# Deposition and fate of trace metals in Finnish bogs and implications for the use of bogs as geological archives

## INAUGURAL – DISSERTATION

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# Summary

Four sampling sites in Finland were selected for this study, each of them with known history of atmospheric metal deposition: Hietajärvi (HIJ), the low-background site; Outokumpu (OUT), near a former Cu-Ni mine; Harjavalta (HAR), near a Cu and Ni smelter and Alkkia (ALK), a site of experimental Cu/Ni application in 1962. The aim of this study is to determine the extent to which the atmospheric deposition of Cu, Ni, Co, Zn and Cd is preserved in peat profiles from ombrotrophic peatlands. The importance of post-depositional processes is studied using two independent approaches: the comparison of metal accumulation rates in peat profiles with monitoring data and emission records, and the comparison of metal concentrations in porewater with those in bulk peat.

ICP-sector-field-MS was used to determine trace metal concentrations in both peat and porewater samples. A new sampling device for the collection of porewater samples from ombrotrophic bogs was developed. A complete sampling protocol was established following strict quality control procedures. Blank values of the sampling devices were as follows (in µg $L^{-1}$): Cd 0.001, Co 0.009, Cr 0.05, Cu 0.07, Mn 0.2, Mo 0.02, Ni 0.10, Pb 0.004, Sc 0.011, V 0.01, Zn 1. Additional contamination by atmospheric dust during the on-site filtration was significant for Cr, Cu and Zn. The high content of humic substances in bog porewaters causes filtration artefacts. A Hesslein-type *in-situ* porewater sampler was used to collect porewater from HIJ and OUT *via* dialysis. Although this method would be less affected by filtration artefacts, it was not possible to establish reliable concentration profiles at these concentration levels with the exception of Co and Mn.

'Background' concentrations for metals in peat were calculated using deep layers at HIJ (in 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). Similar concentrations were found in deep layers of all sites, while they were elevated in upper layers. The metal distribution was independent of the input of mineral dust, the degree of decomposition, and the distribution of S and Fe. The comparison of metal accumulation rates with emission records showed that Cu and Co accurately reflected the atmospheric deposition history of the mining site (OUT), while Ni, Zn and Cd were subjected to post-depositional processes. Although the uncertainties of the $^{210}$Pb age dates and the poor time-resolution between adjacent samples made interpretations at HAR difficult, all metals were found to be mobile. At HIJ and OUT, porewater concentrations were in a similar range (< 8 nM Cu and Ni, < 1.4 nM Co, < 250 nM Zn). Although a limited release of Ni and Zn was indicated at OUT, the generally low concentrations suggested that these metals were re-distributed at an early stage of deposition. High Cd porewater concentrations confirmed post-depositional processes at OUT, whereas Cu was immobile. The crucial point for the retention of different metals at OUT might be the stability of ore-derived dust particles (e.g. chalcopyrite, pyrrhotite) against oxidation in the aerated surface layer of the bog. Porewater concentrations at HAR exceeded those at HIJ and OUT by a factor of 2 (Zn), 10 (Cd), 20 (Co) and 100 (Cu and Ni), confirming post-depositional mobilization of all metals. This might be explained by the deposition of smelter-derived metal oxide particles, which should readily dissolve in the acid conditions of the HAR bog porewater (< pH 3.4).

## Zusammenfassung

Vier Probenahmestellen mit bekannter atmosphärischer Spurenmetall-Deposition wurden beprobt: Hietajärvi (HIJ) als Referenz für die Hintergrundbelastung; Outokumpu, in der Nähe einer ehemaligen Cu-Ni-Mine; Harjavalta (HAR), nahe eines Cu und Ni Hüttenwerks und Alkkia, wo 1962 in einer Feldstudie Metallsalze aufgetragen wurden. Ziel dieser Arbeit ist es herauszufinden, in welchem Ausmaß die atmosphärische Cu, Ni, Co, Zn und Cd Deposition in Torfprofilen aus Hochmooren aufgezeichnet wird. Dies wurde mittels zweier unabhängiger Herangehensweisen studiert: Metall-Akkumulationsraten in Torfproben wurden mit der tatsächlichen Deposition verglichen, und Metallkonzentrationen im Porenwasser wurden mit Gesamtkonzentrationen verglichen.

