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## CHANGES IN THE CONTENT OF BIOAVAILABLE HEAVY METAL COMPOUNDS IN THE SOILS OF THE CRIMEAN MOUNTAIN PLATEAUS AFTER AFFORESTATION

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About 3 thousand hectares of forest stands were created on the surface of the Crimean mountain plateaus in the middle of the 20th century as a result of afforestation. Studies on the influence of these stands on the properties of mountain meadow soils (Phaeozems) showed that under the forest vegetation, the consolidation of structural aggregates, a decrease in the humus content, and an increase in acidity compared to the soils under the meadow vegetation, which could also affect other soil properties, including the mobility of some metals, were observed. The work objective of this research is to conduct a comparative analysis of the content of Pb, Mn, Cu, and Zn compounds available for biota (1 M ammonium acetate) in the soil under mountain meadows, natural beech forest, and artificial forest stands. Following the obtained results, the available Pb, Mn, and Cu compounds accumulated in the afforested mountain meadow soils relative to the adjacent mountain meadows areas. Thus, the average Pb content in the soil layer of 0–10 cm under the mountain pine stands in comparison with the soil under meadow vegetation was 1.6 times higher, Mn – 1.2 times, Cu – 1.2 times. The Pb content was 2.5 times higher, Mn – 1.5 times higher, and Cu – 1.2 times higher under the silver birch stands. The Pb content was 2.2 times higher, Mn – 2.4 times higher, and Cu – 1.5 times higher under Siberian larch stands. The Pb content was 1.9 times higher, Mn – 1.1 times higher, Cu – 1.3 times higher under the sycamore maple stands, compared to the meadow. Differences between afforested and meadow soils in the content of these elements in most cases were significant, except for the Zn content, signs of accumulation of which under artificial stands were not revealed. The Pb, Mn, and Cu content in the brown forest lessive soil (Luvisols) under the oriental beech corresponded to their concentration under the larch, and the Zn content was significantly higher compared to the soil under all species. The main reason for the increase in the mobility of some elements under tree stands is their transition from immobile forms under the influence of increased acidity of afforested soils. Wood litter due to the low content of trace elements in its composition cannot be a source of their accumulation in the topsoil.

**Key words:** *mountain meadow soils, forest stands, trace elements, acidity, heavy metals*

The acidifying effect of artificial forest stands on the soils of former farmland and pastures has been noted in many studies in various natural and climatic zones of the world (Alfredsson et al., 1998; Alriksson, Olsson, 1995; Andersen et al., 2002; Berthrong et al., 2009; Fullerr, Anderson,

1993; Jobbagy, Jackson, 2003; Holubik et al., 2014; Ritter et al., 2003; Wen-Jie et al., 2011). The result of such exposure may be an increase in the concentration of certain trace element compounds available to the biota since pH is a key factor affecting the mobility of the metals in the soil (Reddy et al., 1995;

Sauve et al., 1998; Sherene, 2010). Intensive afforestation of the previously almost treeless mountain plateaus (yailas) of the Crimea began in 1957 and about 3 thousand hectares of artificial forest stands were created on the surface of Karabi, Demerdzhi, and Ai-Petrinskaya yailas until the 1970s (Bagrova, Garkusha, 2009). Their main solid woods, consisting of dozens of separate groves of different species, are concentrated on the Ai-Petri plateau. Among the tree species, scots pine dominates, occupying up to 70% of the area, and solid woods of birch, aspen, maple, hazelnut, larch, pear, spruce, and other species are also observed. The stands occupy relatively flat areas, where mountain meadow soils with a thickness of 50–150 cm have been formed.

Earlier, the authors conducted studies on the influence of artificial stands of pine, larch, and birch on the main properties of mountain meadow soils on the Ai-Petri plateau (Kostenko, 2018). It was found that under forest vegetation, an increase in the proportion of large aggregates in the soil structure composition, a decrease in the humus content, and an increase in acidity and the iron content from organo-mineral compounds had happened in comparison with soils under meadow vegetation. The strongest changes in the structural state of the soils were observed under pine stands, changes in acidity and the iron content were observed under larch stands. The strong acidifying effect of larch stands on the soil was also evidenced by the data following Tkachenko (1939) and Khakimov et al. (2005). A decrease in the humus content was observed under all tree species.

**The work objective** of this paper is a comparative analysis of the content of Pb, Mn, Cu, and Zn compounds available for biota in the soil under artificial forest stands and adjacent areas of mountain meadows.

## MATERIAL AND METHODS

### Study Object

The Ai-Petri plateau belongs to the western yaila system of the Mountainous Crimea with absolute altitudes of 1100–1300 m above sea level. The climatic conditions on site following the weather station "Ai-Petri" (1180

m) are characterized by the average annual rainfall of 1052 mm, the average annual temperature is 5.7 °C, the average temperature in February is -3.8 °C, in July – 15.5 °C. Most of the precipitation (62%) falls during the cold season from November to March.

