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Accumulation of Heavy Metals in the Needles of Scots Pine of the Semipalatinsk Pre-Irtysh Region and Burabay National Park

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Abstract: The purpose of this article is to study pine needles (*Pinus sylvestris L.*) on the territory of the Semipalatinsk Irtysh region and the Burabay National Park to identify the features of the accumulation of heavy metals carried by atmospheric air flows, depending on the age of its formation. To determine the content of chemical elements in needles of the first, second and third year of formation from six experimental plots mass spectrometry method ISO 17294-22003 was used. Its results made it possible to conduct a primary analysis of the accumulation of heavy metals in the needles of Scots pine (*Pinus sylvestris L.*) depending on the year of its formation. Experimental studies revealed a direct correlation between the increase in concentrations of individual metals and the age of the needles. The findings can be used for further scientific research on the use of pine needles (*Pinus sylvestris L.*) as a bioindicator, the impact of the heavy metal composition of the north-east of Kazakhstan on plant organisms, but also used in practice to monitor the state of the environment and the management of forests.

Keywords: evergreen; Green Asia strategy; novel carbon resource sciences

Introduction

This article is devoted to the study of the accumulation of heavy metals in the needles of Scots pine (*Pinus sylvestris L.*) to monitor air pollution in the East Kazakhstan and Akmola regions of the Republic of Kazakhstan with heavy metals. This makes it possible to identify the role of the anthropogenic factor in the accumulation of heavy metals transported by air in living organisms. This is especially important since there are proven deposits of gold, molybdenum, uranium, lead, copper, titanium, zinc, nickel, magnesium, and iron in these areas, their extraction and processing are carried out. Furthermore, the six-lane Astana-Shchuchinsk autobahn leads to the Burabay National Park. The study of the transport of heavy metal particles by air shows the degree of accumulation of heavy metals released into the atmosphere as a result of human activity in living organisms (plants) and allows it to be separated from the accumulation obtained through root nutrition in the territories of heavy metal ores. Such a study makes it possible to identify the features of the combination of heavy metals in the atmosphere of this region, which is the result of human activity.

Such studies help to determine the most effective approach to combating air pollution that adversely affects human health. The dangers of air pollution are highlighted by H. Cometen et al.[1)] and M. Cetin et al.[2)] As they point out, 30 million people die each year from causes related to air pollution, and according to the World Health Organisation, 92% of the world's population lives in regions with polluted air. The main sources of heavy metal pollution are non-ferrous and ferrous metallurgy, quarries and mines for polymetallic ores, road transport, oil, and waste incineration. Thus, 94-97% of lead accumulated by woody vegetation, 84-89% of cadmium, 56-87% of copper, 66-75% of nickel, 58% of mercury are of technogenic origin. The remaining part is extracted by plants from natural sources, notes N.M. Baiseitova.[3)] The level of contamination with heavy metals can be determined by direct methods using special equipment or indirectly using bioindicators. According to Y. Al-Kafri,[4)] the use of bioindicators to detect air pollution gives more reliable results on changes in heavy metal concentrations. The sophisticated equipment used to measure air pollution requires special laboratories to maintain and analyse the results and does not always capture the nuances of the effects of heavy metals on living organisms at different levels of accumulation. Bioindicators, according to V. Voronin and S. Soboleva,[5] is a simpler, more accessible method that allows measuring the accumulation of heavy metals even in the field. Furthermore, bioindicators are often more sensitive to changes in heavy metal concentrations than devices.

The purpose of this study is to investigate the accumulation of heavy metals in pine needles (*Pinus sylvestris L.*) in the Semipalatinsk Irtysh region and the Burabay National Park. The study aims to identify the characteristics of heavy metal accumulation carried by atmospheric air flows, focusing on the influence of needle age. The scientific hypothesis of this study is that there is a correlation between the age of pine needles (*Pinus sylvestris L.*) and the accumulation of heavy metals carried by atmospheric air flows. It is hypothesized that as the needles age, there will be an increase in the concentrations of individual heavy metals present in the needles.

Materials and Methods

To study the degree of heavy metal pollution in the Semipalatinsk Pre-Irtysh area and the Burabay National Park, the Scots pine (*Pinus sylvestris L.*) was selected as a bioindicator, as it is a widely distributed species of woody vegetation, very sensitive to changes in the chemical background of growing conditions.[6] Pine is actively studied and used in various countries as a bioindicator and bio-accumulator of heavy metals. To study the degree of atmospheric air pollution by heavy metals in Semipalatinsk Pre-Irtysh and Burabay National Park, the needles of Scots pine (*Pinus sylvestris L.*) of the first, second and third years of formation were examined (Figure 1).

