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Effect of Industrial Airborne Pollution on the Chemical Composition of Pine Needle Litterfall at the Northern Distribution Limit of Pine Forests

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Abstract—This paper examines the chemical composition of Scots pine litterfall in north taiga pine forests in background conditions and under the impact of emissions from the Severonikel copper–nickel industrial complex. In forests exposed to industrial airborne pollution, the content of fertilizer elements (Ca, Mg, Mn, and Zn) in coniferous litterfall decreases, while the content of heavy metals (Ni and Cu) and values of stoichiometric C/P and N/P ratios increase. This indicates that the quality of plant material to be decomposed by soil biota declines. In background conditions, intrabiogeocoenotic differences in the chemical composition of coniferous litterfall are manifested in a higher content of K and P (supplied with crown and trunk waters) under tree crowns; in intercrown spaces, concentrations of Fe, Zn, Ni, and Cu are higher due to background airborne pollution. In defoliating forests, coniferous litterfall under tree crowns contains more Ca, Mg, K, Mn, P, N, and S due to the intensive leaching of fertilizer elements from tree crowns by acidic precipitation and, as in the case of sulfur, due to its inflow with acidic precipitation. The elevated content of N, P, and K in coniferous litterfall of defoliating forests can be determined by high concentrations of these mobile elements in living needles falling off ahead of normal phenological terms. In background conditions, seasonal variability of the chemical composition of coniferous litterfall in defoliating forests is manifested in high Ca and Mn concentrations in needles due to their accumulation there by the end of the warm season. In sparse technogenic forests, Mg and K accumulate in coniferous litterfall by the end of the growing season, which indicates a disturbance of retranslocation processes under the impact of pollution. In all studied pine forests, the content of Fe and Zn in litterfall significantly decreases by the end of the warm season; in forests exposed to airborne pollution, the content of Ni and Cu decreases as well. This can be explained by their antagonism with Mn and leaching from needles by acidic precipitation during the warm season.

Keywords: coniferous litterfall, chemical composition, pine forests, airborne technogenic pollution, intrabiogeocoenotic variability, seasonal variability

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INTRODUCTION

Fallen assimilating organs represent an active fraction of tree litterfall and act as a source of nutrients available to biota. The elemental composition of leaf/coniferous tree litterfall provides insight into the cycling of matter and soil formation patterns (Meier et al., 2005; Wood et al., 2006, 2009; Vesterdal et al., 2012; Osipov, 2017). Distinct features of the chemical composition of leaf and coniferous litterfall contribute to the formation of phytogenic zones of influence around trees, inhibit the growth of herbaceous plants, and affect the microbial activity and soil composition (Reshetnikova, 2011; Aponte et al., 2013; Chavez-Vergara et al., 2014; Ufimtsev and Egorova, 2016; Kolmogorova and Ufimtsev, 2018). The initial litterfall quality regulates its decomposition rate (Berg, 2000; Wardle et al., 2003; De Marco et al., 2007; Berg and McClaugherty, 2008; Zhang et al., 2008; Rahman et al., 2013; Tu et al., 2014; Lukina et al., 2017; Ivanova et al., 2019). The content of elements in litterfall depends on the tree species (Preston et al., 2006; Ukonmaanaho et al., 2008; Aponte et al., 2013; Jonczak and Parzych, 2014; Boev et al., 2018; Becker et al., 2018; Neumann et al., 2018), stand age (Trap et al., 2013), and topography (Bessonova et al., 2017). Seasonal features of the litterfall chemical composition remain poorly researched (Rautio et al., 1998b; Portillo-Estrada et al., 2013; Jonczak and Parzych, 2014; Chul'diene, 2017).

Within the Kola Peninsula and mainland Murmansk oblast, forest ecosystems are affected by both natural environmental factors (e.g., short growing sea-