The Ai-Petrinsky massif is composed of dense Upper Jurassic limestones, which is the reason for the active development of karst processes. As for the relief, yailas are hilly mountainous plateaus with numerous karst potholes, wells, mines, and caves. Negative landforms are filled with leached products of limestone weathering, which formed the most fertile mountain meadow soils, most of which are currently occupied by artificial forest stands.

According to their morphological structure and properties, these soils are closest to mountain meadow chernozemic soils (Classification ..., 1977), which are formed under meadow steppes on sialitic products of limestone weathering. However, typical chernozemic soils are rare since the main mass of full-profile soils of the plateau is characterized by complete leaching of carbonates, the absence of rock fragments in the profile, and acidic and strongly acidic reactions. The most humous virgin variants of these soils, preserved locally in the bottoms of karst potholes, are characterized by the typical dark gray color of the A horizon with a brown tint. Anthropogenically disturbed soils have grayish-brown color (Kostenko, 2014).

In the modern classification of soils of Russia, mountain meadow soils are not represented, and their closest analog is the type of dark humous soils with the AH-C profile (Classification ..., 2004), which does not cover all the soil diversity of the Crimean yailas.

Following the World Reference Base (WRB) (IUSS Working Group, 2015), mountain meadow soils of the plateau belong to Phaeozems – soils with a dark-colored humous horizon that does not contain secondary carbonates in the profile. Among them, the residual carbonate soils (Calcaric), with signs of clay eluviation (Luvic), underlain by dense rocks from a depth of less than 100 cm (Leptic) and with a dark-colored

humus horizon (Chernic) are observed. The meadow and afforested soils described in the article belong to Phaeozems (soil pit 1353) and Leptic Phaeozems (soil pits 1280, 1281, 1332, 1333, 1351, and 1379).

Mountain forest soils of the Crimea, lying from 300 m above sea level along the southern macroslope of the main ridge and on the plateau, are traditionally referred to as brown mountain forest soils or burozems (Dragan, 2004; Polovitskii, Gusev, 1987). Brown forest soils are characterized by weak profile differentiation into genetic horizons, acid reaction, clay deposition in the entire thickness, the absence of clay leaching, or its weak leaching from the upper horizons (Classification ..., 1977). Following the classification of 2004, burozems are classified as structural-metamorphic soils, which are characterized by acid reaction and weak profile differentiation by clay, and following the WRB – as Cambisols. However, it was difficult to determine the type of soil belonging to the beech forest, since it, in the presence of the main signs of brown soil, is characterized by a strong textural differentiation of the profile, most likely caused by active clay lessivation from the upper horizons. In this regard, the soil of the beech forest was classified as a brown forest lessive soil, which is not represented in the soil classifications of Russia but is described as a texturally differentiated soil without a morphologically significant horizon E (Soil science ..., 1988). The presence of a clayed argic horizon is the basis for assigning the soil of the beech forest (section 1272) to the Reference Soil Group of Luvisols following the WRB.

In the 21<sup>st</sup> century, the territory of Ai-Petri yaila was intensively used for pastures, hayfields, and vegetable gardens for the residents of Yalta before afforestation and then in treeless areas. By the time of the creation of the Yalta Mountain Forest Nature Reserve in 1974, the most fertile soils were severely degraded, so even a long-term stay under the fallow lands did not lead to the restoration of their fertility to the original level. The planting of forests has slowed down the process of humus accumulation, so the organic carbon content in the soils under

all artificial stands is lower than under the grassy vegetation in the areas of mountain meadows adjacent to the stands (Kostenko, 2018).

Soil studies were carried out in stands of mountain pine (*Pinus kochiana* Klotzsch ex K. Koch), silver birch (*Betula pendula* Roth), Siberian larch (*Larix sibirica* Ledeb), and sycamore maple (*Acer pseudoplatanus* L.) planted on the Ai-Petri plateau, according to archival data of the Yalta Mountain and Forest Nature Reserve, in the period from 1958 to 1964. At the time of the study, the age of the stands ranged from 50 to 60 years. To assess the intensity of metal accumulation under forest stands in comparison with natural forests, the same studies were conducted in a natural monodominant beech forest (*Fagus orientalis* Lipsky), the structure of which is dominated by stands of 7–12 decadal age classes (Plugatar, 2015).

Artificial stands of pine, birch, and maple were monodominant communities, the underwood of which consisted of single specimens of rosehip (*Rosa tschatyrdagi* Chrshan.) and hawthorn (*Crataegus taurica* Pojark.). Pine, linden (*Tilia cordata* Mill.), ash (*Fraxinus excelsior* L.) with mountain ash (*Sorbus aucuparia* L.), rosehip, and hawthorn in the underwood were also found in the stands of larch. The trees were planted after plowing the soil according to a thickened scheme of 2 × 0.5–1.0 m, which led to the suppression and loss of a large number of trees by the beginning of this study.