Fig. 1: The map of the Burabay National Park

This investigation also included a comparative analysis of the content of heavy metals in coniferous needles collected from two trial plots (six test plots), including control plots. The first trial site included areas of pine forests located in the Semipalatinsk Pre-Irtysh:

1. Pilot site No. 1 was located within the city of Semey (pilot site – Semey, Silicate Plant district; 50.468442, 80.212024). This site is considered the most polluted.
2. Pilot plot No. 2 (control plot) is established at a distance of 16 km to the north of Semey (control plot – Semey, Staraya Krepost village; 50.498466, 80.090461).
3. Test site No. 3 (control area) is established 18 km eastward from Semey along Semey – Borodulikha highway (control area – Semey, Novopokrovka village; 50.571381, 80.345089).

The second test site included the territories of pine forests of the Burabay National Park:

1. Pilot site No. 4 was located within the Borovoye village, 1.5 km from its centre along the main highway (pilot site – Borovoye, along the highway; 53.074672, 70.276040).
2. Pilot site No.5 (control site) is established on a mountaintop near the Abylaykhan stone throne (pilot site – Borovoye, mountain top; 53.088812, 70.233952).
3. Pilot plot No.6 (control plot) is located 120 km from the village of Borovoye, near the village of Zerenda (pilot plot – Borovoye, Zerenda; 52.887228, 69.142328).

Trees 25-30 years old, 6-9 metres in height and 24-36 cm in diameter were selected for the study. Samples of needles were sorted by age fractions (1-3 years). Chemical elements were determined by inductively coupled plasma mass spectrometry using an iCAP Q quadrupole mass spectrometer from “Thermo Scientific”. The multi-element standard solutions listed in the State system for ensuring the uniformity of measurements of the Republic of Kazakhstan under KZ.03.02.00901-2010 and KZ.03.02.00902-2010 were used to construct the calibration curves. The quality of the measurements was monitored by measuring the calibration solution every 10 samples. If the calibration chart deviated by 8-10% (unsatisfactory calibration result), the instrument was recalibrated with the new background parameters. The analysis was carried out according to ISO 17294-22003: “Water Quality. Application of inductively coupled plasma mass spectrometry (ICP-MS). Part 2: Determination of 62 elements” (state registration number 022/10505 of 27.12.2005).[7)]

Dry samples of plant raw materials for suitability for analysis for the content of heavy metals were previously subjected to autoclave decomposition. A 0.4±0.0001 g sample dry weight of the plant material was placed in a fluoroplastic autoclave liner and 6 cm^3 of concentrate was added. HNO_3 and 2 cm^3 30% N_2O_2. After 40 minutes, the PTFE liner was closed with a lid and inserted into the “BERGHOF” Speedwave Xpert microwave sample decomposition system, clamping it tightly to ensure sealing. The cover of the external casing of the autoclave was clamped with a screw. The system was heated to 190±5°C at 80% capacity and sustained. The total heating and exposure time was 50 minutes. Upon completion of the process, the cooled sample was transferred to a measuring tube and diluted with a 1% solution of nitric acid to a volume of 15 cm^3. This solution was diluted at a ratio of 1:10 and analysed for the content of the elements of interest.

Specific heavy metals (Fe, Be, Al, Cr, Mn, Ni, Cu, Zn, Sr, As, Cd, Cs, Ba, Tl, Pb, U, Co) were selected for analysis based on their toxicity and ecological significance, bioaccumulation potential, association with common pollution sources, existing studies of their impact and regulatory significance. Analysis of these metals in pine needles provided insight into levels of contamination, potential environmental impacts, and will help identify specific sources of contamination in the study area. The selection of these elements for analysis was facilitated by previous studies, which identified them as significant for assessing heavy metal pollution and its effects on ecosystems and human health. By studying these elements in the pine needles of the study area, researchers seek to gain insight into specific patterns of accumulation and potential sources of pollution in the region (Table 1).

Table 1. Environmental effects of metals in the Burabay National Park

Metal	**Detrimental effects**	**Beneficial effects**
Fe	Increased sedimentation, water quality issues	-
Be	Toxic to humans and wildlife	-
Al	-	-
Cr	Water contamination, risks to aquatic life	-
Mn	-	Essential micronutrient for plants
Cu	-	Essential micronutrient for plants
Zn	-	Essential micronutrient for plants
Sr	-	Beneficial for plant growth
As	Water and soil contamination, risks to health	-
Cd	Adverse effects on plant growth, ecosystem	-
Pb	Soil and water contamination, risks to health	-
U	Harmful effects on ecosystems	-
Co	-	Essential trace element for plants

The research carried out using the above methodology and its results are to a large extent unique, as the chemical background of the tree growth areas under study is unique, being influenced both by their geographical location, the wind direction, and the specifics of anthropogenic activity. At the same time, the results of the primary analysis of pine needles (*Pinus sylvestris L.*) samples allow for comparison with the similar unique results obtained from the primary analysis by other authors. To compare the results, the authors made a brief analytical review of the scientific literature on the results of studies of pine needles (*Pinus sylvestris L.*) carried out by scientists from different countries. Particular attention was paid to studies carried out under similar conditions - in national parks and natural forests in mountainous areas, near highways and near non-ferrous metallurgical plants. Such a comparison makes it possible to identify certain trends and features of accumulation of heavy metals transported by atmospheric masses, e.g., correlation with distance from pollution sources (highways, industrial plants).

