

CZECH REPUBLIC

vorosdominik@gmail.com

*Abstract:* The main aim of the study was to evaluate a level of contamination by selected elements (zinc, lead, copper and arsenic) in soils from the southeastern part of Drahaný Upland. In total, it has been collected forty-eight topsoil samples (DV01–DV48) and sixteen surface water samples (W1–W16). The heavy metal concentration has been detected by X-ray fluorescence spectroscopy (XRF) in the topsoil samples and Atomic Absorption Spectroscopy (AAS) in the surface water samples. The heavy metal mobility has been evaluated by the BCR Sequential Extraction Procedure. The Index of Geoaccumulation ( $I_{geo}$ ) reported that the study area rang among uncontaminated or moderately contaminated by heavy metals. According to the Coefficient of Industrial Pollution (CIP) the soils are medium contaminated. The BCR method proved that lead and zinc are the most mobile elements under reducible conditions in the natural background soils, otherwise in the soils of excepted contaminated site, heavy metals have been mostly held in residual fraction. The low mobility of cuprum and arsenic has been reported in the soils. In fact, the copper and arsenic are not supposed to being come into the soil environment and into the plants, either.

*Key Words:* soil contamination, environmental chemistry, sequential extraction procedure, heavy metal mobility, index of geoaccumulation

## INTRODUCTION

The heavy metals and metalloids can cause a risk for an ecosystem and the human health, because of a possible toxicity and a bioavailability in soils. The contamination matter is nowadays actual theme because of many released publications (Alloway 2013, Bradl 2005, Hooda 2010). An origin of heavy metals may come from natural or anthropogenic sources. It is very important to distinguish individual species of heavy metals because some forms of heavy metals are supposed to be more mobile and their releases a long way throughout the soil environment (Sposito 2008). The slight changes in surrounding environmental conditions such as pH and Eh lead very often to metals remobilization. In the last part, the main aim of the study was to evaluate a level of contamination by selected elements (lead, cuprum, zinc and arsenic) in soils from the southeastern part of Drahaný Upland and from the expected contaminated site (ECS). The Drahaný Upland is spread out among the cities Brno, Vyskov, Prostejov, Boskovice and Konice. The area occupies 1 178.62 km<sup>2</sup> and extends to the north from the city Brno. The Cambisols are the most widespread soils in the area (Kozak et al. 2009). These soils are created by weathering of the bedrocks and they are most enriched by an organic matter (Kabata-Pendias 2001). The main source of inorganic elements in the soils comes from the Paleozoic sequences. There are not present industrial sources of pollution in the region.

## MATERIAL AND METHODS

Soil sampling has been passed off into the two groups (background samples) and the expected contaminated site (ECS). The topsoil samples from meadows and woods have been dried and homogenized. The 40 g of sieved soil material (below 0.063  $\mu\text{m}$ ) was weighted down. The Delta Professional Handheld XRF Analyzer has been used to measuring heavy metal contents in topsoil samples. That device has been calibrated and the Mode Geochem-Vanad was used. The time of measuring was 280 seconds. Surface waters, taking from pools and brooks (Hloucela, Klestinek and Bila Voda), have been stabilized 0.5 ml nitric acid/100 ml of sample and analyzed by the Sollars M5- Atomic Absorption Spectroscopy (AAS). A mobility of chosen trace elements has been evaluated in 10 topsoil samples using the BCR Sequential Extraction Procedure (Zemberyova et al. 2006). This method allows us to evaluate heavy metals mobility in the acid (step 1), reducible (step 2) and oxidizable (step 3) environment. The residual fraction presents non-silicate bound metals and they are not expected to release under normally conditions in a nature (Tessier et al. 1979).

### Sequential Extraction Procedure

The soil materials have been leached the reagents with an increasing intensity within steps described below (see Table 1).

