Availability and toxicity of Cu and Ni to Scots pine in different soils

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Abstract
We compared the phytoavailability and within plant mobility of Cu and Ni, as well as the plant mortality, in two contrasting substrates: intact smelter-polluted podzol soil profiles and artificially Cu-Ni contaminated quartz-sand media. Both the uptake and the root-to-shoot transport of Cu and Ni by pine seedlings were clearly higher in the artificially contaminated quartz-sand. No pine mortality took place in the smelter-polluted soils at the levels of metal concentration established as the thresholds for lethal toxicity in the artificial contamination series, although the mortality rate was high in the most contaminated smelter-polluted soil. We further compared the exposure doses and mortality rates in these two substrates with those of an old field experiment, in which a predetermined dose of Cu and Ni was applied on a peat bog in 1962. The Cu dose and the pine mortality response observed at the peat bog site were both lower than those obtained from the most polluted smelter-polluted soil, probably partly because the current Cu and Ni concentrations in the topmost peat layer bear little relation to their original exposure dose.

Keywords: metal mobility, peat, podzol, root uptake, quartz-sand

1 Introduction

Heavy metals from smelting activities have probably affected forest ecosystems since the beginning of metallurgy. The amount of metals accumulated in soil continues to affect vegetation even after emissions have ceased. Increased concentrations of metals in soil can have an effect on plants both by their direct toxicity and by their toxicity to litter decomposing organisms in soil (Baath 1989; Fritze *et al.* 1989; Lukina and Nikonov 1995), which leads to impaired soil-nutrient status. Results about the effects of smelter emissions on soil acidity are rather contradictory (Derome 2000). Derome and Lindroos (1998) report displacement of base cations from cation-exchange sites by copper (Cu) and nickel (Ni) cations in the vicinity of a Cu-Ni smelter, although no signs of acidification were found.

Metal toxicity is dependent on the metal's availability to the plant, which, for its part, is dependent on the soil characteristics and on the plant species in question. The strength of binding of the metal by the soil controls its availability. The pH of the soil solution, Ca content and the dissolved and solid organic matter content are among the key properties of the soil control (Allen 2002). Metals in soils are present in different forms or species with different levels of availability and toxicity. The presence and quality of chelators in nutrient solutions has been shown to affect metal toxicity. For example Taylor and Foy (1985) found different toxicities in wheat exposed to $CuSO_4$ and Cu-EDTA, while FODOR *et al.* (2004) report that poplar seedlings grown with Fe-citrate as their iron source suffered a greater Cd stress than those grown with Fe-EDTA. Distribution of different metal forms in soil is not constant, but varies according to how long the metal has been present in the soil (SAUVE 2002). Therefore, in experiments in which metals have been freshly added as soluble metal salts, the availability of metal differs from that in experiments in which the metals have been added with a complexing matrix, or from that in experiments in which the metal have aged for some period of time.

Although many experimental studies have been carried out on the effects of soil-metal pollution on plants, relatively little attention has been paid to the influence of the chosen substrate on toxicity. Toxic threshold values determined in, e.g. hydroponics, do not necessarily apply in natural conditions where several factors affect metal availability. Therefore, it appears that toxicity tests with soil-grown plants would be ecologically more relevant (DAVIES 1991). However, there are several different solid substrates with varying metal sorption capacities used as soil matrices in experimental studies. According to PATTERSON and OLSON (1983), pine seedlings can support ten times higher metal concentrations when growing in a mineral-soil substrate than when seedlings are germinated on filter paper, and concentrations one hundred times higher when growing in an organic substrate.