Spurenmetall-Konzentrationen wurden mittels ICP-SF-MS bestimmt. Ein neues Gerät zur Entnahme von Porenwasser-Proben in Hochmooren sowie ein vollständiges Probenahme-Protokoll wurde entwickelt, mit folgenden Blindwerten: (in µg $L^{-1}$): Cd 0.001, Co 0.009, Cr 0.05, Cu 0.07, Mn 0.2, Mo 0.02, Ni 0.10, Pb 0.004, Sc 0.011, V 0.01, Zn 1. Die manuelle Filtration an der Probenahmestelle führte zu einer signifikanten Erhöhung der Cr, Cu und Zn Blindwerte. Der hohe Gehalt an Huminstoffen in den Porenwässern führte zu starken Filtrationsartefakten. In HIJ und OUT wurden zusätzlich Porenwasser-Proben mittels Dialyse gewonnen (sog. „Hesslein peeper“). Diese Probenahme-Technik ist weniger anfällig für Filtrationsartefakte, jedoch konnte damit keine zuverlässigen Konzentrationsprofile gewonnen werden (Ausnahme: Co und Mn).

Folgende Hintergrund-Konzentrationen wurden in tiefen Torfschichten in HIJ bestimmt (in µg $g^{-1}$): Cu 1.3 ± 0.2 (n=62), Co 0.25 ± 0.04 (n=71), Cd 0.08 ± 0.01 (n=23) und Zn 4 ± 2 (n=40). Ähnliche Konzentrationen wurden auch in den tieferen Torfschichten der anderen Probenahme-Stellen gefunden, während obere Torflagen erhöhte Metall-Konzentrationen aufwiesen. Die Metallkonzentrationen waren unabhängig vom Bodenstaub-Eintrag, vom Zersetzungsgrad der Torfschichten und von den S und Fe Konzentrationen. Die Cu und Co Akkumulationsraten spiegelten die atmosphärische Deposition in OUT hervorragend wider. Nickel, Zn und Cd wurden dagegen nach der Ablagerung mobilisiert. Trotz Schwierigkeiten bei der Altersbestimmung der Torfproben deuteten die Metall-Akkumulationsraten in HAR auf eine Mobilisierung aller Metalle hin. Porenwasser-Konzentrationen in HIJ und OUT waren niedrig (< 8 nM Cu and Ni, < 1.4 nM Co, < 250 nM Zn). Trotz Anzeichen einer gewissen Freisetzung von Ni und Zn in OUT deuteten sie auf eine Umverteilung der Metalle im Anfangsstadium hin. Hohe Cd bzw. niedrige Cu Konzentrationen im Porenwasser bestätigten die Ergebnisse der ersten Herangehensweise. Die unterschiedliche Mobilität der Metalle basiert vermutlich auf der unterschiedlichen Resistenz der abgelagerten Sulfiderze gegen Oxidation an der Oberfläche des Moores. Porenwasser-Konzentrationen in HAR sind stark gegenüber HIJ und OUT erhöht, vermutlich da dort leichtlösliche Metall-Oxide abgelagert wurden.

## List of original publications and the author's contribution

This thesis is based on the following articles, which are included in the text as separate chapters:

ANALYTICAL SECTION

**Chapter 2**

Rausch, N., L. Ukonmaanaho, T.M. Nieminen, M. Krachler, G. Le Roux, W. Shotyk. A syringe-type sampler for obtaining porewaters from ombrotrophic bogs, and application to trace metal (µg L-1 to sub-µg L-1) determinations. Limnology and Oceanography. Methods submitted (2005)

The paper was initiated and planned jointly by N. Rausch, L. Ukonmaanaho, T. Nieminen, M. Krachler and W. Shotyk. The field work was performed by N. Rausch, T. Nieminen and L. Ukonmaanaho. N. Rausch was responsible for the development of the new sampler, the establishment of the sampling protocol, all analyses and the preparation of the article. Co-authors assisted in field and laboratory work and the interpretation of the data.

**Chapter 3**

Krachler, M., N. Rausch, H. Feuerbacher, P. Klemens. 2005. A new HF-resistant tandem spray chamber for improved determination of trace elements and Pb isotopes using inductively coupled plasma - mass spectrometry. Spectrochimica Achta B (in print).

The paper was initiated and planned jointly by M. Krachler, N. Rausch, H. Feuerbacher and P. Klemens. H. Feuerbacher and P. Klemens developed the new spray chamber. M. Krachler and N. Rausch were responsible for the performance of the analyses. M. Krachler was responsible for the interpretation of the data and the preparation of the article. Co-authors assisted in the interpretation of the data.

PEAT BOGS AS ARCHIVES

**Chapter 4**

Ukonmaanaho, L., T.M. Nieminen, N. Rausch, W. Shotyk. 2004. Heavy metal and arsenic profiles in ombrogenous peat cores from four differently loaded areas in Finland.Water, Air, and Soil Pollution 158: 277-294.

