Concentrations of Cu, Ni and Pb at ombrotrophic peat bogs at a rural site, near a Cu-Ni smelter and near a mine

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Abstract. Concentration of Cu, Pb and Ni was studied in three ombrotrophic peat bogs in Finland: 1) Harjavalta, in the vicinity of a Cu-Ni smelter, 2) Outokumpu, in the vicinity of an earlier used Cu-Ni mine and 3) Hietajärvi, a rural site without any local point sources. At each site a peat sample (15x15x100cm) was taken using a Titanium Wardenaar corer, and the samples were cut into 5 cm slices. Cu, Ni and Pb concentrations were measured by XRF.
The mean concentrations of Cu, Ni and Pb were at their highest at Harjavalta and their lowest at Hietajärvi. Concentrations of Cu and Ni indicated that the Harjavalta site was clearly affected by the proximity of the smelter. The effect of the Cu-Ni mine in Outokumpu was less evident. The effect of local pollution source is indicated by the vertical distribution of Cu and Ni. The distribution was characterized by the highest concentrations occurring in the topmost 40 cm, with a rapid decrease on moving downwards. In the top 40 cm, Ni concentration on average was 14 times higher in Harjavalta than at Outokumpu and 33 times higher than at Hietajärvi. Correspondingly, Cu concentration was 16-fold higher on average in the Harjavalta top 40 cm layer compared to Outokumpu and 100-fold compared to Hietajärvi. While in the bottom layer (40 to 80 cm) there were not great differences in the concentrations of Cu or Ni between sites. In the case of Pb, there was not such decrease on moving downwards of the soil profile, and the between-site differences were of smaller than in the case of Cu and Ni.

Introduction

Peat consists of organic deposited matter produced by the vegetation. In ombrotrophic peat bogs the only source of water and nutrients is through atmospheric deposition, because surface layers of ombrotrophic peat bogs are isolated from the underlying mineral soil and local ground and surface waters (e.g. Damman 1978, Shotyk et al. 1998). In addition, the high organic matter content and anaerobic conditions of peat limit the mobility of metals in peat through adsorption and sulphide formation processes (Wilkin & Barnes 1997). The capacity of ombrotrophic peat bogs to accumulate compounds makes them useful tools in the assessment of contamination level in terrestrial ecosystems.

In Finland heavy metal concentrations of surface layers of ombrotrophic peat bog has been used to estimate heavy metal deposition in regional scale already in early 1970's (Pakarinen 1981, Pakarinen & Tolonen 1976). Some of these trace metal studies have determined the vertical distribution of copper and lead within depth (Kaunisto & Paavilainen 1988), however fewer studies have examined nickel distribution. Heavy metal distributions within depth have used to determine the deposition history of heavy metals, for example in Switzerland long chronologies of lead deposition have been done (Shotyk et al. 1997, Shotyk et al. 1998). For the use of peat cores as archives, it must be proven that the investigated element is permanently fixed at the peat layer and cannot migrate after the decomposition process has started. In this study, the vertical distribution of copper (Cu), lead (Pb) and nickel (Ni) concentrations were studied using a 1-m peat profile with varying heavy metal loads in Finland.

Methods

Study sites

The concentrations and vertical distributions of Cu, Pb and Ni were studied in three ombrotrophic peat bogs in Finland (Fig 1.). The Harjavalta site is located 7 km northeast of the large Cu-Ni smelter (Nieminen et al. 2001). Outokumpu site is located 8 km southeast from a Cu-Ni mine, which operated until the end of 1980s and lastly Hietajärvi site is a background site with no remarkable point sources nearby (Ukonmaanaho 2001). The prevailing wind direction in Finland is from the southwest. Average Cu, Pb and Ni emissions during 1990's in Finland were for Cu 59.4 t yr^{-1}, for Pb 115.4 t yr^{-1} and for Ni 35.1 t yr^{-1} (VYH 2003). Bulk deposition in background areas was 0.30-0.36 mg m^{-2} for Cu, 0.22-0.69 mg m^{-2} for Pb and for Ni 0.08-014 mg m^{-2} in 1999 (Leinonen 2000). In contrast the Harjavalta site, which is 0.5 km distance from smelter, the mean annual Cu deposition during 1993-1998 was 149 mg m^{-2} and for Ni 64 mg m^{-2} (Derome 2000).

