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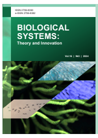

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Biogeochemical cycling of nickel in the hornbeam forest ecosystems of the Middle Dnipro Region

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Abstract. Heavy metals, particularly Ni, are priority pollutants of atmospheric air. Urban green spaces and forest ecosystems play a crucial role in reducing pollution levels. However, they themselves suffer from adverse impacts that induce phytotoxic effects, diminish the resilience of vegetation to pests, diseases, and other negative factors. This study aimed to assess the balance of the biogeochemical cycle of Ni in forest ecosystems to determine the consequences of pollution on vegetation within urbanised environments under varying anthropogenic pressures. Hornbeam forests from two territories of the natural reserve fund of Ukraine were selected as model ecosystems of broad-leaved forests in the Middle Dnipro Region: Holosiivskyi National Nature Park (NNP) and the Kaniv Nature Reserve. The study conducted on these model ecosystems, the methods of atomic absorption spectrophotometry and ICP-OES spectrometry were employed to ascertain the characteristics of Ni accumulation in soils. An evaluation of Ni stocks in the phytomass of hornbeam forests was performed, along with an analysis of the dynamics of metal compound accumulation in the forest litter. Furthermore, Ni's vertical migration rates were assessed using a lysimetric method, and the levels of metal compounds in the deposition process via atmospheric precipitation onto the hornbeam forests were determined. It has been established that the biogeochemical systems of Ni migration in the hornbeam forest of the Kaniv Nature Reserve are characterised by a balanced metal flow. The ecosystem of the hornbeam forest within the Holosiivskyi NNP exhibits an imbalance in the biogeochemical cycle of Ni. Consequently, in the functioning of the Ni biogeochemical cycle within the ecosystem of the Holosiivskyi NNP, the biological component of the "litter-soil-plant" system plays a crucial role, as Ni is actively absorbed by common hornbeam (*Carpinus betulus* L.) and accumulates in the phytomass. The ecosystem of the hornbeam forest of the Holosiivskyi NNP in the conditions of Kyiv is undergoing progressive Ni pollution, which is manifested in the active accumulation by vegetation, which must be taken into account when assessing the condition of existing green spaces and when designing new ones, choosing plants that are resistant to high concentrations of Ni

Keywords: soil; forest litter; leaf fall; atmospheric deposition; bioaccumulation; mineralisation; heavy metal migration

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INTRODUCTION

Urban air pollution is a global problem recognised as a leading factor affecting human health. In urban environments, green spaces and forest ecosystems play a crucial role not only in regulating the microclimate, shielding against noise pollution, and enhancing the aesthetic appeal of urban settings but also in reducing the level of air pollution. Heavy metals, particularly nickel (Ni), after entering a forest ecosystem, accumulate in its components, which can lead to phytotoxic effects and reduce the resistance of green spaces to negative environmental factors. The main mechanisms for reducing the amount of heavy metals in terrestrial ecosystems are migration processes with water flows. It is assumed that a sign of the stability of a forest ecosystem to pollution is the balance of metal input fluxes with fluxes of its removal from the ecosystem. Therefore, to understand the degree of nickel pollution and the consequences of its accumulation in urban green space ecosystems, it is necessary to assess the balance of its biogeochemical cycle under conditions of varying degrees of anthropogenic load.

According to A. Diener & P. Mudu (2021), air pollution worldwide is responsible for over 4 million premature deaths annually. A study by A. Francini *et al*. (2022) demonstrated the crucial role of urban green spaces in reducing air pollution from particulate matter (dust) and aerosols in urban environments. Scientists M. Khodadadi *et al*. (2024) concluded in their study that particulate matter is the primary pollutant with heavy metals, which are absorbed by tree leaves. Research by S. Maksimtsev *et al*. (2021) established that roadside protective forest belts reduce the concentration of dust and aerosols in the atmosphere, which in turn leads to the accumulation of heavy metals in the soil, forest litter, and plant phytomass. At the same time, litter is a key component of the forest ecosystem that regulates the migration processes and bioavailability of chemical elements for plants (Montemagno *et al*., 2022). Meanwhile, in the research of N. Ryzhenko *et al*. (2020), it was shown that the absorption of heavy metals by urban green spaces and suburban forest ecosystems affects the balance of the functioning of biogeochemical cycles of chemical elements and leads to changes in the functional state of green spaces, reducing their resistance to pollutants, including as a result of the appearance of phytotoxic effects. In particular, A. Diener & P. Mudu (2021) showed an increase in defoliation of evergreen plantings in urban park ecosystems during periods of maximum air pollution during the heating season.

Nickel is one of the priority pollutants in atmospheric air. Despite this, the number of studies on its accumulation and migration in forest ecosystems is rather limited. Anthropogenic emissions of nickel, in terms of potential toxicity, are more significant than natural sources of its entry into the environment. It has been established that about 90% of global anthropogenic nickel emissions come from the combustion of petroleum products, which determines its danger specifically for urban ecosystems and the health of urban populations (Begum *et al.,* 2022). It has been shown that nickel causes phytotoxic effects at a concentration of 135 mg/kg in sod-medium podzolic soils and 150 mg/kg for typical low-humus chernozems (Ryzhenko, 2018). Therefore, as a result of the absorption of heavy metals by plants from the atmosphere and soil, a significant increase in their concentration in the forest litter and their subsequent entry into the soil has been shown, which determines their availability for root absorption by plants and poses a potential threat to the normal functioning of forest ecosystems (Maksimtsev *et al.*, 2021; Montemagno *et al.*, 2022). While root uptake from the soil is the primary pathway for Ni entry into higher plants, the possibility of its foliar uptake by plant leaf biomass directly from the atmosphere has been confirmed (Oliveira *et al.*, 2024). Researchers E.F. Infante *et al.* (2021) note that the phenomenon of biomagnification is not typical for nickel in terrestrial ecosystems, and therefore the assessment of absolute values of its accumulation in plant phytomass cannot serve as a correct criterion for the degree of environmental pollution. Therefore, to understand the consequences of nickel entry into green spaces in urbanised environments, it is necessary to analyse the features of the functioning of its biogeochemical cycle under varying degrees of anthropogenic load to assess the balance of fluxes of input and loss of this chemical element and to establish the key ecosystem components that ensure its accumulation.

Hornbeam forests are a zonal type of broadleaved forest ecosystem in the Middle Dnipro

Region that play an important nature conservation role. At the same time, the extremely high efficiency of air purification from heavy metals by common hornbeam plantations in linear protective forest belts of highways has been demonstrated (Maksimtsev *et al.*, 2021). Research by A. Splodytel *et al.* (2021) established a significant accumulation of Mn, Ti, and Pb by common hornbeam. It has been shown that the common hornbeam has a high potential for phytoremediation of soils contaminated with Pb and Zn (Opeña *et al.*, 2022).

Monospecific ecosystems of hornbeam forests are a convenient model for establishing the patterns of functioning of biogeochemical migration systems of heavy metals in broad-leaved forests and determining the criteria for their resistance to polymetallic pollution, and the assessment of the balance of nickel cycle fluxes of these ecosystems, which have undergone varying degrees of anthropogenic impact, has become the aim of a long-term and comprehensive study. To achieve which the following tasks were performed: to establish the features of nickel distribution in soil horizons and its content in groundwater of model forest ecosystems to assess accumulation and vertical migration; to determine the concentration of nickel in atmospheric precipitation and to estimate the annual volumes of its input fluxes into model forest ecosystems, to determine the features of the dynamics of forest litter formation and the content of nickel in its composition to assess its role in the processes of functioning of the biogeochemical migration system "leaf-litter-soil"; to analyse the dynamics of nickel accumulation in the phytomass of the main tree species of the hornbeam forest and to conduct a quantitative assessment of the fluxes of metal input in the composition of leaf fall into the forest litter and soil; and to assess the balance of biogeochemical migration systems of nickel in model forest ecosystems and to determine the ecological factors that determine the features of their functioning.

