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## Landscape geochemical conditions and patterns of inter-element redistribution of heavy metals in landscapes of Kivertsi National Nature Park “Tsumanska Pushcha”

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**Abstract.** Analysis of landscape geochemical conditions of the territory of Kivertsi National Nature Park “Tsumanska Pushcha” was carried out also the levels of pollution of landscapes within the park and adjacent territories were established. Features of the accumulation and distribution of pollutants in the landscapes of the territory under conditions of natural and

Technogenic geochemical anomalies are considered. The landscapes of the studied migration classes (calcium, calcium carbonate, carbonate clayey, acidic calcium) are characterized by a relatively high coefficient of migration intensity due to relatively weak buffering capacity, low water retention capacity and contrasting moisture regime. However, strong gleyed horizons are able to fix contaminants during their surface movement. Using the methods of landscape geochemical research, analytical methods, data on the gross and mobile content of heavy metals were obtained and analyzed. The highest concentrations of manganese and chromium are found in soils differentiated on loess sediments, nickel and copper on glacial sediments. Most of the studied heavy metals exceed the regional geochemical background. In terms of the gross content in soils, trace elements form the following geochemical series:  $Zn > Cu > Pb > Ni > Mn > Cr$ . The accumulation of lead up to 2-3 MPC in forest litters is clearly traced. Dependences of the stability of landscapes to Technogenic pollution on the level of conservation of natural geochemical parameters of soils, the degree of their anthropogenic transformation and the level of heavy metals incomings have been established. All studied plants maximally accumulated Mn, Cu, Cr and minimally Zn and Ti which is consistent with the patterns of migration of these elements in the soil. The high accumulation of heavy metals in the aboveground part of the studied plants indicates a significant removal of elements from the soil, which, in turn, makes it possible to consider certain plant species as potential phytoremediators. According to the average values of the concentration of macro elements in plants, the following geochemical series is established:  $CaO > K_2O > MgO > P_2O_5 > SiO_2 > SO_3 > Al_2O_3 > Fe_2O_3 > Na_2O > TiO_2$ . On the basis of the data obtained, 4 types of biogeochemical bonds between chemical elements in the soil – plant system for the territory of the NPP were identified: V, Ti - soil > plant; Ni - soil < plant; Cr - soil > plant; Mn, Cu - soil < plant.

**Key words:** heavy metals, forms of occurrence, intensity series, accumulations, landscape geochemical conditions

## Ландшафтно-геохімічні умови та закономірності міжкомпонентного перерозподілу важких металів в ландшафтах Ківерцівського національного природного парку «Цуманська Пуща»

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**Анотація.** Здійснено аналіз ландшафтно-геохімічних умов території Ківерцівського національного природного парку «Цуманська Пуща» та встановлено актуальний рівень забруднення ландшафтів в межах парку та суміжних територій. Розглянуто особливості акумуляції та розподілу забруднюючих речовин в ландшафтах території в умовах природних і техногенних геохімічних аномалій. Ландшафти досліджуваних класів міграції (кальцієві, кальцієво-карбонатні, карботатно-

глейові, кислі кальцієві) характеризуються відносно високим коефіцієнтом інтенсивності міграції за рахунок відносно слабкої буферності, низької водоутримуючої здатності та контрастним водним режимом. Однак за наявності потужних оглеєних горизонтів спроможні фіксувати забруднювачі при їх поверхневому переміщенні. З використанням методів ландшафтно-геохімічних досліджень, аналітичних методів, отримано та проаналізовано дані про валовий та рухомий вміст важких металів. Найбільш високі концентрації марганцю та хрому мають ґрунти, що розвинуті на лесових відкладах, нікелю та міді на воднольодовикових відкладах. Більшість досліджуваних важких металів перевищує регіональний геохімічний фон. За валовим вмістом в ґрунтах мікроелементи формують наступний геохімічний ряд:  $Zn > Cu > Pb > Ni > Mn > Cr$ . Чітко простежується накопичення в лісових підстилках свинцю – до 2-3 ГДК. Встановлено залежності стійкості ландшафтів до техногенних забруднень від рівня збереження природних геохімічних параметрів ґрунтів, ступеня їх антропогенної трансформації та рівня надходження важких металів. Всі досліджені рослини максимально накопичували Mn, Cu, Cr і мінімально Zn та Ti, що узгоджується з закономірностями міграції цих елементів в ґрунті. Висока акумуляція важких металів у надземній частині досліджуваних рослин свідчить про значний виніс елементів з ґрунту, який, в свою чергу, дає можливість розглядати окремі види рослин як потенційні фітореєдатори. За величиною середніх значень концентрації макроелементів у рослинах встановлено наступний геохімічний ряд:  $CaO > K_2O > MgO > P_2O_5 > SiO_2 > SO_3 > Al_2O_3 > Fe_2O_3 > Na_2O > TiO_2$ . На основі отриманих даних виділено 4 типи біогеохімічних зв'язків між хімічними елементами в системі ґрунт-рослина для території НПП: V, Ti – ґрунт > рослина; Ni – ґрунт < рослина; Cr – ґрунт > рослина; Mn, Cu – ґрунт < рослина.

*Ключові слова:* важкі метали, форми знаходження, ряд інтенсивності, накопичення, ландшафтно-геохімічні умови

## Introduction.

Most of the newly formed Ukraine's nature conservation objects are concentrated mainly territories, in the past they were actively used in economic activities and therefore are characterized by a significant anthropogenic transformation of landscapes. Analysis landscape geochemical environment is an integral part of the integrated area of research, especially in predicting the migration of contaminants. Geochemical studies of correlation dependences and types of connections of the leading components of landscapes of protected areas, their dynamics makes it possible to predict changes in the functioning of natural complexes determine their resistance to external influences and predict the behavior of pollutants in the natural environment. A reliable indicator of the ecological and geochemical state of the territory is the assessment of the distribution and migration of heavy metals (HM) in soils and in the soil-plant system.

Carrying out such comprehensive natural research is a necessary component of assessing the ecological state of protected areas. In particular, for national nature parks (NNP), where the functions of nature protection are combined with the recreational and economic use of territories. Therefore, for them, the task of landscape-geochemical analysis and the study of inter-component redistribution of heavy metals are especially urgent.

**The main objective of the study** to identify the features of migration and accumulation of pollutants in the landscapes of Kivertsi National Nature Park "Tsumanska Pushcha" in the conditions of natural and man-made geochemical anomalies.

The main objectives of the study:

1. To determine the landscape-geochemical conditions of the research territory and regularities

of inter-element redistribution in the landscapes of Kivertsi NNP "Tsumanska Pushcha";

2. To determine the impact of man-made pollution on changes in the species composition of woody and herbaceous plants in the studied area.
3. Reveal the relationship between the content of heavy metals in the soil-plant system and establish the nature of the accumulation of heavy metals in the organs of woody plants.

