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Assessment of heavy metal concentrations in soils of Western Balkan Mountains

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Abstract

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Concentrations of Fe, Mn, Zn, Pb, Cu and Cd were assessed in some soils of Western Balkan Mountains. In most of the soil profiles the predominant pH_{H2O} was within the range of 4.8 to 5.8. To establish the ongoing accumulation or migration processes of heavy metals in soil profiles they were divided into two groups – with pH_{H2O} lower than 4.8 and above 4.8 in the *A* horizon. Accumulation coefficients (AC) were used to assess these two processes in the studied profiles. It was found clear relationships between copper, pH_{H2O} and the amount of humus in the surface horizon. The accumulation of copper and the amount of humus in A horizon has higher correlation coefficient (r = 0.76) compared to that for copper and pH (r=0.61). The obtained data for zinc AC varied from 0.52 to 1.84. For the iron it was established that all ACs were lower than 1.0 and varied in the range of 0.46 – 0.96. Cadmium in the studied soils was the only metal whose concentrations were higher than the background and precautionary concentration for cadmium concentrations in Bulgarian soils.

Keywords: heavy metal concentrations; soil heavy metal contamination; accumulation coefficients; soil acidity

Introduction

Soils are crucial for all organisms on the planet. They are the most dynamic, complex, and biodiverse habitat that exists (Wall et al., 2015). In just two centuries we have managed to pollute them with organic and inorganic substances that threaten all levels of the ecosystems. One of the most common inorganic threats is heavy metal concentrations in soils. Heavy metals (HMs) and metalloids are hazardous elements. They have high toxicity and low concentration thresholds (Alloway, 2013). In recent decades HMs pollution of the soil has attracted global attention (Ju et al., 2019; Wang et al., 2020).

Plants tend to uptake some HMs and accumulate them in their tissues. In low concentrations heavy metals are important micronutrients, but their higher concentrations have toxic effect for both ecosystems and humans (Sauer & Watabe, 1989; Ohnesorge & Wilhelm, 1991; Castro-Gonzales & Mendez Armenta, 2008; Adimalla, 2019). Soil contamination with heavy metals can create a significant risk to human health (Järup, 2003; Ballabio et al.; 2018; Sihag et al., 2019) due to their bioavailability, bioaccumulation, toxicity and inability to degrade (Bortey-Sam et al., 2015).

Soil parent materials are the natural source of HMs, where they are stored and released in the soil throughout the weathering processes (Horckmans et al., 2005). In some cases, the higher concentrations can be result of natural geogenic sources but often they originate from different anthropogenic activities (Kaur et al., 2020). Their release in soils is complex and includes agrochemicals, metal ore mining waste, emissions of traffic, wastewater irrigation, domestic waste, industrial activities and etc (Zhao et al., 2015).

A large number of studies were focused on HMs concentrations in soils of forest ecosystems, agricultural lands and their remediation (Petrova 1999; Malinova et al., 2018; Serafimova et al., 2019) all over the country.

Soils of forest regions are essential component of the ecosystems and their contamination with heavy metals needs to be observed over time. They stored a large percentage of the worlds soil carbon, minerals, and resources. Nearly 80% of total C in terrestrial ecosystems is stored in soils (Lal, 2008). The organic layers are the most dynamic part of the forest soils. According to Sucharova et al. (2011) HMs that derived from atmospheric depositions are trapped in the litter and their concentrations are especially high in the soils under forest. Heavy metal concentrations depend on several soil parameters such as pH_{H2O}, texture, humus content, parent materials and etc. When pH values in the soil are low heavy metals tend to be more mobile and more bioavailable for the plants. Hence, in forest soils where heavy metal concentrations are higher, and pH values are typically significantly lower compared to agricultural soils, present a higher risk for the ecosystems and therefore human health (Utermann et al., 2019). Analyzing the total concentrations of heavy metals in the soil is often not enough to assess the risk of contamination. The main reason is their different behavior in soil depending on soil characteristics such as soil acidity, content and type of clay minerals and organic matter (Nenova et al., 2015; Tzvetkova et al., 2016).

Therefore the heavy metal concentrations in forest soils must be studied and observed to protect the soils and all the living organisms depending on them, including humans.

