Degradational succession of forest ecosystems in the surroundings of Cu-Ni smelter in the Kola Peninsula

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Abstract

Over the last 60 years, a Ni-Cu smelter "Severonikel" has been operating at Monchegorsk, Russia. The smelter is one of the most powerful sources of pollution in Northern Europe. The effect of "Severonikel" smelter on the adjacent landscape has been to severely damage the surrounding forests. The purpose of presented paper is to describe degradation succession in spruce forests invoking the characteristics of element migration in soil and their uptake by spruce. Sites for the study have been selected in spruce forests with green mosses and dwarf shrubs; the predominant type of soil in these forests is podzol. Sample plots in the polluted areas are present different stages of degradation succession of forest ecosystems: stage of sparse forests, stage of diminished defoliation and stage of defoliation intensification. Air pollution leads to a significant degree of change in precipitation composition and acidity, soil acidity, nutrient cycles in the ecosystem and result in degradation succession in forests. Higher acidity and elevated concentrations of S, Ni, Cu, Fe in atmospheric deposition in the polluted area have been observed. Non-linear changes in the organic horizon acidity in relative to amount of acid-forming substances deposited from the atmosphere can be explained by internal acid formation. In illuvial horizons significant decrease in exchangeable aluminum and increase in extractable and amorphous Al on all stages of degradation have been found. In the organic horizon extractable concentrations of Ni and Cu significantly increased whereas concentrations of Ca, Mg, Mn and Zn decreased in the surroundings of smelter. In mineral soil horizons significant increase in extractable S concentration has been observed on all stages of degradation what can be related to higher amorphous Al. Pollution-induced changes in concentration of organic matter and K, Na, Ca, Mg, Al, Fe, Mn, Zn, N-NH_4, P in soil waters, especially below the crowns, also bear non-linear in relative to distance to the source of pollution character, related to variation in litterfall amount and changes in concentration of the organic matter in soil. Concentrations of Ni and Cu, constitutes of emissions, in waters of both compartments (below and between the crowns) increased with decreasing distance to the smelter. Concentration of S, the main pollutant, linearly increased only in waters between the crowns but no below, where the maximum in this element concentration has been observed on the defoliation intensification stage. In the process of degradational succession non-linear changes in the concentrations of Ca, Mg, K, P and Al in spruce needles have been found. Changes in intensity of elements uptake by spruce can be related to well-known phenomenon of antagonism between elements in pairs Ca-Al, Mg-Al, K-Mg, Ca-K, Ca- P. Concentrations of Mn and Zn decreased whereas concentrations of Ni and Cu increased in spruce needles with decreasing distance to the smelter.

Introduction

Over the last 60 years, a Ni-Cu smelter "Severonikel" has been operating at Monchegorsk. The smelter is one of the most powerful sources of pollution in Northern Europe. The annual amount of pollutants emitted in the period of investigation ranged up to 182 th.tonns of sulfur dioxide, 3.7 th. tonnes of nickel and 2.6 th. tonnes of copper. The effect of "Severonikel" smelter on the adjacent landscape has been to severely damage the surrounding forests. The stability of biogeochemical cycles is a major requirement for the persistence of forest ecosystems. Air pollution leads to a significant degree of change in precipitation composition and acidity, soil acidity, nutrient cycles in the ecosystem and result in degradation succession in forests.

The purpose of presented paper is to describe degradation succession in spruce forests invoking the characteristics of element migration in soil and their uptake by spruce. This work is important for an integrated assessment of forests state on the base of the parameters of biogeochemical cycle,

and for development of approaches to rehabilitation of damaged forests.

Materials and methods

Study objects

The objects under investigation were spruce forests with green mosses and dwarf shrubs, more widely distributed type of forest ecosystems in Northern Fennoscandia. The predominant type of soil is podzol.

Sample plots are located in the background (B) area (200 km away from the smelter) and in the areas subjected to air pollution by emissions of Ni-Cu smelter "Severonikel" (Monchegorsk). Plots in the polluted areas are present different stages of degradation succession of forest ecosystems (Lukina and Nikonov, 1996; 2001): stage of sparse (S) forests (7 km away from the smelter), stage of diminished defoliation (DD) (30 km away) and stage of defoliation intensification (ID) (100 km).

Plot equipment and sampling

Precipitation collectors have been located below and between the crowns. Taking into account vertical (within profile) and horizontal (regulated by trees) variability in soil properties, gravity lysimeters have been located at three different depths below the crowns and between the crowns at each sample plot: below the organic horizon, below 3 horizons (organic+ eluvial + illuvial) and below the whole soil profile. The samples of rainwater and soil water discussed in this paper were collected from 4 sample plots: 7 km, 30 km, 100 km and 200 km away from the smelter during 1999 and 2000 years. The rainwater and percolation water collectors are emptied one-monthly intervals during the snow-free period.

The soil samples were collected from organic nad mineral horizons below and between the crowns, air-dried, sieved over 1.0 mm sieves and fraction of 1mm stored in paper bags in cool room.

The needle samples were taken from the upper third of the crowns with special cutter on the long stick. The needles were separated into current-year needles and previous-year needles and stored in paper bags in cool room.

Analytical methods

Acidity and concentration of Ca, Mg, K, Na, NH_4^+, Al, Fe, Mn, Zn, Ni, Cu, SO_4^{2-}, NO_3^-, Cl^-, P in precipitation and soil waters have been characterized on the basis of data for 1999 and 2000. Metals were determined by AAS; sulphates, nitrates and chlorides - by ion chromatography; P and ammonium – colorimetrically, C as dichromate and permanganate consumption.

