METSÄNTUTKIMUSLAITOKSEN TIEDONANTOJA 769, 2000
Finnish Forest Research Institute, Research Papers 769, 2000

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Academic dissertation

To be presented, with the permission of the Faculty of Agriculture and Forestry, University of Helsinki for public criticism in Auditorium B1, Latokartanonkaari 9, Viikki, on the 26th of May 2000, at 12 o'clock noon.

ROVANIEMI RESEARCH STATION

Derome, J. 2000. Effects of heavy-metal and sulphur deposition on the chemical properties of forest soil in the vicinity of a Cu-Ni smelter, and means of reducing the detrimental effects of heavy metals. Metsäntutkimuslaitoksen tiedonantoja 769. Finnish Forest Research Institute, Research Papers 769. 78 + 46 p. ISBN 951-40-1729-3, ISSN 0358-4283.

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Publisher: Finnish Forest Research Institute, Rovaniemi Research Station. Accepted by Matti Kärkkäinen, Research Director, 29.2.2000

Cover photo: METLA/Erkki Oksanen

Cover design: Jouni Hyvärinen

Hakapaino Oy, Helsinki 2000

ABSTRACT

The study was carried out during 1993-1998 in four Scots pine stands located at distances of 0.5, 2, 4 and 8 km along a transect running approximately to the SE of the Cu-Ni smelter at Harjavalta, SW Finland. Soil condition was investigated by taking soil samples, as well as soil water samples at depths of 5, 20 and 40 cm. Deposition was measured by collecting rainfall and snow samples in an open area and inside the stand. The soil in the stands was treated with limestone, a multi-element mineral fertiliser mixture or a stand-specific fertiliser containing limestone and/or nitrogen. Soil samples were taken 4.5 years after the fertiliser treatments.

The strongly increasing gradient in the accumulation of heavy metals, Mg, P and S in the organic layer of the forest soil with decreasing distance to the smelter appears to be a direct result of heavy metal and sulphur emissions from the smelter. The effects of emissions extend up to a distance of at least 8 km to the SE of the smelter complex. The properties of the forest soil in the immediate vicinity of the Cu-Ni smelter have been drastically altered by emissions during the past 50 years. The accumulation of Cu and Ni in the soil has resulted in a severe deficit of plant-available Ca, Mg and K in the organic layer caused by partial inhibition of the mineralisation of these nutrients from litterfall, and the displacement of these base cations from exchange sites. No signs of soil acidification were found in the organic layer or uppermost mineral soil layers. However, there was an increase in exchangeable acidity and Al deeper in the mineral soil, presumably due to their displacement from the overlying organic and mineral soil layers. The loss in base saturation in the organic and uppermost mineral soil layers close to the smelter was attributed to displacement by Cu and Ni, and not to the effects of acidic deposition. The use of the summation method for determining CEC in heavy-metal polluted soils is not recommended unless other major cations present in such soils are included in the calculations.

The water flux on the plot closest to the smelter has been drastically altered as a result of damage to the tree stand and ground vegetation. The fluxes of Zn, Ni and Cu from the organic layer down into the mineral soil varied owing to differences in their ability to form complexes withorganicmatter and their affinity for cation exchange sites. There was a clear net loss of Zn from the 40 cm-thick soil layer, but a net gain of Cu and Ni. The fluxes of Cu, Ni and Zn at 0.5 km were extremely large compared to those at 4 and 8 km.

Apart from an initial increase in the year of application, liming at all three doses strongly decreased the Cu, Ni and Zn concentrations in the soil solution at the severely contaminated site for the following three years at least. The largest liming dose used in this study, 2000 kg ha^{-1}, thus did not increase the risk of heavy metals being displaced and carried down into the ground water. Liming had only a relatively small reducing effect on free and exchangeable Cu and Ni concentrations in the organic layer at 0.5 km. The lack of a pH increase following liming may be due to the precipitation of Fe, present in very high concentrations close to the smelter, as $Fe(OH)_3$, resulting in the loss of neutralising bicarbonate and hydroxyl ions, but the release of Ca and Mg. Liming strongly increased Ca and Mg availability in the soil. The fast-release components in the correction fertiliser and stand-specific fertiliser increased the supply of macro-nutrients to the tree stand already during the year of application. The dissolution of the slow-release components in the correction fertiliser also ensured an increased supply of Ca, Mg and K throughout the course of the study at the site 8 km from the smelter, but not at 0.5 km.

This study has provided rather comprehensive information about the effects of heavy metal deposition on soil properties close to a point emission source, and has investigated means of alleviating the harmful effects of heavy metal deposition on soil fertility and subsequently the tree stand. Heavy-metal contamination of the forest soil is an extremely serious problem, and every effort must be made to ensure that they remain in an immobilised form. Measures such as correction fertilisation and liming will contribute to this while, at the same time, promoting a recovery in stand growth and the re-establishment of the forest floor vegetation. This will also reduce erosion and reduce the likelihood of the heavy metals being transported down in to the ground water.

Key words: Base saturation, Copper, Element fluxes, Fertilisation, Forest soil, Heavy metal pollution, Liming, Nickel, Zinc,

CONTENTS

LIST OF PUBLICATIONS

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

I Derome, J. and Lindroos, A-J. 1998. Copper and nickel mobility in podzolic forest soils subjected to heavy metal and sulphur deposition in western Finland. Chemosphere 36: 1131–1136.

II Derome, J. and Lindroos, A-J. 1998. Effects of heavy metal contamination on macronutrient availability and acidification parameters in forest soil in the vicinity of the Harjavalta Cu-Ni smelter, SW Finland. Environmental Pollution 99: 225–232.

III Derome, J. and Nieminen, T. 1998. Metal and macronutrient fluxes in heavy-metal polluted Scots pine ecosystems in SW Finland. Environmental Pollution 103: 219–228.

IV Derome, J. and Saarsalmi, A. 1999. The effect of liming and correction fertilisation on heavy metal and macronutrient concentrations in soil solution in heavy-metal polluted Scots pine stands. Environmental Pollution 104: 249–259.

V Derome, J. 2000. Detoxification and amelioration of heavy-metal contaminated forest soils by means of liming and fertilisation. Environmental Pollution 107: 79–88.

ACKNOWLEDGEMENTS

The idea of writing a thesis on the effects of emissions from the Harjavalta smelter on forest soil properties was first proposed by Prof. Eino Mälkönen. His telephone call, which saved me from the seemingly endless minefields of forest liming, marked a turning point in my scientific career. Now that this major undertaking is almost over, I am extremely grateful for his farsightedness.

The field experiments employed in this thesis were planned under the guidance of Prof. Eino Mälkönen, and implemented in the field under the watchful eye of Teuvo Levula. The regular sampling work and other field measurements were carried out as a perfect example of marital teamwork by Teuvo and Sinikka. I am extremely grateful to them both because, without reliable field measurements and sampling, much of the more "scientific" work done indoors would have otherwise been of little real value. The chemical analyses of the soil and water samples were carried out at the laboratories of the Rovaniemi Research Station (Kaarina, Sirpa O, Arja, Anri, Sirpa S, Tarja, Mauri, Leena, Toini), Vantaa Research Centre (Arja, Tuija, Merja-Leena, Pirkko, Maija R, Anneli, Leppis), Joensuu Research Station (Anita and Anki) and Parkano Research Station (Arja and Kari). I would like to thank all the laboratory staff for their top-quality work, and to apologise for my repeated requests for lost results that were always eventually found in my own office!

Marja Huotari has, over the years, performed the unenviable task of maintaining a database containing the tremendous volume of results amassed during the course of the project. Sari Elomaa and Anne Siika helped with the figures, and Helena Poikajärvi has done a marvellous job in getting the manuscript ready for publishing. Their assistance, and that of the head of the Rovaniemi Research Station, Martti Varmola, as well as other members of the station's staff, is gratefully acknowledged.

The soil and soil water studies carried out together with Antti-Jussi Lindroos in Lapland and the Kola Peninsula provided a sound starting point for a number of the articles in this thesis. I am deeply indebted to Antti-Jussi for the rewarding and enjoyable co-operation that has been the hallmark of our "team" for the past ten years at least. Tiina Nieminen, my second co-author, provided me with considerable mental stimulation (mainly during marathon phone calls), and was instrumental in my successful passage over phone calls), and was instrumental in my successful passage over the decisive "3rd article hurdle". She has since acted as an extremely vociferous and persuasive advocate in pleading my case at the Department of Environmental Protection. Anna Saarsalmi, my third co-author, helped to keep my feet on the ground and prevent me from straying beyond the bounds of scientific credibility. Without the support and encouragement of Heljä-Sisko Helmisaari and Eino Mälkönen, the leaders of the two projects in which I have had the pleasure to participate during the past five years, this thesis would never have been carried to completion. I express my sincere thanks to the above and to all the other persons who, over the years, have helped me in a variety of ways.

I would like to thank Prof. Pekka Kauppi, Head of the Department of Limnology and Environmental Protection, and my supervisor, Martin Lodenius, for their assistance. The pre-examiners of my thesis, Ahti Mäkinen and Matti Verta, gave up a considerable amount of their time in reading the manuscript, and I am extremely grateful for their constructive comments and corrections.

Last, but not least, I would like to thank my family, especially my wife Kirsti, for being so patient and understanding, and for providing me with support in a multitude of ways both at work and at home. Her contribution to the analytical side of my thesis has been invaluable. This thesis will no doubt come as a surprise to my sons, Niko and Aleksi, as well as to Paula, Olli and Leena, who perhaps at last will now believe that I don't spend quite all my time playing patience on a laptop.

Rovaniemi, April 2000

John Derome

1 INTRODUCTION

1.1 Copper, nickel and zinc pollution

There is considerable atmospheric deposition of Cu, Ni and Zn in all the industrialised countries. According to a survey based on heavy metal concentrations in forest floor mosses carried out in summer 1990 (Rühling 1994), numerous point sources in Europe were emitting considerable amounts of Cu, Ni and Zn. In Norway, Sweden and Finland, for instance, there were at least 11 point emission sources of Cu and Ni, and at least 4 point emission sources of Zn. In addition, there are major point emission sources of Cu and Ni at Monchegorsk and Nikel on the Kola Peninsula, NW Russia, close to northern Finland and Norway (Rigina and Kozlov 2000). Emissions from the Kola Peninsula are, compared to emissions in Fennoscandia, extremely high: in 1995, 1,600 t of Ni, 900 t of Cu, together with 451 000 t of SO_2. Heavy metals are emitted in the form of particulate material, and the distance that they are transported is, compared to gaseous pollutants, in general relatively short. The transport distance is dependent on factors connected with the production plant, such as the height of the stack and emission levels, as well as on the size of the particles. According to Freedman and Hutchinson (1980a), Cu and Ni in the topsoil were elevated at distances of up to 70 km from the large smelter at Sudbury, Canada. Emissions of Cu and Ni from the Nikel smelter on the Kola Peninsula are detectable in pine needles (Raitio 1995) and forest floor mosses (Kubin et al. 2000) in the NE corner of Finnish Lapland, more than 100 km to the west of the smelter. Owing to the relatively low boiling point of Zn (907°C, as opposed to 2567°C for Cu and 2730°C for Ni), a high proportion of the Zn emitted from smelters is in the form of metal vapour. This means that Zn emissions are likely to be spread over much greater distances, the concentrations in the air subsequently become considerably diluted.

The major point source of Cu and Ni emissions in Finland is the Cu-Ni smelter at Harjavalta, SW Finland (Aunela & Larjava 1990), which accounted for over 90 and 87% of total industrial emissions of Cu and Ni in Finland in 1988. Harjavalta has also been a major source of Zn emissions (ca. 25%). Since the beginning of the

1990's, however, there has been a considerable decrease in heavy-metal emissions (Melanen et al. 1999) as a result of technical modifications to the smelter complex and the construction of a taller smoke stack (Table 1). This is reflected in the results of theheavy-metal moss surveys carried out in 1985, 1990 and 1995 (Kubin etal. 2000), which indicated a steep decrease in Ni concentrations in mosses and a clear, but less marked decrease in Cu concentrations, during the 10-year monitoring period. In southern and central Finland the heavy-metal moss survey is carried out on a 16 x 16 km sampling grid, which makes it suitable for monitoring trends at the national level, but provides no detailed information about deposition in the Harjavalta area itself.

Table 1. Annual emissions (t/year) of SO2, dust, heavy metals and arsenic from the Harjavalta smelter, SW Finland, during 1985-1996. nm = not measured.

Year	SO_2	Dust	Cu	Ni	Zn	As	Pb	Cd	Hg
1985	7800	120	98	47	216	15	55	1.7	nm
1986	7500	1200	126	46	232	17	60	7.1	nm
1987	6900	1800	140	96	160	19	94	3.9	0.017
1988	8500	1000	104	45	100	19	48	3.2	0.012
1989	9500	1000	80	33	190	22	70	3.6	0.028
1990	8800	960	80	31	160	28	80	4.2	0.028
1991	5200	640	80	14	90	18	45	1.6	0.070
1992	4800	280	60	10	12	12	9	1.0	0.070
1993	4700	250	50	7	13	11	6	0.9	0.015
1994	5000	190	40	6	6	5	3	0.6	0.010
1995	3300	70	17	1.4	1.7	0.2	0.5	0.02	0.001
1996*	1700	96	24	1.0	3.0	1.8	0.9	0.09	0.005

***1.1 - 30.6.1996**

A number of studies have been carried out in the area using moss bags (Hynninen 1986), as well as moss, Scots pine and Norway spruce needle and soil samples and moss ball and deposition samplers (Jussila & Jormalainen 1991), to determine heavy-metal deposition patterns at a rather dense sampling intensity. Elevated levels of Cu and Ni were found at distances of up to 10 km from the smelter. Hynninen (1986) presented accumulation values separately for the summer and for the winter period. However, his figures can be converted into approximate annual accumulation values (g/kg dw of moss) based on the period June 1981 to March 1982: 15.7 for Cu, 7.1 for Ni and 2.8 for Zn in the immediate vicinity of the smelter complex, and 0.11 for Cu, 0.11 for Ni and 0.05 for Zn at a distance of about 10 km. The values for Zn appear to be underestimates because emissions of Zn from the smelter in the 1980's were in fact larger than those of Cu and Ni. However, the retention of Zn by mosses is known to be poor (Rühling & Tyler 1970).

1.2 Metallurgical processes at the Harjavalta smelter, SW Finland, and the chemical composition of the emissions

Copper and nickel are produced at the Harjavalta smelter by the flash-smelting pyrometallurgical process in two separate smelters. Copper smelting first started in 1945, and nickel smelting in 1960. A sulphuric acid plant was built at the site in 1947. The raw materials used in copper smelting are chalcopyrite ($CuFeS_2$), as well as some bornite (Cu_5FeS_4) and chalcosite (Cu_2S). The main raw material in nickel smelting is pentlandite ($(Fe,Ni)_9S_8$), the ore also containing varying amounts of pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$). The actual mineral composition of the concentrates has varied to some extent during the lifetime of the smelters. In recent years the main nickel concentrate used at the smelter has been imported from the Mount Keith mine in Australia, and contains 22.7% Ni, 25.5% Fe, 26.8% S, 8.2% MgO, 6.1% SiO_2 and 0.58% Co. In the smelting process, a suspension of finely ground Cu or Ni concentrate is oxidised rapidly in preheated oxygen-enriched air or pure oxygen. The oxidation reaction releases energy, and the reaction products smelt due to the evolution of large amounts of heat. The molten particles coalesce to form the matte (molten metal oxides). Solid flux (primarily quartz sand, SiO_2) is added to the concentrate prior to smelting in order to promote the reactions and to ensure that the slag separates from the matte. The material leaving the flash furnace consists of a suspension of reacted molten concentrate particles, inert flux particles and gases (mainly SO_2, but also some vaporised metals e.g. Zn). The solid and liquid particles separate out from the exhaust stream to form the matte and slag. The exhaust dust consists of CuO, NiO, Fe_2O_3 and other metal oxides, which react with SO_2 in the "cold end" of the exhaust flue to form sulphates. The dust and gases are carried to the electrostatic precipitators for dust recovery, and to the desulphurisation unit for the removal of SO_2 gas. The flue gases were emitted from a 70 m-high stack up until 1994, when it was replaced with a 140 m-high stack. New dust filters were installed and the process technology at the smelters was modified at the same time.

The molten slag is transported out into an open handling area next to the smelter, where it is allowed to cool and finally sprayed with water (while still hot) before being broken up and crushed. The main component of the slag is iron silicate. The slag-cooling and handling area adjoins the forest in which one of the experiments (0.5 km from the smelter) is located. This handling area was considerably enlarged in the latter half of 1994 and, since spring 1995, the experimental stand has been directly exposed to dust and gases carried by the wind from the handling area.

The molten matte is allowed to cool, crushed and then leached with sulphuric acid to release copper or nickel as soluble sulphates inside the plant. The copper sulphate is transported to the nearby town of Pori for electrolytic processing into pure copper. The nickel sulphate is processed into pure nickel metal in a plant adjoining the smelters by the hydrogen reduction method. The plant started operating in August, 1994. Ammonium hydroxide is used to neutralise the sulphuric acid generated in the reduction process, the ammonium sulphate formed being temporarily stored at the plant (Poutanen & Kuisma 1994). The ammonium hydroxide is generated at the plant by mixing water and ammonia (NH_3) gas, which is brought to the site in pressurised, liquid form. Despite strict protection measures, there are sporadic emissions of ammonia from the plant during the unloading and gasification of the ammonia, and the production of ammonium hydroxide.

The composition and amount of emissions from the smelter are dependent on the composition of the raw materials, on the correct functioning of the smelter processes, and on the efficiency of the dust and SO_2 removal processes. The dust mainly consists of metal sulphates.

1.3 The occurrence and behaviour of copper, nickel and zinc in the soil

Copper is a heavy metal that occurs widely in minerals in the bedrock and is therefore also present in the overlying soil (Table 2). It occurs in a number of oxidation states, but Cu^{2+} is the predominant form in non-paludified mineral soils. The non-mineral Cu in soils is primarily in the form of the ion $Cu(H_2O)_6{}^{2+}$, which is adsorbed at mineral surfaces, occluded or co-precipitated by silicate and non-silicate clays, and bound in the form of organically complexed ions (Shuman 1979, McBride 1981). The $Cu(H_2O)_6{}^{2+}$ ion is also predominant in the soil solution of acidic soils, but in neutral and alkaline soils there are several other ionic forms of Cu (e.g. $CuSO_4{}^0$, $Cu(OH)_2{}^0$, $CuCO_3{}^0$, Cu^+, $CuCl^0$, $Cu(Cl_2)^-$) (Mattigod & Sposito 1977). Nickel also occurs naturally in the bedrock and in the soil (Table 2). The non-mineral Ni in acidic soils is primarily in the form of the ions Ni^{2+}, $NiSO_4{}^0$, $NiHCO_3{}^+$ and $NiHPO_4$, depending on the concentrations of sulphate and phosphate, while in neutral and alkaline soils the predominant ionic forms of Ni are $NiCO_3{}^0$, $NiHCO_3{}^+$, Ni^{2+} and $NiB(OH)_4{}^+$ (Sposito & Page 1985). Like copper, Ni is present in a number of different fractions in the soil. Compared to copper and nickel, zinc is a relatively prolific heavy metal in the bedrock and soil (Table 2). The predominant ions in the soil and soil solution are $ZnSO_4{}^0$ and $ZnHPO_4{}^0$.

Table 2. Mean total Cu, Ni and Zn concentrations in the organic layer of Finnish forest soils (Tamminen 2000), in the mineral soil of till soils (Koljonen 1992), and the oxidation states of Cu, Ni and Zn.

Metal	Organic layer mg/kg dw	Mineral soil mg/kg dw	Oxidation states in nature	Oxidation states in the soil
Cu	6.6	24	0, +1, +2, (+3)	+1 (Cu^+), +2 (Cu^{2+})
Ni	8.2	27.2	+1, +2, +3	+2 (Ni^{2+})
Zn	47	66	+2	+2 (Zn^{2+})

Total copper, nickel and zinc in the soil can be divided into six pools: 1) soluble ions and inorganic and organic complexes in the soil solution, 2) exchangeable ions, 3) stable organic complexes in humus, 4) ions adsorbed by Mn, Fe and Al hydroxides, 5) ions adsorbed by clay/humus complexes, and 6) the Cu, Ni and Zn bound in the crystal lattice of soil minerals (Viets 1962, Baker & Senft 1995). In forest soils, the most important components are exchangeable ions, organic complexes and ions adsorbed on Mn, Al and Fe hydroxides (i.e. pools 2 - 4). In unpolluted background areas in Finland, the concentrations of Cu, Ni and Zn in the soil solution in acidic podzolic soils are extremely low, the Cu and Ni concentrations usually being below the detection limit of the analytical equipment used in routine analyses.

Median values of about 0.005 mg/l for Cu, 0.009 mg/l for Ni and 0.018 mg/l for Zn have been reported for soil solution at a depth of 40 cm in four forested catchments in Finland (Ukonmaanaho et al. 1998). These values represent all soluble forms of Cu, Ni and Zn in the soil solution. In the case of Cu, the concentrations of non-complexed ions will be considerably smaller because the soil solution in podzolic soils contains appreciable amounts of dissolved organic matter: the concentrations of the free ion $Cu(H_2O)_6^{2+}$ will be around 50 - 80% of this value (Brügger 1999).

The stability of the complexes formed between metals and organic ligands vary considerably. Schitzner and Skinner (1966, 1967) ranked the stability at pH 3.5 of the complexes formed between divalent metal ions and fulvic acid, derived from the B horizon of a podzolic soil, as follows: $Cu^{2+} > Ni^{2+} > Pb^{2+} > Co^{2+} > Ca^{2+} > Zn^{2+} > Mn^{2+}$. Organic complexes in the solid phase represent the largest pool of Cu (Adediran & Kramer 1987) in the soil. Furthermore, the complexes formed between Cu and humic substances are extremely stable, and the role played by pH in regulating the distribution of Cu between the solid and aqueous phases is relatively small. Copper is absorbed strongly by soils, and it is relatively difficult to displace exchangeable Cu using the extractants normally used to determine exchangeable cations (Fiskell 1965). The stability of organo-Ni and organo-Zn complexes is considerably lower than that of Cu complexes, and Ni and Zn are readily adsorbed on Al and Fe hydroxides (Hickey & Kittrick 1984). Fulvic acids form chelates (soluble complexes) with Zn, thus increasing the solubility and mobility of Zn in the soil. According to Geering and Hodgson (1969), 60 - 75% of soluble Zn is present as soluble organic complexes. In contrast to copper, the distribution of Ni and Zn between the solid and liquid phases is strongly dependent on pH and on the cation exchange capacity of the soil (Sanders et al.1987).

1.4 Harmful effects of elevated copper, nickel and zinc levels

Copper, nickel and zinc are all essential elements for plants and animals at low concentrations, but at high concentrations they can have antagonistic effects which disturb nutrient uptake by plants, as well as direct toxic effects on plant roots and micro-organisms in the soil (Baker & Senft 1995). Copper is one of the most important micro-nutrients, and plays an important role as a prosthetic group in enzyme systems. Copper concentrations in mineral soils in Finland appear to be sufficient to meet the Cu requirements of trees because, although foliar Cu concentrations are relatively low (Raitio et al. 2000), there are no documented reports of stands suffering from Cu deficiencies. At high concentrations, on the other hand, Cu has an antagonistic effect on Mo uptake, causing Mo deficiency (MacKay et al. 1966) and affecting the nitrogen metabolism of trees. Nickel is now considered to be an essential metal for higher plants (Brown et al. 1987) and some micro-organisms (van Baalen & O´Donnell 1978), but the amounts required are so small that it is highly unlikely that trees or soil micro-organisms would suffer from Ni deficiencies. Zinc is also an important micro-nutrient, and is involved in a range of enzymes participating in energy metabolism and in DNA synthesis. Mineral soils in Finland apparently contain sufficient Zn to satisfy the requirements of trees because Zn concentrations in pine and spruce needles are well above the Zn deficiency level (Raitio 1995).

Heavy metals, including Cu, Ni and Zn, are toxic at high concentrations to plants, animals and micro-organisms. The accumulation of high levels of heavy metals can seriously disturb the normal functioning of forest ecosystems. Heavy metal accumulation in the soil can affect nutrient cycling throughout the whole ecosystem by inhibiting litter decomposition (Rühling & Tyler 1974, Freedman & Hutchinson 1980b, Fritze *et. al*. 1989) and subsequently reducing the supply of nutrients released by mineralisation. Elevated levels of Cu, Ni and Zn considerably reduce microbial respiration in laboratory experiments (Change & Broadbent 1981, Doelman & Haanstra 1984), as well as in heavily polluted soils close to smelters (Nordgren et al. 1986). Heavy metals can also have toxic effects on roots and mycorrhizas (Gobl & Mutsch 1985, Colpaert & van Assche 1992, Helmisaari et al. 1999), seriously reducing nutrient uptake. There is a reduction in the growth and vitality of the forest vegetation. The vegetation cover may ultimately be completely destroyed, increasing the risk of soil erosion (Hutchinson & Whitby 1977, Freedman & Hutchinson 1980a, Lukina et al. 1993). The capacity of the ecosystem to bind heavy metals gradually diminishes, increasing the risk of the accumulated heavy metals leaching into the ground water. The maximum permitted concentrations of Cu, Ni and Zn in water intended for human consumption in Finland are 1.0, 0.02 and 3.0 mg/l, respectively (Kujala-Räty 1998).

In addition to the possible antagonistic effects of high concentrations of heavy metals on mineral nutrient uptake, and hence on the nutrient status of tree stands, saturation of the surface soil by heavy metals in the vicinity of metallurgical plants can have an indirect effect on nutrient uptake. Displacement of nutrients in cationic form (e.g. Ca^{2+} and Mg^{2+}) by heavy metals results in the leaching of the displaced cations down into deeper layers in the soil where the proportion of tree roots is lower. Derome et al. (1998), for instance, reported extremely low Ca and Mg concentrations in the organic layer close to a Cu-Ni smelter complex on the Kola Peninsula, NW Russia. Løbersli and Steinnes (1988) reported a decrease in base cations (i.e. Ca and Mg) in the organic layer close to a Cu smelter at Sulitjelma in northern Norway, as well as Hutchinson and Whitby (1977) and Freedman and Hutchinson (1980a) near the Cu-Ni smelter in Sudbury, Canada. In the studies carried out in Norway and Canada, the authors attributed the loss in base saturation to acidic deposition derived from SO_2 emissions from the smelters, although they did conclude that displacement by heavy metals will have contributed to the very low base saturation values.

1.5 Detoxification of heavy-metal polluted soils

The contamination of forest ecosystems by heavy metals such as Cu, Ni and Zn is a serious problem in many industrial regions. The remediation of sites seriously contaminated by heavy metals is a very different problem from the situation on sites contaminated by organic compounds. Considerable advances have been made in recent years in biological methods for degrading organic compounds into non-toxic forms, or removing the soil and destroying the compounds e.g. by combustion at high temperatures.

Heavy metals cannot be destroyed, but can only be converted physically or chemically into non-bioavailable forms on site (*in situ*), or removed along with the soil and treated elsewhere (*ex situ*). A large number of techniques have been developed for the *in situ* and *ex situ* remediation of heavy-metal contaminated soils (Pierzynski 1999).

In situ remediation of the soil is directed at converting the heavy metals in the soil into non-bioavailable forms, or on-site extraction of the heavy metals from the soil. This can be done e.g. by solidification (adding a cementing agent to produce a hardened, non-leachable material), vitrification (heating to produce a glass-like, non-leachable material), encapsulation (covering the soil with an impermeable layer), phytostabilisation (promoting the growth of plants that result in the immobilisation of metals in the soil), attenuation (reducing heavy-metal concentrations in the soil by dilution with uncontaminated material), and soil amendment (reducing the bioavailability of heavy metals with P or other soil amendments). The metals can be extracted from the soil by physical/chemical means such as electromigration (heavy-metal ions migrate, as a result of an electrical current, to electrodes inserted into the soil), or by biological means such as phytoextraction (planting and harvesting of plants that actively accumulate heavy metals).

Physical removal and *ex-situ* treatment of the soil from polluted site has a longer tradition than *in-situ* treatment, and there is obviously greater freedom in the choice of physical and chemical treatments methods that can be used. The removed soil can be treated by solidification and vitrification, as well as washing (removing the metals by means of chelating agents or acids) and leaching (pile-or batch-leaching with chelates or acids). Particle-size segregation (selective removal of the fine fraction containing the highest metal concentrations) is a viable preliminary technique prior to solidification, vitrification, washing or leaching. Soil excavation (soil removal and disposal without any treatment) is the technique most widely used in earlier days.

The physical removal of contaminated soil is a time-consuming and expensive undertaking and, in many cases, the only viable alternative has been to use soil-amendment agents (e.g. liming) to convert the metals into a non-toxic form. Fertilisers can also be added to stimulate nutrient mineralisation, and to replace the plant nutrients that have been lost from the surface soil. Promising results have been obtained in Sudbury, Canada, in the detoxification and restoration of land that is completely deforested as a result of heavy metal deposition from the Cu-Ni smelter (Winterhalder 1983). The main emphasis in restoring the industrial barren area at Sudbury has been to treat the soil with limestone and P fertiliser, and to establish a vegetation cover of grasses and shrubs, on which a cover of broad-leaved trees gradually develops (Lautenbach et al. 1995). In areas where the tree stand is less severely damaged the measures are designed to restore nutrient imbalances and to improve the vitality of the tree stand.

A number of studies have been carried out on the detoxification and restoration of forest land in the immediate vicinity of metallurgical plants (e.g. Bingham et al. 1979). Liming increases soil pH, resulting in the precipitation of heavy metals and a reduction in toxic concentrations in the soil solution (Kreutzer 1995). However, the application of excessive amounts of limestone can result in the dissolution of heavy metals from the organic layer due to the enhanced release of organic complexing agents as a result of an increase in the oxidation and complexation potentials (Göttlein 1989). The soils close to Cu-Ni smelters also frequently suffer from a loss of base cations (Ca and Mg) as a result of their displacement by heavy metals or by protons derived from acidic deposition (SO_2/H_2SO_4) (Løbersli & Steinnes 1988). The application of Mg-rich limestone, for instance, plays a dual role; it reduces heavy metal toxicity and also replenishes the base cation pool important for counteracting soil acidification and maintaining site productivity.

1.6 Aims of the study

The experiments used in this study were established as part of a project investigating the use of liming and correction fertilisers to correct nutrient imbalances in tree stands subjected to acidifying deposition. The experimental stands located along a transect extending from the Harjavalta Cu-Ni smelter, SW Finland, provided a unique opportunity to investigate the possibilities of alleviating nutrient imbalances caused by Cu and Ni deposition from the only major point source of these pollutants in Finland. These experiments have subsequently formed a basis for a project on the "functioning of forest ecosystems subjected to heavy metal deposition", that started in 1992. The results presented in this study therefore rather comprehensively cover the effects of heavy metal deposition on soil properties and heavy-metal and macro-nutrient fluxes between the stand and soil, and are not restricted to the effects of liming and correction fertilisers on soil and soil water parameters.

This thesis is a summary of the results and conclusions published in 5 original articles (Appendices I - V). Some new results are also presented. The aims of the thesis are to determine:

1) the overall pattern of contamination by heavy metals and other elements in forest soil caused by emissions from the Harjavalta Cu-Ni smelter (Papers I and II),
2) the effects of high concentrations of Cu and Ni on soil fertility, primarily the availability of Ca, Mg and K (Paper II),
3) the effects of elevated exchangeable Cu and Ni concentrations in the organic layer on estimates of CEC_{eff} and base saturation obtained by the summation method (Paper II),
4) the effects of heavy-metal and sulphur deposition on soil acidity and base saturation
5) the flux of Cu, Ni, Zn, SO_4 and macro-nutrients in Scots pine ecosystems containing varying levels of accumulated heavy metals and sulphur (Paper III),
6) the effects of liming on elevated concentrations of Cu, Ni and Zn in the soil (Papers IV and V), and
7) the extent to which liming and correction fertilisation can alleviate macro-nutrient deficiencies in the organic layer (Papers IV and V).

2 MATERIAL AND METHODS

2.1 The study sites

Four experiments were established in July, 1992, at distances of ca. 0.5, 2, 4 and 8 km from the Cu-Ni smelter at Harjavalta (61°19' N, 22°9' E), SW Finland. The sites selected for the study were pure Scots pine (*Pinus sylvestris* L.) stands growing on sorted sandy soils. Relatively infertile sites of this type are considered to be especially susceptible to soil acidification (Tamminen and Mälkönen 1986) and the detrimental effects of heavy metal deposition. The experiment at 0.5 km was located to the SW of the smelter complex, and the remaining three experiment along a transect running to the SE of the smelter (Fig. 1). A SE transect was selected because this was the only direction with suitable stands and soils; the smelter complex is located next to the town of Harjavalta, and in all other directions the area is under urban or industrial use, or is otherwise unsuitable owing to the predominance of agricultural fields and till soils. The experiment at 0.5 km had to be located to the SW of the smelter because no forested areas were available at this distance along the SE transect.

The stands in the four experiments were naturally regenerated, young or middle-aged Scots pine stands that had been thinned at a relatively early stage of development. The difference in stand age was rather small (mean 47 ±7 years), but the dominant height, volume and volume growth varied considerably (Table 3). The tree stand at 0.5 km was suffering from severe defoliation. In the middle of the 1980's the stand at 0.5 km had been fertilised with NPK fertiliser (ca. 200 kg N/ha). The vegetation on the sites was originally typical of xerophilous forest sites, but at 0.5 km it was almost completely destroyed (Salemaa and Vanha-Majamaa 1993) and consisted of a few surviving patches of crowberry (*Empetrum nigrum*), with some bog bilberry (*Vaccinium uliginosum*) and *Carex globularis* in wet depressions (Salemaa et al. 1999).

The experiments were located on eskers, the soil consisting of sorted fine or fine/coarse sand with no stones (Table 4). The soils were classified as orthic podsols (Anon. 1988). The organic layer at all 4 sites was relatively thin mor, the thickest organic layer (at 0.5 km) having a clearly pronounced, dry, undecomposed litter layer.

Table 3. Stand characteristics of the untreated plots in July 1992 at the start of the study (Mälkönen et al. 1999).

Distance	Age,	Stems,	Dominant trees		Vol.	Vol. incr.	Needle mass,
Km	yr	no/ha	dbh, cm	height, m	m^3/ha	m^3/ha/yr	kg/ha
0.5	49	1008	14.8	7.6	23.2	0.31	835
2	54	1230	18.2	12.5	85.3	3.78	3805
4	48	1517	17.1	11.1	67.8	2.78	2970
8	40	1552	17.8	12.4	94.5	6.27	3498

Table 4. Forest site type (for Finnish classification, see Cajander 1949) and physical properties of the organic layer and genetic mineral soil horizons of the experimental sites. Stoniness was determined according to Viro (1952). CT = Calluna site type, CT+ = more fertile Calluna site type.

Parameter		Distance from the smelter, km			
		0.5	2	4	8
Forest site type		CT+	CT+	CT	CT
Organic layer					
	Type	mor	mor	mor	mor
	Thickness, cm	2.7	1.7	2.0	2.0
Mineral soil					
	Parent material	sorted fine	sorted fine/	sorted fine	sorted fine
	Texture	sand	coarse sand	sand	sand
	Stoniness, vol%	0	0	0	0
horizon thickness, cm					
	E	15	6	11	8
	Bs	31	39	26	27

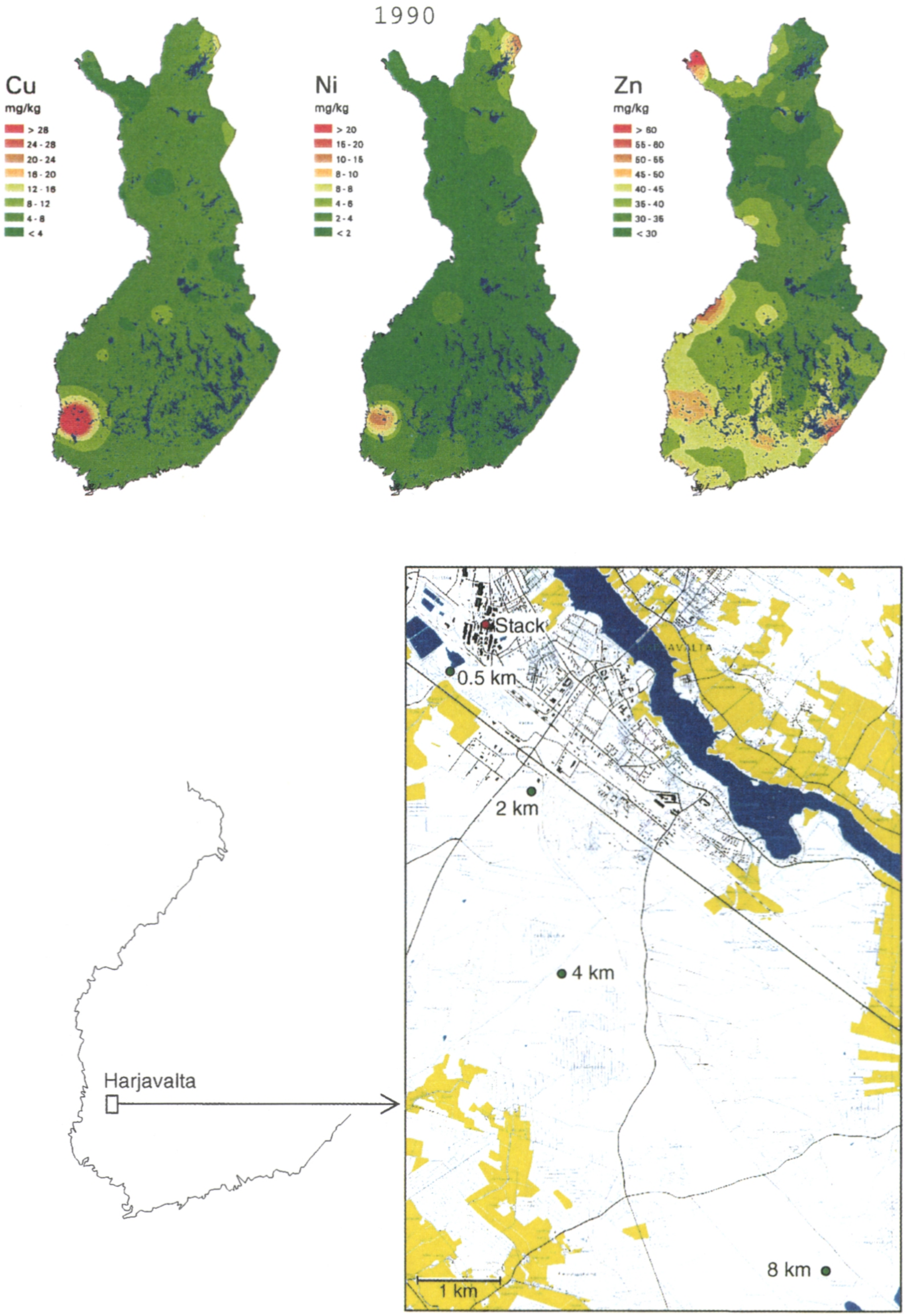

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Figure 1. Location of the experiments at distances of 0.5, 2, 4 and 8 km along a transect running to the SE of the Harjavalta Cu-Ni smelter (stack marked on map), and maps of the Cu, Ni and Zn concentrations in moss samples according to the 1990 heavy-metal moss survey (Kubin2000).