## Materials and methods of research.

The work used the factual material of field landscape geochemical studies carried out in the summer-autumn period of 2018-2019. During field studies, more than 1200 soil samples were taken. The total number of biogeochemical samples of the main NNP plants is more than 640 samples. Sampling was carried out throughout the NNP from the upper part of the humus horizon (0-10 cm) by the envelope method according to DSTU 4287: 2004. Soil samples, which are intended to determine the content of metals, are taken with instruments that do not contain metals. Sampling was carried out in good weather, in the morning before the onset of heat, or at the end of the day (at the same time) conditions for sampling from one polygon were the same. To study the distribution of trace elements along the soil profile, pits with a depth of up to 2 m were laid at individual test sites. Samples were taken every 10 cm of the soil profile. After sampling, the soils were dried; some were passed through a sieve with a 1 mm opening. Samples were quartered and selected for further analysis, which included: complete chemical analysis, analysis of gross content and mobile forms of trace elements, analysis of physicochemical parameters.

The analytical material presented in the article is obtained with the help of classical and modern

analytical methods of analysis. Physics and chemical methods: atomic absorption method (spectrographs S-115, “Saturn-3”) - used to determine the gross and mobile forms of trace elements in soils; emission spectral analysis (spectrograph “EST-1”) - used to determine the content of heavy metals in soils and plants; chemical methods: method of mass spectrometry with inductively coupled plasma (ISR-MS analysis) on devices Elan-6100 and ICP-MS analyzer ELEMENT-2, made in Germany - was used for the determination of trace elements in soils and plants (Institute of Geochemistry, Mineralogy and Ore Formation named after M.P. Semenenko NASU and Institute of Geology of the Poland Academy of Sciences). The results of all the methods used were processed by the method of mathematical statistics and the mean value and interval values were calculated with a confidence level of 95-96%.

Plants were selected together with the root part, digging from the ground at different points of the monitoring sites (spot samples) (GOST 27262-87). Sod grasses were removed from the soil along with the soil monolith to avoid losing most of the root system. A combined sample was formed from plants belonging to one species. The combined sample of plants weighing 1.5 kg consisted of 8-10 spot samples. After selection, the plants were air-dried and crushed. The root part before grinding was pre-cleaned of soil particles to avoid getting them into the sample.

A total of 170 plant samples were analyzed. To detect the degree of absorption of heavy metals in the “soil - plant” system in the studied samples, a chemical analysis of the content of HM I (Pb, Zn), II (Ni, Cu, Cr) and III (V, Mn) hazard classes was performed.

The content of heavy metals in the phytomass of plants was determined in their ash solutions (dry ashing) by atomic absorption spectrometry using the CTE-1 instrument and by mass spectrometry with inductively coupled plasma (ICP-MS), ELEMENT-2 analyzer (Germany) at the Institute of Geochemistry, Mineralogy and Ore Formation NAS of Ukraine. Laboratories have certificates of certification and are provided with the necessary state standards and samples. During ICP-MS method it's used concentrated acids HF, HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, which were further purified using the Sub boiling system. Samples were dissolved one by one in a mixture of hydrofluoric acid recommended for plant decomposition.

Quantitative assessment of toxic trace elements from the soil to plants was performed by calculating the coefficient of biological accumulation (CB),

which is determined by the ratio of metal content per unit mass of the acceptor (plants in terms of its absolute dry weight and donor). To classify CBA, the studied elements were divided into five grades (Avessalomova, 1987):

- 1) elements of energy accumulation: CB - 10n and more;
- 2) elements of strong accumulation: CB - 10n;
- 3) elements of weak accumulation and average capture: CB - 0, n;
- 4) elements of weak capture: CB - 0,0n;
- 5) elements of very weak capture: CB - 0,00n and less.

## Results and Analysis.

**Landscape-geochemical structure of the park territory and its role in accumulation and redistribution of pollutants (heavy metals).** Kivertsi National Nature Park “Tsumanska Pushcha” (Volyn region) formed from large forests near the village of Tsuman and a significant number (over 100) of small forest and meadow areas within the Kivertsi district (total area of 34.5 thousand hectares). In the modern landscape structure of the investigated area dominated landscapes with varying degrees of anthropogenic changes.

When combining landscapes into geochemical classes, the general physicochemical characteristics of soils were taken into account, which determine the patterns of migration of elements in the landscape as a whole. Since the humus horizon of soils is characterized by the highest intensity of all geochemical processes occurring in the landscape, it is its characteristics that are taken as a basis for analyzing landscape-geochemical conditions. The following physicochemical parameters of soils were determined: the content of individual ions, pH of the water extract, pH of the salt extract, determination of the hydrolytic acidity, etc. (Avessalomova I.A., 1978; Alloway, 1995; Vinogradov, 1957; Vorobiova et al., 1980; Zhovynskyi et al., 2012).

The data obtained by the authors (humus content, actual soil acidity, hydrolytic acidity, amount of absorbed bases) were used as the basis for combining the landscapes of the studied area according to the classes of water migration. Almost all geochemical landscapes of the NNP territory are characterized by the oxygen conditions of the soil solution, which is due to the presence of free oxygen. The exception is landscapes in which silty boggy soils are common, where gley restorative conditions are noted. The mineralization of soil solutions is usually low, less than 0.08%. Alkaline-acid conditions vary from slightly

acidic to neutral (the pH value ranges from 4.2–5.1). Due to the following relatively homogeneous characteristics, considerable attention was paid to typomorphic ions dominating in the soils of different landscapes of the region: cations –  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  i  $\text{K}^+$ , and  $\text{Mg}^{2+}$ ; anions –  $[\text{HCO}_3]^-$ ,  $\text{Cl}^-$ .

Within the studied area, geochemical landscapes with such classes of water migration were identified:

*Landscapes of acidic calcium (H-Ca, H-Ca/[H-Fe], H-Ca/H-Fe) classes.*

*Landscapes of acidic geochemical classes with a leading role of hydrogen ion  $\text{H}^+$ :*

*Acidic (H), acidic, acidic gley (H, H-Fe), and acidic gley (H-Fe);*

*Landscapes of calcium (Ca) and calcium carbonate ( $\text{CaCO}_3$ ) classes;*

*Landscapes of acidic calcium (H-Ca, H-Ca | [H-Fe], H-Ca | H-Fe) classes.*

*Landscapes of acid geochemical class.* Relief-forming rocks are water-glacial and alluvial sediments, mainly sandy mechanical composition. Low concentrations of micro- and macronutrients in soil-forming rocks cause soil depletion, which leads to a deterioration of the mineral nutrition of plants.

The results obtained indicate that the soils are depleted in both chalcophilic and siderophilic elements, for most of which there is a level of extreme deficiency (concentration ratio  $\text{Kk} < 0.3$ ). Particularly low concentrations are characteristic of chromium and nickel.

Soddy-podzolic and slightly podzolic clayey sandy and soddy-podzolic clayey-sandy loamy soils are most widespread within the studied area. Often, due to the weakening of the soil runoff, in the soils there are signs of deep gleying in the form of a grayish-gray color of the lower part of the profile, during the transition from the illuvial horizons to the soil-forming rocks. The pH value in the upper part of the profile of such soils is acidic ( $\text{pH} = 3.7\text{--}4.1$ ), gradually approaching slightly acidic with depth ( $\text{pH} = 4.9\text{--}5.2$ ). The accumulation of humic substances is observed in the lower illuvial horizons. The maxim humus content of 2.1% was observed in the illuvial horizon, while in the eluvial horizon the content of humic substances varies from 0.3 to 1.0%.