son and low temperatures) and airborne technogenic pollution. A large mining and smelting enterprise, the Severonikel copper–nickel industrial complex (AO Kol'skaya GMK) is located in the central part of Murmansk oblast; the main components of its emissions are sulfur dioxide and polymetallic dust (Ni and Cu). In the 1990s, the volume of emissions from the Monchegorsk enterprise of Kol'skaya GMK had temporarily decreased (Tsvetkov and Tsvetkov, 2012). According to AO Kol'skaya GMK, Ni, Cu, and SO_2 emissions amounted to 1400, 700, and 129300 t yr^{-1}, respectively, in 1995. Atmospheric pollution causes forest degradation, increases tree defoliation, and disrupts element retranslocation processes within trees (Lukina and Nikonov 1996, 1998; Nieminen and Helmisaari, 1996; Rautio et al., 1998a; Steinnes et al., 2000; Kiikkilä, 2003; Tarkhanov, 2009; Yarmishko and Lyanguzova, 2013; Sukhareva and Lukina, 2014; Vacek et al., 2016). An increase in the Ca inflow with pine litterfall compared to the control zone was registered in the impact zone of Sredneuralsky Copper Smelter (Yusupov et al., 1995). Due to the long-term impact of acidic precipitation and nitrogen saturation in spruce forests of the Czech Republic, concentrations of Ca, Mg, and Mn and the Ca/Al and Mg/Al ratios in the litterfall have decreased, while the N content and N/Mg ratio increased (Kopáček et al., 2010). The decomposition rate of spruce and pine litterfall has decreased in defoliating forests and sparse technogenic forests located in the Severonikel impact zone, and the quality of plant material declined: the initial content of heavy metals (Ni and Cu) increased, while the content of Ca, Mn, K, and Mg decreased (Lukina et al., 2017; Ivanova et al., 2019). To date, no comparative assessments of the chemical composition of tree litterfall components have been performed for a wide range of elements and parameters at the northern distribution limit of forests exposed to airborne technogenic pollution taking into account seasonality and intrabiogeocoenotic variability. Such data will make it possible to assess the state and functioning of forest stands and dynamics of biogeochemical cycles of carbon, nutrients, and heavy metals in forests.

The purpose of this study was to estimate the effect of airborne technogenic pollution from the Severonikel smelter on the chemical composition of pine needle litterfall taking into account the intrabiogeocoenotic and seasonal variability in pine forests at their northern distribution limit.

MATERIALS AND METHODS

The studies were conducted on permanent sampling plots of the Institute of North Industrial Ecology Problems, Kola Science Center, Russian Academy of Sciences, established in north taiga dwarf-shrub–lichen pine forests exposed to emissions from the Severonikel copper–nickel industrial complex (Monchegorsk) within the Kola Peninsula and mainland Murmansk oblast. Based on the pollution level and state of vegetation, the permanent sampling plots represent various stages of a digressive succession. They are located along the pollution gradient in the south-southwestern direction from the smelter at the following distances: 7–10 km from the emission source in sparse technogenic forests (STF), 20–100 km in defoliating forests (DF), and 100–200 km in forests formed in background automorphic conditions (BF) (Lukina and Nikonov, 1998). In terms of the stand composition, all studied objects are pine forests with an admixture of birch and spruce that had been affected by fires in the past.

Pursuant to the ICP Forests recommendations (Ukonmaanaho et al., 2016), litterfall was collected on sampling sites year-round into cotton bags attached to a solid frame at the bottom of the collecting funnel of the litterfall trap. The diameter of the upper part of the funnels is 82 cm; the litterfall trap depth is more than 0.5 m to prevent litterfall blowing-out from the traps. Collectors are installed at a height of 1–1.3 m above the ground to drain water from them. In 1994, litterfall traps were randomly installed in intercrown spaces on the sampling plots (10–15 units per plot); since 2013, they have been installed taking into account intercrown and undercrown spaces. At present, 7–8 litterfall traps are installed on each sampling plot between tree crowns and 4–5 litterfall traps under tree crowns. Sampling is performed twice a year: in early October prior to the permanent snow cover formation and in early June after the snowmelt. The pine needle fraction was isolated from the tree litterfall mass in the laboratory environment.

To determine the chemical composition of fallen Scots pine (*Pinus sylvestris* L.) needles after their isolation from litterfall samples in the laboratory environment, three mixed samples were taken—when possible separately for undercrown and intercrown spaces for analysis—for each of the sampling seasons (October–May and June–September) in 2014–2017; in total, 99 samples were analyzed. These data were supplemented by test results describing the initial composition of needle litterfall sampled once in September 1997 for a decomposition experiment conducted in 1997–1999; these samples were analyzed with a one- to fourfold replication. Computations were performed on an absolutely dry weight basis. The hygroscopic coefficient in the samples was determined by weighing them before and after drying in an oven at a temperature of 105°C. Prior to chemical tests, the studied plant material was crushed and wet ashing was performed using concentrated HNO_3. Concentrations of metals (Ca, Mg, K, Al, Fe, Mn, Zn, Cu, and Ni) were determined using atomic absorption spectrometry (AAnalyst 800). The total N content was determined using the Kjeldahl method, total organic C content (C_{org}) using the Tyurin method, and total P content using the colorimetric method (Vorob'eva, 1998).

