Rapid Screening of Urban Soil Potential Toxic Trace Elements and Organic Matter, Košice City, Slovakia

Lenka Findoráková[1)], Oľga Šestinová[2*)], Jozef Hančuľák[3)]

[1)] Department of Environment and Hygiene in Mining,Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, Košice 040 01, Slovak Republic; email: findorakova@saske.sk; https://orcid.org/0000-0002-2287-3596

[2*)] Department of Environment and Hygiene in Mining,Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, Košice 040 01, Slovak Republic; email: sestinova@saske.sk; https://orcid.org/0000-0003-1684-7882

[3)] Department of Environment and Hygiene in Mining,Institute of Geotechnics, Slovak Academy of Sciences, Watsonova 45, Košice 040 01, Slovak Republic; email: hanculak@saske.sk; https://orcid.org/0000-0002-0374-1555

Abstract

Urban soil survey is necessary in terms of asses the life quality of their inhabitants. From this point of view the detection of the ecological risk in urban soils was done. At first fifteen samples were collected from a depth 0-30cm, in Košice city, Eastern Slovakia around the lake located in the residential zone. In collected samples potential toxic trace elements were established and also the presence of soil organic matter (SOM) was studied, because at present the SOM was recognized as an indicator of sustainable development in the frame of the UN Agenda 2030. SOM and soil organic carbon (SOC) have a positive effect on soil chemical, physical and biological properties. The pH of all studied samples was estimated in the range 6.83-7.42. For rapid screening were used following methods: X-ray fluorescence spectrometry (XRF) and total organic carbon (TOC) analysis. SOM was determined by calculation from the SOC amount. On the basis of XRF analysis it was found that the permitted limits for the elements Co, Ni, Cu, Zn, As were largely exceeded.

Keywords: *rapid screening, urban soil, toxic trace elements, XRF-spectrometry, slovakia*

Introduction

During recent years, soil quality and sustainable soils have become more appreciated as key factors in the long-term development of society. Urban soils research in cities has currently gaining importance especially in connection with the enormously growing urban population (UN 2018). Large cities are increasingly exposed to the risk resulting from the global impacts of climate change, drought or loss of biodiversity. Land occupation and degradation related to urban population growth increase this risk and cause obstacles to future development [1]. Urban park soils are one of the most important media for contaminants. It is needed to study this type of soil because they also represent an environmental risk. Especially children are exposed to health risks, when they come into the contact with pollutants in these soils. Therefore, more and more, the emphasis is on exploring urban soils in terms of their potential risk to human health, since person is with these soils in direct or indirect contact. Urban land, as well as other components of the environment, they should fulfill a basic environmental function and thereby ensure healthy development of the city population. Therefore, it is necessary to study the characteristics of urban park soil pollution. The urban park soils of Eastern Slovakia should be contaminated with inorganic and also with organic pollutants, which come from various anthropogenic activities including industrial activities, transport network, household waste and sludge coming from urban areas as well as fertilizers, pesticides, insecticides, which are dispersed in soil environment [2]. In our previous study we described the characteristics and seasonal variations of atmospheric deposition (AD) of selected elements in the urban and industrial environment of Košice. Detailed analysis of AD showed that in addition to Fe, Mn, and Cr, the ironworks complex is a source of dust particles, aluminum and other observed elements in descending order of lead, zinc, copper, arsenic and cadmium [3] and deposition fluxes at the site Košice-lake were significantly affected mainly by the nearby heating plant (TEKO). Also, it is evident that contamination varies in each city, mainly due to geochemical changes, population density, industrial, and traffic density [4-6] and the pollution sources have a negative impact on fauna, flora, and human health. For the rapid screening of urban park soils in Košice city, specifically soils around the Košice-lake lies in the middle of housing development, X-ray fluorescence spectrometry (XRF) coupled with C,H,N,S and total organic carbon (TOC) analysis were used, because these methods can be used to assess inorganic as well as organic pollutants. It is well known that the X-ray fluorescence spectrometry is a general analytical method which is used to analyses major and trace elements in many materials and also in rocks, minerals, sediments and soils. This method many authors used also to describe urban park soil contamination [7-9] and we also used it because it is a non-destructive method. Obtained results could provide a scientific reference for inorganic and organic risk levels in urban park soils of Košice and find potential pollution sources in the studied urban park area.

