# Uptake of heavy metals by plants from airborne deposition and polluted soils

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The concentrations of sulphur, zinc, copper, lead and cadmium in spring wheat grain and straw, Italian rye grass, timothy and lettuce were studied in a three-year field experiment conducted in southern Finland near a copper-nickel smelter and at nonpolluted control sites.

A pot experiment with copper- and nickel-contaminated soils and with a nonpolluted soil as the control was conducted to determine the copper and nickel concentrations in soils phytotoxic for plants. Forty, 200 or 1000 mg of copper or nickel as cloride was added to 2 litres of soil. The nickel and copper concentrations in the shoots of oats were measured.

The zinc, copper, lead, cadmium and nickel concentrations varied between different plant species and also between experimental years.

Near the smelter, the uptake of nickel by different plant species was very effective, as was copper uptake by lettuce, timothy and Italian rye grass. The same applied to the zinc and cadmium uptake of plants grown on plots. Nickel, cadmium and copper were easily accumulated by plants from air deposition.

In the pot experiment, high nickel concentrations in soil were more phytotoxic for oats than were high copper concentrations. In acidic soil, nickel and copper concentrations lower than 20 and 100 mg/kg of soil, respectively, decreased the dry matter yield of oats shoots. Liming clearly decreased copper and nickel phytotoxity. In the most highly contaminated soil, the addition of Cu 20 mg/kg of soil decreased the yield of oats shoots.

Key words: pollution, bulk deposition, dry deposition, copper-nickel smelter

# Introduction

The most pronounced form of pollution from the metallurgical industry comprises emissions to the atmosphere. There is, however, a scarcity of information on the proportion of elements in deposition that is accumulated by plants from the air direct and the proportion taken up from the soil on which they grow.

In Finland, there are only a few places where heavy metal emissions are high enough to cause problems for agricultural plant production. One of these is the Outokumpu works at Harjavalta,

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southwestern Finland. The main heavy metal source at the Harjavalta Works is a copper-nickel smelter. In the 1980s it accounted for about 1% of the world production of copper and 2% of that of nickel. At the same time the total annual emissions of some elements and SO<sub>2</sub> were as follows: SO<sub>2</sub> 7500 t, particles 2200 t, Cu 300 t, Ni 70 t, Zn 200 t, Pb 50 t and Cd 1.9 t (Provincial Government of Turku & Pori). The emissions were partly stack and partly non-point emissions. There were also some other smaller industrial emission sources of SO<sub>2</sub> and heavy metals.

The purpose of this study was to determine the accumulation by plants of heavy metals from airborne deposition and polluted soils. The Harjavalta Works were established in 1945 but both production capacity and production methods have changed many times since then. Thus, the adjacent soils have been receiving heavy metals over a period of five decades.

The experiments were carried out at Harjavalta and at nonpolluted control sites at Jokioinen in 1985, 1986 and 1988. Further information was collected with a pot experiment conducted in polluted Harjavalta soil and nonpolluted control soil in 1990. In the latter experiment copper and nickel, the elements causing the heaviest pollution of Harjavalta soils, were added to the soils in concentrations intended to yield phytotoxic copper and nickel levels.

# Material and methods

#### **Experimental** fields

The experiment was carried out in 1985 and 1986 at seven experimental sites in southern Finland. Two of these were reference sites located at Jokioinen, in a clean rural area close to the Agricultural Research Centre of Finland:

JOKO (60°48'N, 23°28'E) and JOKN (60°52'N, 23°27'E)

The other five experimental sites were near the Outokumpu works (61°19'N, 22°08'E) at Harjavalta (TAM, POH, PAP and TUP) and at Kokemäki (SAT) 90–100 km northwest of Jokioinen:

TAM 800 m from the smelter to 91° POH 1300 m to 312° PAP 2700 m to 132° TUP 4400 m to 117° SAT 8500 m to 126°

In 1988, the experiment was carried out at three sites only:

JOKA (60°48'N, 23°28'E) at Jokioinen TAMI 800 m from the Harjavalta smelter to 91° and

JOHA 1500 m from the smelter to 51°.

In 1988, a new experimental site, JOHA, was established for the collection of data on the effect of different wind directions from the Harjavalta Works on the heavy metal concentrations of plants.

Plots without any replicates,  $3 \times 3 \text{ m}^2$  in size and growing spring wheat (*Triticum aestivum*, cv. Ruso), timothy (*Phleum pratense*, cv. Tarmo), Italian rye grass (*Lolium multiflorum* L., cv. Amenda) or Australian lettuce (*Lactuca sativa*), were established at each experimental site. A schematic diagram of the experimental field has been presented by Yläranta (1995).

The plough layer (0-25 cm) of experimental soils was sandy except at POH, where it was loam, and at JOK, where it was sandy clay loam (Table 1). On JOKO, JOKN, JOKA and POH fields, the particle size distribution was finer and in other fields coarser in the deeper layer (25-60 cm) than in the plough layer.

Yläranta (1995) has described the use of pots on the plots and the fertilization, management and harvest techniques of the experimental plants. Timothy was sown and managed like Italian rye grass. In 1985 and 1986, rye grass and timothy were cut three times. Lettuce was sown and harvested twice in both years. On JOKA, TAMI and JOHA fields one wheat and lettuce yield and three rye grass yields were harvested in 1988.

					Sa	und
	pH	OC	Clay	Silt	Fine	Coarse
1985 and 1986						
JOKO	5.9	1.8	18	10	34	38
JOKN	5.7	2.0	9	5	62	24
ГАМ	6.0	2.6	4	7	63	26
POH	4.9	2.8	27	36	19	18
PAP	5.3	2.5	8	14	62	16
ΓUP	6.7	2.0	5	13	51	31
SAT	5.8	1.7	10	14	72	1
1988						
JOKA	6.3	2.8	26	16	26	23
ΓΑΜΙ	5.7	2.5	3	7	63	27
JOHA	5.8	1.5	4	7	73	16
Pot soils						
Sandy soil	5.8	6.1	5	6	62	27
Carex peat	6.0	37	-	-	-	_
1990						
Pot experiment						
EPO	4.2	4.3	39	20	38	3
PAP	4.9	2.5	8	15	63	15
TAM	5.6	2.6	4	8	56	33

Table 1. Soil sample means (0-25 cm) of different experimental sites and pots for pH(CaCl<sub>2</sub>), organic carbon content (OC, %) and particle size distribution (clay <0.002, silt 0.002–0.02, fine sand 0.02–0.2 and coarse sand 0.2–2 mm) at experimental sites in 1985 and 1986, 1988 and 1990 (pot experiment).

# Deposition sampling and analytical methods

Two NILU (Norsk Institut for Luftforskning, Lillestrøm, Norway) deposit gauges with 2-litre bottles, one for nitrogen (NSP) and one for sulphur, phosphorus and the heavy metals zinc, copper, lead, cadmium and nickel (ME), were placed on each experimental field. In 1988, dry deposition was collected at TAMI on a 47-mm teflon filter from June 21 to September 27 (Millipore FALP04700, pore size 1  $\mu$ m).

The zinc, copper, lead, cadmium and nickel in the experimental soils were extracted with acid ammonium acetate-EDTA and aqua regia and analysed with ICP-AES (Zn, Cu) and ET-AAS (Pb, Cd, Ni). The zinc, copper, calcium, magnesium, potassium and phosphorus concentrations in the plant samples were determined with ICP-AES and the concentrations of lead, cadmium and nickel with ET-AAS.

Total nitrogen in deposition was determined on NSP samples, and sulphur, phosphorus, zinc, copper, nickel, lead and cadmium were determined on ME samples.

The dry deposition of sulphur, zinc, copper, lead, cadmium and nickel on the teflon filters was determined on the  $HNO_3$ - $H_2O_2$ -HCl digestion solution, that of lead and cadmium with ET-AAS and that of other elements with ICP-AES.

Yläranta (1995) has decribed the bulk and dry deposition sampling and analytical methods in detail. The analytical laboratory that carried out the elemental analysis is participating in the European intercalibration network, EC/BCR.

#### Pot experiment

Two litres of wet EPO clay soil (1672 g of dry matter, Table 1) and 2500 g of wet sandy PAP and TAM soils (2033 g of dry matter) were weighed into 3-litre HD polyethylene pots. TAM and PAP soils were taken from the fields where the TAM, TAMI and PAP field experiments were carried out; EPO soil was taken from a nonpolluted field in a rural area 250 km north of Jokioinen.