MATERIALS AND METHODS

To conduct a comparative assessment of the features of the Ni biogeochemical migration system, two model forest ecosystems of the Ukrainian nature reserve fund were selected: a hornbeam forest of the Holosiivskyi National Nature Park (NNP), which is a unique forest massif within the metropolis of Kyiv, and the Kaniv Nature Reserve, which is one of the oldest forest reserves in Ukraine and, accordingly, represents conditions that are as close to natural as possible. The model plots of the selected hornbeam forests in the nature reserves of the Middle Dnipro Region are similar according to the forest inventory data and are located on flat horizontal sections of the plateau (Table 1).

Table 1. Taxonomic description of model forest ecosystems and indicators of their biological productivity

Quartet/Plot	Area, ha	Stand characteristics	Layer	Age, years	Height, m	Diameter, cm	Yield class	Forest type	Density	Timber stock, m³/ha	Stock of phytomass of dominant tree species, t/ha				Annual phytomass increment, t/ha
											Trunk with bark	Branches	Leaves	Roots	
Holosiivskyi NNP															
26/9	0.8	10Ca. be.	1	70	25	28	I	D_2HO	0.70	320	282.1	45.5	9.3	98.4	2.76
Kaniv Nature Reserve															
15/2	7.0	10Ca. be	1	100	25	28	II	D_1HO	0.70	300	259.7	45.2	7.9	88.6	1.06

Source: developed by the authors based on Ya. Didukh *et al*. (2024)

According to calculations of biological productivity, the mass of timber in the trunks (with bark), branches, and roots of a fresh hornbeam forest D_2HO of the first yield class I, aged 70 years, which corresponds to the hornbeam forest of the Holosiivskyi NNP, is 426 t/ha (Didukh *et al.*, 2024). For the hornbeam forest of the Kaniv Nature Reserve, where the stand corresponds to a dry hornbeam forest D_1HO of the first yield class II, aged 100 years, this value is 393.5 t/ha. Of this, 66%, or

282.1 t/ha for the Holosiivskyi NNP and 259.7 t/ha for the Kaniv Nature Reserve, falls on the trunks with bark. Atmospheric precipitation was collected using rain gauges placed at ground level under the forest canopy, spaced 2 m from the tree trunk according to the method of R. Laskowski *et al.* (1995). The collectors were constructed from plastic containers and funnels with a diameter of 13 cm. The funnels were protected from the ingress of solid particles by a polypropylene mesh with a 5×5 mm mesh size. 4-8 rain collectors were placed on each experimental plot. Water sampling for analysis in the cold period of the year was carried out monthly, in case of heavy rains and in the summer months – within a day after the end of precipitation. To determine the concentration of heavy metals in water, a combined sample from all collectors of the corresponding experimental plot was used. If the volume of collected precipitation exceeded 1 L, the combined sample was divided into multiples of 1 L.

To assess vertical groundwater flow, stationary *zero-tension pan lysimeters* were used. These devices provide a means of measuring the movement of soil water and dissolved substances *in situ* (Schmidt & Henry, 2008; Makowski *et al.*, 2020). The lysimeters were fabricated from sanitary polypropylene without the use of metal components. Each lysimeter had an area of 0.1 m^2. Four lysimeters were installed at a depth of 10-12 cm in each plot to collect vertical soil water flux from the humus horizon. Soil water samples from the lysimeters were collected after intensive rainfall during the growing season or as they filled, once a month. In the case of a small volume of lysimeter water, samples from individual lysimeters were combined to obtain a combined sample volume of 1 L. Samples of atmospheric precipitation and lysimeter water were filtered through medium filtration “white tape” paper filters (pore diameter 7-20 μm) and concentrated by evaporating 1 L to 10 mL on a sand bath without bringing it to a boil, with the addition of 1 mL of 4 N HNO_3 (“special purity”) per 1 L of sample (Nabivanets *et al.*, 1996).

The study was conducted following the Convention on Biological Diversity (1992). Sampling plots for soil sample collection were determined according to DSTU GOST 17.4.3.01:2019 (2019). Point samples were taken using the “envelope” method in three 3×3 m plots from two genetic horizons: the humus horizon at a depth of 5 cm and the eluvial horizon at a depth of 20-25 cm. A combined sample weighing at least 1 kg was prepared for each sampling plot. The combined soil samples were dried at a temperature of 95°C, ground in a porcelain mortar, and the volume was reduced by quartering according to DSTU ISO 11464:2007 (2007). To determine the concentration of heavy metals, *aqua regia* extraction was used by treating 0.5 g of each soil sample with 2 mL of HNO_3 and 6 mL of HCl for 2 hours according to DSTU ISO 11466-2001 (2001).

Samples of forest litter were collected monthly throughout 2018-2023 from 1×1 m plots. The collected material was dried at room temperature and weighed to determine the litter stock. A portion of the litter sample was used to determine the fractional composition, separating leaves, branches, bark, seeds, and undifferentiated fermented mass (dry rot). The mass of each fraction was determined separately. Samples of leaf phytomass of common hornbeam were collected manually from low-hanging branches, or where possible, from fallen trees and branches. Wood samples were collected from fallen trees or large skeletal branches with a diameter of more than 10 cm. Dried samples of phytomass and forest litter were ashed for 12 hours at 450°C. The resulting ash weight of 1 g was boiled in 15 mL of 4 M HNO_3 for 30 minutes. After cooling, the solution was filtered through a paper filter. The filter was washed twice with distilled water to a volume of 10 mL. The determination of heavy metal concentrations was carried out at the Department of Ecology and Zoology of the Educational and Scientific Centre “Institute of Biology and Medicine” using an atomic absorption spectrophotometer C115-M1 (SELMI, Ukraine). Analysis was performed by direct introduction of the liquid sample into an acetylene-air flame. A deuterium background corrector was used to compensate for non-selective absorption by the flame. Analytical data were recorded using a KAS-101 computer-analytical complex. Samples from 2020-2021 were also analysed by inductively coupled plasma optical emission spectrometry (ICP-OES) using an iCAP 6000 ICP Spectrometer (Thermo Fisher Scientific Corporation, USA) at the Institute of Botany of the Leibniz University Hannover (Turcios *et al.*, 2021). The concentration of Ni in solid samples (soil, litter, plant material) was expressed in mg/kg of dry matter, in atmospheric precipitation water – in μg/L, and groundwater – in mg/L. Mean values were represented as the arithmetic mean (*X*), and their variability was assessed as the standard deviation (*SD*). The normality of the data distribution was established using the *Shapiro – Wilk's W-test* as the most sensitive according to Guidance for Data Quality Assessment (2000) and M. Conti *et al.* (2005).

As most measurements were limited in number (3-5 measurements), the non-parametric *Mann-Whitney U-test* was used for pairwise comparisons of sample means with a significance level of $p < 0.05$, as it is the most powerful for small samples according to Guidance for Comparing Background and Chemical Concentrations in Soil for CERCLA Sites (2002). The statistical significance of differences between multiple samples was determined using the One-Way ANOVA (ANOVA Calculator, n.d.). In conducting the research, the authors adhered to ethical norms of ecological design and experimental planning in urban green landscapes (Pataki *et al.*, 2021). Thus, using the aforementioned methods, a comprehensive analysis was conducted on the distribution of Ni concentrations in the main components of model ecosystems of hornbeam forests in the Middle Dnipro Region – atmospheric precipitation, soil genetic horizons, groundwater, leaf litter and leaf fall, wood, and leaf phytomass of common hornbeam. Annual volumes of atmospheric precipitation, the amount of soil infiltration, the dynamics of forest litter stocks, and the phytomass of common hornbeam were determined. This allowed for the determination of Ni stocks in the specified ecosystem components and the assessment of the magnitude of Ni migration fluxes between them.