The paper was initiated and planned jointly by L. Ukonmaanaho, T. Nieminen, N. Rausch and W. Shotyk. The field work was performed by Nieminen, Ukonmaanaho and Rausch. Ukonmaanaho and Nieminen were responsible for the interpretation of the data and the preparation of the article. Rausch was responsible for the sample preparations and assisted in the interpretation of the data.

**Chapter 5**

Rausch, N., T.M. Nieminen, L. Ukonmaanaho, G. Le Roux, M. Krachler, A.K. Cheburkin, G. Bonani, W. Shotyk. 2005. Comparison of atmospheric deposition of copper, nickel, cobalt, zinc and cadmium recorded by Finnish peat cores with monitoring data and emission records. Environmental Science and Technology (accepted for publication).

The paper was initiated and planned jointly by N. Rausch, T. Nieminen, L. Ukonmaanaho and W. Shotyk. The field work was performed by Nieminen, Ukonmaanaho and Rausch. Rausch was responsible for the analytical part (except of age datings and XRF analyses), the interpretation of the data and the preparation of the article. Co-authors provided historical and monitoring data, age datings and XRF data and assisted in the interpretation of data.

## Chapter 6

Rausch, N., T.M. Nieminen, L. Ukonmaanaho, M. Krachler, W. Shotyk. Porewater evidence of metal (Cu, Ni, Co, Zn, Cd) mobilization in an acidic, ombrotrophic bog impacted by a smelter, Harjavalta, Finland and comparison with reference sites. Environmental Science and Technology in review (2005).

The paper was initiated and planned jointly by N. Rausch, T. Nieminen, L. Ukonmaanaho and W. Shotyk. The field work was performed by Rausch, Nieminen and Ukonmaanaho. Rausch was responsible for the analytical part, the interpretation of the data and the preparation of the article. Co-authors assisted in the interpretation of data.

## Appendix 1

Givelet, N., G. Le Roux, A. K. Cheburkin, B. Chen, J. Frank, M. E. Goodsite, H. Kempter, M. Krachler, T. Noernberg, N. Rausch, S. Rheinberger, F. Roos-Barraclough, A. Sapkota, C. Scholz, W. Shotyk. 2004. Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical mineralogical and isotopic analyses. Journal of Environmental Monitoring 6: 481-482.

The paper was initiated and planned jointly by N. Givelet, G. Le Roux and W. Shotyk. The protocol paper was jointly developed during the period of this PhD by all co-authors. N. Rausch contributed to the parts “Quantification of trace elements” (Cd and Ni analyses), “Age dating” (results from Finnish cores) and “Quality control” (analyses of certified reference materials using different analytical methods).

## Appendix 3

Ukonmaanaho, L., T. Nieminen, N. Rausch, A. Cheburkin, G. Le Roux, W. Shotyk. 2005. Recent organic matter accumulation related to some climatic factors in ombrotrophic peat bogs near heavy metal emission sources in Finland. Global and Planetary Changes in review.

The paper was initiated and planned jointly by L. Ukonmaanaho, T. Nieminen, N. Rausch and W. Shotyk. N. Rausch performed the field work jointly with T. Nieminen and L. Ukonmaanaho. N. Rausch prepared all samples and performed the density measurements and carbon analyses. N. Rausch also assisted in the interpretation of the data. Co-authors were responsible for the interpretation of the data, XRF analyses, $^{210}$Pb age dating and the preparation of the article.

## List of abbreviations used

| | |
|---|---|
| ALK | Alkkia site |
| ALK-Ni | Ni-treated site at Alkkia |
| ALK-Cu | Cu-treated site at Alkkia |
| ALK-control | Control site at Alkkia (untreated) |
| AR | Accumulation rate |
| a.s.l. | above sea level |
| b.p.c. | bomb pulse curve |
| Blk | Blank value |
| DOC | Dissolved organic carbon |
| EMMA | Energy-dispersive miniprobe multielement analyzer |
| ESI | Electronic supplementary information |
| GD/XP | Product name for a Whatman syringe filter |
| GF-AAS | Graphite furnace atomic absorption |
| GHP | GHP membrane |
| HA | Humic acid |
| HAR | Harjavalta site |
| HIJ | Hietajärvi site |
| ICP-OES | Inductively coupled plasma optical emission spectrometry |
| ICP-SF-MS | Inductively coupled plasma sector-field mass spectrometry |
| LOD | Limit of detection |
| LOQ | Limit of quantitation |
| NAA | Neutron activation analysis |
| NPP | Net primary production |
| OM | Organic matter |
| OUT | Outokumpu site |
| PC | Polycarbonate |
| PE | Polyethylene |
| PP | Polypropylene |
| PVDF | Polyvinylidendifluoride |
| SEM/EDX | Scanning electron microscopy with energy-dispersive X-ray microanalysis |
| TITAN | Energy-dispersive XRF spectrometer for Ti determination |
| XRF | X-Ray fluorescence spectrometry |

