# Content of chemical elements in *Pinus sylvestris* pine needles

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**Abstract.** Plant organisms absorb heavy metals and pollutants from the atmosphere and are actively used in phytoremediation methods, being in fact a "filter" of ecosystems. Coniferous pine needles are one of the most frequently used objects of monitoring studies, which is due to a wide ecological amplitude and increased sensitivity to anthropogenic changes in the process of ontogenesis. The aim of the study is the ecological assessment of the content and peculiarities of accumulation of chemical elements in the conifers of the undergrowth of common pine (Pinus sylvestris) of different age classes. X-ray fluorescence analysis (Portable X-ray fluorescence analyzer SciAps X-Series X-200, USA) was used to determine the elemental composition of plant samples. The concentration of chemical elements belonging to different classes was determined: vital, conditionally necessary, toxic. The average content of elements is as follows: for 1 year old conifers: K > Ca > Fe > S > P > Mn > Ba > Ti > Zn > Sr > Cr > Cr > Rb > Cu > Ni > Mo > Pb > Zr > V > As > Y. By the conifer of subsequent years of life Ca > K > Fe > S > P > Ba > Mn > Ti > Sr > Sr > Zn > Cr > Cr > Rb > Ni > Cu > Mo > Pb > Zr > V > As > Y.

## 1 Introduction

The kingdom of plants is one of the constituent parts of biological systematics, numbering about 390 thousand species. It is a group of eukaryotic, multicellular organisms capable of synthesizing organic matter through photosynthesis in the process of physiology. Ecological significance of plant organisms besides the production of organic matter is also a number of essential functions necessary for the optimal functioning of the biosphere. In the zonal aspect, the formation of different phytocenoses determines the diversity of landscapes and ecological conditions for other organisms. Herbaceous vegetation in the steppe possesses forage medicinal and honey-bearing properties, in parallel performing environment-forming function for steppe fauna. Ecological role in tundra communities is expressed in providing thermoregulating function of the soil, reducing the contrast between day and night temperatures of the surface layer of the soil. In mountainous regions vegetation performs anti-denudation and anti-avalanche functions, in bog ecosystems it is a source of peat formation. The specificity of forest plantations lies in the production of biomass, regulation

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of carbon and nitrogen cycles, including decomposition and mineralization of organic matter, formation of natural soil fertility.

Biota, namely above-ground and underground parts of plants are the main suppliers of soil organic matter. Based on the elemental chemical composition of plants, it becomes possible to detect processes at the ecosystem level, to identify temporal and spatial changes. Determination of elemental chemical composition is an actual scientific direction within the framework of studying biogeochemical peculiarities of chemical elements behavior in biosphere components, necessary for its sustainable development and functioning.

It is known that plants are able to absorb almost all elements of the periodic system, including heavy metals, from the environment through foliar or root absorption. The study of elemental composition determines the role of environmental factors in the accumulation of chemical elements by plants of different taxa. The concentrations of both basic and toxic elements in plant organs are affected by environmental factors, either directly due to atmospheric pollution or indirectly due to acidification. Within the framework of practical applications, the need for studies on the determination of elemental composition lies in the multifunctionality of the use of plant organisms in various fields [1,2].

Under conditions of increasing anthropogenic load, changes in the accumulation of nutrient elements by photosynthetic organs of woody plants are observed, which in turn is reflected in the elemental chemical composition. In domestic and foreign literature there is a large pool of publications reflecting the results of studies of the elemental composition of woody vegetation, allowing to determine species differences in the absorption of chemical elements.

Plant organisms absorb heavy metals and pollutants from the atmosphere and are actively used in phytoremediation methods, being in fact a “filter” of ecosystems. Thus, assimilating organs of the birch (*Betula pendula*) can actively accumulate heavy metals such as Cu, Ni, Mn. The needles of common pine (*Pinus sylvestris*) accumulate phosphorus compounds, as well as Fe Cu Zn [5, 6]. Often assimilating organs of trees are used in bioecological monitoring to assess the impact of anthropogenic factors. Thus, the needles of common pine are one of the most frequently used objects of monitoring studies, which is due to the wide ecological amplitude and increased sensitivity to anthropogenic changes during the entire ontogenesis [3, 4].