Study Area

The town Košice is bordered on the northwest by the massif of Black Mountain and Volov's hills. To the east, it is surrounded by the Slanske hills wall with volcanic origin. The Košice basin is located in a tectonically lowered area, where quaternary sediments of greater thickness occur. It has a lowland character and development began at the end of the Paleogene, and the

beginning of the Neogene. The geological composition and river relief were created by the rivers Torysa, Hornád, Bodva, and Ida [10]. The study area is one part of Košice, in the concrete Košice - city district called above the Lake. Its name is derived from the water reservoir called Lake, which was originally excavated for the mining of gravel-sands. Initially, the lake was fed by the waters of nearby river Hornád, after modifications it is fed by groundwater. Geographically it is positioned at latitude 48° 41′ 21.48″ North and longitude 21° 17′ 3.84″ East. The studied samples were collected from five sampling sites around the lake. The geographical coordinates are as follows: the first sampling site (S_1) lies at N48°41′38.6304′′, E21°16′54.8616′′, the second (S_2) at N48°41′32.2908′′, E21°17′00.0564′′, the third (S_3) at N48°41′12.4188′′, E21°17′28.8312′′, the fourth (S_4) at N48°41′20.8032′′, E21°17′26.6784 and the fifth (S_5) at N48°41′46.6656′′, E21°17′12.4656′′.

Soils sampling

From each sampling site, three times were soil samples taken, collectively 15 samples. Sampling was performed from horizon A (humic horizon, the topsoil horizon of arable land or grassland, the sample depending on the horizon depth) 30 cm depth and the samples were saved into plastic bags. Then samples were dried at laboratory temperature, quartered, sieved into fractions under 200 µm. Consequently physicochemical properties of five representative urban park soils marked as UPS_1, UPS_2, UPS_3, UPS_4 and UPS_5 were studied. The soil types were established according to the Reference Base for Soil Resources (IUSS Working Group WRB 2015) [11] and the Slovakia soil types (VÚPOP 2019) [12], in this area it is ANTHROSOLS.

Methods

The screening of urban soil potential toxic trace elements and organic matter was done at 5 representative samples, in which starting material was finearth I. Fineearth I is earth, that passes through a sieve with circular holes with a diameter of 2 mm. Fineearth II, was used for all down mentioned analysis. Fineearth II mean that the samples are sieved under the 0.25 mm. In all samples pH was measured with a potentiometric glass electrode in H_2O and KCl solution (ISO/DIS10390).

The risk-element concentrations were determined by SPECTROXEPOS X-ray fluorescence spectrometer (range of elements:Na(11)-U(92), scattering target Mo, Co, Al_2O_3, Pd, HOPG-crystal, X-ray lamp (typeVF50): Pd with Be window, resolution:145keV on lineKα Mn). For XRF analysis 5g of powder sample was homogenized with 1g of Clariant micropowder C (CEREOX BM-0002-1) and pressed with 15 tons pressure to get a pellet with a 32-mm diameter.

Soil total C, H, N, S content was identified by an elementary analyzer Vario MACRO cube (Elemantar Analyse systeme GmbH, Germany) using a thermal conductivity detector. A combustion tube was set up at 1150 °C and the reduction tube at 850 °C. Sulfanilamide (C = 41.81%, N = 16.26%, H = 4.56%, S = 18/0.62%) was used as the C, H, N, S standard.

