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THE EFFECTS OF SIMULTANEOUS LARGE ACIDIC AND ALKALINE AIRBORNE POLLUTANTS ON FOREST SOIL

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Abstract

The effects of air pollutants on soil were studied in Scots pine (*Pinus sylvestris* L.) forests near the boundary of Russia and Estonia. The study area is characterized by large amounts of acidic and basic pollutants, mainly sulphur dioxide (SO_2) and calcium (Ca). Several variables were measured in different horizons of the podzolic soil polluted by emissions from local sources in areas of several thousands of square kilometres. Alkalinization dominates the processes in the soil, since sulphur is absorbed only in small quantities and Ca is much better absorbed. Ca content in humus horizon may rise even to 100 000 mg kg⁻¹ and the pH of originally very acidic soil may rise to 8.3. Total aluminum (Al) content was high in the heavily polluted plots, since emissions contain much Al. On the other hand, the exchangeable Al was very low in these alkaline sites. A larger quantity of exchangeable Al occurred farther from the pollutant sources, even though total Al in these plots was low. These plots had acidic soils in which Al is in exchangeable form. Due to the neutralizing effect of acidic and basic pollutants, forest damage in the study area was not as serious as might be supposed. Complicated pollutant situations must be taken into consideration when pollution-caused environmental protection measures are planned. It is not reasonable to reduce only SO_2 emissions, but necessary to lower the basic emissions at the same time. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: Soil pollution, pine forests, sulphur-emissions, alkaline pollutants, calcium, aluminium.

INTRODUCTION

Large industrial complexes are situated on both sides of the northern boundary between Russia and Estonia, an area heavily polluted by energy production and industry (Haapala *et al.*, 1996a). The largest emissions originate from the energy power plants of Narva in northeastern Estonia, which use shale oil containing 50% inorganic material. These plants are known for their sulphur dioxide (SO_2) emissions: 141 000 t in 1992 and 97 000 t

in 1993 (VTT, 1994), the decline resulting from decreasing energy production.

Less attention has been paid to the dust emissions of these power plants, although these emissions are more massive, being 186 000 t in 1992 and 135 500 t in 1993 (VTT, 1994). Other large sources of particle emissions in the same region are the cement industry of Kunda in northeastern Estonia (82 600 t in 1990; Kallaste *et al.*, 1992) and the Slantsy cement and oil-shale industry on the Russian side (62 800 t in 1990; Haapala *et al.*, 1993). The particle emissions of Narva, Kunda, and Slantsy are together 5–6 times larger than the Finnish particle emissions from industry and energy production combined. In addition, several other large particle-emission sources are situated in the study area, including large-scale mining industry.

Particle emissions in this area are often alkaline, due to their basic cations, mainly calcium (Ca). The pH of fly ash in Kunda is about 12.5. In northeastern Estonia, pH values in excess of 9 have been measured in snow (Kallaste *et al.*, 1992). Alkaline emissions neutralize the acidic effect of sulphurous emissions. Since both alkaline and acidic emissions are simultaneously very high, a peculiar situation prevails in the study area, the effects of which are not yet known.

Studies of air pollutants in the study area have been summarized by Goltsova (1994). Separate studies have been published by Mäkinen (1994), concerning the Estonian side, and by Haapala *et al.* (1993, 1996a) and Seppälä *et al.* (1993), concerning the Russian side. Until now, however, no systematic study of the environmental damage has been published. A good understanding of the situation can be obtained from the map published by Goltsova (1994), in which the number of epiphytic lichen species on pine trunks are shown. According to this map, lichens are missing over a 1000-km² area, and less severe damage occurs over a much larger region. Forest damage is seen in many places, with the injured areas being scattered. The study area is characterized by wide and almost virgin forests, which act as pollutant sinks, suffering from the effects of pollutants and at the same time eliminating these effects.

The special character of alkaline air pollutants on the study area is indicated by exceptional pine epiphytes, namely the lichen *Xanthoria parietina* (L.) Th. Fr. and the green alga *Trentepohlia umbrina* (Chlorophyceae, Chaetophorales), which makes pine trunks appear red (Haapala et al., 1993, 1996a). The effect of acidic and alkaline pollutants is also shown by high concentrations of S and Ca in pine needles (Haapala et al., 1993, 1996a). The effects of air-borne heavy metals are considerable but not severe (Goltsova & Vasina, 1993; Mäkinen, 1994).