The long-term (1971-1988) mean precipitation at a nearby station of the Water and Environment Research Institute was 620 mm (Järvinen & Vänni 1990). According to wind recordings made at a nearby weather station (Fig. 2), the predominant wind direction was from the south, i.e. the greatest amount of deposition (18%) was carried to the north of the smelter during 1993-1996. 10% was carried in the direction of the transect (experiments at 2, 4 and 8 km), and 8% towards the experiment at 0.5 km.

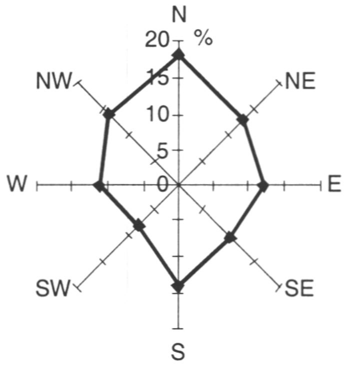

Figure 2. Reverse wind rose (1993-1996) recorded at the Kuuskajaskari weather station (Rauma) of the Finnish Meteorological Institute, ca. 30 km to the SW of the Harjavalta smelter.

2.2 The experimental design, and the liming and fertiliser treatments

The liming and fertiliser treatments were applied on 30 x 30 m plots at the end of May/beginning of June, 1992, using a random design with three repetitions of each treatment at 0.5, 2 and 8 km and four replications at 4 km. The plots were isolated from each other by 5 m-wide buffer strips.

The liming treatment (LT) consisted of Mg-rich (5%) granulated limestone (2000 kg/ha) and a small amount of boron (2 kg/ha). Forest soils in much of Fennoscandia are relatively boron deficient (Lipas et al. 1983), and if limestone is applied then boron is necessary to prevent short-root and mycorrhizal mortality (Lehto 1994) and to minimise subsequent growth losses (Lipas 1990).

The correction fertiliser (CF) consisted of slow-release powdered minerals (apatite 100 kg/ha, calcium/magnesium carbonate 200 kg/ha, biotite 600 kg/ha) and a mixture of fast-release, water-soluble salts. The fertiliser also contained small amounts of Cu (0.8 kg/ha) and Zn (0.8 kg/ha).

The composition of the site-specific fertiliser (SSF) was determined on the basis of needle and soil analyses (Mälkönen et al. 1999). The stand at the experiment located 0.5 km from the smelter had low foliar N and Ca and extremely low Mg concentrations (Papers III and IV), and the organic layer had extremely low exchangeable Ca and Mg concentrations (Paper II). Nitrogen (150 kg /ha) was given in the form of slow-release methylene urea and fast-release ammonium nitrate, and Ca and Mg as Mg-rich granulated limestone (1500 kg/ha). The stands at 2 and 4 km were given nitrogen (150 kg /ha) and limestone (1000 kg/ha), and the stand at 4 km also some phosphate (30 kg/ha). At 8 km only the foliar N concentrations were low, and the SSF treatment was therefore a slightly smaller dose of nitrogen fertiliser (120 kg/ha) only. The amounts of individual nutrients applied in the treatments in the different experiment are given in Table 5.

Table 5. The liming and fertiliser treatments used in the experiments. MU = methylene urea, AN = ammonium nitrate.* = the SSF treatment in the experiment at 4 km also included P fertiliser

Treatment	Nutrient application, kg/ha								
	N	P	K	Ca	Mg	S	B	Cu	Zn
Control									
Liming (LT)				420	100		2.0		
Correction fert. (CF)		31	56	98	61	37	1.3	0.8	0.8
Stand-specific Fertiliser (SSF):									
0.5, 2 and 4 km	75 (MU) 75 (AN)	30*		315	50				
8 km	60 (MU) 60 (AN)								

2.3 Bulk deposition, stand throughfall and soil solution sampling

Bulk deposition was collected in open areas close to the four experiments (0.5, 2, 4, 8 km) using five rainfall collectors (d = 20 cm) during the snowfree period or two snow collectors (d = 36 cm) during the winter. Stand throughfall was collected on one of the untreated plots in three of the experiments (0.5, 4 and 8 km) for the study on metal and micronutrient fluxes (Paper III) using 20 rainfall collectors located systematically inside the stand on the 30 x 30 m plots during the snowfree period, and 6 systematically located snow collectors during the winter. The height of the rainfall collectors was 50 cm above ground level, and of the snow collectors 1.6 m.

Soil solution samples were collected in the form of soil water using zero-tension lysimeters (d = 20 cm) located at depths of 5 cm (4 replications), 20 cm (12 replications) and 40 cm (4 replications), measured from the ground surface, on one of the untreated plots in three of the experiments (0.5, 4 and 8 km) for the study on Cu and Ni mobility (Paper I) and on metal and micronutrient fluxes (Paper III). Zero-tension lysimeters were also installed at a depth of 20 cm (12 replications) on one of the plots given the liming or fertiliser treatment (LT, CF, SSF) in two of the experiments (at 0.5 and 8 km) for the study on heavy metal and macro-nutrient concentrations in the soil solution (Paper IV). The lysimeters consisted of a plastic funnel (d = 20 cm) containing acid-washed, fine quartz fitted to the top of a plastic bottle. The lysimeters were installed by first removing an intact soil core (d = 30 cm) down to the required depth using a special auger, and the lysimeters then placed in a shaft sunk below the removed soil core. The soil core was then carefully replaced. Soil water was removed from the lysimeters by means of a nylon tube leading down into the collection bottle (for more details, see Derome et al. 1991).

Bulk deposition, stand throughfall and soil solution samples (snowfree period only) were collected at ca. 1-month intervals during the period June 1992 to December 1998.

2.4 Soil sampling

Soil samples were taken from all of the plots in the four experiments in May, 1992, prior to the application of the fertilisers (Papers I, II and III), and again in October, 1996, four and a half years after the treatments had been applied (Paper V). Organic layer and mineral soil samples (0 - 5, 5 - 10, 10 - 20 cm layers) were taken at 25 points on each plot in all four experiments. The samples were combined to give one composite sample per layer per plot, and then air-dried. The organic layer samples were milled to pass through a 1-mm sieve, and the mineral soil samples were passed through a 2-mm sieve to remove stones and large roots.

2.5 Chemical analyses

The pH of the bulk precipitation, stand throughfall and soil solution samples was measured, and the remaining part of the samples filtered (0.45 μm membrane filter). Ca, Mg, K, Cu, Ni and Zn were determined by inductively coupled plasma atomic emission spectrometry (ICP/AES) on samples conserved with ultrapure HNO_3 (65%, 0.5 ml/100 ml sample), and NH_4-N, NO_3-N, SO_4-S and PO_4-P directly on non-conserved samples by ion chromatography (IC). Dissolved organic carbon (DOC) was determined by digestion with sodium persulphate under UV radiation on a TOC analyser (Astro).

The pH of the organic and mineral soil samples was determined in distilled water (15 ml sample/25 ml water). Total Ca, Mg, Na, K, Cu, Ni, Fe, Zn, Cd, Pb, Cr, Al, Mn, S and P were determined from the organic layer samples by dry ashing at 550°C, extracting the ash with conc. HCl, and then analysing the solutions by ICP/AES. Total N was determined on a CHN analyser (Leco). Exchangeable Ca, Mg, K, Cu, Ni and Al were determined by extraction with 0.1 M $BaCl_2$ (7.5 g humus or 15 g mineral soil/150 ml extractant, shaking for 2 h), with and without 2% EDTA, followed by filtration and analysis by ICP/AES. Exchangeable acidity was determined from the same extract by titration to pH 7. The Na^+ form of EDTA was used in order to avoid an additional input of protons to exchangeable acidity, which therefore also meant that Na^+ could not be determined nor included in the CEC calculations. Extractable S and P were determined by extraction with 1M ammonium acetate (pH 4.65) (7.5 g humus or 15 g mineral soil/150 ml extractant, shaking for 2 h) followed by filtration and analysis by ICP/AES. Water-extractable (free) Ca, Mg, K, Cu and Ni were determined by extraction with 0.01M NaCl (7.5 g sample/150 ml extractant, shaking for 2 h), followed by analysis by ICP/AES

2.6 Calculations and statistical analyses

Soil parameters

The soil results presented in the individual papers are based on a varying number of plots:

Papers I and III	One plot/experiment, i.e. the untreated plot where stand throughfall and soil water (5, 20 and 40 cm) were collected.
Paper II	Mean values of all the plots in the experiments
Paper V	All the plots in the experiments. The results are expressed as means of the replication plots for each treatment

Fluxes (Paper III)

The annual fluxes for the period 1993-96 were calculated by summing the amounts of individual elements or compounds/m^2 collected during the periods 7.12.1992 - 13.10.1993, 14.10.1993 - 7.11.1994, 8.11.1994 - 6.11.1995, and 7.11.1995 - 12.11.1996. The start of each period was determined by the date when the last soil water sample was obtained prior to the onset of winter, i.e. it was assumed that water collected for the first time after snowmelt each spring was derived from snow that had fallen during the previous winter. Average annual fluxes during the period 1993-96 were calculated from the annual flux values. No water was obtained from the four lysimeters located at a depth of 40 cm at 8 km, and the figures therefore do not include data for this depth and site.

Macro-nutrient and heavy metal availability and cation exchange capacity

The effect of liming and fertilisation treatments on the distribution of macro-nutrients (Ca, Mg, K) and heavy metals (Cu, Ni, Zn) into different forms in the organic layer was investigated in Paper V.

The metals were divided into immobilised, exchangeable and free forms as follows. The immobilised Ca, Mg, K, Cu and Ni concentrations in the organic layer were obtained as the difference between total concentrations (dry digestion, 550°C) and plant-available concentrations ($BaCl_2$+EDTA). Exchangeable Ca, Mg, K, Cu and Ni concentrations in the organic layer were obtained as the difference between plant-available concentrations and water-extractable (free) concentrations.

In Paper II, effective cation exchange capacity (CEC_{eff}) was calculated by summation in three different ways: 1) the sum of the equivalent concentrations of exchangeable Ca, Mg, K and exchangeable acidity, 2) as in 1) but including Cu and Ni obtained without ethylenediamine tetra-acetic acid (EDTA) in the $BaCl_2$ extractant, and 3) as in 1) but including Cu and Ni obtained with EDTA in the $BaCl_2$ extractant. Copper and Ni were included because they are known to be present in high concentrations in the organic layer at the plots closest to the smelter, and it was therefore assumed that they would also occupy a significant proportion of the cation exchange sites.

In Paper V, effective cation exchange capacity (CEC_{eff}) was based on the exchangeable Ca, Mg, K, Cu and Ni concentrations in the organic layer, i.e the difference between plant-available concentrations and water-extractable (free) concentrations. This was done because it was assumed that a considerable amount of these elements would still be present in the soil solution in the organic layer on the plots given the fertilisers and limestone, and not only bound on the cation exchange sites. The $BaCl_2$ extraction solution contained EDTA because, although it was shown in Paper II that the inclusion of EDTA gives an over-estimate for CEC, the determination of plant-available cation conentrations presupposed the use of EDTA.

Statistical analyses

The differences between the experiments were tested for each parameter separately using analysis of variance by the general linear models procedure, and the statistical differences by Tukey's studentised range test. The total element concentrations in the organic layer at different distances from the smelter were grouped by means of factor analysis using the SPSS programme (extraction method: principal component analysis; rotation method: varimax with Kaiser normalisation).

3 RESULTS

3.1 Heavy-metal and sulphur concentrations, acidity status and macro-nutrient availability in the soil and soil water

3.1.1 Heavy-metal and sulphur concentrations

The total concentrations of Cu, Ni, Zn, Fe, Pb, Cd, Cr and S (dry digestion) in the organic layer followed clear increasing gradients with decreasing distance to the smelter complex (Paper II, Table 1). The enrichment factors for total Fe, Cu, Zn, Cd, Pb, Cr and Ni in the organic layer showed similar gradients (Fig. 3). Cu and Ni had clearly accumulated the most, while the accumulation factors for Zn, Cd, Pb, Cr and Fe on the four plots were similar, but considerably lower than those for Cu and Ni. There was no gradient in the total Mn concentrations, total Mn being significantly higher at 2 than at 0.5, 4 or 8 km (Paper II, Table 1).

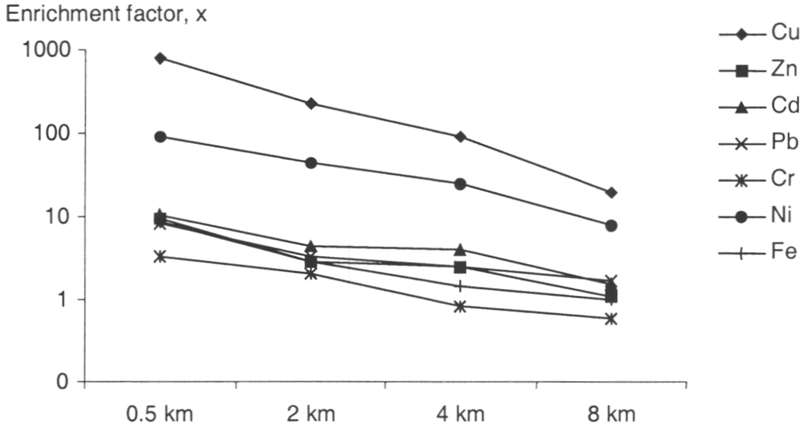

Figure 3. Enrichment of total Cu, Zn, Cd, Pb, Cr, Ni and Fe in the organic layer at distances of 0.5, 2, 4 and 8 km from the Harjavalta smelter. The enrichment factor was calculated as the concentrations of the heavy metals divided by the corresponding mean values for the organic layer of forest soils in southern Finland (Tamminen & Starr 1990).

According to the correlation matrix (Table 6), many of the heavy metals (Fe, Cu, Zn, Cd, Pb, Ni), macro-nutrients (Ca, Mg, K) and other elements (N, P, S) in the organic layer were strongly inter-correlated. Factorial analysis distinguished three groups of elements (Table 7). Group 1 consisted of heavy metals (Cu, Ni, Zn, Fe, Pb, Cd, Cr) and other emission components (S, Mg, P) derived from the smelter complex, and group 2 elements (Ca, K, N, Na) present in the organic layer that are important plant nutrients (apart from Na). Group 3 comprised Al and Mn.

Exchangeable Cu, Ni, Zn, Fe, Pb and Cd and extractable S in the organic layer followed an increasing gradient with decreasing distance from the smelter (Table 8). Exchangeable Cr concentrations in the organic layer were below the analytical detection limit at all distances except 0.5 km.

The mean concentrations of Cu^{2+}, Ni^{2+}, Zn^{2+} and SO_4^{2-} in soil water at a depth of 5, 20 and 40 cm on the untreated plots at 0.5 km during 1992-1996 were extremely high compared to those at 4 and 8 km (Table 9). At 4 and 8 km there was a clear decrease in the concentrations of Cu^{2+}, Ni^{2+}, Zn^{2+} and SO_4^{2-} with increasing depth, but at 0.5 km the highest concentrations occurred at a depth of 20 cm (Paper 1, Fig. 1). In contrast, there were no clear trends in the mean Fe^{3+} and Mn^{2+} concentrations with respect to distance to the smelter or soil depth.

3.1.2 Acidity status

pH and exchangeable acidity

The pH of the organic and 0-5 cm mineral soil layers was relatively constant at different distances along the transect (Paper II, Table 2, Fig. 4). In the 5-10 and 10-20 cm layers, on the other hand, the pH at 0.5 km was between 0.1 and 0.4 pH-units lower than that at distances of 2, 4 and 8 km. The mean pH of soil water at a depth of 5, 20 and 40 cm at 0.5 km was significantly lower during 1992-1996 than at 4 or 8 km (Table 10). There was no clear trend in exchangeable acidity in the organic, 0-5 and 5-10 cm layers along the transect (Paper II, Table 2). In the 10-20 cm mineral soil layer, on the other hand, exchangeable acidity was significantly higher at 0.5 km than at 2,4 and 8 km.

Table 6. Correlation matrix between total heavy metal, aluminium, macro-nutrient (Ca, Mg, K, Na) and phosphorus, sulphur and nitrogen concentrations in the organic layer at distances of 0.5, 2, 4 an 8 km from the Harjavalta smelter. n = 56. * = statistically significant at the 5% risk level, ** = at the 1% risk level, and *** = at the 0.1% risk level.

	P	S	K	Ca	Mg	Mn	Fe	Al	Cu	Zn	Na	Cd	Pb	Cr	Ni
S	0.881***														
K	0.050	0.255													
Ca	0.195	0.311*	0.762***												
Mg	0.891***	0.871***	0.116	0.056											
Mn	-0.213	0.072	0.628***	0.373**	0.040										
Fe	0.948***	0.850***	-0.146	-0.069	0.901***	-0.259									
Al	0.005	0.152	0.692***	0.552***	0.118	0.570***	-0.150								
Cu	0.938***	0.863***	-0.142	-0.036	0.853***	-0.251	0.980***	-0.138							
Zn	0.969***	0.885***	-0.075	0.067	0.863***	-0.273*	0.980***	-0.120	0.982***						
Na	-0.014	0.088	0.521***	0.600***	0.037	0.261	-0.202	0.486**	-0.252	-0.137					
Cd	0.924***	0.901***	0.017	0.154	0.805***	-0.188	0.913***	-0.042	0.954***	0.963***	-0.133				
Pb	0.977***	0.903***	-0.017	0.080	0.911***	-0.195	0.976***	-0.053	0.974***	0.979***	-0.117	0.938***			
Cr	0.747***	0.716***	-0.235	-0.319*	0.865***	-0.186	0.884***	-0.256	0.829***	0.811***	-0.230	0.720***	0.826***		
Ni	0.914***	0.927***	0.016	0.065	0.885***	-0.070	0.940***	-0.023	0.966***	0.953***	-0.179	0.971***	0.956***	0.812***	
N	0.351**	0.514***	0.521***	0.713***	0.203	0.187	0.170	0.437***	0.262	0.314	0.315*	0.328*	0.304*	-0.065	0.365**

Table 7. Total element concentrations in the organic layer at different distances from the smelter grouped into dimensions by means of factor analysis. Extracted using principal component analysis, and rotated by varimax with Kaiser normalisation.

Variable	Factors and sorted loadings (absolute value >0.2)		
	1	2	3
Pb	0.986		
Fe	0.980		
Ni	0.980		
Cu	0.975		
Zn	0.974		
P	0.954		
Cd	0.945		
Mg	0.938		0.240
S	0.924	0.277	
Cr	0.869	-0.379	
Ca		0.928	
N	0.289	0.841	
K		0.695	0.592
Na		0.633	0.269
Mn		0.203	0.887
Al		0.555	0.638

Exchangeable aluminium in the soil and aluminium concentrations in soil water

Exchangeable Al concentrations in the organic and 0-5 and 5-10 cm mineral soil layers at 0.5 km were lower than those at 2, 4 and 8 km (Paper II, Table 2). In contrast, exchangeable Al concentrations in the 10-20 cm mineral soil layer were almost double those at 2, 4 and 8 km. Total Al concentrations in soil water at depths of 5 and 20 cm during 1992-1996 were significantly lower at 0.5 km than at 4 and 8 km, but significantly higher at a depth of 40 cm (Table 10).

Effective cation exchange capacity (CEC_{eff})

When CEC_{eff} was calculated on the basis of the sum of base cations, exchange acidity and exchangeable Ni and Cu (without EDTA), there were no significant differences between the CEC_{eff} of the organic, 0-5, 5-10 and 10-20 cm mineral soil layers at different distances from the smelter (Paper II, Table 3). When Cu^{2+} and Ni^{2+} were excluded, the CEC_{eff} of the organic layer at 0.5 and 2 km was significantly lower than at 4 and 8 km, and when EDTA-extracted Cu^{2+} and Ni^{2+} were included the CEC_{eff} of the organic layer was significantly higher at 0.5 km than at 2, 4 and 8 km.

Table 8. Concentrations (mg/kg dw) of exchangeable (exc.) and extractable (ext.) elements in the organic and mineral soil layers (MS) at different distances from the Harjavalta smelter in the samples taken in 1992. MS = mineral soil. nd = not detected, i.e. below the analytical detection limit (Cr = 0.010 ppm in the extract, Cd = 0.003 ppm).

Layer	$\mathrm{Cu_{exc}}$	$\mathrm{Ni_{exc}}$	$\mathrm{Zn_{exc}}$	$\mathrm{Fe_{exc}}$	$\mathrm{Mn_{exc}}$	$\mathrm{Pb_{exc}}$	$\mathrm{Cr_{exc}}$	$\mathrm{Cd_{exc}}$	$\mathrm{Ca_{exc}}$	$\mathrm{Mg_{exc}}$	$\mathrm{K_{exc}}$	$\mathrm{S_{ext}}$	$\mathrm{P_{ext}}$
Organic layer													
0.5 km	3207^{a}	258^{a}	88.4^{a}	4224^{a}	6.5^{a}	185^{a}	1.99	1.64^{a}	285^{a}	26^{a}	77^{a}	163^{a}	327^{a}
2 km	1044^{b}	157^{b}	67.5^{b}	1936^{b}	73.1^{b}	107^{b}	nd	1.24^{b}	828^{b}	69^{b}	207^{b}	94^{b}	126^{b}
4 km	453^{c}	95^{c}	90.4^{a}	1042^{c}	41.3^{c}	75^{c}	nd	1.20^{b}	1122^{c}	106^{c}	358^{c}	99^{b}	121^{b}
8 km	108c	32^{d}	42.7^{c}	721^{c}	46.8^{c}	56^{c}	nd	0.51^{c}	862^{b}	79^{b}	282^{d}	81^{b}	93^{b}
MS, 0-5 cm													
0.5 km	254^{a}	25.6^{a}	11.2^{a}	239^{a}	0.96^{a}	8.27^{a}	nd	0.24^{a}	41.4^{a}	3.99^{a}	12.4^{a}	11.7^{a}	21.4^{a}
2 km	37^{b}	5.8^{b}	4.1^{b}	192^{ab}	4.98^{b}	4.69^{b}	nd	0.08^{b}	40.0^{a}	6.73^{b}	20.7^{b}	9.6^{ac}	13.5^{b}
4 km	3^{b}	0.4^{c}	1.7^{c}	89^{c}	0.53^{a}	1.71^{c}	nd	nd	11.7^{b}	3.37^{a}	10.3^{a}	5.4^{b}	8.2^{b}
8 km	2^{b}	nd	1.1^{c}	147^{b}	1.03^{a}	2.63^{bc}	nd	nd	12.4^{b}	3.93^{a}	11.8^{a}	6.5^{bc}	12.8^{b}
MS, 5-10 cm													
0.5 km	42.5^{a}	7.39^{a}	3.66^{a}	66^{a}	0.53^{a}	0.38^{a}	nd	0.03	13.4^{a}	1.98^{a}	5.9^{a}	5.3^{a}	10.8^{a}
2 km	4.8^{b}	1.13^{b}	1.36^{b}	163^{b}	2.89^{b}	1.51^{bc}	nd	nd	7.7^{b}	2.80^{b}	15.7^{b}	18.1^{b}	17.6^{bc}
4 km	0.8^{b}	nd	0.68^{bc}	155^{b}	0.24^{a}	1.22^{b}	nd	nd	3.9^{c}	2.11^{a}	7.1^{a}	11.6^{ab}	14.4^{ac}
8 km	0.4^{b}	nd	0.47^{c}	212^{c}	0.42^{a}	1.68^{c}	nd	nd	3.6^{c}	2.42^{ab}	13.0^{b}	16.7^{b}	20.4^{b}
MS, 10-20 cm													
0.5 km	31.0^{a}	5.07	2.64^{a}	117^{a}	0.77^{a}	1.03^{a}	nd	0.02	9.1^{a}	1.66^{a}	5.5^{a}	12.5^{a}	25.2^{a}
2 km	1.7^{b}	nd	0.65^{b}	57^{b}	2.37^{b}	0.10^{b}	nd	nd	4.0^{b}	1.54^{a}	12.4^{b}	37.4^{b}	6.5^{b}
4 km	0.4^{b}	nd	0.12^{c}	79^{c}	0.18^{a}	0.13^{b}	nd	nd	2.3^{c}	1.19^{b}	5.1^{a}	27.2^{c}	6.6^{b}
8 km	0.1^{b}	nd	0.08^{c}	45^{b}	0.42^{a}	nd	nd	nd	1.7^{c}	1.09^{b}	7.2^{a}	25.7^{c}	4.9b

Table 9. Mean Cu, Ni, Zn, Fe, Mn and SO4-S concentrations in soil water at depths of 5, 20 and 40 cm on the untreated plots at distances of 0.5, 4 and 8 km from the Harjavalta smelter during 1992-1996. The standard error of the mean is given in parentheses.

Depth Distance	Cu mg/l	Ni mg/l	Zn mg/l	Fe mg/l	Mn mg/l	SO_4-S mg/l
5 cm						
0.5 km	0.65 (0.09)	0.54 (0.06)	0.34 (0.03)	0.25 (0.11)	0.12 (0.01)	4.43 (0.29)
4 km	0.06 (0.01)	0.02 (0.003)	0.04 (0.004)	0.30 (0.02)	0.15 (0.02)	2.28 (0.18)
8 km	0.02 (0.002)	0.01 (0.001	0.04 (0.003)	0.45 (0.04)	0.13 (0.02)	1.98 (0.18)
20 cm						
0.5 km	1.19 (0.08)	0.95 (0.05)	0.58 (0.08)	0.17 (0.02)	0.20 (0.02)	6.59 (0.44)
4 km	0.03 (0.003)	0.02 (0.003)	0.04 (0.003)	0.31 (0.04)	0.07 (0.008)	1.82 (0.13)
8 km	0.01 (0.002)	0.01 (0.001)	0.04 (0.002)	0.28 (0.03)	0.14 (0.02)	1.89 (0.13)
40 cm						
0.5 km	0.41 (0.05)	0.64 (0.05)	0.44 (0.04)	0.06 (0.007)	0.18 (0.03)	5.29 (0.50)
4 km	0.01 (0.001)	0.01 (0.001)	0.03 (0.003)	0.10 (0.01)	0.07 (0.01)	1.49 (0.11)

Table 10. Mean pH and Al, Ca, Mg, K, NH4-N, NO3-N and PO4-P concentrations in soil solution at depths of 5, 20 and 40 cm on the untreated plots at distances of 0.5, 4 and 8 km from the Harjavalta smelter during 1992-1996. The standard error of the mean is given in parentheses.

Depth Distance	pH	Al mg/l	Ca mg/l	Mg mg/l	K mg/l	NH_4-N mg/l	NO_3-N mg/l	PO_4-P mg/l
5 cm								
0.5 km	4.07 (0.04)	0.15 (0.02)	1.53 (0.12)	0.45 (0.05)	1.47 (0.13)	0.61 (0.16)	0.21 (0.04)	0.11 (0.02)
4 km	4.38 (0.09)	0.35 (0.03)	1.12 (0.11)	0.27 (0.03)	2.03 (0.16)	0.42 (0.09)	0.21 (0.05)	0.18 (0.02)
8 km	4.27 (0.09)	1.02 (0.09)	0.91 (0.09)	0.27 (0.03)	1.78 (0.17)	0.44 (0.10)	0.08 (0.02)	0.11 (0.02)
20 cm								
0.5 km	3.96 (0.03)	0.51 (0.07)	3.05 (0.45)	0.81 (0.12)	2.76 (0.28)	0.98 (0.36)	0.21 (0.10)	0.07 (0.01)
4 km	4.34 (0.06)	1.09 (0.21)	0.44 (0.04)	0.21 (0.02)	2.38 (0.20)	0.20 (0.03)	0.03 (0.01)	0.09 (0.01)
8 km	4.56 (0.05)	0.90 (0.09)	0.82 (0.07)	0.30 (0.02)	1.97 (0.21)	0.27 (0.05)	0.06 (0.02)	0.08 (0.02)
40 cm								
0.5 km	4.43 (0.03)	1.06 (0.07)	1.59 (0.15)	0.57 (0.06)	2.59 (0.26)	0.24 (0.06)	0.25 (0.05)	0.06 (0.01)
4 km	4.76 (0.04)	0.82 (0.08)	0.38 (0.04)	0.15 (0.01)	1.52 (0.16)	0.12 (0.02)	0.03 (0.01)	0.04 (0.01)

Base saturation (BS)

BS was extremely low in the organic layer at 0.5, and significantly depressed at 2 km compared to the situation at 4 and 8 km (Paper II, Table 3). The decrease in BS in the organic layer at 0.5 km especially was due to the high proportion of Cu^{2+} and Ni^{2+} cations occupying cation exchange sites, and not to an increase in exchange acidity (Paper II, Fig. 5). In the 0-5 and 5-10 cm mineral soil layers, on the other hand, BS at both 0.5 and 2 km was higher than that at 4 and 8 km.

3.1.3 Macro-nutrient availability

Calcium

There were no differences in total Ca concentrations in the organic layer along the transect (Paper II, Table 1), apart from the somewhat elevated concentrations at a distance of 4 km. The concentration of non-available (immobilised) Ca at 0.5 km was extremely high compared to that at 2, 4 and 8 km, and that of plant-available (exchangeable) correspondingly low (Table 8). In contrast, plant-available Ca concentrations in the 0-5 cm mineral soil layers at 0.5 and 2 km were significantly higher than those at 4 and 8 km, and in the 5-10 and 10-20 cm layers highest at 0.5 km. Mean Ca^{2+} concentrations in the soil water at depths of 5, 20 and 40 cm during 1992-1996 were higher at 0.5 km than at 4 and 8 km (Table 10).

Magnesium

There was a clear gradient in total Mg concentrations in the organic layer along the transect (Paper II, Table 1), the total Mg concentration at 0.5 km being double that at 4 and 8 km. The proportion of non-available (immobilised) Mg at 0.5 km was even higher than that of Ca, and at 2, 4 and 8 km a considerable part of the Mg was in an unavailable form. The concentrations of plant-available (exchangeable) Mg were correspondingly extremely low, especially at 0.5 and 2 km (Table 8). In contrast, there was no trend in plant-available Mg concentrations in the 0-5, 5-10 and 10-20 cm mineral soil layers along the transect. Mean Mg^{2+} concentrations in the soil water at depths of 5, 20 and 40 cm during 1992-1996 were higher at 0.5 km than at 4 and 8 km (Table 10).

Potassium

There was no trend in total K concentrations in the organic layer along the transect (Paper II, Table 1). The plant available K concentration, on the other hand, was significantly lower at 0.5 km than at 2, 4 and 8 km (Table 8), and non-available K higher at 0.5 km than at 4 and 8 km. There was considerable variation in the plant available K concentrations in the mineral soil layers along the transect, with no clear trends with respect to distance to the smelter. Mean K^+ concentrations in soil water at a depth of 20 and 40 cm during 1992-1996 was higher at 0.5 km than at 4 and 8 km (Table 10).

Ammonium and nitrate

The mean NH_4-N concentrations in soil water at a depth of 5, 20 and 40 cm during 1992-1996 were significantly higher at 0.5 km than at 4 and 8 km (Table 10). The mean NO_3-N concentrations in soil water at a depth of 5 cm were significantly higher at 0.5 and 4 km than at 8 km, and at a depth of 20 and 40 cm higher at 0.5 km.

Phosphorus

There was extremely high accumulation of total P in the organic layer at 0.5 km (Paper II, Table 1). Extractable P concentrations in the organic layer were correspondingly significantly higher at 0.5 km than at 2, 4 and 8 km (Table 8), and slightly elevated in the 0-5 cm mineral soil layer at 0.5 km. There were no clear trends in the mean PO_4-P concentrations in soil water during 1992-1996 at different distances from the smelter (Table 10).

3.2 Chemical composition of bulk precipitation and stand throughfall

There was relatively small year-to-year variation in the amount of bulk precipitation and stand throughfall at the different sites during the period 1993-1998 (Fig. 4). The 6-year mean bulk precipitation was 455 mm (sd ±31 mm) at 0.5 km, 570 mm (sd ±92 mm) at 2 km, 560 mm (sd ±57 mm) at 4 km, and 456 mm (sd ±52 mm) at 8 km. Interception of precipitation by the crown canopy was also relatively constant throughout the study period; 7% (sd ±8%) at 0.5

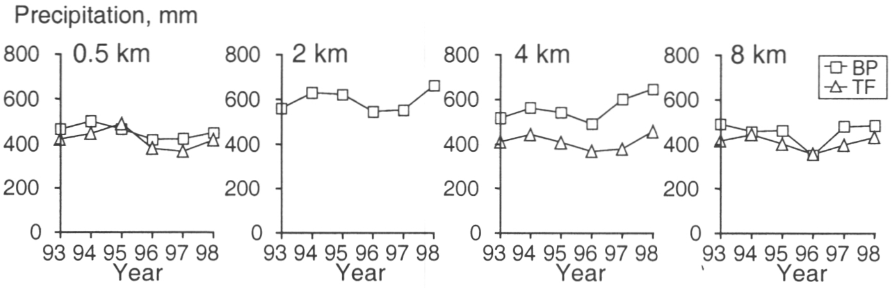

Fig. 4. Annual bulk precipitation (BP) and stand throughfall (TF) at different distances from the Harjavalta smelter during the period 1993-1998.

km, 26% (sd ±6%) at 4 km, and 7% (sd ±7%) at 8 km. Stand throughfall was not collected at 2 km.

There was a clear decreasing gradient in the mean annual deposition of Cu, Ni, Zn, Fe, Ca, Mg, K, total S and NH_4-N during 1993-1998 in both bulk precipitation and stand throughfall with increasing distance from the smelter (Table 11). The pH of both bulk precipitation and stand throughfall was at its highest at 0.5 km from the smelter. The deposition of Cu in bulk precipitation at 0.5 km was more than 50-fold higher than that at 8 km, for Ni 35-fold higher. For the other elements studied the increase was relatively small; for Zn and Fe ca. 5-fold, and for Ca, Mg, total S, NH_4-N and K between 3.5- and 1.5-fold. The corresponding increase in stand throughfall for Cu, Ni, Zn and Fe was much greater than that for bulk precipitation; 106- , 135-, 8- and 13-fold, respectively. SO_4-S and NH_4-N also showed a relatively large increase in stand throughfall compared to bulk precipitation (7.5- and 12-fold, respectively), but for Ca, Mg and K there was only a relatively small increase in stand throughfall.

At 0.5 km from the smelter there was considerable year-to-year variation in the deposition of Ni, Zn, Fe, Ca, Mg, NH_4-N and pH as bulk precipitation (Fig. 5a-c). The deposition of Fe showed a clear, decreasing trend from the relatively high values during the first two years of the study, while pH and NH_4-N indicated an increasing trend from 1995 onwards. Deposition values of all the elements and compounds monitored were higher at 0.5 km in stand throughfall than in bulk precipitation. There was a high peak of Ni deposition in stand throughfall at the end of the study period, and a strongly increasing trend in pH, NH_4-N, total S and K during 1995-1998.

At 2, 4 and 8 km from the smelter, the year-to-year variation for all components in bulk precipitation, apart from Cu and Ni, was relatively small. As was the case at 0.5 km, the deposition of all components in stand throughfall at 4 and 8 km was higher than that in bulk precipitation. There was a peak in the deposition of Cu in 1997 at 2, 4 and 8 km, and a clearly elevated Ni deposition towards the end of the study period at all three distances.

Table 11. Mean pH and mean annual deposition of Cu, Ni, Zn, Fe, Ca, Mg, K, total S and NH4-N (mg/m2) in bulk precipitation (BP) and stand throughfall (TF) during 1993-1998 at different distances from the Harjavalta smelter.