The ground cover under pine, larch, and beech had a projective cover of 5–10%, under birch and maple – 40–70%. The grassy cover under birch stands was dominated with alpine oatgrass (*Helictotrichon schellianum* (Hack.) Kitag.), orchard grass (*Dactylis glomerata* L.), common nipplewort (*Lapsana intermedia* M. Bieb.), milfoil (*Achillea setacea* Waldst. & Kit.), common agrimony (*Agrimonia eupatoria* L.), Briza maxima (*Briza australis* Prokud.), betony (*Betonica officinalis* L.), couch grass (*Elytrigia repens* (L.) Gould). Under the thinned stands of pine, tall oatgrass (*Arrhenatherum elatius* (L.) P. Beauv. ex J.Presl & C.Presl.), orchard grass, and common nettle (*Urtica dioica* L.) grew. Under the larch stands – false-brome

(*Brachypodium sylvaticum* (Huds.) P. Beauv), orchard grass, broad-leaved willowherb (*Epilobium montanum* L.), Roberts geranium (*Geranium robertianum* L.), common nipplewort, wood bluegrass (*Poa nemoralis* L.), and common nettle. Under the canopy of the beech forest, singular specimens of the sweet woodruff (*Galium odoratum* (L.) Scop.) were found.

In conditions of high humidity, the litter of broadleaved species and larch mineralizes quite quickly, so the thickness of the litter under them did not exceed 1–2 cm and only under pine reached 4–6 cm.

The areas of the plateau adjacent to the forest stands belong to the meadow steppe, typical for Ai-Petri yaila, in terms of vegetation composition. According to the obtained results, the dominant species for meadow communities are cereals: alpine oatgrass (*Helictotrichon schellianum* (Hack.) Kitag.), Briza maximum (*Brizaelatior* Sibth. & Sm.), couch grass (*Elytrigia repens* (L.) Gould), wood bluegrass (*Poa pratensis* L.), orchard grass (*Dactylis glomerata* L.), purple-stem cat's-tail (*Phlum phleoides* (L.) H. Karst.), couch grass (*Elytrigia strigosa* (M. Bieb.) Nevski), as well as milfoil (*Achillea setacea* Waldst. & Kit.), betony (*Betonica officinalis* L.), St. John's wort (*Hypericum perforatum* L.), wild basil (*Clinopodium vulgare* L.), creamy strawberry (*Fragaria viridis* (Duchesne) Weston), hedge bedstraw (*Galium mollugo* L.), unspotted lungwort (*Pulmonaria obscura* Dumort.), and some other species.

### Methods of Investigation

Soil pits were dug under artificial stands of forest species and beech, as well as on adjacent areas of mountain meadows up to the depth of dense rocks, samples from which were taken in a continuous column after every 10 cm. Also, at each of the variants, at least 5 samples from the 0–10 cm layer were taken.

In the soil samples, the granulometric composition by the pipette method after pyrophosphate dispersion of soils, pH<sub>KCl</sub>,

hydrolytic or total acidity (Ac<sub>tot</sub>) by the pH-metric method, the content of total organic carbon (C<sub>tot</sub>) according to Tyurin, and the content of mobile forms of Pb, Mn, Cu, and Zn, a 1M ammonium-acetate extract with a pH of 4.8 (Workshop on Agrochemistry, 2001) were determined.

To study the possibility of the elements entering into the soil by biological transfer, samples of birch, maple and beech leaves were taken in mid-August, and immediately after leaf fall – fresh litter of deciduous species, as well as pine from the upper layer of the litter. The content of Pb, Mn, Cu, and Zn in plant samples was determined after dry ashing of leaves and needles. The determination of all elements was carried out in an atomic absorption spectrometer Kvant-2mt.

