Effect of the Industry-Related Air Pollution on the Accumulation of Heavy Metals in the Pine Needles in the Basin of the Selenga River

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Abstract

The concentrations of heavy metals (mercury, cadmium, lead, copper and zinc) in needles of *Pinus sylvestris* growing at the polluted and background territories of the basin of the Selenga River are investigated. The dependence between the metal content of needles and the soil is shown. Using the concentration coefficients for different pollution zones, the rows of metal accumulation in pine needles are arranged; they depict the level of the emission load on forests. In the zone of strong pollution, the highest correlations between the concentrations of lead and cadmium in needles and the morphometric parameters of trees are detected.

INTRODUCTION

The strategy of sustainable development foresees evaluation of the status of natural ecosystems, determination of he scales of the anthropogenic impact on them, as well as the efficient measures aimed at the conservation of territories, first of all those having special importance. That is why the state of the unique ecosystem of Lake Baikal as a region of the world natural heritage attracts much attention of researchers [1]. At present, one of the main anthropogenic factors having a negative effect on the Baikal Natural Territory is the industry-related atmospheric pollution. The specific features of its influence involves changes in the biogeochemical cycles of many elements due to their uncontrollable transport with emissions; as a result, he stable functioning of ecosystems including forest ones gets disturbed.

Such a criterion as the state of tree plants and forest stands has been used for a long time as the informative index adequately depicting the ecological situation in the forests of the Baikal region [2]. To evaluate the degree of industry-related pollution of forest ecosystems, the most acceptable approach is determination of the element composition of assimilation organs of trees [3]. The obtained results allow one to reveal the toxic, deficient or optimal level of elements in plants.

Investigations carried out by us previously showed that the main environmental pollutants in the water-collecting area of Lake Baikal, in the basin of its largest tributary the Selenga River, are sulphur oxides causing weakening of forests over vast territories [4]. In agreement with the level of sulphur content in the needles of *Pinus sylvestris*, the zones of strong, medium and weak pollution of forests were revealed, as well as the background territories where the forest stand is not subjected to pollution. Taking into account the polyelement character of emissions of the large industrial

centres of the Republic of Buryatia situated in the basin of the Selenga, it should be noted that, in addition to sulphur oxides, a substantial contribution into the increased emission load on forest is made also by heavy metals (HM). It is necessary to take into account the fact that the gaseous sulphur-containing compounds that acidify the environment cause an increase in the mobility and hence in the biological activity of metals, which causes a sharp increase in their toxic action on the biota.

The goal of the investigation was to study the accumulation of heavy metals (mercury, cadmium, lead, copper, zinc) in the needles of *Pinus sylvestris* growing at the water-collecting territory of Lake Baikal where large industrial centres of the Republic of Buryatia are situated in Ulan Ude, Gusinoozersk and Nizhneselenginsk.

REGION, SUBJECT AND METHODS OF INVESTIGATION

The forest-coated territory of the basin of the Selenga River (within the boundaries of the Republic of Buryatia) occupying the area about 5 mln ha. Pine forest stands (*Pinus sylvestris* L.), one of the major forest-forming species of the region possessing the high sensitivity to atmospheric pollutants were examined. The features of the natural conditions in the region under investigation, pollution sources, the procedure of field observation of forests by laying test grounds (TG) and taxation characterization of forest stand on TG were reported in [4]. The HM content of the plant samples collected at each TG was determined by means of atomic absorption spectrometry after preliminary dry ashing of the material at 450 °C [5]. To study the effect of soil conditions on HM concentrations in pine needles, soil samples were also taken from the upper (0–30 cm) layer. Determination of the mobile forms of HM was carried out in the 1 M HCl extract after extraction for 1 h.

Analyses for the HM content were carried out in the certified analytical laboratory of the Vinogradov Institute of Geochemistry, SB RAS (Irkutsk). Determination of the elements was carried out with the Perkin-Elmer M 403 atomic absorption spectrophotometer with frame and/or electrothermal atomisation of the matter under investigation. To determine mercury, atomic absorption with cold vapour was involved; lead and cadmium were measured by means of atomic absorption with electrothermal atomisation in the graphite atomizer HGA-72, zinc and copper were detected by means of atomic absorption with flame atomisation in hydrochloric or nitric solution of the soil extract/plant ash [5].

Detection (sensitivity) limits were (mg/kg): mercury 0.005–0.2, lead 0.05–2, cadmium 0.005–0.1, zinc 20–80, and copper 0.5–20.

