



Article Pollution-Induced Changes in the Composition of Atmospheric Deposition and Soil Waters in Coniferous Forests at the Northern Tree Line

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Abstract: This study examines the dynamics of the composition of atmospheric precipitation and soil water in coniferous forests under the influence of atmospheric emissions from the Severonickel Copper–Nickel Smelter in Russia's Murmansk region. We studied dwarf shrub-green moss spruce forests and lichen-shrub pine forests, the most common in the boreal zone. Our results showed a significant intra- (below and between the crowns) and inter-biogeocenotic (spruce and pine forests) variation in the composition of atmospheric precipitation and soil water in forests exposed to air pollution. The concentrations of main pollutants in atmospheric fallout and soil water are tens (sulfates) and hundreds (heavy metals) times higher than in the background areas and typically higher below the crowns. The long-term dynamics (between 1999 and 2020) of the composition of atmospheric fallout and soil water in coniferous forests in the background areas and defoliating forests demonstrates a significant increase in nickel concentrations in aerosols propagating over considerable distances. In pollution-induced sparse forests, a trend was found toward a decrease in the concentration of pollutants, which may indicate a decrease in the fallout of pollutants in the composition of larger particles close to the smelter.

Keywords: coniferous forests; atmospheric fallout; soil water; air pollution; heavy metals; sulfates; pollution-induced degradation; the Arctic

1. Introduction

Intensive industrial development has led to widespread environmental pollution and the relevance of studying and preserving forest ecosystems has increased. Forest ecosystems growing at their northern limit of distribution are exposed to long-term impacts from mining and smelting operations. One of the least studied components of forest biogeocenoses is atmospheric precipitation and soil water, the study of the composition of that makes it possible to obtain more information about the biogeochemical cycles of elements in forest ecosystems. Numerous studies of the chemical composition of atmospheric and soil waters [1–11] showed that the chemical composition of atmospheric precipitation and soil solution changes significantly after contact with the forest canopy, depending on the species composition of woody plants and the impact of air pollution. In turn, the amount and quality of precipitation and soil water has a significant impact on the state of forest ecosystems [1,12]. Between the tree crowns at the northern limit of forest distribution, the precipitation is predominantly atmospheric, while below the crowns autogenic (biogenic) precipitation dominates [13]. When exposed to industrial air pollution, a significant transformation of the composition of atmospheric precipitation and soil water is observed, which consists of consistent changes in acidity and concentrations of heavy metals, sulfates, and nutrients in forests at different stages of degradation.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The Murmansk region is the northernmost region of the European part of Russia and its entire area belongs to the Russian Arctic. For more than eighty years, the forest ecosystems of Murmansk region have been exposed to intense industrial air pollution, which spreads over long distances. The main source of pollution is the Severonickel Smelter (Kola Mining and Metallurgical Company JSC (Murmansk, Russia)), located in the central part of Murmansk region in the city of Monchegorsk. The pollutants that affect the functioning of forest biogeocenoses include acid-forming compounds of sulfur and nitrogen, as well as compounds of heavy metals (nickel, copper, cobalt, lead, cadmium, chromium) [1,14]. The decrease in atmospheric emissions by the smelter and the decrease in the air pollution load on ecosystems causes it to be possible to consider the dynamic trends in the composition of individual components of forest ecosystems [14,15]. To predict the dynamics of biogeochemical cycles of elements in forests and propose measures aimed at increasing their stability under the combined action of natural and anthropogenic factors, it is necessary to estimate the spatial variation in the composition and properties of atmospheric precipitation and soil water, taking into account long-term changes.

The purpose of this study is (1) to assess the chemical composition of atmospheric precipitation and soil water in the northern taiga forests of the Murmansk region at different stages of technogenic digression due to the influence of a copper–nickel smelter, taking into account intra- and inter-biogeocenotic variation based on long-term observations and (2) to assess the long-term dynamic chemical composition of atmospheric fallout and soil water.

2. Materials and Methods

The objects of this study were atmospheric fallout and soil water in dwarf shrub-green moss spruce forests and lichen-shrub pine forests. The field studies were carried out on 6 permanent monitoring sites (PMSs) of the Institute of Industrial Ecology Problems of the North at the KSC RAS in the Murmansk region, Russia (Figure 1). The PMSs were established in typical forest ecosystems of the region in automorphic landscape positions. The PMSs are within transport accessibility for regular surveys. The spread of pollutants from the smelter site is controlled by the height of the pipe stacks (110–160 m), topography, and the strength and direction of the prevailing winds [16]. The predominance of southern and southwestern winds in the region in winter and northern and northwestern winds in summer [17] contribute to the formation of a plume of pollution from the smelter's emissions. The field studies were carried out on 6 permanent monitoring sites representing various stages of pollution-induced degradation: background areas, defoliating forests, and pollution-induced sparse forests (Figure 1). The PMSs are located along the pollution gradient of the Severonickel Smelter at various distances from the source of pollution: in pollution-induced sparse forests at 7–10 km, in defoliating forests at 28–31 km, and in the background (control) areas at more than 150 km [1]. The background site represents the regional background conditions in the study area and meets all the globally recommended criteria for control sites [18]. The soils in pine forests are illuvial-ferruginous podzols (Carbic Podzols, WRB) and in spruce forests are illuvial-humus podzols (Rustic Podzols, WRB) [19,20].

The snow sampling was carried out annually from 1991/95 to 2020 under and between the crowns in triplicate. The snow cores were extracted using a plastic collector for the entire snow depth to the soil surface annually before the start of snowmelt (usually in the first week of April).

The rainwater sampling was carried out annually from 1999 to 2020 using sediment collectors (5 under the crowns, 5 between the crowns), which are plastic pipes with a funnel. A plastic bag is placed inside the pipe and secured with a cap. To prevent the ingress of plant litter, insects, and other particles, the surface of the pipe is covered with a removable fine mesh created with a synthetic material before it is secured with a cap.



Figure 1. Study area: a,b—pollution-induced sparse forests, c,d—defoliating forests, e—background area.

The soil water sampling was carried out annually from 1991/95 to 2020 using gravitytype lysimeters designed by D. Derom [21] (6 per PMS), located at different depths in accordance with the soil horizons (organogenic A0, eluvial E + B, illuvial BC/C), and taking into account the mosaic structure of the biogeocenosis (under the crowns and between the crowns) [17].

During the field sampling campaign, the monthly volume of rain and soil water accumulated in the sediment collectors and lysimeters was measured using plastic measuring utensils. The sampling of lysimetric waters and rainwaters was carried out monthly from May to October.

The water samples were filtered through a blue-ribbon paper filter. The pH was measured potentiometrically, metals (Ca, Mg, Ni, Cu) by atomic absorption spectrophotometry, SO_4^{2-} by ion-exchange chromatography, C by chromatometry or permanganatometry, depending on the concentration. The acid-neutralizing capacity (ANC) was calculated as the difference between the sum of basic cations and anions of mineral acids in mmol/L.

The descriptive statistics and trends to assess the long-term dynamics of the composition of atmospheric precipitation and soil water were prepared in Microsoft Excel 2019. To compare the composition of atmospheric precipitation and soil water at different stages of pollution-induced degradation of Northern taiga forests and to compare the composition of under-crown and inter-crown precipitation, the Mann–Whitney test and the software Statistica 13.3 were used.

3. Results and Discussion

3.1. Composition of Atmospheric Precipitation in the Form of Snow

The winter atmospheric fallout coincides with the period of biological dormancy. In boreal forests, the snow cover is present between one hundred and two hundred days a year, which determines the significant role of precipitation in the form of snow in biogeochemical cycles. Currently, industrial air pollution has a great influence on the formation of the composition of precipitation in the Russian North. A general discussion of the composition of snow fallout in the forests exposed to industrial air pollution, as well as of the effects of the tree canopy on the spatial distribution of elements in atmospheric fallout, is provided in a number of studies [1,7,22–25]. The study revealed a significant influence of forest canopies

on the transformation of snowfall (under the canopy of detection of elements, sometimes several times higher than in open areas), as well as an increase in the concentrations of various pollutants (hundreds for detection, and tens of times for sulfates) when the level of air pollution of industrial origin is exceeded.

