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Assessment of Soil-Water Composition Dynamics in the North Taiga Forests upon the Reduction of Industrial Air Pollution by Emissions of a Copper–Nickel Smelter

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Abstract—This work is aimed at assessing the dynamics of the composition of soil waters in coniferous forests subjected to air pollution from the Severonikel' copper–nickel smelter in Murmansk oblast. The objects of investigations are the most common in boreal zone spruce forests with dwarf shrubs + green mosses and pine forests with dwarf shrubs + lichens. The results show a significant intra- (below the crowns and between the crowns) and interbiogeocenotic (spruce and pine forests) variation in the composition of atmospheric deposition and soil waters in forests under pollution. The atmospheric deposition of pollutants and leaching of their compounds from all soil genetic horizons are tens (sulfates) and hundreds (copper and nickel) times higher than in reference sites and their fluxes below the crowns are usually more intense than between the crowns. Long-term dynamics (from 1993 to 2012) demonstrate reliable trends in the reduction of concentrations and leaching of sulfates and heavy metals from the soil. The molar ratio of basic cations to aluminum (BC/Al) in soil waters from all soil horizons does not drop to the level of critical, whereas for mineral nitrogen the lowest critical level (0.2 mg/L) was exceeded in waters from all horizons at all stages of digression. It was shown that, for the early detection of exceedances of the critical level for mineral nitrogen in soil waters, an evaluation of their composition is necessary not only between the crowns, but also below them.

Keywords: coniferous forests, pollution-induced digression, industrial air pollution, atmospheric deposition, soil waters, heavy metals, sulfates, chemical indicators, spatial variation, many-year dynamics

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INTRODUCTION

Atmospheric industrial pollution is a powerful factor that has a detrimental effect on forests. In the 20th century, the most powerful sources of industrial air pollution in Northern Europe were the enterprises of JSC "Kolskaya Mining & Metallurgical Company" MMC Norilsk Nikel. However, according to reporting on the Monchegorsk KGMK site for 2012, the company has been complying with the maximum permissible emissions standard for 8 years. This contributed to the reduction of emissions of the main pollutants at the Monchegorsk site for 1990–2011: SO_2 (thousand tons) is from 232.5 to 31.3 (7.4 times); Cu (tons/year) is from 1813 to 483.5 (3.7 times); and Ni (tons/year) is from 2712 to 344.8 (7.8 times) (data from MMC Norilsk Nikel).

The main pollutants that have a negative impact on the forest biogeocenoses of the Kola North are acid-forming compounds of sulfur and nitrogen, as well as heavy metals (nickel, copper, cobalt, plumbum, cadmium, chromium, etc.) (Lukina and Nikonov, 1996; Tsvetkov, V.F. and Tsvetkov, I.V., 2012; Derome and Lukina, 2010; Kashulina et al., 2014; Reinmann et al, 1997; Steinnes et al., 2000). Pollution has both direct (fumigation and leaching) and indirect (changes in the composition and properties of soil and soil waters, reduced resistance to disease, etc.) effects on forests. Soil is the most important component of the forest ecosystem, where effective barriers to the downward interspecific migration of pollutants in organic and illuvial soil horizons of the study region are functioning (Koptsik et al., 2016; Lukina and Nikonov, 1996;

Lukin et al., 2008). Soil waters are an informative matrix for assessing the negative impact of pollutants on forest ecosystems. One of the actively developing approaches to such an assessment is the concept of critical loads (Nilsson and Grennfelt, 1988). Critical loads are calculated with use of chemical indicators proposed, inter alia, for the composition of soil waters. These indicators include the molar ratio of basic cations and aluminum (Ca + Mg + K/Al), which is recommended for assessing soil acidification processes, as well as the concentration of mineral nitrogen, which allow assessing the eutrophication level (Kopzik, 2004; Svedrup and Warfvinge, 1993).

An assessment of the composition of atmospheric deposition and soil waters in forests of reference sites on the Kola Peninsula after a sharp decrease in anthropogenic pressures in the period 2002–2008 showed significant intra- and interbiogeocenotic variations in chemical indicators (Lukina et al., 2018).

The aims of this article are (1) to compare the composition of atmospheric deposition and soil waters of forests formed under conditions of high levels of industrial air pollution and forests in reference sites based on many-year dynamics and (2) to assess the composition of atmospheric deposition and soil waters in coniferous forests of the Kola Peninsula at different stages of technogenic forest digression with use of international chemical indicators, taking into account intra- and interbiogeocenotic spatial variation and many-year dynamics.

MATERIALS AND METHODS

The objects of research were soil waters in spruce forests with dwarf shrubs + green mosses and pine forests with lichens at different stages of digression. The soils at the study sites are represented by alpha-humus podzols. The test areas (TAs) are at different distances from the source of pollution—the Severonikel' smelter: 7–10 km are stages of pine and spruce pollution-induced sparse forests, 28–31 km are defoliating forests, and more than 100 km are reference sites (Lukina and Nikonov, 1996, 2003).