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First of all, my sincere thanks to Bill Shotyk for his excellent supervising – he always encouraged me to develop my own ideas, and he was always present to give good advice, support and encouragement whenever I needed them. Thanks for giving me the chance to take part in international cooperations, field trips and conferences, but also for the great time in Heidelberg. Many thanks to my co-supervisor Michael Krachler for all of his help with the analytical part of my thesis in general, and the ICP-SF-MS in particular. Like Bill, he always managed to be "available" for instant advice whenever problems occurred…

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## ANALYTICAL SECTION

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## PEAT BOGS AS ARCHIVES

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# CHAPTER 1

## General Introduction

## 1-1 Background

This project was undertaken in close co-operation with Tiina M. Nieminen and Dr Liisa Ukonmaanaho from the Finnish Forest Research Institute (METLA), who were intimately involved in this study since conception, and helped with all aspects of the field work, bibliographic research (including translations from Finnish into English), and interpreting the results.

### 1-1.1 OMBROTROPHIC PEATLANDS

Peatlands are peat-forming ecosystems in which at least 30 cm of peat have accumulated. Fig. 1 shows their global distribution. They cover approx. 5% of the Earth's total land area (Matthews and Fung 1987) and can be classified into fens and bogs (Gore 1983). Fens, or minerotrophic peatlands, receive their mineral nutrition by waters percolating through mineral soils (Shotyk 1989). Bogs, or ombrotrophic peatlands, are domed and surface layers are hydrologically isolated from the influence of local groundwaters and surface waters. As they are fed by atmospheric deposition only, they are characterised by nutrient-poor conditions (Damman 1986; Dau 1823).

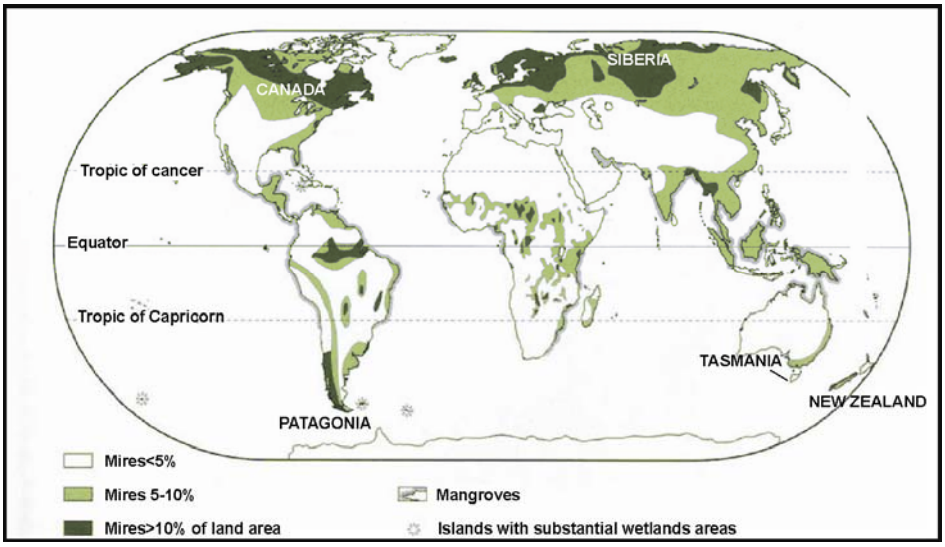
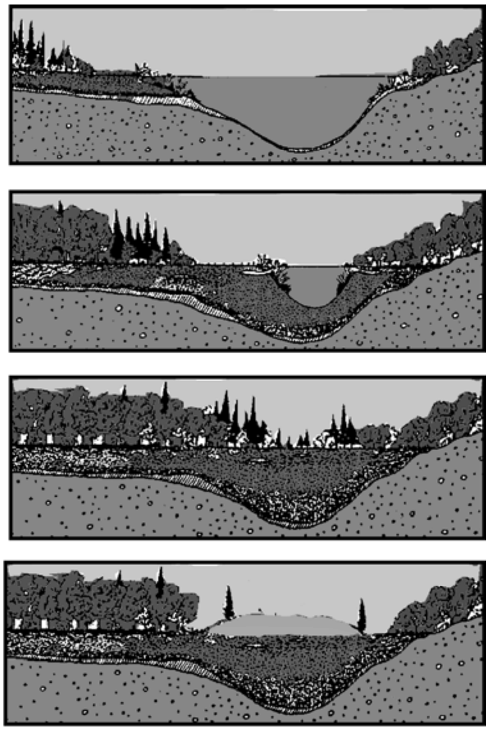


