

Response of Scots pine (*Pinus sylvestris* L.) to a long-term Cu and Ni exposure

Tiina Maileena Nieminen

Finnish Forest Research Institute
Vantaa Research Centre

Plant biology
Department of Biological and Environmental Sciences
Faculty of Biosciences
University of Helsinki

Academic dissertation

To be presented, with permission of the Faculty of Biosciences,
University of Helsinki, for public criticism in Auditorium I of Metsätalo,
Unioninkatu 40 B, on the 17th of June 2005, at 12 o'clock noon.

Helsinki 2005

Supervisor: Docent Heljä-Sisko Helmisaari
Finnish Forest Research Institute
Vantaa, Finland

Reviewers: Dr. Lage Bringmark
Department of Environmental Assessment
Swedish University of Agricultural Sciences
Uppsala, Sweden

Docent Kari Laine
Thule Institute
University of Oulu
Oulu, Finland

Examiner: Professor Nicholas M. Dickinson
Biological & Earth Sciences
Liverpool John Moores University
Liverpool, U.K.

Publisher: Finnish Forest Research Institute, Vantaa Research Centre,
P.O. Box 18, FIN-01301 Vantaa, Finland

Accepted by Kari Mielikäinen, Research Director, 2.5.2005.

Front cover: Experimental pine seedlings cultivated in metal- polluted soil cores
sampled at different distances from a Cu-Ni smelter. Photo: Erkki Oksanen.

ISBN 951-40-1963-6 (printed version)
ISSN 0358-4283
Helsinki 2005
Painopaikka Vammalan Kirjapaino Oy, 2005

ISBN 952-10-2481-X (PDF version)
<http://ethesis.helsinki.fi/>
Helsinki 2005
Helsingin yliopiston verkkojulkaisut

Contents

List of Original Publications	5
Abstract	6
1 Introduction	7
1.1 Copper and nickel pollution in terrestrial ecosystems	7
1.2 Plant responses to excess soil Cu and Ni	8
1.3 Phytoavailability of soil Cu and Ni	10
1.4 Ecological characteristics of Scots pine	11
1.5 Element cycles at the ecosystem level	12
1.6 Aims of the study	13
2 Material and methods	15
2.1 Study area	15
2.2 Emissions from the smelters	17
2.3 Bulk deposition and stand throughfall	21
2.4 Litterfall	22
2.5 Needle sampling in the pine stands along the study gradient	23
2.6 Experimental approaches	24
2.6.1 Soil sampling along the gradient at Harjavalta	24
2.6.2 Artificial exposure treatment	24
2.6.3 Experimental conditions, harvesting and soil sampling at the end of the experiments	24
2.6.4 Chemical analysis of the greenhouse experiments	25
2.6.5 Calculations and statistical treatment of the greenhouse experiments	26
2.6.6 Pine seedling experiment in the field	26
2.7 Peat sampling	27
3 Results and discussion	29
3.1 Recent and past metal deposition at the study area	29
3.1.1 Bulk precipitation and stand throughfall	29
3.1.2 The extent of past metal deposition	30
3.2 Performance of Scots pine in smelter-polluted environment at different phases of its life-cycle	31
3.2.1 History of the forests under study	31
3.2.2 Current growth rate of the study stands	32
3.2.3 Comparison with the experimental seedling cultures	32
3.2.4 Seed crop and seedling establishment	35

3.3 Availability of soil Cu and Ni to Scots pine	36
3.3.1 Soil and soil solution Cu and Ni concentrations as indicators of their availability	36
3.3.2 Cu and Ni concentrations as diagnostic criteria of toxicity	42
3.4 Biogeochemical cycling of elements in the studied forest ecosystems	43
3.4.1 Consequences of a long-term Cu and Ni exposure for element cycling	43
3.4.2 Canopy filtration of dry deposition as a source of element fluxes in the ecosystems	44
3.4.3 Foliar leaching of potassium	45
3.4.4 Nutrient retranslocation in pine foliage	46
3.4.5 Element losses via percolation water	46
3.4.6 Nutrient disturbances	47
4 Conclusions	49
Acknowledgements	51
References	53

List of Original Publications

- I** Nieminen, T.M., Derome, J. and Helmisaari, H.-S. 1999. Interactions between precipitation and Scots pine canopies along a heavy-metal pollution gradient. *Environmental Pollution* 106: 129—137.
- II** Nieminen, T. M., Ukonmaanaho, L. and Shotyk, W. 2002. Enrichment of Cu, Ni, Zn, Pb and As in an ombrotrophic peat bog near a Cu-Ni smelter in Southwest Finland. *The Science of the Total Environment* 292: 81—89.
- III** Nieminen, T. M. 2004. Effects of soil copper and nickel on survival and growth of Scots pine. *Journal of Environmental Monitoring* 6: 888—896.
- IV** Nieminen, T. M. and Saarsalmi, A. 2002. Contents of Cu, Ni and Zn in smelter-polluted soil-plant systems. *Geochemistry: Exploration, Environment, Analysis* 2: 167—174.
- V** Nieminen, T. and Helmisaari H.-S. 1996. Nutrient retranslocation in the foliage of *Pinus sylvestris* L. growing along a heavy metal pollution gradient. *Tree Physiology* 16: 825—831.
- VI** Nieminen, T. M., Derome, J. and Saarsalmi, A. 2004. The applicability of needle chemistry for diagnosing heavy metal toxicity to trees. *Water, Air, and Soil Pollution* 157: 269—279.

Author's contribution

Tiina Nieminen was responsible for the data handling, preparation and writing of all the papers (**I–VI**), as well as for the idea of papers **I**, **III**, **IV** and **VI**. The experimental design of papers **II**, **III**, **IV** and **VI** was also planned by her. Heljä-Sisko Helmisaari was the supervisor of the thesis and paper **V** is based on her suggestion. The field work of paper **V** was planned by Heljä-Sisko Helmisaari. The design of the field experiments (**I**, **V**, **VI**) was provided jointly by Prof. Eino Mälkönen, Heljä-Sisko Helmisaari and John Derome. The idea for paper **II** was initiated by William Shotyk, Liisa Ukonmaanaho and Tiina Nieminen, who also jointly planned the sampling protocol. Anna Saarsalmi provided the litterfall (**IV**) and tree needle results (**VI**) and gave advice on their interpretation. John Derome provided advice in the calculations and in interpreting the results of paper **I** and **VI**.

Abstract

The aim of my thesis was to evaluate the lifelong response of Scots pine to a chronic Cu and Ni exposure in the vicinity of a smelter complex, as well as to study the fate of the pollutants in the studied forest ecosystems. Four study sites were established in pure Scots pine stands growing along an esker at distances 0.5, 2, 4 and 8 km southeast from the main stack of the smelters. In addition, the response of Scots pine to soil Cu and Ni was also studied by performing simulation experiments in a greenhouse.

The rate of Cu and Ni deposition on the forests was estimated by monitoring the current Cu and Ni concentrations in bulk precipitation and stand throughfall, and by estimating the past pollution loads on the basis of the amounts of Cu and Ni accumulated in the surface peat of an adjacent ombrotrophic bog. The measured Cu and Ni deposition at the forest site nearest to the smelters did not appear to be a reliable estimate of current metal input into the ecosystem, because of the high level of internal metal cycling *via* soil dust. The elevated Cu and Ni concentrations in the surface peat sediments of the ombrotrophic bog were interpreted as signs of a higher level of Cu and Ni deposition in the past compared to current deposition in the immediate vicinity of the smelters. In addition, the vertical distribution pattern of Cu suggests that the input of Cu to the peat *via* atmospheric deposition is retained in the top-most peat layers, whereas Ni showed a more even vertical distribution pattern reflecting downward migration. Nickel appeared to be more mobile than Cu also in the polluted forest soils, but this was not reflected as relatively higher Ni uptake by pine roots. The uptake of both Cu and Ni corresponded to their soil contents in the smelter-polluted forest soil, although the uptake rate of inorganic Ni from an artificial quartz sand substrate was, in some cases, higher than that of Cu.

The performance of experimental pine seedlings cultivated in smelter-polluted soil was similar to that of the mature pine stands growing along the study gradient. The variation in the biomass of the seedlings appeared to be related both to the toxicity of Cu and Ni and to the differences in the nutrient status of the experimental soils. However, smelter-induced pollution may affect pines also indirectly through changes in soil nutrient status, which are difficult to distinguish from the natural variation in fertility. The autumnal nutrient retranslocation from senescing needles to overwintering tree compartments was less efficient at the most polluted site compared to that at further distances from the smelters. According to the results of the artificial exposure experiment the lethal threshold for Cu concentration in pine roots would be approx. 1 000 mg kg⁻¹, while the corresponding value for Ni would be 100 mg kg⁻¹, thus indicating a higher toxicity of Ni. The corresponding thresholds for pine stem concentrations were 70 mg Cu kg⁻¹ and 8 mg Ni kg⁻¹. The needle concentrations did not appear to be reliable indicators of Cu and/or Ni toxicity. This was especially true in the field, where the surface contamination of needles by metal-containing particles in the heavily polluted environment further complicated the interpretation of the measured Cu and Ni concentrations. The chloroform washing did not remove all of the metal-containing material attached to the needle surfaces.

I Introduction

I.1 Copper and nickel pollution in terrestrial ecosystems

Although air pollutants may originate from natural sources, such as volcanoes, vegetation fires and salt spray from the oceans, human activities currently have major impacts on the global and regional cycles of most of the trace elements (Nriagu and Pacyna 1988, Nriagu 1990, Ross 1994). Anthropogenic sources of atmospheric copper and nickel are metal mining, smelting and refining, alloying, the petrochemical and fertilizer industries, the burning of fossil fuels, refuse incineration and the use of agricultural amendments (Nriagu and Pacyna 1988, Alloway 1995). The most traditional agrochemical application is the use of copper compounds as fungicides in vineyards since 1885 (Bordeaux mixture: $\text{Ca}(\text{OH})_2 + \text{CuSO}_4$). This practise has resulted in substantial accumulation of Cu in the surface soils of vine growing areas (Brun *et al.* 2001, Parat *et al.* 2002, Ribolzi *et al.* 2002, Chaignon *et al.* 2003). Irrigation by metal-containing sewage water on agricultural fields dates back to the end of the 19th century around some old urban agglomerations in Central Europe (Rebele 2001, Kirpichtchikova 2003). The worldwide use of CCA (chromated copper arsenate) impregnated wood causes environmental contamination by Cu, As and Cr (Chirenje *et al.* 2003, Townsend *et al.* 2004). In Finland, the major sources of Cu are the metallurgical industry, and those of Ni energy production and the use of oil fuel in industry (Jalkanen 2000).

Copper and Ni particulates emitted from mining and smelting are primarily deposited locally, and thus the most severe environmental damage tends to be restricted to limited areas. In many areas, however, metal emissions are associated with SO_2 emissions. The effects of heavy metals on forest trees are connected to irreversible changes in soil processes, while the SO_2 emissions have a direct impact on the above-ground part of trees, but a less permanent effect on the surrounding soils (Winterhalder 1995). Two of the largest and most widely studied Cu-Ni mining and smelting areas in the northern hemisphere are the Sudbury region in Canada (Hutchinson and Whitby 1974, Lozano and Morrison 1981, Winterhalder 1996, Nriagu *et al.* 1998), and the large industrial agglomerations in the Kola Peninsula in NW Russia (Tikkanen and Niemelä 1995, Nöjd *et al.* 1996, Lindroos 1998, Rautio *et al.* 1998, Rigina and Kozlov 2000, Steinnes *et al.* 2000). In Sudbury, the barren land area has been estimated to cover a total surface of 170 km² and a large surrounding semi-barren area is reported to be about 720 km² (Winterhalder 1995, 2000). According to Oleksyn and Innes (2000), the area affected by forest death in the Kola Peninsula is 600–1 000 km². Extensively documented, smaller Cu/Cu-Ni smelting complexes are situated at Gusum, Sweden (Tyler 1984, Bååth 1989, Köhler 1999) and Harjavalta, Finland (Laaksovirta and Silvola 1975, Hynninen 1986, Heliövaara *et al.* 1987, Fritze 1989, 1996, Helmisaari *et al.* 1995, Kiikkilä 2003) as well as a mining and smelting complex at Sulitjelma, Norway (Lobersli and Steinnes 1988).

As a result of the long-range transport of metal-containing aerosols, heavy metals originating from anthropogenic sources have also reached remote areas. For instance, the trace metal profiles determined on Arctic ice cores are in reasonable accord with the calculated historical changes in the rates of anthropogenic emissions into the atmosphere (Nriagu and Pacyna 1988, Boutron *et al.* 1995). Peat and lake sediments can also be used as archives of the past atmospheric metal deposition rates (Gubala *et al.* 1995, Shotyky 1997, Sternbeck and Östlund 2001, Renberg *et al.* 2002). Valuable information about pre-industrial metal concentrations in forest plants can also be obtained from the analysis of old herbarium plants (Lobersli *et al.* 1990).

During the past decade, emissions of heavy metals have decreased in Northern Europe (Melanen *et al.* 1999), which has been reflected in national bioindicator surveys as lowered metal concentrations in forest mosses (Mäkinen 1994, Rühling and Tyler 2001, Steinnes 2001, Poikolainen *et al.* 2004). In Norway, it has been estimated that long-range transport is less important than local sources for Cu and Ni contamination in forest mosses (Steinnes 2001). In Finland, too, local sources have a great impact on the nation-wide distribution of Cu and Ni concentrations in forest mosses (Poikolainen *et al.* 2004).

The weathering of primary minerals is the most important source of trace elements in terrestrial ecosystems in non-polluted areas (Ross 1994, Henderson 1998). Since the amounts of trace elements in the solid soil phase are usually low and weathering processes slow, the release of elements results in very low quantities of available forms (Kabata-Pendias 2001). However, in some cases the weathering of specific metalliferous minerals can result in metal concentrations toxic to non-tolerant-plants, *e.g.* soils derived from ultramafic (serpentine) rocks have a distinctive stunted vegetation adapted to the prevailing elevated Ni concentrations (Brooks 1998).

1.2 Plant responses to excess soil Cu and Ni

Accumulation of metals in toxic amounts in plant substrates affects many metabolic processes, although the sensitivity of different plant species varies widely. According to Jackson *et al.* (1990), Cu toxicity is related to its high affinity for sulfhydryl groups, causing inactivation of sulfhydryl-containing enzymes or altering their catalytic specificity or control. High Cu concentrations stimulate peroxidative degradation of the lipids of membranes, which leads to increased membrane permeability (Marschner 1995, Adriano 2001). Although Cu is a toxic metal at high concentrations, it is also an essential micronutrient (Lipman and MacKinney 1931). Most of the functions of Cu as a plant nutrient are based on the participation of enzymatically bound Cu in redox reactions (Marschner 1995). Consequently, plants need a copper homeostasis mechanism that provides the necessary Cu ions at the required enzymatic sites, while reducing or eliminating their deleterious interactions (Jackson *et al.* 1990).

Nickel has quite recently also been found to be an essential micronutrient for plants (Brown *et al.* 1987), although the role of Ni in plant metabolism remains still largely unknown. At the present time, urease is the only known nickel-containing enzyme in higher plants (Marschner 1995). Only a few studies have been addressed at Ni toxicity (Jackson *et al.* 1990), and the mechanism of Ni toxicity to plants is not well understood (Kabata-Pendias 2001). Leaf chlorosis, stunted growth and dark colour of the roots are

described as symptoms in both Ni and Cu toxicity cases (Marschner 1995, Adriano 2001, Kabata-Pendias 2001).

Baker (1987) divides plants into two main categories with respect to their response to excess amounts of metals in their growing substrate: excluders and accumulators. Excluders survive in polluted soils through avoidance, whereas accumulators survive through a physiological tolerance mechanism. Hyperaccumulator is a term established by Brooks *et al.* (1977) for extreme accumulators that can enrich metal concentrations higher than 1 000 mg kg⁻¹ in their above-ground tissues. The most famous hyperaccumulator is a small perennial shrub (*Alyssum bertolonii* Desv.) that can contain up to 7 900 mg Ni kg⁻¹ in its leaves (Brooks 1998). It grows on ultramafic rocks in Tuscany, and was scientifically documented already in the 16th century by the Italian botanist Cesalpino (Brooks 1998). Even today, there are many more plant species that are known to hyperaccumulate Ni than those hyperaccumulating Cu.

Several biochemical mechanisms appear to be involved in the Cu tolerance of higher plants. Chelating molecules are apparently of crucial importance in Cu tolerance, although their exact role is not well understood (Jackson *et al.* 1990). The immobilization of Cu in cell walls, in cell vacuoles and in nondiffusible Cu-protein complexes has also been related to Cu tolerance (Jackson *et al.* 1990, Kabata-Pendias 2001). Organic acids are believed to play a central detoxifying role in Ni accumulating plants (Lee *et al.* 1978, Yang *et al.* 1997).

Some plant species are suggested to show constitutive tolerance, *i.e.* they possess a tolerance mechanism even though they are not exposed to metals (Baker 1987, Baker and Proctor 1990, Ye *et al.* 1997, Monni *et al.* 2000). Plant populations can also evolve tolerance through heritable adaptation (Baker *et al.* 1986). Although the evolution of metal-tolerant grasses in nature is a classic example of local adaptation (Antonovics *et al.* 1971, Dickinson *et al.* 1996), tolerant ecotypes of long-lived trees are much rarer due to their long generation times. In an exposure study by Kopponen *et al.* (2001), birch clones (*Betula pendula* Roth, *B. pubescens* Ehrh.) from the vicinity of the Harjavalta Cu-Ni smelters in Finland showed better Cu tolerance than birch clones from Zn polluted or non-polluted areas. However, most plant species do not evolve tolerance and are either eliminated from toxic sites (Bradshaw and McNeilly 1981) or survive through gradual acclimatisation by individual plants (Dickinson *et al.* 1991).

The metal excluders possess a restricted metal uptake and transport (Baker 1987). Besides the control of metabolic root uptake, also apoplasmic metal uptake can be restricted by plants through the establishment of a suberin-rich transport barrier in their roots (Schreiber *et al.* 1999). The binding of metals on extracellular binding sites in the root cortex can also be regarded as an exclusion strategy (Baker 1987, McLaughlin 2002). In addition, root uptake restriction can also be based on simple avoidance, expressed as the orientation of the roots into less toxic soil microsites (Turner and Dickinson 1993). Metal avoidance can be facilitated by root associated ectomycorrhizal species, since the spatially large ectomycorrhizal mycelium can efficiently immobilize metals (Galli *et al.* 1994, Colpaert and Assche 1992, Tichelen 1999) and it ameliorates the ability of roots to reach clean soil layers. Metal tolerant strains of mycorrhizal fungi have been isolated from metal polluted soils (Hartley *et al.* 1997). However, according to the review of Godbold *et al.* (1998), ectomycorrhizas do

not universally ameliorate metal toxicity, and amelioration is dependent on the species and on the strain of the ectomycorrhiza, as well as on the metal in question.

1.3 Phytoavailability of soil Cu and Ni

The rate of element uptake from a solution into plants can be described using Michaelis-Menten kinetics: $F = V_{\max} c / (K_m + c)$ (Marschner 1995). In a fundamental work carried out by Epstein and Hagan (1952) ion transport through the membranes of plant cells was regarded as formally equivalent to the relationship between an enzyme and its substrate. Ion uptake by plants has features of saturation kinetics, which is related to the assumption of control (*e.g.* number of binding sites: carriers, permeases; capacity of H^+ efflux pumps). According to the equation, the ion transport rate is dependent on two factors: V_{\max} , which is the maximal transport rate when all available binding sites are loaded, and K_m a constant, equal to the substrate ion concentration (c) giving half of the maximal transport rate. The basic scheme has stood the test of time, and this model is still commonly used as a component in plant uptake models.

However, the formal application of the Michaelis-Menten kinetics is not always in accordance with the experimental results (Marschner 1995). The relationship between the substrate metal content and its uptake is regulated by many factors, such as interactions with other ions in solution or changes in plant uptake processes. For instance, at high metal concentrations damage to cell membranes and transport proteins may also cause a reduction in metal uptake rates, so that the effects of phytotoxicity may be confused with saturation of the uptake mechanisms (McLaughlin 2002). Furthermore, the Michaelis-Menten model depicts basically the short-term element uptake pattern in controlled nutrient solution cultures, which cannot be directly generalized to *in situ* conditions. The presence of the solid matrix in soil strongly affects metal availability, thus turning the substrate metal concentration into a complex concept. As a general rule, the partitioning of metals between the solid and solution phases reduces metal availability, although the distribution between the soil phases is not constant, but varies with time (Allen 2002, Sauvé 2002). The strength of binding of a metal by the soil varies markedly across soils as a consequence of differences in soil properties (Allen 2002). According to Kabata-Pendias (2001), the association of trace elements with specific soil phases and their affinity for each soil constituent is the key factor determining their behaviour in soils (Fig. 1).

Total metal contents in the soil depict the potential availability of metals; in fact total concentrations refer to the complete dissolution of the solid matrix and quantification of its chemical constituents (Sauvé 2002). In mineral soils the real total content is of little relevance in terms of trace element availability, and strong acid digestions are more frequently used instead. The basic aim of the number of more subtle extraction schemas is to estimate the metal pool available to plants or other soil biota (McLaughlin 2002). Since plants access metals in the soil principally through the soil solution, it would be expected that the determination of metal concentrations in the soil solution would provide the best predictor of their availability. However, the prediction capacity of soil solution concentrations appears to be unclear. For example, the effect of pH is contradictory. Although a decrease in pH increases soil solution metal concentrations, it does not enhance the metal uptake by plants to the same extent

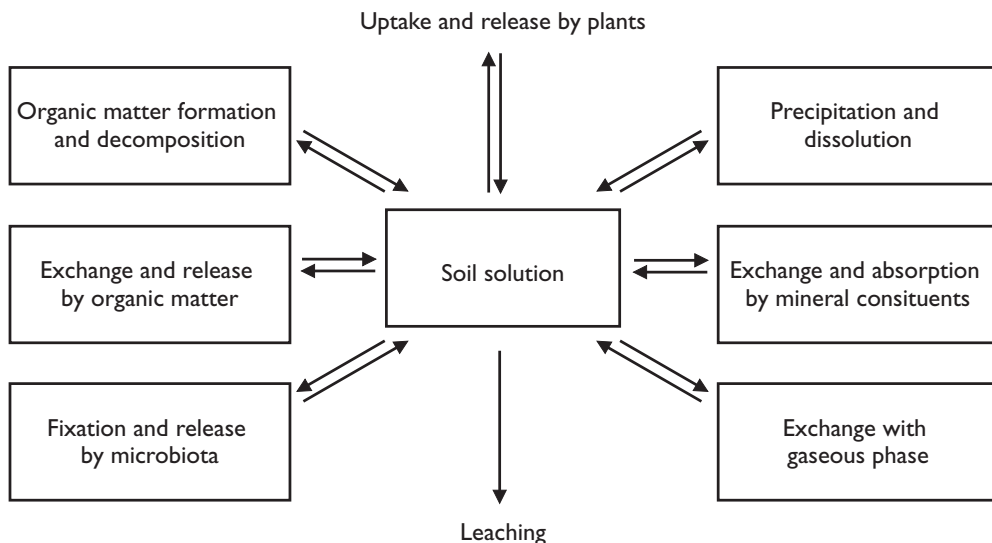


Fig. 1. Schematic diagram of the key interactive processes in the soil system (modified from Kabata-Pendias 2001).

(McLaughlin 2002). On the basis of a model developed in aquatic toxicology (Free Ion activity Model, FIAM), it has been supposed that the use of free ion activities of soil solution would give the best indication of their availability also to terrestrial plants (Sauvé 2002). Nevertheless, at the present time there are insufficient data to determine whether soil solutions or soil extracts are the best indicators to use, and the additional utility of considering free metal ion activities also remains questionable (Allen 2002, McLaughlin 2002).

Copper is known to be a rather immobile element in soils, which is related to the formation of organic complexes (Adriano 2001, Kabata-Pendias 2001). The mobility of Cu in soils is highly dependent on soil pH (Kabata-Pendias 2001). Nickel appears to be relatively mobile in soils with a high complexation ability, due to the apparent remobilization of Ni from solid phases in the presence of organic acids (Kabata-Pendias 2001). The sorption of Ni in soils is largely pH-dependent (Adriano 2001). An average value of 30 mg kg⁻¹ for the total Cu concentration and 20 mg kg⁻¹ for total Ni of world soils have been reported by Adriano (2001).

