Bulgarian Journal of Agricultural Science, 25 (No 3) 2019, 519–526

Coefficients of heavy metal accumulation in forest soils

Diana Malinova[1*], Ludmila Malinova[2], Kameliya Petrova[2], Biser Hristov[3]

[1]*University of Forestry, Faculty of Ecology and Landscape Architecture, 1756 Sofia, Bulgaria*
[2]*University of Forestry, Faculty of Forestry, 1756 Sofia, Bulgaria*
[3]*Institute of Soil Science, Agrotechnologies and Plant Protection "Nikola Poushkarov", 1331 Sofia, Bulgaria*
[*]*Corresponding author:* dianamalinova@yahoo.com

Abstract

Malinova, D., Malinova, L., Petrova, K. & Hristov, B. (2019). Coefficients of heavy metal accumulation in forest soils. *Bulgarian Journal of Agricultural Science*, *25*(3), 519–526

In a number of publications, it is reported that the surface soil layer in forest territories often contains increased heavy metal quantities, but at present there are lack of criteria for evaluation of their origin. In the present studies is assumed that regarding the forest territories, the determination of heavy metal accumulation coefficients in the surface soil layer is a suitable criterion for distinguishing the natural accumulation processes from the aerosol pollution because the use of norms may lead to incorrect assessment of the contamination caused by atmospheric depositions. The accumulation coefficients of Mn, Zn, Cu, Pb and Cd in the surface soil layers were determined. Data obtained from a 16 x 16 km network in landscape of the Balkan Mountains (40 profiles), Rhodope Mountains (33 profiles), Sredna Gora (22 profiles), obtained in the period from 1986 to 2017, as well as the results obtained at 2 intensive monitoring field stations. Results of litterfall and soil solution analysis were assessed for interpretation of the obtained coefficients. The maximum coefficients (3.00 for Mn, 3.43 for Pb, 2.55 for Cu, 2.25 for Cd and 1.86) are the product of natural accumulation processes and are caused by the high soil acidity.

Keywords: forest soil; heavy metals; acidity; coefficient of accumulation

Introduction

The assessment of the natural heavy metal accumulation in the surface soil layers of unpolluted areas is one of the possible methodological approaches to distinguish the additional anthropogenic contribution of heavy metals in soil due to aerosol deposition (Raikov et al., 1983; Mmolawa et al., 2011; Barbieri, 2016). The surface soil layer is of particular concern due to its role as a stable adsorbent of atmospheric metal deposition. In some studies the heavy metal content in litter is reported to be higher than in the soil which affects the decomposition of organic matter and the heavy metal accumulation in forest litter (Laskowski et al., 1993; Jelaska et al., 2007; Jingjun et al., 2008). The analysis of the soil monitoring database in forest ecosystems in Europe (Vanmechelen et al., 1997) confirms the higher content of Mn, Cu, Pb and Cd in litter of acidic soils, compared to the surface mineral soil layer.

An important aim of many environmental studies is to outline the areas where the soil contains potentially toxic materials (Goovaerts et al., 1997), but currently there is still lack of standards for assessment of soil contamination in the forest territories. In order to overcome this problem some authors use the coefficients of heavy metal accumulation (CA) (Mutsch, 1998; Walthert et al., 2004). These coefficients, also known as "enrichment factors" are applied for assessment of the changes in chemical composition of soils in permanent sample plots, for example in Austria for the period from 1986 to 2012 (Smidt et al., 2012). In their study Blaser et al. (2000) concluded that for the assessment of soil pollution it is more appropriate to use the coefficients in comparison with the application of the maximum allowable concentrations because the enrichment factors consider the effects of geological variation on metal abundances. The use of only norms may lead to incorrect conclusion about soil contamination caused by the atmospheric depositions (Malinova, 2014).

The aim of the present study is to calculate the coefficients of heavy metal accumulation (CA) in the surface soil layers of landscapes, distant from industrial and urban centres in order to numerically define the extent of natural accumulation processes as criteria for distinguish them from the aerosol soil contamination.

Materials and Methods

The coefficients of accumulation (CA) of the following heavy metals – Mn, Zn, Cu, Pb, and Cd in the surface soil layer of Cambisols were determined as ratios between their content in the soil layers 0-10 cm and 40-60 cm (or 60-80 cm depending on the depth of the soil). The results of the heavy metal content in soils from the National Environmental Monitoring System, which is a part of the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests, operating under the UNECE – CLRTAP, were used to perform the calculations. Data obtained from permanent sample plots from the 16 x 16 km network in beech (*Fagus Sylvatica* L.) landscape of the Balkan Mountains and the coniferous (pure and mixed stands of *Pinus sylvestris* L., *Picea abies* L., *Abies alba* Mill.) landscape of the Rhodope Mountains and Sredna Gora, as well as the results obtained at 2 intensive monitoring field stations in the Balkan Mountains – „Vitiniya" and „Staro Oryahovo" for the period 1986 – 2008 were used. Summary analysis and assessment of the heavy metal content in soils and forest litter for the respective period were made by Malinova et al. (1998), Pavlova et al. (2001), Kolarov et al. (2002), Pavlova et al. (2006), Malinova (2014). The results were supplemented with new ones, obtained for the period 2009 – 2017.

