Heavy metals in soils under various tree species

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Abstract. The issues of mutual influence of forest and soil attract the attention of researchers not only in theory, but also in practice, especially in the forest-steppe and steppe regions of the country. The researchers drew attention to the rapid changes in soil properties associated with forest planting. In addition, the composition and properties of soils are affected by the rock composition of forest belts. The main chemical, physical, and physical-chemical properties of ordinary chernozems under forest stands, of different rock composition, were studied. The same indicators were investigated in the chernozems occupied by arable land. It is shown that protective forest strips do not significantly affect the physical properties of soils. Chemical and physical-chemical properties change under the influence of wood crops. The gross content and mobile compounds of heavy metals in chernozems occupied by tree species were studied. It is shown that various HM and their compounds have their own characteristics of content and intra-profile distribution. The content and distribution of heavy metals is determined by the pH value, the content and distribution of silty particles, and humus (Corg). In addition, the nature of vegetation and various types of wood species have a significant impact on the content and profile distribution of heavy metals.

1. Introduction

Forest ecosystems play an important role in the biogeochemical circulation of elements. Plants effectively intercept aerosols and settling suspensions of solids from rain, snow, hail, and dust. This position was confirmed experimentally. It was found that the loss of some elements in the forest can be 5-6 times higher than the corresponding indicator for open spaces [1].

Under the influence of the forest growing on the chernozem, there is an expansion and acceleration of the cycle of substances. A larger volume of soil is captured as a result of the development of deep chernozem horizons by the roots. The features of soil development under forest plantations include increased humidity of the upper horizons, lower and more even daily temperature, greater solubility and mobility of organomineral compounds. The cycle involves an additional number of elements that were previously firmly bound in humus, primary and secondary minerals. However, to predict changes in the cycles of elements and substances under the influence of wood species, it is not enough to divide them into deciduous and coniferous. It is necessary to have a more accurate understanding of the effect of individual crops on biogeochemical soil processes [2]. There is very little information in the literature, including foreign literature, about how metals circulate between plants and soil and what their balance is in forest ecosystems [1].
Currently, the influence of forest crops on soil properties is found in the works of many authors. The influence of tree species on the rate of humus (Corg) mineralization is considered [2]. The influence of forest belts on pH is studied [3]. Heavy metals are studied in detail in soils and plants of recreational areas [4]. In connection with the increasing anthropogenic load, the dust-holding capacity of forest belts [5], as well as the influence of all kinds of anthropogenic emissions on the accumulation of heavy metals in plants [6], are studied. The influence of various tree species on the content and features of the intra-profile distribution of heavy metals is not sufficiently covered in the literature. The study of the influence of individual species on soil formation is complicated by the variety of stands and multiple, but not synchronous, changes in forest formation and soil formation processes. To answer questions about the interaction of individual tree species and soils, we need many years of experience with the same age forest crops created in the same soil and environmental conditions [2, 6]. This condition is met by forest belts growing on the territory of the Stone steppe. It should be noted that the study area belongs to the protected area, not experiencing technogenic impact, it is located far from anthropogenic sources of pollution. The obtained data can be used as "background" data for the purpose of conducting regular monitoring studies. Therefore, the purpose of this work was to study the features of accumulation and intra-profile distribution of heavy metals (Mn, Zn, Cu) under the same-age forest plantations of the Stone steppe, consisting of various tree species, located far from sources of anthropogenic pollution. In order to determine the contribution of various tree species to the soil formation process, the vegetation fall of forest plantations was studied.

The stone steppe is located far from all anthropogenic sources of pollution. In background or lightly polluted areas, most heavy metals accumulate in the roots. But roots are not good for biomonitoring [1]. As root hairs and fine roots are closely associated with soil particles and in the collection of material is their loss. This significantly affects the results of the analysis. Thus, in terrestrial plants for the analysis of heavy metals are used mostly leaves. The oldest leaves have the highest concentrations of elements. The analysis of the fall of woody vegetation will allow us to assess the degree of involvement of various heavy metals in the biological cycle of elements. Therefore, the purpose of this work was a comprehensive study of the behavior of heavy metals - Mn, Zn, Cu (their gross content and mobile compounds) in the soil cover and plants on the territory of the Kamennaya Steppe, which is a nature reserve. Consequently, the obtained data are proposed to be used as a "background" in order to conduct a full monitoring of areas prone to pollution.

