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Elemental Composition of the Leaves of Wood Plants under the Conditions of Technogenic Pollution

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Abstract

Chemical composition of assimilating organs of *Pinus Sylvestris* and *Betula pubescens* in the zone affected by the GMK Pechenganikel JSC situated in the northwest of the Murmansk Region near the borders of Finland, Norway and Russia was studied. Anomalously high concentrations of copper and nickel in the leaves (needles) of trees under the conditions of technogenic pollution were revealed. Insufficient provision of pine needles with nutrition elements – phosphorus and potassium – was discovered. Higher concentrations of copper, nickel and sulphur in comparison with their concentrations in pine needles were detected.

Key words: elemental composition, pine, birch, leaves, needles, atmospheric pollution, GMK Pechenganikel JSC, northern taiga forest, the Kola Peninsula

INTRODUCTION

The balanced mineral composition of plants determines their normal growth and development. Under atmospheric pollution, excess amounts of pollutants enter plant tissues as a result of foliar and root absorption. This causes redistribution of many biogenic elements. As a result, the provision of nutrition elements decreases not only for assimilating organs, separate plants, but forest biocenoses in general. The largest source of the emission of acidifying substances into the atmosphere and heavy metal compounds in the Murmansk Region is Pechenganikel Combine, which is in operation since 1946. The critical levels of heavy metals are exceeded at the territory with the area more than 3200 km^2 [1]. Long-term technogenic pollution caused substantial disorder in functioning forest ecosystems, including distortions of the mineral nutrition of plants. Negative consequences for forest ecosystems are observed at a distance up to several ten kilometres from the source. Visible damage of plants, caused by SO_2 emission, is characteristic of different plant species including *Pinus sylvestris* and *Betula pubescens*. In the direct vicinity of the factory there are many dead standing trees; the forest is damaged. A decrease in production capacity during the recent two decades provided the initial indices of the recovery of ecosystems but the processes of pollutant accumulation in different components of forest phytocenoses still go on.

The goal of the work was to study the chemical composition of assimilating organs of foliate (*Betula pubescens* Ehrh.) and coniferous (*Pinus sylvestris* L.) trees in the zone affected by the GMK Pechenganikel.

EXPERIMENTAL

Plant samples were collected at test ground (TG) situated at different distances from the combine. The major type of forest vegetation in the region under study is the birch forest herbosa-suffruticose and suffruticose, as well as pine forest herbosa-suffruticose and suffruticose. The number of studied TG is 23 (Fig. 1): 11 at the territory of Finland (F-1–F-11), 7 – Russia (RUS1, RUS2, RUS3, N6, S3, S10, RUS0), 5 – Norway (PA, PB, PC, PD, N11). Reference TG were laid at the territories of Russia (RUS0) and Finland (F-11) at a distance of 42 and 131 km of the combine, respectively.

The samples of pine needles and birch leaves were collected at the listed objects at the end of the vegetation period (August) in 2004. At each TG, assimilating organs were collected from five trees and united into the mixed sample. Pine needles were classified according to age. The data on the chemical composition of one-year-old needles are presented in the work.

The quantitative chemical analysis of plant samples was carried out at the Centre of Shared Instrumentation for physicochemical analysis methods at the Institute of North Industrial Ecology, Kola Scientific Centre of RAS (Apatity). Analytical examination was carried out according to the State Standard GOST 30178–96 [2] and other generally accepted procedures [3, 4]. The concentrations of chemical elements were determined in the extraction-ventilation box after wet combustion in concentrated nitric acid. The concentrations of Ca, Mg, Fe, Al, Mn, Cu, Ni, and Zn were determined by means of atomic absorption spectrophotometry, K – by means of atomic emis-

