Трансформация экосистем
Ecosystem Transformation

ISSN 2619-0931 Online
www.ecosysttrans.com

DOI: https://doi.org/10.23859/estr-241120
EDN: https://elibrary.ru/mkmyti
UDC 504.064.2: 574.2

Article

Assessing the degree of damage to birch stands in areas of airborne industrial pollution from copper smelter

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Abstract. The article presents the results of assessing vital conditions of forests and pollution levels in the area affected by the "Karabashmed" JSC using a silver birch as the bioindication species. Defoliation, discoloration, and damage indices of tree stands were measured, including the concentration coefficients and total content of heavy metals in birch leaves. It was shown that Cd, Pb, Zn, Ni, and Cu made the greatest contribution to pollution. The highest total content of heavy metals was detected in 1.5 km from the pollution source, while the lowest at a distance of 20 km. In most damaged (by emissions) birch stands, the total content of heavy metals reached 25.1; contamination was characterized as moderate. The obtained quantitative metal concentrations in leaves of silver birch can be applied in establishing threshold values under long-term exposure to metallurgical emissions.

Keywords: heavy metals, silver birch, vital conditions, anthropogenic pollution

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To cite this article: Menshchikov, S.L., Gorbunova, V.D., 2026. Assessing the degree of damage to birch stands in areas of airborne industrial pollution from copper smelter. *Ecosystem Transformation* **9** (2), 181–194. https://doi.org/10.23859/estr-241120

Received: 20.11.2024
Accepted: 14.06.2025
Published online: 29.05.2026

DOI: https://doi.org/10.23859/estr-241120
EDN: https://elibrary.ru/mkmyti
УДК 504.064.2: 574.2

Научная статья

Оценка степени повреждения березовых древостоев в очагах аэротехногенного загрязнения выбросами медеплавильного комбината

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Аннотация. Приведены результаты оценки жизненного состояния древостоя и уровня загрязнения на территории воздействия АО «Карабашмедь» с помощью вида-биоиндикатора березы повислой. Были измерены показатели дефолиации, дехромации, индексы повреждения древостоев, а также коэффициенты концентрации тяжелых металлов и суммарный показатель их концентрации в листьях березы. Показано, что наибольший вклад в загрязнение внесли такие элементы, как Cd, Pb, Zn, Ni, Cu. Максимальное суммарное содержание ТМ обнаружено на расстоянии 1.5 км от источника загрязнения, минимальное – на расстоянии 20 км. В древостоях, наиболее поврежденных выбросами комбината, суммарный показатель концентрации ТМ достиг 25.1, что позволило характеризовать уровень загрязнения как средний. Полученные количественные концентрации металлов в листьях березы повислой могут быть использованы для установления пороговых значений в условиях многолетнего влияния выбросов металлургических предприятий.

Ключевые слова: тяжелые металлы, береза повислая, жизненное состояние, техногенное загрязнение

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Для цитирования: Менщиков, С.Л., Горбунова, В.Д., 2026. Оценка степени повреждения березовых древостоев в очагах аэротехногенного загрязнения выбросами медеплавильного комбината. *Трансформация экосистем* **9** (2), 181–194. https://doi.org/10.23859/estr-241120

Поступила в редакцию: 20.11.2024
Принята к печати: 14.06.2025
Опубликована онлайн: 29.05.2026

Introduction

Industrial development generates enormous amounts of wastes, containing toxic heavy metals (HMs) as well. Insufficient waste treatment leads to pollution of the environment and, subsequently, its degradation.

Anthropogenic pollution is responsible for changes in the elemental composition of plant structures. Typically, elevated levels of HMs result in dysregulation of assimilation of elements necessary for proper plant growth and development, reduced seed germination and root growth, lower production of tree biomass, and suppression of photosynthesis (Ivanov et al., 2011; Malinowska, 2010).

Low pH in soil increases solubility and toxicity of various metals (copper, cadmium, and zinc), thereby causing nitrogen and phosphorus deficiency in plants along with depressed microbial activity (Aguinaga et al., 2021). This may be a key factor of phytotoxicity and lack of vegetation in certain areas (Ferreira et al., 2021). Low pH of mine effluents brings to higher rates of metal release and, consequently, their leaching (Favas et al., 2016; Sahoo et al., 2020).