Metals in soil and plants were determined by AAS methods, P and S – colorimetrically. Soil pH was measured potentiometrically, exchangeable acidity and aluminium were determined by extraction with 1N KCl, followed by titration, total acidity was estimated by extraction with 1M ammonium acetate, pH = 7, followed by titration. Extractable cations were estimated by extraction with 1M ammonium acetate, pH = 4.65 (Halonen et.al, 1983), amorphous Al - by extraction with ammonium oxalate + oxalic acid.

Results and Discussion

1.Atmospheric deposition

Data for acidity and element concentrations in the atmospheric deposition are present in Table 1. It is well known that acidity and composition of atmospheric precipitation passed through the tree canopy are distinct from that of the between-crown sites. Precipitation below the crowns of conifer trees are characterized by higher acidity (Nihlgard, 1971; Ulrich et al., 1971; Messenger, 1975, 1980; Karpachevsky, 1977) resulting from leaching the organic acids and ammonium exchange with protons on the needle surface (Cronan, Reiners, 1983). This phenomenon can also be explained by high capacity of conifer trees for capture of aerosols owing to large surface of their canopy.

As is obvious from Table 1, both inorganic and organic compounds are leaching from aboveground parts of tree plants. Acidity of atmospheric deposition in the polluted areas was significantly higher. Elevated concentrations of emission constitutes, SO_4, Ni, Cu, Fe, and Zn, in deposition below and between the crowns have

been observed. Higher concentration of Al was, probably, related to dusting of areas not covered by plants and organic layer (industrial barrens).

2.Soil

2.1. Acidity of the organic horizon

Background area. Trees, being dominants in forests, control spatial variability in forest soil properties. Accordingly the received opinion soil acidity below the crowns of conifer trees is higher than that of between the crowns (Karpachevskyi, 1978). Results of our numerous investigations showed contrary regularity in the organic horizons (L, F, H) of spruce forests (Lukina and Nikonov, 1998; Lukina et. al, 2002). Presented in this paper data testified that in the background area active acidity and exchangeable Al in the organic horizon of soil between the crowns were also higher (p=0.09 and p= 0.008) than that of below the crowns, total acidity was comparable (Table 2).

The reason for lower acidity of the organic horizon below the crowns could be exchange reactions between calcium and acid (aluminium and proton) cations. Exchangeable Ca in the organic horizon below the crowns of spruce is higher than that of between the crowns what can be explained by higher input of Ca with fall (needles), stemflow, crown waters and lower amount of precipitation below the crowns in comparison with between the crown sites (Lukina et.al, 2002).

Degradation succession stages. Pollution-induced changes in soil acidity were investigated taking into account horizontal spatial heterogeneity of soil (between and below the crown compartments). On the stage of defoliation intensification (ID) spatial variability in soil acidity corresponded to natural regularities. Compared to the background values active acidity and exchangeable Ca in the organic horizon *below the crowns* were significantly higher whereas non-exchangeable acidity was lower. The main reason for higher active acidy may be an increase in fulvic acids concentration because of hydrolysis of accumulative forms of humus by catalytic effect of mineral acids (sulfur acids). In addition to this, higher input of litterfall may also result in

active formation of fulvic acids. Significant decrease in non-exchangeable acidity pointed at drop in participation of weak acids in acidity formation. Elevated concentration of exchangeable Ca was, probably, related to higher mobility of Ca resulted from higher acidity. In the organic horizons *between the crowns* active acidity also increased in comparison with the background.

On the stage of diminished defoliation (DD) differences in the acidity of the organic horizons between the compartments are distinct from that of the background: active acidity of this horizon below the crowns was significantly higher (p=0.003) whereas exchangeable Ca and base saturation were lower (p=0.005 and p=0.023 correspondingly). These pollution - induced changes in spatial heterogeneity in soil properties can be explained by more intense fluxes of acid forming substances below the crowns owing to high capacity of conifer trees for capture of aerosols. Therefore, soil below the crowns is subjected to more strong pollution by acid forming substances in comparison with soil between the crowns at the same distance from the smelters. Compared to the background, active and exchangeable acidity as well as exchangeable aluminum and proton were significantly higher whereas concentrations of base cations and non-exchangeable acidity were lower in the organic horizons *below the crowns*. Intense cation exchange reactions in the soil have resulted in enrichment of the organic horizon with aluminum and protons and depletion of it by base cations. Leaching of weak acids from the organic horizon was observed what was confirmed by data for non-exchangeable acidity. In the organic horizons *between the crowns* comparable pollution-induced changes have been observed: active and exchangeable acidity increased, concentration of base cations and non-exchangeable acidity decreased.

In sparse forests (S) spatial differences in the acidity of the organic horizon were distinct from that of the background and were comparable to that for the previous stage of degradation succession. Compared to the background, in the organic horizons *below the crowns* significant reduction in total and non-exchangeable acidity

has been found. An active acidity and exchangeable protons were comparable to the background despite the intense fluxes of the acid forming substances from the atmosphere. This phenomenon could be explained by decrease in autogeneous acid formation, particularly by reduction in fulvic acids resulted from lower amount of litterfall and active migration of these acids at the previous stages of degradation due to hydrolysis of accumulative forms of humus. This is confirmed by significant widening the ratio Cha : Cfa in the organic horizons at this stage (Lukina and Nikonov, 1996).Like at previous stages of degradation, base saturation was decreasing and exchangeable aluminum was growing in the organic horizon. *Between the crowns* similar pollution-induced changes in the organic horizon acidity have been observed.