Various methods such as X-ray fluorescence chromatographic-mass spectrometric spectrophotometric atomic absorption spectrophotometry are used in ecological and biological studies of elemental analysis of plant samples [2,8].

The aim of the study is the ecological assessment of the content and peculiarities of chemical elements accumulation in the conifers of pine undergrowth (*Pinus sylvestris*) of different age classes. Age classes are understood as annual needles and needles of subsequent years of life.

## 2 Material and methods

The needles of Pinus sylvestris undergrowth of different age classes are used as an object of research. Field studies on sampling were conducted in the summer seasons of 2022-2023, on the territory of the former OPH “Gornaya Polyana” in Pinaceae forest plantations. Territorially, the site is located in Kirovsky district of Volgograd (Fig.1, A). Climatic conditions are arid with sharply pronounced continentality. The average annual air temperature is 9.4ºC and the average annual precipitation is 396 mm. (according to the Volgograd City weather station). Soil and vegetation conditions are characterized as dry-steppe zone of chestnut soils. The soil cover of the site is represented by chestnut, light-chestnut and deluvial-soils. In some areas with a noticeable surface slope, soil horizons are mixed with the parent rock due to erosion, leveling and plantation. Soil-forming rocks on the site are ancient alluvial, Quaternary and Tertiary sediments. Quaternary sediments are deluvial loess-like loams with light and medium mechanical composition, often with interlayers of yellow-brown loam.

The initial field survey of the area included reconnaissance of the area and determination of traditional taxation morphometric characteristics of the stand with selection of representative model trees (Fig.1, B). A total of 17 model trees were sampled throughout the key site. Needles from the model trees were collected using a lopper, and the samples were transported to the laboratory for desktop processing and analysis. In the laboratory, shoots were separated from branches, needles were separated by age classes, and the plant material was brought to a fine, homogeneous powder (powder).

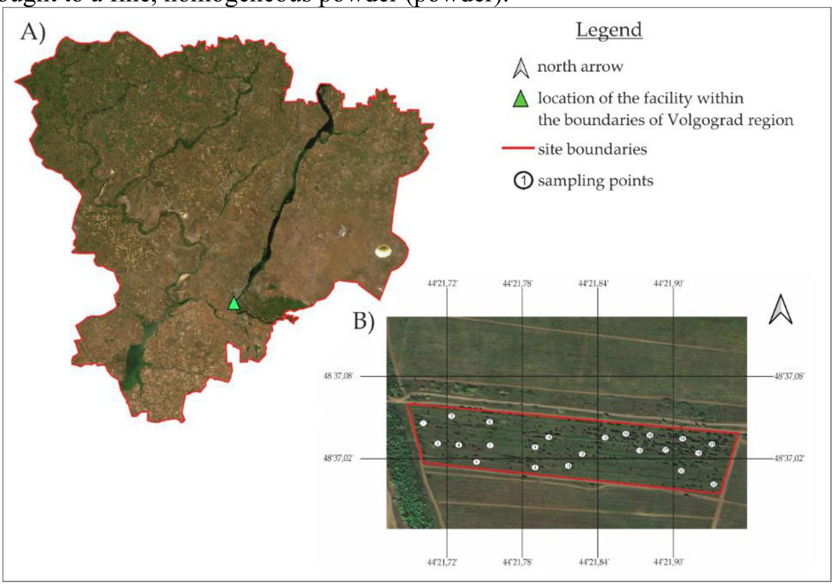


**Fig.1.** Location of the object of research (A), scheme of experiment laying (B).

In the present work, X-ray fluorescence analysis (Portable X-ray fluorescence analyzer SciAps X-Series X-200, USA) is used to determine the elemental composition of plant samples. The method allows qualitative and quantitative analysis of elements using secondary X-rays generated by X-ray irradiation of the sample, makes it possible to quickly and accurately analyze the elemental composition of a large number of samples (Franzini et al., 1972). The main advantage is considered to be non-destructive sample preparation, i.e. no stage of destruction of the material under study by chemical reagents or high temperature.

