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The effect of emissions from the Cu-Ni smelters in the Kola Peninsula on the chemical properties of forest soil

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Academic dissertation
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to be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in Auditorium Pieni Juhlasali of the University's Main Building, Fabianinkatu 33, on 5 June 1998, at 12 o'clock noon.

VANTAAN TUTKIMUSKESKUS

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The effects of sulphur and heavy metal emissions from the Cu-Ni smelters (Monchegorsk and Nikel) in the Kola Peninsula, NW Russia, on the chemical composition of deposition, forest soil and percolation water were studied along two gradient lines running approximately to the west from the point sources through the Kola Peninsula and Finnish Lapland. The role of dissolved organic matter (DOM) in percolation water quality, as well as the reliability of the percolation water acidification parameters (pH and Al concentration), were also investigated. Two Al fractionation methods were also tested.

The deposition pattern caused by the Kola emissions was determined by collecting snowpack samples in open areas, as well as bulk deposition and throughfall samples. The chemical properties of the forest soil were studied by collecting soil (O, E, B and C horizons) and percolation water (by zero-tension lysimeters at depths of 5, 20 and 40 cm) samples. The effects of sample transportation, filtration and storage (+4°C, -20°C) on the percolation water pH and Al concentration were determined by comparing the results obtained using different sample treatment methods. Aluminium fractionation was studied by comparing the results obtained by the ICP/AES and FIA methods. The studied tree stands in Lapland and the Kola Peninsula consisted of Scots pine (*Pinus sylvestris*) and were located on dry or dryish mineral soil sites. The soils were podzols and consisted of sorted sand.

Analysis of the deposition and percolation water/soil solution samples were as follows: pH; total S, P and metals (ICP/AES); NH_4^+, NO_3^-, total reactive Al (FIA); SO_4^{2-}, Cl^- (IC); permanganate consumption (SFS 3036); and DOC (TOC analyser). Aluminium fractionation was performed using a cation exchange column (Amberlite IR 120). The chemical soil parameters were as follows: pH(H_2O); exchangeable base cations, Al and Cu (0.05M $BaCl_2$ extraction, ICP/AES); titratable acidity (0.05M $BaCl_2$ extraction followed by titration with 0.05M NaOH to pH 7); extractable S (1M ammonium acetate extraction, pH 4.65, ICP/AES); and total Cu and Ni (dry digestion, HCl extraction, ICP/AES).

The S, Cu and Ni emissions from Monchegorsk were reflected as elevated concentrations of these elements in the snowpack and percolation water (depth 5 cm) to a distance of about 30 km from the source. The extractable S concentration in the organic layer was relatively high only at distances of less than 10 km from Monchegorsk. The total Cu and Ni concentrations in the organic layer were elevated along the gradient line up to100 km from Monchegorsk, but in the mineral soil only to a distance of 10 km. The pH values of the snowpack, percolation water and forest soil, or the exchangeable H^+ concentration in the O horizon, did not indicate increased acidity near the Monchegorsk smelter. The decreased base saturation and base cation concentration in the O horizon near Monchegorsk were mainly due to elevated exchangeable Al concentrations in the O horizon. External sources of Al are significant near to Monchegorsk.

The total Cu and Ni concentrations were elevated in the organic layer up to a distance of 50-70 km from Nikel, but no signs of elevated concentrations were found in the mineral soil. Slightly increasing S gradients were detected in the snowpack, bulk deposition and throughfall towards Nikel. Increased acidity close to Nikel was not evident according to the pH of the snowpack, forest soil and percolation water. However, the situation better fulfilled the definition of soil acidification because a reduction in the organic layer base saturation and base cation concentrations were found together with an increase in the exchangeable H^+ concentrations near the point source.

The significant negative correlation between percolation water DOM and pH (depth 5 cm) and positive correlation between DOM and Al concentration (depths 5 and 20 cm) indicated the important role of DOM in regulating percolation water quality in forest soils in the background areas. The anionic nature of the DOM was evident because there was a significant positive correlation between DOM and anionic deficit of the percolation water (depth 5 cm). The percolation water total Al concentrations in the soil from Northern Finland do not seem to be a serious threat to trees because they were well below the critical values for Al toxicity, and a significant proportion of the total Al at depths of 5-20 cm was in the non-toxic, organic complexed form.

The effect of transportation, filtration and storage on percolation water pH and total Al concentrations was found to be insignificant in the gradient study, which means that the presented procedures can be recommended. Either of the two methods presented (ICP/AES and FIA) can be used for estimating the concentration of positively charged inorganic Al.

Key words: Cu-Ni smelters, deposition, forest soil, Kola Peninsula, Lapland, percolation water, Scots pine.

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CONTENTS

LIST OF PUBLICATIONS

The thesis is based on the following papers, which are referred to in the text with Roman numerals:

I - Lindroos, A.-J., Derome, J. & Niska, K. 1995. Snowpack quality as an indicator of air pollution in Finnish Lapland and the Kola Peninsula, NW Russia. Water, Air and Soil Pollution 85(4): 2185-2190.

II - Lindroos, A.-J., Derome, J., Nikonov, V. & Niska, K. 1996. Influence of sulphur and heavy metal emissions from Monchegorsk, Northwest Russia, on percolation water quality in *Pinus sylvestris* stands. Scandinavian Journal of Forest Research 11: 97-103.

III - Lindroos, A.-J., Derome, J. & Niska, K. 1995. The relationship between dissolved organic matter and percolation water chemistry in Northern Finland. Water, Air and Soil Pollution 79(1/4): 191-200.

IV - Derome, J., Lindroos, A.-J. & Niska, K. Effects of SO_2 and heavy metal emissions from the Kola Peninsula, NW Russia, on soil acidity parameters in NW Russia and Finnish Lapland. Scandinavian Journal of Forest Research. (in print).

V - Lindroos, A.-J., Derome, J. & Niska, K. 1998. The effect of emissions from Cu-Ni smelters at Nikel, NW Russia, on the quality of bulk deposition, stand throughfall and percolation water in four Scots pine stands in Northern Norway and Finland. Chemosphere 36(4-5): 1101-1106.

VI - Derome, K., Derome, J. & Lindroos, A.-J. 1998. Techniques for preserving and determining aluminium fractions in soil solution from podzolic forest soils. Chemosphere 36(4-5): 1143-1148.

In addition, some new results are presented.

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1 INTRODUCTION

1.1 Soil acidification

The development and status of soil acidity are influenced by many different factors. Acidic deposition, resulting from the chemical reactions in the air between sulphur dioxide or nitrogen oxides and water, may cause anthropogenic soil acidification. According to the acidification theory, soil acidification causes the leaching of base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) from the topmost layers of forest soil and aluminium mobilisation (Abrahamsen 1983, Schulze 1989). Generally it has been shown that acid deposition

- increases the rate of soil acidification (defined as loss of acid neutralising capacity over time)
- leads to losses of base cations from the cation exchange sites
- causes a decrease in soil pH
- releases Al^{3+} ions into the soil solution as a consequence of H^{+} buffering processes (according to the overview in Matzner & Murach 1995).

Acidic deposition can be an important proton source, but there are many other processes that should also be taken into account when estimating soil acidification. The net accumulation of base cations (Ca^{2+}, Mg^{2+}, K^{+}) in the biomass, as well as nitrogen transformation processes, are proton sources in forest soils. The organic acids produced by the partial decomposition of organic matter in the cool and moist climate prevailing in the coniferous forests of the boreal zone, are proton sources causing natural podsol development and acidification of forest soils. As the pH in the organic and eluvial horizons of podsols is often below 4, it must be assumed that this is due to the presence of relatively strong organic acids (Petersen 1976). The release of anions in mineral weathering is also an important proton source (van Breemen et al. 1983, van Breemen et al. 1984, Kallio & Kauppi 1990).

Soil acidification is also dependent on proton-retention processes, i.e. the buffering and neutralising processes in the soil. Protons are consumed in nitrogen transformation processes, biomass accumulation of anions, as well as the release of cations through mineral weathering in the mineral soil (van Breemen et al. 1983, van Breemen et al. 1984, Kallio & Kauppi 1990).

Base cation deposition decreases the acidifying effect of sulphur and nitrogen deposition by supplementing the buffering reactions. Tree age also has a considerable impact on forest soil acidity. Acidity tends to increase with increasing stand age (Bergholm et al. 1985, Hallbäcken & Tamm 1986). This is mainly due to the accumulation of base cations in biomass. Forest management may also affect soil acidity. Clear-felling releases nutrients from the organic matter and increases soil pH (Nykvist & Rosén 1985). Nutrient leaching is usually strong after clear felling, and this may eliminate the positive effect of base cation release from the organic matter. Whole-tree harvesting may have a negative effect on the soil buffering system because base cations are removed along with the harvested organic matter (Nilson et al. 1982). Prescribed burning, as well as forest fires, decreases the soil acidity, and nutrients are released from the burned organic matter (Viro 1969).

The buffering and neutralising reactions are assumed to act effectively over different pH ranges (Table 1, Schwertman et al. 1987), but in natural soil systems these ranges are not necessary very distinct. The ranges cover only the most favourable conditions for each reaction.

Organic acids are important buffering compounds in forest soils. The dissociation of organic acids produces protons in the soil, and the dissolved organic anions are the main anions in the soil solution in natural conditions (Reuss & Johnson 1986). The deposition of strong mineral acids is a major source of sulphate and nitrate anions and protons in soil solution. If the deposition of these compounds is very high, the proportion of organic anions in the soil solution decreases (the dissociation of organic anions decreases) (Krug & Frink 1983). Thus, the dissociation of organic acids is dependent on soil solution pH.

Although, soil acidity is dependent on many natural and anthropogenic factors and complicated chemical, physical and biological processes, a connection between the high anthropogenic deposition of sulphur and nitrogen and soil acidification has been demonstrated in many studies. For example, de Vries et al. (1995) found that sulphur and nitrogen deposition has a clear effect on soil solution SO_4^{2-}, NO_3^- and Al concentrations in the Netherlands. The studied forest stands were located on non-calcareous, acid sandy soils with a tree cover consisting of Scots pine, oak, Douglas fir, black pine, Norway spruce, Japanese larch and beech. Median annual SO_4^{2-} deposition varied from 1283 to 2646 mol_c/ha/yr, and N deposition from 3206 to 5034 mol_c/ha/yr. In the same study, there was a very strong positive correlation between the soil solution concentrations of $SO_4^{2-} + NO_3^-$ and $H^+ + Al^{3+}$.

Table 1. The buffering systems and their pH ranges and chemical reactions in agricultural and forest soils according to Schwertmann et al. (1987). K = metallic cation.

Buffering system	pH range	Buffering reaction
ALKALI EARTH-CARBONATE		
Carbonate	8-6.5	$CaCO_3 + H^+$ <--> $HCO_3^- + Ca^{2+}$
Bicarbonate	7-4.5	$HCO_3^- + H^+$ <--> $CO_2 + H_2O$
VARIABLE-CHARGE CATION EXCHANGE		
Clay minerals (C)	8- <5	$C\text{-}OH]K + H^+$ <--> $C\text{-}OH_2] + K^+$
	6- <3	$C\text{-}OH + H^+$ <-->$C\text{-}OH_2$
Humus (R)	6- <3	$R\text{-}(COO)K + H^+$ <--> $R\text{-}(COO)H + K^+$
	>7-4	$R\text{-}NH_2 + H^+$ <--> $R\text{-}NH_3^+$
SILICATE		
Primary silicates	<7	$\text{-}(SiO)K + H^+$ <--> $\text{-}(SiOH) + K^+$
Clay minerals		
- no perm. charge		$\text{-}(SiO)_3Al + 3H^+$ <--> $\text{-}Si(OH)_3 + Al^{3+}$
- perm. charge		
oct.	<4.5	$Mg(O,OH)^-]K + 3H^+$ <--> $Mg^{2+} + K^+ + 2H_2O$
tetr.		$AlO_2^-]K + 4H^+$ <--> $Al^{3+} + K^+ + 2H_2O$
OXIDE/HYDROXIDE		
Al hydroxide		
Intermed. Al	4.8-3	$Al(OH)_3 + 3H^+$ <--> $Al^{3+} + 3H_2O$
Al-OH-sulphate	4.5-3	$AlOHSO_4 + H^+$ <--> $Al^{3+} + SO_4^{2-} + H_2O$
Fe oxide/hydroxide		
- without reduction	<3	$FeOOH + 3H^+$ <--> $Fe^{3+} + 2H_2O$
- with reduction	<7	$4FeOOH + CH_2O + 8H^+$ <--> $4Fe^{2+} + CO_2 + 7H_2O$
Mn oxide/hydroxide		
- with reduction	<8	$2MnO_2 + 4H^+ + CH_2O$ <--> $2Mn^{2+} + CO_2 + 3H_2O$

In the ore smelting region of Sudbury in Ontario, Canada, the high sulphur deposition has strongly affected the surrounding forests both via direct effects on the vegetation and indirectly through changes in the soil. The boreal forest ecosystem (consisting of *Pinus strobus, Pinus banksiana, Acer rubrum* and *Quercus rubra*) has been destroyed over a large area around the smelters due to SO_2 emissions and soil acidification. Soil acidification has caused the dissolution of a number of metals and this has led to phytotoxic effects (Hutchinson & Whitby 1977).

The connection between sulphur deposition and soil acidification has also been found in many studies carried out in the

Nordic countries. According to Erikson et al. (1992), the acidification of forest till soils is related to the areal distribution of atmospheric deposition, and in SW Sweden soil acidification is detectable even at a depth of 2 m below the ground surface. Acidification has decreased the amounts of base cations in the topmost layers of forest soil in many areas in Central and Southern Sweden. Sulphur adsorption has reached the saturation point in many soils along the west coast of Sweden. According to multi-variable analysis describing the effect of different factors on the soil acidification status, sulphur deposition (H_2SO_4) seems to be the most important single factor determining the geographical distribution of forest soil acidification when moving from the west to east in the southern and central parts of Sweden (Karltun 1994).

An increasing trend in soil acidification has also been reported in many other studies carried out in Scandinavia (Hallbäcken & Tamm 1986, Falkengren-Grerup 1987, Tamm & Hallbäcken 1988). It has not been possible to explain the increasing acidity as a whole without taking into account the effect of acidifying deposition. In a study carried out in Southern Norway, some indications of the relationship between needle loss of Norway spruce (*Picea abies*) and soil acidification have been found (Nellemann & Frogner 1994). There also seems to be a relationship between soil acidification and acidic deposition in the south of Norway (Steinnes et al. 1993). In the southern parts of Scandinavia sulphur deposition has increased tenfold since the beginning of the nineteenth century. A similar trend is also evident for nitrogen deposition (Bernes 1993).

According to Sverdrup et al. (1992), the critical loads of acidifying compounds calculated for forest soils are exceeded in a significant part of the Nordic countries. These model calculations suggest that forest soils located in Southern Finland receive a higher load of acidifying compounds than the soil is able to withstand (Kämäri et al. 1992). However, there has been some uncertainty about the validity of the current approach in the critical load concept, for example concerning the use of Ca/Al ratio in these calculations (Løkke et al. 1996).

1.2 The influence of soil acidification on vegetation

The dissolution of certain metals in soils is dependent on the soil acidity status. In many studies it has been concluded that high aluminium concentrations in soil solution may cause forest damage (Ulrich et al. 1979, Ulrich et al. 1980). The effects of soluble toxic aluminium forms (e.g. Al^{3+}) on plants include a reduction in root growth, changes in the nutrient and water uptake by the roots, changes in the structure of cell walls and a reduction in root respiration (Foy et al. 1978, Hütterman 1985).

There are a number of different forms of dissolved aluminium in soil solution, and only some of them are toxic to plants. At pH values above 4.0, Al^{3+} readily forms soluble mononuclear compounds with hydroxide ions (e.g. $AlOH^{2+}$, $Al(OH)_2^{+}$). Inorganic ligands such as sulphate and fluoride, as well as organic ligands, easily form Al complexes (Haug 1984, Hue et al. 1986). Aluminium also forms polynuclear compounds with hydroxides. Free Al^{3+} is considered to be the most toxic form of the mononuclear aluminium species (Parker et al. 1989). The concentration of all inorganic mononuclear aluminium species is also widely used as a parameter of the aluminium toxicity to plants. However, it has not been possible to demonstrate that the polynuclear aluminium forms are non-toxic to plants. In contrast, the organic aluminium complexes have been shown to be non-toxic (Hue et al. 1986).

In the topmost layers of podsolic soil there are usually considerable amounts of dissolved organic matter. Nilsson and Bergkvist (1983) found that there was a strong positive correlation between the concentrations of dissolved organic carbon (DOC) and soil solution aluminium. The organic aluminium complexes are relatively resistant to an increase in acidity, and the pH has to decrease significantly before the complexes decompose (Derome 1989). The dissolved organic aluminium complexes are the most common aluminium species in the upper layers of podsolic soils (Nilsson & Berqkvist 1983, Lundström 1993).

The high aluminium concentration in soil solution is not the only parameter that explains the negative effects of soil acidification on plants. Aluminium toxicity decreases along with an increase in the concentration of base cations in soil solution, and therefore the Ca/Al molar ratio is generally accepted to be an even more important criterion in estimating the Al toxicity than the Al concentration as such (Rost-Siebert 1983). The critical limit for the Ca/Al molar ratio is usually 1.0. If ratio values are below the critical limit, the soil solution composition may be a limiting factor for plant growth and soil acidification may threaten plant roots (Roelofs et al. 1985, Sverdrup et al. 1990, Sverdrup & Warfvinge 1993, Sverdrup & de Vries 1994, Sverdrup 1995). However, there have been many discussions about the validity of the critical limits set for different parameters (e.g. Ilvesniemi & Starr 1994). No relationship has been found between the base cation/aluminium ratio and forest growth (Örlander et al. 1994, Westling 1995).

It is very difficult to determine the possible negative effects of elevated aluminium concentrations in soil solution on plants in field conditions, because many other chemical processes are also closely involved in soil acidification processes. There do not seem to be any long time series of aluminium concentrations in the soil solution. Therefore, Al toxicity to plants has commonly been studied in laboratory experiments using seedlings and the addition of relatively high concentrations of aluminium salts (Al^{3+}). For example, according to Henriksen et al. (1992) the Ca concentrations in the shoots and roots of *Picea abies* seedlings decreased with increasing aluminium concentrations in the substrate. The growth of spruce seedlings stopped when the Al concentration was 0.74 mM in the nutrient solution.

The resistance of different tree species to elevated aluminium concentrations is not similar. Arovaara and Ilvesniemi (1990a and b) showed that the growth of spruce seedlings is inhibited at somewhat lower aluminium concentrations than for pine seedlings. It is naturally very difficult to compare the results obtained in the laboratory with seedlings to those measured in the field with older trees. Laboratory experiments are useful to clarify the basic dose-response mechanisms but they cannot be used as such to estimate the situation in nature.

1.3 Accumulation of heavy metals in forest soil

The accumulation of heavy metals from point sources in forest soils and their effects on vegetation, as well as on soil biological properties, have been described in a large number of studies. According to Nordgren et al. (1986), the Fe, Pb, Zn, Cu, V, Ni, Se and Cr concentrations in the organic layer clearly increased on moving towards the Rönnskärverken metal smelter located in the north of Sweden. Løbersli and Steinnes (1988) reported on the effects on soil properties of emissions from the Cu smelter at Sulitjelma, Northern Norway. The emissions from the smelter consisted of SO_2,and metals such as Cu, Zn, Pb and Cd. The concentrations of these metals increased in the topmost layers of the forest soil near the smelter. The tree cover consisted of birch. The concentrations decreased significantly with increasing distance from the smelter. Metal contamination was still detectable at a distance of 27 km from the smelter in the prevailing wind direction.

The effects of emissions from the Harjavalta Cu-Ni smelter, western Finland, on the surrounding forests have been studied in many investigations. The Cu and Ni loads in bulk precipitation and stand throughfall have increased, compared to background values, due to the heavy metal emissions. Copper deposition at a distance of 0.5 km from the Harjavalta smelter was 275 mg/m^2 in bulk precipitation and 429 mg/m^2 in stand throughfall during June 1992 - June 1993. The corresponding Ni values were 27 mg/m^2 and 52 mg/m^2 (Helmisaari et al. 1994). The Cu and Ni concentrations in the organic layer of the forest soil have also been relatively high in the immediate surroundings of the smelter (Fritze et al. 1989, Fritze et al. 1994). Almost 50 years' accumulation of heavy metals in the soil has caused direct toxic effects on soil microbes, thus decreasing decomposition and nutrient mineralisation (Helmisaari et al. 1995).

The Cu-Ni smelters and surrounding area in Sudbury, Canada, have been intensively studied, and emissions from the smelters have been found to cause considerable changes in the soil and vegetation (Hutchinson & Whitby 1974, Hutchinson & Whitby 1977). Copper, Ni, Fe and S have accumulated in the litter, soil and vegetation. The role of the organic layer of the soil is important in metal accumulation. The Ni and Cu concentrations in the topsoil were elevated even at a distance of 70 km from the smelters, compared to the values in background areas (Freedman & Hutchinson 1980).

Nickel and copper are effectively absorbed by soil organic matter, but the binding mechanisms are different. Nickel has a high affinity for negatively charged cation exchange sites on soil colloids, and copper readily forms organic complexes. Therefore, the mobilisation of copper is much weaker in the topmost layers of the soil than that of nickel (Steinnes 1992).

Copper concentrations in the soil solution are strongly dependent on the dissolved organic carbon concentrations (DOC). The complexation of heavy metals in the soil solution is connected with the composition of the DOC. Hydrophilic acids are important in the formation of copper complexes in soil solution, while hydrophobic acids play only a minor role. The metal-hydrophilic acid complexes are very resistant to acidification. The hydrophilic acids are the most mobile fraction of the DOC in soil solution (Guggenberger et al. 1994).

1.4 Background and aims of the study

1.4.1 Background

This thesis was carried out as a part of the Lapland Forest Damage Project (Tikkanen 1995a). The Lapland Forest Damage Project was carried out at the Finnish Forest Research Institute during 1989-1995. The project was launched to determine possible connections between the sulphur and heavy metal emissions from the Kola Peninsula, NW Russia, and tree damage observed in Finnish Lapland (Tikkanen 1995b). Information about the huge emissions in the Kola Peninsula first came to light as a result of political changes in the Soviet Union at the end of the 1980s. Crown condition monitoring carried out in Finland during 1986-89 showed that the highest degree of needle loss in Scots pine forests in northern Finland had occurred in the NE corner of Lapland (Jukola-Sulonen et al. 1993). During 1988-89, many forests in Eastern Lapland were also damaged by *Gremeniella abietina* (Lagerb.) Morelet (Kaitera & Jalkanen 1993).

1.4.2 Emissions from the Kola Peninsula

The Cu-Ni smelters in the Kola Peninsula are significant point sources of sulphur and heavy metals. In 1990, for example, the combined emissions of sulphur dioxide from Nikel, Zapoljarnyi and Monchegorsk were double the total emissions in Finland. Lapland's own emissions are very low compared to those of the Kola Peninsula. The sulphur dioxide emissions were 190 000 t from Nikel, 67 000 t from Zapoljarnyi and 233 000 t from Monchegorsk in 1990 (Lapin lääninhallitus 1992). The high emissions are due to the utilisation of sulphur-rich sulphide ore transported from Norilsk, western Siberia. The ore contains about 30% of sulphur (Anttila 1995). The poor environmental technology of the smelters is also an important reason for the high emissions (Anttila 1995).

There was a peak in the total sulphur dioxide emissions of the Kola Peninsula in the middle of the 1980s when emissions amounted to about 700 000 t SO_2 per year. The emissions have since decreased and were about 500 000 t per year in the early part of the 1990s (Blatov et al. 1992, Anttila 1995). The Kola smelters have been in operation since 1940. Although, the emissions from the Kola Peninsula are high, there are much larger emission sources in the Central Europe. The effect of the Kola Peninsula emissions is further accentuated by their northern location and the lack of any other important emission sources in the Calotte region (Anttila 1995).

The smelter activities have also caused high heavy metal emissions in the Kola Peninsula. The annual copper emissions are about 200 t and nickel emissions 300 t in Nikel and Zapoljarnyi. The corresponding values for the Monchegorsk smelters are 2200 t and 3100 t, respectively. These emissions are high compared to the largest source of nickel emissions in Lapland, at Tornio, where the emissions are less than 2 tonnes Ni per year (Lapin lääninhallitus 1992).

1.4.3 The aims of the study

This thesis is a summary of the results which have been published in six journal articles (Appendices I - VI). Some new results are also presented. The aim of the thesis is:

1) to determine the distance to which the sulphur and heavy metal emissions from the Kola Peninsula point sources have an effect on the chemical composition of deposition, forest soil and percolation water,
2) to determine the effects of emissions from the Kola smelters on forest soil acidification processes,
3) to study the role of dissolved organic matter in natural acidification processes and its relationship to percolation water quality,
4) and to estimate the reliability of percolation water parameters (pH, Al concentration) used in soil acidification studies by determining the effects of transportation, pretreatment and storage on percolation water quality. A reliable and flexible protocol for the routine screening of Al fractions in soil solution (primarily inorganic monomeric Al) is also presented.

The deposition pattern of the Kola Peninsula emissions was determined using information obtained from the chemical composition of the snowpack, bulk deposition and stand throughfall. The acidity status and chemical changes in the soil were studied using soil and percolation water material. The effects of sample transportation, pretreatment and storage on percolation water acidification parameters were determined by comparing the results obtained using different sample treatment methods. The screening of inorganic monomeric Al in soil solution samples was tested by two methods (the ICP/AES and FIA methods).

2 MATERIAL AND METHODS

2.1 The gradient method

In the gradient method the area affected by emissions from a point source is investigated along a line running from the source. Indicator parameters are measured along the gradient line. The chemical composition of deposition, forest soil and percolation water with respect to the distance from the Kola Peninsula emission sources was studied using the gradient technique. There are many important aspects to be taken into account when the gradient method is employed for large areas. For example, the natural variation between the sample plots along the gradient line should be as minimal as possible, and sometimes statistical methods have to be used to control the variation. It is also important to eliminate the effects of the other emission sources in the area. These features must be taken into account already in the planning of the study.

The gradient technique was considered to be a suitable method for the study because the forest ecosystems in the north are relatively simple and contain only a low number of different plant species. Also, there are only two major point sources in the study area, Monchegorsk and Nikel. The other sources are insignificant compared to these ore-smelting complexes (Tikkanen 1995b). The gradient technique is a useful tool in large areas, especially when the studied parameters can be measured on an extensive level (samples are taken, for example, only once from each point). Snowpack and soil sampling are widely used to study the distribution of deposition and forest soil chemical properties over large areas (e.g. Tamminen & Starr 1990, Soveri & Peltonen 1995).

2.2 Intensive monitoring

The chemical composition of bulk precipitation, stand throughfall and percolation water was studied on the so-called intensive level. The water samples were collected continuously at monthly periods during the snowfree season. In soil solution studies, intensive continuos monitoring is important due to the large spatial and temporal variation in the chemical properties of the soil solution (Starr 1985) and to difficulties in obtaining water samples during the dry summer months.

2.3 Sample plot network

In this study the chemical composition of the snowpack and forest soil were determined on the extensive-level plots located along the gradient lines running from Monchegorsk and Nikel. Deposition and percolation water were studied on 13 intensive monitoring plots in Finnish Lapland, two plots near the Nikel smelters in Finnmark, Northern Norway, and eight plots on the gradient line running to the west of the Monchegorsk smelters in Russia (Fig. 1).

2.4 Methodological research

The methodological study was performed in order to determine the effects of sample handling and pretreatment on the pH values and aluminium concentrations of the percolation water samples. It is important to minimise the effects of sample transportation, pretreatment and storage on relatively sensitive soil acidification parameters, such as percolation water pH and Al concentration. Possible effects should be taken into account when soil acidification estimates are presented.

The aim of this part of the thesis was to study the effects of different sample treatment techniques on the results of chemical analyses using a number of different pretreatment combinations carried out on parallel subsamples. The second aim was to develop a reliable and flexible protocol for the routine screening of different aluminium fractions in large numbers of samples.

2.5 Vegetation and soil properties of the sample plots in the gradient study

2.5.1 Vegetation

The sample plots were located on as uniform as possible sites as regards stand and soil characteristics in order to minimise the natural variation between the plots. The dry or dryish sites (Cajander 1949)

Fig. 1. The sample plot network of the study.

were dominated by Scots pine (*Pinus sylvestris* L.). The age of the dominant tree layer was 80-200 years. The southern part of the study area lies in the central boreal coniferous zone, and the northern part in the northern boreal coniferous zone. The forest site type of the plots was originally *Empetrum-Cladina* type (EClT). Lingonberry (*Vaccinium vitis-idaea*) and heather (*Calluna vulgaris*) are typical ground vegetation species. However, due to reindeer grazing the sample plots represented very poor site types dominated by lichens and heather (ClT/CT). The most fertile sites represented *Empetrum-Vaccinium* type (EVT). The lichen cover was much stronger on the plots located on the Russian side of the border (Väre & Ohtonen 1995).

Needle loss reflects the overall condition of trees. No needle-loss gradient was found in Scots pine on the Finnish side of the border along the Monchegorsk gradient line (Salemaa et al. 1995). Needle loss varied constantly along the whole line. In contrast, needle loss increased on moving towards Monchegorsk on the Russian side of the border. The defoliation of Scots pine increased strongly at a distance range of 30-60 km from the Monchegorsk smelters (Salemaa et al. 1995). There was only one needle age class left on the plot 10 km from the source. The average needle loss around the smelters was 26%. The corresponding value in NE Lapland was 15% and in Central Lapland 13% (Salemaa et al. 1995).