Additional studies on the heavy metal content in litter and soil from the territories of the "Central Balkan" National Park (Malinova, 2015; Karatoteva et al., 2016), "Bulgarka" Natural Park (Malinova, 2010; Karatoteva et al., 2014) and Petrohan Training and Experimental Forest Range, located in the Balkan Mountains, were conducted.

The heavy metal content in soils was determined by decomposition with Aqua regia and Flame AAS (ISO 11466) Perkin Elmer 5000. The results of litterfall and soil solution from the intensive monitoring field stations "Vitiniya" and "Staro Oryahovo" were analysed in order to evaluate the CA values.

The heavy metal content in litterfall was determined by Flame AAS (ISO 11466) and in soil solution after filtration by AAS Graphite furnace. Analyses were performed in the laboratory of a National Environmental Agency.

The soils were divided into 2 groups:

(1) Soil with $pHCaCl_2$ < 4.2 – these conditions are an indicator of Mn-oxides dissolution, weathering of secondary silicates (clay minerals) and dissolution of Fe-oxides (Ulrich, 1983).

(2) Soil with $pHCaCl_2$ > 4.2 – dissolution of $CaCO_3$, weathering of primary silicates and proton exchange with base cation from exchange complexes (Ulrich, 1983).

To assess the soil conditions where different values of CA occur, the latter were divided into 3 groups: CA < 1.0; CA 1.0 ÷ 1.50 and CA > 1.50.

The statistical analysis of the obtained data was performed using the Statistika 10 software.

Only data from sites that are distant from industrial immission sources were used to perform the CA calculations. The concept of De Vos et al. (2010) that the current heavy metal content is the result of their background concentration plus the contribution of atmospheric depositions was assumed. Regarding the large territories where the research was implemented the contribution of atmospheric depositions cannot be distinguished from the natural background due to the lack of data from the previous periods.

Results and Discussion

The analysis of the obtained coefficients of heavy metal accumulation (CA) in the surface soil layers showed significant variation of the values. No statistically significant differences between the CA in the two studied sites – the beech landscape of the Balkan Mountains and the coniferous one at the Rhodope Mountains and Sredna Gora were determined which enabled the combination of the obtained data.

The CA variation by soil groups – with $pHCACl_2$ < 4.2 and with $pHCACl_2$ > 4.2 was also significant. The statistical analysis showed a slight differentiation of the CA values from $pHCaCl_2$ and the quantity of org. C. The resulting low correlation coefficients are explained by the presence of CA with values below and above 1.0 in both soil groups – with $pHCaCl_2$ < 4.2 and with $pHCaCl_2$ > 4.2 (Table 1). This means that both accumulation and migration processes occurred in the surface soil layers.

However, the results clearly show that in cases of high soil acidity the majority of CA mean values were higher in comparison with the ones in soils with $pHCaCl_2$ > 4.2 (Table 2). The maximum CA values were obtained also from the group of the highly acidic soils. The process of elements'

Table 1. Percentage distribution of the coefficients of heavy metal accumulation (CA) in the surface soil layer of Cambisols by groups in soils with pH$CaCl_2$ < 4.2 and soils with pH $CaCl_2$ > 4.2

Elements	Groups of CA	pH$CaCl_2$ < 4.2	pH$CaCl_2$ > 4.2
		CA (%)	
Mn	<1.0	53	21
	1.0-1.50	32	65
	>1.50	15	15
Pb	<1.0	18	39
	1.0-1.50	38	37
	>1.50	44	24
Cu	<1.0	53	33
	1.0-1.50	25	60
	>1.50	33	7
Zn	<1.0	59	34
	1.0-1.50	32	66
	>1.50	9	–
Cd	<1.0	38	68
	1.0-1.50	62	29
	>1.50	–	4

return to the soil surface through forest litter should be taken into consideration in the forest landscapes. As determined from the analysis, in most of the cases in the studied areas it is characterized by a higher heavy metal content in comparison with the surface soil layer (Malinova, 2014).

The accumulation and migration processes, apart from the mineral soils, occur also in the organic layers as the balance between the heavy metal input and output depends on a number of microbiological activity factors, oxidation and reduction processes, precipitation amounts, etc. (Hernandez et al., 2003). Despite the strong connection of the metals with the organic matter, the release rate of the individual elements from it is different.