The V criterion (Husson et al., 2017) was used to estimate the intrabiogeocoenotic and seasonal variability of the pine needle litterfall chemical composition and the effect of airborne pollution (through the digression stage). The degrees of effect caused by airborne pollution (through digression stages), seasonal variability (warm and cold seasons of the year), and intrabiogeocoenotic spatial variability on the composition of coniferous pine litterfall was estimated taking into account the main elements of the micromosaic (undercrown/intercrown spaces) on the basis of the determination coefficient (R^2) that reflects the contribution of a given factor to the total variance of the studied parameter. The V criterion was computed in the R statistical programming environment (*R Core Team*..., 2017).

RESULTS AND DISCUSSION

Chemical Composition of Pine Needle Litterfall in North Taiga Pine Forests at Different Digression Stages

Airborne pollution has the most significant effect on the content of Mn, Ni, Cu, S, Fe ($R^2 = 0.4–0.7$), P, Ca, Al, and Mg and on the C/P ratio ($R^2 = 0.2–0.3$) in Scots pine litterfall. To a lesser extent, the effect of airborne technogenic pollution is manifested for Zn and the N/P ratio ($R^2 = 0.1$) (Table 1). In pine forests formed in background conditions, pine needle litterfall is distinguished by a relatively high content of Mg, Mn, and Zn and a low content of Al, Fe, Ni, Cu, and S ($p < 0.05$) (Table 2).

Changes in the elemental composition of fallen needles are observed in pine forests exposed to industrial airborne pollution. In defoliating forests, litterfall is distinguished by the lowest content of Ca and Mg, which is consistent with patterns identified under similar conditions for living needles (Lukina and Nikonov, 1998); concurrently, the P content is high ($p < 0.05$) (Table 2). The depletion of pine litterfall of nutrients (Ca, Mg) and the increase in the content of P capable of retranslocation in fallen needles can be explained by the effect of airborne pollution: in the vicinity of smelters, the age of needles on branches decreases, since they fall off not only in phenological terms, and retranslocation processes involving mobile elements are disrupted (Nieminen and Helmisaari, 1996; Lukina and Nikonov, 1998; Rautio et al., 1998a; Nikonov et al., 2004). A higher P content can also be associated with elevated K and N concentrations as a manifestation of a relationship in the N : P : K ratio: an increase in the concentration of one element leads to an increase in the content of others (Sazonova et al., 2005). Calcium and magnesium are less mobile elements, and a decrease in their content may be caused by their leaching from living needles on trees by acidic precipitation (Lukina and Nikonov, 1998). In sparse technogenic forests, litterfall formed by assimilating pine organs is distinguished by high concentrations of Ca, Al, Fe, Ni, Cu, and S and low concentrations of Mn, Zn, and P ($p < 0.05$) (Table 2). The increase in the content of heavy metals (Ni, Cu, and Fe), the main components of emissions from the Severonikel smelter, and a decrease in the content of Mn and Zn in living needles (Sukhareva, 2013) can be explained by antagonism between these elements (Rautio et al., 1998b; Steinnes et al., 2000; Lukina et al., 2005) and between Mn and Fe (Kabata-Pendias and Pendias, 1989; Lukina and Nikonov, 1996; Barber, 1998; Sukhareva and Lukina, 2014). Pollution disturbs the redistribution of mobile elements, which results in their higher content in assimilating organs (Sukhareva, 2013). However, a low P content is observed in coniferous litterfall of sparse technogenic light forests; apparently, this is due to its initially deficient level in pine needles (Sukhareva and Lukina, 2014) and antagonism with Ca, as it occurs in spruce needles at the intense defoliation stage (Lukina et al., 2008). The high content of Ca in pine litterfall and in living pine needles in sparse technogenic forests can be associated with the absorption of calcium from soil waters formed in horizons rich in this element and an inflow of mineral particles from dusty surfaces of technogenic wastelands. In the vicinity of the smelter, where sparse technogenic forests are formed, soil parent rocks contain gabbro- and gabbronorites that are rich in major cations (Lukina and Nikonov, 1996, 1998; Lukina et al., 2008; Anan'eva et al., 2012).

Airborne pollution significantly affects the C/P ratio and, to a lesser extent, the N/P ratio. These ratios characterize the plant material quality for soil biota, including microbial decomposers (Table 1). According to the literature data, the C/P and N/P ratios in *Pinus banksiana* Lamb. needle litterfall in Canada amount to 391 and 10, respectively (Moore et al., 2006). On sampling plots used in this study, the average C/P and N/P ratios in coniferous Scots pine litterfall reach in background conditions 1982 and 11, respectively. In defoliating forests, the C/P and N/P ratios statistically significantly feature the lowest values; while in sparse technogenic forests, these ratios are high. Taking that the N content and C content in litterfall are similar regardless of the digression stage, this phenomenon can be explained by a large difference in the phosphorus concentration: it is high in defoliating forests and low in sparse technogenic forests.