2. Methods and materials

The object of the study was the soils of the forest plantations of Kamennaya steppe, Talovsky district of the Voronezh region (Russian Federation), located within the same forest strip No. 211 (table 1). The forest strip was laid in 1959. The length is 850 m and the width are 22 m. The method of creation is diagonal-group, the site is rhombic, the placement of tree species is accepted as optimal [7].

| Wetland   | N, °   | E, °   |
|-----------|--------|--------|
| Arable    | 51.052328 | 40.747665 |
| Maple     | 51.050580 | 40.748916 |
| Larch     | 51.050917 | 40.746058 |
| Birch tree| 51.051302 | 40.743098 |
| Pine      | 51.051847 | 40.739985 |

The woody composition of the forest belt is represented by: Siberian larch (Larix siberica Ldb.); Holly maple (Acer platanoides L.); common pine (Pinus sylvestris L.); and warty birch (Betula verrucosa Ehrh). Field and laboratory studies were conducted from 2018 to 2019. In total, five full-profile sections were laid to a depth of 150 cm. Four sections were laid in sections of maple, larch, birch and pine forest belt No. 211; the fifth is on arable land, in close proximity to the forest belt. The
soils of the study area were identified as ordinary chernozems (WRB - segregated chernozems). The soil forming rocks for these soils were cover carbonate heavy loams and clays [8].

Soil samples were taken in layers, every 10 cm to a depth of 150 cm: 0-10, 20-30, 40-50...140-150 cm. The soil was placed in boxes and transported to the laboratory. The plant material was selected in the form of the fall of woody vegetation in sections of maple, larch, birch and pine. Plant residues were also placed in boxes and transported to the laboratory. The following analytical works were performed in soil samples under laboratory conditions.

The pH value of the water suspension. Included in the group of electrochemical methods. Its principle is based on the assessment of processes occurring on the surface of the electrode – 10 g of soil passed through a sieve with a hole diameter of 1 mm is taken with an accuracy of ±0.1 g. It is placed in a clean beaker with a capacity of 100 ml (Vekton, St. Petersburg, Russia). Distilled water (25 ml) is poured into a glass. Mix thoroughly with a glass stick and leave for 24 hours. At the end of the settling period, the pH in the supernatant is determined using a potentiometric microprocessor ionomer I-160MI (Aquilon, Moscow, Russia).

Total humus (Corg). The principle of the method is the oxidation of soil carbon K_2Cr_2O_7. The excess K_2Cr_2O_7 after oxidation is titrated with a solution of (NH_4)_2SO_4·FeSO_4·6H_2O - determined in a specially prepared sample: the soil should be devoid of roots and sifted through a sieve with a hole diameter of 0.25 mm. on the tracing paper, take a soil sample of 0.05 g with an accuracy of ±0.0001 g (analytical scales VL-S, Gosmetr, St. Petersburg, Russia). The taken hitch is placed in a dry conical heat-resistant flask with a capacity of 100 ml. The hitch from a burette with a glass tap is poured strictly by drops of 10 ml of 0.4 n solution of the chrome mixture (K_2Cr_2O_7 (Vekton, St. Petersburg, Russia) in the presence of H_2SO_4 pl. 1.84 in the ratio 1:1). The flasks are closed with glass funnels and placed on an electric stove (the working surface of the tile is previously covered with a thin layer of asbestos). The contents of the flask are boiled for 5 minutes, the boiling should not be strong without the release of white vapors from the flask. After boiling, the flask is allowed to cool down to room temperature. Then 5 drops of 0.2% solution of phenylanthranilic acid (C_13H_11NO_2) (Vekton, St. Petersburg, Russia) are added to the contents of the flask and titrated with 0.2 n solution of Mora salt ((NH_4)_2SO_4·FeSO_4·6H_2O) (Vekton, St. Petersburg, Russia) until the color changes to emerald green.