Scots pine (*Pinus sylvestris* L.) seems to be among the most resistant plant species to metal pollution, as studies from the Kola Peninsula in northwestern Russia (LUKINA *et al.* 1993), and in the vicinity of a much smaller Cu-Ni smelter at Harjavalta, southwestern Finland (LAAKSOVIRTA and SILVOLA 1975; MALKONEN *et al.* 1999; NIEMINEN and HELMISAARI 1996) have shown. However, the vitality and growth rate of Scots pine has been greatly reduced in the immediate vicinity of the Harjavalta smelter (NIEMINEN and HELMISAARI 1996; MALKONEN *et al.* 1999; NIEMINEN *et al.* 2000). On the Kola Peninsula the radial growth of mature Scots pines has been affected by pollution for decades within a radius of 30 km south of the Monchegorsk smelter and has ceased altogether within 15 km (NOJD *et al.* 1996; NOJD and REAMS 1996).

The aim of this study was to compare the Cu and Ni uptake by the roots of pine seedlings from podzolic soils impacted by a smelter with that from a Cu-Ni sulphate treated quartz-sand series. In addition we wanted to compare the seedling mortality and the Cu and Ni contents of these series to the pine mortality and peat Cu and Ni contents of an old field experiment in which Cu and Ni sulphate had been applied to a pine bog approx. 40 years ago.

2 Material and methods

2.1 Sampling of the smelter-polluted soil series

A Cu-Ni smelter complex is situated on an esker in the area of Harjavalta township in southwest Finland. The smelting of Cu started in the area in 1945 and Ni smelting in 1960. Four sampling sites were located in pure Scots pine stands growing in sorted sandy soils at distances of 0.5, 2, 4 and 8 km southeast of the main stack of the smelter along the esker. One site, situated at Hämeenkangas, 60 km northeast from Harjavalta, in an area without local emission sources, was chosen as a background site. The texture of the mineral soils is fine or coarse sand, and the soil type is orthic podzol. The organic layer is mor, with a thickness ranging from 1 to 3 cm.

The vegetation of all the sites was originally typical of a boreal xerophilous forest site: with *Pinus sylvestris* L. as the dominant tree species and *Calluna vulgaris* (L.) Hull., *Empetrum nigrum* L., *Vaccinium vitis-idaea* L., *Pleurozium schreberi* (Brid.) Mit., *Dicranum* spp., and *Cladina* spp. as among the most common ground-vegetation species. The sites are of the *Calluna* type, according to the Finnish forest site classification of CAJANDER (1949). However, in the immediate vicinity of the smelter the understorey vegetation is almost completely absent (SALEMAA *et al.* 2001), and the Scots pine stand suffers from retarded growth and severe needle loss (MALKONEN *et al.* 1999). A survey in 1993 (SALEMAA *et al.* 2001) found that lichens were absent up to a distance of 2 km from the smelter, and mosses, excluding *Pohlia nutans* (Hedw.) Lindb., were not frequent until at least of 8 km away.

Intact volumetric soil profiles, including the litter layer and ground vegetation, were taken with an auger (diameter 25 cm, depth 30 cm) from the five sampling sites (0.5, 2, 4, 8 and 60 km) and placed in 10-liter pots. The soil profiles were taken at 25 points located as 5 clusters on each sampling site. A four-year-old, bare-rooted pine seedling (*Pinus sylvestris* L.) was planted in each pot.

A smaller volumetric soil sample for chemical analysis was taken beside each sampling point using 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 to 10 and 10 to 20 cm. The samples of each cluster (5) were bulked together to give five composite samples per layer per site for chemical analysis.

2.3 Artificial Cu-Ni treatment series

Pine seedlings of the same 4-year-old seedling lot were planted in similar 10-litre pots as in the smelter-polluted soil series. Each pot contained 8 litres (11.34 kg) of quartz sand (particle size 0.5–1.5 mm). On the following day quartz-sand plant systems were treated with increasing doses of (1) copper sulphate, (2) nickel sulphate or (3) a combination of both in equal doses (Table 1). Two replicates for each treatment level were made in order to have enough material from each seedling compartments for the chemical analysis. The survival rates of the seedlings are given in Table 1 according to NIEMINEN (2004).