Table 1 BCR three-step Sequential Extraction Procedure

Extraction step	Reagent(s)
1	$\text{CH}_3\text{COOH}$ (40 ml $0.11 \text{ mol}\cdot\text{l}^{-1}$ )
2	$\text{NH}_2\text{OH}\cdot\text{HCl}$ (40 ml $0.5 \text{ mol}\cdot\text{l}^{-1}$ )
3	$\text{H}_2\text{O}_2$ (10 ml $8.8 \text{ mol}\cdot\text{l}^{-1}$ ) then $\text{CH}_3\text{COONH}_4$ (50 ml $1 \text{ mol}\cdot\text{l}^{-1}$ ), pH 2
Residual	Agua regia

**Step 1:** Into the bottle with 1 g of solid material was added 40 ml of  $0.11 \text{ mol}\cdot\text{l}^{-1}$  acetic acid and it was shaken for the 16 hours at room temperature. The extract was separated by centrifugation and decanted into a polyethylene container and stored at  $4^\circ\text{C}$  for analysis. The residuum was used to another step after it had been washed with 20 ml distilled water by shaking for 20 minutes and recentrifuged.

**Step 2:** Into the residuum from step 1 was added 40 ml of  $0.5 \text{ mol}\cdot\text{l}^{-1}$  hydroxylamine hydrochloride and to have a pH 1.5 it was needed to pour 25 ml of  $8.8 \text{ mol}\cdot\text{l}^{-1}$  nitric acid. The solution was shaken for 16 hours at room temperature and centrifuged as well. Into the step 2 residuum was added 10 ml of  $8.8 \text{ mol}\cdot\text{l}^{-1}$  hydrogen peroxide. The solution was digested for an hour at room temperature and occasionally shaken. The watch glass with the solution was heated at  $85^\circ\text{C}$  in a water bath for an hour and subsequently it was poured another 10 ml  $8.8 \text{ mol}\cdot\text{l}^{-1}$  of hydrogen peroxide and digestion was repeated. It was added 50 ml of  $1 \text{ mol}\cdot\text{l}^{-1}$  ammonium acetate after the residuum had been cooled down. The shaking and centrifugation were done in the same manner explained above.

The metal amount in solid materials has been detected by the method of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The level of soil contamination has been evaluated by the Index of Geoaccumulation (Turekian, Wedepohl 1961) and with the Coefficient of Industrial Pollution (Kribek et al. 2014). According to Czech Technical Standard ISO 10390 (CSN 2011) it has been measured Soil Potential Reaction (pH/KCl) within thirteen topsoil samples from the ECS.

