Features of the migration of heavy metals in the forest landscapes of the 'Kamennaya Steppe'

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Abstract. The article examines the influence of woody vegetation on the change in some soil properties. Numerous studies have confirmed the change in the water regime under forest belts. Such dynamics entails the transformation of morphological characteristics and the following basic soil properties: pH of the soil solution, carbon of organic compounds. The evolution of properties causes changes in the total content of heavy metals: nickel (Ni), lead (Pb), cadmium (Cd) and their exchange compounds. The features of the profile distribution of Ni, Pb and Cd in the chernozems of the forest belt have been studied. Elements were determined by atomic absorption spectrophotometry. Carbon of organic compounds - by titrimetric method, pH of soil solution - by potentiometric method. Wood species affect the profile distribution of heavy metals. Correlation analysis revealed a close relationship in the profile distribution of carbon of organic compounds, pH, Ni, Pb. Variational analysis of spatial heterogeneity showed the differences in the studied indicators between arable land and forest belt. A decrease in the coefficient of variation from the forest belt to arable land is noted. The phenomenon is explained by plowing, mixing the soil mass and leveling out spatial differences in the content of carbon of organic compounds, pH, heavy metals.

1. Introduction

The positive meliorative role of forest belts was scientifically substantiated by V V Dokuchaev. He also designed and implemented the first agroforestry measures, including on the territory of the Kamennaya Steppe, where our research was carried out. Later, many scientific publications were devoted to the study of the transformation of the soil cover under the influence of forest belts. The use of field-protective forest plantations in the forest-steppe and steppe zones of the Central Chernozems region is an effective reclamation technique. A favorable reclamation effect is noted in [1]. An increase in the biological cycle under the influence of forest vegetation is noted [2]. Shelter forests increase the productivity of agricultural crops by improving the water balance and water regime. The positive influence of forest belts on erosion processes is undeniable [3]. Since forest belts reduce wind speed, they reduce the harmful effects of dry winds. An important feature of forest belts is the accumulation and uniform distribution of snow in the fields. This leads to an improvement in the water balance, and at the same time to the transformation of soils. It is necessary to note the role of tree
plantations in the binding of carbon to carbon dioxide, which leads to a decrease in the greenhouse effect [4]. Forest belts have become an integral part of the landscape, fulfilling its ecological functions [5]. In addition to an active experiment in nature, mathematical modeling of the processes occurring under forest vegetation is currently used. The data obtained using model experiments indicate that the soil solution carries organic matter, as well as heavy metals [6].

It is known that unique bioclimatic conditions are created in the soils under forest belts, which affect the soil cover. Favorable conditions are created for humus accumulation due to the constant supply of organic matter to the soil in the form of leaf and branch litter. Such drastic changes in soil processes will necessarily be accompanied by the transformation of morphological, physical, physicochemical, chemical, and biological properties of soils. There is a significant difference between the soils of the forest belt and arable land in terms of such physical parameters as bulk density, silt and physical clay reserves. The transformation of (carbon of organic compounds) Corg [3], microbial biomass, respiratory activity, nitrogen fixation [4] is described.

Soils formed in the same type of conditions can be reliably transformed under the influence of forest belts [3]. Forest vegetation affects the morphological, physical, physicochemical, and chemical properties of soils. The literature mentions the ability of woody vegetation (Siberian larch) to accumulate heavy metals [7]. The purpose of this work is to reveal the influence of the forest belts of the Kamennaya Steppe on the transformation of Corg and pH of the soil solution; to study whether the unique soil and climatic conditions of the forest belts of the Kamennaya Steppe affect the profile distribution of the total content and mobile compounds of Ni, Pb and Cd; to determine whether there are significant differences between the chernozems of arable land and forest belts, in terms of the gross content and exchangeable compounds of Ni, Pb and Cd.

2. Methods and materials
Field and laboratory studies were conducted from 2018 to 2020. The studies were carried out on the land-use territory of the Kamennno-Stepnose Experimental Forestry (Talovsky District, Voronezh Region). The objects of research were ordinary, medium-humus, medium-thick, heavy loamy chernozems (Vorony-Calcic (World Reference Base for Soil Resources)), which lie under different sections of tree species of forest belt No. 211 and on adjacent arable land (figure 1). Forest belt No. 211 was laid down in 1959, its length is 850 m and width is 22 m. The forest belt is represented by sections with various tree species: Siberian larch (Larix sibirica Ldb.), Norway maple (Acer platanoides L.), Scots pine (Pinus sylvestris L.) and warty birch (Betula verrucosa Ehrh). The forest belt was laid in a diagonal-group way, the sites are rhombic, the placement is optimal. In each section of the forest belt and on the adjacent arable land, soil sections were laid to the depth of the opening of the parent rocks, which are cover carbonate heavy loams and clays.