Parameter	Type of precipitation	Distance, km			
		0.5	2	4	8
Cu	BP	149	32.3	10.1	2.7
	TF	361		13.5	3.4
Ni	BP	64	9.3	3.2	1.9
	TF	203		4.5	1.5
Zn	BP	16.5	6.3	3.8	3.2
	TF	40.5		7.1	4.8
Fe	BP	33	13.2	7.6	6.9
	TF	100		12.1	8.0
Ca	BP	124	74	58	47
	TF	329		150	106
Mg	BP	39.6	20.8	18.0	15.7
	TF	91.1		43.9	32.6
K	BP	68	48	43	41
	TF	476		241	210
PH	BP	5.08	4.69	4.68	4.71
	TF	4.92		4.51	4.50
Total S	BP	742	390	328	290
	TF	2617		485	355
NH_4-N	BP	590	215	177	157
	TF	1653		208	142

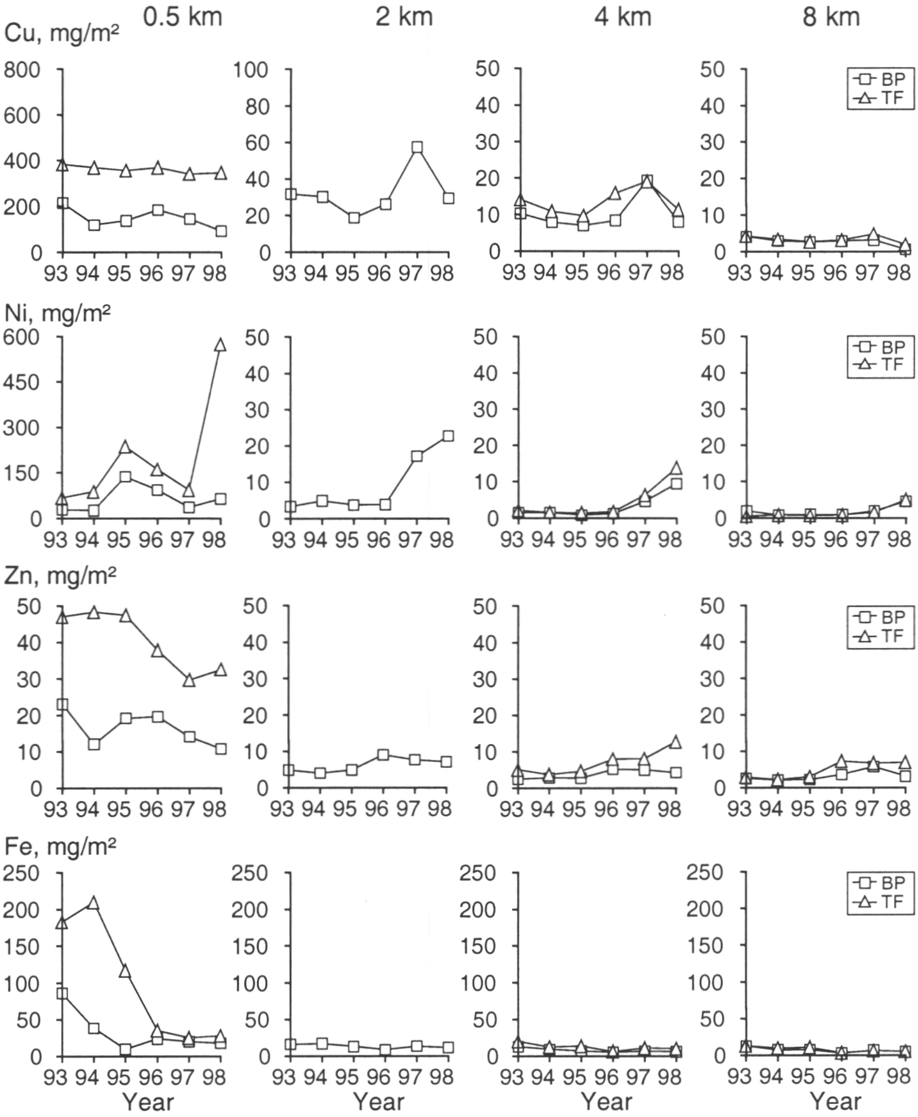

Fig. 5a. Annual deposition of Cu, Ni, Zn and Fe in bulk precipitation (BP) and stand throughfall (TF) at different distances from the Harjavalta smelter during the period 1993-1998.

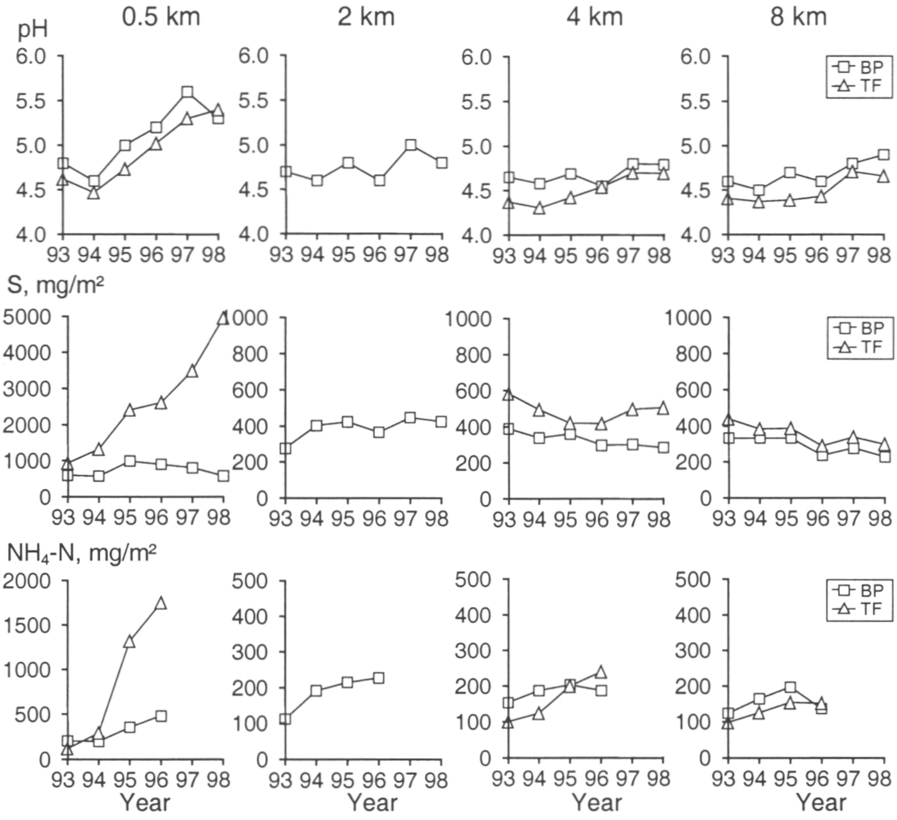

Fig. 5b. Mean pH and annual deposition of S and NH4-N in bulk precipitation (BP) and stand throughfall (TF) at different distances from the Harjavalta smelter during the period 1993-1998.

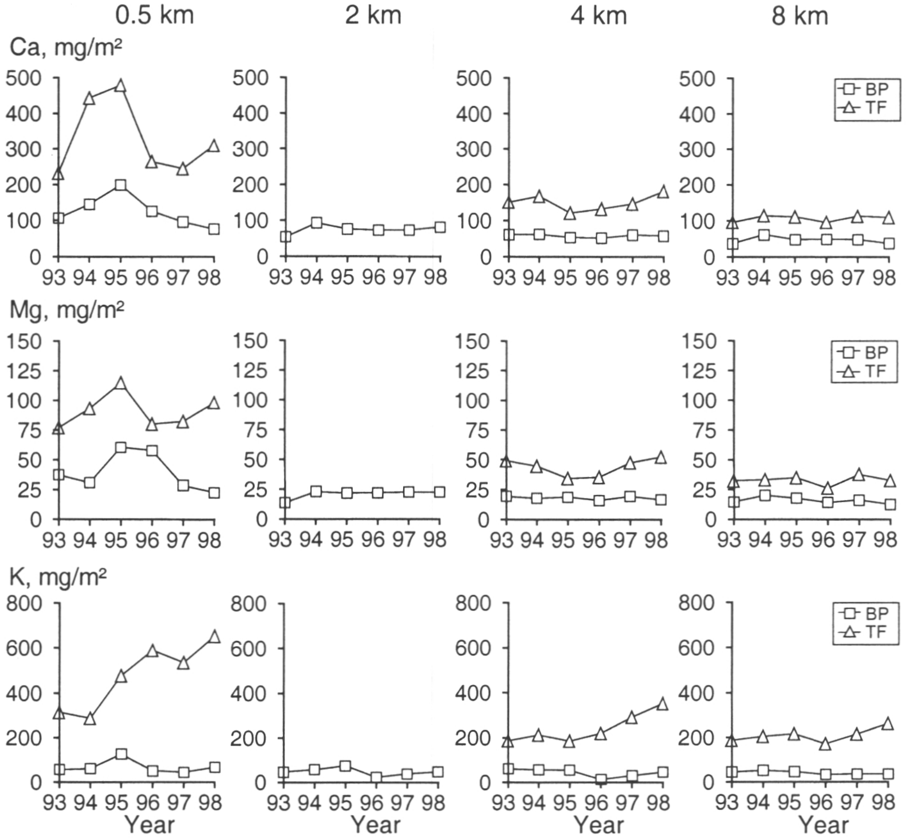

Fig. 5c. Annual deposition of Ca, Mg and K in bulk precipitation (BP) and stand throughfall (TF) at different distances from the Harjavalta smelter during the period 1993-1998.

3.3 Heavy metal and macro-nutrient fluxes within the stands

Water flux

A relatively high proportion of stand throughfall passed down to a depth of 5 cm at the plot at 0.5 km; the flux of soil water at 5 cm depth was 43% of bulk precipitation (Paper III, Fig. 3). At 4 and 8 km the corresponding proportions were only 11 and 18%, respectively. The fluxes of soil water at 20 and 40 cm at 0.5 km were also higher than those at 4 and 8 km. The fluxes of soil water at 5 and 20 cm at 4 and 8 km were very similar, in all cases less than 20% of bulk precipitation.

Copper, nickel, zinc and sulphate

The annual amounts of Cu, Ni and SO_4-S reaching the forest floor in throughfall at 0.5 km were considerably greater than those entering the stand as precipitation (Paper III, Fig. 4); 115% greater for Cu, 85% for Ni and 132% for SO_4-S. The situation at 4 km was somewhat similar although the increases were not as great as at 0.5 km. There were clear differences in the behaviour of Cu and Ni on entering the soil. Copper was retained to a greater extent than Ni in the uppermost soil layers because the flux of Cu in soil water at 5, 20 and 40 cm depths fell relatively sharply with increasing depth at both 0.5 and 4 km compared to the flux entering the soil in throughfall. The flux of Ni at 5 cm depth was greater than that entering the stand in precipitation at both 0.5 and 4 km. The flux of SO4-S was rather similar to that for Cu, especially at 0.5 km.

The effect of the crown canopy on the flux of Zn and the flux of Zn between the soil layers was rather different to that for Cu, Ni or SO_4-S (Paper III, Fig. 4). At 0.5 km the flux of Zn in soil water at 5, 20 and 40 cm depth was greater than that entering the soil in throughfall. Thus at 0.5 km there was a net loss of Zn from the 0-40 cm thick soil layer.

Calcium, magnesium and potassium

The fluxes of Ca, Mg and especially K in throughfall at 0.5 km were much higher than the fluxes entering the stand as bulk precipitation; an increase of 135% for Ca, 87% for Mg and 444% for K (Paper III, Fig. 5). The relative net increases in Ca and Mg were approximately the same at all three distances from the smelter, but for K the relative increase was by far the greatest at the plot at

0.5 km. There was a net loss of Mg from the 0-5 cm thick layer, and an overall net loss of both Mg and K from the 0-40 cm-thick mineral soil layer. The input and output of Ca were approximately the same.

Hydrogen ions and dissolved organic carbon (DOC)

The flux of hydrogen ions in bulk precipitation was the lowest at the plot closest to the smelter (Paper III, Fig. 6). The flux of protons in throughfall increased somewhat compared to that in bulk precipitation at all three distances. At 0.5 km there was a strong increase in the flux of protons passing down to a depth of 5 cm compared to distances of 4 and 8 km. There was a clear decrease in the flux of protons in soil water with increasing depth at all three distances.

No data were available for the flux of DOC in bulk precipitation. There was a strong increase in the flux of DOC in soil water at 5 cm depth at 0.5 km. The correlation between DOC and H^+ at this depth was weak ($r = 0.270$, $p<0.05$, $n = 38$), but it gradually increased with increasing depth (at 20 cm $r = 0.354$, $p<0.01$, $n = 39$; at 40 cm $r = 0.435$, $p<0.001$, $n = 31$). At 4 and 8 km, on the other hand, the only significant but weak correlation between these two parameters was at a depth of 5 cm (at 4 km $r = 0.331$, $p<0.01$, $n = 37$; at 8 km $r = 0.495$, $p<0.001$, $n = 34$).

Ammonium, nitrate and phosphate

At 0.5 km there were relatively large net increases in the flux of NH_4-N and NO_3-N in throughfall, NH_4-N increasing by 150% and NO_4-N by 60% compared to the amounts in bulk precipitation (Paper III, Fig. 7). In contrast, at 4 and 8 km there was a slight net decrease in NH_4-N and no change in NO_3-N in throughfall. The fluxes of NH_4-N and NO_3-N passing down the soil profile in soil water decreased strongly at all three sites compared to the input in throughfall.

At 4 and 8 km there was a clear decreasing trend in the flux of PO_4-P as the precipitation passed down through the canopy and then down through the soil to a depth of 40 cm (Paper III, Fig. 7). At 0.5 km, however, there was a 30% net increase in throughfall, and at 5 cm depth the flux of PO_4-P was still greater than that in bulk precipitation. There was a strong decrease in the flux of PO_4-P reaching depths of 20 and 40 cm at this distance from the smelter.

3.4 Effect of liming and correction fertilisation on heavy-metal concentrations and macro-nutrient availability in the soil and soil water

3.4.1 Heavy metal concentrations

The treatments containing the highest doses of limestone (LT, SSF) significantly reduced the exchangeable Cu concentrations in the organic layer at 0.5 and 4 km (Paper V, Fig. 5), and the LT treatment also at 8 km. The CF treatment had no effect on the exchangeable Cu concentrations at any of the sites, and none of the treatments had any effect on the free Cu concentrations. The three treatments had no significant effect on the exchangeable Ni concentrations in the organic layer, but the free Ni concentrations were reduced significantly by all three treatments at 2 km, and by the LT treatment at 4 km. None of the treatments had any effect on the concentrations of immobilised Cu or Ni at any distance.

At a distance of 0.5 km, all three treatments (LT, CF, SSF) increased the Cu^{2+}, Ni^{2+} and Zn^{2+} concentrations in soil water at a depth of 20 cm in the year following application, but brought about a significant decrease during 1993-95 (Paper IV, Fig. 2). These treatments also increased the Cu^{2+}, Ni^{2+} and Zn^{2+} concentrations during the first year at 8 km, but had no effect in subsequent years.

3.4.2 Acidity and base saturation

At a distance of 0.5 km, only the treatment with the second largest dose of limestone (SSF) increased the pH(H_2O) of the organic layer (Paper V, Table 1), while none of the treatments including limestone had any effect at 2 km. The amount of limestone added at these distances did not appear to have any direct effect on the magnitude of the increase in pH of the organic layer. In contrast, there was a clear relationship between the amount of limestone applied and the increase in pH at both 4 and 8 km.

The two smaller liming treatments temporarily increased soil solution pH at a depth of 20 cm at 0.5 km in the second year after application (Paper IV, Fig. 1), while the largest dose of limestone (LT) significantly reduced the pH of the soil solution throughout the study. In contrast, the largest dose of limestone strongly increased soil solution pH at 8 km.

The liming treatments had no significant effect on exchangeable acidity or exchangeable aluminium in the organic layer at 0.5 km (Paper V, Table 1), while at greater distances from the smelter the effects were very similar to those on pH.

All the liming treatments significantly increased base saturation (Paper V, Table 1). The correlation between pH and base saturation was extremely high at 2, 4 and 8 km, but somewhat lower at 0.5 km. The increase in the proportion of base cations out of CEC following liming at 0.5 km occurred primarily at the expense of the displacement of H^+ and Cu^{2+} ions, with only a small decrease in the proportions of Al^{3+} and Ni^{2+} (Paper V, Fig. 1). At 2, 4 and 8 km, on the other hand, the increase in base saturation resulted in a decrease in the proportions of both H^+ and Al^{3+}.

3.4.3 Macro-nutrient availability

Calcium, magnesium and potassium

The largest limestone treatments (LT, SSF) significantly increased the concentrations of plant-available Ca and Mg in the organic layer at all distances apart from 2 km from the smelter (Paper V, Table 2). The CF treatment had no significant effect on the Ca or Mg concentrations at any of the distances, apart from Mg at 8 km. None of the treatments had an effect on the K concentrations at any distance. All the treatments produced a peak in Ca^{2+}, Mg^{2+} and K^+ concentrations in soil solution at a depth of 20 cm at both 0.5 and 8 km (Paper IV, Fig. 3). This was followed by a significant decrease in the Ca concentration at 0.5 km during 1993-96. All three treatments brought about a relatively long-term increase in the Mg^{2+} concentrations at 0.5 km, and the LT and CF treatments at 8 km. The CF treatment clearly increased the K^+ concentrations in soil solution at 8 km.

Nitrogen

The SSF treatment, which contained nitrogen as ammonium and nitrate, strongly increased the concentrations of both forms of nitrogen during the growing season immediately after application at both 0.5 and 8 km (Paper IV, Fig. 5). The LT and CF treatments, which did not include nitrogen, also somewhat increased the NH_4-

N and NO_3-N concentrations during the same year. There was a strong increase in both the NH_4-N and NO_3-N concentrations in all the treatments, including the untreated plot, at 0.5 km in 1996.

<u>Phosphorus</u>

All three treatments, irrespective of whether they contained P or not, increased the PO_4-P concentrations in soil solution at 0.5 km (Paper IV, Fig. 4). In contrast, the treatments had no effect on the PO_4-P concentrations at 8 km.

4 DISCUSSION

4.1 The overall pattern of contamination by heavy metals and other elements in the forest soil

The properties of the forest soil in the immediate vicinity of the Cu-Ni smelter have been drastically altered by emissions from the smelter during the past 50 years. The strongly increasing gradient in the accumulation of heavy metals, Mg, P and S in the organic layer with decreasing distance to the smelter, appeared to be a direct result of these emissions. According to Tamminen (2000), the average total concentrations of heavy metals in the organic layer of upland forest soil in Finland are 6.6 mg/kg for Cu, 8.2 for Ni, 47 for Zn, 0.4 for Cd, 31 for Pb, and 8.1 for Cr. As the concentrations of these metals (apart from Cr and perhaps Zn) at the sites at 4 and 8 km were well in excess of these average values, it is clear that the heavy-metal pollution gradient extends for a distance of at least 8 km to the SE of the smelter. The total Ni gradient in the organic layer was less steep than that for Cu, suggesting that Ni dust has been carried over greater distances from the smelter stack than Cu. Hutchinson and Whitby (1977) attributed similar differences in the transportation distances of Cu and Ni deposition close to the Sudbury smelter in Canada, to differences in the size of the emitted particles.

The pattern of Cu, Ni and Zn concentrations in the mineral soil differed from that in the organic layer. Copper is known to form more stable complexes with organic matter than Ni and Zn (Alloway 1995), and will therefore be more effectively retained in the organic layer. At the site at 8 km, for instance, the Cu concentration in the organic layer was more than 20-fold the average value for upland forest soils (Tamminen 2000), while those of Ni and Zn were only 5- and 1.3-fold. The fluxes of Cu, Ni and Zn in soil water at 0.5 km also indicated that the mobility of these three metals followed the order Zn > Ni > Cu. The Cu, Ni and Zn concentrations in the soil water collected at depths of 5, 20 and 40 cm at 0.5 km were much higher than the median values of 0.005 mg/l for Cu, 0.009 mg/l for Ni and 0.018 mg/l for Zn at a depth of 40 cm at four background-monitoring ICP/IM plots in Finland

(Ukonmaanaho et al. 1998). At 8 km, on the other hand, the concentrations at 5 and 20 cm were only slightly higher than the background reference values.

There are no data available about Fe emissions, but it can be assumed that the extremely high concentrations of Fe in the organic layer (almost 2%) are derived from the smelter because the ore concentrates used in the smelting processes contained Fe. According to information provided by personnel at the smelter, the dust emissions contain both Fe_2O_3 and $Fe_2(SO_4)_3$. Although the enrichment factor (Fig. 3) for Fe in the organic layer at 0.5 km is extremely small (x 9) compared to that for Cu (x 780), in absolute terms the increase in the Fe concentration compared to background values (Tamminen 2000) is in fact many times greater (from 2,154 to 18,600 mg/kg dw) than that for Cu (from 7.4 to 5,800 mg/kg dw). If we assume that Fe and Cu deposition has been retained equally in the organic layer, and that emissions of Cu and Fe are transported over the same distance, then it can be concluded that Fe emissions during the lifetime of the smelter have been three times higher than those of Cu. However, Fe accumulation in the organic layer will have been further increased by the fact that Fe is a relatively immobile metal that readily forms complexes with organic matter (Schnitzer & Hansen1970) and, being a trivalent cation (Fe^{3+}), has a much higher affinity for cation exchange sites than Cu.

It is not known whether P has been emitted from the smelter, but Kemira Oy's fertiliser plant, which was established next to the smelter in 1948, emitted P at a level of 1 t/year during the 1980's. The factory produced superphosphate and KP fertilisers, and was closed down in 1989. According to Laaksovirta & Silvola (1975), in 1970 and 1971 the bark of pine trees growing about 0.5 km to the SE of the smelter complex contained about 3 g P/kg pine bark. To the NW of the smelter the concentration was ca. 5 g P/kg, and at distances of 4 to 5 km in both directions it fell to below 2 g P/kg. The mean P concentration of pine bark in background area in southern Finland according to the 1985 heavy-metal survey on pine bark carried out in conjunction with the National Forest Inventory was ca. 0.1 g/kg dm (Jarmo Poikolainen, unpublished results). The P concentrations in the organic layer fell sharply with increasing distance from the smelter. The presence of large amounts of Fe in the organic layer could result in the fixation of phosphates as insoluble complexes with Fe and organic matter (Dimma 1981).

There are indications that a high proportion of the accumulated P is in a non-available form because foliar P concentrations in the stand at 0.5 km were not elevated, and PO_4-P concentrations in soil solution were only slightly higher at 0.5 km than at 8 km. The P that has accumulated in the organic layer at 0.5 km is therefore most probably derived from an external source, and is not attributable to disturbances in internal P cycling within the stand.

The reason for the accumulation of Mg but not Ca in the organic layer appears to be due to the fact that the Ni concentrate used in the smelting process contains 8.2% Mg, but no appreciable mounts of Ca. Magnesium is probably present in the dust emissions as e.g. olivine $[(Mg, Fe)_2 SiO_4]$, because the patterns of Fe and Mg accumulation at different distances from the smelter were very similar.

Although SO_2 emissions from the smelter have earlier been relatively high, the strong accumulation of total inorganic S in the organic layer appears to be primarily due to the deposition of dust containing heavy-metal sulphates. The metal oxides formed during the smelting process combine with SO_2 to form sulphates in the "cold-end" of the smelter. Prior to the installation of electrostatic dust precipitators at the end of the 1980's, dust emissions from the smelter were considerable (over 1,000 t/year during the 1980's) (Poutanen & Kuisma 1994). The conclusion that the S is derived from dust emissions, rather than SO_2 emissions, is supported by the fact that there were no signs of excessive acidity in the uppermost soil layers at 0.5 km.

According to emission data provided by Outokumpu Harjavalta Metals Oy, the emissions of Cu, Ni, Zn, Pb, Cd and Cr have been reduced dramatically during the past decade. The temporal patterns of deposition both in the open and within the stand varied considerably during the period 1993-1998, and the deposition patterns at 0.5 km differed considerably from those at the other sites. The main reason for the considerable variation between the sites was their location with respect to the smelter, and the changes and improvements implemented at the smelter complex. The experiment at 0.5 km was located to the SW of the smelter complex and, following the doubling of the height of the stack from 70 to 140 m in 1994, the deposition at this site will have became more dependent on sporadic emissions from the smelter complex and the adjacent slag-handling area. In contrast, the experiments at 2, 4 and 8 km are located to the SE of the stack and, after 1994, have been sporadically subjected to somewhat higher deposition loads. For instance, there were clear peaks in Cu deposition at these three sites in 1997, and in Ni deposition in 1997 and 1998. At the experiment at 0.5 km, it is extremely difficult to distinguish between the contribution of metals, S and P in dust derived from the forest floor and that from dry deposition originating from the slag-handling area and smelter complex. The ground vegetation has been almost completely destroyed at this site (Salemaa & Vanha-Majamaa 1993) and the forest floor is covered in a relatively dry layer of undecomposed forest litter (Fritze et al. 1989). It is almost certain that dust from the degenerated forest floor has passed into the rainfall collectors because the opening at the top of the collectors was only 50 cm above ground level.

The conclusion that the elevated total concentrations of Cu, Ni, Zn, Pb, Cd, Cr, Fe, Mg, P and S in the organic layer in the different experiments are directly derived from deposition is supported by the extremely high correlation between these elements, and the results of the factorial analysis. The reason for the strong intercorrelation between Ca, K, N and Na, but less pronounced correlation with the above group of elements, is presumably due to the fact that these elements are related to the nutrient status of forest soil.

The maximum allowable concentrations of Cu, Ni and Zn in household water in Finland are 1.0, 0.02 and 3.0 mg/l, respectively (Kujala-Räty 1998). The town of Harjavalta uses groundwater from local deposits for the town's drinking-water supply. Although the concentrations measured in this study are for surface water and not groundwater, there are good reasons for comparing them with the allowable concentrations because surface water represents the first stage in the formation of groundwater. The concentrations of Cu and Zn in soil water at all depths on the control plots at distances of 4 and 8 km from the smelter were well below these values, but the mean Ni concentration was approximately the same as the maximum allowable value. At 0.5 km, in contrast, the Ni concentration at 20 cm depth was almost 50 times the permitted value, and for Cu at the same depth slightly above the permitted value. Of the three heavy metals studied, Zn appears to pose the greatest threat to the groundwater reserves in the area. Despite the fact that Zn emissions from the smelter have earlier been higher than those of Cu or Ni, the concentrations of Zn in the surface soil and soil solution are much lower than those of Cu or Ni. This strongly suggests that considerable amounts of Zn have already passed down deeper into the soil, and most probably into the groundwater. This process will have been accelerated by the depressed water-holding capacity of the surface soil close to the smelter.

Since 1995 there have been ever-increasing emissions of gaseous NH_3 from the smelter complex. This has been reflected as elevated pH levels in rainwater both in the open and within the stand at 0.5 km, and strongly increased deposition of NH_4-N and total S in throughfall. By 1998, nitrogen deposition within the stand had reached a level of almost 40 kg N/ha/year, which is almost 8-fold the background nitrogen deposition in this part of Finland (Järvinen & Vänni 1990). The formation of alkaline NH_4OH on the wet surfaces of the needles is presumably efficiently scavenging SO_2 from the air and, following oxidation to $(NH_4)_2SO_4$, is considerably increasing the input of sulphate into the soil.

4.2 Effects of high concentrations of Cu and Ni on Ca, Mg and K availability

Microbial activity in the organic layer at the plots at 0.5 and 2 km has been considerably reduced by the toxic effects of heavy metals on soil microbes (Fritze et al. 1989, cf. Bååth 1989). The humus layer at the plot at 0.5 km was covered by a rather thick layer of relatively undecomposed needle litter (cf. Freedman & Hutchinson 1980b), caused partly by the low rate of needle decomposition (Helmisaari et al. 1994). This has presumably resulted in a reduced rate of Ca, Mg and K mineralisation in the organic layer.

At 0.5 and 2 km the exchangeable Ca, Mg and K concentrations in the organic layer were extremely low, but in the 0-5 cm mineral soil layer relatively high. This deficiency of Ca, Mg and K in the organic layer was reflected as low foliar Ca, Mg and K concentrations on the plot at 0.5 km. Despite the relatively high concentrations of exchangeable Ca, Mg and K in the uppermost mineral soil layer, nutrient uptake by the tree appears to have been severely disturbed by the toxic effect of Cu and Ni on the plant roots and mycorrhizas (cf. Baes & McLaughlin 1987, Helmisaari et al. 1999).

The low concentrations of exchangeable Ca, Mg and K in the organic layer can be explained by the displacement of Ca, Mg and

K by the Cu, Ni and other heavy metals that have gradually accumulated in the organic layer. Copper, especially, is known to bind very strongly to cation exchange sites, and to readily displace other cations (Bloomfield & Sanders 1977). A high proportion of the Ca, Mg and K that has returned to the forest floor layer in the litter appears to have been strongly retained in the organic layer as a result of the depressed microbial activity. The small amounts of Ca, Mg and K that are released through mineralisation, together with the input from throughfall, are not bound in the organic layer, but pass down directly into the underlying mineral soil.

4.3 Effects of elevated exchangeable Cu and Ni concentrations and liming and fertilisation on estimates of CEC_{eff}

Effective cation exchange capacity (CEC_{eff}) was determined in this study by the summation method, i.e. the sum of equivalent concentrations of exchangeable cations, as obtained by extraction with 0.1M $BaCl_2$. The exchangeable cations Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+ and Al^{3+} are known to account for almost 100% of the cations bound on cation exchange sites in forest soils (Hendershot & Duquette 1986). In many cases, however, the term "exchangeable cation" in this context is not entirely correct, because the extract also contains cations that are free in the soil solution, i.e. not occupying cation exchange sites, as well as cations bound to or complexed with soluble organic matter. This source of error can be partly eliminated by subtracting the cation concentrations obtained by extraction with water. However, this correction is not usually considered necessary because the proportion of free cations in forest soils is normally insignificant compared to the proportion of cations bound on exchange sites. However, correction is necessary if large amounts of soluble salts or slow-release compounds have been added to the soil (e.g. as fertiliser or limestone), since this will greatly increase the concentrations of free cations. This procedure was followed in this study when determining the CEC_{eff} of the soil samples taken 5 years after liming and fertilisation. This was justified by the finding that the proportions of free Ca^{2+} and Mg^{2+} out of plant-available Ca and Mg ($BaCl_2$ extract) in the organic layer samples from the plots treated with limestone or the fertilisers were approximately double those on the untreated plots. In the case of K, however, there was no significant difference because most of the K^+ in podsolic forest soils is in fact already free in the soil solution (Derome 1991).

When determining CEC_{eff} by the summation method, the concentrations of exchangeable H^+ and Al^{3+} are not measured directly, but are determined indirectly as the concentration of so-called acidic cations (Huheey 1978) as exchangeable (or titratable) acidity. Both Al^{3+} and Fe^{3+} are acidic cations because their hydrated cations hydrolyse in the soil solution with the release of H^+ (i.e. H_3O^+) (Thomas & Hargrove 1984):

$$\begin{array}{cc} \underline{\text{Hydration}} & \underline{\text{Hydrolysis}} \end{array}$$

$$Al^{3+} + 6H_2O \Leftrightarrow [Al(H_2O)_6]^{3+} \overset{+H_2O}{\Leftrightarrow} H_3O^+ + [Al(H_2O)_5OH]^{2+}$$

The hydration of a metallic ion is the binding of water molecules around the shell of a charged metallic atom (cation). The hydration energy of the hydrated cation is expressed as the charge/size ratio of the cation, and is used to depict the degree of acidity of the cation. If the charge/size ratio is high, the H-O bonds in the water molecules can rupture, i.e. the hydrate ionises to yield hydronium ions (H_3O^+). Both Al^{3+} and Fe^{3+} have a high charge/size ratio (43.6 and 35.5, respectively) owing to their trivalency, and are therefore acidic cations. Hydrated divalent cations such as Ca^{2+}, Mg^{2+} and Mn^{2+} have relatively low charge/size ratios (10.3, 14.3 and 12.5, respectively) and do not ionise. The same applies to the divalent heavy metals, e.g. Cu (14.1) and Zn (13.7) and hence they do not contribute to exchangeable acidity. For instance, according to Leckie and Davis (1979), the hydrolysis constant for Cu^{2+} in solution ($Cu^{2+} + H_2O \Leftrightarrow CuOH^+ + H^+$) is between pH 7.2 to 8.1, and according to Lindsay (1979) pH 7.7. Cu^{2+} is the major form of Cu in solution below pH 6.9.

In podsolic forest soils, the predominant acidic cation in exchangeable acidity in the organic layer is H^+, and in the uppermost mineral soil layers Al^{3+} (Tamminen & Starr 1990, Derome 1991). The contribution of Fe^{3+} in the organic layer is negligible owing to the fact that most of it is in the form of extremely stable organic complexes (Stevenson 1982b). In this study, there was a very strong increasing gradient in exchangeable Fe concentrations in the organic layer with decreasing distance to the smelter, but no corresponding trend for exchangeable acidity. The exchangeable Fe concentration at 0.5 km of 4224 m/kg dw would, for instance, be equivalent to an exchangeable acidity value of 227 meq/kg dw. As exchangeable acidity at this site was in fact only 90.6 meq/kg dw, it is clear that the "exchangeable" Fe was not in an exchangeable form or acting as an acidic cation. The most likely explanation for this is that the Fe extracted by $BaCl_2$ was primarily in the form of organically complexed Fe.

Another serious drawback to the summation method is that it gives a marked underestimate of CEC if the soil naturally (e.g. Mn), or as a result of pollution by heavy metals, contains appreciable amounts of other exchangeable cations. In this study, Cu and Ni together occupied 35% of the cation exchange sites in the organic layer at a distance of 0.5 km, and 12% at 2 km (data not presented). Similar results have been obtained for the organic layer close to the Cu-Ni smelters at Monchegorsk, NW Russia (Derome et al. 1998). The corresponding proportions for the two other relatively abundant heavy metals, Zn and Pb, were below 1%. When Cu and Ni were included in the CEC calculations, the estimates for CEC in the organic layer at 0.5 and 2 km were much higher than those obtained without Cu and Ni. This strongly supports the assumption that their exclusion results in an underestimate of CEC. A decrease in CEC_{eff} has been reported close to a Cu-Ni smelter at Monchegorsk, NW Russia (Lukina & Nikonov 1995) and at Harjavalta (Fritze et al. 1996), but in their studies CEC was calculated using the summation method without including Cu or Ni.

The use of EDTA in the $BaCl_2$ extract for determining CEC_{eff} was also investigated in this study. Methods for determining plant-available Cu in agricultural soils include the use of EDTA (Lundblad et al. 1949) in order to ensure that the Cu released from exchange sites and complexes remains in solution. In organic-rich forest soils, however, there is a strong likelihood that EDTA will also extract Cu from organic complexes, especially at Cu-polluted sites. The Cu in these complexes is not occupying cation exchange sites. In this study the yield of EDTA-extractable Cu from the organic layer was almost double that obtained with $BaCl_2$ alone. It would thus appear that the use of $BaCl_2$ + EDTA for determining CEC_{eff} in Cu-polluted soils strongly overestimates CEC, and is therefore not a recommendable practice. However, $BaCl_2$ + EDTA was used in this study to determine the effects of the liming and fertiliser treatments on the bio-availability of Cu and other metals.

4.4 Effects of heavy-metal and sulphur deposition on soil acidity and base saturation

Rather contradictory results have been presented about the effects of SO_2 and other emissions from Cu-Ni and Cu smelters on soil acidity. Løbersli and Steinnes (1988) reported only a slight decrease in the pH of the organic layer close to a Cu smelter at Sulitjelma in northern Norway. Derome et al. (1998) found no changes near to the Cu-Ni smelters at Monchegorsk and at Nikel, NW Russia, nor Fritze et al. (1989) close to the Harjavalta smelter. In contrast, a decrease in pH has been reported in the organic layer close to a metal refinery in NW England (Watmough & Dickinson 1995), as well as extremely low pH values in the Sudbury smelting region, Canada (Hutchinson & Whitby 1977). A strong decrease in base saturation (BS) was also observed in the organic layer at the sites at Sudbury, at Monchegorsk, at Sulitjelma, and at Harjavalta. BS is a widely used parameter for depicting soil acidification, and there is normally highly significant correlation between pH and BS in the organic and uppermost mineral soil layers (Hallbäcken & Popovic 1985, Derome et al. 1986). A decrease in BS along a gradient running from a point source emitting SO_2 is normally taken as a clear indicator of soil acidification caused by sulphur emissions (e.g. Løbersli & Steinnes 1988). At Harjavalta, however, the low BS values in the organic and 0-5 cm mineral soil layers were not associated with a reduction in pH or exchangeable acidity, nor with an increase in exchangeable aluminium. Løbersli and Steinnes (1988) suggest that the deposition of H^+ and heavy metals has displaced base cations from the organic layer. The only change in acidity parameters at Harjavalta occurred in the 5-10 and 10-20 cm layers. As SO_2 emissions from the smelter fell drastically at the end of the 1980's, it would appear that the loss of base cations from the organic layer is due to displacment by Cu and Ni rather than to SO_2-induced acidification. Furthermore, there are strong signs that Ni and Cu have also displaced exchangeable Al from the organic layer, and that exchangeable H^+ and exchangeable Al^{3+} in the 0-5 cm layer have been displaced by the accumulation of base cations and heavy metals in the same layer. This would explain the increase in exchangeable acidity and exchangeable Al in the deeper 10-20 cm layer.

There are a number of possible explanations for the absence of clear signs of soil acidification in the experiments at 0.5 and 2 km, despite the considerable SO_2 emissions during the 1940's to 1980's. The experiments are located rather close to the emission point source, and there is considerable uncertainty about how rapidly SO_2 emissions are converted in the atmosphere into H_2SO_4 (Joffre et al. 1990). Water is required for the reaction, but the climate in the region is relatively dry; the long-term (1973-1988) mean annual precipitation is ca. 600 mm (Järvinen & Vänni 1990), of which about one third falls as snow. According to the wind direction data from a weather station located about 30 km to the SW, the emission plume from the smelter was directed towards the experiment at 0.5 km about 10% of the time during 1993-1996. Sulphuric acid will of course be formed from SO_2 on the surface of the needles and leaves of the tree stand and forest floor vegetation (Fowler 1980), especially during wet periods. According to the age of the tree stands, however, the previous tree stands at the two sites were clear cut in 1945 and 1940, respectively. The naturally regenerated tree stand at 0.5 km has grown very slowly (mean height of 14.8 m at 47 years), and the forest floor vegetation has been severely damaged and in many places is completely absent. The interception of SO_2 and formation of H_2SO_4 on the needle surfaces during the period when SO_2 emissions were at their highest have thus probably been considerably lower than they would have been in a normally growing pine stand with a healthy forest floor vegetation.

4.5 The flux of Cu, Ni, Zn, SO_4 and macronutrients in the polluted Scots pine ecosystems

Water and element fluxes in forest soil can be measured using zero-tension lysimeters, or estimated using models based on suction-cup lysimeter data (Beier et al. 1988). Zero-tension lysimeters were chosen for this study because the soil at all three sites was extremely homogeneous (fine/coarse sand), and almost completely stone-free. The lysimeter type and installation technique have been successfully employed in a number of studies carried out earlier in Finland on sites of this type (Lindroos et al. 1995). However, the reliability of the results is somewhat reduced by the fact that a variable number of replications were used (4 replications at 5 cm, 12 at 20 cm, and 4 at 40 cm). This problem is somewhat reduced by the fact that the aim of the study was to compare the water and element fluxes in relative terms at different distances from the smelter.

The movement of water is the driving force behind the flux of elements between the different compartments of forest ecosystems. The water flux on the plot at 0.5 km appears to have been seriously disturbed by the damage to the ecosystem caused by emissions from the smelter. Canopy interception has been greatly reduced as a result of the serious decline in tree growth and the high degree of defoliation (Mälkönen et al. 1999). Furthermore, the almost total destruction of the forest floor vegetation (Salemaa & Vanha-Majamaa 1993) and the diminished needle biomass in the tree canopy will have strongly reduced the loss of water from the soil via evapo-transpiration. The low rate of decomposition activity (Fritze et al. 1989) and subsequent accumulation of undecomposed plant litter will have also reduced the water-holding capacity of the organic layer. A high proportion of the precipitation inside the stand passed down to a depth of 5 cm, which presumably means that there will have been less chemical and microbiological interactions between the soil solution and the soil.