2.4 Pine seedlings and experimental conditions

The four-year-old pine seedlings used in the experiment were bare-rooted, and had been raised from selected seeds in the forest nursery of the Finnish Forest Research Institute. A set of 50 reference seedlings from the same four-year-old seedling lot as those planted in experimental pots were measured (average height 31 cm, standard deviation 5.8), weighed and their element concentrations analysed for different compartments at the start of the experiment. The soil-plant systems were cultivated for 17 months (from June, 1994 until October, 1995) in controlled greenhouse conditions without any aerial Cu-Ni load. A period consisting of two growing seasons was considered as an optimal length for the experiment, since the growth of the woody test plant, *Pinus sylvetris* L., is already predominantly predeterminative at the age of five years (LANNER 1976; KANNINEN 1990). Hence, the primary stem growth of the pine seedlings during the first experimental year still largely reflected the environmental conditions of the previous year prior to the experiment.

Day-time temperatures were allowed to follow ambient temperatures during summer months, but the night-time temperature was kept constant at 15 °C. A constant 4 °C level was maintained throughout the winter period. Watering was by drip irrigation using normal tap water with a pH of 5.9, a Cu concentration of 0.35 mg litre^{-1}, Zn concentration of 0.03 mg litre^{-1} and a Ni concentration below the detection limit (0.018 mg litre^{-1}).

At the end of the experiment, pine seedlings were harvested and divided into root, stem, green needles and senescent needle compartments. Those grown in the pots belonging to the same cluster were bulked together to give five composite samples per compartment per site. Senescent needles were collected continuously during the experiment and were stored in a dry place.

Table 1. The Cu and Ni exposure doses of the artificial treatment series, as well as the corresponding soil concentrations.

Treatment Dose/mg per pot	Soil concentration/ mg kg^{-1} dry weight	Number of surviving seedlings	
Cu or Ni treatment		Cu series	Ni series
0	0	2	2
2.4	0.2	2	2
6	0.6	2	2
12	0.7	1	2
24	2.1	2	1
48	4.2	1	2
72	6.3	0	2
96	8.5	1	1
120	10.6	1	0
180	15.9	0	0
240	21.2	0	2
300	26.4	0	1
360	31.7	1	1
480	42.3	0	0
720	63.5	0	0
1440	126.9	0	0
2880	253.9	0	0
Cu + Ni treatment			
0	0	2	
1.2 + 1.2	0.1	2	
2.4 + 2.4	0.2	2	
4.8 + 4.8	0.4	2	
12 + 12	1.1	0	
24 + 24	2.1	1	
36 + 36	3.2	1	
48 + 48	4.2	0	
60 + 60	5.3	0	
120 + 120	10.6	0	
240 + 240	21.2	0	
480 + 480	42.3	0	
960 + 960	84.6	0	

2.5 Sampling at the old field experiment on a pine bog

Peat samples were collected with a Wardenaar corer as monoliths (15 cm × 15 cm × 100 cm) in September 2001 from two test areas (20 m × 20 m each) of an old ore-prospecting simulation experiment at a pine peat bog in Alkkia, southwest Finland. One of the test areas had been treated with copper sulphate and the other with nickel sulphate in 1962. The dose of metal sulphate was 200 kg ha^{-1} in both cases. The surface vegetation, consisting originally mostly of *Sphagnum* species, was still severely damaged at the time of sampling and consisted mostly of unvegetated peat surfaces, approx. 40 years after metal sulphate applications.

2.6 Chemical analysis

Humus and pine seedling samples were dried, weighed and milled to pass through a 1-mm sieve. Total Cu and Ni concentrations were determined from humus and pine seedling samples by dry ashing at 550 °C, followed by extraction with concentrated HCl. As a quality control measure, each furnace loading had one empty crucible (a blank) and a reference sample of known chemical content, which was used to ensure replicability of the analysis. The solutions were analysed by ICP-AES. The pH for humus was determined in water (15 ml sample/25 ml water).