The predominance of sandy rocks within the studied area also determines the main hydrochemical patterns. Low-mineralized surface waters were investigated, and in terms of total hardness they are characterized as “very soft” and “soft”. Surface waters have a reaction of the environment, varying over a wide range from acidic (4.6 pH) to neutral (7.1 pH). An acid reaction is typical for small rivers, which are fed in summer from swampy catchments. Surface waters are

characterized by high iron content, which consistently exceed environmental standards, and in absolute terms is 0.5–2.7 mg/dm. Ground waters are characterized by a similar composition. The ionic composition of groundwater is dominated by bicarbonate ion, the content of which significantly exceeds the content of chloride and sulfate ions. Concentrations of hydrocarbonates and chlorides increase towards the backwater, the content of sulfates is maximal at the watershed. The concentrations of  $\text{Na}^+$ ,  $\text{Mg}^+$  and  $\text{K}^+$  Cations regularly increase from the watershed to the floodplain. Against the background of low concentrations of water-soluble salts, a high concentration of iron stands out sharply, which varies from 0.4 to 4 mg/dm. The lowest indicators of the content of other metals are characteristic of the transit landscapes of the river valley slope. According to the peculiarities of water migration, the elements are arranged in the following row: the elements of medium migration (0.2–1) include iron and nickel, the elements of strong migration in surface and groundwater (in descending order) – zinc, manganese, copper, lead. The obtained values for most trace elements are higher than the average values of water migration coefficients according to V.V. Dobrovolskyi, especially for lead, cadmium and manganese, which indicates their high mobility (1–10) in the conditions of acid reaction of soils and contrast redox conditions, weak expression of radial and lateral geochemical barriers (Dobrovolskyi, 1983).

Thus, the leading factors in the formation of soil composition in landscapes of acidic geochemical class are the dominance of sandy rocks of water-glacial origin, depleted by most elements and contrast redox conditions. Differences in the composition of soils are associated with the peculiarities of vertical and lateral migration of elements, accumulation on landscape-geochemical barriers.

The light particle size distribution of the described soils, low content of metabolic bases and humus do not contribute to the fixation of pollutants in the soil. That is why the landscape-geochemical characteristics of H-class landscapes are favorable for the accumulation of pollutants.

When groundwater lies close to the surface, soils with acidic glaciation (**H, H-Fe - class**) and low pH (less than 5.3) are formed. Landscapes of this class occupy insignificant spaces on denudation interfluvial plains, composed of low-strength water-glacial sands and sandstones, with shallow marls and chalks, with sod-podzolic and sod-gley soils.

In the dominant soil types, the humus content is 1.5–1.7%, the acidity is high ( $\text{pH} 4.6\text{--}5.5$ ), which strongly inhibits the development of biotic processes.



Soils have a higher absorption capacity in comparison with sand analogues: 6-8 mg-eq/100g of soil, but they are also characterized by higher hydrolytic acidity (2.0-3.7 mg-eq/100g of soil).

Sod-podzolic sandy soils are depleted microelements. The concentration of titanium averages ( $n \times 10^{-3}\%$ ) 53.7, manganese 18.76, copper 0.15, nickel 0.27, vanadium 0.89, chromium 0.51, lead 0.36, zirconium 27, 45. In the studied soils occur ( $n \times 10^{-3}\%$ ): molybdenum 0.1-0.2, niobium 0.8-1.0, scandium 0.5-0.8 and yttrium 0.8-2.0. The content of cobalt, bismuth, thallium, cadmium, tin, vanadium, below the sensitivity of the method.

The content of copper, chromium, nickel, exceeds the average level by 2-3 times. Metals, which are often considered as indicators of man-made emissions - lead and cadmium - in sod-slightly podzolic gley sandy-sandy soils are contained in small concentrations that do not exceed the average values for these soil differences. It is recorded that elevated concentrations are characteristic of siderophilic elements, chalcophilic accumulate weakly.

Soddy slightly-medium-podzolic soils, widespread on thick sandy water-glacial deposits, are characterized by a fairly uniform granulometric composition along the entire profile. Dominated by particles of Medium-grained sand with a size of 0.27-0.06 mm, which account for 87-94%. Their distribution by genetic horizons is usually homogeneous, with some decrease in the content of this fraction in the humus-eluvium and an increase in the illuvial horizons.

The amount of dust and physical clay varies between 2-5%.

Process of podsolization in these soils takes place in a fairly acidic environment. The lowest soil reaction is characteristic of the humus-eluvium horizon, pH 2.9-4.2, which is explained by the interaction with humus, which consists mainly of acidic products of organic sediment of coniferous species. Lower along the soil profile, the pH of the medium is in the range of 4.4-5.1. The low content of organic matter and the light granulometric composition of the soils determine the poverty of their absorbing complex. According to our data, in the humus-eluvium horizon of soils, the sum of absorbing bases on average reaches 8-10 mg-eq. per 100 g of soil.

When distributed over the genetic horizons, the number of bases and the capacity of the absorbing complex decrease which is due to a sharp decrease in the humus content with depth.

An insignificant increase in capacity of the absorbing complex in illuvial horizon occurs obviously due to the interaction of iron and aluminum

compounds, which in the form of amorphous hydroxides; lingering in this horizon, partly enter the absorbing complex.

Iron, aluminum and silicon oxides play an important role in podzolic process. These compounds reflect the degree of mobility and forms of migration of elements and determine the concentration and migration of many trace elements. In the studied soils, the content of amorphous forms of iron varies between 0.03-0.20% (average 0.095%), aluminum - 0.04-0.55% (0.25%) and silicon - 0.06-0.90 % (0.23%). There is a decrease in the concentrations of amorphous compounds of iron and aluminum and an increase in the content of mobile forms of silicon in some soils from the highest relief elements to low. This situation is obviously due to changes in physicochemical processes in soils due to terrain, pH, humus and other factors.

H-Fe - class landscapes have high concentrations of iron and manganese, especially in deep soil horizons.

For manganese and copper there is an increase in concentrations in the illuvial horizon of the soil profile, which correlates with an increased number of amorphous compounds of iron and aluminum. Manganese is traced with organic matter, and nickel - with a heterogeneous source of its in. There are concentrations of lead in the humus-eluted horizon, which are associated with man-made input, because in the transition horizons it is not fixed. When considering the geochemical relationship of microelements with each other, a high positive relationship between Mn and Cu can be noted (when any fluctuation of the variable in the geochemical analysis of manganese is transferred to copper and amplifies, due to which continuous fluctuations arise in the interaction, indicates their high (positive) coefficient of interrelation), reliable relationship between Cu and Ni (multiple increase in one variable, which leads to an increase in the other and forms a positive relationship coefficient). Weakly interact with each other: Mn and Pb, Cu and Cr, Ni and Cr. For other pairs of trace elements, this relationship is insignificant.

Comparison of the average concentrations of trace elements in sandy soils in general showed that the soils of the park have an increased content of trace elements, especially zinc, copper and lead.

Landscapes of low above-floodplain terraced plains with meadow air-medium loamy gley soils have a humus content of 2.96% and a high content of exchangeable cations - 24.5 mg-eq./100g.

For low-level floodplains composed of sandy and loamy alluvium, with peat-swamp soils and peat

lands, the content of microelements is highly variable. This indicates sharp differences in the conditions of the entry of microelements into peat deposits, their accumulation by plants and fixation on the peat biogeochemical barrier.

