

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/7589466>

Comparison of Atmospheric Deposition of Copper, Nickel, Cobalt, Zinc, and Cadmium Recorded by Finnish Peat Cores with Monitoring Data and Emission Records

ARTICLE in ENVIRONMENTAL SCIENCE AND TECHNOLOGY · SEPTEMBER 2005

Impact Factor: 5.33 · DOI: 10.1021/es050260m · Source: PubMed

CITATIONS

30

READS

52

8 AUTHORS, INCLUDING:



Nicole Rausch

European Commission

25 PUBLICATIONS 533 CITATIONS

SEE PROFILE



Liisa Ukonmaanaho

Natural Resources Institute Finland (Luke)

45 PUBLICATIONS 686 CITATIONS

SEE PROFILE



Gaël Le Roux

French National Centre for Scientific Research

70 PUBLICATIONS 831 CITATIONS

SEE PROFILE



Michael Krachler

European Commission

142 PUBLICATIONS 3,671 CITATIONS

SEE PROFILE

Comparison of Atmospheric Deposition of Copper, Nickel, Cobalt, Zinc, and Cadmium Recorded by Finnish Peat Cores with Monitoring Data and Emission Records

NICOLE RAUSCH,[†] TIINA NIEMINEN,[‡] LIISA UKONMAANAHO,[‡] GAËL LE ROUX,[†] MICHAEL KRACHLER,[†] ANDRIY K. CHEBURKIN,[†] GEORGES BONANI,[§] AND WILLIAM SHOTYK*,[†]

Institute of Environmental Geochemistry, University of Heidelberg, Im Neuenheimer Feld 236, 69120 Heidelberg, Germany, Finnish Forest Research Institute, Box 18, 01301 Vantaa, Finland, and Institute for Particle Physics, ETH Zuerich, Zurich, Switzerland

This study aims to determine the extent to which the accumulation rates of Cu, Ni, Co, Zn, and Cd in peat cores agree with established histories of atmospheric emission from local point sources. Metals accumulating in three Finnish peat cores with known metal deposition histories have been measured using inductively coupled plasma-sector field mass spectrometry. Samples were age-dated using both ²¹⁰Pb and ¹⁴C (bomb pulse curve). At the Outokumpu (OUT) site as well as the low-background site Hietajärvi (HIJ), ²¹⁰Pb age dates are in excellent agreement with the ¹⁴C bomb pulse curve method results, and the precision is between 1 and 10 years for most of the samples; at the Harjavalta (HAR) site, precision is >6 years. Mean regional “background” concentrations have been calculated from deeper peat layers of the HIJ site ($\mu\text{g g}^{-1}$): Cu, 1.3 ± 0.2 ($n = 62$); Co, 0.25 ± 0.04 ($n = 71$); Cd, 0.08 ± 0.01 ($n = 23$); and Zn, 4 ± 2 ($n = 40$). For layers accumulated within the past 100 years, accumulation rates (ARs) have been calculated. At sites with $<0.06 \text{ g m}^{-2}$ cumulative Ni inventory (HIJ and OUT), ARs of Cu and Co trace the known metal deposition histories very well. At HAR, where metal inventories are much greater, Cu and Co are mobile. ARs of Zn were between 3 and $30 \text{ mg m}^{-2} \text{ year}^{-1}$ and those of Cd between 24 and $140 \mu\text{g m}^{-2} \text{ year}^{-1}$ at all sites and are independent of the chronology of their inputs from the atmosphere.

Introduction

Ombrotrophic peat cores have recently proved to be meaningful archives of recent as well as ancient atmospheric metal deposition, especially for Pb (1–3) and Hg (4–7). In contrast,

there are far fewer studies on the distribution and fate of Cu (8–14), Ni (13, 15), Co (12), Cd (8, 10), or Zn (8, 10–12, 14, 16–18) in ombrotrophic peat bogs. Although some studies have provided evidence that Cu concentrations may reflect the history of ancient mining and smelting (9, 16), Zn is thought to be rather mobile in peat and to be readily redistributed by plants (8, 10, 12, 14, 16–18). In general, however, previous work on these trace metals in ombrotrophic peat tends to suffer from poor temporal resolution, uncertain analytical data, a lack of characterization of the background metal concentration and its natural variation, inaccurate or insufficient age dating, or poorly constrained peat accumulation rates.

Here, peat cores were collected from bogs that had already been subjected to preliminary study (19, 20). Replicate cores were frozen and precisely cut into 1 cm slices and then age dated using both ²¹⁰Pb and ¹⁴C [including the atmospheric “bomb pulse curve” (21)]. This approach has been used successfully for atmospheric deposition of Pb and Hg (22, 23) and offers the promise of detailed, high-resolution reconstructions of atmospheric trace metal deposition, which can be compared with the known metal emission histories of the three sites: Harjavalta, near a Cu–Ni smelter; Outokumpu, near the famous Cu–Ni mine; and Hietajärvi, a “low background” control site that receives atmospheric trace metals predominantly from long-range transport. The main goal of the study is to determine the extent to which the accumulation rates of Cu, Ni, Co, Zn, and Cd in the peat cores agree with the established histories of atmospheric emission from these point sources. If there is disagreement between the metal accumulation rates in the bogs and the emission histories, the second goal is to determine whether these are due to the uncertainty in the age dating methods or whether physical, chemical, or biological processes in the bogs might be responsible for redistributing the metals after their deposition from the air.

Materials and Methods

Study Sites. Peat cores were taken from undisturbed, *Sphagnum*-dominated ombrotrophic peat bogs at Hietajärvi (HIJ), Outokumpu (OUT), and Harjavalta (HAR) (Figure 1). The surface waters have a pH of ~4, which is typical of ombrotrophic bogs. A detailed description of the sampling sites is given elsewhere (19, 20) and summarized here. The HIJ site is located in the Patvinsuo National Park, eastern Finland. As there are no agricultural activities or roads in the vicinity, and no point sources of atmospheric metal pollution within a radius of tens of kilometers, the predominant source of contaminants is from long-range transport (24). The OUT sampling site is located in the Viurusuo mire complex in eastern Finland, 8 km southwest of the town of Outokumpu. A Cu–Ni mine and concentration plant operated at Outokumpu from 1910 until the 1980s, and a small Cu plant operated from 1913 until 1929 (25). At the HAR site, peat samples were taken from a peat bog in the Pyhäsuu mire complex, 6 km northeast of Harjavalta, southwestern Finland, where a Cu smelter has operated since 1945 and a Ni smelter since 1959 (25).

Sampling. Each site was sampled using a titanium Wardenaar corer. The cores were immediately frozen and shipped to the laboratory, where they were sectioned into 1 cm slices with a stainless steel band saw. The edges of each slice were removed, and the residual peat was dried at 105 °C in Teflon bowls and milled with a titanium centrifugal mill equipped with a 0.25 mm sieve. Details of the sample collection and preparation protocol are given elsewhere (26).

* Corresponding author phone: +48-6221-544801; fax: +48-6221-545228; e-mail: shotyk@ugc.uni-heidelberg.de.

[†] University of Heidelberg.

[‡] Finnish Forest Research Institute.

[§] ETH Zuerich.

TABLE 1. Age Dates of ^{210}Pb , ^{14}C Bomb Pulse Curve, and Conventional ^{14}C of the HIJ, OUT, and HAR Cores Obtained from Bulk Peat Samples and Macrofossils

