

Geochemical assessment of iron and manganese accumulation in woody and herbaceous vegetation of forest ecosystems, Northeast Kazakhstan

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ABSTRACT

The article presents the results of a comprehensive geochemical assessment of the iron (Fe) and manganese (Mn) accumulation in woody and herbaceous vegetation of forest ecosystems in the North-East Kazakhstan: the Chaldai ribbon pine forest and the Bayanaul State National Nature Park (BSNP). The study covers four impact zones: protected, natural, anthropogenic and post-fire. A comparative analysis of element concentrations in plants and soils was carried out, and key biogeochemical coefficients were calculated: biotoxicity (PBE), accumulation (Kn), concentration (Kc) and background accumulation (Ko). The results showed that manganese plays a more active role in the biogeochemical cycle, especially in areas with high anthropogenic impact. Iron mainly accumulates in herbaceous forms, but does not reach a physiologically favorable Fe:Mn ratio (2:1), which may indicate stressful conditions for vegetation. In both forest areas, signs of aerotechnogenic pollution were established, while the level of pollution according to the integral indicator Zc was classified as weak. The obtained data confirm the sensitivity of plants to technogenic load and the need for regular environmental monitoring.

Keyword: Iron, Manganese, Needles, Herbaceous plants, Accumulation coefficient, Pollution, Bioindication, Forest ecosystems.

Article type: Research Article.

INTRODUCTION

One of the most significant environmental problems of our time, which is becoming increasingly important, is environmental pollution with heavy metals (HM). The release of HM into the atmosphere has a complex negative impact on the components of the biosphere; soil, vegetation and, indirectly, on human health (Muller 2014). Despite the accumulated information, there is still no consensus in the scientific community regarding the degree of toxicity of heavy metals for plant organisms. According to a number of studies, the most dangerous elements for woody vegetation when they accumulate include cobalt (Co), copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd) and mercury (Hg; Keller 1983). These same metals, including nickel (Ni), are considered the most toxic for higher plants (Galibina *et al.* 2025). In accordance with sanitary and hygienic standards GOST 17.4.102-83, Zn and Cd are classified as highly hazardous elements, and Ni and Mo as moderately hazardous. The United Nations Environment Programme (UNEP) classifies Co and V as priority pollutants. The most toxic elements classified as hazard class I are Hg, Pb, Cd, Zn, As, Se and Be. At the same time, the presence of certain concentrations of biogenic microelements, such as iron (Fe) and manganese (Mn), classified as hazard class III, is of fundamental importance for the normal functioning of living organisms, including plants. Iron occupies a special position among the metals that make up plant tissues and performs key functions in metabolic processes. Its average content in plants is 0.02–0.08% (20–80 mg kg⁻¹ dry weight). Manganese, in turn, actively participates in metabolic

processes and improves the physiological functions of plant organisms. Its average content in plants is about 0.001% (1 mg kg⁻¹ dry weight; Muller 2014). For the sustainable functioning of forest ecosystems, a stable biogeochemical cycle of substances, including the above elements, is necessary. An analysis of scientific literature shows that the impact of heavy metals on the state of natural forest ecosystems and urban forest plantations in Kazakhstan has not been sufficiently studied to date (Hughes 1984; Muller 2003; Kappler & Straub 2005; Vodyanitskii 2009; Grelen & Parzych & Astel 2018; Pielech *et al.* 2025). Industrial zones located in Pavlodar and the Pavlodar region include enterprises in the energy, oil refining and coal sectors, whose activities are accompanied by significant emissions of pollutants into the atmosphere. The main contribution to the formation of gross emissions of pollutants is made by industrial centers: Ekibastuz (48%), Aksu (24%) and Pavlodar (26%). In recent years, the volume of emissions of liquid and gaseous substances into the atmosphere has been wave-like with an upward trend. Thus, if in 2018 the total volume of emissions was 709.3 thousand tons, then by 2022 it increased to 724.2 thousand tons. The emissions are dominated by carbon dioxide, sulfur dioxide, particulate matter (dust) and nitrogen oxides (Zhumadina *et al.* 2023). The areas adjacent to these cities are subject to constant pollution, including emissions of toxic heavy metals, which leads to soil degradation, weakening of the vital activity of plant communities and their subsequent death (Satova *et al.* 2020). Iron and manganese are parts of aerosol emissions from various industries, including ore processing, iron and steel production (Fedorkov 2007; Zhumadina *et al.* 2022). In addition, iron is the most common element in the earth's crust and the most actively used transition metal in the biosphere (Karabalayeva *et al.* 2023). Manganese is widespread in natural components: soil, water and air, where it is present in stable low concentrations (Vasilyev 2023). To assess the degree of technogenic pollution of territories and the accumulation of heavy metals in the biosphere, woody plants are widely used as bioindicators capable of extracting and accumulating elements in various organs. The highest concentrations of HM are usually recorded in the roots, then in the stems and leaves, and to a lesser extent - in the generative organs (flowers, fruits and seeds; Kalabin 2021). The level of accumulation of heavy metals by plants depends on their content in the soil solution, soil reaction (pH), and the species of plants. The aim of this study is to determine the concentrations of biogenic elements - iron and manganese - and assess the degree of their accumulation in Scots pine needles and herbaceous plants in the conditions of two natural territories of North-Eastern Kazakhstan: Chaldai ribbon pine forest and Bayanaul State National Nature Park.