Mn is one of the most mobile metals in soil (Heinrichs et al., 1980) and its content in the soil solution decreases 100 times with the increase of pH$CaCl_2$ by 1 unit (Schulte et al., 1999). Among the obtained CA, the highest value – 3.00 was determined for Mn in soils with pH$CaCl_2$ < 4.2. The conditions, corresponding to the resulting high CA for Mn, were characterized by a relatively narrow pH$CaCl_2$ interval (from 3.6 to 3.7), which is a very strong acidic reaction. These values are an indicator of Mn-oxides dissolution, weathering of secondary silicates (clay minerals) and dissolution of Fe-oxides (Ulrich, 1983). An important characteristic of the soil from the forest landscapes is its high acidity, presence of increased quantity of accessible to plants forms of heavy metals which can easily be absorbed by the plants. This process can be seen by the results obtained from the intensive monitoring field station of the beech stand in the Balkan Mountains – "Vitinya". The soil is highly acidic, with pH$CaCl_2$ = 3.9. High concentrations of Mn and Fe were determined in the lysimeter water. Their mean annual values – 319 μg.l^{-1} – 639 μg.l^{-1} for Mn and 109 μg.l^{-1} – 579 μg.l^{-1} for Fe (for the period 2014-2017) were within the soil variation ranges for the Europe's forests (ICP Forest Manual – part XI 2016), but the maximum values were extremely high and beyond the ranges – 1890 μg.l^{-1} for Mn and 9487 μg.l^{-1}. The obtained results showed that intensive migrations processes occurred in the soil. A part of the released heavy metals from the dissolution of their oxides are leached, but another part is absorbed by the plants in increased amounts. This is illustrated on Fig. 1 for the content of Mn in the litterfall from the same field station. In the period 2009-2016 it exceeded the maximum value for the beech forests in Europe (ICP Forest Manual, part XIII 2016).

Litterfall forms high content of Mn in litter. Under its influence accumulation processes occur in the surface soil layer and it is enriched with Mn. The vertical distribution of Mn in the soil profile is presented on Fig. 2. The high surface

Table 2. Coefficients of heavy metal accumulation (CA) in the surface soil layers, pH$CaCl_2$ and org. C in Cambisols

Value	pH$CaCl_2$,	Org. C g.kg^{-1}	CA				
			Mn	Zn	Cu	Pb	Cd
Soil pH$CaCl_2$ < 4.2							
mean	3.86	43.20	1.34	0.89	1.05	1.39	0.88
SD	0.23	38.05	0.59	0.30	0.74	0.69	0.57
min	3.40	1.69	0.35	0.37	0.27	0.28	0.14
max	4.20	138.8	3.00	1.86	2.55	3.43	2.25
Soil pH$CaCl_2$ > 4.2							
mean	5.26	27.89	1.16	0.95	0.93	1.13	0.76
SD	0.81	21.37	0.47	0.38	0.45	0.46	0.43
min	4.28	4.12	0.29	0.31	0.17	0.28	0.12
max	7.40	83.70	2.17	1.94	1.93	1.90	1.55

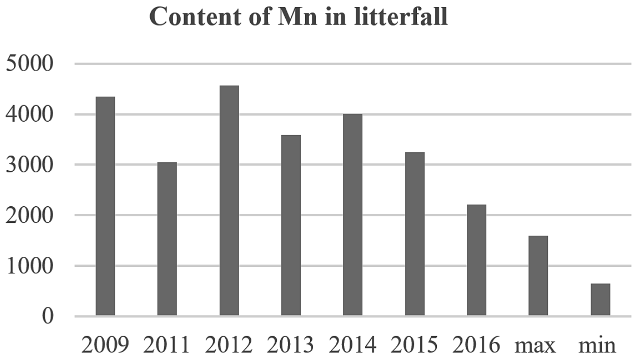

Fig. 1. Content of Mn (µg.g^{-1}) in litterfall at "Vitinya" field station

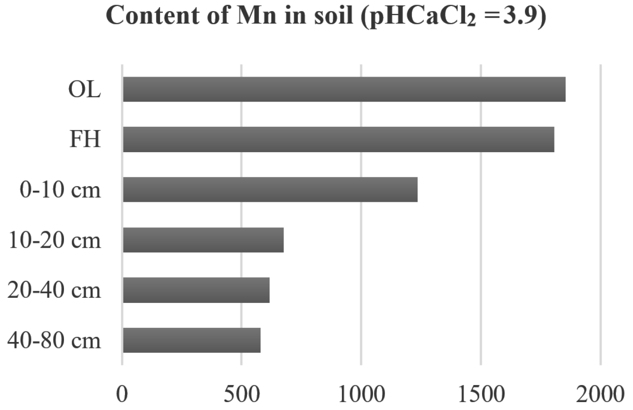

Fig. 2. Content of Mn (mg.kg^{-1}) in the soil profile from the „Vitinya" field station