The type of dominant communities in the reference sites is represented by spruce forests with dwarf shrubs + green moss and pine forests with dwarf shrubs + green moss + lichens; the full tree stand is 0.5 and 0.4, respectively. The mean age of the spruce stand in the reference sites is 200–220 years and for pines it is 160–180 years; the lifetime of spruce needles reaches 13–14 years, and for pine needles it reaches 7–8 years. Defoliating forests are represented by grass-shrub spruce forests and lichen–shrub pine forests (Lukina and Nikonov, 1996) with a full tree stand of 0.4 and 0.3, in which the mean spruce age is 220–240 years old, pine trees are 80–100 years old, and the lifetime of spruce needle decreases compared to the references sites up to 7–9 years and that of pine needles decreases up to 3–5 years. The stage of pollution-induced sparse forests is represented by spruce–birch crowned and pine shrub sparse forests with a full stand of 0.1 and 0.2, respectively; the average age of the spruce was 100–120 years, that of pines was 80–100 years, the lifetime of the spruce needles during the period of high pollution did not exceed 3–5 years, and the lifetime of pine needles was 2–3 years. The portion of dead trees (deadwood and windfall) in spruce forests increases from 6% in reference sites to 20% in defoliating forests and 80% in pollution-induced sparse forests, and in pine forests it is from 6% in reference sites to 10 and 60% in defoliating forests and in pollution-induced sparse forests, respectively. Each TA is equipped with six precipitation collectors for rain deposition (three below the crowns and three between the crowns). Snow was sampled at the end of March–beginning of April during the period of maximum snow accumulation. Rain deposition and soil waters were sampled monthly from early May to early October. Each TA is equipped with gravity-type lysimeters (12 pcs. on TA) located at different depths in accordance with genetic soil horizons (A0, E, Bhfa, and BC/C) and taking into account the mosaic structure of the biogeocenosis (below the crowns and between the crowns) (Lukina and Nikonov, 1996, 1998). Gravitational lysimeters made by John Derom have the least destructive effect on the functioning of forests and are recommended for use in the ICP Forests international program (Nieminen et al., 2013).

Water samples were filtered through a blue ribbon paper filter. The pH was determined potentiometrically, metals were determined by the AAS method (Aanalyst 800), and nitrates and sulfates were determined by ion-exchange chromatography. The chromatograph is made in the form of two separate units: a pump (Water 501 HPLC Pump, Millipore2) and a detector (Waters 431 Conductivity Detector, Millipore). The quality of analyses of soil waters and atmospheric deposition is confirmed by the regular and successful participation of the common use center of INIEP in international interlaboratory comparison tests of the quality of chemical analysis. The standard error of anion determination, including ion exchange chromatography, installed in accordance with the Guide (Clarke et al., 2010) is as follows: for NO_3^- from 5 to 21% and SO_4^{2-} from −3 to 36%. Ammonium nitrogen was determined by the Kjeldahl method (Mahera et al., 2002).

To characterize the composition of atmospheric deposition, data for 1999 to 2012 were used and, for soil waters, data from 1995 to 2012 were used. Since 2000, according to the data of MMC Norilsk Nikel, there has been a decrease in emissions of pollutants into the atmosphere (Nornickel official website).

For soil waters, molar ratios (Ca + Mg + K)/Al and the concentration of mineral nitrogen were calculated as the sum of nitrate and ammonia nitrogen, mg/L.

The descriptive statistics were calculated in Microsoft Excel 2007. In the same program, trends were empirically selected to assess the many-year dynamics of atmospheric depositions and the removal of heavy metal compounds with soil waters. The significance of trends was estimated in the Biomstat 4.11 program (Sokal and Rohlf, 2012) by the p-value associated with *F*-statistics, i.e., the ratio of the explained regression model of dispersion to the unexplained model. To compare the stages of digression, the Mann–Whitney test and the Statistica 10 program were used.

RESULTS

Snow Deposition

In the reference spruce and pine forests (Table 1), the deposition of sulfur compounds with snow in the spaces below the crowns (BelC) was significantly higher ($p < 0.05$) than in the spaces between crowns (BetC), which can be explained by intensive exchange processes on the needle surfaces, as well as by flushing dust from the crown, which has a large absorptive capacity. No significant intrabiogeocenotic differences for pH and heavy metals were found. Interbiogeocenotic differences also turned out to be unreliable ($p > 0.05$). The many-year dynamics of pollutant deposition shows a reliable trend for declines of copper—from 0.48 to 0.05 mg/m^2 ($R^2 = 0.51$); nickel is from 0.2 to 0.05 mg/m^2 ($R^2 = 0.57$) and sulfur is from 238 to 95 mg/m^2 ($R^2 = 0.39$) in spruce forests below the crowns. In pine forests, a tendency to decrease is observed only for sulfur—from 126 to 39 mg/m^2 ($R^2 = 0.37$). In between crown spaces, the tendency to decrease can be observed for nickel deposition in spruce forests—from 0.12 to 0.08 mg/m^2 ($R^2 = 0.39$), nickel is from 0.2 to 0.08 mg/m^2 ($R^2 = 0.32$), and copper is from 0.24 to 0.06 mg/m^2 ($R^2 = 0.35$) in the pine forests; for sulfur, no tendency to decline was found.

In defoliating spruce and pine forests, compared with the reference sites of the main pollutants, deposition with snow increases significantly: nickel is up to 60 times, copper is up to 20 times, and sulphate sulfur is up to 3 times (both in BelC and BetC).

The deposition of compounds of the main pollutants with snow in BelC of pine and spruce forests is up to 2 times higher than in BetC and acidity in BelC is significantly higher, which is associated with the flushing of acid-forming substances from tree crowns. The deposition of the main pollutants in the BelC of spruce forests is 2–5 times higher than that of pine forests, which can be explained by the higher sorbing capacity of the canopy of spruce due to the long and dense crown; in BetC, no reliable interbiogeocenotic differences between spruce forests and pine forests were found.

Many-year deposition dynamics showed a decrease in copper precipitation in BetC from 5 to 0.43 mg/m^2 ($R^2 = 0.5$), in nickel from 7 to 0.54 mg/m^2 ($R^2 = 0.45$), and in sulfur from 188 to 148 mg/m^2 (R^2 0.32) in spruce, as well as in copper from 1.9 to 0.66 mg/m^2 ($R^2 = 0.52$) and in sulfur from 220 to 142 mg/m^2 ($R^2 = 0.57$) in the pine forest. There is no downward trend in spruce or pine forests below the crowns.

In pollution-induced sparse spruce and pine forests, the deposition of nickel with snow is up to 600 times higher, copper is up to 140 times higher, and sulphate sulfur is up to 5 times higher than in the reference sites (Ershov et al., 2016).