Remarked non-linear changes in the organic horizon acidity in relative to amount of acid-forming substances deposited from the atmosphere can be explained by internal acid formation. These changes are, probably, related to intensity of fulvic acid formation depending on the amount of litterfall and on degree of hydrolysis of humus accumulative forms at different stages of forest degradation succession. The maximal acidity of soil was found in defoliating forests where the more intense fulvic acid formation was observed (Lukina, Nikonov, 1996). Close to the smelters, on the stage of sparse forests, where the internal acid formation is diminished, the acidity of soil decreased despite the intense fluxes of acid-forming substances from the atmosphere.

2.2. Acidity of mineral horizons
In the background area acidity of the mineral soil horizons below the crowns was higher than that of between the crowns what is in agreement with existing concepts. These differences were most clearly pronounced in the illuvial horizons (Table 3): active, exchangeable and total acidity below the crowns were significantly ($p=0.002$, $p=0.016$, $p=0.05$ correspondingly) higher. V. V. Ponomareva (1964) supposed that acid reaction in the illuvial horizons is controlled by free reaction-capable groups of fulvic acids.

On the stage of defoliation intensification (ID) *below the crowns* significant decrease in exchangeable aluminum in comparison with the background has been found. Compared to the background, concentration of exchangeable Al was 3-4 times lower, whereas concentration of amorphous and extractable Al was 2-3 times higher (Table 4). Pratt and et al. (1961) and McLean and et al. (1965) have reported that ammonium acetate extracted recently precipitated amorphous Al hydroxides. It has been found that in the pH range of 4 –6 the amorphous Al hydroxides can be formed in interlayers of 3 - layer silicates with labile grid in the process of hydrolysis, polymerization and fixation of Al $^{3+}$ (Jackson, 1959; 1963; Rich, 1960; Carstea, 1968). Explanation for decrease in exchangeable Al can be also leaching of Al from mineral profile. On this stage the Al concentration was higher by a factor of 2 in waters from the organic horizon and by a factor of 6 in waters from mineral profile. The reason for dissolution of Al compounds in mineral horizons could be high concentration of fulvic acids. Probably, dissolution of proto-imogolite on this stage of degradation, characterizing the highest concentration of fulvic acids, migrating from the organic horizon, could be observed. It is known, that fulvic acids are able to dissolve the proto-imogolite when the molar ratio COOH/Al exceeded 8 (Farmer, 1979). Similar, but weakly pronounced, tendencies for changes in acidity of illuvial horizon has been observed in the soil *between the crowns*.

On the stages of diminished defoliation and sparse forests exchangeable Al was higher than on previous stage of degradation but stayed significantly lower in comparison with the background values. Concentration of amorphous Al was significantly higher. Active acidity of illuvial horizon on the stages of diminished defoliation (below and between the crowns)) and in sparse forests (between the crowns) significantly increased in comparison with the background.

2.3.Metals and sulfur in soil
In the organic extractable (ammonium acetate) concentrations of Ni and Cu significantly increased whereas concentrations of Mn and Zn decreased with decreasing distance to the smelter

(Table 5). The explanation could be replacement of nutrient cations with protons, Al^{3+}, Ni^{2+}, Cu^{2+} ions from the soil exchange complex and removal them from root zone. Concentration of extractable Ca in the organic horizon significantly exceeded the background values on stage of defoliation intensification.

Extractable Cu and, especially, Ni increased in eluvial and illuvial horizons close to the smelter what can result from the higher total concentration (Lukina, Nikonov, 1998) and higher mobility of heavy metal compounds in soil profile because of decrease in the organic matter concentration in the organic horizon, the main barrier against downward migration of pollutants. This tendency was more clearly pronounced below the trees. Concentrations of extractable Ca, Mg, Mn and Zn in E horizon in the polluted sites exceeded background values what can be related to leaching of them from the organic horizon.

Concentration of extractable sulphur in the organic horizon on all stages of degradation was comparable to the background values, except for stage of defoliation intensification. In mineral soil horizons significant increase in extractable S concentration has been observed on all stages of degradation. Accordingly existing concept, an important role in sulphate sorption in the soils belongs to Al and Fe hydroxides; surface of colloid particles of these hydroxides is positively charged (Singh et al, 1980). As has been shown above, the concentration of amorphous Al in illuvial horizon was higher under pollution.

3. Soil waters
3.1. Background
Al-Fe humus podzol waters are dilute solutions with total concentration of elements below 1 g/l. Carbon, concentration of which ranged from 3 to 100 mg/l, is predominant element in these waters. Ammonium, calcium and potassium are dominating in cationic part (up to 9, 4 and 5 mg/l correspondingly); sulphates are prevailing among anions (up to 7 mg/l) (Table 6). Concentrations of major part of these elements decreased during migration through the profile owing to existing the barriers in soil profile (organic matter, oxides and hydroxides of Al, Fe, Mn, sulphates etc.) and to biological uptake. Compared to waters from the whole profile, the concentrations of elements in waters from the organic horizon were 2-20 times higher. For nitrates, taken up by living organisms very actively, barriers were pronounced more clearly than for chlorides and, especially, for sulfates.

Besides vertical within profile variability, in forests exists brightly pronounced horizontal spatial variability in composition of these waters, controlled by the dominant tree species, playing medium forming role. Accordingly presented data, concentrations of the organic matter and major part of elements in soil waters below the spruce crowns were significantly higher than those of between the crowns. In waters below the crowns actual acidity was lower, whereas total acidity was significantly higher (Lukina et al, 2002), in comparison with waters between the crowns.