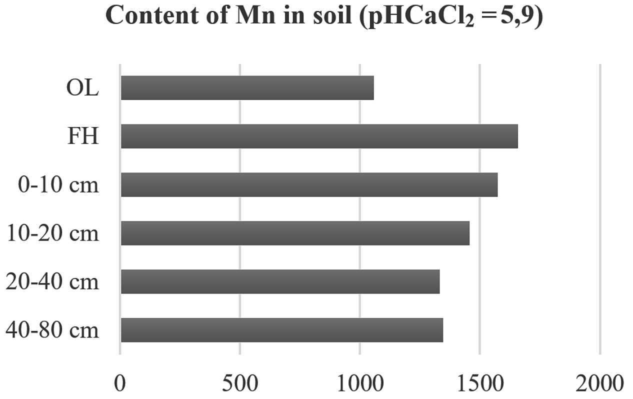

Fig. 3. Content of Mn (mg.kg^{-1}) in the soil profile from the "Staro Oryahovo" field station

concentration appears as air pollution but no actual pollution is determined.

It is appropriate to compare the vertical distribution of Mn in soil profile (Fig. 2) with another one with pHCaCl$_2$ > 4.2, which is the intensive monitoring field station in the Balkan Mountains, in the Staro Oryahovo locality (Fig. 3). In the latter a gradual decrease of Mn content in depth can be seen, and the CA is relatively low – 1.2. In the highly acidic soil (Fig. 2) the obtained CA is high – 2.1. The content of Mn sharply decreases in depth due to the occurring migration processes, resulting in soil Mn impoverishment.

The number of cases with CA of Mn, greater than 1.5, is low – 15 % (Table 1). They occur in soils with high org. C content in the surface horizon ranging from 57.3 g.kg^{-1} to 138.8 g.kg^{-1}. Higher CA are obtained for Mn and Pb (5.90 and 5.45, respectively), but their origin – natural and/or anthropogenic is controversial and therefore these values are excluded from the present analysis (Karatoteva et al., 2018).

CA values < 1.0 are the most common – 53 % (Table 1). They characterize the predominance of the migration and accumulation processes in soils and occur at pHCaCl2 within the range from 3.9 to 4.1. The org. C content varies from 8.1 g.kg^{-1} to 51.5 g.kg^{-1}, which is significantly lower compared to soils with CA >1.5. Concentrations, lower or comparable with the lower layers, are formed in the surface part of these soil profiles. The fact is that in the humus-rich soils there are also CA < 1.0, indicating that the role of high acidity is of greater importance for Mn behaviour.

In soils with pHCaCl$_2$ > 4.2 the mean CA value for Mn is lower in comparison with the one in soils with pHCaCl$_2$ < 4.2 (Table 2). The accumulation processes are slightly expressed in this soil group and the migration processes are discontinued by increasing the pH in the neutral and alkaline spectrum.

Zn is also highly mobile element and its profile distribution is estimated as elluvial – illuvial. According to Sheila (1994) its mobility decreases 100 times by increasing the pH with 1 unit. It is also characterized by a high transfer coefficient between soil and plants (Kadovic et al., 2011). Similar to other metals – Cd, Mn, Pb, the amount of Zn in the forest litter is higher than the one in the surface soil layer and is due to its accumulation in the organic matter (Jones et al., 1988).

The high mobility of Zn is also evident from the obtained CA values. Regarding the soils with pHCaCl$_2$ < 4.2, in 59% of the cases the CA was lower than 1.0. Unlike Mn and Pb the mean CA value was lower than 1.0, meaning predominant migration processes under high acidity conditions. Only 9% of the studied cases were characterized with high CA values – more than 1.5 and they referred to soils with not so strong acidic reaction, ranging from pHCaCl$_2$ 4.0 to pHCaCl$_2$ 4.2, where the movement of Zn in depth was less pronounced. The org. C content was within the ranges from 8.5 to 20.4 g.kg^{-1}.

In the soils with pHCaCl$_2$ > 4.2 the mean CA value of Zn was also lower than 1.0. The profile distribution of Zn in these soils is characterized by close in value concentrations in the different layers, thus forming CA with values about 1.0.