There were four replicates, the experimental plan being as follows:

- 1. Control, no Cu or Ni addition
- 2. Cu addition, 40 mg/pot
- 3. Cu 200 mg
- 4. Cu 1000 mg
- 5. Ni addition, 40 mg/pot
- 6. Ni 200 mg
- 7. Ni 1000 mg

In addition, the treatments in EPO soils were limed with  $Ca(OH)_2$  to increase the pH(CaCl<sub>2</sub>) by 1.5 pH unit (Mäntylahti and Yläranta 1980). The total number of pots in the experiment was 112.

The fertilizers mixed into the whole amount of soil in the pot were pure chemicals (Merck, p.a.) dissolved in deionized water as follows:

Ν	470 mg	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> , NH <sub>4</sub> NO <sub>3</sub>
Р	80 mg	$(NH_4)_2HPO_4$
Κ	350 mg	KCl, $K_2SO_4$
Mg	90 mg	MgCl <sub>2</sub> x 6H <sub>2</sub> O
Ca	60 mg	CaCl <sub>2</sub> x 2H <sub>2</sub> O
S	80 mg	$K_2SO_4$ , $MnSO_4 \times H_2O$ ,
		$ZnSO_4 \times 7H_2O$ ,
		$CuSO_4 \times 5H_2O$
Mn	3.3 mg	$MnSO_4 \times H_2O$
Zn	2.3 mg	$ZnSO_4 \times 7H_2O$
Cu	2.6 mg	CuSO <sub>4</sub> x 5H <sub>2</sub> O
Fe	2.0 mg	FeNa-EDTA
Mo	0.4 mg	Na <sub>2</sub> MoO <sub>4</sub> x H <sub>2</sub> O
В	0.4 mg	H <sub>3</sub> BO <sub>3</sub>

From each pot, 250 ml of soil was put aside and 20 ml of copper or nickel solution was mixed with the rest of the soil. Copper and nickel solutions were prepared from pure chemicals (Merck p.a.), Cu from  $CuCl_2 \times 2H_2O$  and Ni from Ni $Cl_2 \times 6H_2O$ . Seventeen seeds of oats (cv. Veli) were sown on May 29, 1990 in each pot and covered with 250 ml of soil. The shoots of oats were cut on July 9, 1990, dried at 60°C and ground in a hammer mill.

# Results and discussion

#### Soil characteristics

The concentrations of HAAC-EDTA-extractable zinc, copper, lead and nickel were notably lower in the unpolluted soils (JOKO, JOKN and JOKA) than in the other experimental soils (Table 2). The concentrations of zinc, copper and nickel were clearly higher at Harjavalta, near the copper-nickel smelter (TAM, POH, PAP, TAMI and JOHA) than in uncontaminated Finnish soils (Erviö et al. 1990). The lead concentrations in Harjavalta soils were likewise mostly higher than those in Finnish soils on average. Some copper pollution from the Harjavalta smelter can also be seen in the top layer of POH soil (Table 2). Moreover the concentration of cadmium is higher in the soils at Harjavalta than in uncontaminated soils. However, the high heavy metal concentrations were recorded only in the top soil (0-25 cm), implying that only a small fraction of the deposited metals had been leached and accumulated under the plough layer.

Aqua regia (AR) extracts the heavy metals in soils almost totally. The AR values of zinc and copper in polluted Harjavalta soils were clearly higher than those in "clean" JOKN soils. Element concentrations in fine-textured soils are commonly higher than those in coarse mineral soils. The higher clay content of JOKO and JOKA soils may explain why their zinc concentrations were higher than those in TAM soil. The sampling sites TAM and TAMI were close to each other. Thus only a large natural variation

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Table 2. Soil sample means for HAAC-EDTA and aqua regia-extractable Zn, Cu, Pb, Cd, Ni (mg/kg of dry soil).

				-	_						
Site	Layer,		HA	AC-ED	ΟTA			AQUA REGIA			
	cm	Zn	Cu	Pb	Cd	Ni	Zn	Cu	Pb	Cd	Ni
1985, 1986											
JOKO	0-25	2.3	3.3	2.3	0.16	0.8	55	16	8	0.56	21
	25-50	0.7	3.0	2.2	0.32	1.2					
JOKN	0-25	0.9	1.3	2.7	0.14	0.8	13	8	9	0.26	13
	25-50	0.2	0.6	0.6	0.08	0.2					
TAM	0-25	16	190	8.5	0.60	17	61	260	17	0.79	17
	25-50	3.5	18	1.5	0.12	1.0					
POH	0-25	9.9	82	5.1	0.42	12	116	161	22	0.58	40
	25-50	0.8	2.9	1.4	0.18	0.6					
PAP	0-25	22	38	5.6	0.28	3.9	80	67	15	0.41	15
	25-50	2.1	1.6	0.8	0.05	0.3					
TUP	0-25	3.3	12	2.5	0.13	1.3	21	19	7	0.21	6
	25-50	0.3	0.7	0.3	0.05	0.1					
SAT	0-25	0.8	6.1	1.7	0.17	0.7	26	12	11	0.19	11
	25-50	0.3	1.0	0.5	0.09	0.3					
Pot soil											
Sandy soil											
	0-25	1.6	2.2	1.1	0.10	0.4	25	8	8	0.23	9
1988											
JOKA	0-25	2.5	4.5	2.6	0.09	1.0	82	20	14	0.22	23
	30-60	0.4	3.2	1.7	0.02	1.1					
TAMI	0-25	12	142	5.6	0.41	17	320	252	14	0.66	59
	25-50	1.6	1.2	0.5	0.05	0.6					
JOHA	0-25	14	72	3.7	0.32	10	55	127	10	0.44	30
	25-50	0.5	1.9	0.1	0.02	0.1					
Pot soil											
Carex peat											
	0-25	9.5	13	1.4	0.23	5.7	49	42	18	0.47	20
1990											
Pot exp.											
EPO	0-25	1.4	6.1	_	_	4.3					
PAP	0-25	21	35	_	_	4.2					
TAM	0-25	14	104	_	_	16					

in element concentrations in this field can explain the large differences between zinc and nickel concentrations in these soils. The concentrations of AR-extractable zinc and lead in Harjavalta soils were very small compared with those in a polluted soil near an old lead-zinc mine in Spain, for instance (Ansorena et al. 1995). According to the preliminary standards for soil pollution in Poland (Fotyma and Terelak 1994), soils at Harjavalta are heavily polluted with copper, very slightly polluted with zinc, nickel and cadmium and unpolluted with lead.

The heavy metals in contaminated soils were more readily extractable into HAAC-EDTA than the respective concentrations extracted with AR. On average, 70% of AR-extractable cadmium, 50% of copper and 4–30% of zinc were extractable into HAAC-EDTA. Relatively speaking, the

highest HAAC-EDTA-extractable heavy metal concentrations were measured on the coarsest soils (TAM, TAMI and JOHA). Smaller fractions of AR-extractable cadmium (40%), Cu (20%) and Zn (3–19%) were extracted into HAAC-EDTA from nonpolluted, JOKO, JOKN, JOKA and pot soils than from polluted Harjavalta soils. Zn and Ni were easily extractable into HAAC-EDTA from Carex peat pot soil; copper, however, was extractable only with difficulty. Extractable Ni concentrations were very low in nonpolluted mineral soils.

#### Deposition

The annual bulk deposition of zinc, copper, lead and cadmium at Harjavalta and Jokioinen (JOKO, JOKN) can be estimated from the sum of the values measured during the growing period from June 13, 1985 to October 8, 1985 and from October 8, 1985 to May 28, 1986 (Table 3). Copper and cadmium deposition at some Harjavalta sites was tens of times that at Jokioinen, which can be considered a "nonpolluted" rural area in southern Finland.

The bulk deposition of zinc, copper, lead, cadmium and nickel at Harjavalta was really high when compared with Swedish heavy metal deposition values (Andersson and Gustafson 1988). The lead deposition measured here at TAM, POH, PAP, TAMI and JOHA was often also many times higher than that measured alongside roads at Jokioinen and at Nurmijärvi in 1987 and 1988 (Yläranta 1995). The main source of heavy metal deposition at Harjavalta was the copper-nickel smelter. Nickel deposition, too, was therefore high at Harjavalta as measured during the growing period in 1988 (Table 3).

Differences in zinc and lead deposition between Harjavalta and Jokioinen were not as large as in other elements. However, fairly high zinc and lead depositions were measured at JOKO in 1986 (Table 3). These values are probably due to the emissions from a small industrial point source at Jokioinen.