The material was placed in XRF sample containers, which are double open plastic tablets with a lid that provides ventilation for the outer overflow reservoir and a snap ring with serrated edges. Elemental analysis included determination of the following chemical elements: P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Mo, Ba, Pb.

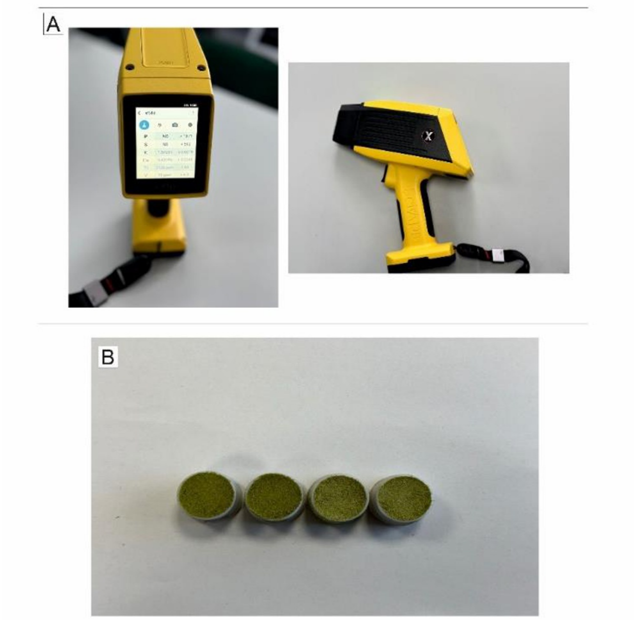


**Fig.2.** Used equipment (A), plant samples to be analyzed (B).

## 3 Results and discussion

As a result of field and desk studies, the elemental composition of the needles of Pinus sylvestris undergrowth of different age classes was determined (Table 1,2).

Chemical elements in plants are subdivided into several classes depending on their importance and significance for plant organisms:

- vital elements, which ensure the normal course of biological processes, the lack of which leads to plant oppression;
- conditionally necessary chemical elements that have a significant biological impact on the metabolic processes occurring in the plant organism;
- toxic chemical elements, the excess of which provokes negative consequences for ontogenesis.

The content of chemical elements belonging to the vital group is established by a large number of studies and scientific works. On the content of chemical elements in plant organisms of the second and third group of elements is not reliably established.

Of the chemical elements determined by us in plant samples, the distribution is as follows: vital chemical elements (K, Ca, S, P, Fe, Mn, Zn, Cr, Cu, Mo), conditionally necessary (Ti, Ni, V), toxic (Ba, Sr, Pb, Rb, Zr, As). Y is not categorized in any class, as there is insufficient information on the content of this element in plant organisms in the scientific literature. The content of chemical elements in plant samples was assessed relative to their clark in aboveground vegetation. Clark represents the established concentration of a chemical element mg/kg in the aboveground vegetation, clark numbers are used when comparing the obtained results with standards [1,7].

*Vital chemical elements.*

The average concentration of calcium in the conifers of the first year of pine is 5693.5±459.9 in conifers of 2-3 years 4401.8±727.5 These values are lower than the established clark values of the chemical element content in terrestrial vegetation. For a number of chemical elements also the values less than clark values are fixed here include Ca, K, S, P, Mn, Zn, Cu. For Fe Cr Mo exceeding of clarks content of chemical elements is noted. The following age peculiarities of the content of chemical elements are noted: in the conifer of 1 year old conifer the higher concentration of the following chemical elements K, Fe, Zn, Cr, Cu, Mo, in the conifer of 2-3 years old Ca, S, P, Mn. The accumulation of 10 vital chemical elements was determined in the conifers of Pinus sylvestris undergrowth and they have the following form K > Ca > Fe > Fe > S > P > Mn > Zn > Cr > Mo in 1-year-old conifers, Ca > K > Fe > S > P > Mn > Zn > Cr > Mo in 2-3-year-old conifers.