The deposition of heavy metals and sulfur with snow in spruce and pine forests in the BelC is 2–3 times higher than in the BetC. Acidity, as well as in defoliating forests, is significantly higher in BelC. Compared with depositions in pine forests, in spruce forests, copper and nickel deposition in BelC are twice as high and, in BetC here, nickel deposition is 1.4 times higher. The many-year dynamics of copper, nickel, and sulfur deposition with snow in spruce and pine sparse forests does not show distinct intrabiogeocenotic differences due to the high variability.

Rain Deposition

In the reference sites of spruce and pine forests (Table 1), heavy metal and sulfate deposition with rain, as with snow, below the crowns of trees is significantly higher (2 to 8 times) than between the crowns. In BelC, the pH value in rain deposition was significantly ($p < 0.05$) lower than in BetC.

The many-year dynamics shows a decrease in the deposition of copper compounds between crowns in spruce forests only; it is from 0.26 to 0.07 mg/m^2 ($R^2 = 0.48$). For nickel and sulfur, significant changes in the many-year dynamics have not been established.

It should be noted that there are interbiogeocenotic variations in the deposition of heavy metals below the crowns: in pine forests, their loss is up to 1.7 times and for sulfates it is up to 3 times lower than in spruce forests. In BetC in pine forests, nickel deposition is 1.4 times lower when compared to spruce forests.

In defoliating spruce and pine forests, depositions of the main pollutants with rain significantly exceed the background: nickel is up to 76 times, copper is up to 24 times, and sulfates is up to 5 times.

The deposition of compounds of these elements with rain in BelC is 6–40 times higher than in BetC (Table 2), as is acidity ($p < 0.05$). Just as in the reference sites, there are interbiogeocenotic differences: the depositions of the compounds of the main pollutants in BelC in pine forests are 1.5 times lower than in spruce forests. No significant differences were found in BetC. The many-year dynamics of depositions of the main pollutants with rain show a downward trend in copper in the BetC of spruce forests and a trend in

Table 1. Acidity and content of copper, nickel (mg/m^2), and sulfate sulfur (g/m^2) in atmospheric depositions (average for the period of 1999–2012)

Stages of digression	Depositions	Spruce forests				Pine forests			
		pH	Ni	Cu	$S{-}SO_4^{2-}$	pH	Ni	Cu	$S{-}SO_4^{2-}$
Below tree crowns									
Reference sites	Rain	4.05*	1	2	0.58	4.16	0.4	1	0.19
		0.05**	0.1	0.2	0.10	0.05	0.1	0.2	0.03
	Snow	4.53	0.1	0.2	0.04	4.54	0.1	0.1	0.02
		0.07	0.02	0.1	0.003	0.09	0.01	0.02	0.002
Defoliating forests	Rain	3.54	39	39	1.40	3.57	30	31	1.02
		0.04	5	6	0.17	0.03	3	7	0.09
	Snow	4.28	6	5	0.13	4.29	2	1	0.06
		0.05	1	1	0.01	0.07	0.3	0.1	0.004
Sparse forests	Rain	3.51	305	266	1.97	3.67	96	118	0.91
		0.04	38	31	0.22	0.05	11	25	0.09
	Snow	4.30	63	31	0.19	4.34	30	13	0.13
		0.06	9	5	0.02	0.06	3	2	0.01
Between tree crowns									
Reference sites	Rain	5.16	0.1	0.6	0.07	4.91	0.1	0.5	0.09
		0.10	0.03	0.1	0.01	0.09	0.03	0.1	0.02
	Snow	4.60	0.1	0.2	0.03	4.60	0.1	0.1	0.02
		0.08	0.01	0.03	0.003	0.09	0.01	0.01	0.003
Defoliating forests	Rain	4.49	1	1	0.17	4.40	1	1	0.16
		0.08	0.2	0.1	0.02	0.05	0.2	0.1	0.02
	Snow	4.50	3	2	0.08	4.50	1	1	0.05
		0.06	0.3	0.3	0.01	0.08	0.2	0.1	0.003
Sparse forests	Rain	4.00	24	18	0.49	4.10	5	3	0.33
		0.03	4	4	0.06	0.05	1	2	0.07
	Snow	4.48	25	9	0.09	4.55	18	7	0.09
		0.06	4	1	0.01	0.07	2	1	0.005

* Average value.

** Standard error.

decline of copper and nickel in the BelC of pine forests (Fig. 1, Table 2).

In pollution-induced sparse spruce and pine forests, rain depositions with nickel are up to 450 times higher, those with copper are up to 130 times higher, and those with sulfate sulfur are up to 5 times higher than in the reference sites.

Like at other stages, rain depositions in BelC are 2–39 times higher, and pH is lower than in BetC. In pine forests, heavy-metal depositions are up to 6 times lower and sulphates are up to 2 times lower than in spruce forests, both in BelC and BetC. The many-year dynamics of sulphates, nickel, and copper rain depositions show the most pronounced decrease in deposition of nickel and copper in pine forests in BelC (Fig. 1).

Thus, atmospheric depositions at all stages of digression are characterized by significant inter- and intrabiogeocenotic variation. The depositions are significantly higher in BelC compared to BetC and in spruce forests compared to pine forests.

Composition of Soil Water

Spatial intrabiogeocenotic variability of the composition of soil waters. In lysimetric waters of spruce and pine forests formed **in reference sites** and sampled from all soil horizons (Table 3), the concentrations of the main pollutants in BelC are significantly higher ($p < 0.05$) than in BetC, which is connected with their inflow with crown waters and higher concentrations of these compounds in soils below the crowns (Lukina and Nikonov, 1996). The exception is copper in the soil waters of spruce forests from the E + B and BC soil horizons: the intrabiogeocenotic differences are not significant ($p > 0.05$) here. In waters from all soil horizons, in BelC of spruce forests, acidity is significantly lower ($p < 0.05$) than in BetC, except for waters from the BC horizons. This is due to a higher concentration of calcium in the crown water and in the soil below the crown of spruce, due to the fact that the litter of spruce needles is rich in calcium. Another explanation is that the dense and low crown of the spruce delays a significant amount of atmospheric depositions, which prevents the intensive removal of bases from the organic horizons (Lukina et al., 2008). In pine forests, on the contrary, in waters of BelC, acidity is higher ($p < 0.05$) than in waters of the BetC. This is due to the high volume of atmospheric deposition, especially trunk water, washing the soil under the pine crowns.