Various mechanisms have been proposed to explain plant tolerance to toxic metals (Baker, 1981). Some woody plant species can accumulate heavy metals from tailings (Brković et al., 2021). In post-industrial habitats, silver birch *Betula pendula* Roth is a pioneer species due to its expansive reproductive strategy and low habitat preferences (Sitko et al., 2022). All these characteristics make silver birch promising for phytoremediation. This species is known to be capable of hyperaccumulating zinc (Dmuchowski et al., 2012). Though silver birch accumulates HMs, it is not a hyperaccumulator plant since concentrations of HMs are not high (Naila et al., 2019).

The aim of this study is to analyze pollution levels in the area of the copper smelter (“Karabashmed” JSC) using the bioindication method for assessing the degree of damage to birch stands (*Betula pendula* Roth).

Materials and methods

The “Karabashmed” JSC (KME), Chelyabinsk oblast is one of the oldest metallurgical enterprises in Russia and a major producer of black copper from copper concentrate. Emissions of its furnace gas contain up to 82% sulfur dioxide, as well as carbon monoxide, nitrogen dioxide, formaldehyde and hydrogen fluoride vapors, inorganic dust, and heavy metals. Together, they have a strong toxic impact on forest ecosystems (Agikov, 2011; Kalabin and Titova, 2011; Koroteeva et al., 2011). In addition, waste piles, slag dumps, and pyrite tailings form dust, being hazardous to human health and the environment (Agikov, 2011). Over the years of the enterprise operation, a huge amount of industrial wastes was discharged into the environment. As a result, the ecological situation and forest state abruptly deteriorated (Bachurina, 2008; Usoltsev et al., 2011). For studies, natural stands of silver birch *Betula pendula* affected by effluents from the “Karabashmed” JSC, the Southern Urals were selected. In this area, northwesterly, southwesterly, and westerly winds prevail. Water bodies within the KME impact territory are polluted by wastes discharged into the Sak-Elga River (Kalabin et al., 2011).

Based on wind patterns and topography, we selected five sample plots (SPs) with birch stands of different pollution level: S-1.5, SV-5, SV-15, SV-20, and SV-24 (Fig. 1) (letters indicate direction, numbers - the distance from the pollution source in kilometers). Sample plot S-1.5 is located 1.5 km north of the emission source on gray mountain forest soil of a flat plain. The mixed-herb mature birch forest here is of seed origin. The trees are of 30–50 year old, approximately 20 m tall with an average trunk diameter of 26 cm. Plots SV-5, SV-15, SV-20, and SV-24 are located 5, 15, 20, and 24 km from the plant, respectively, in birch forests with stand density of 0.7–0.8, mixed grass and forbs on gray mountain forest soils of class7–8. The trees are approximately 25–32 m tall and 31 cm in diameter. A site with the best birch stands in 20 km from KME (SV-20) was selected as the reference one.

Silver birch became the study object due to its predominance throughout. Model trees were selected from the first layer, approximately 100 trees from each site. For bioindication-based assessment of forests, defoliation (percentage of leaf loss) and discoloration (color change) of tree crowns as indicators (Methods for Organization and Implementation of Works 1995), as well as the standard methods for identifying tax indicators (Moiseev, 1987) were employed.