Intra-biogeocenotic variability. In pine and spruce forests at the stages of defoliating forest and pollution-induced sparse forest, the concentrations of Ca, Mg, C, Ni, Cu, and $SO_4^{2^-}$ in the snow water under the crowns are significantly, up to 3 times, higher (p < 0.05)) compared to between the crowns. In the background area, a higher content was found under the crowns for C, Ca, and $SO_4^{2^-}$ (p > 0.05) (Table 1). The revealed pattern is associated with the leaching of these elements from tree tissues, which is due to frequent winter thaws on the Kola Peninsula [24,26]. The pH value of the snow under the crowns is lower than between the crowns at all surveyed PMSs. The acid-neutralizing capacity never dropped to negative values in the background areas and in defoliating pine and spruce forests. The fallout values of compounds of elements did not have pronounced intra-biogeocenotic differences, which is associated, on the one hand, with increased concentrations of elements under the crowns.

Table 1. Concentration of element compounds in snow in spruce and pine forests in 1995–2020, mg/L, ANC in mmol/L.

Stages of Degradation	V, mL	рН	Ca	Mg	С	Ni	Cu	SO_4^{2-}	ANC
Spruce forests (n = 60–69)									
Background UC	<u>1326</u> 83	$\frac{4.81}{0.07}$	<u>0.37</u> 0.02	<u>0.09</u> 0.01	<u>3.29</u> 0.37	<u>0.002</u> 0.001	<u>0.002</u> 0.0002	<u>0.96</u> 0.06	<u>0.02</u> 0.002
Background BC	<u>2241</u> 89	$\frac{4.97}{0.09}$	$\frac{0.27}{0.02}$	<u>0.06</u> 0.005	$\frac{1.56}{0.18}$	<u>0.002</u> 0.0005	<u>0.002</u> 0.0005	$\frac{0.47}{0.03}$	<u>0.01</u> 0.002
Def. UC	$\frac{1506}{100}$	$\frac{4.52}{0.05}$	$\frac{0.58}{0.05}$	$\frac{0.15}{0.01}$	$\frac{2.69}{0.28}$	<u>0.02</u> 0.003	<u>0.02</u> 0.005	$\frac{2.06}{0.19}$	<u>0.005</u> 0.003
Def. BC	<u>2387</u> 126	$\frac{4.79}{0.06}$	$\frac{0.29}{0.02}$	$\frac{0.07}{0.004}$	$\frac{1.60}{0.20}$	<u>0.01</u> 0.002	$\frac{0.005}{0.001}$	$\frac{0.70}{0.03}$	<u>0.01</u> 0.002
Pol. UC	<u>2144</u> 155	$\frac{4.43}{0.06}$	$\frac{0.78}{0.07}$	$\frac{0.20}{0.02}$	<u>2.55</u> 0.28	<u>0.32</u> 0.04	$\frac{0.16}{0.02}$	$\frac{3.53}{0.34}$	$\frac{-0.02}{0.01}$
Pol. BC	<u>2194</u> 123	$\frac{4.68}{0.06}$	$\frac{0.44}{0.03}$	$\frac{0.10}{0.01}$	$\frac{1.47}{0.16}$	<u>0.12</u> 0.01	$\frac{0.05}{0.01}$	$\frac{1.50}{0.08}$	$\frac{-0.001}{0.002}$
			Pin	e forests (n	= 60–75)				
Background UC	$\frac{1104}{71}$	$\frac{4.87}{0.09}$	$\frac{0.38}{0.03}$	$\frac{0.11}{0.03}$	$\frac{3.18}{0.27}$	<u>0.001</u> 0.0003	<u>0.002</u> 0.0005	$\frac{0.71}{0.04}$	$\frac{0.01}{0.003}$
Background BC	<u>1581</u> 67	<u>4.96</u> 0.09	<u>0.29</u> 0.02	<u>0.06</u> 0.005	<u>1.70</u> 0,17	<u>0.001</u> 0.0003	<u>0.001</u> 0.0003	<u>0.52</u> 0.05	$\frac{0.004}{0.001}$
Def. UC	<u>1522</u> 92	$\frac{4.50}{0.06}$	$\frac{0.50}{0.04}$	$\frac{0.13}{0.01}$	<u>2.56</u> 0.22	<u>0.01</u> 0.002	<u>0.01</u> 0.001	$\frac{1.56}{0.08}$	$\frac{0.004}{0.002}$
Def. BC	<u>2307</u> 112	$\frac{4.79}{0.07}$	$\frac{0.30}{0.02}$	$\frac{0.07}{0.004}$	$\frac{1.59}{0.16}$	<u>0.01</u> 0.001	<u>0.003</u> 0.0005	$\frac{0.75}{0.04}$	$\frac{0.004}{0.003}$
Pol. UC	<u>1908</u> 92	$\frac{4.46}{0.05}$	$\frac{0.59}{0.05}$	$\frac{0.17}{0.01}$	$\frac{1.87}{0.18}$	$\frac{0.16}{0.01}$	$\frac{0.08}{0.01}$	$\frac{2.54}{0.14}$	$\frac{-0.01}{0.003}$
Pol. BC	<u>2244</u> 99	$\frac{4.70}{0.05}$	$\frac{0.40}{0.03}$	$\frac{0.10}{0.01}$	$\frac{1.74}{0.18}$	<u>0.08</u> 0.01	$\frac{0.05}{0.01}$	$\frac{1.44}{0.06}$	$\frac{-0.005}{0.002}$

Note: Background—background area, Def.—defoliating forests, Pol.–pollution-induced sparse forests. UC—under the crowns, BC—between the crowns. Above the line—mean value, below the line—standard deviation.

Effects of air pollution. Industrial air pollution has a significant impact on the formation of snow water composition. In defoliating pine and spruce forests, the concentrations of many elements differ from the background area. Under the crowns and between the crowns, there was a significant (p < 0.05) increase in the concentrations of SO_4^{2-} compounds of up to three times, Cu compounds up to four times, and Ni compounds up to seven times compared with the background area. The concentrations of the main nutrients (Ca and Mg) were higher, concentrations C and the pH lower compared to the background area, which is most pronounced under the crowns. In pollution-induced sparse spruce and pine forests, compared to the background area, the concentrations of the main pollutants were significantly higher: SO_4^{2-} up to 4 times, Cu up to 100 times, and Ni up to 130 times under and between the crowns. In addition, there was a decrease in C concentrations and an increase in the actual acidity and concentrations of basic cations in pollution-induced sparse spruce and pine forests compared to the background area, which can be explained both by the influence of air emissions [1] and by the leaching of these elements from the tree canopy. The ANC index under the crowns in spruce and pine forests, as well as between the crowns in spruce forests was significantly lower than in the background area. As in defoliating forests, an increase in pollutant concentrations compared to the background area indicates a significant impact of industrial pollution on forest ecosystems as the source of emissions becomes closer.

Fallout of elements. The fallout of all elements, except for C, in the spruce and pine defoliating forests and pollution-induced sparse forests was significantly higher compared to the background areas both between and under the crowns, which, under pollution conditions, can be associated with (1) an increase in the concentrations of the elements that constitute the emissions, (2) an increase in the concentrations of elements as a result of leaching from damaged needles, and (3) an increase in fallout due to the deterioration of the crowns (defoliation) and an increase in their permeability.

Inter-biogeocenotic variation. When comparing the concentrations and fallout of elements in the snow water in spruce and pine forests at different stages of degradation, significant differences were found only under the crowns of pollution-induced sparse forests, where the concentrations of Cu, Ni, and SO_4^{2-} in the snow water are higher in pollution-induced sparse forests of spruce than of pine.

Multi-year dynamics. In the period from 1991/99 to 2020, the concentrations of elements in the snow of the Northern taiga forests at different stages of pollution-induced degradation are characterized by significant variability.

Under and between the crowns in the background Northern taiga forests, a trend of a major increase in the concentrations of copper and nickel in 2016 and 2017 was found. No other distinct long-term trends were found.

In defoliating forests, the long-term dynamics of the concentrations of elements in snow demonstrates high variability both under and between the crowns. Between the crowns in defoliating forests, a decrease in sulfate concentrations was observed, from 1.1 to 0.87 mg/L ($R^2 = 0.37$) in spruce forests and from 0.87 to 0.62 mg/L ($R^2 = 0.29$) in pine forests. There was a decrease in copper concentrations under the crowns in spruce forests from 0.08 to 0.004 mg/L ($R^2 = 0.36$) and between the crowns from 0.02 to 0.003 mg/L ($R^2 = 0.49$). This may be due to the reduction in pollutant emissions into the atmosphere from the smelter.