The study on heavy metal accumulation in pine needles has limitations including a small sample size, geographic specificity, lack of long-term data, focus on specific heavy metals, limited exploration of underlying mechanisms, and potential influence of external factors.

Results

Pine trees are very sensitive to pollution. It is particularly sensitive to aerial pollution of atmospheric air by both toxic gases and chemical elements of the heavy metal group.[8),9)] It is therefore used as a bioindicator in environmental pollution assessments. The experimental data indicate that there is a definite pattern of redistribution of elements in the coniferous pine needles as the plants grow. Moreover, the accumulation of some elements occurs in close correlation with each other, as previously noted by other authors.[10)-12)] Indicators of the content of heavy metals in the coniferous pine (*Pinus sylvestris L.*) of different years of formation, obtained during the experimental study at six sites of Semipalatinsk Pre-Irtysh and the Burabay National Park, are shown in Table 2; 3.

Table 2. The content of heavy metals (Fe, Be, Al, Cr, Mn, Ni, Cu, Zn, Sr, As) in pine needles (*Pinus sylvestris L.*)

No.	Age of needles, year	Elements content, mg/kg									
		Fe	Be	Al	Cr	Mn	Ni	Cu	Zn	Sr	As
Semey, Silicate Plant district (50.468442, 80.212024)											
1	3	92±8	<0.0004	110±1	2.3±0.1	130±1	3.6±0.02	1.3±0.1	27±1	11±0.1	<0.0015
2	2	55±4	<0.0004	76±1	1.8±0.1	120±1	1.6±0.03	1.5±0.1	25±1	9.7±0.1	<0.0015
3	1	110±8	<0.0004	140±1	1.8±0.1	150±1	5.5±0.1	1.9±0.1	29±1	13±0.1	<0.0015
Semey, Staraya Krepost village (50.498466, 80.090461)											
4	3	78±4	<0.0004	100±1	2.2±0.1	140±1	0.83±0.06	1.3±0.1	22±1	10±0.2	<0.0015
5	2	47±4	<0.0004	71±1	1.2±0.1	100±1	0.34±0.04	1.2±0.1	20±1	9.1±0.1	<0.0015
6	1	53±6	<0.0004	72±1	1.2±0.1	84±1	0.7±0.06	1.2±0.1	19±1	9.1±0.1	<0.0015
Semey, Novopokrovka village (50.571381, 80.345089)											
7	3	100±15	<0.0004	350±1	2.4±0.1	750±1	0.96±0.03	2.4±0.1	63±1	27±0.2	<0.0015
8	2	76±3	<0.0004	180±1	1.3±0.1	330±1	1.2±0.04	1.5±0.1	37±1	12±0.1	<0.0015
9	1	65±6	<0.0004	160±1	1.5±0.1	330±1	0.48±0.02	1.4±0.1	31±1	11±0.1	<0.0015
Borovoye, along the highway (53.074672, 70.276040)											
10	3	190±4	<0.0004	220±1	0.9±0.1	410±1	0.59±0.01	1.7±0.1	45±1	12±0.1	<0.0015
11	2	160±8	<0.0004	230±1	0.9±0.1	380±1	0.66±0.02	2.2±0.1	43±1	12±0.1	<0.0015
12	1	190±11	<0.0004	210±1	0.6±0.1	200±1	1±0.02	2.4±0.1	39±1	9.1±0.1	<0.0015
Borovoye, mountain top (53.088812, 70.233952)											
13	3	69±4	<0.0004	450±1	1.6±0.1	590±1	0.5±0.07	1.7±0.1	42±1	21±0.1	<0.0015
14	2	59±3	<0.0004	370±1	0.6±0.1	350±1	0.17±0.01	1.2±0.1	27±1	15±0.3	<0.0015
15	1	59±3	<0.0004	260±1	1±0.1	280±1	0.22±0.03	1.8±0.1	30±1	11±0.1	<0.0015
Borovoye, Zerenda (52.887228, 69.142328)											
16	3	74±3	<0.0004	86±1	1.7±0.1	150±1	0.74±0.04	3.5±0.1	39±1	13±0.1	<0.0015
17	2	65±9	<0.0004	63±1	1±0.1	110±1	0.57±0.05	2.8±0.1	32±1	8.5±0.1	<0.0015
18	1	54±4	<0.0004	44±1	0.7±0.1	95±1	0.95±0.01	2.7±0.1	31±1	6.7±0.1	<0.0015

Table 3. The content of heavy metals (Cd, Cs, Ba, Tl, Pb, U, Co) in the needles of Scots pine (*Pinus sylvestris L.*)