The gross content of heavy metals was determined as follows. The principle of the methods for determining the heavy metals is based on measuring the optical density of the atomic vapor of the element being determined, obtained by electrothermal atomization of the sample in the graphite furnace of the spectrometer brand (Kortek, Moscow, Russia)- the soil for determining heavy metals is ground in a Jasper mortar to a powder state. The soil is placed in porcelain crucibles and salted in a muffle furnace SNOL (Umega, Lithuania) at 505ºC for 3 h. Take 5 g of calcined soil, with an accuracy of ±0.1 g. It is placed in a dry conical heat-resistant flask with a capacity of 100 ml. Add nitric acid HNO_3 1:1 and boil for 10 min. The concentrated hydrogen peroxide H_2O_2 (concentrated), boil for 10 min. It is cooled, filtered through a dense filter (blue tape). The filtrate is placed in a 50 ml volumetric flask, the volume is brought to the mark with distilled water (Vekton, St. Petersburg, Russia).

Mobile heavy metals compounds were determined in the extract of an acetate-ammonium buffer (AAB) with the pH of 4.8 (Vekton, St. Petersburg, Russia), the soil – solution ratio is 1:10.

Heavy metals in plant litter-on analytical scales VL-S (Gosmetr, St. Petersburg, Russia), take a weight of 1 g. with an accuracy of ±0.0001 g. Previously, the plant material was crushed with scissors. The crushed mass is sifted through a sieve with a hole diameter of 1 mm. The Attachments are placed in porcelain crucibles, moistened with 2 ml of ethyl alcohol (C_2H_5OH) (Vekton, St. Petersburg, Russia) and set on fire in a fume hood. When the flame goes out, the crucibles are placed in the muffle furnace SNOL (Umega, Lithuania) and burned with the door open. After the crucibles stop Smoking, they are removed and cooled in the air. Then 10 drops of concentrated hydrogen peroxide (H_2O_2) (Kortek, Moscow, Russia) are added to each crucible. The crucibles are placed in a muffle furnace SNOL (Umega, Lithuania) and after 10 minutes, when the oxidizer has evaporated, the door is closed. The crucibles are kept for 30 min at 500ºC. If complete combustion has not occurred, the oxidizer is
added to the cooled crucibles again, evaporated and calcined. After complete combustion, the color of the ash should be light gray, almost white. The plant ash is dissolved in 100 ml of nitric acid HNO₃ (1:1) and filtered through a dense filter (blue ribbon) in a 100 ml volumetric flask (Vekton, St. Petersburg, Russia). Then the volume is brought to the label with acid and taken with a pipette of 1 ml. A 100 ml volumetric flask is placed and brought to the label with distilled water.

Quantitative determination of heavy metals in the obtained extracts was performed using the KVANT.Z.ETA atomic absorption spectrometer (Kortek, Moscow, Russia), the sensitivity of detection 0.01 µg/l, precision of 4%. The measurement method is based on the measurement of the absorption capacity (optical density) of the atomic vapor of the element to be determined, obtained by electrothermal atomization of the sample in the graphite furnace of the spectrometer. Measurements of the optical density of an atomic vapor are made at the resonant spectral line of an element emitted by a corresponding hollow cathode lamp. To correct the background (non-atomic) absorption in the spectrometer, the inverse Zeeman effect is used when a parallel alternating magnetic field is applied to the analytical cell. The measured optical density of the atomic vapor of the element to be determined is unambiguously related to the concentration of this element in the analyzed sample by the calibration dependence determined during the calibration process. Calibration is performed using at least four calibration solutions, including the background (zero or blank) solution.

Variational and statistical processing was performed using programs Microsoft Excel.

3. Results and discussion

Determination of the humus (Corg) content showed that the largest amount of humus is typical for soils where larch (7.92±0.98%) and maple (7.58±1.01%) grow. The amount of total organic matter in chernozems under birch (7.07±0.67%) and pine (7.03±0.61%) crops is significantly reduced, the lowest value was obtained in agro-soil (6.11±0.83%). The loss of organic matter as a result of intensive agricultural use is also noted by other authors [8], as well as in our previously published works [9, 10]. At the same time, the capacity of the organ profile is also naturally reduced. So, in the soil under larch and maple, the capacity of the humus horizon is 82 and 84 cm, respectively. In chernozem under birch and pine, it is reduced to 76 and 75 cm, respectively, and in soils under arable land it is the smallest and is 70-72 cm.

