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LANDSCAPE AND GEOCHEMICAL ASSESSMENT OF ECOLOGICAL CONDITION OF ENVIRONMENTAL PROTECTION TERRITORIES

А. О. Сплодитель. ЛАНДШАФТНО-ГЕОХІМІЧНА ОЦІНКА ЕКОЛОГІЧНОГО СТАНУ ПРИРОДООХОРОННИХ ТЕРИТОРІЙ. Здійснено аналіз ландшафтно-геохімічних умов території національного природного парку (НПП) «Нижньосулський», встановлено закономірності розподілу важких металів у сучасному ґрунтовому покриві території НПП «Нижньосулський». Визначено закономірності просторового розподілу потенційно доступних форм важких металів. Встановлена динаміка накопичення Ni, Zn, Cu, V, Pb та інших важких металів в ґрунтовому покриві території протягом 2014-2019 років за рівнями імпаکتного забруднення. Аналіз ландшафтно-геохімічних умов території свідчить, що вони в цілому сприяють як міграції хімічних елементів з поверхневим стоком, так і значному вертикальному їх перерозподілу. Диференціація ландшафтно-геохімічних умов обумовлює фіксацію та акумуляцію значної кількості природних і техногенних хімічних елементів на ландшафтно-геохімічних бар'єрах (механічні, окисно-відновні, кисло-лужні, сорбційні, сорбційно-глейові). Це попереджує інтенсивне забруднення переважної більшості ландшафтних комплексів парку забруднюючими речовинами, які мігрують з сільськогосподарських угідь, що підтверджено результатами аналізу джерел та обсягів забруднення. Аналіз вмісту важких металів у ландшафтних комплексах території НПП «Нижньосулський» засвідчив його залежність від наявних джерел техногенного забруднення, а також високий ступінь відповідності характеру розподілу важких металів загальним закономірностям цих процесів у ґрунтах відповідних типів. Більшість ВМ надходять до Сулинської акваторії переважно під час весняної повені з талими сніговими водами. Було відмічено перевищення Cd^{2+} , Cu^{2+} і Pb^{2+} у воді порівняно з діючими нормами ГДК.

За результатами ландшафтно-геохімічного аналізу НПП «Нижньосулський» можна стверджувати, що територія з екологічної точки зору є слабо забрудненою і може використовуватися для розвитку рекреаційної діяльності з дотриманням низької вимоги.

Ключові слова: ландшафтні комплекси, ландшафтно-геохімічні умови, важкі метали.

А. О. Сплодитель. ЛАНДШАФТНО-ГЕОХИМИЧЕСКАЯ ОЦЕНКА ЭКОЛОГИЧЕСКОГО СОСТОЯНИЯ ПРИРОДООХРАННЫХ ТЕРРИТОРИЙ. Осуществлен анализ ландшафтно-геохимических условий территории национального природного парка (НПП) «Нижнесулский», установлены закономерности распределения тяжелых металлов в современном почвенном покрове территории НПП «Нижнесулский». Анализ ландшафтно-геохимических условий территории свидетельствует, что они в целом способствуют как миграции химических элементов с поверхностным стоком, так и значительному вертикальному их перераспределению. Определены закономерности пространственного распределения потенциально доступных форм тяжелых металлов. Установлена динамика накопления Ni, Zn, Cu, V, Pb и других тяжелых металлов в почвенном покрове территории в течение 2015-2019 годов при различных уровнях импаکتного загрязнения. Дифференциация ландшафтно-геохимических условий обуславливает фиксацию и аккумуляцию значительного количества природных и техногенных химических элементов на ландшафтно-геохимических барьерах (механические, окислительно-восстановительные, кисло-щелочные, сорбционные, сорбционно-глинистые). Это предупреждает интенсивное загрязнение подавляющего большинства ландшафтных комплексов парка загрязняющими веществами, которые мигрируют из сельскохозяйственных угодий, что подтверждено результатами анализа источников и объемами загрязнения. Анализ содержания тяжелых металлов в ландшафтных комплексах территории НПП «Нижнесулский» показал его зависимость от имеющихся источников техногенного загрязнения, а также высокую степень соответствия характера распределения тяжелых металлов общим закономерностям этих процессов в почвах соответствующих типов. Большинство ВМ поступают в акваторию Сулы преимущественно с тальми снеговыми водами. Было отмечено превышение Cd^{2+} , Cu^{2+} и Pb^{2+} в воде по сравнению с действующими нормами ПДК.