3.2. Pollution-induced changes
Pollution-induced changes in concentration of organic matter, metals and non-metals in waters *below the crowns* bear non-linear in relative to distance to the source of pollution character. As a rule, maximal concentrations of all these substances have been observed on the stage of intensification of defoliation. Significant increase in carbon and organic anion concentration in waters on this stage was, probably, related to hydrolysis of accumulative forms of humus by catalytic effect of mineral acids and to increase in litterfall amount. Concentrations of Na, K, Mg, Ca, N-NH$_4$, SO$_4$, Cl, Zn, Mn, Al, Fe were also characterized by pronounced maximal values in soil waters on the stage of defoliation intensification, what could be related to large amount of litterfal, higher solubility of element compounds and intense exchange processes in soil. On the stages of diminished defoliation and sparse forests concentrations of some element compounds (Ca, Na, SO$_4$, Cl, Zn,) sharply decreased in comparison with previous stage but stayed significantly higher the background values. Concentrations of compounds of other elements (K, Mg, C, N-NH$_4$, N- NO$_3$) in waters on the stage of diminished defoliation were comparable to those in the background but on the stage of sparse forests they were significantly below the background values. The reason for this reduction

in element concentrations is depletion of the organic horizon with their mobile compounds because of leaching and of decrease in plant productivity and litterfall amount (Lukina, Nikonov, 1993).

Pollution-induced changes in concentration of C, Fe, N- NH_4 in waters *between the crowns* also bear non-linear in relative to distance to the source of pollution character. Concentrations of these elements reached the maximum on the stage of defoliation intensification. Concentrations of Ca, Mg, Mn, Zn and Cl, in soil waters were, as a rule, higher the background values, while concentration of K significantly decreased.

Concentrations of Ni and Cu, constitutes of emissions, linearly increased in waters of both compartments (below and between the crowns) with decreasing distance to the smelter. Concentration of S, the main pollutant, linearly increased only in waters between the crowns but no below, where the maximum in this element concentration has been observed on the defoliation intensification stage.

3.3. Barriers against downward migration

In defoliating forests, as well as in the background area, concentrations of many elements decreased during migration through the profile what indicates the existing of biogeochemical barriers (biological uptake, organic matter, oxides and hydroxides of Fe, Mn, Al). However these barriers against downward migration of Fe, Al, and C were significantly weaker in defoliating forests, especially on the stage of intensification defoliation. If in the background area the ratios between the Fe, Al, and C concentration in waters from the organic horizon and from the whole soil profile reached 6, 3.5, and 5, on the ID stage they dropped to 2, 1.3, and 3 correspondingly. The reason for barrier deterioration against the downward migration of the organic matter, probably, was hydrolysis of humus resulting in increase in the concentration of fulvic acids with relatively low molecular weight. Iron and Al migrated in complexes with fulvic acids. Additional explanation for intense migration of the organic compounds, for instance carbohydrates, can be suppression of microorganisms (Nikonov, et al, 2001).

Conversely, the barriers against downward migration of nutrients N-NH_4, K, Ca, Mg, Zn and pollutants SO_4, Ni, Cu, were more brightly pronounced in defoliating forests. For Ca and Mg on stage of defoliation intensification and for N and K on the stage of diminished defoliation this barrier was, probably, active uptake by plants (Lukina et al, 1999).

Of particular interest is behavior of sulfates, especially in waters below the crowns: if in the background area the ratio between concentrations of sulfates in waters from the organic horizon and from the whole profile ranged from 0.5 to 1.0, in defoliating forests it can raise to 2.4. The absence of clearly pronounced barriers against migration of sulfates in the background areas could be explained by blocking by the organic matter of exchange positions on the surface of hydroxides or by formation of complexes of the organic matter with $AlSO_4^+$ (Singh and Johnson, 1986). The explanations for brightly pronounced barriers in mineral horizons of soil subjected to air pollution can be an increase in the concentrations of amorphous compounds of Al in mineral part of profile. Amorphous Al hydroxides also can effectively adsorb phosphates (Gorbunov et al., 1961), but in the polluted area we did not observe this phenomenon, probably, because of competition of sulfates.

The barriers against downward migration of heavy metals in soil of defoliating forests, probably, are the organic matter and sulphates, concentration of which were growing in mineral horizons (Lukina and Nikonov, 1996). Also the reason for lower migration ability of heavy metals could be saturation of fulvic acid functional groups with these metal ions resulting in molecular mass significant increase, lowering their migration and chemical activity and formation of associates. But it is necessary to notice, that soil and soil acidity level was not favorable to associate formation.

In sparse forests biogeochemical barriers against downward migration of many determined elements were significantly weaker than in the background and in defoliating forests. This is connected with vegetation cover destruction, inhibition of microbial activity, decrease in the organic matter concentration and destruction of

soil profile. Concentrations of nitrates in waters from the whole profile were significantly higher than in waters from the organic horizon. Probably, nitrates can be displaced from exchange complex in illuvial horizons by sulfates.

4.Element uptake by spruce

4.1.Background

Widely known age-related changes in chemical composition of needles of conifer trees (Mitrofanov, 1977; Humbucker and Remacle, 1991; Helmisaari, 1992, Lukina and Nikonov, 1991) have been confirmed. In the background area the concentrations of mobile elements N, K, P and Mg decreased whereas the Ca, Al, and Mn concentrations increased during the ageing (Table 7). The maximal concentrations of Zn, Ni and Cu have been found in current needles.