The subject of the present study are the heavy metal concentrations of iron, manganese, zinc, lead, copper and cadmium in forest soils of the Lower altitude area of oak forests (0 to 600 m a.s.l.) – *Gray* Luvisols (Gray forest soils) identified by the Basic classification of soils in Bulgaria (Penkov et al., 1992) and from the Middle mountain area of beech and coniferous forests (600 m to 2000 m a.s.l.) – *Dystric-Eutric* Cambisols (Brown forest soils). The main aim of the study was to assess the concentrations of heavy metals in these soils.

Methods and Materials

Study area

The study area falls into the temperate-continental climate region according to the climate zoning of Bulgaria (Velev, 2010). The climate is clearly continental. The average temperature in the lower parts is -1.9° in January and the vegetation rainfall ranges between 450 mm and 500 mm (Koleva-Lizama, 2018). The soil types of the study area were identified as *Gray* Luvisols and *Dystric-Eutric* Cambisols. There are no nearby pollution sources, mining or industrial activities. A total of 16 soil profiles were studied in altitude range of 185 – 812 m a.s.l. (including the two forest zones of Oak forests and Beech/coniferous forests) of Western Balkan Mountains.

For the purposes of the present study, the soils were divided into 2 groups – with pH_{H2O} lower than 4.8 and above 4.8 in the *A* horizon, which allows a clearer characterization of ongoing soil formation processes – accumulation or migration of heavy metals in soil profiles. To assess these processes, accumulation coefficients (AC) were used. They were calculated as the ratio of the amount of a given metal in the surface horizon and in the soil-forming materials.

The collected soil samples were mineralized with aqua regia (HCl and HNO_3 in a ratio of 3: 1). After that the concentrations of Fe, Mn, Zn, Pb, Cu and Cd were determined by atomic absorption spectrometer using Atomic absorption spectrophotometry (Perkin-Elmer Model Analyst 5000). The pH_{H2O} was determined according to ISO 10390, and the amount of humus – Turin's modified method (Kononova, 1963; Filcheva & Tsadilas, 2002). The study was conducted in 2020.

Results

One of the most important factors that determine the behavior of heavy metals in the soil is the pH_{H2O} and the amount of humus. In the studied region of the Western Balkan Mountains soils with pH_{H2O} in the range of 4.8 to 5.8 predominate (Table 1). In two of the profiles the pH_{H2O} is lower than 4.8 (№ 6 and 10). With regard to humus, quantities are established within the range of 1.35 up to 8.61%. Under these conditions, both accumulation and migration processes can be expected for the behavior of heavy metals in the soil profile.

For the predominant group of soils – those with a pH_{H2O} in the range of 4.8 – 5.8, there are clear relationships between copper and pH_{H2O} and the amount of humus in the surface horizon. The results show that with decreasing pH_{H2O} the accumulation processes are replaced by migration ones (Figure 1). This was measured with a AC for copper above and below 1.0, respectively. The approximate value can be pointed as pH_{H2O}=4.9, above which the accumulation of copper in the surface horizon has a stronger manifestation of the two processes.

The relationship between the accumulation of copper and the amount of humus in the surface horizon (Figure 2) has been established by a higher correlation coefficient (r = 0.76) compared to that for copper and pH.

For the other studied heavy metals in the group of soils with pH 4.8 – 5.8 interrelations are established only with the amount of humus in the surface horizon, but not with pH_{H2O}. This applies to the metals zinc, lead and iron. For them, with