In pollution-induced sparse forests, no clear trends of the concentrations of Ni, Cu, and SO_4^{2-} in winter precipitation were identified, with the exception of a decrease in the Cu content in snow between the crowns in pine—from 0.13 to 0.0004 mg/L (R² = 0.34). This may be due to the ongoing deposition of large particles near the smelter.

3.2. Composition of Atmospheric Fallout in the Form of Rain

Atmospheric precipitation in the form of rain plays an important role in the cycling of chemical elements and the functioning of forest ecosystems. The chemical composition of rainfall changes significantly after passing through the forest canopy. During this interaction, physicochemical reactions occur, leading to a change in water acidity and the concentrations of most of the elements contained in it. Currently, atmospheric precipitation chemistry is significantly influenced by air pollution and boreal forests act as a modifier of pollution flows [3,4,7,9,14,25,27-29], etc. The studies show that in the rainwater near the smelter, the concentrations of SO₄²⁻ and the concentrations of the main cations (Ca and Mg) were several times higher than the background values. The content of heavy metals in the rain was higher by an order of magnitude and more than in the background area. It is noted that filtered gas and dust emissions and chimneys are the dominant source of rainwater pollution, the reduction in emissions by the plant itself has significantly reduced the amount of pollutants coming from pipes into rainwater.

Intra-biogeocenotic variability. The composition of rainwater, as well as meltwater, at all stages of degradation in spruce and pine forests is characterized by pronounced intra-biogeocenotic variability: the concentrations of Ca, Mg, Ni, C, Cu, and SO_4^{2-} in the rainwater under the crowns are significantly higher (p < 0.05) than between the crowns (Table 2). In addition, in the rainwater of spruce and pine forests, the ANC index under the crowns are significantly higher than between the crowns and the acidity under the tree crowns also significantly increases. The elevated concentrations of elements under the crowns indicate leaching of element compounds from woody plants [1,5,17].

Table 2. Concentration of element compounds in rainwater in spruce and pine forests in 1999–2020, mg/L, ANC in mmol/L.

Stages of Degradation	V, mL	рН	Ca	Mg	С	Ni	Cu	SO4 ²⁻	ANC	
Spruce forests (n = 85–91)										
Background UC	$\frac{355}{34}$	$\frac{4.23}{0.05}$	$\frac{4.10}{0.25}$	<u>1.32</u> 0.10	<u>86.29</u> 3.75	<u>0.007</u> 0.001	$\frac{0.014}{0.001}$	$\frac{10.97}{0.92}$	$\frac{0.69}{0.04}$	
Background BC	<u>646</u> 42	$\frac{5.42}{0.08}$	$\frac{0.51}{0.05}$	<u>0.12</u> 0.012	$\frac{6.00}{0.77}$	<u>0.003</u> 0.0005	<u>0.003</u> 0.0005	$\frac{1.00}{0.08}$	<u>0.04</u> 0.006	
Def. UC	$\frac{323}{28}$	$\frac{3.60}{0.03}$	<u>6.66</u> 0.52	$\frac{1.60}{0.14}$	<u>55.90</u> 6.13	$\frac{0.31}{0.029}$	$\frac{0.24}{0.030}$	$\frac{33.48}{2.68}$	<u>0.318</u> 0.031	
Def. BC	$\frac{624}{47}$	$\frac{4.84}{0.08}$	<u>0.88</u> 0.09	$\frac{0.16}{0.02}$	$\frac{4.93}{0.34}$	$\frac{0.01}{0.002}$	<u>0.006</u> 0.001	<u>2.93</u> 0.26	<u>0.02</u> 0.004	
Pol. UC	<u>613</u> 51	<u>3.52</u> 0.03	$\frac{4.38}{0.25}$	$\frac{1.14}{0.08}$	<u>28.20</u> 1.68	$\frac{1.41}{0.12}$	$\frac{1.05}{0.11}$	<u>26.93</u> 1.85	$\frac{0.04}{0.02}$	
Pol. BC	<u>631</u> 56	$\frac{4.19}{0.05}$	$\frac{1.38}{0.10}$	$\frac{0.25}{0.02}$	$\frac{4.59}{0.30}$	$\frac{0.09}{0.01}$	$\frac{0.07}{0.01}$	$\frac{6.24}{0.45}$	$\frac{-0.005}{0.005}$	
			Pin	e forests (n	= 85–91)					
Background UC	$\frac{461}{41}$	$\frac{4.46}{0.06}$	$\frac{2.70}{0.16}$	$\frac{0.73}{0.04}$	$\frac{45.03}{1.77}$	<u>0.005</u> 0.0007	<u>0.008</u> 0.0008	$\frac{3.08}{0.22}$	<u>0.35</u> 0.021	
Background BC	<u>727</u> 49	$\frac{5.34}{0.08}$	$\frac{0.48}{0.06}$	<u>0.10</u> 0.009	$\frac{4.81}{0.27}$	<u>0.003</u> 0.001	<u>0.004</u> 0.001	$\frac{1.24}{0.17}$	<u>0.023</u> 0.003	
Def. UC	<u>577</u> 65	$\frac{3.64}{0.03}$	$\frac{4.28}{0.24}$	$\frac{1.04}{0.06}$	$\frac{55.34}{3.03}$	$\frac{0.14}{0.013}$	$\frac{0.10}{0.01}$	$\frac{16.20}{1.05}$	<u>0.346</u> 0.02	
Def. BC	$\frac{640}{46}$	<u>4.72</u> 0.06	$\frac{0.72}{0.06}$	$\frac{0.14}{0.013}$	$\frac{4.61}{0.24}$	<u>0.01</u> 0.001	<u>0.005</u> 0.0006	$\frac{2.70}{0.22}$	<u>0.023</u> 0.003	
Pol. UC	$\frac{571}{45}$	$\frac{3.64}{0.03}$	$\frac{3.51}{0.22}$	$\frac{0.80}{0.05}$	<u>29.82</u> 1.81	$\frac{0.60}{0.05}$	$\frac{0.53}{0.07}$	$\frac{17.28}{1.08}$	$\frac{0.11}{0.01}$	
Pol. BC	<u>616</u> 44	$\frac{4.40}{0.05}$	$\frac{1.01}{0.07}$	$\frac{0.17}{0.01}$	$\frac{4.09}{0.22}$	$\frac{0.04}{0.01}$	$\frac{0.04}{0.01}$	$\frac{4.16}{0.28}$	<u>0.009</u> 0.003	

Note: Background—background area, Def.—defoliating forests, Pol.—pollution-induced sparse forests. UC—under the crowns, BC—between the crowns. Above the line—mean value, below the line—standard deviation.

Effects of air pollution. Rainwater in defoliating spruce and pine forests, compared with the background areas, is characterized by a significant increase in pollutant concentrations: copper up to 17 times, Ni up to 43 times, and sulfates up to 5 times. This pattern is most pronounced under the crowns. The concentrations of Ca and Mg in defoliating spruce and pine forests, compared to the background areas, are significantly higher, both under the crowns (with the exception of magnesium concentrations in spruce forest, *p* > 0.05) and between the crowns, which is explained by the leaching of these elements from tree crowns due to acid rain. When exposed to air pollution, the tissues of woody plants are depleted in inactive elements, such as calcium, which accumulates in aging and often damaged needles [17,30,31]. The concentration of C is significantly reduced compared to the background area, which is due to crown defoliation.

The rainwater in pollution-induced sparse pine and spruce forests, under and between the crowns, differs compared to the background by a sharp increase in the concentrations of pollutants that constitute emissions: Cu up to 75 times, Ni up to 200 times, and SO_4^{2-} up to 6 times. Between the crowns in spruce and pine forests, the concentrations of calcium and magnesium in rainwater are higher compared to the background, which may be due to their high content in industrial emissions and dusting of areas not covered with vegetation (pollution-induced wastelands). In the rainwaters of sparse pine and spruce forests, a decrease in C concentrations is observed compared to the background area due to the degradation of the crowns of woody plants.