Soil samples were taken from each soil section, starting from the surface to a depth of 140-150 cm. The sampling was carried out every 10 cm in layers 10 cm thick. The weight of one sample was 0.5 kg. Each sample was labeled and placed in special bags. In the selected soil samples, the following types of analyzes were carried out according to the methods described below:

2.1. pH of the aqueous suspension by potentiometric method
The method is based on the dependence of the equilibrium potential of the electrode on the active concentration of the detected ion. For the preparation of an aqueous suspension, the ratio of soil - distilled water was used, taken as 1:2.5 (for 10±0.1 g of soil, there is 25 ml of distilled water). The suspension was obtained by thorough mixing with a glass rod of soil, crushed and sieved through a sieve with a hole diameter of 1.0 mm and water in the specified ratio in 100 ml beakers (Vektion, St. Petersburg, Russia). After settling the suspension (24 hours) in the supernatant liquid, the activity of hydrogen ions (pH) was determined by a potentiometric method on an I-160MI microprocessor ionometer (Aquilon, Moscow, Russia). Temperature compensation was performed using an electronic temperature sensor.
Figure 1. A map of the location of research objects (Voronezh region, Talovsky district, Federal state budgetary scientific institution 'Stone-and-steppe experimental forestry'). The numbers indicate the places of selection of soil samples: Arable land, N 51.052328°, E 40.747665° (1); Maple section, N 51.050580°, E 40.748916° (2); Larch section, N 51.050917°, E 40.746058° (3); Birch tree section, N 51.051302°, E 40.743098° (4); Pine section, N 51.051847°, E 40.739985° (5).

2.2. The carbon of organic compounds of the soil and its conversion into humus

The method is based on the oxidation of soil carbon with an excess of potassium dichromate in the presence of sulfuric acid, which is accompanied by the reduction of Cr^6+ to Cr^3+. The soil for the analysis was prepared in a special way. In a laboratory sample, plant roots and other nonspecific organic inclusions were carefully selected using tweezers and a magnifying glass, after which the sample was ground in a mortar and sieved through a sieve with a hole diameter of 0.25 mm. From the prepared laboratory sample, an analytical sample (weighed portion) weighing 0.05±0.0001 g was taken on an (HR-100ARG, A&D Company Ltd, Japan) electronic analytical balance. The weighed portions were placed in chemical heat-resistant conical flasks with a capacity of 100 ml, and then 10 ml of a chromium mixture К₂Cr₂O₇ (Vekton, St. Petersburg, Russia) in the presence of H₂SO₄, density 1.84 g/cm³ in a 1:1 ratio was poured into them from a burette with a glass stopcock. Then the flasks were closed with glass tears and their contents were boiled on laboratory hotplates with an asbestos-coated working surface for 5 minutes (using a stopwatch). After boiling, the contents of the flasks were cooled to room temperature and then titrated with 0.2 N solution of Mohr's salt ((NH₄)₂SO₄·FeSO₄·6H₂O) (Vekton, St. Petersburg, Russia) in the presence of 0.2% solution (5 drops) of phenylanthranilic acid (C₁₃H₁₁NO₂) (Vekton, St. Petersburg, Russia) until the color of the solution turns emerald green. The carbon of soil organic compounds was recalculated to humus using the generally accepted coefficient of 1.724 [8].
2.3. Determination of the gross content of heavy metals

The principle of the method 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. The soil for the determination of heavy metals was ground in a jasper mortar to a powder state. Then the ground, ground into powder, was placed in porcelain crucibles and ashed for 3 hours in a SNOL muffle furnace (Umega, Lithuania) at a temperature of 505 °C. Then, analytical samples (weighed portions) weighing 5.0±0.1 g were taken from the calcined soil, which were placed in heat-resistant chemical flasks with a capacity of 100 ml. Nitric acid (Vekton, St. Petersburg, Russia) was added to the weighed portions in a 1:1 ratio, and the contents of the flasks were boiled on laboratory electric stoves for 10 minutes. After cooling to room temperature, concentrated (30%) hydrogen peroxide (H₂O₂) (Vekton, St. Petersburg, Russia) was added to the contents of the flasks and boiled again for 10 minutes. After the second boiling, the contents of the flasks were cooled to room temperature and filtered through a tight filter (blue ribbon) (Vekton, St. Petersburg, Russia). The volume of the obtained filtrate was placed in a volumetric flask with a capacity of 50 ml and was brought to the mark with distilled water. The resulting extract was used to determine the total content of heavy metals.