On the intensive monitoring sample plot 8 km from the Monchegorsk smelters all the pine trees have died, and the ground vegetation and humus layer at many points are absent owing to widespread fires and subsequent soil erosion (about 40 % of the ground surface area lacked an organic layer). Some species have benefited from the absence of the original ground vegetation (e.g. *Trapeliopsis granulosa, Placynthiels oligotropa* and *P. uliginosa*). The sample plot located 10 km from Monchegorsk was also suffering from a loss of ground vegetation, although the situation was better than that on the plot at 8 km distance (Väre & Ohtonen 1995). The tree stand was suffering from severe needle loss (>60%) (Salemaa et al. 1995).

2.5.2 Bedrock and soil

The bedrock composition varies greatly in Lapland. The largest schist areas in Lapland are the Peräpohja area located in the Kemi-Tornio-Tervola area and the Central Lapland Greenstone belt linked with the Kuusamo schist area. The bedrock is composed of quartzites, phyllites, mica schists, mafic and acid plutonic rocks and dolomite limestones. The greenstone belt consists of mafic and ultramafic rocks. The largest granite gneiss areas are the Pudasjärvi, Koillis-Lappi and Taka-Lappi areas. The bedrock consists of acid plutonic and metamorphic gneisses. The Lapland granulite area extends north-westwards from Nellimö and Korvatunturi in the east to Karigasniemi in the west. Granulite is a metamorphic gneissose rock. The largest area of acidic plutonic rocks in Lapland is located in its central parts. The central Lapland granite area is located between Rovaniemi, Pello, Vaalajärvi and Salla (Simonen 1980).

In Finnish Lapland the Monchegorsk gradient line runs through bedrock areas consisting of volcanic rocks, quartzite and basement gneisses, and in Russia gneisses and gabbro. The major Pre-Quarternary rock areas are composed of granulite, basement gneisses and acid plutonic rocks in Finland, and gneisses and basaltic volcanite in Norway and Russia along the Nikel gradient line (Simonen 1980, Äyräs et al. 1997a).

The ground surface of the sample plots was either flat or sloping slightly eastwards. The soil type on the plots was classified as spodosols (USA Soil Taxonomy) (e.g. Schroeder 1984) or podzols (FAO - World Soil Classification) (FAO-Unesco 1990). The soils had a spodic B horizon enriched in Fe, Al and organic matter below the organic horizon (Of), comprising partly decomposed, fibrous organic matter, and below a bleached E horizon.

The soil on the intensive monitoring plots located in Finland (n = 12) were classified in the field as ferric podzols owing to the presence of a brown to red Bs horizon. Horizons were poorly developed on few studied plots. The thickness of the Of horizon was 1.0 - 4.5 cm, E horizon 0.5 - 7.5 cm, Bs horizon 5.5 - 14 cm and BC horizon 5 - 10 cm. The soil morphology on one of the thirteen plots was not very distinct, and it was therefore classified as an intermediate form between ferric and cambic podzol. The soil had a very thin E horizon (1 cm thick) and a B horizon (9 cm thick) visibly enriched with organic matter and Fe. The soil texture on the plots was sorted sand, except for two plots where relatively unsorted sand was dominant. The mean grain size on the plots was in the grain size classes 0.063 - 0.2 mm or 0.2 - 0.63 mm in all three soil layers (Fig. 2). The sorting index was below 3.0 on all the plots, except one plot were the value was 3.3 (Fig. 3). The content of soil material < 0.063 mm varied between 3 - 20 %, except on one plot where the value was 35 %. The soil organic matter content (loss in weight on ignition, LOI %) was 34 - 82 % in the Of horizon, 1 - 6 % in the E horizon, 0.6 - 5.0 % in the B+BC horizon and 0.3 - 3.0 % in the C horizon. Stoniness on ten of the sample plots was below 10 % and on three plots in the class 10 - 30 %.

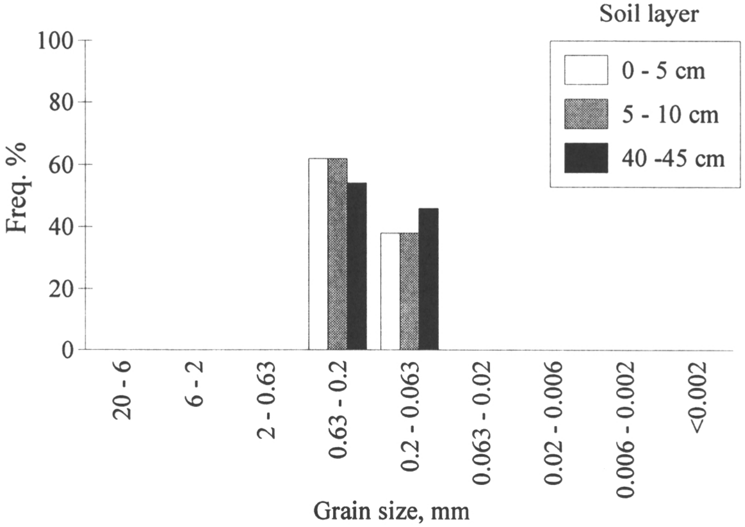

Fig.2. Frequency distribution of the mean grain size values of the intensive monitoring plots located in Finland (n = 13).

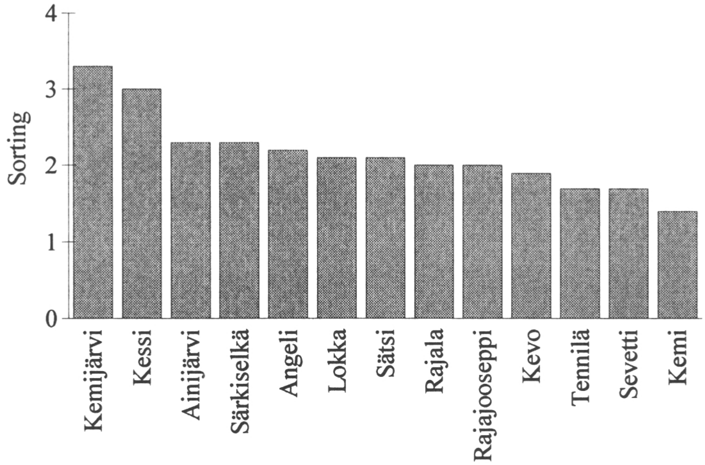

Fig 3. Mineral soil sorting index (square root(d75/d25)) of the intensive monitoring plots located in Finland. Sorting index has been calculated for the soil layer at a depth of 0 - 5 cm.

The soils on the gradient line running westwards from Monchegorsk were classified in the field as ferric podzols, except for one plot which was haplic podzol. Horizons were poorly developed on few studied plots. The horizon thickness of the haplic podzol was: Of horizon 9 cm, E 4.5 cm, Bh 8.5 cm and BC 19 cm. The soil had a continuous albic E horizon and a subhorizon within the spodic B horizon enriched with organic matter. The thickness of the Of horizon in the ferric podzols was 0.5 - 7.5 cm, E horizon 1 - 9.5 cm, Bs horizon 3 - 15 cm and BC horizon 5 - 23 cm. The soils on the plots consisted of sorted sand or gravel except on six plots located in Finland where the soil was sand and gravel-dominated till. The content of <0.063 mm material was 3 - 25 % except on three plots where the value was about 35 %. Stoniness was higher in the soils consisting of coarser material; generally the plots were in stoniness class < 30 %. The organic matter content of the organic horizon along the gradient line is presented in Fig. 4. The content of <0.063 mm material, mean grain size (d50), sorting (So) or stoniness (%) did not correlate with the distance from Monchegorsk along the gradient line. The correlation coefficients were: $r = 0.36$, $p > 0.05$, $n = 26$ (<0.063 mm material); $r = 0.1$, $p > 0.05$, $n = 26$ (d50); $r = 0.29$, $p > 0.05$, $n = 26$ (So) and $r = 0.14$, $p > 0.05$, $n = 21$ (stoniness). The thickness of the Of horizon correlated positively with the distance from Monchegorsk ($r = 0.56$, $p < 0.01$, $n = 22$) due to the fact that the sample plots nearest to the smelters had thin Of layers. The humus layer on the sample plot 8 km from Monchegorsk was thin and absent at many points (see 2.5.1. Vegetation).

The soils on the gradient line running from Nikel were classified in the field as ferric podzols, except for two plots where the soil type was an intermediate form between ferric and haplic podzol. The soil at these two plots had indications of a subhorizon in the B horizon which was enriched with organic matter or iron or both. The E horizon was continuous and albic. The thickness of the Of horizon in the ferric podzols was 0.5 - 3 cm, E horizon 1 - 6.5 cm, Bs horizon 9 -18 cm and BC horizon 10 - 35 cm. Horizons were poorly developed on few studied plots. The soil on the plots consisted of sorted sand, except on three plots in Finland where the soil was sand and gravel-dominated till. The content of <0.063 mm material was 1 - 25 %. Stoniness was higher on the soils composed of coarser material; generally the plots were in stoniness class < 30 %. The organic matter content of the organic horizon along the gradient line is presented in Fig. 5. The content of <0.063 mm material, mean grain size (d50), sorting (So), stoniness (%) or thickness of the Of horizon did not correlate with the distance from Nikel along the gradient line. The correlation coefficients were: $r = 0.30$, $p > 0.05$, $n = 13$ (<0.063 mm material); $r = -0.29$, $p > 0.05$, $n = 13$ (d50); $r = -0.1$, $p > 0.05$, $n = 13$

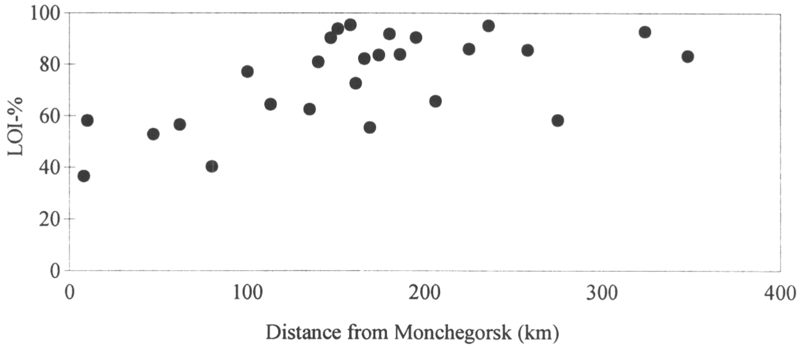

Fig. 4. The organic matter content (LOI-%) in the O horizon along the Monchegorsk gradient line.

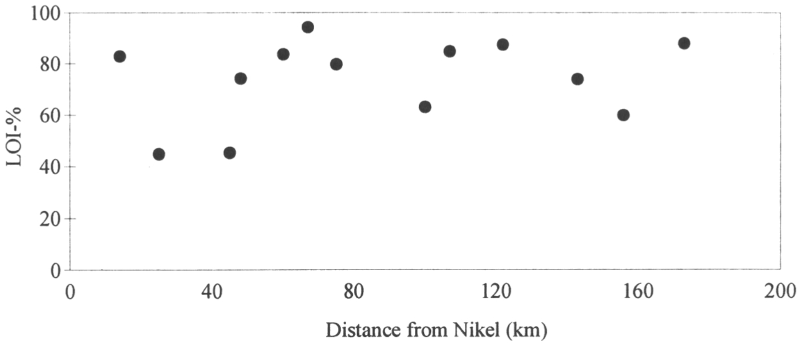

Fig. 5. The organic matter content (LOI-%) in the O horizon along the Nikel gradient line.

(So); $r = 0.27$, $p > 0.05$, $n = 13$ (stoniness) and $r = 0.12$, $p > 0.05$, $n = 13$ (Of horizon).

Sorted glaciofluvial and aeolian sediments cover approximately 10 % of the land area in the calotte region, and these sediments are fairly evenly distributed. The largest esker formations are situated in NW Lapland (Atlas of Finland 1990). The sorted sediments (sand and gravel) composed mainly of quartz and feldspars poorly reflect the chemical characteristics of the underlying bedrock.

2.6 Determination of snowpack chemistry

The aim was to investigate the extent of sulphur and heavy metal deposition in the area lying to the west of the smelter complexes at Nikel and Monchegorsk. The chemical composition of the snowpack was used as an indicator of air pollutants and their deposition. Snow samples were collected from the snowpack along two gradient lines running in a westerly direction from Monchegorsk and Nikel (Fig. 1). Samples were collected in March 1991, 1992 and 1993 before the spring thaw. Precipitation as snow can account for as much as 50 % of the total annual precipitation (Derome et al. 1991). Snow sampling should be carried out before thawing episodes due to their effect on the chemical composition of the snow. According to Johannessen and Henriksen (1978), 44-76 % of the chemical elements in the snowpack are mobilised during the melting of the first one third of the whole snowpack.

The samples were taken in flat open areas, avoiding nearby settlements, roads and forests. Snow samples were taken at six points on the sample plot. The thickness of the snowpack was measured at a total of 33 points. The criteria applied in choosing the sampling points on the sample plot were the flatness of the snowpack surface and similar thickness of the snow cover. A pit was dug in the snow next to the sampling point and a square plastic plate inserted horizontally into the face of the pit at a height of about 5 cm above the ground. The sampling tube was made of clear acrylic plastic (diam. 14.3 cm, length 150 cm) which permitted the integrity of the sample to be checked. The sampling tube was pushed down through the snowpack until it reached the plate. The tube was then removed and the snow sample transferred to a plastic bag. The six samples were combined in the field to give two composite samples. The sampling equipment was acid washed prior to use.

After transport to the laboratory, the samples were allowed to thaw at room temperature and then immediately filtered through filter paper. An aliquot was taken for pH measurement. Samples for metal analysis were preserved by adding Suprapur 65% nitric acid. The S, Cu and Ni determinations were made directly from the unconcentrated melt water by inductively coupled plasma atomic emission spectrophotometry (ICP/AES) (Jarva & Tervahauta 1993).

No attempt was made in sampling, sample pretreatment or analysis to follow the procedures required when analysing extremely small concentrations of heavy metals. The aim of the snowpack survey was to identify macropatterns of metal deposition.

Snowpack analysis has also been used in a number of other studies carried out near smelters as an indicator of deposition (Cerundolo 1992, Baklanov et al. 1993, Tchekin 1993, Äyräs et al. 1995). The formation of the snowpack is naturally not completely the same over extensive areas owing to variations in snowfall, wind patterns and temperature. For this reason the study was restricted to the pH and metal concentrations, and no attempts were made to calculate actual deposition levels.

2.7 Determination of chemical composition of the forest soil

The samples from the organic layer (O horizon) and E, B and C horizons were collected at sample plots located along gradient lines running from Monchegorsk and Nikel (Fig. 1). Samples were taken from 20 sampling points located systematically around the plot proper (300 m^2 in area). Mineral soil samples were taken from the topmost part of each genetic horizons, the sample layer being 7.5 cm thick in each horizon whenever possible. The fresh samples were homogenised by hand by rubbing through a 3 mm (organic layer samples) or 2 mm (mineral soil samples) sieve and the twenty subsamples combined to give one sample per horizon per plot. The samples were kept frozen until analysis.

Soil moisture content was determined by drying overnight in an oven at 105 °C. pH was measured in a soil/water slurry (15:25, v/v), and exchangeable base cations, Al and Cu were determined by extraction with 0.05 M $BaCl_2$ (Hendershot & Duquette 1986, Hendershot et al. 1993). Calcium, Mg, K, Na, Cu and Al were determined from the extract by ICP/AES. Titratable acidity of the organic layer samples was determined by titration with NaOH to pH 7 (Halonen et al. 1983). Exchangeable H^+ in the organic layer was considered to be the difference between titratable acidity and exchangeable Al. Effective cation exchange capacity of the organic layer was obtained as the sum of exchangeable base cations and Cu and titratable acidity. Base saturation (BS, %) was calculated as follows: $(Ca^{2+}+Mg^{2+}+K^{+}+Na^{+})/CEC*100$. The results for the organic layer were calculated on the basis of the organic matter content. The organic matter content was determined as the loss in weight on ignition (LOI %).

Total Cu and Ni were determined by dry digestion at 550 °C in a muffle furnace, followed by extraction of the ash with HCl. Copper and Ni were determined from the extract by ICP/AES. Extractable S of the organic layer was determined by extraction with 1 M ammonium acetate (pH 4.65). Sulphur was measured from the extract by ICP/AES.

2.8 Determination of the chemical composition of bulk deposition, stand throughfall and percolation water

The bulk deposition, stand throughfall and percolation water quality were studied on intensive monitoring plots (Fig. 1). In order to cause minimal disturbance to the sample plot proper (300 m^2), the intensive monitoring work has been performed on a "doughnut"-shaped plot, 300 m^2 in area, surrounding the plot proper. Bulk precipitation was collected at a suitable point in an open area using five rainwater collectors. An open area was considered to be a point where the nearest trees were situated at a distance exceeding the maximum height of the same trees. Stand throughfall was collected using 20 rainwater collectors located systematically on the sample plot. The total surface area of the five bulk deposition collectors was 0.157 m^2 and of the twenty stand throughfall collectors 0.628 m^2.

Percolation water was collected at three depths (5, 20 and 40 cm below ground surface) using a total of 12 gravity lysimeters installed in banks of three at four points around the sample plot. The lysimeters were installed by first removing an intact soil core (diam. 30 cm) down to the required depth, and then inserting the lysimeters in a shaft sunk below the removed soil core. After inserting the percolation water lysimeters, the soil core was carefully replaced. Percolation water was removed from the lysimeters by means of a nylon tube leading down into the collection bottle.

The rainwater and percolation water collectors were emptied at approx. 1-month intervals during the snowfree period. However, collection periods of varying length had occasionally to be used to prevent the rain collectors either overflowing, or to ensure that sufficient sample was obtained for the analyses.

Composite samples were taken from the bulk deposition and stand throughfall collectors. The samples for each percolation lysimeter were analysed separately. A time lag between sampling and pH measurement and pretreatment of the sample in the laboratory ranged from a few hours to two days. The water samples were not filtered prior to pH measurement. The samples were filtered through filter paper and percolation water samples additionally through 0.45 µm membrane filters (ME 25, Schleicher & Schuell). Subsamples for the determination of total S, P and metals by ICP/AES were preserved with 65% Suprapur nitric acid (0.25ml/50 ml sample). NH_4^+ and NO_3^- were determined by flow injection analysis (FIA), and the organic matter concentration as permanganate consumption according to the Finnish standard SFS 3036. Dissolved organic carbon (DOC) was determined on a TOC analyser. SO_4^{2-} and Cl^- concentrations in bulk deposition were determined by ion chromatography.

The experimental study on the effect of different sample treatment techniques on the soil solution chemical parameters were performed using samples collected from three permanent monitoring plots established as part of the ICP Forests project in 1995. The samples consisted of soil solution obtained using zero-tension lysimeters and suction-cup lysimeters. The zero-tension lysimeters were located at a depth of 5, 20 and 40 cm, and the suction-cup lysimeters at 20 and 40 cm. The samples were collected during 1996. Comparison of the sample treatment techniques was performed on the same series of samples for each treatment. No distinction was made between the samples obtained with different types of lysimeters or sampling depths, because the only interest of the study was to investigate possible differences between the sample treatment techniques. The effects of transportation and filtration were studied by means of different pretreatment combinations carried out on parallel subsamples.

The pretreatment combinations were as follows: 1) pH measurement prior to filtration in the field, 2) pH measurement in the field following filtration, 3) pH measurement in the laboratory prior to filtration, and 4) pH measurement following filtration in the laboratory. The samples were filtered through 0.45 µm membrane filters. The effect of storage on aluminium concentrations was investigated by keeping the samples at +4 °C for two weeks, and the effect of freezing by maintaining the samples for two weeks at -20 °C.

Total Al was measured by ICP/AES and total reactive Al by flow injection analysis (FIA). Both analyses were made before and after passage of the sample through a cation exchange column. Exchangeable dissolved Al was calculated as the difference between total Al (ICP) and non-exchangeable Al (ICP), and between total reactive Al (FIA) and non-exchangeable reactive Al (FIA).

2.9 Statistical methods

The relationships between the distance from the smelters and the measured parameters were studied using a linear regression model. Logarithmic transformation ($\log_{10}$) were used in order to ensure that the data corresponded to the requirements of regression analysis. The significance of the regression models was tested using the F- and t-tests.

The relationships between different chemical parameters were studied by calculating Pearsons correlation coefficients. Transformations were used whenever necessary. The statistical differences of the mean values were tested using Student's t-test (paired and unpaired) and ANOVA+Tukey.

3 RESULTS

3.1 The effect of sulphur emissions from the Kola Peninsula on sulphur concentrations in deposition, forest soil organic layer and percolation water

3.1.1 Sulphur concentrations along the Monchegorsk gradient line (I - IV)

The S concentration of the snowpack decreased strongly with increasing distance from the Monchegorsk smelters and reached a rather constant level at about 40 km from the source. The Finnish-Russian border is located at a distance of about 120 km to the west of Monchegorsk. The S concentrations in the snowpack varied from 0.37 to 0.95 mg/kg in the vicinity of the smelters (< 20 km distance). The highest value was obtained at 8 km in March 1991 (I).

The mean S concentration of the snowpack was 0.27 mg/kg along the gradient line running from Monchegorsk. The distance from Monchegorsk explained 75% of the variation in the snowpack S concentrations (regression analysis was performed on samples representing the distance range 8 - 62 km) (I).

Sulphur emissions from Monchegorsk have increased extractable S concentrations in the organic layer at the plot closest to the smelter (730 mg/kg o.m.). Elsewhere along the line there was only a very slight and non-significant increase in S concentration with decreasing distance to the point source (IV).

The S concentration in the percolation water collected at a depth of 5 cm also decreased with increasing distance from Monchegorsk. The highest median S concentration, 7.9 mg/l, was recorded at the plot closest to Monchegorsk (8 km). At a distance of 10 km the median was 5.6 mg/l and at 36 km 7.3 mg/l. The lowest S concentrations occurred at the plots 47 - 80 km from the smelter (2.9 - 3.5 mg/l). There was a significant negative correlation between the distance from the Monchegorsk smelter and the S concentration in percolation water. The distance explained 28 - 40 % of the variation in the percolation water S concentrations during 1991-1993 (II).

The percolation water S concentrations were lower on the plots in Finnish Lapland than in the vicinity of the Monchegorsk smelter. The median S concentration on the plots located in Finland was 3.7 mg/l at a depth of 5 cm. The S concentration did not change with increasing soil depth. The median value was 3.8 mg/l at a depth of 20 and 40 cm (III). The highest plotwise values were recorded at Sevetti and Tennilä; the median S concentrations were 4.4 mg/l and 4.2 mg/l at a depth of 5 cm, respectively (Lindroos et al. 1995).

The sulphur emissions from Monchegorsk were reflected in the sulphur concentrations of the snowpack, organic soil layer and percolation water in the Russian section of the gradient line. In Finland no signs of the Monchegorsk emissions were detected.

3.1.2 Sulphur concentrations along the Nikel gradient line (I, IV, V)

The snowpack S concentration decreased slightly with increasing distance from the Nikel smelters, but the decrease was not as clear as that at Monchegorsk. The distance from Nikel explained 42% of the variation in the S concentration (regression analysis was performed on the distance range 14 - 100 km). The mean value for the gradient line, 0.20 mg/kg, was lower than the corresponding value for the Monchegorsk line. The highest values were recorded at a distance of < 40 km (max. 0.40 mg/kg) (I). The S concentration in bulk deposition and stand throughfall decreased significantly with increasing distance from the Nikel smelters (V).

The Nikel smelters have had no effect on the extractable S concentration of the organic layer (IV). Neither were there any significant differences in the percolation water S concentrations (depth of 5 cm) on moving away from the Nikel smelters (V).

The sulphur emissions from Nikel were reflected in the bulk deposition and stand throughfall, as well as to a some extent in the snowpack. However, the S concentrations in the snowpack did not increase as sharply as those close to Monchegorsk. The emissions from Nikel have had no effect on sulphur concentrations in the soil; neither S levels in the organic layer nor in percolation water.

3.2 The acidity status of deposition, forest soil and percolation water along the gradient lines

3.2.1 The acidity status along the Monchegorsk gradient line (I-IV, unpublished data)

There was no gradient in the snowpack pH values with respect to the distance from Monchegorsk. The mean pH was 4.92 along the gradient line. An exception to the rather constant pH level along the line were the elevated values close to the open-cast mine at Kovdor, 100 km from Monchegorsk (I).

Emissions from Monchegorsk have had no effect on the pH(H_2O) of the organic layer. Exchangeable H^+ in the organic layer was somewhat depressed close to the smelter. However, the difference was not statistically significant. Exchangeable Al in the organic layer increased significantly with decreasing distance to Monchegorsk. The values were rather low and constant at distances greater than 100 km. Base saturation in the organic layer decreased towards Monchegorsk owing to the low values at two of the plots near the smelter (<20% closest to the smelter) (IV).

There were no decreasing pH(H_2O) gradients in the mineral soil horizons on moving towards the emission source. In fact, a significantly increasing gradient was found in the E and B horizons. No significant pH changes along the gradient line were observed in the C horizon (Fig. 6). No gradients were found in exchangeable Al concentrations in the mineral soil horizons (Fig. 7).

The concentration of exchangeable base cations (Ca^{2+}+Mg^{2+}+K^+) followed a similar gradient as the base saturation in the organic layer. The base cation concentration was low at two of the plots near the smelter. In the mineral soil no gradients were found in the base cation concentrations (Fig. 8).

Correlation coefficients were calculated for the combined soil data from the sample plots located on the Finnish side of the border along the two gradient lines in order to estimate the effect of the variation in natural soil factors on the chemical parameters. These correlations were studied using the Finnish plots only due to the possible influence of the emissions from the point sources on the soil chemical properties. Neither pH nor the concentrations of exchangeable Al and base cations in the organic layer and in the mineral soil (E, B and C horizons) correlated with soil factors such as mean grain size, sorting, fine material <0.063 mm, stoniness or thickness of the Of horizon owing to the fact that the variation in these soil properties was relatively small. Exceptions to this were the significant ($p < 0.05$) positive correlations found between

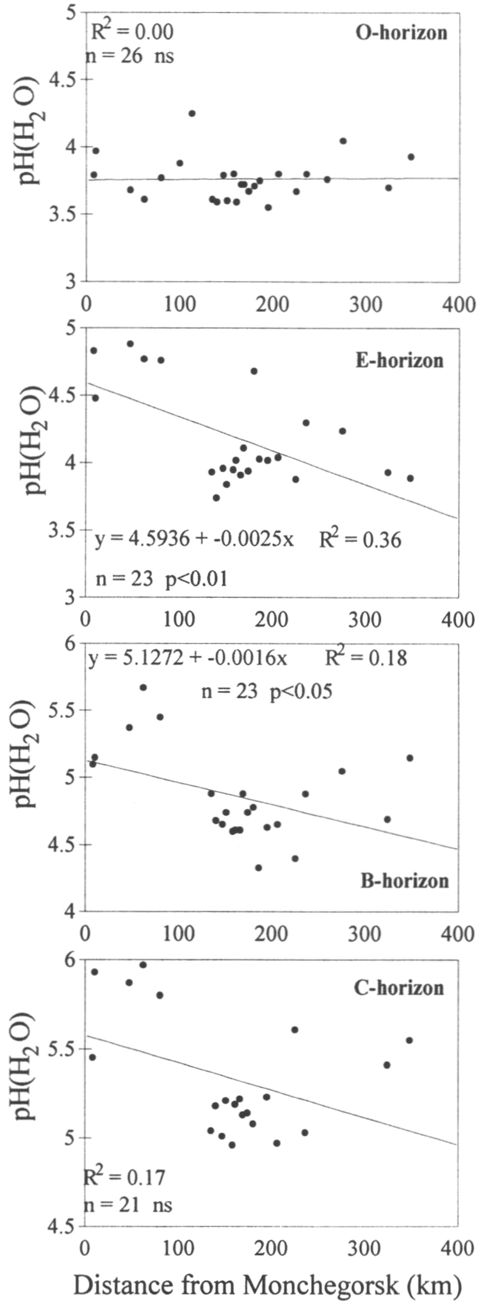

Fig. 6. pH in the different soil horizons along the Monchegorsk gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test).