In waters from all soil horizons **of defoliating** spruce and pine forests, the concentrations of the main pollutants in BelC and BetC are significantly higher compared to the background: for nickel they reach 50 times, for copper they reach 20 times, and for sulfur they reach 7 times.

Intrabiogeocenotic differences show that the concentrations of copper, nickel, and sulphates under the spruce crowns were significantly higher than between the crowns. At the same time, in pine forests the concentration of copper in waters from organic soil horizons BetC was significantly ($p < 0.05$) higher than BelC. Perhaps this is due to the large amount of pine trunk water washing the soil. In contrast to the reference conditions, the acidity of waters from all soil horizons in defoliating spruce and pine forests is significantly lower ($p < 0.05$) in BetC when compared to BelC. In the conditions of industrial air pollution, this can be explained by an increase in the supply of acid-forming substances from the atmosphere, especially under the crowns, and a disturbance in the functioning of the phytocenosis.

In pollution-induced sparse spruce and pine forests, nickel concentrations in soil waters reach 600 times higher, copper is up to 100 times higher, and sulphates reach 20 times higher than in the reference sites. The exception is copper in the waters from the BC horizon in the BetC; the differences are not significant here ($p > 0.05$).

The concentrations of the main pollutants in the soil waters in BelC are significantly higher than in BetC. The acidity of water from all soil horizons in pollution-induced sparse spruce and pine forests in the BelC is significantly higher ($p < 0.05$) than in BetC, except for water from the E + B horizons ($p > 0.05$).

Thus, the composition of soil waters in defoliating forests and in pollution-induced sparse forests is characterized by a significant intrabiogeocenotic variation. Concentrations of copper, nickel, sulphates, and acidity, as a rule, are higher in BelC when compared to BetC.

Table 2. Estimation of the significance of many-year trends in the dynamics of heavy metals, values of *p*

Stage of digression	Nickel	Copper
Atmospheric depositions in the form of rain		
Defoliating spruce forests	nr*	0.001
Defoliating pine forests	0.039	0.002
Spruce sparse forests	nr	nr
Pine sparse forests	0.002	0.0005 0.005
Removal with soil waters from organogenic horizons		
Reference spruce forests	0.002	0.059 0.004
Reference pine forests	0.0005	0.0004 0.0001
Defoliating spruce forests	0.0022	0.004 0.025
Defoliating pine forests	nr	nr
Spruce sparse forests	0.009	>0.0001 0.001
Pine sparse forests	nr	0.0008

* (nr) not reliably.

Spatial interbiogeocenotic variability of soil-water composition. In the waters of the below-crown spaces **of reference** spruce forests from the A0 soil horizons, concentrations of nickel and sulfates, as well as sulfates in waters from E + B and BC horizons, are significantly (up to 2 times) higher than in pine forests. In the waters of the A0 horizons of the BetC of pine and spruce forests, nickel concentrations are almost comparable. The sulfate concentrations in the BetC pine forests in the waters of the E + B and BC horizons reach 3 times lower than in spruce forests; other differences are not significant. The depositions passing through the canopy of woody plants become more concentrated, and the spruce tree performs a deeper transformation than pine due to a longer and denser crown. Acidity in soil waters from all soil horizons in BelC and BetC of pine forests was significantly ($p < 0.05$) higher than in spruce forests, with the exception of waters from the BC horizons of BetC. This can be explained by the higher calcium content in the soils of spruce forests (Lukina and Nikonov, 1996).

In defoliating forests in waters from all soil horizons in BelC and BetC, the concentration of the main pollutants is significantly higher in spruce forests; exceptions are the concentrations of compounds of these