Table 1. Heavy metal concentrations

Profile	Horizon/ Layer	Depth cm	pH_{H2O}	Exch. acidity	Fe	Mn	Zn	Cu	Pb	Cd
				cmol (+).kg^{-1}	mg.kg^{-1}					
1	L	1-0	5.3	0.81	3097	681	34	17	18	1.60
	A	0-8	6.9	0.28	51867	1581	83	44	34	1.96
	Bt1	8-21	6.6	0.46	52427	1469	76	40	33	2.11
	Bt2	21-47	6.5	0.56	49803	1444	141	32	27	2.26
	C	47-↓	6.2	0.64	41423	1107	80	35	23	1.33
2	A	0-5	6.0	0.60	27106	766	61	30	40	1.24
	Bt1	5-14	6.1	0.56	30257	867	53	29	37	1.65
	Bt2	14-20	6.2	0.55	32249	908	71	28	36	1.13
	BC	20-40	6.5	0.46	35329	521	51	26	32	2.23
3	L	1-0	5.4	0.61	1805	1973	30	11	19	1.22
	A	0-6	5.7	0.73	22706	1752	57	18	45	1.91
	Bt1	6-41	4.9	1.30	27369	1332	73	22	37	2.34
	Bt2	41-100	4.7	3.07	48840	151	68	26	36	2.10
	C	100↓	4.8	3.97	49109	830	109	34	27	2.18
4	L	2-1	4.5	1.49	324	991	26	6	14	0.88
	FH	1-0	5.1	0.70	6907	1685	43	13	35	1.21
	A	0-18	5.1	0.55	23693	1825	58	18	57	1.97
	Bt1	18-30	5.0	1.42	37720	828	69	24	45	1.82
	Bt2	30-90	4.7	3.08	50041	606	77	28	55	1.30
	C	90-↓	4.6	3.21	43113	268	85	26	43	1.75
5	L	2-1	5.6	0.71	8824	1077	54	17	29	1.49
	FH	1-0	5.9	0.48	25981	1206	89	33	55	2.05
	A	0-3	6.3	0.45	43617	1184	111	43	63	1.65
	Bt1	3-23	5.0	1.01	46675	1086	111	46	59	1.74
	Bt2	23-40	5.5	0.46	54606	1269	143	111	77	1.71
	BC	40-↓	4.8	1.28	15694	922	44	20	43	0.87
6	L	2-0	5.2	1.10	3598	1589	40	10	17	1.54
	A	0-6	4.6	2.79	18965	1044	43	14	39	1.38
	Bt1	6-30	4.3	3.52	19456	988	45	14	37	1.02
	Bt2	30-45	4.4	2.95	19738	1022	39	11	29	1.83
7	L	1-0	5.4	0.80	5007	764	33	16	18	1.26
	A	0-5	6.0	0.66	37727	789	60	32	42	1.75
	Bt	5-19	4.7	5.14	42111	563	57	33	31	2.21
	C	19-47	4.9	0.56	36740	438	42	39	23	1.84
8	L	1-0	5.1	1.10	1775	1855	40	11	18	0.94
	A	0-4	4.8	1.30	13395	800	35	9	33	1.28
	Bw1	4-30	4.5	2.30	14805	474	31	8	27	1.17
	Bw2	30-41	4.4	1.94	15245	325	27	8	24	1.57
	BC	41-↓	4.6	1.10	14037	454	19	6	21	1.57
9	L	1-0	5.0	1.51	556	1819	35	12	13	0.94
	A	0-1	4.9	1.76	11693	491	32	8	33	1.48
	Bw1	1-10	4.2	3.13	12308	211	28	7	26	1.67
	Bw2	10-34	4.2	2.85	12129	248	30	7	27	1.01
	BC	34-55↓	4.3	3.31	14207	116	27	7	26	1.47

Table 1. Continued

10	L	3-2	5.1	0.72	604	1531	31	12	14	1.01
	FH	2-0	5.7	0.50	8920	2159	64	18	28	1.39
	A turf	0-10	4.3	6.73	23188	397	64	26	45	1.88
	Bw	10-25	4.3	7.05	25684	168	80	25	36	1.60
	BC	25-45↓	4.2	6.43	29065	144	74	31	27	0.97
	L	2-1	5.5	0.82	1495	865	38	14	16	1.35
	FH	1-0	6.1	0.49	6374	897	42	15	25	1.37
11	A	0-9	4.9	1.59	13382	367	32	9	28	0.77
	Bt	9-29	4.6	3.05	13849	251	25	7	19	0.86
	C	29-38↓	4.7	2.12	14365	234	26	8	15	0.81
	Aturf	0-10	5.8	0.46	30478	707	69	25	74	1.60
12	Bw1	10-23	5.6	0.57	32060	765	69	26	75	1.64
	Bw2	23-37	5.4	0.57	33298	822	69	24	75	1.59
	BC	37-63↓	5.2	0.57	33135	856	68	25	71	1.64
	L	1-0	5.8	0.71	2405	1246	45	13	30	1.27
	A	0-10	5.1	0.65	17392	499	43	13	30	0.97
13	B1	10-18	4.6	1.48	18954	327	43	13	24	0.97
	B2	18-30	4.8	0.75	18895	361	40	11	23	1.23
	BC	30-110↓	5.7	0.28	27553	197	56	16	25	1.18
	A	0-4	6.7	0.18	12064	230	37	16	25	0.82
	Bt1	4-17	5.6	0.46	12225	211	38	16	25	0.97
14	Bt2	17-31	5.7	0.28	13123	218	37	15	19	0.82
	BC	31-53	5.6	0.46	14739	193	40	17	16	0.97
	C	53-↓	5.3	0.66	20198	267	56	22	20	1.08
	A	0-27	5.2	0.74	17869	393	44	18	24	1.12
15	Bt	27-42	5.3	0.57	26343	530	55	28	33	1.13
	BC	42-105↓	6.2	0.28	26265	595	56	26	27	1.24
	A	0-3	4.9	1.04	28083	797	59	22	34	1.35
16	Bw1	3-20	4.5	2.05	29463	799	59	21	35	1.23
	Bw2	20-46↓	4.9	0.84	30573	609	65	21	22	1.18