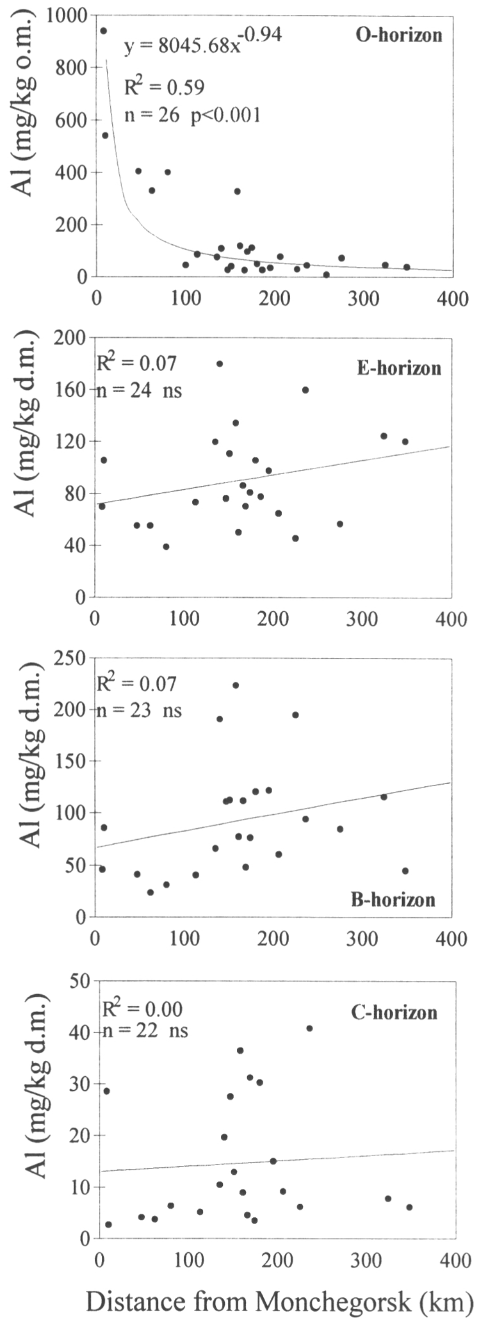

Fig. 7. Exchangeable Al in the different soil horizons along the Monchegorsk gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter, d.m. = dry matter.

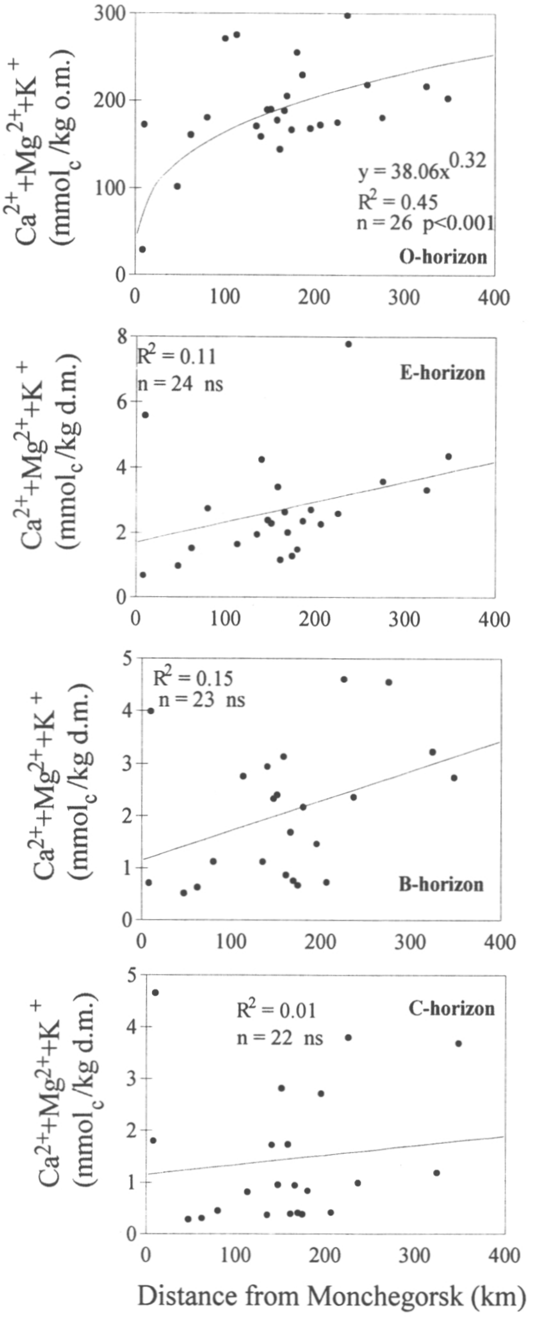

Fig. 8. Exchangeable base cation concentration in the different soil horizons along the Monchegorsk gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter, d.m. = dry matter.

exchangeable Al and the proportion of soil material <0.063 mm in the E and B horizons (r = 0.44 and r = 0.52, respectively, n = 27). However, the correlations were dependent on one or two of the largest fine material values and, when these values were omitted from the analysis, no significant correlations were obtained.

The largest fine material values (about 35 %) occurred on the Monchegorsk gradient line within a distance of about 150 - 220 km from the smelters, where the exchangeable Al concentrations in the mineral soil were also at their highest. Omitting these plots from the regression analysis between the exchangeable Al concentration and the distance from Monchegorsk, did not improve the relationship, and hence these plots do not affect the conclusion.

There was no gradient in the pH of the percolation water (depth 5 cm) with respect to the distance from the Monchegorsk smelters. The lowest pH values were recorded at the plot 36 km from Monchegorsk where the median value was 4.11. On the other plots located in Russia (at a distance range 8 - 80 km) the pH medians varied from 4.31 to 4.75 (II).

The median pH value in percolation water (depth 5 cm) was 4.70 for the plots located in Finland. The pH increased significantly with increasing soil depth from 5 to 20 cm, but not from 20 to 40 cm. The pH medians were 5.26 and 5.41 at depths of 20 and 40 cm, respectively (III). The lowest plotwise pH values in Finland were recorded at Sevetti, where the median pH was 4.35 at a depth of 5 cm (Niska et al. 1995).

According to the pH values in the snowpack, forest soil and percolation water, there was no increase in the acidity status on moving towards Monchegorsk. There was no increase in the H^+ concentration in the organic layer either. However, the increased exchangeable Al levels, as well as the decreased base saturation and base cation concentration in the organic layer, indicate considerable soil changes in the vicinity of the Monchegorsk smelter. There were no statistically significant gradients in the exchangeable Al or base cation concentrations in the mineral soil.

3.2.2 The acidity status along the Nikel gradient line (I, IV, V, unpublished data)

There was no clear gradient in the snowpack pH values with respect to the distance from the Nikel smelters. The pH values were rather constant along the line and the differences between the years 1991, -92 and -93 were negligible. The mean pH along the line was 4.96, i.e. slightly higher than the corresponding value for the Monchegorsk line

(I). No clear gradient was found in the pH of bulk deposition or stand throughfall either (V).

The variation in pH(H_2O) of the organic layer along the Nikel line was considerably greater than that along the Monchegorsk line. Emissions from Nikel have had no effect on the pH of the organic layer. However, there was a significant increase in exchangeable H^+ with decreasing distance to the Nikel smelters. The distance to the Nikel smelter had no significant effect on exchangeable Al concentrations in the organic layer. In contrast, base saturation decreased significantly with decreasing distance to Nikel (IV).

The distance from Nikel did not correlate with the pH(H_2O) in the mineral soil, except in the B horizon where slightly decreasing pH values were observed with decreasing distance to the smelters (Fig. 9). No increasing gradient were found in exchangeable Al in the mineral soil on moving towards Nikel (Fig. 10). The base cation concentration followed a similar gradient to that of base saturation in the organic layer, i.e. a decreasing gradient on moving towards Nikel. The same was also true for the E horizon, but not for the B and C horizons (Fig. 11).

The emissions from Nikel had no effect on the acidity status of percolation water collected at a depth of 5 cm; no decreasing gradient in pH values or increasing gradient in Al concentrations were found with decreasing distance to the point source (V).

According to the pH of deposition, forest soil and percolation water, the acidity status was relatively constant along the Nikel gradient line, and did not increase in the vicinity of the smelters. However, the increased H^+ concentration and decreased base saturation and base cation concentration in the organic layer on moving towards the Nikel smelters may be a sign of acidification. Base cation concentrations were also relatively low in the E horizon near to the point source.

3.3 The role of sulphur deposition and dissolved organic matter in acidification processes (I - V, unpublished data)

The elevated sulphur deposition in the vicinity of the Monchegorsk smelters is not necessarily associated with acidic deposition, because no correlation was found between the sulphur concentration and pH in the snowpack (I). No connection was found between percolation pH and S concentrations either (II). Despite the fact that the extractable S concentration in the organic layer was strongly elevated near Monchegorsk, no decreasing gradient was observed in organic layer pH nor an increasing gradient in exchangeable H^+ (IV). The elevated

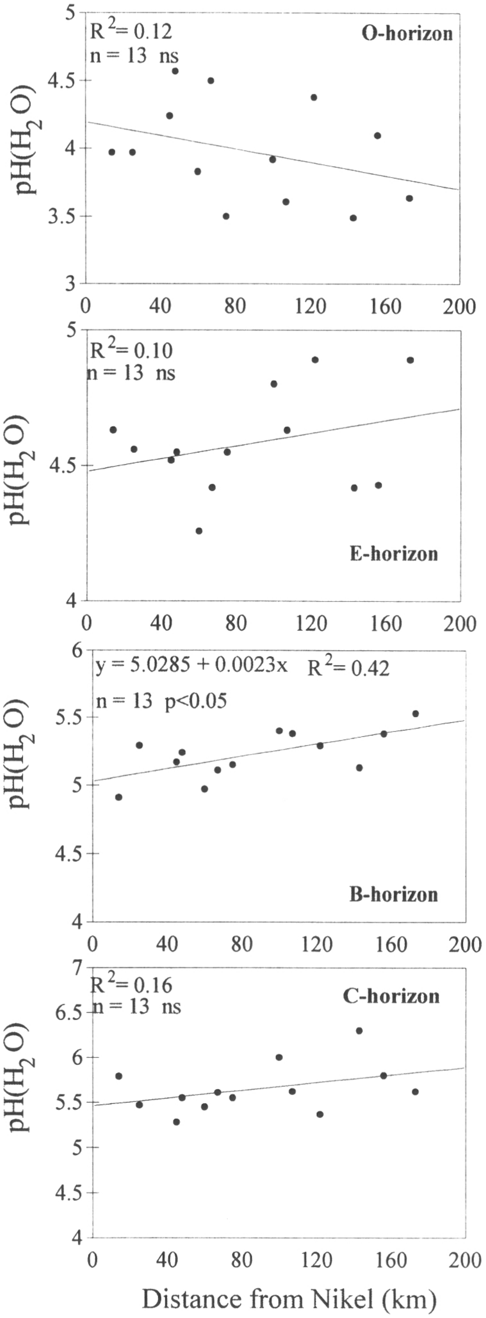

Fig. 9. pH in the different soil horizons along the Nikel gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test).

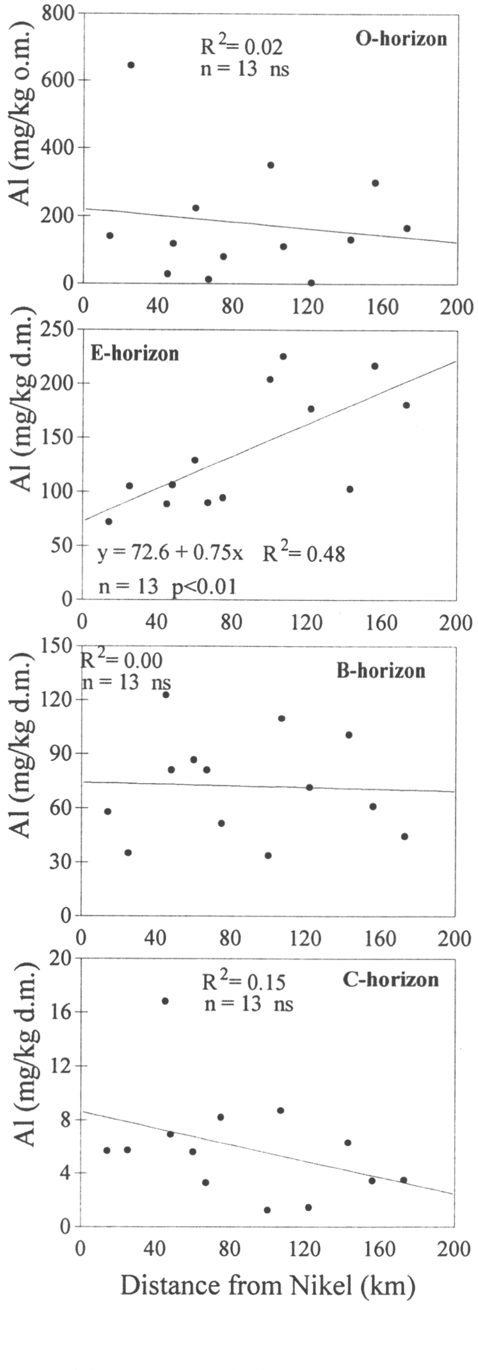

Fig. 10. Exchangeable Al in the different soil horizons along the Nikel gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter, d.m. = dry matter.

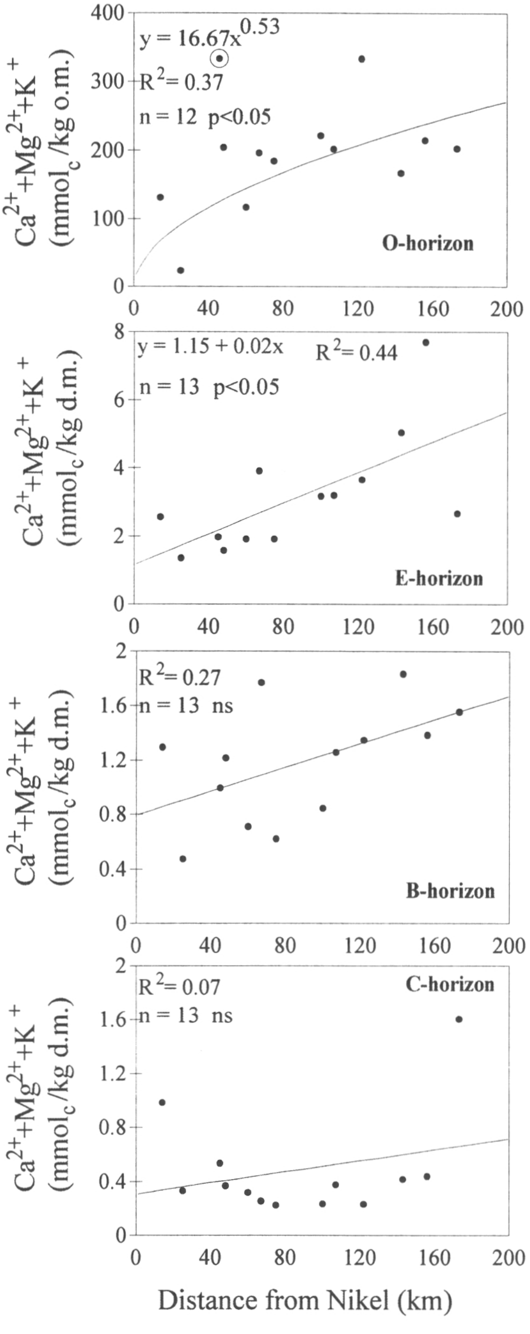

Fig. 11. Exchangeable base cation concentration in the different soil horizons along the Nikel gradient line. The ringed value is excluded from the analysis in order to give a better fit for the regression line along the whole gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter, d.m. = dry matter.

exchangeable Al concentrations, as well as the depressed base saturation and base cation concentration (Fig. 8) in the organic layer in the vicinity of the Monchegorsk smelters are obviously due to processes other than acidification caused by acidic deposition (IV). For example, the deposition of dissolved Al is significantly elevated near Monchegorsk, which is undoubtedly reflected in the organic layer composition (Äyräs et al. 1995).

There was a significant negative correlation between the S concentration and pH in the snowpack along the gradient line running from Nikel. This could indicate that there is a connection between sulphur and acidic deposition. However, this finding is of little significance because the variations in pH and S concentrations along the line were very small (I). The extractable S concentration or pH values in the organic layer did not indicate increased soil acidity on moving to Nikel (IV). Although the concentration of exchangeable H^+ increased and base saturation and base cation concentration (Fig. 11) decreased significantly in the organic layer towards Nikel (IV), the connection between soil changes and the acidifying sulphur deposition is somewhat unclear. However, the situation close to Nikel better fulfils the definition of soil acidification than the situation close to Monchegorsk. There were no increasing S or decreasing pH gradients in the percolation water on moving towards Nikel either (V).

One of the main aims of this study was to determine possible connections between the sulphur dioxide emissions from the Kola Peninsula and acidifying deposition, and their relationship with soil acidification processes. However, the role of natural phenomena in soil acidification processes appears to be dominant in most parts of the study area because no correlation was found between sulphur deposition and soil acidification processes.

On the sample plots located in Finland, significant negative correlation was found between percolation water pH and dissolved organic matter concentration (DOM) at a depth of 5 cm. This indicates that weak organic acids play an important role in controlling percolation water acidity in natural conditions (III). The percolation water DOM concentration decreased significantly with increasing soil depth: 144 mg/l (mean, 5 cm depth), 44 mg/l (20 cm) and 17 mg/l (40 cm). No correlations were found between the percolation water pH and DOM at depths of 20 and 40 cm (III).

The dissociated organic acids in the soil act as anions that readily form complexes with metals. The organic aluminium complexes are non-toxic to plants. On the sample plots in Finland, percolation water DOM correlated positively with the dissolved total aluminium concentration at depths of 5 and 20 cm. The correlation was the strongest at 20 cm depth. This indicates that a high proportion of the dissolved aluminium in the topsoil is in the form of organic complexes (III).

The median total Al concentrations in percolation water (depth 5 cm) were below 1 mg/l on all the plots located in Finland (Niska et al. 1995). The mean value for the whole sample plot network was also very low, 0.68 ± 0.74 mg/l (depth 5 cm). The percolation water Ca/Al molar ratio was 1.3 (depth 5 cm), 3.2 (20 cm) and 8.2 (40 cm) calculated using the median Ca and total Al concentrations for the sample plot network (III). According to de Vries (1993), the critical Ca/Al ratio is <1.0. However, there has been a lot of criticism about the importance of the Ca/Al ratio and its critical value (e.g. Løkke et al. 1996).

The difference between the cation sum (H^+, Ca^{2+}, Mg^{2+}, K^+, Al^{3+}, Mn^{2+}, NH_4^+) and anion sum (SO_4^{2-}, PO_4^{3-}, NO_3^-) in the percolation water (depth 5 cm) indicate that there was an anion deficit in 85 % of the samples collected on the plots located in Finland. The anion deficit correlated positively with the DOM concentration, reflecting the anionic nature of the dissolved organic matter (III).

Dissolved organic matter has a major regulating effect on percolation water acidity in areas subjected to low acidic deposition. The dissolved organic matter controls the acidity, proportion of different aluminium fractions, as well as the ionic balance of the percolation water.

3.4 The effects of copper and nickel emissions from the Kola Peninsula on the chemistry of deposition, forest soil and percolation water

3.4.1 The Cu and Ni concentrations along the Monchegorsk gradient line (I, II, IV, unpublished data)

The Cu and Ni concentrations in the snowpack decreased significantly with increasing distance from the Monchegorsk smelters. The highest concentrations were recorded in March 1991 on the plot (8 km) nearest to the emission source. The Cu concentration was 421 µg/kg and Ni concentration 180 µg/kg. According to the regression analysis performed on the distance range 8 - 38 km, the distance from Monchegorsk explained 70% of the variation in the Cu and 80% in the Ni concentrations in the snowpack (I).

The Cu and Ni concentrations in the percolation water (depth 5 cm) decreased significantly with increasing distance from Monchegorsk. The highest median Cu concentration was 95 µg/l measured on the plot (8 km) nearest to Monchegorsk. The highest Ni median concentration was also determined on the same plot, 561 µg/l. However, there was considerable variation in the Cu and Ni concentrations of the percolation water in the vicinity of the smelters. The distance from Monchegorsk correlated negatively with the Cu and Ni concentrations. Distance explained 38 - 55% of the variation in the Cu concentrations and 77 - 88% in the Ni concentrations of the percolation water (II).

The total Cu and Ni concentrations in the organic layer decreased significantly with increasing distance from the Monchegorsk smelters. The Cu and Ni concentrations were strongly elevated on the plots closest to the point source compared to the other plots along the line. Elevated Cu and Ni concentrations extended for ca. 100 km along the line (IV).

Exchangeable and total Cu concentrations followed a similar gradient along the Monchegorsk line. When the high values of exchangeable or total Cu close to Monchegorsk were excluded from the analysis, no gradients were found in the mineral soil horizons along the line (Figs 12 and 13). Total Ni concentrations were also high in the mineral soil near Monchegorsk. However, the increasing gradient was strongly dependent on the one or two high values measured on the plots nearest to the point source (Fig. 14).

The Cu and Ni emissions from Monchegorsk had a significant effect on the chemical properties of the snowpack, percolation water and forest soil in the vicinity of the smelters. The emissions were reflected in the snowpack only at distances of less than 30 km from the source. The emissions were also detectable in the percolation water at the same distance. Elevated Cu and Ni concentrations in the organic layer were detectable even at a distance of 100 km. Elevated concentrations in the mineral soil were found only on the plots 8 and/or 10 km from Monchegorsk.

3.4.2 The Cu and Ni concentrations along the Nikel gradient line (I, IV, V, unpublished data)

The Cu and Ni concentrations in the snowpack and percolation water were below the analytical detection limit even on the plots located in Finnmark, Northern Norway, relatively close to the emission sources (I, V).

Elevated total Cu concentrations in the organic layer were measured at distances of less than 50 km from the Nikel smelters. The Cu values decreased significantly with increasing distance. The highest values were less than 1/10 of the highest measured values near

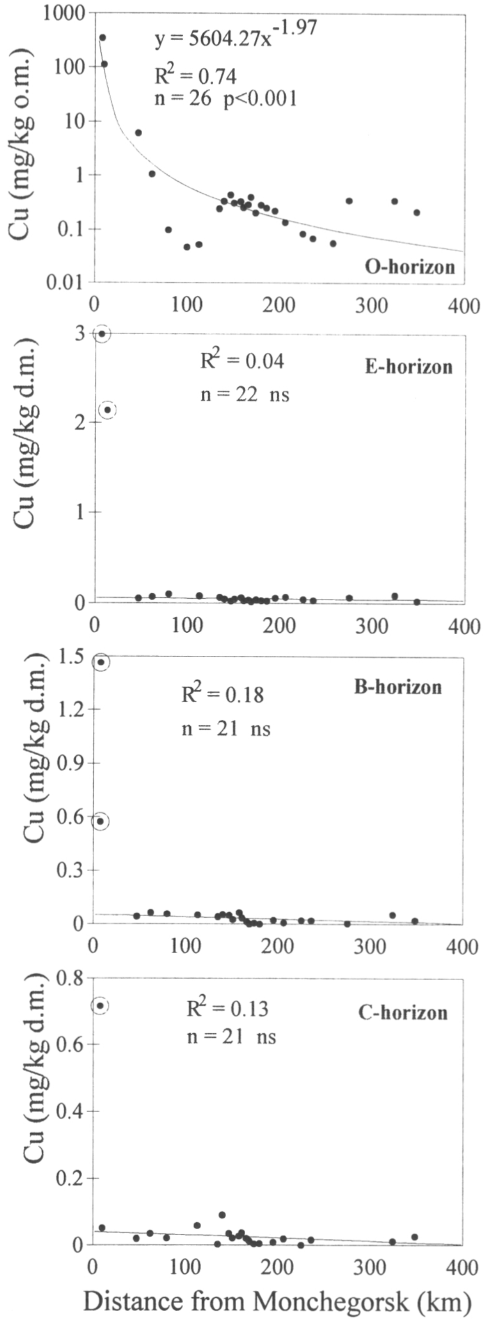

Fig. 12. Exchangeable Cu concentration in the different soil horizons along the Monchegorsk gradient line. Ringed values are excluded from the analysis in order to give a better fit for the regression line along the whole gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter, d.m. = dry matter.

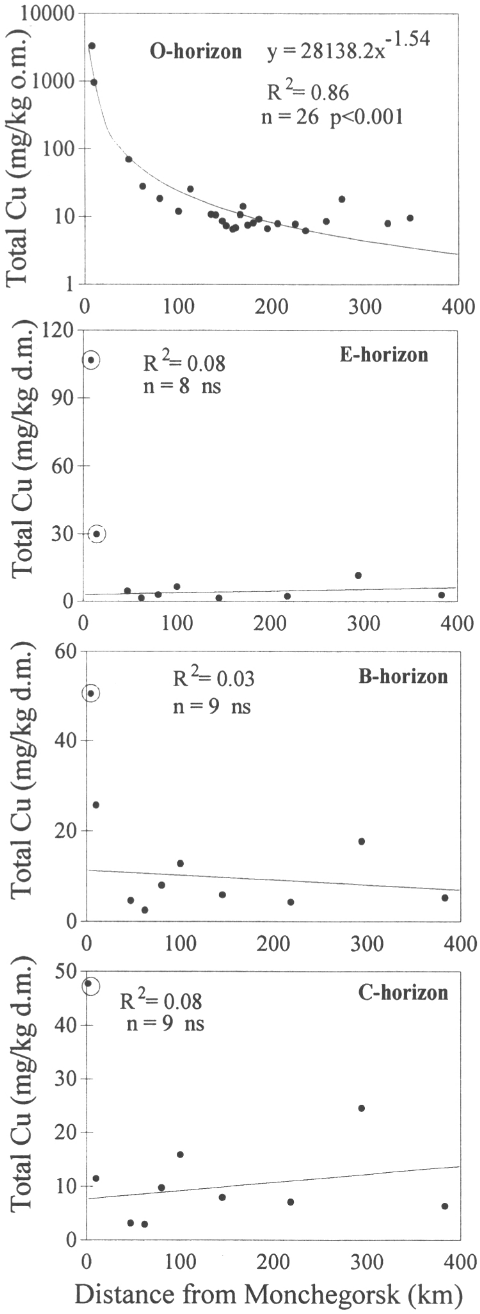

Fig. 13. Total Cu concentration in the different soil horizons along the Monchegorsk gradient line. Ringed values are excluded from the analysis in order to give a better fit for the regression line along the whole gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter, d.m. = dry matter.

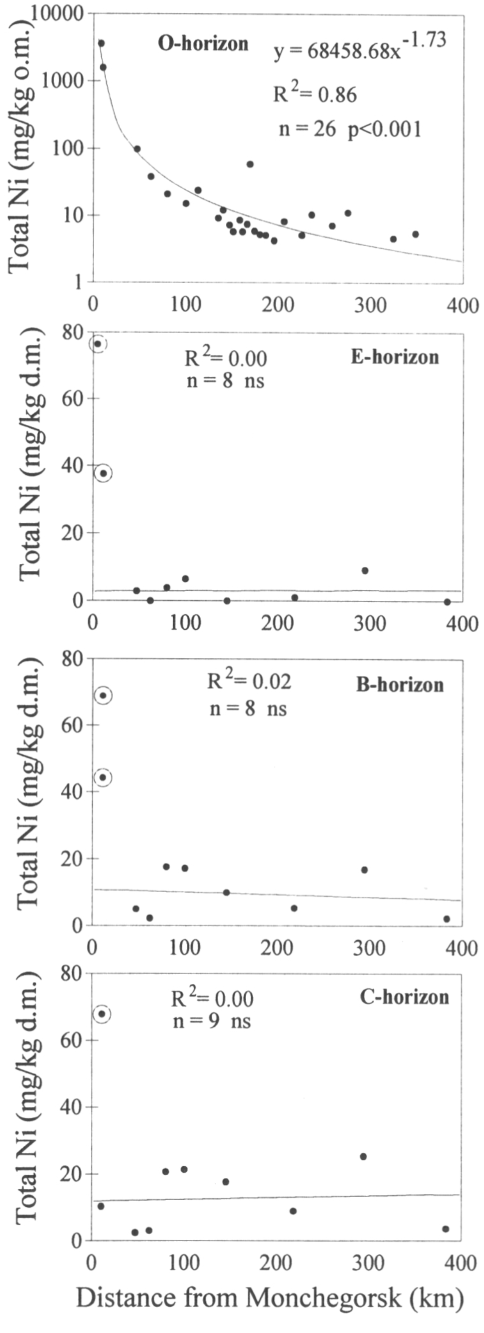

Fig. 14. Total Ni concentration in the different soil horizons along the Monchegorsk gradient line. Ringed values are excluded from the analysis in order to give a better fit for the regression line along the whole gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter, d.m. = dry matter.

Monchegorsk. There was also a significant decreasing gradient in the total Ni concentration of the organic layer with increasing distance from Nikel. Elevated concentrations were still detectable at a distance of about 70 km from the sources. The highest Ni concentrations were also considerably smaller than the corresponding values in the vicinity of the Monchegorsk smelters (IV). No increasing gradients in the Cu or Ni concentrations were found in the mineral soil, except for exchangeable Cu in the E horizon. The exchangeable Cu concentration was the highest on the plot nearest to Nikel (Figs 15, 16 and 17).

Thus, the effects of heavy metal emissions from Nikel were clearly detectable in the chemical composition of the organic layer, but not in deposition or percolation water.

3.5 Percolation water pH and Al concentration - the effects of transportation, pretreatment and storage, and the ICP/AES and FIA methods in Al fractionation (VI)

In the gradient study, percolation water pH was measured in the pretreatment laboratory. This meant that the time lag between sampling and pretreatment ranged from a few hours to a couple of days. The reported pH values are very reliable because transportation, i.e. the time lag between sampling in the field and pretreatment in the laboratory, had only a slight effect on sample pH. The mean pH of the soil solution samples increased significantly due to the time lag, but the increase was only 0.1 pH units (VI).

The percolation water samples were filtered through 0.45 µm membrane filters to remove fine particles from the samples after pH measurement. All the chemical analyses apart from pH were performed only on filtered samples. The effect of filtration on water pH was tested. However, filtration was found to have no statistically significant effect on sample pH (VI). Thus the pH values measured on the unfiltered samples were compatible with the other chemical parameters determined from the filtered samples.