The effects of air pollutants on the forest soil are not known. In this work, these effects were studied in the western part of the Leningrad region, which is affected also by the Narva power plants and other northeastern Estonian sources. Major attention was paid to acid-base problems in the soils. Heavy-metal concentrations were measured, but these findings are reported in a separate article (Haapala et al., 1996b).

MATERIAL AND METHODS

Study area

The study area is situated in the western part of the Leningrad administrative region. The main sources of air pollutants can be seen in Fig. 1. The Narva power plants are situated just west of the study area. The main wind direction is to the northeast toward the study area (Fig. 1, insert).

Studies were performed on 41 sample plots situated in forests of Scots pine, *Pinus sylvestris* (L.), mainly on sandy soils. For total element analyses, 80 sample plots were used. Similar Scots pine forest sites were selected for the study; however, not in every case was this selection possible due to different geological conditions and to the long-term air pollution effect on vegetation and soil. The soil parent material was formed in the last ice age. In all plots, a podzol profile was present. In the north, the underlying ancient rocks are silicates, whereas, in the south, carbonate rocks predominate. The soils in the north are more podzolized, more acidic, and hence contain fewer alkaline cations.

The sample plots were divided into six groups.

- (1) First Slantsy area, distance from Slantsy plants 1–6 km (five sample plots).
- (2) Second Slantsy area, distance 7–20* km (six sample plots).
- (3) Third Slantsy area, distance 15–35* km (seven sample plots).
- (4) First Narva area, distance from Narva power plants 8–20 km (seven sample plots).
- (5) Second Narva area, distance 20–40 km (eight sample plots).
- (6) 'Background' areas (relatively unpolluted), distance from main pollutant sources 40–50 km (eight sample plots).

*The second Slantsy area was longer in the main wind direction (northeast, 20 km) than to other directions (15 km).

On each plot, samples from the humus, eluvial, and illuvial horizons were taken. Two samples on each plot, both of them containing five subsamples, were taken with a cylinder and combined into a single sample for each plot and horizon. The samples were air-dried to constant weight. Particle size, water content and organic matter content were determined, and pH was measured in water (soil to water 1:2 v/v) and in 1 M KCl (1:10 v/v) suspensions; pH was also measured for pine bark samples. Elemental concentrations of Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, S, V and Zn were determined from HNO₃ (total content) and from 1 M ammonium acetate (exchangeable content; 1:10 v/v, pH 4.65) extractions. Exchangeable Al was measured in KCl extracts. For HNO₃ extraction, 1 g of soil was digested in 20 ml of HNO₃ (acid to water 1:1 v/v) for 20 h in 20°C, then 1–2 ml of H₂O₂ was added and boiled for 2 h in 240°C.

Analysis were performed in St. Petersburg in the MECHANOBRA ANALIT laboratory, which participates

Fig. 1. pH in the humus horizon of the Scots pine forests of the study area. Insert: proportional distribution of SO₂ emissions of Narva energy plants in various wind directions (according to Mäkinen, 1994).

in international intercalibration. An inductively coupled plasma emission spectrophotometer (ICP, PST, BAIRD) and an atomic absorption spectrophotometer (PERKIN ELMER, Model No 5100 PC) were used for the measurements. Exchangeable acidity was determined for the 0.1 M BaCl_2 extractions (1:10 v/v) by titration with NaOH to an endpoint of pH 7.00.

For statistical calculations (one-way analysis of variance, Pearson correlations, descriptive statistics), Statistix Version 4.1. was used.