No.	Age of needles, year	Elements content, mg/kg						
		Cd	Cs	Ba	TI	Pb	U	Co
Semey, Silicate Plant district (50.468442, 80.212024)								
1	3	<0.003	0.028±0.003	5.8±0.2	0.015±0.003	3.1±0.01	0.021±0.002	0.056±0.003
2	2	<0.003	0.018±0.001	5±0.1	0.009±0.002	2±0.01	0.028±0.002	0.041±0.003
3	1	0.051±0.009	0.034±0.004	6.6±0.2	0.01±0.001	3.1±0.04	0.022±0.002	0.1±0.004
Semey, Staraya Krepost village (50.498466, 80.090461)								
4	3	0.058±0.009	0.045±0.004	4.5±0.1	0.02±0.003	3.2±0.08	0.014±0.002	0.071±0.005
5	2	0.037±0.004	0.026±0.002	4.3±0.1	0.01±0.001	1.9±0.02	0.013±0.002	0.045±0.002
6	1	<0.003	0.022±0.002	4.8±0.1	<0.0004	1.6±0.04	0.013±0.002	0.053±0.002
Semey, Novopokrovka village (50.571381, 80.345089)								
7	3	0.066±0.013	0.027±0.001	17±0.1	0.013±0.003	1.7±0.03	0.034±0.005	0.086±0.004
8	2	0.045±0.003	0.011±0.001	8.5±0.1	0.01±0.001	0.9±0.02	0.011±0.002	0.042±0.002
9	1	0.038±0.007	0.013±0.002	7.7±0.1	<0.0004	0.94±0.03	0.015±0.001	0.044±0.008
Borovoye, along the highway (53.074672, 70.276040)								
10	3	0.033±0.005	0.023±0.002	5.2±0.1	0.01±0.002	0.99±0.03	0.019±0.002	0.075±0.002
11	2	<0.003	0.021±0.003	5.2±0.1	0.01±0.002	1.2±0.02	0.02±0.004	0.07±0.005
12	1	<0.003	0.037±0.004	6±0.1	0.009±0.001	0.63±0.01	0.033±0.002	0.082±0.006
Borovoye, mountain top (53.088812, 70.233952)								
13	3	0.1±0.028	0.014±0.003	6.3±0.1	0.025±0.004	0.52±0.01	0.015±0.001	0.094±0.01
14	2	0.071±0.012	0.017±0.004	4±0.1	0.012±0.001	0.63±0.03	0.011±0.001	0.11±0.007
15	1	0.19±0.027	0.015±0.003	3.5±0.2	0.01±0.002	0.32±0.02	0.013±0.001	0.043±0.001
Borovoye, Zerenda (52.887228, 69.142328)								
16	3	0.04±0.008	0.012±0.002	6.5±0.1	0.011±0.002	0.73±0.01	0.013±0.001	0.05±0.007
17	2	0.041±0.003	0.008±0.001	4.5±0.1	0.008±0.002	0.62±0.01	0.014±0.002	0.042±0.004
18	1	0.035±0.009	0.008±0.002	3.8±0.1	<0.0004	0.46±0.01	0.008±0.002	0.052±0.006

Figures 2-7 present summarized results from the study, illustrating the accumulation of heavy metals in the needles of Scots pine (*Pinus sylvestris L.*) at the six experimental plots. The figures contain data on the composition of heavy metals in Scots pine needles at each trial site and on the accumulation of heavy metals in the needles of different ages of their formation. The figures represent the results of an initial analysis and synthesis of the data obtained from the study of the needle samples at each of the sites. The identified features of the accumulation of heavy metals in Scots pine needles can be a starting point for further research, both empirical and scientific analysis, and for the comprehensive compilation of the primary results obtained. The results of analyses of Scots pine needles across the Semipalatinsk Pre-Irtysh are presented below (Figure 2-4). Regarding the Burabay National Nature Park, the results of analyses of pine needles were as follows (Figure 5-7).

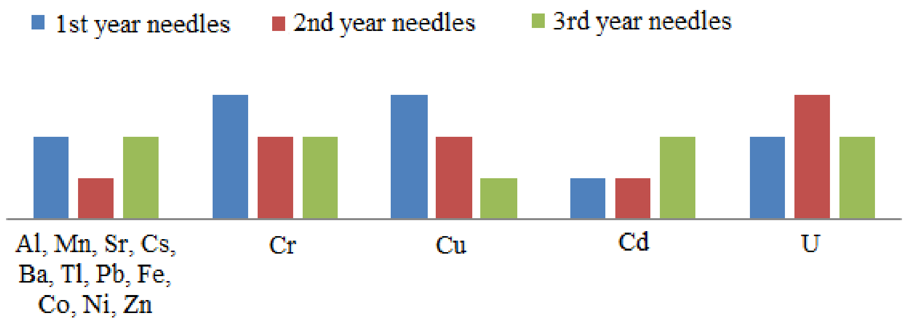

Fig. 2: Accumulation of heavy metals in pine needles by years of their formation at experimental plot No.1 (Semey, Silicate Plant district; 50.468442, 80.212024).