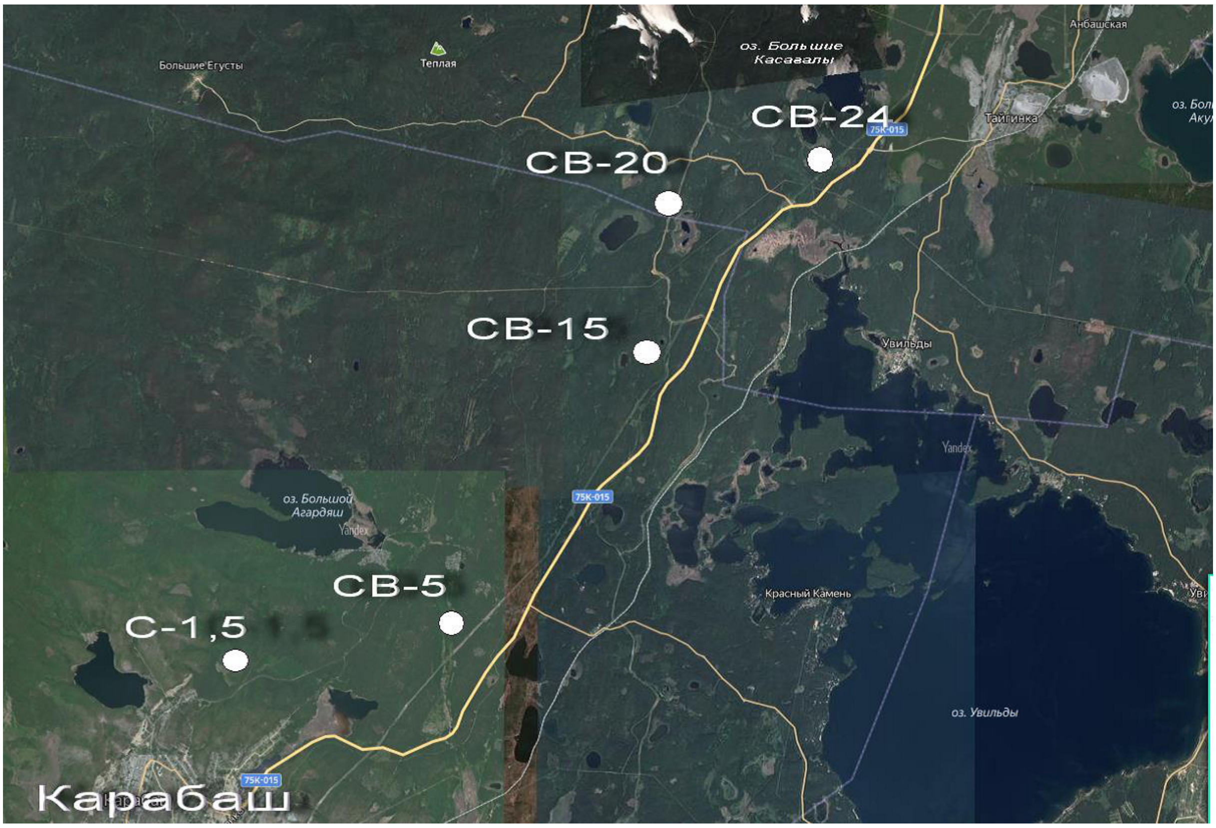

Fig. 1. Location of sample plots at different distances from KME.

The concentration coefficient enables estimation of pollutant content in the man-impacted object relative to the average background level, i.e., in leaves of trees growing under regional background conditions. Concentrations are considered abnormal at Cc ≥ 1.5 (Saet et al., 1990). Concentration coefficients for evaluating the intensity of HM accumulation by silver birch are calculated from the formula:

$$Cc = Ce/Cc,$$

where Cc is the concentration coefficient, Ce is the element content in leaves subject to pollution, and Cc is the element content under background conditions. The values obtained for the most healthy sample plot are used as the background indicators.

The category of tree stands weakness (sanitary condition) was determined in accordance with recommendations of V.A. Alekseev (1989): a tree stand was characterized as healthy at Cc = 1.0–1.5, weakened at Cc = 1.6–2.5, very weakened at Cc = 2.6–3.5, dying at Cc = 3.6–4.6, and dead at Cc ≥ 4.6.

To assess the accumulation of heavy metals in plants, the total content index (TCI) was calculated (Neverova and Kolmogorova, 2003):

$$TCI = \Sigma(Ce - Cc)/Cc.$$

Like other indices of HM contamination, TCI is derived from absolute measurement data without consideration of a geochemical background (Kowalska et al., 2018). In terms of HM total content, N.N. Moskalenko and R.S. Smirnova (1990) identified the following levels of vegetation pollution: critical (10–20); moderate (20–30); high (30–40); very high (40–60); extremely high (60–80 and higher).

To study the variable chemical composition in leaves and individual variability, 10 trees were selected from each plot in the “Karabashmed” JSC area, with one leaf weighing approximately 20 grams sampled from each tree in late July of 2019. Leaves were collected only from shortened shoots forming the main part of the canopy in mature trees and being of the same age due to a synchronous leaf unfolding in spring (Macdonald and Mothersill, 1983). Sample collection and preparation for analysis were made in accordance with the generally accepted methods (Rautio, 2020).