По результатам ландшафтно-геохимического анализа НПП «Нижнесулский» можно утверждать, что территория с экологической точки зрения является слабо загрязненной и может использоваться для развития рекреационной деятельности с соблюдением ряда требований.

Ключевые слова: ландшафтные комплексы, ландшафтно-геохимические условия, тяжелые металлы.

Formulation of the problem. The effectiveness of landscape-geochemical monitoring of protected areas largely depends on the rationalization of the system of ecological regulation and control. A reliable indicator of the ecological and geochemical state of the territory is the assessment of the distribution and migration of heavy metals (HMs) in soils and in the soil-plant system. The toxicity of HMs for protected areas, recreational areas as well as areas used as forest and agricultural lands within the NNP, is determined not only by their gross content. An important indicator is the content of moving

metal forms, which determines the expediency of their determination in the most sensitive components of the landscape.

Material and methods of research. The method of the soil-geochemical survey envisaged the sampling of the soil at a depth of 0-20 cm by the method of envelope as well as the profile of the soil in accordance with the current DSTU 4287:2004, DSTU ISO 10381-2:2004. The extraction of the gross forms of heavy metals contained in the soil was carried out with concentrated HNO_3 in accordance with the requirements, while the extraction of

mobile (fixed) forms of heavy metals – $1n \text{HNO}_3$.

Soil sampling was carried out in several stages in the spring-autumn period of 2015-2017. Plant sampling was performed equally from all the examined areas in two diagonal directions. In total, 970 soil samples, 10 varieties of wood and 25 varieties of herbaceous vegetation were selected. The presence of heavy metals in phytomass of plants was determined in their ash solutions by atomic absorption spectrometry. To assess the degree of hazard of the pollutant element, a concentration factor was used, i.e. the correlation between the concentration of the pollutant and its background content (GOST 17.4.3.06-86) and the total contamination index (Z_c) by Yu. E. Saet [8]. The assessment of the ecological condition of the soil according to the presence of moving forms of heavy metals was carried out by comparing their actual presence in soil based on the maximum permissible concentration and geochemical background for each type of soil.

Identification of previously unsolved parts of the general problem. Heavy metals are among the number of microelements that take an active part in the physiological, biochemical and geochemical processes that determine their localization in the soil. In this case, HMs are partially fixed and become stationary, partly – transform into a ground solution, and then are washed or absorbed by plants. Most of the HMs are fixed in the upper part of the soil profile [7-9].

Depending on the content, patterns of distribution and migration in soils, microelements can be essential and toxic. High concentrations of HMs in the landscapes of NNP generate a number of ecological problems. Accumulation of HMs violates the physical and chemical equilibrium and gives impetus to a number of processes that change the soil properties. In particular, the destruction of the soil absorbing complex occurs, the soil structure changes, the humus becomes dehumidifying, etc. [7,9]. Plants grown on contaminated soils usually contain HMs in excessive amounts. With high toxicity, HMs cause a negative change when they enter the human body.

Control over pollution of the territories by HMs provides for the restriction of their content in the components of the landscape in quantities that do not lead to negative environmental consequences [15,16]. The most effective ways to reduce the environmental risk of HMs contamination can be determined through comprehensive research. Informative in such studies is the determination of the forms of metal found in soils and the peculiarities of their physico-chemical migration, which characterize the ability of the elements to cross into adjacent environments, in particular in plants and groundwater. Without knowing the forms of migration of chemi-

cal elements and their behavior in the trophic chain, it is impossible to correctly assess the orientation of the natural process and give an accurate calculation of the accumulation of the element under study in a particular type of landscape.

The purpose of the article. The practice of systematic research of HMs content in the geosystems of the national natural parks of Ukraine is absent, therefore such background monitoring within the NNP is a relevant task.