The reaction of the medium is most acidified in chernozems where pine (pH=6.41±0.57) and to a lesser extent birch (pH=6.62±0.11) grow. The pH of the water suspension is slightly higher in the chernozem under maple (pH=6.72±0.24) and larch (pH=6.81±0.32) crops. The increase in the alkalinity of the soil suspension under larch culture relative to birch and pine is also noted by other authors [2]. The agro-soil profile is characterized by a neutral and slightly alkaline reaction of the medium over the entire capacity (7.01-8.09). The upper boundary of the carbonate profile in agro chernozem is marked at a depth of 52 cm. In soils under tree crops, there is a decrease in the boiling line to varying degrees, which is obviously due to the chemical composition and pH of the fall, root secretions, compounds extracted by precipitation from the above-ground part of plants, the density of the crowns and, consequently, the ability to delay these precipitation [11]. So, in the black soil, where maple, larch, birch grow, carbonates are found from a depth of 70-74 cm. the lowest carbonate profile falls in the soil under the pine, here its upper border is at the level of 98 cm.

The studies have shown that the content of Mn in the studied soils is less than its Clarke [12] in the lithosphere (1000 ppm), that is, there is a scattering of the element relative to the lithosphere. The content of heavy metals in the soils under all tree species was significantly higher than in the soils of arable land. At the same time, the maximum amount of gross Mn content is observed in the upper 0-10 cm layer of soil under the maple and is 791±20.1 ppm, then in descending order are the soils under larch (558±18.4 ppm), birch (519±11.7 ppm), pine (516±10.4 ppm) and the minimum content is noted in the chernozem of segregation under arable land (500±10.1 ppm) (figure 1a). This phenomenon is to some extent explained by the different percentages of humus under the studied tree species, the amount of which decreases in the same direction, with a minimum amount under arable land. Since Mn has the ability to form strong organomineral complexes.
Figure 1. Profile distribution of heavy metals total content of Mn (a), Zn (b), and Cu (c).

Analyzing the gross content of Mn in the soil profile, it can be noted that the maximum amount of the element is usually confined to the upper horizon with a gradual decrease in its depth, which refers this distribution to the accumulative type. This is especially clear in the soil profile under maple and larch (figure 1a). For birch and pine, the profile distribution becomes more complicated and acquires noticeable signs of accumulative-eluvial-illuvial distribution, with two characteristic maxima of accumulation of the gross Mn content, in the upper part of the profile and at a depth of 100-110 cm. This type of distribution is also observed in the soil under arable land, with the only difference that the eluvial minimum in the profile is higher (80-90 cm) than in soils under woody vegetation, which is probably due to less intensive soaking of the soil profile in arable conditions. Researchers also emphasize the ability of heavy metals to be fixed by humus substances in the upper soil layer, and in the lower ones by clay minerals, carbonates, and minerals with a variable charge [13-15].

The results of the correlation analysis show that the intra-profile distribution of the gross Mn content is closely related to the amount of humus (Corg) in the soils under larch and birch (r reaches 0.98). Under the same tree species, there is a close negative correlation with pH. No correlation was found under other tree stands and in arable soils.

The share of Mn exchangeable compounds in the upper soil horizons accounts for from 3 to 6 % of the total content. As for the above forms, the content of mobile Mn decreases in a row: larch (39.5±1.21 ppm) > maple (35.6±1.15 ppm) > birch (20.9±1.11 ppm) > pine (20.5±1.17 ppm) > arable land (19.1±1.07 ppm), but a different phenomenon is observed in the profile distribution. If the gross
Mn content in the profile was distributed according to the accumulative type, the mobile ones in all soils have an eluvial distribution type (figure 2a). At the same time, the content of mobile Mn increases down the soil profile under maple and larch by approximately 1.4 times, under birch and pine by 2.8 times, and under arable land by 3.0 times. This difference is primarily due to the different amount of gross Mn content, as well as the different intensity of absorption by woody and herbaceous crops. The results of the correlation analysis showed a close relationship between the profile distribution of mobile Mn, humus and pH under all tree species and under arable land.