The content of heavy metals (cadmium, cobalt, chromium, copper, iron, nickel, lead, manganese and zinc) in KME emissions was determined by atomic absorption spectrophotometry using a novAA-300 spectrophotometer (AnalyticJena, Germany). The result was expressed in mg/kg dry weight. To interpret the findings, we used the scale presented by A. Kabata-Pendias (1989) providing normal (or sufficient) concentrations of microelements (mg/kg dry weight): Cd – 0.05–0.2; Co – 0.02–1; Cr – 0.1–0.5; Cu – 5–30; Ni – 0.1–5; Pb – 5–10; Zn – 27–150 and excessive (or toxic) ones: Cd – 5–30; Co – 15–50; Cr – 5–30; Cu – 20–100; Ni – 10–100; Pb – 30–300; Zn – 100–400.

The obtained material was analyzed using Microsoft Excel 2007 and the statistical analysis method in STATISTICA V. 10 (StatSoft Inc., USA). We employed one-way analysis of variance (ANOVA) to reveal differences between five groups, followed by determination of the significance of differences through applying the Fisher's exact test. The relationship between the element content in plants and the vital condition of trees was tested by means of the parametric Pearson r-test. The level of statistical significance made up 5%.

Results and discussion

Table 1 presents the data on forest state at different distance from the “Karabashmed” JSC. For instance, birch woods located closer to the pollution source (C-1.5) are most damaged. The level of defoliation is 59.5%, discoloration – 52%, and the damage index – 3.3 that is 2.7, 3.3 and 2 times higher than under background conditions. Sample plots located at distances from 15 to 24 km are best preserved compared to other sites. In plots S-15, S-20, and S-24, stands of trees are characterized as weakened and in S-1.5, S-5 as severely weakened. Birch stands in 24 km from KME turn out to be in a poorer condition. This is explained by terrain, wind speed and other factors, which are driving in the mountainous regions. Thus, KME has a negative effect on health of birch forests that is manifested by increased defoliation, discoloration, and deterioration of their state.

The total content of HMs in birch leaves was studied at a different distance from the “Karabashmed” JSC, including the contribution of each metal to the total accumulation. The total content of HMs in leaves increased with the proximity to the source of pollution. For instance, at a distance of 1.5 km it was the highest (2100 mg/kg dry weight), while in 20 km from KME this indicator made up 1034 mg/kg. Furthermore, at a distance of 20 km (background), the content of almost all studied heavy metals in leaves was the lowest compared to other sites.

The concentrations of iron, manganese, and zinc in leaves of silver birch significantly exceeded the content of other elements (Fig. 2) that was supported by the Jurković research on HM accumulation in tree leaves (Jurković et al., 2023). In our study, manganese, as one of the most important micronutrients in plants (Alejandro et al., 2020), had the highest concentration (648–1294 mg/g). Recent investigations also report about its bioaccumulation by silver birch (Çomaklı and Bingöl, 2021; Zapata-Carbonell et al., 2020).

Table 1. Characteristics of birch stands at a different distance from “Karabashmed” JSC. * – Values significantly differ for S-1.5 at $p < 0.05$.

Sample plot	Average defoliation, %	Average discoloration, %	Condition category
S-1.5	59.5 ± 3.4	52 ± 4.5	3.2 ± 0.1
SV-5	42.8 ± 6.1*	16.7 ± 5.6*	2.6 ± 0.2*
SV-15	25.6 ± 3.2*	8.5 ± 2.6*	2.1 ± 0.07*
SV-20 (background)	22 ± 2.5*	16.1 ± 4.2*	1.6 ± 0.07*
SV-24	39.5 ± 5.1*	17.8 ± 2.8*	2.4 ± 0.2*