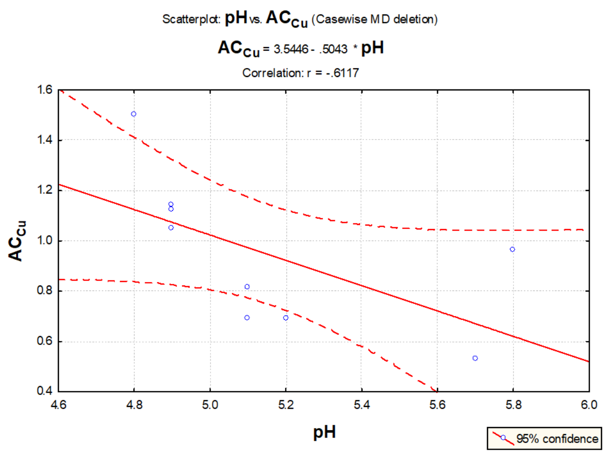

Fig. 1. Relationship between pH and coefficient of accumulation (AC) of copper in soils from the region of Western Balkan Mountains

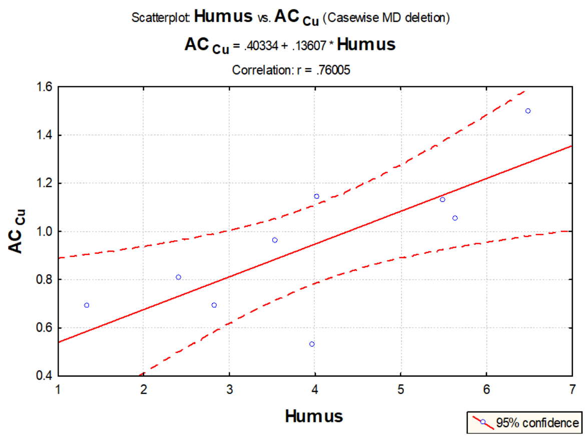

Fig. 2. Relationship between the humus content and the coefficient of accumulation (AC) of copper in soils from the region of Western Balkan Mountains

the increase of the amount of humus in the *A* horizon, the values of AC also increase. No similar dependences have been found for the behavior of manganese and cadmium.

The obtained values for AC of zinc varied from 0.52 (profile 3) to 1.84 (profile 8), which is a wide range. The reason for that on the one hand is the very low content of zinc in the surface soil horizon in some of the profiles. Intensive migration processes are evident in profile 4 (AC = 0.52), profile 13 (AC = 0.77), profile 15 (AC = 0.79) and others. On the other hand, there is a clear accumulation of zinc in the surface horizon of profile 8 (AC = 1.84), profile 11 (AC = 1.23), profile 9 (AC = 1.19).

The results are similar for the behavior of lead. However, only two profiles have a AC lower than 1.0. These are profiles 12 (AC = 0.99) and 13 (AC = 0.89). In the remaining AC they are in the range 1.20 – 1.67, and the profile distribution of lead shows clearly expressed accumulation processes in the surface horizon.

For iron, all ACs are lower than 1.0. They vary in the range of 0.46 – 0.96 and are primarily the result of the increasing concentration of the element in the direction of the soil-forming rock (Figures 3, 4, 5).