The most sensitive biological instruments for

measuring the deposition of heavy metals in terrestrial ecosystems are certain mosses (Hertz 1991). Using the moss technique Rühling et al. (1987, 1992) measured copper and nickel concentration of over 28 and 30 mg/kg in dry moss samples in the Harjavalta region. These values are the highest ever measured in northern Europe including Denmark, Estonia, Finland, Iceland, Latvia, Lithuania, Norway, Sweden and adjacent areas of Russia.

Sulphur emissions from the Outokumpu Harjavalta Works during the experimental period from 1985 to 1986 amounted to about 7500 metric tons of  $SO_2$ . In spite of this, the annual bulk deposition of sulphur at experimental sites at Harjavalta was only some kilograms per hectare (Table 3), being almost equal to the values measured at Jokioinen. The only available explanation is that most of the  $SO_2$  emissions were spread over a large area instead of being deposited locally. The annual nitrogen deposition, too, was only some kilograms per hectare, presumably because there are no special NO or  $NO_2$ sources at Harjavalta.

The lead concentration in air (Fig. 1) was ten times and the cadmium concentration tens of times that of the "background" values (Yläranta 1995). The lead concentration was still, on average, clearly lower than that measured in air at 13 sites in or near London, UK in 1985 and 1986 (Jensen and Laxen 1987). Between the end of June and the beginning of July the lead concentration had a very clear peak. At Harjavalta, occasional peak concentrations were also typical of bulk depositions. The simultaneous lead and cadmium peaks were obviously due to unexpected malfunctions in industrial processes. The mean concentrations of other elements in dry deposition at TAMI, the lead and cadmium deposition at the same experimental site and the values measured from June 21 to September 27, 1988 200 m from a road at Jokioinen (JO II, Yläranta 1995) 200 m from a road were as follows (ng m<sup>-3</sup>):

	S	Zn	Cu	Pb	Cd	Ni
TAMI	880	140	30	73	2.5	13
JOII	720	10	1.6	7.9	0.06	4.2

Table 3. Precipitation (Prec.) and bulk deposition of some elements at the experimental sites in 1985, 1986 and 1988.

Site and time	Prec.	Ν	S	Zn	Cu	Pb	Cd	Ni	
period	mm	kg	kg ha-1		g ha-1				
13.6-8.10.1985									
JOKO	243	2.2	2.8	66	16	16	0.14	-*)	
JOKN	250	2.7	2.7	20	201	14	0.15	-	
ГАМ	243	2.7	3.6	190	1100	170	4.3	_	
POH	232	2.9	3.7	92	410	46	2.6	-	
PAP	253	2.2	2.6	95	230	170	1.3	_	
ΓUP	236	1.9	2.3	41	78	20	0.46	_	
SAT	240	2.4	2.3	36	43	25	0.33	-	
8.10.1985-28.5.1986									
JOKO	208	3.4	2.7	67	6	42	0.23	_	
JOKN	165	2.9	2.3	15	5	12	0.18	_	
ГАМ	224	3.9	4.4	420	2600	130	10.4	_	
POH	227	5.8	6.5	320	1200	83	5.3	_	
PAP	219	3.3	2.9	160	290	230	1.7	_	
ΓUP	228	2.8	2.5	48	110	23	0.79	-	
SAT	277	3.6	2.8	37	60	22	0.44	-	
28.5-22.10.1986									
IOKO	349	3.1	3.2	26	7	21	0.16	-	
IOKN	334	3.0	3.2	18	8	15	0.14	-	
ГАМ	314	3.1	4.8	260	2200	82	31.7	-	
POH	312	3.2	4.6	150	1000	58	6.9	-	
PAP	291	2.6	3.2	120	410	42	2.6	_	
ΓUP	298	2.4	2.8	29	97	20	3.0	_	
SAT	300	2.9	2.9	34	79	40	15.8	-	
31.5-27.9.1988									
IOKA	243	2.1	2.2	20	33	8	0.17	24	
ΓAMI	315	1.8	3.3	140	1200	62	3.1	490	
IOHA	311	1.9	2.7	79	410	28	1.0	165	

\*) not measured

Although the concentrations of elements in dry deposition are not given in "g ha<sup>-1</sup>", we can deduce from the values shown that the dry deposition of most elements at TAMI has been very low compared with the bulk deposition (Table 3). Exceptions to this "rule" are sulphur and zinc. Heavy metal concentrations in the air were clearly higher than in the "clean" background area at Jokioinen. It is surprising that sulphur deposition was equally high at both sites.

#### Metal accumulation by plants

#### Field experiments

In 1985 and 1986, the yields varied clearly from growing site to growing site but not very much within the pots grown in plots (Table 4–9). No abnormal differences in calcium, magnesium, potassium, phosphorus or sulphur concentrations were seen between plants grown on plots and those grown in pots. Therefore, except for sulphur, these figures are omitted from the final results.

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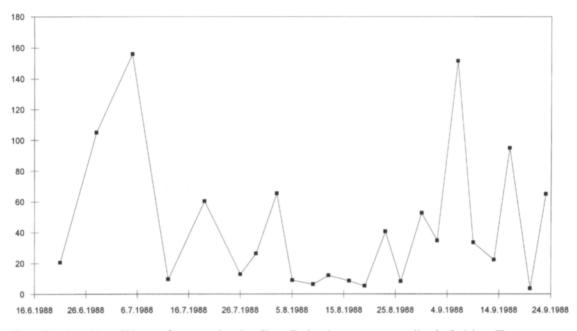
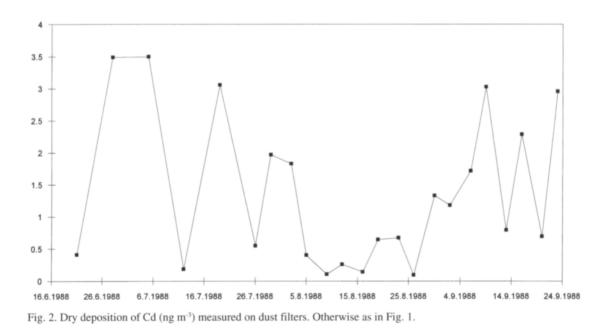


Fig. 1. Dry deposition of Pb (ng m<sup>-3</sup>) measured on dust filters. Each point represents sampling for 3–4 days. The squares are joined by a line to ease readability.

The concentrations of zinc, copper, lead, cadmium and nickel varied between different plant species and also to some extent between the experimental years. The differences in the sulphur concentrations of plants were smaller than were those in heavy metals.



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Table 4. Mean dry matter yield, g/plot (Y) or pot (A), S, and heavy metal concentrations (mg/kg of dry
matter) of first yield of lettuce at Jokioinen (JOKO) and (JOKN), Harjavalta (TAM, POH, PAP, TUP) and