depth (cm)	material ^{210}Pb dated	date ^{210}Pb year A.D.	material ^{14}C dated	^{14}C AMS	lab no.	date ^{14}C year B.P.	$\delta^{13}\text{C}$	date cal year A.D. (B.C.)
Hietajärvi								
6.5	bulk	1985 \pm 2	Sph ^a	^{14}C bpc	ETH-28610	-2230 \pm 40	-28.0	1979 \pm 1
7.5	bulk	1982 \pm 2						
8.5	bulk	1979 \pm 2						
9.5	bulk	1975 \pm 2	Sph	^{14}C bpc	ETH-28611	-2885 \pm 40	-24.8	1973 \pm 1
10.5	bulk	1972 \pm 2						
11.5	bulk	1968 \pm 2	Sph	^{14}C bpc	ETH-28612	-4155 \pm 40	-28.8	1967 \pm 1 1963 \pm 1
12.5	bulk	1964 \pm 3	Sph	^{14}C bpc	ETH-28613	-3460 \pm 40	-31.9	1963 \pm 1
13.5	bulk	1959 \pm 3	Sph	^{14}C bpc	ETH-28614	-785 \pm 40	-30.8	1957 \pm 1
44.5			Sph	conventional ^{14}C	ETH-28660	955 \pm 45	-25.4	1000–1164 (95%) 1167–1188 (5%)
54.5			Sph	conventional ^{14}C	ETH-28661	1145 \pm 45	-25.6	778–986 (100%)
74.5			Carex	conventional ^{14}C	ETH-28662	2480 \pm 50	-28.2	(BC 779–479) (87%) (BC 470–446) (5%) (BC 444–411) (8%)
Outokumpu								
7.5	bulk	1986 \pm 5	Sph	^{14}C bpc	ETH-28605	-1470 \pm 40	-28.5	1986 \pm 1
8.5	bulk	1984 \pm 5						
9.5	bulk	1981 \pm 5						
10.5	bulk	1978 \pm 6						
11.5	bulk	1975 \pm 6	Sph	^{14}C bpc	ETH-28606	-2825 \pm 40	-27.3	1973 \pm 1
12.5	bulk	1972 \pm 7						
13.5	bulk	1969 \pm 7						
14.5	bulk	1966 \pm 8	Sph	^{14}C bpc	ETH-28607	-4435 \pm 40	-27.1	1964 \pm 1
16.5	bulk	1962 \pm 9	Sph	^{14}C bpc	ETH-28608	-4710 \pm 40	-28.6	1964 \pm 1 1965 \pm 1
17.5	bulk	1958 \pm 10	Sph	^{14}C bpc	ETH-28609	-3015 \pm 40	-27.2	1963 \pm 1
49.5			Sph	conventional ^{14}C	ETH-28656	415 \pm 45	-25.6	1420–1525 (76%) 1557–1630 (24%)
69.5			Sph	conventional ^{14}C	ETH-28657	945 \pm 45	-26.3	1017–1192 (100%)
79.5			Carex	conventional ^{14}C	ETH-28658	1505 \pm 45	-25.6	471–479 (5%) 531–622 (89%) 630–637 (4%)
Harjavalta								
3.5	bulk	1985 \pm 9	Sph	^{14}C bpc	ETH-28615	-1335 \pm 40	-30.2	1988 \pm 1
4.5	bulk	1982 \pm 10						
6.5	bulk	1978 \pm 11	Sph	^{14}C bpc	ETH-28616	-3355 \pm 40	-30.0	1971 \pm 1
7.5	bulk	1973 \pm 13						
8.5	bulk	1967 \pm 15	Sph	^{14}C bpc	ETH-28617	-1735 \pm 40	-28.9	1982 \pm 1
9.5	bulk	1961 \pm 18	Sph	^{14}C bpc	ETH-28618	-3840 \pm 40	-28.9	1962 \pm 1
10.5	bulk	1954 \pm 22	Sph	^{14}C bpc	ETH-28619	-2540 \pm 40	-29.0	1962 \pm 1
39.5			Sph	conventional ^{14}C	ETH-28664	560 \pm 45	-25.2	1302–1370 (53%) 1381–1435 (47%)
59.5			Sph	conventional ^{14}C	ETH-28665	830 \pm 45	-25.6	1055–1088 (6%) 1121–1139 (4%) 1156–1282 (88%)
69.5			Sph	conventional ^{14}C	ETH-28666	875 \pm 45	-23.1	1038–1143 (45%) 1149–1255 (55%)

^a *Sphagnum* species.

Representativeness. The distribution of Cu, Ni, and Zn in the OUT and HAR cores is similar to the distribution seen in replicate cores described elsewhere (19). Other studies also found replicate cores recording similar metal concentrations (6, 9, 11, 16, 27).

Age Dating. Recent peat samples were age dated using ^{210}Pb (CRS model) (28). The activities of ^{210}Pb were determined in bulk samples of peat powder using low-background gamma spectrometry (GCW 4028, HPGE, Canberra, Australia). Estimated errors in ^{210}Pb age dates are based on error propagation of ^{210}Pb counting errors and density variability. As an independent check on the ages obtained using ^{210}Pb , the atmospheric bomb pulse of ^{14}C was used to date five samples more recent than A.D. 1950 selected from each peat core. Ages of older peat samples were obtained using conventional ^{14}C age dating. All ages given in the text, except where noted, were obtained using ^{210}Pb .

Macrofossils of *Sphagnum* moss were identified in selected slices using optical microscopy, carefully removed, prepared using a standard procedure for plant material (29), and then age dated (^{14}C) using accelerator mass spectrometry (AMS) at the ETH Zürich. In two highly decomposed samples

in which no *Sphagnum* could be identified, *Carex* fibers were selected (Table 1). For dating using the bomb pulse curve (bpc), ages were graphically evaluated using the calibrated ^{14}C bpc of the northernmost northern hemisphere (30). For samples older than 1800, calibrated (bomb-corrected) radiocarbon ages were presented as 2σ ranges (95% confidence limit) and calculated using the program CalibETH (31).

Trace Metal Analyses. Powdered samples were digested in duplicate using a microwave-heated high-pressure autoclave (ultraCLAVE II, MLS) employing high-purity reagents (subboiled HNO_3 , H_2O_2 , and HBF_4) as described elsewhere (15). ICP-sector field MS (ICP-SF-MS, Element2, Thermo Electron) was used to determine Cd, Co, Cu, Ni, and Sc concentrations in the HIJ and OUT cores, whereas ICP-OES (Vista MPX, Varian Inc.) was used to determine these elements in the HAR core. For ICP-SF-MS analyses, digests with a dilution factor of ~ 500 were spiked with $1\ \mu\text{g L}^{-1}$ In as internal standard element and primed by a self-aspirating inert sampling introduction system (Micro-Flow PFA-100 nebulizer and Scott-type spray chamber made of PFA). For ICP-OES analysis, digests with a dilution factor of ~ 50 were analyzed using an inert Sturman–Masters cyclone spray chamber and

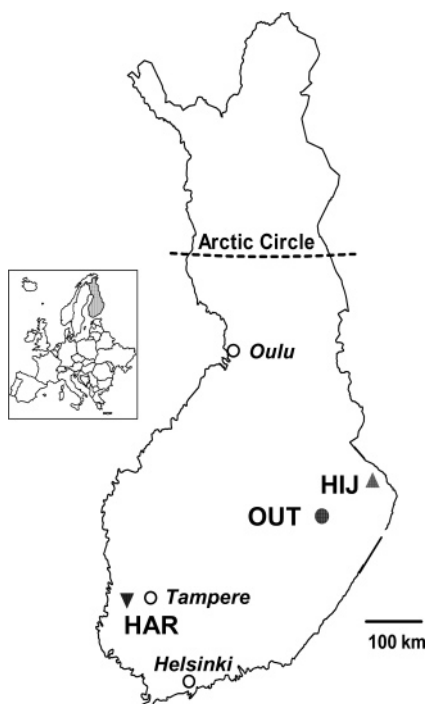


FIGURE 1. Map of Finland with the location of the sampling sites indicated: HIJ, Hietajärvi; OUT, Outokumpu; HAR, Harjavalta.

V-slit nebulizer using Sc as internal standard element for the Cu, Ni, Co, and Cd determinations. Method detection limits for ICP-OES analysis, referring to solid samples, were as follows: Cu, $0.03 \mu\text{g g}^{-1}$; Ni, $0.05 \mu\text{g g}^{-1}$; Co, $0.05 \mu\text{g g}^{-1}$; Cd, $0.006 \mu\text{g g}^{-1}$. Cobalt concentrations approached the limit of detection of ICP-OES in the HAR samples below 30 cm.

Quality Control and Intermethod Comparison. Plant reference materials were digested in duplicate with every batch of samples and analyzed together with samples. For ICP-SF-MS measurements, NIST SRM 1573 A Tomato Leaves and CTA-OTL-1 Oriental Tobacco Leaves were used. For ICP-OES analyses, CTA-VTL-2 Virginia tobacco leaves was used. Results obtained for Cd, Co, Cu, Ni, and Sc were within the certified range. An intermethod comparison based on regression analysis of 10 HAR peat samples showed excellent correlation ($r \geq 0.99$; $n = 10$) between ICP-SF-MS and ICP-OES analyses for all elements, with relative systematic errors of $\leq 3\%$ for Cd, Co, Cu, and Ni and 13% for Sc concentrations.

Further Analyses. Zn and Sr were determined using an energy-dispersive miniprobe X-ray fluorescence multielement analyzer as described elsewhere (32). For Ca, a new X-ray fluorescence spectrometer was used (33). Percentage light absorption of NaOH extracts (8%) of peat samples was determined using a UV-Vis spectrometer ($\lambda = 550 \text{ nm}$) as a proxy of peat decomposition as described elsewhere (34). Density was calculated after determining the thickness ($\pm 0.1 \text{ mm}$) and dry weight of three single plugs with defined areas.