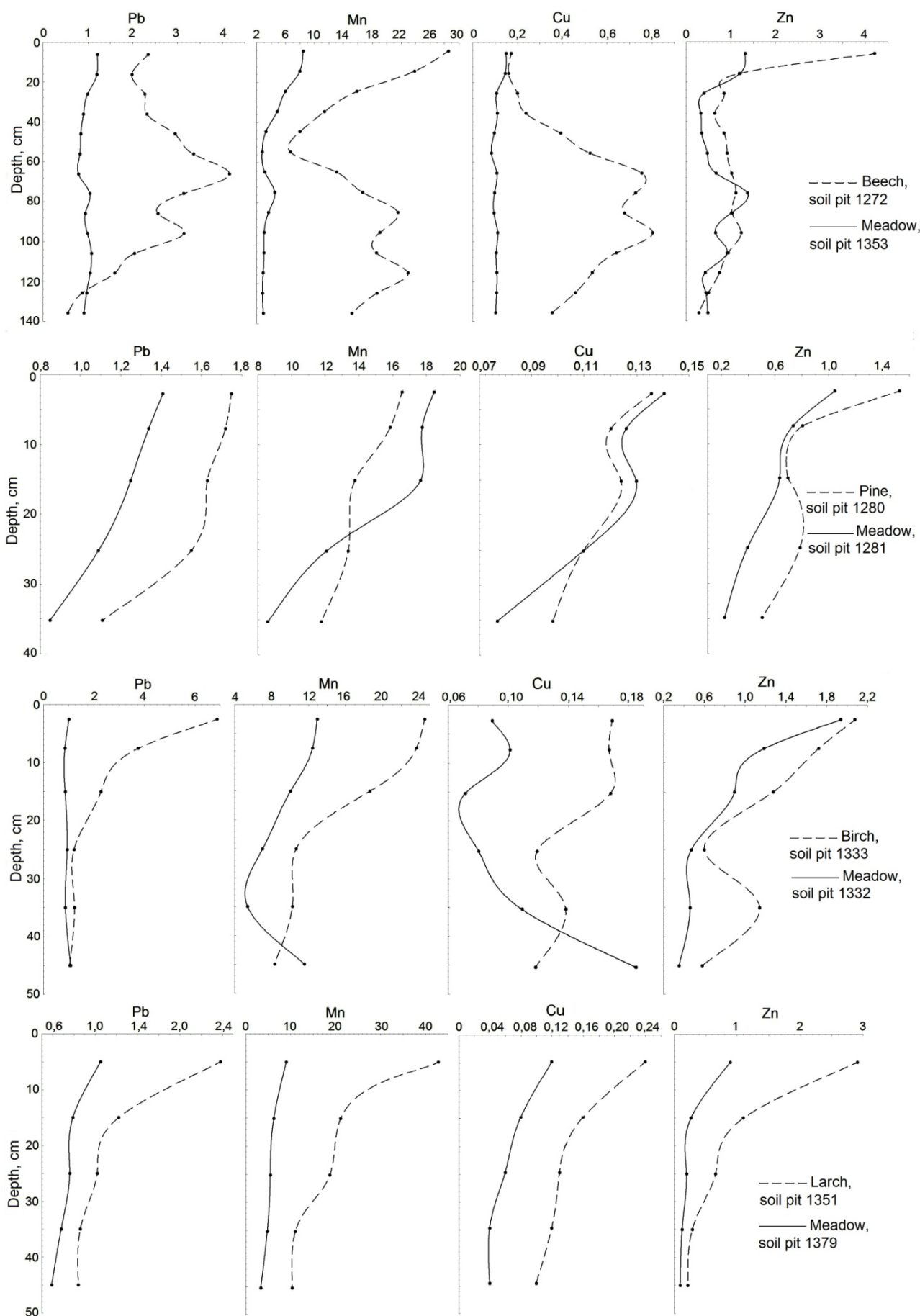
Moisture measurements in the soil profile under natural beech forest, larch stands, and meadow vegetation were carried out on October 10, 2014, using an HH2 Delta-T electronic moisture meter.

Statistical processing of the results was carried out using the STATISTICA 6 software package and an online service for calculating the Mann-Whitney criterion.

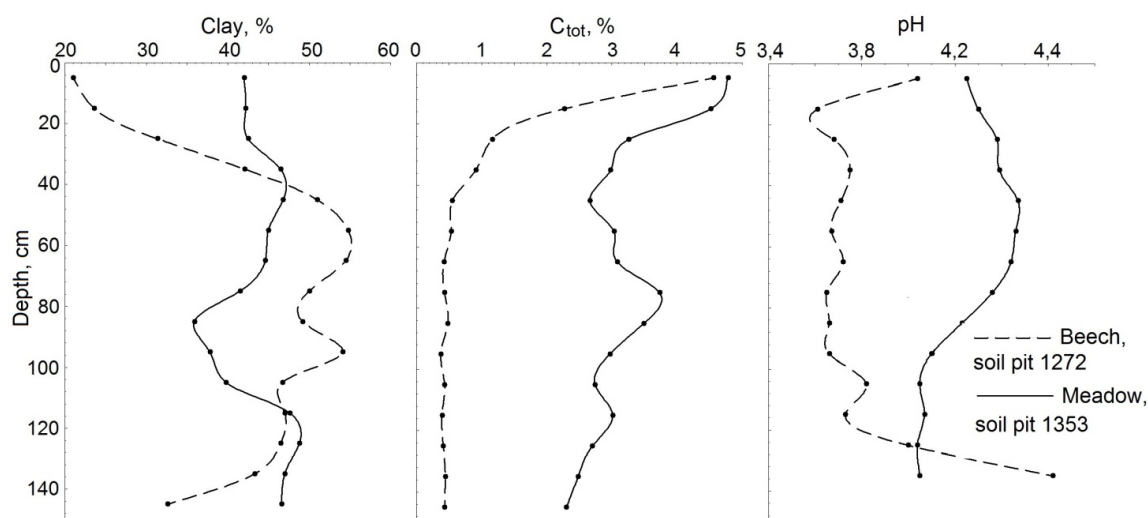
### RESULTS AND DISCUSSION

The results of comparative studies of the content and nature of the profile distribution of trace elements in brown forest soil under beech forest and mountain meadow soil of the Ai-Petri plateau indicate a strong influence of vegetation type on these parameters.