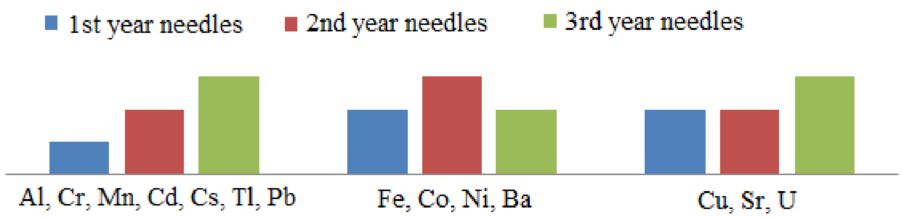

Fig. 3: Accumulation of heavy metals in pine needles by years of their formation at experimental plot No.2 (Semey, Staraya Krepost village; 50.498466, 80.090461).

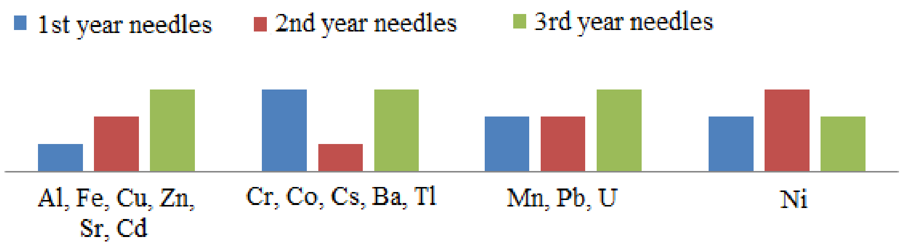

Fig. 4: Accumulation of heavy metals in pine needles by years of their formation at experimental plot No.3 (Semey, Novopokrovka village; 50.571381, 80.345089).

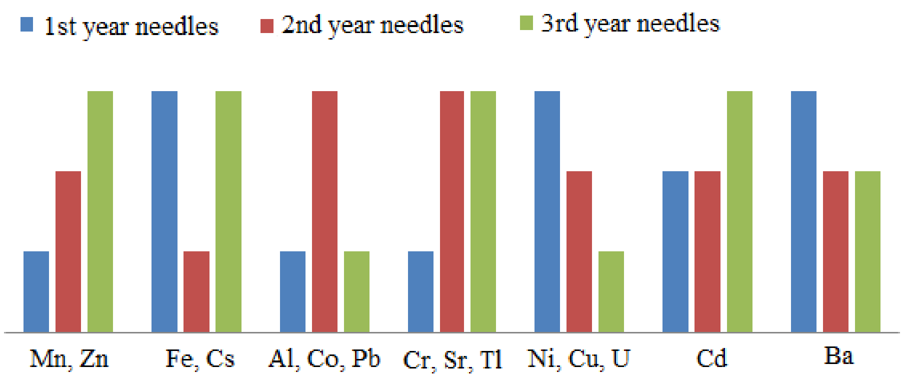

Fig. 5: Accumulation of heavy metals in pine needles by years of their formation at experimental site No. 4 (Borovoye, along the highway; 53.074672, 70.276040).

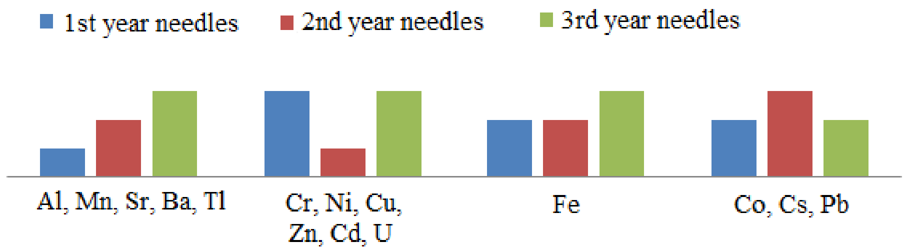

Fig. 6: Accumulation of heavy metals in pine needles by years of their formation at experimental site No. 5 (Borovoye, mountain top; 53.088812, 70.233952).

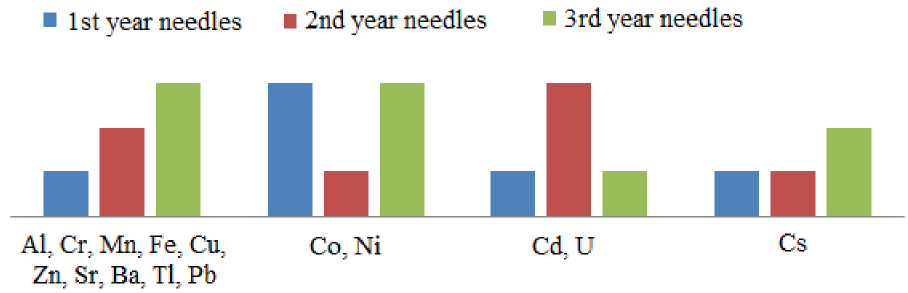

Fig. 7: Accumulation of heavy metals in pine needles by years of their formation at experimental site No.6 (Borovoye, Zerenda; 52.887228, 69.142328).