The effect of the time lag between filtration and analysis on soil solution aluminium concentrations was also tested. Filtration removes fine particles which are potential sources or sinks of aluminium. However, filtration in the field or in the laboratory had no significant effect on the total Al or fractionated non-exchangeable Al concentrations in soil solution (VI).

In the gradient study the percolation water samples were conserved with Suprapur nitric acid and then stored in a refrigerator for a couple of weeks before ICP/AES analysis. When the pH of the

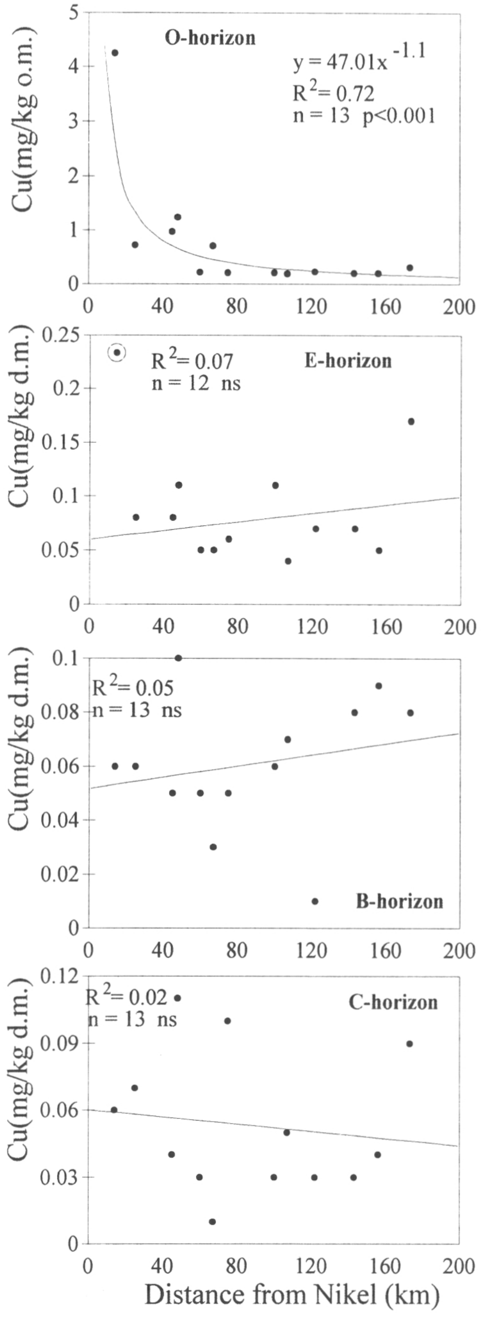

Fig. 15. Exchangeable Cu concentration in the different soil horizons along the Nikel gradient line. The ringed value is excluded from the analysis in order to give a better fit for the regression line along the whole gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter, d.m. = dry matter.

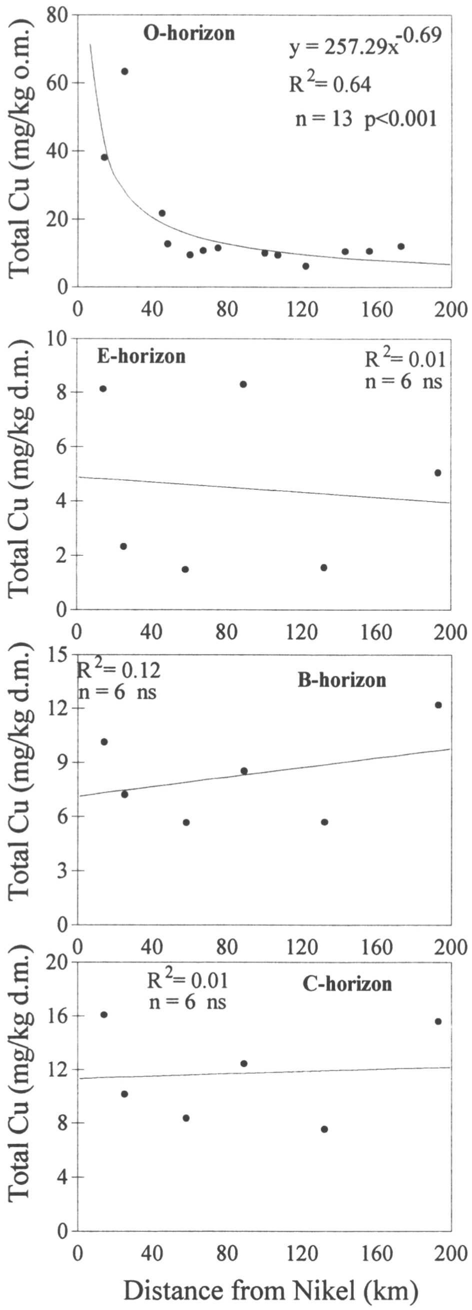

Fig. 16. Total Cu concentration in the different soil horizons along the Nikel gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter, d.m. = dry matter.

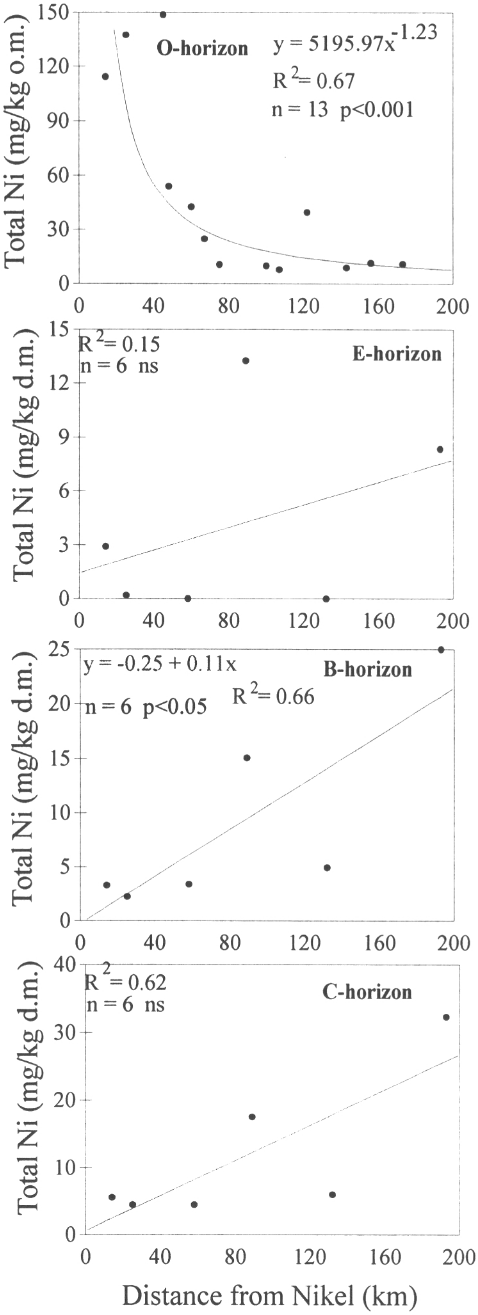

Fig. 17. Total Ni concentration in the different soil horizons along the Nikel gradient line. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter, d.m. = dry matter.

sample was adjusted to <3.7 there was no change in the total Al or non-exchangeable Al concentrations after two weeks' storage. Two weeks' storage without pH adjustment did not change the total Al concentration in soil solution either. Thus, if total Al only is measured and the analysis can be performed within two weeks, it is not necessary to preserve the sample. However, preservation is a useful tool when the samples must be stored for several weeks before analysis. Freezing the samples was also found to be an inappropriate storage technique because it resulted in a strong decrease in the total Al concentrations (VI). The total Al concentration and pH measurements of the percolation water samples in the gradient study appeared to be very reliable, and the effect of transportation, filtration and storage on the pH and total Al values insignificant.

The second aim of this part of the study was to compare the results obtained for Al fractions (primarily positively charged Al ions, inorganic monomeric Al fraction) in soil solution by the ICP/AES and FIA methods. The concentration of dissolved exchangeable Al determined indirectly by ICP/AES and by FIA was very similar, which means that either of these two methods can be used for determining the positively charged Al fraction, but if non-exchangeable reactive Al fraction (i.e. organically complexed monomeric Al) is required then FIA is also necessary (VI).

4 DISCUSSION

4.1 The effects of emissions from Monchegorsk

According to this study the emissions from Monchegorsk have had no clear effect on the chemical properties of the forest soil or percolation water in Finnish Lapland. The study sites were considered to be very sensitive to anthropogenic deposition because they represent dry, rather infertile forest types. The main reason for the negligible effect of the Monchegorsk emissions is the low deposition of sulphur compounds and heavy metals in Finland. The distribution of emissions is controlled by the prevailing winds that, depending on the season, are from the north, south or north-west (Barcan 1993). The high fell chain located on the westerly side of Monchegorsk also restricts the transport of emissions directly to the west (Mikkola 1995).

Sulphur emissions from Monchegorsk were detectable as elevated S concentrations in the snowpack only at distances of less than 30 km to the south and west of the smelters. Sulphur deposition is not necessarily connected with acidic deposition because there was no corresponding pH gradient in the snowpack. Snowpack sampling is a widely used, reliable method for estimating deposition acidity. For example, according to Soveri and Peltonen (1995), the highest concentrations of acidifying components (H^+, SO_4^{2-}, NO_3^- and NH_4^+) in the snowpack in Finland occur in the southern parts of the country, and there is a significant positive correlation between the H^+ and SO_4^{2-} concentration. High concentrations of H^+, SO_4^{2-}, NO_3^- and NH_4^+ in snow in south-eastern Norway have been attributed to the long-range transport of pollutants (Wright & Dovland 1977).

Äyräs et al. (1995) collected snow samples in March/April 1994 from three catchments near the Monchegorsk smelters and from two catchments located in background areas in Naruska and Pallas in Finnish Lapland. The pH of filtered snow meltwater was higher near Monchegorsk than at Naruska and Pallas, where there are no significant local emission sources. Median S concentrations in filtered snow meltwater (825 ppb) and filter residues (200 ppb) were strongly elevated near Monchegorsk compared to the catchments in the background areas. These results are in very good agreement with the results obtained in this thesis.

In contrast to the results of this thesis and those of Äyräs et al. (1995), Lukina & Nikonov (1995) reported that the pH of summer- and winter-time precipitation has declined in the polluted area near Monchegorsk. According to them, there is only partial neutralisation of protons by alkaline particles in the emissions, and the pH in summer- and winter-time precipitation between the tree crowns was positively correlated with distance from the emission source. However, the distance explained only 23 % of the variation in the precipitation pH values in summer and 27 % in winter. Baklanov et al. (1993) collected snowpack samples at varying distances from Monchegorsk during late spring in 1991. Samples were collected both in the vicinity of the smelter (the nearest point at about 10 km) and from remote locations to the east of the point source. Despite the higher SO_4^{2-} concentrations in snow near Monchegorsk, the pH was not significantly lower. The authors concluded that this appears to be a result of acidity reducing reactions by the other deposited compounds.

The dust emissions are significant in the Kola Peninsula, and there are some indications of their ability to reduce deposition acidity (Anttila 1995). According to this thesis, the exceptionally high pH values in the snowpack (over 6.0) along the part of the Monchegorsk gradient line close to the open-cast mine at Kovdor suggest that the dust input is important. Reimann et al. (1996) reported even higher pH values (7.2) in filtered snow meltwater in the vicinity of the large open-cast mine only a few kilometres to the east of the Nikel smelter. The authors assumed that this was due to dust input from the mining of basic rocks and handling of the stockpiles of ore.

According to this thesis, the chemical properties of the forest soil or percolation water did not indicate increased soil acidity due to sulphur deposition along the part of the gradient line in the immediate vicinity of Monchegorsk. The sulphur concentration of the organic layer and the sulphur concentration in percolation water (depth 5 cm) clearly increased in the vicinity of Monchegorsk, but the lack of any pH or H^+ gradient suggests that deposition has so far had no effects on these acidity parameters. In theory, buffering and neutralisation reactions in the soil could maintain the pH of percolation water at the background levels even in areas with high levels of acidifying deposition. The effect of acidifying compounds should, however, be reflected in the pH of deposition especially. According to Reuss & Johnson (1986), soil solution may become acidified rapidly even though the pH of the soil itself is little affected. Acidifying sulphur deposition may affect soil and percolation water in different ways.

The pH of percolation water (depth 5 cm) was at its lowest at a distance of about 30 km from Monchegorsk. Slightly lower pH values were detected in 1991 and 1993, but not in 1992. The pH values in the vicinity of the smelter were not lower than those at more distant parts along the gradient line. Lukina & Nikonov (1995) reported increased concentrations of DOC, base cations, SO_4^{2-}, Cl^-, $NH_4^+$and Al in percolation water collected below the humus layer of pine stands at distances of about 30-40 km to the south and west of Monchegorsk. They concluded that the increased concentrations of base cations could be explained by displacement of these cations from the cation exchange sites by protons derived from atmospheric deposition. Other explanations which they proposed for the increased concentrations of these compounds was the increased concentration of DOC, the mineralization of large amounts of litterfall, and the leaching of elements from the damaged needles.

Reimann et al. (1997) measured the pH($CaCl_2$) of the topsoil (0-5 cm) in three catchments near Monchegorsk and three in Finland. The mean pH was 2.8 in the vicinity of Monchegorsk, 3.0 about 25 km to the south and 3.6 about 50 km to the east of the source. The corresponding values for the Finnish catchments were 2.6 (Kirakka), 3.1 (Naruska) and 3.2 (Pallas). These values do not indicate any strong acidification near the smelter compared to background areas and, according to the authors, pH showed a strong dependence on lithology. The catchments were located mainly on till soils, and had spruce stands except for Kirakka (pine stand). The Monchegorsk catchment is in the forest death area.

According to this thesis, the base saturation of the organic layer was lower in the vicinity of the smelters compared to the other parts of the line. One explanation for the high exchangeable Al concentrations in the organic layer and related decrease in base saturation could be an external source of Al near to the Monchegorsk smelters. The pH values and base cation concentrations in the mineral soil horizons did not decrease on moving towards the smelters, and neither was the exchangeable Al concentration in the mineral soil elevated. The high levels of Al deposition near Monchegorsk compared to background areas support the conclusion that an external source of Al is reflected in the chemical composition of the organic layer. According to Äyräs et al. (1995), the Al concentration in snow meltwater is significantly higher in Monchegorsk and Kirovks than that in central Finnish Lapland. Filter residue analysis of the snow meltwater also showed that the Al concentration was at its highest near Monchegorsk. The increased total Al concentrations in the percolation water collected below the organic layer in the vicinity of Monchegorsk is partly due to dust from the area seriously affected by soil erosion (Lukina & Nikonov 1995). In addition, Mäkinen (1994) reported high (5 times the background) Al concentrations in moss samples. The organic layer is very thin near the smelters and absent at many points (about 40 % of the soil surface lacks an organic layer).

Furthermore, the considerable changes in the functioning of the forest ecosystems are undoubtedly reflected in the chemical properties of the remaining organic layer.

Reimann et al. (1997) reported that the effect of open-cast mining and waste dumps of alkaline rocks from the nephelinite industry near Kirovsk can be seen e.g. as elevated Al concentrations in the topsoil (0-5 cm) in a nearby catchment. The studied catchment was located only 50 km to the east of Monchegorsk. The bedrock below the till soil in the catchment was composed with nephelinite, the tree cover consisted of spruce and birch. Aluminium was determined by aqua regia digestion.

The results of this thesis indicated that copper and nickel emissions from Monchegorsk were reflected in the snowpack as clearly increasing Cu and Ni gradients on moving towards the emission sources. Elevated Cu and Ni values were also found in the forest soil and percolation water. The Cu and Ni concentrations in the snowpack were relatively high at distances of less than 30 km from the smelters. In the percolation water (depth 5 cm), elevated concentrations were detected even on the plot located at 31 km.

The gradients of total and exchangeable Cu and total Ni concentrations in the organic layer were much longer than those in the snowpack or percolation water, and extended to about 100 km from Monchegorsk. This could be due to the fact that these soil parameters represent the accumulation of heavy metals in the organic layer during a longer time period than those of percolation water. However, elevated Cu and Ni values were only found in the mineral soil on the plots 8 and 10 km from Monchegorsk.

The decrease in the base saturation of the organic layer in the vicinity of the Monchegorsk smelters compared to that in other parts of the study area is partly due to the deposition of copper, aluminium and nickel. A higher proportion of cation exchange sites was occupied by Cu^{2+} and Al^{3+} , thus reducing the base saturation. The decreasing effect of heavy metals on base saturation can be considerable. According to Derome & Lindroos (1998), the loss in base saturation in the organic and uppermost mineral soil layers close to the Harjavalta Cu-Ni smelter is due to the displacement of base cations by Cu^{2+} and Ni^{2+}, and not to acidic deposition. In many other studies there has also been a dramatic fall in base saturation in the organic layer close to the smelters, but only a marginal decrease in humus pH (e.g. Løbersli & Steinnes 1988, Fritze et al. 1989).

According to this thesis, Cu and Ni emissions from Monchegorsk are strongly reflected in the organic layer and even in the mineral soil layers (including the C horizon). The Cu and Ni emissions from Monchegorsk are very high compared to those at

Nikel. On the other hand, the base cation status has decreased and the exchangeable Al concentration increased only in the organic layer.

According to many other studies, the high Cu and Ni emissions from the Monchegorsk smelters are reflected in the surrounding environment. For example, Karaban & Gytarsky (1995) reported that the concentrations of nickel and copper in rainwater over the area adjacent to the emission sources in Monchegorsk (10-12 km from the smelter) were respectively 3-8 and 8-20 times higher than those observed in areas 40 km from the smelter. Many heavy metals, including Cu and Ni, were enriched in snow meltwater and filter residues in the catchments studied near Monchegorsk (Äyräs et al. 1995). Reimann et al. (1997) collected topsoil samples (0-5 cm) from catchments in Russia, Finland and Norway. According to their results, the Cu and Ni median concentrations (aqua regia) in the topmost layers of the till soils were about 600 times higher close to Monchegorsk than in the Finnish catchments. Boyd et al. (1997) concluded that high heavy metal concentrations in the topsoil of the same catchment near Monchegorsk are due to anthropogenic activity since the Ni and Cu concentrations were 1 to 2 order of magnitude higher in the topsoil samples than in the C-horizon samples. The catchment was located only 5 km to the south of Monchegorsk. The role of the organic horizon is important in accumulating heavy metals from deposition. According to Räisänen et al. (1997), Ni, Cu, Co and As were strongly enriched in the organic horizon in the contaminated sites near Monchegorsk, Kurka and Zapoljarnij compared to parent tills and podzols in the background areas. The organic horizon of Al-Fe-humus podzolic soils under pine stands has sharply diminished the rate of downward Cu and Ni migration near the smelters in Monchegorsk (Nikonov et al. 1993, Nikonov et al. 1994).

Äyräs et al. (1997a) reported heavy metal anomalies in terrestrial moss. The Cu and Ni anomalies originating in Monchegorsk showed a clear north-south pattern around Monchegorsk. The patterns closely followed the main topographical features and the main wind direction (north-south). To the west background levels were reached at approximately the Russian/Finnish border. This finding is in close agreement with the pattern of elevated total Cu and Ni concentrations in the organic layer under pine forests observed in this thesis along the Monchegorsk gradient line. Lippo et al. (1995) also reported elevated Ni concentrations on the Finnish side of the border in mosses, lichens and bark in the north-eastern parts of Lapland due to the influence of the Nikel and Monchegorsk smelters.

The shape of the so-called inner visible-damage zone around the forest death areas in Monchegorsk reflects the distribution of emissions from the smelters. The conifers within this zone show marked defoliation and epiphytic lichens have disappeared. The zone extends ca. 30 km south from Monchegorsk, i.e. about the same distance where S, Cu and Ni concentrations are elevated in the snowpack and percolation water. The zone extends about 40 km north of Monchegorsk. The inner visible-damage zone extends no further than 25 km west of the emission sources due to the Monche fells (Mikkola 1995, Tikkanen 1995c).

The increasing S, Cu and Ni gradients in snowpack, forest soil and percolation water with decreasing distance to the emission sources are in good agreement with the chemical composition of the pine needles. The chemical composition of needles is widely used as an indicator of the nutrient balance of trees and the effects of air pollutants (e.g. Zöttl & Hüttl 1986, Raitio 1995). The high sulphur dioxide emissions have increased the sulphur concentrations of the pine needles in the vicinity of the Kola smelters (Raitio et al. 1995). The Cu and Ni concentrations also increase with decreasing distance to the point sources. The maximum S, Cu and Ni concentrations in pine needles near Monchegorsk occurred on the plot 10 km from the source (Raitio 1992). On the plot located nearest to Monchegorsk (8 km) all the pine trees are dead.

4.2 The effects of emissions from Nikel

According to this thesis, sulphur emissions from Nikel have had no clear effect on the chemical properties of forest soil and percolation water. There was only a slight increase in the S concentrations of the snowpack with decreasing distance to Nikel. No pH gradient was observed. The S concentration in bulk deposition and in stand throughfall increased significantly with decreasing distance to Nikel. However, no decreasing pH gradient was found. The S concentration and pH of the organic layer were relatively constant along the whole gradient line. In addition, there was no clear decreasing pH gradient in the mineral soil either. There were no gradients in the S concentration or pH in the percolation water. These findings do not support the assumption of strongly increased acidity due to sulphur emissions at Nikel. On the other hand, the elevated H^+ concentrations and depressed base saturation of the organic layer in the vicinity of Nikel may be a sign of increased soil acidification. Furthermore, the base cation concentration in the E horizon decreased on moving towards Nikel. Some changes were also observed in these parameters on the Finnish side of the border.

Bulk sulphur deposition is higher in Norway near Nikel compared to Finnish Lapland (Anttila 1995). According to some studies there are signs of the acidifying effects of the Nikel emissions.

For example, according to Kähkönen (1996), the relatively high sulphur concentrations in the organic layer, and the sulphate concentrations in acidic and poorly buffered lakes, indicate that sulphur deposition in NE Lapland is derived from the Nikel smelters. Water quality studies in the border areas between Norway and Russia have indicated some signs of acidification in small lakes (Traaen et al. 1992). Lappalainen et al. (1995) studied the possible effects of acid deposition on sensitive fish populations in north-eastern Finnish Lapland. They concluded that the waters near the eastern border of northern Finnish Lapland are threatened by acidification since very low alkalinity values were measured in a group of small upland ponds.

On the other hand, large amounts of alkaline dust particles are deposited in the immediate vicinity of the smelter and this can lead to soil alkalinization (Bruskina et al. 1994). Koptsik & Mukhina (1995) studied sandy podzols in tills and glaciofluvial sediments under pine and birch forests. The sample sites were located at different distances and directions from the Nikel smelter. The O horizon of the podzols near the smelter contained higher concentrations of exchangeable base cations compared to remote sites (40-100 km). Exchangeable acidity in the O horizon increased significantly with distance. Gustafsson (1996) studied spodic B horizons in glacial tills on the sampling transect running from northernmost Sweden to north-easternmost Norway, only 10 km from the Nikel smelter, in order to determine whether there is any evidence of strong soil acidification. Because the pH(H_2O) was >4.8 in all the soils and the exchangeable Ca/Al ratio was high, there were no evidence for strong acidification. According to the results of this thesis and other studies, it can be concluded that it is very difficult to drawn any general conclusions about the effect of sulphur emissions from Cu-Ni smelters in the Kola Peninsula on soil acidification processes. This is due to the fact that many other processes also affect the chemical characteristics of the soil, such as heavy metal, aluminium and dust/particle emissions as well as natural variation (wind direction, topography, soil properties etc.).

According to this thesis, the effect of heavy metal emissions from Nikel were not clearly detectable in the chemical composition of deposition or percolation water. The Cu and Ni concentrations in the snowpack and percolation water were below the analytical detection limit even on the plots located in Finnmark, Northern Norway, relatively close to the emission sources. Äyräs et al. (1995) and Reimann et al. (1996) reported high heavy metal concentrations (including Cu and Ni) as well as S, and Al concentrations in snow in the vicinity of the smelters at Nikel and Zapoljarnij. According to them, the snowpack pH values indicated that the least acidic values can be found close to the emission sources, and that the most acidic values in the background areas in Finland. Karaban & Gytarsky (1995) measured the highest concentrations of SO_4^{2-} , Ni and Cu in rainwater (open area) at a distance of 6-8 km from Nikel. At 30 km from the source the concentrations decreased significantly and became constant. No marked dependence was observed between the pH and the distance from the emission sources.

In this thesis, elevated total Cu concentrations in the organic layer were found at distances of less than 50 km from the Nikel smelters. Relatively high total Ni concentrations were also detected even at a distance of about 70 km from the sources. Exchangeable Cu concentrations were high only in the organic layer and E horizon at the plot nearest to Nikel. Heavy metal deposition was not reflected in the other mineral soil layers. Along the Nikel gradient line, heavy metals appear to accumulate only in the topmost layers of the soil. The lower emissions of Cu and Ni from Nikel compared to Monchegorsk are reflected as lower concentrations in the forest soil.

High heavy metal concentrations in moss have been reported over large areas around Nikel, NE Finland and Norway, reflecting high atmospheric deposition (Rühling et al. 1992, Rühling 1994). Heavy metal concentrations in terrestrial moss indicated that Ni appears to travel farther west than Cu from Nikel (Äyräs et al. 1997a). This finding is in good agreement with the results presented in this thesis for total Cu and Ni in the organic layer. Äyräs et al. (1997b) reported that both terrestrial moss and humus (O horizon) give the same picture for the distribution of Cu and Ni from Nikel, with a very steep gradient from east to west and background levels being reached about 30-50 km from the Nikel smelters. In this thesis the effects of Cu and Ni emissions were also detected at somewhat greater distances in the organic layer.

4.3 The acidity status of the percolation water in northern Finland

According to this study, percolation water acidity is strongly connected with natural factors in the northern Finland. Percolation water acidity is controlled by organic acids in the topmost layers of the soil. Organic acids are formed as a result of the decomposition of litter in the cool and moist conditions prevailing in coniferous forests. They are weak acids and important buffering compounds. The dissociation of organic acids releases hydrogen ions into percolation water. Dissociation is reversed if the percolation water pH decreases due to acidic deposition (Krug & Frink 1983). The results of this thesis indicated that there was a significant negative correlation between percolation water pH and dissolved organic matter concentration at a depth of 5 cm on the plots located in Finland. The high Al, Ca and Mg concentrations were also associated with the high DOM concentrations. In deeper layers of the soil, DOM no longer had a corresponding effect on percolation water acidity and nutrient status because the DOM concentration strongly decreased with increasing soil depth. The DOM is precipitated in the B horizon of podzolic soil. The amount of organic matter in the mineral soil is usually higher than that in the organic layer (Viro 1969).

Percolation water can become very acidic as it passes down through a naturally acid humus layer even though no mineral anions are present in the solution. The low pH of percolation water dissolves, for example, aluminium from minerals into the solution, and the Al in turn forms complexes with the dissolved organic anions. The decrease in the Al activity in the solution due to this process causes increasing Al mobilisation from minerals. When the capacity of the organic anions to form chelates and complexes with the cations (e.g. aluminium) is consumed, the organic complexes precipitate (Reuss & Johnson 1986).

The total Al concentrations in the percolation water correlated positively with DOM at depths of 5 and 20 cm on the plots located in Finland. This indicates that a high proportion of the dissolved aluminium is in the form of dissolved organic complexes in the rooting zone. Dissolved organic Al complexes have been shown to be non-toxic to roots (e.g. Hue et al. 1986). The median values of the total Al concentration in the percolation water (depths 5 - 40 cm) were also below 1 mg/l on the Finnish plots. De Vries (1993) has suggested that the toxic Al concentration would be around 1.8 mg/l. According to Arovaara and Ilvesniemi (1990a and b), the growth of Norway spruce seedlings is inhibited when the concentration of soluble inorganic Al is 10 - 50 mg/l in the nutrient solution. The corresponding value for Scots pine seedlings is 20 - 50 mg/l. The presence of Al in the percolation water of northern Finnish soils therefore does not seem to be a serious threat to trees because the total Al concentrations are well below the presented limit values and, in addition, a significant proportion of the total Al is in the non-toxic form.

According to this thesis, the total Al concentration in the percolation water decreased with increasing soil depth. The pH also increased with depth, which is a typical phenomenon in forest soils due to the buffering and neutralising processes (Helmisaari & Mälkönen 1989, Soveri & Ahlbeg 1990). An increase in percolation water pH in the soil means that the concentration of Al^{3+} remains low, which is an important feature considering that the proportion of the organic Al complexes is relatively low in the deeper layers of the soil (Lundström 1993). The percolation water pH controls the Al concentration in the C horizon because the dissolved organic matter precipitates in the B horizon.

The anionic nature of DOM was clearly evident according to the ion balance calculations. The difference between the inorganic cations and anions in the percolation water (depth 5 cm) indicated a considerable anion deficit that correlated positively with the DOM concentration. The connection between the DOM and pH values, as well as between DOM and Al complexes, can be explained by the formation of organic anions and their presence in the soil solution.

The base cation/aluminium ratio in soil solution is widely used as an acidification parameter (e.g. Roelofs et al. 1985, Sverdrup et al. 1990). In this study Ca/Al molar ratio in percolation water, calculated using the median Ca and total Al concentrations for the whole sample plot network in Finland, was above the presented critical value of 1.0 at depths of 5 - 40 cm. At values below 1.0, root effects can in theory occur. If only the inorganic fraction of total Al were to be used in these ratios, the ratio values would have been higher. The positive correlation between the total Al and DOM in the percolation water at depths of 5 and 20 cm indicates that total Al is not a suitable parameter in the ratio. The Al toxicity is connected with the inorganic and not organic Al fractions.