MATERIALS AND METHODS

The object of this study is woody and herbaceous plants growing in the territories of the Chaldai ribbon pine forest and the Bayanaul State National Nature Park (BSNP), located in the North-east Kazakhstan. The Chaldai ribbon pine forest is a unique relict pine forest that formed, according to paleogeographic data, more than a million years ago, after the end of the last glaciation. Stretching from Semey along the Irtysh to Barnaul and further to the Ob River, it includes five ribbon structures and is characterized by a sharply continental climate, arid conditions and a sandy substrate. Ribbon pine forests are considered natural formations of exceptionally high ecological value and are represented on the planet in only two regions: Canada and in the territory of Russia and Kazakhstan, while more than half of the area of this type of forest is concentrated within Kazakhstan (Fig. 1). In the East Kazakhstan region, the total area of ribbon pine forests is 662.2 thousand hectares, of which 62.3% are covered by forest (411.4 thousand hectares), with a total timber reserve of about 30 million m³. These forests are classified as especially valuable forests of the first group with pronounced climate-regulating, sanitary-hygienic, soil-protective and water-protective functions (Kappler & Straub 2005; Vodyanitskii 2009; Pielech *et al.* 2025). Meanwhile, there are only two unique ribbon pine forests on the planet. The first is in Canada. The second is on the territory of Russia and Kazakhstan. Moreover, more than half of it is in Kazakhstan (Fig. 1). The Chaldai forest massif is one of the specially protected natural areas aimed at preserving biodiversity and ensuring sustainable nature management. However, a significant part of its area has been degraded due to forest fires and illegal logging. According to current data, the area of burnt areas is about 62 thousand hectares, the restoration of which will require significant time and resource costs. According to satellite remote sensing data, the study area is characterized by eleological alluvial-accumulative relief with a predominance of dunes, ridges, ranges and closed depressions, most pronounced in the southwestern part of the forest (Fig. 2). According to morphometric features, the relief is divided into small forms (height up to 3 m), medium (3-7 m) and large (more than 7 m), in the structure of which ridges, areas of sand, rubble and hollows alternate. The climate of the Chaldai region is characterized by sharp continentality: the average temperature in January is -18–19 °C, and in July: +20...+21 °C. The annual precipitation varies within 245–300 mm. Periods of short-term rains are followed by long droughts.

In the summer months, the relative humidity drops to 20% and below. The greatest frequency of winds is observed from the southwest and northwest directions, which causes stable dry winds (Adegboye *et al.* 2019).

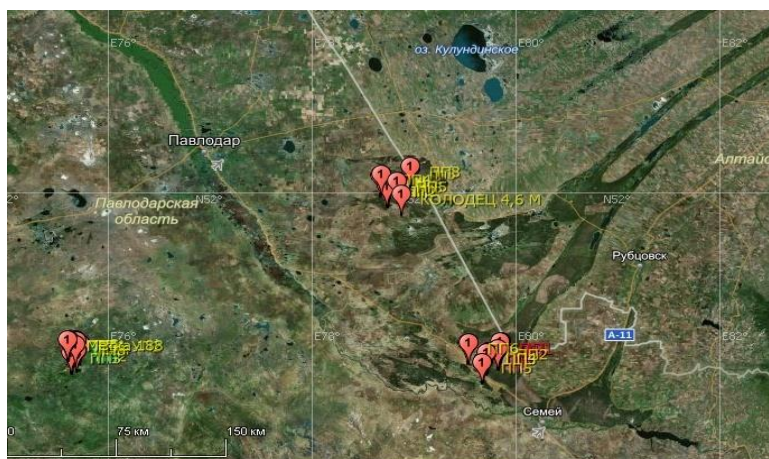


Fig. 1. Satellite image of the study area.

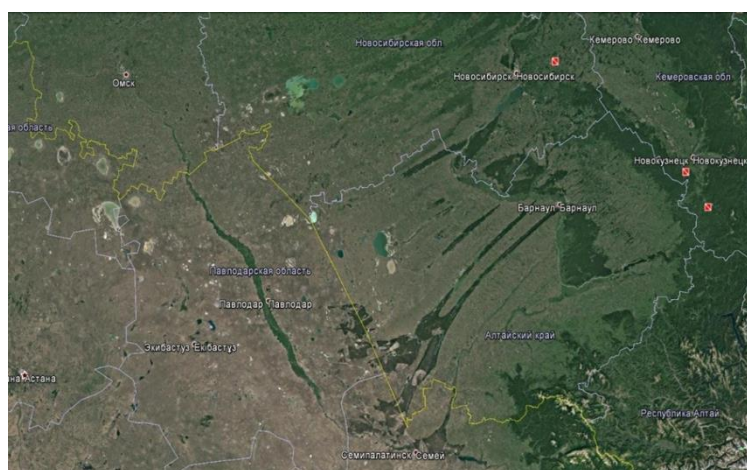


Fig. 2. Satellite image of the Chaldai pine forest.