Overall, industrial airborne pollution has a significant effect on the chemical composition of litterfall formed by assimilating organs of pine trees: the quality of plant material to be decomposed by microorganisms declines due to a decrease in the content of fertilizer elements (Ca, Mg, Mn, and Zn) and an increase in the heavy metal content and C/P and N/P ratios.

Table 1. Estimated effects of airborne technogenic pollution (through digression stages) and intrabiogeocoenotic and seasonal variability on the chemical composition of litterfall formed by assimilating organs of Scots pine trees

Factor		Parameter															
		Ca	Mg	K	Al	Fe	Mn	Zn	Ni	Cu	S	P	N	C_{org}	C/N	C/P	N/P
Airborne technogenic pollution N = 99–111	R^2	**0.26**	**0.18**	0.01	**0.20**	**0.37**	**0.71**	**0.10**	**0.70**	**0.63**	**0.47**	**0.29**	0.03	0.01	0.03	**0.26**	**0.08**
	p	**0**	**0**	0.75	**0**	**0**	**0**	**0.003**	**0**	**0**	**0**	**0**	0.21	0.54	0.28	**0**	**0.01**
Intrabiogeocoenotic variability N = 32–34	Background																
	R^2	0.11	<0.01	**0.28**	0.04	**0.20**	<0.01	**0.34**	**0.23**	**0.17**	0.01	**0.14**	0.05	0.02	0.01	0.11	0.02
	p	0.06	0.76	**0.001**	0.27	**0.01**	0.81	**0.001**	**0.004**	**0.02**	0.55	**0.03**	0.21	0.42	0.51	0.06	0.40
	Defoliating forests																
	R^2	**0.45**	**0.31**	**0.17**	<0.01	0.01	**0.18**	0.10	0	<0.01	**0.14**	**0.35**	**0.15**	<0.01	**0.13**	**0.31**	0.01
	p	**0**	**0.001**	**0.02**	0.76	0.59	**0.02**	0.07	1.00	0.92	**0.03**	**<0.001**	**0.03**	0.93	**0.04**	**0.001**	0.71
	Sparse technogenic forests																
	R^2	**0.30**	<0.01	0.08	<0.01	0.01	0.08	<0.01	0.01	0.04	<0.01	0.08	<0.01	<0.01	<0.01	0.09	0.07
	p	**0.001**	0.85	0.12	0.73	0.66	0.11	0.71	0.61	0.26	0.73	0.12	0.86	0.77	0.83	0.10	0.13
Seasonal variability N = 32–34	Background																
	R^2	**0.21**	0	<0.01	0.05	**0.49**	**0.57**	**0.22**	<0.01	**0.26**	**0.14**	**0.29**	0.08	0.01	0.02	**0.23**	0.02
	p	**0.01**	0.98	0.84	0.20	**0**	**0**	**0.01**	0.73	**0.002**	**0.03**	**0.001**	0.10	0.59	0.46	**0.004**	0.42
	Defoliating forests																
	R^2	**0.19**	0.03	<0.01	**0.17**	**0.74**	**0.51**	**0.39**	**0.87**	**0.66**	0.12	0.01	0.11	0.08	0.06	0.01	**0.20**
	p	**0.01**	0.32	0.87	**0.02**	**0**	**0**	**<0.001**	**0**	**0**	0.05	0.57	0.06	0.11	0.17	0.63	**0.01**
	Sparse technogenic forests																
	R^2	0.06	**0.34**	**0.26**	<0.01	**0.43**	**0.35**	**0.65**	**0.67**	**0.47**	0.01	0.09	0.10	0.04	0.03	0.04	<0.01
	p	0.16	**<0.001**	**0.003**	0.76	**0**	**<0.001**	**0**	**0**	**0**	0.52	0.08	0.07	0.28	0.36	0.25	0.70

R^2 is the determination coefficient reflecting the contribution of a given factor to the parameter variance and *p* is the probability of a type I error.

Table 2. Chemical composition of fallen pine needles in pine forests at various digression stages ($N = 32–38$)