Concentrations of lead and nickel are close to the average values calculated for the studied area. The lead content in peat lands is not correlated with any of the other elements. A high reliable positive correlation was noted between the content of copper, nickel, iron and manganese in peat lands.

Landscapes of H, H-Fe-class are characterized by changing conditions of lateral migration of pollutants, which contribute to high mobilization of chemical elements. Due to the presence of thick gleyed horizons in the soil profile, landscapes with soils characterized by a heavy granulometric composition are capable of fixing pollutants (during their surface movement) on gley landscape-geochemical barriers (**LGB**). On sorption LGB fixation of pollutants occurs due to the high capacity of cation exchange and high humus content, and the variation of pH determines the fixing capacity of pollutants on LGB acid-base type.

**Landscapes of calcium and calcium carbonate ( $\text{Ca}$ ,  $\text{CaCO}_3$ ) classes.** Geochemical characteristics of this class of landscapes are associated with participation in the migration of carbonate rocks. Mobile calcium compounds determine the neutral and slightly alkaline reaction of the soil and the saturation of the absorbing complex of Ca and Mg. Such conditions contribute to the accumulation of humus.

Due to the increased biological accumulation, Cu, Mn, Pb, Zn accumulate in soils. Copper, manganese and lead have a positive correlation with the humus content, that is, they are contained in the soil in the form of complexes.

The wide distribution of landscapes of the calcium-carbonate class of water migration is explained by the superior carbonate rocks. In coniferous-broad-leaved and broad-leaved forest landscapes, while maintaining the zonal type of vegetation with a predominance of deciduous species, such geochemical conditions are also provided by the capacity and intensity of the biological cycle, as a result of which a large amount of calcium and organic matter gets into the soil every year with precipitation. Within the framework of the NNP and in the territories adjacent to the park, the landscapes of the calcium and calcium-carbonate class are, first of all, denudation plains, composed directly of dense carbonate rocks (marl and chalk), with soddy-carbonate and soddy-podzolic secondary carbonated sandy loamy soils formed on the weathering crust of chalk. The slopes

of the denudation interfluvial plains are inclined (3–50), composed of loess-like loams, underlain by chalk deposits, with soddy carbonate and podzolized black earth, light loamy, weakly fertile soils, characterized by high fertility (humus content 1.95–2.2%), are predominant among the exchangeable cations of Ca (20.82 mg-eq/100g), slightly alkaline reaction (7.3–7.5%) and strong fixation of substances and nutrients.

The floodplains of a higher level (2.7–3 m above the water line) are characterized by soddy calcareous sandy loamy soils, alluvial soddy sandy loamy and light loamy soils. They are also characterized by a high content of humus (up to 2.4%), the pH of the soils of these landscapes shifts towards neutral – 6.4–7.4. The content of exchangeable cations reaches 20–21 mg-eq/100g.

The conducted analysis of microelement composition shows that for alluvial sod layered soils there is a uniform distribution in the profile of copper, Nickel, chromium, and insignificant differentiation of manganese and lead content in eluvial-illuvial with accumulation in the turf horizon. In the distribution of zinc, there is a clearly pronounced minimum in the middle part of the profile, and accumulations in the lower, gleying part of the profiling.

Thus, the vertical distribution of trace elements in the landscape depends on a number of factors. Biogenic accumulation, which is characteristic of zinc, cadmium, and to a lesser extent manganese and lead, causes an increase in the concentrations of these elements in the soil cover.

In the landscapes of these classes, pollutants, namely heavy metals, have a low migration capacity and are almost never removed from the soil.

**Landscapes of acidic calcium (H-Ca, H-Ca | [H-Fe], H-Ca | H-Fe) classes** formed on low inter-river plains (185–195 m), composed of thin water-glacial sands and sandy loams, with shallow occurrence of marls and chalk, in conditions of sufficient and increased moisture. Such landscapes are characterized by a rather high amount of absorbed cations (18.75–24.4 mg-eq/100g) and humus (2.52–2.95%), acidity varies from neutral to weakly alkaline – 6.4–7.4. Soils of this class contain a significant number of silty particles (from 17% to 28%). Physical and chemical properties of soils cause biogenic accumulation of Zn, Cu, Mn and reduction of Co, Ni removal.

Landscapes of these classes are characterized by a relatively high coefficient of migration intensity due to relatively weak buffering, low water holding capacity and contrast water regime. However, in the presence of strong gleyed horizons are able to fix pollutants during their surface movement.

### ***Content of toxic elements in the landscapes of National Natural Park “Tsumanska Pushcha”.***

It has been established that the indicators of the accumulation of heavy metals in soils of the NNP are significantly higher than average data for Kivertsevs-ki district of the Volyn region.

Anthropogenic impact, in addition to agricultural activities, associated here with large enterprises, in particular PJSC “Tsuman”, LLC “Tanforan”, LLC “Kaminskiy Timber and Venuses”, “Ukrlesservice”, spontaneous dump of Tsumansky production department of housing and communal services p.g.t. Tsuman and Kadyshe village), PAF “Vistula”, “Lutskvodokanal”, etc.

Wastes of enterprises are substances of I - IV classes of danger. In particular, waste containing aluminum, vanadium, chromium and their compounds, lead (including Batteries for storage purposes or broken ones), iron carbonyls, etc.

Most of the studied HM exceeds the regional geochemical background. Migration and spreading of each metal along the profile of Soddy weakly - medium podzolic soils has its own specifics. The greatest accumulation of copper and zinc occurs in forest litters, and in mineral part of the profile it has a weakly expressed eluvial-iluvial character. Content of nickel, cobalt and manganese become increases with depth

of its accumulation in soil, which are characteristic of the chemical composition of glacial sediments (Lubben et al., 1991; Sauerbeck et al., 1991).

It is noted that the amount of chromium, manganese and cobalt is higher in soil-forming rocks than in forest litters. Spreading along the profile of chromium, no regularities were found. The average HM content in the main soil types of the NNP territory is presented in Tables 1 and 2.

By gross content of micronutrients in soil we can arrange in the following series of geochemical: Zn> Cu> Pb> Ni> Mn> Cr. Accumulation of lead in forest litters up to 2-3 LOC is clearly traced.

Obtained data about accumulation of heavy metals in soils of the NNP territory are of significant importance, since they are the basis for identifying spatial patterns of soil pollution and establishing the local geochemical background.

Most of heavy metals are spread unevenly in the soil cover. High values of the coefficient of variation (V) - more than 34% typical for heterogeneous set of data on concentration of all studied HMs (Table 5). The highest rate of variation was found for lead concentration - 170%, and the lowest values were obtained for content of chromium - 34% and zinc - 36%.