An increase in the acidity of rainwater between and under the crowns was found, which indicates a high level of industrial air pollution. Compared to the background areas, the indicator of the acid-neutralizing capacity was significantly (p < 0.05) lower in the rainwater of defoliating spruce forests and pollution-induced sparse pine and spruce forests under and between the crowns. This pattern is explained by a lower content of organic acids due to thinning of crowns, due to the premature fall of needles and a significant increase in the concentration of sulfates under the influence of technogenic air pollution [1].

Fallout of elements. In pine and spruce forests at all stages of degradation, the fallout of compounds of elements has clear intra-biogeocenotic differences: the fallout of elements with rain under the crowns is in most cases significantly higher than between the crowns. At the same time, between the crowns, the amount of atmospheric precipitation in spruce and pine forests in the background area, as well as in defoliating spruce forests, is up to two times higher than under the crowns. In defoliating pine forests and pollutioninduced sparse spruce and pine forests, the differences in precipitation levels are leveled, which is associated with the thinning of tree crowns due to the impact of pollution. In defoliating forests and pollution-induced sparse forests, the deposition of SO_4^{2-} , Cu, and Ni is much higher, both under and between the crowns compared to the background area. This can be explained by an increase in their concentrations and an increase in the volume of precipitation due to an increase in the transmission capacity of the tree crowns. Fallouts, as well as carbon concentrations in rain in defoliating forests and pollution-induced sparse forests, are significantly lower compared to the background area, with the exception of defoliating pine forests, here the differences are not significant (p > 0.05). Similar results were obtained in earlier studies, where it was found that in pollution-induced sparse forests, the concentration of carbon in atmospheric fallout was lower compared to the background values, which is associated with a sharp decrease in the mass of needles and a significant influx of sulfates, nitrates, and chlorides with emissions from the copper–nickel smelter [1].

Inter-biogeocenotic variability. In the background area, the concentrations Ca, Mg, C, Ni, Cu, and SO_4^{2-} between and under the crowns are significantly higher in spruce forests compared to pine forests. In the background area and in defoliating forests, the pH and ANC values are higher in pine forests than in spruce forests. In defoliating spruce forests, the concentrations of elements in rain under tree crowns are significantly higher than in pine forests, with the exception of C concentrations. In pollution-induced sparse forests, the pH and ANC values are higher in the pine forest compared to the spruce forest, the

concentrations of Ca, Mg, Ni, Cu, and SO_4^{2-} , on the contrary, are higher in the spruce forest, both under the crowns and between the crowns of the trees.

In the background area and in defoliating forests, the volume of precipitation penetrating through the tree canopy is significantly higher in pine forests. There were no differences in the amount of precipitation in the pollution-induced sparse forests. The fallout of Ca, Mg, Ni, Cu, and SO_4^{2-} is significantly higher under the crowns in spruce forests, which is associated with higher concentrations in the rain. The elevated concentrations of element compounds in the rainfall under the crowns of spruce forests are associated with a larger surface area and more pronounced barrier functions of spruce tree crowns [1,11,13].

Multi-year dynamics. The atmospheric fallout of element compounds with rain during the period from 1999 to 2020 at different succession stages of coniferous forests is characterized by high variability. In the background areas, during the period from 1999 to 2020, under and between the crowns of Northern taiga forests, a trend of increasing Ni concentrations was found, most pronounced in pine forests (Figure 2). This can be explained by an increase in the level of pollutants in industrial emissions in the form of aerosols propagating over considerable distances, which indicates an increase in pollution loads [32,33].



Pine UC

Pine BC

Figure 2. Long-term dynamics of nickel concentrations in the rainwater in the background spruce and pine forests: UC—under the crowns, BC—between the crowns.

Under the crowns in defoliating pine forests, a trend was observed toward decreasing copper concentrations in the rainwater from 0.14 to 0.04 mg/L ($R^2 = 0.32$). No other significant trends were found in the long-term dynamics of the concentrations of main pollutants in the rainwater in defoliating forests and pollution-induced sparse forests.

3.3. Soil Water Composition

The soil is the most important component of the forest ecosystem and serves as an accumulator for most of the elements present in the biosphere. The soil solution is the most active phase of the soil. Since the soil water is in direct contact with plant roots, information on soil water composition is of high indicative value for assessing the possible negative impacts on forests. The chemical composition of soil water enables it to be possible to obtain information on the availability of nutrients and compounds of elements potentially toxic to biota in soils [34–36]. According to studies, significant intraprofile variability can be observed in the soil waters of boreal forests, which is expressed in a decrease in the concentrations of all elements with depth and is explained by the presence of biogeochemical barriers. It is also possible to observe pronounced intra-biogeocentric variability; soil waters in under-crown spaces are more concentrated and acidic than in intercrown spaces, which is due to the formation of intense flows of acid-forming substances with crown and stem waters. The variability of the composition of soil waters depending on the type of biogeocenosis is noted: it is shown that in the soil waters of spruce forests, the concentrations of elements, as a rule, are higher than in pine forests.

When approaching the source of pollution, there is a violation of the functioning of all components of the biogeocenosis, in connection with this, the concentrations of nutrients in soil water and the ANC index decrease, and an increase in the concentrations of the compounds of the elements included in the emissions is observed. These changes are most noticeable in woody, especially in spruce, parcels due to the high sorption capacity of the crowns of coniferous trees.

Intra-biogeocenotic variability. In the background area, in lysimetric water samples from all soil horizons in spruce and pine forests, the concentrations of Ca, Mg, C, Ni, Cu, and SO_4^{2-} were significantly (p < 0.05) higher under the crowns than between the crowns (Tables 3–5), which is associated with the leaching of element compounds from plant tissues by atmospheric precipitation. An exception is the concentration of Cu in the water from the A0 soil horizon in pine forests, as well as in the water from the BC soil horizon in spruce and pine forests (p > 0.05).

The soil water acidity under spruce crowns in the background area is significantly lower (p < 0.05) than between the crowns. This is explained by the higher Ca concentration in crown rainwater and in the soils under spruce. In addition, the dense and low spruce crowns retain a significant amount of precipitation, which prevents the intensive removal of bases from the soil. The organogenic and mineral horizons of soils under spruce trees are richer in available calcium compounds, the content of which in the falling needles of spruce is much higher than in pine [36]. In pine forests, significant differences in water acidity in the under-crown and inter-crown spaces were not found.

The ANC index in the water samples from all soil horizons under and between the crowns in the background spruce and pine forests decreases with depth and has a positive value. A decrease in the ANC index with depth can be observed in spruce and pine forests under and between the crowns, which is associated with a decrease in the concentrations of low molecular weight aliphatic organic acids [37]. In spruce and pine forests, the ANC index in the soil water under the crowns is significantly higher than between the crowns, with the exception of soil waters from the illuvial horizons of pine forests.

The intra-biogeocenotic differences in defoliating pine and spruce forests show that the concentrations of Ca, Mg, Cu, Ni, and SO_4^{2-} in the soil water from all soil horizons under the crowns are significantly higher than between the crowns. It should be noted that in pine forests, the concentration of Cu in the soil water from the soil horizon A0 between the crowns is significantly (p < 0.05) higher than under the crowns. In contrast to the background area, the acidity of soil water in defoliating spruce forests is significantly lower (p < 0.05) between the crowns compared to under the crowns. Under 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 disruption in the functioning of the phytocenosis. In defoliating spruce forests, the ANC index in the soil

water from all soil horizons between the crowns is significantly higher than under the crowns, which may be due to the intense flow of acid-forming substances with precipitation under spruce crowns. In defoliating forests, the acidity and composition of atmospheric fallout is controlled by two additional factors—the level of atmospheric pollution and the degree of damage to the tree canopy. Under the conditions of aerotechnogenic pollution, due to the presence of the tree canopy, the lower tiers of vegetation, the soils of the undercrown spaces, and the trees themselves are exposed to a more powerful technogenic impact than the vegetation and soils of the inter-crown spaces [27]. The ANC indicator has a positive value in the soil water of spruce and pine forests under the crowns and between the crowns.