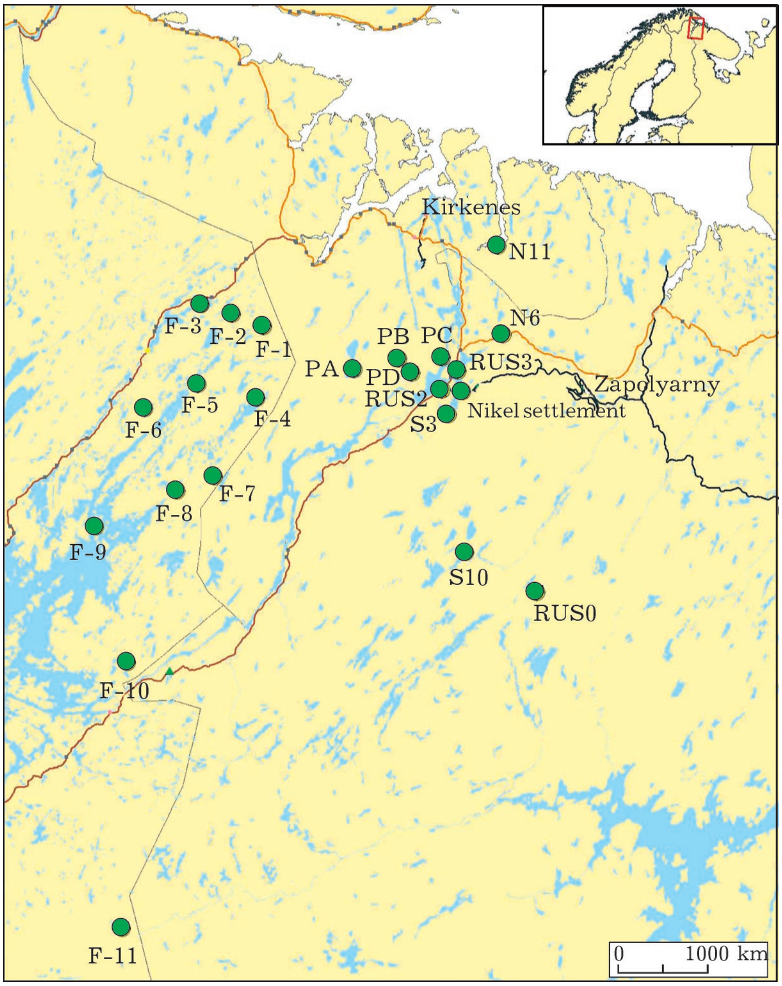

Fig. 1. Schematic map of the location of test ground at the frontier territories of Russia, Norway and Finland.

sion spectrometry, P – with the help of photocolorimetry on the basis of the intensity of colouring of the phosphorus-molybdenum complex (Lawry–Lopez method), S – by means of turbidimetry.

The error of measurements does not exceed ±(3–5) %. The accuracy and correctness of the methods and results of measurements were evaluated according to GOST R ISO 5725-4–2002 [5].

RESULTS AND DISCUSSION

Pinus sylvestris L.

Under the background conditions, rather low concentrations of Ni and Cu are detected in the coniferous trees of the northern taiga forests: the average concentrations are 1.4 and 2.0 mg/kg, respectively [6, 7]. It is known that the income of copper and nickel into plants plays important role in metabolism processes. Copper activates separate enzymes and entire enzyme systems connected with the reduction-oxidation reactions in cells [8]. Nickel in plants participates in a number of enzymatic reactions: carboxylation, hydrolysis of peptide bonds *etc*. Copper and nickel are necessary for plants in small concentrations. However, the excess amounts of heavy metals can prevent the intake of other nutrition elements causing distortions of the balance of mineral composition [9].