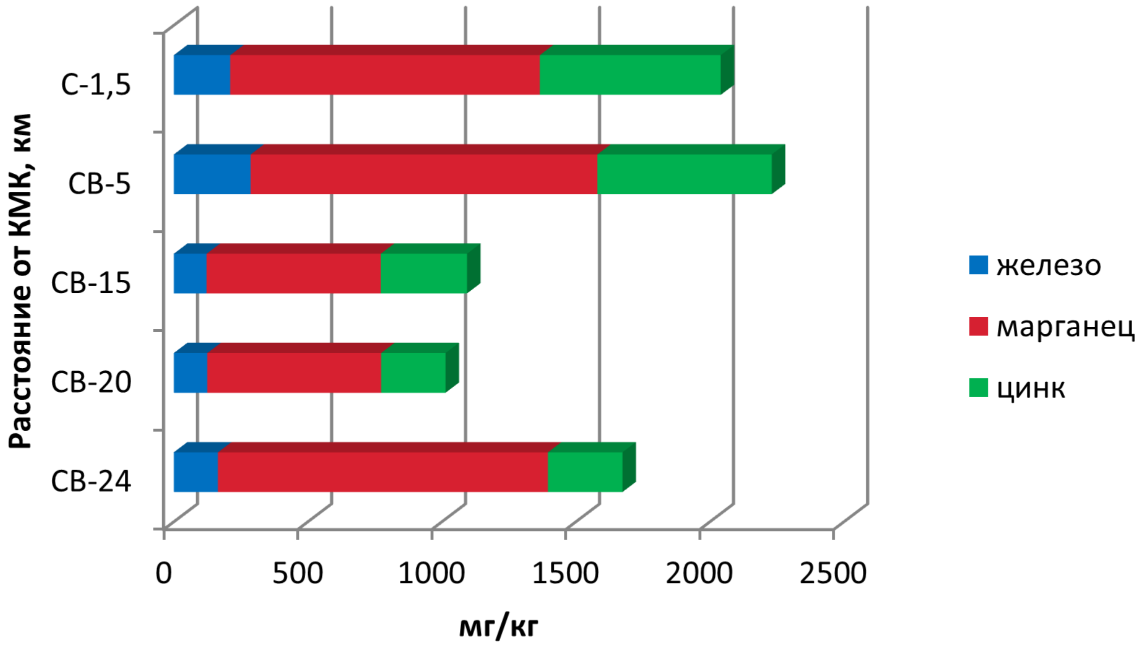

Fig. 2. Iron, manganese, and zinc contents in silver birch leaves at different distances from KME.

In plots, which are the nearest to the pollution source, the content of metals of hazard classes 1[1] (Cd, Pb, Zn) and 2 (Cu, Fe) in birch leaves was significantly higher than in sites situated 15 km or more from KME (Figs. 3, 4). Cadmium exceeded the background level by 7 and 3.5 times in plots S-1.5 and SV-5, respectively. Zinc and iron concentrations showed 3- and 2.3-fold excess in SV-1.5 and SV-5. In all sites, zinc exceeded toxic concentrations (Kabata-Pendias and Pendias, 1989). It is known that silver birch acts as a selective accumulator of zinc: its leaves accumulate this element in elevated quantities even in pristine habitats (Urazgildin and Suleimanov, 2022). In 15–24 km from the plant, concentrations of cadmium, chromium, iron, copper, lead, and zinc varied insignificantly.

Copper concentrations at sites S-1.5, SV-5 were 2.5 and 2 times higher than the background values.

Studies suggest that Cu^{2+} ions play an important role in plant metabolism (Williams et al., 2000); its bioaccumulation rate varies greatly depending on plant species (Lange et al., 2017; Reeves et al., 2018; Xiao et al., 2008).

Lead accumulation in birch leaves increased from 1.5–3 mg/kg to 12 mg/kg in more distant sites (S-1.5).

Nickel content was high in all sample plots (22.5–27.8 mg/kg), with the exception of SV-20 (10.3 mg/kg). Worth noting that the average nickel content in the Earth's crust is approximately 20 mg/kg (Kabata-Pendias and Pendias, 1989). Nickel is extracted from pyrrhotite (Fe(1−x)S), which can contain up to 5% of nickel, pentlandite $(FeNi)_9S_8$, chalcopyrite ($CuFeS_2$), and gersdorffite (NiAsS) present in gold-bearing ore (Fashola et al., 2016). There is no scientific evidence of a significant part of nickel in plant metabolism.

The calculation results of the concentration coefficients and total content of HMs in leaves of silver birch are given in Table 2. In 1.5–5 km from the pollution source, values of concentration coefficients for birch leaves were several times greater than the background ones for all elements. Cadmium, lead, zinc, nickel, and copper contributed most to pollution; the highest values were recorded for cadmium. Birch leaves accumulated nickel in elevated quantities even in remote sites (Cc varies from 2.2 to 2.7). At a distance of 5 km (NE-5), the concentration coefficients for cobalt, chromium, iron, manganese, and nickel were higher than at sites situated closer to KME.