The background concentrations of the elements in pine needles were determined at TG situated at a distance of 50–200 km from the industrial centres. To estimate the level of element accumulation in the needles under the industry-affected conditions, the concentration coefficients (K_c) with respect to the mean background concentration were calculated [6].

The mathematical treatment of the results was carried out using standard methods; the following statistical indices were determined: M – arithmetic mean, m – error of mean, lim – variation limits, V – variation coefficient, %, r – correlation coefficient, n – repeatability [7].

RESULTS AND DISCUSSION

Concentrations of heavy metals in pine needles under the background conditions

To determine the level of tree provision with the elements of mineral nutrition and to evaluate the degree of their pollution under the action of atmospheric industrial emission, it is necessary to known the initial (background) chemical composition of the subject under investigation, in particular pine needles. Results of analyses showed that among the investigated HM the highest zinc concentration is observed in the needles. In some cases zinc concentration exceeds that of copper, lead, cadmium and mercury by several orders of magnitude. This is likely to be connected with the fact that zinc is included in more than 200 enzymes belonging to all the six classes of the enzyme catalogue and plays important biochemical functions in plants in connection with the metabolism of proteins, hydrocarbons, lipids, nucleic acids [8]. The minimal concentration in

the needles of background pine trees was detected for mercury. It should be noted that the concentrations of mercury, lead and cadmium in the needles at the background TG was lower than the toxicity threshold if the latter is estimated according to [9]. On the basis of the data obtained, the following row of element concentrations in the needles of pine trees growing at the background territories of Transbaikalia can be ranged:

$$\frac{\text{Zn}}{n\cdot 10^{-3}\%} > \frac{\text{Cu}}{n\cdot 10^{-4}\%} > \frac{\text{Pb}}{n\cdot 10^{-5}\%} > \frac{\text{Cd}}{n\cdot 10^{-6}\%} > \frac{\text{Hg}}{n\cdot 10^{-7}\%}.$$

The chemical composition of plants is formed under the action of a large number of factors. They can be divided into two groups: internal (physiological and biochemical) and external (ecological), connected with the geological, soil, climatic and other environmental conditions of the plant habitats [10]. No significant differences are detected in the comparison of our data on metal concentrations in the needles of pine trees growing under different conditions (from different types of forest). This points to the existence of an adaptive mechanism directed at the provision of the level of chemical elements necessary for the life of plants. Analysis of the data showed that under the background conditions relatively stable concentrations of chemical elements are characteristic of pine needles, with variation within ±10 % around the mean values (K_c = 0.9–1.1). This confirms that the mean background HM content can serve as a reliable criterion to evaluate the level of industrial pollution of pine forest in the region under investigation.

The effect of edaphic conditions on metal accumulation in pine needles was considered for the examples of lead (a toxic element), copper and zinc (necessary microelements) (Table 1).

One can see that the soil of he background TG is characterized by rather high concentration of the mobile form of lead. This fact is likely to be connected with the regional feature of the soil in Transbaikalia; this soil is characterized by the higher lead content than its clarke in the lithosphere (by a factor of 2.2) [12]. At the same time, correlation analysis did not reveal a reliable connection between lead content of the soil and of pine needles (r = 0.15, $P \geq 0.05$, n = 30). The coefficient of biological accumulation (CBA) of lead, calculated as the ratio of the element concentration in needles to the concentration of its mobile form in soil, turned out to be much smaller than unit for pine (0.026±0.002), which is an evidence of the weak intake of this element by plants. This may be due to the fact that the admission of lead to the top organs of plants from the root system is limited by the protective physiological and biochemical mechanisms, so that its accumulation proceeds *via* the background barrier type [13, 14].

TABLE 1

Concentrations of the mobile forms of heavy metals in soil at the background test grounds, mg/kg

Element	$M\pm m$	lim	V, %	MPC [11]
Zn	4.9±0.5	3.4–6.6	32	23
Cu	2.1±0.2	1.5–2.6	24	3
Pb	5.1±0.4	3.8–6.9	21	6

The average content of the mobile copper form in soil for a number of TG approached the MPC, too, which points to rather high mobility of this element in the soil of the region. However, the majority of plants absorb copper according to the barrier type: the high concentration of this element in soil and in rocks is not always accompanied by an adequate increase of copper concentration in plants [14]. Correlation analysis showed that under the background conditions there is a weak positive dependence of copper content in pine needles on its concentration in soil (r = 0.37, P = 0.05, n = 30), CBA = 1.0.