Investigations showed that the concentrations of heavy metals (copper and nickel) in pine needles in the zone affected by GMK Pechenganikel near the frontiers of Russia, Norway and Finland exceed the normal level substantially (Table 1). At the territory of Russia, near the factory (RUS3, 2.6 km from the source) Ni concentration in one-year-old needles is 9 times higher and Cu – 6 times higher than the reference values (RUS0). At the territory of Norway nickel and copper concentrations are

TABLE 1

Elemental composition of one-year-old pine needles at different distances from Pechenganikel Combine at test grounds (TG) situated in the frontier region of Russia, Norway and Finland, mg/kg of abs. dry matter

TG	Distance, km	Ca	K	P	S	Mg	Mn	Al	Fe	Zn	Ni	Cu
RUS3	2.6	3710	3884	1071	801	971	531	407	237	18	54	24
RUS2	5.1	3256	4420	1127	753	880	608	292	161	20	37	16
RUS1	5.2	3445	4569	1116	800	778	655	257	171	21	35	20
S3	7.0	2585	3097	1002	873	1028	389	337	249	24	43	22
PC	8.1	2721	3945	932	799	805	469	193	69	30	16	10
PD	11.9	2649	3382	1078	777	1145	558	297	47	27	9	7
N6	12.3	2722	4501	1359	955	709	516	429	217	21	56	24
PB	15.3	3571	3492	1189	908	1401	685	199	54	33	11	7
PA	23.3	3070	3785	951	761	832	952	253	40	39	6	4
S10	32.8	3123	3996	1207	731	1053	883	261	90	53	18	4
RUS0	42.2	1696	3907	1259	599	877	588	224	36	28	6	4
F-4	42.3	2710	3511	1200	949	993	500	298	97	39	16	12
F-1	42.7	2222	3349	1022	777	924	394	218	39	41	4	4
F-2	49.4	2539	3763	1074	795	882	568	200	37	42	2	3
F-7	53.7	2386	3611	1157	812	1185	357	251	45	35	5	5
F-5	54.0	2287	3480	1000	741	892	302	224	46	37	16	12
F-3	55.8	3024	4013	1081	795	953	674	210	37	39	2	3
F-8	61.7	3475	4502	1187	826	1130	361	322	44	51	3	4
F-6	65.0	2578	3497	1023	712	927	515	158	38	44	3	4
F-9	79.3	2822	4146	1283	820	1253	717	269	41	44	4	4
F-10	90.0	2193	4516	1209	704	963	424	252	31	40	2	3
F-11	131.0	2602	4395	951	686	974	837	307	28	52	1	3

1.5–9 times higher than the reference values. At the territory of Finland in the sampling site situated most closely to the pollution source (F-4) the concentration of Ni in needles is 2.6 times higher and Cu content is 3 times higher than the reference values (RUS0), and 16 and 4 times higher, respectively, in comparison with the most remote monitoring station (F-11). Substantial accumulation of Ni and Cu in pine needles near the factory can be connected not only with the absorption of pollutants from soil but also with the foliar absorption.

The concentrating coefficient (K_C) used in biogeochemical studies allows one to estimate the level of pollutants in an object under study in the case of technogenic load with respect to the average background content, that is, in the needles of the trees growing under the regional background conditions. Concentrations are considered as anomalous if $K_C \geq 1.5$ [10]. The data on concentrating coefficients for the needles of all the studied TG are presented in Fig. 2, *a*. One can see that in the zone affected by the factory the concentrations of heavy metals in the needles are substantially higher than the background values. As the distance from the pollution source becomes shorter, K_C values increase. The maximal K_C values were discovered at the Russian TG. Judging from K_C values, the concentrations of heavy metals in pine needles at the studied territory near the frontier should be considered as anomalous. It should be noted that the anomalously high level of nickel and copper accumulation in pine needles is also conserved at a large distance from the factory, which is the evidence of the long-term propagation of atmospheric emissions.

Under the conditions of the strong technogenic pollution, not only the concentrations of heavy metals in needles increase but also their