The water flux at the plots at 4 and 8 km was in good agreement with water fluxes reported for corresponding sites in background areas in northern Finland (Derome & Väre 1995). The relatively low amount of precipitation reaching a depth of 5, 20 and 40 cm at 4 and 8 km well illustrates the hydrological conditions prevailing in Finnish mineral soils: the ground is frozen for a long period, surface runoff can be relatively high, and the precipitation during summer relatively low. The low interception of rainfall in the stand at 8 km compared to that at 4 km is rather surprising, because the needle mass of the stand at 8 km is much greater than at 4 km (Mälkönen et al. 1999). However, only relatively weak relationships have been reported between rainfall interception and stand parameters in coniferous stands in Fennoscandia (Strand 1998).

The high flux of dissolved organic carbon (DOC) passing down to a depth of 5 cm at 0.5 km suggests that morphological changes have taken place in the organic layer. The polysaccharides excreted by soil micro-organisms play an important role in binding humic substances into aggregates, thus reducing their solubility (Stevenson 1982a). In the dry, relatively toxic conditions in the organic layer close to the smelter, the formation of aggregates may be considerably reduced, thereby increasing the dissolution of humic substances. The greater flux of DOC in the soil at 0.5 km could also be explained by the leaching of low molecular-weight compounds from the relatively undecomposed litter that has accumulated on the forest floor. The presence of high concentrations of heavy metals in the organic layer may have also increased the amount of DOC in the soil olution as a result of the formation of soluble chelates between metals and low molecular-weight organic compounds (Schnitzer & Khan 1972). The proportion of weak acids in the DOC collected at 0.5 km differed somewhat from that in the DOC at 4 and 8 km; the correlation between DOC and hydrogen ions in soil solution at 5 cm in the heavily polluted stand was considerably weaker than that at 20 and 40 cm. In podsolic soils, organic matter normally plays an important role in regulating soil solution acidity in the surface layers. Lindroos et al. (1995) reported strong correlation between DOC concentrations and pH in soil solution at 5 cm depth on similar types of site in Northern Finland, but no correlation at 20 and 40 cm. In this study, the correlations for all three depths at 4 and 8 km were very similar to those reported by Lindroos et al. (1995). The formation of complexes between heavy metals and dissociated weak organic acids would explain the abnormally low acidic reaction in soil solution at 5 cm at 0.5 km.

The increase in the fluxes of Cu, Ni, Zn, SO_4-S, Ca, Mg, K and PO_4-P in throughfall at 0.5 km compared to bulk precipitation was much greater than that at 4 or 8 km. There are several possible reasons for this; the washing off of dry deposition accumulating in the tree crowns (Fowler 1980), exchange reactions between precipitation and the foliage (Ulrich 1983, Parker 1983), and the accumulation of dust from the forest floor in the crowns and rainfall collectors. The low needle mass of the stand at 0.5 km (Mälkönen et al. 1999) means that the surface area of the foliage capable of intercepting dry deposition is considerably reduced. However, the amounts of heavy metals intercepted by the canopy were extremely high (Nieminen et al. 1999). Exchange between precipitation and the needles accounts for at least a part of the increase in Ca and Mg. Foliar leaching is even more important in the case of K, because there are no signs of smelter-derived deposition of K at this site (Nieminen et al. 1999). The relatively high flux of PO_4-P in throughfall suggests that part of the net increase in Cu, Ni, Zn and SO_4-S is derived from dust from the forest floor. Phosphate is not normally leached from the tree crowns (Helmisaari & Mälkönen 1989), and at a distance of 4 and 8 km there was a net reduction in PO_4-P in throughfall. Furthermore, foliar P concentrations in the tree stand at 0.5 km were similar to those at 4 and 8 km.

The fluxes of Cu, Ni, Zn, Ca, Mg and K down through the uppermost 0-5 cm soil layer at the plot at 0.5 km rather well reflected, apart from those for K and Cu, the affinity of these metals for cation exchange sites. The lyotropic series depicting the preferential binding of these metals to cation exchangers is $K^+ < Mg^{2+} = Zn^{2+} < Cu^{2+} < Ni^{2+} < Ca^{2+}$ (Bohn et al. 1985). The decrease in K in the 0-5 cm layer was much greater than would be expected on the basis of its affinity for cation exchange sites. However, the cycling of K within forest ecosystems is known to be very efficient: K is strongly leached from the crown canopies, but effectively recovered in the surface layers (Helmisaari & Mälkönen 1989). This was fully supported by the results for the plant-available K concentrations in the mineral soil. At 0.5 km, the concentrations in the 0-5 cm mineral soil layer were appreciable, but extremely low at 10-20 cm despite the high input of K into the soil in throughfall. The actual mechanism involved is not known, but it appears to be relatively unaffected by the toxic effects of heavy metals on the roots and mycorrhizas (Gobl & Mutsch 1985), because needle K concentrations were relatively high at this site.

Copper was more strongly retained in the 0-5 cm layer than Ni or Zn. However, Cu is known to form stable complexes with organic matter (Baker & Senft 1995) and much of the Cu will therefore be bound strongly to the organic matter rather than occupying cation exchange sites. The stability of the complexes formed between heavy metals and organic matter follow the order: Cu > Fe = Al > Mn = Co > Zn (Alloway 1995). The higher mobility of Ni in the organic layer compared to Cu was supported by the Cu/Ni ratios in the organic layer and uppermost mineral soil layers in the experiments along the transect. There was a clear net loss of Zn from the 40 cm-thick soil layer at 0.5 km, i.e. the Zn output in the leachate at 40 cm depth was greater than the Zn input in either bulk deposition or stand throughfall. For Cu and Ni, on the other hand, there was a net gain.

The high fluxes of Ca, K and especially Mg down to a depth of 5 cm at 0.5 km compared to the fluxes at 4 and 8 km indicated strong leaching of these base cations from the organic layer. This was supported by the low exchangeable Ca, Mg and K concentrations in the organic layer in the experiment at 0.5 km.

The fluxes of NH_4-N and NO_3-N in throughfall were considerable at 0.5 km. There is normally a net decrease in both NH_4-N and NO_3-N in throughfall (Hyvärinen 1990), as was the case at 4 and 8 km. In summer 1995, however, elevated pH values and relatively high NH_4-N concentrations were observed in the precipitation samples collected at 0.5 km, and this has continued sporadically up until the end of 1998. This was due to ammonia emissions from the smelter. As there was no clear increase in the amounts of NO_3-N in bulk precipitation, it would appear that there has been some nitrification either on the needle surfaces in the tree crowns or, more likely, in the precipitation collectors. Nitrification is promoted by low acidity and high NH_4-N concentrations. Despite the low microbial activity in the surface soil and poor stand growth at 0.5 km, the relatively large flux of NH_4-N and NO_3-N passing into the soil in throughfall were efficiently taken up from the soil water.

4.6 Effects of limestone on soil acidity and elevated concentrations of Cu, Ni and Zn in the soil

Dolomitic limestone was applied in these experiments in order to alleviate possible soil acidification caused by SO_2 emissions from the smelter (as expected on the basis of e.g. Hutchinson & Whitby 1977, Løbersli & Steinnes 1988, Watmough & Dickinson 1995), to counteract the reduction in nutrient mineralisation caused by depressed microbiological activity in the soil (Fritze et al. 1989), to reduce the toxic levels of heavy metals in a plant-available form in the soil, and to provide a source of Ca and Mg for the tree stands with a disturbed nutrient status (Mälkönen et al. 1999).

The amounts of limestone used in the three treatments varied considerably: 200 kg/ha in the correction fertilisation, 1000 to 1500 kg/ha in the stand-specific fertilisation (not applied at 8 km) and 2000 kg/ha in the liming treatment. The results obtained at 4 and 8 km with the liming treatments were similar to those reported for liming experiments on forest soil in Fennoscandia and Central Europe (Derome et al. 1986, Nihlgård et al. 1988, Kreutzer 1995): a strong increase in pH and base saturation, and a corresponding strong decrease in exchangeable acidity and exchangeable Al concentrations. In contrast, liming had only a relatively small effect on acidity parameters in the organic layer at 0.5 km, and at 2 km the effects were restricted to an increase in BS and a decrease in exchangeable acidity. The average increase in the pH of the organic layer following application of 2000 kg limestone/ha (LT) was much smaller than the corresponding increase given by 1500 kg/ha (SSF). The pH values for the organic layer on the three replicate plots at 0.5 km 4.5 years after the treatments were 3.73, 3.48 and 3.49 (average 3.57) for the control, 3.91, 3.77 and 3.65 (average 3.87) for the LT treatment, but 4.41, 4.42 and 3.91 (average 4.25) for the SSF treatment. As the limestone was spread by hand on the plots and there were a total of 20 systematically selected sampling points on each plot, it can be assumed that these results are representative of the actual effects of the limestone applications on the acidity of the organic layer.

The dissolution of limestone in forest soils is a slow process that depends on the particle size of the limestone, the amount of precipitation, and the acidity of the precipitation if the limestone is spread on the soil surface (Kreutzer 1995). All these factors will have been approximately the same for the plots given the LT and SSF treatments at 0.5 km. Furthermore, the limestone appears to have been dissolved to the same extent because both treatments brought about a similar increase in the concentrations of available Ca and Mg and the BS values. The conditions in the experiment at 0.5 km differ considerably from those at 4 and 8 km: at 0.5 km the flux of water down the soil profile was considerably greater and there were very high concentrations of heavy metals, especially Fe, in the organic layer. These two features could have a strong effect on the conflicting neutralising behaviour of the limestone at 0.5 km. When Mg-rich limestone dissolves it releases Ca^{2+}, Mg^{2+}, HCO_3^- and OH^- ions into the soil solution. The total Fe concentrations in the organic layer were extremely high, up to 2%, the Fe presumably being in the form of $Fe_2(SO_4)_3$. In the presence of HCO_3^- and OH^- ions, the Fe^{3+} will be precipitated as $Fe(OH)_3$, thus consuming a considerable proportion of the neutralising effect of the limestone. In waterway liming experiments carried out in Finland and Sweden, there have been problems with the inactivation of limestone gravel placed in stream beds in order to neutralise the stream water running into lakes and other waterways from forested areas (Vähänäkki 1994). The limestone rapidly becomes covered in a film of precipitated iron that prevents dissolution of the limestone and inactivates its neutralising effect. In addition to Fe, there were also considerable amounts of other heavy metals (e.g. Cu, Ni, Zn) in the organic layer, and they will correspondingly react with the HCO_3^- and OH^- ions and be precipitated. Thus, in the presence of large amounts of Fe (and other heavy metals), we can expect that the dissolution and neutralisation of limestone will result in the release of Ca and Mg, but have little acidity reducing effect on the surrounding organic layer. This would explain the situation in the LT treatment, but not in the SSF treatment.

The water flux was measured on one of the three replicate plots in each treatment at 0.5 km. The amount of water passing down to 20 cm during the 5-year study on the SSF plot was relatively similar to that on the untreated plot, but on the LT plot the amount of water was 25% times higher than that on the SSF plot. This suggests that moisture has been retained less effectively in the organic layer on the LT plot than on the SSF plot, and there will have been less interaction between the limestone and soil solution, and between limestone and the acidic organic matter. It is not possible to determine the effect of the nitrogen fertilisers (ammonium nitrate and methylene urea) in the SSF treatment on the dissolution of limestone on the basis of the analyses carried out in this study, but both ammonium nitrate and methylene urea are deliquescent compounds, i.e. they absorb water from the air, and they may have slightly increased the moisture content of the organic layer for a short period after applicaton.

Although liming has considerably decreased the concentrations of Cu and Ni in the soil solution at 20 cm at 0.5 km especially, it only marginally decreased the free and exchangeable Cu concentrations in the organic layer, and had almost no effect on the exchangeable Ni concentrations. The main reason for this appears to be the relatively weak effect of liming on soil acidity at this site. However, liming has also had only negligible effects on Cu and Ni concentrations in the organic layer at greater distances from the smelter, even though at these sites liming had a relatively strong effect on the pH of the organic layer. The total, exchangeable and free Cu and Ni concentrations in the organic layer at the site at 0.5 km were extremely high, and so even a slight increase in the concentrations of toxic forms of Cu and Ni is likely to be important from the point of view of the soil micro-organisms and root development.

4.7 Alleviation of Ca and Mg deficiencies in the organic layer

Correction and stand-specific fertilisers were applied in this study in order to correct the nutrient imbalances in the tree stand indicated by the needle and soil analyses carried out prior to establishment of the experiments. The stand located 0. 5 km from the smelter had depressed needle Ca and Mg concentrations. In Finland, trees do not normally suffer from Ca and Mg deficiencies, and long-term fertilisation experiments with Ca and Mg have not given positive growth increases. However, low needle Mg concentrations have been reported in a pine stand on a similar type of site close to the Cu-Ni smelter at Monchegorsk (Raitio1995), and a growth response has been obtained with dolomitic limestone in a pine stand growing on an infertile dry site, with known Ca and Mg deficiencies, in western Finland (Raitio 1990). Although none of the stands along the gradient were suffering from a serious nitrogen deficiency, nitrogen is normally the growth-limiting factor in tree stands in Finland.

All the treatments applied in this study (apart from the stand-specific fertiliser at 8 km) contained varying amounts of Ca and Mg, and the correction fertiliser treatment also contained K. Liming increased Ca and Mg availability in the organic layer at 0.5 km, and even more strongly at greater distances from the smelter. As there were clear shortages of these two important macro-nutrients in the organic layer, it would appear that this increase in plant-available Ca and Mg has contributed to the partial recovery of microbial activity (Fritze et al. 1996) and stand growth on the site at 0.5 km (Mälkönen et al. 1998). Apart from a steep increase in the Ca and Mg concentrations in the soil solution during the first year after application, none of the treatments had a very strong long-lasting effect on Ca or Mg in the soil solution.

The correction fertiliser had no effects on available Ca and Mg concentrations at 0.5 km, nor on the K concentrations at any of the distances. In this respect, the correction fertiliser had only minor short-term effects on the macro-nutrient status of the organic layer, although it has rather strongly increased Ca, Mg and K concentrations in the soil solution at 0.5 km. This is not a surprising result, because most of the Ca, Mg and K in the correction fertiliser was in the form of slow-release components, and only a relatively small proportion as water-soluble salts.

All the treatments increased the PO_4-P concentration in the soil solution at 0.5 km, despite the fact that only the correction fertiliser contained P. The organic layer at this site has elevated total P concentrations, and it is highly likely that both liming and the stand-specific fertiliser treatment have had a promoting effect on P mineralisation in the organic layer. However, as the needle P concentrations were relatively normal at all distances from the smelter, this increase in P availability is not likely to be of decisive importance from the point of view of the tree stand.

The large peak in the NH_4-N and NO_3-N concentrations produced by the stand-specific fertiliser in the soil solution at 0.5 and 8 km in the same year as application, was clearly derived from the fast-release ammonium nitrate component in the fertiliser. The slow-release nitrogen fertiliser, methylene urea, had no effect on the NH_4-N and NO_3-N concentrations during the last 4 years of the study. According to Martikainen et al. (1989), methylene urea produces elevated soil NH_4-N concentrations in the laboratory for at least two years, without the formation of NO_3-N, and the effect can persist in the soil for 7 - 14 years after application. The fact that the NH_4-N concentrations in the soil solution did not increase during the 2 to 5-year period after application suggests that the NH_4-N released from the methylene urea was efficiently utilised by the soil microbes and vegetation. The liming treatment resulted in slightly elevated NH_4-N and NO_3-N concentrations at both sites. This suggests that the increased Mg and Ca concentrations and elevated pH values in the organic layer caused by liming has had a short-term stimulating effect on both N mineralisation and nitrification (Tamm & Petersson 1969).

5 CONCLUSIONS

The main conclusions to be drawn from the results of this study are as follows:

1) The strongly increasing gradient in the accumulation of heavy metals, Mg, P and S in the organic layer with decreasing distance to the smelter appears to be directly or indirectly a result of heavy metal and sulphur emissions from the smelter. The effects of emissions extend up to a distance of at least 8 km to the SE of the smelter complex.
2) The properties of the forest soil in the immediate vicinity of the Cu-Ni smelter have been drastically altered by emissions during the past 50 years. The accumulation of Cu and Ni in the soil has resulted in a severe deficit of plant-available Ca, Mg and K in the organic layer caused by partial inhibition of the mineralisation of these nutrients from litterfall and the displacement of these base cations from exchange sites.
3) The use of the summation method for determining CEC in heavy-metal polluted soils is not recommended unless other major cations present in such soils are included in the calculations. Neither is CEC determination using a neutral salt solution containing EDTA to solubilise exchangeable/complexed Cu recommended because a high proportion of this Cu is presumably not bound on cation exchange sites.
4) Sulphur deposition does not appear to have affected soil acidity. No signs of soil acidification were found in the organic layer or uppermost mineral soil layers. However, there was an increase in exchangeable acidity and Al deeper in the mineral soil, presumably due to their displacement by heavy metals from the overlying organic and mineral soil layers. The loss in base saturation in the organic and uppermost mineral soil layers close to the smelter was attributed to displacement by Cu and Ni, and not to the effects of acidic deposition.
5) The water flux on the plot closest to the smelter has been drastically altered as a result of damage to the tree stand and

ground vegetation. The fluxes of Zn, Ni and Cu from the organic layer down into the mineral soil varied owing to differences in their ability to form complexes with organic matter and their affinity for cation exchange sites. This was reflected in the distribution of heavy metals down the soil profile. There was a clear net loss of Zn from the 40 cm-thick soil layer, but a net gain of Cu and Ni. The fluxes of Cu, Ni and Zn at 0.5 km were extremely large compared to those at 4 and 8 km.

6) Apart from an initial increase in the year of application, liming at all three doses strongly decreased the Cu, Ni and Zn concentrations in the soil solution at the severely contaminated site for the following three years at least. The largest liming dose used in this study, 2000 kg ha^{-1}, thus did not increase the risk of heavy metals being displaced and carried down into the ground water. Liming had only a relatively small reducing effect on free and exchangeable Cu and Ni concentrations in the organic layer at 0.5 km. The lack of a pH increase following liming may be due to the precipitation of Fe, present in very high concentrations close to the smelter, as $Fe(OH)_3$, resulting in the loss of neutralising bicarbonate and hydroxyl ions, but the release of Ca and Mg. Liming strongly increased Ca and Mg availability in the soil.

7) The fast-release components in the correction fertiliser and stand-specific fertiliser increased the supply of macro-nutrients to the tree stand already during the year of application. The dissolution of the slow-release components in the correction fertiliser also ensured an increased supply of Ca, Mg and K throughout the course of the study at the site 8 km from the smelter, but not at 0.5 km.

This study has provided rather comprehensive information about the effects of heavy metal deposition on soil properties close to a point emission source, and has investigated means of alleviating the harmful effects of heavy metal deposition on soil fertility. Heavy-metal contamination of the forest soil is an extremely serious problem, and every effort must be made to ensure that the metals remain in an immobilised form in the surface layers of the soil. Liming with Mg-rich limestone appears to be the most feasible means of achieving this goal. However, liming alone will not be sufficient to return the water flux in the soil back to its original condition close to the smelter. The major disturbances in the moisture conditions and water flux in the organic layer constitute a considerable risk of heavy metals passing down into the ground water. The addition of partly decomposed organic mulches to the forest floor would increase the water-retaining capacity of the soil, stimulate microbial activity and macro-nutrient mobilisation, and reduce erosion and the dust problem. This would also considerably accelerate the re-establishment of forest-floor vegetation, contribute to a recovery in the tree stand, and promote the binding of heavy metals in the soil. Because the situation is already so serious in the vicinity of the smelter, efforts should be made to further reduce emissions.

Future research work at these sites should concentrate on fractionation of the forms and species of heavy metals (especially Fe) in the soil, in order to gain a deeper understanding of the effects of ameliorating agents on heavy metal availability. Samples should also be taken down to the ground water table in order to determine the distribution of heavy metals, especially zinc, in the overburden, and thus assess the risk of heavy metals being carried into the groundwater. The effects of emissions of gaseous ammonia from the smelter on the tree stand and the possible leaching of nitrate also require further study.

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CORRECTIONS

- **Paper I**, p.1132, para 2, line 1, and p. 1133, Table 1. Distances are 0.5, 2, 4 and 8 km, and not 0.5, 3, 4 and 8 km.
- **Paper I,** page 1133, Table 1. The units in the table are mg/kg dry mass, and not mg/100 g dry mass.
- **Paper II,** page 226, column 1, line 35. the number of plots in the experiment at 2 km was 12, and not 16.
- **Paper II,** page 226, column 1, line 45. the mineral soil layers sampled were 0-5, 5-10 and 10-20 cm.
- **Paper II,** p. 226, column 2, line 7. The correct extraction ratio is: 7.5 g sample 150 ml^{-1} extractant.
- **Paper II,** page 226, column 2, line 29. In the hydrolysis reaction the correct form for copper hydroxide should be $CuOH^{+}$, and not $CuOH^{2}$.
- **Paper III,** page 221, Table 2. The correct units for the needle element concentrations are mg kg^{-1} for Cu, Ni, Zn and S, g kg^{-1} Ca, Mg, K, N and P.
- **Paper III,** page 223, Fig. 4d. The scale of SO_4-S values on the y axis should be 0, 0.5, 1.0, 1.5, 2.0, 2.5 g m^{-}

PAPER I

Reprinted from Chemosphere, Vol. 36(4-5), Derome, J. & Lindroos, A-J. Copper and nickel mobility in podzolic forest soils subjected to heavy metal and sulphur deposition in western Finland, 1131-1136, Copyright 1998, with permission from Elsevier Science.

Pergamon

Chemosphere, Vol. 36, No. 4-5, pp. 1131-1136, 1998
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0045-6535/98 $19.00+0.00

PII: S0045-6535(97)10184-9

COPPER AND NICKEL MOBILITY IN PODZOLIC FOREST SOILS SUBJECTED TO HEAVY METAL AND SULPHUR DEPOSITION IN WESTERN FINLAND

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Received in Italy 14-19 September 1996; accepted 1 February 1997

ABSTRACT

The distribution of copper and nickel down the soil profile has been investigated at 4 plots along a heavy metal and sulphur gradient extending for a distance of up to 8 km from a copper smelter in Western Finland. Emissions from the smelter have earlier been at a relatively high level, but were considerably reduced at the beginning of the 1990's prior to the start of the experiment. Soil samples were taken in 1991, and soil water quality has been monitored using zero-tension lysimeters (5, 20 and 40 cm depth) during the growing season in 1992-1994. The organic layer and mineral soil on the plot nearest to the smelter contains considerable amounts of Cu and Ni. The Cu/Ni ratio in the organic layer was much higher than that in the underlying mineral soil, indicating that Cu is more strongly adsorbed in the organic layer than Ni. Copper concentrations in percolation water showed a peak at 20 cm depth, while for Ni the concentrations at 40 cm were higher than those at 5 cm. The lower Cu and Ni concentrations at 5 cm depth could be signs of a gradual detoxification of the surface soil, i.e. the gradual leaching of the mobile Cu and Ni components down to greater depths. ©1998 Elsevier Science Ltd

1. INTRODUCTION

During the past two decades a large number of studies have been carried out on the effects of heavy metal deposition in the vicinity of copper and nickel smelters in the boreal and tundra zones [1, 2, 3, 4]. The emissions from the smelters e.g. at Sudbury, Canada, and at Harjavalta, Finland, have already been considerably reduced [2], and we are now in a position to make preliminary assessments of the possibilities of alleviating and even rectifying the adverse effects of heavy metals on forest and tundra ecosystems.

The results presented in this study are part of a correction fertilization project currently being carried out close to a Cu-Ni smelter on the west coast of Finland. The project is testing a range of fast- and slow-acting fertilizers with the aim of improving tree vitality and the nutrient status of the tree stand and soil. The project was started in 1991, and the results presented here are restricted to the soil samples taken before the fertilization treatments were applied. The percolation water samples have been collected from the control plots. The aim of this report is to assess the severity of Cu and Ni contamination of the surface soil and soil water, and to determine whether changes can already be detected following the drastic reductions in emissions of SO_2 and heavy metals at the end of the 1980's.

2. MATERIAL AND METHODS

The smelter at Harjavalta, western Finland, started processing copper in 1945 and nickel in 1960. Gaseous emissions from the smelter are primarily SO_2, and the particulate emissions mainly consist of Cu and Ni, as well as smaller amounts of Zn, Pb, Cd, As and Hg. A sulphuric acid plant next to the smelter utilizes a high proportion of the SO_2 produced in the smelter. In recent years the emissions of both SO_2 and heavy metals have been drastically reduced by changes in process technology, and the installation of new filters and a taller smoke stack. In 1994 annual SO_2 emissions totalled 5 000 t, Cu 40 t. and Ni 6 t [2].

A series of four monitoring plots were established in 1991 in Scots pine stands at distances of 0.5, 3, 4 and 8 km along a gradient running due east of the smelter. The soil on all the plots has developed from sorted coarse sand and is classified as orthic podzol, and the forest site type is Calluna (dryish site, relatively infertile). Soil samples were taken at 20 systematically located points from the organic layer and at 0-5, 5-10, 10-20 and 20-40 cm depth in the mineral soil in 1991. Composite samples were prepared for each layer. After air-drying and determination of moisture content (105°C, 24 h), the exchangeable Cu and Ni contents were determined by extraction with 0.1 M $BaCl_2$ + EDTA (7.5 g humus or 15 g mineral soil/150 ml), followed by analysis by ICP/AES. Zero-tension lysimeters were installed at depths of 5 cm (4 repl.), 20 cm (20 repl.) and 40 cm (4 repl.), measured from the ground surface, on three of the plots (0.5, 4 and 8 km). Samples were taken monthly during the snowfree period (ca. May - October). The samples were filtered through membrane filters (0.45 μm), preserved with nitric acid, and Cu and Ni analysed by ICP/AES.

Owing to the problems involved in comparing gravimetric results for the organic and mineral soil layers, the Cu/Ni ratio was calculated for each layer on all four plots in order to estimate the distribution of Cu and Ni down the soil profile. During the period 1985-90 the Cu/Ni ratio in emissions from the smelter ranged from 1.5 to 2.6 (av. 2.3), but in 1991 it rose to 6.0 [1].

3. RESULTS AND DISCUSSION

There was a strongly increasing trend in both Ni and Cu concentrations in most of the soil layers on moving towards the smelter (Table 1). There was also a clear trend for decreasing Ni and Cu contents with increasing depth in the mineral soil. According to these results, the deposition and accumulation of Cu and Ni in the soil extends to at least 4 km from the smelter. At the site closest to the smelter, the Cu/Ni ratio in the organic layer was much higher than that in the mineral soil layers, the difference increasing with soil depth. This trend indicates that Cu has been more strongly retained than Ni in the organic layer, as well as in the uppermost mineral soil layers. Copper is known to form rather stable complexes with organic matter, and in this respect is expected to be less mobile than Ni in the soil [5]. The ratio also decreased in both the organic layer and 0-5 cm mineral soil layer with increasing distance from the smelter. This suggests that Ni emissions are transported over longer distances than Cu emissions, i.e. the Cu deposition gradient is shorter and steeper than that of Ni. Hutchinson & Whitby [6] have also reported differences in the transportation distances of Cu and Ni emissions, which they attribute to differences in particulate size. If we accept the conclusion that Ni is lost from the organic layer at a faster rate than Cu, then the amount of Ni deposition falling on the soil surface has been underestimated in our study.

Table 1. Copper and nickel contents (mg/100 g dry mass) in the organic and mineral soil layers on sample plots located at different distances from the emission source.

Distance from smelter		Organic layer	Mineral soil 0-5 cm	5-10 cm	10-20 cm	20-40 cm
0.5 km	Cu	2304	259	76.8	46.9	29.0
	Ni	118	17.3	8.02	4.52	2.62
	Cu/Ni	19.5	15.0	9.6	10.4	11.2
3 km	Cu	1079	29.1	4.65	2.99	2.42
	Ni	161	5.07	1.29	bdl	bdl
	Cu/Ni	6.7	5.7	3.6	-	-
4 km	Cu	525	4.3	1.09	0.68	0.74
	Ni	107	1.01	bdl	bdl	bdl
	Cu/Ni	4.9	4.3	-	-	-
8 km	Cu	125	1.32	0.28	bdl	0.03
	Ni	32.2	bdl	bdl	bdl	bdl
	Cu/Ni	3.9	-	-		

bdl = below the analytical detection limit, the Cu/Ni ratio therefore not determined.

The results for Cu and Ni concentrations in percolation water at distances of 0.5, 4 and 8 km from the smelter are in good overall agreement with the soil results (Fig. 1). However, the distribution down the soil profile was somewhat different: at 0.5 km distance Cu concentrations in percolation water were highest at 20 cm depth compared to 5 and 40 cm, while Ni concentrations were higher at both 20 and 40 cm depth. In contrast, further away from the smelter (4 and 8 km) Cu and Ni concentrations were highest at 5 cm depth. Although the percolation water results cover only a three-year period, the overall trend in both Cu and Ni

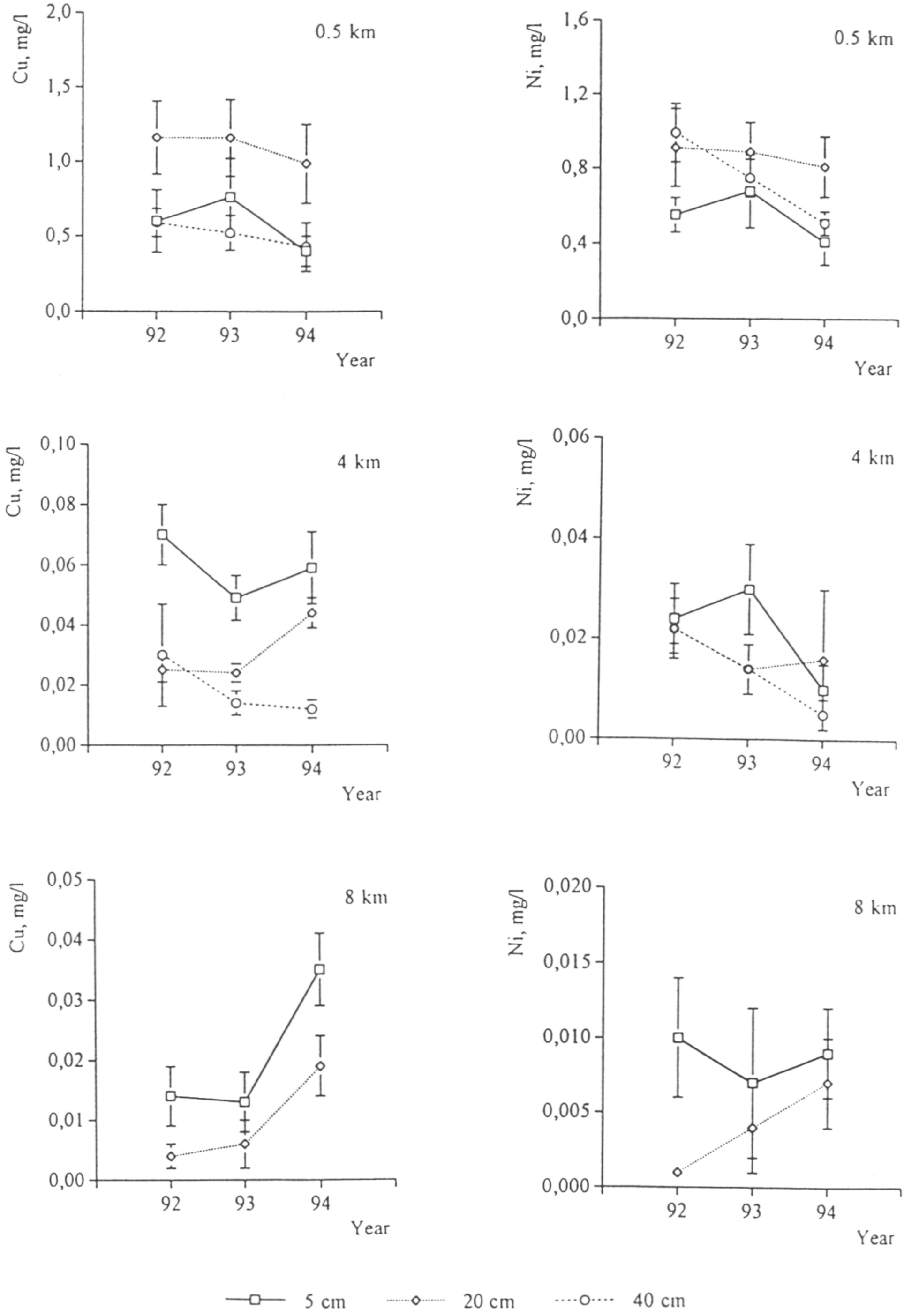

Fig. 1. Copper and nickel concentrations in percolation water at depths of 5, 20 and 40 cm at a distance of 0.5, 4 and 8 km from the Cu-Ni smelter. The bars indicate the standard errors of the means.

concentrations indicates that a slight decrease in Cu and Ni concentrations is taking place over time at the closest plot (0.5 km), while at 8 km the Cu and Ni concentrations in percolation water are gradually increasing. The gradual decrease in the concentrations of these two metals in percolation water during 1992-94 at the two closest plots may reflect the decrease in Cu and Ni at the beginning of the 1990's [2].

Although the pool of accumulated Cu and Ni in the organic layer is considerable, there is reason to believe that accumulated Cu especially is not in a very labile (i.e. easily released) form. This is supported by the fact that the yield of exchangeable Cu from the soil samples was increased markedly (results not shown) by the use of EDTA + $BaCl_2$ compared to $BaCl_2$ alone. The Cu/Ni ratio in percolation water was much lower than that in the soil samples: ca. 1 on the average for 5, 20 and 40 cm depths at 0.5 km distance compared to ca. 13 on the average for the organic + 0 to 40 cm mineral soil layers (Table 2). In contrast to the situation in the soil samples, there was little variation in the Cu/Ni ratio of percolation water down the soil profile at the plot closest to the smelter. At 4 km, however, the pattern was similar to that for the soil, i.e. less Cu with respect to Ni. The concentrations in percolation water reflect the end result of interactions between rainwater as it percolates down through the soil. The results for 8 km should be treated with caution owing to the extremely low Cu and Ni concentrations.

Table 2. Copper and nickel contents (mg/l) in percolation water collected using zero-tension lysimeters at 5, 20 and 40 cm depth on sample plots located at different distances from the emission source.

	Distance from smelter								
	0.5 km			4km			8 km		
Depth	Cu	Ni	Cu/Ni	Cu	Ni	Cu/Ni	Cu	Ni	Cu/Ni
5 cm	0.587	0.547	1.1	0.060	0.021	2.9	0.021	0.009	2.3
20 cm	1.102	0.870	1.3	0.031	0.017	1.8	0.010	0.004	2.5
40 cm	0.513	0.750	0.7	0.019	0.014	1.4	ns	ns	-

ns = no samples obtained from this depth.

To summarise, Cu and Ni emissions were reflected in the organic layer at a distance of up to 4 km at least from the smelter. The Cu and Ni contents in the mineral soil layers followed a similar pattern for the organic layer, except that Ni contents in the 10 - 20 cm layer were below the detection limit already at a distance of only 3 km. There was strong evidence of Cu accumulation in the organic layer, Ni being less readily bound and more uniformly distributed down the soil profile at 0.5 km from the smelter. The highest

Cu and Ni concentrations in percolation water at the plot closest to the smelter occurred at a depth of 20 cm, and Cu and Ni concentrations showed a slightly decreasing trend at all depths on this plot during the period 1992-94. This may be due to the gradual depletion of mobile forms of Cu and Ni from the humus layer following the drastic reduction in Cu and Ni emissions at the beginning of the 1990's.

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PAPER II

Reprinted from Environmental Pollution 99, Derome, J. & Lindroos, A-J. Effects of heavy metal contamination on macronutrient availability and acidification parameters in forest soil in the vicinity of the Harjavalta Cu-Ni smelter, SW Finland, 225-232, Copyright 1998, with permission from Elsevier Science.

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Environmental Pollution 99 (1998) 225–232

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Effects of heavy metal contamination on macronutrient availability and acidification parameters in forest soil in the vicinity of the Harjavalta Cu–Ni smelter, SW Finland

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Received 22 April 1997; accepted 23 October 1997

Abstract

Four experiments were established (1992) in Scots pine stands at distances of 0.5, 2, 4 and 8 km along a line running to the SE of the Cu–Ni smelter at Harjavalta, SW Finland, in order to investigate the effects of Cu and Ni emissions on macronutrient availability and estimates of cation exchange capacity (CEC) and base saturation (BS). The accumulation of Cu and Ni (total, exchangeable) in forest soil close to the smelter has resulted in a deficit of base cations (exchangeable Ca, Mg, K and BS) in the organic layer caused by inhibition of mineralisation and the displacement of base cations from cation exchange sites by Cu and Ni cations. No signs of soil acidification were found in the topmost layers of the soil measured as a change in pH, exchangeable acidity and Al. The determination of CEC by the summation method in heavy-metal polluted forest soils is not recommended unless heavy metal cations are also included in the calculations. © 1998 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Heavy metal pollution; Forest soil; Copper; Nickel; Base saturation

1. Introduction

The effects of SO_2 and heavy metal deposition on soils in the immediate vicinity of Cu–Ni smelters in the northern hemisphere were rather well documented, e.g. in south-western Finland by Fritze et al. (1989), in Norway by Løbersli and Steinnes (1988) (Cu smelter only), at Monchegorsk in NW Russia by Lukina and Nikonov (1995), and in Canada by Hutchinson and Whitby (1977) and Freedman and Hutchinson (1979). Forest soils close to these point sources have become saturated with Ni and Cu, and the vegetation was destroyed either as a direct result of high levels of SO_2, or indirectly through nutrient imbalances in the soil or the toxic effects of Cu and Ni on roots and mycorrhizas (Freedman and Hutchinson, 1980; Nordgren et al., 1986). Raitio (1992) has reported low foliar Mg and Mn concentrations in Scots pine growing near the Cu–Ni smelter at Monchegorsk, NW Russia, and Helmisaari et al. (1995) have reported low foliage Mg concentrations in the immediate vicinity of the Cu–Ni smelter at Harjavalta, SW Finland. The low concentrations of Mn, Ca and Mg in the leaves of birch (*Betula spp.*) and blueberry (*Vaccinium myrtillus*) near a smelter in Norway were associated with a decrease in the exchangeable concentrations of these nutrients in the organic layer (Løbersli and Steinnes, 1988). Fritze et al. (1989) also reported a clear decreasing gradient in exchangeable Ca, Mg, K and Mn concentrations in the organic layer with decreasing distance to the smelter at Harjavalta.