The concentration of mobile zinc in soil at the background TG is much lower than the established MPC. Correlation analysis revealed an essential positive connection between the element concentration in pine needles and in soil (r = 0.64, $P \geq 0.05$, n = 30). The CBA for zinc turned out to be rather high for pine (7.3), which is an evidence of the active (barrier-free) accumulation of this element by plants. So, among the considered HM, only the level of zinc content in soil can have a strong effect on its content in pine needles.

In general, the concentrations of chemical elements in pine needles at the background TG situated in the sites with different growing conditions were shown to be relatively stable. This proves the existence of a mechanism of selective accumulation of the elements of mineral nutrition directed at the maintenance of stable and vitally favourable state for this species. It may be concluded on the basis of the data obtained that under the background conditions the chemical composition of pine needles is determined to a larger extent by the inherently fixed biochemical features of tree types.

Heavy metal content of pine needles under the conditions of the industrial atmospheric pollution

Under the conditions of industrial pollution, substantial changes in HM concentrations are observed in the needles (Table 2). The most clearly exhibited accumulation is characteristic of lead; its concentration in pine needles exceeded the mean background value at the major part of the investigated territory (60 % TG of their total number). In this situation, high concentrations of this element (K_c = 4.5–4.7) were revealed at the territories of industrial centres; the medium level of accumulation (K_c = 1.5–2.8) is characteristic of the territories situated at a distance up to 40 km, as well as in the vicinity of large settlements and at a number of watershed heights. In the absence of evident sources of lead emission in sampling sites, its accumulation is connected most probably with the propagation over large distances with the submicron fraction of aerosol from industrial emissions formed in high-temperature processes at power stations and other facilities [15].

Pollution of the investigated territory with cadmium has a local character, judging from cadmium accumulation in pine needles. Pollution with cadmium almost completely embraces the territory of the Nizhneselenginsk industrial centre propagating over the distance up to 40 km, and the zone of the Ulan Ude centre. The detected slight increase in cadmium content of pine needles at the territory within the distance up to 20 km from the Gusinoozersk industrial centre and at the territories adjacent to a number of large settlements provides the evidence of the presence of local regions of weak pollution.

The concentrations of mercury, copper and zinc were within the mean background range for the major part of the investigated territory. Local accumulation of copper was revealed only at the territory of industrial centres where

TABLE 2

Concentrations of heavy metals in the needles of *Pinus sylvestris* under industrial pollution, mg/kg

Location of test grounds	Industrial centre and distance from it, km	Hg	Cd	Pb	Cu	Zn
	The region of strong pollution					
Ulan Ude	Ulan Ude, industrial zone	0.012 (1.3)	0.024 (1.6)	0.56 (4.7)	3.7 (1.8)	31.1 (0.8)
Zaozerny settlement	Gusinoozersk, industrial zone	0.013 (1.4)	0.020 (1.3)	0.55 (4.6)	3.1 (1.5)	30.9 (0.8)
Selenginsk settlement	Nizhneselenginsk, industrial zone	0.012 (1.3)	0.045 (3.0)	0.54 (4.5)	3.5 (1.7)	22.8 (0.6)
	The region of medium pollution					
Erkhirik village	Ulan Ude, 15	0.011 (1.2)	0.020 (1.3)	0.31 (2.6)	2.1 (1.0)	32.4 (0.9)
Ubienny ridge	Gusinoozersk, 16	0.011 (1.2)	0.018 (1.2)	0.18 (1.5)	2.1 (1.0)	31.9 (0.9)
Gasan mountain	Nizhneselenginsk, 12	0.010 (1.1)	0.023 (1.5)	0.21 (1.7)	2.1 (1.0)	34.9 (1.0)
	Region of weak pollution					
Onokhoy settlement	Ulan Ude, 40	0.006 (0.7)	0.019 (1.3)	0.16 (1.3)	2.1 (1.0)	31.8 (0.9)
Korolkov fold	Gusinoozersk, 40	0.019 (2.1)	0.016 (1.1)	0.31 (2.6)	2.1 (1.0)	37.2 (1.0)
St. Tataurovo village	Nizhneselenginsk, 40	0.013 (1.4)	0.024 (1.6)	0.24 (2.0)	2.1 (1.0)	33.8 (0.9)
Mean background concentration		0.009	0.015	0.12	2.1	36.3

Notes. 1. K_c values are given in brackets. 2. Pollution regions were distinguished on the basis of sulphur content in pine needles [4].

copper content exceeded the background value by a factor of 1.5–1.8.