Study sites were located at undrained ombrotrophic bogs with a sparse tree (*Pinus sylvestris*) cover. Most of the ground layer in all sites consisted of *Sphagnum* species eg. *Sphagnum fuscum*, *S. balticum*, *S. angustifolium* or *S. magellanicum*, all of which more or less indicate ombrotrophy. In addition some dwarf shrubs (eg. *Andromera polifolia, Empetrum nigrum, Ledum palustre* and *Vaccinium* species) and a few herbs such as *Carex globularis* and *Rubus chamaemorus* exists in varying amounts at each site.

Peat sampling analyses

At each sampling site, two peat cores (15cm x 15cm x 100cm) were taken using a Titanium Wardenaar corer. The living *Sphagnum* moss layer was removed from the top of the cores, and one of the cores was cut into 5 cm slices with a titanium knife and packed in plastic bags. In the laboratory the peat samples were dried at 105º C in acid-washed Teflon bowls and macerated in a centrifugal mill equipped with a Ti rotor and 0.25 mm sieve. Selected trace elements were measured by EMMA-XRF (Cheburkin & Shotyk 1996). Anova with a probability of Tukey tests was used on the data to test for differences in mean concentrations between sites and two depth classes. Because of non-normal distribution logarithm transformed data was used.

The other core was cut into 1 cm slices and the upper 30 cm slices were used for detailed macrofossil identification. The aim of the macrofossil identification was to provide well-identified *Sphagnum* fragments for a future radiocarbon AMS dating.

In addition, for deeper layers, a Russian core was used, getting a half-cylinder 50 cm long, 12 cm wide sample. These deeper samples were taken from the borehole of the Wardenaar corer, but at least 50 cm below the bottom of the hole to get undisturbed core for conventional radiocarbon dating, which was done from the bulk peat in Heidelberg University.

Results and discussion

Concentrations

Overall, measured concentrations of the heavy metals in upper (0-40 cm) and deeper layers (40-80 cm) of the peat cores were at their highest at Harjavalta and their lowest at Hietajärvi (Table 1). The differences in concentrations show a strong regional pattern and relationship with local pollution sources. Concentration of Cu at the Outokumpu and especially at the Harjavalta site was higher than the average measured concentrations of surface peat in Finland. However Veijalainen has (1998) reported relatively similar average Cu concentration (378 mg kg^{-1}) as we had (334 mg kg^{-1}) from surface peat at 5 km distance from the Harjavalta smelter. A nickel concentration at Harjavalta upper layer was significantly greater ($p<0.05$) than in the other sites, but similar to levels found by Veijalainen (1998). At Outokumpu and Hietajärvi sites Ni concentrations were relatively low, indicating that these concentrations may be similar to normal background concentrations in Finland. Lead concentration at Harjavalta was comparable to the result of Veijalainen (1998) (49 mg kg^{-1}). Concentration of Pb at Outokumpu and Hietajärvi was slightly higher than the background result, which Pakarinen (1981) reported (3.8-8.3 mg kg^{-1}). However, his results were based on deeper peat layers (total depth 4.0-6.7 m).

Nevertheless, the Pb concentrations found in our study are relatively small compared to the results of Shotyk (1996) which were obtained from two mires in the Jura mountains where the maximum Pb peaks were over 80 mg kg^{-1}. Jensen (1997) reported Pb concentrations changing from 0.59 to 227 mg kg^{-1} in the uppermost 35-cm-layers of six ombrotrophic mires located far from distinct local sources in Sweden and Norway. Correspondingly Cu concentrations of these same sites ranged from 0.1 to 18.7 mg kg^{-1}.