## RESULTS AND DISCUSSION

### Lead distribution

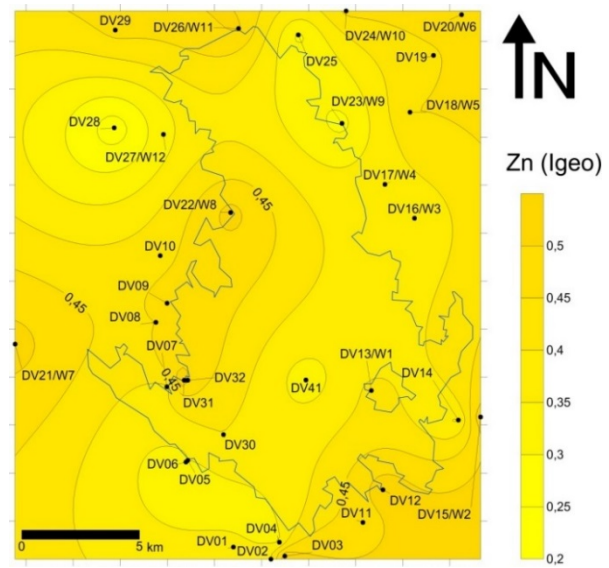
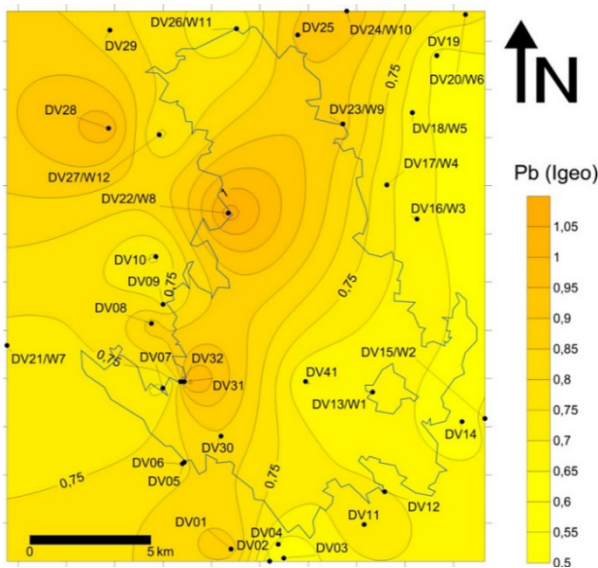
The lead contents in topsoil samples from natural background reached  $80 \text{ mg}\cdot\text{kg}^{-1}$ , DV22;  $50 \text{ mg}\cdot\text{kg}^{-1}$ , DV08;  $60 \text{ mg}\cdot\text{kg}^{-1}$ , DV24 and  $65 \text{ mg}\cdot\text{kg}^{-1}$ , DV28. These soil materials showed as approximately twice higher lead content as the rest of them around  $30 \text{ mg}\cdot\text{kg}^{-1}$ . The higher lead concentration in soils may be related to the weathering of surrounding bedrock in the Stribrna Hill, which is situated in the southeastern part of Drahaný Upland. There are galena and cerussite veins (Posmourny 2000). According to the  $I_{\text{geo}}$  values, the natural background soils are supposed to be uncontaminated as far as moderately contaminated by lead and that area belongs to the category  $I_{\text{geo}}$  1–2 (see Figure 1).

**Zinc, copper and arsenic distribution**

The zinc contents in topsoil samples from natural background reached  $89 \text{ mg} \cdot \text{kg}^{-1}$ , DV08;  $105 \text{ mg} \cdot \text{kg}^{-1}$ , DV22;  $92 \text{ mg} \cdot \text{kg}^{-1}$ , DV24 and  $52 \text{ mg} \cdot \text{kg}^{-1}$ , DV28. The copper contents contained in topsoil samples DV24,  $36 \text{ mg} \cdot \text{kg}^{-1}$ ; DV22,  $15 \text{ mg} \cdot \text{kg}^{-1}$ ; DV08,  $8 \text{ mg} \cdot \text{kg}^{-1}$  and DV28,  $5 \text{ mg} \cdot \text{kg}^{-1}$  and arsenic concentration reached values  $21 \text{ mg} \cdot \text{kg}^{-1}$ , DV22;  $21 \text{ mg} \cdot \text{kg}^{-1}$ , DV28;  $18 \text{ mg} \cdot \text{kg}^{-1}$ , DV08;  $17 \text{ mg} \cdot \text{kg}^{-1}$ , DV24. According to the  $I_{\text{geo}}$  values the natural background soils seem to be uncontaminated by zinc ( $I_{\text{geo}}$  category 1; see Figure 2), copper ( $I_{\text{geo}}$  category 0–1) and arsenic ( $I_{\text{geo}}$  category 1). Apparently, the enrichment of those inorganic elements in soils comes from natural sources, comparing with the copper, arsenic and zinc natural contents in fluvial sediments in the southeastern part of Drahaný Upland (Abraham et al. 1994).