Lettuc	e	JOKO	JOKN	TAM	POH	PAP	TUP	SAT
1985								
Yield	Υ	1131	1354	1437	856	1420	1127	1256
Yield	А	11.5 bc	11.3 bc	11.9 <sup>b</sup>	19.7 <sup>a</sup>	7.5 <sup>d</sup>	8.9 cd	10.9 bc
Zn	Y	35 d	28 <sup>d</sup>	96°	193 <sup>a</sup>	141 <sup>b</sup>	30 <sup>d</sup>	30 <sup>d</sup>
Zn	Α	43 abc	34 °	36 bc	52 <sup>ab</sup>	55 ª	34 °	$40^{\text{ abs}}$
Cu	Y	4.7 °	3.7 °	67 ª	60 <sup>a</sup>	40 <sup>b</sup>	14 °	11 °
Cu	Α	8.1 °	4.0 °	33 ab	40 ª	29 <sup>b</sup>	7.1 °	7.3°
Pb	Y	0.33 °	0.28 °	1.75 <sup>b</sup>	3.55 ª	0.76 °	0.44 °	0.46 °
Pb	А	0.31 °	0.17 °	0.80 <sup>b</sup>	2.81 ª	0.75 °	0.19°	0.22 °
Cd	Υ	0.65 f	1.52 °	3.25 b	5.41 a	1.12 de	1.00 °	1.35 cd
Cd	А	0.51 bc	0.45 °	0.53 bc	0.70 <sup>a</sup>	0.62 ab	0.51 bc	0.55 bc
Ni	Y	0.90 <sup>d</sup>	1.06 d	11.4 <sup>b</sup>	36.0 <sup>a</sup>	4.88 °	1.58 <sup>d</sup>	1.78 <sup>d</sup>
Ni	Α	0.82 <sup>cd</sup>	0.46 <sup>d</sup>	3.22 <sup>b</sup>	6.04 <sup>a</sup>	1.58 °	0.44 <sup>d</sup>	0.58 cd
S	Y	2.29°	2.73 d	3.70 <sup>b</sup>	4.76 <sup>a</sup>	4.58 ª	2.67 <sup>d</sup>	3.21 °
S	А	3.59 <sup>b</sup>	3.31 <sup>b</sup>	3.79 <sup>b</sup>	2.60 °	4.19 ª	3.38 <sup>b</sup>	3.33 b
1986								
Yield	Υ	2910	2025	1930	995	1786	2390	1981
Yield	А	20.5 <sup>a</sup>	18.2 ab	13.5 bc	21.1 ª	11.1 °	16.2 abc	16.8 abs
Zn	Υ	34 °	35 °	88 <sup>b</sup>	184 ª	85 <sup>b</sup>	30 °	32 °
Zn	Α	50 ª	41 <sup>bc</sup>	45 <sup>ab</sup>	49 <sup>a</sup>	40 <sup>bc</sup>	35 °	35 °
Cu	Υ	5.3 °	4.4 °	47 ª	49 <sup>a</sup>	49 ª	15 <sup>b</sup>	22 <sup>b</sup>
Cu	А	8.8 <sup>cd</sup>	6.4 <sup>d</sup>	31 <sup>b</sup>	58 ª	27 в	13 cd	16 °
Pb	Υ	0.31 °	0.17 °	0.80 <sup>b</sup>	2.81 a	0.75 °	0.19 °	0.22 °
Pb	А	0.22 °	0.30 °	1.94 ª	2.23 ª	2.09 <sup>a</sup>	0.56 ª	1.28 <sup>b</sup>
Cd	Υ	0.53 °	1.25 °	3.50 <sup>b</sup>	4.94 <sup>a</sup>	0.76 °	0.93 °	1.34 °
Cd	А	0.54 <sup>b</sup>	0.60 <sup>b</sup>	0.96 <sup>a</sup>	0.77 <sup>ab</sup>	0.68 <sup>b</sup>	0.55 b	0.57 <sup>b</sup>
Ni	Υ	0.86 ef	0.61 <sup>f</sup>	29.3 b	51.6 ª	13.4 °	4.66 dfe	5.28 d
Ni	А	0.41 °	0.30 °	18.8 <sup>b</sup>	27.9 ª	6.47 °	3.58 d	3.36 d
S	Υ	2.52 °	2.61 °	3.54 <sup>b</sup>	4.38 ª	2.87 °	2.78 °	2.70 °
S	Α	2.59 °	2.74 bc	3.55 ª	2.46 °	2.66 °	3.05 <sup>b</sup>	2.45 °

Means not marked with a common letter differ from each other at the 1% significance level (Tukey's HSD, Honestly Significant Difference test). The plots and pots were tested separately.

In most cases the element concentrations were highest at the experimental sites TAM and POH (Table 4-8) and TAMI and JOHA (Table 9). The element concentrations at POH often differed from those measured in the "clean area" and at JOKO, JOKN and JOKA, but also from those measured at TUP and SAT, both of which are farther from the Outokumpu Harjavalta Works than are TAM, POH, PAP, TAMI and

Kokemäki (SAT) in 1985 and 1986.

JOHA. The zinc, copper, lead, nickel and sulphur concentrations in timothy grown at JOKO and JOKN were at the same level but the cadmium concentrations were at a somewhat higher level than the reported average in Finland (Mäkelä-Kurtto et al. 1993).

In all cases nickel accumulation by different plant species was intense at Harjavalta. Copper was effectively accumulated by lettuce, timothy

Table 5. Mean dry matter yield, g/plot (Y) or pot (A), S, and heavy metal concentrations (mg/kg of dry matter) of spring wheat grain and straw at Jokioinen (JOKO) and (JOKN), Harjavalta (TAM, POH, PAP, TUP) and Kokemäki (SAT) in 1985.

		JOKO	JOKN	TAM	POH	PAP	TUP	SAT
Grain								
Yield	Y	2364	2740	3003	2529	3784	4746	3650
Yield	А	20.7 <sup>b</sup>	22.0 <sup>b</sup>	29.5 ª	31.7 ª	30.2 ª	20.3 b	21.3 <sup>b</sup>
Zn	Y	30 °	29 °	62 ª	64 <sup>a</sup>	49 <sup>b</sup>	35 °	31 °
Zn	А	33 <sup>ab</sup>	34 <sup>ab</sup>	32 <sup>ab</sup>	32 <sup>ab</sup>	30 b	35 ª	32 ab
Cu	Υ	2.3 °	3.4 °	10 <sup>a</sup>	8.2 <sup>b</sup>	6.2 °	6.2 °	4.6 d
Cu	А	3.7 °	5.2 <sup>b</sup>	7.1 ª	5.3 b	5.1 <sup>b</sup>	5.1 <sup>b</sup>	4.6 <sup>b</sup>
Pb	Υ	0.053 °	0.018 <sup>f</sup>	0.072 <sup>a</sup>	0.045 <sup>d</sup>	0.064 <sup>b</sup>	0.032°	0.030°
Pb	А	0.015 f	0.021 °	0.073 <sup>b</sup>	0.035 °	0.083 a	0.027 <sup>d</sup>	$0.015^{f}$
Cd	Y	0.029 f	0.031 f	0.25 ª	0.17 <sup>b</sup>	0.063 °	0.059 <sup>d</sup>	0.037°
Cd	А	0.034 <sup>d</sup>	0.031 °	0.057 <sup>a</sup>	0.048 <sup>b</sup>	0.038 °	0.046 <sup>b</sup>	0.034 <sup>d</sup>
Ni	Y	0.14 <sup>b</sup>	0.10 <sup>b</sup>	13.2 ª	13.5 ª	0.54 <sup>b</sup>	0.40 <sup>b</sup>	0.20 <sup>b</sup>
Ni	А	0.10 <sup>b</sup>	0.10 <sup>b</sup>	3.28 ª	3.67 ª	0.28 <sup>b</sup>	0.24 <sup>b</sup>	0.10 <sup>b</sup>
S	Υ	1.67 ª	1.69 <sup>a</sup>	1.69 <sup>a</sup>	1.75 ª	1.76 ª	1.70 ª	1.68 a
S	А	1.98 abc	2.03 ab	2.09 ª	$1.92  {}^{\rm bc}$	1.83 °	2.04 ab	1.94 <sup>ab</sup>
Straw								
Yield	Y	4049	4830	5266	8538	5614	5487	2740
Yield	А	30.1 <sup>b</sup>	36.0 <sup>a</sup>	39.7 ª	38.0 ª	40.0 <sup>a</sup>	34.8 ab	35.8 ab
Zn	Υ	8.7 <sup>d</sup>	7.3 <sup>d</sup>	97.3 ª	73.8 <sup>b</sup>	39.2 °	12.8 <sup>d</sup>	8.2 <sup>d</sup>
Zn	А	11.7 <sup>b</sup>	9.9 <sup>b</sup>	24.9 ª	24.0 ª	12.5 <sup>b</sup>	10.3 <sup>b</sup>	9.7 <sup>b</sup>
Cu	Υ	1.8 °	2.1 °	74.7 ª	36.5 b	6.5 °	6.5 °	3.7°
Cu	А	2.9 °	3.4 °	172.6 ª	78.9 <sup>b</sup>	9.9°	7.8 °	5.3°
Pb	Υ	0.79 °	0.78 °	3.25 ª	2.11 <sup>b</sup>	2.77 ab	1.21 °	0.59 °
Pb	А	0.93 °	1.02 °	4.92 ª	3.47 <sup>b</sup>	4.98 <sup>a</sup>	1.37 °	0.71 °
Cd	Y	0.057 °	0.058 °	0.976 <sup>a</sup>	0.647 <sup>b</sup>	0.126 °	0.103 °	0.077 °
Cd	А	0.072 <sup>b</sup>	0.059 <sup>b</sup>	0.334 ª	0.259 <sup>a</sup>	0.083 b	0.075 <sup>b</sup>	$0.060^{b}$
Ni	Υ	0.34 °	0.16 °	31.90 ª	12.04 <sup>b</sup>	1.42 °	1.30 °	1.18 °
Ni	А	0.22 °	0.16 °	52.0 ª	19.92 <sup>b</sup>	1.96 °	1.32 °	0.44 °
S	Υ	0.82 °	0.91 °	1.69 <sup>a</sup>	1.53 a	1.60 <sup>a</sup>	1.51 a	1.11 <sup>b</sup>
S	А	1.11 °	1.17 °	1.64 ª	1.50 ab	1.34 bc	1.50 ab	1.52 ab

Statistical tests as in Table 4.

and Italian rye grass, as were zinc and cadmium by plants grown on plots.