Results and Discussion

Evaluation of ^{210}Pb Age Dating. Activities of unsupported ^{210}Pb decline toward zero below approximately 40 cm in the OUT core and below approximately 15 and 25 cm in the HAR and HIJ cores, respectively (Figure 2). In HAR, the lower ^{210}Pb inventory (Figure 2) is due to the proximity to the Baltic Sea and not to differences in precipitation ($\sim 600 \text{ mm}$ at all sites). Due to the lower activity of unsupported ^{210}Pb , the age uncertainty calculated by error propagation (35) is higher for the HAR samples ($\pm 6\text{--}75$ years for the past century) than for the OUT ($\pm 3\text{--}30$ years) and HIJ ($\pm 1\text{--}8$ years) samples. The ^{210}Pb activities were determined in bulk peat samples,

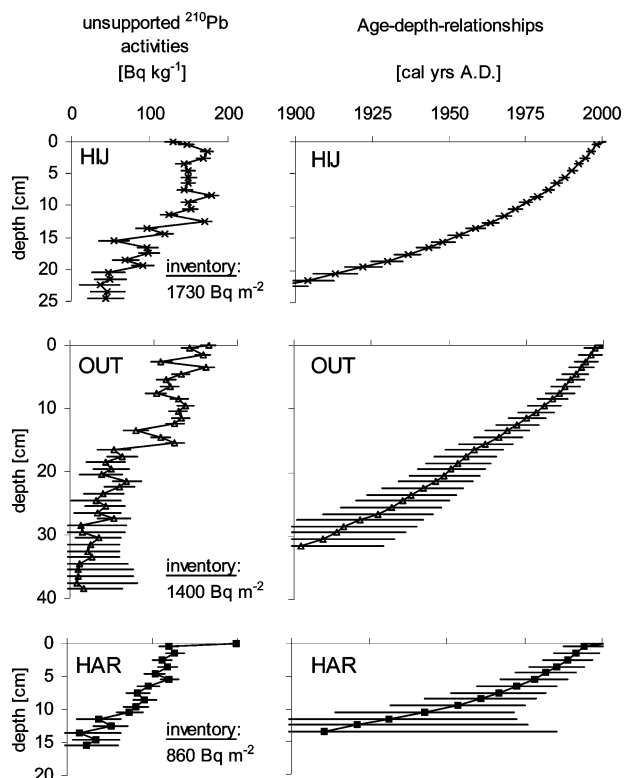


FIGURE 2. Age dating using ^{210}Pb : unsupported ^{210}Pb activities and age–depth relationships of the HIJ, OUT, and HAR cores.

which are representative of the entire peat slice, which is 1 cm thick (26). In contrast, the age dates obtained using the bpc of ^{14}C require a measurement of the percent modern carbon (PMC), relative to A.D. 1950, in a single plant macrofossil that has been removed from the peat slice and weighs but a few milligrams. A plant macrofossil that was obtained toward the top of the peat slice might have an age younger than the average ^{210}Pb age, and one taken near the bottom of the slice an older age, depending on the length of time represented by the slice. Good agreement between the two dating methods means that the ^{14}C age falls within the range of ^{210}Pb age, and this should be the case if the macrofossil was obtained from the center of the plug removed from the slice for subsampling. Good agreement is found in the HIJ and OUT samples (Table 1). Due to the greater error of the ^{210}Pb dating of the HAR samples, the ^{14}C AMS bpc age dates generally fall within the range of ^{210}Pb ages, too, although some samples show a high bias to the ^{14}C bpc age. However, the samples at 10 and 11 cm depths have similar ^{14}C bpc age dates, suggesting that macrofossils may not have originated from the center of these slices. Additionally, the ^{14}C bpc age of the sample from 9 cm is much younger than the overlying sample. In the peat core at HAR, therefore, although the ^{14}C bpc dates do not constrain the ^{210}Pb ages, this reflects subsampling difficulties rather than a problem with the age dates themselves. Because the ^{210}Pb age dates are consistent with the ^{14}C bpc (HIJ and OUT) and because they were obtained using bulk samples representing the entire peat slice, all dates referred to in the text are those obtained using ^{210}Pb .

Peat Accumulation. Age dating using ^{210}Pb allows continuous dating of peat layers accumulated within the past 150 years, thereby allowing the age–depth relationship of the core to be reconstructed (Figure 2) and yielding the accumulation rates of the elements of interest. The age–depth models show that peat accumulation is nonlinear. Moreover, bogs that are situated close together, such as HIJ and OUT, may exhibit very different growth rates.

Regarding the past 100 years, growth rates are low at HAR (0.15 cm year⁻¹), compared to OUT (0.32 cm year⁻¹) and HIJ (0.22 cm year⁻¹). If the past 1000 years are considered using calibrated ¹⁴C age dates (Table 1), greater growth rates are found at HAR and OUT (0.080 cm year⁻¹) than at HIJ (0.057 cm year⁻¹). These differences highlight the importance of detailed age dating for each peat core. The HIJ core covers a much longer time period (until ~630 B.C.) than either the HAR or OUT cores (until ~1100 A.D.).

Trophic Status of the Cores. Given that the thickness of the ombrotrophic peat layer depends to some extent on the overall depth of the peat deposit as well as the mineralogical composition of the underlying substrate, the possible importance of trace metal migration into the peat profile from mineral weathering at the peat–sediment interface needs to be considered. Ca and Sr are two of the most dynamic elements in peat in the sense that they are readily supplied to the porewaters in the basal peat layer from mineral weathering and because they will rapidly diffuse upward into the peat column from that interface (1, 36). The concentrations of Ca found in all three peat cores are well within the range reported for continental ombrotrophic peat bogs (see Supporting Information). At HAR, the Sr concentrations are typically between 6 and 8 μg g⁻¹, which are similar to the average value for Sr (7 μg g⁻¹) at a continental, ombrotrophic peat bog in Switzerland (EGR) (Figure 3). At HIJ and OUT, the values in the surface layers are comparable with the values from EGR, but somewhat higher below 10 and 30 cm, respectively. However, the Sr concentrations normalized to absorbance are constant below 30 cm, which shows that variations in dust deposition and decay of organic matter, not upward migration from basal sediments, control the Sr concentration profile (Supporting Information).

Preindustrial “Background” Concentrations. The HIJ site is situated within a national park in an area that is mainly forested, which further reduces emissions of local soil dust. Furthermore, the HIJ core includes very old peat layers (up to 630 B.C. cal ¹⁴C years), which predate anthropogenic contributions from long-range transport. For these reasons, the HIJ core is well suited to determine the natural “mean regional background” concentrations (MRB) for metals in these peat bogs. In fact, the constantly low concentrations of Cu, Co, Cd, and Zn in the deeper layers of the HIJ core provide the following MRB values (μg g⁻¹): Cu, 1.3 ± 0.2 (*n* = 62); Co, 0.25 ± 0.04 (*n* = 71); Cd, 0.08 ± 0.01 (*n* = 23); and Zn, 4 ± 2 (*n* = 40) (Figure 4). The Cu, Co, Cd, and Zn concentrations in the deeper parts of both the HAR and OUT cores are constantly at these MRB values, which confirms that the MRB values presented here are representative for southern Finland. Furthermore, in the aforementioned peat bog EGR from Switzerland, the lowest Cu, Co, Cd, and Zn concentrations are in good agreement with the Finnish MRB values (10), which suggests that they might have an even broader validity. The background concentrations of these metals are independent of the local bedrock, which is Archaean gneiss at HIJ, mica schist at OUT, dolerites at HAR, and calcareous rocks at EGR in Switzerland (see below for further discussion) (36, 37). In contrast, Ni concentrations slightly increase downward in the HIJ profile, so that reliable MRBs could not be calculated. However, the lowest Ni concentrations found in very old (>5320 ¹⁴C years B.P.) layers of the Swiss peat bog average 0.46 ± 0.09 μg g⁻¹ Ni (*n* = 18) (15). This value fits very well with the lowest concentrations of Ni found in the middle part of the HIJ core and is used here for the MRB value.