RESULTS AND DISCUSSION

Nickel concentrations in the genetic horizons of the soils in the studied model ecosystems did not differ significantly: in the Holosiivskyi NNP, the humus layer contained an average of 11.2 ± 1.1 mg/kg, and in the eluvial layer – 9.6 ± 3.3 mg/kg; in the Kaniv Nature Reserve, the average nickel concentration in the humus layer was 8.3 ± 2.1 mg/kg, and in the eluvial layer it was slightly higher – 10.5 ± 3.9 mg/kg, however, the difference was statistically insignificant (*Mann–Whitney*, $p = 0.129$). Thus, the uniform distribution of nickel concentration across the soil profile may indicate its vertical migration in the soils of both studied ecosystems. A similar situation was described for the vertical distribution of Ni in forest ecosystems of the parks "Levice" and "Želiezovce", in south-western Slovakia (Pivková *et al.*, 2022). Nickel concentrations in the soils of the studied ecosystems did not exceed the MPC for hazardous substances in soils (Resolution of the Cabinet of Ministers of Ukraine No. 1325, 2021). Also, no exceedances of background nickel concentration values for arable lands of the forest-steppe zone were found, which is on average 26 mg/kg (range 10-80 mg/kg) (Chornyy, 2018) and were lower than the total nickel content in the soils of the Holosiivskyi forest, which was 20 mg/kg (Samchuk *et al.,* 2019).

Given the absence of significant differences in soil nickel concentrations between the studied hornbeam forest ecosystems, estimates of metal stocks in genetic horizons were found to be similar. Specifically, in the humus layer of Holosiivskyi NNP and Kaniv Nature Reserve, metal stocks were 6.73 ± 0.60 $kg \times ha^{-1}$ and 4.95 ± 1.30 $kg \times ha^{-1}$, respectively. In the eluvial horizon, due to its greater thickness, the mass of accumulated metal was 21.6 ± 7.3 $kg \times ha^{-1}$ and 23.6 ± 6.4 $kg \times ha^{-1}$, respectively. Lysimetric analysis of groundwater allowed for the estimation of the magnitude of vertical migration fluxes of heavy metals to the eluvial horizon of the soils of the studied ecosystems. The total annual soil infiltration for the hornbeam forest of Holosiivskyi NNP was 13.5 L/m^2 (135 $m^3 \times ha^{-1}$), and for the Kaniv Nature Reserve – 29.3 L/m^2 (293 $m^3 \times ha^{-1}$). In the conditions of the Holosiivskyi NNP ecosystem, the maximum nickel concentration in groundwater was characteristic of July and was 4.81 ± 0.59 mg/L. In the Kaniv Nature Reserve, its maximum concentration was observed in November-December and corresponded to the range of 2.28-2.83 mg/L, which is 1.7-2.1 times lower.

Despite differences in maximum concentration, the average annual concentration of Ni in lysimeter waters of the studied ecosystems was not statistically different and was 1.83 ± 0.22 mg/L for the Holosiivskyi NNP ecosystem and 1.74 ± 0.21 mg/L for the Kaniv Nature Reserve. Similar concentrations of Ni in groundwater were shown in a review by R. Michopoulos (2021).

Specifically, in groundwater in brown forest soils at a depth of 35 cm, the concentration of Ni reached 4 mg/L, while in podzolic soils, the concentration of Ni was 2 mg/L, which the author explains by the higher content of organic matter in podzolic soils. The calculated value of the vertical migration flux of Ni with groundwater to the eluvial horizon in the conditions of the Kaniv Nature Reserve ecosystem during the year was 51.1 ± 6.2 g×ha^{-1}×year^{-1}, which is 2.9 times higher than the level established for the Holosiivskyi NNP ecosystem, where it was 17.6 ± 1.9 g×ha^{-1}×year^{-1}, reflecting the larger volume of soil infiltration in the Kaniv Nature Reserve.

It is well-known that wet deposition via atmospheric precipitation is a primary pathway for heavy metals into terrestrial ecosystems (Hůnová *et al.*, 2023). Moreover, transboundary transport of air masses and wet deposition processes determine the input of most chemical elements into European forest ecosystems (Schlutow *et al.*, 2021). The average concentration of Ni in atmospheric precipitation within the studied ecosystems did not differ significantly and was 4.5 ± 0.9 µg/L in the Holosiivskyi NNP ecosystem and 4.1 ± 0.4 µg/L in the Kaniv Nature Reserve ecosystem (*Mann-Whitney,* p = 0.684). The established range clearly corresponds to the average Ni concentration in atmospheric precipitation for background regions of central Greece, which was 4.58 µg/L (Michopoulos, 2021), but exceeded the value shown by N. Ezaldin (2023) for Iraq (Kurdistan) – 1.96 µg/L, which may reflect the overall level of industrial development in the region. It was established that the concentration of Ni in atmospheric precipitation under the canopy of the Holosiivskyi NNP was highest at the beginning of the growing season in May-June, after which there was a gradual decrease in its concentration (Fig. 1).

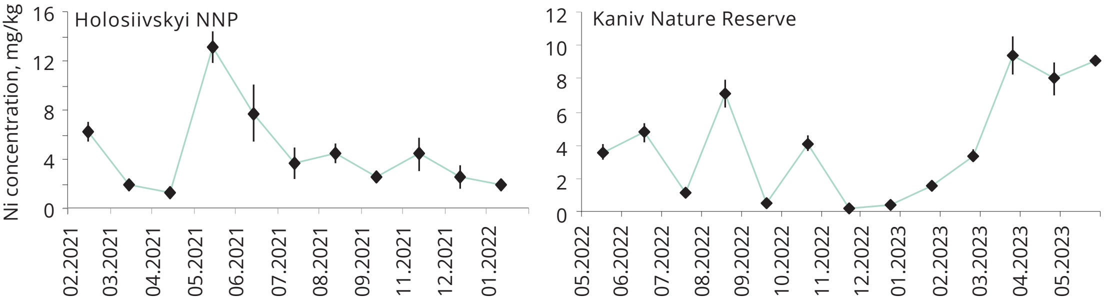

Figure 1. Annual dynamics of Ni concentration in atmospheric precipitation in hornbeam forest ecosystems of Holosiivskyi NNP and Kaniv Nature Reserve

Source: developed by the authors

In the Kaniv Nature Reserve, the concentration of Ni exhibited significant variability with a tendency to increase during the spring period. Such seasonal dynamics may reflect processes of metal leaching from young leaves, as the main accumulation of Ni occurs during its unfolding and growth through root uptake from the soil, as shown by the studies of A. Paul *et al.* (2021) and R. Michopoulos (2021).

An assessment of the annual input of Ni via atmospheric precipitation for both ecosystems revealed similar values: according to the Holosiivskyi NNP ecosystem, 29.1 ± 4.1 g×ha^{-1}×year^{-1} was deposited during 2021, and for the Kaniv Nature Reserve ecosystem, it was 38.8 ± 4.1 g×ha^{-1} ×year^{-1}. Thus, on the scale of large forest areas, the volumes of wet deposition of metals with atmospheric precipitation are more influenced by the regional transport of pollutants with air masses than by local emissions from individual pollution sources near the model forest ecosystem, which is confirmed by the results of studies by P. Michopoulos (2021). Analysis of the seasonal dynamics of heavy metal concentrations in the wood of common hornbeam throughout the year showed no statistically significant differences.