**Fig. 1.** Distribution of peatlands expressed as a proportion of the land surface of the world. Map redrawn from Lappalainen by permission of the International Peat Society in (Charman 2002).

Bogs develop in areas where precipitation exceeds evapotranspiration and surface runoff. In addition the basement must be relatively impermeable to water. They form by either the in-filling of shallow lakes (terrestrialization) as shown in Fig. 2 or by water-logging of terrestrial soils (paludifiction) (Gore 1983). Due to the excess of water and the low nutrient supply specialized vegetation develops, dominated by species of *Sphagnum* moss.



Small lake developped in a basin left by the retreating glaciers

Progressive filling of the lake by detritus of aquatic plants and microorganisms (often gyttja)

Terrestrialization of the ecosystem: a fen is formed, typical plants are *Carex*, *Eriophorium*

*Sphagnum* species replace minerotrophic vascular plants

**Fig. 2**. Development of a peat bog after the ice retreat at the end of the last glaciation (from Le Roux 2005).

### 1-1.2 BIOGEOCHEMICAL PROCESSES DURING PEAT ACCUMULATION

*Sphagnum* plants grow at the apex, whereby deeper parts of the plants die. In layers above the water table (‘acrotelm’), aerobic decomposition prevails, with decay rates of approx. 2-4% per year. In layers below the water table (“catotelm”) the rate of decay is strongly retarded (0.1-0.000001% per year) (Swift et al. 1979). Therefore, the accumulation rate of organic matter is not only controlled by the plant growth rate and the resistance of plant species to decomposition, but also the elevation of the acrotelm (Clymo and Hayward 1982). The latter one is controlled by the water table, which fluctuates in relation to rainfall, run-off, evaporation and the hydraulic conductivity of the peat layers.

As a result of the decomposition of organic matter, bog waters are rich in dissolved organic carbon (DOC), averaging 50 mg $L^{-1}$ (Thurman 1985). Due to the low supply of mineral dust (atmospheric deposition only), the acids produced *via* the decomposition of organic matter ($CO_2$ and organic acids) are not neutralized, resulting in acid bog waters (approx. pH 4) (Shotyk 1988; Steinmann and Shotyk 1997). In this special environment, three potential dissolution reactions for deposited Fe-minerals are reported (Shotyk 1992): reductive dissolution, ligand-promoted dissolution, and proton-promoted dissolution. A known feature is the dissolution of Fe minerals and the subsequent bacteria-mediated precipitation in oxygenated drainage waters (Shotyk 1992; Steinmann and Shotyk 1997). In uncontaminated bogs the formation of Fe sulfides, carbonates and phosphates is in general prevented by the low rate of supply of metals, the formation of metal-organic complexes, the low pH, sulfate concentrations below the lower limit of dissimilatory sulfate reduction and the low supply of P (Steinmann and Shotyk 1997). In turn, the anaerobic conditions diminish the solubility of those elements which are less soluble under these conditions such as Cu and U (Shotyk 1989). A general scheme of the most important processes is given in Fig. 3. The interaction of metals with the organic matter is described in the following chapter.