Bayanaul State National Nature Park (BSNP), the second object of the study, is located on the outskirts of the Central Kazakhstan Uplands. The park is included in the list of specially protected natural areas and is characterized by a unique floristic diversity - about 460 plant species, including endemic forms such as Bayanaul pine and black alder. Pine stands grow mainly on granite rocks, forming a unique landscape complex (Fig. 3). The plant community also includes birch, aspen, rose hips, currants, hawthorn and up to 50 species of relict flora. The park has a continental climate, with an average January temperature of -13.7°C (min -17.8°C) and July $+14.6^{\circ}\text{C}$ (max $+32.6^{\circ}\text{C}$). The average annual precipitation is about 340 mm (from 190 to 494 mm by years), with an average wind speed of 2.9 m s^{-1} . Sandstorms, typical for the nearby steppe regions, are practically not observed here due to the relief features. Snow cover is insignificant, the summer period is often accompanied by droughts, but the climatic continentality is softened by the geomorphological position of the BGNP (Kolbin & Kustarnikov 2023). The analysis involved samples of Scots pine needles and herbaceous plants collected from four types of sites: dunes, flat areas, and along motorways and dirt roads. The samples were collected in the summer-autumn period (late July - early August), when the plants are in the flowering and fruiting phases. The grass cover is dominated by sedges, turf grasses and forbs. The site for collecting control samples was located 20 km from the nearest settlement with a minimum level of anthropogenic impact. Collection, transportation and preparation of plant material were carried out in accordance with the requirements of current GOSTs and approved guidelines (Liu *et al.* 2023). Samples of needles and herbaceous plants were pre-washed from surface dust with distilled water (volume 250 mL), dried on filter paper and placed in a drying chamber to constant weight. The Fe and Mn contents were determined in the accredited laboratory of Eco NUS LLC (Karaganda) using atomic emission spectrometry with inductively coupled plasma on a SPECTRO ARCOS device. The following parameters were calculated for quantitative biogeochemical assessment:

The biotic index (BI) is the ratio of the element content in plant material (C_p , mg kg^{-1}) to its Clarke concentration in the lithosphere (C_{lit} , mg kg^{-1}), according to the following formula (Muller 2014):

$$\text{PBE} = C_p / C_{lit} \quad (1)$$



Fig. 3. Rocks overgrown with pine.

where C_p is the total content of the element in plants (mg kg^{-1}); and C_{lit} is the Clarke of the element in the lithosphere (mg kg^{-1}). Clarke values are taken from the works of A.P. Vinogradov (Eronat *et al.* 2019): for Fe: 51,000 mg kg^{-1} , and for Mn: 900 mg kg^{-1} . Accumulation of chemical elements in the leaves of woody and herbaceous plants was assessed using the concentration coefficient (K_c), which is the ratio of the element content in plant leaves to its concentration in leaves growing in background areas (Masserov & Masserov 2023). Some authors call this ratio the accumulation coefficient (K_a ; Pielech *et al.* 2025).

$$K_c = C_p / C_f, \quad (2)$$

where C_p : concentration of TM in dry plant mass (mg kg^{-1}); and C_f : concentration of TM in leaves of background areas (mg kg^{-1}). To characterize the distribution of elements between living matter and the abiotic environment, accumulation coefficients (K_n) were determined. K_n is the ratio of the concentration of TM in the dry mass of plants (mg kg^{-1}) to the concentration of TM in the mobile form in the soil (mg kg^{-1} ; Muller 2014). The authors call this coefficient the accumulation index and denote it as I_a (Pielech *et al.* 2025).

$$K_n = C_p / C_n, \quad (3)$$

where C_p – concentrations of TM in dry plant mass (mg kg^{-1}); and C_n : concentrations of mobile form of heavy metals in soil (mg kg^{-1}). The hazard coefficient (HQ) is the ratio of the metal content in the soil or plants to the maximum permissible concentration of the metal in the soil or plants (Vodyanitskii 2009).

$$K_o = C_{n/p} / \text{MPS}_{n/p}, \quad (4)$$

where $C_{n/p}$: concentration of metal in soil or plants, and $\text{MPS}_{n/p}$: maximum permissible concentration of metal in soil or plants (mg kg^{-1}). In the case of iron, instead of MAC, we take the critical concentration. To characterize the linear relationship between the content of heavy metals in the organs of herbaceous and woody plants and their content in the soil, Pearson correlation coefficients were calculated. We expressed the two-way correlation relationship through regression indicators using formulas and equations that provide a clear idea of the form and tightness of the correlation relationship between the features. The obtained experimental data were processed by variational statistical methods, which are described in the manual by N.A. Plokhinsky using the Microsoft Excel program (Totubaeva *et al.* 2023).