Figure 1 Lead distribution through the soils from southeastern part of Drahaný Upland

Figure 2 Zinc distribution through the soils from southeastern part of Drahaný Upland

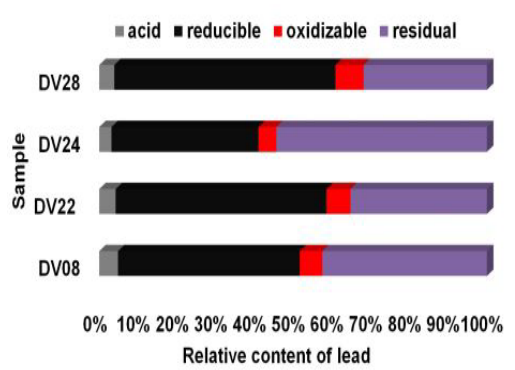
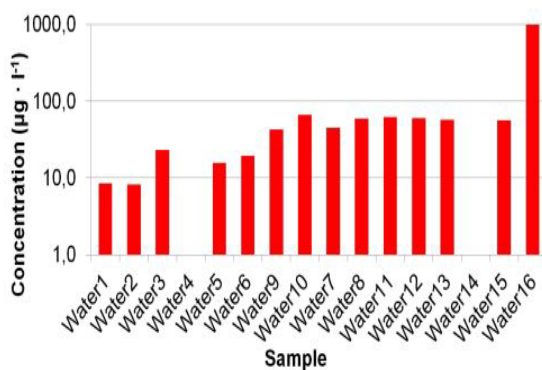


**Lead mobility**

In the natural background soils has lead been released under acid conditions less of the 9% total lead amount, therefore the higher lead contents,  $41\text{--}64 \mu\text{g} \cdot \text{l}^{-1}$ , have been noticed in pools and backwaters (see Figure 3), nearby the soils that are moderately contaminated  $I_{\text{geo}}$  1–2. Measured lead values in surface water samples exceeded values both natural background W1–12 and W13–W16 from ECS as well, except of not detected samples, determining by the Regulation of Government No. 61/2003, Coll. (MŽP 2015). The lead mobility has mostly noticed in reducible fraction which is bound to Fe-Mn oxides (Tessier et al. 1979). The lead concentration in an extract reached values  $0.678 \text{ mg} \cdot \text{l}^{-1}$ , DV08;  $1.280 \text{ mg} \cdot \text{l}^{-1}$ , DV22;  $0.580 \text{ mg} \cdot \text{l}^{-1}$ , DV24 and  $0.954 \text{ mg} \cdot \text{l}^{-1}$ , DV28, therefore lead appears to be readily mobile under reduction conditions, almost 50% total amount (see Figure 4).

Figure 3 Lead concentration in the surface water samples from southeastern part of Drahaný Up-

Figure 4 Percent amount of released lead in the soils samples from natural back-



### Zinc, copper and arsenic mobility

However, the nearby natural waters have been enriched by zinc, increasing of the measured values has been noticed in pools (samples W2, W3, W5 and W6) around east margin of the ECS (see Figure 5). The zinc mobility has mostly noticed in reducible fraction, because the most amount of dissolved zinc was detected in the topsoil samples DV08,  $0.678 \text{ mg} \cdot \text{l}^{-1}$ ; DV22,  $1.280 \text{ mg} \cdot \text{l}^{-1}$ ; DV24,  $0.580 \text{ mg} \cdot \text{l}^{-1}$  and DV28,  $0.954 \text{ mg} \cdot \text{l}^{-1}$ , therefore we suppose to zinc is readily mobile under reduction conditions of approximately 50% total amount (see Figure 6). The copper content has not been detected in the natural background surface waters (W1–W12) neither arsenic, so it was under acid conditions releasing into the soil of  $<0.005 \text{ mg} \cdot \text{l}^{-1}$  copper and  $<0.007 \text{ mg} \cdot \text{l}^{-1}$  arsenic, nonetheless their mobility is negligible, because the overwhelming majority of copper ( $>85\%$ ) and arsenic content ( $>89\%$ ) has been held in residual fraction and these elements are not supposed to be transported throughout the soil environment because the fraction presents non-silicate bound metals and they are not expected to release under normally conditions in a nature (Tessier et al. 1979).