In the profile of meadow soil, the content of most elements is lower, and the spread of values is smaller in comparison with the soil of a beech forest (Figure 1). It is due to the large differences between soils in the main characteristics – the content of clay, organic matter, and pH values (Figure 2), which affect the accumulation of total and mobile forms of trace elements (Tobratov et al., 2007). The differences between the pits in the content of all elements, except Zn, are significant at the level of  $p \leq 0.01$ .



**Figure 1.** Profile distribution of Pb, Mn, Cu, and Zn compounds available for biota in the soil under natural beech forest, artificial tree stands, and mountain meadows



**Figure 2.** Profile distribution of clay,  $C_{tot}$ , and pH values in the soil under beech forest and meadow vegetation

**Table 1.** Results of multiple correlation analysis ( $n=16$ )

Element	Multiple correlation coefficients	Partial correlation coefficients		
		Clay	$C_{tot}$	$Ac_{tot}$
Pb	0.94	0.72**	0.58*	0.88**
Mn	-	-	0.67**	-
Cu	-	0.85**	-	-
Zn	0.95	0.69**	0.92**	-

Note: \* – correlation coefficients are significant at the level of  $p \leq 0.05$ , \*\* –  $p \leq 0.01$

Following the results of multiple correlation analysis (Table 1), the content of mobile Pb in the soil of beech forest is associated with all of these soil factors, Zn – with the content of clay and  $C_{tot}$ , Mn – with the  $C_{tot}$  content, and Cu – with the clay content.

The mobility of metals can also be influenced by the peculiarities of the hydrological regime of soils formed under different types of vegetation. It is obvious that with a comparable amount of precipitation, the humidity of the forest soil in comparison with the meadow will be higher due to the lower evaporation of the shaded surface, which is also protected by a layer of forest litter. The results of measurements of soil moisture in a beech forest in the layers of 10–15, 30–35, and 50–55 cm were, respectively,  $25.4 \pm 1.8$ ,  $35.7 \pm 2.2$ , and  $34.4 \pm 0.9\%$ , and the meadow –  $29.5 \pm 1.7$ ,  $28.6 \pm 2.9$ , and  $27.4 \pm 2.5\%$  of the volume of soil at a significance level of differences following the Mann-Whitney

criterion  $\leq 0.01$ . As can be seen, due to autumn precipitation, the soil moisture in the layer of 10–15 cm was higher in open areas under meadow vegetation, and deeper layers – under the forest vegetation.

Judging by the profile distribution of trace elements in the soil of the beech forest (Figure 1), the distribution of Mn is most strongly influenced by humidity, which determines the redox conditions of the soil. In the upper, more desiccated part of the 0–60 cm profile, the Mn content is closely related to  $C_{tot}$  ( $r = 0.94$ ;  $n = 7$ ), sharply decreasing with depth. Within the wetter layer of 60–80 cm, the Mn content increases sharply and varies within close values up to 130 cm, indicating that the readily mobile  $Mn^{2+}$  compounds are formed under periodically developing reducing conditions (Azarenko, 2013; Orlov et al., 2005) in the middle and lower parts of the profile.

The impact of the forest on the soils under artificial stands occurs only within a few

decades from the moment of the formation of a sufficiently closed canopy that prevents the growth of grasses. During this period, a change in some chemical properties of afforested soils has happened, which, however, did not affect the fundamental soil indicators, including the content and nature of the profile distribution of granulometric elements and organic matter. Therefore, despite the change in the concentration of metal compounds available for biota under forest stands, the nature of their profile distribution in most cases is close to the distribution of elements under meadow vegetation (Figure 1). Over the entire profile, the soil under the pine contained more Pb and Zn (Figure 1). The upper part of the profile contained more Mn and Cu under the meadow, in the lower part – under the pine, which is due to the higher acidity of the meadow soil in the layer of 0–40 cm at the site of pit 1281 ( $Ac_{tot} = 8.9 \text{ cmol}(+)/\text{kg}$ ) compared to the afforested area, where the average profile value of  $Ac_{tot}$  was  $7.8 \text{ cmol}(+)/\text{kg}$ . In this regard, the difference between the pits at the level of  $p \leq 0.05$  was significant only for Pb.