4.2. Pollution-induced changes

In the process of degradation succession non-linear changes in the concentrations of Ca, Mg, K, P and Al in spruce needles in relative to amounts of pollutants deposited from the atmosphere have been found. The maximal exceeding the background concentrations for Ca and Mg has been observed on the ID stage (Figure). In contrast, the K, P and Al concentrations in spruce needles on this stage decreased in comparison with the background. On the DD and S stages the Ca and Mg concentrations were significantly lower the background level. On stage of diminished defoliation (DD) the Mg concentrations were even below the deficiency level (700 mg/kg, accordingly Huettl, 1993), individual trees suffered deficiency of calcium. The K concentrations in needles on the DD and S stages significantly increased. On the DD stage concentrations of Al in needles was also significantly higher the background level but decreased in sparse forests (S stage)?

Changes in concentration of elements in needles have often not been corresponded to variation in composition of soil waters where these elements are present in the most bio-available forms. Accordingly the composition of soil water concentrations of all elements in waters on the ID stage were significantly higher the background

values because of higher litterfall amounts and soil acidity. On the DD stage concentrations of K in spruce needles significantly increased whereas in soil waters concentrations of this element decreased. Despite the comparable to the background concentration of Mg and elevated concentration of Ca in soil waters concentration of these elements in needles decreased on this stage.

Changes in intensity of elements uptake by spruce can be related to well-known phenomenon of antagonism between elements in pairs Ca-Al, Mg-Al, K-Mg, Ca-K, Ca -P. In sparse forests decreased concentration of P in needles corresponded to significant reduction of phosphate and total phosphorous concentrations in soil waters.

Concentrations of Mn and Zn decreased whereas concentrations of Ni and Cu increased in spruce needles with decreasing distance to the smelter. The Fe concentration in spruce needles increased only in sparse forests (S stage). The explanation for lower level of Mn and Zn in plants could be replacement of nutrient cations with protons, Al^{3+}, Ni^{2+}, Cu^{2+} ions from the soil exchange complex and removal them from root zone. Antagonism in pairs Ni-Mn, Cu-Mn, Zn – Ni, Zn- Cu, Fe, Mn, Fe –Zn is also well-known phenomenon (Kabata-Pendias, Pendias, 1989).

Conclusions

1. Air pollution resulted in higher acidity and elevated concentrations of S, Ni, Cu, Fe in atmospheric deposition. These tendencies were most clearly pronounced in deposition below the crowns.
2. Non-linear changes in the organic horizon acidity in relative to amount of acid-forming substances deposited from the atmosphere can be related to intensity of fulvic acid formation depending on the amount of litterfall and on degree of hydrolysis of humus accumulative forms at different stages of forest degradation succession. In illuvial horizons significant decrease in exchangeable aluminum and increase in extractable and amorphous Al on all stages of degradation has been observed. Active

acidity in illuvial horizons increased close to the smelter.

3. In the organic horizon extractable concentrations of Ni and Cu significantly increased whereas concentrations of Ca, Mg, Mn and Zn decreased in the surroundings of smelter. The explanation could be replacement of nutrient cations with protons, Al^{3+}, Ni^{2+}, Cu^{2+} ions from the soil exchange complex and removal them from root zone. Concentration of Ca on stage of defoliation intensification exceeded background values below the crowns.

4. Elevated extractable Cu and, especially, Ni in eluvial and illuvial horizons close to the smelter can result from higher total concentration and higher mobility of heavy metal compounds in soil profile. On all stages of degradation concentration of extractable sulphur increased in mineral soil horizons what can be related to higher amorphous Al.

5. In the process of degradation succession non-linear changes in concentration of organic matter and K, Na, Ca, Mg, Al, Fe, Mn, Zn, N-NH$_4$, P in soil waters, especially below the crowns have been observed. This is related to variation in litterfall amount and changes in the concentration of the organic matter in soil. Significant increase in carbon and organic anion concentration in waters on stage of defoliation intensification was, probably, related to hydrolysis of accumulative forms of humus by catalytic effect of mineral acids and to increase in litterfall amount.

6. Concentrations of Ni and Cu, constitutes of emissions, in soil waters of both compartments (below and between the crowns) increased with decreasing distance to the smelter. Concentration of S, the main pollutant, linearly increased only in waters between the crowns but no below, where the maximum in this element concentration has been observed on the defoliation intensification stage.

7. In the process of degradation succession non-linear changes in the concentrations of Ca, Mg, K, P and Al in spruce needles have been found. On stage of defoliation intensification the maximal exceeding the

background concentrations has been observed for Ca and Mg whereas concentrations of K and Al decreased. On stages of diminished defoliation and sparse forests an inverse tendency for these elements has been observed. Concentrations of Mn and Zn decreased whereas concentrations of Ni and Cu increased in spruce needles with decreasing distance to the smelter.

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Table 1. Chemical composition of atmospheric deposition in spruce forests for non-snowing period, mg/l

Degra-dation stage	pH	C	Ca	Mg	K	Al	Fe	Zn	Ni	Cu	SO$_4$
B	4,67* 5,58**	47,5 9,4	1,88 0,27	0,45 0,13	5,27 0,78	0,05 0,03	0,06 0,02	0,003 0,003	0,003 0,004	0,007 0,016	9,90 1,04
ID	3,99 5,10	23,8 2,7	4,81 0,40	1,20 0,09	6,80 0,42	n.d. n.d.	n.d. n.d.	n.d. n.d.	0,08 0,009	0,12 0,019	23,90 2,09
DD	3,51 4,20	35,0 1,8	7,77 1,42	1,67 0,27	6,61 0,54	0,39 0,09	0,12 0,05	0,026 0,005	0,48 0,06	0,72 0,18	42,95 7,80
S	3,73 3,97	18,1 4,4	3,47 1,86	0,97 0,47	1,68 1,11	0,28 0,11	0,17 0,09	0,045 0,011	1,71 0,56	2,33 0,61	28,98 14,53

1)* -– below the crowns;**– between the crowns;

2) Here and in tables 2 – 8 stages of degradation : B – background, ID – stage of defoliation intensification; DD- stage of diminished defoliation: S –sparse forests.