Parameter		V criterion			Mean value for the stage			Standard deviation for the stage			General mean	General standard deviation	p		
		BF	DF	STF	BF	DF	STF	BF	DF	STF			BF	DF	STF
Ca	mg/kg	–0.40	–4.40	4.77	4398	3875	5056	1154	584	591	4448	950	0.69	0	0
Mg		3.18	–4.24	1.02	445	311	407	162	111	80	389	134	<0.01	0	0.31
K		–0.09	0.70	–0.60	684	725	658	198	505	389	689	380	0.93	0.49	0.55
Al		–4.67	2.15	2.56	376	549	558	72	167	237	493	191	0	0.03	0.01
Fe		–4.93	–1.01	5.97	135	213	356	65	125	159	234	153	0	0.31	0
Mn		7.42	0.44	–7.90	1072	755	367	282	126	99	734	347	0	0.66	0
Zn		2.48	0.67	–3.15	941	776	426	902	559	332	715	671	0.01	0.50	<0.01
Ni		–5.61	–3.02	8.64	4	69	387	3	22	193	153	202	0	<0.01	0
Cu		–5.72	–2.36	8.11	2	20	78	2	6	43	33	41	0	0.02	0
S		–6.00	0.24	5.80	207	411	597	187	187	141	403	235	0	0.81	0
P		–0.72	5.23	–4.47	307	371	267	79	68	51	314	79	0.47	0	0
N		0.30	1.38	–1.65	3434	3599	3156	1203	973	932	3393	1053	0.77	0.17	0.10
C_{org}	%	0.36	0.74	–1.10	57	57	56	4	7	4	57	5	0.72	0.46	0.27
C/N		1.28	–1.48	0.19	210	173	196	143	57	55	193	96	0.20	0.14	0.85
C/P		0.70	–4.76	4.02	1982	1618	2199	491	268	418	1937	467	0.48	0	<0.01
N/P		0.65	–2.80	2.10	11	10	12	4	2	3	11	3	0.52	0.01	0.04

(BF) background forests, (DF) defoliating forests, (STF) sparse technogenic forests, and (p) probability of a type I error.

Intrabiogeocoenotic Variability of the Pine Needle Litterfall Chemical Composition in Pine Forests at Different Digression Stages

As is known, the elemental composition of litterfall formed by assimilating plant organs and the presence of secondary metabolites in it contribute to the formation of phytogenic zones of influence around trees (Aponte et al., 2013; Kolmogorova and Ufimtsev, 2018). In background conditions, the spatial intrabiogeocoenotic variability of the coniferous litterfall composition is most pronounced for Zn, K ($R^2 = 0.3$), Ni, Cu, and Fe ($R^2 = 0.2$) and least pronounced for P ($R^2 = 0.1$) (Table 1). Plant material sampled under tree crowns is distinguished by a higher content of mobile K and P ($p < 0.05$), which may be due to the inflow of potassium with crown and trunk waters and, possibly, due to a larger proportion of young needles in litterfall under tree crowns (Table 3). In intercrown spaces, fallen pine needles contain more Fe, Zn, Ni, and Cu ($p < 0.05$), which may be due to background airborne technogenic pollution caused by the transfer of pollutants in aerosols spreading over considerable distances (Ershov et al., 2019).

In defoliating pine forests, spatial variability is most pronounced for Ca and P ($R^2 = 0.4–0.5$), Mg, Mn, K, N, and the C/P ratio ($R^2 = 0.2–0.3$); by contrast, it is practically not manifested for S and the C/N ratio (Table 1). Needle litterfall in undercrown spaces is distinguished by a higher content of Ca, Mg, K, Mn, P, N, and S ($p < 0.05$) (Table 3), which is associated with their intensive supply with crown and trunk waters as a result of the leaching of fertilizer elements from tree crowns (Ca, Mg, K, Mn, and P) and the inflow of S with acidic precipitation. The C/N and C/P ratios are higher in intercrown spaces ($p < 0.05$) (Table 3) due to the lower P content there and similar C concentrations in litterfall and in undercrown spaces. On a waste rock heap (in reclaimed areas previously occupied by overburden rocks from a coal pit), the total P content in Scots pine litterfall also reaches the maximum in undercrown and near-crown zones of closed artificial stands (Kolmogorova and Ufimtsev, 2018). In sparse technogenic forests, spatial variability is clearly pronounced only for Ca ($R^2 = 0.3$), whose content in coniferous litterfall is higher under tree crowns ($p < 0.05$) (Table 3), which may be associated with intense leaching of Ca from needles and its subsequent inflow into litterfall with precipitation. The absence of differences in the content of other elements and their ratios in sparse pine forests can be explained by a high transparency of their crowns damaged by the pollution impact.