Enrichment of Cu, Ni, Co, Zn, and Cd in Upper Peat Layers. The greatest concentrations of all metals of interest are found within the upper layers of the HAR core (Figure 4). Peaks of Cu and Cd concentrations occur in layers slightly below those of Ni, Co, and Zn, corresponding to the different

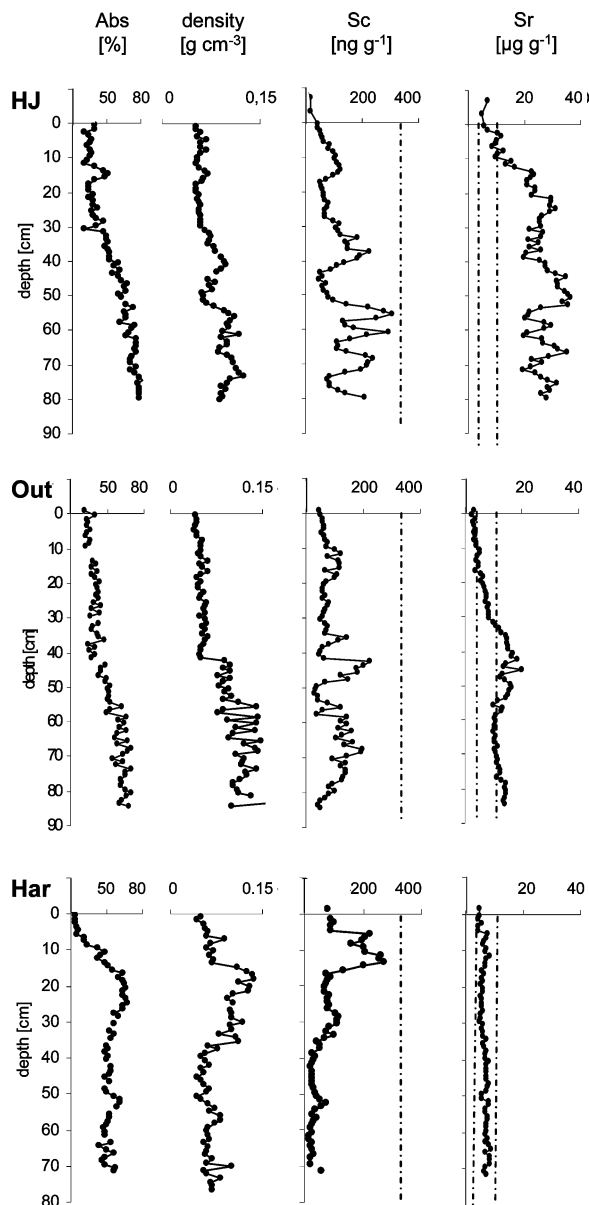


FIGURE 3. Depth profiles of absorption, density, and Sc and Sr concentrations for HIJ, OUT, and HAR. Dashed lines indicate typical values of ombrotrophic bogs from Switzerland.

onsets of the Cu and Ni smelting activities (1945 and 1959, respectively). At the OUT site, elevated concentrations are found in layers corresponding to mining activities, with sharp, distinct peaks for Cu and Co. In contrast, Ni, Zn, and Cd show broad peaks, and even though these elements are strongly enriched in the OUT ores (Table 2), their maximum values at best slightly exceed the maximum concentrations at HIJ. At the HIJ site, Cu and Ni are slightly enriched (1.9 and 3.5 times, respectively) in the uppermost peat layers compared to MRB values, whereas Cd and Zn are enriched up to 7 and 28 times in the upper part of the core.

Influence of Mineral Matter Abundance on Trace Metal Distribution. The concentration of Sc can be taken as an indicator of the abundance of mineral material in the peat cores, consisting mainly of silicates and derived primarily from atmospheric soil dust (1).

Assuming that for preindustrial times the input of natural soil dust determines the Cu, Ni, Co, Zn, and Cd distribution, the “lithogenic” fraction of these metals can be estimated using the product of Sc concentrations and the metal/Sc ratio of the natural dust. As there are strong regional

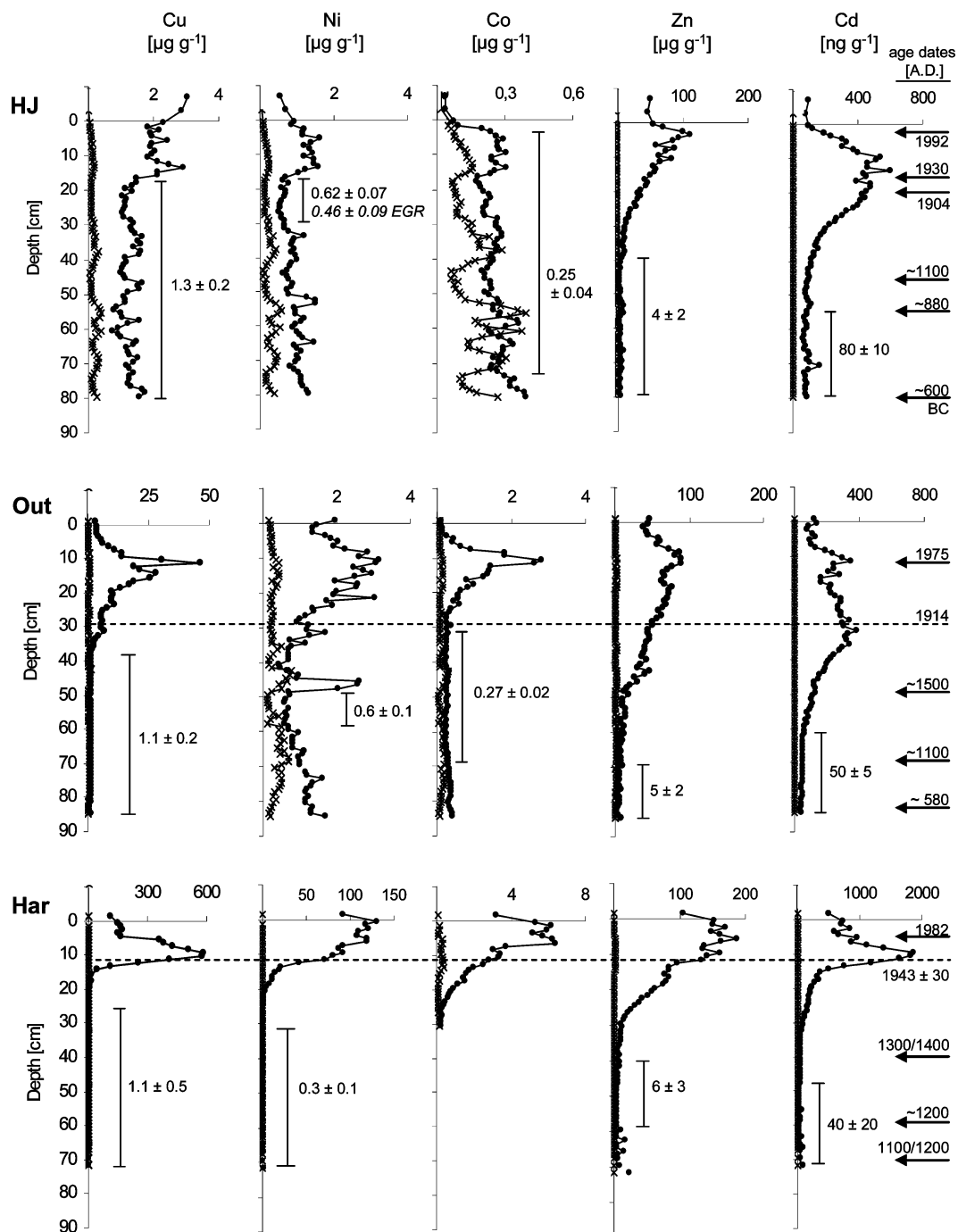


FIGURE 4. Concentrations of Cu, Ni, Co, Zn, and Cd (●) and calculated concentrations of lithogenic Cu, Ni, Co, Zn, and Cd concentrations (×) at the HJ, OUT, and HAR cores. For layers of constant metal concentrations, mean values are given. The horizontal dashed line refers to the onset of mining (OUT) and smelting (HAR), as derived from the ^{210}Pb chronologies.

differences in the “soil dust” composition among the three sites, the metal/Sc ratios of local tills (37) were taken instead of average crustal values. However, the lithogenic fractions at most account for ca. 50% of total Co, 40% of Ni, 20% of Zn, 15% of Cu, and <1% of Cd in the preindustrial layers of the HJ core (Figure 4); in peat layers below 50 cm (>880 A.D.), the profiles of lithogenic and total metals are more similar. Comparable results are obtained when Ti is used instead of Sc. These findings are consistent with other studies (8, 10). In general, this may be explained by the enrichment of trace metals in the clay-rich, fine fraction of aerosols produced during physical and chemical weathering and are subject to long-range transport. As shown in the background concentrations (Figure 4), the influence of local bedrock

composition is negligible (see above). Further studies are necessary to determine whether there are other significant natural sources of these metals or if dust inputs have varied in composition with time.