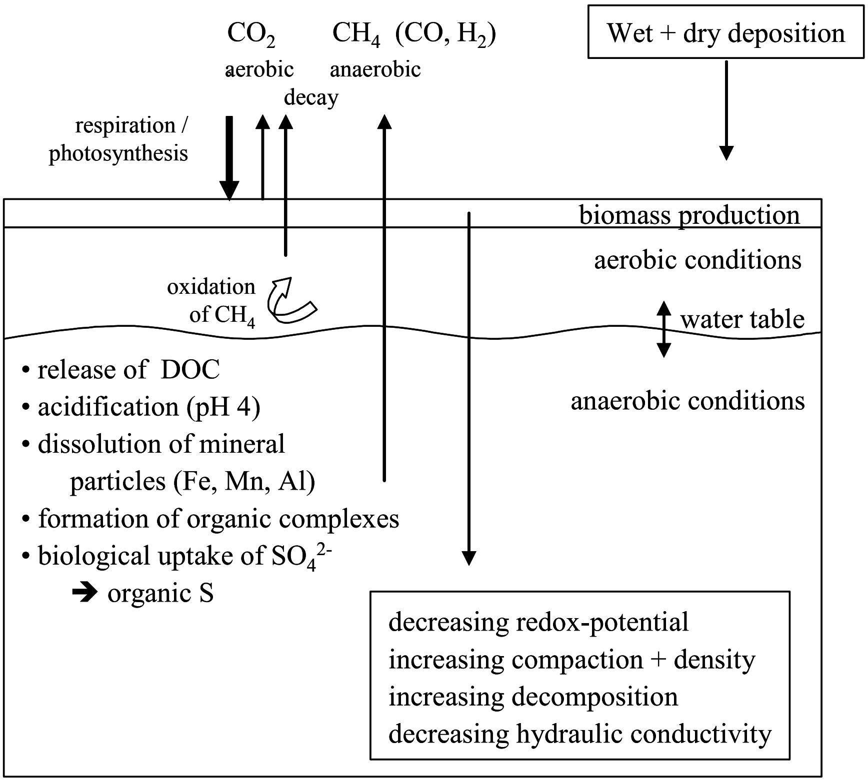


**Fig. 3.** Scheme of the most important processes in ombrotrophic peat layers.

### 1-1.3 METAL RETENTION BY THE ORGANIC MATTER

Due to the nutrient-poor conditions at bogs, the living plants have developed specific strategies to efficiently retain metals. Sphagnum mosses are composed of imbricate leaves, spirally arranged at branches which are either spreading or pendent (Clymo and Hayward 1982). The high surface area results in an efficient trapping of metals from the atmosphere (Erisman et al. 1998). The leaves themselves are one cell thick with cell walls (hyaline cell) of a high cation exchange capacity. This allows a relatively unrestricted exchange of solutes between the atmosphere and the living plant tissue (Livett 1988). With increasing decomposition, the proportion of metal-binding "humic substances" increases at the expense of less resistant plant constituents (e.g. hemicelluloses). These humic substances are widely known for their metal binding capacities (Tipping 2002).

In general, some divalent cations such as Cu adsorb to peat mainly as inner-sphere complexes, i.e. specifically adsorbed. Zinc and Cd, as well as monovalent cations, are predominantly bound as outer-sphere complexes (Ringqvist and Öborn 2002; Twardowska and Kyziol 1996; Twardowska and Kyziol 2003). Inner-sphere complexes tend generally to be much more stable than outer-sphere complexes (Sposito 1984). Much less is known about the binding of Ni, and the results in the literature are inconsistent (Crist et al. 1996; Tummavuori and Aho 1980). Although peat is well-known to reduce trace metal concentrations in polluted waters (Allen 1996; Chauvet 2003; Coker and Dilabio 1979; Eger et al. 1981), a common viewpoint on the exact retention mechanism is still under investigation. The most recent laboratory studies show that metal sorption on peat is dependent on a variety of factors: the botanical origin of the peat, the pH, the presence of competing as well as complexing ions, the ionic strength of the solution, metal concentrations of the solution and even the contact mode between the solution and the peat (Fattahpour Sedeh et al. 1996; Ho and Mckay 2000; Ho et al. 2002; Ringqvist and Öborn 2002; Twardowska and Kyziol 2003). Therefore, predictions of the adsorption behavior of dissolved metals in natural ecosystems are rather difficult.

### 1-1.4 PEAT BOGS AS ARCHIVES OF ATMOSPHERIC METAL DEPOSITION

Knowledge and understanding of historical trends in pollutant deposition can provide an useful analogue for the prediction and assessment of impacts of contemporary environmental contamination (Jones and Hao 1993; Monna et al. 2004). As a prerequisite, the pre-anthropogenic, “pristine” metal deposition rate must be quantified. Geological archives also allow monitoring of the long-term effects of policy changes such as the Clean Air Act, as well as the introduction of new technical developments. Furthermore, archives can provide new insight into the identification of ancient metallurgical activities such as mining, ore processing and smelting even when archaeological evidence is scarce and written sources are absent (Le Roux et al. 2004).