*Conditionally essential chemical elements.*

In conifers of Pinus sylvestris undergrowth of 1 year old on average 47±3.4 mg/kg of titanium was accumulated (from 40 to 52 mg/kg), in conifers of 2-3 years old 82±6.6 mg/kg (from 59 to 90 mg/kg). The obtained values are significantly higher than clarks by 47 and 82 times, respectively. Ni concentration ranges from 7.6 to 10.4 mg/kg in 1-year old conifers and from 7.9 to 9.2 mg/kg in 2-3-year old conifers. These values also exceed the clark values. In conifers of 1-year old Pinus sylvestris undergrowth the concentration of V ranges from 1 to 1.7 mg/kg, in conifers of 2-3 years from 0.9 to 2 mg/kg. Average values of vanadium content are insignificantly less than clark values. In general, the concentration of conditionally necessary chemical elements is higher in conifers of 2-3 years old. The content of three conditionally necessary elements in two age classes of needles was determined and it has the following sequence Ti > Ni > V.

*Toxic elements.*

The average Ba concentration in 1-year old conifers was 90±4 mg/kg in 2-3-year old conifers 201±5.6 mg/kg. The obtained data exceed the clark values by 6 and 14 times, respectively. The content of Sr in 1 year old conifers ranges from 27 to 49 mg/kg in conifers of 2-3 years from 56 to 78 mg/kg. Strontium concentrations in the studied samples exceed the clark values. The average content of Pb in the studied plant samples in pine of 1 year is 1.7±0.4 mg/kg in pine of 2-3 years 2±0.6 mg/kg. The values of lead concentration obtained by us are lower than the clark values. The average concentration of Rb in 1-year old conifers is 11.7±1.2 mg/kg (from 9.3 to 15 mg/kg) in 2-3-year old conifers 12.1±1.2 mg/kg (from 9.9 to 14.5 mg/kg), respectively. Zr accumulation in 1-year old pine varied from 1 to 1.9 mg/kg with an average value of 1.5±0.3 in 2-3 year old pine from 1.2 to 2 mg/kg with an average value of 1.6±0.2. As concentration was 1.2±0.2 mg/kg in 1-year old pine and 1.2±0.3 mg/kg in 2-3 year old pine. These values are 6.5 times higher than the clark.

In two age classes of needles the distribution of elements was in the following sequence Ba > Sr > Rb > Pb > Zr > As in two age classes of needles.

According to the established standards, the maximum permissible concentration (OFS.1.5.3.0009.15) of Pb in vegetation should not exceed 6.0 mg/kg for As 0.5 mg/kg [7]. Thus, in our case the content of lead does not exceed the maximum permissible concentration, while the maximum permissible concentration of arsenic is exceeded by 2.4 times.

**Table 1**. Concentration of chemical elements in conifers of *Pinus sylvestris* undergrowth, mg/kg

| Chemical element | Clark terrestrial plants, mg/kg | Average element content in conifers 1 year | Ratio to clark, % | Average content of the element in conifers 2-3 years | Ratio to clark, % |
|---|---|---|---|---|---|
| K | 14000 | 5693 | 41 | 4402 | 31 |
| Ca | 18000 | 3407 | 19 | 5137 | 29 |
| S | 3407 | 881 | 26 | 1152 | 34 |
| P | 2300 | 257 | 11 | 274 | 12 |
| Fe | 140 | 999 | 714 | 1322 | 944 |
| Mn | 630 | 110 | 17 | 120 | 19 |
| Ba | 14 | 90 | 643 | 201 | 1436 |