1.4 Ecological characteristics of Scots pine

Scots pine (*Pinus sylvestris* L.) has the widest geographical amplitude of all pine species. It forms the northern timberline in Fennoscandia, and the southernmost Scots pine populations can be found in Spain (Atlas Flora Europaeae 1973). It grows on a wide range of soils, including peat, and tolerates both acid and slightly alkaline soil conditions, although its volume production is highest on well-drained acid soils (Kujala 1958). Scots pine is not susceptible to drought but, as a pioneer tree species (Hämät-Ahti *et al.* 1989), it does not tolerate shade. Abundant seed crops are produced

irregularly, every 3 to 6 years, with light crops in intervening years (Sarvas 1962a, Koski and Tallqvist 1978). The rooting system of Scots pine is deep (Laitakari 1927), and it is associated with ectomycorrhizal fungi.

Natural fires, as well as slash-and-burn cultivation, have historically played an important role in Finnish forests (Tolonen 1983), and this has led to a dominance of Scots pine since it is relatively resistant against fires and has an efficient colonization capacity on burned soils (Sarvas 1962b). At the present time, Scots pine is still the dominant tree species in Finnish forests. Being the most important raw material for the Finnish forest industry, it has been favoured by forest management practices (Tomppo 2000). However, in several studies Scots pine has been reported to be relatively sensitive to air-borne pollutants (Huttunen *et al.* 1983, Laine *et al.* 1994, Bäck *et al.* 1995, Innes 1995), and it appears to be especially susceptible to sulphur dioxide (Huttunen and Laine 1983, Katainen *et al.* 1984, Huttunen *et al.* 1985, Turunen *et al.* 1997). Extensive studies on the performance of Scots pine under the impact of sulphur dioxide and heavy metal emissions from the Ni-Cu smelters on the Kola Peninsula have recently been reported by Nöjd (1996) and Rautio (2000).

1.5 Element cycles at the ecosystem level

In the 1950s element cycling at the ecosystem level became a subject of extensive study. The concept of whole-ecosystem studies *in situ* was introduced by H.T. Odum's early works on strontium (Sr) cycling and energy and material flows in aquatic ecosystems (Odum 1951, 1957), in which he connected element geocycles with biotic cycles. Later, he pioneered large-scale whole-ecosystem studies in rain forests of Puerto Rico and in ecosystems under the impact of anthropogenic inputs, *i.e.* surface waters and swamps affected by waste water (referred to by Mitsch and Day 2004).

Already in the 1950s, Ovington (1957, 1959) studied biomass production and nutrient cycling in Scots pine plantations at different stages of development. However, in the 1970s the application of the whole-ecosystem concept in forests became strongly developed in research on the relationship between acidic deposition and forest functioning. Mathematical models can serve as important tools in describing and predicting the characteristics of biogeochemical cycling, *e.g.* the MAGIC model developed by Cosby *et al.* (1985). Also processes that cannot be directly measured can be described by modelling, *e.g.* mineral weathering by the PROFILE model (Sverdrup and Warfvinge 1990, Jonsson *et al.* 1995). Ulrich (1974, 1981, 1992) built up the system analysis concept of forest functioning by dividing the forest ecosystem into compartments that exchange elements with each other and across ecosystem boundaries. The aim of this kind of approach is a quantitative evaluation of the compartments and element fluxes within the forest ecosystem.

In Finland, Mälkönen (1974) published the annual nutrient budgets of Scots pine stands at different developmental stages, and in a birch stand (Mälkönen 1977) already in the 1970s. Later on, Helmisaari (1995) and Helmisaari *et al.* (2002) studied biomass production and nutrient cycling in a chronosequence of Scots pine stands in eastern Finland. Saarsalmi *et al.* (1985) and Saarsalmi and Mälkönen (1989) studied nutrient cycling in *Alnus incana* (L.) Moench stands, and Saarsalmi (1984) also in a *Salix* 'Aquatica Gigantea' plantation. Major nutrient and acidity budgets at the catchment

scale have been determined in remote areas by Forsius *et al.* (1995), and at the forest stand level by Ukonmaanaho and Starr (2002).

Paavilainen (1980, 1984) studied the relationship between fertilization and nutrient cycling in peatland forests. Furthermore, Finér (1992) published an extensive report about the nutrient dynamics of Scots pine in drained peatland ecosystems. Nieminen (2003) studied the consequences of clear-cutting on nutrient output from drained Scots pine mires, while Piirainen *et al.* (2004) reported the effects of forest clear-cutting on the nutrient fluxes in podzol soils. Although studies on nutrient cycling in Finnish forests are relatively frequent, the cycling of heavy metals has rarely been included in such studies. Ukonmaanaho *et al.* (2001) presented heavy metal budgets for two forested catchments in background areas of Finland, Bringmark and Lundin (2004) recently reported results on heavy metal stores and fluxes in several European sites including Finland, while Starr *et al.* (2003) estimated the importance of weathering for ecosystem heavy metal budget in a background forest area. However, no studies on either nutrient or heavy metal cycling in heavy metal polluted forest ecosystems have been realised in Finland prior to the present study.

1.6 Aims of the study

The aim of my thesis was to evaluate the lifelong response of Scots pine to a chronic Cu and Ni exposure in the vicinity of a smelter complex. The focus of the research articles of this thesis is on juvenile (**III, IV, VI**) and mature phases (**I, V, VI**) of the lifecycle of pine. The rate of Cu and Ni exposure was studied by **1**) monitoring the current deposition level (**I, VI**), **2**) estimating the past pollution load on the basis of the accumulated amounts of metals in the surface peat of an adjacent ombrotrophic bog (**II**), **3**) estimating the soil Cu and Ni content and their phytoavailability (**III, IV**), and **4**) performing simulation experiments (**III-IV**).

The determination of metal exposure rates and plant responses for long-lived trees is a complex task, because only the current status can be measured by direct means. I have traced the past metal deposition and plant response patterns on the basis of production and emission records provided by the smelter company, vertical metal distributions in peat sediments, and pine annual ring chronologies.

Most of the studies dealing with the effects of heavy-metals on plants have been conducted as a short-term exposure without considering the relevance of the assessment for long-term exposure. The life-cycle approach with terrestrial plants has been rare, even with annual crops and herbaceous plants. In order to cover a full lifecycle of long-lived plants, such as trees, extensive long-term investigations are needed. Our current understanding of the response of trees to high metal loads is mostly based on data from the early life phases, *i.e.* on the responses of newly germinated seedlings or on seed germination trials. Therefore, in my experimental manipulations (**III, IV**), I used seedlings that had already reached the age of 4 years. The duration of the experiments was extended to 17 months in order to study the responses over two successive growing seasons.

As the persistence of a tree stand in a polluted environment is largely dependent on the functioning of nutrient cycling in the ecosystem, my studies on the responses in the mature phase were concentrated on different aspects of the nutrient cycling in

the studied forests (I, V). In addition, the fluxes of Cu and Ni were studied. Therefore, the approach of this study could be included in the field of ecotoxicology which, according to Cairns and Mount (1990), is a study of the fate and effect of toxic agents in ecosystems.

The interactions between the tree canopy and metal deposition loads (I), as well as the internal nutrient cycling of the trees (V), were studied along a pollution gradient. In addition, the consistency between foliar metal concentrations over successive time intervals and measured metal deposition loads was studied, and the diagnostic value of foliar concentrations evaluated (VI).

The specific aims of the thesis were:

- to determine the current metal input to the ecosystems along the smelter pollution gradient
- to trace the past input loads and amounts accumulated in the soil
- to evaluate the availability of Cu and Ni to Scots pine in polluted soils
- to define the responses of Scots pine seedlings to soil Cu and Ni exposure in controlled conditions
- to determine the efficiency of internal nutrient cycling in mature pine stands growing along the smelter-pollution gradient
- to estimate the critical toxicity thresholds for Cu and Ni concentrations in plant tissues and soil
- to estimate the proportion of surface contamination out of needle total metal concentrations

2 Material and methods

2.1 Study area

Harjavalta (61°19′N 22°9′E) is a small industrial town situated in southwestern Finland, about 30 km from the coast, in the southern boreal coniferous zone (Ahti *et al.* 1968). The long-term (1960–1990) mean annual temperature at a near-by weather station of the Finnish Meteorological Institute is +4.0°C and the annual precipitation 558 mm. The area has been subjected to a heavy pollution load since 1945, due to the relocation of a large metal smelter from eastern Finland to Harjavalta during the final stages of World War II. At that time Harjavalta was a completely rural area with practically no industry (Poutanen and Kuisma 1998).

The smelter was reconstructed on a forested esker running in a NW-SE direction. The sorted sand heathland was considered as ideal for the rapid reconstruction of the plant owing to the urgent need for copper for military purposes (Poutanen and Kuisma 1998). Copper smelting started at Harjavalta in 1945 and nickel smelting in December 1959, and a nickel refinery was built in 1960. The blister copper produced by smelting has been transported to a copper refinery in Pori, located some 30 km from Harjavalta. There has never been any ore mining at Harjavalta.

The heathland Scots pine forest growing in the immediate vicinity of the smelter died during the first years of industrial activities (Poutanen and Kuisma 1998). The dead pine stands were left uncut until the mid 1950s, which aroused a lot of publicity and gave a nationwide negative image to the smelter. However, owing to the lack of any scientific documentation of the damage, the exact rate and extent of this forest damage remains unclear. Poutanen and Kuisma (1998) report that Docent Esko Kangas was asked by the smelter company to evaluate the damaged area in 1946. He concluded that the damage was limited to the immediate vicinity of the smelter. However, it is worth noting that the forested area in this part of Finland was, and still is, relatively limited due to the intensive agricultural use of land. In practice, only the relatively infertile sites not suitable for crop cultivation, like this sorted sand esker, had been left in a forested state. Poutanen and Kuisma (1998) further report that, in 1946, altogether 47 farmers reported that pollution-induced damage had taken place in their fields. The total surface area of the affected fields was reported to be almost 100 hectares.

Public concern arose again in the 1970s because of the visible damage in gardens and forest trees in the vicinity of the smelters. This initiated several scientific research works carried out in the area. A comprehensive review of the studies carried out since 1975 in and around the Harjavalta area has been published by Kiikkilä (2003). A systematic survey of the condition of forests in Harjavalta and neighboring municipalities was carried out for the first time in 1979 by the regional Forest Centre of Southwest Finland, and it has subsequently been repeated every fifth year. The purpose of the survey is to determine the reduction of growth rates in forests considered to be affected by smelters, in order to determine appropriate compensation to be paid to forest owners by the smelter company. In 1985 the surface area, estimated to be affected by smelting, was 550 hectares. Fifteen years later, in 2000, the area had

enlarged to 700 hectares, and the most distant forest site considered to be affected was located 6.6 km from the smelters. The mean reduction in volume growth of the affected stands compared to control stands was 16%.

In 1992, the Finnish Forest Research Institute established study plot clusters (each plot 625–900 m² in size) in pure Scots pine stands growing along the esker at distances of 0.5, 2, 4 and 8 km southeast from the main stack of the smelters (Fig. 2.)

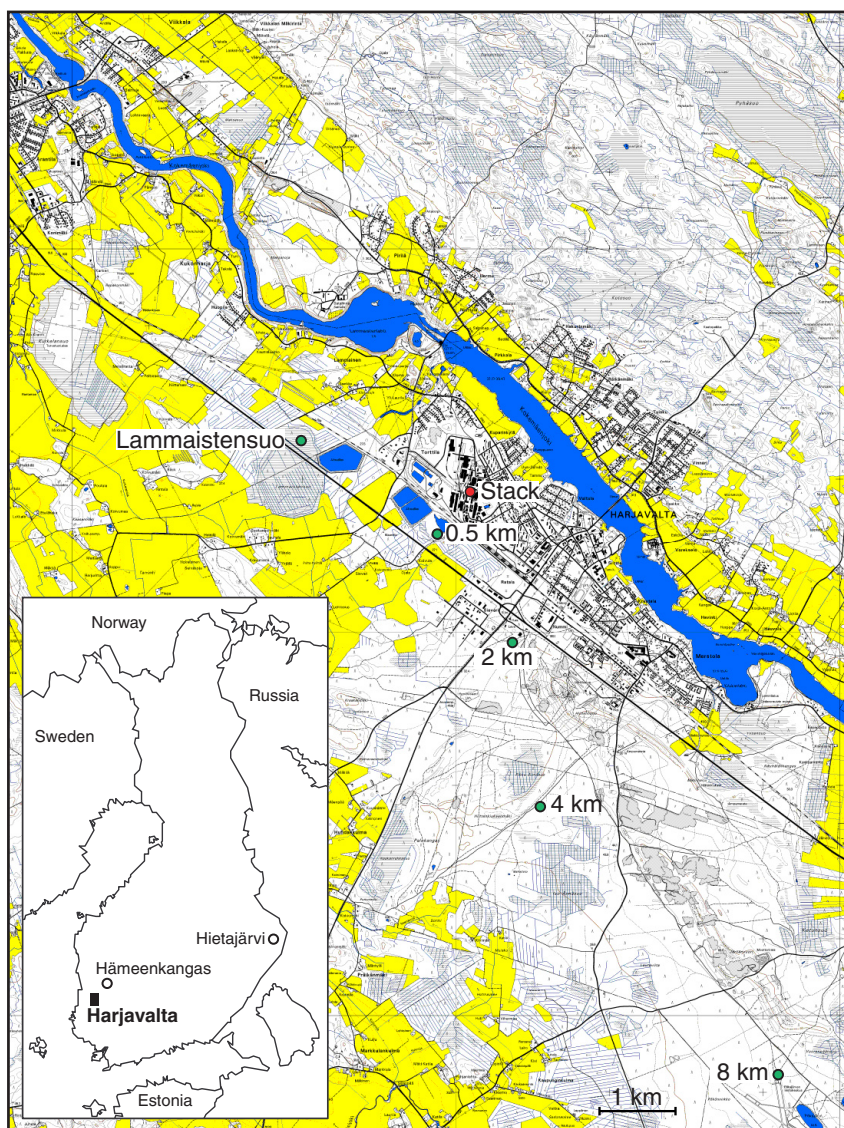


Fig. 2. Location of the Harjavalta study area, the forest background site at Hämeen kangas, and the reference peat bog at Hietajärvi in Finland. The study sites at Harjavalta are situated at distances of 0.5, 2, 4 and 8 km from the main stack of the Cu-Ni smelters, and the peat bog sample plot (Lammaistensuo) 2.4 km west from the stack.

(Mälkönen *et al.* 1999). The field data of this thesis (**I**, **III–VI**) have mostly been collected from these plots. The study plots are located on bedrock consisting of Jotnian olivine diabase. The soil comprises sorted glaciofluvial sediments, which poorly reflect the chemical properties of the underlying bedrock. One sampling site, situated at Hämeen kangas, 60 km northeast from Harjavalta (Fig. 2), in an area without any local pollution sources, was chosen as a background site. The texture of the mineral soil at all sites is fine sand, excluding the sites at 2 (fine/coarse) and 60 (coarse) km, and the soil type is orthic podzol (according to FAO-UNESCO 1998). The organic layer is mor, with a thickness ranging from 1 to 3 cm.

After almost 50 years of smelting activities the esker was still mostly covered by Scots pine forests, even though the large industrial complex and numerous sand pits caused by intensive sand extraction, have made the forests relatively fragmented (Fig. 2). The understorey vegetation of all sites is, or has originally been, typical of xerophilous forest sites: *Calluna vulgaris* (L.) Hull., *Empetrum nigrum* L., *Vaccinium vitis-idaea* L., *Pleurozium schreberi* (Brid.) Mit., *Dicranum spp.*, *Cladina spp. etc.* The understorey vegetation in the stand at 0.5 km is seriously damaged. According to a survey of understorey vegetation carried out in 1993 by Salemaa *et al.* (2001), lichens were absent up to a distance of 2 km, and mosses, excluding *Pohlia nutans* (Hedw.) Lindb., were not frequent until a distance of 8 km. In 1996, a remediation experiment (Kiikkilä 2002) was started at the same Scots pine site where the 0.5 km study plot is located. Needles of field-grown Scots pine seedlings in this experiment were used in Paper **VI**.

In addition, two ombrotrophic peat bogs were chosen as sampling sites in 1999 for studying airborne metal accumulation (**II**): Lammaistensuo bog situated 2.4 km west from the main stack of the smelter and a reference site, Hietajärvi bog, situated in the Patvinsuo National Park in eastern Finland, without any local pollution sources within tens of kilometres (Fig. 2). Hietajärvi catchment has been systematically monitored since 1989 as a part of the UN-ECE International Cooperative Programme of Integrated Monitoring for the effects of long-range transboundary air pollution on forest ecosystems (Ukonmaanaho *et al.* 1998). The polluted Lammaistensuo site is located in the concentric raised bog zone, and the Hietajärvi site in a transition area between the eccentric raised bog zone and the northern aapa mire zone according to Ruuhijärvi (1983).

Both bog sites were undrained ombrotrophic bogs with a sparse Scots pine cover. The field layer of both sites was dominated by *Eriophorum vaginatum* L., but at the polluted Lammaistensuo bog only two species, *Pohlia nutans* (Hedw.) Lindb. and *Cladopodiella fluitans* (Nees) Buch, occurred in the ground layer and a large part of the bog consisted of unvegetated peat surfaces. The ground layer vegetation of the background site in Hietajärvi consisted of *Sphagnum* species typical to a pristine ombrotrophic pine bog, *e.g.*, *S. angustifolium* C. Jens. and *S. fuscum* (Schimp.) Klinggr.

2.2 Emissions from the smelters

The chemical composition of the raw material used for smelting has naturally a great impact on the composition of the emissions. Up until the early 1970s, the ores

used for smelting were mainly domestic sulphidic minerals from the Outokumpu mine in eastern Finland. Chalcopyrite (CuFeS_2) was the most important copper and pentlandite ($(\text{Ni, Fe+Co})_9\text{S}_8$) nickel mineral of the Outokumpu ore body (Mäkinen 1938, Disler 1953, Parkkinen and Reino 1985). Only ore concentrates have been used at the Harjavalta smelters, so no ore crushing or concentrating has taken place at Harjavalta. However, the transport and handling of the ore concentrates have produced dust emissions especially during the earlier periods of smelters' lifetime but, after some technical improvements realised in the 1970's, the direct ore-concentrate-dust emissions have been drastically decreased (Poutanen and Kuisma 1994). At present, the ore concentrates used for smelting are bought worldwide from different mining companies.

Metals are emitted from the smelter stacks as components of fugitive dust release. Regular monitoring of stack emissions was started in 1985 by Outokumpu Harjavalta Metals Oy (Table 1). Most of the combustion gases were emitted from a 70 m high main stack up until 1994, when it was replaced by a 140 m-high stack. At present, 80% of the Ni and Zn is emitted from the 140-m-high main stack (Saari *et al.* 1998). Copper is mainly (60%) emitted from a smaller 40-m-high stack (Saari *et al.* 1998). The Harjavalta smelter complex is one of the largest point sources in Finland (Melanen *et al.* 1999), and its metal emissions account for a large proportion of the total national emissions (Table 2). During the past decade, the emissions from Harjavalta smelters have drastically decreased owing to improvements in process technology and the installation of more efficient filter systems.

Stack emissions for the earlier operating period of the smelters (1945–1984) have been estimated according to the production rates provided by Outokumpu Harjavalta

Table 1. Annual sulphur dioxide and heavy metal emissions from the Harjavalta smelters during 1985–2003. Arsenic (As) measurements were started in 1993 (Source: Outokumpu Harjavalta Metals Oy).

Year	SO ₂	Cu	Ni	Zn	Pb	As
tonnes per year						
1985	8000	98	47	216	55	
1986	7500	126	46	232	60	
1987	7000	140	96	162	94	
1988	8000	104	45	103	48	
1989	9500	80	33	190	70	
1990	8804	80	31	160	80	
1991	5200	80	14	90	45	
1992	4800	60	10	12	9.0	
1993	4700	50	7.0	13	6.0	11
1994	5000	40	6.0	6.0	3.0	5
1995	3230	17	1.4	1.7	0.5	0.2
1996	3200	49	1.2	5.0	1.7	4.0
1997	3000	69	2.9	13.9	3.9	9.7
1998	3041	23	1.7	6.1	2.3	10
1999	3392	5.9	0.8	4.2	1.0	1.8
2000	3002	6.6	1.2	1.1	0.2	0.8
2001	3387	7.4	0.8	3.0	0.7	1.6
2002	3300	11.6	0.6	1.5	0.4	0.5
2003	3000	6.0	0.6	0.9	0.3	0.4

Metals Oy (Fig. 3). During the early 1940s, the sulphur in the combustion gases was not covered, and the SO₂ emissions were even greater than the amounts of copper produced. In the worst year, 1947, the copper production was 26 000 tonnes and the SO₂ emissions were 35 000 tonnes (Poutanen and Kuisma 1994). The construction of a sulphuric acid factory in 1947 considerably reduced the SO₂ emissions, especially after the start of full-time processing in 1949 (Poutanen and Kuisma

Table 2. Annual total sulphur dioxide and heavy metal emissions in Finland during 1990–2002 (Source: Finnish Environment Institute).

Year	SO ₂	Cu	Ni	Zn	Pb	As
tonnes per year						
1990	260000	94	67	571	326	33.2
1991	194000	91	45	381	248	22.1
1992	141000	66	37	284	175	10.0
1993	123000	54	26	260	100	14.3
1994	114000	49	34	316	60	9.3
1995	96000	27	34	322	57	3.5
1996	105000	55	25	191	35	7.2
1997	99000	72	28	70	19	12.3
1998	90000	27	21	71	20	12.4
1999	87000	-	-	-	-	-
2000	74000	19	33	71	38	4.6
2001	85000	19	33	69	38	5.2
2002	82000	28	36	88	40	3.7

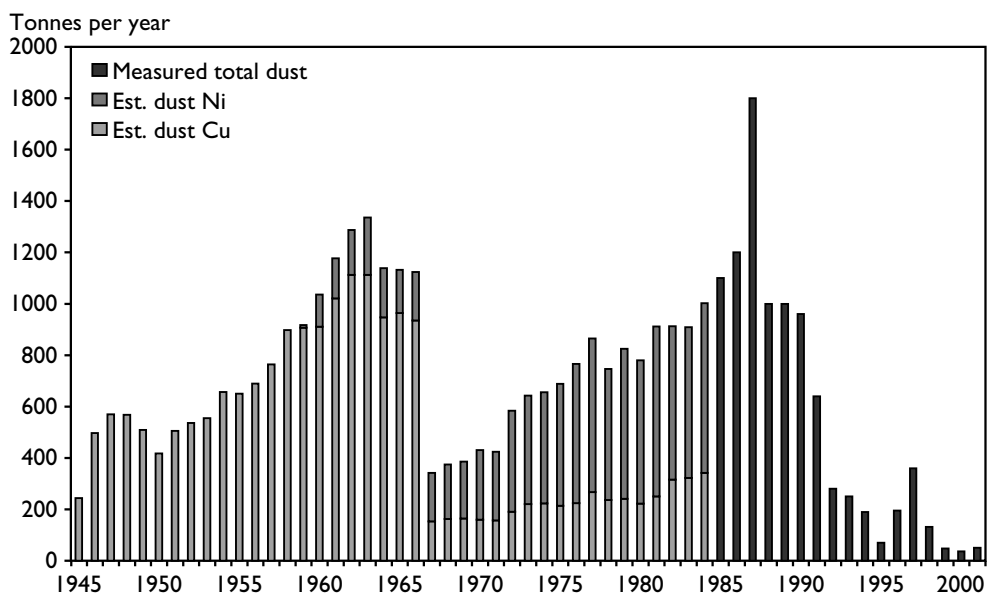


Fig 3. Production-based estimates of dust emissions from the Cu and Ni processes during 1945–1984. Regular measurement of stack-emitted dusts was started in 1985 (Source: Outokumpu Harjavalta Metals Oy).

1994). The flash-smelting process, an innovation of the Outokumpu company that was introduced in metal smelting in 1949, further improved the recovery of the SO₂ gases.