There are several kinds of geological archives, of which alpine and polar snow and ice, lake sediments, and peat bogs have been studied most intensively (Livett 1988). They are very different with respect to accessibility, time span, temporal resolution, and ability to preserve various records of environmental change. The particular advantages of peat bogs as archives of atmospheric deposition are as follows: (1) The surface layers are hydrologically isolated from the influence of local groundwaters and surface waters, and are fed exclusively by atmospheric deposition (see above). (2) The Sphagnum species efficiently collect airborne particulates due to their branched structure and retain dissolved metals due to their high cation exchange capacity (Clymo 1983; Swaine et al. 1984). (3) Unlike ice-cores, which predominantly record long-range atmospheric transport, peat bogs are significantly affected by local and regional metal inputs. With their broad geographic distribution and their long accumulation history, peat bog archives are ideal for quantifying regional differences in deposition histories (Le Roux et al. 2004). Although there are published studies of peat bog archives in the literature (Glooschenko 1986; Jones and Hao 1993; Stewart and Fergusson 1994), the most crucial point is the possibility of post-depositional migration of metals (Coleman 1985; Livett 1988; Shotyk 1996; Urban et al. 1990). Until now, only Pb and Hg have been shown to be immobile in peat layers (Benoit et al. 1998; Farmer et al. 1997; Givelet et al. 2003; MacKenzie et al. 1997; Pheiffer-Madsen 1981; Shotyk et al. 1996; Vile et al. 1995; Vile et al. 1999; Weiss et al. 1999). Due to the binding capacity of peat for Cu, this element is generally thought to be immobile and variations in its concentration profile probably reflect atmospheric history. In contrast, Zn is probably redistributed after deposition, e.g. by plants (Espi et al. 1997; Jones 1987; Livett 1988; Livett et al. 1979). There are few studies of Ni, Co and Cd in peat profiles, and the general findings related to mobility are inconclusive (Jones and Hao 1993; Krachler et al. 2003; MacKenzie et al. 1998; Monna et al. 2004; Stewart and Fergusson 1994). In fact, the importance of post-depositional migration has not yet been investigated in any systematic way for either Cu, Ni, Co, Zn or Cd.

## 1-2 Aim of the study

The ultimate objective of this study is to determine the extent to which the atmospheric deposition of Cu, Ni, Co, Zn and Cd is preserved in peat profiles from ombrotrophic peatlands. The importance of post-depositional processes is studied using two independent approaches:

- **High resolution reconstructions of atmospheric metal deposition in ombrotrophic peat are compared with the known metal deposition histories.** Four sites were selected with established chronologies of anthropogenic, atmospheric emission/deposition of Ni, Cu, Cd, Zn and Cd.
- **Porewater profiles of the same sites were compared with bulk concentrations** to quantify the release of metals from the solid phases supplied by atmospheric dust particles.

Specifically, the aims using the first approach are: Reconstruct the local metal deposition/emission history in detail from the literature. Reconstruct metal accumulation rates in the different peat cores using accurate and reproducible analytical methods for the elements of interest, but also for age dating. Compare the different analytical methods used for consistency (e.g. ICP-SF-MS with ICP-OES; $^{210}$Pb with $^{14}$C bomb pulse curve age dating). Compare metal accumulation rates with the local history for consistency. Calculate natural, pre-anthropogenic metal concentrations in peat.

For the second approach, a new porewater sampler had to be developed which yielded low blank values for trace metals. A sampling protocol had to be established following strict quality control procedures. The performance of the ICP-SF-MS analysis had to be optimized on the reduction of blank levels. Porewater samples had to be collected and analyzed from all sites.

The underlying goal is to study the interactions between atmospheric metal deposition and organic matter accumulation.