The accumulation of heavy metals by plants from the soil and airborne deposition could be evaluated with the experimental design used. The soil at Harjavalta was found to have been polluted since 1945 by emissions from various industrial processes, mainly from the smelter, whereas pot soils were not polluted (Table 2).

There were differences within the plants grown in different soils and at different sites;

this, too, affected the element concentrations in plants. However, using the concentrations of elements measured in plants grown at clean JOKO, JOKN and JOKA sites we can compare the accumulation by plants of elements from the soil on the plot with that from airborne deposition.

The mobility of copper and lead in plants is slight (e.g. Gorlach and Gambuś 1992), as shown by the low copper and lead concentrations of wheat grain (Tables 5 and 6). The root tissue is the primary site of accumulation of copper but

Table 6. Mean dry matter yield, g/plot (Y) or pot (A), S, and heavy metal concentrations (mg/kg of dry matter) of spring wheat grain and straw at Jokioinen (JOKO) and (JOKN), Harjavalta (TAM, POH, PAP, TUP) and Kokemäki (SAT) in 1986.

		JOKO	JOKN	TAM	POH	PAP	TUP	SAT
Grain								
Yield	Y	2503	2675	3509	2475	4870	3194	2487
Yield	А	16.4 ab	10.1 <sup>b</sup>	22.7 ª	21.3 a	20.1 ª	16.8 <sup>a</sup>	22.1 ª
Zn	Y	32 cd	31 <sup>cd</sup>	67 ª	68 <sup>a</sup>	44 <sup>b</sup>	37 bc	27 d
Zn	А	42 <sup>b</sup>	57 ª	36 °	44 ь	35 °	35 °	35 °
Cu	Y	3.2 <sup>d</sup>	2.3 °	9.6 ª	8.0 <sup>b</sup>	5.0 °	5.9°	5.0 °
Cu	А	3.5 bc	3.6 bc	6.5 ª	6.1 <sup>a</sup>	4.1 <sup>b</sup>	3.2°	3.1 °
Pb	Y	0.044 <sup>d</sup>	0.077 <sup>a</sup>	0.053 b	0.075 <sup>a</sup>	0.046 <sup>d</sup>	0.049 °	0.051 bx
Pb	А	0.045 ª	0.022 <sup>d</sup>	0.039 <sup>b</sup>	0.038 b	0.027 °	0.029 °	0.011 °
Cd	Υ	0.030 f	0.061 °	0.304 <sup>a</sup>	0.193 <sup>b</sup>	0.042 <sup>d</sup>	0.060 °	0.035 °
Cd	А	0.033 f	0.081 <sup>b</sup>	0.099 <sup>a</sup>	0.078 °	0.037 °	0.045 d	0.046 d
Ni	Y	0.040 <sup>b</sup>	0.106 <sup>b</sup>	11.30 ª	9.69 <sup>a</sup>	0.65 b	0.538 <sup>b</sup>	0.38 b
Ni	А	0.032 °	0.078 °	3.66 <sup>a</sup>	2.79 <sup>b</sup>	0.412 °	0.300 °	0.128 °
S	Υ	1.84 <sup>a</sup>	1.79 <sup>ab</sup>	1.79 ab	1.68 bc	1.55 °	1.77 <sup>ab</sup>	1.72 al
S	А	1.85 <sup>bc</sup>	$1.98 \ ^{ab}$	$1.87 {}^{\rm bc}$	2.12 ª	1.93 abc	2.03 ab	1.71 °
Straw								
Yield	Υ	2904	3281	5331	3193	5236	4500	3363
Yield	Α	23.9 <sup>b</sup>	20.6 b	33.9 ª	38.0 ª	27.8 ab	25.3 ab	27.2 at
Zn	Υ	8.5 °	7.8 °	105 <sup>a</sup>	69 <sup>b</sup>	23 °	10 °	6.8 °
Zn	А	12 ь	20 ª	20 <sup>a</sup>	14 <sup>b</sup>	13 <sup>b</sup>	11 <sup>b</sup>	12 <sup>b</sup>
Cu	Υ	1.9 °	1.8 °	32.0 <sup>a</sup>	19.7 <sup>b</sup>	6.8 °	4.9°	6.1 °
Cu	А	2.6 <sup>d</sup>	2.7 <sup>d</sup>	25.6 ª	21.0 <sup>b</sup>	8.6 °	4.8 <sup>cd</sup>	5.5 °
Pb	Υ	0.412 °	0.531 °	2.19 ª	1.391 <sup>b</sup>	0.638 °	0.572°	0.795°
Pb	Α	0.456 b	0.491 <sup>b</sup>	1.71 <sup>a</sup>	1.58 a	0.789 <sup>b</sup>	0.505 <sup>b</sup>	0.646 <sup>b</sup>
Cd	Υ	0.055 °	0.101 °	1.39 ª	0.958 <sup>b</sup>	0.128 °	0.132 °	0.127 °
Cd	Α	0.084 °	0.128 °	0.485 <sup>a</sup>	0.388 <sup>b</sup>	0.125 °	0.109 °	0.130 <sup>b</sup>
Ni	Υ	0.054 °	0.054 °	11.47 ª	8.006 <sup>b</sup>	1.616 °	1.046 °	1.118 °
Ni	А	0.094 °	0.064 °	8.43 ª	7.73 ª	1.91 <sup>b</sup>	0.738 bc	0.860 <sup>b</sup>
S	Y	0.93 <sup>cd</sup>	0.79 <sup>d</sup>	1.89 <sup>a</sup>	1.42 <sup>b</sup>	1.04 °	1.35 <sup>b</sup>	0.82 d
S	Α	0.82 <sup>b</sup>	1.00 <sup>b</sup>	1.69 <sup>a</sup>	1.41 ab	1.02 <sup>b</sup>	1.42 ª	0.83 <sup>b</sup>

Statistical tests as in Table 4.

also of nickel when environmental levels of copper and nickel are high (Bagatto and Shorthouse 1991). Vegetation is contaminated by lead mainly through the retention of particulate matter (Thomas et al. 1984). It is thus evident that most of the copper and lead in plants have been accumulated from airborne deposition.

The increased nickel and cadmium concentrations in plants grown on plots and in pots at Harjavalta showed that these elements were easily accumulated by plants from airborne deposition. Lettuce took up high concentrations of cadmium in PAP and TAM soil, a finding that is consistent with that of Gardiner et al. (1995). They reported that the mobility of cadmium into plants from soil appears to be greater than the mobility of zinc, copper and nickel.

The yields of and the element concentrations in plants determined from the second and third yields in 1985, 1986 and 1988 confirmed the results presented here.

Table 7. Mean dry matter yield, g/plot (Y) or pot (A), S, and heavy metal concentrations (mg/kg of dry matter) of first yield of timothy at Jokioinen (JOKO) and (JOKN), Harjavalta (TAM, POH, PAP, TUP) and Kokemäki (SAT) in 1985 and 1986.