It was shown that in sites next to the pollution source, the HM total content significantly elevated

[1] MG 2.1.7.730-99. Hygienic assessment of soil quality in populated areas.

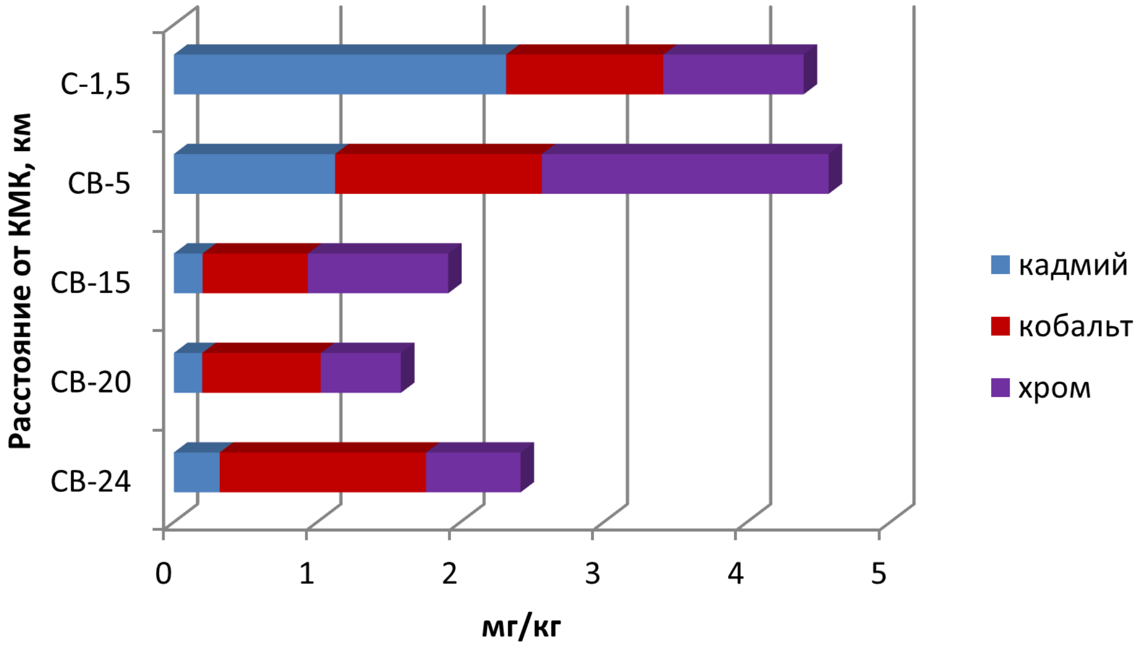

Fig. 3. Cadmium, cobalt, and chromium contents in silver birch leaves at different distances from KME.