To characterize the average content of heavy metals in the soils of the NNP, the arithmetic and

**Table 1.** Average HMs indicators in genetic bedding rocks of soil, most typical for the territory of NNP

Bedding rock, depth	Mn	Pb	Cr	Ni	Zu	Cu
<i>Sod-slightly podzolic sandy on water-glacial sands and sand lined with Neogene-Paleogene sediments (sands and loams)</i>						
Ho, 0-2 cm	430.0	38.0	23.2	26.2	274.7	23.5
HE, 2-4 cm	176.2	6.2	26.8	13.1	222.5	9.2
E, 4-20 cm	278.4	6.4	28.2	17.4	251.4	19.1
I, 20-60 cm	292.6	5.2	29.1	11.3	232.6	17.4
PI, 60-130 cm	271.5	6.0	19.2	11.7	221.8	18.6
<i>Sod-medium podzolic sandy loam, on water-glacial sediments, with deep bedding of chalk rocks</i>						
Ho, 0-2 cm	367.3	29.1	29.4	31.0	310.7	32.9
HE, 2-5 cm	259.0	7.9	34.2	23.6	227.4	11.2
E, 5-28 cm	383.6	7.0	34.1	26.3	254.9	11.7
I, 28-43 cm	510.3	5.1	38.6	25.4	267.1	14.2
IP, 43-124 cm	554.7	4.6	40.1	25.7	253.9	20.2
<i>Peat-boggy on ancient alluvial sandy and loamy sediments</i>						
ТНкор, 0-14 cm	362.9	19.6	28.3	27.6	341.3	29.3
HPK, 14-26 cm	341.5	10.2	37.5	24.3	320.5	15.7
Phggl, 26-31 cm	346.2	13.4	44.3	26.3	343.1	17.4
P(h)KGl, 31-46 cm	362.5	9.0	43.2	25.4	346.8	19.2
<i>Soddy carbonate sandy loam on eluvium of carbonate rocks</i>						
Ho, 0-2 cm	320.4	38.3	26.3	26.0	494.3	22.2
HK, 2-26 cm	280.6	27.5	34.4	24.3	363.9	16.4
HPK, 26-43 cm	210.2	34.7	36.7	32.6	381.8	18.6
PK, 43 > cm	168.6	24.2	34.3	31.8	382.0	21.2

geometric mean values were calculated. This is due to the fact that the indicators of the concentration of elements in soils vary greatly and do not obey the law of equable spreading. As a result, arithmetic mean strongly depends on the presence of small number of samples with higher levels of elements. In such cases, it would be more correct to use geometric mean to estimate the HM content in the soil \*.

\* Geometric mean  $N$  of numbers is equal to the root of the  $N$  degree from the product of these numbers, in this case - product of all obtained values of the content of a particular chemical element. Such an indicator is always less than arithmetic mean, in terms of its value, large deviations and fluctuations between individual values in the studied set of indicators are much less affected.

High value of the standard deviation ( $\sigma$ ) is an indication of the average values of sporadic. Minim

of the soil cover of the territory. In connection with increases of heavy metals content in soil, their accumulation by plants increasing too. However, with distance from pollution sources, the content HM in plants decreases by 10-20 mg/kg. The excess content of Pb, Zn, Cu and Mn is detected in plants on constant test areas of NPP (points 17-19, 41-19), closest to the emission sources along the line of the prevailing wind direction. Differences in the content of metals in plants that grow under conditions of minim and maxim anthropogenic load, are for Mn and Zn - 6-7 times, Cu - 4-5 times, Ni and Pb - 4 times, Cr - 2 times. Similar trends in the accumulation and distribution of heavy metals in soils and plants during the two seasons of research in 2018-2019.

As a result of the study, the interdependence between the mineral composition of soils and the level of ash content of plants was established. The needles

**Table 2.** Total content of micronutrients in the soils of NNP

Element	Average values	Limits of oscillation	K <sub>Ci</sub>	Background values [9]	Average values	Limits of oscillation
	mg/kg				mg/kg	
	Content of gross forms				Content of mobile forms	
Mn	420	8.1-830	1.06	395	0.89	0.27-1.9
Cr	30.4	5.2-60.8	0.7	39	0.48	0.33-0.9
Ni	25.5	6.3-50.7	2.1	12	0.8	0.6-1.6
Zn	350	60.3-700	5	42	1.1	0.5-2.1
Cu	25.4	6.5-50.4	3.1	8	1.7	0.9-3.4
Pb	30.5	6.4-60.5	2.7	11	0.6	0.38-1.2

standard deviation was obtained for chromium concentrations - 30.5, and maxim for manganese 341.0.

Table 3 also presents characteristics of the average values of the HM content in soils of the NNP. The average content of all studied HMs exceeds their regional background values.

of Scots pine (*Pinus sylvestris*), which grows on sod-slightly podzolic sandy soils developed on glacial sands, has an average ash content of 3.25%, and alluvial sands - 1.52%, pine branches - respectively 2.81 and 1.68%, hanging birch leaves (*Betula pendula*) - 4.76 and 3.52%, branches 4.19 and 1.15%.

**Table 3.** Statistical indicators of HMs content in NNP soils, mg/kg

Element (background)	Arithmetic mean	Geometric mean	Maxim value	Minimal value	$\sigma$	V, %
<b>Mn (395)</b>	420	81.9	830	8.1	341.0	81
<b>Pb (11)</b>	30.5	19.6	60.5	6.4	52.1	170
<b>Cr (39)</b>	30.4	8.1	60.8	5.2	10.5	34
<b>Ni (12)</b>	25.5	17.8	50.7	6.3	11.6	45
<b>Zn (42)</b>	350	205.9	700	60.3	76.7	36
<b>Cu (8)</b>	29.4	19.8	60.4	6.5	21.4	72

General patterns of HM distribution in typical plants of the stud area.

The dependence of the HM content in NNP plants on the level of technogenic load and the properties

There is a certain pattern - the richer the mineral composition of the soil, the higher the percentage of plant ash (Dobrovolskyi, 1983). In addition, despite the variability of ash content of plants growing in



different landscape conditions, a direct relationship between soil chemical composition and ash content could not be detected. The average chemical composition of plants typical for the territory of the NNP species is presented in table 4.

in sands lined with chalk deposits, with sod gleyed and meadow-swampy lowland soils level, composed of sandy and loamy alluvium, with peat-swamp soils. The latter are dominated by silicon oxide (up to 43%). The concentration of other elements in such landscape

**Table 4.** Chemical composition of plants typical the NNP species,% on ash, (ICP-AES)

Plants	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MnO	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
<b>Silver birch (<i>Betula pendula</i>):</b>											
<i>leaf</i>	3.62	0.72	0.13	0.07	-	26.90	14.80	3.71	-	-	-
<i>tree branches</i>	1.67	0.74	1.51	0.06	0.41	39.87	5.71	1.84	7.11	0.85	5.93
<b>Alder alder (<i>Alnus incana</i>):</b>											
<i>leaf</i>	2.49	0.98	1.49	0.09	0.07	40.05	6.65	2.76	14.11	1.09	6.42
<i>tree branches</i>	3.61	0.69	1.83	0.09	0.39	43.86	3.12	2.14	6.65	1.75	2.89
<b>Scots pine: (<i>Pinus sylvestris</i>)</b>											
<i>pine needles</i>	3.21	0.41	4.07	-	-	13.02	17.22	4.21	-	-	-
<i>tree branches</i>	6.12	0.82	3.84	-	-	36.17	7.41	1.54	-	-	-
<b>Hornbeam: (<i>Carpinus betulus</i>)</b>											
<i>leaf</i>	2.43	0.61	0.92	-	-	35.01	5.26	2.34	-	-	-
<i>tree branches</i>	1.81	0.32	1.12	-	-	39.23	-	3.23	-	-	-
<b>Raspberry (<i>Rubus idaeus</i>)</b>	3.58	0.65	0.16	0.06	-	21.09	6.84	3.69	-	-	-
<b>Shaggy sedge (<i>Carex brizoides</i>)</b>	32.41	1.12	3.43	0.02	0.34	13.94	6.54	5.98	-	-	6.78
<b>Wood pea (<i>Lathyrus sylvestris</i>)</b>	31.76	1.78	0.73	0.17	-	7.60	7.09	-	-	-	5.02