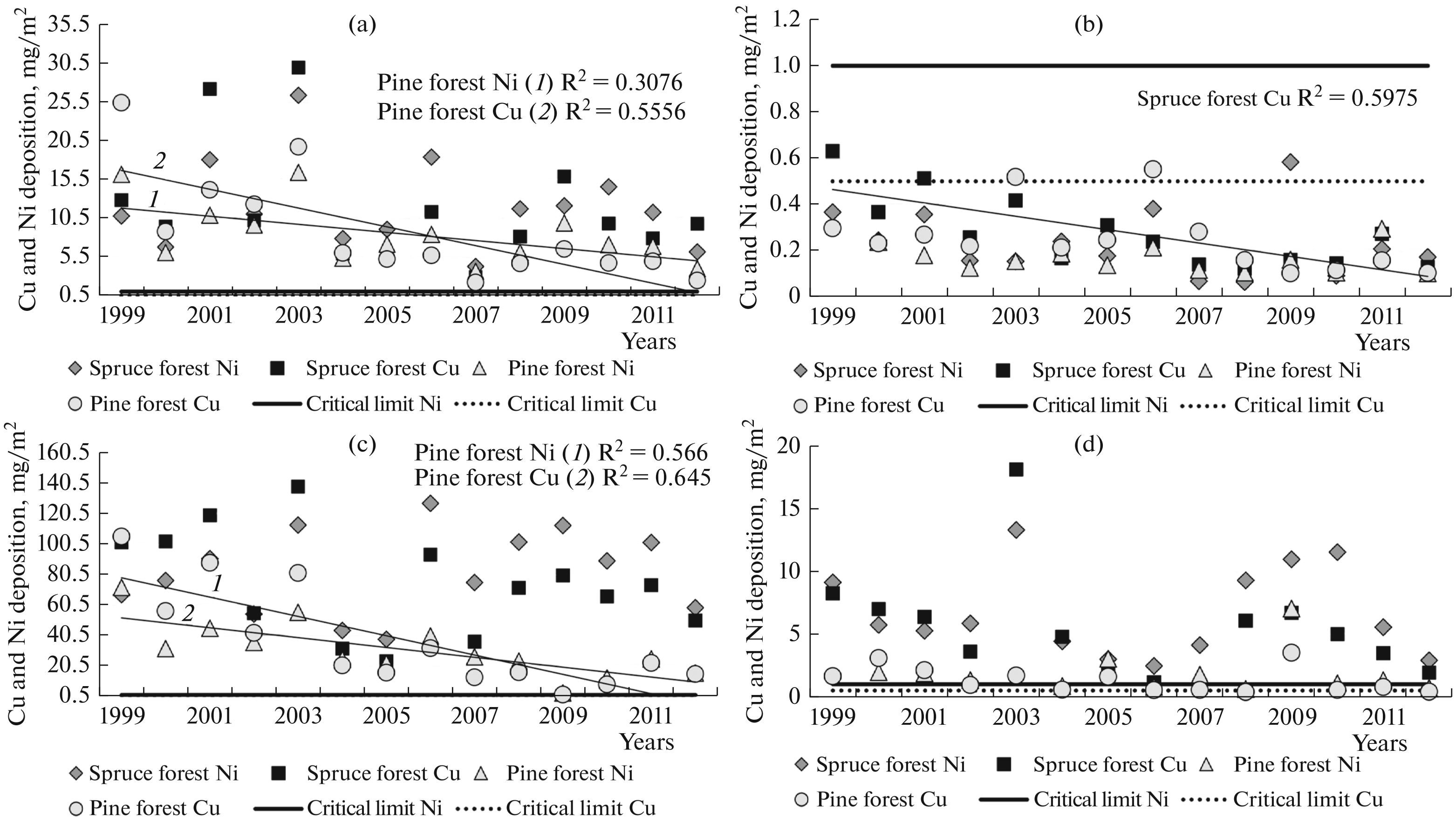

Fig. 1. Nikel and copper rain deposition. Defoliating forests: (a) below crowns and (b) between crowns; sparse forests: (c) below crowns and (d) between crowns.

Table 3. Acidity, content of copper, nickel, sulphates, BC/Al indicator, and Nmin indicator in the soil waters of spruce and pine forests, mg/L

Type of states	Depth	Spruce forests						Pine forests					
		pH	Ni	Cu	SO_4^{2-}	BC/Al	N min	pH	Ni	Cu	SO_4^{2-}	BC/Al	N min
Below tree crowns													
Reference sites	A0	4.39*	0.004	0.01	6.78	26.68	0.64	3.66	0.003	0.01	2.57	8.78	0.42
		0.063**	0.0004	0.001	0.57	1.64	0.06	0.039	0.0002	0.001	0.23	0.62	0.06
	E + B	5.01	0.002	0.01	4.61	11.64	0.24	4.17	0.002	0.01	2.46	2.14	0.30
		0.11	0.0003	0.002	0.39	1.39	0.03	0.04	0.0002	0.001	0.19	0.21	0.03
	BC	4.99	0.002	0.01	7.80	34.15	0.16	4.69	0.002	0.004	6.03	16.41	0.28
		0.09	0.0002	0.001	0.63	8.16	0.03	0.07	0.0002	0.001	0.29	2.64	0.04
Defoliating forests	A0	3.53	0.23	0.26	28.16	22.76	0.27	3.64	0.02	0.02	6.54	10.88	0.22
		0.02	0.02	0.02	1.91	1.40	0.02	0.02	0.002	0.001	0.41	0.68	0.02
	E + B	3.91	0.13	0.04	24.51	3.90	0.21	4.53	0.01	0.01	8.79	21.48	0.28
		0.03	0.01	0.003	1.53	0.55	0.03	0.10	0.001	0.001	0.46	5.20	0.05
	BC	4.29	0.06	0.01	14.75	7.36	0.28	4.54	0.06	0.02	11.52	13.12	0.22
		0.05	0.01	0.002	1.08	0.54	0.05	0.08	0.01	0.004	0.90	1.68	0.05
Sparse forests	A0	3.79	1.26	1.11	31.44	12.18	0.37	3.62	1.13	0.68	22.74	16.55	0.28
		0.04	0.11	0.13	2.06	0.83	0.09	0.04	0.09	0.06	1.43	0.92	0.04
	E + B	4.42	0.94	0.16	17.36	21.99	0.70	4.06	0.62	0.16	17.24	7.82	0.24
		0.04	0.08	0.02	1.15	3.86	0.17	0.04	0.05	0.02	1.00	0.88	0.03
	BC	4.06	0.62	0.16	17.24	7.82	0.24	4.18	0.72	0.17	19.54	14.23	0.33
		0.04	0.05	0.02	1.00	0.88	0.03	0.04	0.07	0.02	1.50	0.81	0.05
Between tree crowns													
Reference sites	A0	4.19	0.001	0.01	0.96	14.98	0.54	3.89	0.002	0.01	1.00	11.69	0.49
		0.05	0.0001	0.001	0.08	1.46	0.08	0.05	0.0002	0.001	0.13	0.94	0.04
	E + B	4.59	0.001	0.005	2.96	8.42	0.25	4.41	0.001	0.01	1.11	3.44	0.26
		0.07	0.0001	0.001	0.23	1.84	0.04	0.08	0.0001	0.001	0.12	0.73	0.03
	BC	4.73	0.001	0.01	4.23	51.43	0.16	5.04	0.001	0.01	1.75	6.57	0.22
		0.10	0.0001	0.001	0.44	19.81	0.03	0.11	0.000	0.001	0.27	0.92	0.06
Defoliating forests	A0	3.86	0.06	0.03	6.95	13.31	0.20	4.13	0.02	0.03	3.17	11.97	0.32
		0.04	0.005	0.002	0.64	2.58	0.02	0.04	0.002	0.002	0.32	1.47	0.04
	E + B	4.41	0.01	0.01	5.50	7.71	0.21	4.75	0.01	0.01	3.79	18.83	0.15
		0.06	0.002	0.003	0.23	0.78	0.02	0.06	0.001	0.001	0.26	1.76	0.02
	BC	4.44	0.02	0.01	7.47	9.90	0.21	4.70	0.003	0.004	4.07	38.44	0.20
		0.05	0.002	0.001	0.40	1.20	0.03	0.07	0.001	0.001	0.29	6.49	0.03
Sparse forests	A0	4.05	0.84	0.20	21.40	15.68	0.60	4.18	0.30	0.12	14.41	18.16	0.32
		0.04	0.07	0.02	1.75	1.29	0.11	0.03	0.02	0.01	0.95	0.90	0.04
	E + B	4.42	0.47	0.04	13.64	12.87	0.73	4.59	0.27	0.05	10.68	33.48	0.18
		0.04	0.05	0.01	0.91	2.14	0.16	0.05	0.02	0.01	0.50	8.62	0.02
	BC	4.55	0.55	0.01	10.98	44.32	2.66						
		0.04	0.07	0.002	0.60	9.53	0.55						

* Average value.