Important sources of heavy metals in the surroundings of the industrial plant are the different types of slag generated by the smelting processes, which have primarily been stored at the plant site. During the piling period, the uncovered slag heaps are a source of wind-borne dust emissions. The recycling and use of slag as land-fill and construction material further complicates the distribution pattern of slag-originating dust particles. An Environmental Impact Assessment report (EIA, Finnish law 10.6.1994/468), carried out by Geoinsinöörin Oy (2000) gives some details about the recent use of slag. Copper slag has been used in railroad ballast between Kokemäki and Pori, as well as in constructing a sound abatement barrier at the eastern end of the industrial area in the middle of the 1990s. The slag-cooling and handling area, which adjoins one of the study sites (0.5 km), is based on a Ni slag foundation, and the Ni slag has been used in the ballast of two railroad bridges inside the industrial area. In 1990, in order to reduce the overall dust emissions, the company started to transport the Cu slag in sludge form and to store it in land basins.

The composition and amounts of industrial wastes generated by smelting activities are given in the EIA report (Geoinsinöörin 2000). The main components of both Cu and Ni slag are fayalite (Fe₂SiO₄), magnetite (Fe₃O₄) and a glassy matrix. The elemental impurities are bound in fayalite and the glassy matrix (Table 3). The annual amounts produced in the end of the 1990s were *ca.* 320 000 tonnes of Cu slag and *ca.* 150 000 tonnes of Ni slag. In addition, gypsum (*ca.* 5 000 tonnes per year) and iron (*ca.* 20 000 tonnes per year) precipitates are generated in small amounts.

The EIA report also sums up the wide range of fuels used by the complex (Geoinsinöörin 2000). Most of the energy requirements are supplied by the ignition of sulphur in the ore concentrates (flash smelting), but also oil, coke and propane are used to some extent. The annual consumption of fossil fuels is *ca.* 25 000 tonnes, and

Table 3. Total mean concentrations of the potentially harmful elements in smelter slag in 1996 compared to the mean background values of mineral soils in Finland (Koljonen 1990). Concentrations in slag are determined by Outokumpu Harjavalta Metals Oy. Table modified from Geoinsinöörin (2000).

element	background	Cu slag		Ni slag	
	concentration ppm	concentration ppm	enrichment	concentration ppm	enrichment
As	7.2	700	100 x	5	0.7 x
Cd	0.3	22	70 x	<1	<3.3 x
Co	10	400	40 x	2100	210 x
Cr	50	n.d.	-	1100	22 x
Cu	25	4100	160 x	1400	56 x
Ni	20	1400	70 x	2800	140 x
Pb	17	3800	220 x	99	6 x
Sb	0.7	370	530 x	0	0 x
Sn	5	2100	420 x	40	8 x
Zn	50	18100	360 x	500	10 x

the annual amount fuel needed by the smelters' transport vehicles is about 3 000 tonnes. Kerosene is used in the nickel fabrication processes, and its annual losses through ventilation of the industrial hall are *ca.* 30 tonnes according to the measurements made by the factory. The corresponding emissions of Ni as ventilation losses are about one tonne per year.

In 1995 a new reduction method for the production of nickel was adopted. Ammonia (NH₃) is used in the process, and ammonium sulphate ((NH₄)₂SO₄) is formed as a by-product. According to the EIA report, the ammonia emissions through process gas ventilation were *ca.* 750 tonnes in the year 2000 (Geoinsinöörin 2000). Sporadic emissions of ammonium sulphate -dust can also take place during loading operations.

2.3 Bulk deposition and stand throughfall

Bulk (free) precipitation and stand throughfall were collected at three sites along the Harjavalta study gradient, at 0.5, 4 and 8 km distances, as well as at the 60 km Hämeen kangas background site. Bulk deposition was collected in open areas close to the tree stands using 5 rainfall collectors (diameter = 20 cm) during the snow-free period, and 2 snow collectors (d = 36 cm) during the winter. Stand throughfall was collected using 20 rainfall collectors located systematically inside the stand on a 30 m × 30 m plot, and 6 systematically located snow collectors during the winter. Samples were collected at 1-month intervals during the period June 1992 to December 1998.

Water samples from the rainfall collectors on the same plot were combined to give one composite sample per plot at each sampling date. The volume and pH of the samples were measured and the remaining part of the samples filtered through a 0.45 µm membrane filter. Samples for the determination of Ca, Mg, K, Fe, Cu, Ni and Zn by inductively coupled plasma/atomic emission spectrometry (ICP-AES) were acidified with ultrapure 65% HNO₃ (0.5 ml/100 ml sample). Ammonium, NO₃⁻, SO₄²⁻ and PO₄³⁻ were determined by ion chromatography. Dissolved organic carbon (DOC) was determined by digestion with sodium persulphate under UV radiation on a total organic carbon analyzer.

Bulk precipitation and stand throughfall samples at 0.5, 4 and 8 km distances during the snow-free period from June 1992 to December 1996 were used in Paper **I**. Bulk precipitation from June 1992 to December 1996 at the 0.5 km stand was used in Paper **II**. Both snow-free and winter period samples of stand throughfall during the year 1993 at 0.5, 4, 8 and 60 km were used in Paper **IV** in order to calculate the Cu and Ni fluxes *via* throughfall. Bulk precipitation and stand throughfall samples of the autumnal needle senescence period from July 1992 to September 1992 were used in Paper **V**. Both snow-free and winter period samples of the bulk precipitation and stand throughfall during the period from June 1992 to December 1998 were used in Paper **VI**.

In Papers **I**, **V** and **VI**, the net throughfall deposition was calculated as the difference between throughfall deposition (rainfall collectors inside the stand) and bulk deposition (rainfall collectors in an open area). In Paper **I** the sums of anions and cations were derived from the ionic concentrations (mol_e L⁻¹) of each sample. The Pearsson

coefficients of correlation between DOC and the anion deficit were calculated. Deposition loads ($\text{mol}_c \text{ m}^{-2}$) were calculated by multiplying the concentrations by the amount of water (L m^{-2}) at each sampling date for both bulk precipitation and throughfall. The average deposition for each element was calculated as the arithmetic mean of the deposition values of all sampling dates from July 1992 to November 1996 ($n = 34$).

Canonical discriminant analysis was carried out in order to obtain the best combination of element variables in bulk precipitation and throughfall that discriminated the study stands from each other. The statistical significance of the effect of the canopy on the amounts of water and elements in precipitation was tested using the paired t-test (difference between the amount in bulk precipitation and that in throughfall).

In Paper V, nutrient net throughfall values for the autumnal senescence period were used as indices of needle nutrient leaching for this period at 0.5 and 8 km distances. Net throughfall from the whole canopy (mg m^{-2}) was transformed to net throughfall from the senescing needle mass by multiplying the net throughfall from the whole canopy by the ratio between the three-year-old needle mass and the total needle mass (equation (4) in V).

In Paper VI, mean annual Cu, Fe, Ni and Zn deposition in net throughfall and stand throughfall were calculated for the calendar years 1993–1998 on the basis of the amount of these metals in precipitation and the metal concentrations in the precipitation samples.

2.4 Litterfall

Tree litterfall was collected by 12 litter traps systematically located inside the pine stand at 0.5, 4 and 8 km distances along the Harjavalta study gradient and at the Hämeenkangas background study site at 60 km distance during the period July 1992 to December 1998. The litter traps were emptied every second week during March–July, and weekly during August–November up until the formation of a permanent snow cover.

Green and senescent needles, as well as pine seeds, were separated from the rest of the litterfall. The number of seeds and needles were calculated, and all litter compartments were dried at 70°C for 48 h, weighed and milled. Needle unit weight (mg needle^{-1}) was determined for each sample. Total P, Ca, K, Mg, Mn, Fe, Cu, Ni and Zn concentrations were determined by dry ashing, followed by extraction with a concentrated HCl. The solutions were analyzed using ICP-AES. Nitrogen and sulphur concentrations of finely ground needles were determined by Leco analyzers. Annual seed crops were calculated for the period 1993–1998.

In Paper IV, area-specific Cu, Ni and Zn deposition values (mg m^{-2}) were calculated from the concentrations and amounts of sample related to the surface area of the collectors for the sampling period of the year 1993.

In Paper V, the litter needle mass per unit area was calculated by dividing the total mass of the collected litter needles (kg) by the surface area of the litter traps (m^2). The nutrient content of litter needles (mg m^{-2}) was calculated by multiplying the nutrient concentrations of litter needles (mg kg^{-1}) by the litter needle mass (kg m^{-2}) (equation (3)

in V). The relative element content per needle ($\mu\text{g needle}^{-1}$) was calculated by dividing the area-based content by the number of needles per unit area.

2.5 Needle sampling in the pine stands along the study gradient

Summer needles were collected in the middle of July 1992 from 8–10 trees per study site at 0.5, 4 and 8 km along the Harjavalta gradient and at the 60 km Hämeenkangas background site. The sample trees were randomly selected from five size-class groups representative of each stand. One random branch from the upper, middle and lower crown was sampled on each tree. One-hundred needle pairs were collected from each needle age-class on each branch, and the needles from the upper, middle and lower branch of the same tree were combined to form a sample of 300 needle pairs *per* sample tree.

The needle samples were dried at 70°C for 48 h, weighed and milled. Needle unit weight (mg needle^{-1}) was determined for each sample, and total element concentrations were determined in the same way as for the litter needles.

In Paper I, the needle element pools (mg m^{-2}) were calculated by multiplying the needle element concentrations (mg kg^{-1}) by the corresponding needle mass (kg ha^{-1}).

In Paper V, three-year old needle samples were used to calculate the senescing needle mass by multiplying the litter needle mass (kg m^{-2}) by the ratio between three-year-old green needle unit mass and litter needle unit mass (equation (1) in V). The nutrient content of the needles prior to senescence (mg m^{-2}) was calculated by multiplying the three-year-old needle mass (kg m^{-2}) by the nutrient concentration of the three-year-old green needles (equation (2) in V).

Winter needles for Paper VI were collected twice from three replicate plots in the 0.5 km stand: in January 1992 and in February 1998. The needle samples were taken from five sample trees, randomly selected from the dominant crown layer on each of the plots, *i.e.* from 15 trees in both sampling years. Only current-year needles (C) growing on the third to fifth branch of the whorl, counting from the top, on the southern side of the crown were sampled. The needle samples were dried (70°C for 48 h) and analyzed separately for each tree. The concentrations of Cu, Fe, Ni and Zn were determined from finely ground needles by wet digestion ($\text{HNO}_3 + \text{H}_2\text{O}_2$), followed by analysis by ICP-AES. To estimate the internal pool of metals in the needles, additional needles were collected in 1998 from five pine trees from the buffer zone around two of the replicate plots. The needles were sampled in the same way as described above. Half of the needles were washed with chloroform as recommended by Raitio (1995), and the other half were dried (70°C for 48 h) without any washing. The fresh needles were washed in chloroform for 1 min while stirring with a glass rod. The chloroform was then decanted off, the needles dried on filter paper, and then dried in the same way as the unwashed needles. The Cu, Fe, Ni and Zn concentrations of both washed and unwashed needles were determined according to the same method as for the regular needle samples. The statistical significance of the differences in needle nutrient concentrations between the washed and unwashed samples and between the two sampling years were tested using paired t-test.

2.6 Experimental approaches

2.6.1 Soil sampling along the gradient at Harjavalta

Intact volumetric soil profiles including the litter layer and ground vegetation were taken with an auger (diameter 25 cm, depth 30 cm) at the five sampling sites (0.5, 2, 4, 8, and 60 km) and placed in 10-liter pots. One 4-year-old, bare-rooted pine seedling (*Pinus sylvestris* L.) was planted on the 2nd of June 1994 in each pot. The soil profiles were taken at 25 points in 5 clusters on each site. A smaller volumetric soil sample was taken for chemical analysis next to each sampling point with a small auger (diameter 3.8 cm, depth 30 cm). The loose litter was removed from the top of the sample, and the sample was divided into the humus layer and two mineral soil layers: 0–10 and 10–20 cm. The samples from each cluster (5) were bulked to give five composite samples per layer per site. These samples were used in Papers **III** and **IV**.

2.6.2 Artificial exposure treatment

Pine seedlings of the artificial exposure experiment of Paper **III** were from the same 4-year-old seedling lot as those planted in the smelter-pollutes soil cores. They were planted on the 2nd of June 1994 in similar 10-litre pots as for the smelter-polluted-soil. Each pot contained 8 litres (11.34 kg) of quartz sand (particle size 0.5–1.5 mm). On the following day the soil-plant systems were treated with increasing doses of 1) copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), 2) nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), or 3) a combination of both in equal doses (Table 1 in **III**). Two replicate seedlings were treated with each treatment dose in order to ensure a sufficient amount of plant material for chemical analysis. All the treatments were given as a water solution. The seedlings were fertilized twice during the experiment: 5th of July 1994, and 2nd of July 1995 using a commercial fertilizer. The total amount of nutrients added per pot in fertilization were 155 mg N, 55 mg P, 355 mg K, and 22 mg Mg. These doses were relatively low because achieving optimal nutrient conditions, which are unlikely to occur in natural conditions, was not the aim of the fertilization. At the end of the experiment soil samples were taken for chemical analysis with a small auger (diameter 3.8 cm) from the artificial quartz sand exposure pots. The samples from both replicates were combined to give one composite sample per treatment level.

2.6.3 Experimental conditions, harvesting and soil sampling at the end of the experiments

The four-year-old pine seedlings used in the experiment were bare-rooted and had been raised from selected seed in the forest nursery of the Finnish Forest Research Institute at Suonenjoki, eastern Finland. A set of 50 reference seedlings of the same 4-year-old seedling lot as those planted in the experimental pots were measured (average height 31 cm, standard deviation 5.8), weighed, and the element concentrations in the different compartments (roots, stem, needles) analysed at the start of the experiment. All the soil-plant systems (total number 185) were cultivated for 17 months (from June, 1994 until October, 1995) in controlled greenhouse conditions at the Ruotsinkylä field station

(60°21'N, 25°00'E) of the Finnish Forest Research Institute. A period consisting of two growing seasons was considered to be the optimal length for the experiment, since the primary stem growth of the woody test plant (*Pinus sylvestris* L.) starts to be predominantly prederminative already at the age of 5 years (Lanner 1976, Kanninen 1990). Hence, the primary stem growth of the experimental seedlings during the first year still largely reflected the environmental conditions of the previous year, which naturally also affects the biomass production.

Day temperatures were allowed to follow the ambient temperature during the summer months, but the night temperature was kept at 15°C. A constant temperature of +4°C was maintained throughout the winter period. The seedlings were watered by drip irrigation using ordinary tap water with a pH of 5.9, Cu concentration 0.35 mg L⁻¹, Zn concentration 0.03 mg L⁻¹ and Ni concentration below the quantification limit (< 0.018 mg L⁻¹).

At the end of the experiment the pine seedlings were harvested and divided into root, stem and needle compartments. Green needles were collected by age classes: current needles (C), one-year-old (C+1) needles, and two-year-old and older needles (C+2). Senescent needles were collected throughout the course of the experiment and were stored in a dry place prior to analysis. The pine seedling data are presented in Papers III–IV.

At the end of the experiment soil samples for chemical analysis were taken using a small auger from each pot. The soil samples were divided into layers and those belonging to the same clusters were bulked together to give five composite samples per layer per site, as in field sampling prior to the experiment. These soil samples were compared to those taken in the field prior to the experiment in Paper IV.

2.6.4 Chemical analysis of the greenhouse experiments

The pine seedling samples were dried at 70°C for 48 h and weighed in order to obtain the biomass of the individual seedling compartments. The compartments of the seedlings grown in the smelter-polluted soil pots, and belonging to the same cluster, were bulked to give five composite samples per compartment per site. The replicate seedling compartments of the artificial quartz sand exposure were combined to give one composite sample per compartment per treatment level. The humus samples were dried, weighed and milled to pass through a 1-mm sieve. Total Cu, Ni, P, Ca, Mg and K concentrations were determined on the humus and pine seedling samples by dry ashing at 550°C, followed by extraction with concentrated HCl. The solutions were analysed by ICP-AES, and the total N and S concentrations were determined on the milled humus samples on LECO analysers. Exchangeable element concentrations were determined on the humus samples by extraction with 1M ammonium acetate (pH 4.65) with 2% EDTA (25 ml humus *per* 250 ml extractant, shaking for 1 h), followed by filtration and analysis by ICP-AES. The mineral forest soil samples were dried, weighed and passed through a 2-mm sieve to remove stones and large roots. The sieved portion of each sample was weighed. Exchangeable element concentrations were determined from the sieved mineral forest soil and from the quartz sand samples in the same way as for the humus samples. The pH of the quartz sand samples was determined in water (15 ml sample *per* 25 ml water).

2.6.5 Calculations and statistical treatment of the greenhouse experiments

The net uptake of Cu and Ni by the pine seedlings was determined by calculating the amount of metal per compartment sample (roots, stem, green needles and senescent needles). As these compartment samples were composite samples taken from 5 seedlings, the values were divided by five in order to obtain the value per seedling. Finally, metal uptake was obtained by summing up all the compartments per seedling, and then subtracting the average element content of the reference seedlings from the element content of each experimental seedling.

The data were analysed using SAS V8 statistical package. Simple linear regression equations were calculated for the relationships between the exchangeable Cu and Ni content of the quartz sand series at the end of the experiment and the amount of Cu and Ni originally added. The dependence of seedling biomass on the Cu and Ni content of the quartz sand media was calculated as a simple linear regression equation for all treatment series using ln-transformed treatment dose values. The independent variables were logarithmically (ln) transformed in order to linearize the asymptotic relationship with the dependent variable.

To find the variables that best explained the variation in biomass of the smelter-polluted-soil- grown seedlings, multiple regression analysis was performed using the Cu, Ni, Ca, K, Mg, and P contents of the smelter-polluted soil cores as independent variables. The calculation of the element contents of the smelter-polluted soil cores (mg *per* pot) is explained in detail in Paper IV. All possible regression models were fitted to the data with all possible combinations of the independent variables. The best model was found to be the model with Cu, Ni and P as independent variables. The multiple regression procedure was repeated using the total Cu, Ni, N, S, P, Ca, K, and Mg concentrations in the humus as independent variables. The humus Cu and N concentrations were found to be the best explaining variables.

Regression equations between seedling metal uptake and soil Cu and Ni content were calculated as simple linear models. Pearson correlation coefficients were calculated between soil Cu and Ni contents and the Ca, K, Mg, P, Cu and Ni concentrations of the roots, stem, senescent needles and green needles.

In Paper IV, the soil Cu, Ni and Zn concentrations are presented as an average value of the five replicate samples. The nonexchangeable metal concentration was obtained by subtracting the exchangeable concentration from the corresponding total concentration. The statistical significance of the differences between the concentration before and after the incubation period was tested by paired t-test.

2.6.6 Pine seedling experiment in the field

The field grown pine seedlings of Paper VI were planted in June, 1996, as 2-year-old containerised (peat containers) seedlings in the immediate vicinity of the study stand at 0.5 km distance from the smelters. Three experimental squares (5 m × 5 m) were established, and 49 seedlings were planted in each square. The seedlings were planted in soil pockets filled with 'clean' mulch consisting of a mixture of municipal compost

and woodchips. These seedlings were therefore grown in unpolluted soil in the field, but exposed to the heavy-metal deposition from the smelters.

Needles from the seedling experiment in the field were collected by needle-age classes in September 1998, when the seedlings had reached the age of 5 years. Needle samples were taken from three seedlings per square, and then bulked together to give one sample per square, *i.e.* a total of 3 samples of each needle-age class. The needle samples were dried (70°C, 48 h) and analysed by dry ashing and extraction with HCl, followed by analysis by ICP-AES.

2.7 Peat sampling

The peat core (15 cm depth × 5 cm × 5 cm) in Paper II was taken from the surface layer of the Lammaistensuo bog at Harjavalta, 2.4 km from the Cu-Ni smelters. A reference core was taken from the background bog at Hietajärvi in eastern Finland. The cores were frozen and cut into 1 cm slices using a stainless steel band saw at the University of Berne. All peat samples were dried at 105°C in acid-washed Teflon bowls, and milled in a centrifugal mill equipped with a titanium rotor and 0.25 mm titanium sieve. The milling was carried out in a Class 100 laminar flow clean air cabinet to prevent possible contamination of the peat samples by laboratory dust. Selected trace elements were measured using the Energy-dispersive Miniprobe Multielement Analyzer (EMMA-XRF) (Cheburkin and Shotykhin 1996) at EMMA Analytical Inc., Elmvale, Ontario, Canada. The instrument was calibrated using certified standard reference plant materials.

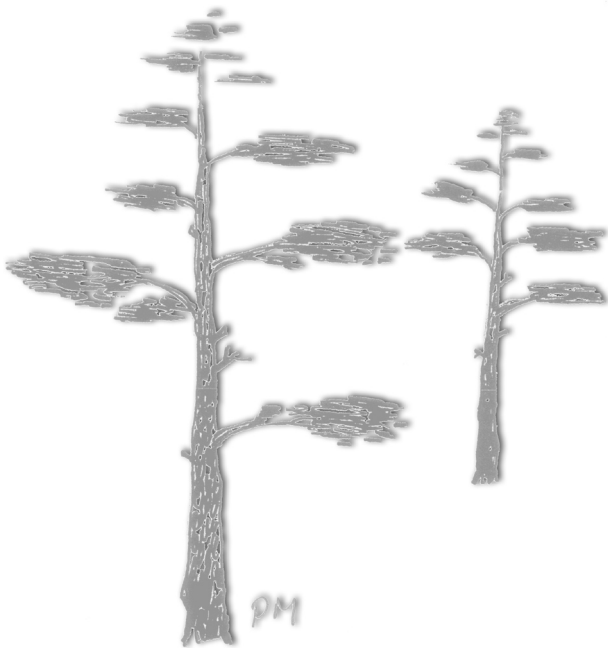
In order to separate the natural variation in element concentrations with depth from changes due to anthropogenic deposition, enrichment factors (EF) were calculated according to the following formula:

$$EF = (X/Ti)_{\text{peat}} / (X/Ti)_{\text{crust}},$$

where the data of Wedepohl (1995) was used for the values of the Earth's crust. The calculated enrichment factors (EF) show the extent of the changes in element abundances in the profile relative to crustal values. We acknowledge that pre-anthropogenic (X/Ti) peat values may exceed those of the crust, but it is helpful to have a common reference level for comparison between the two cores, and with our published values.

Pollution factors (PF) were calculated for comparison between the polluted (Harjavalta) and the reference site (Hietajärvi). The average and median element concentrations of the Harjavalta core were divided by the corresponding concentrations of the Hietajärvi core. These PF values thus merely indicate the extent of pollution at the Harjavalta bog compared to that of the Hietajärvi bog.

The bulk density value of 87 g dm⁻³ reported by Veijalainen (1984) for the Harjavalta peat bog was used to estimate the total amounts of the studied elements in the 15-cm-surface-peat layer. It was assumed that this 15-cm surface-peat contains all the peat formed since the smelting activities started. Thus the total amount of Cu and Zn was divided by the duration of Cu smelting (55 years) in order to obtain a rough estimate of the average annual deposition during the smelter history. Nickel was correspondingly divided by 40, since Ni smelting started in 1959.



3 Results and discussion

3.1 Recent and past metal deposition at the study area

3.1.1 Bulk precipitation and stand throughfall

The deposition of metals (Ca^{2+} , Mg^{2+} , Fe^{3+} , Zn^{2+} , Cu^{2+} , Ni^{2+}), NH_4^+ and SO_4^{2-} through bulk precipitation and stand throughfall was the greatest at 0.5 km (Fig. 1 in **I**). As an average for the whole study period, Cu^{2+} and Ni^{2+} were clearly the most abundant heavy metals in both bulk and throughfall deposition. The element concentration of bulk precipitation changes during passage through the tree canopies (Helmisaari and Mälkönen 1989, Hyvärinen 1990, Bringmark *et al.* 2001, Ukonmaanaho 2001). Forest canopies are efficient at intercepting dry deposition (Hultberg 1985), which is reflected in stand throughfall as a strong enhancement of the dry deposited elements. In addition to canopy-intercepted dry deposition, throughfall also contains elements leached out from the living and dead foliar tissues (Tukey 1980, Parker 1983, Godt *et al.* 1986). Despite the sparse tree cover at 0.5 km, the amounts of metals intercepted as dry deposition by the canopy were extremely high, since a high proportion of the metals in throughfall were derived from the canopy (Fig. 1 in **I**). The results of canonical discrimination analysis demonstrated that the composition of both bulk precipitation and stand throughfall at 0.5 km was clearly different from that at 4 and 8 km (Fig. 2 in **I**).