It was found that in plants that are characteristic of the landscapes of floodplain terraces composed of ancient alluvial sands, with sod-hidden and slightly podzolic gley sandy and clay-sandy soils, for denudation interfluvial plains and sandy loams, composed of low-thickness, with sod-podzolic and humus-carbonate clay-sandy and sandy soils, as well as for inter-annual plains composed of water-ice-sand sands and sandy loams, with deep deposits of marls and chalk, with sod-low-podzolic sandy loams and sandy loams the content of which ranges from 11.82 to 43.17%. The concentration of other elements is slightly lower. The following geochemical series can be established by the value of the average values of the concentration of macronutrients in plants: CaO>K<sub>2</sub>O>MgO>P<sub>2</sub>O<sub>5</sub>>SiO<sub>2</sub>>SO<sub>3</sub>>Al<sub>2</sub>O<sub>3</sub>>Fe<sub>2</sub>O<sub>3</sub>>Na<sub>2</sub>O>TiO<sub>2</sub>.

The composition of mineral components differs slightly from the background landscapes of the landscapes of the erosion and river network, namely - beams with sloping slopes in water-glacial sands, and

conditions forms the following geochemical series: SiO<sub>2</sub>>CaO>MgO>SO<sub>3</sub>>P<sub>2</sub>O<sub>5</sub>>Al<sub>2</sub>O<sub>3</sub>>Fe<sub>2</sub>O<sub>3</sub>>TiO<sub>2</sub>. The content of CaO and SiO<sub>2</sub> fluctuates in the highest percentages in plants (table 4).

The study of the most common species of plants growing on soils of different mechanical composition, found that the largest number of trace elements contain plants growing on sod-podzolic sandy-sandy soils, and the least on peat-swamp soils and peatlands (table 5).

In our opinion, this is due to the different intensity of plant uptake of elements. Plants that grow on soils poor in trace elements are characterized by greater intensity in terms of their absorption from the soil. Confirmation of the different intensity of plant uptake of elements from soils of different mechanical composition is the coefficients of biological absorption of the elements presented in table 6.

The largest amounts of plants absorb manganese, nickel and copper. Chromium and titanium are less

**Table 5.** The content of chemical elements in plants in their confinement to soils typical of the NNP area (average values for plants of different species, mg / kg), (ICP-MS)

Soil	Pb	Cu	Ni	Cr	Mn	Ti
Sod-slightly podzolic sandy on water glacial sands	9.6	18.9	5.8	2.7	360	28
Sod-weak (medium) podzolic sandy on water glacial sands	11.3	17.2	4.1	2.1	165	22
Sod carbonate light loam on forest-like loams	5.7	9.7	1.8	1.7	164	24
Alluvial layered sand on alluvial sands	8.3	13.5	3.5	1.3	67	11.3
Peatland low-power degradation	14.1	14.7	1.0	1.1	74	10.7

**Table 6.** The coefficient of biological absorption of plants growing on soils, typical (characteristic) for the territory of the NNP

Soil	Pb	Cu	Ni	Cr	Mn	Ti
Sod-slightly podzolic sandy on water glacial sands	2.37	34.8	8.32	1.34	33.16	0.39
Sod-weak (medium) podzolic sandy on water glacial sands	1.42	24.3	2.75	0.91	6.86	0.18
Sod carbonate light loam on forest-like loams	1.12	5.74	1.26	0.35	5.44	0.16
Alluvial layered sand on alluvial sands	0.78	21.76	3.57	0.41	6.25	0.08
Peat land low-power degradate	0.56	6.94	0.63	0.29	4.37	0.17

biologically active elements (Adriano, 2001; Andersen et al., 2004; Pinsky et al., 1989). They are characterized by rate of biological uptake of less than one. Smaller amounts of lead are absorbed, the amount of which in plants averages 12.4%. Manganese, titanium, nickel, copper and lead are present everywhere in plants.

It is established that plants that grow on sod-podzolic sandy soils are characterized by a high content of manganese, as well as copper and nickel. They are characterized by low titanium content. Plants growing on sod-podzolic sandy soils are characterized by low levels of chromium and titanium. However, they have an increased accumulation of copper, manganese and nickel.

For loamy soils, there are similar trends the accumulation of HM as in sandy soils, except for nickel. Based on the obtained data, 4 types of biogeochemical relationships between chemical elements in the soil-plant system for the territory of the NNP were identified: V, Ti – soil > plant; Ni – soil < plant; Cr – soil > plant; Mn, Cu – soil < plant.

HM content in woody shrub plants of the NNP territory.

The results of analytical studies of the geochemical composition of woody shrub plants NNP “Tsumanska Pushcha” (Table 7) show that in the largest quantities they accumulate **manganese**. The max-

im concentration of the element was noted for Silver birch (*Betula pendula*) - 1020 mg / kg. For other plant species, the content of trace elements is much lower than the average: in samples of Scots pine (*Pinus sylvestris*), alder gray (*Alnus incana*) 2-3 times, sharp-leaved willow (*Salix acutifolia*) in 4 times.

**Titanium** maxim accumulates raspberry (*Rubus idaeus*) 80.0 mg/kg, aspen (*Populus tremula*) 60.3 mg/kg and hazel (*Corylus avellana*) 59.63. Interspecific differences in the content of the element reach 10-20 mg / kg.

The investigated NNP plants accumulate titanium in small quantities in comparison with the average values of the element content obtained for similar species of plants in the natural region as a whole. The average value of titanium in Ukrainian Polissia for pine is 21.2 mg/kg, in the park 3.80; for willow is 18.4 and 4.87, hornbeam - 25.2 and 4.87 mg/kg. From the bush vegetation, the increased content of titanium was found in samples of brittle buckthorn - 12.11 mg / kg (with average values of 3.4 mg/kg).