For mercury, considered as one of the most toxic elements [16], a weak tend for accumulation in pine needles was observed at the territories of industrial centres. At the same time, an increase in mercury concentration by a factor of 1.4–2.1 was recorded within the radius of 40 km from the Gusinoozersk and Nizhneselenginsk industrial centres, which may be due to the natural anomalies of this element.

As far as zinc is concerned, some decrease in its concentration in needles is observed at the territory of industrial centres, which may be due to leaching this element from needles with acid precipitation. In addition, the antagonism of this element with copper, iron and cadmium is possible [9], which is indirectly evidenced by an increase in the concentrations of these elements in needles by a factor of several units.

The analysis of HM content of pine needles in the wood stands differing in pollution degree showed that an increase in the concentrations of lead, cadmium and copper is observed in the region of strong pollution, while the amount of zinc decreases. In this situation, the character of metal accumulation somewhat differs depending on the level and specific composition of industrial emissions. For instance, at the territory of the Nizhneselenginsk industrial centre (with the Selenginsk Pulp and Paper Mill and Plants of Construction Materials as the sources of pollution), the highest accumulation in pine needles is observed for lead (K_c = 4.5), cadmium (K_c = 3.0) and copper (K_c = 2.0). At the territory polluted with the emissions from the Ulan Ude industrial centre (heat plants, machinery construction, production of construction materials), the concentration of lead increases substantially (K_c = 4.7), while the concentrations of cadmium (K_c = 1.6) and copper (K_c = 1.8) correspond to the medium accumulation level. Under the action of pollutants from the Gusinoozersk industrial centre (Gusinoozersk State Regional Power Plant) on tree stands, the concentration of lead in needles increases (K_c = 4.6), while the concentrations of cadmium (K_c = 1.3) and copper (K_c = 1.5) correspond to the weak level of accumulation. In general, the following row of metal accumulation in pine needles is characteristic of the strongly polluted region (calculated as an average for three industrial centres): $Pb_{4.6} - Cd_{2.0} - Cu_{1.7} - Hg_{1.3} - Zn_{0.7}$.

With an increase in the distance from emission sources, the concentrations of the investigated metals decrease. Nevertheless, in the region with the medium degree of pollution (at a distance of 16 km from the industrial zone), the concentration of lead in pine needles exceeded the mean background value by a factor of 1.5–2.6, cadmium 1.2–1.5, while the level of copper turned out to be comparable with the mean background value; the row of metal accumulation in pine needles was $Pb_{1.9} - Cd_{1.3} - Hg_{1.2} - Cu_{1.0} - Zn_{0.9}$. In the region of weak pollution, lead conserved its leading position in accumulation rows; in addition, an increased level of cadmium and mercury was detected in pine needles. The row of accumulation in needles was: $Pb_{1.9} - Hg_{1.4} - Cd_{1.3} - Cu_{1.0} - Zn_{0.9}$.

Effect of soil conditions on the changes of the elemental composition of pine needles under industry-related pollution

The concentrations of the mobile forms of lead, copper and zinc is the soil of polluted territories were investigated. For lead, the content varied within the range 2.4–8.0 mg/kg, with the mean value (5.0±0.5) mg/kg. A half of the recorded values varied within the range from 2.4 to 4.8 mg/kg (50 % of cases) increasing to 7–8 mg/kg at the territories of industrial centres. Correlation analysis revealed a significant positive correlation (r = 0.56, $P \geq 0.05$, n = 15) between the concentrations of lead in soil and in pine needles in the TG situated at the territories of industrial centres, while the correlation turned out to be uncertain at the background territories. In addition, an increase in the CBA of lead was observed at the polluted TG (0.1 against 0.03 for the background). On the basis of the data obtained; we may conclude that the action of industrial emission weakens the general physiological status of trees and distorts the barrier mechanisms that limit lead intake to the top organs; as a consequence, this element may now enter the needles not only from the atmosphere but also from soil.