The average concentration of Ni in the wood of common hornbeam from the Holosiivskyi NNP was 2.63 ± 0.25 mg/kg, while in the Kaniv Nature Reserve, it was 3 times lower at 0.88 ± 0.26 mg/kg. To estimate the stocks of accumulated Ni in woody biomass, it was conditionally assumed that its concentration did not significantly differ in the wood of trunks, branches, and roots (some wood samples were obtained from large skeletal branches). For the Holosiivskyi NNP ecosystem, it was established that the wood of common hornbeam contained high stocks of Ni, estimated at 11.2 ± 1.25 kg/ha, while in the Kaniv Nature Reserve they were significantly lower and amounted to 0.35 ± 0.02 kg/ha. The dynamics of Ni concentration in the leaf biomass of common hornbeam during the growing season showed significant differences in the studied model forest ecosystems (Fig. 2).

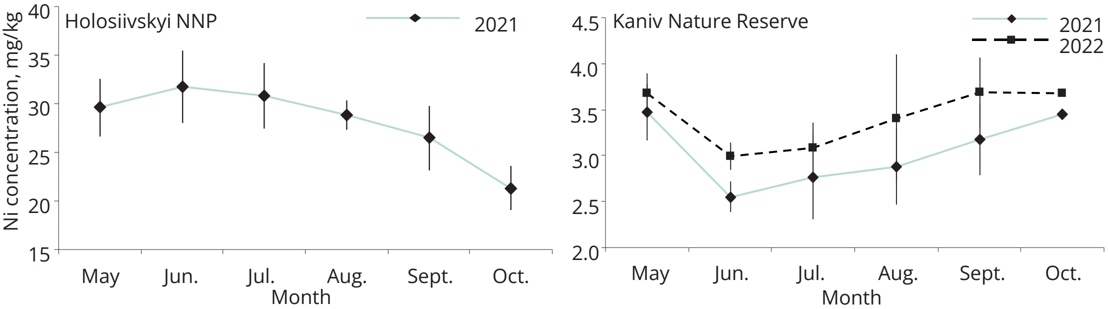

Figure 2. Dynamics of Ni concentration in the leaf biomass of common hornbeam during the growing season in hornbeam forest ecosystems

Source: developed by the authors

In the Holosiivskyi NNP, the maximum accumulation of the metal was characteristic of May-June, when the concentration was 29.6-31.7 mg/kg. Subsequently, there was a gradual decrease in the metal concentration in the leaves, reaching a minimum before leaf fall in October at 21.3 ± 2.28 mg/kg (1.5 times less compared to June). Such accumulation of the metal at the beginning of the growing season indicates its predominant intake from the soil during the process of root feeding of plants, as shown by other researchers (Paul *et al.*, 2021; Tisserand *et al.*, 2024). The subsequent decrease in metal concentration may be associated with both an increase in leaf biomass and dilution of the initial amount of metal ("*dilution effect*"), as well as leaching of the metal from the leaf biomass by atmospheric precipitation (Tőzsér *et al.*, 2023).

Conversely, in the Kaniv Nature Reserve, the concentration of Ni in common hornbeam leaves did not change significantly throughout the growing season (ANOVA, $p = 0.089$), although it was slightly higher in May (3.5-3.7 mg/kg) than in June (2.6-2.9 mg/kg). Subsequently, up until the leaf fall, there was a tendency for Ni concentration to increase. A similar constancy of Ni concentration throughout the growing season was described for *Phyllanthus rufuschaneyi*, where the metal concentration differed by only 0.2% in young and old leaves, indicating the formation of a metal stock in the early stages of leaf growth (Tisserand *et al.*, 2024). To estimate the amounts of leaf litter input, the results of the analysis of the seasonal dynamics of the component composition of the forest litter in the studied hornbeam forests were used, assuming that the mass of fallen leaves does not change significantly within a month after its entry into the litter. Calculations of the amount of leaf litter that entered the litter of both ecosystems during the year showed close values: for the Holosiivskyi NNP – 3,200 kg×ha^{-1}, for the Kaniv Nature Reserve – 2,500-3,600 kg×ha^{-1} (Table 2).

Table 2. Calculated values of Ni input into the forest litter via leaf fall in hornbeam forest ecosystems of Holosiivskyi NNP and Kaniv Nature Reserve

Month/ Year	Mass of leaf fraction in the litter, kg×ha^{-1}		Leaf fall input, kg×ha^{-1}	Amount of Ni input into forest litter via leaf fall, g×ha^{-1}	
	X	SD		X	SD
Holosiivskyi NNP					
07.21	400	50	-	-	
08.21	1,500	40	1,100	31.7	01.7

Table 2. Continued

Month/ Year	Mass of leaf fraction in the litter, kg×ha^{-1}		Leaf fall input, kg×ha^{-1}	Amount of Ni input into forest litter via leaf fall, g×ha^{-1}	
	X	SD		X	SD
09.21	1,900	150	400	10.6	1.3
10.21	3,200	140	1,300	27.7	3.0
11.21	3,300	200	100	2.1	0.2
12.21	3,600	200	300	6.4	0.7
Total			3,200	78.5	6.8
Kaniv Nature Reserve					
09.21	320	50	-	-	-
10.21	480	60	1,550	5.3	0.6
11.21	570	40	950	3.3	0.4
Total			2,500	8.6	1.0
06.22	30	10	-	-	-
07.22	40	10	120	0.4	0.02
08.22	80	20	310	1.1	0.1
09.22	140	10	650	2.4	0.4
10.22	260	20	1,190	4.4	0.4
11.22	340	40	830	3.0	0.3
12.22	390	30	500	1.8	0.2
Total			3,600	13.1	1.5

Source: developed by the authors

To calculate the flow of Ni in fallen leaves, the concentration in the leaves for the corresponding month and the mass of leaf litter that accumulated during that time in the forest litter were considered. It was established that the beginning of leaf fall and the formation of a new annual litter in hornbeam forests in the Middle Dnipro Region begins in July-August and ends in November-December. Despite changes in the concentration of Ni in the biomass of common hornbeam during the growing season, the main factor determining its input into the litter is the amount of leaf fall per month. As a result, from August to December 2021, 78.5 ± 6.8 g×ha^{-1} of Ni entered the litter of the hornbeam forest in Holosiivskyi NNP, while in the Kaniv Nature Reserve, this value in 2021 was 6-9 times lower and amounted to 8.6 ± 1.0 g×ha^{-1}, and in 2022 – 13.1 ± 1.5 g×ha^{-1}.

The concentration of Ni in the forest litter of the Holosiivskyi NNP during 2018-2019 and 2020-2021 ranged from 5.7 to 17.6 mg/kg; in the Kaniv Nature Reserve, it was 4.2-5.4 times lower, at 1.3-3.2 mg/kg. The seasonal dynamics of Ni concentration in the forest litter with the onset of leaf fall is characterised by an increase, with maximum metal accumulation occurring in November (Fig. 3).