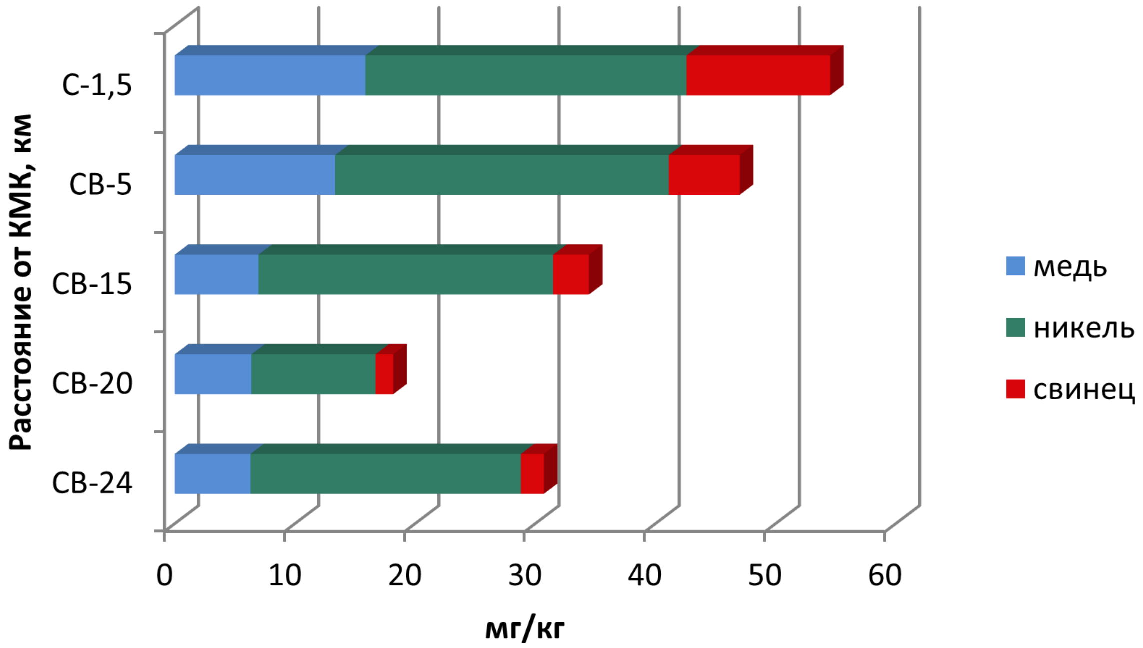

Fig. 4. Copper, nickel, and lead contents in silver birch leaves at different distances from KME.

Table 2. Показатели загрязнения ТМ листьев березы повислой.

Sample plot	Cc									TCI
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	
S-1.5	11.56	1.32	1.75	2.49	1.6857	1.78	2.59	8.08	2.81	25.1
SV-5	5.63	1.74	3.57	2.09	2.2941	1.99	2.69	3.99	2.71	17.7
SV-15	1.01	0.88	1.75	1.09	0.9786	1.00	2.38	2.017	1.34	3.5
SV-24	1.60	1.73	1.18	0.99	1.318	1.90	2.18	1.29	1.16	4.4

with increasing concentrations of cadmium and lead, including zinc and copper, but to a lesser extent (Table 2). These metals discharged by the “Karabashmed” JSC belong to hazard class 1 and class 2 (toxic and extremely toxic)[2]. Correlation analysis showed a positive relationship between the HM total content and vital conditions of tree stands. With rising HM total content, defoliation ($r = 0.92$, $p < 0.05$), discoloration ($r = 0.79$, $p < 0.05$) increased and the sanitary condition worsened ($r = 0.93$, $p < 0.05$).

TCI was the highest in the most damaged S-1.5: vegetation pollution was assessed as moderate (Moskalenko and Smirnova, 1990). In SV-5, even with its severely weakened tree stands, the contamination was the lowest. In sites SV-24 and SV-15, the pollution was also the least. Besides, the concentration coefficients for Co, Cr, Fe, Mn, and Ni in 5 km from the KME were greater than at a distance of 1.5 km. Values of Co, Cd, Fe, and Mn at a distance of 24 km (the most remote area) exceeded those in 15 km from the pollution source. We assume that the assessment scale for the HM total content proposed by N.N. Moskalenko and R.S. Smirnova (1990) does not account for vital conditions of forest stands; it should be revised and updated.

Conclusion

The obtained results demonstrate the negative effect of the “Karabashmed” JSC on silver birch stands in northeastern and northern directions. We noted a deterioration in forests located closer to the pollution source: defoliation increased by 2.7, discoloration by 3.3 and damage index by 2 times, as compared to remote sample plots.

The highest HM total content (2100 mg/kg) in birch leaves was found in sites situated at a distance of 1.5 km, while the lowest (1034 mg/kg) in 20 km from the plant. The metal content of hazard classes 1 (cadmium, lead, zinc) and 2 (copper and iron) significantly increased towards the pollution source. Moreover, the concentration coefficients for Co, Cr, Fe, Mn, and Ni were higher in 5 km from KME than at a distance of 1.5 km, while for Co, Cd, Fe, and Mn they were greater for a site at a distance of 24 km (the most remote site) than in 15 km from the pollution source.

With proximity to KME, the HM total content significantly increased, primarily because of cadmium and lead and, to a lesser extent, owing to zinc and copper. Correlation analysis revealed a relationship between the HM total content and vital conditions of trees: with elevation of the HM total content, defoliation and discoloration intensified and the sanitary state of forest worsened.

Overall, despite the increased concentrations of HMs in birch leaves and forest deterioration in the contaminated zones, the airborne anthropogenic loads do not bring to birch stands destruction for long. The obtained quantitative concentrations of metals in leaves of silver birch can be used for establishing the threshold values under the long-term exposure to emissions from metallurgical enterprises.

[2] MG 2.1.7.730-99. Hygienic assessment of soil quality in populated areas.

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