Figure 5 Zinc concentration in the surface water samples from southeastern part of Drahaný Upland

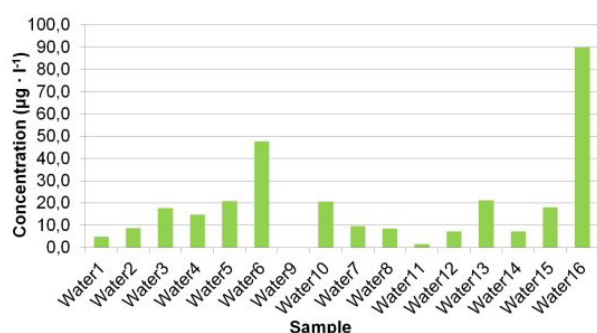
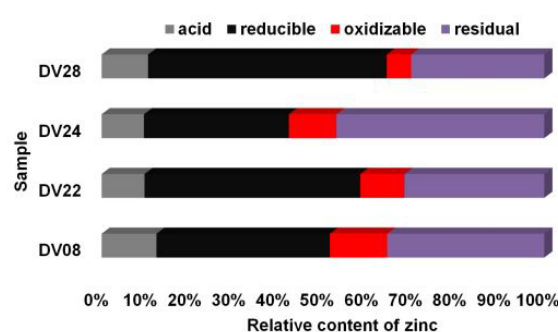


Figure 6 Per cent amount of released zinc in the soil samples from natural background



### Expected contaminated site

This area serves as a training facility for an individual training of military personnel and is divided to the training ranges. Lead concentration reached mostly higher values in top soil samples taking from a range of Hand-Thrown Grenades DV43,  $288 \text{ mg} \cdot \text{kg}^{-1}$ ; DV44,  $181 \text{ mg} \cdot \text{kg}^{-1}$  and DV48,  $142 \text{ mg} \cdot \text{kg}^{-1}$  and of Infantry Shooting Range DV45,  $134 \text{ mg} \cdot \text{kg}^{-1}$ ; DV46,  $293 \text{ mg} \cdot \text{kg}^{-1}$  and DV47,  $455 \text{ mg} \cdot \text{kg}^{-1}$ . According to the Coefficient of Industrial Pollution the soils are medium contaminated by heavy metals (see Figure 7) and in the surroundings of ranges the soils appear to be particularly similar to the natural background. The pH/KCl is ranged from 3.2 to 6.6 in the soils which are not affected by anthropogenic activity. The alkaline soils have been evaluated in a range of Hand-Thrown Grenades (range of 7.8–8.5) and intensively acid soils at an Infantry of Shooting Range (3.4–3.6). The oxidative conditions (414.34–663.58 mV) are presented in the soils. The soil alkalinity prevents from the heavy metal mobilization, otherwise in the acid conditions may be lead and zinc remobilized (Kabata-Pendias 2001).

### Heavy metals mobility

The lead, zinc and copper concentration are presented in natural waters, so called pools at an Infantry Shooting Range within surface water samples (W15–W16). These waters have been most enriched by copper ( $139.6 \mu\text{g} \cdot \text{l}^{-1}$ ), zinc ( $89.3 \mu\text{g} \cdot \text{l}^{-1}$ ) and lead ( $944.5 \mu\text{g} \cdot \text{l}^{-1}$ ) as well. The copper ( $0.029\text{--}0.255 \mu\text{g} \cdot \text{l}^{-1}$ ), zinc ( $0.047\text{--}0.170 \mu\text{g} \cdot \text{l}^{-1}$ ) and lead ( $0.602\text{--}5.553 \mu\text{g} \cdot \text{l}^{-1}$ ) dissolution have been reported under mildly acidic condition. The origin of lead, zinc and copper in soils may come from the ammunition. A brass (compound of zinc and copper) is meant to make cartridge casing and lead is used to increase penetrative power of a bullet (Plihal 2010). The overwhelming majority of lead ( $>75\%$ ; see Figure 8), zinc ( $>85\%$ ; see Figure 9), copper ( $>85\%$ ) and arsenic content ( $>96\%$ ) have been held in residual fraction and these elements are not supposed to be mobilized through the soil environment.