Table 2. Comparison of the organic horizon acidity parameters (mgeqv/100g) with one- way variance analysis

Parameter	Below the crowns								Between the crowns							
	B, n= 34	B - ID		B- DD		B- S			B, n= 24	B - ID		B - DD		B - S	
		ID, n=12	p	ЗД, n=21	p	P, n=8	p			ID, n=12	p	ЗД, n=23	p	P, n=15	p
Ca	14,0	21,3	***	8,12	***	4,06	***		12.1	11.8	NS	10,6	NS	9,59	*
Mg	3,87	4,32	NS	1,58	***	1,34	***		5.16	4.14	NS	2,22	**	2,16	**
K	2,83	1,84	***	1,44	***	0,56	***		2.57	2.28	NS	1,91	**	0,86	***
Na	0,55	0,28	***	0,33	**	0,18	***		0.44	0.23	**	0,19	***	0,14	***
pH	4,32	4,11	*	3,94	***	4,20	NS		4.2	3.95	**	4,13	NS	4,08	NS
TA	167,8	151,3	*	161,7	NS	123,4	***		160.4	157.3	NS	141,3	**	137,5	***
EA	7,53	7,12	NS.	14,7	***	12,43	**		9.31	9.65	NS	13,2	***	13,71	***
EAl	2,89	2,81	NS	7,87	***	7,97	***		4.45	4.55	NS	7,0	**	7,6	***
EH	4,65	4,31	NS	6,84	**	4,46	NS		4.87	5.11	NS	6,18	*	6,11	NS
NEA	160,3	144,1	*	147,0	*	110,9	***		151.1	148.5	NS	128,1	***	123,8	***
Bspot, %	11	15	**	7	***	5	***		11	10	NS	10	NS	8	**
BS ef,%	73	77	NS	45	***	33	***		68	66	NS	54	***	48	***

1) Here and in Table 3: B - background; ID- defoliation intensification stage; DD- diminished defoliation stage; S – sparse forests.
2) TA – total acidity, mgeqv/100 g; EA – exchangeable acidity, mgeqv/100 g; EAl – exchangeable aluminum, mgeqv/100 g; OH – exchangeable protons, mgeqv/100 g; NEA – non-exchangeable acidity, mgeqv/100 g; BSpot – potential base saturation, %; BSef – effective base saturation, %;.
3) NS – not significant; * - p < 0,05; ** - p < 0,01; *** - p << 0,001;

Table 3. Comparison of the illuvial horizon acidity parameters with one- way variance analysis

Parameter	Below the crowns							Between the crowns						
	B, n=34	B - ID		B - DD		B- S		B, n=24	B - ID		B - DD		B- S	
		ID, n=12	p	DD, n=21	p	S, n=8	p		ID, n=12	p	DD, n=23	p	S, n=15	p
Ca	0.65	0.61	NS	0,34	**	0.70	NS	0.38	0.51	NS	0,25	NS	0.84	NS
Mg	0.18	0.09	NS	0,08	**	0.09	NS	0.13	0.10	NS	0,08	*	0.10	NS
K	0.09	0.05	NS	0,08	NS	0.09	NS	0.07	0.05	NS	0,07	NS	0.08	NS
Na	0.10	0.03	NS	0,04	*	0.05	NS	0.07	0.04	NS	0,03	**	0.04	NS
pH	4.82	5.12	*	4,53	**	4.85	NS	5.15	5.1	NS	4,63	***	4.82	***
TA	15.5	12.5	**	14,6	NS	15.8	NS	14.0	12.4	NS	13,9	NS	15.9	*
EA	3.01	0.96	***	2,11	*	1.79	*	2.15	1.53	NS	1,84	NS	2.06	NS
EAl	2.78	0.81	***	1,88	**	1.63	*	1.99	1.35	NS	1,63	NS	1.77	NS
EH	0.23	0.15	*	0,24	NS	0.16	NS	0.16	0.18	NS	0,21	NS	0.29	NS
BSp, %	5.9	5.9	NS	3,6	**	5.4	NS	4.18	5.58	*	2,8	*	5.9	NS
Bsef, %	25.3	46.8	***	22,6	NS	33.7	NS	23.5	35.9	NS	20,6	NS	32.7	NS
NEA	12.54	11.53	NS	12,52	NS	1.65	NS	11.9	10.9		12,1	NS	13.9	**

Table 4. Total, amorphous and extractable Al in illuvial horizon, g/kg

Stage of degradation	Below the crowns		Between the crowns		
	Amorphous	Extractable	Total	Amorphous	Extractable
B	6,46	1,22	75,8	7,58	1,57
ID	19,5	4,25	66,1	14,3	3,82
DD	16,0	2,33	71,4	12,0	2,83
S	30,8	3,70	70,3	32,4	2,52