Presentation of the main research material. The data from the territory of NNP “Nyzhniolsulskyi” were used for the analysis of the behavior of the HMs. The territory is sufficiently studied and there is a significant amount of landscape geochemical data obtained by the author during landscape and geoscience surveys (field as well as analytical), collected from funds and literary sources. The data are organized into the geoinformation system (GIS). Integrated GIS includes several layers of thematic data, in which information on vegetation, hydrography, soil covering, landscapes, land use structure, etc. is organized. The structuring of the available information is performed for the formation of the information module of landscape geochemical GIS. As a result, the following subject sections are determined: information on landscapes and soils of the territory (cartographic information), meteorological section, and soil-geochemical section.

Map information is represented by a landscape, a landscape geochemical map and the map of soils with a scale of 1: 25000 in a vector format [1,2] and the map of soil forming rocks with a scale of 1: 200 000. The meteorological information summarized by the data of Ukrainian Hydrometeorological Center includes the average monthly air temperature and precipitation. It is used for the study of fast soil-geochemical processes that respond to changes in weather conditions and the identification of natural and man-made trends. The soil-geochemical section is represented by the database (DB) with a two-level structure. The first level is a ground cut, which is determined by the number, the date of the description and the geographical coordinates, which allows to transfer information from the database to the map. The description of the section includes information on the factors of soil formation and the name of the soil.

The second level of the database is the morphological properties of the individual soil horizons (color, character of color, humidity, type of structure, granulometric composition, new formations and inclusion, the nature of the transition and the form of the boundary) and tables with relevant analytical data. The first table includes physico-chemical indicators of soil horizons (pH, humus content, physical clay content, moving iron content,

etc.). The second and third tables present the content of moving and gross forms of HMs. The data obtained during field and laboratory work are structured as sets of numerical information.

The landscape-geochemical GIS contains the coordinates and descriptions of more than 280 soil sections, as well as the results of chemical analyses: the content of humus, pH, concentration of gross and moving (in extract of 1n HCl) forms of Mn, Zn, Cu, Pb, Ni, Cr and moving Fe forms in the genetic horizons of the main types of soils common in the studied area.

The mobility of heavy metals was determined as the fraction of the separation of their moving forms contents in the soil by the content of gross forms, multiplied by 100%.

The mapping of the landscape-geochemical research was carried out using GIS-analysis and simulation methods.

The functional module of GIS includes:

- the spatial-temporal analysis of data using the apparatus of mathematical statistics and expert assessments;

- the development of geochemical and mathematical models for the description of migration and transformation of chemical elements in various landscape conditions;

- the construction of electronic maps of individual features and complex soil-geochemical maps of various purposes, content, on various time based on information from the soil-geochemical database on thematic maps (landscape, topography, vegetation);

- the creation of digital models of geochemical fields by the method of landscape-oriented interpolation;

- the construction of maps of dynamics of soil-geochemical indicators on the basis of several time-scale maps.

The structural and functional heterogeneity of the landscapes of the territory of the NNP, the excellent types of interactions and directions of migration flows lead to uneven redistribution of microelements and their compounds in the lateral and radial directions.

Lateral migratory flows contribute to spatial heterogeneity of landscapes. In turn, the radial heterogeneity of the landscapes reflects the nature of the interaction and the relationship between its components such as soil and soil forming rock, soil-surface water, soil-plant, etc. [12,13,21].

For the territory of the NNP "Nyzhniosulskyi", we investigated the laws of lateral and radial redistribution and behavior of HMs in soils as the most sensitive component of the landscape.

To carry out the research, the following tasks were performed: 1) control platforms were established within the NNP and adjacent territories; 2) the

selection of soil and vegetation samples; 3) the physical and chemical parameters of soils were investigated; 4) the content of gross and moving forms of heavy metals in the soil covering was determined; 5) the ecological state of landscapes was estimated on the basis of calculated concentration factors and total pollution index.