Influence of Organic Matter Decay on Trace Metal Distribution. In the cores from HJ and OUT, the peat layers where trace metals are most enriched (Figure 4) are poorly decomposed (Figure 3). At HAR, too, the greatest absorbance values clearly underlie the peaks in metal concentration. Therefore, the decomposition of organic matter, which would lead to a relative enrichment of solid particles due to mass loss, cannot explain the variations in trace metals concentrations. We note further that peat density and absorbance profiles show similar variations. Peat density therefore

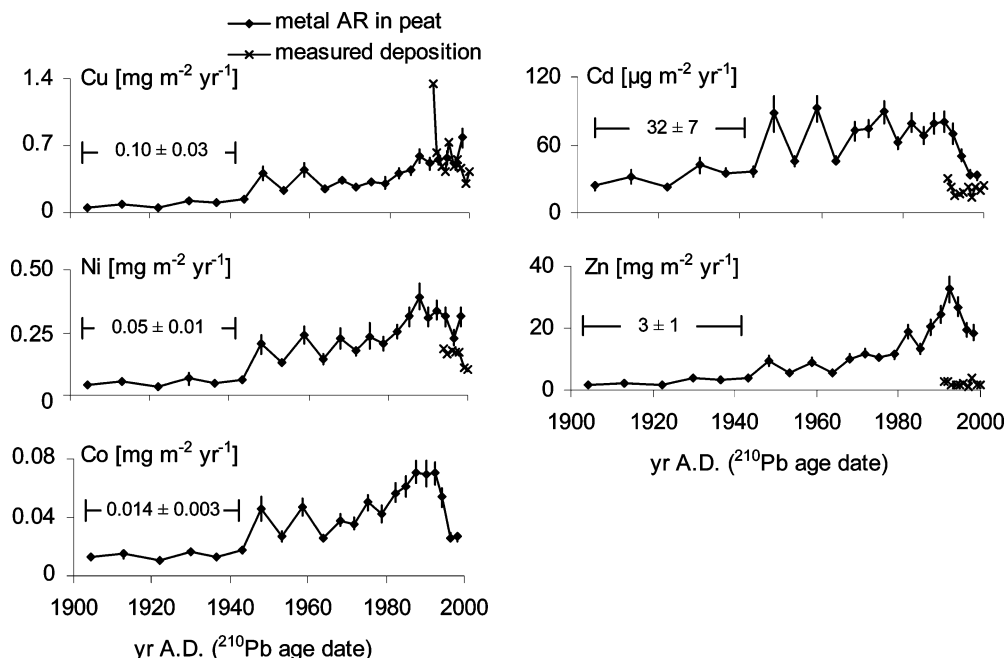


FIGURE 5. ARs of Cu, Ni, Co, Zn, and Cd in peat (HIJ) and atmospheric bulk deposition (wet + dry) at open area as monitored at HIJ.

TABLE 2. Characterization of the Upper Continental Crust (UCC) and Main Sources of Trace Elements at Outokumpu and Harjavalta

	UCC ^a (μg g ⁻¹)	Outokumpu ore ^b (wt %)	Vuonos Cu ore ^c (wt %)	Vuonos Ni ore ^c (wt %)	Harjavalta emissions ^d (t year ⁻¹)
Cu	25	3.8	2.45	0.07	6–140
Ni	56	0.1	0.13	0.33	0.6–96
Co	24	0.2	0.16	0.05	na ^e
Cd	0.1	na	na	na	0.02–7.1
Zn	65	0.8	1.6	0.06	0.9–232

^a After ref 53. ^b After ref 54. ^c After ref 51. ^d Range of annual emissions for the period 1985–1999 (20). ^e No data available.

compensates for variations in the degree of humification of the peats when metal accumulation rates are calculated.

Influence of Deposition History on Trace Metal Distribution. If the elements are retained by the peat column, after their deposition, the elevated concentrations in the upper peat layers should reflect increases in rates of atmospheric supply. In fact, if the element profiles are well preserved and if the cores are accurately age dated, then the chronology of accumulation of these elements should match the chronology of their emissions. As noted earlier, atmospheric deposition has been monitored at the low-background site HIJ for some time, and the emissions of metals from the OUT mine and the HAR smelter can be reconstructed from historical records of mining and smelting. The metal accumulation rates (ARs) and associated errors for the upper peat layers can be calculated using the ²¹⁰Pb CRS age model as described elsewhere (35). The use of ARs instead of absolute concentrations or enrichment factors allows direct comparisons between the cores, as differences in peat growth rate and density (humification) are taken into account.

Metal Accumulation Rate versus Deposition History at Hietajärvi. Copper, Ni, and Co ARs were low at the beginning of the 19th century and increased considerably from ~1945 onward (Figure 5). The greatest ARs of all metals of interest occur during the 1990s except Cd, which has elevated ARs since 1968. Monitoring of annual bulk deposition started only in 1990 in the vicinity of the coring site (38–47). Prior to this, there were various possible trace metal sources for

this area (including settlement, forest fires, and paper and pulp production, as well as long-range transport of pollutants). In the absence of deposition data prior to 1990, it is not possible to interpret the earlier part of the HIJ record. However, the HIJ record is a valuable reference site for comparison with the other sites (see below).

Monitored Cu deposition varies between 0.3 and 0.74 mg m⁻² year⁻¹, which is in good agreement with the Cu ARs for this period. Despite this, there is one outlier in measured Cu deposition (1.3 mg m⁻² year⁻¹ in 1991) that does not fit with Cu ARs. Due to the limited monitoring data it is not possible to decide if this value is an outlier or if it reflects a general trend of decreasing Cu deposition at this remote site. Accumulation rates of Ni slightly exceed the monitored deposition of these metals, suggesting that the deposition rates (obtained by monitoring) may have underestimated the true inputs. Studies of Erismäki (48) showed that the effective atmospheric deposition to a given ecosystem is strongly dependent on the roughness and wetness of the surface. For example, living *Sphagnum* plants with their raised stems can effectively filter solid particles from the air stream, whereas bulk deposition samplers represent an aerodynamic obstacle causing wind streams to divert from the opening as well as creating turbulent flow. As in Finland Cu and Ni have different emission sources (metallurgical processes, and energy production and the use of oil fuel, respectively), the effective deposition might differ between those elements (49). Alternatively, the elevated Ni accumulation rate could be due to postdepositional processes. The retention of Co in the peat layers cannot be assessed, as monitoring data for Co are lacking.

Zinc ARs are decoupled from true deposition. This is consistent with some studies suggesting that Zn might be recycled by higher plants (14, 17). Cadmium ARs of uppermost samples are in the same range as monitored deposition; however, in deeper layers, Cd ARs were much greater. Although there are no deposition records available for comparison, monitoring studies based on forest mosses showed that Cd deposition from long-range transport was ~3 times higher in 1985 than in 2000 (50); the decline in Cd AR at HIJ is consistent with this trend.

Metal Accumulation Rate versus Emission History at Outokumpu. The area was fairly inaccessible until the

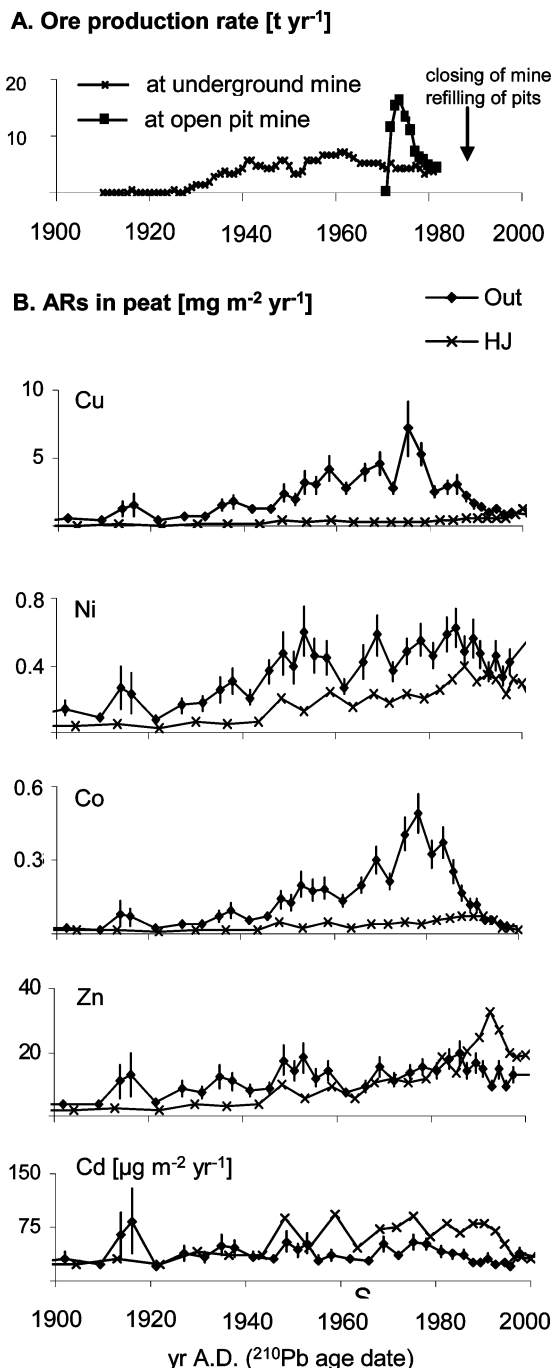


FIGURE 6. (A) Ore production rates at the Outokumpu mines. (B) ARs of Cu, Ni, Co, Zn, and Cd in peat.