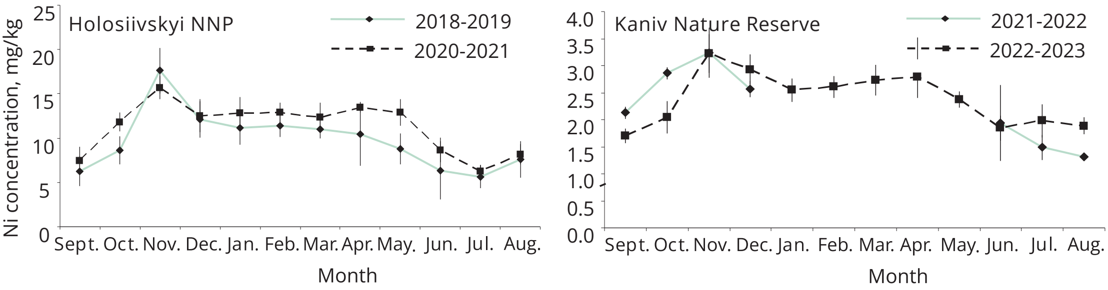

Figure 3. Annual dynamics of Ni concentration in the forest litter of the hornbeam forests in Holosiivskyi NNP and Kaniv Nature Reserve

Source: developed by the authors

In the Holosiivskyi NNP, the maximum concentration of Ni in November 2018 and 2020 was 17.6 ± 0.1 mg/kg and 15.7 ± 0.1 mg/kg, respectively. Meanwhile, the leaf biomass of common hornbeam in October before leaf fall contained 21.3 ± 2.3 mg/kg of this chemical element. In the ecosystem of the Kaniv Nature Reserve, the maximum concentration of Ni in the litter in November 2021 was 3.2 ± 0.5 mg/kg, and in 2022, it was 3.2 ± 0.4 mg/kg, which is 4.9-5.4 times less than in the Holosiivskyi NNP. The leaves of common hornbeam in October before falling contained 3.5-3.7 mg/kg of this chemical element. Thus, leaf fall serves as an important source of Ni input into the forest litter of the studied hornbeam forests. A similar phenomenon has been described by many other researchers, who have shown that leaf fall is the main flux that enriches the soil with Ni and Zn (Michopoulos, 2021; Bani *et al.*, 2024; Tisserand *et al.*, 2024).

An assessment of the dynamics of accumulated Ni in the forest litter of model forest ecosystems showed that it corresponds to the annual cycle of concentration changes – during the period of active formation of the forest litter, the stocks of the metal accumulate, reaching a maximum in November (Fig. 4).

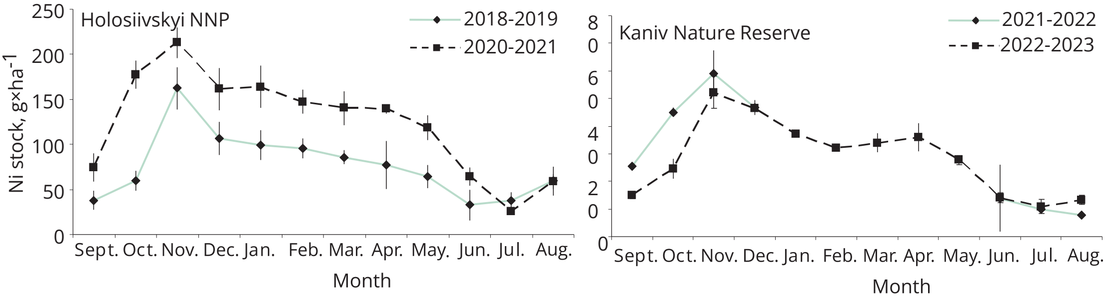

Figure 4. Annual dynamics of Ni in the forest litter of the hornbeam forests in Holosiivskyi NNP and Kaniv Nature Reserve

Source: developed by the authors

In the Holosiivskyi NNP ecosystem, the mass of accumulated Ni in the forest litter was significantly higher, 1.3-7.5 times greater, than the amount of the metal in the forest litter of the Kaniv Nature Reserve ecosystem. Moreover, in 2020-2021, the stocks of Ni in the forest litter of the hornbeam forest of the Holosiivskyi NNP were 1.3-3.0 times higher due to larger volumes of formed litter. In November 2018, in the Holosiivskyi NNP, the amount of Ni in the litter was 162 ± 40 g×ha^{-1}, and in November 2020, it was 213 ± 10 g×ha^{-1}. By December 2018, in the hornbeam forest of the Holosiivskyi NNP, the amount of Ni in the litter had decreased by 34% from the maximum volume in November, and in December 2020, this decrease in Ni stocks was 24%. In the ecosystem of the Kaniv Nature Reserve, in November 2021, the mass of accumulated metal in the litter was 59 ± 83 g×ha^{-1}, and in November 2022, it was 52 ± 6 g×ha^{-1}. Just one month later, in December 2021, there was a decrease in Ni stocks to 47 ± 3 g×ha^{-1} (by 21%), and in December 2022, to 47 ± 7 g×ha^{-1} (by 20%). Subsequently, from December to July-August, there was a gradual decrease in the amount of the chemical element until reaching a minimum at a level of 25-33 g×ha^{-1} in the Holosiivskyi NNP and 8-11 g×ha^{-1} in the Kaniv Nature Reserve, which was 79-88% of the metal accumulated in autumn.

To assess heavy metal fluxes in the model ecosystems, a 13-month period was chosen for which a complete dataset is available on metal stocks in the forest litter, volumes of metal input from atmospheric precipitation, lysimetric measurements, and estimates of the mass of fallen leaves in the forest litter. For the hornbeam forest ecosystem of the Holosiivskyi NNP, the assessment was conducted for the period from January 2021 to January 2022, and the ecosystem of the Kaniv Nature Reserve – from June 2022 to July 2023.

Over the year, the total accumulation of Ni in the forest litter of the hornbeam forest in the Holosiivskyi NNP was 115 ± 17 g×ha^{-1}×year^{-1}, which corresponds to the calculated value of the total input of the metal into the ecosystem through leaf fall and wet deposition processes from the atmosphere – 108 ± 10 g×ha^{-1}×year^{-1} (Table 3).

Table 3. Balance of Ni inputs and outputs in the biogeochemical cycle of the hornbeam forest ecosystem of the Holosiivskyi NNP

Month/Year	Ni stock, g×ha^{-1}		Accumulation of Ni in the forest litter/ Output from the forest litter, g×ha^{-1}		Total Ni input (leaf fall + atmospheric precipitation),g×ha^{-1}		Ni input from leaf fall, g×ha^{-1}		Ni input from atmospheric precipitation, g×ha^{-1}		Soil Ni infiltration, g×ha^{-1}	
	X	SD	X	SD	X	X	SD	SD	X	SD	X	SD
01.2021	164.0	6.5	-	-	-	-	-	-	-	-	-	-
02.2021	147.4	14.3	-16.7	10.4	6.5	-	-	-	6.51	0.82	2.05	0.25
03.2021	140.2	16.2	-7.1	15.3	0.5	-	-	-	0.50	0.05	-	-
04.2021	139.3	10.5	-0.9	13.4	0.6	-	-	-	0.59	0.13	-	-
05.2021	118.5	7.9	-20.8	9.2	9.8	-	-	-	9.83	0.98	4.48	0.55
06.2021	64.4	1.9	-54.1	4.9	1.8	0.5	-	-	1.78	0.55	2.70	0.33
07.2021	25.3	0.2	-39.1	1.1	2.3	0.8	-	-	2.25	0.81	6.11	0.75
08.2021	58.8	0.9	33.4	0.5	34.7	2.2	31.7	1.7	2.97	0.52	0.10	0.01
09.2021	58.8	3.0	0.1	2.0	11.1	1.4	10.6	1.3	0.55	0.08	-	-
10.2021	87.2	1.3	28.4	2.1	27.7	3.0	27.7	3.0	-	-	-	-
11.2021	107.0	5.9	19.7	3.6	3.5	0.7	2.1	0.2	1.41	0.45	-	-
12.2021	140.5	12.2	33.5	9.1	8.2	1.3	6.4	0.7	1.76	0.66	2.19	0.27
01.2022	101.8	10.8	-38.7	11.5	1.0	-	-	-	0.98	0.07	-	-
Total accumulation, g×ha^{-1}×year^{-1}			115.1	17.3	107.7	9.9	78.5	6.8	29.1	4.1	-	-
Total output, g×ha^{-1}×year^{-1}			-177.4	26.7	-	-	-	-	-	-	17.63	1.90
Ni accumulation in annual tree growth, g×ha^{-1}×year^{-1}			7.3	0.8								
Ni stocks in tree biomass, g/ha			11,218	1,153								
Ni stocks in 0-5 cm soil layer, g/ha			6,725	637								
Ni stocks in 5-20 cm soil layer, g/ha			21,647	7,347								

Source: developed by the authors

Meanwhile, the main contribution to Ni input was provided by leaf fall, which during the formation of new annual litter during November-December 2021 accounted for 73% of the total amount of the metal. Atmospheric precipitation accounted for 27% of the total amount of the metal – 29 ± 4 g×ha^{-1}×year^{-1}.