Table 3. Intrabiogeocoenotic variability of the chemical composition of fallen pine needles in pine forests at various digression stages

Parameter		V criterion		Mean value		Standard deviation		General mean	General standard deviation	p
		ICS	UCS	ICS	UCS	ICS	UCS			
Background (N = 15–17)										
Ca	mg kg^{-1}	1.88	−1.88	4357	3848	977	436	4103	788	0.06
Mg		0.31	−0.31	397	391	66	56	394	61	0.75
K		−3.07	3.07	555	745	113	187	650	180	<0.01
Al		−1.11	1.11	354	381	67	75	367	71	0.27
Fe		2.57	−2.57	156	99	80	26	128	65	0.01
Mn		0.25	−0.25	1000	986	190	143	993	166	0.80
Zn		3.23	−3.23	1533	504	1009	145	1051	899	<0.01
Ni		2.77	−2.77	4	2	3	1	3	2	0.01
Cu		2.34	−2.34	2	2	1	1	2	1	0.02
S		0.61	−0.61	227	188	190	187	207	187	0.54
P		−2.16	2.16	273	334	60	91	303	82	0.03
N		−1.28	1.28	3025	3531	916	1332	3278	1155	0.20
C_{org}	%	−0.82	0.82	56	57	4	4	57	4	0.41
C/N		0.68	−0.68	230	196	177	105	213	144	0.50
C/P		1.86	−1.86	2150	1834	478	472	1992	494	0.06
N/P		0.85	−0.85	12	11	4	3	11	4	0.39
Defoliating forests (N = 15–17)										
Ca	mg kg^{-1}	−3.75	3.75	3405	4213	319	548	3835	607	<0.01
Mg		−3.10	3.10	246	304	38	50	277	53	<0.01
K		−2.29	2.29	497	606	81	152	555	134	0.02
Al		0.32	−0.32	587	570	171	144	578	155	0.75
Fe		0.55	−0.55	239	215	154	100	226	127	0.59
Mn		−2.34	2.34	713	818	140	93	768	127	0.02
Zn		1.80	−1.80	1046	710	667	300	867	526	0.07
Ni		−0.0002	0.0002	70	70	24	23	70	23	1.00
Cu		0.10	−0.10	20	20	6	7	20	6	0.92
S		−2.09	2.09	338	476	149	196	411	187	0.04
P		−3.30	3.30	322	384	37	48	355	53	<0.01
N		−2.16	2.16	3134	3858	783	968	3519	946	0.03
C_{org}	%	0.09	−0.09	57	57	8	6	57	7	0.93
C/N		2.00	−2.00	196	155	68	40	174	57	0.05
C/P		3.08	−3.08	1783	1493	268	178	1629	265	<0.01
N/P		−0.38	0.38	10	10	2	2	10	2	0.70
Sparse technogenic forests (N = 16–17)										
Ca	mg kg^{-1}	−3.08	3.08	4703	5374	407	630	5049	626	<0.01
Mg		0.20	−0.20	395	390	79	61	392	69	0.84
K		1.58	−1.58	582	492	173	146	536	163	0.11
Al		0.35	−0.35	599	570	230	252	584	239	0.73
Fe		0.45	−0.45	387	362	168	156	374	160	0.65
Mn		−1.62	1.62	322	366	81	71	344	78	0.10
Zn		0.38	−0.38	500	457	358	279	479	317	0.70
Ni		0.52	−0.52	416	379	220	190	397	202	0.60
Cu		1.15	−1.15	88	70	58	31	79	46	0.25
S		0.35	−0.35	605	588	128	156	597	141	0.72
P		1.58	−1.58	271	246	36	52	258	46	0.11
N		−0.18	0.18	2950	2996	690	779	2974	726	0.86
C_{org}	%	0.30	−0.30	56	55	4	5	56	4	0.77
C/N		0.22	−0.22	200	196	55	53	198	53	0.82
C/P		−1.65	1.65	2097	2332	331	453	2218	410	0.10
N/P		−1.53	1.53	11	12	3	3	12	3	0.13

(ICS) intercrown spaces, (UCS) undercrown spaces, and (p) probability of a type I error.

Table 4. Seasonal variability of the chemical composition of fallen pine needles in pine forests at various digression stages