RESULTS AND DISCUSSION

Acidity and alkalinity of the soil

The original acidic podzolic soil has become neutral or even alkaline over wide areas (Fig. 1) as a result of areal pollutants. These contaminants have accumulated over the last 30 years after the beginning of the intense industrialization of this region. This finding was somewhat unexpected, since the area was known for the acidic sulphurous pollutants originating from the Narva energy plants. Some earlier soil pH measurements in Estonia did not reveal such a strong alkaline effect (Mäkinen, 1994). The alkaline effect is not only restricted to the surface soil. In the vicinity of Slantsy's pollutant sources, even our deepest samples (30 cm) showed a $\text{pH}_{\text{H}_2\text{O}}$ value of 8.3. Soils in equilibrium with CaCO_3 have a pH of 8.3 (Thomas & Hargrove, 1984). Compared to the forest liming, this alkaline effect reaches to deeper horizons, since the effect of forest liming is found only in the humus horizon, which has a great capacity for base neutralizing (Kreutzer, 1995).

In the study area, most alkaline sample plots are located in close proximity to the Slantsy cement and oil-shale works (Figs 1 and 2). Sample plots 10–20 km from Slantsy were less acidic than those situated at an equal distance from the Narva power plants. The difference was statistically significant (one-way analysis of variance,

LSD(T) pairwise comparison of means, rejection level 0.05). The same was true when the sample plots at a distance of 20–40 km from these two pollutant sources were compared.

On peripheral sample plots, the alkaline effect was lacking. For instance, in the northern part of the Kurgal Peninsula about 45–50 km north of Narva, an unchanged silicate podzol profile was identified with a humus pH clearly lower than 4 and the pH of underlying soil horizons about 5. These spatial differences were also observed in the eluvial horizon (Fig. 2). In many sample plots, pH values exceeded 7. On the other hand, the eluvial horizon in the periphery zone was generally acidic. The illuvial horizon was also alkaline in some plots. The highest pH value (8.3) was measured in the eluvial horizon of some of the profiles of soils near the Slantsy cement and oil-shale works.

In places where airborne pollutants had the greatest alkaline effect on soil pH, the illuvial horizon was generally less alkaline than the upper horizons, with the exception of area 2 (Slantsy 7–20 km), where the alkaline effect was relatively stronger in deeper horizons (Fig. 2). In places where the alkaline effect was very small, the humus horizon was mostly acidic horizon ('background').

In comparison to other cases of alkaline air pollution, the effects in the study area were truly on a massive scale. In the Niepolomice forest (Poland, 25 km north-east of Kraków), effects of different industrial dusts on the soil were studied experimentally. In the most alkaline case, plots were treated with dust from a cement plant totalling 75 t ha^{-1} over 1.5 years. The dust contained 47% CaO at pH 9.5. After 5 years, the maximum pH for the topsoil was 7.7. Below the uppermost 5-cm soil layer, the maximum was pH 6.1 (Greszta, 1988a,b). In Kalkkiranta (Finland, 25 km east of Helsinki), the long-lasting effect of a limestone quarry changed the pH of a podzolic humus soil of the surrounding forest from about 4 to over 7 (Huttunen *et al.*, 1990). Even in this case, however, the alkaline effect is smaller than that of

Fig. 2. pH in different horizons of the Scots pine forests in different parts of the study area. SI 1–6 km, SI 7–20 km, and SI 15–35 km mean distance from Slantsy, Na 8–20 km and Na 20–40 km mean distance from Narva (see Material and Methods section).

Slantsy. Only minor changes in soil pH have been caused by liming experiments in Finnish coniferous forests, in which limestone additions were 2 t ha^{-1} . Humus pH 20 years after that liming was only one pH unit higher than before the liming, the effect being even less in mineral soil, although almost all limestone Ca still remained in the soil (Derome & Pätälä, 1990).

Soil calcium

The alkaline effect observed in the soil was mainly caused by Ca-containing compounds, the content of which is high in both the Narva and Slantsy emissions. The highest total Ca content of humus was $100\,000 \text{ mg kg}^{-1}$ (in the vicinity of Slantsy, Fig. 3). On the Estonian side of the boundary, high Ca concentrations in soil have also been measured (Mäkinen, 1994), although not so high as in the present study. In the Polish Niepolomice forest the highest total Ca content was $21\,500 \text{ mg kg}^{-1}$ (Greszta, 1988a,b).