The total annual losses of Ni from the forest litter of the hornbeam forest in Holosiivskyi NNP were 177 ± 27 g×ha^{-1}×year^{-1}, which is 1.5 times higher than the amount of accumulated metal – 115 ± 17 g×ha^{-1}×year^{-1}. The imbalance between the accumulation and output of Ni from the forest litter in Holosiivskyi NNP is 62 g×ha^{-1}×year^{-1}. An analysis of the balance of Ni losses from the forest litter and its input over individual months showed that the forest litter loses more Ni for most of the year than it receives from atmospheric precipitation. At the same time, during the period of active formation of new annual litter in August-October, there is a correspondence between the input of Ni with leaf fall (70 g×ha^{-1} ×year^{-1}) and an increase in its accumulation levels in the forest litter. At the same time, the losses of Ni from the Holosiivskyi NNP ecosystem with vertical groundwater flow per year were only 18 ± 2 g×ha^{-1}×year^{-1}, indicating the absence of active removal of the metal from the hornbeam forest ecosystem of Holosiivskyi NNP.

An assessment of Ni accumulation in the annual growth of common hornbeams revealed significant amounts of the accumulated metal – 7 ± 1 g×ha^{-1}×year^{-1} is fixed annually in the woody biomass of common hornbeams. In the leaf biomass, a significantly larger amount of Ni accumulates annually – 79 ± 7 g×ha^{-1}×year^{-1}, which, after leaf fall, returns to the soil during the decomposition of litter and becomes available for absorption by the root system of common hornbeam. At the same time, there is no active leaching of Ni by groundwater, as evidenced by its higher concentration in the humus layer (11.2 mg/kg) compared to the eluvial layer (9.6 mg/kg). Thus, in the ecosystem of the hornbeam forest of the Holosiivskyi NNP, the main part of the Ni biogeochemical cycle is provided by the "littersoil-plant" system, when Ni is extracted from the soil during root uptake and actively accumulates in the biomass of common hornbeam. The main part of the metal from fallen leaves (about 91%) returns to the soil, from where it is again absorbed by plant root systems, while the other part is fixed in the annual growth of common hornbeam wood. Approximately 91% of the metal from fallen leaves returns to the soil, where it is again absorbed by plant root systems, while the remaining portion is fixed in the annual growth of common hornbeam wood.

The leaching of Ni during vertical migration through the soil profile is negligible, indicating an accumulation of the metal in the ecosystem. A similar situation has been described for soils in Albania, where it was shown that plants absorb Ni from deep soil layers and redistribute it to the upper soil layer, leading to the enrichment of the litter with Ni due to the input of leaf fall (Bani *et al.*, 2024). Such a biogeochemical cycle is sensitive to excessive metal input from external sources, which can lead to the accumulation of Ni in the ecosystem. In particular, a comparison of the amount of Ni entering the hornbeam forest ecosystem of the Holosiivskyi NNP from atmospheric precipitation (29 ± 4 g×ha^{-1}×year^{-1}) and the amounts leached from the soil (18 ± 2 g×ha^{-1}×year^{-1}) indicates a significant imbalance in the biogeochemical cycle of this chemical element. Over the year, the total accumulation of Ni in the forest litter of the hornbeam forest of the Kaniv Nature Reserve was 48 ± 4 g×ha^{-1}×year^{-1} (Table 4).

Table 4. Balance of Ni inputs and outputs in the biogeochemical cycle of the hornbeam forest ecosystem of the Kaniv Nature Reserve

Month/Year	Ni stock, g×ha^{-1}		Accumulation of Ni in the forest litter/ Output from the forest litter, g×ha^{-1}		Total Ni input (leaf fall + atmospheric precipitation), g×ha^{-1}		Ni input from leaf fall, g×ha^{-1}		Ni input from atmospheric precipitation, g×ha^{-1}		Soil Ni infiltration, g×ha^{-1}	
	X	SD	X	SD	X	X	SD	SD	X	SD	X	SD
06.2022	13.82	3.17	-	-	-	-	-	-	-	-	-	-
07.2022	9.82	4.67	-4.00	3.92	4.77	0.55	0.37	0.02	4.40	0.54	1.06	0.13
08.2022	7.85	1.52	-1.97	3.10	3.54	0.39	1.06	0.08	2.48	0.30	-	-
09.2022	14.91	2.18	7.05	1.85	3.74	0.61	2.40	0.45	1.35	0.16	15.72	1.92
10.2022	24.57	5.26	9.66	3.72	7.06	0.77	4.37	0.45	2.69	0.33	-	-
11.2022	52.25	5.83	27.69	5.55	3.49	0.36	3.05	0.31	0.44	0.05	15.00	1.83
12.2022	46.51	7.06	-5.75	6.45	5.55	0.64	1.84	0.19	3.72	0.45	11.28	1.38
01.2023	37.02	6.44	-9.49	6.75	0.14	0.02	-	-	0.14	0.02	-	-
02.2023	32.11	5.16	-4.91	5.80	0.27	0.03	-	-	0.27	0.03	-	-
03.2023	33.95	4.52	1.84	4.84	0.49	0.06	-	-	0.49	0.06	-	-
04.2023	35.88	6.02	1.92	5.27	1.18	0.14	-	-	1.18	0.14	-	-
05.2023	27.72	4.39	-8.16	5.21	10.03	1.22	-	-	10.03	1.22	8.08	0.99

Table 4. Continued

Month/Year	Ni stock, g×ha^{-1}		Accumulation of Ni in the forest litter/ Output from the forest litter, g×ha^{-1}		Total Ni input (leaf fall + atmospheric precipitation), g×ha^{-1}		Ni input from leaf fall, g×ha^{-1}		Ni input from atmospheric precipitation, g×ha^{-1}		Soil Ni infiltration, g×ha^{-1}	
	X	SD	X	SD	X	X	SD	SD	X	SD	X	SD
06.2023	14.22	3.57	-13.49	3.98	6.33	0.77	-	-	6.33	0.77	-	-
07.2023	10.93	4.02	-3.30	3.80	5.25	0.05	-	-	5.25	0.00	-	-
Total accumulation, g×ha^{-1}×year^{-1}			48.16	4.25	51.83	3.35	13.08	1.49	38.75	4.09	-	-
Total output, g×ha^{-1}×year^{-1}			-51.06	4.88	-	-	-	-	-	-	51.14	6.24
Ni accumulation in annual tree growth, g×ha^{-1}×year^{-1}			0.94	0.07								
Ni stocks in tree biomass, g/ha			347.2	24.3								
Ni stocks in 0-5 cm soil layer, g/ha			4,953	1,340								
Ni stocks in 5-20 cm soil layer, g/ha			23,637	6,409								

Source: developed by the authors

The estimated total annual loss of Ni from the litter was found to be 51 ± 5 g×ha^{-1}×year^{-1}, which is not statistically significantly different (*Mann–Whitney*, $p = 0.109$) from the total accumulation of the metal (the difference is only 3 g×ha^{-1}×year^{-1}). This indicates a balanced state of the nickel biogeochemical cycle in the hornbeam forest of the Kaniv Nature Reserve, where the amount of metal entering the litter is balanced by the processes of its output from the ecosystem.