Timot	hy	JOKO	JOKN	TAM	POH	PAP	TUP	SAT
1985								
Yield	Y	1925	2339	2717	2076	2201	2316	2800
Yield	А	18.9 <sup>b</sup>	19.8 <sup>b</sup>	26.1 ª	19.7 <sup>b</sup>	25.3 ª	22.6 ab	25.9ª
Zn	Υ	26 <sup>b</sup>	25 b	88 a	88 a	87 ª	28 <sup>b</sup>	24 <sup>b</sup>
Zn	Α	29 <sup>b</sup>	37 ª	36 a	35 <sup>a b</sup>	38 ª	32 <sup>ab</sup>	36 ª
Cu	Υ	4.6 <sup>d</sup>	4.6 d	28.7 ª	20.7 <sup>b</sup>	16.5 <sup>b</sup>	9.5°	7.6 cd
Cu	Α	4.5 °	6.3 bc	13.5 ª	14.4 ª	9.4 <sup>b</sup>	6.2 bc	6.9 bc
Pb	Y	0.30 °	0.31 °	1.25 ª	1.00 <sup>b</sup>	0.26 °	0.38 °	0.42 °
Pb	Α	0.24 °	0.32 °	0.56 <sup>b</sup>	0.97 <sup>a</sup>	0.18 °	0.25 °	0.31 °
Cd	Υ	0.047 <sup>b</sup>	0.049 <sup>b</sup>	0.442 ª	0.445 <sup>a</sup>	0.076 <sup>b</sup>	0.105 <sup>b</sup>	0.056 <sup>b</sup>
Cd	Α	0.036 °	0.056 °	0.062 b	0.150 ª	0.041 d	0.041 d	$0.029^{f}$
Ni	Υ	0.78 <sup>d</sup>	1.08 <sup>d</sup>	13.46 <sup>b</sup>	23.98 ª	6.28 °	1.88 <sup>d</sup>	1.60 <sup>d</sup>
Ni	Α	0.48 <sup>d</sup>	0.76 cd	1.40 <sup>b</sup>	3.80 ª	1.25 bc	0.50 <sup>d</sup>	$0.56^{d}$
S	Y	1.50 °	1.98 <sup>d</sup>	2.72 ab	2.44 bc	2.87 ª	2.32°	2.18 cd
S	А	1.38 °	1.79 <sup>b</sup>	1.85 <sup>b</sup>	1.91 <sup>b</sup>	2.26 ª	1.83 <sup>b</sup>	$1.80^{b}$
1986								
Yield	Y	3783	4405	3536	4236	2952	4231	4091
Yield	Α	28.2 ª	23.5 ª	22.9 ª	32.3 ª	27.8 ª	24.5 ª	28.7ª
Zn	Y	25 °	21 °	93 a	72 <sup>b</sup>	62 в	33°	22°
Zn	Α	25 в	26 <sup>b</sup>	40 <sup>a</sup>	29 <sup>b</sup>	29 <sup>b</sup>	29 <sup>b</sup>	23 <sup>b</sup>
Cu	Υ	4.0 <sup>cd</sup>	3.0 <sup>d</sup>	29.8 ª	19.5 <sup>b</sup>	9.3 °	8.9 °	5.5 cd
Cu	А	3.6 °	4.3 °	28.1 ª	13.4 <sup>b</sup>	6.2 °	6.5 °	4.1 °
Pb	Υ	0.26 bc	0.15 °	1.36 a	1.14 <sup>a</sup>	0.57 <sup>b</sup>	0.29 bc	0.20 °
Pb	А	0.24 <sup>d</sup>	0.23 <sup>d</sup>	1.68 <sup>a</sup>	0.97 <sup>b</sup>	0.64 °	0.26 <sup>d</sup>	$0.20^{d}$
Cd	Υ	0.030 <sup>d</sup>	0.035 °	0.251 ª	0.176 <sup>b</sup>	$0.031^{d}$	0.029 de	$0.028^{\circ}$
Cd	А	0.019 <sup>f</sup>	$0.016^{f}$	0.246 <sup>a</sup>	$0.078^{b}$	0.034 °	$0.024^{d}$	$0.024^{d}$
Ni	Υ	0.47 °	0.57 °	20.72 <sup>b</sup>	25.41 ª	2.38 °	1.47 °	1.04 °
Ni	Α	0.12 °	0.28 °	14.57 ª	6.34 <sup>b</sup>	1.18 °	0.65 °	0.30 °
S	Y	1.49 <sup>d</sup>	1.64 cd	2.09 abc	2.39 a	1.79 bcd	2.21 ab	1.62 <sup>d</sup>
S	А	1.73 <sup>cd</sup>	1.86 bcd	2.68 <sup>a</sup>	2.12 bc	1.97 bcd	2.23 ab	1.59 <sup>d</sup>

Statistical tests as in Table 4.

#### Pot experiment

The addition of 200 mg of Cu and 1000 mg of Ni per pot increased the amounts of soluble salts in pot soils (Table 10). These increments were very clear with the largest additions of copper or nickel. The bulk of the copper and nickel added to the soils was in HAAC-EDTA-extractable form at the end of the experiment.

The largest addition of copper and nickel (1000 mg/pot) killed the oats in EPO soils. Liming, which raised the soil  $pH(CaCl_2)$  by 1.5–1.7

pH unit, saved the plants, and yields increased almost to the control level. Liming lowered the HAAC-EDTA-extractable copper and nickel concentrations in the soil and the concentrations of these elements in the oats shoots. However, liming had a minor effect on the copper concentrations in oats shoots because these concentrations were largely independent of the copper added to the soils. Likewise in the pot experiment carried out by Gorlach and Gambuś (1992) liming of acidic soil combined with the addition

Table 8. Mean dry matter yield, g/plot (Y) or pot (A), S, and heavy metal concentrations (mg/kg of dry matter) of first yield of rye grass at Jokioinen (JOKO) and (JOKN), Harjavalta (TAM, POH, PAP, TUP) and Kokemäki (SAT) in 1985 and 1986.

		JOKO	JOKN	TAM	POH	PAP	TUP	SAT
1985								
Yield	Y	2578	2890	2732	2939	2985	2572	2641
Yield	А	34.9 ª	26.6 bc	28.1 bc	32.7 ab	17.0 <sup>d</sup>	25.2°	27.7 bc
Zn	Y	20 °	19 °	49 <sup>b</sup>	68 <sup>a</sup>	73 ª	21 °	21 °
Zn	А	21 °	22 °	22 °	35 ª	28 <sup>b</sup>	21 °	21 °
Cu	Υ	4.3 °	4.9°	38.1 ª	37.2 ª	30.8 <sup>a</sup>	13.7 <sup>b</sup>	10.8 bc
Cu	А	4.0 °	6.2 de	22.5 b	31.6 ª	13.3 °	8.3 d	6.8 de
Pb	Y	0.66 bc	0.26 °	1.18 <sup>b</sup>	3.25 ª	0.49 °	0.27 °	0.24 °
Pb	А	0.78 <sup>b</sup>	0.20 °	0.78 <sup>b</sup>	3.21 ª	0.38 bc	0.19 °	0.21 °
Cd	Y	0.06 °	0.16 <sup>b</sup>	0.37 ª	0.42 ª	0.15 <sup>b</sup>	0.10 bc	0.109 bc
Cd	А	0.066 °	0.069 <sup>d</sup>	0.089 <sup>b</sup>	0.101 a	0.074 °	0.056 f	0.042 g
Ni	Υ	0.9 <sup>d</sup>	1.4 <sup>d</sup>	14.0 <sup>b</sup>	23.0 ª	6.1 °	1.60 <sup>d</sup>	1.84 <sup>d</sup>
Ni	А	0.52 °	0.86 °	1.90 <sup>b</sup>	4.37 ª	0.82 °	0.60 °	0.66°
S	Υ	1.61 °	2.08 <sup>b</sup>	3.90 <sup>a</sup>	3.51 ª	3.52 ª	2.26 <sup>b</sup>	2.52 <sup>b</sup>
S	А	1.81 <sup>d</sup>	2.29°	2.79 <sup>b</sup>	2.16 <sup>cd</sup>	3.73 ª	2.80 <sup>b</sup>	2.49 bc
1986								
Yield	Υ	4445	3286	3168	3087	2655	2935	2383
Yield	А	18.1 °	25.0 bc	31.7 ь	43.2 ª	29.0 <sup>b</sup>	29.8 <sup>b</sup>	28.9 <sup>b</sup>
Zn	Υ	20 <sup>d</sup>	23 <sup>d</sup>	46 <sup>b</sup>	41 °	53 ª	21 d	22 d
Zn	А	25 bcd	29 <sup>ab</sup>	28 <sup>ab</sup>	22 <sup>d</sup>	30 ª	23 cd	26 ab
Cu	Υ	4.5 <sup>d</sup>	4.6 <sup>d</sup>	45.9 ª	25.3 <sup>b</sup>	28.0 <sup>b</sup>	12.3 °	14.9°
Cu	Α	5.5 d	5.6 <sup>d</sup>	30.0 ª	21.6 <sup>b</sup>	21.3 в	9.6 <sup>cd</sup>	13.2°
Pb	Υ	0.38 <sup>cd</sup>	0.24 <sup>d</sup>	1.89 <sup>a</sup>	1.29 <sup>b</sup>	1.68 <sup>a</sup>	0.56 °	0.55 °
Pb	Α	0.41 <sup>cd</sup>	0.25 d	1.39 ª	1.20 ab	1.48 a	0.59 cd	0.78 bc
Cd	Υ	0.06 °	0.20 <sup>b</sup>	0.50 <sup>a</sup>	0.46 <sup>a</sup>	0.19 <sup>b</sup>	0.11 °	0.243 b
Cd	А	0.053 f	0.091 °	0.209 <sup>b</sup>	0.248 ª	0.163 °	0.092°	0.133 <sup>d</sup>
Ni	Υ	0.74 °	0.88 °	33.30 <sup>b</sup>	38.21 ª	9.35°	3.09 <sup>d</sup>	4.62 <sup>d</sup>
Ni	Α	0.37 °	0.32°	15.09 <sup>a</sup>	10.42 <sup>b</sup>	5.81 °	1.59 de	3.37 d
S	Υ	1.46 <sup>d</sup>	2.03 <sup>cd</sup>	3.92 ª	2.67 bc	3.00 <sup>b</sup>	2.93 <sup>b</sup>	1.86 <sup>b</sup>
S	А	1.31 d	1.32 <sup>d</sup>	2.53 ª	1.56 °	1.65 °	2.13 <sup>b</sup>	1.22 d

Statistical tests as in Table 4.

of peat and phosphatic fertilizer diminished the phytoavailability of nickel, thus reducing its uptake by oats.