Stages of Degradation	V, mL	pН	Ca	Mg	С	Ni	Cu	SO_4^{2-}	ANC
			Sprue	ce forests (n	= 88–120)				
Background UC	$\frac{1305}{72}$	$\frac{4.41}{0.04}$	$\frac{6.37}{0.39}$	$\frac{1.60}{0.10}$	<u>84.92</u> 4.63	<u>0.006</u> 0.0004	$\frac{0.01}{0.001}$	$\frac{7.11}{0.52}$	$\frac{0.64}{0.04}$
Background BC	$\frac{1054}{73}$	$\frac{4.23}{0.04}$	$\frac{1.51}{0.11}$	$\frac{0.34}{0.023}$	$\frac{28.39}{1.84}$	<u>0.003</u> 0.0004	<u>0.006</u> 0.0006	$\frac{0.94}{0.07}$	$\frac{0.20}{0.014}$
Def. UC	<u>1152</u> 52	<u>3.52</u> 0.02	<u>6.15</u> 0.28	$\frac{1.16}{0.05}$	<u>37.21</u> 1.77	<u>0.23</u> 0.015	<u>0.26</u> 0.015	<u>29.14</u> 1.51	$\frac{0.151}{0.014}$
Def. BC	$\frac{709}{58}$	$\frac{3.84}{0.03}$	$\frac{3.58}{0.17}$	$\frac{0.81}{0.04}$	$\frac{54.93}{2.30}$	<u>0.08</u> 0.006	$\frac{0.035}{0.002}$	$\frac{6.66}{0.48}$	$\frac{0.34}{0.017}$
Pol. UC	$\frac{1641}{65}$	$\frac{3.96}{0.04}$	$\frac{4.62}{0.21}$	$\frac{1.25}{0.06}$	<u>16.90</u> 1.27	$\frac{1.31}{0.08}$	$\frac{0.82}{0.10}$	$\frac{28.47}{1.53}$	$\frac{-0.03}{0.01}$
Pol. BC	<u>722</u> 80	$\frac{4.20}{0.04}$	$\frac{3.94}{0.27}$	<u>0.93</u> 0.06	<u>16.36</u> 1.57	<u>0.70</u> 0.06	<u>0.15</u> 0.02	$\frac{18.06}{1.40}$	<u>0.029</u> 0.007
			Pine	e forests (n =	= 83–139)				
Background UC	$\frac{1089}{65}$	<u>3.79</u> 0.03	$\frac{4.48}{0.24}$	$\frac{0.93}{0.05}$	$\frac{82.75}{4.17}$	$\frac{0.004}{0.0004}$	<u>0.008</u> 0.0007	<u>2.23</u> 0.16	$\frac{0.57}{0.037}$
Background BC	$\frac{1100}{76}$	$\frac{3.90}{0.03}$	$\frac{2.17}{0.14}$	$\frac{\underline{0.46}}{0.028}$	$\frac{44.84}{2.79}$	$\frac{0.003}{0.001}$	$\frac{0.009}{0.002}$	$\frac{1.02}{0.10}$	$\frac{0.331}{0.024}$
Def. UC	<u>828</u> 70	<u>3.63</u> 0.02	<u>3.85</u> 0.24	$\frac{0.79}{0.04}$	<u>55.62</u> 2.58	$\frac{0.04}{0.004}$	<u>0.02</u> 0.00	<u>7.92</u> 0.41	$\frac{0.303}{0.02}$
Def. BC	$\frac{1779}{54}$	$\frac{4.17}{0.03}$	$\frac{1.99}{0.10}$	$\frac{0.44}{0.020}$	$\frac{28.06}{1.19}$	<u>0.02</u> 0.002	<u>0.03</u> 0.002	<u>2.96</u> 0.23	$\frac{0.177}{0.010}$
Pol. UC	<u>1613</u> 57	$\frac{3.63}{0.03}$	$\frac{5.49}{0.27}$	$\frac{1.36}{0.07}$	<u>36.93</u> 1.94	$\frac{1.21}{0.07}$	$\frac{0.68}{0.05}$	<u>26.04</u> 1.23	$\frac{0.12}{0.02}$
Pol. BC	<u>1302</u> 55	<u>4.21</u> 0.03	<u>3.02</u> 0.13	$\frac{0.81}{0.04}$	$\frac{17.47}{1.07}$	$\frac{0.31}{0.02}$	$\frac{0.11}{0.01}$	$\frac{12.86}{0.69}$	$\frac{0.069}{0.006}$

Table 3. Concentration of element compounds in the soil water from organic soil horizons (A0) in spruce and pine forests in 1995–2020, mg/L, ANC in mmol/L.

Note: Background—background area, Def.—defoliating forests, Pol.—pollution-induced sparse forests. UC—under the crowns, BC—between the crowns. Above the line—mean value, below the line—standard deviation.

In pollution-induced sparse forests, the concentrations of Ca, Mg, Cu, C, Ni, and SO_4^{2-} and the acidity are significantly higher in the soil water under the crowns compared between the crowns. In spruce forests, the ANC indicator has a negative value in the soil water both under and between the crowns.

Effect of air pollution. In the soil water under the crowns of defoliating spruce and pine forests, the concentrations of the main pollutants are much higher in comparison with the background areas: sulfates up to 4 times, copper up to 30 times, and nickel up to 40 times, which is most pronounced under the crowns. In the soil waters from all soil horizons under

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and between the crowns of spruce forests, the acidity of lysimetric waters increases in comparison with the background areas. In pine forests, in comparison with the background areas, the acidity also increases in the soil water from A0 horizons under-the crowns and in the soil water from BC horizons, both under and between the crowns. However, in the soil water from the E + B horizons in pine forests, on the contrary, a decrease in actual acidity was observed compared to the background. This may be due to an increase in the concentration of bases associated with the composition of parent rocks. In soil under crown waters in defoliating spruce and pine forests, the value of the ANC index is significantly lower than in the background area, except for waters from the A0 horizons of spruce forest soils in inter-crown spaces [1,36].

Table 4. Concentration of element compounds in the soil water from eluvial soil horizons (E + B) in spruce and pine forests in 1995–2020, mg/L, ANC in mmol/L.

Stages of Degradation	V, mL	рН	Ca	Mg	С	Ni	Cu	SO_4^{2-}	ANC	
Spruce forests (n = 88–120)										
Background UC	$\frac{554.44}{114.75}$	$\frac{4.98}{0.08}$	$\frac{3.62}{0.45}$	$\frac{1.07}{0.12}$	$\frac{52.34}{5.44}$	$\frac{0.005}{0.001}$	$\frac{0.008}{0.002}$	<u>5.87</u> 0.59	$\frac{0.30}{0.04}$	
Background BC	<u>641.19</u> 106.87	$\frac{4.76}{0.08}$	$\frac{1.39}{0.12}$	$\frac{0.41}{0.03}$	$\frac{21.90}{1.73}$	$\frac{0.004}{0.002}$	$\frac{0.006}{0.001}$	$\frac{2.54}{0.20}$	$\frac{0.12}{0.01}$	
Def. UC	<u>755.35</u> 58.63	<u>3.91</u> 0.02	<u>3.69</u> 0.18	$\frac{1.05}{0.05}$	$\frac{22.35}{0.95}$	$\frac{0.128}{0.007}$	<u>0.037</u> 0.003	<u>22.97</u> 1.22	$\frac{0.04}{0.01}$	
Def. BC	<u>590.03</u> 78.35	$\frac{4.41}{0.04}$	$\frac{1.58}{0.11}$	$\frac{0.41}{0.03}$	<u>21.64</u> 1.78	$\frac{0.015}{0.002}$	$\frac{0.016}{0.002}$	<u>5.29</u> 0.19	$\frac{0.10}{0.01}$	
Pol. UC	<u>962.15</u> 90.30	$\frac{4.49}{0.03}$	$\frac{3.25}{0.20}$	$\frac{0.90}{0.05}$	$\frac{9.71}{0.72}$	$\frac{0.81}{0.06}$	$\frac{0.15}{0.01}$	$\frac{15.47}{0.87}$	$\frac{-0.02}{0.01}$	
Pol. BC	<u>815.66</u> 77.83	$\frac{4.53}{0.03}$	$\frac{3.09}{0.14}$	$\frac{0.71}{0.03}$	<u>9.35</u> 0.67	$\frac{0.47}{0.03}$	$\frac{0.04}{0.00}$	$\frac{13.15}{0.68}$	$\frac{-0.02}{0.01}$	
			Pine	forests (n =	= 83–139)					
Background UC	<u>1166.18</u> 78.45	$\frac{4.30}{0.03}$	<u>2.07</u> 0.10	$\frac{0.73}{0.03}$	<u>46.54</u> 1.77	$\frac{0.004}{0.001}$	<u>0.007</u> 0.001	<u>2.29</u> 0.17	$\frac{0.30}{0.02}$	
Background BC	$\frac{710.36}{90.84}$	$\frac{4.46}{0.05}$	$\frac{1.23}{0.07}$	$\frac{0.36}{0.02}$	<u>29.77</u> 1.65	$\frac{0.003}{0.001}$	$\frac{0.005}{0.001}$	$\frac{1.08}{0.11}$	$\frac{0.20}{0.01}$	
Def. UC	<u>376.22</u> 56.68	$\frac{4.55}{0.04}$	$\frac{3.03}{0.24}$	<u>0.90</u> 0.06	<u>24.22</u> 1.94	$\frac{0.049}{0.007}$	$\frac{0.011}{0.001}$	$\frac{10.56}{0.56}$	$\frac{0.08}{0.01}$	
Def. BC	<u>774.93</u> 90.61	$\frac{4.83}{0.05}$	$\frac{0.86}{0.05}$	$\frac{0.24}{0.02}$	<u>18.28</u> 1.72	<u>0.006</u> 0.001	<u>0.005</u> 0.001	<u>3.63</u> 0.21	<u>0.03</u> 0.00	
Pol. UC	782.15 65.70	$\frac{4.14}{0.03}$	<u>3.03</u> 0.13	$\frac{0.89}{0.04}$	<u>15.76</u> 1.06	<u>0.61</u> 0.03	$\frac{0.13}{0.01}$	$\frac{16.49}{0.66}$	<u>0.01</u> 0.01	
Pol. BC	774.68 67.97	$\frac{4.63}{0.05}$	<u>2.52</u> 0.12	$\frac{0.70}{0.04}$	$\frac{12.29}{0.94}$	$\frac{0.26}{0.03}$	$\frac{0.05}{0.01}$	$\frac{10.18}{0.48}$	$\frac{0.04}{0.00}$	