The soil under birch contained

significantly more Pb, Mn, and Cu, especially in the upper part of the profile, with a slight difference in Zn compared to meadow soil. At the bottom of the pit, when moving to the underlying rock, these differences were neutralized (Figure 1), and they were significant for Pb at the level of  $p \leq 0.01$ , and Cu –  $p \leq 0.05$ .

The greatest difference in the content of all the studied elements was observed between meadow soil and the soil under larch, where it was significant at the level of  $p \leq 0.05$  for Pb, Cu, and Zn and at the level of  $p \leq 0.01$  for Mn. As can be seen in Figure 1, these differences decreased with depth but persisted up to the underlying rocks.

In comparison with the soil under the meadow, the available Pb compounds were significantly more accumulated in the soil layer of 0–10 cm under stands of all species, Mn – under larch and birch, Cu – under all species except pine, and the difference in the content of Zn between the soils under forest stands and meadow vegetation was unreliable (Table 2). Under the natural beech forest, a significantly higher content of available compounds of all metals, including Zn, was observed.

**Table 2.** Statistical indicators on the content of elements in the soil layer of 0–10 cm

Vegetation	Number of repetitions	Content, mg/kg			
		Pb	Mn	Cu	Zn
Pine	23	$1.93 \pm 1.27^{**}$	$15.3 \pm 5.9$	$0.29 \pm 0.22$	$0.91 \pm 0.31$
Meadow	24	$1.20 \pm 0.59$	$12.9 \pm 5.9$	$0.25 \pm 0.16$	$0.91 \pm 0.32$
Birch	16	$1.93 \pm 0.94^{**}$	$16.6 \pm 6.6^{**}$	$0.13 \pm 0.03^*$	$1.21 \pm 0.92$
Meadow	17	$0.78 \pm 0.24$	$11.0 \pm 3.9$	$0.11 \pm 0.04$	$1.06 \pm 0.47$
Larch	10	$2.70 \pm 1.23^{**}$	$24.1 \pm 8.4^{**}$	$0.21 \pm 0.03^{**}$	$1.48 \pm 0.53$
Meadow	7	$1.24 \pm 0.25$	$10.1 \pm 2.8$	$0.14 \pm 0.04$	$1.33 \pm 0.29$
Maple	5	$1.37 \pm 0.46^*$	$5.1 \pm 1.0$	$0.10 \pm 0.02^*$	$0.68 \pm 0.32$
Meadow	5	$0.74 \pm 0.11$	$4.5 \pm 0.9$	$0.08 \pm 0.02$	$0.70 \pm 0.20$
Beech	16	$2.25 \pm 1.39^{**}$	$25.8 \pm 9.4^{**}$	$0.15 \pm 0.04^{**}$	$3.77 \pm 1.73^{**}$
Meadow	12	$0.81 \pm 0.21$	$11.0 \pm 3.9$	$0.11 \pm 0.02$	$1.20 \pm 0.45$

Note: \* – the significance level of the differences following the Mann-Whitney criterion  $\leq 0.05$ , \*\* –  $\leq 0.01$ .

The main reason for the increase in the mobility of elements under forest stands is the increase in soil acidity, which is observed under all forest species, except for maple,

where the differences in the values of  $Ac_{tot}$  in comparison with meadow soil are insignificant (Table 3).

**Table 3.** Acidity, the content of clay and organic carbon in the soil layer of 0–10 cm

Vegetation	Number of repetitions	pH	Ac <sub>tot</sub> , cmol(+)/kg	C <sub>tot</sub> , %
Pine	23	4.18	9.3 ± 2.9*	3.22 ± 0.76
Meadow	24	4.51	7.2 ± 2.01	3.64 ± 0.74
Birch	16	4.13	8.9 ± 3.1**	3.42 ± 0.85**
Meadow	17	4.79	5.4 ± 3.1	4.45 ± 0.88
Larch	10	3.76	16.2 ± 1.4**	3.61 ± 0.36**
Meadow	7	4.62	9.0 ± 0.9	4.83 ± 0.59
Maple	5	4.90	6.24 ± 1.49	4.08 ± 0.26
Meadow	5	5.31	4.34 ± 1.95	4.98 ± 1.46
Beech	16	3.73	13.0 ± 4.3**	4.16 ± 0.74
Meadow	12	4.79	6.6 ± 1.3	4.0 ± 0.64

Note: \* – the significance level of the differences following the Mann-Whitney criterion  $\leq 0.05$ , \*\* –  $\leq 0.01$ .