discovery of the ore deposit led to the foundation of the town of Outokumpu. Two different ore bodies can be distinguished: the Cu-rich "Outokumpu" ore body, which was excavated by means of an underground mine from 1912 to 1989, and the "Vuonos" ore body with two different ore types, mined between 1972 and 1982, by both underground and open pit methods (51, 52). These ore bodies not only differ from each other in their chemical composition (Table 2) but are also inhomogeneous. The ores were further processed by milling and concentrating, and tailings were stored in open waste heaps. During the first 20 years these tailings still contained considerable concentrations of metals due to an inefficient concentrator process; additionally, a test plant refined small amounts of Cu until 1929 (25). All things considered, the ore production rate (Figure 6) is only an approximate guide to local metal emissions.

During the early years of the 20th century, ARs of Cu and Ni slightly exceed the ARs at HJ, whereas ARs of Co and Cd are similar to those of the low-background site (Figure 6). From 1931 ± 17 onward, ARs of Cu and Co strongly increase, corresponding to the increasing production of Cu/Co-rich ores at underground mines. The greatest ARs of Cu and Co occur in peat layers accumulated during the period of additional open pit mining (1975/1978). The continuously decreasing Cu and Co ARs since 1986 ± 5 coincide with the decline of the mining industry since 1983 and subsequent refilling of the open pit. In summary, the Cu and Co ARs obtained by the peat core provide an accurate reflection of the known history of production of these metals. Slight differences between Cu and Co ARs from 1975 ± 6 onward could be due to the changeover to separate grinding grades for different ore types in 1977 (55). Nickel ARs increase slightly with the beginning of the mining industry at the Outokumpu ore body. However, in contrast to Cu and Co, there is no peak resulting from the open pit at Vuonos. This is even more remarkable considering that the ore of Vuonos contains 3 times more Ni than the OUT ore. In addition, Ni ARs recorded by the OUT core are twice that of the low-background site, whereas Cu and Co ARs are up to 23 and 10 times higher, respectively. Clearly, the Ni ARs obtained using the peat core are not an accurate reflection of the local Ni emission history, and this reflects postdepositional mobility. Zinc ARs are very similar to ARs at HJ, regarding both absolute values as well as the temporal trend. Therefore, the distribution of Zn seems to be more dependent on natural processes operating within the peat bog rather than the local deposition history. Similarly, Cd ARs do not reflect mining impacts, and overall variations in Cd ARs are small.

Metal Accumulation Rate versus Emission History at Harjavalta. At Harjavalta, a copper smelter has operated since 1945 and a Ni smelter since 1959. Ore concentrates were purchased from all over the world. From the beginning of smelting operations until 1984, estimations of dust emissions based on production data have been available (20); since 1985, the company has monitored the emissions of Cu, Ni, Zn, and Cd (Figure 7). Emissions from other metal and chemical industrial companies in the industrial area of Harjavalta or surrounding towns should be of minor importance compared to the substantial emissions from the smelter stack. The slag produced during smelting is stored in basins at the plant site. The granulated Ni slag (together with Cu slag until 1990) is piled in uncovered heaps and could act as an additional source of dust emission (19, 20).

The Cu ARs are considerably enhanced from 1931 ± 40 to 1978 ± 11 and from 1989 ± 8 to 1994 ± 7. Despite the large uncertainties in the ²¹⁰Pb ages for older samples of the HAR core (see above), the ARs trace the high Cu emissions in the early years of smelting and in the late 1980s quite well (Figure 7). However, when only the average values of ²¹⁰Pb age dates are considered, the increase in Cu AR in "1931" predates the true beginning of Cu smelting at HAR in 1945 by ~14 years. However, the spatial difference between the sample accumulated in "1931" and the overlying sample accumulated in "1943" is only 1 cm. Therefore, the difference (14 years) between the increase in Cu ARs (peat) and the known beginning of smelting activity is a consequence of the great uncertainties in the ²¹⁰Pb age dates and the time resolution between adjacent samples, rather than downward Cu migration. Similar to Cu, the timing of the beginning of increasing Ni ARs cannot be determined with sufficient reliability. Nickel ARs are enhanced during the early period of Cu smelting, probably due to the Ni impurities (together with Co and Zn) in the Cu concentrates used at the Harjavalta smelter (56). With the beginning of Ni smelting, Ni ARs increase until a maximum value in 1994 ± 7. A similar shape in ARs is obtained for Co, implying that Co is enriched in Ni

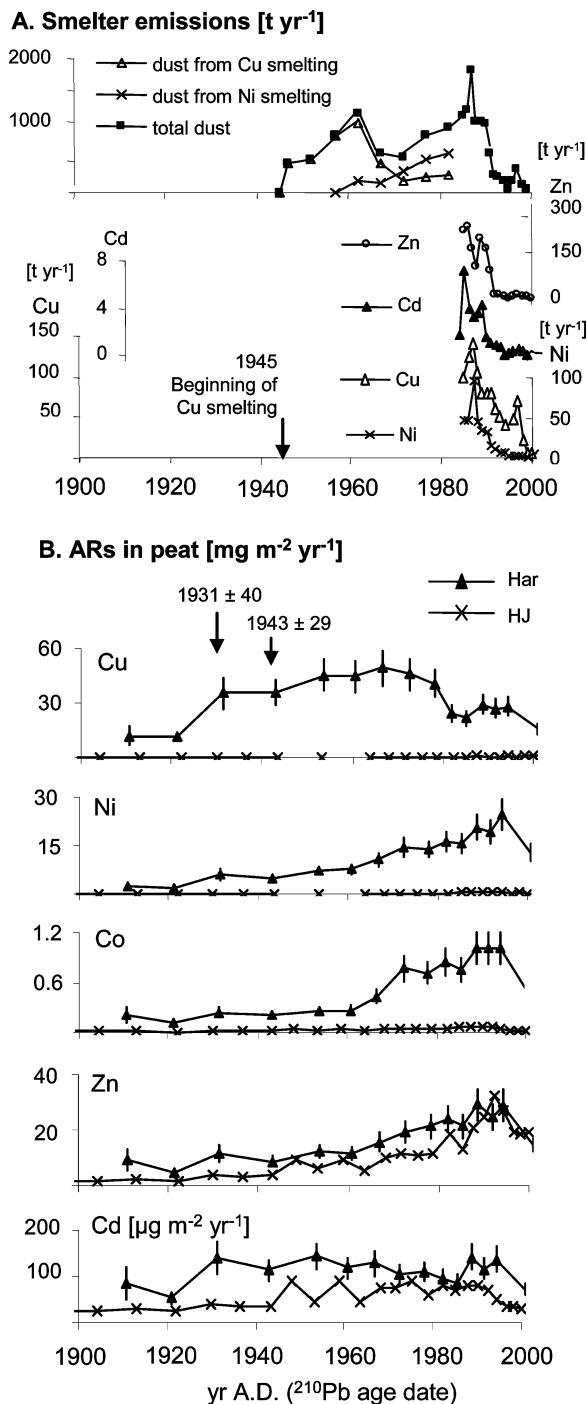


FIGURE 7. (A) Emissions at the Harjavalta smelter. (B) ARs of Cu, Ni, Co, Zn, and Cd in peat. See text for explanations.

concentrates. In summary, Cu, Ni, and Co reflect the general trends in deposition history. Zinc and Cd ARs do not reflect smelting impacts: Zn and Cd ARs at HAR are similar to those at HIJ.