4.4 The effect of transportation, filtration and storage on the percolation water pH and total Al concentrations, and the two Al fractionation methods

In water quality studies, sampling, transportation, pretreatment and storage are important factors that could have an effect on the measured chemical parameters. The effects of storage on samples can be due, for instance, to aluminium adsorption on the walls of the sample bottles and to changes in the composition of dissolved organic matter. When the pH value of a sample is relatively high, changes in the proportions of different Al fractions can take place if the carbon dioxide water-air equilibrium is affected. This could happen during the different steps of sample treatment procedures. pH is a very sensitive parameter and, according to the analysis manuals for water samples, pH should be measured as soon as possible after sampling, which in practice means already in the field (Jarva & Tervahauta 1993). The effect of sample storage on the surface water and soil solution aluminium concentrations, and especially the different Al fractions, has been studied to some extent (e.g. Rögeberg &

Henriksen 1985, Sullivan et al. 1986, Bérden et al. 1994, Andrén 1995). The effects of transportation, filtration and storage on the total Al concentration and pH of soil solution were studied as a part of this thesis using the same sample handling procedures as in the gradient study. The aim was to ensure that the measured acidification parameters are reliable. The effect of transportation, filtration and storage on the pH and total Al concentrations of the percolation water samples in the gradient study was found to be insignificant. This means that similar procedures can also be used in future studies.

Although the mean pH of the soil solution samples in the sample treatment study was somewhat higher than the mean pH values in the gradient study, the pH range was rather large and covered the same pH values measured in Lapland and in the Kola Peninsula. The pH values in the experiment varied from 4.5 to 7.1 while the mean pH values on the sample plots located in Lapland were 4.8 , 5.3 and 5.4 at depths of 5, 20 and 40 cm, respectively. The pH of the samples remained stable during transportation or filtration regardless of the pH level. The total Al concentrations were very similar in both studies.

pH adjustment is a commonly used technique to preserve water samples prior to analysis. Despite the fact that no preserving method is fully adequate (Jarva & Tervahauta 1993), pH adjustment with HNO_3 seems to be a very good method for total Al in soil solution. The total Al concentration remained constant when the sample was stored at + 4 °C for two weeks even though the pH was not adjusted. pH adjustment should naturally be used whenever possible because it makes the results more reliable. Freezing the samples is not an appropriate storage technique because it results in a strong decrease in total Al concentrations.

The relationship between DOM and total Al concentration in percolation water indicates that the organic Al complexes play an important role in the topmost layers of podzolic soils. This finding raises a need for accurate analysis of the different Al fractions in soil solution especially when the total Al concentration is relatively high. Both the ICP/AES and FIA methods gave comparable results for the exchangeable Al fraction in soil solution (positively charged Al ions), and thus either of the methods can be used for estimating aluminium toxicity.

5 CONCLUSIONS

According to this thesis, it can be concluded that:

1a) The sulphur, copper and nickel emissions from Monchegorsk are reflected as elevated S, Cu and Ni levels in snowpack and percolation water to a distance of about 30 km from the source along the gradient line. In the organic layer the S concentration is elevated due to emissions only at a distances of less than 10 km from the source. Copper and Ni emissions are reflected in the organic layer composition even up to 100 km from Monchegorsk, but in the mineral soil only up to 10 km.

1b) The effect of sulphur emissions from Nikel on the chemical properties of deposition, forest soil and percolation water is not clear. There are increasing S gradients in the snowpack and in bulk deposition and stand throughfall on moving towards Nikel. However, there are no S gradients in the soil or percolation water. The Cu levels in the organic layer are elevated up to 50 km from the smelter. The Ni levels also are relatively high in the organic layer to a distance of 70 km. There are no clear signs of the effects of copper and nickel emissions in the mineral soil. Copper and nickel emissions are not reflected in the chemical composition of the percolation water or snowpack.

2a) No signs of decreased pH values in the soil can be found due to the emissions from Monchegorsk along the gradient line even in the vicinity of the smelter. The acidity of the snowpack, forest soil or percolation water do not indicate that the sulphur emissions from the smelters have strongly increased acidity. Decreased base cation levels in the organic layer near Monchegorsk is most likely due to an external input of aluminium. Accumulation of copper and nickel in the forest soil can also have a decreasing effect on base saturation.

2b) The effect of emissions from Nikel on soil acidity status is not clear. However, the situation better fulfils the definition of soil acidification because a reduction in the base cation status of the organic layer was found to be associated with an increase in the H^+ concentrations in the organic layer.

It is not possible to draw any general conclusions about soil acidification due to sulphur emissions from the Kola Peninsula in the sector running towards Finland from the point sources. The high SO_2 emissions are a potential acidifying factor, but there are many other processes in many parts of the Kola Peninsula and Finland that may have a strong effect on soil chemical characteristics. In the vicinity of the smelters these include heavy metal and aluminium deposition as well as dust and particle emissions.

3) The role of dissolved organic matter is important as regards percolation water acidity and quality in the background areas. The connection found between DOM and pH values, as well as between DOM and total Al concentrations, can be explained by the anionic nature of DOM in percolation water. Because the DOM forms organic complexes with the Al in percolation water, it decreases the potential toxic effects of the total aluminium concentrations. The presence of Al in the percolation water of northern Finnish soils does not seem to be a serious threat to trees because the total Al concentrations are well below the limit values and, in addition, a significant proportion of the total Al is in the form of non-toxic organic complexes at depths of 5-20 cm.

4a) The effect of transportation, filtration and storage on percolation water pH and total Al concentrations was found to be insignificant in the gradient study, which means that the procedures used are satisfactory.

4b) Either of the two presented methods (ICP/AES, FIA) can be used for determining positively charged, inorganic Al ions in soil solution.

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I

Paper I

Reprinted from Water, Air and Soil Pollution, Volume 85(4), 1995, 2185-2190, Snowpack quality as an indicator of air pollution in Finnish Lapland and the Kola Peninsula, NW Russia, Lindroos, A.-J., Derome, J. & Niska, K., 4 figures, © 1995 Kluwer Academic Publishers, with kind permission from Kluwer Academic Publishers.

SNOWPACK QUALITY AS AN INDICATOR OF AIR POLLUTION IN FINNISH LAPLAND AND THE KOLA PENINSULA, NW RUSSIA

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Abstract. Bulk snow samples were collected from the snowpack in open areas along two sampling lines running to the west from the Cu-Ni smelters at Nikel and Monchegorsk, NW Russia, during 1991-1993. The aim of the study was to estimate the area affected by sulphur and heavy metal deposition from the smelters. Snowpack quality was used as an indicator of deposition during winter time. The total sulphur, copper and nickel concentrations in the snowpack decreased significantly ($p < 0.001$) with increasing distance from the smelters along the sampling line running directly to the west from Monchegorsk. The deposition pattern was similar each winter during 1991-1993. The pH values did not correlate with the corresponding sulphur concentrations, and there was no decreasing pH gradient in the snowpack on moving towards Monchegorsk. The effects of sulphur emissions from Monchegorsk on snowpack chemistry were not detectable on the Finnish side of the border. The 3-year mean of the total sulphur concentration was 0.27 mg/kg, and of the pH values 4.92, along the sampling line running to the west of Monchegorsk. The total sulphur concentrations near the smelters (< 20 km) varied between 0.37 and 0.95 mg/kg. The effect of the Cu-Ni smelters at Nikel on snowpack quality was not detectable in northern Finnish Lapland. The 3-year mean for total sulphur was 0.20 mg/kg and for pH 4.96 along the sampling line running to the west of Nikel.

Key words: Cu, Cu-Ni smelters, Kola Peninsula, Lapland, Ni, pH, S, snowpack

1. Introduction

The copper-nickel smelters in the Kola Peninsula, NW Russia, are significant emission sources of sulphur dioxide and heavy metals. The SO_2 emissions from Petshenganikel in 1990 were 190 000 tonnes, from the adjoining smelter at Zapoljarnyi 67 000 t, and from Monchegorsk 233 000 t. Annual copper and nickel emissions from Petshenganikel were 200 t and 300 t, respectively. The emissions for Monchegorsk were 2 200 t of copper and 3 100 t of nickel per year (Lapin lääninhallitus, 1992).

These industrial emissions have caused considerable changes in the forest ecosystems surrounding the smelter complexes (Kalabin *et al.*, 1990; Kauhanen and Varmola, 1992; Kozlov *et al.*, 1993; Kryuchkov, 1991; Tikkanen, 1995). The trees and ground vegetation were completely destroyed in the immediate vicinity of the smelters (Lukina *et al.*, 1993).

Emissions of sulphur dioxide and heavy metals from smelters have been reported to cause serious environmental damage (e.g. Hutchinson and Whitby, 1974; 1977). Sulphur

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deposition can also cause soil acidification (Berden *et al.*, 1987). According to Nordgren *et al.* (1985, 1986), the microbiological properties in the vicinity of smelters can also change.

The aim of this study was to investigate the extent of sulphur and heavy metal deposition in the area lying to the west of the smelter complexes at Nikel and Monchegorsk. The chemical composition of the snowpack was used as an indicator of air pollutants and their deposition.

2. Material and Methods

Snow samples were collected in March 1991, 1992 and 1993 from the snowpack along two lines running through Russia and Finnish Lapland to the west of the smelter complexes at Nikel and Monchegorsk (Figure 1). Because the sampling was carried out as early as in March, the effect of thawing episodes on snowpack concentrations was considered to be insignificant. The snow was sampled in open areas with a uniform snowpack as far away as possible from roads and settlements. The samples were taken at points not affected by the tree cover.

The samples were allowed to thaw in the laboratory and then filtered through filter paper. pH was measured on the samples, which were then conserved with nitric acid prior to analysis of total sulphur (S), copper (Cu) and nickel (Ni) by inductively coupled plasma atomic emission spectrophotometry (ICP/AES). The sampling procedure and analyses are described in detail in Derome *et al.* (1993).

The formation of the snowpack is naturally not completely the same over extensive areas owing to variations in snowfall, wind patterns and temperature. For this reason the study was restricted to the pH and concentrations of S, Cu and Ni, and no attempts were made to calculate actual deposition levels. Variations in the chemical composition of the snowpack were studied in relation to the distance to the emission sources using a linear regression model.

The snowpack in the study area represented snowfall for the period October to March, the annual precipitation in the area ranging from ca. 380 - 580 mm.

3. Results

3.1. EFFECT OF EMISSIONS FROM MONCHEGORSK ON THE ACIDITY AND SULPHUR, COPPER AND NICKEL CONCENTRATIONS IN THE SNOWPACK

No trends were found in the pH of the snowpack with increasing distance from the emission source along the line running to the west from Monchegorsk (Figure 2). The only clear exception to the rather constant pH level along the line were the relatively high pH values close to the open-cast mine at Kovdor, 100 km from Monchegorsk. The mean pH value for the three-year period along the line was 4.92.

Fig. 1. The sampling lines (A and B) extending to the west of Monchegorsk and Nikel.

Snowpack S concentrations fell sharply with increasing distance from Monchegorsk (Figure 2). The S concentration reached a constant level at a distance of about 40 km from the emission source. The mean S concentration for the three-year period along the line was 0.27 mg/kg, but at a distance of less than 20 km the S concentration varied from 0.37 to 0.95 mg/kg. The S concentration did not correlate with the snowpack pH along this line ($r = 0.06$, $n = 99$, $p > 0.05$).

The effect of distance from the emission source at Monchegorsk on snowpack S concentrations was investigated using regression analysis. The analysis was performed on the samples collected during the 3-year period at distances of 8 - 62 km from the emission source. Samples taken at distances greater than 62 km were omitted from the analysis because the emissions clearly no longer had any effect on snowpack composition. The concentrations were transformed logarithmically ($\log_{10}$) in order to give a better fit for the regression line. The distance from Monchegorsk explained 75% of the variation in the S concentration of the snowpack (Table I).

The Cu and Ni concentrations in the snowpack were determined along the line up to a distance of 120 km from the emission source during the 3-year period, but not on the Finnish side of the border (>120 km) in 1992 and 1993. The results for 1991 indicated that the Cu and Ni concentrations in the snowpack at a distance of more than 120 km from the emission source were below the detection limits of the analytical equipment. Both the Cu and Ni concentrations in the snowpack fell sharply with increasing distance from the smelter (Figure 3). The highest concentrations were recorded in 1991 close to the smelter (8 km), the Cu concentration being 421 µg/kg and Ni concentration 180 µg/kg. Regression analysis was performed on the samples collected over the distance 8 - 38 km from the smelter (Table I). According to the model, distance explained 70% of the variation in the Cu concentration and 80% of the Ni concentration. Log_{10} transformations were used in the analysis.

TABLE I

Regression analysis between distance (km) from the Monchegorsk smelters and the snowpack S, Cu and Ni concentrations

Regression line	R^2	n	p*	Distance range from the smelters (km)
log S (mg/kg) = 0.27 + (-0.51 log km)	0.75	23	< 0.001	8 - 62
log Cu (µg/kg) = 4.41 + (-2.19 log km)	0.70	13	< 0.001	8 - 38
log Ni (µg/kg) = 3.29 + (-1.53 log km)	0.80	13	< 0.001	8 - 38

*F-test, H_0: ß=0

3.2. EFFECT OF EMISSIONS FROM NIKEL ON THE ACIDITY AND SULPHUR CONCENTRATION IN THE SNOWPACK

There was no clear gradient in the snowpack pH values with increasing distance from the Nikel smelter (Figure 4). The 3-year mean pH value was 4.96. The snowpack S concentration decreased gradually with increasing distance (Figure 4). The 3-year mean snowpack S concentration along the line was 0.20 mg/kg. Statistically significant correlation was found between the S concentration and the pH of the snowpack ($r = -0.54$, $n = 31$, $p < 0.01$). However this finding is of little meaning because the variations in pH and S concentration along this line were very small.

According to regression analysis performed on the untransformed values over the distance range 14 - 100 km, the distance to Nikel explained 42% of the variation in the snowpack S concentration ($R^2 = 0.42$, $n=17$, $p < 0.01$). In this case, too, the drop in the S concentration with increasing distance was relatively small.

4. Discussion

According to the results of this study, the effects of sulphur emissions from Monchegorsk on snowpack composition extend for a distance of 30 km from the emission point source. In this case sulphur deposition was not necessarily associated with acidic deposition because no gradient was found in the snowpack pH values. The copper and nickel emissions were also clearly reflected in the snowpack composition in the immediate vicinity of the smelter, although not as far as 30 km. The results rather well reflect the spread of emissions and their wet deposition from the Monchegorsk smelter towards Finland in the west, which in actual fact are relatively low owing to the prevailing wind directions (Anttila, 1995). Also, the high fell chain running in a north-south direction on the western side of Monchegorsk undoubtedly reduces the spread of emissions to the west.

The effects of emissions from Nikel on the chemical composition of the snowpack in northern Lapland were not as clear. The S concentrations increased with decreasing distance to the emission source, but nowhere near as sharply as close to Monchegorsk.

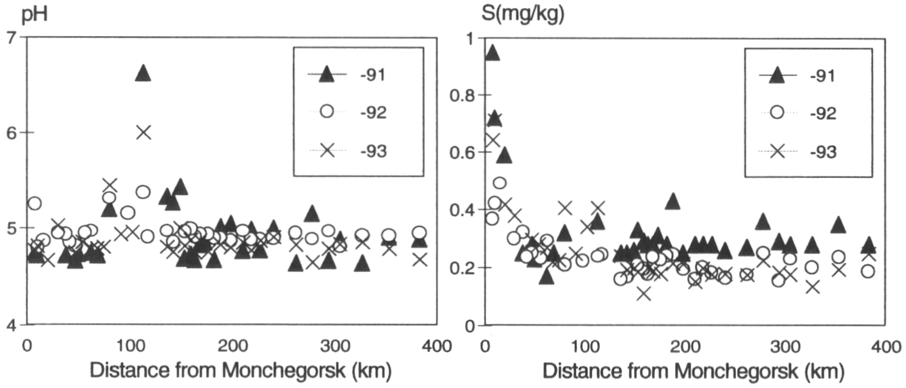

Fig. 2. Snowpack pH and S concentration along the sampling line running from Monchegorsk in 1991, 1992 and 1993.

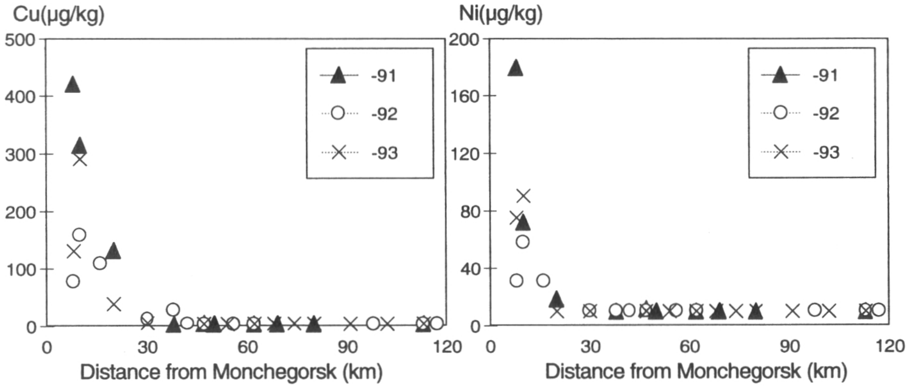

Fig. 3. Snowpack Cu and Ni concentrations along the sampling line running from Monchegorsk in 1991, 1992 and 1993.

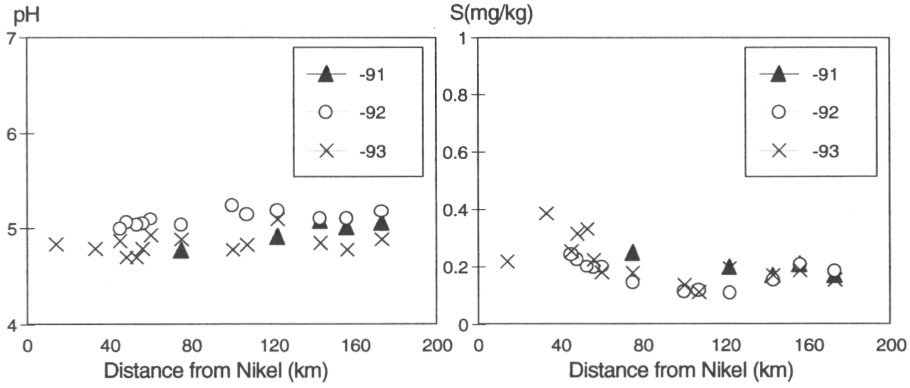

Fig. 4. Snowpack pH and S concentration along the sampling line running from Nikel in 1991, 1992 and 1993.

According to Tikkanen and Mikkola (1993), damage to the forest ecosystems is clearly visible in the surroundings of the smelters, and the severity of the damage increases sharply on moving towards the emission sources. The effects of emissions outside the major damage zones can only be identified using the most sensitive plant indicator techniques. The pattern in the chemical composition of the snowpack obtained in this study was in good agreement with the areal distribution of forest damage, especially in the Monchegorsk area. For instance, sulphur, copper and nickel concentrations in Scots pine needles in the area surrounding Monchegorsk decreased sharply with increasing distance from the point emission source (Raitio *et al.*, 1993).

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Paper II

Lindroos, A.-J., Derome, J., Nikonov, V. & Niska, K. 1996. Influence of sulphur and heavy metal emissions from Monchegorsk, Northwest Russia, on percolation water quality in *Pinus sylvestris* stands. Scandinavian Journal of Forest Research 11: 97-103.

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Influence of Sulphur and Heavy Metal Emissions from Monchegorsk, Northwest Russia, on Percolation Water Quality in *Pinus sylvestris* Stands

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Percolation water chemistry was studied in the Kola Peninsula, Northwest Russia, in order to determine the distance to which S, Cu and Ni emissions from Monchegorsk have an effect on water quality in forest soils. Samples were collected at a depth of 5 cm below the ground surface on seven sample plots located in the sector running to the south and southwest from the point source. The tree stands consisted of Scots pine (*Pinus sylvestris* L.) and were located on dry or dryish mineral soil sites. The soil type was iron–humus podzol and the texture class was sorted fine sand or sand. There was an increasing gradient in the S, Cu and Ni concentrations in the percolation water during 1991–1993 on moving towards the point source. Copper and Ni concentrations were relatively high even at a distance of 30 km from Monchegorsk. Percolation water pH values did not correlate with the corresponding S concentrations. *Key words: Cu, deposition, Ni, percolation water, S, Scots pine.*

INTRODUCTION

The effects of sulphur dioxide and heavy metal deposition on forest soil in the vicinity of Cu–Ni smelters have been described rather extensively in a number of investigations carried out around Sudbury in Canada (Hutchinson & Whitby 1974), in Harjavalta in western Finland (Fritze et al. 1989), at Sulitjelma in northern Norway (Løbersli & Steinnes 1988), and in the Kola Peninsula in Russia (Kozlov et al. 1993). The soil in the immediate vicinity of the smelters has become partially saturated with Ni and Cu (Freedman & Hutchinson 1980, Nordgren et al. 1986). Acidic deposition may result in the leaching of nutrients from the topsoil and the dissolution of toxic elements (Tyler 1981). The leaching of mineral nutrients from the surface soil layers presupposes, however, that the sulphate is in a mobile form (Singh et al. 1980). Percolation water studies have demonstrated that the organic horizon in podzolic soils acts as an efficient biogeochemical barrier to the downward passage of Cu and Ni, but not to sulphurous compounds (Petrova et al. 1993).

In 1990 annual emissions of SO_2, Cu and Ni from the Cu–Ni smelter at Monchegorsk, Kola Peninsula, northwest Russia, were approximately 233 000 t, 1800 t and 2900 t, respectively (Anon. 1991). The forest vegetation is totally destroyed over an area extending for ca. 20 km from the smelter complex, and varying degrees of forest damage occur over an area encompassing tens of thousands of hectares. Russian researchers have divided the area into five zones on the basis of damage severity (Kalabin et al. 1990, Kryuchkov 1991).

The aim of this study is to determine the concentrations of S, Ni and Cu in percolation water collected at forest sites located at varying distances from the Cu–Ni smelter at Monchegorsk, northwest Russia. The sampling sites were located in a sector running to the south and southwest of the smelter. Information about S and heavy metal levels in forest

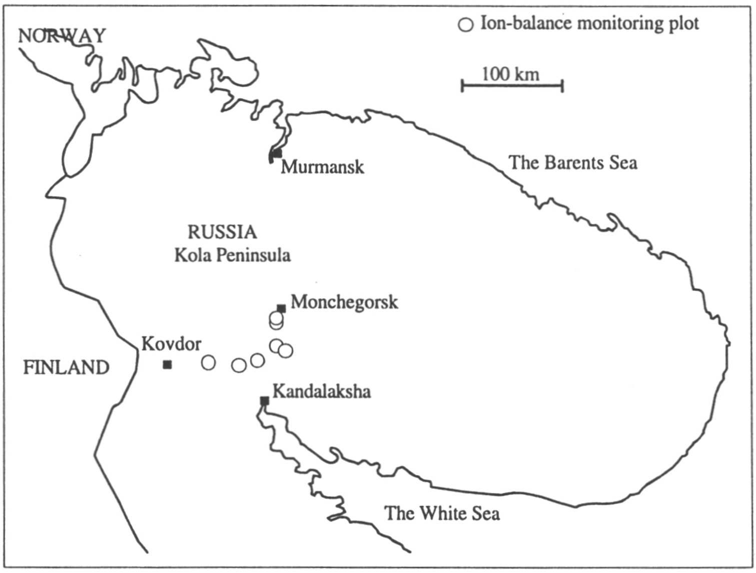

Fig. 1. Location of the ion-balance monitoring plots in the Kola Peninsula, northwest Russia.

soils is needed to complement the results already obtained about the direct effects of these pollutants on the above-ground components of the forest ecosystems in the area.

MATERIAL AND METHODS

The percolation water was collected during 1991–1993 from the seven so-called ion-balance monitoring plots located in a sector running to the south and southwest of the Monchegorsk Cu–Ni smelter complex in the Kola Peninsula, northwest Russia (Fig. 1). The actual location of the plots was largely determined by accessability in the area, i.e. the plots were close to the road network. The tree stand on the plots consists almost solely of Scots pine (*Pinus sylvestris* L.) with an average age of over 80 yrs. The stands are located on dry or dryish mineral soil sites (see Cajander (1949) for Finnish forest site classification). The ground vegetation consists primarily of heather (*Calluna vulgaris*) and lichens (*Cladonia* spp.). The soil type is iron–humus podzol, and the soil texture class is rather well sorted fine sand or sand. The organic matter content in the humus layer and the mineral soil, and the thickness of the genetic horizons are shown in Table 1. On the sample plot 8 km from Monchegorsk all the pine trees have died, and the ground vegetation and humus layer at many points are absent owing to widespread fires and subsequent soil erosion (see Lukina et al. (1993) for details of the vegetation cover). The tree stand at 10 km was suffering from severe needle loss (>60%) and was of low vitality; needle loss at all the other plots was below 25% (Tikkanen 1995).

The percolation water lysimeters were located at four points around the circular sample plots (300 m^2). There were three lysimeters at depths of 5, 20 and 40 cm (from the ground surface) at each point. The 5-cm-depth lysimeters at the plot closest to Monchegorsk were located at points with an intact humus layer.

Table 1. *Soil horizon thickness and organic matter content (loss in weight on ignition, LOI) on the seven ion-balance monitoring plots in the Kola Peninsula*

Ranges given in parentheses

Horizon	Thickness (cm)	LOI (%)
O	2.8 (1.5–6.5)	57.2 (42.2–91.7)
E	3.5 (2.1–4.6)	3.3 (1.3–5.5)
B + BC	10.8 (5.9–27.5)	3.0 (1.2–5.2)
C		1.2 (0.6–2.3)

The lysimeters were installed by first removing an intact soil core (30 cm diameter) down to the required depth, and then inserting the lysimeters in a shaft sunk below the removed soil core. After inserting the percolation lysimeters, the soil core was carefully replaced (Derome et al. 1993). The lysimeters were emptied at intervals of about 1 month during the snow-free period in 1991–1993. Percolation water was obtained only sporadically from depths of 20 and 40 cm during the study period and hence the results presented here are confined to the 5 cm depth.

pH was measured on the water samples, after which they were filtered through filter paper and a membrane filter (0.45 μm). A 50 ml amount of sample was conserved with superpure nitric acid (0.25 ml) for subsequent determination of the total S, Ni and Cu concentrations by inductively coupled plasma atomic emission spectrometry (ICP/AES, ARL 3580).

The relationships between the distance to Monchegorsk smelters and the percolation water concentrations were studied using a linear regression model. Logarithmic transformations ($\log_{10}$) were used in order to ensure that the data corresponded to the requirements of regression analysis better. The significance of the regression coefficient was tested using the *F*-test (Ho: $\beta = 0$).

RESULTS

There was a clear increasing gradient in the sulphur concentration in the percolation water at 5 cm depth during all three years on moving towards the emission point source at Monchegorsk. The only major divergence from the gradient occurred at a distance of 31 km in 1993. The highest median S concentration in the whole material, 7.9 mg l^{-1}, occurred on the plot closest to the smelter complex. The highest individual value (34.9 mg S l^{-1}) was recorded on the same plot in 1993 (Fig. 2, Tables 2 and 3).

The copper concentrations also increased on moving towards the point source in all years. In 1991 and 1992 the Cu concentration was relatively high at 10 km distance, and in 1993 also up to 31 km. The highest median Cu concentration during the study period was 0.095 mg l^{-1}, and the highest individual value was 1.688 mg l^{-1} (1993). Both were recorded at 8 km distance. There was considerable variation in the percolation water Cu concentrations recorded close to the point source; even very low concentrations were recorded (Fig. 3, Tables 2 and 3).

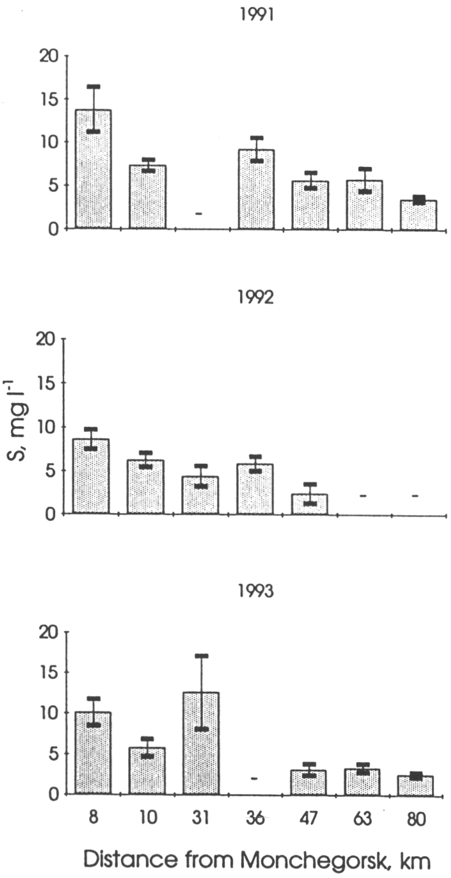

Fig. 2. Sulphur concentration (mean ± SE) in percolation water in the sector running south and southwest from Monchegorsk in 1991, 1992 and 1993 (– = no data).