Differences in the average copper content between plants of different species are 10-14 mg/kg. High concentrations of this microelement are noted for common hazel (*Corylus avellana*) – 23.90 mg/kg, buckthorn brittle (*Frangula alnus*) – 21.37 mg/kg and raspberries (*Rubus idaeus*) – 20.3 mg/kg. Among woody plants, an increased copper content

**Table 7.** The average content of trace elements in woody and shrub plants NNP “Tsumanska Pushcha”, mg / kg, (ICP-AES)

№	Type of vegetation	Ash content, %	Mn	Cu	V	Pb	Ti	Cr	Zn	Ni
1	Scots pine ( <i>Pinus sylvestris</i> )	3.25	290.7	6.41	0.89	0.93	3.80	1.32	-	2.78
2	Sharp-leaved willow ( <i>Salix acutifolia</i> )	5.17	167.2	6.94	-	0.62	4.87	2.54	-	1.34
3	Silver birch ( <i>Betula pendula</i> )	4.39	611.2	10.11	5.86	6.84	5.92	5.23	5.21	6.41
4	Alder alder ( <i>Alnus incana</i> )	5.78	501.2	8.63	1.17	0.92	12.32	4.3	6.5	2.30
5	Hornbeam ( <i>Carpinus betulus</i> )	4.11	532.6	5.69	5.87	2.61	4.87	5.96	-	-
6	Large-leaved cherries ( <i>Prunus avium</i> )	4.87	563.1	-	4.87	-	5.23	4.34	-	3.26
7	Aspen ( <i>Populus tremula</i> )	5.61	562.3	10.8	4.9	3.5	60.3	4.5	-	11.2
8	Hazel ( <i>Corylus avellana</i> )	8.76	382.6	23.90	-	2.92	59.62	-	-	2.96
9	Buckthorn brittle ( <i>Frangula alnus</i> )	9.11	889	21.37	4	1.36	12.11	4	9.3	3.61
10	Raspberries are common ( <i>Rubus idaeus</i> )	7.64	860	20.3	3.4	-	80.0	3.5	50	-
	Background (Heavy metals in soils of Ukraine P, 2006)		277	13.5	3.4	5	-	3.6	-	2.6

was recorded for aspen (*Populus tremula*) - 10.8 mg/kg. It was determined that deciduous trees of the stud area contain slightly higher copper concentrations than conifers. The maxim concentration of copper in conifers is typical for Scots pine (*Pinus sylvestris*) - 8.7 mg/kg. In general, NNP plants accumulate copper by 5-8 mg/kg less than in the territory adjacent to the NNP.

The **nickel** content in plants is insignificant - mostly lower than background concentrations. Its maxim amount is observed in aspen (*Populus tremula*) 18.5 mg/kg, the average content is 11.2 mg/kg, the minimum in holly willow (*Salix acutifolia*) - 0.9 mg/kg at an average content of 1.34 mg/kg, which corresponds to the background content of the element. Among deciduous tree species in terms of nickel content, hanging birch (*Betula pendula*) differs and buckthorn brittle (*Frangula alnus*) (6.41 i 3.61 mg/kg accordingly).

The average content of **vanadium** in the ash of Scots pine (*Pinus sylvestris*) is 0.89 mg/kg, of deciduous trees - in the silver birch (*Betula pendula*) - 5.86 mg/kg, hornbeam common (*Carpinus betulus*) - 5.87 mg/kg and aspen (*Populus tremula*) - 4.9 mg/kg. The average content of vanadium in the analyzed samples is 2-3 times lower than the background values for plants of similar species.

The **zinc** content in most of the studied plants of the territory was below the sensitivity limit of the analysis. However, high levels of its content are recorded for raspberries (*Rubus idaeus*) - 50 mg/kg on sod podzolic gley sandy soils and brittle buckthorn (*Frangula alnus*) - 9.3 mg/kg on sod-slightly podzolic sandy soils near the village Yaromel.

The accumulators of lead are silver birch (*Betula pendula*), aspen (*Populus tremula*) and common hazel (*Corylus avellana*). The minim amount of trace elements is typical for specimens of willow (*Salix acutifolia*) - 0.5 mg/kg.

Coefficients of biological accumulation (CBA) of heavy metals by plants (table 8) calculated on the basis of the results of mass spectrometry analysis with inductively coupled plasma (ICP-MS), obtained for plant and soil samples of key areas of NNP.

For sod-slightly podzolic sandy soils of test areas 17-19, 23-19, 26-19 is characterized by a higher accumulation of HM plants compared to test areas 29-19, 41-19 due to the low buffering capacity of sandy soil. The value of KBP sandy soils is 1.5-5 times higher than in loamy soils.

The values of CBA on the sample areas located near the sources of pollution, in some cases were lower than in remote. Obviously, this is due to both the

predominant uptake by plants of metals from the soil and the manifestation of the protective mechanisms of plants with increasing mobility of HM in the soil.

According to the value of the absolute HM content in the studied plants, the following geochemical series can be formed:

Sedge shaking (*Carex brizoides*):

Mn>Cu>Ni>Cr=Pb>V>Ti>Zn;

Common bracken (*Pteridium aquilinum*):

Ti>Mn>Cu=Pb=V>Cr>Ni>Zn;

Forest rank (*Lathyrus sylvestris*):

Mn>Ni=Cu>Pb>Cr=V>Zn>Ti;

Lily of the valley (*Convallaria majalis*):

Mn>Cu>Ni>Pb>V=Cr=Zn>Ti;

Raspberry (*Rubus idaeus*):

Mn>Pb=Zn=Cu=Ni>V=Cr>Ti;

Buckthorn brittle (*Rhamnus frangula*):

Mn>Cr>Cu>Pb>Ni>Zn>Ti>V;

Hazel common (*Corylus avellana*):

Cu>Mn>Ni>Cr>Pb=V>Zn>Ti;

Willow Sharp-leaved (*Salix acutifolia*):

Mn>Cr>Ni>V>Cu=Pb>Zn>Ti;

Aspen (*Populus tremula*):

Mn>Cr>Cu=V>Ni>Zn=Pb>Ti;

Male bugbug (*Dryopteris filix-mas*):

Cu>Mn>Ni>Pb>V=Cr>Zn>Ti;

Birch hung (*Betula pendula*):

Mn>Ni>V=Pb>Cu>Cr>Zn>Ti;

Yarrow (*Achillea millefolium*):

Mn=Ni>Pb=Cu>V=Cr>Zn>Ti;

Hornbeam (*Carpinus betulus*):

Mn>Cu=V>Ni=Pb>Cr>Zn>Ti.

It should be noted that there is not always a clear pattern between the values of the gross forms of HM and indicators of CBA. Probably, metal compounds adsorbed from the atmospheric air play an important role in the accumulation of HM by the aboveground part of plants. The plants that grow close to potential sources of contamination, We found a higher content of the test TM. The main part of the excess of the background values by elements was found on the test plots of the northwest direction. All studied plants accumulated as much as possible Mn, Cu, Cr and minimally Zn and Ti which is consistent with the patterns of migration of these elements in the soil (Vinogradov A.P., 1957).