Parameter		V criterion		Mean value for the season		Standard deviation for the season		General mean	General standard deviation	p
		CS	WS	CS	WS	CS	WS			
Background (N = 13–20)										
Ca	mg kg^{-1}	–2.64	2.64	3675	4402	455	842	4103	788	0.01
Mg		–0.03	0.03	394	394	64	60	394	61	0.98
K		–0.20	0.20	643	655	241	130	650	180	0.84
Al		1.29	–1.29	386	354	48	83	367	71	0.20
Fe		4.01	–4.01	181	90	65	29	128	65	<0.01
Mn		–4.35	4.35	846	1096	149	71	993	166	0
Zn		2.59	–2.59	1547	711	1196	370	1051	899	0.01
Ni		0.35	–0.35	4	3	2	3	3	2	0.72
Cu		2.91	–2.91	3	2	1	1	2	1	<0.01
S		2.14	–2.14	289	150	183	171	207	187	0.03
P		3.11	–3.11	355	266	99	40	303	82	<0.01
N		1.64	–1.64	3666	3006	1397	890	3278	1155	0.10
C_{org}	%	–0.55	0.55	56	57	5	4	57	4	0.58
C/N		–0.75	0.75	191	229	117	162	213	144	0.46
C/P		–2.78	2.78	1710	2189	515	378	1992	494	0.01
N/P		–0.83	0.83	10	12	3	4	11	4	0.41
Defoliating forests (N = 12–20)										
Ca	mg kg^{-1}	–2.44	2.44	3496	4038	449	607	3835	607	0.01
Mg		1.02	–1.02	289	269	68	42	277	53	0.31
K		0.17	–0.17	560	552	205	71	555	134	0.86
Al		2.31	–2.31	659	529	145	142	578	155	0.02
Fe		4.78	–4.78	364	143	106	21	226	127	0
Mn		–3.97	3.97	654	837	120	67	768	127	<0.01
Zn		3.46	–3.46	1283	618	644	190	867	526	<0.01
Ni		5.20	–5.20	97	53	11	7	70	23	0
Cu		4.53	–4.53	26	16	5	2	20	6	0
S		1.95	–1.95	495	361	176	179	411	187	0.05
P		–0.58	0.58	348	359	62	47	355	53	0.56
N		1.87	–1.87	3922	3277	1262	611	3519	946	0.06
C_{org}	%	–1.59	1.59	54	58	3	8	57	7	0.11
C/N		–1.39	1.39	156	185	68	48	174	57	0.16
C/P		–0.50	0.50	1599	1647	232	288	1629	265	0.62
N/P		2.46	–2.46	11	9	3	2	10	2	0.01

Table 4. (Contd.)

Parameter		V criterion		Mean value for the season		Standard deviation for the season		General mean	General standard deviation	*p*
		CS	WS	CS	WS	CS	WS			
Sparse technogenic forests (N = 12–20)										
Ca	mg kg^{-1}	–1.42	1.42	4857	5174	651	592	5049	626	0.16
Mg		–3.31	3.31	343	424	49	62	392	69	<0.01
K		–2.87	2.87	435	602	130	151	536	163	<0.01
Al		0.32	–0.32	601	574	208	261	584	239	0.75
Fe		3.70	–3.70	502	292	156	96	374	160	<0.01
Mn		–3.33	3.33	288	381	74	57	344	78	<0.01
Zn		4.48	–4.48	802	284	260	135	479	317	0
Ni		4.62	–4.62	599	266	169	70	397	202	0
Cu	mg kg^{-1}	3.86	–3.86	117	54	53	11	79	46	<0.01
S		–0.65	0.65	577	609	145	141	597	141	0.52
P		1.73	–1.73	275	247	49	41	258	46	0.08
N		1.81	–1.81	3258	2789	921	511	2974	726	0.07
C_{org}	%	1.11	–1.11	57	55	3	5	56	4	0.27
C/N		–0.94	0.94	188	205	56	51	198	53	0.35
C/P		–1.16	1.16	2115	2285	356	437	2218	410	0.25
N/P		0.39	–0.39	12	12	3	3	12	3	0.70

(CS) cold season (October to May inclusive), (WS) warm season (June to September inclusive), and (*p*) probability of a type I error.

Seasonal Variability of the Pine Needle Litterfall Chemical Composition in Pine Forests at Different Digression Stages

In background pine forests, seasonal variability is manifested to the greatest extent for Mn and Fe ($R^2 = 0.5–0.6$) and to the least extent for P, Cu, Zn, Ca, and the C/P ratio ($R^2 = 0.2–0.3$); for S, it is practically not manifested (Table 1). Plant material sampled after the cold season (October–May) is distinguished by a high content of Fe, Zn, Cu, P, and S; after the warm season (June–September), it is distinguished by high concentrations of Ca and Mn and a higher C/P ratio ($p < 0.05$) (Table 4). According to literature sources, the larch litterfall sampled in spring was 10% richer in N and 40% depleted of Ca compared to litterfall sampled in autumn (Chul'diene, 2017). Two main periods of C and N inflow into the soil with Scots pine litterfall were identified in forests of Finland: May–October and November–April; the inflow registered in the first period is greater with a maximum in September (Portillo-Estrada et al., 2013). In the year of 2007, the content of Mn and Zn in pine needle litterfall in pine forests of Poland was higher in autumn; in 2009, it was higher in spring (Jonczak and Parzych, 2014). According to Finnish researchers (Rautio et al., 1998b), first-year pine needles in Russian forests feature (similar to our case) a high content of Fe, Cu, P, and S in spring and Ca and Mn in autumn. It must be noted that the increase in the content of Zn and Fe in needle litterfall during the winter period is not consistent with patterns identified for living needles in background conditions of the Kola Peninsula: for 2 years, the content of zinc and iron in living needles there was higher in August compared to June (Lukina and Nikonov, 1996).