The conducted works allowed to determine the distribution of HMs depending on the factors of their migration and to assess the trends in the change of their content. The interpretation of the obtained results revealed the nature of the effect of hydrogenogenic iron, organic matter, mold fraction, Eh and pH of the medium on the maintenance of hydrogen forms of the HMs. The analysis of the mechanisms and processes that determine the picture of the spatial distribution of HMs in the soils of the territory of the NNP allowed to establish their general patterns.

Landscapes of the territory are dominated by the landscape hole of the segment-ruffed and segment-island floodplains. The soil cover of these holes are dominated by alluvial turf, usually salted, sometimes carbonate, glued soils in the lower part of the profile [16-21].

We carefully studied the landscapes of moraine-loess and loess terraced plains of deep humus surface slightly alkaline slightly mid-loamy black soil and with saline meadow- black soil deep mid-loamy salines on the moraine and loess loams, turf underdeveloped sandy soils of varying degrees of gleying on fluvio-glacial sand and alluvial turg gley deep-solar soils on sediments of different granulometric composition.

Anthropogenic impact, besides agricultural activity, is associated here with large enterprises, in particular Poltava Mining and Processing Plant in Komsomolsk, Ukrtatnafta in Kremenchuk, Kremenchuk Steelmaking Plant, Kremenchuk Petroleum Product (petroleum station 55, Chornobaivskyi district), Ukrnafta (gas station number 230/05, Irkliy village, Chornobaivskyi district), NadezhdaRetail (gas station, Chernobay), Ukrtransgas (village Mala Burimka, Chornobaivskyi district), Kremenchuk Petroleum Product Service (storage and sales of oil products), the stock of the poison chemicals of the Chorolskaya Agrochemistry, etc.

Wastes of enterprises include substances of I-IV classes of danger. In particular, spent mercury lamps, oils and motor oils, zinc slag, spent x-rays and lubricating liquids, ferrous metal cuttings, spent electrodes and batteries for lead accumulators, galvanic sludges, non-ferrous metal scrap (aluminum, copper, brass, bronze, nickel, aluminum cuttings), marble carbide, etc.

In soil samples, selected on the territory of the NNP, the gross amount of lead was the highest. The

concentration of Pb is 25-40 mg/kg and exceeds the background and MAC, which are respectively 8-10 mg/kg and 30 mg/kg. The increased content of gross forms of copper, titanium, and chromium was recorded. The excess of the background in virtually all studied soil samples was recorded for V (content reaches 50-60 mg/kg) and Ti (3000-4000 mg/kg). The content of these chemical elements is within the limits of the MAC, but sometimes the values obtained exceed it and equals, respectively, 60-70 mg/kg and 5700 mg/kg [56]. The amounts of Ni (6-8 mg/kg) and Co (3-5 mg/kg) in the soil are close to the background, and a slight excess of their background values was observed at points 101-15, 107-15, 108-15, 129-15. The concentration of Mo and Zn is relatively low (within the limits of 1-2 mg/kg and 50 mg/kg respectively) and is below the background values. However, Zn is characterized by local excesses at monitoring points 32-15, 102-15, 110-15, 113-15, 129-15 (80-100 mg/kg).

The analysis of the data shows that the distribution of HMs in soils is uniformly-accumulative in its nature, but several basic laws may be distinguished, which can be traced within the studied area:

- The distribution of Pb is fundamentally different from the distribution of other studied HMs. Pb compounds are concentrated, mostly in the humus profile, with a gradual permanent migration to lower horizons. The migratory capacity of Pb is on average 10-14%, in the humus horizon the migration capacity is $15 \pm 8\%$, which indicates its exogenous origin. The latter may be due to the use of gasoline fuels for the extraction and processing of petroleum products as well as waste of lead batteries and electrodes;

- Zn and Cu are mostly localized in the upper transition profile, as well as in the humus horizon. The migratory capacity of these HMs in soils is low; for Zn it is 7% practically irrespective of the profile, for Cu it is <4-5%, and for Cr it is 4%, with the highest index in the humus horizon of 8%. An indication of such distribution is the endogenous origin of the above-mentioned HMs due to the transformation of soil-forming rocks;