The monthly average amounts of canopy derived Cu^{2+} (net throughfall) during 1992–1996 at 0.5, 4 and 8 km were 0.27, 0.004 and 0.0007 mol_c m⁻², respectively, and the corresponding amounts of Ni^{2+} 0.047, 0.0007 and 0.0007 mol_c m⁻² (Fig. 1 in **I**). Although foliar leaching of Cu^{2+} and Ni^{2+} cannot be completely ruled out, most of the canopy derived Cu^{2+} and Ni^{2+} at 0.5 km originates from the wash-off of previously dry-deposited material. This can be concluded from the ratios between the annual fluxes (mg m⁻² year⁻¹) and needle pools (mg m⁻²) of Cu and Ni (Table 5 in **I**). The annual Cu flux during 1992–1996 was nine times greater than the needle pool of Cu, and that of Ni almost 14 times higher. According to Pfirrmann *et al.* (1990), the leaching of most cations from spruce foliage represents only slightly more than 1% of the total content in the needles. In our experimental needle washing approach, a statistically significant proportion (40%) of Ni was removed from needles by chloroform washing (Table II in **VI**). In contrast, the difference between the Cu concentrations in the chloroform-washed and unwashed samples was not statistically significant. These results suggest that although the overall deposition of Ni is lower, the canopy deposited Ni is relatively more susceptible than Cu to wash-off from the canopy by rainfall.

The relatively high amount of NH_4^+ in both bulk precipitation and stand throughfall at 0.5 km (**I**) was caused by NH_3 emissions from the nickel-processing plant (Derome *et al.* 2004). The NH_3 emissions have had an increasing effect on S deposition by scavenging SO_2 from the air (Derome *et al.* 2004). Although SO_4^{2-} was the most abundant ion, both in bulk precipitation and in throughfall at all sites (**I**), only the amounts at 0.5 km were greater than those reported for Finnish background areas

(Helmisaari and Mälkönen 1989, Hyvärinen 1990, Ukonmaanaho 2001). Throughfall enhancement of SO_4^{2-} has also been reported in several earlier studies, and it is assumed to be mainly due to the canopy interception and subsequent wash-off of sulphur-rich, dry deposition (Mayer and Ulrich 1978, Probst *et al.* 1990, Cape *et al.* 1992, Hultberg and Grennfelt 1992, Lindberg and Lovett 1992).

The annual metal throughfall deposition values during 1993–1998 at the 0.5 km site (Fig. 2 in **VI**) do not follow the trends of the stack emissions (Table 1). Copper deposition in throughfall remained relatively constant during the study period, while there was a decrease in throughfall deposition of Zn. In the case of Ni, there was a very strong increasing peak in throughfall deposition in 1998 (Fig. 2 in **VI**), which is consistent with the observation of increased Ni concentrations in forest mosses in 2000 compared to 1995 in the surroundings of the Harjavalta smelters (Poikolainen *et al.* 2004), but inconsistent with the simultaneous decrease in stack-emissions of Ni (Table 1). Therefore, other sources of metals have to be of more importance for the measured metal deposition than the current stack-emissions. Possible sources of metals are the slag produced during smelting (*cf.* Chapter 2.2.), as well as wind-borne dust derived from the forest floor, where a considerable accumulation of metals has taken place during the more than 50 years lifetime of the smelters (**I**).

3.1.2 The extent of past metal deposition

The extent of pollution in the immediate vicinity of the Harjavalta smelters was determined by comparing metal concentrations in peat and precipitation samples to the values measured in corresponding media at the reference site Hietajärvi in eastern Finland (Fig. 2) The metal contents in the surface peat of the Lammaistensuo bog adjacent to the smelters (Fig. 2) reflect much higher Cu and Ni pollution rates than the current bulk precipitation at the 0.5 km site (**II**). This can, at least partly, be explained by the earlier considerably higher emission levels. (Table 1, Fig. 3). In addition to the stack emissions, possible sources of Cu and Ni are the slags formed during the smelting processes (Table 3). The wind-borne slag dust may have had a greater impact on metal deposition in the surrounding areas in earlier days prior to the recent technical improvements in slag handling. On the other hand, the direct effect of a recent influx of sludge runoff on the surface peat of the study bog cannot be completely ruled out. In spring 1998, the holding dam of a sludge basin adjacent to the bog burst and a considerable amount of sludge was released into the surroundings despite active clean-up efforts. Furthermore, the precipitation data are not fully comparable with the peat contents, since insoluble particles were excluded from the bulk precipitation samples by filtration, and the peat samples, parting turn, included all chemical and mineralogical forms.

Peat sediments can be used as indicators of past metal deposition only in the case of relatively immobile elements, such as Pb (Mackenzie *et al.* 1998, Shotyk *et al.* 1998, Weiss *et al.* 1999). According to our current study, Cu also appeared to be strongly retained by the peat (**II**). In contrast, Ni is known to be much more mobile than Cu in an organic matrix (Bergkvist *et al.* 1989, Kabata-Pendias 2001), and hence also more susceptible to downward migration in a peat profile.

3.2 Performance of Scots pine in smelter-polluted environment at different phases of its life-cycle

3.2.1 History of the forests under study

The deleterious effect of SO₂ gases on coniferous trees has been documented in numerous studies (e.g. Whitby 1939, Kikuzawa 1973, Huttunen 1975, Hutchinson and Whitby 1977, Legge *et al.* 1996), and *Pinus sylvestris* L. has proved to be among the most SO₂ sensitive species of the *Pinaceae* family (Caput *et al.* 1978, Genys and Heggstad 1978, Katainen *et al.* 1984). Therefore, it is most probable that the forest dieback, known to have occurred during the first years of smelting activities at Harjavalta, was caused by the direct toxic effects of SO₂. However, after the start of efficient sulphur recovery in 1949 and consequently improved air quality, the pine stands in the vicinity of the smelter were still able to recover. As the mean age of the 0.5 km study stand, 52 years in 1996, is approximately the same as the duration of smelting activities, it appears that the forest dieback of the early days was not totally complete. At least some of the young seedlings survived or new ones were rapidly established.

The radial growth series of the study stands indicate an abrupt decrease in growth rates of the 0.5 km stand in the mid-1970s (Fig. 4), which reflects the deterioration in growth conditions at the site. The critical threshold in soil metal accumulation may have been passed by that time. The vegetation damage area appeared to be at its largest in the 1970s (Laaksovirta and Silvola 1975), and public concern was also aroused at that time by the visible vegetation injuries in the gardens and forests surrounding smelters (Poutanen and Kuisma 1994). The decrease in radial growth of the 0.5 km stand was followed by a sudden increase (Fig. 4) due to the NPK fertilization applied

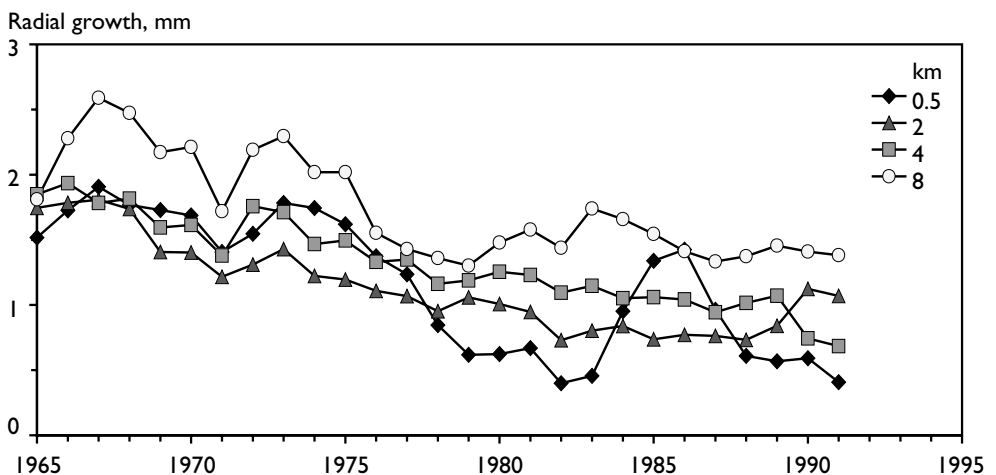


Fig. 4. Radial growth of trees in the experimental stands during 1965–1991 (modified from Mälkönen *et al.* 1999)

in 1983 (Mälkönen *et al.* 1999) containing *ca.* 120 kg N ha⁻¹. The effect of fertilization followed a normal response pattern and levelled off in the late 1980s.

3.2.2 Current growth rate of the study stands

All of the study stands are naturally regenerated middle-aged stands in which thinnings were carried out at an early stage (Mälkönen *et al.* 1999). The Harjavalta tree stands were measured in 1992 and 1996, and the Hämeen kangas background site in 1991 and 1995, in order to determine the volume increment, *i.e.* the difference in stand volume between the measurement years (Mälkönen *et al.* 1999). The overall low growth rate of the study stands (Table 4) reflects the poor fertility of the sites. The extremely low growth of the stand growing next to the smelters is related to the adverse effects of smelting activities (**I** and **III–V**), but the differences between the other stands are much more difficult to interpret. Their growth characteristics are not clearly related to distance and can simply indicate silvicultural and natural, between-site variation (Mälkönen *et al.* 1999, Nieminen *et al.* 2000). However, the role of pollution as a factor affecting growth also at greater distances cannot be completely ruled out. The indirect effects of metal pollution on tree growth, through deterioration of the nutrient status of the soil, are difficult to distinguish from the natural variation in soil fertility between sites subjected to low to moderate pollution conditions. The current growth rate of the stands, expressed as the annual volume increment during the last 5-year-period, is clearly different from the predicted increment estimate modelled by functions presented by Nyyssönen and Mielikäinen (1978), only in the case of the 0.5 km stand (Table 4).

3.2.3 Comparison with the experimental seedling cultures

The results of the greenhouse experiment, in which pine seedlings were cultivated in soil cores transported from the field plots, showed a relatively similar variation in the biomass production rates as the mature pine stands (Fig. 1 in **III**, Figs. 5 and 6). These results indicate that soil factors have a major impact on the current biomass

Table 4. Stand characteristics at different distances from the Harjavalta smelters. (Modified from Nieminen *et al.* 1998.)

Distance from the smelter, km	0.5	2	4	8	60
Age of the study stands in 1992, years	49	54	48	40	in 1991 45
Stems, no ha ⁻¹ in 1992	1008	1230	1517	1552	in 1991 2063
H _{dom} , m in 1992	7.6	12.5	11.1	12.4	in 1991 9.2
Stem volume in 1992, m ³ ha ⁻¹	23	85	68	95	in 1991 48
Annual volume increment, m ³ ha ⁻¹ year ⁻¹ (1992–1996)	0.3	3.8	2.8	6.3	(1991–1995) 3.3
Predicted volume increment for the five year period, m ³ ha ⁻¹ year ⁻¹ (according to Nyyssönen and Mielikäinen 1978)	1.6	4.4	4.2	6.2	3.7

production of Scots pine at the study plots, and that the current level of deposition is of minor importance.

However, the production rate of the 0.5 km seedlings was, in relative terms, even lower than that of the corresponding pine stand in the field. In fact the seedlings in the 0.5 km soil cores hardly grew at all, and they did not have any net biomass production during the experiment (III). Due to their limited photosynthetic capacity, survival has probably been strongly based on the consumption of storage carbon compounds. Furthermore, only four of the original 25 seedlings survived up until the end of the 17-month experimental period (III); at first site, this appears to conflict with the fact that the pine stand, with a current density of more than 1 000 trees per hectare, has been growing in the same polluted site for more than 50 years. However, in reality, the trees have not been growing for over 50 years in soil that is as polluted as it is now. Soil pollution has taken place gradually during the period of smelting activities, and metal accumulation has reached a level at which no natural seedling establishment can take place at 0.5–1 km distance from the smelters (Riissanen 1998, Salemaa and Uotila

Fig. 5. Needle mass of Scots pine seedlings grown in soil cores transported from a smelter-pollution gradient. C = current needles, C+1 = previous-year needles and C+2 = two-years-old and older needles.

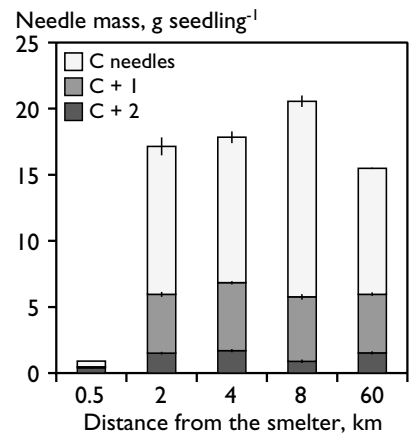
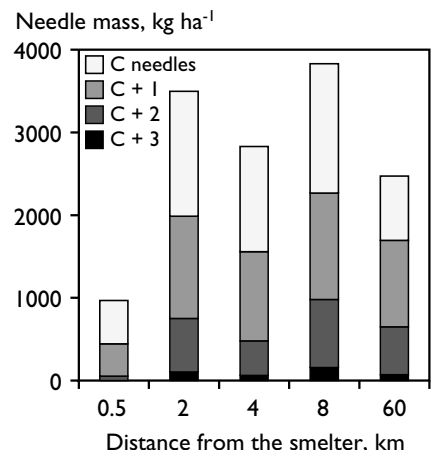


Fig. 6. Needle mass of Scots pine stands growing along a smelter pollution gradient (Nieminen et al.1998). C = current needles, C+1 = previous-year needles, C+2 = two-years-old needles and C+3 = three-years-old and older needles.



2001). According to Dickinson *et al.* (1996) trees can remain relatively healthy in the presence of high levels of contamination that build up slowly over time. Lepp *et al.* (1997) report that seedlings of broad-leaved herbs in a vicinity of a copper rod rolling factory in England were more sensitive to Cu than older herbs. Due to the cessation of reproduction close to Harjavalta smelters, the Scots pine stand at 0.5 km can no longer be considered as tolerant to the prevailing pollution level. According to the definition given by Baker and Walker (1989), tolerance enables a plant to establish, survive and reproduce in the presence of a particular pollutant.

Another possible factor explaining the better survival and growth rate of the mature trees at the 0.5 km field site compared to the greenhouse grown 0.5 km-seedlings is the impact of selection pressure. The heavy metal load, and also the SO₂ exposure in the early period of smelter activities, may have subjected the trees to a strong selection pressure with the result that only the most resistant individuals have survived at the site. During their *ca.* 50-year life-cycle, the pines have also had time to acclimatise to the gradually increasing heavy-metal concentrations in the soil. According to Baker (1987), Baker and Walker (1989), and Dickinson *et al.* (1991), the metal resistance of long-lived plants, such as trees, is primarily based on the phenotypic plasticity of individuals rather than on a constitutive tolerance, although the precise mechanisms allowing survival in metal-contaminated environments still remain unclear (Turner and Ross 1994).

Trees growing in metalliferous soils can also avoid metals by penetrating their roots in less polluted soil pockets and deep uncontaminated soil layers (Tyler *et al.* 1989, Dickinson *et al.* 1991, Turner and Dickinson 1993, Watmough and Dickinson 1995). Thus, a heterogeneous dispersal and availability of metals in soil may explain the survival of mature trees at 0.5 km.

Finally, the genetic tolerance of root-associated mycorrhizal species plays an important role in the heavy metal resistance of woody plants (*e.g.* Bradley *et al.* 1982, Dixon 1988, Wilkinson and Dickinson 1995). The spatially large ectomycorrhizal mycelium may immobilize metals in their cell walls (Colpaert and Assche 1992, Tichelen 1999, Ahonen-Jonnarth 2000), and facilitate the ability of roots to reach clean soil layers, thus avoiding the metals (Turner and Dickinson 1993). The mycorrhizas may have alleviated heavy-metal toxicity in the field in the mature stands (Nieminen *et al.* 2000). In the 0.5 km plant-soil systems grown in the greenhouse, on the other hand, there was no possibility for mycorrhizal infection by new fungal species during the experiment, because a relatively high supply of carbohydrates from the host plant is needed for the initiation of a mycorrhizal infection (Harley and Smith 1983).

The major contribution of soil contamination to the high mortality rate of the greenhouse-grown-seedlings is confirmed by the low mortality of the field-grown pine seedlings (see VI). These field-seedlings were planted in June 1996 in soil pockets filled with “clean” mulch as a part of the remediation experiment (Kiikkilä 2002) established next to the 0.5 km study site. In September 2004, after nine growing seasons, the survival rate of the seedlings was as high as 96% (unpublished results). Hence, planting in unpolluted organic mulch proved to be an efficient way to mitigate the toxic effects of soil contamination, even under the impact of the current atmospheric smelter emissions.

3.2.4 Seed crop and seedling establishment

The annual seed crops on the three study plots showed an overall decreasing trend with decreasing distance to the smelters (Table 5); this was of course partly due to the decreasing stand density. However, even the seed crops of the most polluted 0.5 km stand are at a normal level. Lehto (1956) reported 16 seeds *per m*² as a mean value for CT stands, and 30 seeds *per m*² for VT stands. Sarvas (1949) found that the average annual crop from seed-tree stands on CT sites in southern Finland was 18.5 seeds *per m*². He also concluded that sites with a poor growth rate produced smaller seed crops than those with a higher growth rate. According to Koski and Tallqvist (1978), the seed crop of Scots pine varies from 18 to 216 seeds *per m*². Therefore, the seed production of the study stands closest to the smelter cannot be the reason for the lack of natural seedling establishment. Similar results were obtained by Kozlov and Zvereva (2004) near the Monchegorsk Ni-Cu smelters in northwest Russia. They concluded that the high level of pollution had not decreased the seed production of mountain birch (*Betula pubescens ssp. czerepanovii* (Orlova) Hämet-Ahti).

Salemaa and Uotila (2001) concluded from their seed bank studies in Harjavalta soils that viable pine seeds occurred even in the most contaminated soil, but that seedling establishment was unsuccessful. According to several studies on the lack of tree seedling establishment in metal-polluted substrate, seed germination does not seem to be affected, but the development of the radicle is disturbed (Patterson and Olson 1983, Wotton *et al.* 1986, Komulainen *et al.* 1994). Niini and Raitio (1993) found that the radicles of germinated pine seedlings were not able to penetrate into soil derived from a forest in the vicinity of the Harjavalta smelters.

Consequently, pine seedlings appear to be more susceptible than mature pines to the current elevated soil metal contents. The seed production of mature trees, which is considered to be a decisive phase in the assessment of population survival by Ernst and Nelissen (2000), was not severely affected. Nevertheless, the disturbed development of the seedling radicle is most likely the crucial phase preventing the establishment of seedlings at the most polluted study site. According to Ernst *et al.* (1992), long-term survival of plants in metal-enriched environments is possible only if they can detoxify the metals and protect their roots from an excess of metals. At the most polluted Harjavalta site, the pine seedlings do not appear to be able to protect their roots, although mature pines survive at the same site.

Table 5. The annual pine seed crops during 1993–1998 at plots at three distances from the Cu-Ni smelters.

Distance from the smelters	1993	1994	1995	1996	1997	1998
	number of seeds per m ²					
0.5 km	45	45	28	26	105	12
4 km	26	32	64	60	111	32
8 km	188	133	57	42	98	41

3.3 Availability of soil Cu and Ni to Scots pine

3.3.1 Soil and soil solution Cu and Ni concentrations as indicators of their availability

Based on the present study, the uptake pattern of Scots pine appeared to be closer to that of an accumulator plant than of an excluder plant (Baker 1987) in both the case of Cu and Ni (Figs. 4 and 5 in **III**). The soil Cu, Ni, N and P contents were the best explainers of the biomass production of the seedlings grown in smelter-polluted soil in paper **III**. The exceptionally low production rate of the 60 km background site is undoubtedly due to the poor soil nutrient status (Table 6), while the stunted growth

Table 6. The mean total and exchangeable concentrations in the humus layer along the smelter pollution gradient, as well as the exchangeable mineral soil concentrations (n = 5, standard deviation is given beside the mean value).

Distance, km	0.5		2		4		8		60	
Humus, pH	4.1		3.8		3.5		3.9		4.1	
Mineral soil pH										
0-10 cm	4.1		4.1		3.9		4.2		4.9	
10-20 cm	4.1		4.6		4.6		4.6		4.8	
Humus concentrations g kg ⁻¹										
N _{tot}	4.68	1.0	5.58	0.8	5.32	1.4	6.10	1.2	2.58	0.4
S _{tot}	0.65	0.12	0.56	0.06	0.40	0.05	0.33	0.04	0.30	0.04
P _{tot}	0.42	0.08	0.49	0.1	0.47	0.04	0.42	0.1	0.26	0.02
P _{extr}	0.14	0.02	0.18	0.05	0.15	0.01	0.14	0.03	0.07	0.01
Ca _{tot}	0.45	0.1	1.13	0.3	1.07	0.1	0.91	0.2	0.50	0.2
Ca _{exch}	0.24	0.06	1.13	0.2	0.80	0.1	0.80	0.2	0.35	0.1
K _{tot}	0.25	0.03	0.38	0.05	0.43	0.03	0.40	0.05	0.28	0.02
K _{exch}	0.06	0.01	0.19	0.04	0.29	0.03	0.26	0.05	0.11	0.01
Mg _{tot}	0.17	0.03	0.26	0.03	0.26	0.04	0.28	0.06	0.35	0.09
Mg _{exch}	0.02	0.006	0.10	0.02	0.13	0.03	0.11	0.03	0.07	0.03
Mineral soil exchangeable concentrations mg kg ⁻¹										
P 0-10 cm	7.1	1.2	35.6	20.1	13.0	7.2	32.4	6.6	8.3	3.7
P 10-20 cm	42.6	21.2	37.3	16.1	22.9	9.0	19.7	3.2	4.2	0.8
Ca 0-10 cm	21.9	7.0	36.0	17.7	10.7	2.4	16.5	5.1	8.6	3.4
Ca 10-20 cm	11.6	3.4	13.2	6.7	6.5	1.4	5.5	1.5	4.0	0.8
K 0-10 cm	13.4	5.3	18.6	8.8	10.0	1.1	13.6	1.6	25.0	7.3
K 10-20 cm	9.0	1.4	12.8	5.1	8.7	1.6	10.3	2.1	12.4	5.5
Mg 0-10 cm	3.0	0.9	8.0	4.5	3.5	1.3	5.5	2.1	4.5	2.2
Mg 10-20 cm	1.8	0.4	1.6	0.5	1.4	0.3	1.5	0.5	1.2	0.4

of the 0.5 km site mainly reflects the deleterious effects of the high soil Cu and Ni contents (Table 7). The low soil nutrient content at Hämeen kangas has been reported also by Raitio (1990a).

Since plants access metals in the soil primarily through the soil solution, the soil solution concentration of a specific metal would appear to be a good indicator of its availability. The Cu and Ni concentrations in zero-tension soil water collected at the Harjavalta field sites followed the same decreasing pattern with increasing distance as did the soil concentrations (Table 8). However, although the soil solution Ni concentrations were almost as high as those of Cu at the 0.5 km site, this was not reflected in the Cu:Ni ratio of the pine tissues of the present study. According to the tissue concentrations of the greenhouse grown seedlings of the present study (Fig. 7 and 8), as well as to their net uptake rates (Fig. 5 in IV), the ratio between Cu and Ni availability at the most polluted 0.5 km site would be relatively close to 10:1, which is about the same as their ratio in the soil (Fig. 8, Table 7, III, IV). Thus, the soil concentrations of the present study appeared to be better indicators of Cu and Ni availability than the soil solution concentrations of the same site presented by Derome (2000). However, the use of root concentration as an availability indicator is problematic due to the strong affinity of Cu for the negatively charged exchange sites in the root cortex (McLaughlin 2002). This cortex-bound Cu would appear as elevated root Cu concentrations, even if no real uptake through the plasma membrane had taken place (cf. III).