Nickel showed a similar trend to Cu on moving towards the point source in 1991 and 1992. The nickel concentrations up to 31 km distance were at a constant, relatively high level in 1993. The highest median Ni concentration during the 3-yr period occurred at the plot closest to the point source (0.561 mg l^{-1}), which was also the plot with the highest individual value, 2.891 mg l^{-1} (in 1993). The nickel concentration also varied considerably close to Monchegorsk (Fig. 4, Tables 2 and 3).

There was no clear pH gradient with respect to the distance from the emission source (Fig. 5). The lowest pH values during the 3-yr period were recorded at a distance of 36 km from the smelter complex (Table 2). No correlation was found between the pH values

Table 2. *Percolation water composition 1991–1993*

	Distance from Monchegorsk (km)							
		8	10	31	36	47	63	80
S (mg l^{-1})	Median	7.86	5.63	3.72	7.34	3.09	3.51	2.89
	Mean	10.82	6.32	7.54	7.66	3.97	4.35	2.96
	SD	6.86	3.03	7.54	3.13	2.89	3.45	1.19
	Minimum	2.16	2.59	1.65	3.83	0.94	1.48	1.03
	Maximum	34.88	16.65	25.06	15.52	12.41	18.86	6.18
	n	31	25	13	11	27	28	27
Cu (mg l^{-1})	Median	0.095	0.063	0.008	0.021	0.006	0.007	0.006
	Mean	0.347	0.134	0.082	0.02	0.012	0.013	0.01
	SD	0.466	0.182	0.135	0.014	0.024	0.015	0.016
	Minimum	0.005	0.005	0.004	0.004	0.004	0.004	0.004
	Maximum	1.688	0.72	0.379	0.049	0.131	0.058	0.089
	n	31	26	13	11	27	28	27
Ni (mg l^{-1})	Median	0.561	0.323	0.016	0.043	0.016	0.014	0.018
	Mean	0.691	0.45	0.21	0.043	0.015	0.014	0.016
	SD	0.613	0.494	0.338	0.035	0.005	0.005	0.009
	Minimum	0.102	0.079	0.01	0.01	0.01	0.01	0.01
	Maximum	2.891	2.542	1.037	0.125	0.029	0.027	0.057
	n	30	26	13	11	27	28	27
pH	Median	4.75	4.46	4.51	4.11	4.31	4.43	4.57
	Mean	4.87	4.48	4.38	4.18	4.31	4.42	4.54
	SD	0.54	0.38	0.44	0.31	0.25	0.32	0.19
	Mininum	4.07	3.92	3.63	3.64	3.82	3.58	4.08
	Maximum	5.82	5.75	4.94	4.66	4.93	4.96	4.85
	n	30	27	15	13	29	28	27

Table 3. *Linear regression equations for the S, Cu and Ni concentration (mg l^{-1}) in percolation water and the distance (km) from Monchegorsk for the years 1991, 1992 and 1993*

(F-test, Ho: $\beta = 0$)

1991			
$\log S = 1.39 + (-0.41 \log km)$	$r = -0.63$	$p < 0.001$	$n = 56$
$\log Cu = 0.07 + (-1.22 \log km)$	$r = -0.70$	$p < 0.001$	$n = 57$
$\log Ni = 1.29 + (-1.68 \log km)$	$r = -0.93$	$p < 0.001$	$n = 56$
1992			
$\log S = 1.33 + (-0.50 \log km)$	$r = -0.53$	$p < 0.01$	$n = 25$
$\log Cu = (-1.27 \log km)$	$r = -0.62$	$p < 0.001$	$n = 25$
$\log Ni = 1.83 + (-2.27 \log km)$	$r = -0.88$	$p < 0.001$	$n = 25$
1993			
$\log S = 1.31 + (-0.49 \log km)$	$r = -0.61$	$p < 0.001$	$n = 81$
$\log Cu = 0.30 + (-1.32 \log km)$	$r = -0.74$	$p < 0.001$	$n = 81$
$\log Ni = 1.10 + (-1.66 \log km)$	$r = -0.88$	$p < 0.001$	$n = 81$

and the corresponding sulphur concentrations in any of the study years (1991, $r = -0.11$, $n = 57$, $p > 0.05$; 1992, $r = -0.38$, $n = 22$, $p > 0.05$; 1993, $r = -0.07$, $n = 78$, $p > 0.05$).

DISCUSSION

According to snowpack studies, deposition in the vicinity of the smelter complex contains large

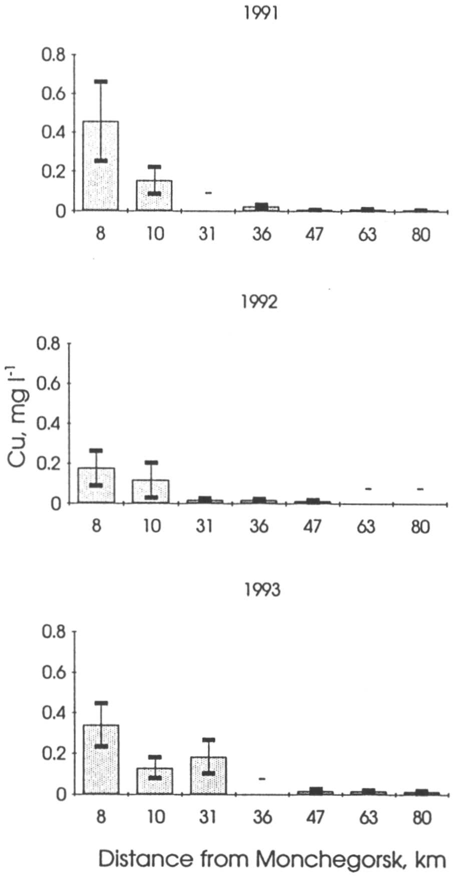

Fig. 3. Copper concentration (mean ± SE) in percolation water in the sector running south and southwest from Monchegorsk in 1991, 1992 and 1993 (– =no data).

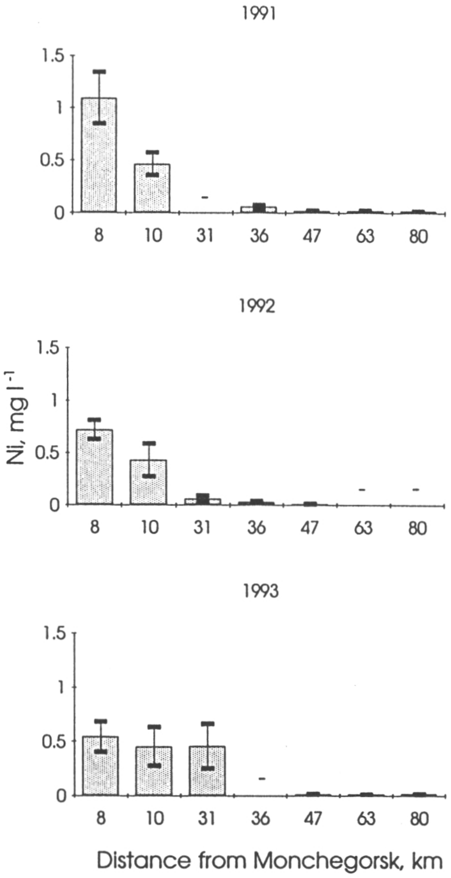

Fig. 4. Nickel concentration (mean ± SE) in percolation water in the sector running south and southwest from Monchegorsk in 1991, 1992 and 1993 (– =no data).

amounts of S, Cu and Ni, but the pH values are in most cases close to those recorded in background areas (Derome et al. 1992, Baklanov et al. 1993). In a study carried out on the same plots, Petrova et al. (1993) reported that the mean S deposition in throughfall during June–July 1991 at a distance of 8 km was 226 mg m^{-2} (totally destroyed tree cover), whereas the S deposition at a distance of 80 km was 78 mg m^{-2} (healthy stand). The corresponding values for Cu were 116 and 1.0 mg m^{-2}, and for Ni 22.6 and 0.1 mg m^{-2}. The increase in S concentrations at distances of 30–40 km from the point source may be attributable to the high needle litterfall at these points compared with close to the smelter. Needle analysis has also shown that S, Cu and Ni concentrations increase sharply with decreasing distance to the point source (Raitio 1992). Deposition patterns in the area are strongly affected by the predominant wind directions, which, depending on the season, are primarily the north, south or northwest (Barcan 1993). The high range of fells located to the west of Monchegorsk tend to restrict the transport of emissions directly to the west.

Empirical data concerning S, Cu and Ni emissions from Monchegorsk, as well as their deposition in the snowpack and the forest floor and their concentrations in pine needles, are in good agreement with the pattern of S, Cu and Ni concentrations in percolation water along the study sector. The Cu and Ni concentrations in percolation water collected from immedi-

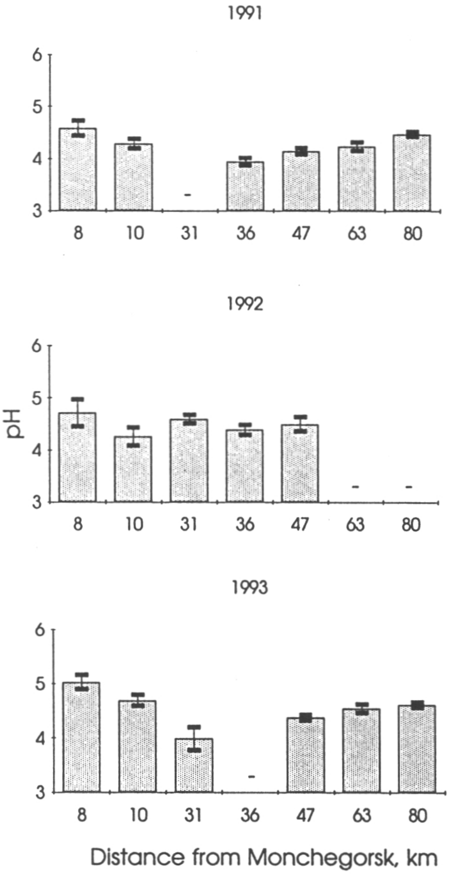

Fig. 5. pH (mean ± SE) in percolation water in the sector running south and southwest from Monchegorsk in 1991, 1992 and 1993 (— = no data).

ately below the organic layer were still relatively high at a distance of 30 km from the point source. At distances of over 40 km the concentrations decreased strongly; this corresponds to the sharp drop in deposition levels caused by the fact that the plots were located to the southwest of the emission source, and the deposition levels were therefore strongly reduced by the topography and prevailing wind directions. The sulphur concentrations in percolation water were also high close to the smelter complex.

No decreasing pH gradient was found with decreasing distance to the point source suggesting that deposition has not yet had any significant acidifying effect on percolation water even close to the smelter complex. One explanation for this somewhat surprising result could be that the major component in the deposition on forest soils close to the smelter is non-acidic, particulate material containing S, Cu and Ni compounds.

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Paper III

Reprinted from Water, Air and Soil Pollution, Volume 79(1/4), 1995, 191-200, The relationship between dissolved organic matter and percolation water chemistry in Northern Finland, Lindroos, A.-J., Derome, J. & Niska, K., 5 figures, © 1995 Kluwer Academic Publishers, with kind permission from Kluwer Academic Publishers.

THE RELATIONSHIP BETWEEN DISSOLVED ORGANIC MATTER AND PERCOLATION WATER CHEMISTRY IN NORTHERN FINLAND

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Abstract. The aim of this study was to investigate the relationship between dissolved organic matter and chemical constituents of percolation water collected at 5, 20 and 40 cm depths from 13 ion-balance sampling plots located along lines extending through Finnish Lapland from Cu-Ni smelters in the Kola Peninsula, Russia. All the monitoring plots have as uniform as possible stand and site characteristics. The plots were located in Scots pine stands on dry and dryish sites with genetic horizons characteristic of Fe-humus podsols. The soil type on most of the sites was sorted fine sand or sand. Significant positive correlations were found between dissolved organic matter (DOM) and total dissolved Al concentrations at 5 and 20 cm, but not at 40 cm. A significant negative correlation was found between DOM and pH at 5 cm, but not at 20 or 40 cm. The anion deficit was positively correlated with DOM at 5 cm in the percolation water. Organic matter thus plays an important role as an anion in percolation water, and regulates water pH in the surface soil. A high proportion of dissolved Al was in the form of organic complexes. Total dissolved Al levels were well below the toxic limits for pine.

1. Introduction

Organic matter plays a major role in soil-forming processes in coniferous forests in the boreal zone. The organic layer is the main source of the protons causing podzolisation of the upper strata of the mineral soil, and the transport of organic matter by percolation water and its precipitation in the B horizon are significant phenomena characteristic of podzolic soils. Organic matter has been found to have a strong effect on soil water pH and the occurrence of different Al species, and is an important anion and proton donor in the ionic balance of water systems (e.g., Nilsson and Bergkvist, 1983; Derome, 1989; Kortelainen and Mannio, 1990; Gobran and Tipping, 1993). The total amount of organic matter in the upper layers of the mineral soil is considerable, and on many sites is greater than that in the organic layer (Viro, 1969). The amount and vertical distribution of organic matter in the mineral soil are of crucial importance for the maintenance of soil fertility by providing cation exchange sites and retaining moisture. The behavior of organic matter in the soil and soil water should be taken into account when attempting to distinguish between natural and anthropogenic soil acidification in areas subjected to elevated acidic deposition.

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The aim of this study was to investigate the relationship between dissolved organic matter and chemical constituents of percolation water collected from forested sites in northern Finland. Detailed information was needed about this relationship in order to be able to distinguish between natural podzolisation phenomena and possible changes in the soil and percolation water caused by SO_2 and heavy metal emissions. The study was conducted on ion-balance sampling plots located along gradient lines extending from Cu-Ni smelters in the Kola Peninsula, Russia, established as part of the Lapland Forest Damage Project. This paper concentrates on the correlations between dissolved organic matter and a number of percolation water parameters; no attempt is made to investigate seasonal or regional trends in these parameters. These matters will be dealt with in subsequent publications.

2. Material and Methods

The percolation water data were collected during 1989–1991 from 13 permanent ion-balance monitoring plots located in Finnish Lapland along lines running to the NW, W and SW from the emission point sources in Russia (Monchegorsk, Nikel) (Figure 1). A gradient approach is being employed in the Lapland Forest Damage Project, and all the monitoring points along the lines have as uniform as possible stand and site characteristics. The sample plots were located on dry and dryish sites (see Cajander, 1949, for Finnish site classification) with genetic horizons characteristic of iron-humus podsols. The particle size distribution and organic matter content in the different horizons are given in Table I. The soil type on the sites was sorted fine sand or sand, apart from two sites which represented an intermediate form between sorted and till soil. The 80 to 200-yr-old tree stands were dominated by Scots pine (*Pinus sylvestris*) and the ground vegetation consisted primarily of dwarf shrubs (*Calluna vulgaris*) and lichens (*Cladonia* spp.). Percolation water was collected from gravity lysimeters located at three different depths (5, 20 and 40 cm below the ground surface) at four points around the circular monitoring plots (300 m^2 in size). The lysimeters were emptied at 3 to 4-week intervals during the snowfree period (May – October). Annual precipitation in the region ranges from 380 to 580 mm.

The pH of the water samples was measured and the samples then filtered through filter paper and a membrane filter (0.45 μm). Fifty mL of each sample were treated with superpure nitric acid (0.25 mL) and used for the determination of metals and total dissolved P and S by inductively coupled plasma atomic emission spectrometry (ICP/AES). The remainder of the sample was used for determining $NH_4{}^+$ and $NO_3{}^-$ by flow injection analysis (FIA), and the organic matter concentration as permanganate consumption according to the Finnish standard SFS 3036. Sodium ion was omitted from the ionic balance calculations because Cl^- was not determined. The experimental design of the ion-balance monitoring plots and the analyses are described in detail in Derome *et al.* (1991).

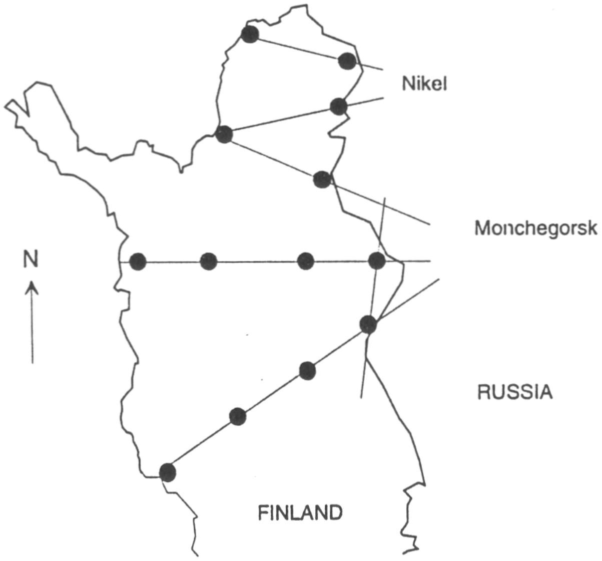


Fig. 1. Location of the ion-balance monitoring plots.

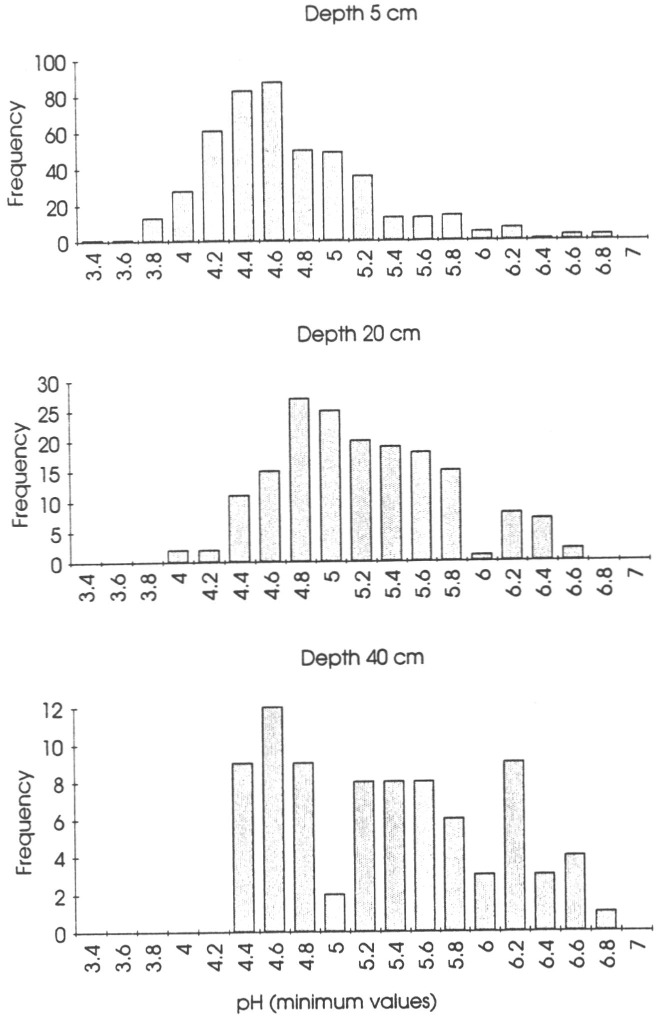
TABLE I

Means of thickness, organic matter content (loss in weight on ignition, LOI), and sand, silt and clay content by soil horizon on the 13 ion-balance monitoring plots. Ranges given in parentheses

Horizon	Thickness (cm)	LOI (%)	Sand (%)	Silt (%)	Clay (%)
Ao	2.3 (1.0–4.4)	55.5 (33.7–82.4)	–	–	–
E	4.1 (0.6–7.6)	2.6 (1.0–6.0)	81.3 (60.0–96.3)	13.1 (3.3–31.4)	1.3 (0.0–4.1)
B + BC	14.1 (10.4–24.1)	2.1 (0.6–5.0)	82.3 (60.2–97.2)	11.4 (2.0–31.7)	1.2 (0.1–2.4)
C	–	1.0 (0.3–3.0)	79.0 (40.4–99.4)	11.4 (0.0–36.6)	1.0 (0.0–3.3)

3. Results

There was considerable variation in the chemical composition of the percolation water sampled at the same depth on the different plots even though the material had been collected from sample plots where the variation in stand properties had been minimized. Despite this variation between the plots, the concentrations of chemical constituents followed a similar trend down the soil profile. The concentrations of



Depth 5 cm

Depth 20 cm

Depth 40 cm

Fig. 2. Frequency distribution of the percolation water pH values at different depths.

soluble Ca, Mg, Al, K, Fe, Mn, NH_4^+, and dissolved P and organic matter decreased on moving from a depth of 5 to 20 cm. There were no changes in total dissolved S and NO_3^- concentrations, while soluble Na concentration showed a slight increase between depths of 5 and 20 cm. Only the concentrations of dissolved Al, K, Fe and organic matter decreased further on moving deeper to 40 cm (Table II). Percolation water pH increased on moving from a depth of 5 to 20 cm, but did not differ substantially between 20 and 40 cm (Table II, Figure 2).

Significant positive correlations were found between dissolved organic matter and total dissolved Al concentrations at 5 and 20 cm depth, but not at 40 cm (Figure 3). A significant negative correlation was found between dissolved organ-

TABLE II

The chemical composition of the percolation water at different depths

	Depth cm	Mean	Median	S.D.	Min	Max	n	t-test 5/20 cm	t-test 20/40 cm
pH	5	4.81	4.70	0.56	3.56	6.98	469	$p < 0.001$	
	20	5.31	5.26	0.56	4.06	6.64	172		n.s.
	40	5.44	5.41	0.71	4.41	6.93	82		
Ca, mg L^{-1}	5	1.41	0.98	1.43	0.02	7.41	393	$p < 0.001$	
	20	0.78	0.62	0.65	0.02	3.48	127		n.s.
	40	0.90	0.73	0.68	0.05	2.61	63		
Al, mg L^{-1}	5	0.68	0.50	0.74	0.00	7.39	393	$p < 0.001$	
	20	0.30	0.13	0.40	0.00	1.87	127		$p < 0.01$
	40	0.15	0.06	0.26	0.00	1.40	63		
Mg, mg L^{-1}	5	0.43	0.30	0.47	0.01	2.99	393	$p < 0.05$	
	20	0.35	0.29	0.26	0.01	1.30	127		n.s.
	40	0.35	0.37	0.24	0.01	1.10	63		
Na, mg L^{-1}	5	1.10	0.70	1.25	0.07	9.03	393	$p < 0.05$	
	20	1.31	1.11	0.84	0.09	5.17	127		n.s.
	40	1.24	1.10	0.83	0.11	6.12	63		
K, mg L^{-1}	5	2.00	1.37	2.04	0.00	11.81	393	$p < 0.001$	
	20	0.81	0.55	0.88	0.00	5.28	127		$p < 0.01$
	40	0.43	0.24	0.82	0.00	6.09	63		
Fe, mg L^{-1}	5	0.52	0.38	0.50	0.00	4.47	393	$p < 0.001$	
	20	0.16	0.09	0.17	0.00	1.01	127		$p < 0.001$
	40	0.09	0.04	0.12	0.00	0.58	63		
Mn, mg L^{-1}	5	0.29	0.19	0.30	0.00	2.50	393	$p < 0.001$	
	20	0.12	0.06	0.17	0.00	1.29	127		n.s.
	40	0.17	0.08	0.20	0.00	0.90	63		
NH_4^+–N mg L^{-1}	5	1.15	1.02	0.59	0.00	4.25	303	$p < 0.001$	
	20	0.87	0.85	0.26	0.42	1.78	86		n.s.
	40	0.92	0.78	0.39	0.44	2.28	48		
S, mg L^{-1}	5	4.49	3.68	2.87	0.41	17.79	393	n.s.	
	20	4.31	3.75	2.40	1.29	17.81	127		n.s.
	40	4.12	3.77	2.17	1.01	10.42	63		
P, mg L^{-1}	5	0.19	0.07	0.34	0.00	3.36	393	$p < 0.001$	
	20	0.03	0.00	0.04	0.00	0.24	127		n.s.
	40	0.03	0.00	0.05	0.00	0.28	63		
NO_3^-–N, mg L^{-1}	5	0.02	0.00	0.08	0.00	1.03	295	n.s.	
	20	0.03	0.00	0.16	0.00	1.37	84		n.s.
	40	0.02	0.00	0.06	0.00	0.34	46		
Permanganate consumption, mg L^{-1} (Dissolved organic matter)	5	144	116	107	12	711	263	$p < 0.001$	
	20	44	26	38	5	148	88		$p < 0.001$
	40	17	16	8	4	42	44		

ic matter concentration and pH at 5 cm depth, but not at 20 and 40 cm depth (Figure 4).

The ionic balance of the percolation water was investigated by determining the difference between the cation sum ($H^+ + Ca^{2+} + Mg^{2+} + K^+ + Al^{3+} + Fe^{3+} + Mn^{2+} + NH_4{}^+$) and anion sum ($SO_4{}^{2-} + PO_4{}^{3-} + NO_3{}^-$). There was an anion deficit in 85% of the water samples collected at 5 cm depth. The anion deficit was positively correlated with the dissolved organic matter concentration in the percolation water collected at this depth (Figure 5).

4. Discussion

Total dissolved Al concentrations in the percolation water collected in the surface layers (depths of 5 and 20 cm) of the podzol soil profiles correlated positively with the corresponding dissolved organic matter concentrations. This is in agreement with the finding that most of the Al present in the surface layer of podzolic soils is in the form of organic complexes (Nilsson and Bergkvist, 1983; Lundström, 1993). Organic Al complexes have been shown to be non-phytotoxic (e.g. Hue *et al.*, 1986), the toxicity of Al to plants being more dependent on free Al^{3+} than on total dissolved Al concentrations (Parker *et al.*, 1989). Total dissolved Al concentrations obtained in this study were relatively low (0.68 ± 0.74 mg L^{-1} at a depth of 5 cm). According to Arovaara and Ilvesniemi (1990), the growth of spruce seedlings is inhibited at soluble inorganic Al concentrations of 10–50 mg L^{-1}, and of pine seedlings at 20–50 mg L^{-1}. The presence of Al (determined as total Al) in the percolation water of northern Finnish soils is probably therefore not a serious threat to roots and mycorrhizae because the rooting zone is primarily restricted to the humus layer and the uppermost mineral soil layer.

In this study the percolation water pH increased with increasing soil depth, which is a feature characteristic of podzolic soils in Finland (e.g., Helmisaari and Mälkönen, 1989; Soveri and Ahlberg, 1990). An increase in soil water pH deeper in the soil means that the concentrations of Al^{3+} in the soil solution remain low (Derome, 1991), which is an important feature considering that the organic matter concentration is relatively low at such depths.

Organic matter plays a pH-regulating role in the surface layers of the soil (depth 5 cm) because the humus compounds formed as a result of plant litter decomposition in cool, humid conditions are weak, organic acids. Deeper down in the soil (depths of 20 and 40 cm) the organic matter concentration no longer appears to have any effect on percolation water pH owing to the relatively low concentrations of organic matter.

Organic matter plays an important role in maintaining the ionic balance of water systems where it acts as an anion (e.g., Kortelainen and Mannio, 1990; Derome, 1992; Lundström, 1993). The anionic nature of the organic matter in the percolation water collected in dry and dryish soils in northern Finland was most

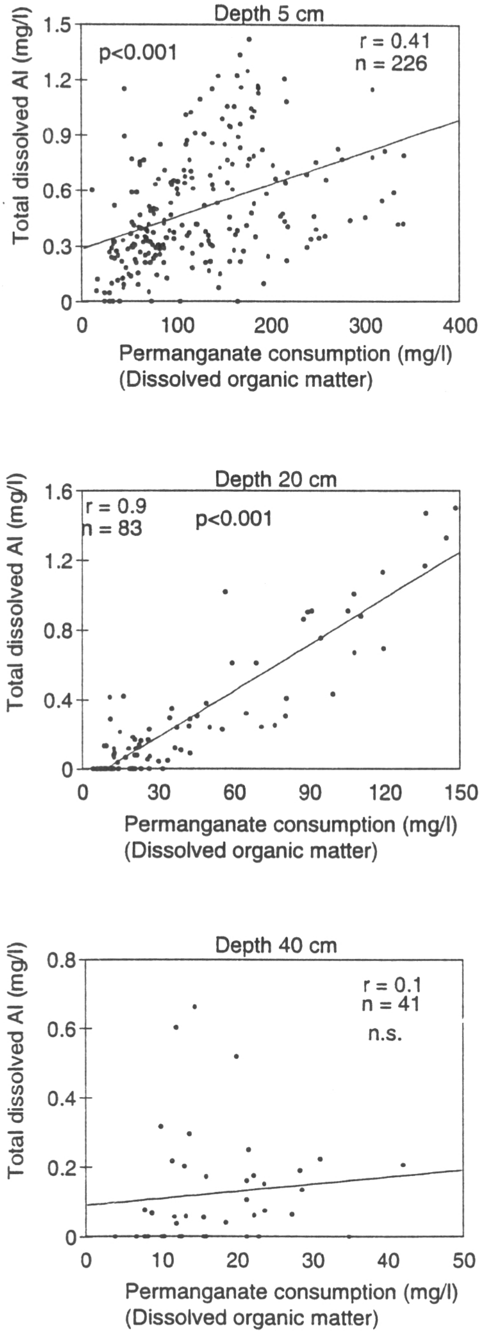


Fig. 3. The relationship between dissolved organic matter (permanganate consumption) and total Al concentrations in percolation water at depths of 5, 20 and 40 cm.