Statistical analysis

Statistical processing of the experimental data was carried out using the Statistica 6.0 program.

RESULTS

The study showed that the concentrations of biogenic elements - iron (Fe) and manganese (Mn) - in the leaves of woody and herbaceous plants within the study areas vary widely, which may be due to differences in environmental conditions and the level of anthropogenic load. The study revealed significant variations in the

content of biogenic elements - iron (Fe) and manganese (Mn) - in Scots pine needles and herbaceous plants in the Chaldai ribbon pine forest and Bayanaul State National Nature Park (BSNP). The main objective was to assess the accumulation levels and ratios of these elements, as well as to diagnose potential environmental stress in forest ecosystems, taking into account background, natural, anthropogenic and post-fire conditions (Table 1). Based on the data obtained, it was established that the average iron content in pine needles in the Chaldai pine forest varies from 293.15 to 403.41 mg kg⁻¹, and the manganese content – from 123.4 to 522.3 mg kg⁻¹. In herbaceous plants, the iron concentration reaches 1126.98 mg kg⁻¹ in the post-fire zone, while manganese varies within the range of 135.7–309.4 mg kg⁻¹. In the BGNNP, a similar picture is observed with peaks of iron content up to 1164.04 mg kg⁻¹ and manganese up to 378.5 mg kg⁻¹ in anthropogenic zones. The assessment of the biological availability of elements was carried out using the biotic index of elements (BIE), which allows us to determine the involvement of Fe and Mn in biogeochemical cycles. In pine needles, the BIE of manganese exceeded the threshold value (0.3) in 5 of the 8 studied zones, while for iron it remained significantly lower (0.006–0.014). This indicates an active role of manganese in metabolic processes and a passive role of iron. In herbaceous plants, a similar trend was less pronounced: BIE of Mn > 0.3 was observed only in the protected area of the Chaldai pine forest and in the anthropogenic zone of the BGNNP settlement. The ratio between iron and manganese (Fe:Mn), optimal at a value of about 2:1 for normal plant functioning, was disturbed in all the studied zones. In pine needles, this indicator fluctuated from 0.5:1 to 3.6:1, which may indicate a biochemical imbalance. A particularly sharp imbalance (up to 13.3:1) was recorded in the herbaceous leaves in the BGNNP route zone, which potentially reflects stress load and excess iron with a lack of manganese. An additional indicator is the concentration coefficient (Kc), reflecting the level of technogenic pollution. For iron, the Kc values exceeded one in the herbaceous plants of the post-fire zone of Chaldai (1.18) and in the anthropogenic zones of BGNNP (up to 2.11), indicating a possible contribution from atmospheric sources. For manganese, the Kc values > 1 were recorded mainly in tree needles, especially in the natural and anthropogenic zones of Chaldai (up to 1.78), which allows us to talk about airborne technogenic pollution with Mn. The accumulation coefficient (Kn), calculated as the ratio of the element content in the plant to its concentration in the soil, demonstrated a high level of manganese accumulation. In herbaceous leaves, the values of Kn, Mn reached 13.1 in the natural zone of Chaldai and 9.32 in the anthropogenic zone. Iron, however, accumulated in significantly smaller quantities (Kn < 0.1 in all zones), which confirms the hypothesis of its predominant entry from the soil and low mobility. Correlation analysis between the content of elements in the soil and plants revealed a statistically significant positive relationship between the iron content in the soil and herbaceous plants ($r = 0.58$), while there was no correlation for Fe in pine needles ($r = 0.01$). The opposite trend is observed for manganese: a strong positive correlation between the Mn content in the soil and needles ($r = 0.72$) and a negative relationship with the grass cover ($r = -0.49$), which emphasizes the differences in the mechanisms of bioavailability between the types of vegetation. The study revealed variations in the content of biogenic elements (Fe and Mn) in pine needles in different areas of the Chaldai ribbon pine forest and the Bayanaul National Nature Park. The data are summarized in a table that includes calculations of the PBE, concentration and accumulation factors, as well as the Fe:Mn ratio, which allows us to judge the level of bioaccumulation and potential physiological risks (Table 1). The data presented in Table 1 allow us to make a comparative assessment of the content of biogenic elements iron (Fe) and manganese (Mn) in the needles of Scots pine growing in different zones of the Chaldai ribbon pine forest and the Bayanaul State National Nature Park (BSNP). The highest iron content in the needles was noted in the anthropogenic zone of the BGNNP (settlement): 717.05 mg kg⁻¹, which is almost 2.5 times higher than in the needles of the zone after the fire of Chaldai (293.15 mg kg⁻¹). In other zones, the iron content fluctuates from 358.49 to 640.51 mg kg⁻¹. The maximum concentration of manganese was recorded in the needles of the Chaldai natural zone - 522.3 mg kg⁻¹. The minimum was found in the needles of the Zhasybai zone of the BGNNP (117.5 mg kg⁻¹). This indicates a high accumulation of Mn in conditions where less pollution is possible, but a greater supply of the element from the soil. The optimal physiological ratio of iron and manganese for normal plant life is $\approx 2:1$. However, in all zones of Chaldai, except for the anthropogenic one (2.9:1), an imbalance towards manganese is observed (for example, 0.5:1 in the protected area). In BGNNP, on the contrary, the excess of iron over manganese is more pronounced - from 2.9:1 to 3.6:1, which may indicate potential physiological stress of plants. According to the standard, the values of PBE ≥ 0.3 indicate active involvement of the element in the biogeochemical cycle. In pine needles, the PBE of iron (PBE - Fe) in all zones is below 0.3, which indicates weak biological involvement of iron. At the same time, the PBE of manganese (PBE_Mn) exceeds the threshold value only in one zone - the natural zone of Chaldai (0.5803), and approaches