Note: Background—background area, Def.—defoliating forests, Pol.—pollution-induced sparse forests. UC—under the crowns, BC—between the crowns. Above the line—mean value, below the line—standard deviation.

In technogenic light forests, the concentrations of the main pollutants in soil waters are significantly higher than in the background area: up to 10 times for SO_4^{2-} , up to 100 times for Cu, and up to 500 times for Ni, which is more pronounced in the under-crown space. The pH value of soil water in the under-crown spaces of pine woodlands, under-crown and inter-crown spaces of spruce woodlands is lower compared to the background. In the spruce and pine light forests, in soil waters, with the exception of waters from the soil horizon A0 of the under-crown spaces of the spruce forest, an increase in the concentrations of Ca and Mg is observed compared to the background territory, which is explained by

parent rocks rich in bases. In sparse forests, the value of the ANC index in the soil water under and between the crowns is lower than in the background area. There is a decrease in C concentrations in waters from all soil horizons in defoliating pine and spruce forests and technogenic light forests under crowns compared to the background, which is due to the degradation of the state of the forest stand and crown defoliation.

Table 5. Concentration of element compounds in the soil water from illuvial soil horizons (IS) in spruce and pine forests in 1995–2020, mg/L, ANC in mmol/L.

Stages of Degradation	V, mL	pН	Ca	Mg	С	Ni	Cu	SO_4^{2-}	ANC
Spruce forests (n = 88–120)									
Background UC	<u>629.46</u> 99.87	$\frac{5.17}{0.08}$	<u>2.38</u> 0.19	<u>0.85</u> 0.06	$\frac{\underline{24.08}}{2.73}$	<u>0.003</u> 0.001	<u>0.005</u> 0.001	<u>7.56</u> 0.55	$\frac{0.13}{0.02}$
Background BC	$\frac{608.00}{165.72}$	$\frac{4.73}{0.09}$	$\frac{1.19}{0.15}$	$\frac{0.40}{0.06}$	$\frac{14.20}{1.30}$	$\frac{0.001}{0.000}$	<u>0.007</u> 0.001	$\frac{3.95}{0.40}$	$\frac{0.05}{0.01}$
Def. UC	<u>886.00</u> 204.66	$\frac{4.34}{0.04}$	<u>2.35</u> 0.16	$\frac{0.71}{0.05}$	<u>11.16</u> 1.09	$\frac{0.06}{0.01}$	$\frac{0.01}{0.00}$	$\frac{13.18}{0.91}$	$\frac{0.01}{0.01}$
Def. BC	$\frac{652.40}{84.91}$	$\frac{4.47}{0.03}$	<u>1.72</u> 0.10	$\frac{0.46}{0.02}$	<u>14.18</u> 1,50	$\frac{0.02}{0.00}$	$\frac{0.01}{0.00}$	$\frac{7.18}{0.30}$	$\frac{0.05}{0.01}$
Pol. UC	<u>1350.28</u> 95.10	$\frac{4.56}{0.04}$	<u>3.96</u> 0.17	$\frac{1.21}{0.09}$	$\frac{14.15}{1.40}$	<u>1.22</u> 0.11	$\frac{0.50}{0.05}$	<u>22.06</u> 1.33	$\frac{-0.05}{0.01}$
Pol. BC	<u>1452.82</u> 101.46	$\frac{4.68}{0.03}$	$\frac{3.59}{0.15}$	$\frac{0.72}{0.03}$	$\frac{7.36}{1.34}$	$\frac{0.43}{0.05}$	$\frac{0.01}{0.00}$	$\frac{10.72}{0.79}$	$\frac{-0.06}{0.01}$
			Pine	forests (n =	= 83–139)				
Background UC	$\frac{286.81}{40.93}$	$\frac{4.71}{0.05}$	$\frac{1.68}{0.15}$	$\frac{0.53}{0.03}$	<u>24.99</u> 1.86	<u>0.002</u> 0.000	$\frac{0.004}{0.000}$	$\frac{5.37}{0.27}$	$\frac{0.11}{0.01}$
Background BC	<u>547.66</u> 85.31	$\frac{4.91}{0.06}$	$\frac{1.25}{0.08}$	<u>0.38</u> 0.03	<u>27.27</u> 1.87	$\frac{0.004}{0.001}$	<u>0.005</u> 0.001	$\frac{1.51}{0.17}$	$\frac{0.17}{0.02}$
Def. UC	$\frac{531.47}{85.85}$	$\frac{4.43}{0.05}$	<u>3.90</u> 0.31	$\frac{1.11}{0.08}$	$\frac{34.90}{3.35}$	$\frac{0.11}{0.01}$	$\frac{0.03}{0.01}$	<u>13.95</u> 0.86	$\frac{0.12}{0.02}$
Def. BC	<u>918.34</u> 145.59	$\frac{4.83}{0.06}$	$\frac{1.07}{0.14}$	$\frac{0.32}{0.03}$	$\frac{13.04}{1.87}$	<u>0.003</u> 0.001	$\frac{0.004}{0.001}$	$\frac{4.10}{0.22}$	$\frac{0.04}{0.01}$
Pol. UC	<u>956.56</u> 72.96	$\frac{4.19}{0.03}$	<u>5.81</u> 0.36	$\frac{1.43}{0.09}$	<u>19.88</u> 0.96	<u>1.12</u> 0.11	$\frac{0.30}{0.04}$	<u>24.64</u> 1.67	<u>0.02</u> 0.01

Note: Background—background area, Def.—defoliating forests, Pol.—pollution-induced sparse forests. UC—under the crowns, BC—between the crowns. Above the line—mean value, below the line—standard deviation.

The increase in water acidity and concentrations of the main pollutants in defoliating forests and pollution-induced sparse forests indicates a significant negative impact of industrial air pollution on forest biogeocenoses. The decrease in the ANC index in defoliating forests and pollution-induced sparse forests compared to the background areas is associated with a decrease in the concentrations of low molecular weight aliphatic acids and an increase in the concentrations of mineral acid anions.

Removal of elements. In the background area in the Northern taiga forests, the removal of elements with lysimetric waters has high variability. Under the crowns, in the soil water from all soil horizons in spruce forests and from A0 and E + B horizons in pine forests, the removal of the majority of elements is significantly higher than between the crowns. This is due to the higher concentration of elements in the soil water under the crowns.