The concentrations of exchangeable Ca were correspondingly very high. Exchangeable Ca, like other basic cations, is accumulated by air pollution in the humus horizon (Table 1). Near Slantsy the highest concentrations were over $20\,000 \text{ mg kg}^{-1}$ in the humus horizon (Fig. 4), 7000 mg kg^{-1} in the eluvial horizon and over 1000 mg kg^{-1} at the depth of 30 cm in the illuvial

horizon. The highest values were almost twofold greater than those reported for the Finnish Kalkkiranta forest near the limestone quarry (Huttunen *et al.*, 1990). Differences in Ca content between different parts of the study area were great (Figs 3 and 4). Total Ca contents were about tenfold greater near Slantsy than in the peripheric zone. In fact, soil Ca values were increased across the entire study area. Even 60 km northeast from the pollutant sources, soil Ca content was about twofold the background values, which were approximately $4000 \pm 1000 \text{ mg kg}^{-1}$ (Tamminen & Starr, 1990). On the other hand, some comparatively low Ca concentrations were also measured.

Ca pollution has greater effects on soil near Slantsy than in the surroundings of Narva. The differences are similar in total and extractable contents. These differences were also detected in deeper soil horizons. At the 30 cm depth, area numbers 1 and 2 around Slantsy differed significantly from all other areas in their Ca contents, the greatest concentrations being also in this case about tenfold greater than in the least polluted areas.

High Ca content may have an important impact on forest soil and the whole ecosystem (Kreutzer, 1995). Positive effects are de-acidification of soil, reduction in mobility of toxic species of Al and heavy metals and

Fig. 3. Total calcium content in the humus horizon of the Scots pine forests in different parts of the study area. The bars of the columns indicate standard deviation. For further explanations, see Fig. 2.

Table 1. Total and exchangeable (different horizons) element content (mg kg^{-1}) of the Scots pine forest soil of the study area

	Al	S	Ca	Ba	K	Mg	Na
Total <i>n</i>	80	78	80	80	80	79	79
Humus mean	4857	1201	11 730	74	1599	837	82
SD	3636	726	14 100	36	1868	831	56
Exchangeable <i>n</i>	41	41	41	41	41	41	41
Humus mean	54	313	7137	18	390	346	25
SD	75	578	5893	12	211	292	22
Eluvial mean	45	25	967	6	47	54	5
SD	13	28	1733	10	41	88	6
Illuvial mean	83	18	190	3	18	14	6
SD	264	17	268	4	16	26	7

improvement in humus quality resulting from better conditions for soil organisms (Metzner & Meuwes, 1991; Derome *et al.*, 1994; Kreutzer, 1995). An increase in soil Ca content may also have negative effects, such as an increase in nitrate concentration of seepage water, reduction in the humus store, mobilization of copper and lead as organic complexes, induction of boron deficiency and damage to roots and their mycorrhizae (Lehto, 1984, 1994; Kreutzer, 1995). Many of these effects have been observed in liming experiments, and the effects of Ca are in many cases indirect. In the study area, the increase in soil Ca content was totally uncontrolled, and in many places much greater than in normal liming.

Other basic cations

Total concentrations of magnesium (Mg), potassium (K), sodium (Na), and barium (Ba) have clearly increased in the same sample plots as Ca, and they correspond to Ca fluctuations. All are considered to originate from the same pollutant sources. The amounts of Mg and K are so high that they have a considerable

effect on soil alkalinity. However, the Ca content was clearly most dominant. The exchangeable-element content of Mg, K, and Ba correlated well with that of calcium, but Na did not (Table 2).

The amount of alkaline cations was very high compared to that of similar soil types in Finland (Tamminen & Starr, 1990) and, especially in the case of K, was much higher than soil K content in ash experiments in Niepolomice, Poland (Greszta, 1988a,b). On the most-polluted plots, even more than 90% of the K was in non-exchangeable form.

Soil aluminum

The amount of Al differs from that of alkaline cations. Total Al content was very high in the plots that showed high concentrations of alkaline cations (Fig. 5). The correlation of total Al with total alkaline cations was strongly positive (Table 2), as a result of air pollution, which contains a lot of Al from Narva and Slantsy. On the other hand, concentrations of exchangeable Al (mainly Al^{3+}) differed substantially in distribution, being very low in sample plots where total Al and Ca

Fig. 4. Exchangeable calcium content in humus horizon of the Scots pine forests in different parts of the study area. For further explanations, see Figs 2 and 3.