it in the post-fire zone (0.4632) and the protected zone (0.3257), indicating the greater significance of Mn in metabolic processes.

Table 1. Content of iron and manganese, their ratio and biotic index (BI) in the needles of woody plants in the studied areas of the Chaldai pine forest and BGNPP.

Zone	Plant type	Fe (mg kg ⁻¹)	Mn (mg kg ⁻¹)	Fe:Mn	PBE _Fe	PBE _Mn	Kc_Fe	Kc_Mn	Kn_Fe	Kn_Mn
Chaldai: a protected area	Pine needles	403.41	293.15	0.5:1	0.008	0.3257	0.88	1.78	0.01	6.7
Chaldai: natural	Pine needles	358.49	522.3	0.7:1	0.007	0.5803	0.9	0.42	0.015	13.1
Chaldai: anthropogenic	Pine needles	363.49	123.4	2.9:1	0.007	0.1371	0.73	1.42	0.01	4.8
Chaldai: After the fire	Pine needles	293.15	416.9	0.7:1	0.006	0.4632			0.007	9.3
BGNPP: Zhasybay	Pine needles	390.28	117.5	3.3:1	0.008	0.1305	1.64	1.9	0.01	2.31
BGNPP: natural	Pine needles	640.51	223.1	2.9:1	0.012	0.2479	1.17	3.22	0.01	2.26
BGNPP: route	Pine needles	455.42	378.5	1.2:1	0.009	0.4206	1.17	1.67	0.01	2.49
BGNPP: village	Pine needles	717.05	196.7	3.6:1	0.014	0.2186			0.02	2.66

Thus, the needles of woody plants show a consistently low level of iron inclusion in biogeochemical cycles, despite its high absolute content in some zones. This indicates its possible passive form in plant tissues or insufficient bioavailability. Manganese demonstrates a more active participation in the physiological processes of plants, especially in the Chaldai natural zone, which is confirmed by increased PBE. Violation of the Fe:Mn ratio, especially with an excess of one of the elements, can be associated with anthropogenic load (including man-made emissions and fires), and indicates a possible physiological stress of plants in a number of zones. The greatest environmental risk was identified in the anthropogenic zones of the BGNPP, where high concentrations of iron and manganese are accompanied by their biological activity, indicating pollution and the possibility of their entry from both the soil and the atmosphere. Thus, the table reflects the differentiated distribution of metals in pine needles, allowing this biological object to be used as an indicator of the state of forest ecosystems. Thus, the conducted comprehensive analysis showed that manganese has greater mobility and involvement in biogeochemical processes compared to iron, and its accumulation depends on both soil and atmospheric sources. Violation of the optimal Fe:Mn ratio and excess of MAC in some zones indicate local environmental stress, especially in post-fire and anthropogenic areas. A set of biogeochemical indicators allows for effective diagnosis of the current state of forest ecosystems and making informed decisions in the context of environmental protection activities. Visualization of the spatial distribution of iron (Fe) and manganese (Mn) concentrations in woody and herbaceous plants of the Chaldai pine forest is presented in Fig. 4. The X-axis shows the studied zones (protected, natural, anthropogenic and the zone after the 2017 fire), and the Y-axis shows the metal content in mg mg kg⁻¹. As can be seen from the diagram (Fig. 4), the iron content is significantly higher in herbaceous plants compared to woody plants in almost all zones, especially in the post-fire zone, where the concentration reaches 1126.98 mg mg kg⁻¹. A similar trend is observed for manganese: in the natural zone and after the fire, the Mn content in herbaceous plants (522.3 and 416.9 mg mg kg⁻¹, respectively) significantly exceeds similar values in tree needles (293.15 and 213.7 mg mg kg⁻¹). This confirms the more pronounced ability of herbaceous species to accumulate heavy metals, probably due to more active contact with the soil and atmospheric environment. A similar visualization was made for the territory of the Bayanul State National Nature Park (BSNP), which is shown in Fig. 5. Analysis of the diagram (Fig. 5) shows that in the anthropogenic (route) zone, the iron content in herbaceous plants reaches its maximum values (1164.04 mg mg kg⁻¹), exceeding the critical concentration by more than 1.5 times. Manganese concentrations also vary by zone, with the highest content noted in herbaceous plants of the anthropogenic settlement zone (310.2 mg mg kg⁻¹), while in tree leaves the maximum value was found in the anthropogenic route zone (378.5 mg mg kg⁻¹). The data confirm that zones with increased technogenic impact (route, and settlement) are characterized by a higher accumulation of metals, especially in the grass cover, which indicates intense air pollution and active metal influx from the atmosphere. Thus, both graphic images confirm