The trees in the control and experimental plots exhibited a direct correlation between the increase in concentrations of individual metals and the age of the needles. The study found that in the needles of Scots pine (*Pinus sylvestris L.*), regardless of the environmental conditions of the study area, the accumulation of metals such as Al, Mn, Fe, Cr, Zn increases with age. Mn, Cr, Fe and Zn are biogenic trace elements, while aluminium is one of the elements likely to have some effect on plant metabolism, but the role of this element (along with Ba, Cu, U, Cs) in plants and its biogenic significance require further study.

It has also been determined that the needles in the second year of formation exhibit an increase in the concentration of certain chemical elements, and then either the needles die off or the concentration decreases. This pattern can be explained by the leaching of these elements as the cuticle of the needles breaks down. Such variations in the deviations of values indicate the adaptability of pine to pollution. It is also possible that under the influence of environmental factors or the protective mechanisms of the plant itself, little-studied mechanisms of blocking the toxic effect of absorbed metals are activated. When studying the content of heavy metals in Scots pine needles (*Pinus sylvestris L.*) in the territory of Semipalatinsk Pre-Irtysh and Burabay State National Nature Park, the following pattern in their accumulation (bioaccumulation) was noted, which can be represented by the following series of elements (1):

$$\text{Mn>Al>Fe>Zn>Sr>Ba>Ni>Pb>Cu>Cr>Co>Cs=U>Tl>Cd>As>Be} \quad (1)$$

The heavy metal accumulation series obtained in this study consists of more chemical elements (17) than the accumulation series presented in the scientific literature by other authors. This may be indicative of the wide variety of minerals that are extracted and processed in the region by human industrial activity. The established pattern (1) agrees well with the data of various authors on the physiological role of individual elements. Thus, Mn, Fe, Zn, Sr, which are at the beginning of this row, are biogenic trace elements, without which the organism cannot grow, develop, and complete its natural life cycle. The same applies to elements such as Cu, Cr, Co. The elements Al and Ba in this series are very close to the biogenic elements, but their biogenic value has not been proven. The final elements in this series are Tl, Cd, As, which are highly toxic.[13)] The degree of toxicity of heavy metals can be represented by the following sequence (2):

$$\text{Cu>Ni>Cd>Zn> Pb>Hg>Fe>Mo>Mn} \quad (2)$$

Studies of various plant species with different ability to accumulate heavy metals have allowed heavy metals to be divided into four groups depending on the degree of bioaccumulation: elements of intensive absorption (Cd, Cs, Rb), elements of medium absorption (Zn, Mo, Cu, Pb, As), elements of weak absorption (Mn, Ni) and elements that are difficult for plants to access (Se, Fe, Va). It was found that in Scots pine (*Pinus sylvestris L.*) elements of intensive absorption (e.g., Cd, Cs) are less accumulated in the needles, and those difficult to access for plants (Fe, Ba) and elements of low absorption (Mn, Ni) have a high degree of accumulation in this organ.

Other researchers describe a similar but slightly different composition of these groups: elements of intense absorption (Cd, Cs, Rb); elements of medium absorption (Zn, Mo, Cu, Pb, Co, As); elements of low absorption (Mn, Ni, Cr); elements difficult for plants to access (Se, Fe, Ba, Te). One of the indicators of heavy metal pollution in the atmosphere is the age of the needles, as the accumulation of heavy metals in them, exceeding the critical limit, leads to diseases and the complete dying off of the needles. This critical limit for the concentration of base metals is 50-100 times higher than the reference value. As evidenced by I. Juranovic Cindric et al.,[14] the average age of the needles of the Scots pine (*Pinus sylvestris L.*) in the background areas is usually 5-9 years. Studies conducted at six trial plots in the Semipalatinsk Pre-Irtysh and the Burabay National Nature Park did not find pine plants with needles older than five years. This indicates significant cross-border transport of air pollutants and their dispersion over large areas.

Discussion

Scots pine (*Pinus sylvestris* L.) has proved to be a good indicator of airborne pollution, with high sensitivity, and is used in many countries for biomonitoring of atmospheric air pollution. An example is more than half a century of biomonitoring of changes in air and forest soil chemistry in two mature stands of Scots pine (*Pinus sylvestris L.*) as described by J. Pritzel et al.,[15] which allowed conclusions to be drawn about the dependence of forest ecosystem condition on changes in the chemical composition of anthropogenic emissions. However, the mechanisms of heavy metal uptake and accumulation through the surface of the needles are still largely understudied.