Exchangeable Cu and Ni concentrations were analysed from the humus samples by extraction with 1M ammonium acetate (pH 4.65) containing 2 % EDTA (25 ml humus/ 250 ml extractant, shaking for 1 h), followed by filtration and analysis by ICP-AES. Mineral forest soil samples and quartz-sand samples were dried, weighed and passed through a 2-mm sieve to remove stones and large roots. The extraction and solution analysis were carried out with humus for exchangeable Cu and Ni.

The peat samples were cut into 5 cm slices with a titanium (Ti) knife and packed in plastic bags. To calculate the peat density, three plugs of fixed dimensions were subsampled from each slice and their dry weight was determined. The samples were dried at 105 ºC in acid-washed Teflon bowls and milled in a centrifugal mill equipped with a Ti rotor and 0.25 mm sieve. Copper and Ni concentrations were measured from samples representing the upper 50 cm part of the cores using an energy-dispersive miniprobe x-ray fluorescence multi-element analyzer (CHEBURKIN and SHOTYK 1996).

2.7 Calculations and statistical analysis

The net Cu and Ni uptake by pine seedlings was determined by calculating firstly the amount of Cu and Ni per compartment (roots, stem, green needles and senescent needles). This was obtained by multiplying the metal concentrations of the compartment by the dry mass of that compartment. As these compartment samples were, in the case of the smelter-polluted series, composite samples taken from 5 seedlings, and in the case of the artificial treatment series, from two seedlings, the values were divided by five or by two in order to obtain a value per seedling. Finally, the Cu-Ni uptake was obtained by summing up all the compartments per seedling and then subtracting the average Cu-Ni content of the reference seedlings.

Average soil Cu and Ni concentrations were calculated for humus and mineral soil layers at each distance from the smelter where samples were taken. The total mass of Cu and Ni in peat columns until the depth of 50 cm was calculated on the basis of bulk density and the metal concentration of each slice by summing the metal contents of individual slices.

3 Results and discussion

3.1 Cu and Ni uptake by experimental seedlings

The ratio between Cu and Ni uptake by the seedlings grown in smelter-polluted soil was proportional to their ratio in soil (Fig.1, Table 2). Most of each metal was incorporated in roots and the root-to-shoot transport remained low. The extremely low biomass growth of the seedlings grown in the most polluted 0.5 km soil cores explains the lowest uptake values (NIEMINEN 2004). The Cu and Ni uptake in the artificially treated quartz-sand series was higher than that in the smelter-polluted soil series (Fig. 2), as was the root-to-shoot transport of both Cu and Ni. The difference in uptake patterns between the smelter-polluted soil and quartz-sand series is in agreement with earlier studies. The origin of metal is known to greatly affect its availability. GRUPE and KUNZE (1987 and 1988), for example, report a higher Cu and Ni uptake by cereals from a soil with added Cu and Ni than from lithogenic Cu and Ni sources, and MISHRA and KAR (1974) found that Ni was more easily absorbed by plants when supplied in ionic form than in organic form. No ore-bearing minerals are found in the bedrock consisting of Jotnian olivine diabase or in the sorted glaciofluvial sediments of the smelter-polluted soil sites. This means that a lithogenic origin of excess Cu and Ni is not plausible. However, organic forms of both Cu and Ni are most probably dominant in the smelter-polluted soil. Chelation and complexing are the key reactions governing Cu behaviour in most natural soils. Nickel also appears to occur mainly in organically bound forms in the surface soil horizons (KABATA-PENDIAS 2001).

Copper is known to be efficiently bound onto root surfaces due to its high affinity for the negatively charged carboxylic groups of the cell walls of the apoplastic free space of the roots (MARSCHNER 1995). However, although Ni does not have a corresponding affinity for the negatively charged cation exchange sites in the root cortex (KABATA-PENDIAS 2001), it was also mostly incorporated in roots in the smelter-polluted soil series. In the artificial treatment series, the metals showed an opposite pattern: Cu was translocated from root to shoot as efficiently as Ni. According to MCLAUGHLIN (2002), there is a competitive interaction between different metals in terms of root uptake, e.g. between Cu^{2+} and Zn^{2+}. This kind of competition could reduce Cu uptake to some extent, since the smelter-polluted soil was moderately polluted by Zn (NIEMINEN and SAARSALMI 2002).