The calculated total input of Ni from leaf fall and wet deposition from atmospheric precipitation is a similar value – 52 ± 13 g×ha^{-1}×year^{-1}. Unlike the Holosiivskyi NNP ecosystem, in the conditions of the Kaniv Nature Reserve, 75% of the total input of Ni into the hornbeam forest is determined by processes of wet deposition with atmospheric precipitation – 39 ± 4 g×ha^{-1}×year^{-1}, and 25% – by the amount of metal that entered as part of fallen leaves (13 ± 2 g×ha^{-1}×year^{-1}). In the conditions of the Holosiivskyi NNP ecosystem, wet deposition as part of atmospheric precipitation gives a similar value of metal input into the ecosystem – 29 ± 4 g×ha^{-1}×year^{-1}. A comparison of the total Ni input into the Kaniv Nature Reserve ecosystem (52 ± 3 g×ha^{-1}×year^{-1}), groundwater runoff (51 ± 6 g×ha^{-1}×year^{-1}), and the total amount of Ni output from the litter (52 ± 5 g×ha^{-1}×year^{-1}) indicates the presence of a balance between the input and loss of metal in the ecosystem.

However, unlike the Holosiivskyi NNP ecosystem, in the Kaniv Nature Reserve, an increase in metal concentration to 10.5 ± 3.9 mg/kg is observed in the eluvial soil horizon at a depth of 20 cm, which may indicate its active vertical migration through the soil profile and leaching from the upper humus horizon. In particular, the volumes of groundwater runoff of Ni over the year exceed 1.3 times the amount of metal entering from atmospheric precipitation, which is 51 ± 6 g×ha^{-1}×year^{-1} and 39 ± 4 g×ha^{-1}×year^{-1}, respectively. Therefore, the main pathway for Ni input into the Kaniv Nature Reserve ecosystem, unlike the Holosiivskyi NNP ecosystem, is atmospheric precipitation, which accounts for 75% of the total metal input. The amount of Ni entering with atmospheric precipitation corresponds to the amount of metal that was removed during leaching by vertical groundwater flow to the eluvial layer. The fixation of Ni in the annual growth of common hornbeam wood is insignificant and amounts to 0.94 ± 0.07 g×ha^{-1}×year^{-1}.

A review of recent scientific publications has revealed a lack of comprehensive studies on the biogeochemical cycle of Ni in European forest ecosystems. Most publications are dedicated to studying the accumulation of Ni by plants in model experiments to use them for phytoremediation of contaminated soils (Rosatto *et al.*, 2021; Samreen *et al.*, 2021; Reis *et al.*, 2024). In natural ecosystems, research focuses on studying the features of Ni accumulation in individual components of forest ecosystems – biomass (McQueen *et al.*, 2023), litter (Zhao *et al.*, 2024) and soil (Brandão *et al.*, 2022). In his review, P. Michopoulos (2021) attempted to estimate the magnitude of Ni fluxes in European forest ecosystems, but a complete assessment of the balance of the metal's biogeochemical cycle was not carried out. The most complete analysis of the Ni biogeochemical cycle was conducted in the studies of A. Paul *et al.* (2021) and R. Tisserand *et al.* (2024), that dedicated to studying the functioning of specific tropical ecosystems of Ni hyperaccumulator plants used for industrial extraction of metallic nickel from Ni-rich soils. Therefore, the results of such studies can only be partially used to compare the processes of Ni migration in European broad-leaved forest ecosystems.

As a result of the analysis of the main Ni fluxes in model hornbeam forest ecosystems of the Middle Dnipro Region, significant differences in the functioning of the metal's biogeochemical cycle were revealed. In the Holosiivskyi NNP ecosystem, the main pathway for metal input is leaf fall, which accounts for 73% of the metal volume. At the same time, in the Kaniv Nature Reserve, leaf fall accounts for only 25% of the total metal input (Fig. 5).

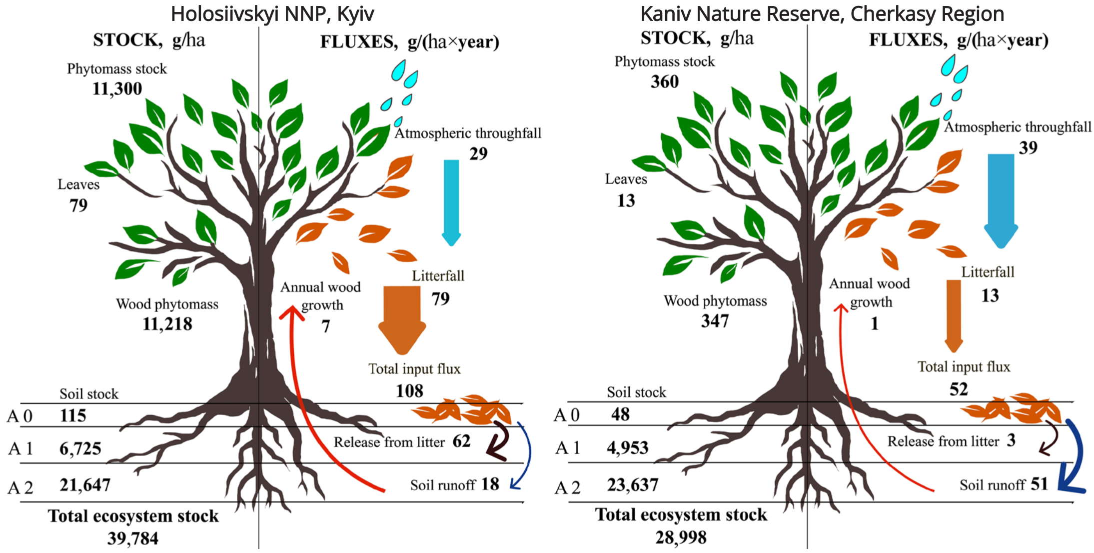

Figure 5. The biogeochemical cycle of Ni in the hornbeam forest ecosystems of the Holosiivskyi NNP and the Kaniv Nature Reserve

Source: developed by the authors

Similar values were indicated in the study by R. Tisserand *et al.* (2024), where leaf fall from the tropical nickel hyperaccumulator tree *P. rufuschaneyi* provided 74% of the total metal flux in the ecosystem formed on nickel-enriched soils. Despite the fact that the gross concentration of nickel in the soils of the hornbeam forests studied by authors does not differ significantly, in the Holosiivskyi NNP there is active accumulation of nickel by biomass, as a result of which the estimated nickel stocks in the leaf biomass of common hornbeam from Holosiivskyi NNP are 6 times greater (79 g/ha) than in the Kaniv Nature Reserve (13 g/ha). The differences in metal stocks in the wood were even more significant.

In the common hornbeam wood of Holosiivskyi NNP, 11.3 kg/ha of Ni is concentrated, which is 31 times more than in the common hornbeam wood of the Kaniv Nature Reserve – 0.35 kg/ha, which respectively accounts for 28% and 1.2% of the total metal stocks in the ecosystem. In tropical forest ecosystems formed on nickel-rich ultramafic serpentine rocks, the main part of this metal is concentrated in the plant biomass. This phenomenon was revealed in the study by A. Paul *et al.* (2024) when 90.3% of the total nickel stocks of the ecosystem were concentrated in the biomass of the tropical nickel hyperaccumulator tree *Pycnandra acuminata*. As a result of Ni fixation in the biomass of common hornbeam, the volumes of leaching by vertical groundwater flow in Holosiivskyi NNP are 2.8 times smaller, where the value of this component of the metal flow is 18 g×ha^{-1}×year^{-1}. In the Kaniv Nature Reserve, leaching to the eluvial soil layer is 51 g×ha^{-1}×year^{-1} and corresponds to the amount of annual Ni input with atmospheric precipitation. As a result, the forest litter of the hornbeam forest of the Kaniv Nature Reserve contains 2.4 times less nickel than the litter of the Holosiivskyi NNP ecosystem. Estimates of the magnitude of soil Ni infiltration, presented in the study by P. Michopoulos (2021), showed similar values. In particular, in a spruce forest in central Germany, the Ni flux was estimated at 11.5 g×ha^{-1}×year^{-1}. In a mixed stand of Norway spruce, birch, and aspen in Finland, the annual leaching of nickel was 6.2 g×ha^{-1}×year^{-1}. In the northeast of France, quite high Ni fluxes in the soil solution were found, amounting to 43 g×ha^{-1}×year^{-1} (Michopoulos, 2021).