Among broad-leaved species, maple and oak are classified as Mn concentrators. According to [16, 17] in forest landscapes, wood species are 5-10 times richer in Mn than grasses (with the exception of hydrophytes). With additional moisture, birch and willow are also Mn concentrators, and on acidic rocks – pine. According to the data obtained, the Mn content in the litter of the studied rocks decreases in a row: Holly maple (99.1±12.7 ppm) > Siberian larch (89.7±15.3 ppm) > warty birch (57.4±10.0 ppm) > common pine (41.8±12.4 ppm). Thus, the highest accumulation coefficient (N) is typical for Holly maple (0.13), and the lowest (N=0.08) for common pine. The maple species makes the greatest contribution to Mn biogeochemistry, compared to other forest plantations studied.

The obtained data showed that the Zn content in the studied soils is higher than the clarke of the soil and the lithosphere [12]. From the data obtained, it follows that the gross content of Zn, as well as Mn in soils under tree species is significantly higher compared to the soil of arable land. Moreover, the same sequence of quantitative Zn content in soils under different crops is maintained. The highest amount of gross Zn content in the upper soil layer is observed under larch – 145±11.5 and maple-136±10.8, less – under birch – 110±16.8, pine – 106±14.2 and arable land – 98±11.8 ppm (figure 1b). The increased content of Zn in chernozems under larch and maple is explained by the high content of humus (Corg), and the nature of the biological cycle that contributes to the accumulation of Zn under these rocks. The distribution of the gross Zn content in the soil profile under maple and larch is characterized by an accumulative type, but in contrast to Mn, the distribution curve has signs of regressive accumulation.

The attention is drawn to the features of the profile distribution of the gross Zn content in soils under birch, pine and arable land, where the accumulative-eluvial-illuvial type of distribution is most clearly observed (figure 1b). At the same time, the eluvial zone (the lowest content of the element in the profile) in arable soils is marked at a depth of 60-70 cm, in the soil under the birch – 80-90 cm, and in the soil under the pine – 120-130 cm. This difference in the profile distribution of the gross Zn content is primarily due to the structure of the soil profiles of the studied soils and, in particular, the depth of the carbonate horizon, as well as the features of the hydrological regime of these soils.

Correlation analysis data indicate a close relationship between the distribution of gross Zn content with humus (Corg) under larch and birch, and with pH under all tree species and arable land.

The share of exchangeable Zn in the upper part of the profile of the studied soils is from 2.01 to 9.86 % of the gross content and increases with depth. It should be noted that in the profile of all studied soils, the exchangeable Zn is distributed by eluvial type (figure 2b). Exchangeable Zn is an easily accessible element of plant mineral nutrition. It is actively involved in biogeochemical cycles, especially from the upper soil horizons, where there is a concentration of root systems of woody and herbaceous vegetation. High correlation coefficients indicate a close relationship between the profile distribution of mobile Zn compounds with humus (Corg) and pH.

Zn refers to elements of medium and intensive accumulation in plants. Among wood species, the most intensively concentrated Zn is birch [1, 16], which is confirmed by our research. So the Zn content in the fall of woody vegetation decreases in the following series: warty birch (42.8±6.3 ppm) > Holly maple (27.8±4.9 ppm) > Siberian larch (22.7±1.8 ppm) > common pine (21.8±3.6 ppm). The highest accumulation coefficient Zn=0.39 is typical for birch, the lowest-0.16 is for larch.

Cu content in the studied soils is close to the clarke of the lithosphere and slightly higher than the Clarke of soils [12]. Cu, along with many heavy metals, refers to elements closely related to organic matter. The data obtained by us also indicate a high organophilicity of Cu. The total Cu content is accumulated in the upper humus horizon of the studied soils, and the increase in the concentration of
these compounds depends on the percentage of humus content. In soils under larch that have the maximum amount of organic matter, the gross Cu content reaches the maximum and is 45.9±7.8 ppm (figure 1c). In soils under arable land, where as a result of agricultural use there was a decrease in the humus (Corg) content and the amount of Cu in the same 0-10 cm layer is only 19.4±11.0 ppm.