| | | | | | |
|---|---|---|---|---|---|
| Ti | 1 | 47 | 4700 | 82 | 8200 |
| Zn | 100 | 43 | 43 | 29 | 29 |
| Sr | 26 | 41 | 158 | 65 | 250 |
| Cr | 0.23 | 21 | 9130 | 19 | 8261 |
| Cu | 14 | 9.2 | 66 | 8.5 | 61 |
| Ni | 3 | 8.6 | 290 | 8.7 | 290 |
| Mo | 0.9 | 5.8 | 644 | 5.1 | 567 |
| Pb | 2.7 | 1.7 | 63 | 2 | 74 |
| Rb | 20 | 11.7 | 9 | 12.1 | 9 |
| Zr | 0.64 | 1.5 | 234 | 1.6 | 250 |
| V | 1.6 | 1.4 | 88 | 1.4 | 88 |
| As | 0.2 | 1.2 | 650 | 1.2 | 650 |
| Y | – | 0.7 | – | 0.7 | – |

**Table 2.** Statistical indicators of chemical elements concentration in coniferous conifers of *Pinus sylvestris* undergrowth, mg/kg

| Chemical element | Needle class | n | min | Q1 | med | Q3 | max | M | s | CV, % |
|---|---|---|---|---|---|---|---|---|---|---|
| K | 1 year | 17 | 4991 | 5400 | 5693 | 5820 | 6551 | 5693.5 | 459.9 | 8 |
| | 2-3 years old | 17 | 3800 | 4052 | 4105 | 4390 | 6410 | 4401.8 | 727.5 | 17 |
| Ca | 1 year | 17 | 2650 | 3082 | 3381 | 3610 | 4126 | 3407.4 | 428.8 | 13 |
| | 2-3 years old | 17 | 4230 | 4910 | 5180 | 5437 | 5889 | 5137.1 | 440.8 | 9 |
| S | 1 year | 17 | 598 | 756 | 871 | 891 | 1502 | 881.2 | 237 | 27 |
| | 2-3 years old | 17 | 789 | 985 | 1104 | 1169 | 1758 | 1151.9 | 288.6 | 25 |
| P | 1 year | 17 | 244 | 251 | 254 | 264 | 279 | 256.8 | 10 | 4 |
| | 2-3 years old | 17 | 258 | 265 | 274 | 282 | 294 | 273.6 | 10.8 | 4 |
| Fe | 1 year | 17 | 976 | 991 | 1000 | 1007 | 1012 | 998.6 | 100.4 | 2 |
| | 2-3 years old | 17 | 1100 | 1265 | 1325 | 1370 | 1560 | 1322.4 | 120.7 | 9 |
| Mn | 1 year | 17 | 91 | 101 | 110 | 112 | 139 | 110.5 | 13 | 12 |
| | 2-3 years old | 17 | 108 | 115 | 120 | 122 | 135 | 119.8 | 8 | 7 |
| Ba | 1 year | 17 | 85 | 89 | 90 | 91 | 101 | 90.5 | 4 | 4 |
| | 2-3 years old | 17 | 190 | 199 | 201 | 203 | 215 | 201.5 | 5.6 | 3 |
| Ti | 1 year | 17 | 40 | 45 | 47 | 49 | 52 | 47.1 | 3.4 | 17 |
| | 2-3 years old | 17 | 59 | 80 | 82 | 85 | 90 | 81.6 | 6.6 | 21 |
| Zn | 1 year | 17 | 37 | 42 | 43 | 44 | 48 | 42.8 | 3 | 17 |
| | 2-3 years old | 17 | 25 | 28 | 29 | 30 | 33 | 28.5 | 2 | 21 |
| Sr | 1 year | 17 | 27 | 40 | 41 | 45 | 49 | 48 | 6 | 15 |
| | 2-3 years old | 17 | 56 | 60 | 65 | 68 | 78 | 64.6 | 3 | 8 |
| Cr | 1 year | 17 | 17 | 20 | 21 | 22 | 24 | 21.2 | 1.9 | 9 |
| | 2-3 years old | 17 | 16 | 18 | 19 | 21 | 24 | 19.4 | 2 | 15 |
| Cu | 1 year | 17 | 8 | 9 | 9.2 | 9.4 | 10 | 9.2 | 0.5 | 5 |