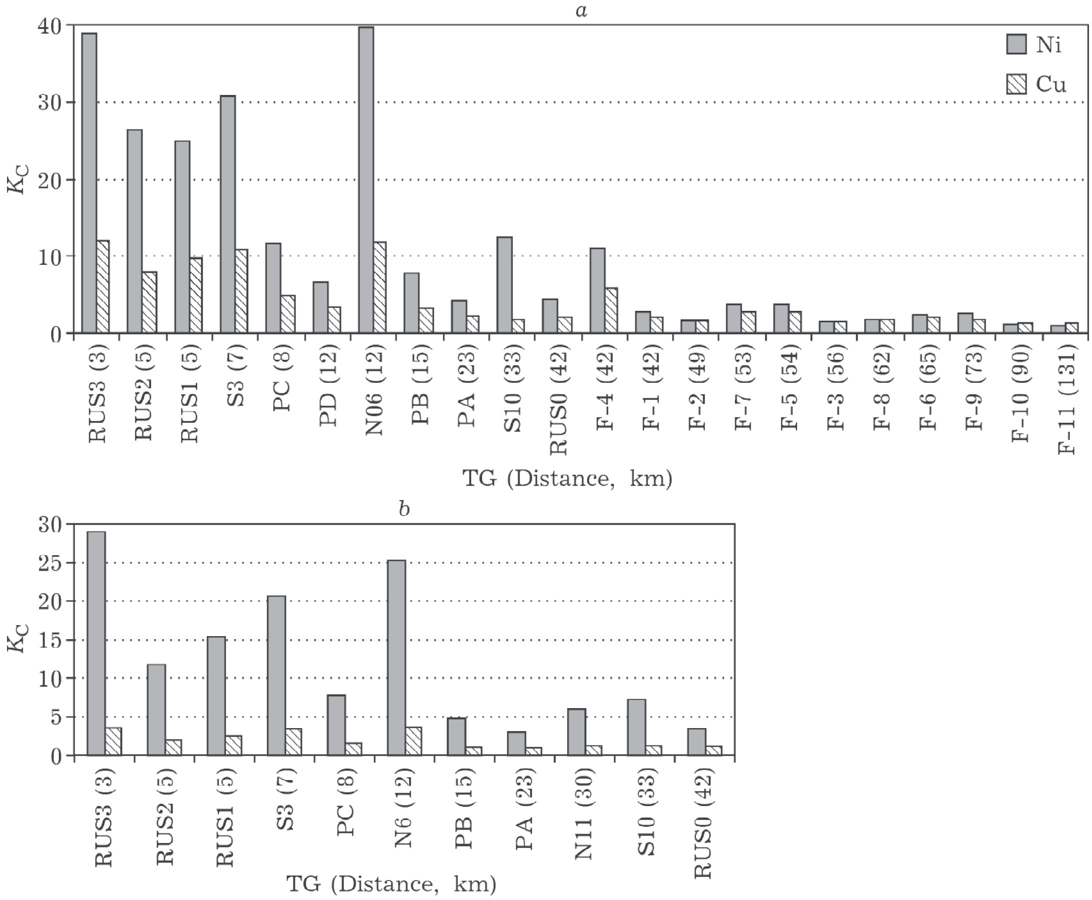

Fig. 2. Concentrating coefficient (K_C) for nickel and copper in one-year-old pine needles (*a*) and in birch leaves (*b*) at the studied test grounds (TG) situated at different distances from the combine.

normal ratio changes. According to the results of pine needle studies in background regions [11], copper content exceeds or is close to nickel concentration, which is determined by the physiological need for these microelements in plants. In our case, this ratio changes in the inverse direction almost in all the studied TG. An exception is some remote TG situated at the territory of Finland. Changes of the Ni/Cu ratio under atmospheric pollution were also reported by other researchers; the reasons are both the effect of antagonism in element absorption and the differences in the rates of their absorption from soil [11, 12]. It was established that nickel, as opposed to copper, more intensively moves from roots to the top organs. For example, about 30 % of nickel absorbed by roots is transported into leaves [14]. Another reason can be the prevalence of nickel in emissions [13]. This is also the reason of its increased content in assimilating organs because a substantial part of particles gets deposited on leaf surface as a result of sedimentation processes near the sources of emissions or in the form of aerosol particles at a large distance from the combine.