Figure 2. Profile distribution of heavy metals exchangeable compounds of Mn (a), Zn (b), and Cu (c).

Down the soil profile under larch and maple, there is a very gradual decrease in the gross Cu content with a minimum metal content at a depth of 140-150 cm. in the chernozems under birch, pine and arable land, there are 2 maximum accumulations of the element – in the humus and carbonate horizons. This phenomenon seems to be related to the features of seasonal-variable migration of carbonates under various tree species. The results of the correlation analysis revealed a close relationship in the profile distribution of the gross Cu content with humus and pH in soils under maple and larch r=0.98.

In the profile distribution of exchangeable Cu, there is a distinct eluvial type of profile distribution, that is, an increase in it in the lower part of the soil profile (figure 2c), which is due to the intensive consumption of Cu by plants from the upper horizons. As a result, there is a strong correlation between the intra-profile distribution of mobile Cu and humus (Corg) and pH r=0.81. The percentage of cu mobility ranges from 3.46 to 13.1 %.
According to literature data, the weakest concentrators among Cu trees are warty birch and common aspen [1, 16]. According to our data, the highest Cu content is also characteristic of warty birch (31.4±8.2 ppm), followed in descending order by Holly maple (16.6±2.5 ppm) > Siberian larch (11.5±1.6 ppm) > common pine (5.4±1.2 ppm). The highest accumulation coefficient is typical for warty birch, equal to 1.48, the lowest is for Siberian larch - 0.25.

Conclusion
The studied soils have a heavy particle size distribution, with a predominance of silty particle size distribution. According to the humus (Corg) content, chernozems are classified as medium humus. The maximum content of organic matter is confined to the upper horizons under the rocks of larch and maple. Wood species contribute to the conservation and some increase in organic matter in the soil profile. In addition, they enhance the penetration of organic matter into deeper layers of the soil profile, which leads to an increase in the thickness of the humus horizon.

The most influential effect on the pH of the soil solution is ordinary pine. This phenomenon is associated with root secretions that have an acidic reaction. In general, under all tree species there is a decrease in the depth of the carbonate horizon. This is due to the chemical composition of the litter, its pH, root emissions and the ability of tree species to retain moisture.

Relative to the lithosphere, Mn scattering is observed in the studied soils. The level of Zn content slightly exceeds the clarke of the lithosphere, and it is dispersed relative to the lithosphere. The amount of Cu in the studied soils is close to the clarke of the lithosphere.

In the chernozems of Kamennaya steppe, under all tree species, there is a biogenic accumulation of the gross content of Mn, Zn, Cu with the maximum content in the soils under larch, then the soils under maple, birch, pine and arable land follow in descending order, which may be due to the corresponding content of humus, the amount of which decreases in the same row.

Exchangeable compounds Mn, Cu, Zn have an eluvial type of intra-profile distribution, concentrating mainly in the lower part of the soil profile, which is associated with their consumption by plants as food elements, as well as features of the carbonate-calcium regime of the studied soils. The results of the correlation analysis revealed the closest relationship between the profile distribution of the gross content of heavy metals, humus and pH in soils under larch and maple. For exchangeable forms of heavy metals compounds, this relationship is observed under all tree species and arable land. Among the studied heavy metals the least mobile compounds are Zn.

Of the studied wood species, the Mn concentrator is the Holly maple, which is characterized by the highest accumulation coefficient. The Zn and Cu concentrator is the warty birch. The gross content and exchangeable forms of heavy metals in all studied soils do not exceed the MPC [17] set for chernozem soils. Due to the ever-increasing level of anthropogenic load, there is a regular supply of heavy metals to the soil cover. Through biogeochemical chains, heavy metals are able to enter the body of plants and humans. Therefore, it is necessary to regularly conduct biomonitoring studies of soils and plants. And the data obtained by us can be used as "reference" (background) values for the purpose of conducting monitoring studies.

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