Organic share (OS) and carbonates content (CC) were established by mass loss annealing to 550 °C and 850°C, respectively. Total organic carbon (TOC) in all samples was determined using TOC (marked as SOC-soil organic carbon) by company Ekolab s.r.o., Košice, Slovakia according to Norm. STN EN 13137.

Results

The soil type was determined based on the representation of soil particles according to their size, i.e. representation of grain size fractions of soil particles by sieve analysis. This analysis was also done because based on soil texture, which is the most stable soil characteristic, it decisively affects a number of soil properties. In our studied samples, according to the ČSN ON 736518, it was found three fraction types known as *sand* marked as the fraction **IV** (100-2000 µm) which represents 70.6-89.1%, the second one is called *silty-sand* marked as the fraction **III** (50-100 µm), which represents 7.4-12.3% and the third fraction found in our samples was *silt* fraction **II** (10-50 µm) which represents 0.5-17.1% (Figure 1). The fraction **IV** was the most represented in all samples. In the classification scale according to Novák (1949), the % representation of particles < 0.01 mm is also used to determine the soil type [13]. According to this classification, the soil type of the studied samples is as follows: samples, both soil types fall under the classification of *light soils*.
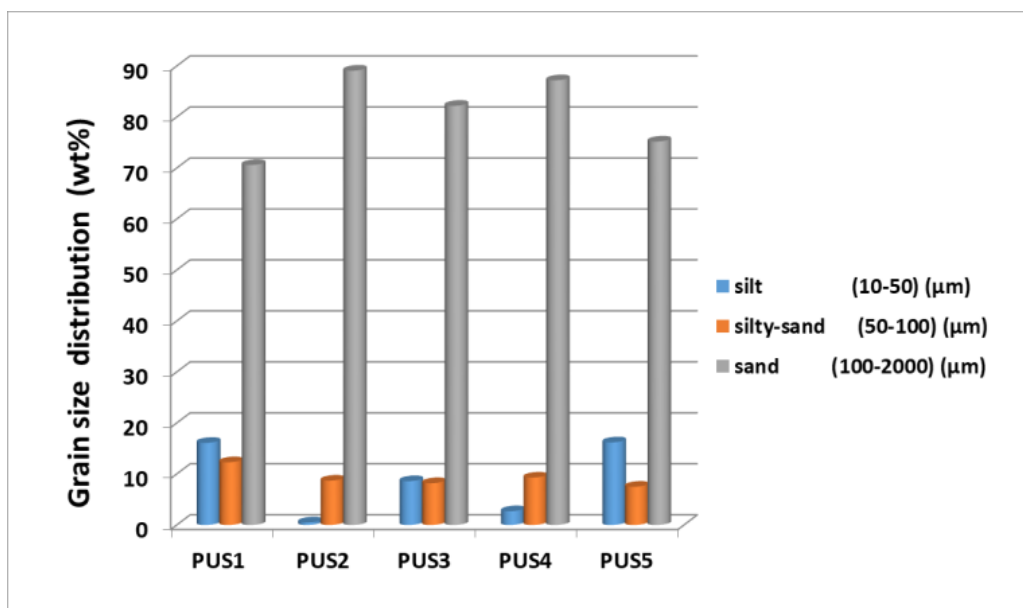

Fig. 1. Grain size samples distribution (wt.%).

Methodology for ecological risk assessment

For the evaluating the ecological risk of single pollutants, the single factor pollution index was used:

$$P_i = C_i/S_i \qquad (1)$$

where P_i is the environmental quality index of pollutant i in the soil, C_i is the concentration of pollutant i in the soil (mg/kg), S_i is background value [14]. The classification standard of the environmental quality index:

$P_i \leq 1$ means non-contamination
$1 < P_i \leq 2$ means slight contamination
$2 < P_i \leq 3$ means medium contamination
$P_i > 3$ means heavy contamination.