In many of the earlier-mentioned studies, there has also been a dramatic fall in base saturation in the organic layer close to the smelter, but only a marginal decrease in pH: Løbersli and Steinnes (1988) found a slight decrease in the pH of the organic layer close to the smelter, while Fritze et al. (1989) reported no effect on organic layer pH. Base saturation (BS) is widely used as a measure of soil acidity (Berdén et al., 1987), a decrease in base saturation being considered to indicate soil acidification (de Vries et al., 1989). The cation exchange capacity (CEC), i.e. the total number of cation exchange sites on the solid phase in the soil, is usually determined by the so-called summation method. In this method the major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, Al^{3+}) occupying the exchange sites are displaced by the cation of a neutral salt, e.g. $BaCl_2$, KCl or NH_4NO_3, and the displaced

PII: S0269-7491(97)00185-1

cations analysed. CEC is calculated as the sum of the equivalent concentrations of base cations and exchangeable acidity (EA), which mainly consists of H^+ and Al^{3+}. The drawbacks to this method include the rather large error derived from summing the results of five different analyses ($Ca^{2+} + Mg^{2+} + K^+ + Na^+ + EA$), as well as the fact that cation exchange capacity will be rather strongly underestimated in soils where, for natural or anthropogenic reasons, there are abnormally high levels of other cations present on the cation exchange sites. Determining CEC by methods involving multiple extractions or recovery of the displacing cation (Grove et al., 1982) would be less affected by such problems, but these methods are rarely used because they are rather laborious and time consuming.

The aim of this study was to determine whether the presence of relatively high levels of Cu and Ni in forest soil near the Cu–Ni smelter at Harjavalta, SW Finland has: (1) has had a detrimental effect on soil fertility, primarily the availability of Ca, Mg and K; (2) affects estimates of CEC in the organic layer obtained by the summation method; and (3) whether base saturation is affected by heavy metal accumulation. Owing to the dramatic decrease in SO_2 and heavy metal emissions during the past few years (Helmisaari et al., 1995), the site at Harjavalta provides an ideal opportunity to study the effect of heavy metals on the surface soil in the absence of heavy emissions of SO_2.

2. Material and methods

The four experiments used in this study were established in 1992 for compensatory fertilisation studies. The experiments are located in Scots pine stands along a line running to the SE of the smelter. The experiments at 0.5 and 8 km from the smelter had 12 sample plots and those at 2 and 4 km had 16 sample plots (each 30×30 m). The forest site type varied from *Vaccinium* to *Calluna* (for the Finnish forest type classification, see Cajander, 1949) (dry to dryish sites, relatively infertile). The soil in the experiments consisted of sorted fine sand (coarse/fine sand at 2 km) and is classified as orthic podzol. The thickness of the organic layer varied from 2–3 cm. Soil samples were taken from all the plots in the four experiments in May, 1992 prior to the application of the fertilisers. The organic layer and mineral soil samples (0–5, 5–10, and 20–30 cm layers) were taken at 25 points on each plot in all four experiments. The samples were combined to give one composite sample per layer per plot, and then air-dried. The organic layer samples were milled to pass through a 1 mm sieve, and the mineral soil samples were passed through a 2 mm sieve to remove stones and large roots. pH was determined in water (15 ml sample 25 ml^{-1} water). Total Ca, Mg, Na, K, Cu, Ni, S, Fe, Zn, Cd, Pb, Cr, Al and Mn were determined from the organic layer samples by dry ashing at 550°C, extracting the ash with conc. HCl, and then analysing the solutions by inductively coupled plasma atomic emission spectrometry (ICP/AES). Total N was determined on a CHN analyser. Exchangeable Ca, Mg, K, Cu, Ni and Al were determined by extraction with 0.1 M barium chloride (10 g sample 100 ml^{-1} extractant, shaken for 2 h), with and without 2% EDTA, followed by analysis by ICP/AES, and exchangeable acidity by titration to pH 7. EDTA is available in two forms; a protonated form and a Na form. The Na form was used in this study in order to avoid an additional input of protons to exchangeable acidity. However, this meant that Na could not be included in the CEC calculations.

Cation exchange capacity was calculated by summation (Hendershot and Duquette, 1986) in three different ways: (1) the sum of the equivalent concentrations of exchangeable Ca, Mg, K and exchangeable acidity; (2) as in (1) but including Cu and Ni obtained without EDTA in the $BaCl_2$ extractant; and (3) as in (1) but including Cu and Ni obtained with EDTA in the $BaCl_2$ extractant. Copper and Ni were included because they are known to be present in high concentrations in the organic layer and uppermost mineral soil layers at the plots closest to the smelter (Fritze et al., 1989), and it was therefore assumed that they would also occupy a significant proportion of the cation exchange sites. According to Leckie and Davies (1979), the hydrolysis constant for Cu^{2+} in solution ($Cu^{2+} + H_2O \Longleftrightarrow CuOH^2 + H^+$) is between pH 7.2 and 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. Although similar data are not available for Ni, laboratory tests involving the titration to pH 7.0 of Cu and Ni salts dissolved in 0.1 M $BaCl_2$ showed that neither of these cations contribute to exchangeable acidity (data not shown). The results were calculated as average values for the 12 to 16 plots in each experiment. The differences between the experiments were tested for each layer separately using variance analysis, and the statistical differences by the Tukey test.

3. Results

3.1. Sulphur, heavy metals and aluminium

The total concentrations of copper, nickel, sulphur, iron, zinc, cadmium, lead and chromium in the organic layer of the four experiments showed a clear increasing gradient with decreasing distance to the smelter complex (Table 1). The total Al concentration was not affected by distance to the smelter. There was an increasing gradient with decreasing distance to the smelter for exchangeable Cu and Ni in both the organic and mineral soil layers (Fig. 1). The Cu and Ni concentra-

Table 1
Mean total element concentrations (mg kg^{-1}) in the organic layer at distances of 0.5, 2, 4 and 8 km from the Cu–Ni smelter at Harjavalta

Distance (km)	Cu	Ni	S	Fe	Zn	Cd	Pb	Cr
0.5	5799^{a}	462^{a}	1235^{a}	18617^{a}	516^{a}	4.95^{a}	314^{a}	31.4^{a}
2	1648^{b}	224^{b}	818^{b}	6069^{b}	158^{b}	2.10^{b}	128^{b}	19.0^{b}
4	658^{c}	124^{c}	668^{b}	3167^{c}	137^{b}	1.90^{b}	93^{bc}	7.9^{c}
8	147^{c}	39^{d}	411^{c}	2154^{c}	61^{c}	0.73^{c}	64^{c}	5.5^{c}

Distance (km)	Al	Mn	Ca	Mg	K	Na	P	N
0.5	1561^{a}	33.0^{a}	968^{a}	444^{a}	382^{a}	37.9^{a}	1225^{a}	8608^{ab}
2	1761^{a}	90.0^{b}	904^{a}	313^{b}	437^{ab}	40.5^{ab}	533^{b}	7944^{ab}
4	1695^{a}	53.1^{a}	1226^{b}	225^{c}	466^{b}	44.7^{b}	527^{b}	9150^{a}
8	1762^{a}	58.1^{a}	971^{a}	207^{c}	397^{a}	43.2^{ab}	439^{b}	7350^{b}

Means marked with the same letter are not significantly different ($p < 0.05$, $n = 56$).

tions in the organic layer are not directly comparable with those in the mineral soil layers because the bulk density of the organic layer is much lower. However, the exchangeable Cu concentrations in all four layers were ca 10 times greater than those of Ni. The gradients of both the Cu and Ni concentrations in the mineral soil layers were much shorter than those in the organic layer; significantly higher Cu and Ni concentrations only occurred in the mineral soil on the plots at 0.5 and 2 km from the smelter.

3.2. *Macronutrients*

The patterns for total calcium, magnesium, potassium, nitrogen and phosphorus were somewhat different to those for most of the heavy metals (Table 1). The total magnesium and phosphorus concentrations in the organic layer increased significantly on moving towards the smelter complex; the total calcium, potassium, sodium and nitrogen concentrations were relatively constant, and the total manganese concentration close to the smelter was significantly depressed. The distribution of calcium, magnesium and potassium into non-exchangeable and exchangeable forms in the organic layer changed on moving towards the smelter (Fig. 2). There was a statistically significant decrease ($p < 0.05$) in the concentrations of exchangeable calcium, magnesium and potassium at a distance of 0.5 km from the smelter compared to the situation at 8 km, and a corresponding significant increase ($p < 0.05$) in non-exchangeable Ca at 0.5 km and for Mg and K at 0.5 and 2 km (Fig. 2).

In the mineral soil, the pattern for the base cation concentrations (exchangeable Ca + Mg + K) along the heavy metal gradient was rather different to that in the organic layer (Fig. 3). The base cation concentration in the 0–5 cm mineral soil layer close to the smelter was significantly higher than that at 2, 4 or 8 km ($p < 0.05$); deeper in the soil the difference between the experiments was not statistically significant.

3.3. *Soil acidity and acidification parameters*

Soil acidity was estimated using two different parameters, soil pH and exchangeable acidity. The deposition and accumulation of heavy metals and sulphur have not had any short- or long-term effects on soil acidity, i.e. on pH (Fig. 4) or on exchangeable acidity (Table 2), in the organic layer and uppermost mineral soil layer (0–5 cm). Deeper in the mineral soil, however, there was a significant decrease in pH (5–10 and 10–20 cm), and significant increase in exchangeable acidity (10–20 cm) at 0.5 km compared to 2, 4 and 8 km. There was a significant decrease ($p < 0.05$) in exchangeable aluminium concentration in the organic layer and 0–5 and 5–10 cm mineral soil layers and a significant increase ($p < 0.05$) in the 10–20 cm layer at 0.5 km compared to 2, 4 and 8 km. Soil pH and the exchangeable aluminium concentration were highly

Table 2
Mean pH, exchangeable acidity (EA) and exchangeable aluminium concentrations in the organic and mineral soil layers at different distances from the Harjavalta smelter

Distance (km)	0.5	2	4	8
Organic layer				
pH	3.5^{a}	3.7^{a}	3.6^{a}	3.6^{a}
EA, meq kg^{-1}	90.6^{a}	72.8^{b}	93.8^{a}	84.7^{ab}
Exch. Al, mg kg^{-1}	181^{a}	281^{b}	313^{b}	327^{b}
Mineral soil layers 0–5 cm				
pH	3.8^{a}	3.9^{a}	3.8^{a}	3.8^{a}
EA, meq kg^{-1}	15.5^{a}	20.3^{b}	16.0^{a}	24.4^{c}
Exch. Al, mg kg^{-1}	66.3^{a}	142^{b}	108^{c}	182^{d}
5–10 cm				
pH	3.9^{a}	4.1^{bc}	4.0^{b}	4.2^{c}
EA, meq kg^{-1}	20.1^{a}	13.4^{a}	13.6^{a}	14.4^{a}
Exch. Al, mg kg^{-1}	63.4^{a}	105^{b}	112^{b}	114^{b}
10–20 cm				
pH	4.0^{a}	4.3^{b}	4.3^{b}	4.4^{b}
EA, meq kg^{-1}	11.8^{a}	5.0^{b}	6.6^{b}	5.0^{b}
Exch. Al, mg kg^{-1}	88.4^{a}	43.6^{bc}	55.5^{b}	38.0^{c}

Means marked with the same letter are not significantly different ($p < 0.05$, $n = 56$).

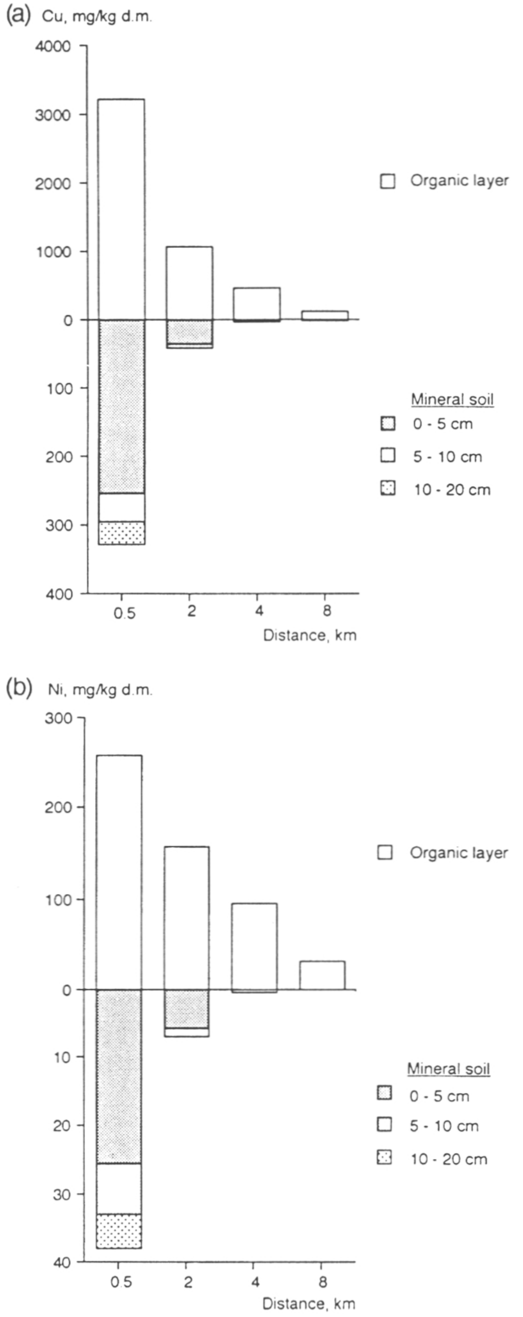

Fig. 1. Exchangeable copper (a) and nickel (b) concentrations in the organic and mineral soil layers at different distances from the Harjavalta smelter.

significantly correlated in the four layers at all distances from the smelter ($r = 0.736$, $n = 223$, $p < 0.001$).

3.4. *Cation exchange capacity and base saturation*

According to the calculations made on the basis of the sum of base cations, exchange acidity and exchangeable Ni and Cu (without EDTA), there were no significant differences in the CEC of the organic or 0–5, 5–10 and 10–20 cm layers at different distances from the smelter (Table 3). Not including Cu and Ni gave a statistically significant ($p < 0.001$) underestimate for CEC in the organic layer at 0.5 and 2 km, and the inclusion of EDTA-extracted Cu and Ni gave a significant ($p < 0.001$) overestimate in the 0–5 cm layer at 0.5 km.

There was a significant decrease in the BS of the organic layer with decreasing distance to the smelter (Table 3). In the mineral soil layers, the BS values in the 0–5 and 5–10 cm mineral soil layers were significantly larger at distances of 0.5 and 2 km from the smelter, compared to 4 and 8 km. The main reason for this trend is apparent from Fig. 5, which shows the proportion of cation exchange sites occupied by different cations. In the organic layer at 0.5 km a significantly ($p < 0.001$) higher proportion of the cation exchange sites were occupied by heavy metals, especially Cu. There were no significant differences between the proportions of hydrogen ions and aluminium (i.e. exchangeable acidity) at different distances from the smelter, but the proportions of the base cations — Ca^{2+}, Mg^{2+} and K^{+} — were significantly reduced ($p < 0.001$) at 0.5 km.

4. Discussion

Sulphur and copper, nickel and other heavy metals in the emissions were deposited over a distance of at least 8 km to the SE of the smelter. The gradient for total Ni in the organic layer was much flatter than that for Cu, suggesting that there are differences in the distribution pattern of these two heavy metals. Hutchinson and Whitby (1977) attributed similar differences in the transportation distances of Cu and Ni deposition, close to the Sudbury smelter in Canada, to differences in the size of the emitted particles. The accumulation of Cu and Ni in the organic layer differs from that in the mineral soil: the Cu/Ni ratio in the organic layer at 0.5 km distance is 19.5, and decreases with increasing depth to 10.4 in the 10–20 cm mineral soil layer (Derome and Lindroos, in press). Copper is known to form more stable complexes with organic matter than Ni (Mellor and Maley, 1947). Retention of Cu and Ni in the organic layer is supported by the fact that elevated exchangeable Cu and Ni concentrations in the mineral soil extended over a distance of less than 4 km from the smelter.

Microbial activity in the organic layer at the plots at 0.5 and 2 km was considerably reduced by the toxic effects of heavy metals (primarily Cu and Ni) on soil microbes (Bååth, 1989; Fritze et al., 1989). The humus layer at the plot at 0.5 km was covered by a rather thick layer of undecomposed needle litter (cf. Freedman and Hutchinson, 1980), caused partly by the high rate of needle fall (34% of the total needle biomass in autumn 1992) and the low rate of needle decomposition (Helmisaari et al., 1994). The large increase in non-exchangeable Ca, Mg and K in the organic layer close to the smelter also indicates that mineralization of these nutrients was strongly reduced.

Fritze et al. (1989) studied the same gradient using double the number of plots (8 plots in 8 km) with logarithmic spacing, and reported a strong increase in total Mg towards the smelter, no effect for potassium, and a reduction for calcium. No data are available for Mg and

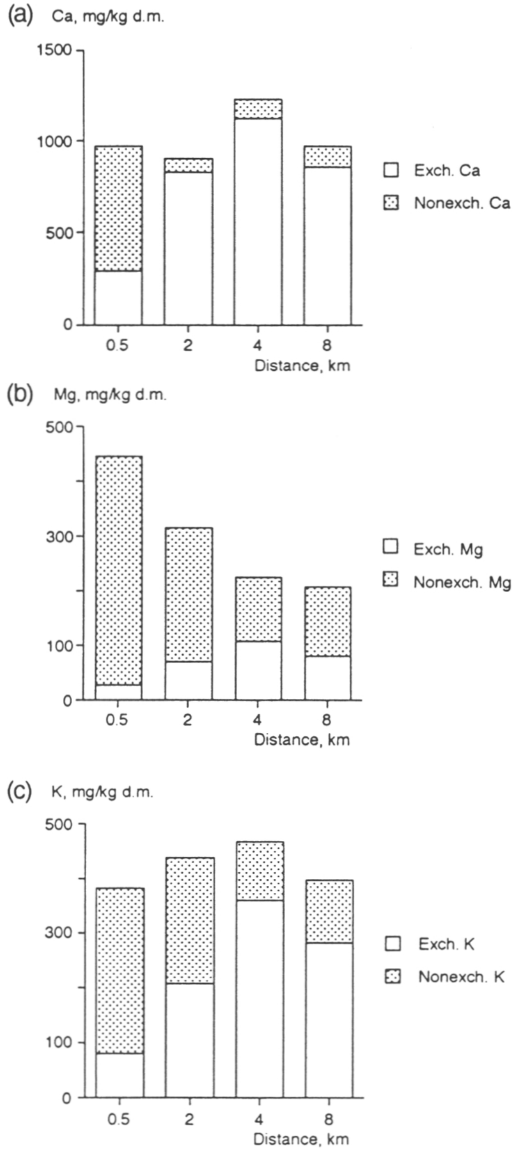

Fig. 2. Exchangeable and non-exchangeable calcium (a), magnesium (b) and potassium (c) concentrations in the organic layer at different distances from the Harjavalta smelter.

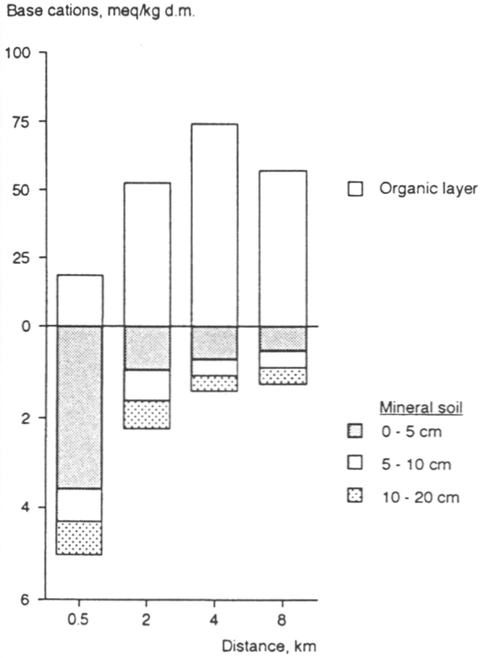

Fig. 3. Base cation concentrations (exchangeable $Ca+Mg+K$) in the organic and mineral soil layers at different distances from the Harjavalta smelter.

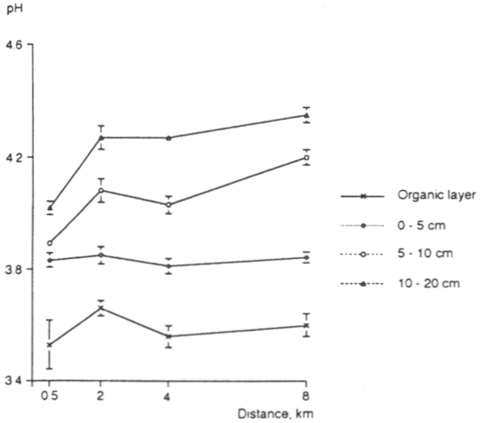

Fig. 4. pH(H_2O) in the organic and mineral soil layers at different distances from the Harjavalta smelter. The bars indicate the standard errors of the means.

Table 3

Mean estimates of cation exchange capacity (CEC) and base saturation (BS) obtained as the sum of base cations + exchangeable acidity (1), base cations + exchangeable acidity + exchangeable Cu and Ni (2), and base cations + exchangeable acidity + exchangeable Cu_{EDTA} and Ni_{EDTA} (3) Means marked in bold type differ significantly ($p < 0.001$, $n = 12$ or 16) from corresponding means calculated according to (1), (2) or (3).

Layer/distance (km)	CEC			BS		
	(1)	(2)	(3)	(1)	(2)	(3)
Organic layer						
0.5	**111**	**170**^{a}	**220**	**16.8**	**10.9**^{a}	**8.5**
2	**119**	**136**^{a}	**157**	**41.1**	**36.0**^{b}	**31.2**
4	170	177^{a}	187	44.1	42.4^{c}	39.9
8	145	146^{a}	149	41.3	40.8^{c}	40.1
Mineral soil layers 0–5 cm						
0.5	**18.0**	**23.7**^{a}	**26.9**	**14.3**	**10.9**^{a}	9.6
2	22.1	22.8^{a}	23.3	12.9	12.5^{a}	12.3
4	17.0	17.1^{b}	17.1	7.0	7.1^{b}	7.0
8	25.8	25.8^{a}	25.9	5.6	5.6^{b}	5.6
5–10 cm						
0.5	21.2	22.3^{a}	22.8	7.7	7.1^{a}	6.8
2	14.4	14.5^{b}	14.6	6.9	6.8^{a}	6.8
4	14.3	14.3^{b}	14.3	4.3	4.3^{b}	4.3
8	15.0	15.0^{b}	15.0	4.4	4.4^{b}	4.4
10–20 cm						
0.5	12.6	13.3^{a}	13.8	13.7	10.1^{a}	9.1
2	5.3	5.4^{b}	5.4	17.5	17.1^{a}	16.7
4	6.7	6.7^{b}	6.7	5.6	5.6^{a}	5.6
8	5.3	5.3^{b}	5.3	4.8	4.8^{a}	4.8

Means marked with the same letter in the two central columns are not significantly different ($p < 0.05$, $n = 56$).

P emissions from the smelter, but the clear increasing gradient does suggest that earlier emissions may have contained these two elements in appreciable amounts: P emissions from the fertiliser factory adjoining the smelter were 1 t yr^{-1} in 1987, but emissions almost completely ceased in 1989 (Helmisaari et al., 1994).

There was a strong decrease in exchangeable Ca, Mg and K in the organic layer at 0.5 and 2 km distance, and a corresponding increase in the 0–5 cm mineral soil layer. Thus, although there are potentially abundant amounts of Ca, Mg and K for the trees in the organic layer close to the smelter, there is a severe shortage of these macronutrients in a plant-available form. This is presumably the reason for the strongly reduced Ca, Mg and K levels in the pine needles (Nieminen and Helmisaari, 1996) on the plot at 0.5 km. The trees appear to be unable to utilise the relatively high concentrations of exchangeable Ca, Mg and K in the uppermost mineral soil layer. This may be caused by the toxic effect of Cu and Ni on the plant roots and mycorrhizas (Baes and McLaughlin, 1987), and subsequently severe disturbances in nutrient uptake.

The apparent contradiction between the effects of heavy metal deposition on exchangeable Ca, Mg and K in the organic layer and in the uppermost mineral soil layer can be explained by the displacement of Ca, Mg and K by the Cu and Ni that have gradually accumulated in the organic layer. Copper, especially, is known to bind very strongly to cation exchange sites, and to readily displace other cations (Bloomfield and Sanders, 1977). A high proportion of the deposited Cu and Ni was retained in the organic layer, and much less has passed into the 0–5 cm mineral soil. Thus, although a high proportion of the Ca, Mg and K that has returned to the organic layer in the litter is still strongly retained, the small amounts of Ca, Mg and K that are released through mineralization, together with the input from throughfall, are not bound in the organic layer, but pass down into the mineral soil layer.

The method used to determine CEC in this study was the summation method. The cations normally used in

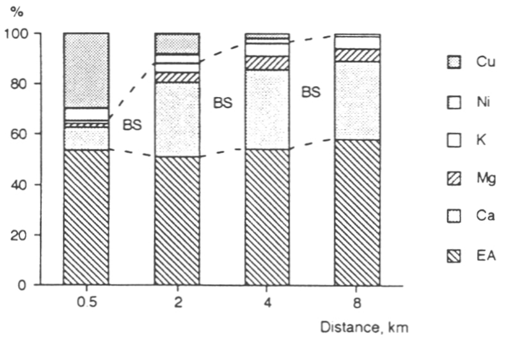

Fig. 5. Relative proportion of different cations occupying cation exchange sites in the organic layer at different distances from the Harjavalta smelter. BS = base saturation, EA = exchangeable acidity.

such CEC calculations are the base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and the so-called acidic cations (determined as exchangeable acidity). These cations are known to account for almost 100% of the cations bound on cation exchange sites (Hendershot and Duquette, 1986). In soils that naturally, or as a result of pollution, contain appreciable amounts of other cations, the summation method will therefore give an underestimate of CEC. In this study, Cu and Ni occupied 35% of the cation exchange sites in the organic layer at a distance of 0.5 km, and 12% at 2 km. When Cu and Ni were included in the CEC calculations, the estimates for organic layer CEC at 0.5 and 2 km were much higher than those obtained without Cu and Ni. This strongly supports the assumption that their exclusion results in an underestimate for CEC. The use of EDTA in the $BaCl_2$ extract was also tested in this study. Methods for determining available Cu in agricultural soils include the use of EDTA (Lundblad et al., 1949) in order to ensure that the Cu released from exchange sites and complexes remains in solution. In organic-rich forest soils, however, there is a strong likelihood that EDTA will also extract Cu from organic complexes. The Cu in these complexes is not exchangeable Cu. In this study the yield of EDTA-extractable Cu from the organic layer was almost double that obtained with $BaCl_2$ alone. We can thus conclude that $BaCl_2$ + EDTA for determining CEC in Cu-polluted soils strongly overestimates CEC, and is therefore not a recommendable practice. There were reports of a decrease in CEC close to a Cu–Ni smelter at Monchegorsk, NW Russia (Lukina and Nikonov, 1995) and at Harjavalta (Fritze et al., 1996), but in these studies CEC was calculated using the summation method without including Cu or Ni.

In a study of this sort, a decrease in BS along a gradient running from a point source is normally taken as a clear indicator of soil acidification caused by sulphur emissions (e.g. Løbersli and Steinnes, 1988). However, the low BS values in the organic layer were not associated with a reduction in pH or exchangeable acidity, nor with an increase in exchangeable aluminium. Neither were the elevated BS values in the 0–5 cm mineral soil layer associated with an increase in soil pH or a decrease in exchangeable acidity. Løbersli and Steinnes (1988) suggest that the deposition of H^+ and heavy metals has displaced base cations from the organic layer. The only increase in acidification in the study in hand occurred in the 5–10 and 10–20 cm layers. As SO_2 emissions from the smelter fell drastically at the end of the 1980s, it would appear that the loss of base cations from the organic layer is caused by Cu and Ni accumulation rather than to SO_2 induced acidification. In addition, there are strong signs that Ni and Cu have also displaced exchangeable Al from the organic layer, and that the reduction in exchange acidity and exchangeable Al in the 0–5 cm layer is caused by the displacement of these two components by the base cations that have accumulated in the same layer. This would explain the increase in EA and exchangeable Al in the 10–20 cm layer.

5. Conclusions

The accumulation of Cu and Ni in forest soil close to the Cu–Ni smelter at Harjavalta, SW Finland, has resulted in a severe deficit of Ca, Mg and K in the organic layer as a result of strong inhibition of the mineralization of these nutrients from litterfall and their displacement from cation exchange sites. The trees appear to be unable to utilise the Ca, Mg and K that have accumulated in the topmost mineral soil layer as a result of displacement from the organic layer. No signs of soil acidification were found in the organic layer or the uppermost mineral soil layers, but there was an increase in exchangeable acidity and Al deeper in the mineral soil. This was considered to be caused by their displacement from the overlying organic and mineral soil layers. The loss in BS in the organic and uppermost mineral soil layers close to the smelter was attributed to displacement by Cu and Ni, and not to acidic deposition. Base saturation is therefore not a useful measure of soil acidification in heavy-metal polluted soils. The use of the summation method for determining CEC in heavy-metal polluted soils is not recommended unless other major cations present in such soils are included in the calculations. Neither is CEC determination using a neutral salt solution containing EDTA to solubilise exchangeable/complexed Cu recommended because a high proportion of this Cu is presumably not bound on cation exchange sites.

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PAPER III

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Environmental Pollution 103 (1998) 219–228

ENVIRONMENTAL
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Metal and macronutrient fluxes in heavy-metal polluted Scots pine ecosystems in SW Finland

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Received 1 April 1998; accepted 6 June 1998

Abstract

Cu, Ni, Zn, SO_4–S and macronutrient fluxes in Scots pine ecosystems were investigated during 1992–1996 at distances of 0.5, 4 and 8 km from the Harjavalta Cu–Ni smelter, SW Finland. The flux of water percolating down to a soil depth of 5 cm at 0.5 km was more than double that at 4 and 8 km. There was a net loss of Zn from the 40-cm thick soil layer, but a net gain for Cu, Ni and SO_4–S. Copper was more strongly retained in the organic layer than Ni. Cu, Ni and Zn fluxes at 0.5 km were extremely large compared to those at 4 and 8 km. The fluxes of Ca, Mg, K and PO_4–P to a depth of 5 cm at 0.5 km distance were much higher than the input via bulk precipitation, and the flux of Mg higher than the input in throughfall. There was a net loss of Mg and K at a depth of 40 cm compared to the input via bulk precipitation. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Copper; Element fluxes; Forest soil; Nickel; Soil pollution; Zinc

1. Introduction

Heavy metals and sulphur dioxide derived from anthropogenic sources have caused serious damage to forest ecosystems in areas close to a number of emission sources in the boreal forest zone. The effects of huge emissions from nickel and copper mining and smelting activities in Sudbury, Canada (Hutchinson and Whitby, 1974; Freedman and Hutchinson, 1980a), and in the Kola Peninsula, NW Russia (Boltneva et al., 1983; Kozlov et al., 1993; Tikkanen, 1994; Nöjd et al., 1996), have been extensively documented. A much smaller Cu–Ni smelter unit has been operating in Harjavalta (61°19′ N, 22°9′ E), SW Finland, since 1945. Although emissions of SO_2 and heavy metals from the smelter have been considerably reduced in recent years (Helmisaari et al., 1995), 50 years' accumulation of pollutants has had a considerable effect on Scots pine ecosystems in the vicinity of the smelter (Laaksovirta and Silvola, 1975; Fritze et al., 1989; Heliövaara and Väisänen, 1989; Helmisaari et al., 1995).

Heavy metal accumulation in forest soil may affect nutrient cycling throughout the whole ecosystem by inhibiting litter decomposition (Rühling and Tyler, 1974; Freedman and Hutchinson, 1980b; Fritze et al., 1989) and subsequently reducing the supply of nutrients released by mineralisation (Derome and Lindroos, 1998a). Heavy metals can also have toxic effects on roots and mycorrhizas (Gobl and Mutsch, 1985; Colpaert and Van Assche, 1992), and nutrient uptake can be seriously reduced. There is a reduction in the growth and vitality of the forest vegetation. The vegetation cover may ultimately be completely destroyed, increasing the risk of soil erosion (Hutchinson and Whitby, 1977; Freedman and Hutchinson, 1980a; Lukina et al., 1993). The capacity of the ecosystem to bind heavy metals gradually diminishes, increasing the likelihood of the accumulated heavy metals gradually leaching into the ground water.

Sulphur dioxide and heavy metal emissions have been drastically reduced in recent years in many parts of western Europe (e.g. Strand, 1998), but the pollutants that have earlier accumulated in forest ecosystems continue to affect the functioning of such ecosystems. For this reason, the flux of heavy metals within and out of forest ecosystems needs to be continuously monitored.

The aims of this study were to investigate (1) the flux of Cu, Ni, Zn and SO_4–S in Scots pine ecosystems containing varying levels of accumulated heavy metals and sulphur, and 2) the possible effects of these pollutants

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PII: S0269-7491(98)00118-3

on the flux of macronutrients. Element fluxes between the different strata in the ecosystems were quantified using bulk deposition, stand throughfall, and percolation water collected at different depths down the soil profile.

2. Material and methods

2.1. Study sites

Three sample plots were established in July 1992 at distances of 0.5, 4 and 8 km from the Cu–Ni smelter at Harjavalta (61°19′ N, 22°9′ E), SW Finland. Emissions from the smelter primarily comprise Cu, Ni, Zn and SO_2 (Fig. 1). During the 1980s, annual emissions from the neighbouring fertiliser factory (Kemira Ltd.) were 600 t nitrogen oxides, 30 t chloride, 0.8 t fluoride and 1 t phosphorus. However, production at the factory ceased in 1989. The plots were located in pure Scots pine stands growing on dry mineral soil sites along an esker running to the SE of the smelter. The vegetation on the sites was originally typical of xerophilous forest sites. The ground vegetation on the plot at 0.5 km was almost completely destroyed (Salemaa and Vanha-Majamaa, 1993), and the pine stand suffering from retarded growth and severe needle loss (Table 1, Mälkönen et al., 1998). The stands located at 4 and 8 km appeared to be relatively unaffected. The thickness of the organic layer varied from 1 to 3 cm, the underlying mineral soil consisted of sorted fine sand, and the soil was classified as orthic podzol. Despite the SO_2 emissions from the smelter, there were no signs of increased soil acidity. However, the organic layer at 0.5 km especially was suffering from a strong deficit of base cations, and consequently low BS values (Derome and Lindroos, 1998a). The uppermost mineral soil layer had elevated base cation concentrations.

2.2. Bulk deposition, stand throughfall and soil solution

Bulk deposition was collected in open areas close to the three stands using five rainfall collectors ($d=20$ cm) during the snowfree period or two snow collectors ($d=36$ cm) during the winter. Stand throughfall was collected using 20 rainfall collectors located systematically inside the stand on the 30×30 m plots during the snowfree period and six systematically located snow collectors during the winter. The height of the rainfall collectors was 50 cm above ground level.

Soil solution samples were collected in the form of percolation water using zero-tension lysimeters ($d=20$ cm) located at depths of 5 cm (four replications), 20 cm (12 replications) and 40 cm (four replications) measured from the ground surface. The lysimeters consisted of a plastic funnel ($d=20$ cm) containing acid-washed, fine quartz fitted to the top of a plastic bottle. The lysimeters were installed by first removing an intact soil core ($d=30$ cm) down to the required depth using a special auger, and the lysimeters then placed in a shaft sunk below the removed soil core. The soil core was then carefully replaced. Percolation water was removed from the lysimeters by means of a nylon tube leading down into the collection bottle (for more details, see Derome et al., 1991).

Bulk deposition, stand throughfall and soil solution samples (snowfree period only) were collected at 1-month intervals during the period June 1992 to December 1996.

Table 1
Characteristics of the soil and tree stand on the study plots in 1991

Parameter	Distance from the smelter (km)		
	0.5	4	8
Thickness of horizons			
Ao (cm)	3	2	1
E (cm)	15	11	8
Bs (cm)	31	26	27
Mineral soil texture	Sorted fine sand		
Stoniness (%)	0	0	0
Stand age (years)	47	45	38
Number of trees ha^{-1}	1008	1517	1552
Mean height (m)	7.6	11.1	12.4
Stem volume (m^3 ha^{-1})	23.2	67.8	94.5
Volume increment (m^3 ha^{-1} year)	0.31	2.78	6.27
Needle mass (kg ha^{-1})	861	2862	3900

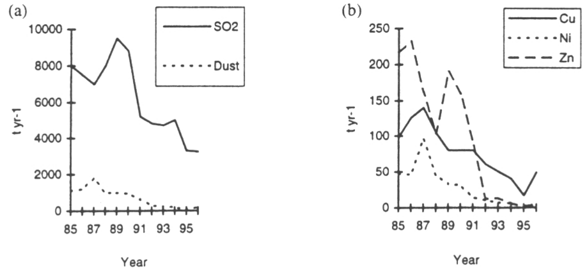

Fig. 1. Annual SO_2, dust, Cu, Ni and Zn emissions from the Harjavalta smelter, SW Finland, during the period 1985–1996.

2.3. *Soil and needle samples*

Samples were taken from the organic layer and mineral soil (0–5, 5–10, 10–20, 20–30 cm depth) at 25 systematically selected points on the three plots in May 1992. The organic layer samples were taken using a steel cylinder ($d = 58$ mm), and the mineral soil samples using a soil auger ($d = 21$ mm). The samples from the same layer were bulked to give one sample per layer.

Needles were collected in mid-July 1992 from 10 trees per plot. The sample trees were randomly selected from five size classes representative of the stand on each plot. One branch from the upper, middle and lower crown were randomly selected from each tree. One hundred 1-year-old fascicles were collected from each excised branch and combined to form a sample of 300 fascicles per tree.

2.4. *Chemical analyses*

Needle Cu, Ni, Zn, Ca, Mg, K, P and S concentrations were determined from finely ground needle samples by dry ashing (550°C) and extraction of the ash with conc. HCl. The solutions were analysed by inductively coupled plasma atomic emission spectrometry (ICP/AES). Total N was determined on a CHN analyser.