- Alkaline conditions contribute to the reduction of the content of the moving forms of all investigated pollutants. However, the influence of pH on the behavior of Sr was not detected. In Cu, Pb, Ni in the reducing gluten medium, the concentration of moving forms decreases, in Zn it slightly increases;

- The content of the moving forms Cu, Zn, Pb, Cr, Ni increases according to the content of the moving Fe and usually leads to the accumulation of moving forms of these elements;

- A moving Mn form has a significant effect on the behavior of the HMs. Their concentration in-

creases a number of moving forms of Co, Zn, Pb, Ni and decreases Cu and Cr;

- The moving forms of Mn, Cr, Ni have a direct positive relationship with their gross concentrations. The inverse relationship between these indices is characteristic of Cu, while it is absent in Pb and Zn. The behavior of Cu is distinguished by the greatest individuality, therefore it was not possible to track its laws.

The gross metal concentrations in the soil profile of the alluvial turf sandy soils are reduced by 1.5-2 times compared with the loamy analogues. Most clearly, this pattern is manifested in Cr, V, Ni, Zn, and the concentration of Cu and Pb is less sensitive to the change in the granulometric composition of the horizons. The humus horizons of alluvial sandy soils are characterized by a less contrasting decrease in gross metal concentrations compared to loamy soils. This indicates the convergence of the content of elements in the humus horizons of soils on various soil forming rocks. The content of the mobile forms of Mn, Pb, Cu, Zn in sandy soils is 2-3 times, while Cr, Ni is 10-15 times lower compared with loamy soils.

In typical black earths and turf loamy soils, a soil forming rock is a forest-like loam that is bedrocked with moraine. The content of humus is slightly higher – from 1,5 to 3,3%. The pH value is practically the same for both types of soils, but for turf soils, its variability is significantly higher – from 4 to 6.1. This contributes to the accumulation of heavy metal cations due to the reduction of their migration capacity when consolidated in the soil-absorbing complex. The average content of metals in typical low-humus loamy black earths is 30-40% higher on average than in sod-podzolic loamy soils, which is probably due to inland drainage. The gross content at the sampling points (115-15, 118-15, 124-15) is higher than the background values; in some cases, the excess MAC was recorded: Ni - 60 mg/kg (with background values 22 mg/kg), Ti - 3000 mg/kg (2250 mg/kg), V - 50-60 mg/kg (41 mg/kg), Cr - 50-60 mg/kg (49 mg/kg), Cu - 80-100 mg/kg (12-16 mg/kg), Pb - 40-50 mg/kg (10 mg/kg).

Absolute values of moving metal forms and their mobility in turf soils are close to the corresponding values of alluvial loamy soils, only in Cr content in the humus horizon is almost 2 times lower. The variability of the moving metal forms is also preserved at the previous level in most of the elements, except for Pb and Sr, in which it grows 1.4-2.2 times (Fig. 1, Fig. 2).

Turf sandy soils on fluvioglacial sands with absolute content of gross and moving forms of metals are close to turf-podzolic with similar granulometric composition.