Copper uptake was somewhat greater than the uptake of Ni when they were applied alone as single treatments. In the single treatment series, in the case of both the Cu and the Ni treatment, the uptake increased with exposure rate, but in the case of the combination treatment only the Ni uptake increased with increasing exposure rates. The overall Cu uptake in the combination treatment series remained at a lower level than in the Cu single treatment series. The fact that the lethal metal dose was clearly lower in the combination treatment series than in the single treatment series (Table 1; NIEMINEN 2004) suggests that the Ni uptake suppressed that of Cu.

The survival rate of the seedlings grown in the smelter-polluted 0.5 km soils was low, although only one of the seedlings died during the first experimental year. By the end of the 17-month experiment only 4 of the original 25 seedlings had survived (NIEMINEN 2004). In contrast to the smelter-polluted soil series, the deaths of the seedlings growing in the quartz-sand series took place at the beginning of the experiment, during the first few days following the metal sulphate treatments (NIEMINEN 2004). Therefore, it appears that the acute toxicity caused by the artificial metal-sulphate exposure, which is associated with metal uptake into the above-ground parts of the pine seedlings, is a result of different physiological response processes to those involved in the toxicity caused by the metals accumulated in the smelter-polluted soil.

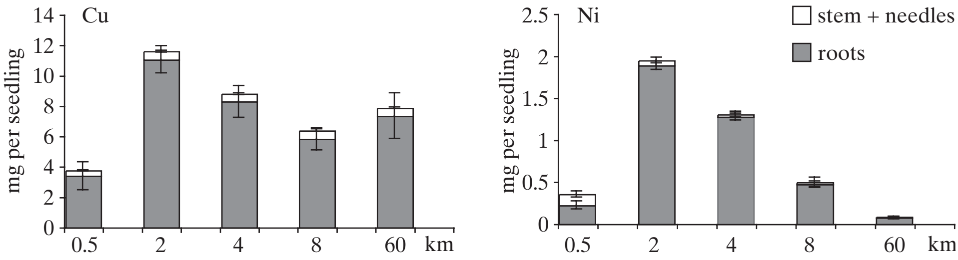

Fig. 1. Uptake of Cu and Ni into roots and above-ground parts of the pine seedlings grown in the smelter-polluted soil series.

Table 2. The mean 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 total		exchangeable mg kg^{-1} d.w.		Mineral layer concentration 0–10 cm layer		10–20 cm layer	
	mean	sd	mean	sd	mean	sd	mean	sd
Cu								
0.5	2665	1178	2072	380	59	23	22	18
2	1465	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.	

The metals of the smelter-polluted soil, which have been accumulating in the soil for several decades, have most probably formed complexes with organic compounds. The availability and mobility of organically bound metals differ greatly from those of the cationic forms. The most obvious toxicity symptoms in the seedlings grown in the smelter-polluted soil cores transported from the 0.5 km site were disturbed root formation and the production of short, brown lateral roots. These symptoms have been reported as typical of damage caused by Cu in soil (SCHULZE *et al.* 2005). Apparently, lethal metal-toxicity levels were reached in the soil cores of the 0.5 km site, and seedlings died due to root deterioration, effectively without any metal accumulation into the aboveground parts of the seedlings. Hence, the thresholds for metal concentration levels in plant tissues established in artificial treatment series do not appear to be good indicators of the toxic exposure limits for soils with long-term contamination.