According to I O Plekhanova et all. [9] the total content of heavy metals does not provide comprehensive knowledge about the ecological situation, as well as about their effect on plants [10]. To do this, it is necessary to have information about the mobile compounds available to plants. Exchangeable compounds of heavy metals were determined in an extract of ammonium acetate buffer (AAB) pH 4.8 units. (Vekton, St. Petersburg, Russia), the ratio of soil-solution 1:10 [11]. The quantitative determination of heavy metals in the obtained extracts was carried out on a KVANT.Z-ETA atomic absorption spectrophotometer (Kortek, Moscow, Russia), the detection sensitivity was 0.01 μg/L, the accuracy was 4%.

Variational-statistical processing was carried out using the STATISTICA 10 and Microsoft Excel software package. The map shown in figure 1 was digitized using the GIS tools of the SASPlanet and MapInfo Professional programs. The geographic coordinates of the locations of the soil profiles were determined using GPS navigators from Garmin.

3. Results and discussion

The humus content and its forms are always not only a reflection of the life of the soil biota, but are also determined by the dynamic nature of humus formation. In turn, humus formation is determined by the intensity of the biological cycle, the development of vegetation, as well as the relationship with environmental factors [2]. All this is reflected in the percentage of humus and Corg. The data obtained indicate that the maximum humus/Corg content is observed in the 0-10 cm layer of the studied chernozems. With the maximum content under the maple (7.61/4.41±0.57%), the minimum under arable land (5.78/3.35±0.82%). The loss of organic matter from arable soils is associated with the processes of its enhanced mineralization as a result of plowing. In addition, the annual removal of nutrients with the harvest is not fully replenished by the application of organic fertilizers. As a result, it leads to significant losses of humus. There is a significant loss of Corg from the upper layer of arable land in comparison with the forest belt [3]. Down the profile of all studied areas, there is a gradual decrease in the content of organic matter. In the parent rock, it does not exceed 0.11±0.15%. As O G Chertov and M A Nadporozhskaya in her work [2] different forest stands affect the forms of humus, in our work we traced the influence of different species on the percentage of humus, provided that a homogeneous soil and climatic territory was studied. According to the data obtained, the humus/Corg content decreases in the following order: soils under maple (7.61/4.41±1.02%)>birch (7.01/4.07±1.01%)>larch (6.46/3.75±1.02%)>pine (6.23/3.61±0.83%). The influence of litter on the nature of the litter, and subsequently on the organic matter and humus content, is also emphasized in [12]. As a result of the transformation of the water regime, excretion of forest litter and coniferous litters, desorption of organic substances from the solid phase occurs. In a more mobile state, they are able to migrate into deeper layers of the soil profile. This situation explains the more extended humus
profile in the chernozems under the tree species of the forest belt. Under larch and maple, the thickness reaches 82 and 84 cm, respectively, under birch 76 cm, pine 75 cm, and in soils under arable land it is reduced to 70 cm.

Differences in the modes of migration of carbonate compounds are characteristic of chernozems under arable land and forest belt. In the forest belt, relatively cool microclimatic conditions are formed due to the retention of moisture. The retained moisture is able to migrate along the soil profile, which leads to the movement of the carbonate horizon into deeper layers. So, in chernozems under arable land, the boundary of the carbonate horizon occurs at a depth of 50 cm. While under tree species, the boiling line sinks to a depth of 70-80 cm. The maximum depth to which carbonates have sunk is 98 cm. It was recorded under a pine crop. This phenomenon is possibly related to the specificity of pine root secretions. Root excretions of woody species are weakly acidic in nature, which affected the pH of the soil solution. And if in arable soils the reaction of the medium is neutral (pH=7.01±0.57), then in chernozems under the forest belt, it becomes slightly acidic and decreases in the following sequence: (pH=6.81±0.83) larch>(pH=6.72±0.21) maple>(pH=6.62±0.56) birch>(pH=6.41±0.41) pine.