It is worthwhile to make a brief review of studies on the accumulation of heavy metals in the needles of Scots pine (*Pinus sylvestris L.*), made by other authors in conditions similar to those of Semipalatinsk Pre-Irtysh and the Burabay National Park in order to direct further comparative analysis of the obtained research results presented in this article. The main sources of heavy metal pollution are mining and their industrial processing, as well as highways. All of these sources are in the vicinity of the sites investigated by the authors and polluted by their emissions. Therefore, when analysing such investigations, attention was paid to the distance of pine forests from the source of pollution, the combination of heavy metals depending on the dominant sources, and the accumulation of heavy metals in the needles depending on the age of their formation. The authors investigating the accumulation of heavy metals in the needles of Scots pine (*Pinus sylvestris L.*), depending on the proximity to non-ferrous metallurgy enterprises, state that, in general, their accumulation decreases along the distance from the source of pollution. Although there are deviations for individual metals. There is also a difference in the degree of absorption between different types of trees, even of the same species.[16]

Atmospheric emissions from ferrous and non-ferrous metallurgy plants consist mainly of sulphur dioxide and heavy metal particles (Cu, Pb, Cd, Zn, Fe, Ni, Co, etc.). Thus, H.A.A. Alaqouri et al.[8] investigated the features of the accumulation of heavy metals in pine needles near the magnesium plant, focusing on the change in their concentrations depending on the age of the needles and the distance from the plant. A study of samples of Scots pine needles (*Pinus sylvestris L.*) shows its efficiency as a bioindicator for monitoring the concentration of heavy metals in the air, in particular magnesium. A decrease in magnesium concentrations was noticeable with increasing distance from the pollution source. No such correlation was observed for Al, Fe, Mn and Ca. The direct correlation between the accumulation of heavy metals in conifers and the distance to industrial plants is also confirmed by the study of V. Popovic et al.[17]

The second main source of heavy metal pollution is highways. This is important in the context of this study, as the Astana-Schuchinsk Autobahn is located in the immediate vicinity of Burabay National Park, and the study areas of the Semipalatinsk Pre-Irtysh are close to large cities and industrial centres with intensive road infrastructure. Lead and cadmium are the main heavy metals in road emissions, and both are highly toxic. The content of lead and cadmium is inversely related to the distance of trees from the road. Plants located by the roadside show lead concentrations 10-100 times higher compared to plants located farther away. Cadmium concentrations are 11-17 times higher in plants by the roadside compared to plants farther away from the road. Also, heavy metal concentrations can increase by up to 60% in the lowlands and upwind compared to the flat landscape.[18)-19] This is evidenced in a study by N.M. Baiseitova (2014). Monitoring lead and cadmium in the air is very important because of the high toxicity of these metals and their long elimination period from the body. Thus, the half-life of cadmium from the human body is about 10 years. The use of Scots pine as a bioindicator is more effective than deciduous trees, as the needles have a large absorption area and waxy surface to trap metal particles. Scots pine (*Pinus sylvestris L.*) is also a good bioindicator for Mo and Ag, and a bioaccumulator for K and Na.

The study by R. Kozlowski and M. Strzyz[20] in the Świętokrzyskie National Park (Poland), where roads of different traffic levels are the main close sources of pollution, is of interest in the context of this investigation. The study confirmed the direct dependence of the concentration of Zn, Pb on the distance to the highways, as well as on the intensity of traffic. The lead content in the exhaust gases has decreased slightly due to its partial replacement in petrol by zinc. The authors note that the highest concentrations of these metals, along with Cu, Cd and Ni, were observed in the uplands, as the Świętokrzyskie Mountains, where the park is located, are elevated above the surrounding terrain. As such, strontium was detected in addition to the heavy metals' characteristic of automotive emissions. Cu, Cd, Sr, and Ni may be emissions from enterprises in the Upper Silesian industrial area, trapped by pine forests growing in the mountainous area of Świętokrzyskie National Park.

Research conducted by S. Ayan et al.[21] in Kerey and Dzhanibek Khan Park in Astana, the capital of Kazakhstan, aimed to trace the dependence of heavy metal accumulation in five tree species, including Scots pine (*Pinus sylvestris L.*) on traffic density on the roads close to the park. Heavy metal pollution near highways is caused by exhaust fumes (Pb, Cd and Zn, used as fuel additives), abrasion of car tyres (Cd and Zn), and brake pads (Cu and Ni).[22)-24)] The study confirmed that concentrations of Pb, Cd and Zn increase with higher traffic densities and decrease with greater distance from the road. There is also an increased level of concentration of these metals on curved sections of the road. In addition to the above-mentioned metals, elevated contents of Ni, Cr, Li, Co, Fe were detected in areas close to the roads. Comparison of the heavy metal accumulation capacity of different tree species makes it possible to assess the efficiency of their use as bioindicators, depending on the potential combination of chemical elements in the air at different sites, as well as to prioritise their use for the purposes of extraction, accumulation, and purification of air from toxic impurities.[25] The ability of different tree species to accumulate heavy metals and the nature of their accumulation has been studied by authors such as J. Jonczak et al.,[26] in national parks, arboretums, respectively in Lisičine (Croatia) and Mlyňany (Slovakia), and in nature reserves.[27]