the conclusions obtained in the tabular and correlation form: biogeochemical accumulation of iron and manganese is more pronounced in herbaceous forms of vegetation, especially under technogenic impact.

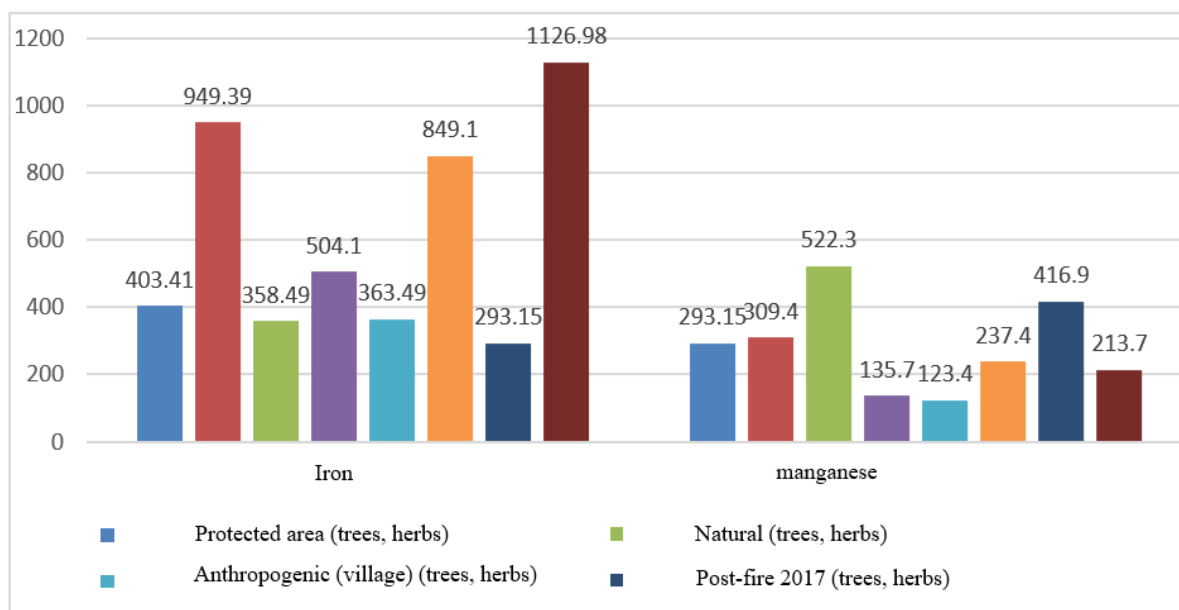


Fig. 4. Diagram of iron and manganese content in leaves of woody and herbaceous plants of the Chaldai pine forest.