On the basis of the single factor pollution index (Table 1) it was found that the contamination of samples by toxic elements is as follow: Ni<Co<Zn<As<Cu. The non-contamination was found in the case Cr and heavy contamination was in the case of As and Cu. According to pollution factor it is evident that sampling sites S1 and S5 were the most contaminated mainly with Cu and As. In the case Zn, Co, Ni there was slight contamination in all studied samples. This is assumption was confirmed by XRF spectrometry as it is seen from table 2.

Tab. 1. The single factor pollution index characterizing the ecological risk of single pollutants.

Single factor pollution index (P_i)	Cr	Co	Ni	Cu	Zn	As
PUS₁	0.5	**1.2**	**1.3**	**3.3**	**1.3**	**4.5**
PUS₂	0.5	**1.7**	**1.5**	**2.8**	**1.5**	**2.2**
PUS₃	0.5	**1.7**	**1.3**	**2.8**	**1.2**	0.9
PUS₄	0.5	**1.7**	**1.3**	**2.7**	**1.1**	0.9
PUS₅	0.5	**1.5**	**1.2**	**3.4**	**1.8**	2.2

The contamination of samples were assess according to the limit risk element values (LV) in agricultural land due to law No. 508/2009 coll. act of the National Council of the Slovak Republic 220/2004 coll. on the agricultural land protection (Ministry of Agriculture 2022) and also according to mean concentrations of WAV (World average values), and EAV (European average values) described by Kabata-Pendias [15]. Also the contamination was assessing due to background values of soils which were calculated from geochemical database of uncontaminated Slovakian soils [16]. Exceeded concentration limits according to law No. 508/2009 were in the following order: Co<Ni<Zn<As<Cu. The most contaminated localities were locality S₂ and S₅ with all mentioned toxic elements except for Cr. The highest concentrations were in the case Cu and As, approximately two and three times more than limit value.

Tab. 2. Descriptive statistics of risk element concentrations (mg/kg) in park urban soils (PUS) around sites S₁-S₅ and those in other worldwide sites.

	Cr	Co	Ni	Cu	Zn	As
PUS₁						
min	73.5	9.5	60.7	185.7	184.1	110.7
max	74.9	18.3	65.3	217.8	193.9	113.9
mean	74	**13.3**	**63.1**	**199.8**	**188.3**	**112.4**
PUS₂						
min	67.1	11.5	67.9	134.3	191.7	39.4
max	86.2	27.3	85.2	187.4	236.1	63.4
mean	75.9	**18.7**	**75.1**	**167.9**	**220.2**	**54.0**
PUS₃						
min	63.9	14.4	56.7	143.2	154.9	22.5
max	86.0	24.5	68.5	186.4	190.9	26.1
mean	75.5	**19.4**	**63.9**	**167.8**	**178.7**	24.7
PUS₄						
min	69.9	15.4	64.0	164.4	149.6	21.0
max	87.0	24.3	67.8	160.5	185.3	25.3
mean	81.0	**19.7**	**65.7**	**163.3**	**161.8**	22.7
PUS₅						
min	*63.7*	*13.4*	*57.5*	*181.1*	*254.9*	*45.8*
max	82.4	20.5	66.8	217.1	270.8	60.3
mean	71.7	**16.8**	**62.2**	**203.2**	**265.3**	**54.8**
Background	**82.2**	-	**26**	**18**	**60**	**6.8**
LV	**150**	**11.3**	**50**	**60**	**150**	**25**
WAV	**59.5**	-	**29**	**38.9**	**70**	**6.8**
EAV	**94.8**	-	**37**		**68.1**	**11.6**
[17]	31.5	-	24.7	35.5	86.9	-
[18]	10.9	5.6	17.9	12.6	62.4	6.3

*Min-minimun, Max-maximum, "Background " - median background soil values according to Šefčík et al. [16], LV-limit value according to law No. 508/2009, SR 220/2004, WAV-World average value, EAV- Europan average value