A statistical analysis of the obtained data on the content of Corg and pH of the environment to determine the spatial differences between arable land and a forest belt showed a regular decrease in the coefficient of variation V from 20±5.3% (forest belt) to 9±1.7% (arable land). This phenomenon is explained by the fact that as a result of plowing, the spatial differences of these soil properties are leveled. In the forest belt, soil conditions are determined by the nature of the vegetation, which makes the difference. An identical pattern is noted in [3].

The clarke of Ni in the lithosphere is 58 ppm, and the clarke of soil is 40 ppm [13]. The gross Ni content in the studied soils is close to the clarke of soils and the clarke of the lithosphere. It should be noted a natural increase in the total metal content down to the parent rock. This is due to the enrichment of the studied parent rocks with this element. In addition, colloids and silty particles have a high sorption capacity for heavy metals, including Ni. A feature of the studied carbonate mantle clays is their high content of silty and colloidal fractions. The vegetation cover also influences the accumulation and distribution of metal. In the upper 0-10 cm layer, the total Ni content decreases in the following order: maple (47.9±1.23 ppm)>birch (45.4±1.47 ppm)>arable land (43.2±1.78 ppm)>larch (33.0±1.11 ppm)>pine (32.5±1.07 ppm). Down the profile there is a gradual decrease in the gross content of the element. The metal is capable of forming organomineral complex compounds. Therefore, following a decrease in Corg along the profile, a decrease in the amount of Ni also occurs. The close relationship in the profile distribution of Ni and Corg is confirmed by the result of correlation analysis. The highest correlation coefficient is observed in chernozems under maple and birch, r=0.97 and 0.88, respectively. In the soils of the forest belt, leaching processes are more intensive. The behavior of the metal obeys a general pattern, and therefore the limit of accumulation in the parent rock is noticeably reduced in the forest belt as compared to arable land (figure 2). In all studied soils, the gross Ni content does not exceed the maximum permissible concentration (MPC) Ni=100 ppm [14].

In the 0-10 cm layer, the following content of exchangeable Ni compounds is noted: maple (1.45±0.51 ppm)>birch (1.43±0.33 ppm)>larch (1.19±0.32 ppm)>pine (1.15±0.17 ppm)>arable land (1.09±0.16 ppm). This distribution is closely correlated with the Corg content (r=0.95). A characteristic feature of exchangeable Ni compounds is the uniformity of the profile distribution in all studied soils according to the eluvial type. There is a gradual increase in exchangeable Ni down the soil profile. It should be noted that the distribution of the element in the chernozems of the forest belt is more even (figure 3), which is associated with more intense leaching processes. In general, the element is inactive, since the percentage of exchangeable compounds is (3.03±0.97%).

The clarke of Pb in the lithosphere is 16 ppm, and the clarke of soil is 20-25 ppm [13]. The Pb content in the studied soils is close to the clarke of soils and exceeds the clarke of the lithosphere. The data show that the total Pb content accumulates in the upper horizons of chernozems due to the interaction of the element with molecules of humic acids, forming strong chelate compounds. The following series of decrease in the total Pb content is formed: maple (24.7±4.3 ppm)>arable land
(23.9±3.87 ppm)>birch (21.7±3.11 ppm)>larch (18.2±2.57 ppm)>pine (17.1±2.09 ppm). Down the profile, there is a gradual decrease in the metal content to a depth of 60-70 cm (figure 2). Further to the parent rock, the accumulation of the total Pb content is again observed as a result of interaction with the metal with the silty and colloidal fraction. The closest positive correlation is observed between the profile distribution of total Pb and humus (r=0.79). The gross Pb content in the studied soils does not exceed the MPC=30 ppm [14].

The largest amount of exchangeable Pb compounds in the 0-10 cm layer is noted on arable land (1.18±0.17 ppm), possibly due to anthropogenic introduction of elements as an admixture in fertilizers, as well as due to the processing of arable soils with agricultural machinery. Then, in decreasing order, there are soils under maple (1.17±0.15 ppm)>birch (1.16±0.11 ppm)>pine (1.14±0.09 ppm)>larch (1.11±0.10 ppm). As for Ni, the eluvial type of the profile distribution of exchangeable Pb compounds is noted with a gradual increase downward toward the parent rock (figure 3). Most Pb compounds are inactive, like many heavy metals; it is strongly sorbed by soils [14]. According to the data obtained, the percentage of mobility does not exceed 7%.