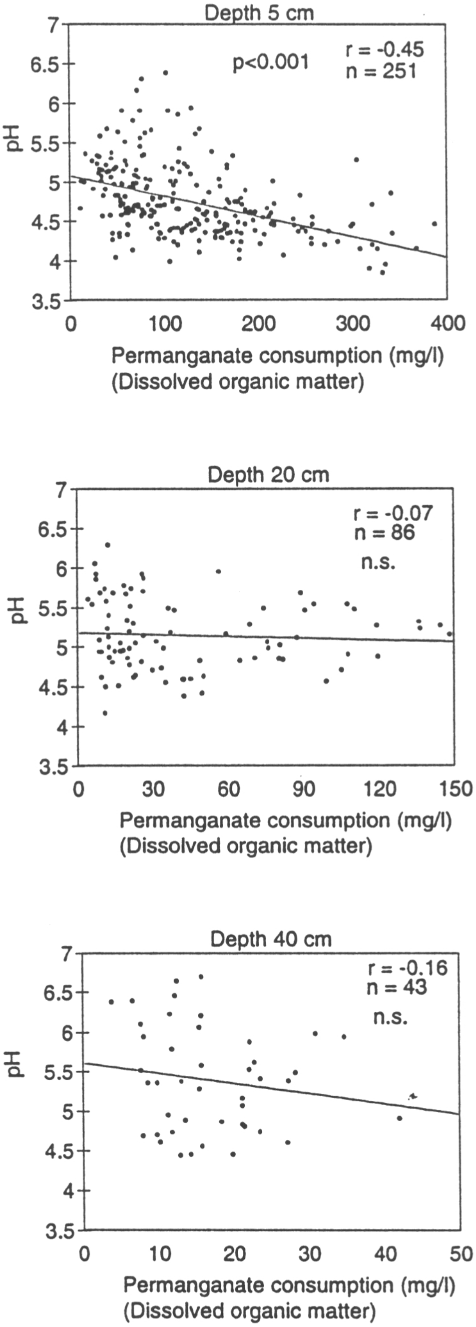


Fig. 4. The relationship between dissolved organic matter (permanganate consumption) and pH in percolation water at depths of 5, 20 and 40 cm.

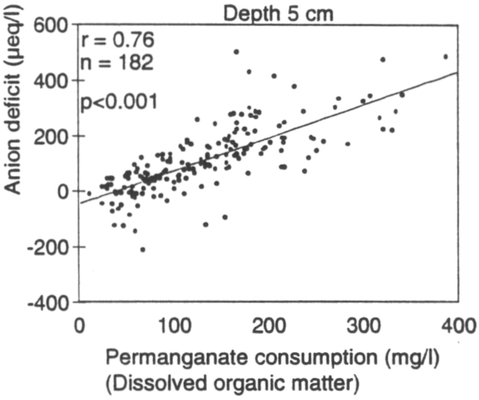


Fig. 5. The relationship between dissolved organic matter (permanganate consumption) and the anion deficit in percolation water at a depth of 5 cm.

clearly apparent in the surface soil layers where the organic matter concentration was the highest. A clear connection was found between the anion deficit and organic matter concentration of the percolation water.

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Paper IV

Derome, J., Lindroos, A.-J. & Niska, K. Effects of SO_2 and heavy metal emissions from the Kola Peninsula, NW Russia, on soil acidity parameters in NW Russia and Finnish Lapland. Scandinavian Journal of Forest Research. (in print).

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EFFECTS OF SO_2 AND HEAVY METAL EMISSIONS FROM THE KOLA PENINSULA, NW RUSSIA, ON SOIL ACIDITY PARAMETERS IN NW RUSSIA AND FINNISH LAPLAND

Running headline: EFFECTS OF SO_2 AND HEAVY METAL EMISSIONS

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ABSTRACT

Derome, J.[1], Lindroos, A.-J.[2] and Niska, K.[1] ([1]Rovaniemi Research Station, the Finnish Forest Research Institute, P.O. Box 16, FIN-96301 Rovaniemi, Finland, and [2]Vantaa Research Centre, the Finnish Forest Research Institute, P.O. Box 18, FIN-01301 Vantaa, Finland). *Effects of SO_2 and heavy metal emissions from the Kola Peninsula, NW Russia, on soil acidity parameters in NW Russia and Finnish Lapland.*

The effects of SO_2 and heavy metal emissions derived from Cu-Ni smelters in the Kola Peninsula, NW Russia, on soil acidity parameters in the western parts of the Kola Peninsula and Finnish Lapland are presented. Organic layer samples were collected at 39 sampling plots along lines running to the west from two emission point sources (Monchegorsk, Nikel) in the Kola Peninsula. The tree cover on the sample plots consisted of *Pinus sylvestris L.* growing on dry sites. The soil type was podsolic and soil texture sorted sand. The effects of emissions from the Monchegorsk smelters on the properties of the organic layer along the sampling line can be divided into two zones: up to a distance of ca. 100 km from the smelters there were distinct gradients in the total Cu and Ni and exchangeable Al concentrations and to some extent in base saturation (BS), but not in extractable S concentrations, while at greater distances to the west the emissions appear to have had no detectable effects. Despite the very low BS values close to the Monchegorsk smelter, there were no differences in pH or in exchangeable H^+ concentrations with increasing distance from the smelter. Total Cu and Ni concentrations were elevated close to the Nikel smelter but were considerably lower than those at corresponding distances from Monchegorsk. Extractable S concentrations along the Nikel line were not affected by emissions. BS showed a decrease with decreasing distance to Nikel, but there were no clear relationships for pH or exchangeable Al. In contrast, exchangeable H^+ increased with decreasing distance to the point source. A reduction in BS in heavy-metal polluted soils should not be taken as an absolute indication of soil acidification caused by acidic deposition, because metals can also effectively displace base cations from cation exchange sites. *Key words: Acidity, Al, base saturation, Cu, forest soil, Ni, organic layer, S, Scots pine.*

INTRODUCTION

Sulphur and heavy metal emissions from the Cu-Ni smelters in the Kola Peninsula, NW Russia, have caused serious damage to forest ecosystems in the immediate vicinity of the emission point sources (Kozlov et al. 1993), and are also considered to pose a serious threat to tree vitality and soil condition over extensive areas in northern Fennoscandia. High levels of S deposition can decrease base saturation and increase acidity and soluble Al concentrations in the soil (Ulrich 1981, Berdén et al. 1987). High Al concentrations are harmful to plant roots and mycorrhizas and limit tree growth (Foy 1974, 1988). Heavy metals have been reported to accumulate in the topmost layers of the soil close to heavy metal smelters (e.g. Freedman & Hutchinson 1980, Nordgren et al. 1986, Løbersli & Steinnes 1988, Fritze et al. 1989, Derome & Lindroos 1998).

Annual sulphur dioxide emissions in the Kola Peninsula totalled about 600 000 - 650 000 t at the end of 1980s and beginning of the 1990s (Tuovinen et al. 1993, Luzin et al. 1994). Of this total, the Cu-Ni smelters at Nikel accounted for 260 000 - 370 000 t, and the Monchegorsk smelters for 210 000 - 250 000 t. The SO_2 concentrations in the air increase with decreasing distance to the Kola smelters. The annual mean SO_2 concentration exceeds 20 $\mu g\ m^{-3}$ over wide areas around the point sources (Tuovinen et al. 1993). In 1990, the annual Cu and Ni emissions from Nikel were 200 t and 300 t, respectively, and for Monchegorsk 2200 t and 3100 t (Anon. 1992). According to a survey of the chemical composition of the snowpack in the region (Äyräs et al. 1995), there is also considerable deposition of Fe, Al and other metals in the form of dust originating from soil erosion or open-cast mining activities.

The high emission levels have had disastrous effects on the environment around the smelters. The forests over an area of 400 - 500 km^2 around Monchegorsk have been completely destroyed and the affected area is even larger around Nikel (Tikkanen 1995). The emissions are reflected as elevated S, Cu and Ni concentrations in the snowpack and rainwater near the smelters (Karaban & Gytarsky 1995, Lindroos et al. 1995, Äyräs et al. 1995, Reimann et al. 1996). The sulphur and heavy metal concentrations in percolation water collected from forest sites also increase with decreasing distance to the Monchegorsk smelters (Lindroos et al. 1996). Strongly elevated S concentrations in Scots pine needles have been reported within a distance of 40 km from the smelters (Raitio et al. 1995). High heavy metal concentrations in moss have been detected over large areas in the Kola Peninsula, NE Finland and Norway (Rühling et al. 1992, Rühling 1994).

This study was carried out as a part of the Lapland Forest Damage Project (1989-95), the aim of which was to determine the effects of emissions from the Cu-Ni smelters at Monchegorsk and Nikel, NW Russia, on the condition of forest ecosystems in Finnish Lapland and in the part of Russia lying between the smelters and the Russian-Finnish border. The aim of this soil study is to determine the effects of emissions of acidifying compounds (SO_2)and heavy metal emissions, as well as other factors associated with the smelting and mining industry, on soil acidity and base cation status in the organic layer of forested sites along two gradients running to the west of the Cu-Ni smelters at Monchegorsk and Nikel. The importance of Cu in the displacement of base cations from cation exhange sites is also examined.

MATERIAL AND METHODS

The soil samples for the study were collected at 39 sample plots located along two gradient lines (26 and 13 plots, respectively) running approximately to the west from two emission point sources (Monchegorsk and Nikel) in the Kola Peninsula, NW Russia (Fig. 1). The tree cover on the sample plots consisted of rather pure Scots pine (*Pinus sylvestris L.*) stands, which were at least 80 years old and growing on dry sites with a ground vegetation mainly comprising heather (*Calluna vulgaris*) and lichens (*Cladonia* spp.). The soil type was podsolic, and on most of the plots the soil texture was sorted sand. The terrain was either flat or sloping slightly to the east, i.e. towards the smelters.

Soil samples were taken from the organic layer at 20 systematically selected points on each of the 39 plots, and combined to give one bulk sample per plot. The moist humus samples were homogenised by hand by rubbing through a 3 mm sieve and kept frozen (-20 °C) until analysis. The soil moisture content was determined by drying for 24 hours in an oven at 105 °C, and the loss in weight on ignition following ignition in a muffle furnace at 550 °C. pH was measured in a soil/water slurry (15:25, v/v). Total Cu and Ni were determined by dry digestion at 550 °C in a muffle furnace, followed by extraction of the ash with HCl. Copper and Ni were determined from the extract by inductively coupled plasma/atomic emission spectrometry (ICP/AES). Extractable S was determined by extraction with 1 M ammonium

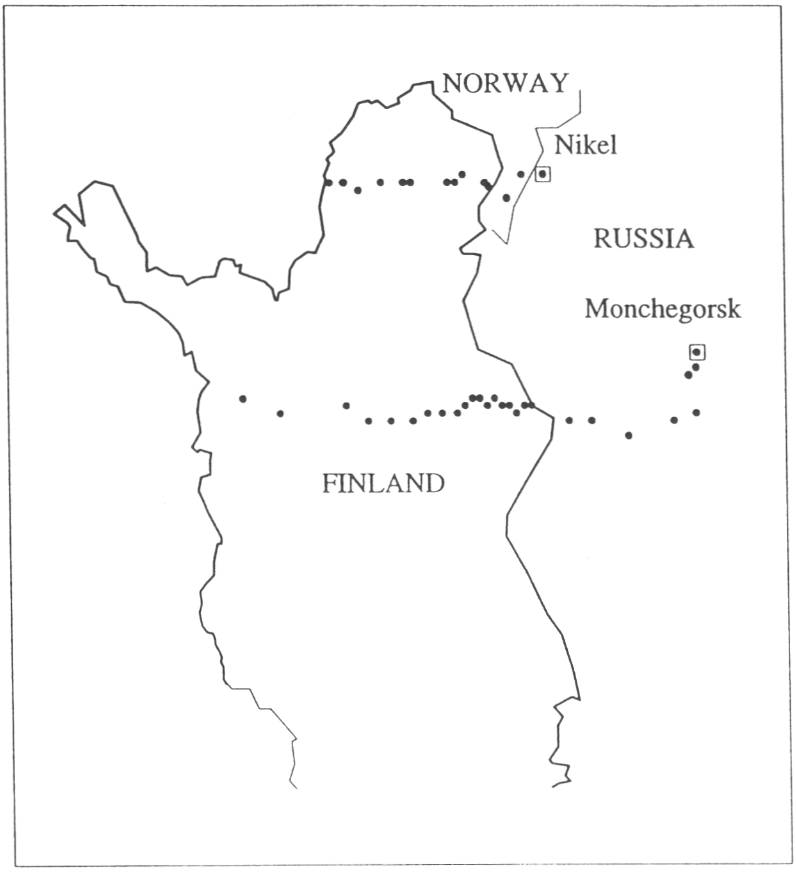

Fig. 1. Location of the emission sources and the soil sampling plots in NW Russia, Norway and Finnish Lapland.

acetate (pH 4.65), and total S in the extract analysed by ICP/AES. Exchangeable base cations and exchangeable Al and Cu were determined by extraction with 0.05 M $BaCl_2$ (27:200, v/v). Calcium, Mg, K, Na, Cu and Al were analysed from the extract by ICP/AES. Titratable acidity was determined by titration of an aliquot of the $BaCl_2$ extract with 0.05 M NaOH to pH 7. Exchangeable H^+ was obtained as the difference between titratable acidity and exchangeable Al. Effective cation exchange capacity (CEC) was obtained as the sum of base cations, exchangeable Cu and titratable acidity. Copper was included in the CEC calculation because it is known to be present in high concentrations in the organic layer close to Cu smelters, and it was therefore assumed that it would also occupy a significant proportion of the cation exchange sites. According to Leckie and Davis (1979), the hydrolysis constant for Cu^{2+} in solution ($Cu^{2+} + H_2O \Leftrightarrow CuOH^2 + H^+$) is between pH 7.2 to 8.1, and according to Lindsay (1979) pH 7.7. Cu^{2+} is the major ion in solution below pH 6.9. This means that the contribution of Cu to exchangeable acidity will be negligible. Base saturation was calculated as the proportion of base cations (Ca + Mg + K + Na) out of CEC. The results were calculated on the basis of the organic matter content rather than dry weight owing to the difficulties involved in obtaining mineral soil-free samples from the rather thin organic layer on these dry, rather infertile sites.

The relationships between the distance to the smelters and element concentrations and acidity parameters in the organic layer were studied using regression models. The statistical significance of each model was tested using the F-test, and the regression coefficient and constant using the t-test. Logarithmic transformations (log10) were used in some cases in order to ensure that the data fully corresponded to the requirements of regression analysis.

RESULTS

Sulphur emissions from the Monchegorsk smelter have increased the extractable S concentration in the organic layer only on the plot closest (8 km) to the smelter (Fig. 2a); elsewhere along the line there was no significant relationship between the S concentration and distance to the smelter. The Nikel smelter has had no effect on extractable S concentrations on any of the plots (Fig. 2b). The gradients for the total Cu (Fig. 2c, d) concentrations in the organic layer were relatively short along both lines; elevated Cu concentrations extended for ca. 100 km along the Monchegorsk line, and for ca. 50 km along the Nikel line. The gradients for total Ni (Fig. 2e, f) were somewhat longer, especially along the Nikel line. In contrast to Cu, elevated Ni concentrations were found up to a distance of 70 km from the Nikel smelter.

Emissions from the Monchegorsk or Nikel smelters have had no effect on the pH(H_2O) of the organic layer (Fig. 3a, b). The variation in pH along the Nikel line was considerably greater than that along the Monchegorsk line. Exchangeable H^+ in the organic layer along the Monchegorsk line appeared to be slightly lower close to the smelter than at other points along the line (Fig. 3c). However, the model depicting the differences was not statistically significant. Along the Nikel line, in contrast, there was a significant increase ($p < 0.01$) in exchangeable H^+ with decreasing distance to the smelter (Fig. 3d). Exchangeable Al in the organic layer showed a significant increase ($p < 0.001$) with decreasing distance to the Monchegorsk smelter (Fig. 3e). At distances greater than 100 km from the smelter, however, the exchangeable Al concentrations were rather low and remained relatively constant. The distance to the Nikel smelter had no significant effect on exchangeable Al concentrations in the organic layer (Fig. 3f).

Base saturation (BS) in the organic layer was only 12% on the plot located 8 km from Monchegorsk, and somewhat depressed (47%) at the plot located at 50 km (Fig. 3g). BS on all the other plots along the line was over 60%. Although the regression equation showed a significant decrease ($p < 0.001$) in BS with decreasing distance to the smelter, exclusion of the two depressed BS values resulted in a non-significant regression model, suggesting that emissions from the smelter have in fact had only a very small overall effect on BS along the gradient line. There was a significant decrease ($p < 0.05$) in BS with decreasing distance to the smelter at Nikel (Fig. 3h).

At 8 km along the Monchegorsk line, the proportion of base cations occupying cation exchange sites was extremely low, about 12%, and that of Al almost 50% (Fig. 4). The decrease in base saturation was primarily due to the depressed Ca concentration. The proportion of Cu was also relatively high at this point. The proportion of sites occupied by exchangeable H^+ was rather constant, even at the plot only 8 km from the smelter. The pattern for the Nikel line was different. The proportion of exchange sites occupied by Cu was insignificant and the proportion of exchangeable Al remained rather constant. However, the proportion of H^+ showed a clear increasing trend with decreasing distance to the smelter. The loss in base

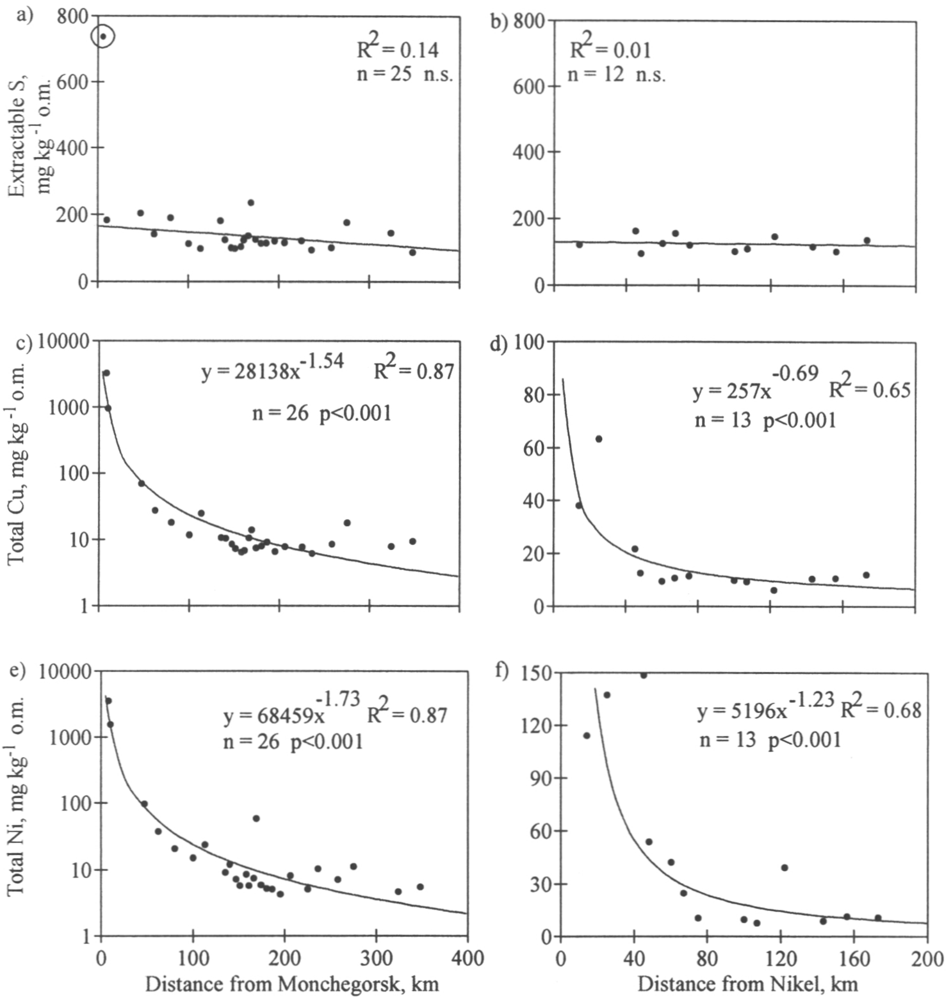

Fig. 2. Extractable S (a, b), total Cu (c, d) and total Ni (e, f) concentrations in the organic layer at different distances from the emission point sources at Monchegorsk and Nikel. The ringed value (outlier) in (a) was excluded from the regression analysis. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter.

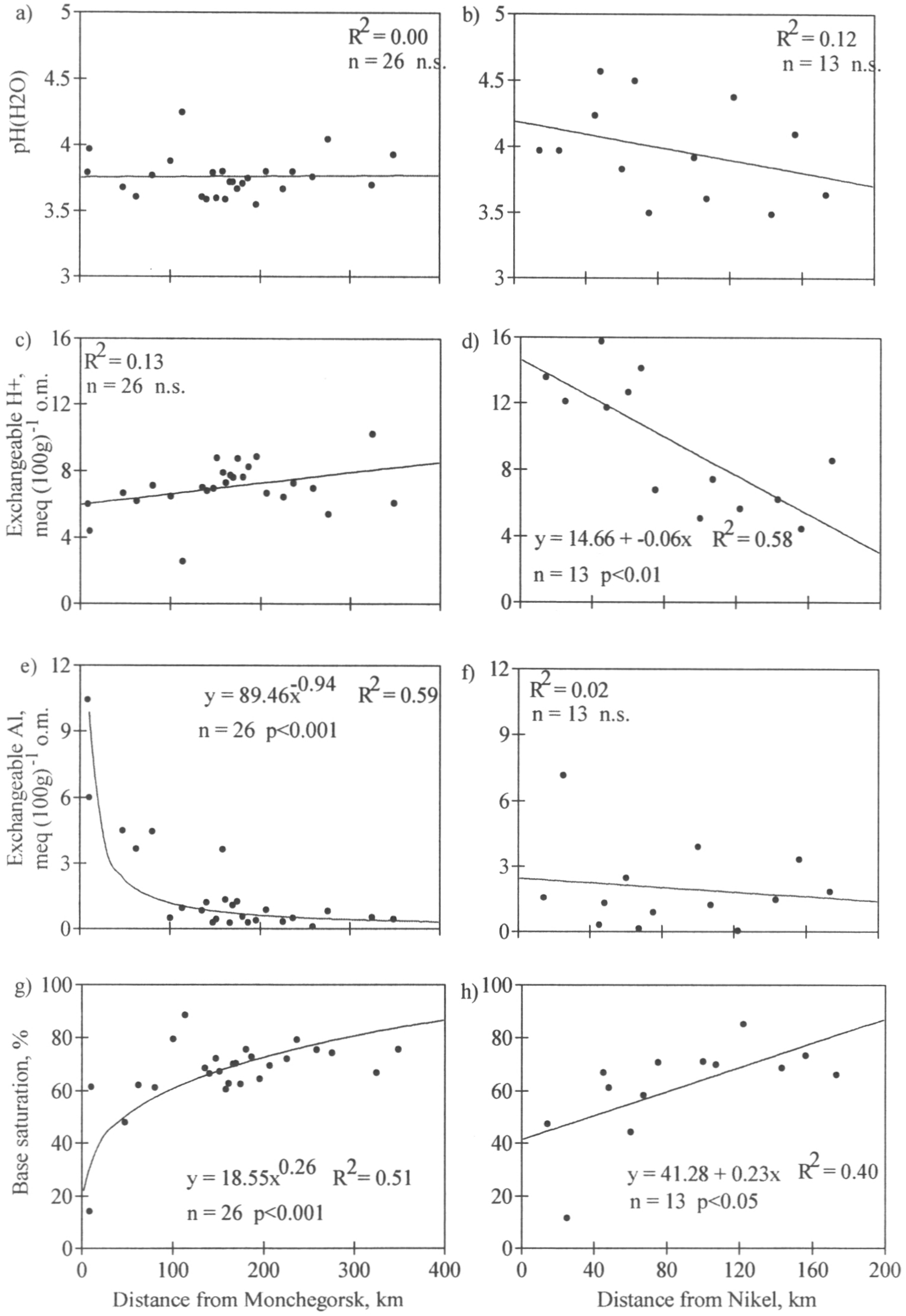

Fig. 3. pH (a, b), exchangeable H+ (c, d), exchangeable Al (e, f) and base saturation (g, h) in the organic layer at different distances from the emission point sources at Monchegorsk and Nikel. Only statistically significant functions are presented. The p value indicates the statistical significance of the model (F-test). o.m. = organic matter.

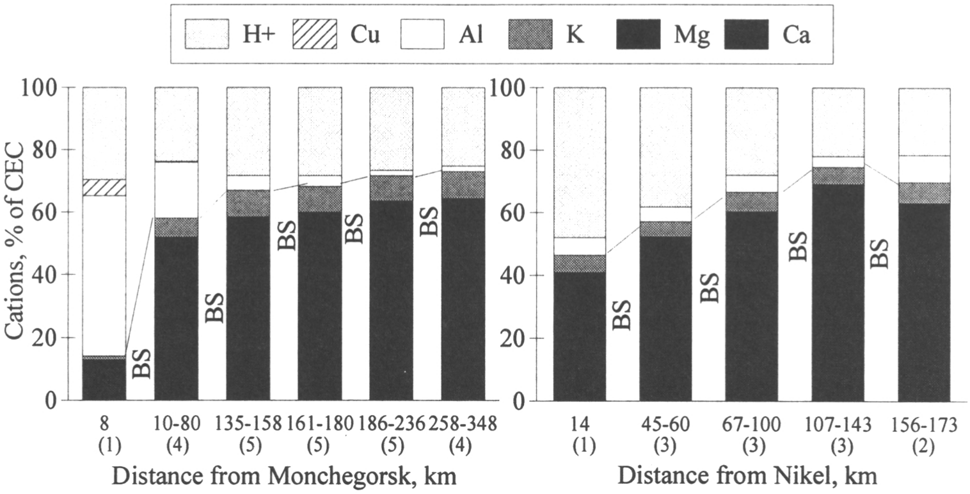

Fig. 4. Relative proportion of different cations occupying cation exchange sites in the organic layer at different distances from the Monchegorsk (on the left) and Nikel (on the right) smelters. CEC = cation exchange capacity. BS = base saturation. The columns in the histogramme represent the value for one plot (Monchegorsk line 8 km, Nikel line 14 km) or the mean value of plot groups in different sections along the two sampling lines. The number of plots (n) is given in parentheses.

saturation close to the smelter was much less than that near Monchegorsk.

DISCUSSION

The effects of emissions from the Monchegorsk smelters on the chemical properties of the organic layer along the sampling line can be divided into two zones: up to a distance of ca. 100 km from the smelters there were distinct gradients in the total Cu and Ni and exchangeable Al concentrations and BS (50 km only), but not in extractable S concentrations, while at greater distances to the west the emissions appear to have had no detectable effects. The first four plots in this 100 km section of the Monchegorsk line are located approximately to the S and SSW of the smelter, and the two remaining ones to the SW. Owing to the prevailing northerly and southerly wind directions (Tikkanen & Niemelä 1995), these plots are frequently exposed to high SO_2 levels and high Cu and Ni deposition. The plots located at distances of greater than 100 km from the smelters are sheltered to a considerable extent by the high range of fells lying to the west of Monchegorsk.

Low BS values close to Ni-Cu smelters are generally considered to be due to soil acidification caused by high emissions of acidifying SO_2 (e.g. Løbersli & Steinnes 1988). Fritze et al. (1989) also reported low BS values, elevated Cu and Ni concentrations, but relatively constant H^+ concentrations, in forest humus close to a Ni-Cu smelter in western Finland. They did not determine exchangeable Al. Despite the very low BS values close to the Monchegorsk smelter, there were no differences in pH or in exchangeable H^+ concentrations with increasing distance from the smelter. According to snowpack sampling (Lindroos et al. 1995), there are no signs of acidic deposition in the area during the winter months at least. Although there was high deposition of S and Cu and Ni, snowpack pH relatively close to the smelter was close to 5. The dust emitted from the smelter and deposited within adjacent areas contains, in addition to Cu, Ni and other heavy metals, ca. 19% S, of which ca. 7% is sulphate. Percolation water along this section of the line showed elevated S, Cu and Ni concentrations at 5 cm depth up to a distance of about 40 km, but only slightly depressed pH values at 30 - 50 km (Lindroos et al. 1996). The strong reduction in base saturation 8 km from the smelter was mainly due to the increased proportion of Cu and Al occupying cation exchange sites, and to Al at 10 - 80 km from the smelter. In a study carried out in SW Finland close to a Cu-Ni smelter with strongly reduced S, Cu and Ni emissions (Derome & Lindroos 1998), a corresponding decrease in base saturation 0.5 and 2 km from the smelter was found to be due to the displacement of base cations by Cu in the organic layer, and not to an input of protons derived from earlier SO_2 emissions. Neither pH nor exchangeable Al concentrations in the organic layer were correlated with distance to the smelter. In the case of Monchegorsk, however, the simultaneous presence of elevated exchangeable Al concentrations, but relatively constant pH, extractable S and exchangeable H^+ concentrations, suggests an external source of Al. Äyräs et al. (1995) reported high Al concentrations (over 5 times the background values) in the snowpack in the Monchegorsk area. They separated water-soluble Al and particulate Al, and found that the concentrations in both fractions were very high. Water-soluble Al is in the form of Al^{3+}, which is the same as exchangeable Al in the soil, and this has undoubtedly contributed to the increased concentrations of exchangeable Al in the organic layer in this part of the line. In addition, Mäkinen (1994) reported high (5 times the background) Al concentrations in moss samples, and Lukina and Nikonov (1992) elevated foliar Al concentrations in Scots pines in the same area. These reports lend further support to the assumption that the increased exchangeable Al concentrations are due to Al derived from external sources, such as dust from spoil heaps at the open-cast mines, as well as possibly from the Al smelter located less than 100 km to the south at Kandalaksha, rather than to soil acidification caused by acidic deposition. The release of Al^{3+} from cation exchange sites and from organic-Al complexes in the organic layer require pH values of between 3 - 3.5 (Derome 1989), which are considerably lower than the values measured in this study.