Above mentioned law applies only for agricultural soils and not for park urban soils. But up today there is not a law for urban soils in Slovakia and in Europe, so we adhered to the aforementioned law. The concentrations of toxic elements were also done in all studied samples in individual grain size fractions. As it was mentioned above the main fraction was sand. In this fraction in all studied samples the toxic elements concentrations were lower than in the silt fraction as you can see from Figure 2, where was shown only two example samples, because this trend was found in all studied samples. Comparing concentrations in silt and sand fraction it was found that in all studied samples the concentrations of Cr, Cu, Zn, As were approximately 1.5 times higher than in the sand fraction. Only Cu silt concentration was 2-3 times higher than sand concentration in the all case.
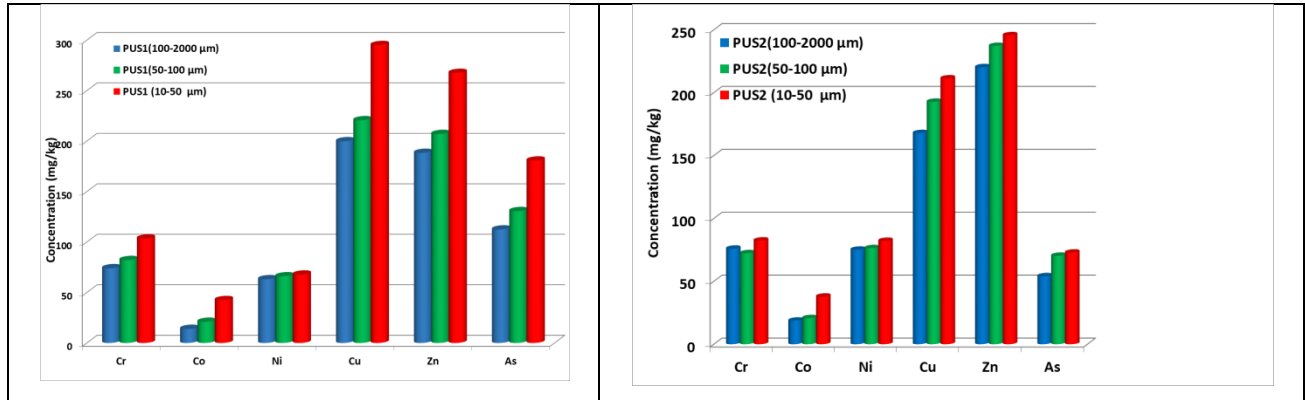

Fig. 2. Comparison of concentrations in samples PUS₁ and PUS₂ in individual particle size fractions.

Considering the soil quality assessment, we also focused on monitoring the carbonate contents and soil organic matter, which have a great importance in the element mobilization. Soil organic matter (SOM) has a significant part in the accumulation and regulation of the nutrient regime, in the accumulation of water and regulation of its regime, in the thermoregulation of soils, and participates in the binding of inorganic and organic substances. So from this point of view it is necessary to study also SOM. Considering that a quantitative indicator of soil organic matter (SOM) in the soil is the SOC content, which is closely related to the soil type, granular composition and degree of cultivation. But soil organic carbon (SOC) refers only to the carbon component of organic compounds. Soil organic matter (SOM) is difficult to measure directly, so laboratories tend to measure and report SOC. In this study the SOC share was also monitored. In studied samples SOC amount was in the range 2.41-3.72% (Table 3), which represents strongly humus soils according to Sotáková [19]. It is well known that about 58% of the all SOM exists as carbon. Based on this fact it is possible to estimate the percentage of SOM from the SOC% using the conversion factor 1.72 (derived from 100/58).

$$\text{Organic matter (\%)} = \text{total organic carbon (\%)} \times 1.72 \qquad (1)$$

This conversion factor may vary in different soils, but 1.72 provides a reasonable estimate of SOM for most purposes [20]

In the case of our samples it was found very high correlation between SOM and organic share (OS). The correlation coefficient was 0.9534. So the amount of soil organic matter based on the equation 1 is in the case of our samples in very good correlation.