In two of the studied sites the soils have a very strongly acid reaction. Their soil reaction in the surface horizon is in the range of 4.3 (profile 10) and 4.6 (profile 6), which is why they are considered separately from the other profiles. It is known that pH values <4.8 are an indicator of the presence of free fulvic acids in the soil solution (Ganev, 1990). The reason for such advanced acidification could be with anthropogenic or natural origin. Numerous studies from different countries written in the middle and in the end of the 20th century has proven that soil acidification is under the influence of increased deposition of acidic airborne pollutants. It is also established that pH of about 4.0 is the critical limit that enhances carbon mobilization (Funakawa et al., 2006). There are no large sources of acidic immissions in the air in the studied area, which could be the source of such high soil acidity. The reason for such advanced acidification in the soil could be a combination of the different soil formation factors. The analysis shows that the soil in both profiles is under the acidifying influence of the litterfall. In profile 6 the organic layer is formed of leaves, twigs and fruits from Eu-

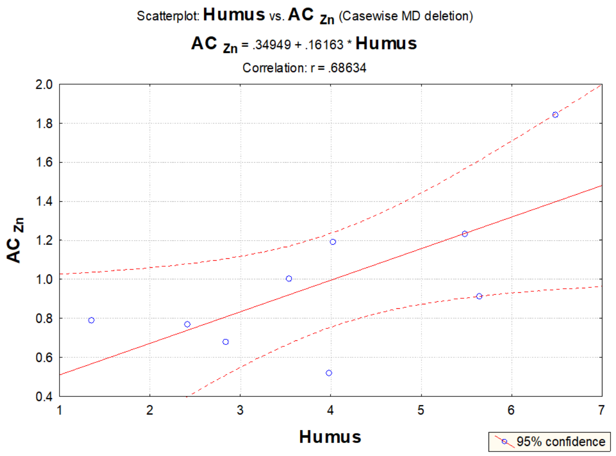

Fig. 3. Relationship between humus content and zinc accumulation coefficient (AC) in soils from the region of Western Balkan Mountains

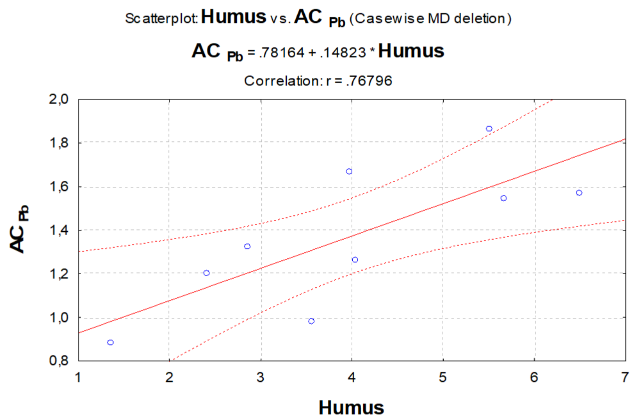

Fig. 4. Relationship between the humus content and the accumulation coefficient (AC) of lead in soils from the region of Western Balkan Mountains

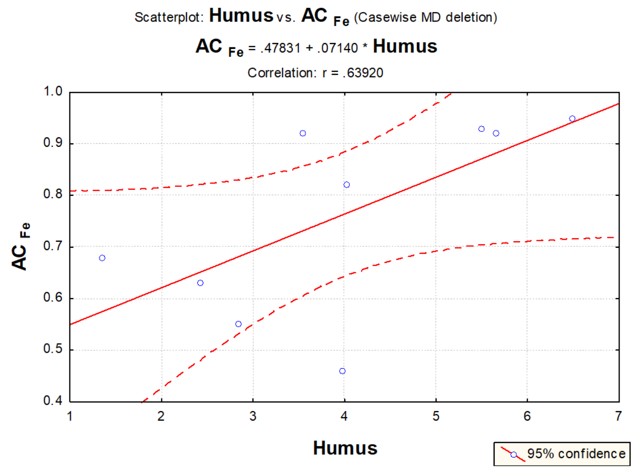

Fig. 5. Relationship between the humus content and the coefficient of accumulation (AC) of iron in soils from the region of Western Balkan Mountains

ropean beech (*Fagus sylvatica* L.), Macedonian pine (*Pinus peuce* Gris.), Scots pine (*Pinus sylvestris* L.) and in profile 10 – European beech and Scots pine. The lowest pH in the surface horizon of all studied soil profiles is the one in profile 10. The soil organic layer was formed of European beech and Scots pine litterfall. European beech is known for its strong acidifying effect on the soils (Falkengren-Grerup & Bjork, 1991; Peters, 1997) and it was established also for the region of Western Balkan Mountains (Malinova & Petrova, 2019). The soil-forming rocks in both profiles are acidic – quartz porphyry (profile 6) and shale (profile 10). The amount of humus in the surface horizon of profile 6 is 4.5%, and for profile 10 – 1.0%.