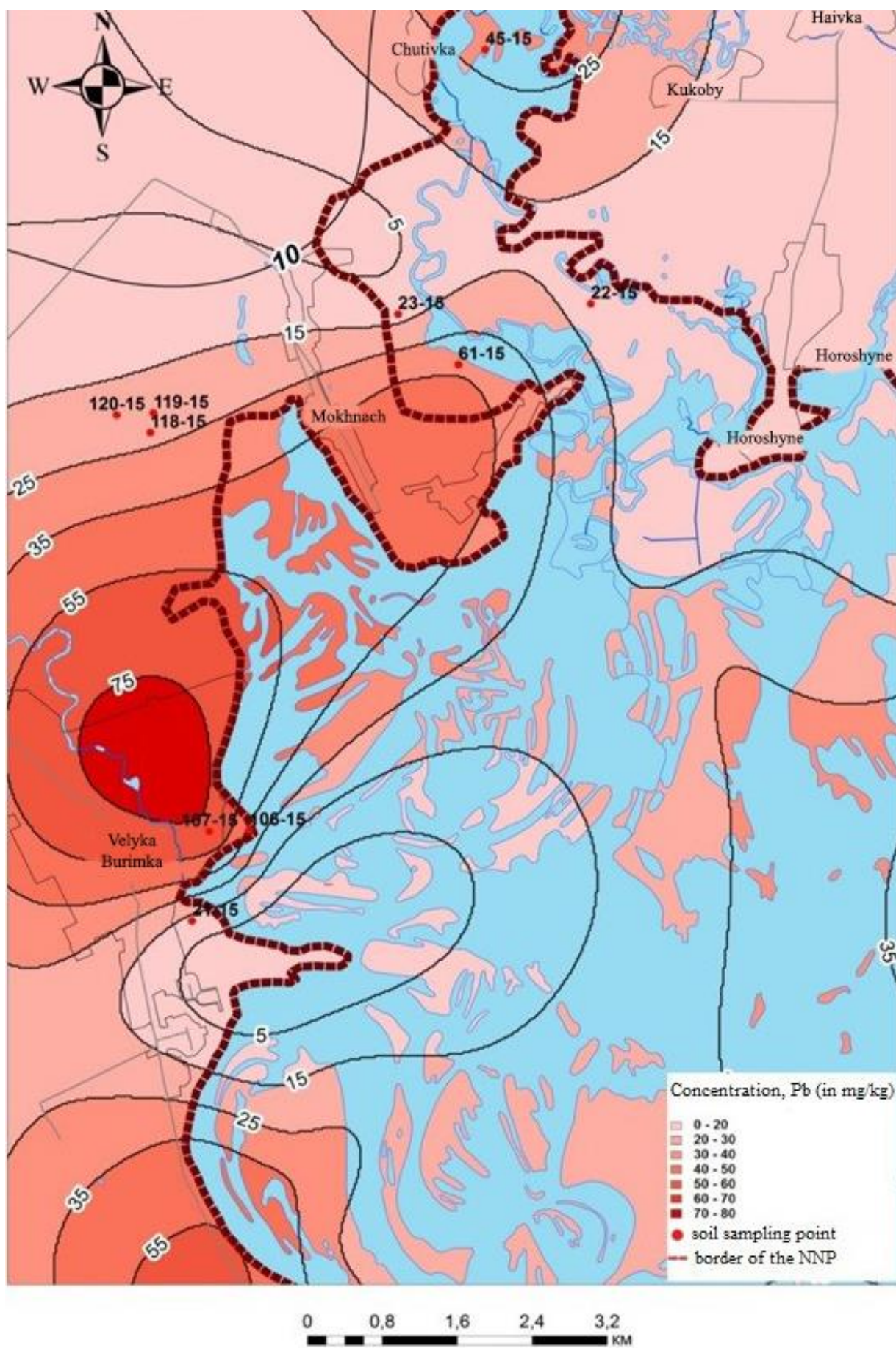


Fig. 1. Distribution of Pb in the modern soil cover of the territory of the NNP "Nyzhniosulskyi"