Table 2. Correlations (Pearson) for total (tot, df = 77) and exchangeable (exc, df = 39) element content in the humus horizon of the Scots pine forests of the study area

	Al	S	Ca	Ba	K	Mg
S tot	0.192					
S exc	-0.026					
Ca tot	0.894**	0.137				
Ca exc	-0.386*	0.013				
Ba tot	0.775**	0.359**	0.689**			
Ba exc	-0.218	0.022	0.595**			
K tot	0.927**	0.135	0.952**	0.688**		
K exc	-0.096	0.025	0.504**	0.548**		
Mg tot	0.886**	0.196	0.959**	0.696**	0.961**	
Mg exc	-0.333*	0.008	0.932**	0.584**	0.639**	
Na tot	0.746**	0.321**	0.801**	0.655**	0.857**	0.867**
Na exc	0.063	0.628**	0.028	0.004	0.303	0.151

* $\alpha \leq 0.05$, ** $\alpha \leq 0.01$.

content was high (Fig. 6). Exchangeable Al was high in plots with low Ca content and low pH, even though their total Al content was very small. The correlation of exchangeable Al with exchangeable Ca was negative (Table 2). When total and exchangeable Al contents were compared, differences between sample plots were quite striking. The ratio of total Al to exchangeable Al in polluted areas was greater than 1000 and in less polluted samples was about 10. Unlike basic cations, Al is not accumulated in the humus horizon (Table 1).

These differences are caused by soil acidity-alkalinity interactions. Because acidification mobilizes Al, much exchangeable Al can be found in acidic soil, despite the total Al content not being very high. In alkaline soil, Al is in insoluble form, and only very little occurs in an exchangeable form. Another reason for this low Al content is the cation-exchange reaction in which Ca exchanges ionized Al from soil into soil water (Alva & Sumner, 1990).

Similarly, the ratio of exchangeable Ca to exchangeable Al changed enormously in different parts of the study area. Near Slantsy the ratio of Ca^{2+} to Al^{3+} was higher than 10 000, whereas in less polluted acid mineral soils it was under 0.1 (Fig. 7).

Exchangeable acidity

Exchangeable acidity (EA) showed an almost similar areal distribution as that of Al (Fig. 8). EA values were low in areas with much Ca, high pH and little exchangeable aluminum and were high for the opposite relationship. In heavily polluted sites, Ca and other cations have forced out those hydrogen ions that were bound to the negatively charged soil particles. EA had its highest positive correlation with exchangeable Al (in humus $r = 0.933$, $df = 38$) and a negative correlation with pH (in humus -0.729) and exchangeable Ca (in humus -0.376).

Fig. 5. Total aluminum content in humus horizon of the Scots pine forests in different parts of the study area. For further explanations, see Figs 2 and 3.

Fig. 6. Exchangeable aluminum content in humus horizon of the Scots pine forests in different parts of the study area. For further explanations, see Figs 2 and 3.

Sulphur in soil

The highest total S content in humus horizon was 4200 mg kg^{-1} , and in four cases its value was higher than 3000 mg kg^{-1} (Fig. 9). In different parts of the study area, changes in S content differed from those of most other elements, especially Ca (Figs 9 and 10). The highest soil S contents were in areas 4 and 5 (to the north and northeast of Narva). This finding indicates the very high S emissions of the Narva energy plants, about tenfold those of Slantsy (Synthesis Report, 1991), even though the differences are not statistically significant

due to the very great variations inside the areas. However, it must be remembered that the effects of air pollutants from Narva and Slantsy cannot be separated totally, since the distance between them is only about 25 km.

Soil S content in the study area was not very great, considering the large S emissions from the local pollutant sources and especially when it is compared to the very high Ca content of the soil. Similar observations have been made in another area heavily polluted by S, namely Montsegorsk in the Kola Peninsula, where soil S content is almost similar to that in the present area

Fig. 7. Ratio of exchangeable Ca/Al in various horizons of the podzolic soil of the Scots pine forests of the study area.