Investigation of sulphur accumulation in plants is very important, especially for evaluations of the effect on forest biocenoses caused by factories emitting sulphur dioxide as the dominant pollutant. Under the conditions of the north, with its short vegetation period, the major route of sulphur income into the needles is its stomatal penetration [15]. It was discovered that the concentration of sulphur in needles at he studied TG increases by 10–60 % in comparison with the reference grounds (RUS0, F-11). The high concentrations of Fe and Al were detected both directly near the factory (at the distance of 3–5 km) and at a larger distance from it (7–12 km). High concentrations of iron were detected even at remote TG (N6, F-4), at a distance of more than 30 km from the factory.

In spite of the high adaptivity of plants to specific environmental conditions and the ability of self-controlling the mineral composition, distortions and deviations of different kinds arise in the case of the strong technogenic action. As a rule, they are connected with leaching of nutrition elements from the soil and assimilating organs, as well as with excessive intake of heavy metals and sulphur into the plant organism, which accompanies this process. As a result, the ratio of major macro- and microelements in the plant changes.

Under the conditions of air pollution, an increase in calcium concentration in needles is observed. This can be connected with its active absorption from the organogenic horizon, where this element was detected in higher concentrations than those observed in background regions [1]. It is known that the main source of mineral nutrition of boreal plants with the root nutrition strategy is the organogenic horizon. The major part of absorbing roots of the plants with the root nutrition strategy are situated in this horizon or directly under it, which allows capturing nutrition elements that are carried with soil water [16]. An increase in calcium concentration in pine needles under these conditions can be also explained by the absorption of this element from soil water formed in the mineral horizons enriched with these elements because of the specific features of soil-forming rocks.

Quite contrary, the concentration of zinc in needles decreases. A decrease in Zn content and an increase in the concentrations of nickel, copper and iron are likely to be due, to a substantial extent, to the manifestation of the known antagonism in pairs: Zn–Ni, Zn–Co, and Fe–Zn. Under the conditions of industrial air pollution, soils can become depleted of zinc as a result of the substitution of zinc cations by protons and heavy metal cations (incorporated in emissions) in the soil absorbing complex [16, 17]. Another reason of needle depletion of this element is leaching of metal cations from the leaves by acid precipitation.

In the region under study, as a rule, the level of P and K in needles decreases below the deficit level (for phosphorus, the deficient level of its content in one-year-old needles does not exceed 1.1–1.2 g/kg, for potassium 4 g/kg [18]. It should be noted that the levels of deficit for these elements were revealed not only at TG near the combine but also at the reference grounds: RUS0 – potassium deficit, F-11 – phosphorus deficit. Magnesium content was comparable with that for reference grounds or slightly exceeded it, which can be explained by variations in the composition of the soil-forming rock.

TABLE 2

Elemental composition of birch leaves at the test grounds (TG) situated at different distances from GMK Pechenganikel (2000 and 2004), mg/kg of abs. dry matter

TG	Distance, km	Ca	K	P	S	Mg	Mn	Al	Fe	Zn	Ni	Cu
RUS3	2.6	4708	7833	2157	1337	2697	361	26	182	90	87	21
RUS2	5.1	5479	7355	2314	1054	2567	912	15	108	109	35	11
RUS1	5.2	5001	8517	2085	1349	2737	930	15	123	121	46	15
PC	8.1	5503	7820	1933	1777	2862	1640	28	78	86	14	10
PB	15.3	5840	5713	2004	1561	2984	930	21	63	105	14	7
N6	12.3	5106	9695	2606	1525	2308	1026	20	204	129	76	22
PA	23.3	8036	6366	1954	1362	2381	1981	19	59	123	9	5
N11	30.0	6649	5251	2171	1546	3514	1391	28	67	82	18	8
RUS0	42.2	5695	7738	2790	964	2374	946	15	60	133	10	7

In general, the studies of pine needles showed that the concentrations of elements prevailing in the emissions from GMK Pechenganikel (S, Ni, Cu, and Fe) increase substantially in the zone affected by the emissions from this combine. The deficient level of potassium and phosphorus in the needles was revealed on the basis of the leaf diagnostics. This may be connected with disturbance of the assimilation of these elements by pine due to the manifestation of antagonism between Ca and K, Ca and P.