The concentration of iron is characterized by an increase in soil depth in both profiles, which is considered as its normal behavior. The absence of accumulation processes is also evident from the values of CA, which are less than 1.0 and are respectively 0.96 in profile 6 and 0.80 in profile 10. The results obtained in this study are not sufficient to prove the migration processes of iron, but in the study of Malinova & Petrova (2019) has been established a vertical migration of iron in very highly acidic soils in the region of the Western Balkan Mountains.

Manganese is considered as one of the most mobile metals (Heinrichs & Mayer, 1980; ICP-Forest and ICP-IM, 2002). The results of the obtained data confirmed it. Under the influence of very strongly acid reaction in the *A* horizon there is a very low accumulation of manganese in profile 6 (CA = 1.02). The soil reaction in profile 10 is even more acidic, but CA = 2.76. This could be explained by the specifics of the forest stand. The litter formed on the soil profile is torn due to thinnings of the stand and the appearance of turf. In these areas, under the influence of grass vegetation, biogenic-accumulation processes take place. Nevertheless, the results show latent migration of manganese outside the soil profile. An indicator for this is the significant difference between the amount of manganese in the litter and in the surface soil horizon – Aturf. According to Vanmechelen et al. (1997), this difference increases with the increasing of soil acidity and respectively migration processes. In Bulgaria, there are currently no standards for estimating the concentrations of manganese in soils, so no comparison can be made with specific criteria.

Zinc is characterized by high mobility and removal outside the soil profile in an acidic environment (McBride et al., 1997; Alloway, 2009). The obtained coefficient for accumulation of zinc in the leached soil (profile 6) is 1.10 and shows the predominance of the accumulation processes over the migration ones. In the Cambisols (profile 10) was established AC =0.86, which indicates the removal of zinc outside the soil profile. Despite the weak accumulation processes, it should be noted that the concentration of zinc in these profiles is very low. It is lower than the background concentration for this element indicated for Bulgarian soils in Regulation 3 (2008) – 88 $mg.kg^{-1}$. The cause of migration processes in both profiles is due to the high acidity.

The behavior of lead in the studied soils shows clearly expressed accumulation processes, under the influence of which the obtained accumulation coefficients are higher than 1.0. The obtained ACs are 1.34 in profile 6 and 1.67 in profile 10. This behavior is typical for lead due to its tendency to bind to the organic matter, which concentration is highest in the surface horizon (Mohamed et al., 2010; Huang et al., 2011). Its profile distribution in the studied soils shows a gradual decrease of the concentrations in depth. Hence, high acidity is not a leading process in the profile distribution for this metal. Compared to the criteria for lead content in Bulgarian soils (Regulation 3/2008), the obtained results are assessed as corresponding to the precautionary concentration (45 $mg.kg^{-1}$).

Cadmium in the studied soils is the only metal whose concentrations are high – higher than the background and precautionary concentration for cadmium content in Bulgarian soils. It is one of the most toxic substances in soils. In profile 10 its concentration (1.88 $mg.kg^{-1}$) approaches the maximum permissible concentration – 2 $mg.kg^{-1}$ (Regulation 3/2008). The obtained results show the course of migration processes in profile 6 (CA 0.75). The concentration of cadmium increases in the depth of the profile. The exact opposite process was observed in profile 10 – cadmium accumulates in the *A*turf horizon.

Conclusion

The obtained data for AC showed that some of the heavy metals accumulate in the surface horizon. Their behaviour depends in most of the cases on pH values of the soil. It was found that with the increase of the amount of organic matter in the *A* horizon of the soil, the accumulation coefficients of zinc, lead and iron also increase. No such dependences were established for the behaviour of manganese and cadmium. It should be noted that AC of lead were higher than 1.0, which showed a clearly expressed accumulation processes. High cadmium concentrations in the studied soils oppose a great concern and must be observed over time.

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