An increase in the mobility of metals with a decrease in pH, including under the influence of tree stands, is described by different authors. The results of studies of Andersen et al. (2004) indicate an increase in acidity under 34-year-old coniferous stands compared to unforested soil, which the authors attribute to an increase in the mobility of Cd and Zn in the upper soil layer under fir, and Cu, Ni, and Pb under spruce. Following the results of studies of Bergkvist (1987), who studied the influence of spruce, beech, and unforested areas on the acidity of the soil solution and the mobility of metals in the lysimetric experiment, the lowest pH values and the highest mobility of metals were observed under spruce, the lowest – under unforested areas. Römken and Solomon (1998) note that despite the higher total Cd and Zn content in arable soils due to the application of manure and mineral fertilizers, the concentration of these elements in the soil solution was higher in the more acidic soil under the forest.

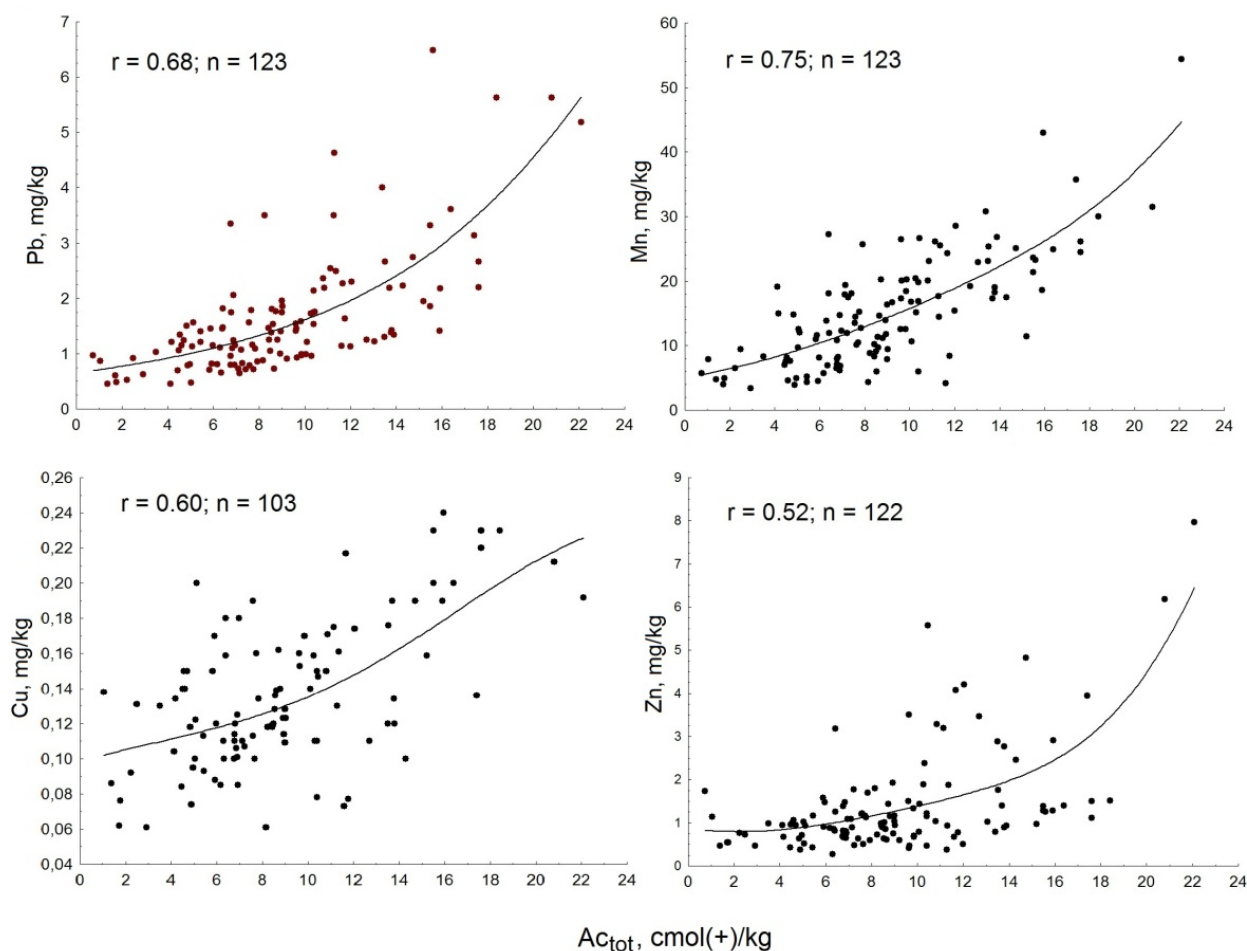
The content of organic matter either did not affect or had a very weak and multidirectional effect on the content of mobile forms of some metals in afforested soils. Thus, in the soil under the pine, a weak positive relationship with C<sub>tot</sub> was revealed only with Zn ( $r = 0.48$ ;  $n = 23$ ), under the birch – a negative relationship with Cu ( $r = -0.53$ ) and Zn ( $r = -0.63$ ;  $n = 17$ ). The effect of clay on the metal content in all cases was insignificant.