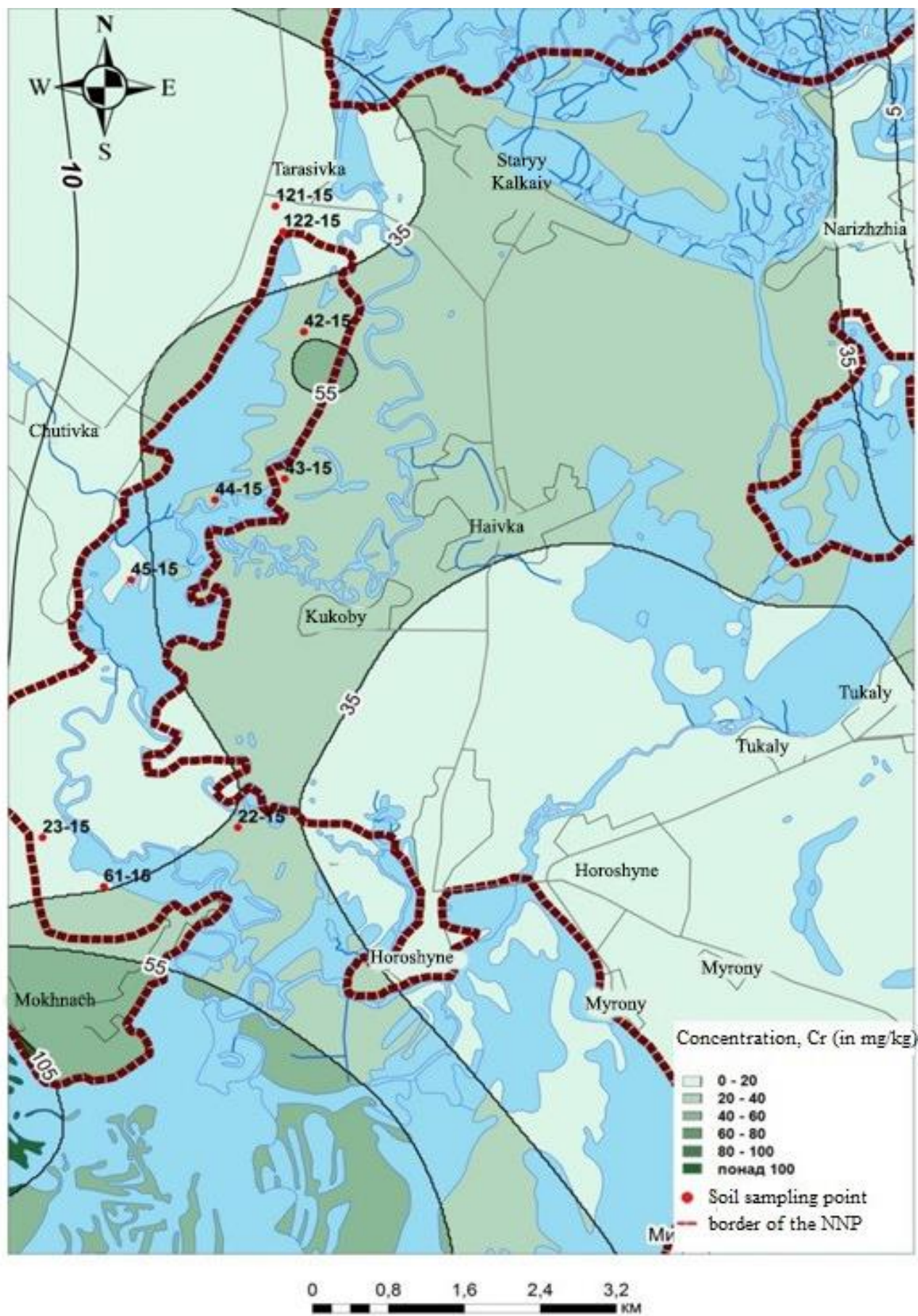


Fig. 2. Distribution of Cr in the modern soil cover of the territory of the NNP “Nyzhniosulskiy”

Alluvial turf glued saline soy sandy soils are characterized by the layering of soil-forming deposits, the presence of buried humus horizons, and high content of humus – 1.9-2.96%. The influence of groundwater is manifested in the gluing either of the lower part or the entire profile, as well as in the alkalinity of the soil solution. Therefore, the lower horizons are characterized by a reducing weak-alkaline (pH > 7) reaction.

Due to the light granulometric composition of soil formation rocks and significant deviation of the bottom of the valley of the Sul River, the moving forms of the HMs are carried out from alluvial soils, that is why they are 1.3-1.5 times frequent there less than in soils of the plain-terraced plains, with the exception of Ni. Alluvial turf gley soils have the highest concentration of HMs, which is explained by the deposition of elements coming from the inland side drain.

Among the marsh soils, turf-gley soils are predominant in lowland marshes in old-age declines. In these soils, besides the ground waters, a specific role is played by the specific marsh vegetation, which determines the acidic reaction of the medium of the upper horizon – pH 4.7-5.4, and the accumulation of organic matter. The content of most metals in marsh soils is almost the same as in turf loamy soils, with the exception of (Cu and Mn). The gross content of Cu (50-100 mg/kg) is 8-10 times, and Mn (660 mg/kg) is 2-3 times higher than the background indices, respectively, 5.3 and 166 mg/kg.