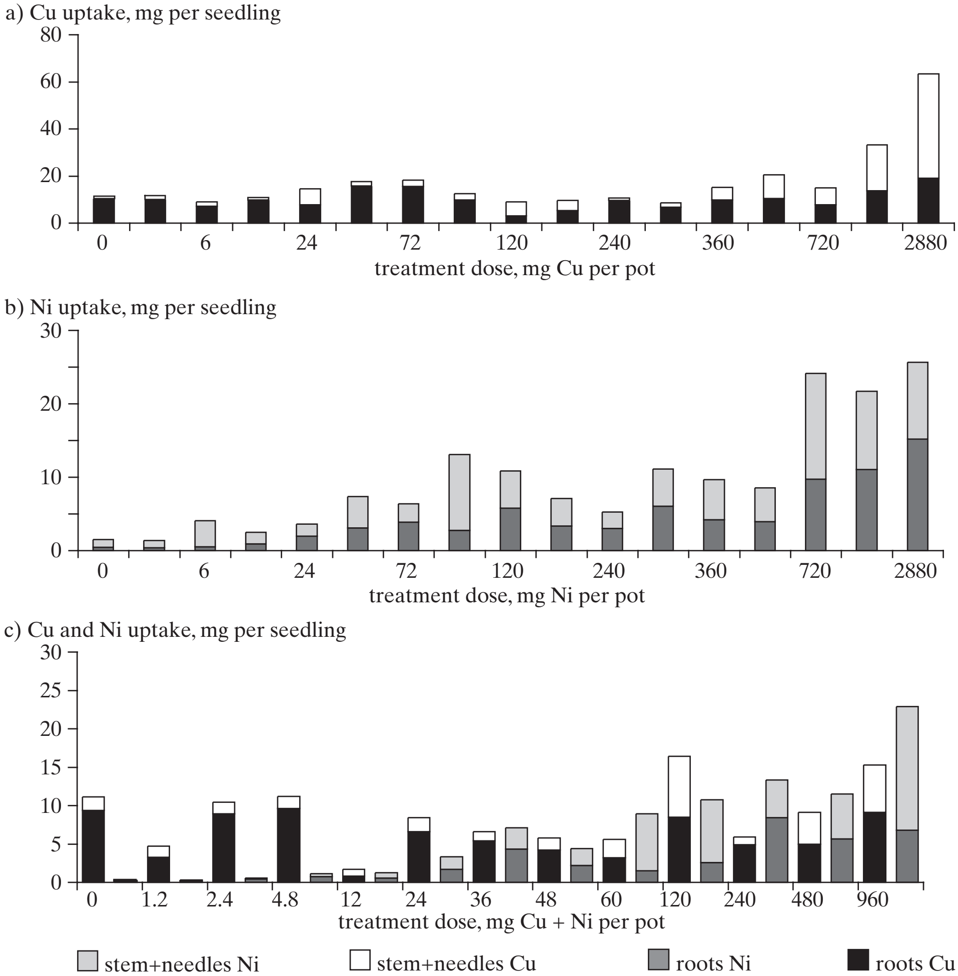

Fig. 2. Uptake of Cu and Ni into roots and above-ground parts of the pine seedlings grown in the artificially contaminated quartz-sand series. a) Cu-treatment series, b) Ni-treatment series, and c) Cu- + Ni-treatment series.

3.2 Cu and Ni contents in the pine seedling substrates vs. peat contents in the Alkkia experiment

The soil Cu and Ni concentrations were found to be extremely high at the most polluted 0.5 km site (Table 2). The ratio between Cu and Ni was roughly 10:1 at the two most polluted (0.5 and 2 km) sites. The lethal threshold value (approx. 30–40 mg kg^{-1}) of the artificial single treatment series (Table 1) was exceeded only in the case of Cu in the upper mineral soil layer of the 0.5 km soil, however, the much lower lethal threshold limit (3–4 mg kg^{-1})

established in the combination treatment series is taken as a threshold, both the Cu and Ni concentrations exceed this limit in the 0.5 km and 2 km soils, and the Cu concentration is still above the limit in the 4 km soils. However, signs of metal toxicity, such as high mortality and clear reduction in biomass growth, were observed only in seedlings grown in 0.5 km soils (NIEMINEN 2004).