Regarding Cu the mean CA value for the soils with pHCaCl$_2$ < 4.2 is 1.0. In 53% (Table 1) of the examined cases the surface soil layers contained concentrations of Cu, comparable with those in the layer 40-60 cm. High coefficients above 1.5 were determined only in 22% of the studied soils. The maximum CA was 2.55, determined in soils with pHCaCl$_2$ 3.5 – 3.6 and with high org. C content – from 80 g.kg^{-1} to 84.3 g.kg^{-1}. In that case the accumulation of Cu is also caused by its high content in the litterfall where it is two times higher than the maximum value (14 µg.kg^{-1}) for the European forests (ICP Forest Manual, part XIII 2016). The retention of Cu in the mineral soil is only in the surface layer, similar to Mn.

CA between 1.0 – 1.50 (60% of the studied cases) prevailed in the soils with pHCaCl$_2$ > 4.2. They occurred in soils with pHCaCl$_2$ from 4.3 to 7.2 and strongly varying org. C content – from 4.2 g.kg^{-1} to 43.2 g.kg^{-1}. The distribution of Cu content in depth of the soil layers was relatively uniform – low concentrations and absence of strong and clearly expressed accumulation processes. High coefficients – above 1.50 were determined in soils with pH within the range pHCaCl2 5.2 – pHCaCl$_2$ 5.9 and not very high org. C content – from 22 g.kg^{-1} to 26 g.kg^{-1}. The heavy metal immobilisation and accumulation in the surface soil layer in such cases is the result of hydroxide precipitation, complex binding with the organic matter, etc. The stability of complex formation with the organic matter is extremely high and unlike Zn and Pb, Cu can hardly be washed away (Kumpiene et al., 2008).

The behaviour of Pb is characterized by the active binding with the organic matter which is determined by its high ionic radius. In some studies (Dumoulin et al. 2017) the content of soluble Pb is estimated to be low and according to other studies it is characterized by a high affinity to solubility (Harvey et al., 2017). According to Faytondziev (1984) the balance between the input and output of Pb from the surface soil layer is directed mostly to accumulation. This is also confirmed in areas with a significant acid contamination, where the Pb concentrations in the surface soil layers also increase (Harvey et al., 2017).

The resulting CA values for Pb showed a slightly expressed dependence from the content of org. C (r = 0.44) and pHCaCl$_2$. Nevertheless, the highest CA – over 1.5 occurred in humus –rich soils with very high acidic reaction (org. C 60.0 g.kg^{-1} – 138.8 g.kg^{-1} and pHCaCl$_2$ 3.5 – 4.2). These cases were 44% (Table 1). The maximum CA value for Pb is high – 3.43 (Table 2). The CA with values from 1.0 to 1.5 represented 38% (Table 1), so it can be concluded that the accumulation processes predominate regarding the behaviour of Pb.

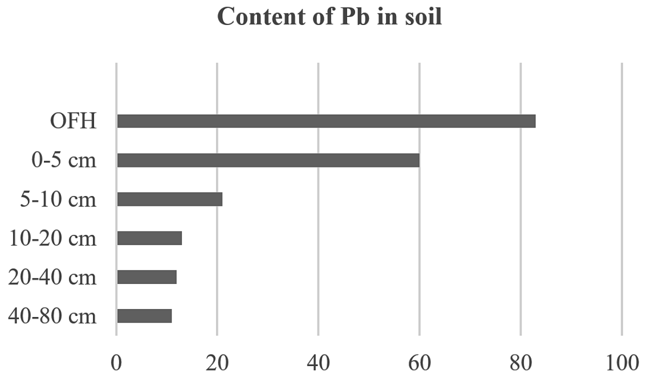

Fig. 4. Content of Pb (mg.kg^{-1}) in the soil profile from the "Vitinya" field station

The conditions under which the migration processes dominated, i.e. CA < 1.0 represented the smallest share – 18% (Table 1) and were characterised by low org. C content (7.4 g.kg^{-1} – 22.2 g.kg^{-1}). The pHCaCl$_2$ values of these soils did not differ from the group with CA above 1.5.

The profile distribution of Pb (Fig. 4) is similar to the one of Mn in the acidic soil from the "Vitinya" field station (Fig. 2). The accumulation processes primarily affect the surface soil layer. In depth there is sharp decrease of its amount. These processes are also related to the influence of the organic matter which enters the soil surface.

Regarding the assessment of Pb content in the litterfall no comparison can be made with the values for the European forests due to the absence of such values in the source used (ICP Forest Manual, part XIII 2016). For the purposes of this study the mean value (MV) of Pb content in litterfall was calculated for the period 2009 – 2016 for the stand from the "Staro Oryahovo" field station where the soil is with pHCaCl$_2$ = 5.9. The increased content of Pb in the litterfall in the acidic soil compared to the MV is presented in Fig. 5.

The accumulation of Pb in the surface soil layer is due to the litterfall enrichment – a characteristic feature of the soils with high acidity, which explains the high CA values.