Postdepositional Mobility. Cumulative metal inventories (Table 3) show that the peat bog at HAR has been severely affected by atmospheric Cu, Ni, and Co contamination, with up to 60 (Cu), 30 (Ni), and 7 (Co) times greater inventories than at the low-background site (HIJ). For peat samples predating the beginning of smelting activity (1911/1920), ARs of Cu, Ni, and Co are up to 120, 40, and 20 times greater at HAR than at HIJ and OUT. Although the region around HAR was settled and industrialized much earlier, this alone cannot explain these high ARs. Age dates cannot be determined

TABLE 3. Metal Inventories in Peat Accumulated since ~1100 A.D.

	Cu (mg m ⁻²)	Ni (mg m ⁻²)	Co (mg m ⁻²)	Zn (g m ⁻²)	Cd (mg m ⁻²)
HIJ	49	28	7.1	1.0	8.2
OUT	240	64	22	1.7	7.8
HAR	3200	970	56	2.4	16

precisely for that period at the HAR core; however, the slow increase in the ARs at the beginning of the smelting activity (1945) is inconsistent with the huge emissions at a time predating the installation of air filters. The most likely reason for the elevated ARs is therefore downward migration of these metals, after their release from the smelter and deposition on the bog surface, on the order of a few centimeters (Figure 4). We assume that most metals emitted from the smelter are metal oxides or sulfates, which might dissolve more rapidly in the acid, anoxic bog waters than sulfides, which are deposited at OUT (Table 2). Inventories of Zn and Cd at HAR are only twice those of HIJ, although up to 230 t year⁻¹ Zn and 7 t year⁻¹ Cd are released at the smelter (Table 2). Long-range transport contributes significantly to the atmospheric deposition of these elements in Finland (57, 58). The comparatively low inventories at HAR indicate that a considerable fraction of the Zn and Cd inventories were leached out of the profile.

The results show that the behavior of Cu, Ni, and Co cannot be generalized and might be controlled by the mineralogy of deposited particles. Further studies are needed to explain retention and mobilization mechanisms of these metals.

Acknowledgments

Financial support was provided by the German Research Foundation (Grant SH 89/1-1 to W.S. and M.K.) and the Finnish Forest Research Institute. We thank K. Taimi, K. Lyytikäinen, W. Roberts, and L. Hirvisaari for their assistance in the field work, C. Scholz for help with ICP-OES measurements, H. Wild for the humification measurements, M. Väiranta and N. Schnyder for the macrofossil separations, P. Van der Knaap for additional help, and especially H. Kempter and N. Givélet for very useful discussions.

Supporting Information Available

Mass accumulation rates (S1) and Sc and Sr concentrations normalized to absorbance as well as Ca concentrations (S2) of HIJ, OUT, and HAR. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Shotyk, W.; Weiss, D.; Kramers, J. D.; Frei, R.; Cheburkin, A. K.; Gloor, M.; Rees, S. Geochemistry of the peat bog at Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 ¹⁴C yr BP. *Geochim. Cosmochim. Acta* **2001**, *65*, 2337–2360.
- Vile, M. A.; Wieder, R. K.; Novak, M. Mobility of Pb in Sphagnum-derived peat. *Biogeochemistry* **1999**, *45*.
- Weiss, D.; Shotyk, W.; Kramers, J. D.; Gloor, M. Sphagnum mosses as archives of recent and past atmospheric lead deposition in Switzerland. *Atmos. Environ.* **1999**, *33*, 3751–3763.
- Givélet, N.; Roos-Barracough, F.; Shotyk, W. Predominant anthropogenic sources and rates of atmospheric mercury accumulation in southern Ontario recorded by peat cores from three bogs: comparison with natural “background” values (past 8000 years). *J. Environ. Monit.* **2003**, *5*, 935–949.
- Roos-Barracough, F.; Shotyk, W. Millennial-scale records of atmospheric mercury deposition obtained from ombrotrophic and minerotrophic peatlands in the Swiss Jura Mountains. *Environ. Sci. Technol.* **2003**, *37*, 235–244.