The concentration of the mobile form of copper in the soil of the territories under investigation varied within the range 0.9–3.4 mg/kg, with the mean value (2.2±0.2) mg/kg. Copper concentrations exceeding the MPC are characteristic of the territories of industrial centres, which is likely to be due to the arrival of copper into soil with aerial industrial emissions. At the same time, correlation analysis showed the absence of a significant correlation between the concentrations of copper in soil and in needles ($r = 0.26$, $P = 0.05$, $n = 15$) at the territories of industrial centres, which is an evidence of mainly foliar copper intake in pine needles at these TG.

The concentration of the mobile form of zinc in soil at the investigated territory varied from 1.6 to 6.4 mg/kg, with the mean value of (4.5±0.4) mg/kg, which is much lower than the accepted MPC. For the territories of industrial centres, we observed a decrease in the concentration of zinc in soil, not very high correlation between its concentration in soil and in needles ($r = 0.61$, $P = 0.05$, $n = 15$), and less intense accumulation of this element by plants (CBA = 5.5). This fact is likely to be due to the manifestation of the antagonism of Zn with the accumulation of other HM or with Zn leaching from soil.

So, under the conditions of atmospheric industrial pollution, an increase in the concentrations of mobile lead and copper forms in soil is observed, both due to the arrival of these metals with aerial emissions and due to an increase in their mobility caused by the acidation of soil solution. As a result of weakening of the physiological state of trees, the barrier mechanisms are distorted, which can be one of the sources of the excessive amounts of HM in the top organs of plants, along with the atmospheric arrival.

Visual and morphometric indices of pine needles and sprouts under the conditions of industrial pollution

An imbalance of the elemental chemical composition of needles causes changes in the intensity and direction of plant metabolism; therefore, the growth parameters of trees are distorted. The analysis of the visual and morphometric indices of pine trees over the pollution regions showed that an approach to the emission source is accompanied by an increase in tree crown defoliation up to 60 %, decrease in the needle lifetime to three years, a decrease in sprout length by 40–80 %, needle length by 10–50 %, needle mass by 50–80 %, the number of needles per one sprout by 40–80 % of the background level (Table 3).

The high coefficients of the correlation of the considered indices with HM accumulation in pine needles were revealed for the tree stands in the region of strong pollution. For example, the concentrations of lead and cadmium in the needles of these trees exhibit a positive correlation with the level of crown defoliation (for

TABLE 3

Visual and morphometric indices of pine needles and sprouts over pollution regions

Pollution region	Crown defoliation level, %	Age of needles, years	Mass of needles per one sprout, g / Number of needles per one sprout, sp.	Needle length, cm / Sprout length, cm
Strong	60	3	1.61–1.98 / 93–100	4.1–4.9 / 7.3–11.0
Medium	45	4	1.75–2.12 / 107–126	4.3–5.3 / 8.0–12.0
Weak	35	4–5	1.98–2.47 / 119–174	5.5–5.7 / 12.8–16.4
Background territory	20–25	5–6	2.41–4.32 / 145–193	5.6–6.9 / 14.2–17.6

lead, $r = 0.64$; for cadmium, $r = 0.56$, $P = 0.05$, $n = 43$) and a negative correlation with the length of sprouts, needles, with needle mass, as well as with the number of needles per one sprout (for lead, $r = -0.78...-0.86$; for cadmium, $r = -0.46...-0.64$, $P = 0.05$, $n = 22$), while for copper and mercury the correlations turned out to be insignificant. For the trees growing in the region with medium level of pollution, the closeness of correlations decreases, while in the region of weak pollution and under the background conditions the correlation coefficients are uncertain. Therefore, under the conditions of strong pollution lead and cadmium to a high extent promote an increase of the emission load and in combination with other toxicants serve as one of the important factors affecting the status of tree stands.

CONCLUSION

The results obtained provide evidence that the highest accumulation of HM in pine needles is observed at the territories of industrial centres(Ulan Ude, Gusinoozersk and Nizhneselenginsk). The accumulation of HM in pine needles in the region of string industrial pollution is connected with the income not only from the atmosphere but also from polluted soil as a result of distortion of the barrier mechanisms due to tree depression. The rows of accumulation, composed on the basis of concentrating coefficients, depict the level of emission load on tree stands, as well as the contribution from separate elements into the phytotoxic effect caused by the multicomponent atmospheric pollution on the physiological state of trees. The high level of HM accumulation in pine needles in the region of strong pollution and their effect on the morphometric parameters of the trees provide the necessity to monitor the concentrations of a number of toxic metals in the emissions of industrial enterprises. At present, mainly the monitoring of lead is carried out in the Republic of Buryatia.

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