The great importance of Cd for the environment derives from its high mobility (Bak et al., 1997; Dokmeci et al., 2009). It is easily extracted from the litter and is present in

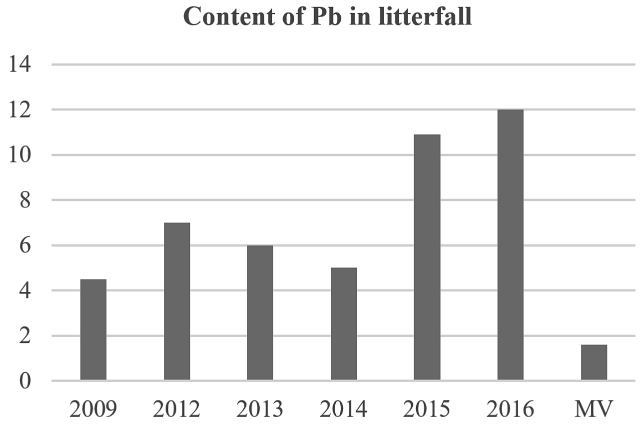

Fig. 5. Content of Pb (µg.g^{-1}) in litterfall from the "Vitinya" field station
*MV – mean value of the Pb content in litterfall for the period 2009-2016 in stands with neutral soil ("Staro Oryahovo" field station)

the solution in ionic form and soluble organic compounds (Jones et al., 1988). A large part of its total amount is in the form of exchange cations (Vanmechelen et al., 1997).

One of the lowest mean CA values of all studied soils with pHCaCl$_2$ < 4.2 was determined for Cd – 0.88. The maximum value was 2.25 and referred to soil with pHCaCl$_2$ = 3.3 and very low org. C content – 5.42 g.kg^{-1}. The organic matter is an important Cd adsorbent therefore its low amount contributes to the high mobility. The profile distribution of Cd in the highly acidic soil from the "Vitinya" field station is presented on Fig. 6. The change in the content of Cd from litter in the surface soil layer is very sharp as the difference is 8.2 times. For comparison, this difference is 4.6 for Zn, 2.0 for Pb, 1.5 for Cu, and 1.4 for Mn in the same soil profile.

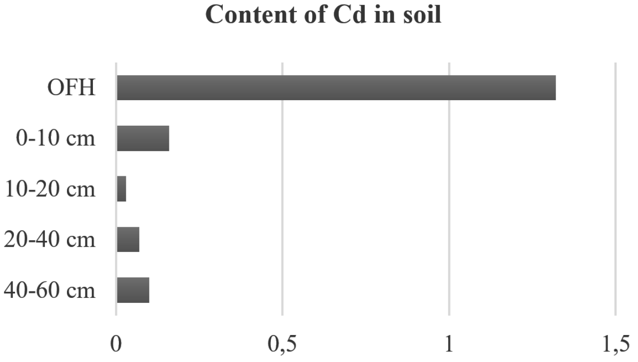

Fig. 6. Content of Cd (mg.kg^{-1}) in the soil profile from the "Vitinya" field station

The higher mobility of Cd in the surface soil layer explains the lower CA values obtained from acidic soils in comparison with CA in the other elements.

The CA of Cd, lower than 1.0, predominated in the soils with pHCaCl$_2$ > 4.2. One third of the coefficients exceeded 1.0 and only 1 value was above 1.50. These results referred to soils with average to high org. C content – from 22.5 g.kg-1 to 42. 8 g.kg^{-1}.

Similar coefficients for the soils in Bulgaria were calculated in 1983 (Raikov et al., 1983) for agricultural lands. Their values are significantly more homogenous and vary about 1.5. In contrast, in soils from the forest landscapes under the influence of litter, functioning to restore the elements absorbed by the plants back in the soil, the accumulation processes occur regardless of pH. This characteristic should be taken into consideration in the evaluation of the heavy metal content in forest soils to distinguish the natural accumulation processes from pollution with aerosol origin.

Conclusions

The obtained coefficients of heavy metal accumulation present quantitative values of the natural environmental degree of heavy metal accumulation in the surface soil layers of Cambisols. The coefficient values for beech landscape in the Balkan Mountains and the coniferous landscape of the Rhodopes and Sredna Gora do not differ. Their maximum values – 3.00 for Mn, 3.43 for Pb, 2.55 for Cu, 2.25 for Cd and 1.86 for Zn could serve to distinguish the naturally occurring accumulation processes from aerosol contamination with heavy metals. The coefficients allow the implementation of contamination risk assessment of grass species in pastures, medicinal plants, mushrooms, etc., as well as the development of criteria for their protection.

Acknowledgements

The present research was supported by the Executive Environment Agency – Ministry of Environment and Water, Projects No. 76/2011, No. 97/2014 of University of Forestry and Project BG05M2OP001-2.009-0034 „Support for the Development of Scientific Capacity at the University of Forestry" funded by OP „Science and Education for Smart Growth", co-funded by European Union through European Structural and Investments Funds.