Distribution

The effect of local pollution source is indicated also by the vertical distributions of Cu and Ni, which were characterized by the highest concentrations occurring in the topmost 40-cm, with a rapid decrease on moving down the profile (Figs 2a,b,c). Copper concentrations were 16-fold higher on average in the top 40 cm layer at Harjavalta compared to Outokumpu and 100-fold higher compared to Hietajärvi. Correspondingly, Ni concentrations in the top 40-cm were significantly ($p<0.05$) higher at Harjavalta than at other sites, being on average 14 times higher at Harjavalta than at Outokumpu and 33 times higher than at Hietajärvi, respectively. While in the deeper layers (40 to 80 cm) there were no great differences in the concentrations of Cu or Ni between sites.

With respect to Pb there was not a clear decrease while moving downwards in the profile, excluding Harjavalta. At all sites, the peak in the Pb concentration was between 10-50 cm. Lower Pb concentrations in the uppermost surface peat is suggested to reflect the introduction of unleaded gasoline at the beginning of the 1990's. Previous studies have indicated that Pb deposition in Finland as well as in Europe and North America have significantly decreased in recent decades (e.g. Ukonmaanaho 2001, Renberg et al. 2000).

Macrofossil composition and the age of the peat profiles

Vertical studies about macrofossil composition showed that at least up to a depth of 30 cm, the peat consisted mostly of remains of *Sphagnum* species and thereafter, species composition varied more. However, in the Harjavalta peat profile, *Sphagnum* species exist solely up to 15 cm, changing after that to a more heterogenic composition including remains of *Eriohorum* sp., *Andromera* etc.

The radiocarbon dated ages of bulk samples from the depth of 150 cm varied considerably. At Hietajärvi, the estimated age was 2600 years, and at Outokumpu 1500 years, but at Harjavalta only 350 years. Therefore, it is evident that a reliable comparison between sites and with the pollution history cannot be done until an independent chronology is developed for each site by means of radiocarbon AMS dating of the identified *Sphagnum* fragments.

Conclusions

Concentrations of Cu and Ni in peat profiles indicate that the Harjavalta site, which is located at a distance of 7 km from the Harjavalta Cu-Ni smelter, was clearly affected by the smelter. The effect of the Cu-Ni mine in Outokumpu was less evident. The effect of local pollution sources is demonstrated also by the vertical distributions of Cu and Ni, which were enriched in the upper layers (0-40 cm) of the peat and rapidly decreased on moving downwards. Lead was clearly enriched in the upper layers only at the Harjavalta site.

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Table 1. Average concentration (mg kg^{-1}) and standard deviation (sd) of Cu, Pb and Ni in surface layer (top-40 cm) and bottom layer (40-80 cm) of the peat in each site (n=8). Means within columns followed by same letter are significantly different from each other by Tukey tests (p<0.05).

Site	Layer	Cu			Pb			Ni		
		mean		sd	mean		sd	mean		sd
Harjavalta	top 40 cm	333.4	abcde	*(338.20)*	28.9	abc	*(17.90)*	83.9	abcde	*(81.32)*
Outokumpu		21.4	afgh	*(15.93)*	12.0	d	*(6.11)*	6.1	a	*(1.44)*
Hietajärvi		3.3	bf	*(1.05)*	11.3		*(4.55)*	2.5	b	*(1.31)*
Harjavalta	40-80 cm	3.9	c	*(1.11)*	5.7	a	*(0.54)*	3.4	e	*(3.58)*
Outokumpu		2.8	dg	*(1.66)*	7.5	b	*(3.76)*	2.5	c	*(1.02)*
Hietajärvi		1.9	eh	*(0.65)*	5.3	cd	*(4.13)*	1.2	d	*(0.94)*