Tab. 3. Elemental CHNS, soil organic carbon (SOC), organic share (OS), carbonate contents (CC) in (wt. %) and pH (mean values).

	C	H	N	S	SOC	OS	CC	pH(KCl)	pH(H2O)
PUS₁	3.34	0.70	0.33	0.15	2.41	6.0	9.2	7.45	8.11
PUS₂	5.30	0.65	0.38	0.09	3.30	7.1	14.5	7.50	8.09
PUS₃	4.30	0.74	0.43	0.07	3.72	7.8	10.7	7.52	8.00
PUS₄	2.50	0.53	0.29	0.04	2.26	5.0	6.9	7.40	8.12
PUS₅	3.35	0.65	0.38	0.06	2.75	6.6	8.8	7.36	8.03

The values of soil active and exchange reaction were in the interval 7.36-8.12, which indicates strongly alkaline soils. This alkalinity can be caused by a higher carbonate contents (table 3), which are a very important part of the soil mineral content and are a protection against constant acidification of the soil. The more carbonates the soil contains, the higher is its ability to resist acidification. The total carbonate content of 6.9-14.5% indicates that the studied soils are calcareous.

Conclusion

The soils of the studied location are characterized by the A horizon, a strongly alkaline soil reaction with a predominance of the sand fraction in their granular composition. Exceeded concentration limits according to law No. 508/2009 were in the following order: Co<Ni<Zn<As<Cu. The most contaminated sites were S₂ and S₅ with all mentioned toxic elements except for Cr. The highest concentrations were in the case Cu and As, approximately two and three times more than limit value. The studied samples were strongly humus according to SOC amount 2.41-3.72% and calcareous according to total carbonate content 6.9-14.5%. Very high correlation (0.9534) between SOM and organic share (OS) was found. Based on our previous study detailed analysis of atmospheric deposition showed that in addition to Fe, Mn, and Cr, the ironworks complex is a source of dust particles, aluminum and other observed elements in descending order of lead, zinc, copper, arsenic and cadmium and deposition fluxes at the site Košice-lake were significantly affected mainly by the nearby heating plant (TEKO). According to these results the atmospheric

deposition results in high levels of heavy metals in heavily industrialized areas. Concentrations of certain heavy metals in park urban soils, especially Zn, Cu, As, in humus layers show regional gradients reflecting patterns of atmospheric deposition.

References

1. J. Sobocká, M. Saksa, J. Feranec, D. Szatmári, J. Holec, H. Bobáľová, A. Rášová, Mapping of environmentally sensitive areas in Bratislava city, J. Soil Sediments. DOI: https://doi/org/10.1007/s11368-020-02682-4 (2020).

2. L. Findoráková, O. Šestinová, M. Kováčová, M. Assessment of potential sediment contamination using screening methods (XRF, TGA/MS) taking into account principles of green chemistry, eastern slovakia. Environ. Earth Sci., 76(3) doi: 0.1007/s12665-017-6433-zM, (2017).

3. J. Hančuľák, O. Šestinová, L. Findoráková, Characteristics and seasonal variations of atmospheric deposition of selected elements in the urban and industrial environment of košice (slovakia). Paper presented at the IOP Conference Series: Earth and Environmental Science, , 906(1) (2021), doi:10.1088/1755-1315/906/1/012100

4. A. Aboubakar, A. Douaik, Y.C. Mfopou Mewouo, B.A. Madong, A. Dahchour, S. El Hajjaji, Determination of background values and assessment of pollution and ecological risk of heavy metals in urban agricultural soils of Yaoundé. Cameroon, J Soil Sediment 21:1437–1454, (2021), https:// doi. org/ 10. 1007/s11368- 021- 02876-4

5. H. Zhu, N. Liu, H. Chen, J. Lei, Kinetic analysis on chemical interactions between plants and soil in pyrolysis and combustion. Fire Saf J 126, (2021), https:// doi. org/ 10. 1016/j. fires af. 2021. 103473