In defoliating spruce forests, the removal of elements with soil water is higher under the crowns than between the crowns. In defoliating pine forests in the soil water from the A0 horizon, the removal of Ca, Mg, C, Cu, and Ni increases in the water between the crowns. This can be explained by the large amount of soil water between the crowns compared to under the crowns. The removal of sulfates, copper, and nickel in the soil water in defoliating Northern taiga forests increases (p < 0.05) compared to the background area.

In pollution-induced sparse forests, the removal of elements with soil water under the crowns is higher than between the crowns. The removal of the main pollutants with water from soil horizons in sparse spruce and pine forests is significantly higher than in the background area. It should be noted that the amount of soil water from all soil horizons under the crowns in sparse forests is higher than in the background area, with the exception of soil water from the E + B horizon in pine forests. This can be explained both by an increase in the volume of precipitation due to thinning of the crowns and an increase in their transmission capacity when exposed to pollution and with a smaller volume of water absorption from the soil by the remaining living plants.

Inter-biogeocenotic variability. In the soil water from all soil horizons under the crowns of background spruce forests, the concentrations of Ca, Mg, SO_4^{2-} , and Ni in the soil water from the A0 horizon are significantly higher than in pine forests. The precipitation passing through the forest canopy becomes more concentrated and spruce undergoes a deeper transformation than pine, due to a longer and denser crown. Between the crowns, in the soil water from the A0 horizon, the concentrations of elements are either comparable or higher in pine forests. In the soil water from mineral horizons, generally, inter-biogeocenotic differences similar to the soil water from organogenic soil horizons were observed. The acidity of the soil water from all soil horizons under and between the crowns in pine forests is significantly higher than in spruce forests (with the exception of the soil water from the BC horizons between the crowns. This can be explained by a higher calcium content in the soils of spruce forests [1]. In defoliating spruce forests, in the soil water from all soil horizons under and between the crowns, the concentrations of most elements are significantly higher than in pine forests. In spruce forests, the ANC index in the soil water under the crowns is lower and, between the crowns, higher compared to pine forests. In the context of industrial air pollution, this can be explained by a higher flux of acid-forming substances under the crowns of spruce, known to intercept more acid-forming substances that the more open pine crowns. In pollution-induced sparce spruce forests, in the soil water from all soil horizons, the concentrations of sulfates, calcium, and nickel are higher than in pine forests. The water acidity is higher under the crowns of pine forests. The ANC index is lower in the soil water of spruce forests, both under and between the crowns, which is due to a more intense flux of acid-forming substances under the crowns of spruce forests.

Multi-year dynamics. In the Northern taiga forests, the long-term dynamics of element concentrations in soil waters are characterized by high variability.

In background spruce forests in the soil water from organogenic soil horizons, the long-term dynamics (in the period from 1999 to 2020) shows a trend of increasing Ni concentrations: under the crowns from 0.005 to 0.008 mg/L ($R^2 = 0.47$) and between the crowns from 0.002 to 0.009 mg/L ($R^2 = 0.39$). In the background pine forests, this trend was not found; on the contrary, there is a trend under the crowns toward decreasing Cu concentrations from 0.01 to 0.001 mg/L ($R^2 = 0.46$).

In defoliating forests in the soil water from A0 soil horizons, trends toward increasing concentrations of Ni, Cu, and SO_4^{2-} in recent years were found under the crowns (Figure 3). At this stage of degradation, a decrease in sulfate concentrations in the soil water from organic soil horizons between the spruce crowns from 10 to 5 mg/L ($R^2 = 0.46$) and from 10 to 2 mg/L ($R^2 = 0.61$) in pine was found. In spruce forests, there was a decrease in sulfate concentrations in soil water from 43 to 18 mg/L ($R^2 = 0.33$) (horizons E + B) and from 20 to 13 mg/L ($R^2 = 0.61$) (horizon BC).



Figure 3. Long-term dynamics of the concentrations of the main pollutants in the soil water under the crowns from the organogenic soil horizon in defoliating spruce and pine forests.

In the soil water in pollution-induced sparse forests, a trend was found of decreasing concentrations of the main pollutants (Cu, Ni, SO_4^{2-}). The most significant trends toward lower concentrations of copper, nickel, and sulfates were observed in the soil water from the organic soil horizon in sparse spruce forests, both under and between the crowns (Figure 4). The observed trends toward lower concentrations of the main pollutants at the pollution-induced sparse forest stage may indicate a decrease in the fallout of pollutants in the composition of large particles near the smelter.

Thus, despite the decrease in the level of pollutants in the emissions of the Severonickel Smelter, in the Northern taiga forests, the long-term dynamics of the concentrations of the main pollutants in atmospheric fallout and soil water in the background area and in defoliating forests demonstrate significant trends toward their increase, which is most pronounced for nickel concentrations. This may be due to an increase in nickel concentrations in aerosols propagating over considerable distances. However, it is worth noting the decrease in the concentrations of the main pollutants in atmospheric fallout and soil water in pollution-induced sparse spruce and pine forests, which may indicate a decrease in pollutant fallout as part of larger particles near the smelter.



Figure 4. Long-term dynamics of the concentrations of the main pollutants in the soil waters from the organogenic soil horizon in pollution-induced sparse spruce forest.

4. Conclusions

1. At different stages of the pollution-induced degradation of the Northern taiga forests, the concentrations of elements in snow, rain, and soil water, their atmospheric fallout, and their removal with soil water in spruce forests are, as a rule, higher than in pine forests. This is explained by the fact that spruce modifies atmospheric fallout and soil water more strongly than pine, due to a longer and dense crown. The concentrations of elements in atmospheric and soil water, as well as their atmospheric fallout and removal with soil water are, as a rule, higher under the crowns of spruce and pine than between the crowns, which is associated with the leaching of element compounds from tree crowns, litter, and soils.

- 2. In defoliating forests and pollution-induced sparse forests, the concentrations of heavy metals and sulfates increase in snow, rain, and soil water compared to the background areas. At these stages of pollution-induced forest degradation, an increase in the concentrations of calcium and magnesium in snow, rain, and soil water was found, which is associated with their leaching from the tree canopy, litter, and soils. In defoliating forests and pollution-induced sparse forests, compared to the background areas, an increase in the actual acidity of atmospheric and soil water, caused by an increase in the number of acid-forming substances, was found. A decrease in carbon concentrations in atmospheric fallout and soil water was found, which is explained by a decrease in the amount of litter due to the degradation and death of trees.
- 3. Long-term dynamics (from 1999 to 2020) of the composition of atmospheric fallout and soil water in coniferous forests in the background areas and defoliating forests demonstrate significant trends toward the increase in nickel concentrations in recent years. This may be due to an increase in nickel concentrations in aerosols propagating over considerable distances. In the pollution-induced sparse forests, there was a trend toward a decrease in the concentration of pollutants, which may indicate a decrease in the fallout of pollutants in the composition of larger particles near the smelter.
- 4. Our results clearly demonstrate that the study of the composition and properties of atmospheric fallout and soil water in forest ecosystems should take into account both inter- and intra-biogeocenotic variability.

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References

- Lukina, N.V.; Nikonov, V.V. Biogeochemical Cycles in the Forests of the North under Aerotechnogenic Pollution, Part. 1; Izd-vo KNC RAN: Apatity, Russia, 1996; 216p.
- Ratkin, N.E. Quantitative assessment of the aerotechnogenic flow of matter to the underlying surface by the calculation method. *Vestnik MGTU* 2000, *3*, 145–164.
- Fischer, R.; Mues, V.; Ulrich, E.; Becher, G.; Lorenz, M. Monitoring of atmospheric deposition in European forests and an overview on its implication on forest condition. *Appl. Geochem.* 2007, 22, 1129–1139. [CrossRef]
- Dauval'ter, V.A.; Dauval'ter, M.V.; Saltan, N.V.; Semenov, E.N. Effect of emissions from a mining and smelting plant on the chemical composition of atmospheric fallout (Monchegorsk polygon). *Geoekologiya* 2009, 3, 228–240.
- Derome, J.; Lukina, N. Interaction between environmental pollution and land-cover/land-use change in Arctic areas. In *Eurasian* Arctic Land Cover and Land Use in a Changing Climate; Gutman, G., Reissell, A., Eds.; Springer: Dordrecht, The Netherlands, 2010; pp. 269–290. [CrossRef]
- Lorenz, M.; Becher, G. Forest Condition in Europe, 2012 Technical Report of ICP Forests. Work Report of the Thünen Institute for World Forestry. ICP Forests, Hamburg. 2012. 159p. Available online: https://www.econstor.eu/handle/10419/96596 (accessed on 3 October 2022).