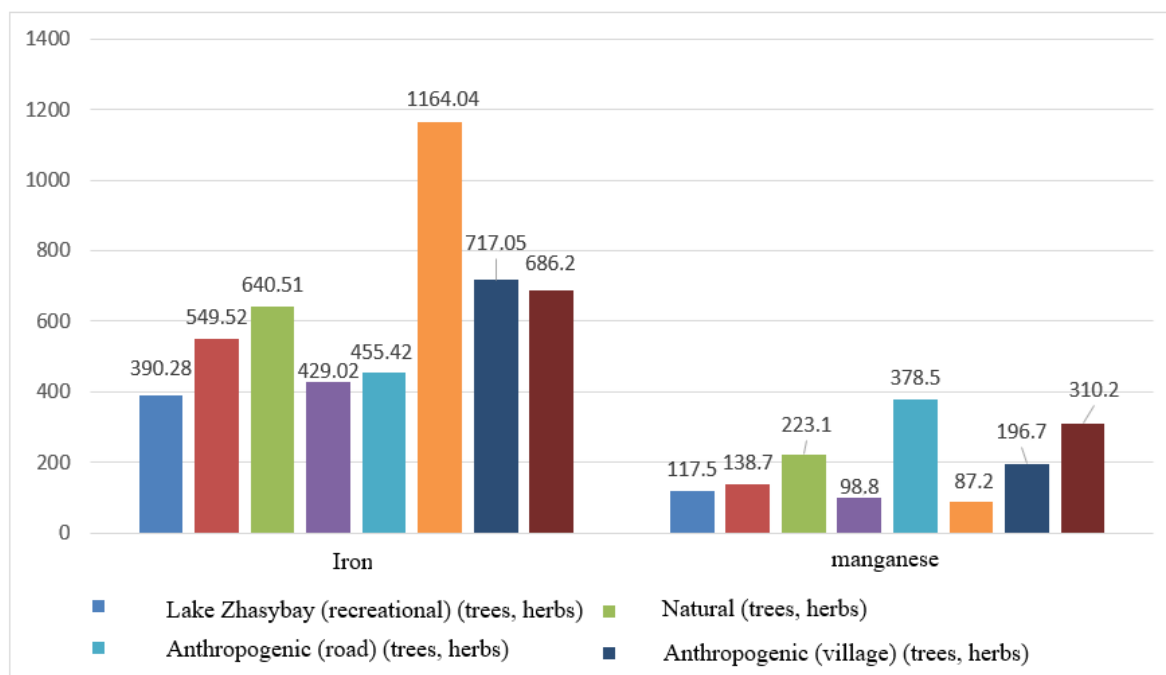


Fig. 5. Diagram of iron and manganese content in leaves of woody and herbaceous plants of the BGNNP.

The established values exceed critical concentrations, which allows us to judge the unfavorable environmental situation in certain areas of the studied territories. The results of chemical analysis of iron (Fe) and manganese (Mn) contents in needles of trees and leaves of herbaceous plants in the areas of the Chaldai ribbon pine forest and Bayanaul State National Nature Park (BGNNP) allow us to identify a number of patterns. Within the Chaldai pine forest, the highest iron content in Scots pine needles was recorded in the protected area (403.41 mg kg⁻¹), while the maximum manganese concentration was noted in the natural area (522.3 mg kg⁻¹). In BGNNP, the content of both biogenic elements in needles was minimal in the recreational area, while the highest values in anthropogenic areas, indicating the influence of anthropogenic factors. When comparing the Fe:Mn ratio, none of the studied areas showed the physiologically favorable ratio of 2:1, necessary for the normal functioning of conifers (see also Figs. 4 and 5). In the Chaldai pine forest, the most imbalanced ratio is observed in the

anthropogenic zone (2.9:1), and in the BGNNP - in the settlement zone (3.6:1). These indicators confirm the fact of disturbed mineral provision and possible functional stress of plants caused by technogenic pollution. The biotic index of elements (BIE), reflecting the participation of a chemical element in the biogeochemical cycle, for iron in all zones of both forest massifs did not exceed the standard value of 0.3. On the contrary, manganese in the needles of the Chaldai pine forest reached $BIE > 0.3$ in three of the four zones, except for the anthropogenic one. In the BGNNP, similar values were noted only in the anthropogenic (route) zone, where the BIE for Mn was 0.4206, which indicates the active inclusion of this element in biological processes under pollution conditions. The values of the concentration coefficient (Kc), showing the degree of accumulation of elements in plants in relation to background values, for iron in the needles of all the zones of Chaldai were below 1, which indicates the absence of excess accumulation. However, Kc for Mn exceeded one in zones with pronounced anthropogenic impact (natural and after a fire), which may indicate the entry of manganese from the atmosphere. In BGNNP, $Kc > 1$ for both elements in all zones, confirming the aerotechnogenic origin of pollution. The background accumulation coefficient (Ko) for iron in the soils of Chaldai generally did not exceed the threshold values, with the exception of the protected area, while manganese was not hazardous in all zones. In BGNNP, the situation is reversed: Ko for Fe exceeded 1 in all zones, which confirms the geochemical load on the soils. Manganese is hazardous only in the route zone (Ko = 1.09). The accumulation coefficient (Kn) for iron in the needles of all the Chaldai and BGNNP zones remained below one, while the Kn for manganese varied from 2.3 to 13.1, which confirms its entry from both the soil and the atmosphere. Analysis of the grass cover confirms similar trends. In the Chaldai pine forest, the iron concentration in the grass exceeds the critical value in the protected, anthropogenic and post-fire zones, while manganese reaches dangerous values only in the protected zone. In the BGNNP, the MPC excess for Fe was found only in the anthropogenic (route) zone, and for Mn - in the village zone. The Fe:Mn ratio in the grasses also does not correspond to the optimal one and fluctuates from 2.2:1 to 13.3:1, indicating a biochemical imbalance. The PBE coefficient for iron in the grasses did not reach the standard values in all zones of both forests. Manganese, on the contrary, demonstrates participation in the biogeochemical cycle in the Chaldai nature reserve zone and the BGNNP settlement zone. The Kc values for iron exceeded one in the Chaldai grasses (post-fire zone) and in both anthropogenic zones of the BGNNP. For manganese, the Kc values > 1 are observed only in the BGNNP settlement zone, which indicates a combined pathway of element intake. The accumulation coefficients (Kn) for iron in the grasses of all zones were significantly lower than one. For manganese, the Kn values in Chaldai ranged from 3.4 to 9.3, and in the BGNNP - from 1.0 to 4.2, with the exception of the route zone, where Kn was less than one. These data confirm the atmospheric pathway of Mn accumulation in most cases. Correlation analysis showed the presence of an average direct relationship between the iron content in soil and grasses ($r = 0.58$), a weak relationship with tree leaves ($r = 0.01$) and a positive relationship for Mn in needles ($r = 0.72$), which demonstrates the mobility of the element and its dependence on environmental factors. Considering the location of the forests under study in the zone of active technogenic impact, especially in the Pavlodar region, where up to 20% of industrial emissions in Kazakhstan are formed, the obtained data indicate biogeochemical stress in the plant-soil systems of the region. The main sources of pollution are metallurgical and energy enterprises that emit heavy metals, including Fe and Mn, into the atmosphere and soil. Studies indicate an excessive content of HM in the soils of the Irtysh region (Al-Rbeawi 2023), which is confirmed by the results of this work. Thus, technogenic pollution with heavy metals has a negative impact on the functional state of forest biocenoses, disrupts biogeochemical cycles and reduces the sustainability of ecosystems. The obtained values of the integral pollution index ($Zc < 16$) allow us to classify the studied territories as a zone of low pollution, however, the dynamics of HM accumulation requires further monitoring and the application of environmental measures.