The inconsistency between the Cu:Ni ratio in soil solution and the Cu:Ni ratio in the aboveground tissues of the experimental pine seedlings, may be partly due

Table 7. The mean Cu and Ni concentrations of the experimental soil cores collected along the pollution gradient (n = 5, standard deviation is given beside the mean value. n.d. = not detected i.e. below the detection limit).

Distance from the smelter, km	Humus layer concentration,				Mineral soil concentration,			
	total		exchangeable		0-10 cm layer,		10-20 cm layer,	
	mg kg ⁻¹ d.w.							
	mean	sd	mean	sd	mean	sd	mean	sd
Cu								
0.5	2665	1178	2072	380	59	23	22	18
2	1456	487	1188	145	17	4	3	0.5
4	522	230	385	79	3	1	0.9	0.2
8	102	34	74	10	2	0.4	0.4	0.2
60	6	1.7	3	0.9	0.8	0.7	0.4	0.1
Ni								
0.5	216	105	138	31	10	2.6	n.d.	
2	158	39	111	12	3	0.8	n.d.	
4	100	27	70	10	0.6	0.6	n.d.	
8	32	12	21	3	n.d.		n.d.	
60	16	3	1	0.3	n.d.		n.d.	

Table 8. Mean element concentrations and pH in soil solution at different distances from the Harjavalta smelter (n.m. = not measured, s.e. = standard error of the mean). Modified from Derome (2000).

Distance	Depth	0.5 km		4 km		8 km	
		mean	s.e.	mean	s.e.	mean	s.e.
		mg L ⁻¹					
Cu	5 cm	0.65	0.09	0.06	0.01	0.02	0.002
	20 cm	1.19	0.08	0.03	0.003	0.01	0.002
	40 cm	0.41	0.05	0.01	0.001	n.m.	
Ni	5 cm	0.54	0.06	0.02	0.003	0.01	0.001
	20 cm	0.95	0.05	0.02	0.003	0.01	0.001
	40 cm	0.64	0.05	0.01	0.001	n.m.	
NH ₄ -N	5 cm	0.61	0.16	0.42	0.09	0.44	0.10
	20 cm	0.98	0.36	0.20	0.03	0.27	0.05
	40 cm	0.24	0.06	0.12	0.12	n.m.	
NO ₃ -N	5 cm	0.21	0.04	0.21	0.05	0.08	0.02
	20 cm	0.21	0.10	0.03	0.01	0.06	0.02
	40 cm	0.25	0.05	0.03	0.01	n.m.	
SO ₄ -S	5 cm	4.43	0.29	2.28	0.18	1.98	0.18
	20 cm	6.59	0.44	1.82	0.13	1.89	0.13
	40 cm	5.29	0.50	1.49	0.11	n.m.	
PO ₄ -P	5 cm	0.11	0.02	0.18	0.02	0.11	0.02
	20 cm	0.07	0.01	0.09	0.01	0.08	0.02
	40 cm	0.06	0.01	0.04	0.01	n.m.	
Ca	5 cm	1.53	0.12	1.12	0.11	0.91	0.09
	20 cm	3.05	0.45	0.44	0.04	0.82	0.07
	40 cm	1.59	0.15	0.38	0.04	n.m.	
K	5 cm	1.47	0.13	2.03	0.16	1.78	0.17
	20 cm	2.76	0.28	2.38	0.20	1.97	0.21
	40 cm	2.59	0.26	1.52	0.16	n.m.	
Mg	5 cm	0.45	0.05	0.27	0.03	0.27	0.03
	20 cm	0.81	0.12	0.21	0.02	0.30	0.02
	40 cm	0.57	0.06	0.15	0.01	n.m.	
pH	5 cm	4.07	0.04	4.38	0.09	4.27	0.09
	20 cm	3.96	0.03	4.34	0.06	4.56	0.05
	40 cm	4.43	0.03	4.76	0.04	n.m.	

to the fact that the sampled soil solution was zero-tension soil solution, which does not necessarily correspond to the soil water fraction surrounding the roots of the vegetation. It is generally assumed that soil solution sampled by tension lysimeters would give a better idea of plant-available element concentrations, whereas gravimetric soil solution provides better information about the movement of elements between the soil horizons (Derome *et al.* 2002).

Furthermore, in the case of Cu, the soil solution concentrations appear to be relatively close to the chemical equilibrium status of a saturated system, where pH is a more important controlling factor than the soil Cu pool. In an experimental

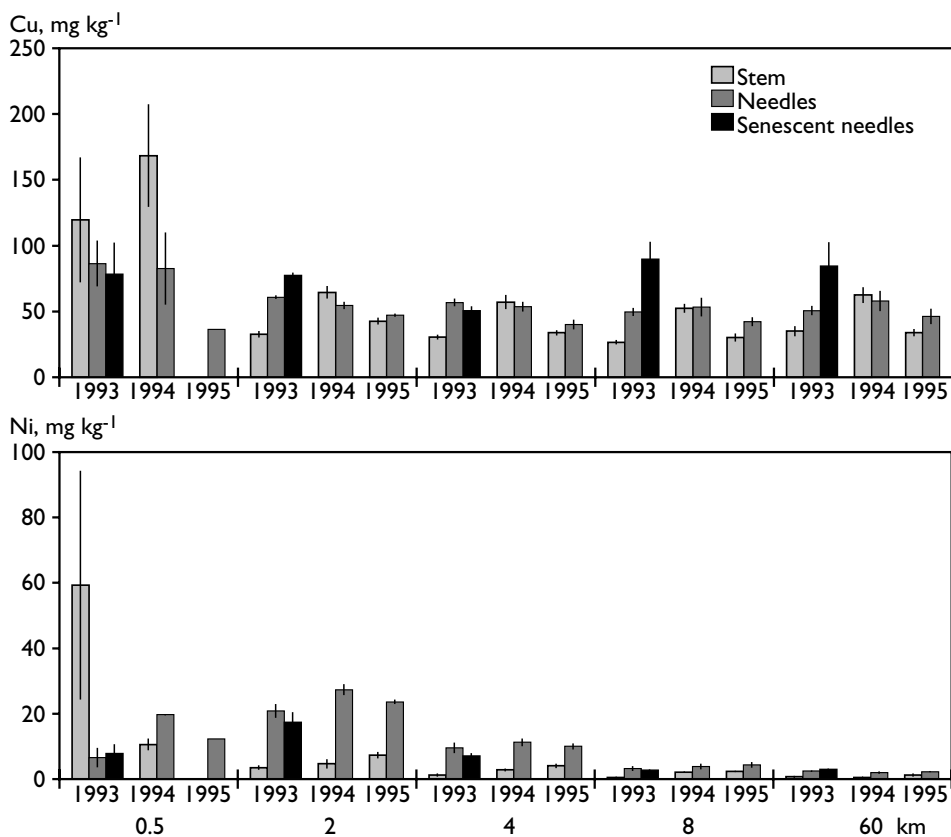


Fig. 7. The mean Cu and Ni concentrations of the above-ground compartments of the seedlings grown in smelter-polluted soil, $n = 5$, except for the 1994 ($n = 4$) and 1995 ($n = 1$) compartments of the 0.5 km. The bar indicates the standard error of the mean. (Note also that the 1994 and 1995 samples of 0.5 km represent only 1 seedling, while the other samples represent 5 seedlings bulked together.)

approach reported by Herms and Brümmer (1980) and Brümmer and Herms (1983), Cu concentration in an equilibrium solution of a sandy podzol with constant total Cu content varied between 0.4 and 4 as a function of pH (Fig. 9). The soil used in this experiment was sampled from the A horizon of an uncontaminated sandy gleyic podzol site, and adjusted to give an excessive total concentration of 100 mg Cu kg⁻¹ (Herms 1982). The soil solution Cu concentrations of the 0.5 km study site (Table 7) follow relatively closely the pH dependence curve of the equilibrium solutions of the sandy podzol (Fig. 9), even though the experimental soil solution was obtained by vacuum filtration (Herms 1982). Consequently, the differences in the Cu concentrations of the soil solution between different depths at the 0.5 km site are presumably merely due to pH changes rather than to changes in the total soil Cu concentration. According to Herms and Brümmer (1980), the increase in Cu solubility over the pH range 6 to 8 (Fig. 9) is due to increasing solubility of Cu complexing organic substances. The increase at low pH values is supposed to be mainly due to dissociation of the metal-organano-complexes, resulting in the release of free Cu²⁺ ions (Herms and Brümmer

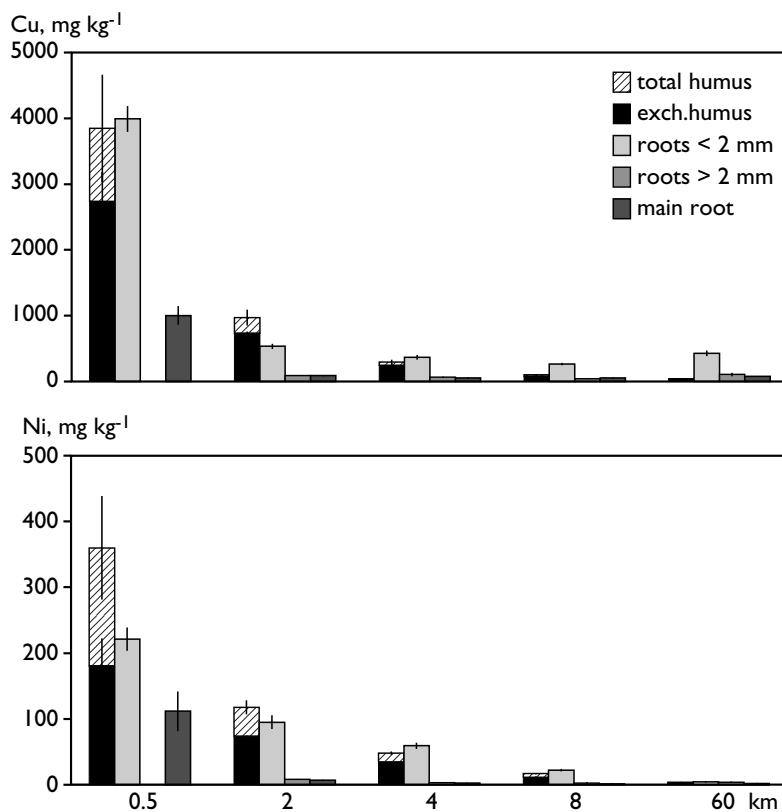


Fig. 8. The mean Cu and Ni concentrations of the humus and below-ground compartments of the pine seedlings. $n = 5$. The bar indicates the standard error of the mean.

1980), which are considered to be the most toxic Cu fraction (Sauvé 2002). According to McLaughlin (2002), the pH-related changes in soil solution metal concentrations are not clearly reflected in plant metal uptake.

Higher solubility of Ni in comparison to Cu in acid soils enriched with organic matter has been reported by several authors (Adriano 2001, Kabata-Pendias 2001). According to Ashworth and Alloway (2004), the role of organic matter in Cu and Ni mobilization is of dual nature. It promotes the mobility of both metals, since neither of them are very mobile if added in inorganic form to an inorganic substrate, but the mobility of Ni is enhanced more by the organic matter than that of Cu. The high immobilization rate of Cu and especially Ni in the quartz sand media of study III (Fig. 10) supports the statement of Ashworth and Alloway (2004) about the low mobility of inorganic Cu and Ni in an inorganic matrix.

Although the higher Ni mobility was reflected as higher leaching of Ni compared to Cu in the field at the sites adjacent to the smelters (II, Derome and Nieminen 1998), Ni uptake by Scots pine did not appear to be more efficient than that of Cu on the basis of the experiments of the present study (III, IV). According to Sauvé *et al.* (1996), studies on the link between metal concentrations in soil solution and metal uptake are rather rare, but there are numerous limitations to assume that the phytoavailable portion of

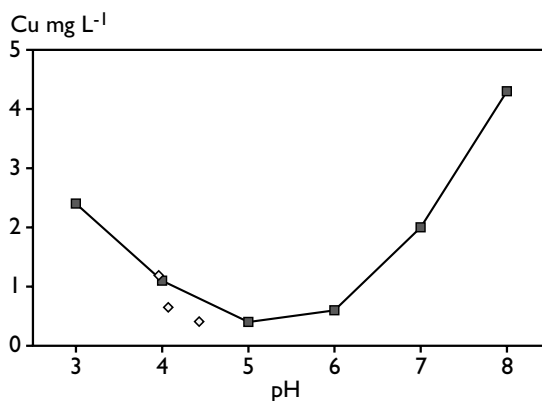


Fig. 9. Cu concentrations in relation to pH in an equilibrium solution of a sandy podzol. (Modified from Herms and Brümmer 1980). \diamond symbols refer to the Cu concentrations measured at different depths of the 0.5 km soils by Derome (2000).

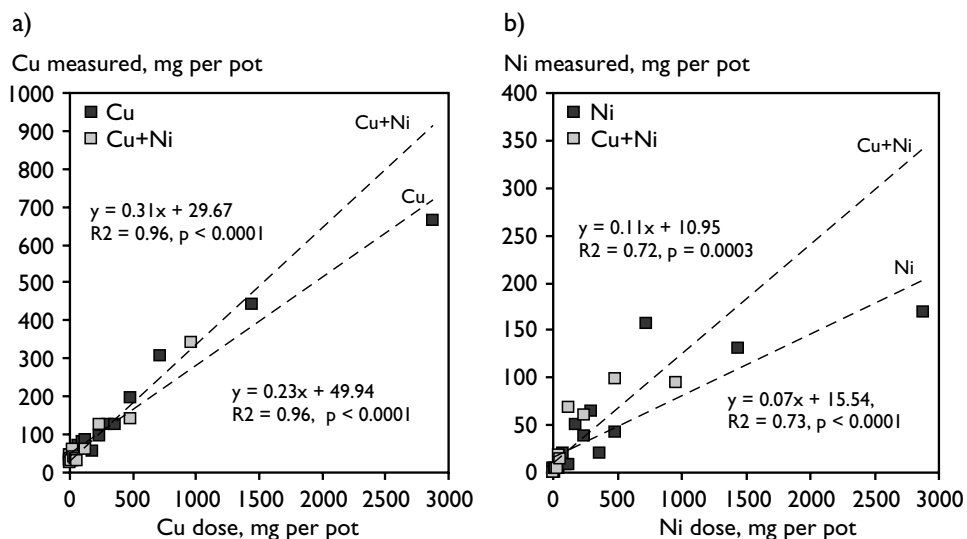


Fig. 10. The exchangeable Cu (a) and Ni (b) contents of the quartz sand substrates after the 17-month experimental period in relation to the Cu/Ni treatment doses originally added.

a metal would be that occurring in the soil solution. Furthermore, when plant uptake causes a depletion of a metal in solution, it is highly unlikely that determining the metal concentration in solution will provide a good predictor of plant metal concentrations or uptake (McLaughlin 2002). The soil's capacity to supply metal to the soil solution is of crucial importance for availability (Ernst and Nelissen 2000, McLaughlin 2002). And, *vice versa*, according to Allen (2002) it is the strength of binding of the metal by the soil that controls its phytoavailability. Assessment of the pool of solid-phase metal that buffers the solution metal concentrations is a means of accounting for this supply rate term. In fact, all the wide range of extraction techniques developed so far aim at measuring this pool (McLaughlin 2002).

3.3.2 Cu and Ni concentrations as diagnostic criteria of toxicity

The lethal substrate thresholds estimated on the basis of the artificial quartz sand treatment series (III) are quite different (32 mg kg^{-1} for Cu and 3.2 mg kg^{-1} for Ni) from the critical threshold values for the solution concentrations presented *e.g.* by Lozano and Morrison (1982). They report substantial growth reductions in hydroponically cultivated white pine and white spruce seedlings when the concentrations of Ni and/or Cu had reached 10 mg L^{-1} . However, solution concentrations cannot as such be directly compared with mineral soil concentrations. On the basis of Chapter 3.3.1., it is evident that soil solution concentration as high as 10 mg L^{-1} are not realistic. Neither can the mineral soil concentrations be directly compared with the concentrations of an organic matrix. Thus, the experimentally defined lethal thresholds for Cu and Ni concentrations in the substrate (III) cannot be generalized to cover different edaphic conditions. According to Patterson and Olson (1983), pine seedlings can support ten times higher metal concentrations when growing in a mineral soil substrate compared to seedlings growing in nutrient solution, and hundred times higher concentrations when growing in an organic substrate.

The lethal threshold values for root and stem Ni and Cu concentrations responded correspondingly to the substrate threshold: $940 \text{ mg Cu kg}^{-1}$ and 80 mg Ni kg^{-1} in the roots, and 70 mg Cu kg^{-1} and 8 mg Ni kg^{-1} indicating a higher toxicity of Ni compared to Cu. However, the greater toxicity of Ni was evident only in the presence of Cu (III, Nieminen 1998). The differences in pine mortality between the Cu and Ni treatments were small when given as inorganic single metal treatment in quartz sand media. Both Cu and Ni concentrations in the roots and stems of the 0.5 km soil cores clearly exceeded the lethal threshold values of the quartz sand experiments, and the root Ni concentrations of the 2 km soil cores were close or even greater than this limit (III). On the basis of the present study (III), root and stem concentrations appeared to be relatively reliable indicators of Cu and Ni toxicity.

The results of the Cu and Ni concentrations in the needles of the experimental seedlings were rather contradictory (III). The mobility of Cu and Ni within a plant is most probably related to the chemical form of the metal taken up by the plant (Jackson *et al.* 1990). According to the present study (III), Ni would appear to be more mobile in Scots pine in an inorganic form than in the forms present in forest soils. Therefore, needles did not prove to be as advantageous as roots and stem as toxicity indicators (III).

Furthermore, the needles of mature pines and young seedlings sampled from the field at the 0.5 km site had much higher Cu and Ni concentrations than those of the experimental seedlings (VI). This was undoubtedly due to the high surface contamination of the needles as a consequence of the high dry deposition load of metal-containing particles from the current smelter emissions and from the degraded forest floor (VI). Surface contamination may bias also the stem concentrations in the field. Hence, the metal concentrations of above-ground plant tissues in a heavily polluted environment have little relevance in terms of a plant's physiological response, although they may be useful as indicators of metal accumulation. Conifer needles have been widely used as indicators of the sulphur deposition rate, both in nationwide studies (Raitio *et al.* 2000) and in the vicinity of industrial towns (Huttunen *et al.* 1985).

3.4 Biogeochemical cycling of elements in the studied forest ecosystems

3.4.1 Consequences of a long-term Cu and Ni exposure for element cycling

The biogeochemical cycling of elements involves the exchange of elements between the various compartments within the ecosystem (Adriano 2001). Element cycles and exchange processes of the degraded 0.5 km forest site have been greatly affected by the long-term pollution load (Fig. 11). The atmospheric input has brought large amounts of heavy metals (II), especially Cu and Ni, derived from the smelter emissions. These have been deposited on the tree canopy (VI) and washed down to the forest-floor by

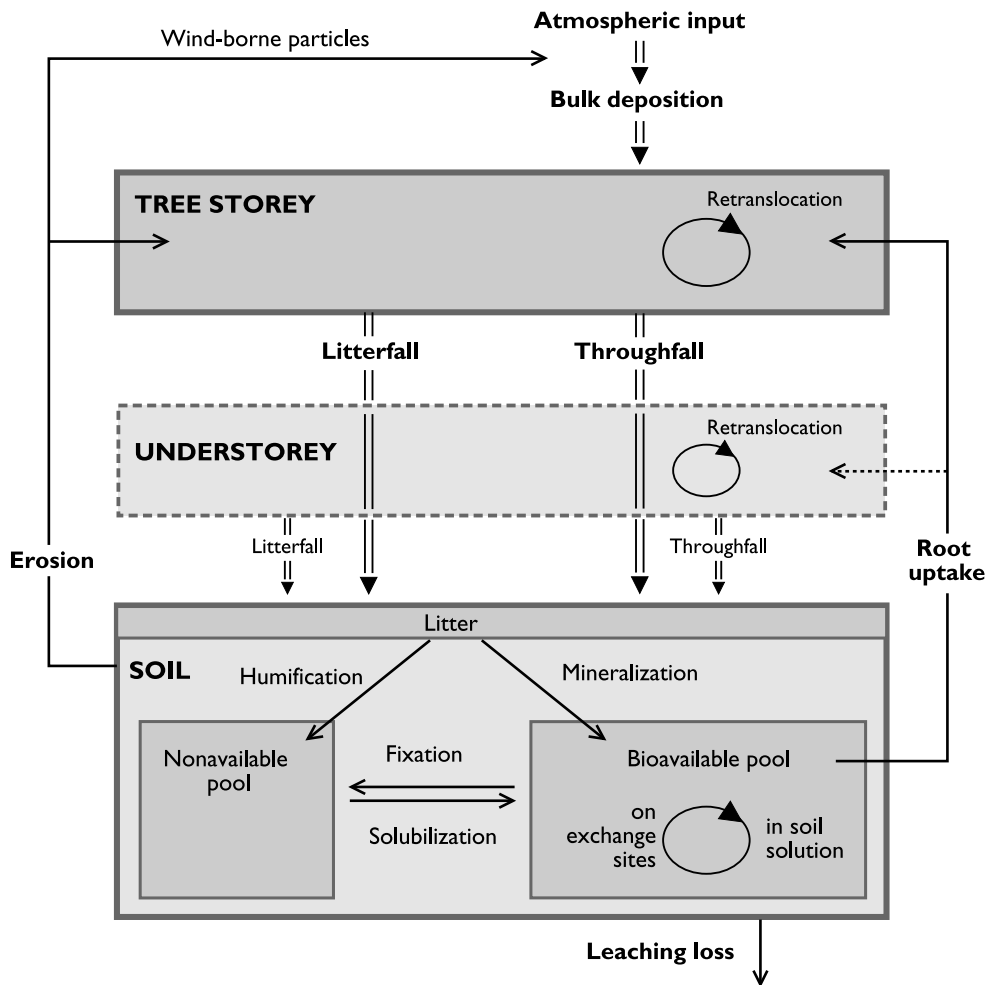


Fig 11. A generalized model depicting element cycles in a degraded forest ecosystem.

rain in the throughfall flux (I), as well as transported as surface contaminants of the litter compartments in the litterfall flux (IV, V). The wind-borne dust from the degraded forest floor has recycled these metals back into the tree canopy, from where they have been again deposited onto the forest floor in the throughfall and litterfall fluxes (I).

The almost completely lacking understorey vegetation does not participate in the element cycling, and the denuded soil is exposed to wind and soil erosion. Copper accumulates in the upper-most organic layers of the soil, preventing seedling establishment and the formation of a new understorey. Nickel, on the other hand, has a higher mobility and higher potential for downwards leaching (II), but is most probably also involved in the inhibition of seedling establishment. Both metals cause nutrient depletion from the phytoavailable pool in the soil through displacement and by retarding litter mineralisation due to their toxicity to soil microbes. The displaced nutrient cations are susceptible to leaching from the root zone. Both Cu and Ni interfere with root nutrient uptake by impairing the normal functioning of the roots (III). The deterioration of the roots causes severe growth retardation of the above-ground parts of the trees, which is reflected as a low internal nutrient retranslocation efficiency (V) and low organic matter input to the forest floor *via* the litterfall flux. However, despite the low litter input, large amounts of litter have accumulated on the forest floor as a consequence of the strongly retarded mineralisation processes.

3.4.2 Canopy filtration of dry deposition as a source of element fluxes in the ecosystems

The lack of understorey vegetation (Salemaa *et al.* 2001), as well as the retarded organic matter mineralization (Fritze *et al.* 1989, Fritze *et al.* 1996) and, consequently, low water holding capacity of the organic layer (Derome and Nieminen 1998), expose the barren soil to wind-erosion, which seldom takes place under normal conditions in boreal forests. The wind-borne soil dust contains large amounts of heavy metals that have accumulated in the soil during the *ca.* 50-year-period of smelting activities (Table 7, Derome and Lindroos 1998). This affects the composition of bulk precipitation and especially the stand throughfall fluxes, thus making it difficult to quantify the atmospheric input by means of precipitation sampling (I).