** Standard error.

elements in the waters of the BC horizons in BelC and copper in the waters from A0 horizons in the BetC—the differences are not significant here. Acidity in waters from all soil horizons in BelC and BetC in spruce forests is significantly higher than in pine forests. In the conditions of industrial air pollution, this can be explained by the increase in the flow of acid-forming substances under the crown of spruce, which absorbs a large amount of substances compared to the high and openwork crown of pine.

In pollution-induced sparse spruce forests in BelC and BetC, the concentrations of Cu, Ni, and SO_4^{2-} in waters from all soil horizons are significantly higher ($p < 0.05$) than in pollution-induced sparse pine forest, except for concentrations in the waters from the BC horizons. Just as in defoliating forests, acidity in waters from all soil horizons in BelC and BetC in spruce forests is significantly higher than in pine forests.

Thus, the composition of soil waters at all stages of digression is characterized by significant interbiogeocenotic variation. Element concentrations are usually higher in soil waters in the BelC of spruce forests compared to pine.

Dynamics of concentrations and removal of elements in soil waters. In the reference spruce forests, the many-year dynamics of the content of pollutants demonstrates significant variability, and no reliable patterns have been found.

In defoliating spruce forests, many-year dynamics showed a decrease in nickel concentrations from 0.2 to 0.1 mg/L ($R^2 = 0.45$), copper from 0.2 to 0.1 mg/L ($R^2 = 0.49$), and sulfates from 28 to 12 mg/L ($R^2 = 0.38$) in the waters of the A0 horizons in the BelC, whereas in the BetC the decrease is observed only for sulfates: from 10 to 6 mg/L ($R^2 = 0.42$). In pine forests, declining trends over the years can be observed for copper from 0.02 to 0.01 mg/L ($R^2 = 0.41$) and for sulphates from 10 to 5 mg/L ($R^2 = 0.52$) in waters from the A0 horizons of the BelC: in the BetC it can be observed only at sulfate concentrations from 10 to 2 mg/L ($R^2 = 0.49$). This can be explained by a decrease in industrial air load.

The many-year dynamics of the removal of compounds of nickel, copper, and sulphates in BelC and copper in BetC with groundwaters of spruce forests showed a tendency to increase from 1993 to 2003 and then to decrease from 2003 to 2012 for nickel and copper (Fig. 2). Patterns in the many-year dynamics of the removal are explained by a positive interrelation, not only with their concentrations, but also with the amount of air depositions. Thus, in spruce forests a positive interrelation was found between the volumes of air depositions and the removal of heavy metals and sulfur compounds with soil waters, both in BelC and BetC ($r = 0.55$ and $r = 0.54$, respectively). The many-year dynamics of depositions volume showed a trend to increase from 364 to 632 mm from 1993 to 2007, and then a decrease (to 455 mm) by 2012. Thus, the composition and properties of soil waters are greatly influenced not only by the level of pollution, but also by the amount of depositions, which has significantly varied on the Kola Peninsula in recent decades (Semenov et al., 2006). The combined effect of the industrial air pollution level and amount of depositions is clearly manifested in defoliating spruce forests.

In pollution-induced sparse spruce and pine forests (Fig. 2), the many-year dynamics of concentrations and removals of the main pollutants show a decrease; this can be explained by a decrease in the industrial air load of the smelter.

DISCUSSION

Atmospheric Depositions

On the basis of the research results, it was established that the deposition of compounds of heavy metals and sulfur exceeds the reference levels many times even after a significant reduction in emissions of pollutants into the atmosphere. It is advisable to compare the levels of deposition of pollutants from the atmosphere at the sites of the presented research with the critical level established in international practice. Moreover, since, based on the results of our studies, significant intra- and interbiogeocenotic differences of depositions with snow and rain were established, comparisons should be made with regard to these differences. The critical level of total depositions (with rain and snow) of sulfate sulfur from the atmosphere in Central Lapland is 0.3 g/m^2 per year (Korhola et al., 1999). The level of critical limits for atmospheric deposition of nickel and copper is 10 and 5 g/ha per year (Reinds et al., 2006).

In the reference spruce and pine forests, the excess of the critical load of sulfate sulfur deposition can be observed only in spruce forests in the BelC (2 times). **In defoliating** spruce and pine forests, the excess of this load level is also observed only in BelC: for spruce forests by 5 times and for pine forests 3.5 times; no excess is observed in BetC. **In pollution-induced** sparse spruce and pine forests in the BelC, the deposition of sulfur compounds exceeded the critical level by 7 and 3.5 times, respectively, and by 2 and 1.4 times in BetC.