CONCLUSION

The conducted chemical analysis of iron (Fe) and manganese (Mn) contents in woody and herbaceous plants of the Chaldai ribbon pine forest and Bukovo-Grachevsky State National Nature Park (BGNNP) revealed spatial heterogeneity in the accumulation of elements in the zones of the ecological gradient. In the Chaldai pine forest, the highest iron content in the needles was recorded in the protected zone, manganese - in the natural zone, while in BGNNP the minimum concentrations of both elements are typical for background areas. In all the studied zones, the iron content does not exceed critical values, while manganese concentrations in the needles in many cases exceed the standards. The biotic indices (BI) for iron in all zones of the Chaldai pine forest and BGNNP remain below the threshold value ($BI \geq 0.3$), indicating its limited participation in the biogeochemical cycle. Manganese, on the

contrary, demonstrates a high degree of involvement in the circulation of substances, especially in areas subject to technogenic impact. In pine needles, this element plays the role of a biogeochemical indicator mainly in the Chaldai pine forest and in the anthropogenic zone of the BGNPP. In the Chaldai pine forest, the values of the concentration coefficient (K_c) of iron in pine needles do not exceed one, indicating its low input into the aboveground biomass. In the BGNPP, $K_c > 1$ for both iron and manganese in all zones, indicated significant aerotechnogenic pollution. Increased values of the accumulation coefficients (K_n) for manganese (up to 13.1 in the Chaldai pine forest and up to 2.7 in the BGNPP) confirm its input not only from the soil, but also from the atmosphere. The soils of both territories, with the exception of the BGNPP route zone, remain relatively safe in terms of Mn content. Iron, on the contrary, is characterized by exceeding threshold levels in many zones. A comparative analysis of the iron and manganese content in needles and herbaceous vegetation showed a predominant accumulation of iron in herbaceous forms, while manganese is concentrated to a greater extent in needles. In the Chaldai pine forest, the concentration of manganese in grass varies unevenly, demonstrating a wave-like character, whereas in the BGNPP the maximum iron content was recorded in the grass of the recreational and highway zones, and manganese - in the recreational and settlement zones. In the pine needles of the Chaldai pine forest, excess of critical iron concentrations was found in the protected, anthropogenic and post-fire zones; manganese - in the protected zone. In the BGNPP, excess iron was recorded only in the highway zone, and manganese - in the settlement zone. These facts indicate local pollution and selective accumulation of elements near sources of technogenic impact. In all the studied forest ecosystems, the iron content in herbaceous plants significantly exceeds the manganese concentration. The physiologically optimal ratio of $Fe:Mn \approx 2:1$, which ensures normal plant metabolism, is achieved only in the village zone of the BGNPP. In other zones, especially in the Chaldai pine forest, deviations from the norm are observed, which may indicate a violation of metabolic processes and a general stress state of phytocenoses. It was found that the elements Cd, Cu, Mn and Zn ($PBE \geq 0.3$) actively participate in the biogeochemical cycle in the Chaldai pine forest, and in the BGNPP - mainly Cd and Zn. High values of the accumulation coefficient ($K_n > 1$) for most heavy metals indicate their entry from both the soil and the atmosphere. Correlation analysis confirmed the presence of a close relationship between the content of heavy metals in the soil and in the leaves ($r_{xy} = 1$), which indicates a cumulative effect of technogenic pollution. Despite the fact that the integral pollution indicator ($Z_c < 16$) classifies both studied areas as territories with a low level of pollution, the identified signs of excessive accumulation of individual elements, their unbalanced ratios and participation in the cycle indicate stable anthropogenic loads that pose a potential threat to ecosystem stability. Increased technogenic impact in combination with climate change can lead to further transformation of natural complexes and a decrease in their environmental stability.

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