- 7. De Vries, W.; Dobbertin, M.H.; Solberg, S.; van Dobben, H.F.; Schaub, M. Impacts of acid deposition, ozone exposure and weather condition on forest ecosystem in Europe: An overview. *Plant Soil* **2014**, *380*, 1–45. [CrossRef]
- 8. Waldner, P.; Thimonier, A.; Pannatier, E.G.; Etzold, S.; Schmitt, M.; Marchetto, A.; Rautio, P.; Derome, K.; Nieminen, T.M.; Nevalainen, S.; et al. Exceedance of critical loads and of critical limits impacts tree. *Ann. For. Sci.* **2015**, *72*, 929–939. [CrossRef]
- 9. Pascaud, A.; Sauvage, S.; Coddeville, P.; Nicolas, M.; Croisé, L.; Mezdour, A.; Probst, A. Contrasted spatial and long-term trends in precipitation chemistry and deposition fluxes at rural stations in France. *Atmos. Environ.* **2016**, *146*, 28–43. [CrossRef]
- 10. Maas, R.; Grennfelt, P. Towards Cleaner Air. In *Scientific Assessment Report 2016*; EMEP Steering Body and Working Group on Effects of the Convention on Long-Range Transboundary Air Pollution; UNECE: Geneva, Switzerland, 2016; pp. 1–50.
- 11. Kowalska, A.; Astel, A.; Boczoń, A.; Polkowska, Ż. Atmospheric deposition in coniferous and deciduous tree stands in Poland. *Atmos. Environ.* **2016**, *133*, 145–155. [CrossRef]
- 12. Nikonov, V.V.; Koptsik, G.N. (Eds.) Acid Rainfall and Forest Soils; Izd-vo KNC RAN: Apatity, Russia, 1999; 320p.
- 13. Nikonov, V.V.; Lukina, N.V. Effect of spruce and pine on the acidity and composition of atmospheric deposition in the north-taiga forests of the industrial-developed region. *Ecology* **2000**, *2*, 97–105. [CrossRef]
- 14. Kashulina, G.; Caritat, P.; Reimann, C. Snow and rain chemistry around the "Severonikel" industrial complex, NW Russia: Current status and retrospective analysis. *Atmos. Environ.* **2014**, *89*, 672–682. [CrossRef]
- 15. Lyanguzova, I.V.; Goldvirt, D.K.; Fadeeva, I.K. Spatiotemporal dynamics of the pollution of al-fe-humus podzols in the impact zone of a nonferrous metallurgical plant. *Eurasian Soil Sci.* **2016**, *49*, 1189–1203. [CrossRef]
- 16. Fedorkov, A.L. Adaptation of Conifers to the Stressful Conditions of the Far North; Izd-vo UroRAN: Ekaterinburg, Russia, 1999; 98p.
- 17. Lukina, N.V.; Nikonov, V.V. Nutritional Regime of Northern Taiga Forests; Izd-vo KNC RAN: Apatity, Russia, 1998; 316p.
- 18. ICP Forests. Forest Monitoring Methodology under the International Program ICP Forests; ICP Forests: Moscow, Russia, 2008; 46p.
- 19. Belov, N.P. Soils of the Murmansk Region; Belov, N.P., Baranovskaja, A.V., Eds.; Izd-vo Nauka: Moscow, Russia, 1969; 147p.
- Chertov, O.G.; Men'shikova, G.P. Changes in forest soils under the influence of acid precipitation. Izvestija AN SSSR. Ser. Biol. 1983, 6, 110–115.
- Derome, J.; Niska, K.; Lindroos, A.-J.; Valikangas, P. *The Ion Balance Monitoring Plot Network. The Lapland Forest Damage Project*; Russian-Finnish Cooperation Report; Rovaniemi Research Station, The Finnish Forest Research Institute: Rovaniemi, Finland, 1993; pp. 49–57.
- 22. Helmisaari, H.-S.; Mälkönen, E. Acidity and nutrient content of throughfall and soil leachate in three *Pinussylvestris* stands. *Scand. J. For. Res.* **1989**, *4*, 13–28. [CrossRef]
- 23. Gandois, L.; Tipping, E.; Dumat, C.; Probst, A. Canopy influence on trace metal atmospheric inputs on forest ecosystems: Speciation in throughfall. *Atmos. Environ.* **2010**, *44*, 824–833. [CrossRef]
- 24. Ershov, V.V.; Lukina, N.V.; Orlova, M.A.; Zukert, N.V. Dynamics of snowmelt water composition in conifer forests Exposed to Airborne Industrial Pollution. *Russ. J. Ecol.* 2016, 47, 46–52. [CrossRef]
- 25. Sukhareva, T.A.; Ershov, V.V.; Isaeva, L.G.; Shkondin, M.A. Analyzing the status of northern taiga forests amid reduced Severonikel emissions. *Tsvetnye Met.* **2020**, *8*, 33–41. [CrossRef]
- 26. Jakovlev, B.A. (Ed.) The Climate of the Murmansk Region; Knizhnoe izdatel'stvo: Murmansk, Russia, 1961; 200p.
- 27. Nikonov, V.V.; Lukina, N.V.; Bezel, V.S.; Bel'skij, E.A.; Bespalova, A.V.; Golovchenko, A.V.; Gorbacheva, T.T.; Dobrovol'skaja, T.G.; Dobrovol'skij, V.V.; Zukert, N.V.; et al. *Scattered Elements in Boreal Forests*; Izd-vo Nauka: Moscow, Russia, 2004; 616p.
- 28. Cvetkov, V.F.; Cvetkov, I.V. Industrial Pollution and Forest; Izd-vo IPC SAFU: Arhangelsk, Russia, 2012; 312p.
- 29. Ershov, V.V.; Isaeva, L.G.; Sukhareva, T.A.; Lukina, N.V.; Danilova, M.A.; Smirnov, V.E. Assessment of the composition of rain deposition in coniferous forests at the northern tree line subject to air pollution. *Russ. J. Ecol.* **2020**, *51*, 319–328. [CrossRef]
- Back, J.; Turunen, M.; Ferm, A.; Huttunen, S. Needle structure and epiphytic microflora of Scots pine (*Pinussylvestris* L.) under heavy ammonia deposition from fur farming. *Water Air Soil Pollut.* 1997, 100, 119–132. [CrossRef]
- Sukhareva, T.A.; Lukina, N.V. Mineral composition of assimilative organs of conifers after reduction of atmospheric pollution in the Kola Peninsula. *Russ. J. Ecol.* 2014, 45, 95–102. [CrossRef]
- Park, K.; Hung, D.D. Characterization of metal aerosols in PM10 from urban, industrial, and Asian Dust sources. *Environ. Monit.* Assess. 2008, 160, 289–300. [CrossRef]
- 33. Wang, Z.-M.; Biswas, P. Nickel Speciation and aerosol formation during combustion of Kerosene Doped with Nickel Nitrate Aerosol in a Premixed Burner. *Aerosol Sci. Technol.* **2010**, *33*, 525–535. [CrossRef]
- 34. Koptsik, G.N.; Smirnova, I.E.; Lukina, N. The effect of industrial aerial pollution on the composition of soil solutions in podzols. *Eurasian Soil Sci.* 2007, 40, 203–214. [CrossRef]
- Ershov, V.V.; Isaeva, L.G.; Gorbacheva, T.T.; Lukina, N.V.; Orlova, M.A.; Smirnov, V.E. 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. *Contemp. Probl. Ecol.* 2019, 12, 97–108. [CrossRef]
- Lukina, N.V.; Poljanskaja, L.M.; Orlova, M.A. Nutrient Regime of Soils of Northern Taiga Forests; Izd-vo Nauka: Moscow, Russia, 2008; 342p.
- 37. Artemkina, N.A.; Gorbacheva, T.T.; Lukina, N. Low-molecular organic acids in soil water in forests of the Kola. *Lesovedenie* **2008**, *6*, 37–44.