Closer relationships between soil properties and the metal content in the 0–10

cm layer was observed in the soil under the natural beech forest. According to the data of multiple correlation analysis, the Pb content is associated with all soil indicators with a high degree of significance ( $R = 0.92$ ;  $r_{\text{clay}} = 0.58$ ;  $r_{\text{C}} = -0.70$ ;  $r_{\text{Ac}} = 0.93$ ;  $n = 16$ ), manganese – with C<sub>tot</sub> and Ac<sub>tot</sub> ( $R = 0.74$ ;  $r_{\text{C}} = -0.52$ ;  $r_{\text{Ac}} = 0.67$ ), as well as zinc ( $R = 0.82$ ;  $r_{\text{C}} = -0.57$ ;  $r_{\text{Ac}} = 0.74$ ). Least of all, the content of Cu, associated only with the content of C<sub>tot</sub>, depended on soil properties ( $r = -0.65$ ). The positive correlation with clay and Ac<sub>tot</sub> is quite natural since the minerals of the finely dispersed part of the soil are the main source of trace elements, and the acidity affects their mobility. The multidirectional influence of C<sub>tot</sub> on the content of the studied metals shows that these bonds can be random since organic matter is not the main source of trace elements in forest soils, but humic and fulvic acids can bind metal ions entering the soil from various sources to insoluble organo-mineral complexes (Orlov et al., 2005).

When analyzing the entire data set for afforested and meadow soils, Ac<sub>tot</sub> is the only factor that has a significant impact on the content of the studied elements. Ac<sub>tot</sub> correlates most closely with the content of Pb and Mn (Figure 3), which are characterized by the greatest difference between the soils under forest stands and meadow vegetation (Table 2). A less close correlation is observed between Ac<sub>tot</sub> and Cu, and the weakest correlation is between Ac<sub>tot</sub> and Zn since the amount of zinc with an increase in soil acidity under the influence of forest stands has not changed much.





**Figure 3.** Effect of  $Ac_{tot}$  on the content of elements in the soil layer of 0–10 cm of mountain meadow fallow lands, and afforested soils

Among the reasons for the increase in the content of some elements in the upper layer of the soil under forest stands, the possibility of their introduction with tree litter was also considered. As the results of fresh leaves analysis showed, they contained a particular amount of all the studied elements, except Pb (Table 4), which for several decades of growing artificial stands could lead to the accumulation of Mn, Cu, and Zn in the upper layer of the soil. However, in the fresh litter of deciduous trees, only Zn was found out among all elements, and in much lower concentrations than in live leaves (Table 4). The concentrations of the remaining elements

were below the detection limit. Among all the species planted during the plateau afforestation, only pine litter could be a source of trace elements, primarily zinc, entering the soil, but it is not confirmed by the results of determining its content in the soil layer of 0–10 cm (Table 2). At the same time, the high zinc content in the layer of 0–10 cm under the beech (Table 2) and a sharp decrease in its concentration with depth (Figure 1) indicate the possibility of zinc accumulation due to plant litter under the condition of prolonged exposure of the forest to the soil.

**Table 4.** The content of ash and elements in fallen and fresh leaves and needles

Tree	Ash, %	Pb	Mn	Cu	Zn
		mg/kg			
2018 litter					
Pine	2.62	n.d.	2.46	2.13	30.7
Larch	5.25	n.d.	n.d.	n.d.	12.7
Birch	4.82	n.d.	n.d.	n.d.	1.21
Maple	9.27	n.d.	n.d.	n.d.	6.73
Beech	5.63	n.d.	n.d.	n.d.	6.38
Leaves selected on August 15, 2019					
Birch	4.42	n.d.	16.1	4.21	92.6
Maple	9.03	n.d.	7.67	6.14	30.7
Beech	5.45	n.d.	24.8	5.66	26.3

n.d. – not detected.

### CONCLUSION

The growth of artificial forest stands on the mountain meadow soils of the Ai-Petri plateau over 60 years caused an increase in their acidity relative to the adjacent areas of mountain meadows and the accumulation of some trace elements.

The greatest difference between the content of elements available for biota in the soil layer of 0–10 cm under forest stands and meadow vegetation was found for Pb and Mn (except for maple), and much smaller for Cu and Zn.

In comparison with the soil of a natural beech forest, only under larch in a layer of 0–10 cm, a higher or similar content of all elements, except for Zn, was observed. The

increased Cu content under the pine is explained by its increased content in the soil of the meadow areas adjacent to the pine stands.

The main reason for the increase in the mobility of some elements under tree stands is their transition from immobile forms under the influence of increased acidity of afforested soils.

The absence or extremely low content of elements in the litter excludes the possibility of their accumulation in the upper soil layer under relatively young stands as a result of the mineralization of needles and leaves, but the long-term growth of the beech forest leads to the accumulation of available Zn.

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