In copper-polluted PAP soil, copper additions retarded the growth of oats, and the addition of 1000 mg of Cu per pot almost killed the oats in PAP and TAM soil. When the yields of oats shoots were very small the copper concentrations in the shoots had increased. In TAM soil even the smallest copper addition, 40 mg/pot, decreased oats yield, implying that in TAM soil the copper concentration is already so high that it can be phytotoxic for plants.

Additions of nickel to PAP and TAM soils retarded the growth of oats very clearly. The addition of as little as 200 mg of Ni per pot impeded the growth of oats, and the addition of 1000 mg/pot killed the oats plants in both soils. As in EPO soil, the copper concentrations in plants were low but nickel concentrations high in TAM and PAP soils.

Risk assessment values collected by Finne-

Table 9. Mean dry matter yield (g/plot or pot) and heavy metal concentrations (mg/kg of dry matter) of spring wheat grain and straw, rye grass and lettuce at Jokioinen (JOKA) and at Harjavalta (TAMI, JOHA) in 1988.

		Plots			Pots	
	JOKA	TAMI	JOHA	JOKA	TAMI	JOHA
Wheat,						
grain						
Yield	2110	2530	2424	13.4 <sup>b</sup>	24.2 ª	21.6 ª
Zn	34 °	49 ª	44 <sup>b</sup>	76 ª	50 °	63 <sup>b</sup>
Cu	4.3 °	9.3ª	8.0 <sup>b</sup>	4.7 <sup>b</sup>	6.7 <sup>a</sup>	6.8 ª
Pb	0.03 ª	0.07 <sup>a</sup>	0.09 <sup>a</sup>	0.04 <sup>a</sup>	0.05 <sup>a</sup>	0.08 <sup>a</sup>
Cd	0.03 °	0.12 ª	0.07 <sup>b</sup>	0.04 <sup>b</sup>	0.03 °	0.05 ª
Ni	0.1 °	14.2 ª	7.2 <sup>b</sup>	0.06 <sup>b</sup>	6.8 <sup>a</sup>	7.0 ª
Wheat,						
straw						
Yield	2120	4290	5016	26.4 <sup>b</sup>	36.2 ª	44.4 ª
Zn	7.5 <sup>b</sup>	32.5 ª	25 ª	53 ª	34 <sup>b</sup>	29 <sup>b</sup>
Cu	2.3 °	47.3 ª	18.7 <sup>b</sup>	3.7 <sup>b</sup>	23.6 ª	9.3 ª
Pb	0.34 °	2.07 ª	1.21 b	0.18 b	0.79 <sup>a</sup>	0.67 ª
Cd	0.04 °	0.51 ª	0.19 <sup>a</sup>	0.12 ª	0.11 <sup>b</sup>	0.08 °
Ni	0.1 °	19.4 <sup>a</sup>	5.3 b	0.1 °	8.0 <sup>a</sup>	2.4 <sup>b</sup>
Rye						
grass						
Yield	1780	1990	2410	49.3 ª	44.8 <sup>b</sup>	33.8 <sup>b</sup>
Zn	21 в	58 ª	51 ª	38 ª	37 ª	36 ª
Cu	6.4 °	54 ª	34 <sup>b</sup>	6.3 °	37.3 ª	21.9 <sup>b</sup>
Pb	0.22 °	1.71 ª	1.22 b	0.29 °	1.38 a	0.95 b
Cd	0.11 °	0.35 ª	0.24 <sup>b</sup>	0.117 <sup>b</sup>	0.120 ª	0.092 °
Ni	0.9 °	40.7 <sup>a</sup>	23.0 b	0.7 °	19.2 ª	6.8 <sup>b</sup>
Lettuce						
Yield	840	696	1640	22.5 b	25.9 ab	36.1 ª
Zn	31 °	154 ª	73 <sup>b</sup>	47 <sup>b</sup>	50 <sup>b</sup>	61 ª
Cu	6.6 <sup>b</sup>	20.4 ª	19.3 <sup>a</sup>	5.6 <sup>b</sup>	15.2 ª	11.8 ª
Pb	0.67 <sup>a</sup>	0.70 <sup>a</sup>	0.85 <sup>a</sup>	0.25 <sup>a</sup>	0.48 <sup>a</sup>	0.49 ª
Cd	0.40 <sup>b</sup>	2.26 ª	1.14 <sup>ab</sup>	0.28 <sup>a</sup>	0.28 <sup>a</sup>	0.32 ª
Ni	0.8 °	36.2 ª	12.1 <sup>b</sup>	0.5 °	7.8 ª	4.9 <sup>b</sup>

Statistical tests as in Table 4.

cy (1987) from polluted soils show that such soils can pose a risk to humans, animals, plants and water. According to a Dutch assessment based on the demand that soil retain its 'multifunctionality', soil is polluted and clean up necessary when copper and nickel concentrations exceed 500 mg/kg of soil (Moen et al. 1985). The present study showed that this limit is too high for both of these elements in Finland. In acidic soil (EPO), a nickel concentration of less than 20 mg/ kg of soil and a copper concentration of less than 100 mg/kg of soil clearly reduced the dry matter yields of oats shoots. In polluted PAP and TAM soils these risk values were somewhat higher but then  $pH(CaCl_2)$  was higher than in EPO soil. From the investigations of the effect of particular heavy metals on plants it follows, however, that their tolerance to an increased heavy metal

Table 10. Mean dry matter yields (g/plot or pot), copper and nickel concentrations (mg/kg of dry matter) and uptake (mg/ pot) of oats shoots in pot experiment in EPO, PAP and TAM soils in 1990. No Li. = No liming. EC = electrical conductivity ( $10^{-4}$  x S/cm), pH = CaCl,, Extract. = HAAC-EDTA-extractable concentrations of copper and nickel.