References

Bak, J., Jensen, J., Larsen, M. M., Pritzl, G., & Scott-Fordsmand, J., (1997). A heavy Metal Monitoring Programme in Denmark. *Sci Total Environ.* 207:179-186 https://doi.

org/10.1016/S0048-9697(97)00262-3.

Barbieri, M., (2016). The Importance of Enrichment Factor (EF) and Geoaccumulation Index (Igeo) to Evaluate the Soil Contamination. *J Geol Geophys*, 5: 237 doi:10.4172/2381-8719.1000237.

Blaser, P., Zimmermann, S., Luster, J., & Shotyk, W., 2000. Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils. *Sci. Total Environ*, 249:257-280, https://doi.org/10.1016/S0048-9697(99)00522-7.

De Vos, B., Iost, S., & Cools, N. (2010). Soil and soil solution research: separate tracks leading to an integrated approach within ICP Forest. Research for ecosystem function and restoration of heavy metal polluted forests. In: John Demore–Ambassador for forest monitoring in Europe, Finnish Forest Research Institute, Finland, pp 25-26.

Dokmeci, H., Ongen, A., & Dagdeviren, S. (2009). Environmental toxicity of cadmium and health effect. *J Environ Prot Ecol*, 10: 84-93.

Dumoulin, D., Billon, G., Proix, N., Frérot, H., Pauwels, M., & Saumitou, P. (2017). Laprade: Impact of a zinc processing factory on surrounding surficial soil contamination. *J Geochem Explor*, 172: 142-150.

Faytondzhiev, L. (1984). Behavior of lead. In: Problems of soil contamination. Zemizdat, Sofia, pp 130-136.

Goovaerts, P., Webster, R., & J-P. Duboi (1997). Assessing the risk of soil contamination in the Swiss Jura using indicator geostatistic. *Environ Ecol Stat*, 4:31-48.

Harvey, J., Rouillon, M., Dong, C., Ettler, V., Handley, H. K., Taylor, M. P., Tyson, E., Tennant, P., Telfer, V., & Trinh, R. (2017). Geochemical sources, forms and phases of soil contamination in an industrial city. *Sci Total Environ*, 584-585:505-514.

Heinrichs, H., & Mayer, M. (1980). The role of forest vegetation in the biogeochemical cycle of heavy metals. *J Environ Qual*, 9:111-118 DOI10.2134/jeq1980.00472425000900010025x.

Hernandez, L., Probst, A., Probst, J. L., & Ulrich, E. 2003. Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. *Sci Total Environ*, 312:195-219.

ICP Forests Manual (2016a). Sampling and Analysis of Soil. In: Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests, UNECE – CLRTAP, Part X, 115 https://www.icp-forests.org/pdf/manual/2016/Manual_2016_Part_X.pdf.

ICP Forests Manual (2016b). Sampling and Analysis of Soil Solution. In: Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests, UNECE – CLRTAP, Part XI, 29, https://www.icp-forests.org/pdf/manual/2016/Manual_2016_Part_XI.pdf.

ICP Forests Manual (2016c). Sampling and Analysis of Litterfall. In: Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests, UNECE – CLRTAP, Part XIII, 15. https://www.icp-forests.org/pdf/manual/2016/Manual_2016_Part_XIII.pdf.

Jelask, A., Blanusa, S. M., Durbesić, P., & Jelaska, D. (2007). Heavy metal concentrations in ground beetles, leaf litter, and soil of a forest ecosystem. *Ecotox Environ Safe*, 66:74-81.

Jingjun, S., Wang, H., Kimberley, M. O., Beecroft, K., Magesan, G. N., & C. Hu. (2008) Distribution of heavy metals in a sandy forest soil repeatedly amended with biosolids. *Aust J Soil Res, 46*(7):502-508 DOI10.1071/sr07203.

Jones, K. C., Watts, S. A., Harrison, A. F., & Dighton, J. (1988). The distribution of metals in the forest floor of aged conifer stands at a plantation in Northern England. *Environ Pollut,* 51:31-47.

Kadovic, R., Snežana, B., Dragica, O., Ivana, B., & Nada, D. (2011). Assessment of heavy metal content in soil and grasslands in national park of the lake plateau of the N.P. "Durmitor" Montenegro. *Afr J Biotechnol*, 10:5157-5165.

Karatoteva, D., & Malinova, L. (2016). Macro and microelement contents in soil from some grassland landscape of „Central Balkan" national park. *Bulg J Agric Sci.*, *2*(4): 580-583.