The current emissions from smelting activities most probably cause an increased atmospheric input of metals into the forests close to the area. However, the relatively effective methods used in our studies for deposition measurement do not correctly quantify the input flux in degraded forests, although they are supposed to give reliable estimations of atmospheric inputs in normal conditions (Helmisaari and Mälkönen 1989, Hyvärinen 1990, Ukonmaanaho and Starr 2002). The stand throughfall flux contains exudates from the canopy, elements originating from foliar leaching, and elements from the wash-off of previously dry deposited material. Distinguishing between these three sources is difficult, and the separation of dry deposition derived from the internal cycling of dust from dry deposition originating from outside the ecosystem boundaries is even more problematic. Therefore, the exact atmospheric input into the 0.5 km ecosystem remains unclear, although our results suggest that sources other than the stack emissions make a major contribution to metal enrichment in bulk precipitation and stand throughfall (I, V and VI).

Canopy filtration of soil-borne dust also affects the litterfall fluxes. Although the quantity of annual litterfall was at its lowest at 0.5 km, the Cu and Ni fluxes *via* litterfall were *ca.* 100 times higher at 0.5 km than at 4 km during 1993 (Nieminen *et al.* 1998). An undeterminable proportion of the dry deposited metal particles attached to the surface of litter needles and other litter compartments is derived from internal dust cycling in the ecosystem. In addition, the litter traps can, to some extent, directly capture wind-born soil dust.

3.4.3 Foliar leaching of potassium

The high rate of K leaching from the needle tissues at 0.5 km stand suggested that K cycling has been altered by the heavy pollution load (I). As a monovalent cation, K⁺ is highly susceptible to foliar leaching even in normal forest conditions (Helmisaari and Mälkönen 1989, Hyvärinen 1990, Stachurski and Zimka 2000, 2002) and the throughfall flux is usually a more important pathway for K cycling than the litterfall flux (Ranger *et al.* 1994, Helmisaari 1995). Enhanced canopy leaching of K has been observed in forest stands suffering from low tree vitality in a number of earlier studies (*e.g.* Alenäs and Skärby 1988, Gjengedal 1996).

The tree canopy was an important source of K at all the distances studied (Fig. 1 in I). However, the amount of K in net throughfall was greatest at 0.5 km, even though the stand K needle pool was the lowest at this site (Fig. 1 and 3 in I). Since net throughfall K is considered to be almost completely derived from foliar leaching (Parker 1983), and no smelter-derived deposition of K was observed, the biological cycling of K in the soil-plant system at 0.5 km appeared to be accelerated (I). This is supported by the fact that the needle K concentrations were at their highest at 0.5 km (Appendix in I).

Accelerated root K uptake would be needed to maintain the needle concentrations at the observed level under the constant loss of K through foliar leaching. However, the results of the greenhouse-grown experimental seedlings do not support the assumption of a more efficient K uptake by the roots (III). A decrease in root K concentrations with increasing metal exposure was found both in the smelter-polluted-soil grown and in the artificially treated seedling series (III). In the smelter-polluted-soil grown seedling series, this pattern was also reflected in the above ground parts of the seedlings (III). Excessive amounts of both Cu and Ni have been reported to cause damage to the cell membranes, which is reflected as an enhanced efflux of K from plant tissues (Baker and Walker 1989, Marschner 1995, Adriano 2001, Kabata-Pendias 2001).

One possible reason for the differences in K status between the field-grown trees and the greenhouse grown seedlings, could be that the pine roots in the field could be associated with a highly adapted microsymbiont. Wallander and Wickman (1999) reported that *Paxillus involutus*, growing in symbiosis with *Pinus sylvestris*, was able to access the K in microcline, which is a common mineral in acid bedrock. In contrast, the other ectomycorrhizal fungi used in their experiment, *Suillus variegatus*, could not mobilise K from the mineral, nor could the pine seedlings cultivated without root symbionts (Wallander and Wickman 1999).

A shortage of K in the smelter-polluted –soil cores could have developed relatively rapidly in the kind of experimental conditions in which the throughfall

and litterfall fluxes of K were completely absent. Since K does not form stable organic complexes, it is the most mobile nutrient and is rapidly cycled in soil-plant systems (Switzer and Nelson 1972, Marschner 1995). According to Ranger (1995), the same K^+ ion can be absorbed several times during one growing season by the same plant. However, this kind of K deficiency would affect all the experimental seedlings at all distances, and should not be aggravated with increasing soil Cu and Ni concentrations.

3.4.4 Nutrient retranslocation in pine foliage

The autumnal nutrient retranslocation of mobile nutrients, especially P and K, was less efficient in the 0.5 km pine stand than at the other distances (Table 3a in V). This was not in agreement with the supposition that internal retranslocation would be of more importance in trees growing on infertile soils (Zimka and Stachurski 1976, Miller *et al.* 1979). Conditions in polluted soils are often relatively similar to those in infertile soils, as continuous exposure to pollution leads to a continual deterioration in soil nutrient status (Freedman and Hutchinson 1980, Bååth 1989, Fritze *et al.* 1989, Derome and Lindroos 1998). However, according to Nambiar and Fife (1987), Nambiar *et al.* (1991) and Saur *et al.* (2000), the growth rate of the trees, rather than the availability of nutrients in the soil, is the main factor controlling retranslocation, which is fully consistent with our results concerning less efficient retranslocation in the pine stand with the lowest growth rate (V).

Furthermore, retranslocation is not necessarily related to senescence (Nambiar *et al.* 1991). Fife and Nambiar (1982, 1984) reported that significant retranslocation occurred even in young needles of *Pinus radiata* L. Retranslocation can be divided into two phenomena: autumnal nutrient withdrawal from senescing foliage, which was determined in our study (V), and nutrient translocation from the living foliage during aging (Meier *et al.* 1985). There is no mathematical formula that could fully take into account both of these phenomena (Ranger 1995); mathematical means can only provide an estimate of the net retranslocation amount during the time lag between measurements.

At the ecosystem scale, the retranslocation process determines the quality of the falling needle litter which, in turn, has a great effect on litter decomposition and mineralization processes (Zimka 1991). According to our results, the N, P and K status of the litter needles was highest at 0.5 km (Fig. 1 in V).

3.4.5 Element losses via percolation water

The fluxes of Ca, Mg, K and P carried down to a depth of 5 cm in the soil as soil leachates were much higher than the fluxes entering the soil as bulk precipitation, while at 40 cm depth there was a net loss of only Mg and K (Derome and Nieminen 1998). The Mg loss in the 0.5 km stand was reflected as low soil (Table 5) and needle (Appendix in I) Mg concentrations but, in the case of K, the needle concentrations were even higher than at further distances from the smelters (Appendix in I).

The satisfactory K status of the needles suggests, however, that the trees are in fact obtaining sufficient K from the soil. Since the rooting system of pine stands growing

on sandy soils is typically deep (Laitakari 1927), we would expect that the roots are able to reach soil layers deeper than 40 cm, and satisfy their K requirements from these layers. However, the root depths measured at Harjavalta (Helmisaari *et al.* 1999) and Hämeenkangas (Raitio 1990b) do not support this assumption, since most of the fine roots in both areas were found in the upper 10 cm layer. Direct access to K in minerals by ectomycorrhizal pine roots has also been reported (*cf.* Wallander and Wickman 1999 in Chapter 3.4.2).

There were clear differences in the partitioning of Cu and Ni between the solid and solution phases in the soil at 0.5 km site. 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 decreased more sharply with increasing depth (Derome and Nieminen 1998). The flux of Ni at 5 cm depth was greater than that entering the stand in precipitation both at 0.5 and 4 km (Derome and Nieminen 1998). The relatively low Cu:Ni ratio in percolation water concentrations at the 0.5 km site compared to the corresponding ratio in soil concentrations (Table 6 and 7) reflects greater solubility of Ni compared to Cu.

The behaviour of Cu and Ni in percolation water fluxes is consistent with the results obtained in study **II**. The vertical gradient in Cu concentrations in the surface peat of the Harjavalta bog suggests that the Cu supplied to the peat through atmospheric deposition was strongly retained by the bog (**II**). The relatively high Ni values at deeper depths compared to Cu indicated post-depositional downward migration, since Ni smelting in the Harjavalta area started 15 years later than Cu smelting (**II**). However, the changes that occurred in the exchangeable Cu and Ni pools in different layers of the smelter-polluted soil cores during the 17-month–experimental period of study **IV** (Table 4 in **IV**) did not indicate higher downwards migration of Ni compared to Cu.

The Cu:Ni ratio of ca. 10:1 observed in the peat of the Harjavalta bog (*cf.* Chapter 3.1.2) is in good correspondence with the Cu:Ni ratio in the humus layers of the 0.5 and 2 km sites (Table 6), which suggests that the binding capacity of organic matter is the key factor determining their current distribution pattern in these soils. Copper has been reported to form much more stable complexes with natural organic ligands than does either Ni or Zn (Bergkvist *et al.* 1989, Baker and Senft 1995). According to Kabata-Pendias (2001), Ni in peaty soils is in easily soluble organic forms. Ashworth and Alloway (2004) stress the importance of dissolved organic matter in promoting the mobility of both Cu and Ni in a sandy loam soil, but point out that the soil mobility of Ni is more enhanced by the presence of organic matter.

3.4.6 Nutrient disturbances

Based on the results of the experimental approach applied in the present study, the Ca, K and Mg dynamics of pine seedlings was affected by exposure to soil Cu and Ni (**III**). The decreased concentrations of these nutrients in the roots of both the artificial treatment series and the smelter-polluted-soil grown seedlings as a function of increasing Cu and Ni concentrations, indicate adverse effects of excess Cu and Ni. According to Ross and Kaye (1994), toxic heavy metals have disruptive effects on the structure and functioning of the plasma membrane of roots, and thus the kinetics of

nutrient uptake. An efflux of K has been reported to occur as a consequence of metal-induced damage to the plasma membrane of the root cells (Baker and Walker 1989).

The nutrient disturbances in the smelter-polluted-soil grown seedlings were more severe and were also reflected in the above-ground parts of seedlings (II). In addition, the low needle Mg concentrations of the mature pines growing at the 0.5 km site indicated Mg deficiency (I). In the smelter-polluted soil-plant systems, the changes in nutrient status can be caused both by the interference by Cu and Ni in the root nutrient uptake processes and by the low soil nutrient contents caused by excess Cu and Ni. The deficiency of macronutrients in polluted forest soil at Harjavalta has been caused both by the displacement of base cations by Cu and Ni (Derome and Lindroos 1998), and by retarded mineralisation of the litter due to the toxicity of soil Cu and Ni to litter-decomposing microbes (Fritze *et al.* 1989, 1996) and soil fauna (Haimi and Siira-Pietikäinen 1996). Litter accumulation is a well documented phenomenon in heavily metal-impacted forest ecosystems (Tyler 1975, Strojan 1978, Freedman and Hutchinson 1980, Berg *et al.* 1991). According to Berg *et al.* (1991), the low mineralisation rate at heavy metal polluted site was caused by changes both in litter quality and in soil factors. At moderate and low pollution levels, metal-induced nutrient disturbances are difficult to distinguish from natural variations in soil fertility.

4 Conclusions

Accurate determination of the current Cu and Ni input to the forest ecosystem closest to the smelter (0.5 km) was not possible by means of deposition measurements owing to the high importance of internal cycling *via* soil dust. The lack of understorey vegetation and the low water-holding capacity of the soil organic layer at the 0.5 km site make the forest soil susceptible to wind erosion. Wind-borne, metal-containing dust is an additional source of Cu and Ni in bulk deposition, and especially in stand throughfall, due to the high capacity of forest canopies to intercept and filter out dry deposition. In contrast to the situation at 0.5 km, the amounts of deposition measured at greater distances along the smelter-pollution gradient can be treated as relatively reliable indicators of the atmospheric input to the ecosystems.

The surface peat sediments of an ombrotrophic bog adjacent to the smelters revealed that the estimated mean annual accumulation of Cu and Ni based on peat contents is higher than the current annual bulk deposition load at the 0.5 km site. The vertical distribution pattern of Cu suggests that Cu supplied to the peat by atmospheric deposition is strongly retained in the top-most peat layers, whereas Ni shows a more even distribution pattern reflecting downwards migration. The behaviour of Ni was different to that of Cu also in the polluted forest soil at distances of 0.5-4 km. The humus layer was the most important sink for Cu, since it was clearly enriched in the uppermost soil layer, but in the case of Ni this was less evident. The exchangeable Ni pools of the underlying *ca.* 20 cm thick mineral soil layer appeared to be equal or higher than the corresponding pools of the humus layer along the whole smelter-pollution gradient.

There were no clear differences between the availability of Cu and Ni to Scots pine from polluted forest soil, since the uptake of both elements to the above ground parts of the pine seedlings responded according to their soil contents. In this study, both total and exchangeable Cu and Ni concentrations in the forest soil horizons appeared to be related to the available pools of soil Cu and Ni. In the artificial quartz sand experiment, on the other hand, the uptake of inorganic Ni was enhanced in the presence of equal amounts of inorganic Cu, while the uptake of Cu appeared to be inhibited in the presence of Ni.

The variation in the biomass of the experimental pine seedlings cultivated in smelter-polluted-soil cores appeared to be related both to the toxicity of Cu and Ni and to differences in the nutrient status of the experimental soils. However, Cu and Ni pollution may also affect pine stands indirectly through changes in soil nutrient status, and this is difficult to distinguish from the natural fertility variation in low-to-moderate pollution conditions. The biomass production of the experimental seedlings showed a very similar pattern to those of the growth and biomass production parameters measured in the field in earlier studies along the same smelter-pollution gradient.

Autumnal nutrient retranslocation from senescing needles to overwintering tree compartments was less efficient at the most polluted 0.5 km site compared to further distances along the smelter-pollution gradient. This finding is in good agreement with the current, widely accepted concept about the growth rate of trees as a driving force behind the retranslocation intensity.

The critical Cu and Ni concentrations determined in the present study for the quartz sand substrate give only a very approximate indication of the toxicity limits for natural soils. They can, at least to some extent, be compared to metal concentrations in the mineral soil horizons, but they are not valid in organic-rich substrates. However, the threshold concentrations determined for the pine seedling compartments should also be valid in a broader sense. The lethal threshold of *ca.* 1000 mg kg⁻¹ for Cu in roots and 100 mg kg⁻¹ for Ni in roots indicates that Ni has a higher toxicity. The corresponding thresholds for stem concentrations were 70 mg Cu kg⁻¹ and 8 mg Ni kg⁻¹. The needle concentrations were rather contradictory, and did not appear to be reliable indicators of Cu and/or Ni toxicity.

In heavily polluted environments the surface contamination of above-ground tree compartments by metal containing particles further complicates the interpretation of the measured tissue concentrations. Washing the samples prior to analysis is generally considered to remove the surface contaminants, but the results of the present study demonstrated that a routine needle washing procedure did not remove all the metal-containing material attached to the needle surfaces. In this study, more than half of the Cu in the pine needles was present as surface contaminants at the most polluted 0.5 km site. In the case of Ni, the pine needles exposed to aerial deposition contained tens of times more Ni than the needles protected from aerial deposition. Therefore, surface contamination poses a severe risk to herbivores by considerably increasing their metal intake.

The prevention of Cu and Ni dispersion through soil erosion and leaching losses is of ultimate importance in avoiding the spread of pollution to surrounding ecosystems. The downwards leaching of Ni is a potential risk for groundwater quality, while inhalation and exposure through the digestive tract can pose health risks for the wild fauna and local human population. This is especially the case because soil-derived dust appears to be of more importance from the point of view of air quality than the current stack emissions in the immediate vicinity of the smelters.

The sustainability of pine stands growing in soils as polluted as that at 0.5 km cannot be maintained without some form of soil remediation to ensure natural seedling establishment. The aim of remediation is to either remove or immobilize the toxic metals in the soil. Several techniques are available for cleaning up polluted soil, of which the phytoextraction techniques are currently among the most studied ones. In phytoextraction, metal-accumulating plants are cultivated in polluted soil and harvested at the time when their metal content is at its maximum.

The primary aim of applying soil ameliorating agents, such as lime, zeolites, apatite or Fe and Mn oxides, is to immobilize toxic metals, as well as in some cases to facilitate the recovery of soil microbial activity, *e.g.* by spreading “clean” organic matter on the polluted soils. However, the long-term effects of these treatments on metal mobility in different soil conditions are difficult to predict. Therefore, considerable care should be taken to avoid the risk of enhanced metal leaching. A deeper understanding of the effects of ameliorating agents on metal mobility would be a challenge for future research.

Acknowledgements

This thesis has been carried out at the Finnish Forest Research Institute (Metla) over a period of several years. I wish to express my sincere gratitude to all who have contributed to the successful completion of my thesis.

I would like to thank Dr. Heikki Pajuoja and Doc. Jari Varjo, directors of the Vantaa Research Centre of Metla, as well as Prof. emer. Eino Mälkönen, who was the leader of research in the field of forest soil during most of the time that I was preparing my thesis, for providing me with excellent working facilities. The current leader of research on forest soil, Prof. Hannu Ilvesniemi, is acknowledged for his comments and constructive criticism on my dissertation plan.

I am indebted to Eeva Ruokonen from Boliden Harjavalta for fruitful co-operation throughout the years of Metla's Harjavalta studies, as well as to Matti Nummi from the Regional Forest Centre of Southwest Finland, for providing me with the results of the forest condition surveys in the Harjavalta area. I also wish to thank the Niemi Säätiö for additional financial support.

I express my warmest thanks to my supervisor Doc. Heljä-Sisko Helmisaari from Metla for suggesting the study subject, and for her continuous encouragement throughout the study. I am also deeply grateful to all my other co-authors: Doc. John Derome, Dr. Anna Saarsalmi, Dr. Liisa Ukonmaanaho from Metla, and Prof. William Shotyk from Heidelberg University in Germany. Practically all I know about scientific writing in English I have learned from John. He also introduced me to the wonders of water fluxes in forest ecosystems. Anna has several times brought my confused thoughts to a scientifically sound structure through her remarkable ability to listen and pick-up the essential points from my endless talk. My collaboration with Liisa and Bill has turned a new page in my scientific career. Our first joint paper, which is included in this thesis, was the start to an adventurous project on wild pristine peatlands. Liisa's friendship and trust in my scientific skills has supported me even through the worst periods of my doctoral project. I thank Anna, Liisa and John for commenting on the summary paper, and John also for revising the language of the thesis.

I am extremely grateful to the Professor of Terrestrial Plant Ecology at the Helsinki University, Heikki Hänninen, whose acquaintance marked a turning point in my seemingly hopeless attempt to attain the doctoral degree. His constructive attitude and encouragement is warmly acknowledged. He has also kindly commented on the manuscript of the summary paper. Dr. Lage Bringmark and Doc. Kari Laine are greatly acknowledged for acting as official pre-reviewers of the thesis.

All the researchers involved in Metla's Harjavalta projects have contributed to my thesis at different phases of the work. I want to especially thank Mikko Kukkola for his crucial role in handling the tree data from the Harjavalta field gradient, as well as Maija Salemaa, Oili Kiikkilä, Satu Lyyra (née Monni) and Ilkka Vanha-Majamaa for fruitful and enjoyable cooperation. I am grateful to Oili also for her valuable suggestions about how to improve my summary paper.

I want to thank Pirkko Rättö for her professional guidance through administrative matters that I would never be able to solve on my own. Hillevi Sinkko and Annikki Viitanen are also acknowledged for all the administrative help they have provided. The

chemical analyses of my samples have been carried out at Metla's Central Laboratory in Vantaa, at Metla's laboratory of the Rovaniemi Research Station, and in EMMA Analytical Inc., Canada. I want especially to thank Kirsti Derome, Andriy Cheburkin, Maija Jarva, Kerttu Nyberg, Maija Ruokolainen and Arja Tervahauta, as well as the lab professionals of the forest soil sector, Anneli Rautiainen and Pirkko Ronkainen. Sari Elomaa is especially acknowledged for performing her extraordinary skills in the layout and figures of my summary paper. Anne Siika has performed outstanding work with great patience on many of the figures in the papers. The staff of Metla's library has also been of invaluable help in providing easy access to scientific literature.

Sinikka and Teuvo Levula are responsible for most of the regular sampling work, and they have also offered their skilled assistance in the field, of which I am extremely grateful. Teuvo has played a crucial role also in the implementation of the field experiments. Juhani Mäkinen is acknowledged for patient and careful soil sample collection for my greenhouse experiment, and Kauko Taimi for his valuable help in peat sampling. I also want to thank Kaarina Pynnönen and Satu Peltola for taking such good care of my pine seedlings during the experimental period and at harvesting time. I am also grateful to Pentti Salonen and Anna-Maija Kokkonen for keeping my computer in shape throughout the years.

I owe sincere thanks to many colleagues and friends at Metla for their supportive attitude, discussions and therapeutic conversations concerning my thesis. I especially want to thank Leila Korpela, Martti Lindgren, Päivi Merilä, Heikki Nuorteva, Pekka Saranpää and Aino Smolander. Without you all, and your friendship, there hardly would be a thesis. I feel privileged also to have such friends, outside the forest research field, to whom my doctoral thesis is not of much importance. They have helped me to keep my feet on the ground and not let the doctoral project ruin all my social life. I thank all my dear friends for that, and especially the very special Eija Happonen who I have known since our early childhood.

I am also deeply indebted to my dear family. First of all, I want to thank my mother, Ulla-Maj Nieminen, whose loving support I have always been able to take for granted. I feel that I have been supported also by all the love given by my late father, Jaakko Nieminen, whose memory lives strongly within me. My brave little sister, Tea Nieminen, has shown me the way by becoming a doctor already quite many years ago. I am extremely grateful to my husband, Pasi Miettinen, and our children, Anniina and Tuomas, for all the love and support they have provided in a multitude of ways. Although Pasi himself attained his doctoral degree already in an early stage of life, he has been amazingly patient and understanding throughout the years of my struggles.

Thank you all!

Helsinki, 2.5.2005,

Tiina Nieminen

Ajatuksen pallopintaa äärellistä / rajatonta
(Markku Lahtela)

References

- Adriano, D.C. 2001. Trace elements in terrestrial environments. Biogeochemistry, bioavailability, and risks of metals. Springer-Verlag. New York. 867 p.
- Ahti, T., Hämet-Ahti, L. & Jalas, J. 1968. Vegetation zones and their sections in northwestern Europe. *Annales Botanici Fennici* 5: 9-211.
- Ahonen-Jonnarth, U., Hees, P.A.W. van, Lundström, U. & Finlay, R. 2000. Production of organic acids by mycorrhizal and non-mycorrhizal *Pinus sylvestris* seedlings exposed to elevated concentrations of aluminium and heavy metals. *New Phytologist* 146: 557-567.
- Alenäs, I. & Skärby, L. 1988. Throughfall of plant nutrients in relation to crown thinning in a Swedish coniferous forest. *Water, Air, and Soil Pollution* 38: 223-237.
- Allen, H. 2002. Terrestrial ecosystems: an overview. In: Allen, H. (ed.). *Bioavailability of metals in terrestrial ecosystems: Importance of partitioning for bioavailability to invertebrates, microbes, and plants*. Setac Press. pp. 1-5.
- Alloway, B.J. 1995. The origin of heavy metals in soils. In: Alloway, B.J. (ed.). *Heavy metals in soils*. Blackie Academic & Professional. London. pp. 38-57.
- Antonovics, J., Bradshaw, A.D. & Turner, R.G. 1971. Heavy metal tolerance in plants. *Advances in Ecological Research* 7: 1-85.
- Ashworth, D.J. & Alloway, B.J. 2004. Soil mobility of sewage sludge-derived dissolved organic matter, copper, nickel and zinc. *Environmental Pollution* 127: 137-144.
- Atlas Flora Europaeae 2. 1973. Gymnospermae (Pinaceae to Ephedraceae). Jalas, J. & Suominen, J. (eds.). Committee for Mapping the Flora of Europe and Societas biologica Fennica Vanamo. Helsinki. Finland. 40p., 50 maps.
- Bååth, E. 1989. Effects of heavy metals in soil on microbial processes and populations. *Water, Air, and Soil Pollution* 47: 335-379.
- Bäck, J., Huttunen, S., Turunen, M. & Lamppu, J. 1985. Effects of acid rain on growth and nutrient concentrations in Scots pine and Norway spruce. *Environmental Pollution* 89: 177-187.
- Baker, A.J.M. 1987. Metal tolerance. *New Phytologist* 106: 93-111.
- Baker, A.J.M., Grant, C.J., Martin, M.H., Shaw, S.C. & Whitebrook, J. 1986. Induction and loss of cadmium tolerance in *Holcus lanatus* L. and other grasses. *New Phytologist* 102: 575-585.
- Baker, A.J.M. & Proctor, J. 1990. The influence of cadmium, copper, lead, and zinc on the distribution and evolution of metallophytes in the British Isles. *Plant Systematics and Evolution* 173: 91-108.
- Baker, A.J.M. & Walker, P.L. 1989. Physiological responses of plants to heavy metals and the quantification of tolerance and toxicity. A review. *Chemical speciation and bioavailability* 1: 7-17.
- Baker, D.E. & Senft, J.P. 1995. Copper. In: Alloway, B.J., (ed.). *Heavy metals in soils*. Blackie Academic and Professional. London. pp. 11-37.
- Berg, B., Ekbohm, G., Söderström, B. & Staaf, H. 1991. Reduction of decomposition rates of Scots pine needle litter due to heavy-metal pollution. *Water, Air, and Soil Pollution* 59: 165-177.
- Bergkvist, B., Folkesson, L. & Berggren, D. 1989. Fluxes of Cu, Zn, Pb, Cd, Cr, and Ni in temperate forest ecosystems. *Water, Air, and Soil Pollution* 47: 217-286.
- Boutroun, C. F., Candelone, J.-P. & Hong, S. 1995. Greenland snow and ice cores: unique archives of large-scale pollution of the troposphere of the northern hemisphere by lead and other heavy metals. *The Science of the Total Environment* 160/161: 233-241.
- Bradley, R., Burt, A.J. & Read, D.J. 1982. The biology of mycorrhiza in the Ericaceae. VIII: The role of mycorrhizal infection in heavy metal resistance. *New Phytologist* 91: 197-210.
- Bradshaw, A.D. & McNeilly, T. 1981. Evolution and pollution. *The Institute of Biology's studies in biology* no. 130. Edward Arnold. London. 76 p.
- Bringmark, L. & Lundin, L. 2004. Report on the assessment of heavy metal stores and fluxes at ICP IM sites. In: Kleemola, S. & Forsius, M. (eds.). 13th Annual report 2004. UNECE Convention on Long-range Transboundary Air Pollution. International Cooperative Programme on Integrating Monitoring of Air Pollution Effects on Ecosystems. Finnish Environment Institute 710. pp. 27-32.