The dried organic layer samples were milled to pass through a 1 mm sieve, and the mineral soil samples passed through a 2 mm sieve. Extractable Cu, Ni, Zn, Ca, Mg, K and extractable P were determined by extraction with 0.1 M $BaCl_2$, followed by analysis by ICP/AES.

The pH of the rainwater and percolation water samples was measured, and the remaining part of the samples filtered (0.45 μm membrane filter). Ca, Mg, K, Cu, Ni and Zn were determined by ICP/AES, and NH_4–N, NO_3–N, SO_4–S and PO_4–P by ion chromatography (IC). Dissolved organic carbon (DOC) was determined by digestion with sodium persulphate under UV radiation on a TOC analyser.

2.5. *Calculation of the results*

The annual fluxes for the period 1993–1996 were calculated by summing the amounts of individual elements or compounds m^{-2} collected during the periods 7.12.92–13.10.93, 13.10.93–7.11.94, 7.11.94–6.11.95, and 6.11.95–12.11.96. The start of each period was determined by the date when the last percolation water sample was obtained prior to the onset of winter, i.e. it was assumed that percolation water collected for the first time each spring was derived from snow that had fallen during the previous winter. Average annual fluxes during the period 1993–1996 were calculated from the annual flux values. No percolation water was obtained from the four lysimeters located at a depth of 40 cm at 8 km, and the figures therefore do not include data for this depth and site.

3. Results

3.1. *Element concentrations in the pine needles and soil*

Needle Cu, Ni, Zn and S concentrations in the stand 0.5 km from the smelter were significantly higher than those in the stands at 4 and 8 km (Table 2). There were no differences in the Ca or P concentrations between any of the plots, but the Mg concentration was lower and the K concentration higher in the stand at 0.5 km.

There was a clear increasing gradient in the exchangeable Cu, Ni and Zn and extractable P concentrations in the organic layer and different mineral soil layers on moving towards the smelter (Table 3). In addition, there was a clear decrease in the concentrations of Cu, Ni and Zn with increasing depth in the mineral soil at 0.5 km, and for Cu and Zn at 4 km. The trends for Ca, Mg and K were not as clear, but the concentrations of these three macronutrients in the organic layer at the plot closest to the smelter were considerably smaller than those at the two other plots. In contrast, the concentrations of Ca, Mg and K in the 0–5 cm mineral soil layer at 0.5 km were clearly elevated compared to the concentrations in the same layer at the two other plots.

Table 2
Needle Cu, Ni, Zn, S, Ca, Mg, K, N and P concentrations in the 1-year-old Scots pine needles at different distances from the Harjavalta smelter

Element (mg ha^{-1})	Distance from the smelter (km)		
	0.5	4	8
Cu	211a	20.0b	8.74b
	(13.7)	(1.61)	(0.55)
Ni	43.5a	7.79b	5.08b
	(1.60)	(0.78)	(0.67)
Zn	82.8a	36.9b	33.4b
	(3.74)	(3.86)	(2.10)
S	832a	377b	406b
	(60.9)	(20.9)	(27.3)
Ca	1.86a	2.10a	1.90a
	(0.17)	(0.31)	(0.16)
Mg	0.41a	0.52a	0.62b
	(0.05)	(0.02)	(0.05)
K	5.30a	3.98b	4.43c
	(0.32)	(0.14)	(0.22)
N	9.88a	8.30b	9.70a
	(0.31)	(0.25)	(0.21)
P	0.98a	0.90a	0.99a
	(0.05)	(0.03)	(0.03)

The standard error of the mean is given in parentheses ($n = 10$). Values marked with different letters differ significantly ($p < 0.05$, pairwise comparisons of means by the Tukey test) from each other.

Table 3
Exchangeable Cu, Ni, Zn, Ca, Mg and K and extractable P in the organic and mineral soil layers at different distances from the Harjavalta smelter

Layer	Exchangeable (mg kg^{-1})						Extractable (mg kg−1)
	Cu	Ni	Zn	Ca	Mg	K	P
0.5 km							
Organic layer	4654	415	125	582	39.9	132	490
Mineral soil (cm)							
0–5	266	24.8	10.3	40.5	14.3	14.3	26.6
5–10	27.4	5.35	2.87	11.0	2.20	5.70	8.32
10–20	15.9	3.24	1.78	6.10	1.30	bdl	21.3
20–30	12.1	2.07	1.37	4.40	0.70	bdl	19.2
4 km							
Organic layer	554	121	90.2	1215	114	456	141
Mineral soil (cm)							
0–5	3.28	0.84	1.91	13.6	3.20	12.5	6.50
5–10	0.62	bdl	0.61	2.80	1.60	8.50	15.3
10–20	0.29	bdl	0.36	2.10	1.10	8.00	5.60
20–30	0.63	bdl	0.30	3.30	0.90	7.30	3.70
8 km							
Organic layer	121	36.9	47.3	885	84.4	291	97.5
Mineral soil (cm)							
0–5	1.54	bdl	1.05	10.6	3.50	9.10	14.9
5–10	0.40	bdl	0.42	3.50	2.20	8.50	16.9
10–20	bdl	bdl	bdl	1.40	1.00	bdl	4.30
20–30	0.19	bdl	bdl	3.00	0.90	bdl	3.90

bdl, below detection limit.

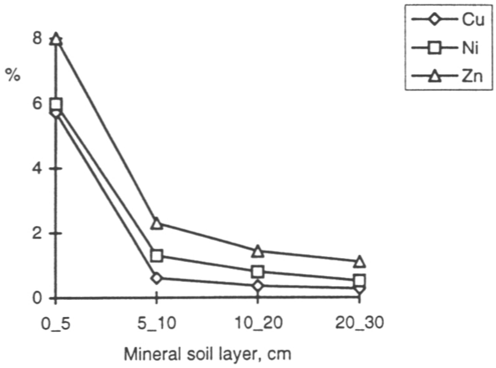

Fig. 2. Proportion (as %) of exchangeable Cu, Ni and Zn in the different mineral soil layers at 0.5 km compared to the concentrations in the organic layer.

Large amounts of Cu, Ni and Zn were present in the organic layer at 0.5 km, but the distribution of these three elements down the mineral soil indicated that their retention in the organic layer was a selective process, i.e. despite the higher amounts of Cu in the organic layer, proportionally more Ni and Zn had passed down into the mineral soil (Fig. 2). The relative proportion of Zn in the mineral soil was three times greater, and that of Ni two times greater than that of Cu.

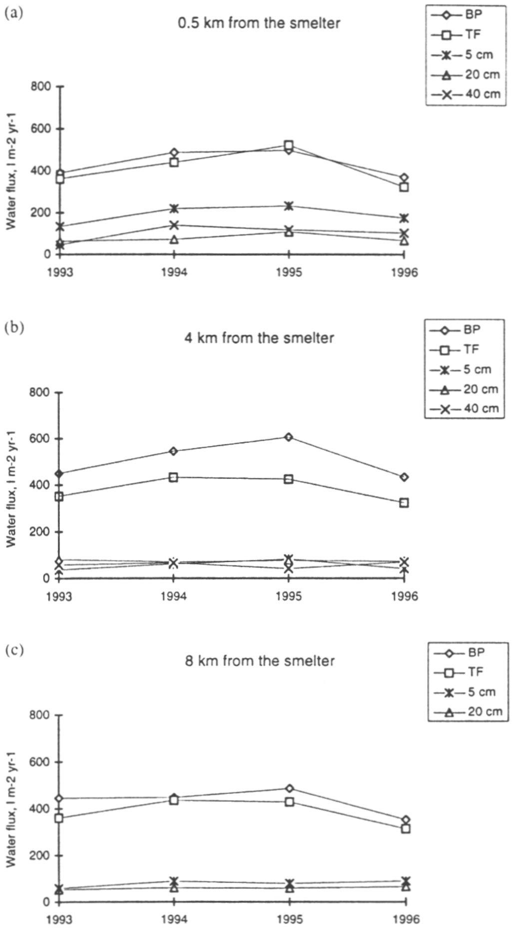

Fig. 3. The annual flux of water (l m^{-2} $year^{-1}$) in bulk deposition (BP), stand throughfall (TF) and percolation water at different depths down the soil profile (5, 20 and 40 cm from the ground surface) at different distances from the smelter.

3.2. *Water flux*

The amount of water intercepted by the crown canopy at 0.5 km was very small, only 6%; throughfall was about 94% of bulk precipitation (Fig. 3). The needle mass in the stand on this site was the lowest of all three sites, only 22% of the needle mass in the stand at a distance of 8 km from the smelter (Table 1). At a distance of 4 km from the smelter, interception by the crown canopy was much higher than at 8 km, 25% compared to 10%. However, the needle mass at 4 km was only 75% of that in the stand at 8 km.

A relatively high proportion of stand throughfall passed down to a depth of 5 cm at the plot at 0.5 km; the flux of percolation water at 5 cm depth was 43%

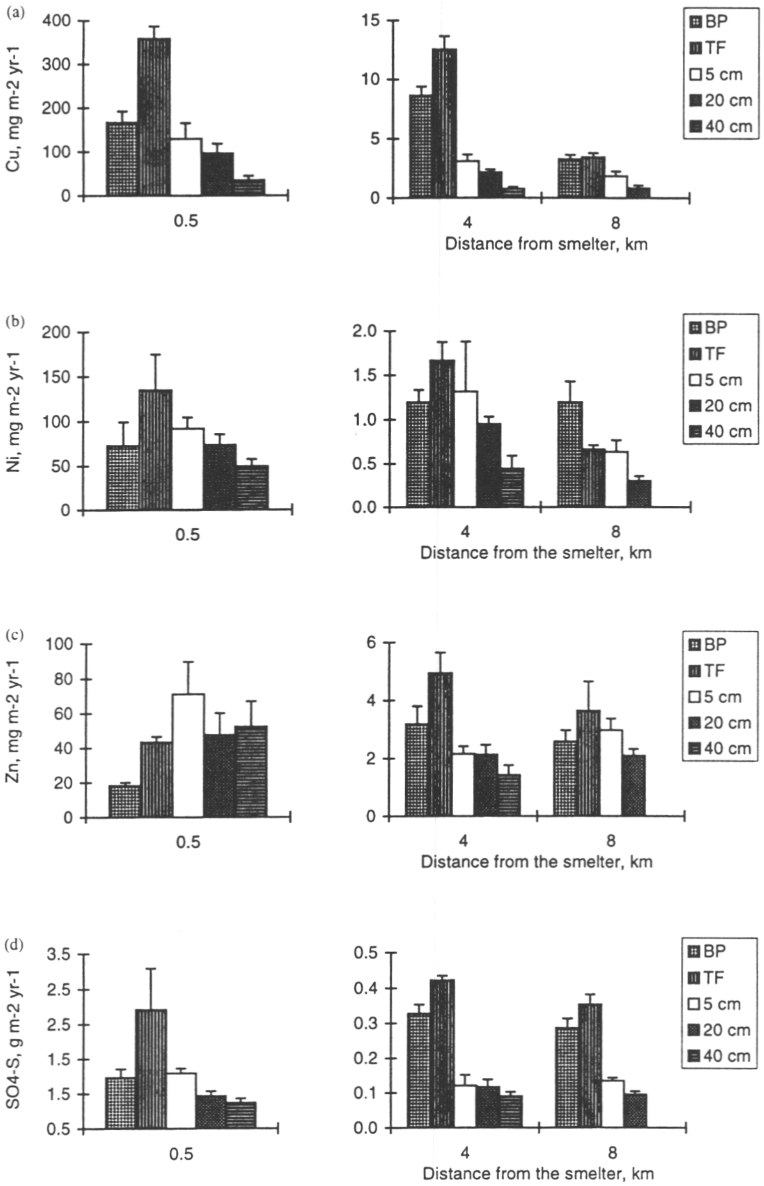

Fig. 4. The mean annual flux of Cu, Ni, Zn and SO_4–S (mg m^{-2} $year^{-1}$) in bulk deposition (BP), stand throughfall (TF) and percolation water at different depths down the soil profile (5, 20 and 40 cm from the ground surface) at different distances from the smelter during the period 1993–1996. The bars indicate the standard error of the mean. Note the different scales on the *y* axes.

of bulk precipitation. At 4 and 8 km the corresponding proportions were only 11 and 18%, respectively. The fluxes of percolation water at 20 and 40 cm at 0.5 km were also higher than those at 4 and 8 km. The fluxes of percolation water at 5 and 20 cm at 4 and 8 km were very similar, in all cases less than 20% of bulk precipitation.

3.3. Copper, nickel, zinc and sulphate

The annual amounts of Cu, Ni and SO_4–S reaching the forest floor in throughfall at 0.5 km were considerably greater than those entering the stand as precipitation (Fig. 4); 115% greater for Cu, 85% for Ni and 132% for SO_4–S. The situation at 4 km was somewhat similar although the increases were not as great as at 0.5 km. The values for Cu and Ni at 8 km should be treated with caution because in many cases the concentrations of these two metals in the water samples were close to or below the detection limit of the analytical equipment. There were clear differences in the behaviour of Cu and Ni on entering the soil. Copper was retained to a greater extent than Ni in the uppermost soil layers because the flux of Cu in percolation water at 5, 20 and 40 cm depths fell relatively sharply with increasing depth at both 0.5 and 4 km compared to the flux entering the soil in throughfall. The flux of Ni at 5 cm depth, for instance, was greater than that entering the stand in precipitation at both 0.5 and 4 km. The flux of SO_4–S was rather similar to that for Ni, especially at 0.5 km.

The effect of the crown canopy on the flux of Zn and the flux of Zn between the soil layers was rather different to that for Cu, Ni or SO_4–S. At 0.5 km the flux of Zn in throughfall was larger than that in bulk precipitation, and the flux in percolation water at 5, 20 and 40 cm depth greater than that entering the soil in throughfall. Thus at 0.5 km there was a net loss of Zn from the 0–40 cm thick soil layer.

3.4. Calcium, potassium and magnesium

The fluxes of Ca, Mg and especially K in throughfall at 0.5 km were much higher than the fluxes entering the stand as bulk precipitation; an increase of 135% for Ca, 87% for Mg and 444% for K (Fig. 5). The relative net increases in Ca and Mg were approximately the same at all three distances from the smelter, but for K the relative increase was by far the greatest at the plot at 0.5 km. There was a net loss of Mg from the 0–5 cm thick layer, i.e. more Mg passed out of this layer than entered it in throughfall, and even at 20 and 40 cm depths the loss of Mg was appreciable. Both K and Ca appeared to be less mobile in the soil than Mg, because the fluxes of K and Ca passing down to a depth of 40 were equivalent to about 45% of the input from throughfall, but for Mg about 80%. At 4 and 8 km, the differences between the retention of Mg compared to that of Ca and of K were not so pronounced.

3.5. Hydrogen ions and dissolved organic carbon (DOC)

The flux of hydrogen ions in bulk precipitation was the lowest at the plot closest to the smelter (Fig. 6). The flux of protons in throughfall clearly increased compared to that in bulk precipitation at all three plots. At 0.5 km there was a strong increase in the flux of protons passing down to a depth of 5 cm compared to the situation at the other plots. There was a clear decrease in the flux of protons in percolation water with increasing depth at all three plots.

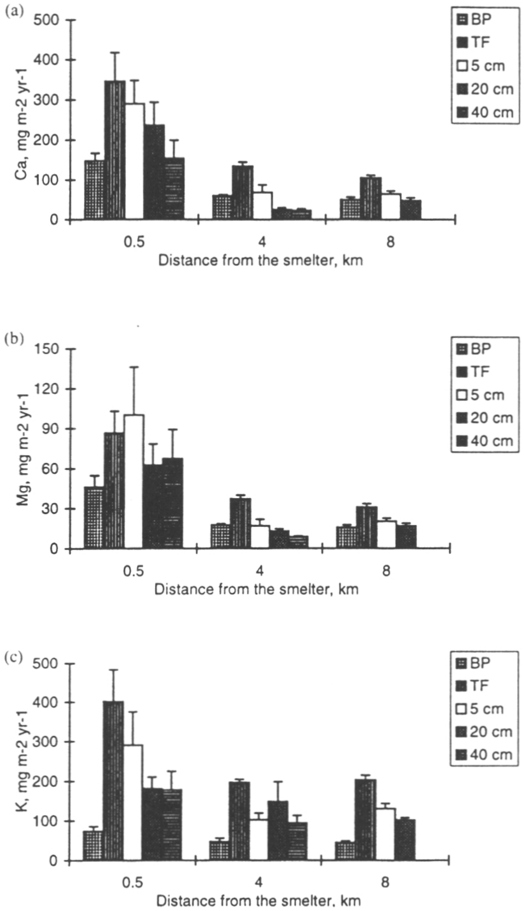

Fig. 5. The mean annual flux of Ca, Mg and K (mg m^{-2} $year^{-1}$) in bulk deposition (BP), stand throughfall (TF) and percolation water at different depths down the soil profile (5, 20 and 40 cm from the ground surface) at different distances from the smelter during the period 1993–1996. The bars indicate the standard error of the mean.

No data were available for the flux of DOC in bulk precipitation. There was an increase in the flux of both DOC and hydrogen ions in percolation water at 5 cm depth at 0.5 km, but the correlation between DOC and H^+ at this depth was relatively weak ($r=0.270$, $p<0.05$, $n=38$), and gradually increased with increasing depth (at 20 cm, $r=0.354$, $p<0.01$, $n=39$, and at 40 cm, $r=0.435$, $p<0.001$, $n=31$). In contrast, at 4 and 8 km, the only significant correlation between these two parameters was at a depth of 5 cm (at 4 km, $r=0.331$, $p<0.01$, $n=37$, at 8 km, $r=0.495$, $p<0.001$, $n=34$).

3.6. Ammonium, nitrate and phosphate

At 0.5 km there were relatively large net increases in the flux of NH_4–N and NO_3–N in throughfall, NH_4–N

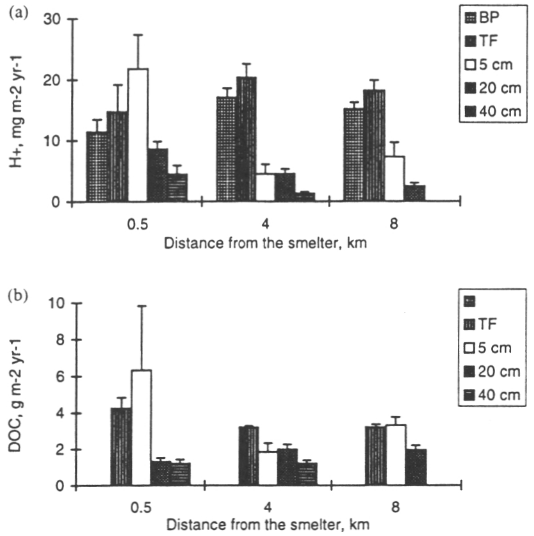

Fig. 6. The mean annual flux of hydrogen ions (H^+) and dissolved organic carbon (DOC) (mg m^{-2} $year^{-1}$) in bulk deposition (BP), stand throughfall (TF) and percolation water at different depths down the soil profile (5, 20 and 40 cm from the ground surface) at different distances from the smelter during the period 1993–1996. The bars indicate the standard error of the mean.

increasing by 150% and NO_4–N by 60% compared to the amounts in bulk precipitation (Fig. 7). In contrast, at 4 and 8 km there was a slight net decrease in NH_4–N and no change in NO_3–N in throughfall. The fluxes of NH_4–N and NO_3–N passing down the soil profile in percolation water decreased strongly at all three sites compared to the input in throughfall.

At 4 and 8 km there was a clear decreasing trend in the flux of PO_4–P as the precipitation passed down through the canopy and then down through the soil to a depth of 40 cm. At 0.5 km, however, there was a 30% net increase in throughfall, and at 5 cm depth the flux of PO_4–P was still greater than that in bulk precipitation. There was a strong decrease in the flux of PO_4–P reaching depths of 20 and 40 cm at this plot.

4. Discussion

Flux measurements in forest soil can be measured or estimated using either zero-tension lysimeters or suction-cup lysimeters (Beier et al., 1988). Both approaches have their advantages and disadvantages, and the final choice of technique is highly dependent on the availability of supporting data (e.g. water tension and matric potential measurements) and on the type of soil involved. Zero-tension lysimeters were chosen for this study because the soil and tree stands at all three sites are (or were originally) extremely homogeneous and there were no stones in the sorted, fine sand. Furthermore, the lysimeter type and installation technique have proved to be highly successful in earlier studies carried out in Finland on sites of this type (e.g. Derome and Väre, 1995). The use of zero-tension lysimeters rather than suction-cup lysimeters was also supported by reports that the chemical composition of percolation water is not necessarily the same as that of soil solution samples collected when the water content is below field capacity (Beier et al., 1988). Percolation water is the medium responsible for element fluxes in the soil. The reliability of the results obtained here for the water and element fluxes is somewhat reduced by the fact the a relatively limited number of lysimeters were employed. The installation of more would have improved the reliability but would have undoubtedly had a disturbing effect on the water flux itself. However, the intention was not to calculate mass balances, but rather to

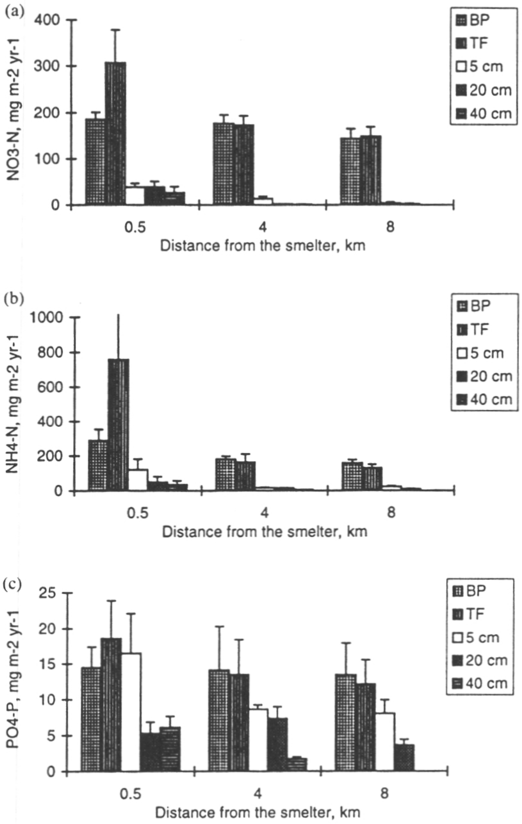

Fig. 7. The mean annual flux of NO_3–N, NH_4–N and PO_4–P (mg m^{-2} $year^{-1}$) in bulk deposition (BP), stand throughfall (TF) and percolation water at different depths down the soil profile (5, 20 and 40 cm from the ground surface) at different distances from the smelter during the period 1993–1996. The bars indicate the standard error of the mean.

compare the water and element fluxes in relative terms at different distances from the smelter.

The driving force behind the flux of elements between the different compartments of forest ecosystems is the movement of water. Although the chemical properties of the individual elements and compounds, as well as the biological and geochemical processes involved, have an effect on the rate and magnitude of the fluxes, the water flux is still the most important determining factor. The water flux on the plot at 0.5 km appears to have been seriously disturbed by the damage to the ecosystem caused by heavy metal and SO_2 emissions from the Cu–Ni smelter. The interception of precipitation by the tree canopy has been greatly reduced as a result of the dramatic decline in tree growth and the high degree of defoliation (Mälkönen et al., 1998), and the almost total destruction of the ground vegetation (Salemaa and Vanha-Majamaa, 1993) has resulted in a high proportion of the water falling as throughfall passing down to a depth of at least 5 cm in the soil. The forest floor is covered in a layer of dry, undecomposed plant litter (Fritze et al., 1989) and the microbiological activity of the whole organic layer is severely depressed (Fritze et al., 1996). As a result, the water holding capacity of the organic layer appears to be considerably reduced, and there will be less chemical and microbiological interactions between the percolation water and soil.

The water flux at the plots at 4 and 8 km was in good agreement with water fluxes reported for background areas in northern Finland (Derome and Väre, 1995). The relatively low proportion of precipitation reaching a depth of 5, 20 and 40 cm at 4 and 8 km well illustrates the hydrological conditions prevailing in Finnish mineral soils; a long winter period with frozen ground and subsequently relatively high surface runoff during snowmelt, and rather dry summers when much of the water passing into the soil is returned to the atmosphere through evapo-transpiration. The rather low interception of rainfall in the stand at 8 km compared to that at 4 km is rather surprising, because the needle mass and growth of the stand at 8 km are much greater than at 4 km (Mälkönen et al., 1998). However, only relatively weak relationships have been reported between rainfall interception and stand parameters in Fennoscandia (Strand, 1998). The average length of the period when precipitation falls as snow in the west of Finland is about 5 months, and the behaviour of snowfall often varies markedly between stands for reasons not necessarily related to stand properties.

The strong increase in the flux of DOC passing down to 5 cm at 0.5 km suggests that morphological changes have taken place in the organic layer. The humic substances formed as a result of microbiological decomposition of the litter are normally strongly aggregated by the polysaccharides excreted by micro-organisms in the soil, thus reducing their solubility (Stevenson, 1982). In the dry, relatively sterile conditions in the organic layer close to the smelter, the binding capacity of these aggregates may be considerably reduced. Increased dissolution of this humic material would increase the flux of organic matter carried down into the underlying layers by the percolation water. The carbon reported as DOC in this study does not include particulate carbon because the samples were filtered through 0.45 μm membrane filters. The properties of the DOC collected at 0.5 km apparently differ somewhat from the DOC at 4 and 8 km, because in the heavily polluted stand the correlation between DOC and hydrogen ions in percolation water at 5 cm depth was considerably weaker than that at 20 and 40 cm. In podsolic soils, organic matter plays an important role in regulating percolation water acidity in the surface layers. Lindroos et al. (1995) reported strong correlation between DOC concentrations and pH in percolation water at 5 cm depth on similar types of site in Northern Finland, but no correlation at 20 and 40 cm. In this study, the correlations for all three depths at 4 and 8 km were very similar to those reported by Lindroos et al. (1995).

Current or earlier emissions from the smelter have resulted in a considerable increase in the fluxes of Cu, Ni, Zn and SO_4–S in throughfall at 0.5 km compared to bulk precipitation. There were also considerable increases in the flux of Ca, Mg, K and PO_4–P at the same plot. There are several possible reasons for this; the washing off of dry deposition accumulating in the tree crowns (Fowler, 1980), exchange reactions between precipitation and the foliage (Parker, 1983; Ulrich, 1983), and the accumulation of dust from the forest floor in the crowns. The last-mentioned is not an input into the ecosystem because it is derived from earlier deposition that has accumulated on the forest floor. Emissions of metals from the smelter have been substantially reduced in recent years (Fig. 1; see also Helmisaari et al., 1995), and the very low needle mass and poor growth of the stand (Mälkönen et al., 1998) mean that the capacity of the crown canopy to intercept dry deposition has been greatly reduced. Exchange between precipitation and the surviving needles may account for part of the increase in Ca and Mg. This is probably even more applicable to K, because the relative increase was even greater and closely followed the trend for foliar K concentrations (Nieminen and Helmisaari, 1996). The strong increase in PO_4–P in throughfall suggests that much of the net increase of Cu, Ni, Zn and SO_4–S in throughfall is in fact derived from dust from the forest floor. Phosphate is not normally leached from the tree crowns (Helmisaari and Mälkönen, 1989), and at a distance of 4 and 8 km in fact there is a net reduction in PO_4–P in throughfall, i.e. interception of PO_4–P. Furthermore, foliar P concentrations in the tree stand at 0.5 km were the same as those at 4 and 8 km. Phosphorus emissions from the smelter are believed to be negligible.

The assumption that the increase in PO_4–P, and therefore also of heavy metals and SO_4–S, is primarily attributable to dust from the forest floor being carried up into the tree crowns in this relatively open stand, as well as into the precipitation collectors, is further supported by the accumulation of relatively large amounts of extractable P in the organic layer at this site. The high levels of extractable P are presumably due to P emissions from the fertiliser factory, that stopped operating in 1989.

The differences in the transport of heavy metals (Cu, Ni, Zn) and alkali and alkaline earth metals (Ca, Mg, K) down to a depth of 5 cm in the soil at the plot at 0.5 km were, apart from K and Cu, in rather good agreement with the affinity of these metals for cation exchange sites. The lyotropic series depicting the preferential binding of these metals to weak cation exchangers (e.g. humus substances) is $K^+ < Mg^{2+} = Zn^{2+} < Cu^{2+} < Ni^{2+} < Ca^{2+}$ (Bohn et al., 1985). The retention of potassium in the surface layers was much greater than would be expected on the basis of its affinity for cation exchange sites. However, potassium is known to be strongly leached from crown canopies but efficiently recovered in the surface layers (Helmisaari and Mälkönen, 1989). This was fully supported by the results for the K concentrations in the mineral soil; at 0.5 km, the concentrations in the 0–5 cm layer were appreciable, but extremely low at 10–30 cm despite the high input of K into the soil in throughfall. The actual mechanism involved is not known, but potassium uptake must be considerable, despite the toxic effects of heavy metals (Gobl and Mutsch, 1985), because needle K concentrations were relatively high at this site. Copper, in turn, was more strongly retained in the 0–5 cm layer than Ni or Ca. However, Cu is known to readily form stable complexes with organic matter (Baker and Senft, 1995) and much of the Cu will therefore be bound strongly to the organic matter rather than occupying cation exchange sites. The stability of the complexes formed between heavy metals and organic matter follow the order: $Cu > Fe = Al > Mn = Co > Zn$ (Alloway, 1995). The greater mobility of Ni in the organic layer compared to Cu was supported by the results of the soil analyses, and it has also been demonstrated on the basis of the Cu/Ni ratios in the organic layer and uppermost mineral soil layers at the plots along this gradient (Derome and Lindroos, 1998b).

The large fluxes of Ca, K and especially Mg down to a depth of 5 cm at 0.5 km compared to the fluxes at 4 and 8 km indicated strong leaching of these base cations from the organic layer. This assumption was supported by the low exchangeable Ca, Mg and K concentrations in the organic and mineral soil layers at the plot 0.5 km from the smelter. According to Derome and Lindroos (1998a), the considerable reduction in the amount of base cations in the organic layer at the site at 0.5 km, and corresponding accumulation in the uppermost mineral soil layers, is due to the displacement of base cations by Cu especially.

The strong increase in the flux of NH_4–N and NO_3–N in throughfall at 0.5 km was an unexpected result. There is normally a net decrease in both NH_4–N and NO_3–N in throughfall (Hyvärinen, 1990), as was the case at 4 and 8 km. In August 1995, however, elevated pH values and relatively high NH_4–N concentrations were noted in the precipitation samples collected at 0.5 km, and this continued sporadically throughout 1996. It is now known that liquid ammonia is being used in the production of by-products at the smelter. This was reflected even more strongly in NH_4–N in throughfall at 0.5 km, as well as to some extent in the form of NO_3–N. As there was no clear trend in the amounts of NO_3–N in bulk precipitation at different distances from the smelter, it would appear that there has been some nitrification either on the needle surfaces in the tree crowns or, more likely, in the precipitation collectors. Nitrification is promoted by low acidity and high NH_4–N concentrations. Despite the low microbial activity in the surface soil and poor stand growth at 0.5 km, the relatively large flux of NH_4–N and NO_3–N passing into the soil in throughfall were efficiently scavenged from the percolation water.

5. Conclusions

The water flux on the plot closest to the smelter has presumably been drastically altered as a result of damage to the tree stand and ground vegetation. The flux of water passing down to a depth of 40 cm on this site was much greater than that on the plot located 4 km from the smelter, but the actual fluxes of Zn, Ni and Cu from the organic layer down into the mineral soil varied owing to differences in their ability to form complexes with organic matter and their affinity for cation exchange sites. The same phenomenon had a corresponding effect on the heavy metal concentrations down the soil profile. There was a clear net loss of Zn from the 40 cm-thick soil layer, i.e. the Zn output in leachate at all depths was greater than the Zn input in either bulk deposition or stand throughfall. In contrast to Zn, there was a net gain of Cu and Ni. Copper was retained more efficiently than Ni in the surface soil, presumably due to its ability to form stable complexes with organic matter. There is a possibility that Zn especially may eventually pass into the groundwater. The fluxes of Cu, Ni and Zn at 0.5 km were extremely large compared to those at 4 and 8 km. The flux of Ca, Mg, K and PO_4–P carried down to a depth of 5 cm at 0.5 km were much higher than the input, but at 40 cm there was a net loss of only Mg and K. The surface soil at all distances from the smelter retained both NH_4–N and NO_3–N extremely effectively.

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PAPER IV

Reprinted from Environmental Pollution 104, Derome, J. & Saarsalmi, A. The effect of liming and correction fertilisation on heavy metal and macronutrien concentrations in soil solution in heavy-metal polluted Scots pine stands, 249-259, Copyright 1999 with permission from Elsevier Science.

ELSEVIER

Environmental Pollution 104 (1999) 249–259

ENVIRONMENTAL
POLLUTION

The effect of liming and correction fertilisation on heavy metal and macronutrient concentrations in soil solution in heavy-metal polluted scots pine stands

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Received 30 June 1998; revised 17 September 1998; accepted 17 September 1998

Abstract

Two experiments were established in 1992 in Scots pine stands (*Pinus sylvestris* L.) on relatively infertile sites at distances of 0.5 and 8 km to the SE of the Cu–Ni smelter at Harjavalta, SW Finland, in order to investigate the effects of liming, correction fertiliser and site-specific fertiliser treatments on heavy metal and nutrient concentrations in the soil solution. Liming decreased soil solution acidity at 8 km, but increased it at 0.5 km. At 8 km liming brought about a long-term increase in the Ca and Mg concentrations, and correction fertilisation a corresponding long-term increase in the K concentrations. The situation at 0.5 km was the opposite; despite the increase immediately after application, there was a long-term reduction in the Ca concentrations as a result of the liming, and correction and stand-specific fertilisation. At 0.5 km all the treatments containing varying doses of limestone clearly decreased the Cu, Ni and Zn concentrations in soil solution during 1993–1995 compared to the control. © 1999 Elsevier Science Ltd.. All rights reserved.

Keywords: Correction fertilisation; Heavy metals; Liming; Macronutrients; Soil pollution;

1. Introduction

The contamination of forest ecosystems by heavy metals such as Cu, Ni and Zn is a serious problem in industrial areas in the northern hemisphere. A number of studies have been carried out on the detoxification and restoration of forest land in the immediate vicinity of metallurgical plants (Bingham et al., 1979; Lautenbach et al., 1994). The removal of contaminated soil is a time-consuming and expensive undertaking and, in many cases, the only viable alternative has been to use liming to convert the metals into a non-toxic form and to add fertilisers to stimulate nutrient mineralisation and to replace the plant nutrients that have been lost from the surface soil (Lautenbach et al., 1994). Liming increases soil pH, resulting in the precipitation of heavy metals and a reduction in toxic concentrations in the soil solution (Kreutzer, 1995). However, the application of excessive amounts of limestone can result in the dissolution of heavy metals from the organic layer due to the enhanced release of organic complexing agents as a result of an increase in the oxidation and complexation potentials (Göttlein, 1989). The soils close to Cu–Ni smelters also frequently suffer from a loss of base cations (Ca and Mg) as a result of their displacement by heavy metals (Derome and Lindroos, 1998) or by protons derived from acidic deposition (SO_2/H_2SO_4) (Løbersli and Steinnes, 1988). The application of Mg-rich limestone, for instance, plays a dual role; it reduces heavy metal toxicity and also replenishes the base cation pool important for counteracting soil acidification and maintaining site productivity. Many soils containing high levels of heavy metals in fact contain appreciable amounts of plant nutrients in a non-available form (Derome and Lindroos, 1998).

Microbial activity is severely depressed by the toxic effects of heavy metals (Fritze et al., 1989) and there is often an accumulation of forest litter owing to the inhibition of nutrient mineralisation (Rühling and Tyler, 1974). The purpose of fertilising such sites is thus to provide the tree stand and other vegetation with a temporary supply of nutrients that will enable them to survive up until the point where there has been a recovery

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PII: S0269-7491(98)00183-3

in microbial activity and nutrient mineralisation. A number of studies have been carried out on the use of fertilisers in both a fast- and slow-release form (Aarnio et al., 1995). However, measures of this sort do not permanently rectify the problem, and the only long-term solution presupposes strong reductions in heavy metal emissions and eventual removal of the accumulated heavy metals from affected sites.

The Cu–Ni smelter unit has been operating in Harjavalta, SW Finland, since 1945. Although emissions of SO_2 and heavy metals from the smelter have been considerably reduced in recent years (Helmisaari et al., 1995), the long-term accumulation of pollutants has had a considerable effect on Scots pine stands in the vicinity of the smelter (Laaksovirta and Silvola, 1975; Fritze et al., 1989; Heliövaara and Väisänen, 1989; Helmisaari et al., 1995).

The aims of this study were to determine the extent to which (1) the fast- and slow-release components of the fertilisers are carried down into the root layer of the soil, (2) liming decreases the concentrations of toxic copper, nickel and zinc in the soil solution, (3) correction fertilisers increase the Ca, Mg, K and P concentrations in the soil solution, and (4) liming causes the displacement and leaching of heavy metals from the surface soil of a heavy-metal saturated pine stand.

2. Material and methods

In June 1992 two liming and correction fertilisation experiments were established in pure Scots pine (*Pinus sylvestris* L.) stands located at distances of 0.5 and 8 km from the Cu–Ni smelter at Harjavalta (61°19′ N, 22°9′ E), SW Finland. The experiments were located on relatively infertile sites located along an esker running to the SE of the smelter. The ground vegetation on the plot at 0.5 km was almost completely destroyed (Salemaa and Vanha-Majamaa, 1993), and the pine stand suffering from retarded growth and severe needle loss. The stand located at 8 km appeared to be relatively unaffected. The average thickness of the organic layer at 0.5 km was 3 cm and at 8 km 1 cm, and the underlying mineral soil consisted of sorted fine sand. The soil type was orthic podzol. Despite the SO_2 emissions from the smelter, there were no signs of increased soil acidity at either of the sites. The chemical properties of the organic and uppermost mineral soil layers are presented in Table 1 (see Derome and Lindroos (1998) for details of the sampling and analytical procedures).