In the reference spruce and pine forests, there is no excess of the level of critical loads for nickel observed in either the BelC or the BetC. The level of critical limits for copper in BelC is exceeded in spruce forests up to 5 times and in pine forests is up to 3 times, and in BetC it reaches 1.5 times in pine and spruce forests. **In defoliating** spruce and pine forests, the critical load level for nickel in BelC of spruce forests is 44 times and for copper it is 87 times; in BelC of pine tree for nickel it is 31 times and for copper it is 64 times. In BetC, excess amounts in spruce forests for nickel reach 3.4 times and, for copper, 5.7 times; for nickel they are 2 times in pine forests and, for copper, 2.8 times. **In pollution-induced sparse forests** of BelC,

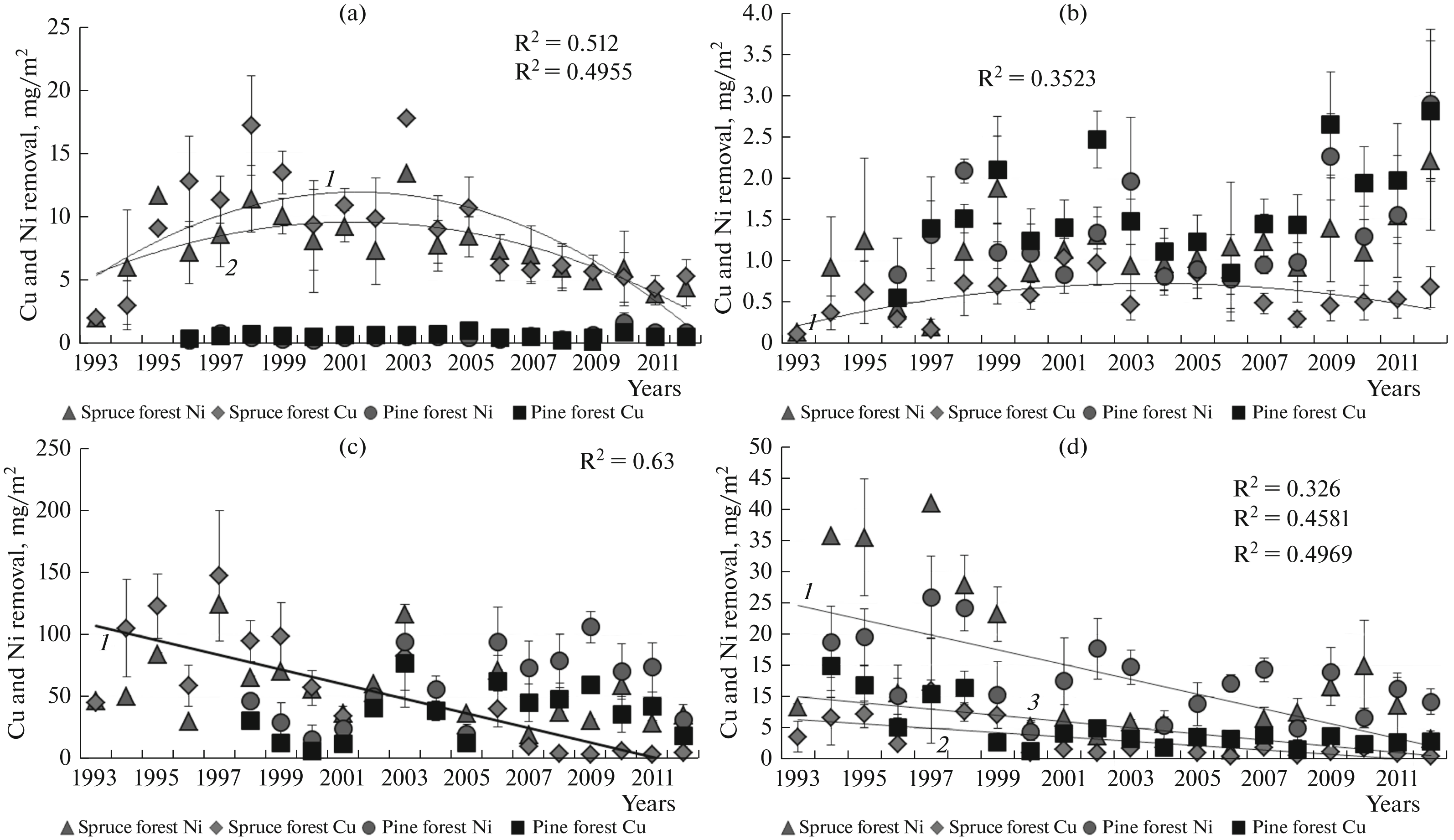

Fig. 2. Removal of copper and nickel with soil waters from organogenic horizons in spruce and pine forests. Defoliating forests: (a) below crowns and (b) between crowns; sparse forest: (c) below crowns and (D) between crowns.

depositions of nickel and copper with atmospheric depositions exceed the level of critical loads by 370 and 600 times in spruce forests and 120 and 260 times in pine forests, respectively. In BetC, the level of critical loads of heavy metals is significantly lower: 49 and 54 times in spruce forests and 23 and 20 times in pine forests, respectively.

Thus, the results of these studies demonstrate that taking into account not only interbiogeocenotic but also intrabiogeocenotic differences in the composition of the atmospheric depositions of element compounds will allow an earlier diagnosis of critical-load exceedances at different stages of technogenic digression. Data on atmospheric deposition in BelC of spruce forests are more informative for identifying exceedances of critical loads, not only in reference conditions, but also at the stages of pronounced technogenic digression.

Assessment of the Critical Level of Soil-Water Characteristics at All Stages of Digression for the Functioning of Woody Plants

These studies demonstrate the significant excess of reference levels of removal of the compounds of heavy metals and sulfur with soil waters and significant spatial intra- and interbiogeocenotic differences. To estimate the critical-level exceedances, spatial differences were taken into account and international chemical indicators such as the molar ratio of basic cations and aluminum and the concentration of mineral nitrogen in the soil solution were used: for the first indicator, this level is for forests with dominants *Pinus sylvestris* and *Picea abies*, which are <1.2 and >0.2 mg/L, respectively (Iost et al., 2012).

Molar Ratios of Basic Cations and Aluminum

In spruce and pine forests in waters from all soil horizons, at all stages of digression, the BC/Al index significantly exceeds the critical values in BelC and BetC.