![Figure 2](image.png)

**Figure 2.** Profile distribution of heavy metals total content of Ni (a), Pb (b), and Cd (c).

The clarke of Cd in the lithosphere is 0.1 ppm, the clarke of soil is 0.3-0.5 ppm [13]. The Cd content in the studied soils is close to the clarke of soils and higher than the clarke of the lithosphere. Compared to Ni and Pb, Cd has a lower affinity for soil organic matter. A weak dependence on the soil moisture regime, redox conditions, Fe, Mn compounds is noted [14]. Due to this, the total Cd
content is relatively evenly distributed over the profile of the studied soils (0.35±0.08 ppm), with only a slight increase to the parent rock of 0.48±0.03 ppm (figure 2). The parent rock is enriched with a silty fraction. Like all metals, Cd is strongly sorbed by the muddy and colloidal fraction of soils. The results of the correlation analysis did not reveal a correlation between the profile distribution of the total Cd content with Corg and pH (r=0.11 and r=0.15, respectively). The gross content of Cd in the studied soils is not exceeded by the MPC=1 ppm [14].

The maximum and minimum content of exchangeable Cd compounds in the studied soils is 0.014-0.061 ppm. Exchangeable compounds as well as the total content are relatively evenly distributed in the profile of the studied soils (figure 3). Correlation analysis data also confirmed the absence of a relationship. The correlation coefficient with Corg is 0.22, with a pH of 0.17. Exchangeable Cd compounds are more mobile than Ni and Pb compounds. Their percentage of mobility reaches 10.4±1.01%. This phenomenon is explained by the lower affinity for Corg, as well as the greater solubility of their compounds [14].

![Figure 3](image-url)  
**Figure 3.** Profile distribution of heavy metals exchangeable compounds of Ni(a), Pb(b), and Cd(c).

It should be noted that the availability of heavy metals and, above all, such hazardous pollutants as Pb and Cd, is much higher than their transfer to the extract of the acetate-ammonium buffer [15]. Cd is very often an accompanying element of organic and mineral fertilizers. It is included in their composition as an impurity. But its removal by plants [16] and migration along the profile is much higher than the introduction. The so-called negative balance of Cd is created [17]. In addition, the
sorption capacity of the silty fraction of chernozems keeps the studied heavy metals in a difficult-to-reach state \[18\]. Therefore, there is no contamination with this element of the soil cover.

The coefficient of variation, which determines the spatial differences in the content of heavy metals, revealed spatial heterogeneity in the chernozems of the forest belt. As in the case of Corg and pH, plowing leads to the leveling of spatial differences in the heavy metals content \(V=3\pm0.5\%\). As for the forest belt, different tree species introduce spatial heterogeneity in the content of heavy metals \(V=17\pm1.12\%\).

4. Conclusion
Chernozems of the Kamennaya Steppe, located under arable land and forest belt, significantly differ from each other in morphological characteristics, in the content of Corg, pH, as well as in the total content and exchangeable compounds of Ni, Pb and Cd. A statistical analysis of the obtained data on the content of Corg and pH of the environment to determine the spatial differences between arable land and a forest belt showed a regular decrease in the coefficient of variation from a forest belt to arable land. This phenomenon is explained by the fact that as a result of plowing, the spatial differences of these soil properties are leveled. In the forest belt, woody vegetation introduces spatial heterogeneity not only in the humus content and pH of the soil solution, but also in the content of heavy metals.

The profile distribution of the total content of Ni and Pb in the profile of the studied soils is characterized by the uniformity of distribution with two maxima of accumulation - the upper and lower in the parent rock. In the chernozems of the forest belt, a deeper profile leaching of the studied heavy metals is noted as a result of the transformation of the water regime. The exchangeable compounds Ni and Pb are characterized by the eluvial type of profile distribution. The profile distribution of the gross content and exchangeable compounds of Cd is more even, since the metal interacts less actively with the organic matter of the soil. The distribution of the element weakly depends on the water regime and redox conditions. The obtained correlation coefficients indicate a close relationship between the profile distribution of Corg, pH, and the total content and mobile compounds of Ni and Pb. No correlation was found between soil properties and Cd distribution.

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