| | 2-3 years old | 17 | 7.4 | 8.2 | 8.6 | 8.9 | 9.4 | 8.5 | 0.5 | 9 |
| Ni | 1 year | 17 | 7.6 | 8.3 | 8.6 | 9 | 10.4 | 8.6 | 0.5 | 6 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 2-3 years old | 17 | 7.9 | 8.4 | 8.7 | 8.9 | 9.2 | 8.7 | 0.4 | 8 |
| Mo | 1 year | 17 | 5.1 | 5.6 | 5.8 | 6 | 6.8 | 5.8 | 0.4 | 7 |
| | 2-3 years old | 17 | 4 | 5 | 5.1 | 5.2 | 5.9 | 5.1 | 0.5 | 9 |
| Pb | 1 year | 17 | 0.8 | 1.5 | 1.8 | 1.9 | 2.2 | 1.7 | 0.4 | 23 |
| | 2-3 years old | 17 | 0.9 | 2 | 2.2 | 2.5 | 2.9 | 2.1 | 0.6 | 29 |
| Rb | 1 year | 17 | 9.3 | 11.1 | 11.6 | 11.9 | 15 | 11.7 | 1.2 | 10 |
| | 2-3 years old | 17 | 9.9 | 11.8 | 12.1 | 12.8 | 14.5 | 12.1 | 1.2 | 10 |
| Zr | 1 year | 17 | 1. | 1.4 | 1.5 | 1.6 | 1.9 | 1.5 | 0.3 | 17 |
| | 2-3 years old | 17 | 1.2 | 1.5 | 1.6 | 1.8 | 2 | 1.6 | 0.2 | 14 |
| V | 1 year | 17 | 1 | 1.2 | 1.4 | 1.4 | 1.7 | 1.4 | 0.2 | 15 |
| | 2-3 years old | 17 | 0.9 | 1.1 | 1.4 | 1.5 | 2 | 1.4 | 0.3 | 28 |
| As | 1 year | 17 | 0.8 | 1 | 1.3 | 1.3 | 1.5 | 1.2 | 0.2 | 19 |
| | 2-3 years old | 17 | 0.8 | 0.9 | 1.2 | 1.2 | 2 | 1.2 | 0.3 | 29 |
| Y | 1 year | 17 | 0.4 | 0.6 | 0.7 | 0.7 | 0.8 | 0.7 | 0.1 | 15 |
| | 2-3 years old | 17 | 0.4 | 0.6 | 0.7 | 0.7 | 0.8 | 0.7 | 0.1 | 16 |

## 4 Conclusions

Field work to collect plant material and desktop processing allowed us to determine the elemental composition of the needles of Pinus sylvestris undergrowth of different age classes. The average content of elements is as follows: for conifers of the 1st year: K > Ca > Fe > S > P > Mn > Ba > Ti > Zn > Sr > Cr > Cr > Rb > Cu > Ni > Mo > Pb > Zr > V > As > Y. By conifers of subsequent years of life Ca > K > Fe > S > P > Ba > Mn > Ti > Sr > Sr > Zn > Cr > Cr > Rb > Ni > Cu > Mo > Pb > Zr > V > As > Y. Higher contents of K, Zn, Cr, Cu, Mo were observed in 1 year old needles compared to 2-3 year old needles. Macroelements K, Ca, S, P, Fe are accumulated to a greater extent in plant samples. According to the established regulations, the maximum permissible concentration (OFS.1.5.3.0009.15) of Pb in vegetation should not exceed 6.0 mg/kg for As 0.5 mg/kg. So in our case, the content of lead does not exceed the maximum permissible concentration, while the content of arsenic exceeds the established value by 2.4 times.

## 5 Acknowledgements

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