Thus, the presented study of model hornbeam forest ecosystems in the Middle Dnipro Region has shown that forest ecosystems in urban conditions (Holosiivskyi NNP) and in natural conditions (Kaniv Nature Reserve) do not significantly differ in the concentration of Ni in soils, groundwater, and atmospheric precipitation, which can lead to a false understanding of the level of anthropogenic load on such ecosystems. However, an analysis of Ni accumulation levels in common hornbeam biomass showed significant differences, when the Ni stocks in hornbeam wood in Holosiivskyi NNP exceeded the metal stocks in Kaniv Nature Reserve by more than 30 times. The Ni stocks in the leaf biomass of hornbeam in Holosiivskyi NNP were 6 times higher, and the stocks in the forest litter were 1.3-7.5 times higher. Accordingly, a significant amount of nickel accumulated in the biomass of common hornbeam in Holosiivskyi NNP led to significant changes in the functioning of the nickel biogeochemical cycle, compared to the conditions of the Kaniv Nature Reserve, when the input of nickel from atmospheric precipitation and leaf fall was not balanced by the loss in the process of leaching by vertical groundwater flow, which led to the retention and accumulation of the metal in the ecosystem. The authors' results confirm the features of the nickel biogeochemical cycle described by other authors in conditions of natural geochemical anomalies of polymetallic deposits when the main part of the nickel biogeochemical cycle is provided by the "litter-soil-plant" system. The main part of the metal (over 90%) returns to the soil as part of leaf fall, from where it is again absorbed by plant root systems. The constant additional input of nickel as part of atmospheric precipitation and the slow leaching of the metal with groundwater creates a danger of continued accumulation of nickel in the biomass to levels that can cause phytotoxic effects in woody plants in urban environments. The imbalance of the nickel biogeochemical cycle in Holosiivskyi NNP indicates the presence of anthropogenic pollution of the ecosystem with this metal.

CONCLUSIONS

A comprehensive, multi-year assessment of the balance of Ni biogeochemical migration fluxes in model hornbeam forest ecosystems of Holosiivskyi NNP and Kaniv Nature Reserve has established that the main input of Ni into the Holosiivskyi NNP hornbeam forest ecosystem was through leaf fall, which, during the formation of a new annual litter layer, provided 73% of the total amount of the metal – 79 ± 7 g×ha^{-1}×year^{-1}. Atmospheric precipitation accounted for 27% – 29 ± 4 g×ha^{-1}×year^{-1}. Losses of Ni from the Holosiivskyi NNP ecosystem with vertical groundwater flow per year amounted to 18 ± 2 g×ha^{-1}×year^{-1}, indicating an imbalance in the Ni biogeochemical cycle. The slow removal of the metal from the ecosystem by groundwater runoff leads to the accumulation of Ni in the soil – with a higher concentration in the humus layer compared to the eluvial layer. As a result of active root uptake of Ni by plants, it accumulates in the biomass – 7 ± 1 g×ha^{-1}×year^{-1} is accumulated annually in the woody biomass of common hornbeam, and 79 ± 7 g×ha^{-1}×year^{-1} in the leaf biomass. It is shown that after leaf fall, Ni returns to the soil and becomes available for absorption by the root system of plants. In the hornbeam forest ecosystem of Holosiivskyi NNP, the main part of the Ni biogeochemical cycle is provided by the "litter-soil-plant" system. In the hornbeam forest ecosystem of Kaniv Nature Reserve, 75% of the total Ni input is provided by the process of wet deposition with atmospheric precipitation – 39 ± 4 g×ha^{-1}×year^{-1}. Leaf fall accounts for 25% of this chemical element – 13 ± 2 g×ha^{-1}×year^{-1}. A comparison of the total Ni input into the Kaniv Nature Reserve ecosystem (52 ± 3 g×ha^{-1}×year^{-1}), groundwater runoff to the eluvial soil layer (51 ± 6 g×ha^{-1}×year^{-1}) and the total amount of Ni output from the litter (52 ± 5 g×ha^{-1}×year^{-1}) indicates the presence of a balance between the input and loss of the metal in the hornbeam forest ecosystem of Kaniv Nature Reserve, and the main migration processes are provided by the "atmosphere-litter-soil" system.

The conducted research reveals the presence of complex mechanisms of heavy metal migration in forest ecosystems. To determine the functional state of urban green spaces and forest ecosystems, it is necessary to assess the degree of balance of heavy metal biogeochemical cycles, which will allow for the prediction of risks of toxicant accumulation in component parts with the aim of developing measures to increase resistance to pollution. This must be considered when designing new plantings resistant to heavy metal pollution.

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CONFLICT OF INTEREST

None.

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Біогеохімічний цикл нікелю в умовах екосистем грабових дібров Середнього Придніпров'я

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Анотація. Важкі метали, зокрема Ni, є пріоритетними забруднювачами атмосферного повітря. Міські зелені насадження та лісові екосистеми зменшують рівень забруднення, проте самі зазнають негативного впливу, що викликає фітотоксичні ефекти, зменшує стійкість зелених насаджень до шкідників, хвороб та інших негативних чинників. Метою дослідження було провести оцінку збалансованості біогеохімічного циклу Ni в лісових екосистемах для визначення наслідків забруднення зелених насаджень в умовах урбанізованого середовища за різниці антропогенного навантаження. Як модельні екосистеми широколистяних лісів Середнього Придніпров'я було обрано грабові діброви двох територій природно-заповідного фонду України: Національний природний парк (НПП) «Голосіївський» та Канівський природний заповідник. У дослідженні, проведеному на цих модельних екосистемах, були використані методи атомно-абсорбційної спектрофотометрії та ICP-OES спектрометрії для з›ясування особливостей накопичення Ni в ґрунтах, проведено оцінку запасів у фітомасі деревної породи грабових дібров та динаміку накопичення сполук металу у лісовій підстилці, оцінено величини потоків вертикальної міграції Ni лізиметричним методом, визначено рівні надходження сполук металу в процесі осадження у складі атмосферних опадів на територію грабових дібров. Встановлено, що біогеохімічні системи міграції Ni грабової діброви Канівського природного заповідника характеризуються балансом потоків металу. Екосистема грабової діброви НПП «Голосіївський» характеризується незбалансованістю біогеохімічного циклу Ni. Як наслідок, у забезпеченні функціонуванні біогеохімічного циклу Ni в екосистемі НПП «Голосіївський» основну роль відіграє біологічна складова системи «підстилка-ґрунт-рослина», коли Ni активно поглинається рослинами грабу звичайного (*Carpinus betulus* L.) та накопичується у фітомасі. Екосистема грабової діброви НПП «Голосіївський» в умовах міста Києва зазнає прогресуючого забруднення Ni, що проявляється у активному накопиченні рослинністю, що необхідно враховувати при оцінках стану існуючих зелених насаджень та при проєктуванні нових, обираючи рослини, які є стійкими до високих концентрацій Ni

Ключові слова: ґрунт; лісова підстилка; листяний опад; атмосферне осадження; біоакумуляція; мінералізація; міграція важких металів