Figure 7 Soil contamination map of the ECS in southeastern part of Drahaný Upland.

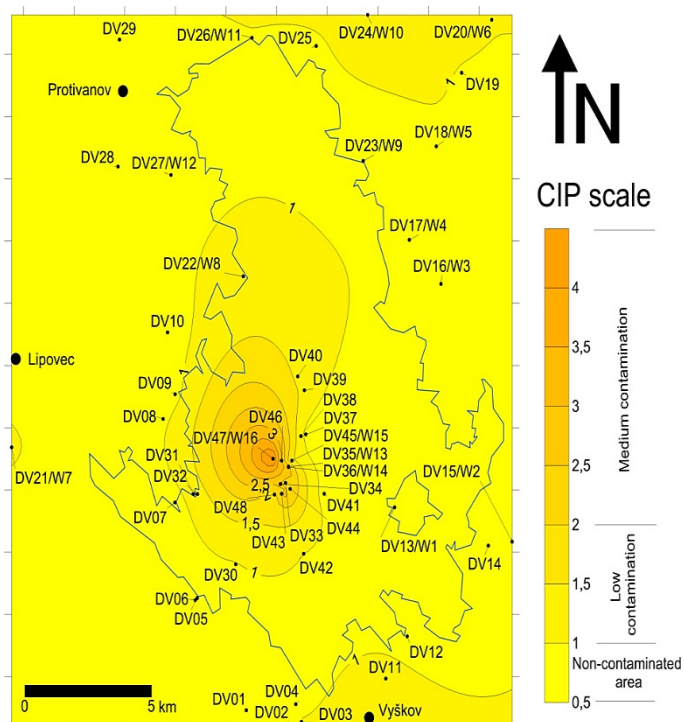


Figure 8 Per cent amount of released lead in the soil samples from the ECS

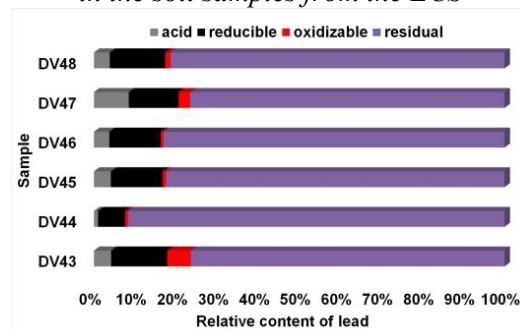
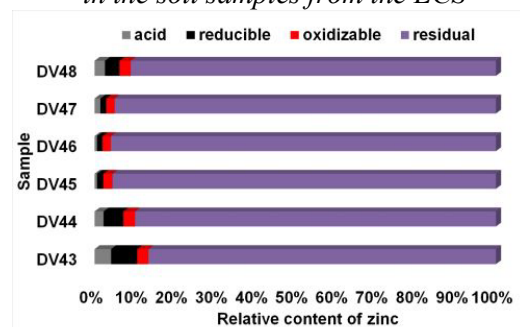


Figure 9 Per cent amount of released zinc in the soil samples from the ECS



## CONCLUSION

It was evaluated soil contamination by lead, zinc, copper and arsenic and their mobility in the southeastern part of Drahaný Upland. The natural background soils are uncontaminated by zinc, copper and arsenic, otherwise moderately lead contamination have been reported. Among the most mobile inorganic elements belong to the natural background soils zinc and lead. They are supposed to be readily mobilized under reduction condition through the soil environment and bioavailable for the biota (Fedotov, Miro 2007). The totally copper and arsenic immobilization in the natural background soils prevent to the possible bound into the biota. On the other hand, the ECS soils are medium contaminated by selected elements, which are all of them mostly immobilized, therefore they cannot come to the biota (Fedotov, Miro 2007). According to the total mobile fraction, the heavy metal mobility in soils decreases in following order: Zn>Pb>Cu>As.