The comparison between the metal concentrations in the quartz-sand media and those in the humus of the smelter-polluted soil is limited by the large difference in density of these two matrices. The same holds true for metal concentrations in the peat of the old field experiments where Cu and Ni sulphates were applied on a pine bog (Fig. 3). The extremely high concentrations relative to those of the pine seedling substrates are largely explained by the low density of the peat matrix. Somewhat surprisingly, the ratio between the peat Cu and Ni concentrations is roughly the same (10:1) as the Cu:Ni ratio in the smelter-polluted soil, although the original dose applied on the bog was the same for both metals (200 kg ha^{-1}). Thus, it appears that, in the absence of current atmospheric metal deposition, the metal concentrations in these soils reflect more the sorption capacity of the soil than the original exposure dose. Copper was found to be concentrated in the upper 15 cm peat layer, while the Ni concentrations were also elevated at deeper depths. This suggests that Ni is more mobile than Cu and has more downward migration as many previous studies have also shown (DEROME and NIEMINEN 1998; UKONMAANAHO *et al.* 2001; NIEMINEN *et al.* 2002, UKONMAANAHO *et al.* 2004; RAUSCH *et al.* 2005a).

A comparison of the Cu and Ni contents of the peat profiles, calculated as area-based doses (Fig. 3), with the contents of the upper 30-cm layer of the smelter-polluted soil cores (humus + mineral soil layers) reveals that the remaining Cu_{exch} dose in the 0.5 km soil exceeded the dose applied on the Alkkia pine bog: 270 kg Cu_{exch} ha^{-1}, 28 kg Ni_{exch} ha^{-1} at 0.5 km; 40 kg Cu_{exch} ha^{-1}, 6 kg Ni_{exch} ha^{-1} at 2 km; 10 kg Cu_{exch} ha^{-1}, 2.5 kg Ni_{exch} ha^{-1} at 4 km; 4 kg Cu_{exch} ha^{-1}, 0.5 kg Ni_{exch} ha^{-1} at 8 km and 1 kg Cu_{exch} ha^{-1}, 0.1 kg Ni_{exch} ha^{-1} at 60 km (NIEMINEN and SAARSALMI 2002). This indicates a higher exposure rate in the smelter-polluted 0.5 km soil than the 200 kg Cu ha^{-1} applied on the Alkkia bog, especially since the smelter-polluted soil Cu contents were not based on a total digestion of soil. The extraction method used (ammonium acetate +EDTA) is supposed to give a rough estimate of the exchangeable proportion of Cu. Correspondingly, the 17 % mortality rate observed in 1990 at the Cu-treated Alkkia peatland site (VEIJALAINEN 1998) is lower than the 86 % mortality rate of the pine seedlings grown in the smelter-polluted 0.5 km soils. The reference mortality percentage we took from an untreated area of the Alkkia bog is 2 % (VEIJALAINEN 1998).

The pine mortality rate at the Ni-treated Alkkia site was 38 % (VEIJALAINEN 1998), indicating higher toxicity of Ni compared to Cu under peatland conditions. The higher toxicity of Ni in the Alkkia bog may be related to its higher mobility in peat, which in turn, reflects the partitioning of Ni from the solid to the aqueous phase (RAUSCH *et al.* 2005b). The remaining amount of Ni_{exch} in the smelter-polluted 0.5 km soil was much lower than the Ni dose applied on the Alkkia site.

The lethal threshold doses established in the artificial quartz-sand treatments were 75 to 100 kg ha^{-1} for Cu or Ni alone and 7.5–10 kg ha^{-1} for Cu + Ni in combination. As these thresholds were exceeded in the soils at the Alkkia test sites and the smelter-polluted 0.5, 2 and 4 km sites, we would expect all the pine grown in these soils to be dead. It is well known that metal bioavailability may change over time because changes in the soil conditions often affect metal availability (ALLEN *et al.* 2002). Therefore, the quality of soil and the duration of "aging" in soil are at least as important as the total Cu-Ni dose supplied for the phytoavailability and toxicity of Cu and Ni. Consequently, risk assessments, based simply on testing samples to which soluble metal salts, are unlikely to be predictive of the toxic effects of metals in field sites (ALLEN *et al.* 2002).