Some authors, such as A. Wegiel et al.,[9] take another step in the study of the properties of Scots pine (*Pinus sylvestris L.*) not only as a bioindicator of heavy metals in atmospheric air and soils, but also as their bioaccumulator for cleaning air and soils from elements harmful to living organisms. They investigated the dependence of accumulation levels of metals such as cadmium (Cd), nickel (Ni), chromium (Cr) and lead (Pb) on plantation density. A significant direct correlation was established between the density and mass of the stands of Scots pine (*Pinus sylvestris L.*) and the accumulation of Cd and Cr. Phytoextraction uses plants that are able to accumulate heavy metals without their toxic effects. The properties of Scots pine for phytoextraction are not widely investigated, but due to its unpretentious growth conditions and large distribution range, it can be considered as an effective phytoextractor. Research into the relationship between heavy metal accumulation and plantation density is important not only scientifically, but also practically for forest management. The purpose of the plantation as a phyto-extractor determines the decision to conduct felling. In this case, instead of thinning, the site is clear-cut and the mass of trees is disposed of, based on the nature of the contamination, which is removed by phytoextraction.[28)-30)]

Plants that collect heavy metals from the air can thereby purify the air from heavy metals.[31),32)] Heavy metals accumulate in different parts of plants in different ways. Different plants also tend to have varying degrees of heavy metal accumulation, as evidenced in a study by R. Gamrat.[33] Therefore, depending on the combination of heavy metals in a particular area, it is important to choose as bioindicators the plants that are most sensitive to it or the plants that accumulate heavy metals the most for air purification.[34),35)] Depending on the performance of the desired function, the most effective plant species are determined. In the current study, Scots pine (*Pinus sylvestris L.*) was chosen to measure the accumulation of heavy metals. The needles of Scots pine (*Pinus sylvestris L.*) of the first, second and third years of formation were examined. Conifers, which include Scots pine, are used to measure the accumulation of heavy metals from the atmosphere, as the needles stay on the tree for several years and are covered with a layer of a waxy substance that traps the heavy metal particles. Pine forests of the Republic of Kazakhstan cover an area of 832 thousand ha, of which ribbon forests of Pre-Irtysh make up 58%, or 545 thousand ha.[36] It should be noted that western, north-western, and south-western wind directions prevail in the territory of Semipalatinsk Pre-Irtysh and Burabay National Park, bringing particles of heavy metals from industrial mining and processing areas, as well as from the Astana-Shchuchinsk autobahn (Burabay National Park).

Based on the analysis of various studies, the authors can conclude that the proposed study is aimed at filling the gaps in the existing literature by studying the patterns of accumulation of heavy metals in the needles of Scots pine of different ages. This will make it possible to identify specific combinations of pollutants and their sources, give an idea of the influence of the place of growth on the accumulation of metals and contribute to the management of forest areas using pine as a bioindicator and bioaccumulator of heavy metals.

Conclusions

This study highlights the potential of Scots pine needles (*Pinus sylvestris L.*) as bioindicators for heavy metal accumulation and continuous monitoring of air pollution. The research focused on the accumulation of heavy metals in pine needles aged 1-3 years in the Semipalatinsk Pre-Irtysh and the Burabay National Park, which are in proximity to major pollution sources. The study found that the content of Al, Mn, Sr, and Zn increases with needle age, indicating a process of bio-accumulation. The accumulation of heavy metals in pine needles follows a distinct pattern, with biogenic trace elements accumulating in higher amounts compared to highly toxic elements. The elemental composition of pine needles is influenced by the specific location of growth, reflecting the intensity of the biogeochemical metal cycle.

The findings of this study contribute to the scientific understanding of heavy metal accumulation and the potential impacts of anthropogenic pressure on the ecosystem. Further research is necessary to explore and compare heavy metal accumulations in Scots pine needles. Such studies will provide a scientific basis for the management of woodlands, using Scots pine as a bioindicator and bioaccumulator. This information can aid in air purification, assessing heavy metal involvement in plant ecosystems, and evaluating the potential toxicity of wood materials.

The knowledge gained from this study can contribute to the development of strategies for mitigating air pollution and improving environmental management. It can help identify pollution sources, assess environmental impact, guide policy and regulation development, establish monitoring programs, and inform forest management and conservation efforts. Further research on heavy metal accumulation in pine needles offers opportunities to expand geographic scope, establish long-term monitoring, conduct comparative studies, investigate mechanisms, explore ecotoxicological effects, and develop practical applications for environmental management.

The scientific value of this work lies in its contribution to the understanding of heavy metal accumulation in pine needles, specifically focusing on Scots pine (*Pinus sylvestris L.*) in the Semipalatinsk Pre-Irtysh region and the Burabay National Park. The purpose and objectives of the study were accomplished.

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