Table 5. Extractable concentrations of metals and sulfur in soil, mg/kg

Stage of degradation	Horizon	Ca	Mg	Mn	Zn	Ni	Cu	S
				Below the crowns				
B	O	2815	462	411	41,0	4,0	4,4	153
ID	O	4258	518	394	38,7	29,0	12,0	205
DD	O	1639	181	143	24,0	141	331	117
S	O	883	131	16	13,0	587	1205	172
				Between the crowns				
B	O	2267	593	202	28,0	2,3	3,3	142
ID	O	2360	497	294	27,9	7,7	2,7	160
DD	O	2054	290	217	31,0	145	109	113
S	O	2546	296	99	25,0	640	404	140
				Below the crowns				
B	E	49	5	2	0,3	0,3	0,1	6
ID	E	106	14	14	0,9	0,5	0,3	27
DD	E	52	9	3	0,8	8,0	12,0	12
S	E	107	13	2	1,4	55,0	31,0	32
				Between the crowns				
B	E	17	4	1	0,08	0,01	0,01	3
ID	E	86	14	1	0,6	0,2	0,3	6
DD	E	34	9	4	1,0	2,4	0,4	10
S	E	203	19	10	0,4	2,9	20,0	24
				Below the crowns				
B	B	130	20	13	1,4	0,6	1,1	2
ID	B	122	11	3	1,0	1,0	1,2	94
DD	B	59	10	45	1,3	8,3	10,0	58
S	B	133	9	17	1,7	35,0	9,0	109
				Between the crowns				
B	B	74	16	8	1,0	0,6	0,6	38
ID	B	102	12	2	0,7	0,7	1,0	59
DD	B	33	6	27	1,0	1,6	0,5	59
S	B	128	19	8	2,3	7,0	0,7	108

Table 6. Soil water composition, μg eqv/l, 1999-2000

Stage of degra-dation	pH	H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	Al^{3+}	Fe^{3+}	Mn^{2+}	Zn^{2+}	Ni^{2+}	Cu^{2+}	SO_4^{2-}	NO_3^-	Cl^-	AD	C, mg/l	P, mg/l	$P-PO_4$, mg/l
O horizon, below the crowns																				
B	4,67	33	171	72	114	20	342	48,6	9,6	13,6	0,83	0,14	0,31	71	16	49	690	56,5	0,928	0,648
ID	4,08	108	606	222	134	120	664	92,9	8,6	53,5	4,23	2,47	2,15	811	12	175	1021	86,9	0,622	0,494
DD	3,50	343	245	76	71	85	211	60,4	8,6	16,3	1,74	8,44	9,47	644	21	113	358	35,2	0,282	0,243
S	3,57	280	220	79	60	56	137	82,2	9,8	1,8	1,76	37,25	40,21	652	6	109	238	19,1	0,225	0,16
O horizon, between the crowns																				
B	4,49	39	36	13	42	11	202	19,2	2,9	1,9	0,44	0,05	0,45	31	9	31	297	35,5	0,434	0,278
ID	3,86	158	144	60	10	24	367	62,8	12,3	9,9	1,56	0,32	0,64	53	2	51	744	52,3	0,061	0,022
DD	3,92	129	114	43	8	19	192	33,7	8,5	29,3	1,94	1,64	3,02	110	4	53	416	44,7	0,092	0,058
S	3,95	117,1	201	94	27	22	174	67,8	7,0	14,6	5,23	41,65	9,09	492	10	70	210	19,2	0,101	0,041
O+E+B horizons, below the crowns																				
B	5,19	12,3	72	52	108	30	176	57,5	4,4	1,5	0,49	0,08	0,17	163	6	64	280	33,4	0,065	0,02
ID	4,61	31,4	346	182	226	141	157	125,0	17,2	17,0	3,74	1,04	1,59	770	10	367	102	41,3	0,291	0,231
DD	4,02	101,1	128	60	50	53	117	130,5	6,9	6,0	2,57	4,72	0,97	439	2	67	136	16,0	0,056	0,028
S	4,61	24,7	144	99	32	98	99	70,6	1,8	3,9	4,98	49,00	10,34	393	93	143	5	15,1	0,031	0,005

Table 6. Soil water composition, µg eqv/l, 1999-2000 (cont'd)																			
O+E+B horizons, between the crowns																			
B	5,80	1,6	13	3	5	20	23	2,8	4,4	0,3	0,35	0,08	0,30	26	2	24	23	9,0	0,238	0,024
ID	4,64	58,5	58	41	9	30	161	42,7	6,1	3,2	0,39	0,12	0,33	101	3	41	265	23,9	0,039	0,012
DD	4,71	19,5	43	21	11	18	22	21,9	0,7	1,1	0,41	0,24	0,15	120	2	42	-5	11,6	0,006	0,005
S	4,44	40,4	133	59	14	27	83	55,4	2,7	2,4	1,82	17,81	0,42	257	116	50	13	11,5	0,121	0,011
O+E+B +BC horizons, below the crowns																			
B	5,34	10,6	71	49	31	38	121	13,9	1,6	1,5	0,54	0,14	0,34	178	4	67	88	10,9	0,038	0,009
ID	4,64	24,7	165	114	76	117	153	70,9	3,9	8,3	1,61	0,37	0,46	400	3	176	149	26,5	0,074	0,023
DD	4,47	34,0	89	39	10	32	64	110,6	2,0	7,4	0,72	1,84	0,42	263	2	35	92	10,3	0,017	0,005
S	4,51	32,5	185	87	31	69	78	122,9	1,6	2,6	3,62	45,09	18,58	430	61	121	65	17,4	0,026	0,005
O+E+B +BC horizons, between the crowns																			
ID	5,05	15,2	28	21	4	35	72	19,5	5,2	0,3	0,33	0,16	0,53	60	2	39	100	14,2	0,058	0,005
DD	4,86	13,8	25	29	4	30	92	23,4	0,3	0,5	0,28	0,22	0,09	99	2	40	77	11,0	0,012	0,005
S	4,32	59,4	215	91	21	34	90	94,0	3,2	4,2	2,60	36,76	4,37	316	199	72	54	12,8	0,046	0,005