- Bringmark, L. Ruoho-Airola, T., Starr, M., Porvari, P., Verta, M., Lundin, L. & Forsius, M. 2001. Progress report of the assessment of heavy metal stores and fluxes. In: Kleemola, S. & Forsius, M. (eds.). 10th Annual Report 2001. UN ECE Convention on Long-range Transboundary Air Pollution. International Cooperative Programme on Integrating Monitoring of Air Pollution Effects on Ecosystems. Finnish Environment Institute 498. pp. 26-29.
- Brooks, R.R. 1998. General introduction In: Brooks, R.R. (ed.). Plants that hyperaccumulate heavy metals. Their role in phytoremediation, microbiology, Archaeology, mineral exploration and phytomining. CAB International. New York pp. 1-14.
- Brooks, R.R., Lee, J., Reeves, R.D. & Jaffré, T. 1977. Detection of nickeliferous rocks by analysis of herbarium specimens of indicator plants. *Journal of Geochemical Exploration* 7: 49-57.
- Brown, P.H., Welch, R.M., Cary, E.E. & Checkai, R.T. 1987. Beneficial effects of nickel on plant growth. *Journal of Plant Nutrition* 10: 2125-2135.
- Brümmer, G.W. & Herms, U. 1983. Influence of soil fraction and organic matter on the solubility of heavy metals in soils. In: Ulrich, B. & Pankrath, J. (eds.). Effects of accumulation of air pollutants in forest ecosystems. D. Reidel Publishing Company, Dordrecht. pp. 233-243.
- Brun, L.A., Maillet, J., Hinsinger, P. & Pépin, M. 2001. Evaluation of copper availability to plants in copper-contaminated vineyard soils. *Environmental Pollution* 111: 293-302.
- Cairns, J. (Jr.) & Mount, D.I. 1990. Aquatic toxicology. Part 2. *Environmental Science & Technology* 24: 154-161.
- Cape, J. N., Sheppard, L. J., Fowler, D., Harrison, A. F., Parkinson, J. A., Dao, P. & Paterson, I. S. 1992. Contribution of canopy leaching to sulphate deposition in a Scots pine forest. *Environmental Pollution* 75: 229-236.
- Caput, C., Belot, Y., Auclair, D. & Decourt, N. 1978. Absorption of sulphur dioxide by pine needles leading to acute injury. *Environmental Pollution* 16: 3-15.
- Chaignon, V., Sanchez-Neira, I., Herrmann, P., Jaillard, B. & Hinsinger, P. 2003. Copper bioavailability and extractability as related to chemical properties of contaminated soils from wine-growing area. *Environmental Pollution* 123: 229-238.
- Cheburkin, A.K. & Shotykh, W. 1996. An energy-dispersive Miniprobe Multielement Analyzer (EMMA) for direct analysis of Pb and other trace elements in peats. *Fresenius' Journal of analytical Chemistry* 354: 688-691.
- Chirenje, T., Ma, L.Q., Clark, C. & Reeves, M. 2003. Cu, Cr and As distribution in soils adjacent to pressure-treated decks, fences and poles. *Environmental Pollution* 124: 407-417.
- Colpaert, J.V. & Assche, J.A. van 1992. Zinc toxicity in ectomycorrhizal *Pinus sylvestris*. *Plant and Soil* 143: 201-211.
- Cosby, B.J., Hornberger, G.M. & Galloway, J.N. 1985. Modelling the effects of acid deposition: assessment of lumped parameter model of soil water and streamwater chemistry. *Water Resources Research* 21: 51-63.
- 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. Finnish Forest Research Institute. Research Papers 769. 78 p.
- Derome, J. & 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.
- Derome, J. & Nieminen, T. 1998. Metal and macronutrient fluxes in heavy-metal polluted Scots pine ecosystems in SW Finland. *Environmental Pollution* 103: 219-228.
- Derome, J., Lindroos, A.-J., Derome, K. & Niska, K. 2002. Soil solution quality during 1998-2000 on 13 of the Level II plots. Forest condition monitoring in Finland. National report 2001. The Finnish Forest Research Institute. Research Papers 879: 70-88.
- Derome, J., Nieminen, T. & Saarsalmi, A. 2004. Sulphur dioxide adsorption in Scots pine canopies exposed to high ammonia emissions near a Cu-Ni smelter in SW Finland. *Environmental Pollution* 129: 79-88.
- Dickinson, N.M., Turner, A.P. & Lepp, N.W. 1991. How do trees and other long-lived plants survive in polluted environments. *Functional Ecology* 5: 5-11.
- Dickinson, N.M., Watmough, S.A. & Turner, A.P. 1996. Ecological impact of 100 years of metal processing at Prescot, northwest England. *Environmental Reviews* 4: 8-24.
- Disler, J. 1953. Die Kupferkieslagerstätte von Outokumpu, Finnland. *Bulletin de la Commission géologique de Finlande* 161:1-108.

- Dixon, R.K. 1988. Response of ectomycorrhizal *Quercus rubra* to soil cadmium, nickel and lead. *Soil Biology and Biochemistry* 20: 555-559.
- Epstein, E. & Hagan, C.E. 1952. A kinetic study of the absorption of alkali cations by barley roots. *Plant Physiology* 27: 457-474.
- Ernst, W.H.O. & Nelissen, H.J.M. 2000. Life-cycle phases of a zinc- and cadmium-resistant ecotype of *Silene vulgaris* in risk assessment of polymetallic mineral soils. *Environmental Pollution* 107: 329-338.
- Ernst, W.H.O., Verkleij, J.A.C. & Schat, H. 1992. Metal tolerance in plants. *Acta Botanica Neerlandica* 41: 229-248.
- FAO-UNESCO 1988. *Soil Map of the World, World Soil Resources Report*, Food and Agriculture Organization of the United Nations, Rome, 60, 119 p.
- Fife, D.N. & Nambiar, E.K.S. 1982. Accumulation and retranslocation of mineral nutrients in developing needles in relation to seasonal growth of young radiata pine trees. *Annals of Botany* 50: 817-829.
- Fife, D.N. & Nambiar, E.K.S. 1984. Movement of nutrients in radiata pine needles in relation to the growth of shoots. *Annals of Botany* 54: 303-314.
- Finér, L. 1992. Biomass and nutrient dynamics of Scots pine on a drained ombrotrophic bog. Finnish Forest Research Institute. Research Papers. 420. 43 p.
- Forsius, M., Kleemola, S., Starr, M. & Ruoho-Airola, T. 1995. Ion mass budgets for small forested catchments in Finland. *Water, Air, and Soil Pollution* 79: 19-38.
- Freedman B. & Hutchinson, T.C. 1980. Effects of smelter pollutants on forest leaf litter decomposition near a copper-nickel smelter at Sudbury, Canada. *Canadian Journal of Botany* 58: 108-132.
- Fritze, H., Niini, S., Mikkola, K. & Mäkinen, A. 1989. Soil microbial effects of a Cu-Ni smelter in southwestern Finland. *Biology and Fertility of Soils* 8: 87-94.
- Fritze, H., Vanhala, P., Pietikäinen, J. & Mälkönen, E. 1996. Vitality fertilization of Scots pine stands growing along a gradient of heavy metal pollution: short-term effects on microbial biomass and respiration rate of the humus layer. *Fresenius' Journal of Analytical Chemistry* 354: 750-755.
- Galli, U., Schüepp, H. & Brunold, C. 1994. Heavy metal binding by mycorrhizal fungi. *Physiologia Plantarum* 92: 364-368.
- Genys, J.B. & Heggstad, H.E. 1978. Susceptibility of different species, clones and strains of pines to acute injury caused by ozone and sulfur dioxide. *Plant Disease Reporter* 62: 687-691.
- Geoinstituutti Oy 2000. *Outokumpu Harjavalta Metals Oy. OMG Harjavalta Nickel Oy. Tuotantotasovaihtoehtot ja kiinteiden prosessijätteiden läjitys. Ympäristövaikutusten arviointiselostus. Yhteysviranomaisen Lounais-Suomen ympäristökeskus. (In Finnish.) Environmental Impact Assessment. EIA. 79 p.*
- Gjengedal, E. 1996. Effects of soil acidification on foliar leaching and retranslocation of metals in vascular plants. *Water, Air, and Soil Pollution* 86: 221-234.
- Godbold, D.L., Jentschke, G., Wintz, S. & Marschner, P. 1998. Ectomycorrhizas and amelioration of metal stress in forest trees. *Chemosphere* 36: 757-762.
- Godt, J., Schmidt, M. & Mayer, R. 1986. Processes in the canopy of trees: internal and external turnover of elements. In: Georgii, H-W. (ed.). *Atmospheric pollutants in forest areas*. D. Reidel Publishing Company. Dordrecht, pp. 263-274.
- Gubala, C.P., Landers, D.H., Monetti, M., Heit, M., Wade, T., Lasorsa, B. & Allen-Gill, S. 1995. The rates of accumulation and chronologies of atmospherically derived pollutants in Arctic Alaska, USA. *The Science of the Total Environment* 160/161: 347-361.
- Haimi, J. & Siira-Pietikäinen, A. 1996. Decomposer animal communities in forest soil along a heavy-metal pollution gradient. *Fresenius' Journal of Analytical Chemistry* 354: 672-675.
- Hämät-Ahti, L., Palmén, A., Alanko, P. & Tigerstedt, P.M.A. 1989. *Suomen puu- ja pensaskasvio. Woody Flora of Finland. (In Finnish. English Summary.) Dendrologian seura. Helsinki. 290 p.*
- Harley, J.L. & Smith, S.E. 1983. *Mycorrhizal symbiosis*. Academic Press, London. 483 p.
- Hartley, J., Cairney, J. W.G. & Meharg, A.A. 1997. Do ectomycorrhizal fungi exhibit adaptive tolerance to potentially toxic metals in the environment? *Plant and Soil* 189: 303-319.
- Heliövaara, K., Väisänen, R., Braunschweiler, H. & Lodenius, M. 1987. Heavy metal levels in two biennial pine insects with sap-sucking and gall-forming life-styles. *Environmental Pollution* 48: 13-23.

- Helmisaari, H.-S. 1995. Nutrient cycling in *Pinus sylvestris* stands in eastern Finland. *Plant and Soil* 168-169: 327-336.
- Helmisaari, H.-S. & Mälkönen, E. 1989. Acidity and nutrient content of throughfall and soil leachate in three *Pinus sylvestris* stands. *Scandinavian Journal of Forest Research* 4: 13-28.
- Helmisaari, H.-S., Derome, J., Fritze, H., Nieminen, T., Palmgren, K., Salemaa, M. & Vanha-Majamaa, I. 1995. Copper in Scots pine forest around a heavy-metal smelter in southwestern Finland. *Water, Air, and Soil Pollution* 85: 1727-1732.
- Helmisaari, H.-S., Makkonen, K., Olsson, M., Viksna, A. & Mälkönen, E. 1999. Fine-root growth, mortality and heavy-metal concentrations in limed and fertilized *Pinus sylvestris* (L.) stands in the vicinity of a Cu-Ni smelter in SW Finland. *Plant and Soil* 209: 193-200.
- Helmisaari, H.-S., Makkonen, K., Kellomäki, S., Valtonen, E. & Mälkönen, E. 2002. Below- and aboveground biomass, production and nitrogen use in Scots pine stands in eastern Finland. *Forest Ecology and Management* 165: 317-326.
- Henderson, P.-J., McMartin, I., Hall, G.E., Percival, J.B. & Walker, D.A. 1998. The chemical and physical characteristics of heavy metals in humus and till in the vicinity of the base metal smelter at Flin Flon, Manitoba, Canada. *Environmental Geology* 34: 39-58.
- Herms, U. 1982. Untersuchungen zur Schwermetalllöslichkeit in Abhängigkeit von pH, Redoxbedingungen und Stoffbestand von Böden und Sedimenten. Dissertation. Agrarwissenschaftlichen Fachbereiches der Christian-Albrechts-Universität. Kiel. 269 p.
- Herms, U. & Brümmer, G. 1980. Einfluss der Bodenreaktion auf Löslichkeit und tolerierbare Gesamtgehalte an Nickel, Kupfer, Zink, Cadmium und Blei in Böden und kompostierten Siedlungsabfällen. *Landwirtschaftlichen Forschung* 33: 408-423.
- Hultberg, H. 1985. Budgets of base cations, chloride, nitrogen and sulphur in the acid Lake Gårdsjön catchment, SW Sweden. *Ecological Bulletins* 37: 133-157.
- Hultberg, H. & Grennfelt, P. 1992. Sulphur and seasalt deposition as illustrated by throughfall input and streamwater output. *Environmental Pollution* 75: 215-222.
- Hutchinson, T.C. & Whitby, L.M. 1974. Heavy metal pollution in the Sudbury mining and smelting region of Canada, I. Soil and vegetation contamination by nickel, copper and other metals. *Environmental Conservation* 1: 123-132.
- Hutchinson, T.C. & Whitby, L.M. 1977. The effect of acid rainfall and heavy metal particulates on a boreal forest ecosystem near the Sudbury smelting region of Canada. *Water, Air, and Soil Pollution* 7, 421-438.
- Huttunen, S. 1975. Studies on forest vegetation in air pollution damage area. *Acta Universitatis Ouluensis. Series A. Biology* 2. University of Oulu. Oulu. pp. 1-37.
- Huttunen, S. & Laine, K. 1983. Effects of air-borne pollutants on the surface wax structure of *Pinus sylvestris* needles. *Annales Botanici Fennici* 20: 79-86.
- Huttunen, S., Karhu, M. & Laine, K. 1983. Air pollution induced stress and its effects on the photosynthesis of *Pinus sylvestris* L. in Oulu. *Aquilo Series Botanica* 19: 275-285.
- Huttunen, S., Laine, K. & Torvela, H. 1985. Seasonal sulphur contents of pine needles as indices of air pollution. *Annales Botanici Fennici* 22: 343-359.
- Hynninen, V. 1986. Monitoring of airborne metal pollution with moss bags near an industrial source at Harjavalta. *Annales Botanici Fennici* 23: 83-90.
- Hyvärinen, A. 1990. Deposition on forest soils. Effect of tree canopy on throughfall. In: Kauppi, P., Anttila, P. & Kenttämies, K. (eds.). *Acidification in Finland*. Springer-Verlag, Berlin, pp. 199-213.
- Innes, J.L. 1995. Influence of air pollution on the foliar nutrition of conifers in Great Britain. *Environmental Pollution* 88: 183-192.
- Jackson, P.J., Unkefer, P.J., Delhaize, E. & Robison, N.G. 1990. Mechanism of trace metal tolerance in plants. In: Katterman, F. (ed.). *Environmental injury to plants*. Academic Press. San Diego. pp. 231-255.
- Jalkanen, L. 2000. Atmospheric inorganic trace contaminants in Finland, especially in the Gulf of Finland area. *Finnish Meteorological Institute Contribution* 29. 106 p.
- Jonsson, C., Warfvinge, P. & Sverdrup, H. 1995. Uncertainty in predicting weathering rate and environmental stress factors with the PROFILE model. *Water, Air, and Soil Pollution* 81: 1-23.
- Kabata-Pendias, A. 2001. *Trace elements in soils and plants*. CRC Press. Boca Raton. 413 p.
- Kanninen, M. 1990. Havupuiden pituuskasvu. In: Lahti, T. & Smolander, H. (eds.). *Johdatus metsien perustuotantobiologiaan*. (In Finnish.) *Silva Carelica* 16: 183-206.

- Katainen, H.-S., Karjalainen, R., Mäkinen E., Jokinen, J. & Kellomäki, S. 1984. Effects of SO₂ on photosynthesis and peroxidase activity in Scots pine needles. *European Journal of Forest Pathology* 14: 33-42.
- Kiikkilä, O. 2002. Remediation through mulching with organic matter of soil polluted by a copper-nickel smelter. Finnish Forest Research Institute. Research Papers 831. 57 p.
- Kiikkilä, O. 2003. Heavy-metal pollution and remediation of forest soil around the Harjavalta Cu-Ni smelter, in SW Finland. *Silva Fennica* 37: 399-415.
- Kikuzawa, K. 1973. On sulphur dioxide gas injury to the Japanese Red Pine forests. *Journal of the Japanese Forestry Society* 55: 182-184.
- Kirpichtchikova, T., Manceau, A., Lanson, B., Marcus, M.A. & Jacquet, T. 2003. Speciation and mobility of Zn, Cu and Pb in a truck farming soil contaminated by sewage irrigation. *Journal de Physique IV France* 107: 695-698.
- Köhler, H.-R., Eckwert, H., Triebskorn, R. & Bengtsson, G. 1999. Interaction between tolerance and 70kDa stress protein (hsp70) induction in collembolan populations exposed to long-term metal pollution. *Applied Soil Ecology* 11: 43-52.
- Koljonen, T. 1990. Geokemia. Suomen Kartasto. *Geologia* 123-126. pp. 40-42.
- Komulainen, M., Vieno, M., Yarmishko, V.T., Daletskaja, T.D. & Maznaja, E.A. 1994. Seedling establishment from seeds and seedbanks in forests under long-term pollution stress: a potential for vegetation recovery. *Canadian Journal of Botany* 72: 143-149.
- Kopponen, P., Utriainen, M., Lukkari, K., Suntioinen, S., Kärenlampi, L. & Kärenlampi, S. 2001. Clonal differences in copper and zinc tolerance of birch in metal-supplemented soils. *Environmental Pollution* 112: 89-97.
- Koski, V. & Tallqvist, R. 1978. Results of long-time measurements of the quantity of flowering and seed crop of forest trees. (In Finnish. English Summary). *Folia Forestalia* 364. 60 p.
- Kozlov, M.V. & Zvereva, E.L. 2004. Reproduction of mountain birch along a strong pollution gradient near Monchegorsk, northwestern Russia. *Environmental Pollution* 132: 443-451.
- Kujala, V. 1958. *Pinus sylvestris* L. –Mänty. In: Jalas, J. (ed.). *Suuri kasvikirja II*. (In Finnish.) WSOY. Porvoo. pp. 143-152.
- Laaksovirta, K. & Silvola, J. 1975. Effect of air pollution by copper, sulfuric acid and fertilizer factories on plants at Harjavalta, W. Finland. *Annales Botanici Fennici* 12: 81-88.
- Laine, K., Lähdesmäki, P., Pakonen, T., Kontunen-Soppela, S., Salonen, E., Tolvanen, A., Virtanen, R., Mäenpää, E., Saari, E. & Havas, P. 1994. Environmental stress and the biochemical and physiological response of plants: studies on the Scots pine and bilberry. *Aquilo Series Botanica* 32: 33-39.
- Laitakari, E. 1927. Männyn juuristo. Morfologinen tutkimus. Thesis. (In Finnish.) Suomalaisen kirjallisuuden seuran kirjapainon osakeyhtiö, Helsinki, 306 p.
- Lanner, R.M. 1976. Patterns of shoot development in *Pinus*. In: Cannell, M.G.R. & Last, F. (eds.). *Tree physiology and yield improvement*. Academic Press. London. pp.223-243.
- Lee, J., Reeves, R.D., Brooks, R.R. & Jaffré, T. 1978. The relation between nickel and citric acid in some nickel-accumulating plants. *Phytochemistry* 17: 1033-1035.
- Legge, A.H., Nosal, M. & Krupa, S.V. 1996. Modelling the numerical relationships between chronic ambient sulphur dioxide exposures and tree growth. *Canadian Journal of Forest Research* 26: 689-695.
- Lehto, J. 1956. Studies on the natural reproduction of Scots pine on the upland soils of southern Finland. (In Finnish. English Summary.) *Acta Forestalia Fennica* 66. 100 p.
- Lepp, N.W., Hartley, J., Toti, M. & Dickinson, N.M. 1997. Patterns of soil copper contamination and temporal changes in vegetation in the vicinity of a copper rod rolling factory. *Environmental Pollution* 95: 363-369.
- Lindberg, S. E. & Lovett, G. M. 1992. Deposition and canopy interactions of airborne sulfur: results from the integrated forest study. *Atmospheric Environment* 26A: 1477-1492.
- Lindroos, A.-J. 1998. The effects of emissions from the Cu-Ni smelters in the Kola Peninsula on the chemical properties of forest soil. Finnish Forest Research Institute. Research Papers 676. 73 p.
- Lipman, C.B. & MacKinney, G. 1931. Proof of the essential nature of copper for higher green plants. *Plant Physiology* 6: 593-599.
- Lobersli, E.M. & Steinnes, E. 1988. Metal uptake in plants from a birch forest area near a copper smelter in Norway. *Water, Air, and Soil Pollution* 37: 25-39.