Betula pubescens Ehrh.

Birch is a typical tree of boreal forests. Unlike for coniferous trees, investigations of the chemical composition of birch are not so numerous. Nevertheless, several specific features of mineral composition can be marked for this species. The assimilating organs of birch are distinguished by rather high content of mineral elements (5.2 % per dry matter) [19]. Calcium and potassium dominate among ash constituents. It is known that birch is a concentrator of zinc [20]. We also established that birch leaves contain zinc at a high concentration (Table 2). Along with zinc, birch also accumulates magnesium. So, concentrations of magnesium and zinc in birch leaves exceed those in pine needles (see Tables 1 and 2). At the reference ground (RUS0) rather high sulphur content – more than 900 mg/kg – was revealed in the assimilating organs of birch. The concentration of iron in birch leaves is also higher than in coniferous trees.

Under the action of aerial technogenic pollution, the concentrations of major pollutants, first of all nickel, copper and sulphur, in birch leaves increase substantially. At the territory of Russia, nickel concentration in birch leaves at the TG is 7–8 times higher than the reference level (RUS0), copper content is 2–3 times higher. At the territory of Norway the concentrations of these metals in birch leaves at the TG are 2–3 times higher than the reference level. The data on K_C calculated for birch leaves are shown in Fig. 2, *b*. The background regional nickel and copper content in birch trees (3 and 6 mg/kg, respectively) are used in calculations [7]. The highest K_C was detected at the territory of Russia at a distance of 12–15 km from the pollution source. The concentrating coefficients for nickel are substantially higher than K_C for copper.

Under technogenic pollution, sulphur concentration in birch leaves increases by 30–60 %. It should be noted that Cu, Ni, S are accumulated in birch leaves in higher concentrations than they are in the assimilating organs of pine. Near the source of pollution, the concentrations of iron and aluminium also increase in birch leaves. Quite contrary, the assimilating organs of birch are depleted of such nutrition elements as calcium, magnesium, zinc.

A comparative analysis of the chemical composition of assimilating organs, carried out in 2000 and 2004, showed that the concentrations of major pollutants – sulphur and heavy metals (Cu, Ni, Fe) – somewhat decreased (Table 3). Nevertheless, the leaves are still deplet-

TABLE 3

Elemental composition of birch leaves at test ground (TG) situated at different distances from GMK Pechenganikel (2000 and 2004), mg/kg of abs. dry matter

TG	Distance, km	Ca	K	P	S	Mg	Mn	Al	Fe	Zn	Ni	Cu
S3	7.0	6814 4770	7782 6950	2285 2210	1794 1527	2992 2378	481 385	252 68	572 264	198 120	68 62	29 20
S10	32.8	5943 5506	6813 7225	2437 2297	1209 962	2686 2173	1299 931	61 48	209 125	175 126	24 22	8 7

Note. Data for 2000 are in the numerator, and data for 2004 are in the denominator.

ed of the most important nutrition elements (Ca, Mg, Mn, and Zn), which undoubtedly has a negative effect on the plant organism functioning in general. Hence, in spite of a decrease in the emission of pollutants into the atmosphere, it is still not a proper time to speak about the normalization of the mineral composition of plants at the territories affected by the copper-nickel industry.

CONCLUSION

The elemental composition of the assimilating organs of woody plants is substantially transformed under the action of such a stress-forming factor as atmospheric pollution. The concentrations of elements present in the emissions from the GMK Pechenganikel JSC, especially nickel, copper and sulphur, substantially increase in the leaves of woody plants. Birch leaves accumulate higher concentrations of heavy metals and sulphur than the assimilating organs of pine do. It was established that under the conditions of heavy pollution the concentrations of P and K reach the levels determined as deficient for pine. Insufficient provision of pine needles with these elements was revealed for the studied territories of Russia, Norway and Finland. It is reasonable to use the assimilating organs of coniferous and foliate trees that are very sensitive to growing conditions in bioindicator studies for the purpose of evaluating the state of forest biocenoses.

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