The liming and fertiliser treatments (Table 2) were applied on 30 × 30 m plots using a random design with three repetitions of each treatment. The liming treatment (LT) consisted of Mg-rich (5%) granulated limestone and a small amount of boron. Forest soils in inland parts of Scandinavia are relatively boron deficient (Lipas et al., 1983), and if limestone is applied then boron is necessary to prevent short-root and mycorrhizal mortality (Lehto, 1994) and to minimise subsequent growth losses (Lipas, 1990). The correction fertiliser (CF) consisted of slow-release powdered minerals (10% apatite, 20% calcium and magnesium carbonate, 60% biotite) and a mixture of fast-release, water-soluble salts. The fertiliser also contained small amounts of Cu and Zn. The composition of the site-specific fertiliser (SSF) was determined on the basis of needle and soil analyses (Mälkönen et al., 1997). The stand at the experiment located 0.5 km from the smelter had low foliar N and Ca and extremely low Mg concentrations (Table 3), and the organic layer had extremely low exchangeable Ca and Mg concentrations (Table 1). Nitrogen was given in the form of slow-release methylene urea and fast-release ammonium nitrate, and Ca and Mg as Mg-rich granulated limestone. At 8 km only the foliar N concentrations were low, and the SSF treatment was therefore a slightly smaller dose of nitrogen fertiliser.

Table 1
pH, base saturation (BS), exchangeable acidity (EA), cation exchange capacity (CEC) and exchangeable Ca, Mg, K and Al in the organic layer and 0–5, 5–10 and 10–20 cm mineral soil layers (MS) in the experiments located 0.5 and 8 km from the smelter (sampling prior to liming or fertilisation)

Soil layer	pH	BS (%)	EA (meq kg^{-1})	CEC (meq kg^{-1})	Ca_{exc} (mg kg^{-1})	Mg_{exc} (mg kg^{-1})	K_{exc} (mg kg^{-1})	Al_{exc} (mg kg^{-1})
Organic layer								
0.5 km	3.53	10.9[a]	90.6	170	285[a]	25.6[a]	78[a]	181[a]
8 km	3.60	40.8[a]	84.7	146	862[a]	78.5[a]	282[a]	327[a]
MS, 0–5 cm								
0.5 km	3.83	10.9	15.5[a]	23.7	41.3[a]	3.99	12.4	66[a]
8 km	3.84	12.5	24.4[a]	25.8	12.4[a]	3.93	11.8	182[a]
MS, 5–10 cm								
0.5 km	3.89[a]	7.1	20.1	22.3[a]	13.4[a]	1.98	5.9[a]	63[a]
8 km	4.20[a]	6.8	14.4	15.0[a]	3.35[a]	2.42	13.0[a]	114[a]
MS, 10–20 cm								
0.5 km	4.02[a]	10.1	11.8[a]	13.3[a]	9.14[a]	1.66	5.47	88[a]
8 km	4.35[a]	17.1	5.0[a]	5.3[a]	1.66[a]	1.09	7.22	38[a]

Values marked with the same letter differ significantly ($p < 0.05$) from each other. (Derome and Lindroos, 1998).

Table 2
The liming and fertiliser treatments used in the experiments. MU = methylene urea, AN = ammonium nitrate

Treatment	Nutrient application (kg ha^{-1})								
	N	P	K	Ca	Mg	S	B	Cu	Zn
Control	–	–	–	–	–	–	–	–	–
Liming (LT)	–	–	–	420	100	–	2	–	–
Correction fertiliser (CF)	–	31	56	98	61	37	1.3	0.8	0.8
Stand-specific fertiliser (SSF):									
0.5 km	75 (MU) 75 (AN)	–	–	315	50	–	–	–	–
8 km	60 (MU) 60 (AN)	–	–	–	–	–	–	–	–

Zero-tension lysimeters were installed on one plot representing each treatment in the two experiments in June 1992. Twelve lysimeters ($d = 20$ cm) were located systematically on each plot at a depth of 20 cm measured from the ground surface. The construction and installation of the lysimeters and sampling technique are described in detail in Derome et al. (1991). Precipitation in the open and on the plots inside the stand were measured during 1992–1996 (see Derome and Nieminen, 1998, for details of the sampling procedures).

Soil solution samples were collected at 1-month intervals during the snowfree period from June 1992 to December 1996. Samples from the same plot were combined. The pH was measured, and the remaining part of the samples filtered (0.45 μm membrane filter). Calcium, Mg, K, Cu, Ni and Zn were determined by inductively coupled atomic emission spectrophotometry (ICP/AES), and NH_4–N, NO_3–N, SO_4–S and PO_4–P by ion chromatography (IC).

Table 3
Mean element concentrations in the needles and needle dry weight in the pine stands before fertilisation in the experiments located 0.5 and 8 km from the smelter (sampled in January 1992)

Element	0.5 km	8 km
N, g kg^{-1}	11.3^{a} (0.24)	12.4^{a} (0.15)
P	1.59 (0.03)	1.50 (0.03)
K	4.87 (0.08)	4.92 (0.07)
Ca	1.42^{a} (0.06)	1.94^{a} (0.06)
Mg	0.56^{a} (0.02)	0.98^{a} (0.02)
S	1.32^{a} (0.04)	1.09^{a} (0.02)
Mn, mg kg^{-1}	153^{a} (7)	304^{a} (10)
Cu	167^{a} (8)	10.8^{a} (0.3)
Zn	84.8^{a} (2.7)	59.5^{a} (1.3)
Fe	890^{a} (30)	61.4^{a} (1.2)
B	19.5^{a} (0.6)	13.0^{a} (0.5)
Al	188^{a} (6)	445^{a} (14)
Dry weight, mg/needle	8.3^{a} (0.4)	12.5^{a} (0.4)

The standard error of the mean is given in parentheses. Values marked with the same letter differ significantly ($p < 0.001$) from each other. (Mälkönen et al., 1997).

3. Results

3.1. *Acidity and heavy metal and macronutrient concentrations in the soil solution*

Liming at a dose of 2000 kg ha^{-1} decreased soil solution pH at 0.5 km, but increased it at 8 km (Fig. 1). The CF treatment included limestone (140 kg dolomite ha^{-1}), but this increased pH only during the first year after application at 0.5 km, and not at all at 8 km. The SSF treatment at 0.5 km also included limestone (1500 kg dolomite ha^{-1}), and this increased pH to the same extent in 1993 as the CF treatment.

The Cu and Ni concentrations in the soil solution on the control plot at 0.5 km were more than 100 times higher than those at 8 km, and the Zn concentrations about 10 times higher (Fig. 2). There was an increase in the Cu and especially Zn concentrations on the control plot at 0.5 km towards the end of the monitoring period (1995–1996).

Immediately after application of the CF treatment there was a sharp increase in the Cu and Zn concentrations at both 0.5 and 8 km. The SSF treatment, which did not contain Cu or Zn also caused a similar, short-term increase in the Cu, Ni and Zn concentrations at both distances. All of the treatments at 0.5 km contained varying doses of limestone, and clearly decreased the Cu, Ni and Zn concentrations during 1993–1995. The treatments had no systematic effects on the extremely low Cu, Ni and Zn concentrations at 8 km.

The Ca and Mg concentrations in the soil solution on the control plots at 0.5 km were almost double those at 8 km (Fig. 3). The K concentrations, on the other hand were about the same. The treatments at both 0.5 and 8 km strongly increased the Ca, Mg and K concentrations during the year of application. The LT treatment at 8 km brought about a long-term increase in the Ca and Mg concentrations, and the CF treatment a corresponding long-term increase in the K concentrations. At

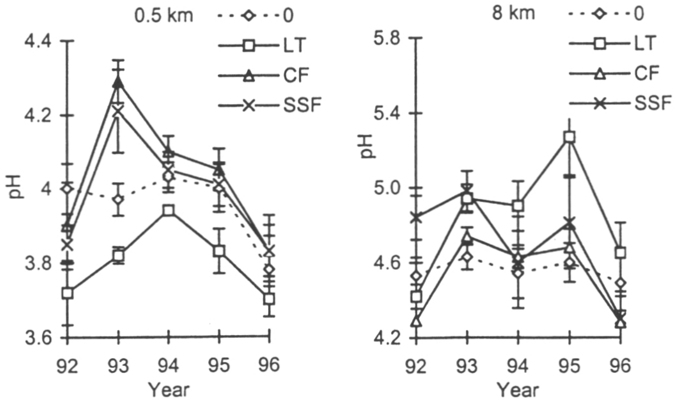

Fig. 1. Effect of liming (LT), correction fertilisation (CF) and stand-specific fertilisation (SSF) on the pH of the soil solution at a depth of 20 cm at a distance of 0.5 and 8 km from the Harjavalta smelter during 1992–1996. O = control. The bars indicate the standard error of the mean, *n* varying from 7 to 9 depending on the number of sampling times in the respective years.

0.5 km, the SSF treatment resulted in a long-term increase in the Mg concentrations, while the LT, CF and SSF treatments produced a clear long-term reduction in the Ca concentrations.

The PO_4–P concentrations on the control plots at 0.5 and 8 km were rather similar (Fig. 4). At 0.5 km, all the treatments increased the PO_4–P concentrations irrespective of whether they contained P. At 8 km the treatments had no significant effect on the PO_4–P concentrations.

The mean SO_4–S concentration at the plot at 0.5 km was more than three times higher than that at 8 km (Fig. 4). All the treatments, apart from SSF at 8 km, strongly increased the SO_4–S concentrations at both 0.5 and 8 km in the year of application. In the last year of the experiment there was a strong increase in the soil solution SO_4–S concentrations in all three treatments at 0.5 km compared to the control plot.

The NH_4–N and NO_3–N concentrations on the control plots at 0.5 and 8 km were extremely low, below 0.05 mg l^{-1} (Fig. 5). The SSF treatment resulted in very high NH_4–N and NO_3–N concentrations at 0.5 and 8 km during the year the treatment was applied. Liming also resulted in relatively high NH_4–N and NO_3–N concentrations at both sites during the treatment year. There were no differences between the NH_4–N and NO_3–N concentrations on the control and treated plots in subsequent years at 8 km. In 1996 there was a sharp increase in the NH_4–N and NO_3–N concentrations on all the plots, irrespective of the treatment, at 0.5 km.

3.2. Amounts of water, macronutrients and Cu, Ni and Zn passing down to 20 cm depth

Precipitation in the open and stand throughfall at distances of 0.5 and 8 km were very similar (Table 4). In contrast, the amounts of percolation water collected at a depth of 20 cm on the individual plots at both 0.5 and 8 km varied considerably. The average amount of percolation water collected on the four plots at 0.5 km was about 22% of stand throughfall, and on the plots at 8 km only about 10%.

The amounts of Ca, Mg, K, NH_4–N, NO_3–N, PO_4–P, SO_4–S, Cu, Ni and Zn passing down to a depth of 20 cm on the control plot at 0.5 km were much greater than those at 8 km; more than 15-fold for NO_3–N, 5-fold for Ca, NH_4–N and SO_4–N, 3-fold for Mg, and 2-fold for K and PO_4–P (Table 5). However, the total amount of percolation water collected on the control plot at 0.5 km was only about 1.5 times that on the control plot at 8 km.

The increase in the amount of Ca passing down to a depth of 20 cm on the plot treated with 2 t/ha of Mg-rich limestone was relatively similar in both of the experiments, the proportion of added Ca being 0.8% and 0.6%, respectively (Table 5). For Mg, on the other hand, the amount of Mg at 0.5 km was almost 3-fold that at 8 km; 9% and 3.2%, respectively. At 0.5 km liming reduced the amounts of Cu and Ni carried to a depth of 20 cm to 67% and 85% of the amounts on the control plot, despite the fact that the amount of percolation water on the limed plot was in fact almost 60% greater than that on the control. Liming had no effect on the amount of Zn.

None of the Ca added in the correction fertiliser mixture passed down to a depth of 20 cm at either 0.5 or 8 km (Table 5). In contrast, some Mg was carried down to 20 cm at both sites, the amount at 0.5 km being more than double that at 8 km. The proportion of the added K passing down to 20 cm was very high (22%) at 0.5 km. 62% of the total amount of K added was in the form of fast-release K fertiliser (KCl), and the amount of K passing down to 20 cm was thus equivalent to about 35% of the fast-release K fertiliser. Only a very small proportion of the P added passed down to a depth

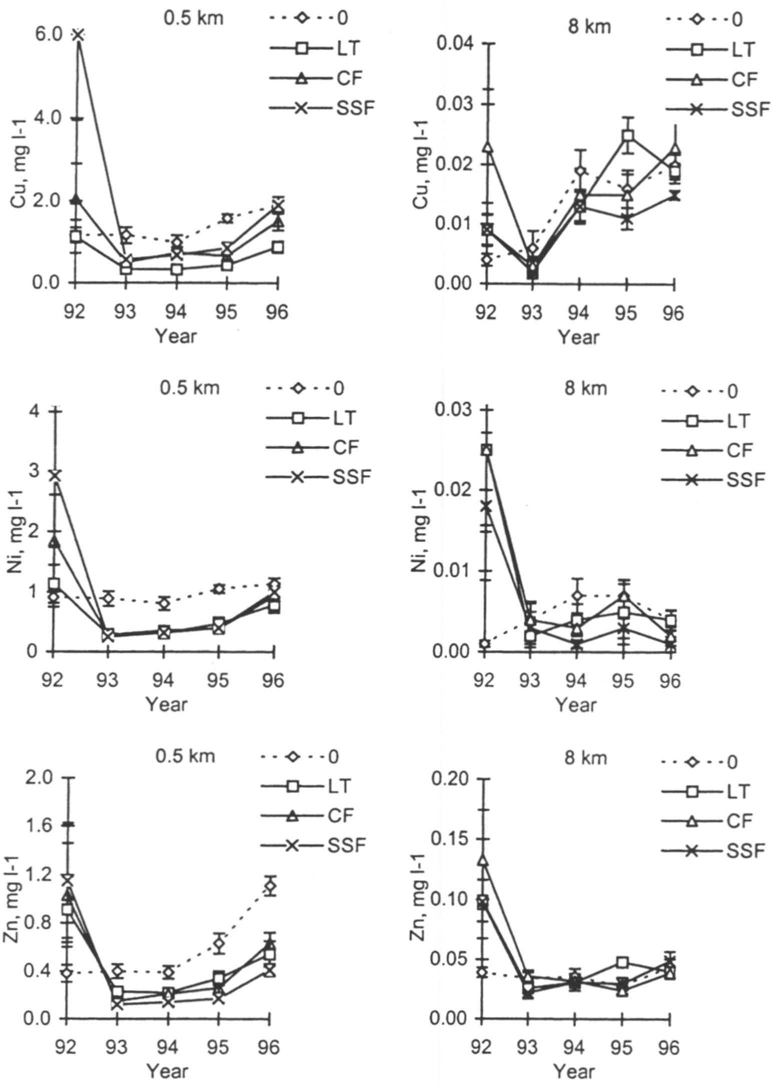

Fig. 2. Effect of liming (LT), correction fertilisation (CF) and stand-specific fertilisation (SSF) on the Cu, Ni and Zn concentrations in the soil solution at a depth of 20 cm at a distance of 0.5 and 8 km from the Harjavalta smelter during 1992–1996. O = control. The bars indicate the standard error of the mean, *n* varying from 7 to 9 depending on the number of sampling times in the respective years.

of 20 cm at 0.5 km, and none of the P at 8 km. The amount of S passing down to 20 cm at 0.5 km was about 50% of the amount added in the fertiliser at 0.5 km, but only about 7% of that at 8 km. At 0.5 km, the correction fertiliser decreased the amount of Cu carried down to 20 cm by about 14%, Ni by about 25%, and Zn by about 25%. The amount of percolation water on the CF plot at 0.5 km was about 13% greater than that on the control. At 8 km the correction fertiliser had no effect on the amount of Cu, Ni or Zn in the percolation water, despite the fact that the fertiliser contained 0.8 kg ha^{-1} of both Cu and Zn.

The site-specific fertilisation treatment used in the stand at 0.5 km included Mg-rich limestone (Table 5). About 10% of the Ca added reached a depth of 20 cm, but for Mg the corresponding value was about 35%.

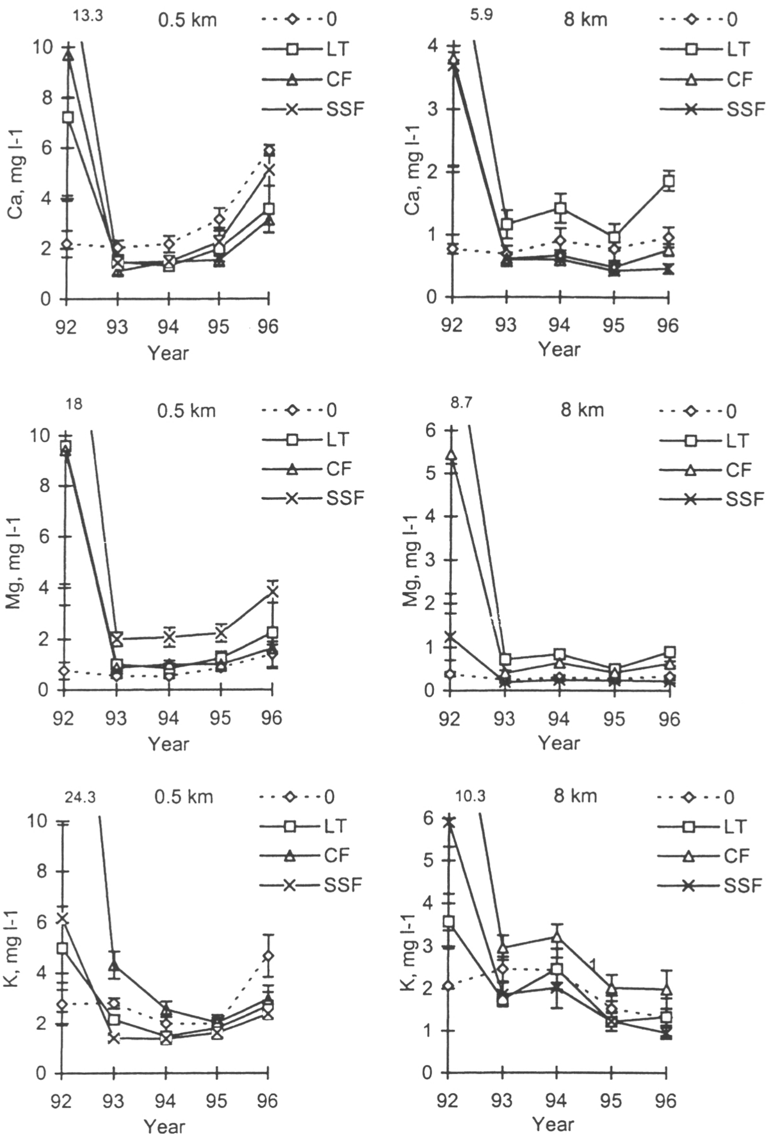

Fig. 3. Effect of liming (LT), correction fertilisation (CF) and stand-specific fertilisation (SSF) on the Ca, Mg and K concentrations in the soil solution at a depth of 20 cm at a distance of 0.5 and 8 km from the Harjavalta smelter during 1992–1996. O = control. The bars indicate the standard error of the mean, *n* varying from 7 to 9 depending on the number of sampling times in the respective years.

One third of the nitrogen fertiliser, calculated as total N, added at 0.5 km reached a depth of 20 cm, but almost none at 8 km. The SSF treatment at 0.5 km strongly increased the amounts of Ni and especially Cu in the percolation water.

4. Discussion

The organic layer in the stand closest to the smelter is strongly deficient in exchangeable Ca, Mg and K, but contains considerable amounts of Ca, Mg and K in an

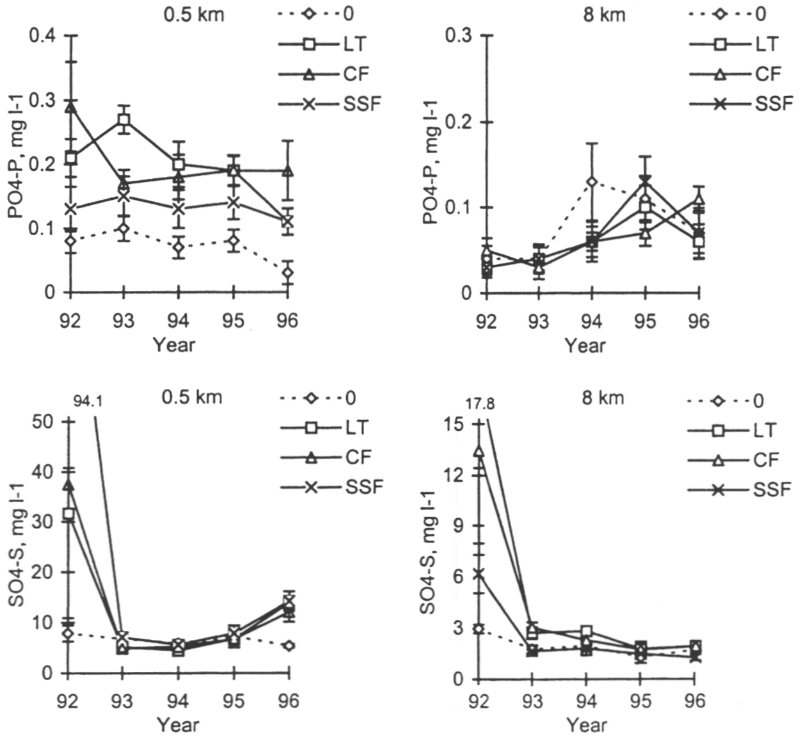

Fig. 4. Effect of liming (LT), correction fertilisation (CF) and stand-specific fertilisation (SSF) on the PO_4–P and SO_4–S concentrations in the soil solution at a depth of 20 cm at a distance of 0.5 and 8 km from the Harjavalta smelter during 1992–1996. O = control. The bars indicate the standard error of the mean, *n* varying from 7 to 9 depending on the number of sampling times in the respective years.

unavailable form (Derome and Lindroos, 1998). The underlying mineral soil, in contrast, contains high concentrations of exchangeable Ca, and relatively normal levels of Mg and K. The organic layer also has elevated concentrations of total and exchangeable P (Derome and Lindroos, 1998). The accumulation of toxic levels of heavy metals (primarily Cu, Ni, Zn) has resulted in severe inhibition of decomposition activity in this layer (Fritze et al., 1996), nutrient uptake by the roots and mycorrhizas has been strongly reduced (Baes and McLaughlin, 1987; Colpaert and Van Assche, 1992), and exchangeable Ca, Mg and K displaced from the organic layer (Derome and Lindroos, 1998).

The effect of the liming treatments on soil solution acidity was different at the two sites; soil solution acidity decreased considerably at 8 km, but increased at 0.5 km. In contrast, the correction fertiliser and stand-specific fertiliser treatments, which at 0.5 km contained smaller amounts of limestone, slightly decreased acidity in the year following application. A short-term increase in soil solution acidity following liming has also been reported by Nohrstedt (1992). According to Derome and Lindroos (1998), aluminium and to some extent protons have been displaced by heavy metals from the organic and 0–10 cm mineral layers at 0.5 km, and there is accumulation of both aluminium and exchangeable acidity in the 10–20 cm layer. The decrease in the exchangeable Al concentrations in the uppermost soil layers was also reflected in the depressed foliar Al concentrations.

At 0.5 km all three treatments clearly decreased Ca concentrations at 20 cm, apart from the year when the treatments were applied. Nohrstedt (1992) also reported a decrease in soil solution Ca concentrations at a depth of 50 cm following application of 1000 kg ha^{-1} of limestone. The initial input of Ca^{2+} derived from the treatments may have displaced some of the relatively abundant protons and aluminium on the exchange sites in the 10–20 cm mineral soil layer, resulting in reduced Ca concentrations and higher acidity in the soil

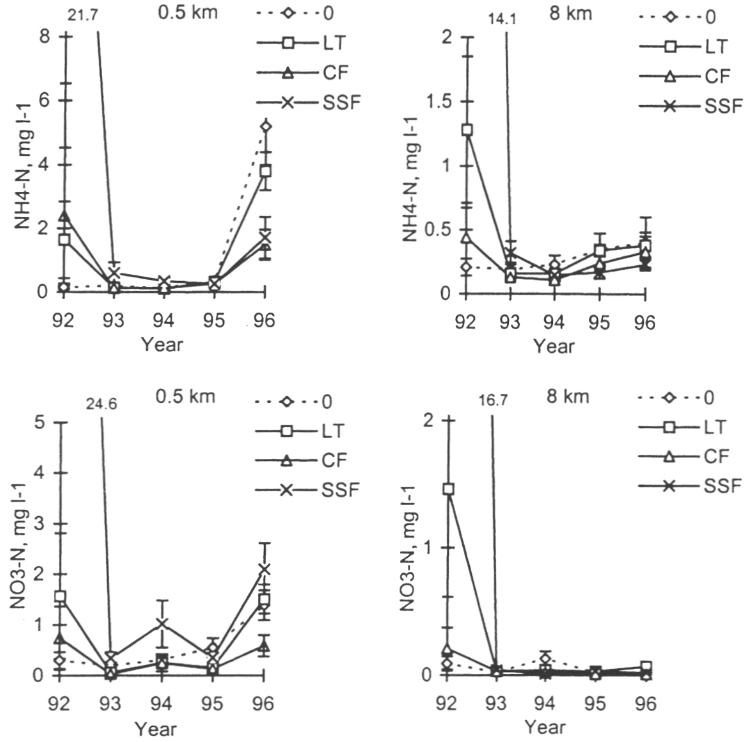

Fig. 5. Effect of liming (LT), correction fertilisation (CF) and stand-specific fertilisation (SSF) on the NH_4–N and NO_3–N concentrations in soil solution at a depth of 20 cm at a distance of 0.5 and 8 km from the Harjavalta smelter during 1992–1996. O = control. The bars indicate the standard error of the mean, *n* varying from 7 to 9 depending on the number of sampling times in the respective years.

solution. This conclusion is to some extent supported by the fact that the situation at 8 km was quite the opposite; the liming treatments reduced soil solution acidity and increased Ca concentrations. The positive growth response of the tree stand at 0.5 km given by the liming and stand-specific fertiliser treatments and the increase in foliar Ca concentrations (Mälkönen et al., 1997), indicates that there has been a considerable recovery in nutrient uptake by the tree stand. Increased nutrient uptake could also contribute to the decrease in soil solution Ca concentrations and increased soil solution acidity (Nilsson et al., 1982).

Table 4
Mean annual precipitation, stand throughfall and amounts of percolation water collected at a depth of 20 cm during the period 1992–1996 on the plots given different fertiliser treatments at a distance of 0.5 and 8 km from the smelter

Distance, (km) Treatment	0.5	8
	Amount of water, (l m^{-2})	
Precipitation in the open	436	442
Stand throughfall (control plot only)	412	404
Percolation water:		
Control	74	54
Liming	113	48
Correction fertilisation	84	41
Stand-specific fertilisation	91	28

Despite a temporary increase in the Cu, Ni and Zn concentrations in soil solution at a depth of 20 cm during the treatment year at 0.5 km, all three treatments subsequently decreased the concentrations of these three heavy metals. The treatment with the highest dose of limestone (2 t ha^{-1}) had the longest-lasting effect. The correction fertiliser treatment contained small amounts of Cu and Zn (0.8 kg ha^{-1} each), but the main reason for the short-term increase in these three heavy metals was undoubtedly displacement of Cu, Ni and Zn from cation exchange sites by the large amount of base cations (Ca, Mg, K) released into the soil solution following dissolution of the limestone and fertilisers. A flush of non-fertiliser cations in soil solution has earlier been reported following fertiliser application (Matzner et al., 1983). The treatments had no clear effects on the very low Cu, Ni or Zn concentrations at 8 km.

The correction fertiliser contained Ca, Mg and K in both a fast- and slow-release form. The fast-release

Table 5
Total amounts of Ca, Mg, K, NH_4–N, NO_3–N, PO_4–P, Cu, Ni and Zn carried down to a depth of 20 cm in percolation water during the period 1992–1996 following the different treatments on the plots located at 0.5 and 8 km from the smelter. Proportion of added nutrients refers to the difference between the treated and control plots, expressed as a percentage of the amount of nutrients added. O = control, LT = liming, CF = correction fertiliser, SSF = site-specific fertiliser

Treatment	Ca (kg ha^{-1})	Mg (kg ha^{-1})	K (kg ha^{-1})	Tot–N (kg ha^{-1})	NH_4–N (kg ha^{-1})	NO_3–N (kg ha^{-1})	PO_4–P (kg ha^{-1})	SO_4!–S (kg ha^{-1})	Cu (kg ha^{-1})	Ni (kg ha^{-1})	Zn (kg ha^{-1})
0.5 km											
O	10.8	2.9	8.9	9.9	3.6	2.1	0.3	23.5	4.6	3.5	2.2
LT	14.0	11.9	12.4	13.1	4.4	2.7	1.1	53.3	3.1	3.0	2.3
CF	10.2	7.6	21.3	8.2	2.6	1.1	0.9	41.6	4.0	2.6	1.6
SSF	20.1	24.6	11.5	59.9	23.6	26.8	0.6	118	8.4	4.2	1.8
8 km											
O	2.2	0.8	4.8	3.1	0.5	0.1	0.2	4.5	0.03	0.01	0.10
LT	4.7	4.0	4.2	3.6	0.8	0.6	0.1	8.5	0.03	0.03	0.10
CF	2.1	2.3	7.0	2.2	0.4	0.1	0.1	7.3	0.03	0.01	0.09
SSF	1.0	0.4	2.4	4.4	1.3	1.3	0.1	2.1	0.01	0.00	0.05
Proportion of added nutrients (%)											
0.5 km											
LT	0.8	9.0									
CF	0.0	7.5	22			2.0	49				
SSF	9.5	36		33							
8 km											
LT	0.6	3.2									
CF	0.0	2.5	4.0			0.0	7.4				
SSF				1.1							

component was clearly evident as a strong peak in the Ca and Mg concentrations at both 0.5 and 8 km, and in the K concentration at 8 km during the same year as application. The slow-release component at 8 km appeared to have increased the Ca, Mg and K throughout the 5-year study period. The soil solution at a depth of 20 cm is still within the reach of the tree roots, and hence slightly elevated concentrations at this depth do not necessarily indicate a risk of leaching losses.

All the treatments increased the PO_4–P concentration at 0.5 km, despite the fact that only the correction fertiliser contained any P. The organic layer at this site contains elevated levels of total P (Derome and Lindroos, 1998), primarily due to the depressed rate of litter decomposition (Fritze et al., 1996), and it is highly likely that both liming and the stand-specific fertiliser treatment have had a promoting effect on P mineralisation in the organic layer. At 8 km, in contrast, none of the treatments had any effect on PO_4–P concentrations in the soil solution at 20 cm.

The stand-specific fertiliser produced a large peak in the NH_4–N and NO_3–N concentrations in the soil solution at 0.5 and 8 km in the same year as application; this was clearly derived from the fast-release ammonium nitrate component (75 and 60 kg/ha, respectively) in the fertiliser. The slow-release component, methylene urea (60 kg/ha), had no effect on the NH_4–N and NO_3–N concentrations during the last four years of the study. According to Martikainen et al. (1989), methylene urea produces elevated soil NH_4–N concentrations in the laboratory for at least two years, without the formation of NO_3–N, and the effect can persist in the soil for 7–14 years after application. The fact that the NH_4–N concentrations in the soil solution did not increase during the 2–5-year period after application suggests that the NH_4–N released from the methylene urea was efficiently utilised by the tree stand. The liming treatment resulted in slightly elevated NH_4–N and NO_3–N concentrations at both sites. This suggests that the increased Mg and Ca concentrations and elevated pH values in the organic layer caused by liming has had a short-term stimulating effect on both N mineralisation and nitrification (Tamm and Petersson, 1969).

The dissolution of the limestone and the slow-release components of the fertilisers depends on the particle size of the minerals and the amount and acidity of the precipitation (Kreutzer, 1995). In this respect, the sites at 0.5 and 8 km were almost identical (Derome and Nieminen, 1998). Precipitation in the open and stand throughfall were very similar, but the amount of water passing to a depth of 20 cm at 0.5 km appeared to be about 1.5 times greater than at 8 km. This was due to the lower canopy coverage of the tree stand, almost total destruction of the ground vegetation (Salemaa and Vanha-Majamaa, 1993) and lower water-holding capacity of the thick undecomposed litter layer (Derome and Nieminen, 1998) at the site closest to the smelter.

The liming and correction fertiliser treatments both markedly decreased the amounts of Cu and Ni carried down to a depth of 20 cm at 0.5 km, and for Zn only in the case of the correction fertiliser treatment. There are two processes associated with these treatments that have opposite effects on the mobility and movement of the heavy metals down the soil profile. The high pH values resulting from the addition of limestone will decrease the amounts of metals in the soil solution through precipitation, while the increase in SO_4–S concentrations associated with correction fertilisation especially will increase the likelihood of them being transported in the percolation water. Nickel, for instance, forms a soluble complex with sulphate ($NiSO_4^0$) (Sposito and Page, 1984). The stand-specific treatment at 0.5 km, in contrast, strongly increased the amount of Cu and Ni carried down to a depth of 20 cm, despite the fact that it included limestone. However, this treatment involved the addition of relatively large amounts of nitrate, and strongly increased the amounts of sulphate in the soil solution. The reducing effect of the limestone application in this treatment on Cu and Ni at 0.5 km was presumably outweighed by the presence of very large amounts of anions that increased the mobility of Cu and Ni.

There were clear differences between the two sites with respect to the proportions of added Ca, Mg, K, PO_4–P, SO_4–S and total N carried down to a depth of 20 cm. Although this could reflect differences in the rate of dissolution of the fast- and slow-release components of the fertilisers at the two sites, more likely explanations include the greater amounts of percolation water transporting the anions and cations down the soil profile at 0.5 km, the saturation of the cation exchange sites in the organic layer with Cu, Ni, Zn and other heavy metals (Derome and Lindroos, 1998), thus reducing base cation absorption, the presence of large amounts of accumulated SO_4–S in the surface soil layers, and the addition of relatively large amounts of anions (sulphate, nitrate, phosphate) in the fertilisers.

The proportions of the three base cations carried down to 20 cm followed the order Ca < Mg < K at both sites (see also Derome and Nieminen, 1998). This can be explained on the basis of their mobility, i.e. varying affinity for cation exchange sites. Mg is known to have a lower affinity for cation exchange sites than Ca, and K a lower affinity than Mg (Bohn et al., 1985). The greater mobility of Mg and K at the site at 0.5 km has presumably been further promoted by the high SO_4–S concentrations, derived from deposition from the smelter, present in the surface soil and soil water. The downward movement of cations in podsolic soils is normally strongly limited by the low concentrations of inorganic anions in the soil solution (Krug and Frink, 1983). A relatively high proportion of the N added as ammonium or nitrate in the stand-specific treatment was carried down to a depth of 20 cm at 0.5 km. However, this does not necessarily mean a reduced supply of N to the tree stand at 0.5 km, because this treatment increased the foliar N concentrations already during the growing season following application, and has given a considerable increase in tree growth at both sites (Mälkönen et al., 1997). The proportion of P added in the correction fertiliser treatment passing down to 20 cm was very small at 0.5 km and negligible at 8 km.

5. Conclusions

The fast-release components in the correction fertiliser and stand-specific fertiliser increased the supply of macronutrients to the tree stand already during the year of application. The dissolution of the slow-release components in the correction fertiliser also ensured an increased supply of Ca, Mg and K throughout the course of the study at the site 8 km from the smelter, but not at 0.5 km. In contrast, the effects of slow-release methylene urea were not reflected in the NH_4–N and NO_3–N concentrations in the soil solution, presumably due to efficient uptake by the trees of these growth-limiting nitrogen compounds.

Apart from an initial increase in the year of application, liming at all three doses strongly decreased the Cu, Ni and Zn concentrations in the soil solution at the severely contaminated site for the following three years at least. The largest liming dose used in this study, 2000 kg ha^{-1}, thus did not increase the risk of heavy metals being displaced and carried down into the ground water.

The increase in macronutrient concentrations and decrease in heavy metal concentrations in the soil solution resulting from the treatments suggest that the application of macronutrients and liming agents is the major cause of the recovery of the severely affected pine stand located only 0.5 km from the smelter, and that liming together with correction fertilisation provides an effective means of increasing the capacity of pine stands to withstand heavy-metal pollution.

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PAPER V

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Environmental Pollution 107 (2000) 79–88

ENVIRONMENTAL
POLLUTION

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Detoxification and amelioration of heavy-metal contaminated forest soils by means of liming and fertilisation

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Received 21 January 1999; accepted 18 May 1999

Abstract

Four experiments were established in 1992 in Scots pine stands (*Pinus sylvestris* L.) on relatively infertile sites at distances of 0.5, 2, 4 and 8 km to the south-east of the Cu–Ni smelter at Harjavalta, south-west Finland, in order to investigate the effects of liming, correction fertiliser and site-specific fertiliser treatments on heavy metal (Cu, Ni) and macronutrient (Ca, Mg, K) availability in the organic layer. The organic layer samples were analysed for total, plant-available ($BaCl_2$ + EDTA) and water-extractable Ca, Mg, K, Cu and Ni. A high proportion of the Cu and Ni at 0.5 km was in a non-toxic, immobilised form. Liming had only a relatively small reducing effect on free and exchangeable Cu and Ni concentrations at 0.5 km. The lack of pH increase following liming may be due to the precipitation of Fe, present in very high concentrations close to the smelter, as $Fe(OH)_3$, resulting in the loss of neutralising bicarbonate and hydroxyl ions, but the release of Ca and Mg. Liming strongly increased Ca and Mg availability. The correction fertiliser had no effect on Ca or K availability at any of the sites. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Detoxification; Liming; Fertilisation; Copper; Nickel

1. Introduction

Heavy-metal polluted soils have for long been recognised as a serious problem in industrialised parts of Western Europe (Alloway, 1995) and North America (Hutchinson and Whitby, 1977), and it has recently become apparent that the problems in Eastern Europe and Russia are in many cases even more extensive (Kozlov et al., 1993). In heavily polluted areas of this sort there are usually two main forest damage zones (Tikkanen and Niemelä, 1995): an industrial barren zone relatively close to the point emission source where the tree and ground vegetation are completely destroyed, and an outer zone where the vegetation is progressively suffering from serious damage but is capable, if emissions are drastically reduced, of slow recovery. Promising results have been obtained in Sudbury, Canada, in the detoxification and restoration of land that is completely deforested as a result of heavy metal deposition from the Cu–Ni smelter (Winterhalder, 1983). The main emphasis in restoring the industrial barren area has been to treat the soil with limestone and P fertiliser, and to establish a vegetation cover of grasses and shrubs, on which a cover of broad-leaved trees gradually develops (Lautenbach et al., 1995). In areas where the tree stand is less severely damaged the measures are designed to restore nutrient imbalances and to improve the vitality of the tree stand. The tree stands usually suffer from shortages of Ca and Mg (Raitio, 1992; Mälkönen et al., 1999) as a result of soil acidification (Løbersli and Steinnes, 1988) or the displacement of base cations from the organic layer by heavy metals (Derome and Lindroos, 1998). Liming has proved to be an appropriate measure for reducing heavy-metal toxicity and stimulating litter decomposition (Fritze et al., 1996). Nitrogen is the main mineral nutrient restricting tree growth in the boreal coniferous forest zone (Mälkönen et al., 1990), and there is usually a shortage of available nitrogen in heavy-metal polluted soils owing to the inhibitory effect of heavy metals on microbial activity (Fritze et al., 1989). The purpose of liming and fertilising such sites with Ca, Mg and N is thus to provide the tree stand and other vegetation with a temporary supply of nutrients that will enable them to

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PII: S0269-7491(99)00132-3

survive up until the point where there has been a recovery in microbial activity and nutrient mineralisation.