- Lobersli, E.M., Steinnes, E. & Odegard, M. 1990. A historical study of mineral elements in forest plants from South Norway. *Environmental Monitoring and Assessment* 15: 111-129.
- Lozano, F.C., & Morrison, I.K. 1981. Disruption of hardwood nutrition by sulfur dioxide, nickel and copper air pollution near Sudbury, Canada. *Journal of Environmental Quality* 10: 198-204.
- Lozano, F.C., & Morrison, I.K. 1982. Growth and nutrition of white pine and white spruce seedlings in solutions of various nickel and copper concentrations. *Journal of Environmental Quality* 11: 437-441.
- MacKenzie, A.B., Logan, E.M, Cook, C.T. & Pulford, I.D. 1998. A historical record of atmospheric depositional fluxes of contaminants in west-central Scotland derived from an ombrotrophic peat core. *The Science of the Total Environment* 222: 157-166.
- Mäkinen, A. 1994. Biomonitoring of atmospheric deposition in Finland, Estonia and Kola Peninsula, based on the chemical analysis of mosses. *Publications from the Department of Botany, University of Helsinki* 19. Helsinki. 28 p.
- Mäkinen, E. 1938. Die Kupfererzlagertstätte Outokumpu in Finnland und ihre Verwertung. *Metall und Erz* 2: 25-33.
- Mälikönen, E. 1974. Annual primary production and nutrient cycle in some Scots pine stands. *Communications Instituti Forestalis Fenniae* 84.5. 87 p.
- Mälikönen, E. 1977. Annual primary production and nutrient cycle in a birch stand. *Metlan julkaisu* 91. 35 p.
- Mälikönen, E., Derome, J., Fritze, H., Helmisaari, H-S., Kukkola, M., Kytö, M., Saarsalmi, A. & Salemaa, M. 1999. Compensatory fertilization of Scots pine stands polluted by heavy metals. *Nutrient cycling in Agroecosystems* 55: 239-268.
- Marschner, H. 1995. *Mineral Nutrition of Higher Plants*. Academic Press. Cambridge. 889 p.
- Mayer, R. & Ulrich, B. 1978. Input of atmospheric sulphur by dry and wet deposition to two central European forest ecosystems. *Atmospheric Environment* 12: 375-377.
- McLaughlin, M.J. 2002. Bioavailability of metals to terrestrial plants. In: Allen, H. (ed.). *Bioavailability of metals in terrestrial ecosystems: Importance of partitioning for bioavailability to invertebrates, microbes, and plants*. Setac Press. pp. 39-68.
- Meier, C.E., Grier, C.C. & Cole, D. W. 1985. Below and aboveground N and P use by *Abies amabilis* stands. *Ecology* 66: 1928-1942.
- Melanen, M., Ekqvist, M., Mukherjee, A.B., Aunela-Tapola, L., Verta, M. & Salmikangas, T. 1999. Atmospheric emissions of heavy-metals in Finland in 1990s. *The Finnish Environment* 329. Finnish Environment Institute. Helsinki. 92 p.
- Miller, H.G, Cooper, J.M., Miller, J.D. & Pauline, O.J. 1979. Nutrient cycles in pines and their adaptation to poor soils. *Canadian Journal of Forest Research* 9: 19-26.
- Mitsch, W.J. & Day, J. W. Jr. 2004. Thinking big with whole-ecosystem studies and ecosystem restoration – a legacy of H.T. Odum. *Ecological Modelling* 178: 133-155.
- Monni, S., Salemaa, M. & Millar, N. 2000. The tolerance of *Empetrum nigrum* to copper and nickel. *Environmental Pollution* 109: 221-229.
- Nambiar, E.K.S. & Fife, D.N. 1987. Growth and nutrient retranslocation in needles of *Radiata* pine in relation to nitrogen supply. *Annals of Botany* 60: 147-156.
- Nambiar, E.K.S., Fife, D.N., Kaufmann, M.R. & Landsberg, J.J. 1991. Nutrient retranslocation in temperate conifers. *Tree Physiology* 9:185-207.
- Nieminen, M. 2003. Effects of clear-cutting and site preparation on water quality from a drained Scots pine mire in southern Finland. *Boreal Environment Research* 8: 53-59.
- Nieminen, T. 1998. The effect of soil copper and nickel on survival and growth of Scots pine saplings. *Chemosphere* 36: 745-750.
- Nieminen, T., Helmisaari, H-S, Kukkola, M. & Saarsalmi, A. 1998. Puuston biomassa ja ravinnepitoisuudet. In: Mälikönen, E. (ed.). *Ympäristömuutos ja metsien kunto. Metsien terveydentilan tutkimusohjelman loppuraportti*. (In Finnish.) *Metsäntutkimuslaitoksen tiedonantoja* 691. pp. 202-204.
- Nieminen, T., Derome, J., Helmisaari, H.-S., Janhunen, S., Kukkola, M. & Saarsalmi, A. 2000. Response of tree stands to heavy metal loading. In: Mälikönen, E. (ed.). *Forest condition in a changing environment - the Finnish case*. Kluwer Academic Publishers. Dordrecht. pp. 278-283.

- Niini, S. & Raitio, H. 1993. Männyntaimien alkukehitys saastuneessa maassa. In: Hyvärinen, A., Jukola-Sulonen, E.-L., Mikkilä, H., Nieminen, T. (eds.). *Metsäluonto ja ilmansaasteet*. (In Finnish.) *Metsäntutkimuslaitoksen tiedonantoja* 446: 181-183.
- Nöjd, P. 1996. Effects of emissions from the nickel-copper smelter in Monchegorsk, northwestern Russia, on the radial growth of Scots pine. The Finnish Forest Research Institute. *Research Papers* 615. 52 p.
- Nöjd, P., Mikkola, K. & Saranpää, P. 1996. History of forest damage in Monchegorsk, Kola; a retrospective analysis based on tree rings. *Canadian Journal of Forest Research* 26: 1805-1812.
- Nriagu, J.O. 1990. Global metal pollution poisoning the biosphere. *Environment* 32: 7-33.
- Nriagu, J.O. & Pacyna, J.M. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333: 134-139.
- Nriagu, J.O., Wong, H.K.T., Lawson, G. & Daniel, P. 1998. Saturation of ecosystems with toxic metals in Sudbury basin, Ontario, Canada. *The Science of the Total Environment* 223: 99-117.
- Nyysönen, A. & Mielikäinen, K. 1978. Estimation of stand increment. (In Finnish. English Summary.) *Acta Forestalia Fennica* 163. 40 p.
- Odum, H.T. 1951. The stability of the world's strontium cycle. *Science* 114: 407-411.
- Odum, H.T. 1957. Trophic structure and productivity of Silver Springs, Florida. *Ecological Monographs* 27: 55-112.
- Oleksyn, J. & Innes, J.L. 2000. Air pollution and forests in heavily industrialized regions: an introduction. In: Innes, J.L. & Oleksyn, J. (eds.). *Forest dynamics in heavily polluted regions*. IUFRO 1 Research Series. CAB International. Wallingford. p. 1-8.
- Ovington, J.D. 1957. Dry-matter production of *Pinus sylvestris* L. *Annals of Botany* 21: 287-314.
- Ovington, J.D. 1959. The circulation of minerals in plantations of *Pinus sylvestris* L. *Annals of Botany* 23: 229-239.
- Paavilainen, E. 1980. Effect of fertilization on plant biomass and nutrient cycle on a drained dwarf-shrub pine swamp. Finnish Forest Research Institute. *Research Papers* 98. 71 p.
- Paavilainen, E. 1984. Fertilization and nutrient cycle in peatland forests. (In Finnish. English Summary.) *Suo* 35: 91-93.
- Parat, C., Chaussod, R., Lévêque, J., Dousset, S. & Andreux, F. 2002. The relationship between copper accumulated in vineyard calcareous soils and soil organic matter and iron. *European Journal of Soil Science* 53: 663-669.
- Parker, G.G. 1983. Throughfall and stemflow in the forest nutrient cycle. *Advances in Ecological Research* 13: 58-133.
- Parkkinen, J. & Reino, J. 1985. Nickel occurrences of the Outokumpu type at Vuonos and Keretti. In: Papunen, H. & Gorbunov, G.I. (eds.). *Nickel-copper deposits of the Baltic shield and Scandinavian Caledonides*. Geological Survey of Finland. *Bulletin* 333: 178-188.
- Patterson, W. A. & Olson, J.J. 1983. Effects of heavy metals on radicle growth of selected woody species germinated on filter paper, mineral and organic soil substrates. *Canadian Journal of Forest Research* 13: 233-238.
- Pfirrmann, T., Runkel, K. H., Schramel, P., Eisenmann, T., Blank, L.W. & Lutz, C. 1990. Mineral and nutrient supply, content and leaching in Norway spruce exposed for 14 months to ozone and acid mist. *Environmental Pollution* 64: 229-253.
- Piirainen, S., Finér, L., Mannerkoski, H. & Starr, M. 2004. Effects of forest clear-cutting on the sulphur, phosphorus and base cations fluxes through podzolic soil horizons. *Biogeochemistry* 69: 405-424.
- Poikolainen, J., Kubin, E., Piispanen, J. & Karhu, J. 2004. Atmospheric heavy metal deposition in Finland during 1985–2000 using mosses as bioindicators. *The Science of the Total Environment* 318: 171-185.
- Poutanen, P. & Kuisma, M. 1998. Puoli vuosisataa kuparia ja nikkeliä. *Outokummun Harjavallan tehtaata*. Gummerus Kirjapaino Oy. Jyväskylä. 192 p.
- Probst, A., Dambrine, E., Viville, D. & Fritz, B. 1990. Influence of acid atmospheric inputs on surface water chemistry and mineral fluxes in a declining spruce stand within a small catchment (Vosges massif, France). *Journal of Hydrology* 116: 101-124.
- Raitio, H. 1990a. The foliar chemical composition of young pines (*Pinus sylvestris* L.) with or without decline. In: Kauppi, P., Anttila, P. & Kenttämies, K. (eds.). *Acidification in Finland*. Springer Verlag, Berlin, pp. 701-715.

- Raitio, H. 1990b. Decline of young Scots pines in a dry heath forest. *Acta Universitatis Ouluensis A* 216. 40 p.
- Raitio, H. 1995. Influence of sample washing on the foliar chemical composition. A review. 3rd Meeting of the forest foliar expert panel. International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests- ICP Forests , 6-8 November 1995. Vienna. 8 p.
- Raitio, H., Tamminen, P., Tuovinen, J-P. & Anttila, P. 2000. Tree nutrient status. In: Mälkönen, E. (ed.). Forest condition in a changing environment - The Finnish case. Kluwer Academic Publishers. The Netherlands. pp. 93-102.
- Ranger, J., Colin-Belgrand, M. & Nys, C. 1994. Le cycle biogéochimique des éléments majeurs dans les écosystèmes forestiers. Importance dans le fonctionnement des sols. *Etude et Gestion des Sols* 2: 119-134.
- Ranger, J. 1995. Le cycle biogéochimique des éléments nutritifs dans les écosystèmes forestiers. INRA. Centre de Nancy. Champenoux. 108 p.
- Rautio, P. 2000. Nutrient alterations in Scots pines (*Pinus sylvestris* L.) under sulphur and heavy metal pollution. *Acta Universitatis Ouluensis A353* University of Oulu. Oulu. 52 p.
- Rautio, P., Huttunen, S., Kukkola, E., Peura, R. & Lamppu, J. 1998. Deposited particles, element concentrations and needle injuries on Scots pines along an industrial pollution transect in northern Europe. *Environmental Pollution* 103: 81-89.
- Rebele, F. 2001. Management impacts on vegetation dynamics of hypereutrophicated fields at Berlin, Germany. *Applied Vegetation Science* 4: 147-156.
- Renberg, I., Brännvall, M.-L., Bindler, R. & Emteryd, O. 2002. Stable lead isotopes and lake sediments – a useful combination for the study of atmospheric lead pollution history. *The Science of the Total Environment* 292: 45-54.
- Ribolzi, O., Valles, V., Gomez, L. & Voltz, M. 2002. Speciation and origin of particulate copper in runoff water from a Mediterranean vineyard catchment. *Environmental Pollution* 117: 261-271.
- Rigina, O. & Kozlov, M. 2000. The impacts of air pollution on the northern taiga forests of the Kola Peninsula, Russian Federation. In: Innes, J.L. & Oleksyn, J. (eds.). *Forest dynamics in heavily polluted regions*. CABI Publishing. Wallingford. pp. 37-65.
- Riissanen, N. 1998. Männyn luontainen uudistuminen Harjavallan gradientilla. Metsäympäristön hoidon ja suojelun pro gradu. (In Finnish.). University of Joensuu. Faculty of Forestry. 36 p.
- Ross, S.M. 1994. Retention, transformation and mobility of toxic metals in soils. In: Ross, S.M. (ed.). *Toxic metals in soil-plant systems*. John Wiley & Sons Ltd. Chichester. pp. 63-152.
- Ross, S.M. & Kaye, J. 1994. The meaning of metal toxicity in soil-plant systems. In: Ross, S.M. (ed.). *Toxic metals in soil-plant systems*. John Wiley & Sons Ltd. Chichester. U.K. pp. 27-61.
- Rühling, Å. & Tyler, G. 2001. Changes in atmospheric deposition rates of heavy metals in Sweden. *Water, Air, and Soil Pollution: Focus* 1: 311-323.
- Ruuhijärvi, R. 1983. The Finnish mire types and their regional distribution. In: Gore, A.J.P., (ed.). *Ecosystems of the World. Mires: Swamp, Bog, Fen and Moor. Regional Studies*. Elsevier. Amsterdam pp. 47-67.
- Saari, H., Kartastenpää, R. Lindgren, K. & Tuomi, V. 1998. Hiukkas- ja rikkidioksiditutkimus Harjavallassa keväällä 1997. Ilmatieteen laitos. Helsinki. 58 p.
- Saarsalmi, A. 1984. Biomass production and nutrient and water consumption in *Salix 'Aquatica Gigantea'* plantation. (In Finnish. English Summary.) *Folia Forestalia* 602. 29p.
- Saarsalmi, A. & Mälkönen, E. 1989. Biomass production and nutrient consumption in *Alnus incana* stands. (In Finnish. English Summary.) *Folia Forestalia* 728: 16 p.
- Saarsalmi, A., Palmgren, K. & Levula, T. 1985. Biomass production and nutrient and water consumption in an *Alnus incana* plantation. (In Finnish. English Summary.) *Folia forestalia* 628. 24p.
- Salemaa, M. & Uotila, T. 2001. Seed bank composition and seedling survival in forest soil polluted with heavy metals. *Basic and Applied Ecology* 2: 251-263.
- Salemaa, M., Vanha-Majamaa, I. & Derome, J. 2001. Understorey vegetation along a heavy-metal pollution gradient in SW Finland. *Environmental Pollution* 112: 339-350.
- Sarvas, R. 1949. Seed-tree cutting as a regeneration method in Scots pine forest of Southern Finland. *Communicationes Instituti Forestalis Fenniae* 37.5: 1-43.

- Sarvas, R. 1962a. Investigations on the flowering and seed crop of *Pinus silvestris*. *Communicationes Instituti Forestalis Fenniae* 53.4: 1-198.
- Sarvas, R. 1962b. The development of tree species composition of the forests of Southern Finland during the past two thousand years. *Communicationes Instituti Forestalis Fenniae* 55.4: 1-14.
- Saur, E., Nambiar, E.K.S. & Fife, D.N. 2000. Foliar nutrient retranslocation in *Eucalyptus globulus*. *Tree Physiology* 20: 1105-1112.
- Sauvé, S. 2002. Speciation of metals in soils. In: Allen, H. (ed.). *Bioavailability of metals in terrestrial ecosystems: Importance of partitioning for bioavailability to invertebrates, microbes, and plants*. SETAC Press. Pensacola. pp. 7-37.
- Sauvé, S., Cook, N., Hendershot, W.H. & McBride, M. 1996. Linking plant tissue concentration and soil copper pools in urban contaminated soils. *Environmental Pollution* 94: 154-157.
- Schreiber, L., Hartmann, K., Skrabs, M. & Zeier, J. 1999. Apoplastic barriers in roots: chemical composition of endodermal and hypodermal cell walls. Review article. *Journal of Experimental Botany* 50: 1267-1280.
- Shoty, W. 1997. Summary of the workshop on peat bog archives of atmospheric metal deposition. *Water, Air, and Soil Pollution* 100: 213-219.
- Shoty, W., Weiss, D., Appleby, P.G., Cheburkin, A.K., Frei, R., Gloor, M., Kramers, J.D., Reese, S. & van der Knaap, W.O. 1998. History of atmospheric lead deposition since 12,370 ¹⁴C yr BP from a peat bog, Jura mountains, Switzerland. *Science* 281: 1635-1640.
- Stachurski, A. & Zimka, J.R. 2000. Atmospheric input of elements to forest ecosystems: a method of estimation using artificial foliage placed above rain collectors. *Environmental Pollution* 110: 345-356.
- Stachurski, A. & Zimka, J.R. 2002. Atmospheric deposition and ionic interaction within a beech canopy in the Karkonosze Mountains. *Environmental Pollution* 118: 75-87.
- Starr, M., Lindroos, A.-J., Ukonmaanaho, L., Tarvainen, T. & Tanskanen, H. 2003. Weathering release of heavy metals from soil in comparison to deposition, litterfall and leaching fluxes in a remote, boreal coniferous forest. *Applied Geochemistry* 18: 607-613.
- Steinnes, E. 2001. Metal contamination of natural environment in Norway from long range atmospheric transport. *Water, Air, and Soil Pollution: Focus* 1: 449-460.
- Steinnes, E., Lukina, N., Nikonov, V. Aamlid, D. & Royset, O. 2000. A gradient study of 34 elements in the vicinity of a copper-nickel smelter in the Kola peninsula. *Environmental Monitoring and Assessment* 60: 71-88.
- Sternbeck, J., Östlund, P. 2001. Metals in sediments from the Stockholm region: geographical pollution patterns and time trends. *Water, Air, and Soil Pollution: Focus* 1:151-165.
- Strojan, C.L. 1978. Forest leaf litter decomposition in the vicinity of a zinc smelter. *Oecologia* 32: 203-212.
- Sverdrup, H. & Warfvinge, P. 1990. The role of weathering and forestry in determining the acidity of lakes in Sweden. *Water, Air, and Soil Pollution* 52: 71-78.
- Switzer, G.L. & Nelson, L.E. 1972. Nutrient accumulation and cycling in loblolly pine (*Pinus taeda* L.) plantation ecosystems: the first twenty years. *Proceedings. Soil Science Society of American Journal* 36: 143-147.
- Tichelen, K.K. van, Vanstraelen, T. & Colpaert, J.V. van 1999. Nutrient uptake by intact mycorrhizal *Pinus sylvestris* seedlings: a diagnostic tool to detect copper toxicity. *Tree Physiology* 19: 189-196.
- Tikkanen, E. & Niemelä, I. (ed.). 1995. *Kola peninsula pollutants and forest ecosystems in Lapland*. Gummerus. Jyväskylä. Finland. 82 p.
- Tolonen, K. 1983. The post-glacial fire record. In: Wein, R.W. & MacLean, D.A. (eds.). *The role of fire in northern circumpolar ecosystems*. *Scope* 18. New York. John Wiley & Sons. pp. 21-44.
- Tomppo, E. 2000. Kavupaikat ja Puusto. In: Reinikainen, A., Mäkipää, R., Vanha-Majamaa, I. & Hotanen, J.P. (eds.). *Kasvit muuttuvassa metsäluonnossa*. (In Finnish. English Summary.) Tammi. Helsinki. pp. 60-83.
- Townsend, T., Tolaymat, T., Solo-Gabriele, H., Dubey, B., Stook, K. & Wadanambi, L. 2004. Leaching of CCA-treated wood: implications for waste disposal. *Journal of Hazardous Materials* B114: 75-91.
- Tukey, H. B. 1980. Some effects of rain and acid mist on plants, with implications for acid precipitation. In: Hutchinson, T.C. and Havas, M. (eds.). *Effects of acid precipitation on terrestrial ecosystems*. Plenum Press. New York. pp. 141-150.

- Turner, A. P. & Dickinson, N.M. 1993. Survival of *Acer pseudoplatanus* L. (sycamore) seedlings on metalliferous soils. *New Phytologist* 123: 509-521.
- Turner, A.P. & Ross, S.M. 1994. The responses of plants to heavy metals. In Ross, S. M. (ed.). *Toxic metals in soil-plant systems*. John Wiley & Sons Ltd, Chichester, U.K. pp. 153-187.
- Turunen, M., Huttunen, S., Percy, K.E., McLaughlin, C.K. & Lamppu, J. 1997. Epicuticular wax of subarctic Scots pine needles: response to sulphur and heavy metal deposition. *New Phytologist* 135: 501-515.
- Tyler, G. 1975. Heavy metal pollution and mineralisation of nitrogen in forest soils. *Nature* 255: 701-702.
- Tyler, G. 1984. The impact of heavy metal pollution on forests: a case study of Gusum, Sweden. *Ambio* 13: 18-25.
- Tyler, G., Balsberg-Påhlsson, A.M., Bengtsson, G., Bååth, E., Tranvik, L. & Pålsson, A.M.B. 1989. Heavy-metal ecology of terrestrial plants, microorganisms and invertebrates. A review. *Water, Air, and Soil Pollution* 47: 189-215.
- Ukonmaanaho, L. 2001. Canopy and soil interaction with deposition in remote boreal forest ecosystems: a long-term integrated monitoring approach. Finnish Forest Research Institute. Research Papers 818. 69 p.
- Ukonmaanaho, L. & Starr, M. 2002. Major nutrients and acidity: budgets and trends at four remote boreal stands in Finland during the 1990s. *The Science of the Total Environment* 297: 21-41.
- Ukonmaanaho, L., Starr, M., Hirvi, J.-P., Kokko, A, Lahermo, P., Mannio, J., Paukola, T., Ruoho-Airola, T. & Tanskanen, H. 1998. Heavy metal concentrations in various aqueous and biotic media in Finnish Integrated Monitoring catchments. *Boreal Environment Research* 3: 235-249.
- Ukonmaanaho, L., Starr, M., Mannio, J. & Ruoho-Airola, T. 2001. Heavy metal budgets for two headwater forested catchments in background areas of Finland. *Environmental Pollution* 114: 63-75.
- Ulrich, B. 1974. The nutrient cycle in forest ecosystems as influenced by fertilization. International symposium on forest fertilization, Paris, France, 3-7 December, 1973. *FAO-IUFRO*. pp. 23-34.
- Ulrich, B. 1981. Theoretische Betrachtung des Ionenkreislaufs in Waldökosystemen. (In German. English Summary.) *Zeitschrift für Pflanzenernährung und Bodenkunde* 144: 647-659.
- Ulrich, B. 1992. Forest ecosystem theory based on material balance. *Ecological Modelling* 63: 163-183.
- Wallander, H. & Wickman, T. 1999. Biotite and microcline as potassium sources in ectomycorrhizal and non-mycorrhizal *Pinus sylvestris* seedlings. *Mycorrhiza* 9: 25-32.
- Watmough, S.A. & Dickinson, N.M. 1995. Dispersal and mobility of heavy metals in relation to tree survival in an aerially contaminated woodland soil. *Environmental Pollution* 90: 135-142.
- Wedepohl K.H. 1995. The composition of the continental crust. *Geochimica et Cosmochimica Acta* 59: 1217-1232.
- Weiss, D., Shotyk, W., Appleby, P.G., Kramers, J.D. & Cheburkin, A.K. 1999. Atmospheric Pb deposition since the industrial revolution recorded by five Swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources. *Environmental Science & Technology* 33: 1340-1352.
- Whitby, G. S. 1939. The effects of sulphur dioxide on vegetation. *Chemical Index* 58: 991-999.
- Wilkinson, D.M. & Dickinson, N.M. 1995. Metal resistance in trees: the role of mycorrhizae. *Oikos* 72: 298-300.
- Winterhalder, K. 1995. Early history of human activities in the Sudbury area and ecological damage to the landscape. In: Gunn, J.M. (ed.). *Restoration and recovery of an industrial region. Progress in Restoring the smelter-damages landscape near Sudbury, Canada*. Springer-Verlag, New York. pp. 17-31.
- Winterhalder, K. 1996. Environmental degradation and rehabilitation of the landscape around Sudbury, a major mining and smelting area. *Environmental Reviews* 4: 185-224.
- Winterhalder, K. 2000. Landscape degradation by smelter emissions near Sudbury, Canada and subsequent amelioration and restoration. In: Innes, J.L. & Oleksyn, J. (eds.). *Forest dynamics in heavily polluted regions*. IUFRO 1 Research Series. CAB International, Wallingford. p. 87-120.

- Wotton, D.L., Jones, D.C. & Phillis, S.F. 1986. The effect of nickel and copper deposition from mining and smelting complex on coniferous regeneration in the boreal forest of northern Manitoba. *Water, Air, and Soil Pollution* 31: 337-341.
- Yang, X.E., Baligar, V.C., Foster, J.C. & Martens, D.C. 1997. Accumulation and transport of nickel in relation to organic acids in ryegrass and maize grown at different Ni levels. *Plant and Soil* 196: 271-276.
- Ye, Z.H, Baker, A.J.M., Wong, M.H. & Willis, A.J. 1997. Zinc, lead and cadmium tolerance, uptake and accumulation by *Typha latifolia*. *New Phytologist* 136: 469-480.
- Zimka, J.R. 1991. Analysis of processes of element transfer in forest ecosystems. *Polish Ecological Studies* 15: 135-212.
- Zimka, J.R. & Stachurski, A. 1976. Vegetation as a modifier of carbon and nitrogen transfer to soil in various types of forest ecosystems. *Ecologia Polska* 24: 493-451.