In defoliating pine forests, seasonal variability is more pronounced for the content of Ni, Fe, Cu, Mn, Zn ($R^2 = 0.4–0.9$), Ca, and Al and for the N/P ratio ($R^2 = 0.2$) (Table 1). Coniferous litterfall of the cold season features higher concentrations of Al, Fe, Zn, Ni, and Cu and a wide N/P ratio, while litterfall of the warm period, similar to the background conditions, is distinguished by high concentrations of Ca and Mn ($p < 0.05$) (Table 4). The elevated content of fertilizer elements in litterfall sampled after the growing season is determined by the more active absorption of elements from the soil and their redistribution within the tree during the warm period. The retranslocation of Ca and Mn inside trees is impossible; as a result, these elements accumulate during the warm season and

remain in fallen needles in background conditions and in defoliating pine forests, which is consistent with patterns identified for living needles (Lukina and Nikonov, 1996).

In sparse technogenic forests, seasonal differences are most clearly manifested for Ni, Zn, Cu, and Fe ($R^2 = 0.4–0.7$) and, to a lesser extent, for Mn, Mg, and K ($R^2 = 0.3$) (Table 1). Coniferous litterfall of the cold period of the year contains more Fe, Zn, Ni, and Cu; pine needles fallen during the warm season, more Mg, K, and Mn ($p < 0.05$) (Table 4); while in living needles, K and Mg are mobile, and their content decreases at the end of summer (Lukina and Nikonov, 1996). The accumulation of K and Mg by the end of the growing season can indicate a disturbance of retranslocation processes under the impact of pollution (Nieminen and Helmisaari, 1996).

A significant (by almost two times) decrease in the content of Fe and Zn in litterfall after the end of the growing season in all studied pine forests and a decrease in the content of Ni and Cu ($p < 0.05$) (Table 4) in pine forests exposed to airborne pollution is not typical for aging but still living needles. In background conditions, this phenomenon can be explained by the potential antagonism between these elements and Mn ions (Lukina et al., 2008); in areas affected by airborne technogenic pollution, it is supplemented by their leaching and flushing from the needle surface by acidic precipitation during the summer season.

CONCLUSIONS

Industrial airborne pollution has a significant effect on the chemical composition of litterfall formed by assimilating organs of pine trees. It is established that in north taiga pine forests exposed to technogenic airborne pollution caused by emissions from the Severonikel copper–nickel industrial complex, the content of fertilizer elements (Ca, Mg, Mn, and Zn) in Scots pine litterfall decreases, while the content of heavy metals (Ni and Cu) and values of stoichiometric C/P and N/P ratios increase. This indicates that the quality of plant material to be decomposed by soil biota declines.

Both in background conditions and under the impact of airborne technogenic pollution, the chemical composition of litterfall formed by assimilating organs of pine trees is distinguished by a significant intrabiogeocoenotic variability. In background conditions, coniferous litterfall features a higher content of K and P (supplied with crown and trunk waters) under tree crowns; in intercrown spaces, concentrations of Fe, Zn, Ni, and Cu are higher due to background airborne pollution. In defoliating forests, higher concentrations of Ca, Mg, K, Mn, P, N, and S in coniferous litterfall under tree crowns are determined by their increased inflow with crown and trunk waters due to the leaching of compounds containing these elements by acidic precipitation.

Seasonal variability in the chemical composition of pine litterfall has common features in background pine forests and in pine forests exposed to airborne technogenic pollution. Both in background conditions and in defoliating forests, fallen needles that enter litterfall traps during the warm (June–September) season are distinguished by a high content of Ca and Mn, because the retranslocation of these elements inside trees is impossible and they accumulate during the growing season. In sparse technogenic forests, Mg and K accumulate in coniferous litterfall by the end of the growing season, which indicates a disturbance of retranslocation processes under the impact of pollution. A significant decrease in the content of Fe and Zn in litterfall after the end of the growing season in all studied pine forests and a decrease in the content of Ni and Cu in pine forests exposed to airborne pollution can be explained by the antagonism between elements and their leaching and flushing from the needle surface by acidic precipitation during the summer season.

Overall, airborne technogenic pollution affects the chemical composition of coniferous litterfall in pine forests of the north taiga forest zone and contributes to seasonal variability both in the redistribution of elements within trees and in spatial features of the inflow of elements with litterfall, which can directly affect the state of forest ecosystems in the north and the fulfillment of their ecosystem functions.

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COMPLIANCE WITH ETHICAL STANDARDS

Conflict of Interest

The authors declare that they have no conflict of interest.

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