## REFERENCES

- Abraham M., Simek J., Luna J., Svestka J., Hulka L., Zacek M., Haje J., Grym V. 1994. *The regional heavy mineral prospecting in the Czech Republic, atlas of maps 1:200 000, sheet 24 Brno*: Brno. Ministry of Economy CR.
- Alloway B. J. [ed.] 2013. *Heavy Metals in Soils, Trace Metals and Metalloids in Soils and their Bioavailability*. 3<sup>rd</sup> ed: Reading. Springer.
- Bradl H. B. [ed.] 2005. *Heavy metals in the Environment: origin, interaction and remediation*, 1<sup>st</sup> edition: London. Elsevier Academic Press.
- CSN ISO 10390. 2011. *The soil quality – determination of pH*. 2<sup>nd</sup> ed.: Geneva. The Office for Standards, Metrology and Testing.
- Fedotov P. S., Miro M., Violante A. [ed.], Huang P. M. [ed.], Gadd G. F. [ed.] 2007. Fractionation and mobility of trace elements in soils and sediments. In: *Biophysico-chemical processes of heavy metal and metalloids in soil environments*: Hoboken. John Wiley & Sons, Inc.
- Hooda P. S. [ed.] 2010. *Trace elements in soils*: Chichester. John Wiley & Sons, Ltd.

- Kabata-Pendias A. 2001. *Trace elements in soils and plants*. 3<sup>rd</sup> edition: Florida. CRC Press.
- Kozak J., Nemecek J., Boruvka L., Lerova Z., Nemecek K., Kodesova R., Janku J., Jacko K., Hladik K., Zadorova T. 2009. *Soil Atlas of Czech Republic*. 2<sup>nd</sup> revised edition: Prague. Czech University of Agriculture.
- Kribek B., Majer V., Pasava J., Knesl I., Kamona F., Mapani B., Mwiya S., Kawali L., Kandjii I., Keder J. 2014. Impact of ore processing on the environment in the Tsumeb area, Namibia. *Communs Geological Survey of Namibia*, 15: 111–116.
- MZP. 2015. Government Regulation No. 61/2003 Coll., on indicators and values of permissible surface water pollution and wastewater treatment, details of the permit to discharge wastewater into the surface water and into the sewerage systems, and on sensitive areas, as amended by the Government Regulation No. 229/2007 Coll., and the Government Regulation No. 23/2011 [online] April 30, 2015. Available from: [http://www.mzp.cz/C1257458002F0DC7/cz/pripustne\\_znecistení\\_vod\\_narizení/\\$FILE/OOV-NV\\_61\\_2003-20110610.pdf](http://www.mzp.cz/C1257458002F0DC7/cz/pripustne_znecistení_vod_narizení/$FILE/OOV-NV_61_2003-20110610.pdf)
- Plihál B. 2010. *Ammunition sets III: Ecology in ammunition disposal and explosives*: Brno. University of Defence.
- Posmourny K. 2000. Mineral deposits. In: *Explanatory notes to the file of geological and environmental thematic map of natural resources at a scale of 1:50 000, a sheet 24-23 Protivanov*: Prague. Czech Geological Survey.
- Sposito G. 2008. *The chemistry of soils*. New York: Oxford University Press.
- Tessier A., Campbell P. G. C., Bisson M. 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*, 51(7): 844–851.
- Turekian K. H., Wedepohl, K. H. 1961. Distributions of the elements in some major units of the earth's crust. *Geological Society of America Bulletin*, 72(2): 175–192.
- Zemberyova M., Bartekova, J., Hagarova, I. 2006. The utilization of modified BCR three-step sequential extraction procedure for the fractionation of Cd, Cr, Cu, Ni, Pb and Zn in soil reference material of different origins. *Talanta*, 70(5): 973–978.