The regularities of the radial redistribution of HMs on the genetic horizons of the characteristic soils of the NNP were studied on the example of the points of the complex description. In the studied soil profiles, similar tendencies of radial redistribution of heavy metals were recorded.

In particular, the content of Pb grows down the profile. Cu is usually accumulated in the upper soil horizon, which is explained by anthropogenic impact, as well as its bioaccumulation [15,17-21]. This is confirmed by our research as well. Chromium compounds are also washed along with downstream moisture streams. The content of nickel practically does not change on the profile of the studied soil sections. The given data on the distribution of pollutants in the soil cover of landscapes of the NPP is an example that illustrates the relevance of this analysis, especially for protected areas.

Conclusions. The analysis of heavy metals in the landscape complexes of the territory of NNP “Nyzhniosulskyi” confirmed its dependence on available sources of technogenic pollution. It also confirms a high degree of compliance of the character of HMs distribution with general laws of these processes in soils of the corresponding types. The main direction of further research should be improvement of the system of landscape and geochemical monitoring of the territories, where there are nature protection objects, and adjacent territories for the purpose of detection of pollution centers and improvement of ways of reducing their concentration to allowable norms.

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LANDSCAPE AND GEOCHEMICAL ASSESSMENT OF ECOLOGICAL CONDITION OF PROTECTED TERRITORIES

Purpose. The problem of environmental pollution by heavy metals is one of the most important problems of the present and the near future. The compounds of these elements are characterized by high toxicity, mobility and ability to bio-accumulation. The aim of the study was to establish the main regularities of trace elements of the national natural park (NNP), to determine the indicators of their mobility for assessment of state of environment.

Scientific novelty. The article discusses the features of distributing of heavy metals in the components of landscapes of the territory of the national natural park for realization of control and settlement of his concentration in accordance with the set norms.

Results. The analysis of the landscape-geochemical conditions of the territory of the national natural park “Nyzhniosulskyi” has been performed. Consistent patterns of heavy metals distribution in the modern soil of the territory of NNP “Nyzhniosulskyi” have been determined. The analysis of landscape-geochemical conditions of the territory indicates that they generally contribute to the migration of chemical elements with land runoff as well as their significant vertical redistribution. The differentiation of landscape-geochemical conditions causes the fixation and accumulation of a significant number of natural and man-made chemical elements on the landscape-geochemical barriers (mechanical, redox, acid-alkaline, sorption, sorption-gley). This prevents from intense pollution of the vast majority of landscape regions in the park by polluting substances migrating from agricultural lands, which is confirmed by the results of the analysis of pollution sources and volumes.

It was shown, that processes of transformation and migration of heavy metals compounds in the soil profile are determined by physical and chemical properties of soils. The analysis of the content of heavy metals in the soils of NNP “Nyzhniosulskyi” has shown that, the distribution of heavy metals is uniformly dispersive, but the variations in the content of certain heavy metals can range from $\pm 7\%$ to $\pm 25\%$ - 35% . The greatest bioaccumulation capacity is expressed in biogenic microelements – manganese and cuprum.

The analysis of heavy metals content in the landscape regions of NNP “Nyzhniosulskyi” has confirmed its dependence on available sources of technogenic contamination as well as the high degree of compliance of the nature of heavy metals distribution to the general laws of these processes in the soils of the relevant types. Most heavy metals get into the Sulyn aquatorium mainly during spring flood with snow melt water.

The excess of Cd^{2+} , Cu^{2+} and Pb^{2+} in water has been noted in comparison with the current threshold level value regulations.

According to the results of the landscape-geochemical analysis of the NNP “Nyzhniosulskyi”, it can be stated that the territory from the ecological point of view is poorly contaminated and can be used for the development of recreational activities in compliance with a number of requirements.

Practical significance. The results of this study have been introduced into practice of the NNP “Nyzhniosulskyi” in organizing and conducting research work, for planning tourist and recreational activities, forming tourist routes, and organizing recreational infrastructure.

Keywords: landscape regions, landscape-geochemical conditions, heavy metals.

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