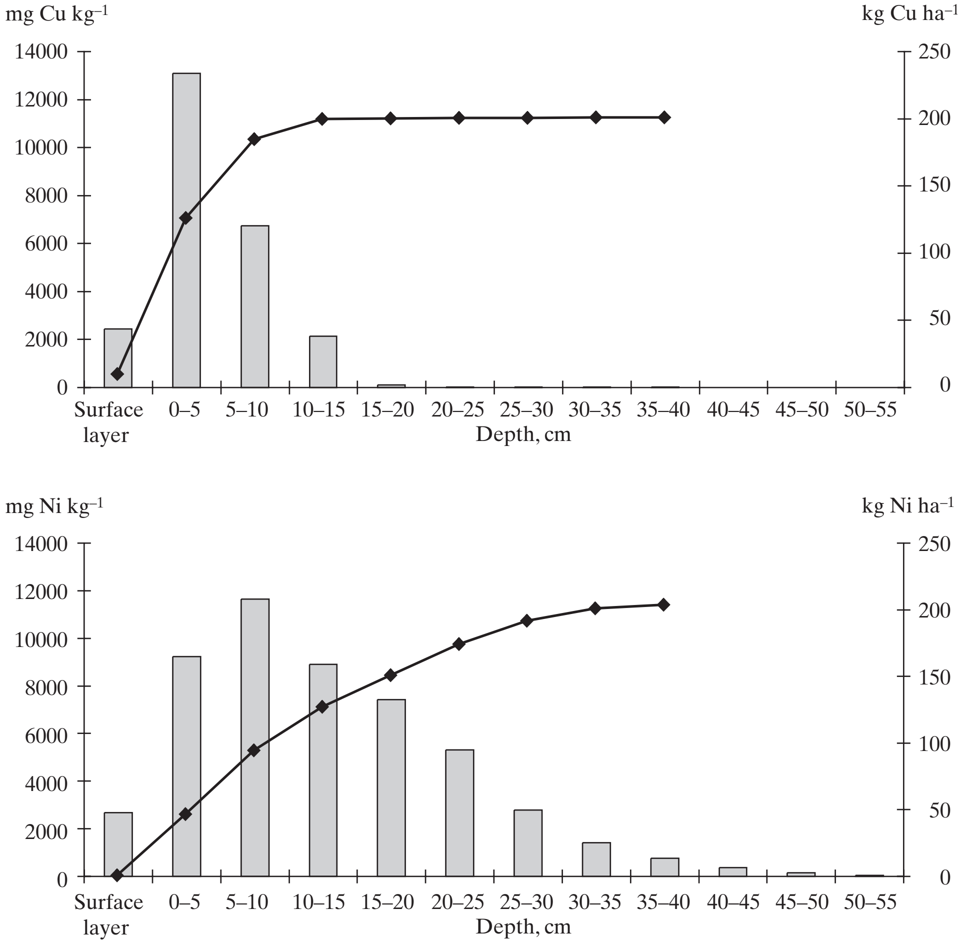

Fig. 3. Vertical distribution of Cu and Ni concentrations (left axis) in peat columns sampled from a pine bog site treated with either a) copper sulphate or b) nickel sulphate in 1962. The line presents the cumulative amount of Cu and Ni incorporated into the peat layer above each depth (left axis).

4 Conclusions

The uptake and the within-plant mobility of Cu and Ni were lower in the the smelter-polluted soil – pine seedling systems compared to artificially contaminated quartz-sand – pine seedling systems: Exposure to metal in the soil can lead to the death of a plant without causing clearly elevated metal concentrations in the shoot.

The phytoavailability and toxicity of Cu and Ni in soil are greatly dependent on the specific characteristics of the different soil substrates in which they are found and on the duration of storage within the soil. The use of metal concentrations alone to indicate the intensity of metal exposure can be misleading since they do not permit comparison between different edaphic conditions or between different metals.

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