The aims of this study were to determine: (1) whether liming decreases the toxic concentrations of exchangeable Cu, Ni and Zn in the soil; and (2) the extent to which liming and slow-release mineral fertilisers can alleviate the shortage of Ca, Mg and K concentrations in the organic layer of pine stands along a heavy-metal deposition gradient near the Cu–Ni smelter at Harjavalta, south-west Finland.

2. Materials and methods

Four liming and correction fertiliser experiments were established in Scots pine (*Pinus sylvestris* L.) stands located at distances of 0.5, 2, 4 and 8 km along a line running to the south-east of the Harjavalta Cu–Ni smelter (61°19′N, 22°9′E), south-west Finland. Emissions from the smelter primarily comprise Cu, Ni, Zn and SO_2 (Helmisaari et al., 1995), and in recent years they have been strongly reduced (Derome and Nieminen, 1998). The forest site type varied from the *Vaccinium* to the *Calluna* type (dry to dryish sites, relatively infertile; for the Finnish forest type classification see Cajander, 1949). The ground vegetation in the stand at 0.5 km was almost completely destroyed (Salemaa and Vanha-Majamaa, 1993), and the pine stand suffering from retarded growth and severe needle loss (Mälkönen et al., 1999). The soil in the stands consisted of sorted fine sand (coarse/fine sand at 2 km) and is classified as orthic podzol. The thickness of the organic layer varied from 1 to 3 cm. Despite the SO_2 emissions from the smelter, there were no signs of increased soil acidity close to the smelter (Derome and Lindroos, 1998). However, the organic layer at 0.5 km especially was suffering from a strong deficit of base cations, and consequently low base saturation (BS) values, but the uppermost mineral soil layer at this site had strongly elevated base cation concentrations.

The liming and fertiliser treatments were applied on 30×30 m plots using a random design with three repetitions of each treatment at 0.5, 2 and 8 km and four replications at 4 km. The liming treatment (LT) consisted of Mg-rich (5%) granulated limestone (2000 kg/ha) and a small amount of boron (2 kg/ha). The correction fertiliser (CF) consisted of slow-release powdered minerals (apatite 100 kg/ha, calcium/magnesium carbonate 200 kg/ha, biotite 600 kg/ha) and a mixture of fast-release, water-soluble salts. The fertiliser also contained small amounts of Cu (0.8 kg/ha) and Zn (0.8 kg/ha). The amounts of individual macro- and micronutrients applied are given in Derome and Saarsalmi (1999)). The composition of the site-specific fertiliser (SSF) was determined on the basis of needle and soil analyses (Mälkönen et al., 1999). The stand at the experiment located 0.5 km from the smelter had low foliar N and Ca and extremely low Mg concentrations (Derome and Saarsalmi, 1999), and the organic layer had extremely low exchangeable Ca and Mg concentrations (Derome and Lindroos, 1998). Nitrogen (150 kg/ha) was given in the form of slow-release methylene urea and fast-release ammonium nitrate, and Ca and Mg as Mg-rich granulated limestone (1500 kg/ha). The stands at 2 and 4 km were given nitrogen (150 kg/ha) and limestone (1000 kg/ha), and the stand at 4 km also received phosphate (31 kg/ha). At 8 km only the foliar N concentrations were low, and the SSF treatment was, therefore, a slightly smaller dose of N fertiliser (120 kg/ha) only.

Soil samples were taken from all the plots in the four experiments in October, 1996, 4.5 years after the treatments had been applied. Organic layer samples were taken at 25 points on each plot in all four experiments. The samples were combined to give one composite sample per plot, and then air-dried. The samples were milled to pass through a 1-mm sieve. pH was determined in water (15 ml sample/25 ml water).

Total Ca, Mg, K, Cu, Ni and Zn were determined from the samples by dry ashing at 550°C, extracting the ash with concentrated HCl, and then analysing the solutions by inductively coupled plasma atomic emission spectrometry (ICP/AES). Plant-available Ca, Mg, K, Cu, Ni and Al were determined by extraction with 0.1 M barium chloride + 2% EDTA (7.5 g sample/150 ml extractant, shaking for 2 h), followed by analysis by ICP/AES, and exchangeable acidity by titration to pH 7. As the Na form of EDTA was used in this study, this meant that Na could not be included in the CEC calculations. Water-extractable (free) Ca, Mg, K, Cu and Ni were determined by extraction with 0.01M NaCl (7.5 g sample/150 ml extractant, shaking for 2 h), followed by analysis by ICP/AES.

The immobilised Ca, Mg, K, Cu and Ni concentrations in the organic layer were calculated as the difference between total concentrations and plant-available concentrations ($BaCl_2$ + EDTA). Exchangeable Ca, Mg, K, Cu and Ni concentrations in the organic layer were calculated as the difference between plant-available concentrations and water-extractable concentrations. This was done because it was assumed that a considerable amount of these elements would still be present in the soil solution in the organic layer on the plots given the fertilisers and limestone, and not only bound on the cation exchange sites. Cation exchange capacity (CEC) was calculated by the summation method (Hendershot and Duquette, 1986) as the sum of the equivalent concentrations of exchangeable Ca, Mg, K, Cu and Ni and exchangeable acidity. CEC values for the mineral soil layers were based directly on the concentrations obtained using $BaCl_2$ + EDTA. Cu and Ni were included because they are known to be present in high concentrations in the organic layer at the plots closest to the smelter, and it was therefore assumed that they would also occupy a significant proportion of the cation exchange sites (Derome and Lindroos, 1998). The results were calculated as average values for the 2–3 replicates of each treatment in the individual experiments. The differences between the experiments were tested for each parameter separately using variance analysis, and the statistical differences by the Tukey test.

3. Results

3.1. *Cation exchange capacity (CEC_{eff}) and acidity parameters*

None of the treatments had a statistically significant effect on CEC_{eff} (Table 1). All the treatments, apart from the SSF treatment at 8 km, contained varying amounts of limestone. There was no significant correlation between CEC_{eff} and pH at 0.5 km for all the treatments combined, but at 2 and 8 km the correlation was highly significant (Table 1), and at 4 km significant. The relatively large limestone applications (LT, SSF) significantly ($p < 0.05$) increased the BS in the organic layer at all distances from the smelter (Table 2), while the CF treatment increased BS significantly only at 4 and 8 km. The correlation between pH and BS was extremely high at 2, 4 and 8 km (Table 1), but much lower at 0.5 km.

The pH of the organic layer on the plots given treatments containing relatively large amounts of limestone (LT, SSF) was greater than that on the controls at all four distances (Table 2). However, the increase was statistically significant ($p < 0.05$) only in the experiments located at 4 and 8 km, apart from a strong increase at 0.5 km with the SSF treatment, and there appeared to be no clear relationship between the increase in pH and the amount of limestone added at 0.5 and 2 km.

At 0.5 km none of the liming treatments had a significant effect on exchangeable acidity, and at 2 km only the largest dose of limestone significantly reduced exchangeable acidity (Table 2). At 4 and 8 km both of the large limestone applications (LT, SSF) significantly decreased exchangeable acidity. The correlation between pH and exchangeable acidity was extremely high at 2, 4 and 8 km (Table 1), but somewhat lower at 0.5 km.

Table 1
Correlation between pH (H_2O) and effective cation exchange capacity (CEC_{eff}), base saturation (BS), and exchangeable acidity (EA) and exchangeable Al (Al_{exc}) concentrations in the organic layer 4.5 years after the treatments at different distances from the Harjavalta smelter. The treatments at each distance are combined[a]

	Distance from the smelter (km)			
	0.5 ($n = 12$)	2 ($n = 12$)	4 ($n = 16$)	8 ($n = 12$)
CEC_{eff}	−0.028	0.742^{***}	0.545^{*}	0.872^{***}
BS	0.788^{**}	0.970^{***}	0.952^{***}	0.974^{***}
EA	-0.840^{**}	-0.981^{***}	-0.971^{***}	-0.936^{***}
Al_{exc}	-0.815^{*}	-0.980^{***}	-0.951^{***}	-0.958^{***}

[a] Statistical significance, $* = p < 0.05$; $** = p < 0.01$; $*** = p < 0.001$.

Table 2
Effect of liming and fertilisation on the effective cation exchange capacity (CEC_{eff}), base saturation (BS), pH and exchangeable acidity (EA) and exchangeable Al concentrations in the organic layer 4.5 years after the treatments at different distances from the Harjavalta smelter[a]

	Distance from the smelter (km)			
	0.5	2	4	8
CEC_{eff} (meq/kg dw)				
O	170	227	153	220
LT	285	381	219	258
CF	178	279	180	226
SSF	117	290	150	145
BS (%)				
O	9.7	55.7	35.5	37.7
LT	51.2^{*}	91.2^{*}	87.4^{*}	94.9^{*}
CF	11.6	58.3	47.7^{*}	55.2^{*}
SSF	57.0^{*}	76.2^{*}	79.0^{*}	37.4
pH (H_2O)				
O	3.57	3.78	3.11	3.20
LT	3.87	4.44	4.08^{*}	4.45^{*}
CF	3.69	3.82	3.37^{*}	3.40
SSF	4.25^{*}	4.08	3.80^{*}	3.23
EA (meq/kg dw)				
O	96.1	87.5	108.8	71.5
LT	71.1	26.4^{*}	30.8^{*}	14.3^{*}
CF	85.3	77.1	88.2	66.1^{*}
SSF	55.1	50.7	44.1^{*}	89.3
Exchangeable Al (mg/kg dw)				
O	158	252	411	238
LT	153	42	85^{*}	17^{*}
CF	159	233	314	230
SSF	74	128	147^{*}	282

[a] O, control; LT, liming; CF, correction fertilisation; SSF, stand-specific fertilisation.

*Statistically significant ($p < 0.05$) difference compared to the control.

None of the liming treatments had any effect on exchangeable Al at 0.5 and 2 km, but there was a significant decrease in exchangeable Al at both 4 and 8 km (Table 2). The correlation between pH and exchangeable Al was extremely high at 2, 4 and 8 km (Table 1), but much lower at 0.5 km.

The increase in the proportion of base cations out of CEC brought about the liming treatments (LT and SSF) at 0.5 km occurred primarily at the expense of H^+ and Cu^{2+} (Fig. 1), the proportions of Al^{3+} and Ni^{2+} being affected only slightly. At this distance the correction

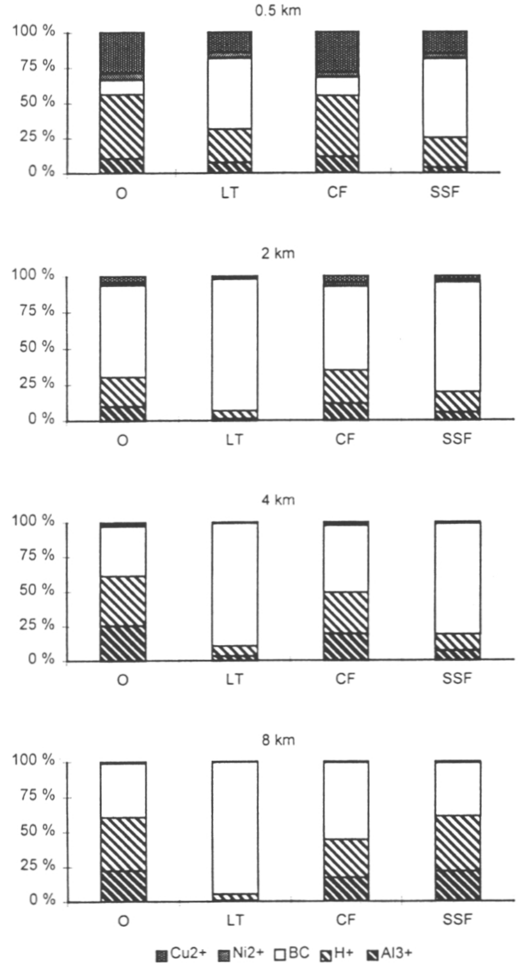

Fig. 1. Relative distribution (as % of cation exchange capacity) of Cu^{2+}, Ni^{2+}, base cations (BC = Ca^{2+}, Mg^{2+}, K^{+}), hydrogen ions (H^{+}) and Al^{3+} occupying cation exchange sites in the organic layer 4.5 years after the treatments at distances of 0.5, 2, 4 and 8 km from the Harjavalta Cu–Ni smelter. O, control; LT, liming; CF, correction fertilisation; SSF, site-specific fertilisation.

Table 3
Effect of liming and fertilisation on the plant-available Ca, Mg, K, Cu and Ni concentrations in the organic layer 4.5 years after the treatments at different distances from the Harjavalta smelter[a]

	Distance from the smelter (km)			
	0.5	2	4	8
Ca (mg/kg dw)				
O	391	3479	1248	879
LT	2343*	6929	4745*	5381*
CF	453	2606	1752	1593
SSF	2526*	3878	3443*	1062
Mg (mg/kg dw)				
O	44	291	140	107
LT	285*	561	507*	491*
CF	48	273	259	223*
SSF	261*	442	419*	120
K (mg/kg dw)				
O	101	428	432	334
LT	123	447	401	319
CF	88	478	498	435
SSF	119	398	455	456
Cu (mg/kg dw)				
O	1740	409	111	14.3
LT	1113	117	35.5*	2.0*
CF	1541	353	98.3	14.7
SSF	1176	223	54.0*	21.0
Ni (mg/kg dw)				
O	308	201	76.3	22.7
LT	203	144	52.3	15.3*
CF	187	173	76.5	25.3
SSF	238	149	56.5	29.7

[a] O, control; LT, liming; CF, correction fertilisation; SSF, stand-specific fertilisation.

*Statistically significant ($p < 0.05$) difference compared to the corresponding component on the control.

fertiliser had no affect on the distribution of cations. In contrast, the situation at 2, 4 and 8 km was somewhat different since both H^{+} and Al^{3+} were strongly reduced by these two treatments (SSF at 8 km did not include limestone).

3.2. *Macronutrient and heavy metal concentrations*

The relatively large limestone applications (LT, SSF) significantly increased the concentrations of plant-available Ca and Mg in the organic layer at all distances apart from 2 km from the smelter (Table 3). The CF treatment had no significant effect on the Ca or Mg concentrations at any of the distances, apart from Mg at 8 km. None of the treatments had an effect on the K concentrations at any distance.

Although in general the plant-available Cu and Ni concentrations on the treated plots were lower than those on the control plots, the difference was only significant for Cu at 4 and 8 km on those plots given the larger doses of limestone, and for Ni only at 8 km.

3.3. *Distribution of Ca, Mg, K, Cu and Ni into immobilised, exchangeable and free forms*

3.3.1. *Calcium*

On the control plots the total Ca concentrations in the organic layer were very similar at 0.5, 4 and 8 km, but much higher at 2 km (Fig. 2). The distribution of Ca at 0.5 km differed clearly from that at the other three sites in that a relatively high proportion of the Ca was in an immobilised form; 66% compared to 17, 2 and 1% at 2, 4 and 8 km, respectively. The corresponding proportions for exchangeable Ca were 26, 76, 86 and 88%. The proportion of free Ca was extremely low at all distances.

The LT significantly ($p < 0.05$) increased the concentration of exchangeable and free Ca compared to the control at all distances. The Cf treatment had no effect on the free and exchangeable Ca concentrations, apart from a significant ($p < 0.05$) increase in free Ca concentration at 8 km. The varying amounts of limestone included in the stand-specific treatment (SSF) at 0.5, 2 and 4 km significantly ($p < 0.05$) increased the exchangeable Ca concentration at 0.5 and 4 km, and the free Ca concentration at all three sites.

3.3.2. *Magnesium*

The two sites at 0.5 and 2 km had considerably higher total Mg concentrations in the organic layer than those at 4 and 8 km (Fig. 3). An extremely high proportion of the Mg at 0.5 km was in an immobilised form; 94% compared to 62, 37 and 46% at 2, 4 and 8 km, respectively. The corresponding proportions for exchangeable Mg were much lower than those for Ca; 3, 30, 40 and 36%. The proportion of free Mg was extremely low at 0.5 and 2 km, but over 20% at 4 and 8 km.

The Mg-rich LT significantly ($p < 0.05$) increased the concentration of exchangeable and free Mg compared to the control at all distances, except for exchangeable Mg at 2 km. The CF treatment increased the exchangeable Mg concentration only at 8 km, and significantly

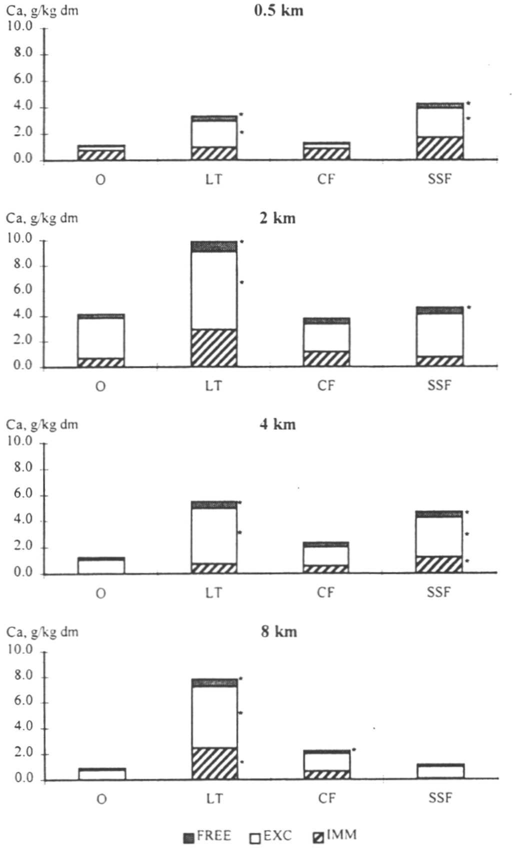

Fig. 2. Distribution of total Ca into immobilised (IMM), exchangeable (EXC) and free forms in the organic layer 4.5 years after the treatments at distances of 0.5, 2, 4 and 8 km from the Harjavalta Cu–Ni smelter. O, control; LT, liming; CF, correction fertilisation; SSF, site-specific fertilisation. The asterisk indicates a statistically significant ($p < 0.05$) difference compared to the corresponding component on the control plots.

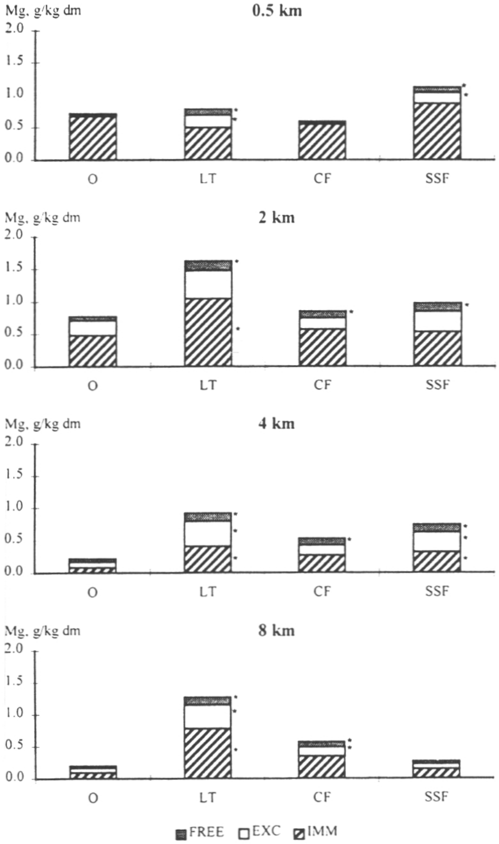

Fig. 3. Distribution of total Mg into immobilised (IMM), exchangeable (EXC) and free forms in the organic layer 4.5 years after the treatments at distances of 0.5, 2, 4 and 8 km from the Harjavalta Cu–Ni smelter. O, control; LT, liming; CF, correction fertilisation; SSF, site-specific fertilisation. The asterisk indicates a statistically significant ($p < 0.05$) difference compared to the corresponding component on the control plots.

($p < 0.05$) increased the free Mg concentration at 2, 4 and 8 km. The varying amounts of Mg-rich limestone included in the stand-specific treatment (SSF) given at 0.5, 2 and 4 km significantly ($p < 0.05$) increased the exchangeable Mg concentration at 0.5 and 4 km, and the free Mg concentration at all three sites.

3.3.3. *Potassium*

On the control plots the total K concentrations in the organic layer varied between 400 and 600 mg/kg at the four sites, with the highest value at 2 km and the lowest at 8 km (Fig. 4). The distribution of K into different components at 0.5 km was very different from that at the other three sites because almost all the K was in an immobilised and free form. Immobilised K at 0.5 km accounted for 80% of the total K compared to 29, 11 and 18% at 2, 4 and 8 km, respectively. The corresponding proportions for free K were 16, 53, 69 and 66%, but only 4, 17, 20 and 15% for exchangeable K.

The only treatment involving the addition of K fertiliser was the CF, but this had no significant effect on exchangeable or free K concentrations at any distance. The LT and SSF treatments had no effect on the partition of K between immobilised, exchangeable and free forms, apart from the significant decrease in immobilised K given by liming at 0.5 km.

3.3.4. *Copper and nickel*

There was a clear increasing gradient in the total Cu and Ni concentrations in the organic layer on the control plots with decreasing distance to the smelter (Figs. 5 and 6). The proportion of Cu in an immobilised form

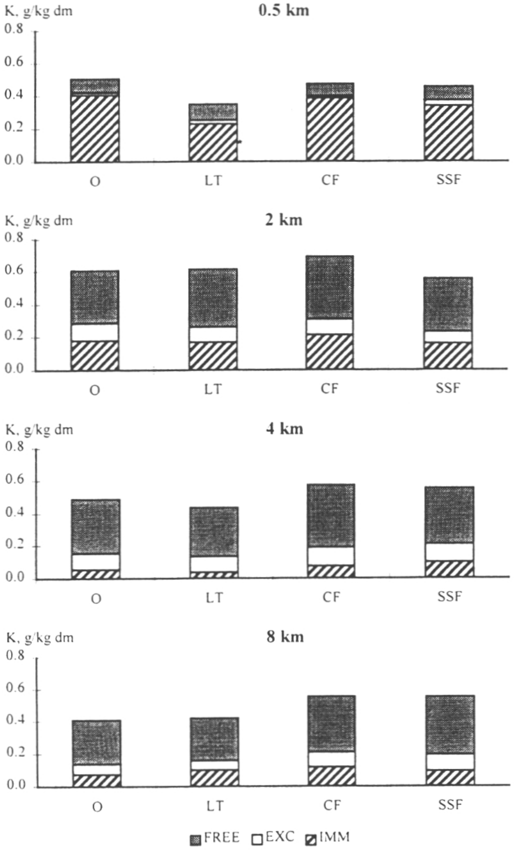

Fig. 4. Distribution of total K into immobilised (IMM), exchangeable (EXC) and free forms in the organic layer 4.5 years after the treatments at distances of 0.5, 2, 4 and 8 km from the Harjavalta Cu–Ni smelter. O, control; LT, liming; CF, correction fertilisation; SSF, site-specific fertilisation. The asterisk indicates a statistically significant ($p < 0.05$) difference compared to the corresponding component on the control plots.

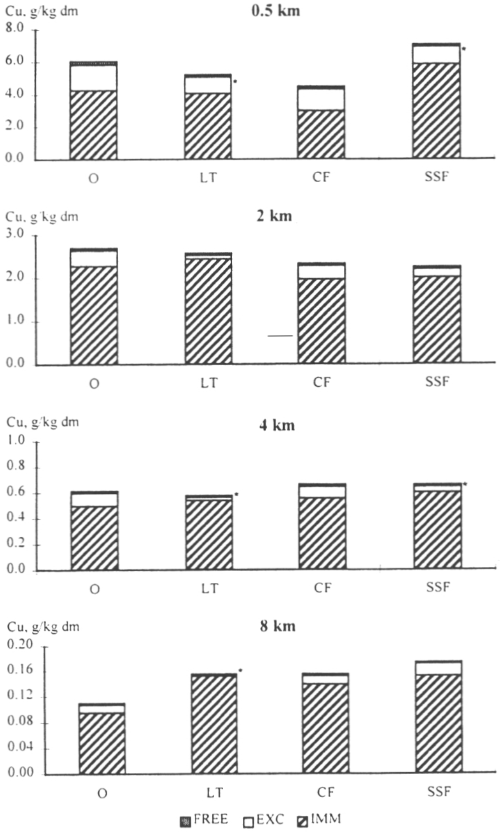

Fig. 5. Distribution of total Cu into immobilised (IMM), exchangeable (EXC) and free forms in the organic layer 4.5 years after the treatments at distances of 0.5, 2, 4 and 8 km from the Harjavalta Cu–Ni smelter. O, control; LT, liming; CF, correction fertilisation; SSF, site-specific fertilisation. The asterisk indicates a statistically significant ($p < 0.05$) difference compared to the corresponding component on the control plots. Note the different scales on the y axis.

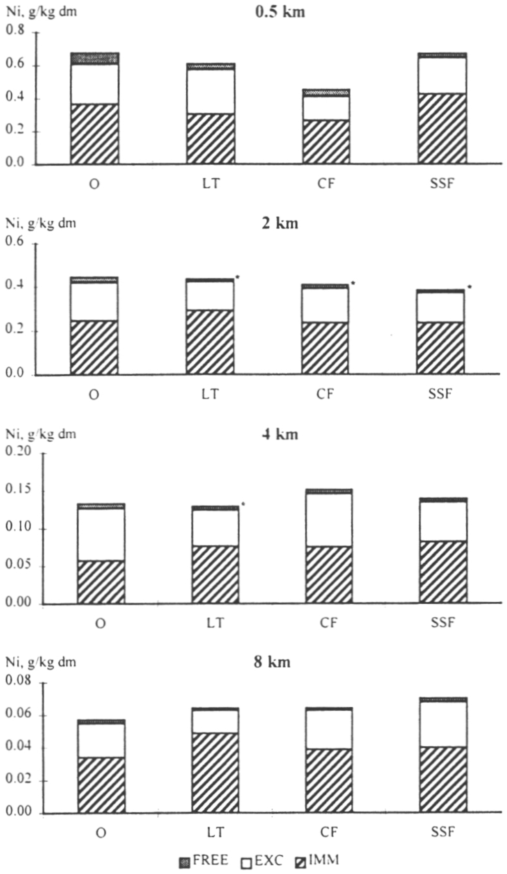

Fig. 6. Distribution of total Ni into immobilised (IMM), exchangeable (EXC) and free forms in the organic layer 4.5 years after the treatments at distances of 0.5, 2, 4 and 8 km from the Harjavalta Cu–Ni smelter. O, control; LT, liming; CF, correction fertilisation; SSF, site-specific fertilisation. The asterisk indicates a statistically significant ($p < 0.05$) difference compared to the corresponding component on the control plots. Note the different scales on the y axis.

was much greater than that of Ni (81 compared to 53%), and the proportion of exchangeable Cu correspondingly smaller (17 compared to 41%). Only 2–5% of the total amount of Cu and Ni was in a free form. The relative proportions of the different components of Cu and Ni were surprisingly constant at all four distances, irrespective of the great differences in concentrations.

The LT significantly ($p < 0.05$) reduced the exchangeable Cu concentration at 0.5, 4 and 8 km. The same treatment reduced significantly ($p < 0.05$) the free Cu concentration at 0.5 km, but not any of the other sites. The SSF treatment at 4 km, which included liming, significantly ($p < 0.05$) reduced the exchangeable Cu concentrations only at 0.5 and 4 km. The CF treatment had no significant effect on exchangeable or free Cu at any of the sites.

Overall, the effect of the treatments on the Ni concentrations was much smaller than that for Cu, since there was no statistically significant change in the exchangeable Ni concentrations at any of the sites. In contrast to Cu, however, the free Ni concentrations were reduced significantly ($p < 0.05$) by all three treatments at 2 km, and by the LT treatment at 4 km.

4. Discussion

The amounts of limestone used in the three treatments varied considerably: 200 kg/ha in the correction fertilisation, 1000–1500 kg/ha in the stand-specific fertilisation (not applied at 8 km) and 2000 kg/ha in the liming treatment. Liming had only a relatively small effect on acidity parameters in the organic layer at 0.5 km compared to the situation at 4 and 8 km, and at 2 km the effects were restricted to an increase in BS and a decrease in exchangeable acidity. The results obtained at 4 and 8 km were in agreement with those reported for forest liming in stands located in areas not subjected to heavy-metal deposition (Derome et al., 1986; Nihlgård et al., 1988; Kreutzer, 1995). There was a strong increase in pH and base saturation, and a corresponding strong decrease in exchangeable acidity and exchangeable Al concentrations. In contrast to the results of an earlier study on the same series of experiments (Fritze et al., 1996), the increase in the CEC_{eff} of the organic layer as a result of liming was not statistically significant. However, the low number of treatment replications (3–4) was presumably too small to account for the natural variation between the plots in the same experiment. Furthermore, in this study CEC_{eff} was calculated by first subtracting the water-soluble base cation concentrations from the cation concentrations given by $BaCl_2 + EDTA$ extraction in order to obtain the actual exchangeable base cation concentrations, and hence a more reliable but lower estimate of CEC_{eff}. The use of this procedure was verified by the significant increase in water-extractable Ca and Mg following liming. As this procedure was not followed in the study reported by Fritze et al. (1996), their CEC_{eff} values are probably considerable over-estimates of the effect of liming on CEC_{eff}.

The effects of the LT proper on the acidity parameters in the organic layer at 0.5 km were only slight and, in a number of respects, rather contradictory. There was a strong increase in BS, but no effect on pH or on the exchangeable acidity or exchangeable Al concentrations. In contrast, the SSF treatment, which included 1500 kg limestone/ha, strongly increased pH, as well as BS. The correlations between pH and BS, exchangeable acidity and exchangeable Al in all the treatments at 0.5 km were much weaker than those at 2, 4 or 8 km. These parameters are normally strongly correlated with pH (Nihlgård et al., 1988). These rather conflicting results for the effects of the LT and SSF treatments on the acidity properties of the organic layer at 0.5 km are supported by the results for the effects of the LT and SSF treatments on soil solution pH and Ca concentrations at a depth of 20 cm observed in a study carried out on the same experiment at 0.5 km (Derome and Saarsalmi, 1999). Following a strong increase in the Ca concentrations in the soil solution during the first year after application of the treatments, there has been a long-term significant decrease in the Ca and Mg concentrations and pH of the soil solution on the LT plot, but no effect on the SSF plot.

The experiment at 0.5 km differs considerably from those at 2, 4 and 8 km: at 0.5 km the flux of water down the soil profile is considerably greater (Derome and Nieminen, 1998), and there are very high concentrations of total Fe in the organic layer (Derome and Lindroos, 1998). These two features could have a strong effect on the dissolution and neutralising behaviour of the limestone. The dissolution of Mg-rich limestone takes place as follows:

$$CaMg(CO_3)_2 + 2H_2O \Longleftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- + 2OH^-$$

The total Fe concentrations in the organic layer are extremely high, up to 2%, (Derome and Lindroos, 1998), the Fe presumably being in the form of $Fe_2(SO_4)_3$. In the presence of high levels of Fe^{3+} the following reaction will also occur:

$$Fe^{3+} + HCO_3^- + 2OH^- \Longleftrightarrow Fe(OH)_3 \downarrow + CO_2 \uparrow$$

In other words, Fe will be precipitated and, at the same time, a considerable proportion of the neutralising capacity of the limestone will be consumed. In addition to Fe, there is also considerable accumulation of other heavy metals (e.g. Cu, Ni, Zn) in the organic layer (Derome and Lindroos, 1998), and they will correspondingly react with the HCO_3^- and OH^- ions and be precipitated. Thus, in the presence of large amounts of Fe (and other heavy metals), we can expect that the dissolution and neutralisation of limestone will result in the release of Ca and Mg, but have little acidity reducing effect on the surrounding organic layer. In waterway liming experiments carried out in Finland and Sweden, there have been problems with the inactivation of limestone gravel placed in stream beds in order to neutralise the stream water running into lakes and other waterways from forested areas (Vähänäkki, 1994). The limestone rapidly becomes covered in a film of precipitated iron that prevents dissolution of the limestone and inactivates its neutralising effect.

The almost total destruction of the ground vegetation (Salemaa and Vanha-Majamaa, 1993) at 0.5 km has resulted in a high proportion of the water falling as throughfall passing down to a depth of at least 5 cm in the soil (Derome and Nieminen, 1998). The forest floor is covered in a layer of dry, undecomposed plant litter (Fritze et al., 1989) and the microbiological activity of the whole organic layer is severely depressed (Fritze et al., 1996). As a result, the water holding capacity of the organic layer appears to be considerably reduced, and there will be less chemical interactions between precipitation and the fertilisers/liming agents, and hence smaller effects on the chemical properties of the organic layer. Furthermore, the amount of water passing down to 20 cm during the 5-year study on the LT plot was almost 50% greater than that on the SSF plot (Derome and Saarsalmi, 1999). This will have also had an effect on the rate of dissolution of the limestone and other fertilisers.

The sequence of events on the LT plots at 0.5 km following liming could be explained as follows: following gradual dissolution of the limestone, Ca and Mg have been released into the soil solution, but the released neutralising ions have been almost completely consumed through the precipitation of Fe and other heavy metals. As a result of the decreased water-holding capacity, there has been less interaction between the limestone and the surface organic layer, and the released Ca and Mg have been carried down deep into the organic layer, where they have displaced hydrogen ions from the cation exchange sites, increasing BS. The displaced hydrogen ions have, in turn, been carried down into the mineral soil, reducing percolation water pH, e.g. at 20 cm depth. Similar pulses of hydrogen ions following liming have been reported in other studies (e.g. Nohrstedt, 1992).

This appears to hold true on the LT plots, but not on those given the SSF treatment, in which liming, at a dose of 1500 kg/ha, was given together with nitrogen fertiliser (NH_4NO_3). On these plots, the water flux was relatively similar to that on the control plots (Derome and Saarsalmi, 1999), suggesting that moisture has been retained more effectively in the organic layer and that there has been more interaction between the organic matter and the limestone. The effect of the precipitation of Fe and other heavy metals in reducing the pH increase has presumably been less, and there has also been a greater increase in BS. The chemical analyses carried out in this study do not permit conclusions to be drawn about the role played by the addition of NH_4NO_3, which is a rather hydroscopic salt, on the dissolution and chemical reactions of the limestone.

Although liming has considerably decreased the concentrations of Cu and Ni in the soil solution at 20 cm at

0.5 km especially (Derome and Saarsalmi, 1999), it only marginally decreased the free and exchangeable Cu concentrations in the organic layer, and had almost no effect on the Ni concentrations. The main reason for this appears to be the relatively weak effect of liming on soil acidity at this site. However, liming has also had only negligible effects on Cu and Ni concentrations in the organic layer at greater distances from the smelter, even though at these sites liming had a relatively strong effect on the pH of the organic layer. The total, exchangeable and free Cu and Ni concentrations in the organic layer at the site at 0.5 km were extremely high, and so even a slight increase in the concentrations of toxic forms of Cu and Ni are likely to be important from the point of view of the soil micro-organisms and root development.

Liming strongly increased Ca and Mg availability in the organic layer at 0.5 km especially, as well as at greater distances from the smelter. There were clear shortages of these two important macronutrients in the organic layer, and it would appear that this increase in plant-available Ca and Mg has contributed to the partial recovery of microbial activity (Fritze et al., 1996) and stand growth on the site at 0.5 km (Mälkönen et al., 1999). Deficiencies of Ca and Mg can, under certain conditions, restrict tree growth. In contrast, the correction fertiliser had no effects on available Ca and Mg concentrations at 0.5 km, but an increasing effect with increasing distance from the smelter. Similarly, the free K concentrations increased, but not significantly, at all distances apart from 0.5 km. In this respect, the correction fertiliser had only minor short-term effects on the macronutrient status of the organic layer, although it has rather strongly increased Ca, Mg and K concentrations in the soil solution at 0.5 km (Derome and Saarsalmi, 1999). This is not a surprising result, because most of the Ca, Mg and K in the correction fertiliser was in the form of slow-release components, and only a relatively small proportion as water-soluble salts.

5. Conclusions

A high proportion of the Cu and Ni that has accumulated in the organic layer at a distance of 0.5 km from the smelter was in a non-toxic, immobilised form, and the concentration of exchangeable Cu and Ni much higher than free forms of these metals. Liming had only a relatively small reducing effect on the high concentrations of free and exchangeable Cu and Ni at a distance of 0.5 km from the smelter, as well as at 2, 4 and 8 km. One reason for this may be the absence of the normal increase in pH following liming, due to the precipitation of Fe, present in very high concentrations in the organic layer close to the smelter, as $Fe(OH)_3$. This would result in the loss of neutralising bicarbonate and hydroxyl ions, but the release of Ca and Mg into the soil. Another possible contributing factor is the strong increase in the amount of water percolating down the soil profile, resulting in a drier organic layer, lower rate of limestone dissolution, and less interactions between the dissolved limestone and surrounding organic matter.

Liming strongly increased Ca and Mg availability in the organic layer and has undoubtedly helped to alleviate the severe deficiency of Ca and Mg in the organic layer. The correction fertiliser, consisting of a mixture of finely ground minerals and readily soluble salts, had no effect on Ca or K availability at any of the sites during the 5-year course of the study, but significantly increased Mg availability at distances greater than 0.5 km from the smelter. The amounts of readily soluble Ca, Mg and K were rather small compared to the amounts already present in the organic layer, and hence these addition are not likely to be seen in e.g. exchangeable Ca, Mg and K concentrations. The correction fertiliser was primarily intended as a long-term measure, and the effects of this treatment will presumably start to become evident in the organic layer after a much longer period of time.

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Hakapaino 2000

ISBN 951-40-1729-3 ISSN 0358-4283