Fig. 8. Exchangeable acidity in humus horizon of the Scots pine forests in different parts of the study area. For further explanations, see Figs 2 and 3.

(Menshikova *et al.*, 1993). The S level of the soil was of the same order of magnitude as that of Norrleden, Sweden (Nömmik *et al.*, 1984) or around Oulu in northern Finland (Ohtonen *et al.*, 1989).

This relatively low level of S in the soil is not easy to explain, since the chemical reactions of S in soil are very complicated. Especially under these exceptional conditions, very great differences in soil S content were found even between sample plots situated near each other.

Only a small portion of the S is absorbed in the surface horizons of podzolic soil (Neary *et al.*, 1987). This probably results from the fact that sulphate ions and other negatively charged S ions cannot replace the negatively charged hydroxyl ions in the surface of soil humus and inorganic colloid particles. The absorption of sulphate is also strongly dependent on soil pH, the optimum being under pH 4. In less acidic soils, sulphate

absorption is greatly weakened (Nömmik *et al.*, 1984). These experimental studies support the finding that only relatively small amounts of S will be found in podzolic soils simultaneously polluted by S and Ca, the total effect being alkalinization of the soil.

CONCLUSIONS

The soil of the pine forests in the study area has been polluted by emissions from local sources over areas comprising several thousands square kilometres. The area is characterized by both acidic and alkaline pollutants, mainly S and Ca. They neutralize each other's effects. However, the absorption of these elements occurs differently. S (mainly deposited as sulphate) is absorbed only in small quantities, making the S content

Fig. 9. Total sulphur content in humus horizon of the Scots pine forests in different parts of the study area. For further explanations, see Figs 2 and 3.

Fig. 10. Exchangeable sulphur content in humus horizon of the Scots pine forests in different parts of the study area. For further explanations, see Figs 2 and 3.

of the soil not as high as could be expected in the light of such massive pollution. Because Ca is absorbed much more efficiently, its level in soil rises very high, in the humus layer even to 100 000 mg kg⁻¹. Alkalinization dominates the processes of the soil. The transport of S and Ca pollutants differs, since S is mainly transported in its gaseous form as SO₂ and Ca in particle form. For that reason, the greater proportion of the Ca is deposited at a shorter distance than that of S. This may sharpen the basic-acidic gradient of the study area, which was very obvious.

The effects of such soil pollution on this forest ecosystem is not known. In many parts of the study area, forests are already dead or are suffering from air pollutants. Their injurious effects may have many causes in various ways, including gaseous SO₂ interactions. The absence of epiphytic lichens in an area of about 1000 km² indicates this kind of damage. It is also possible that the alkalinization of pine trunks may contribute to the death of those lichens that are adapted to acidic conditions. This theory is supported by the fact that some epiphytic species did occur on the trunks of pine trees in these polluted areas. These included the lichen *Xanthoria parietina* and the alga *Trentepohlia umbrina*, which grow in these ecosystems on Scots pine trunks that are less acidic or on alkaline bark.

The long-term role of soil alkalinization on forests is not yet known. Because pine forest vegetation is adapted to very acid soil, soil alkalinization must negatively impact these areas. An important cause of damage to trees may be via damage to mycorrhizae, which are sensitive to changes in soil acidity.

It could be argued that the forest damage in the study area is not so serious, considering the massive scale of pollution. This may in part be due to the neutralizing effect of acidic and alkaline pollutants. However, if uncontrolled pollution lasts for much longer periods, unanticipated changes should be expected. An indication of this can be found in the great alterations taking place in the soil.

The complicated pollutant situation of the study area must be taken into consideration when environmental protection measures are planned. Major attention has been paid to reducing SO₂ emissions from the Narva energy plants. This is important to decrease the injurious effects of gaseous SO₂. However, the main problem in the immediate area around the plants comes from alkaline deposition. Therefore, any decrease in the acidic proportion of the deposition may cause even more problems in the soil. It is necessary to reduce both acidic and alkaline emissions at the same time.

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