In reference and defoliating spruce forests and reference pine forests, the BC/Al index in soil waters decreases from the A0 to the BC horizon, both below and between the crowns of trees, which is associated with the active absorption of the main cations by plants. In pollution-induced sparse forests, no similar distinct trend was found due to deep disturbances in the functioning of biogeocenoses.

Intrabiogeocenotic differences in the BC/Al index in spruce and pine forests at all stages of digression in waters from all horizons in most cases are significant ($p < 0.05$). In spruce forests, BC/Al in waters from all soil horizons in reference conditions and in waters from A0 horizons in defoliating forests, as well as in waters from E + B horizons in pollution-induced sparse forests in the BelC, is significantly higher than in BetC, which is related to a high concentration of calcium in soils below the crowns, whereas the opposite is observed for aluminum, or there are no differences (Lukina and Nikonov, 1996).

In BelC and BetC of defoliating spruce forests, the BC/Al index in waters from all horizons is up to 5 times lower than in the reference area, which indicates the processes of soil depletion by basic cations. In defoliating pine forests, the BC/Al indicator in the waters from the A0 horizons reaches 1.5 times higher under the crowns and 5 times higher between crowns in the waters from all horizons than in the reference sites, which may be due to the deep root system of pine, unlike spruce, which is able to draw nutrients from the deep mineral horizons of soils that are rich in basic cations under these conditions and with intensive cation-exchange processes in soils.

In pollution-induced sparse spruce forests, the BC/Al indicator in the waters of the E + B horizons is up to 2 times higher than in the reference sites, both in BelC and in BetC. In pollution-induced sparse pine forests, this indicator in the waters of the A0 and E + B horizons is up to 9 times higher in the BelC and the BetC than in the reference sites. This is associated with rich soil-forming rocks with an admixture of gabbronorites near the smelter.

Thus, the BC/Al indicator in the soil waters of pine and spruce forests, both below the crowns and between the crowns of trees, significantly exceeds the critical values. This can be explained by the relative richness of the soil bases at research sites, especially near the smelter.

Nitrogen Mineral

In the reference sites of spruce and pine forests, the Nmin indicator in the soil waters decreases with the depth of the soil, both in BelC and BetC, which can be explained by active biological absorption. In defoliating forests and in pollution-induced sparse forests due to disruption of the functioning of phytocenoses, this trend is observed only in pine forests and only between the crowns of trees.

For mineral nitrogen, the critical level during the observation period, covering a high level of air pollution (1995–2000), was exceeded even in reference spruce and pine forests in waters from all soil horizons, both in BelC and BetC. Previously, on the basis of data obtained during the period of a sharp decrease in loads—2002–2008 (Lukina et al., 2018)—as well as on the basis of data from the following years of 2009–2012 additionally analyzed in this study, it was not seen that the critical levels of mineral nitrogen in waters from the mineral horizons of the soils of reference forests were exceeded. It can be concluded that the reduction in emissions could have led to some optimization of the nitrogen status of the soil waters.

In defoliating spruce and pine forests, the excess of the critical level of Nmin is observed in the waters from A0 and BC of spruce forests in the BelC and in the waters from the A0 horizons in the BelC and E + B in the pine forests. In pollution-induced sparse spruce and pine forests, the critical level Nmin is exceeded, both in BelC and BetC in waters from all horizons, except for the water of their E + B horizons in pine forests between tree crowns.

In reference spruce and pine forests, intrabiogeocenotic differences for Nmin in waters from all horizons are not reliable ($p > 0.05$), except for waters from A0 spruce forest soil horizons, which confirms ideas about the limitations of leaching of nitrogen compounds (a limiting factor of growth and productivity of boreal forests) from crowns of woody plants (Piirainen et al., 1998). In defoliating forests and sparse forests, on the contrary, there are higher concentrations of mineral nitrogen in the BelC in the soil waters, which can be explained by atmospheric pollution and leaching of nitrogen compounds from tree crowns with damaged needles.

CONCLUSIONS

As a result of conducted researches, significant inter- and intrabiogeocenotic variability of the composition of atmospheric depositions in spruce and pine forests at different stages of technogenic digression was established. The concentration of elements in atmospheric depositions that has passed through the forest canopy is higher than between tree crowns. It is confirmed that the spruce tree transforms depositions more strongly than pine, which is explained by its denser and more extended crown.

The revealed exceedances of critical loads in atmospheric depositions of sulphate sulfur and heavy metals at the stages of technogenic digression indicate the continuing negative impact of industrial air pollution on forest biogeocenoses, while the emission of pollutants into the atmosphere is decreasing.

The composition of soil waters at all stages of digression is also characterized by significant inter- and intrabiogeocenotic variation. The concentrations of elements are usually higher in the soil waters of the spaces below crowns when compared to the spaces between crown and in the spruce forests when compared to the pine forests.

The data on the many-year dynamics of concentrations of heavy metals and sulphates in soil waters are highly variable and show a downward trend, which may indicate a gradual decrease in technogenic load. However, an analysis of the data and a comparison with background values indicates a significant effect of industrial air pollution on forests. The combined effect of the level of pollution and the amount of depositions, which is clearly manifested in spruce defoliating forests, is manifested on the removal of compounds of elements with soil waters that are components of emissions.

The BC/Al index in the soil waters of pine and spruce forests, both below the crowns and between the crowns of trees at all stages of digression, significantly exceeds the critical values. This can be explained by the richness of soil-forming rocks and the soils of the region of research with basic cations. The relatively low values of this indicator in waters from the upper soil horizons of defoliating spruce forests when compared to the reference sites can be explained by the processes of soil depletion by the main cations compared to the reference sites.

The critical level for mineral nitrogen is exceeded at all stages of digression, while in the below-crown spaces the excess is, as a rule, higher than in the between-crown ones.

For the early detection of exceedances of the critical level of concentrations of mineral nitrogen in the soil waters at all stages of digression, it is necessary to assess their composition both in between-crown spaces and below-crown spaces.

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COMPLIANCE WITH ETHICAL STANDARDS

The authors declare that they have no conflict of interest. This article does not contain any studies involving animals or human participants performed by any of the authors.

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