6. H. Haghnazar, J.A. Cunningham, V. Kumar, E. Aghayani, M. Mehraein, COVID-19 and urban rivers: effects of lockdown period on surface water pollution and quality - a case study of the Zarjoub River, north of Iran. Environ Sci Pollut Res., (2022) , https:// doi. org/ 10.1007/ s11356- 021- 18286-5

7. W. Wan, H. Hu, M. Qu, W. Li, C. Zhang, J. Kang, B. Huang, Rapid estimation of soil cation exchange capacity through sensor data fusion of portable XRF spectrometry and vis-NIR spectroscopy. Geoderma, 363, doi:10.1016/j.geoderma.2019.114163, (2020)

8. X. Shengguo, R. Korna, F. Jiarong, K. Wenshun, W. Lou, J. Wang, F. Zhu, Spatial distribution, environmental risks, and sources of potentially toxic elements in soils from a typical abandoned antimony smelting site, J. Environ. Sci., 127, pp.780-790, ISSN 1001-0742, https://doi.org/10.1016/j.jes.2022.07.009 , (2023)

9. R. Measurement, M. Mitaphonna1, N. Ramli, N. Ismail, N. Idris, Evaluation of Geochemical Signature in Soil Sampled from a 2004 Indian Ocean Tsunami-stricken Region in Aceh Province Located in the Western Part of Indonesia Using Scanning Electron Microscopy–Energy Dispersive X-ray (SEM-EDX) Spectroscopy and Its Compatibility with X-ray Fluorescence (XRF) Philippine Journal of Science 152 (1): pp. 485-499, (2023).

10. M. Zeleňáková, J. Vinayakam, S. Arjun, D. Káposztásová, H. Hlavatá, Dynamic analysis of meteorological parameters in Košice climatic station in Slovakia. Water 10(6):702 (2018).

11. IUSS Working Group WRB (2015) World Reference Base for Soil Resources 2014, update 2015 International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106. FAO, Roma IT EU, 192 p

12. VÚPOP (2019) Pôdny portál SR. www. podne mapy. sk

13. A. Zaujec, J. Chlpík, J. Nádašský, N. Szombathová, E. Tobiašová, Pedológia a základy geológie. 1 vyd. Nitra : SPU, 2009. 399 s. ISBN 978-80-552-0207-5.

14. M. Sun, T. Wang, X. Xu, L. Zhang, J. Li, Y. Shi, Ecological risk assessment of soil cadmium in Chinas coastal economic development zone a meta-analysis. Ecosyst Health Sustain 6(1), (2020), https://doi. org/ 10. 1080/ 20964 129. 2020. 17339 21

15. A. Kabata-Pendias, Trace elements in soils and plants, (2011) 4th edn. CRC Press, Taylor and Francis Group

16. P. Šefčík, S. Pramuka, A. Gluch, Assessment of soil contamination in Slovakia according index of geoaccumulation. (2008) Agriculture 54:119–130.

17. S. Z. Yaghoubi, S. A. Hosseini, G. N. Bidhendi, A. Sharafati, Assessment of heavy metals in contaminated soils of urban parks in Tehran, Iran, International Journal of Environmental Science and Technology (2022) 19:12303–12314, https://doi.org/10.1007/s13762-022-04454-8

18. M. Salee, D.A. Sens, S. Somji, D. Pierce, Y. Wang, A. Leopold, M. Ehsanul Haque, S.H. Garrett, Contamination Assessment and Potential Human Health Risks of Heavy Metals in Urban Soils from Grand Forks, North Dakota, USA (2023)Toxics 11(2), pp. 132

19. S. Sotáková, Organická hmota a úrodnosť pôdy. Príroda, Bratislava. (1982) 234 s.

20. F. Hoyle, Managing soil organic matter: A practical guide, Grains Research and Development Corporation, Kingston, (2013) ISBN 978-1-921779-56-5.