The length of the Nikel line was only half that of the Monchegorsk and there was no clear division into zones as regards the effects of emissions on the organic layer. Maximum total Cu and Ni concentrations close to the smelter were considerably lower than those at corresponding distances from Monchegorsk. Extractable S concentrations in the organic layer throughout the sampling line were of a similar order of magnitude to those along the Monchegorsk line. All the plots on the Nikel line are located due west of the smelter, and the dominant wind directions are from the northwest, north and south. Nikel is located in a river valley running in a N-S direction between rather low ranges of fells.

The effects of emissions from the Nikel smelter on acidity parameters in the organic layer along the sampling line were somewhat different from those in the first 100 km of the Monchegorsk line. BS showed a decrease with decreasing distance to the smelter, but for exchangeable Al there was no clear relationship. In contrast, exchangeable H^+ was strongly related to the distance to the point source. In this respect the effect of emissions on the organic layer better fulfil the definition of soil acidification caused by acidic deposition than the situation close to Monchegorsk, despite the fact that extractable S concentrations along the Nikel line were also not affected by emissions.

The results of this study raise the question of whether a reduction in BS in the heavy-metal polluted soil in the vicinity of the Monchegorsk smelter can in fact be considered a result of soil acidification caused by acidic deposition. For instance, Freedman & Hutchinson (1980) and Løbersli & Steinnes (1988) reported soil acidification on the basis of strongly reduced BS values, even though other soil acidity parameters showed only minor changes. In contrast, Derome & Lindroos (1998) concluded that a strong reduction in BS in the organic layer less than 2 km from a Cu-Ni smelter in SW Finland was due to the displacement of base cations from this layer by heavy metals, primarily Cu. The displaced base cations accumulated strongly in the underlying 0-5 cm mineral soil layer.

In conclusion, the effect of the Monchegorsk smelters is reflected in the total Cu and Ni and exchangeable Al concentrations and to some extent BS in the organic layer, but not in extractable S concentrations up to a distance of ca. 100 km from the smelters, while at greater distances to the west the emissions appear to have had no detectable effects. The strong reduction in base saturation near Monchegorsk was mainly due to the increased proportion of Cu and especially Al occupying cation exchange sites but not H^+. Total Cu and Ni concentrations were elevated close to the Nikel smelter but were considerably lower than those at corresponding distances from Monchegorsk. Extractable S concentrations along the Nikel line were not affected by emissions. Because BS showed a decrease and exchangeable H^+ an increase with decreasing distance to Nikel, the effect of emissions on the organic layer better fulfil the definition of soil acidification than the situation close to Monchegorsk. A reduction in BS in heavy-metal polluted soils should not be taken as an absolute indication of soil acidification caused by acidic deposition because metals can also effectively displace base cations from cation exchange sites.

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Paper V

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THE EFFECT OF EMISSIONS FROM Cu-Ni SMELTERS AT NIKEL, NW RUSSIA, ON THE QUALITY OF BULK DEPOSITION, STAND THROUGHFALL AND PERCOLATION WATER IN FOUR SCOTS PINE STANDS IN NORTHERN NORWAY AND FINLAND

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ABSTRACT

The effects of industrial emissions from Nikel, NW Russia, on the chemical composition of bulk deposition, stand throughfall and percolation water (depth 5 cm) were studied in four Scots pine stands. The plots were located on dry sites with genetic horizons characteristic of iron-humus podsol. The ground vegetation consisted of *Calluna vulgaris* and *Cladonia* spp.. The highest S concentrations in bulk deposition and in stand throughfall were recorded on the sample plot (14 km) closest to Nikel. The S concentration in stand throughfall decreased gradually with increasing distance from Nikel. The pH of stand throughfall was somewhat lower on the plots located at 14, 33 and 58 km from Nikel compared to that at 132 km. There was no clear gradient in the percolation water pH or S concentrations with respect to the point source. The copper and nickel concentrations in percolation water were very low, even at the plot (14 km) closest to the point source. The lowest pH values and highest Al, Ca and Mg concentrations in percolation water were recorded on the plot where the DOC concentrations were also the highest.

INTRODUCTION

The effects of sulphur and heavy metal emissions on the surrounding forest ecosystems have been investigated in a number of studies carried out in the Kola Peninsula and Fennoscandia. For instance, Løbersli and Steinnes [1] reported that particulate emissions of Cu, Zn, Pb and Cd from the Sulitjelma Cu smelter in Norway had a clear effect on the surface soil in birch stands close to the smelter. Metal contamination was still detectable at a distance of 27 km downwind from the smelter. Emissions from the Cu-Ni smelter at Harjavalta, SW Finland, have strongly increased Cu concentrations in the soil and vegetation of Scots pine stands located close to the smelter. The accumulation of heavy metals in the soil over the past 50 years has had a clear toxic effect on soil micro-organisms, and reduced organic matter decomposition and nutrient mineralisation [2].

The effect of emissions from the Cu-Ni smelters in the Kola Peninsula, NW Russia, on the environment in Finland, Norway and Russia have been studied extensively [3, 4, 5]. The forests over an area of ca. 40 000 - 50 000 ha around the Monchegorsk smelter complex have been destroyed by sulphur and heavy metal emissions, and the area of dead forest around the Nikel smelters is even greater [3]. Emissions from Monchegorsk are clearly evident as elevated S, Cu and Ni concentrations in the snowpack and percolation water on forested sites, but no decrease in pH values has been reported [6, 7].

$S0_2$ emissions from Nikel and the adjacent Zapoljarnyi smelters amounted to 257 000 tonnes in 1990. Total Cu emissions were 200 t, and Ni emissions 300 t [8]. The aim of this study is to determine whether emissions from Nikel are detectable in the chemical composition of bulk deposition, stand throughfall and percolation water at sites in Finland and Norway located at varying distances to the west of Nikel.

MATERIAL AND METHODS

The bulk deposition, stand throughfall and percolation water data were collected at four intensive monitoring plots during the period June - October in 1992 and 1993. Two of the plots were located in Finnmark, northern Norway, at distances of 14 and 33 km to the west of Nikel, and two in northern Lapland, Finland, at distances of 58 and 132 km (Fig. 1). Sites with as similar as possible soil and stand properties were selected. The age of the Scots pine (*Pinus sylvestris* L.) stands was at least 80 years. The stands were growing on dry or dryish sites [9] with a vegetation cover dominated by heather (*Calluna vulgaris*) and reindeer lichens (*Cladonia* spp.). The genetic soil types were iron-humus podsols, and the soil texture sorted sand. The circular plots were 300 m^2 in size.

Bulk deposition was collected using 5 precipitation collectors located in an adjacent open area. Stand throughfall was collected using 20 precipitation collectors located systematically in the stand. Composite samples were taken from the bulk deposition and stand throughfall collectors. Percolation water was collected at depths of 5, 20 and 40 cm (four replications) at four points in the stand. Owing to the relatively low precipitation in the area, insufficient samples were obtained from depths of 20 and 40 cm; the results for 5 cm depth only are presented here. The samples from each lysimeter were analysed separately. Precipitation and percolation water sampling was carried out at intervals of ca. one month. pH was measured in the laboratory as soon as possible after sampling. The water samples were filtered (0.45 µm membrane filters), and subsamples for the determination of total sulphur and metals conserved with 65% Suprapur nitric acid (0.25 ml/50 ml sample). Total S, Al, Ca, Mg, Cu and Ni concentrations were determined by ICP/AES. Dissolved organic carbon (DOC) was determined on a TOC analyser. SO_4^{2-} and Cl^- concentrations in bulk deposition were determined (by ion chromatography) in order to estimate the proportion of total S derived from marine sources [10]. The sample plot design, sampling regime and chemical analyses are described in more detail in [11].

RESULTS

The highest mean S concentration in bulk deposition, 1.1 mg/l, occurred at the plot (14 km) located in Norway closest to Nikel. The difference between this plot and the plots (58 and 132 km) located in Finland was statistically significant (ANOVA and Tukey, $p<0.05$) (Fig. 2). An even clearer increasing trend in S concentrations was found when the results were corrected for the marine S input.

The mean S concentration in stand throughfall was higher than the corresponding value for bulk deposition on all the plots. A gradual increase in S concentrations was found with decreasing distance to the point source. The highest mean value, 1.3 mg/l, also occurred on the plot closest to Nikel (Fig. 2). The difference between this plot (14 km) in Norway and the plot (132 km) in Finland was statistically significant ($p<0.05$).

The lowest mean pH values of bulk deposition and stand throughfall occurred at a distance of 33 km from the point source. The mean pH value of bulk deposition at the plot closest to Nikel was similar to that at the plot farthest away (132 km). If the plot closest to Nikel is ignored, then there is a rather weak decreasing trend in the mean pH of bulk deposition and stand throughfall with decreasing distance to the point source (Fig. 2). The mean pH of stand throughfall was lower than that of bulk deposition on all the plots.

No clear increasing or decreasing trends in pH and DOC, Al, S, Ca and Mg concentrations in percolation water were found on moving towards Nikel. The values on the plot (14 km) closest to Nikel were in all cases statistically equal to those measured on at least two of the other plots. The lowest mean pH value occurred on the plot located 58 km from the point source: the highest DOC, Al, Ca and Mg concentrations were also found on this plot. The mean S concentrations were rather similar on all four plots (Fig. 3). The Cu and Ni concentrations in percolation water were below the analytical detection limit even on the plot closest to Nikel.

DISCUSSION

The higher S concentrations and lower pH values in stand throughfall compared to the corresponding values for bulk deposition are due to the effects of dry deposition interception and within-stand nutrient cycling on the ionic composition of the precipitation passing through the stand canopy. In natural nutrient cycling for instance, sulphur is returned to the soil as a result of the leaching of dead biomass in the tree crown by precipitation. However, the increase in S concentrations in precipitation close to Nikel is undoubtedly primarily due to sulphur emissions, either as a result of the interception of SO_2 or the deposition of particulate material containing sulphur. Annual mean SO_2 concentrations recorded at Svanvik, Norway, at a weather station very close to the 14 km plot, ranged from 6 - 15 $\mu g/m^3$ during 1989-92. The corresponding values for Kevo, close to the 132 km plot, ranged from 1 - 3 ug/m^3 [12]. The SO_2 concentrations increase very steeply close to the Kola smelters. The annual mean SO_2 concentration exceeds 20 $\mu g/m^3$ over extensive areas around the smelters on the Kola Peninsula [13].

No clear trend was found in this study in the pH of bulk deposition or stand throughfall on moving towards the point source, and hence it was not possible to demonstrate any relationship between rainfall acidity and S concentrations. The extent of the area (running to the west) affected by emissions from the Nikel smelters has earlier been surveyed on the basis of chemical snowpack analysis [6]. Snowpack S concentrations increased on moving towards Nikel, but the relative increase compared to the mean concentration for more distant parts of the gradient line was very small. Similarly, no unambiguous gradient was found in snowpack pH values.

The emissions from Nikel had no effect on the chemical composition of the percolation water collected below the organic layer (5 cm); no increasing or decreasing trends were found in pH or S concentrations with respect to distance to the emission source. The heavy metal concentrations in percolation water at the site closest to Nikel even, did not exceed the analytical detection limits. The high Al, Ca and Mg concentrations on the plots in Finland were clearly associated with the high DOC concentrations, which has been reported in other studies [14].

CONCLUSIONS

The S concentration in bulk deposition increased with decreasing distance to the point source due to the SO_2 emissions or particulate material containing sulphur.

The increase in S concentrations in stand throughfall close to Nikel compared to the corresponding values in bulk deposition is partly due to the emissions from the smelter. Sulphur is also returned to the soil in stand throughfall in natural within-stand nutrient cycling.

Figure 1. Location of the intensive monitoring plots.

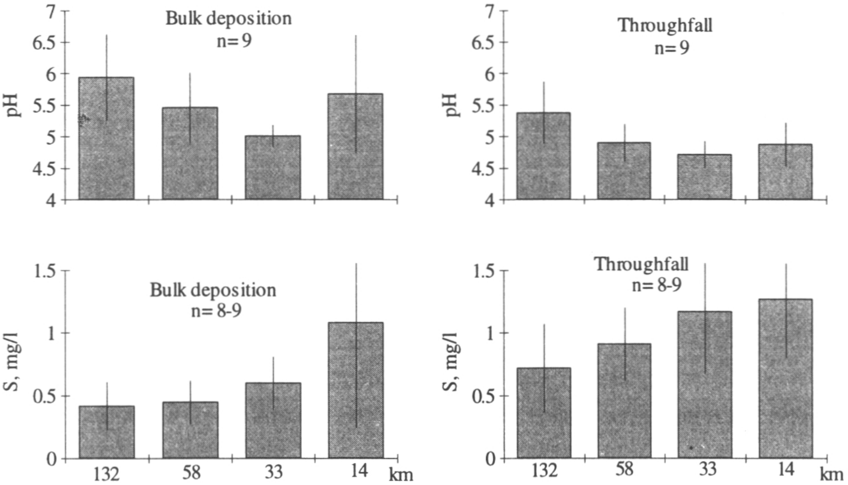

Figure 2. pH and sulphur concentration (mean, S.D.) of bulk deposition and stand throughfall during the 1992 and 1993 growing seasons. Distance of the sample plots from Nikel is indicated.

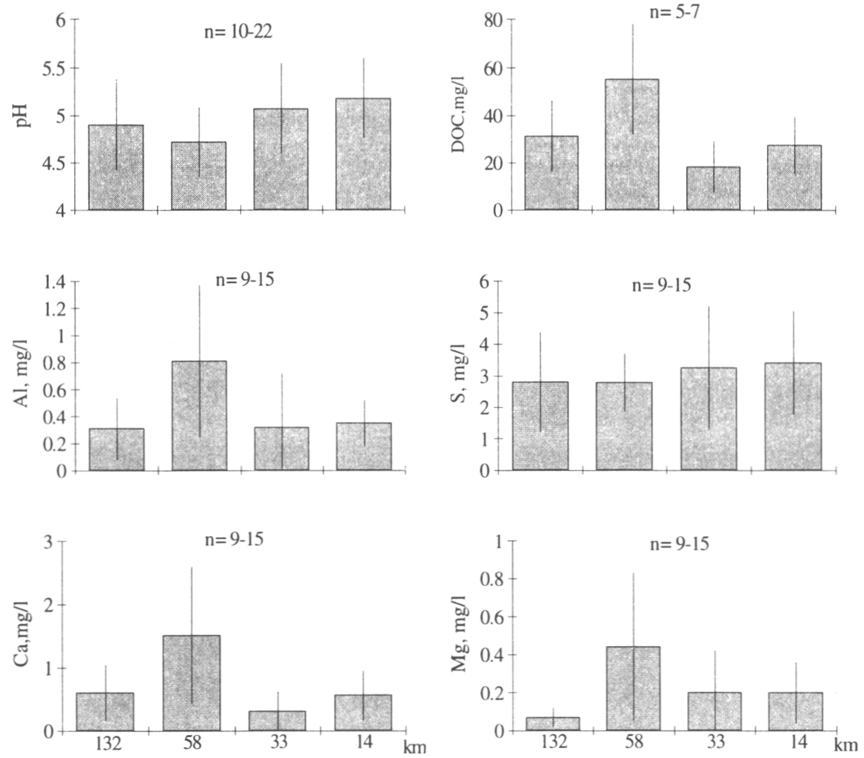

Figure 3. Chemical composition of percolation water collected at a depth of 5 cm below the ground surface during the 1992 and 1993 growing seasons. Mean values with S.D. and the distances of the sample plots from Nikel are indicated.

Sulphur deposition is not necessarily associated with acidic deposition close to the point source because no clear gradient was found in the bulk deposition or stand throughfall pH values.

The chemical composition of the percolation water was not affected by the sulphur and heavy metal emissions from Nikel even at the plot closest to Nikel.

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Paper VI

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TECHNIQUES FOR PRESERVING AND DETERMINING ALUMINIUM FRACTIONS IN SOIL SOLUTION FROM PODZOLIC FOREST SOILS

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ABSTRACT

The purpose of the study was 1) to determine techniques for minimising the effects of transportation and storage on the concentrations of different Al fractions in soil solution samples, and 2) to determine a suitable method for analysing monomeric Al concentrations in water samples from humus-rich podzolic soils. Aluminium fractionation was performed on a cation exchange column and the fractions were analysed by ICP/AES and FIA. A time lag of a few hours to two days between sampling and pretreatment appeared to have no effect on total Al concentrations, even though the samples were not preserved with acid. Freezing the samples was not an appropriate storage technique because it resulted in a strong decrease in total Al concentrations. Storage (+4°C) had a detrimental effect on the proportion of exchangeable monomeric Al, but this problem was overcome by fractionating the samples immediately on arrival at the laboratory. Adjustment of sample pH to <3.7 permitted storage of the fraction for at least 2 weeks before analysis by ICP/AES or FIA. Either of these two techniques can be used for determining exchangeable monomeric Al, but if the non-exchangeable reactive Al fraction (i.e. organically complexed Al) is required then analysis by FIA is necessary. ©1998 Elsevier Science Ltd

INTRODUCTION

The Al concentrations and molar Ca/Al ratio in soil solution are widely used for estimating soil acidification and the exceedance of critical loads of acidifying nitrogen and sulphur compounds [1, 2, 3]. These parameters are normally based on total Al concentrations in the soil solution, and not on the monomeric Al fraction (e.g. Al^{3+}), which is the Al species considered responsible for the toxic effect on roots and mycorrhizas [4]. Considerable work has been carried out on Al fractionation during the past decade, and numerous techniques have been developed for use in the laboratory [5, 6] as well as in the field [7]. While most of the laboratory techniques represent the state of the art, relatively little attention has been paid to practical aspects such as sample transportation, storage and pretreatment [8]. The establishment of standardised European monitoring networks involving the regular sampling of soil solution or leachates implies that Al fractionation needs to be carried out on large numbers of samples within a rather tight time schedule.

The first aim of the study was to determine the effects of sample transportation, storage and pretreatment on the subsequent determination of Al fractions in the laboratory. The second aim was to develop a reliable and flexible protocol for the routine screening of aluminium fractions in large numbers of samples. The results obtained for aluminium fractions, primarily positively charged ions, by ICP/AES and FIA were also compared.

M ATERIAL AND METHODS

The water samples were collected from three of the permanent monitoring plots established in Finland in summer 1995 as part of the European Programme for the Intensive Monitoring of Forest ecosystems (ICP Forests, level II). Two of the plots (one Norway spruce stand and one Scots pine stand) were located near Tammela in southern Finland, and the third (Scots pine) near Rovaniemi in northern Finland. The samples consisted of soil solution obtained using zero-tension lysimeters and suction cup lysimeters. The gravity lysimeters were located at a depth of 5, 20 and 40 cm, and the suction-cup lysimeters at 20 and 40 cm. Samples were collected, whenever possible, at two-week intervals during June - August, 1996. No distinction is made in this report between samples obtained with different types of lysimeter or different sampling depth. The volume of the samples and the number of lysimeters yielding water samples varied considerably during the study owing to variation in the amount of precipitation at the three sites. Transport from the Rovaniemi plot to the Rovaniemi Research Station took only a few hours, but from Tammela on the average 1.5 days by express post.

The effects of transportation and filtration were investigated by means of a number of different pretreatment combinations carried out on parallel sub-samples: 1) pH measurement prior to filtration in the field, 2) pH measurement in the field following filtration, 3) pH measurement in the laboratory prior to filtration, and 4) pH measurement following filtration in the laboratory. The samples were filtered through 0.45 µm membrane filters (ME 25, Schleicher & Schuell). The effect of storage on aluminium fractionation was investigated by keeping the samples at +4°C for two weeks, and the effect of freezing by maintaining the samples for two weeks at -20°C.

Total aluminium in the samples was determined by inductively coupled plasma atomic emission spectrometry (ICP/AES) both before and after passage through a cation exchange column containing Amberlite IR 120. Total reactive aluminium was determined by flow injection analysis (FIA) by the pyrochatecol violet method both before and after passage through the same type of cation exchange column. Preliminary tests with the column/FIA method showed that the pH of samples analysed directly by FIA as well as the fraction obtained from the exchange column had to be adjusted to <3.7 prior to the FIA runs. The FIA gave very low Al values without pH adjustment, presumably due to absorption on the walls of the sample containers or to precipitation of aluminium hydroxides. pH adjustment was performed immediately after passage through the column.

The results obtained by ICP/AES correspond to total aluminium concentrations in a water sample, and those obtained by the FIA method to total reactive aluminium. Passing the samples through a cation exchange column removes positively charged aluminium ions, e.g. Al^{3+}, $Al(OH)_2^+$, $Al(OH)^{2+}$ and $AlSO_4^+$ (referred to in this study as exchangeable Al). The different fractions analysed using a combination of ICP/AES and FIA, and the abbreviations used for the fractions, are depicted in Fig. 1. Exchangeable Al was calculated as the difference between ICP(tot. Al) and ICP(non exch. Al), and between FIA(tot. react. Al) and FIA(non exch. react Al).

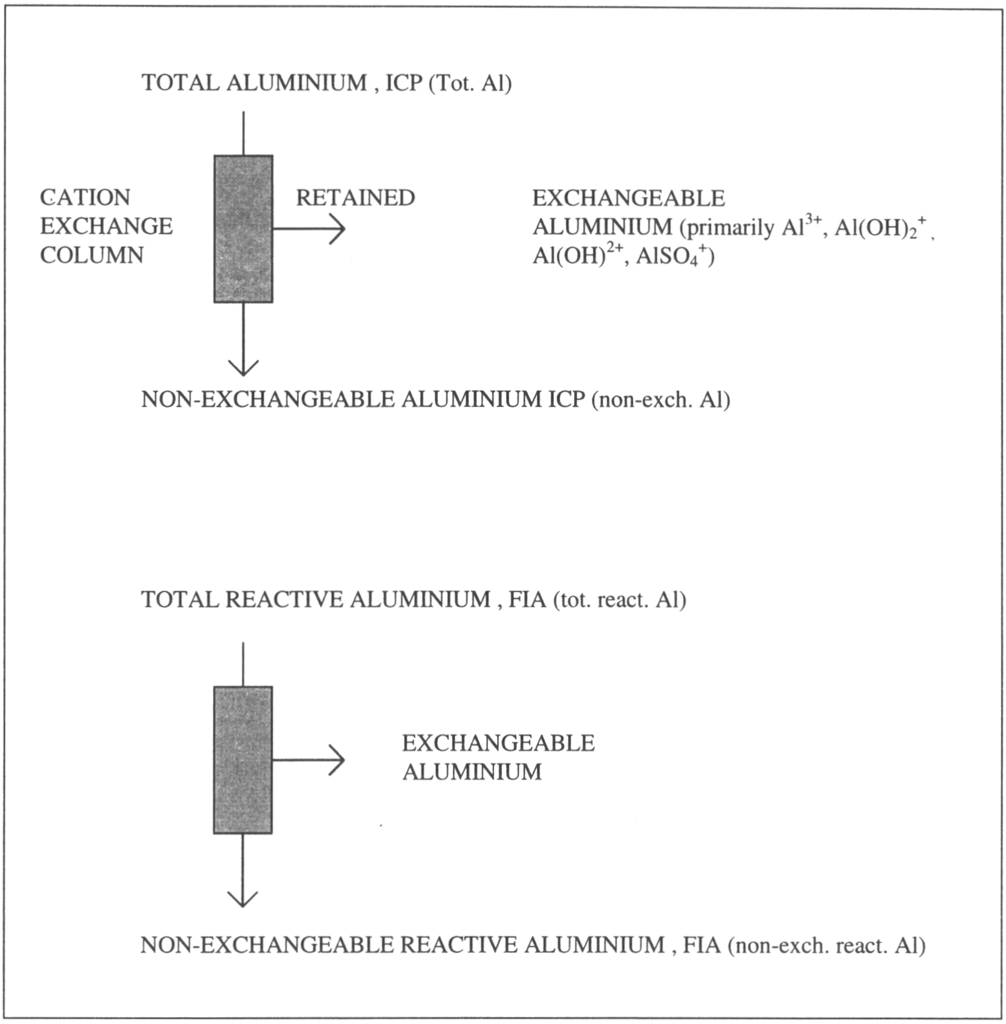

Figure 1. Schematic diagramme of aluminium fractionation by cation exchange.

RESULTS AND DISCUSSION

Transportation, i.e. the time lag between sampling in the field and pretreatment in the laboratory, had only a slight effect on sample pH (Table 1). Although statistically significant, the increase was only 0.1 pH unit and was most probably due to the high pH of many of the samples. The effect of filtration on sample pH was not statistically significant.

Table 1. Effect of a time lag during transportation and filtration on the pH of the soil solution samples (statistical differences tested using the Student's t-test, paired observations, n = 28, *** = p <0.001).

	pH	pH	difference
	in the field	in the laboratory	
time lag (transportation)	6.19 ± 0.69	6.31 ± 0.71	0.12***
	before filtration	after filtration	
filtration	6.24 ± 0.69	6.29 ± 0.75	0.05

Filtration in the field or in the laboratory had no significant effect on ICP(tot. Al) or ICP(non exch. Al) (Table 2). However, storage in a refrigerator for two weeks at +4°C slightly increased the concentration of ICP(non exch. Al). This suggests that the concentration of exchangeable monomeric Al in the samples had decreased slightly during storage. Storage at -20°C, followed by fractionation, strongly reduced the concentration of ICP(tot. Al), but increased that of ICP(non exch. Al). This reduction in total Al was undoubtedly due to the precipitation of a considerable portion of the Al in the form of fine particles, which rapidly clogged the nebuliser of the ICP/AES instrument.

Table 2. Effect of a time lag during transportation and storage on aluminium fractions determined by ICP/AES (without pH adjustment).

Sample	Total Al, mg/l mean	Non exchangeable Al, mg/l mean
Rovaniemi (n = 4)		
filtration in the field fractionated immediately	0.49	0.15
filtration in the laboratory fractionated immediately	0.48	0.15
stored at +4°C for 2 weeks followed by fractionation	0.49	0.19
Tammela (n = 6)		
filtration in the laboratory fractionated immediately	0.85	0.11
stored at +4°C for 2 weeks followed by fractionation	0.86	0.12
stored at -20°C for 2 weeks followed by fractionation	0.53	0.20

The concentration of exchangeable Al determined indirectly by ICP/AES and by FIA was very similar (Fig. 2). The slight underestimation given by FIA for this Al component is presumably due to small differences between the Al standards used for the two instruments rather than to quantification differences, because the same cation exchange column was used to remove exchangeable monomeric Al.

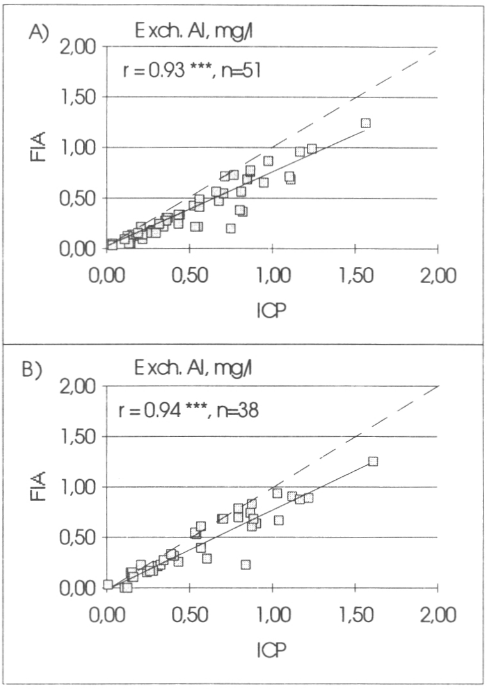

Figure 2. Concentration of the exchangeable Al fraction in soil solution measured by ICP/AES and by FIA immediately (A), and after 2 weeks storage (B) (pH adjustment <3.7).

CONCLUSIONS

The monitoring of soil solution Al fractions in samples collected from a geographically widely dispersed sample plot network poses considerable problems for both the field work and the laboratory. The samples should preferably be analysed as rapidly as possible, but in practice this is not always feasible. Sample pretreatment techniques which lengthen the time that the samples retain their authenticity are invaluable in monitoring work. The results obtained in this preliminary study are rather encouraging. A time lag of a few hours to two days between sampling and pretreatment appeared to have no effect on total Al concentrations, even though the samples were not conserved with acid. Freezing the samples was not an appropriate storage technique because it resulted in a strong decrease in total Al concentrations. Storage (+4°C) had a detrimental effect on the proportion of exchangeable monomeric Al, but this problem can be overcome by fractionating the samples immediately on arrival at the laboratory. When the pH of the fraction was adjusted to <3.7, the fractionated sample could be stored for at least 2 weeks before analysis by ICP/AES or FIA. Either of these two techniques can be used for determining positively charged inorganic Al, but if the non-exchangeable reactive Al fraction (i.e. organically complexed Al) is required then FIA is also necessary.

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