- (6) Benoit, J. M.; Fitzgerald, W. F.; Damman, A. W. H. The biogeochemistry of an ombrotrophic bog: evaluation of use as an archive of atmospheric mercury deposition. *Environ. Res. A* **1998**, *78*, 118–133.
- (7) Pheiffer Madsen, P. Peat bog records of atmospheric mercury deposition. *Nature* **1981**, *293*, 127–130.
- (8) Monna, F.; Petit, C.; Guillaumet, J.-P.; Jouffroy-Bapicot, I.; Blanchot, C.; Dominik, J.; Losno, R.; Richard, H.; Leveque, J.; Chateau, C. C. History and environmental impact of mining activity in Celtic Aeduan Territory recorded in a peat bog (Morvan, France). *Environ. Sci. Technol.* **2004**, *38*, 665–673.
- (9) Mighall, T. M.; Abrahams, P. W.; Grattan, J. P.; Hayes, D.; Timberlake, S.; Forsyth, S. Geochemical evidence for atmospheric pollution derived from prehistoric copper mining at Copa Hill, Cwmystwyth, mid-Wales, UK. *Sci. Total Environ.* **2002**, *292*, 69–80.
- (10) Shotyk, W.; Krachler, M.; Martinez-Cortizas, A.; Cheburkin, A. K.; Emons, H. A peat bog record of natural, pre-anthropogenic enrichments of trace elements in atmospheric aerosols since 12,370 14C yr BP, and their variation with Holocene climate change. *Earth Planet. Sci. Lett.* **2002**, *199*, 21–37.
- (11) Kettles, I. M.; Bonham-Carter, G. F. Modelling dispersal of metals from a copper smelter at Rouyn-Noranda (Québec, Canada) using peatland data. *Geochem. Expl. Environ. Anal.* **2002**, *2*, 99–110.
- (12) MacKenzie, A. B.; Logan, E. M.; Cook, G. T.; Pulford, I. D. A historical record of atmospheric depositional fluxes of contaminants in west-central Scotland derived from an ombrotrophic peat core. *Sci. Total Environ.* **1998**, *222*, 157–166.
- (13) Holynska, B.; Ostachowicz, B.; Ostachowicz, J.; Samek, L.; Wachniew, P.; Obidowicz, A.; Wobrauschek, P.; Strel, C.; Halmetschlager, G. Characterisation of 210Pb dated peat core by various X-ray fluorescence techniques. *Sci. Total Environ.* **1998**, *218*, 239–248.
- (14) Livett, E. A.; Lee, J. A.; Tallis, J. H. Lead, zinc and copper analyses of British blanket peats. *J. Ecol.* **1979**, *67*, 865–891.
- (15) Krachler, M.; Mohl, C.; Emons, H.; Shotyk, W. Atmospheric deposition of V, Cr, and Ni since the late glacial: Effects of climatic cycles, human impacts, and comparison with crustal abundances. *Environ. Sci. Technol.* **2003**, *37*, 2658–2667.
- (16) Kempter, H.; Frenzel, B. The impact of early mining and smelting on the local tropospheric aerosol detected in ombrotrophic peat bogs in the Harz, Germany. *Water, Air Soil Pollut.* **2000**, *121*, 93–108.
- (17) Espi, E.; Boutron, C. F.; Hong, S.; Pourchet, M.; Ferrari, C.; Shotyk, W.; Charlet, L. Changing concentrations of Cu, Zn, Cd and Pb in a high altitude peat bog from Bolivia during the past three centuries. *Water, Air Soil Pollut.* **1997**, *100*, 289–296.
- (18) Sugden, C. L.; Farmer, J. G.; MacKenzie, A. B. Isotopic ratios of lead in contemporary environmental materials from Scotland. *Environ. Geochem. Health* **1993**, *15*, 59–65.
- (19) Ukonmaanaho, L.; Nieminen, T.; Rausch, N.; Shotyk, W. Heavy metal and arsenic profiles in ombrogenous peat cores from four differently loaded areas in Finland. *Water, Air Soil Pollut.* **2004**, *158*, 261–277.
- (20) Nieminen, T. M.; Ukonmaanaho, L.; Shotyk, W. Enrichment of Cu, Ni, Zn, Pb and As in an ombrotrophic peat bog near a Cu–Ni smelter in southwest Finland. *Sci. Total Environ.* **2002**, *292*, 81–89.
- (21) Jungner, H.; Sonninen, E.; Possnert, G.; Tolonen, K. Use of bomb-produced C-14 to evaluate the amount of CO₂ emanating from 2 peat bogs in Finland. *Radiocarbon* **1995**, *37*, 567–573.
- (22) Shotyk, W.; Goodsite, M. E.; Roos-Barracough, F.; Givélet, N.; Le Roux, G.; Weiss, D.; Cheburkin, A. K.; Knudsen, K.; Heinemeier, J.; Van der Knaap, W. O.; Norton, S. A.; Lohse, C. Accumulation rates and predominant atmospheric sources of natural and anthropogenic Hg and Pb on the Faroe Islands since 5420 14C yr BP recorded by a peat core from a blanket bog. *Geochim. Cosmochim. Acta* **2005**, *69*, 1–17.
- (23) Shotyk, W.; Goodsite, M. E.; Roos-Barracough, F.; Frei, R.; Heinemeier, J.; Asmund, G.; Lohse, C.; Hansen, T. S. Anthropogenic contributions to atmospheric Hg, Pb and As deposition recorded by peat cores from southern Greenland and Denmark dated using the 14C “bomb pulse curve”. *Geochim. Cosmochim. Acta* **2003**, *67*, 3991–4011.
- (24) Ukonmaanaho, L.; Starr, M.; Mannio, J.; Ruoho-Airola, T. Heavy metal budgets for two headwater forested catchments in background areas of Finland. *Environ. Pollut.* **2001**, *114*, 63–75.
- (25) Kuusma, M. *Kuparikaivoksesta Suuryhtiöksi, Outokumpu 1910–1985*; Forssan kirjapaino Oy: Forssa, Finland, 1985.
- (26) Givélet, N.; Le Roux, G.; Cheburkin, A.; Chen, B.; Frank, J.; Goodsite, M. E.; Kempter, H.; Krachler, M.; Noernberg, T.; Rausch, N.; Rheinberger, S.; Roos-Barracough, F.; Sapkota, A.; Scholz, C.; Shotyk, W. Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses. *J. Environ. Monit.* **2004**, *6*, 481–492.
- (27) Kempter, H.; Frenzel, B. Zur Bedeutung von ombrotrophen Mooren als Archive der atmosphärischen Deposition. *Telma* **1997**, *27*, 107–130.
- (28) Appleby, P. G.; Oldfield, F. The calculation of lead-210 dates assuming a constant rate of supply of unsupported 210Pb to the sediments. *Catena* **1978**, *5*, 1–8.
- (29) Shore, J. S.; Bartley, D. D.; Harkness, D. D. Q. *Sci. Rev.* **1995**, *14*, 373.
- (30) Goodsite, M. E.; Rom, W.; Heinemeier, J.; Lange, T.; Ooi, S.; Appleby, P. G.; Shotyk, W.; van der Knaap, W. O.; Lohse, C.; Hansen, T. S. High-resolution AMS 14C dating of post-bomb peat archives of atmospheric pollutants. *Radiocarbon* **2001**, *43*, 453.
- (31) Niklaus, T. R.; Bonani, G.; Simonius, M.; Suter, M.; Wolfli, W. CalibETH—an interactive computer-program for the calibration of radiocarbon-dates. *Radiocarbon* **1992**, *34*, 483–492.
- (32) Cheburkin, A. K.; Shotyk, W. An energy-dispersive miniprobe multielement analyzer (EMMA) for direct analysis of Pb and other trace elements in peats. *Fresenius' J. Anal. Chem.* **1996**, *354*, 688–691.
- (33) Cheburkin, A. K.; Shotyk, W. Energy-dispersive XRF spectrometer for Ti determination (TITAN). *X-Ray Spectrom.* **2005**, *34*, 73–79.
- (34) Blackford, J. J.; Chambers, F. M. Determining the degree of peat decomposition for peat-based palaeoclimatic studies. *Int. Peat J.* **1993**, *5*, 7–24.
- (35) Appleby, P. G. In *Tracking Environmental Change Using Lake Sediments*; Last, W. M., Smol, J. P., Eds.; Kluwer: Dordrecht, The Netherlands, 2004; Vol. 1, pp 171–202.
- (36) Steinmann, P.; Shotyk, W. Chemical composition, pH, and redox state of sulfur and iron in complete vertical porewater profiles from two *Sphagnum* peat bogs, Jura Mountains, Switzerland. *Geochim. Cosmochim. Acta* **1997**, *61*, 1143–1163.
- (37) Koljonen, T., Ed. *The Geochemical Atlas of Finland. Part 2: Till*; Geological Survey of Finland: Espoo, Finland, 1992.
- (38) Leinonen, L.; Juntto, S. *Ilmanlaatumittauksia—Air Quality Measurements 1991*; Finnish Meteorological Institute: Helsinki, Finland, 1992.
- (39) Leinonen, L. *Ilmanlaatumittauksia—Air Quality Measurements 1992*; Finnish Meteorological Institute: Helsinki, Finland, 1993.
- (40) Leinonen, L. *Ilmanlaatumittauksia—Air Quality Measurements 1993*; Finnish Meteorological Institute: Helsinki, Finland, 1994.
- (41) Leinonen, L. *Ilmanlaatumittauksia—Air Quality Measurements 1994*; Finnish Meteorological Institute: Helsinki, Finland, 1996.
- (42) Leinonen, L. *Ilmanlaatumittauksia—Air Quality Measurements 1995*; Finnish Meteorological Institute: Helsinki, Finland, 1997.
- (43) Leinonen, L. *Ilmanlaatumittauksia—Air Quality Measurements 1996*; Finnish Meteorological Institute: Helsinki, Finland, 1998.
- (44) Leinonen, L. *Ilmanlaatumittauksia—Air Quality Measurements 1998*; Finnish Meteorological Institute: Helsinki, Finland, 1999.
- (45) Leinonen, L. *Ilmanlaatumittauksia—Air Quality Measurements 1997*; Finnish Meteorological Institute: Helsinki, Finland, 1999.
- (46) Leinonen, L. *Ilmanlaatumittauksia—Air Quality Measurements 1999*; Finnish Meteorological Institute: Helsinki, Finland, 2000.
- (47) Leinonen, L. *Ilmanlaatumittauksia—Air Quality Measurements 2000*; Finnish Meteorological Institute: Helsinki, Finland, 2001.
- (48) Erisman, J. W.; Mennen, M. G.; Fowler, D.; Flechard, C. R.; Spindler, G.; Grüner, A.; Duyzer, J. H.; Ruigrok, W.; Qyers, G. P. Deposition monitoring in Europe. *Environ. Monit. Assess.* **1998**, *53*, 279–295.
- (49) Jalkanen, L. *Atmospheric Inorganic Trace Contaminants in Finland, Especially in the Gulf of Finland Area*; Contribution 29; Finnish Meteorological Institute: Helsinki, Finland, 2000.
- (50) Poikolainen, J.; Kubin, E.; Piispanen, J.; Karhu, J. Atmospheric heavy metal deposition in Finland during 1985–2000 using mosses as bioindicators. *Sci. Total Environ.* **2004**, *318*, 171–185.
- (51) Parkkinen, J.; Reino, J. Nickel occurrences of the Outokumpu type at Vuonos and Keretti. *Bull. Geol. Survey Finland* **1985**, *333*, 178–188.

- (52) Laznicka, P. *Precambrian Empirical Metallogeny—Precambrian Lithologic Associations and Metallic Ores*; Elsevier Science: Amsterdam, The Netherlands, 1993; Vol. 2a.
- (53) Wedepohl, K. H. The composition of the continental crust. *Geochim. Cosmochim. Acta* **1995**, 59, 1217–1232.
- (54) Mäkinen, E. Die Kupfererzlagertätte Outokumpu in Finnland und ihre Verwertung. *Metall Erz* **1938**, 2, 25–33.
- (55) Kauppinen, H. Vuonoksen kuparimalmityypit ja rikastamon syötteet. Summary: The copper ore types and concentrator feeds in Vuonos. *Vuoriteollisuus* **1978**, 36, 16–21.
- (56) Pongrácz, E., Ed. *Proceedings of the Waste Minimization and Resources Use Optimization Conference*; Oulu University Press: Oulu, Finland, 2004.
- (57) Rühling, A.; Rasmussen, L.; Pilegaard, K.; Mäkinen, A.; Steinnes, E. Survey of atmospheric heavy metal deposition in the Nordic countries in 1985—monitored by moss analyses. *Nord* **1987**, 21.
- (58) Ilyin, I.; Ryaboshapko, A.; Afinogenova, O.; Berg, T.; Hjellbrekke, A.-G.; Lee, D. S. *Lead, Cadmium and Mercury Transboundary Pollution in 2000*; EMEP/MSC-E/CCC Report, 2002.

Received for review February 8, 2005. Revised manuscript received May 20, 2005. Accepted June 9, 2005.

ES050260M