			Extract.			Concentr.	Uptake	
	EC		mg/pot		g/pot	mg/kg	mg/pot	
		pН	Cu	Ni	Yield	Cu Ni	Cu	Ni
EPO Cu								
No Li.								
Control	5 °	4.5 ª	13 <sup>d</sup>	10 b	7.7 ª	6.5 <sup>b</sup> 14.1 <sup>b</sup>	0.05	0.11
Cu 40	5 °	4.5 ª	39°	10 b	8.8 <sup>a</sup>	8.6 <sup>b</sup> 14.6 <sup>b</sup>	0.08	0.13
200	9 <sup>b</sup>	4.4 ab	165 <sup>b</sup>	12 a	5.1 <sup>b</sup>	17.1 ° 27.6 °	0.09	0.14
1000	16 a	4.2 <sup>b</sup>	845 ª	13 a	_*)		_	_
Liming								
Control	5 <sup>b</sup>	4.5 <sup>b</sup>	13°	10 a	7.7 <sup>b</sup>	6.5 bc 14.1 a	0.05	0.11
Con./ Li	7 <sup>b</sup>	6.1 <sup>a</sup>	15 °	7 <sup>b</sup>	10.0 <sup>a</sup>	4.9° 2.3 <sup>b</sup>	0.05	0.02
Cu 40	7 <sup>b</sup>	6.2ª	56 °	7 <sup>b</sup>	8.6 ab	7.5 <sup>abc</sup> 2.4 <sup>b</sup>	0.06	0.02
200	8 b	6.1 ª	148 <sup>b</sup>	6 bc	9.8 ª	8.1 ab 2.8 b	0.08	0.03
1000	13 ª	6.0 ª	670 ª	5°	5.7 b	9.4 ª 3.7 b	0.05	0.02
EPO Ni		0.0	010	-			0100	0.04
No Li.								
Control	5°	4.5 ª	13 <sup>ab</sup>	10 °	7.7 ª	6.5 <sup>a</sup> 14.1 <sup>b</sup>	0.05	0.11
Ni 40	6°	4.5 a	13 a	49 °	6.8 <sup>b</sup>	5.1 <sup>b</sup> 70.6 <sup>b</sup>	0.03	0.48
200	10 <sup>b</sup>	4.3 <sup>b</sup>	12 ab	210 в	0.4 °	1.8° 395.4°	0.00	0.15
1000	15 ª	4.4 b	11 <sup>b</sup>	986 ª	-		-	-
Liming	10			200				
Control	5 <sup>b</sup>	4.5 <sup>b</sup>	13 <sup>b</sup>	10 °	7.7	6.5 <sup>a</sup> 14.1 <sup>c</sup>	0.05	0.11
Con./ Li	7 <sup>b</sup>	6.1 ª	15 a	7 °	10.0	4.9 <sup>b</sup> 2.3 <sup>d</sup>	0.05	0.02
Ni 40	7 b	6.1 ª	16ª	30 °	9.0	1.4 ° 6.0 °d	0.01	0.05
200	7 <sup>b</sup>	6.2 ª	16 ª	92 <sup>b</sup>	9.9	4.7 <sup>b</sup> 26.5 <sup>b</sup>	0.05	0.26
1000	14 ª	6.0 <sup>a</sup>	14 ab	444 a	7.0	3.6 <sup>b</sup> 71.1 <sup>a</sup>	0.02	0.48
PAP Cu	14	0.0	14		7.0	5.0 71.1	0.02	0.40
Control	5 b	5.1	73 <sup>d</sup>	8	11.9 ª	10.7° 10.9°	0.13	0.13
Cu 40	5 b	5.1	107 °	8	11.1 ª	11.6° 11.9°	0.13	0.13
200	7 <sup>b</sup>	5.0	238 b	8	10.9 ª	14.1 <sup>b</sup> 16.3 <sup>b</sup>	0.15	0.19
1000	16 ª	4.9	238° 930°	9	0.5 <sup>b</sup>	14.1 10.5 18.7 a	0.13	0.19
PAP Ni	10	4.7	950	7	0.5	10.7 20.7	0.01	0.01
Control	5°	5.1 ª	73	8 d	11.9 ª	10.7 ° 10.9 °	0.13	0.13
Ni 40	5 °	5.1 ª	73	41 °	11.5 ª	9.9 a 45.5 b	0.13	0.15
200	12 <sup>b</sup>	4.9 <sup>b</sup>	73	181 <sup>b</sup>	4.3 <sup>b</sup>	7.0 <sup>b</sup> 175.6 <sup>a</sup>	0.03	0.32
1000	12 °	4.9 <sup>ab</sup>	72	925 ª			0.03	0.75
TAM Cu	17	5.0	15	143	_		-	_
Control	5°	5.6ª	325 °	36	12.7 ª	13.7 <sup>b</sup> 40.6 <sup>b</sup>	0.17	0.52
Cu 40	5°	5.6ª	325°	34	10.4 <sup>b</sup>	14.7 <sup>b</sup> 41.2 <sup>b</sup>	0.17	0.52
200	9 <sup>b</sup>	5.4 <sup>ab</sup>	476 <sup>b</sup>	34 36	7.1 °	13.0 <sup>b</sup> 47.8 <sup>b</sup>	0.15	
1000	16ª	5.3 <sup>b</sup>	476° 1136°	30	0.4 d	29.9 a 77.8 a	0.09	0.34
TAM Ni	10.	5.5	1130	57	0.4 -	29.9 11.8	0.01	0.03
Control	5 b	5.6	325	36 °	12.7 ª	13.7 40.6 <sup>b</sup>	0.17	0.52
Ni 40	5°	5.5		50 °	12.7 - 11.7 <sup>ab</sup>			
200	9 <sup>b</sup>	5.5 5.4	316 312	176 <sup>b</sup>	5.5 <sup>b</sup>	12.8 65.8 <sup>ab</sup> 11.6 150.3 <sup>a</sup>	0.15	0.77
1000	15 ª	5.4 5.5	312	176° 943 °	5.5 °	11.6 150.3 ª	0.07	0.65

Means not marked with a common letter differ from each other at the 1% significance level (Tukey's HSD, Honestly Significant Difference test). / \*) oats dead

content depends on the plant species, and is different for different metals (e.g. Gorlach and Gambuś 1992).

The copper and nickel uptake by oats shoots was very small (Table 10).

# Conclusions

Concentrations of zinc, copper, lead, cadmium and nickel varied between different plant species and also between experimental years. Differences in sulphur concentrations between plants were small. The lead and copper concentrations of wheat grain were low, even at polluted sites. Especially nickel but also cadmium and copper were easily taken up by plants from soil and also accumulated from airborne deposition. In acidic soil, nickel and copper concentrations lower than 20 mg/kg and 100 mg/kg of soil, respectively, decreased the dry matter yields of oats shoots. Liming clearly lowered copper and nickel phytotoxity.

In the pot experiment, the smallest addition of copper into TAM soil, 20 mg/kg of soil, decreased the yield of oats shoots. Thus, in the most highly polluted acidic soils at Harjavalta, the copper concentration is so high that it may decrease the yield of plants.

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# SELOSTUS

### Kasvien raskasmetallien otto ilmasta ja saastuneesta maasta

Toivo Yläranta Maatalouden tutkimuskeskus

Sinkin, kuparin, lyijyn, kadmiumin ja nikkelin kertymistä lehtisalaattiin, vehnän jyviin ja olkiin, timoteihin ja italianraiheinään tutkittiin vuonna 1985, 1986 ja 1988 Harjavallassa ja sen ympäristössä sekä vertailupaikkakunnalla Jokioisissa. Harjavallassa toimivat Outokumpu Oy:n Harjavallan tehtaat ovat vuodesta 1945 lähtien levittäneet ympäristöönsä raskasmetalleja, erikoisesti kuparia ja nikkeliä. Keskeisin Outokumpu Oy:n Harjavallan tehtaista on ollut kupari- ja nikkelisulatto, joka on lajissaan Suomen ainoa. Harjavallassa on toiminut eräitä muitakin raskasmetallien, erikoisesti lyijyn, päästölähteitä. Tutkimuksessa selvitettiin raskasmetallien kertymistä kasveihin ilmasta ja saastuneesta maasta. Koepaikat sijaitsivat eri etäisyydellä ja eri suunnissa Outokumpu Oy:n tehtaista. Koepaikkojen valinnalla pyrittiin selvittämään raskasmetallien kulkeutumisetäisyyden ja -suunnan vaikutusta viljelykasvien raskasmetallipitoisuuteen.

Jokioisissa vuonna 1990 läpiviedyssä astiakokeessa tutkittiin, mikä viljelymaan kupari- ja nikkelipitoisuus pienentää viljelykasvin satoa. Kahteen harjavaltalaiseen kuparilla ja nikkelillä saastuneeseen hienohietamaahan lisättiin 40, 200 ja 1000 mg kuparia tai nikkeliä kahta maalitraa kohti. Vertailumaana oli Maatalouden tutkimuskeskuksen Etelä-Pohjanmaan tutkimusasemalta (EPO) noudettu saastumaton savimaa, joka samojen raskasmetallilisäysten lisäksi kalkittiin.

Kasvilajien raskasmetallipitoisuudet olivat erisuuria. Myös eri koepaikoilla kasvaneen kasvin raskasmetallipitoisuudet vaihtelivat selvästi. Vehnän jyvien kupari- ja lyijypitoisuudet olivat pieniä kaikilla koepaikoilla. Nikkeli kertyi kasveihin helposti ilmalaskeumasta. Myös kupari ja kadmium siirtyivät helpohkosti ilmasta kasveihin.

Astiakokeessa nikkeli oli kuparia myrkyllisempi kauralle. Happamassa EPO-maassa pienehköt nikkelija kuparipitoisuudet, Ni 20 mg ja Cu 100 mg maalitraa kohti, pienensivät kauran versojen satoa. EPOmaan kalkitseminen pienensi selvästi nikkelin ja kuparin myrkyllisyyttä. Pahimmin saastuneessa Harjavallan maassa pienin kuparilisäys, Cu 20 mg maalitraa kohti, pienensi ohran versojen satoa. Harjavallassa saattaakin olla happamia viljelymaita, joissa maan korkea kuparipitoisuus voi vähentää kasvien kasvua.