Considering the distribution of elements in plants characteristic of the stud area, it can be stated that nickel is mostly accumulated in aspen (*Populus tremula*) (site 31-19) - 50 mg/kg, in the smallest amount accumulated by willow (*Salix acutifolia*) - 4 mg/kg on low-power peat lands in the floodplain of the Rudka River (site 30-19). The maxim content of manganese (800

**Table 8.** Coefficients of biological accumulation (CBA) of heavy metals by plants key areas of NNP «Tsumanska Pushcha»

№ site	Plant	Soil	The content of elements (mg / kg) in the plant (numerator, or - the number from the top) and in the soil (denominator or - the number from the bottom) biological accumulation coefficient (CBA)															
			Mn	CBA	Ni	CBA	Ti	CBA	V	CBA	Cr	CBA	Zn	CBA	Cu	CBA	Pb	CBA
16-19	Sedge shaking (Carex brizoides)	Alluvial layered sandy loam	400		3		80		2		2		10		20		2	
			100	4	5	0.6	500	0.16	6	0.3	5	0.4	100	0.1	20	1	5	0.4
17-19	Bracken (Pteridium aquilinum)	Sod-slightly podzolic sandy	500		2		3000		40		4		100		6		30	
			300	1.6	6	0.3	300	10	40	1	10	0.4	600	0.16	6	1	30	1
23-19	Forest rank (Lathyrus sylvestris)	Sod-slightly podzolic sandy	600		4		80		3		3		60		8		20	
			300	2	5	0.8	2000	0.04	10	0.3	10	0.3	600	0.1	10	0.8	40	0.5
24-19	Lily of the valley (Convallaria majalis)	Sod-medium podzolic sandy loam	800		2		60		2		2		20		10		15	
			300	2.6	3	0.6	800	0.07	10	0.2	8	0.2	100	0.2	10	1	30	0.5
25-19	Raspberry (Rubus idaeus)	Sod podzolic sandy gleyey	1000		5		80		3		3		50		20		10	
			200	5	10	0.5	600	0.1	8	0.3	10	0.3	100	0.5	50	0.4	20	0.5
26-19	Buckthorn brittle (Rhamnus frangula)	Sod-slightly podzolic sandy	1000		2		10		4		4		10		19		7	
			200	5	6	0.3	400	0.02	300	0.01	8	0.5	200	0.05	40	0.47	16	0.43
29-19	Hazel (Corylus avellana)	Sod carbonate light loam	400		10		50		10		14		67		20		3	
			300	1.3	20	0.5	1000	0.05	30	0.3	30	0.46	300	0.2	10	2	10	0.3
30-19	Sharp-leaved (Salix acutifolia)	Shallow peat bog	300		4		30		3		3		10		5		3	
			300	1	8	0.5	500	0.06	8	0.37	5	0.6	80	0.1	16	0.3	13	0.3
31-19	Aspen (Populus tremula)	Peat bog shallow degraded	500		3		50		4		4		20		10		3	
			400	1.25	50	0.06	2000	0.02	40	0.1	20	0.2	400	0.05	60	0.1	60	0.05
33-19	Male bugbug (Dryopteris filix-mas)	Sod gley (peat) sandy loam	800		10		80		5		5		10		50		3	
			200	4	5	2	1000	0.08	10	0.5	10	0.5	100	0.1	2	25	5	0.6
37-19	Male bugbug (Betula pendula)	Turf gley sandy	800		6		45		4		2		35		3		4	
			150	5.3	12	0.5	1000	0.04	11	0.36	8	0.25	210	0.16	10	0.3	11	0.36
41-19	Yarrow (Achillea millefolium)	Sod carbonate light loam	300		15		10		5		8		29		21		5	
			400	0.75	20	0.75	1500	0.006	30	0.16	50	0.16	400	0.07	40	0.5	10	0.5
48-19	Hornbeam (Carpinus betulus)	Turf podzolic sandy	500		3		40		5		5		40		5		19	
			750	0.6	7	0.4	1000	0.04	10	0.5	20	0.25	200	0.2	10	0.5	46	0.4



mg / kg) and copper (50 mg / kg) was recorded in the Male bugbug (*Dryopteris filix-mas*), which growing on sod gley (peat) sandy-loamy soils near the village Zhuravychi (site 33-19), concentration of manganese exceeds its background value by 3 times (277 mg/kg). Common bracken (*Pteridium aquilinum*) (site 17-19) accumulates a significant amount of titanium (3000 mg/kg), lead (30 mg/kg), zinc (100 mg/kg).

Interspecific differences between plants in terms of the content of the above elements are significant. Forest rank (*Lathyrus sylvestris*) sod-slightly podzolic sandy soils (site 23-19) accumulates titanium, manganese and zinc. A number of plants are characterized by the simultaneous accumulation of several HM, causing high values of reliable pollution. Common hornbeam (*Carpinus betulus*) sod-podzolized sandy loam soils (site 48-19) is characterized by a simultaneous high content of manganese (500 mg/kg), titanium (40 mg/kg) and lead (18 mg/kg).

Yarrow (*Achillea millefolium*) sod carbonate light loam soils concentrates nickel (15 mg/kg) and copper (21 mg/kg). Willow sharp-leaved (*Salix acutifolia*) in peat bogs it is characterized by the minim content of all studied HM, with the exception of manganese.

In a pine tree near the village Yaromel maxim amount of nickel is recorded in samples of lily of the valley (*Convallaria majalis*). This plant, compared to others, has a higher content of manganese (680 mg/kg) and titanium (89 mg/kg). Sedge shaking (*Carex brizoides*) alluvial layered sandy soils is released in the presence of copper (20 mg/kg). Very few trace elements are accumulated Scots pine (*Pinus sylvestris*) (from 0.7 to 4.31 mg/kg).

Titanium accumulat in significant quantities by Hazel common (*Corylus avellana*) and birch hung (*Betula pendula*) (48-50 mg/kg) turf gley sandy soils. Its maximal number (except for common) is recorded in samples of raspberries (*Rubus idaeus*), growing on sod podzolic gley sandy soils, and is 80 mg/kg.

The concentration of copper varies from 2.12 in the male bugbug (*Dryopteris filix-mas*) to 21.34 mg/kg in yarrow (*Achillea millefolium*). A lot of copper was found in sedge shaking (*Carex brizoides*) and raspberry (*Rubus idaeus*) (up to 20 mg/kg). In general, it can be noted that the copper content in plants of the NNP territory increases with an increase in their biological productivity.

The high accumulation of HM in the aboveground part of the studied plants indicates a significant removal of elements from the soil, which, in turn, makes it possible to consider certain plant species as potential phytoremediators. Another indicator that testifies to the high accumulating capacity of the forest

rank (*Lathyrus sylvestris*), male bugbug (*Dryopteris filix-mas*), and yarrow (*Achillea millefolium*) is the prevalence of HM in the aerial part over the root. It should be noted that a high concentration of HM does not have a toxic effect on these plant species, which may indicate their tolerance to anthropogenic pollution.

## Conclusions.

Spatially, the landscape-geochemical structure of the NNP and adjacent territories is represented by calcium, calcium-carbonate, carbonate-gley, acid calcium geochemical classes of landscapes.

Analysis of the content of heavy metals in the soils of the territory showed its non-uniform distribution and dependence on the available sources of anthropogenic impact. The highest concentrations of manganese and chromium are found in soils developed on loess deposits, and nickel and copper on glacial deposits.

The first results of studying the microelement composition of the vegetation of the investigated NNP make it possible to conclude that woody and shrub plants of the park territory are characterized by an increased content of manganese, titanium, copper and lead in comparison with similar species of plants that are common in other parts of the Polissia region. Within each phytocenosis there are plants-concentrators of a certain element. In particular, plants with high ability to accumulate HM belong: common bracken (*Pteridium aquilinum*), raspberries (*Rubus idaeus*) and forest rank (*Lathyrus sylvestris*). The supply of elements in phytocenoses depends on the chemical composition of plants, their total biomass, which is determined by the mineral composition and soil moisture conditions.

The main direction of further research should be further study of the distribution of macroelements and microelements in different genetic types of soils; establishment of the reference content of elements in geochemical landscapes to establish the intensity of migration and the nature of the distribution of elements; determination of pathological and specific plant diseases due to the geochemical features of the landscape.

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