Table 7. Chemical composition of spruce needles, mg/kg

| Degradation stage	Ca	Mg	K	Al	Fe	Mn	Zn	Ni	Cu	P	S
Current needles											
B, n=5	7115	1050	5878	98	32	1588	53	2.2	2.0	1512	641
ID, n=5	8137	1316	5067	80	33	949	56	9.7	2.8	1426	1108
DD, n=5	5689	952	7495	126	33	785	38	26.7	6.3	1558	1453
S, n=5	3107	907	7516	70	82	107	28	83.0	23.3	1337	1469
1-year needles											
B, n=5	7855	930	4962	123	34	1760	59	1.5	1.9	1336	670
ID, n=5	9544	1181	4415	93	36	1043	57	9.3	2.8	1168	1158
DD, n=5	6711	890	6406	165	36	806	42	28.8	7.1	1315	1802
S, n=5	4966	801	6298	71	72	166	27	80.4	21.7	948	1776
Many-years needles											
B, n=5	11047	629	3734	155	33	1985	58	1.6	1.6	1051	708
ID, n=5	12621	794	3470	140	37	935	56	8.4	2.9	841	1413
DD, n=5	7241	679	5812	236	29	719	34	26.4	6.4	1066	2116
S, n=5	4975	630	6126	75	70	165	20	82.4	24.5	920	2271
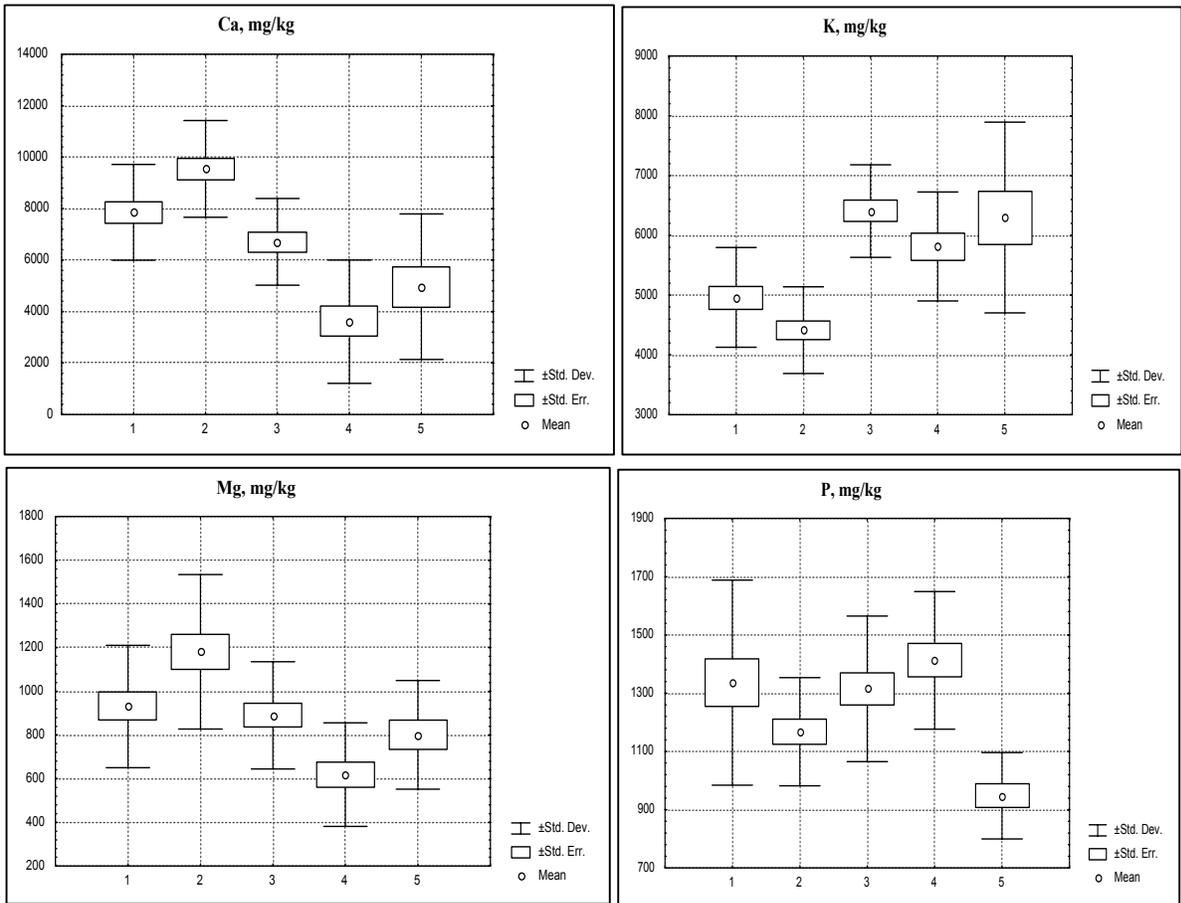
Figure. Element concentration in 1-year needles
1-background; 2-stage ofdefoliation intensification; 3-stage of diminished defoliation 1; 4-stage of diminished defoliation 2; 5-sparse forests