Karatoteva, D., Malinova, L., & Petrova, K. (2018). Coefficients of Heavy Metal Accumulation in Soils from Different Forest Landscapes. International Scientific Conference GREDIT'2018 – Green Development, Green Infrastucture, Green Technology, Book of abstracts, Oral session 4: Agriculture, Agro ecology, Food Quality safety. Skopje, March 2018, pp 90.

Karatoteva, D., Tsvetkova, E., & Bezlova, D. (2014). Heavy metals and arsenic in soils from grasslands in Bulgarka nature park. *Bulg J Agric Sci.*, *20*(1): 73-78.

Kolarov, D., Pavlova, E., Pavlov, D., Doncheva-Boneva, M., Tsvetcova, N., Malinova, L., Nicolova, M., Bezlova, D., & Bencheva, S. (2002). Intensive monitoring of forest ecosystems in Bulgaria. Publ. house UF, Sofia, 160.

Kumpiene, J., Lagerkvist, A., & Maurice, C. (2008). Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments – A review. *Waste Management,* 28:1215-225.

Laskowski, R., & Berg, B. (1993) Dynamics of some mineral nutrients and heavy metals in decomposing forest litter. *Scand J Forest Res, 8*:446-456.

Malinova, D. (2010). Investigation on soil polution of diferent landscapes on the trerritory of „Bulgarka" Natura park. Bulgarian Academy of Science, Sofia, *Forest Science* ISSN 0861-007X, (2):75-84.

Malinova, L. (2015). Study of Cambisols in "Central Balkan" National park for the purpose of soil monitoring. Soil science agrochemistry and ecology. ISSN 0861-9425. XLII. (1). Agricultural Academy, Sofia,36-42.

Malinova, L. (2014). Physicochemical and Chemical Soil Parameters from the Forest Ecosystems Monitoring Network [dissertation]. University of Forestry, Sofia.

Malinova, L., Pavlova, E., & Doncheva-Boneva, M. (1998). Regional Levels of Macro-and Microelements in Some Components of Common Pine and Spruce Ecosystems in the Western Rhodopes. Balkan Ecology (1). PublishScieSet-Agri Co. LTD. 99-108.

Mmolawa, K., Likuku, A. S., & Gaboutloeloe, G. K. (2011) Assessment of heavy metal pollution in soils along major roadside areas in Botswana. *African Journal of Environmental Science and Technology*, 5:186-196.

Mutsch, F., 1998. Indication of long-range transport of heavy metals based on the Austrian Forest Soil Monitoring System. *Envi-*

ron Sci Pollut Res, 1:81-87.

Pavlova, E., & Malinova, L. (2001). Nutrition Status Assessment in the Soil/Plant System. *Journal of Environmental Protection and Ecology* (2):2. Balkan Environmental Association. ISSN 1311-5065. 396-401.

Pavlova, E., Pavlov, D., Doncheva-Boneva, M., Malinova, L., Rosnev, B., Mirchev, P., Petkov, P., Georgiev, G., Grozeva, M., Velizarova, E., et al. (2006). 20 Years Monitoring of Forest Ecosystems in Bulgaria. In: ICP-Forest. Assessment and Monitoring of Air Pollution Effects on Forest. Minerva Press, Sofia. 238.

Raikov, L., H. Chuldjiyan, & Faytondzhiev, L. (1983). Mapping and Diagnostics of Soil Pollution with Heavy Metals. *Journal of Soil Science and Agrochemistry*, 1:42-49.

Schulte, E. E., & Kelling, K. A. (1999) Soil and Applied Manganese. In: Understanding Plant Nutrients. Cooperative Extension Publications, University of Wisconsin-Extension, pp 1-4.

Sheila, R. M. (1994) Retention, Transformation and Mobility of Toxic Metals in Soil. In: Toxic Metals in Soil-Plant System. Dept. of Geography, University of Bristol, pp 139.

Smidt, S., Jandl, R., Bauer, H., Fürst, A., Mutsch, F., Zechmeister, H. & Seidel, C. (2012). Trace Metals and Radionuclides in Austrian Forest Ecosystems. In: *The Biosphere*. *InTech*, 5:94-118.

Ulrich, B., (1983). Soil Acidity and its Relations to Acid Deposition. In: Effects on accumulation of Air Pollution on Forest Ecosystems. Reidel, Boston, pp 1-29.

Vanmechelen, L., Groenemans, R., & Van Ranst, E. (1997). Forest Soil Condition in Europe. International Co-operative Programme on Assessment and Monitoring of Air Pollution on Forest, UN-ECE, 261.

Walthert, L., Zimmermann, S., Blaser, P., Luster, J., & Lüscher, P. (2004). Waldböden der Schweiz Band 1. Grundlagen und Region Jura. Verlag, Bern.

Received: March, 28, 2019; *Accepted:* April, 19, 2019; *Published:* June, 30, 2019