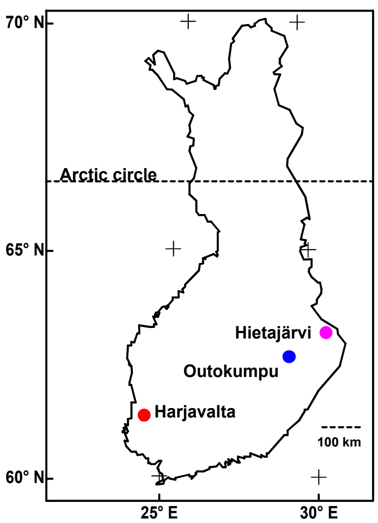

Fig 1. Location of sampling sites

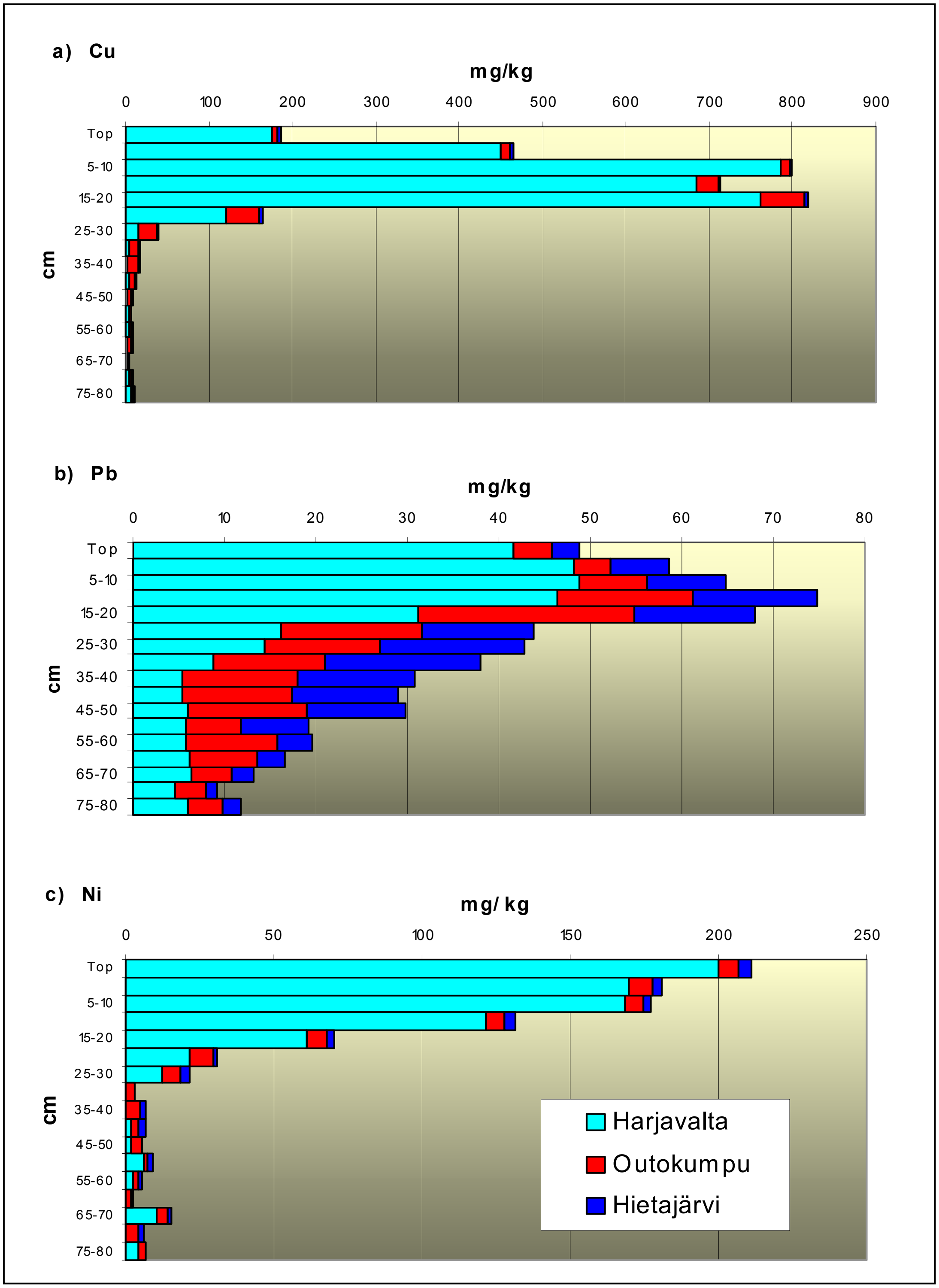

Fig. 2 Vertical distribution of a) Cu, b) Pb and c) Ni at three ombrotrophic peat bogs in Finland.