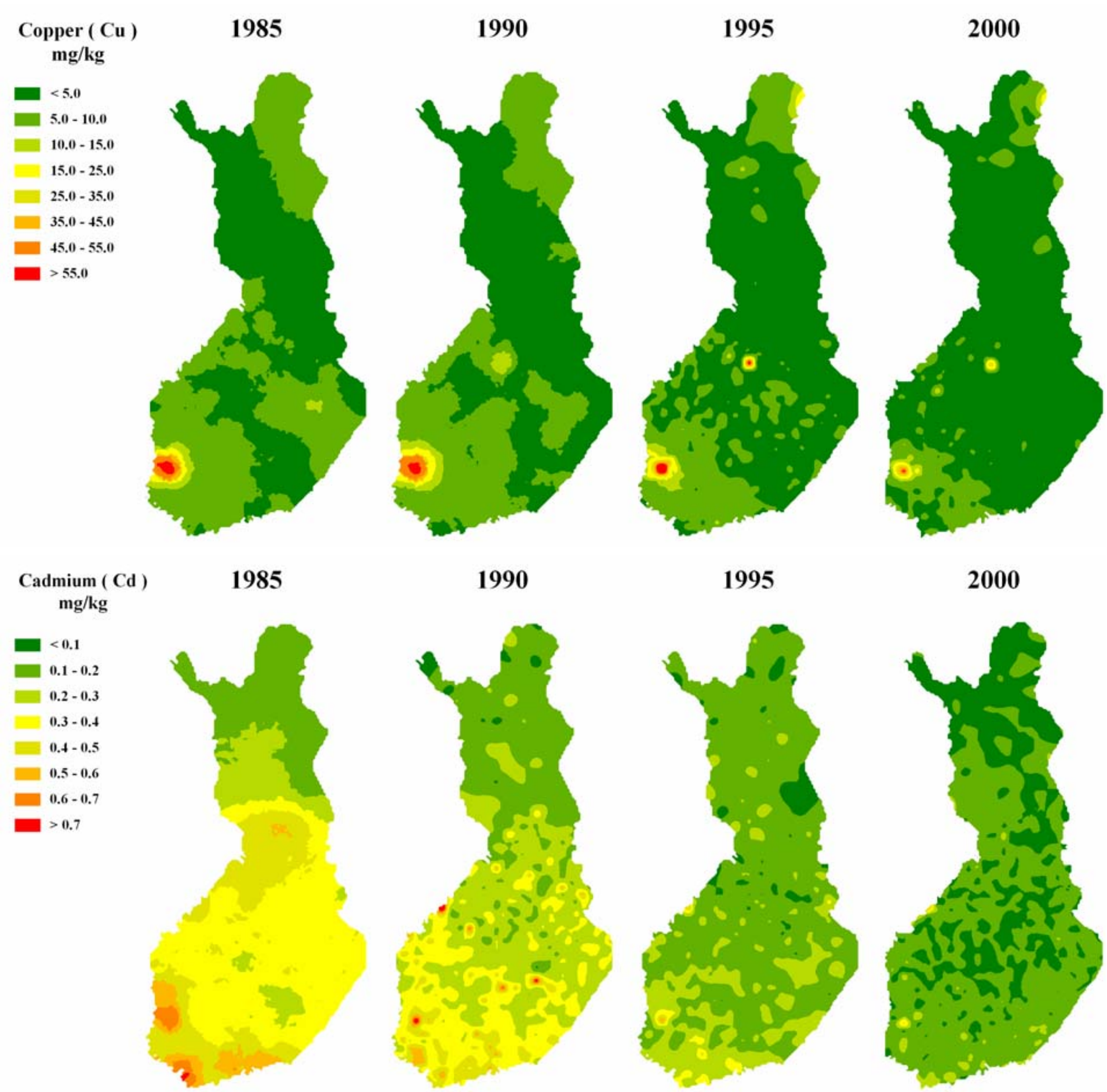


**Fig. 4.** Concentrations of Cu and Cd in mosses in 1985, 1990, 1995 and 2000 as an indicator of atmospheric metal deposition in Finland (from Poikolainen 2004, with permission).

## 1-3 Materials and Methods

### 1-3.1 SAMPLING SITES

Four sampling sites in Finland were selected for this study, each of them with known history of trace metal deposition: Hietajärvi (HIJ), the low-background site; Outokumpu (OUT), near the famous Outokumpu Cu-Ni mine; Harjavalta (HAR), near a Cu and Ni smelter and Alkkia (ALK), a site of experimental Cu/Ni application in 1962 (see Chapter 4, Fig. 15). Site characteristics and the history of metal deposition are described in detail in Chapter 4 to 6, and are summarized in Table 1.

The significance of the HAR and OUT point sources on atmospheric metal deposition in Finland is shown in Fig. 4. The atmospheric deposition of Cu (and Ni) is much more restricted to the vicinity of the point sources than the deposition of Cd. As indicated by monitoring studies, Cu and Ni deposition at HIJ has been at low-background levels since at least 1985, while Cd deposition is still affected by long-range transport, mainly originating from the St. Petersburg area and Estonian oil shale fueled power plants (Ilyin et al. 2002; Jalkanen 2000; Poikolainen et al. 2004). Moreover, extensive forest fires which are still common at Eastern Finland and Russia are important natural sources of Cd (Nriagu and Pacyna 1988).

### 1-3.2 SAMPLING PROCEDURES

#### 1-3.2.1 Peat samples

At each site, two peat cores were taken in September 2001 using a titanium Wardenaar corer (Givelet et al. 2004). One core was cut into 5 cm slices using a Ti knife, and peat samples were packed into plastic bags. This core was used for a preliminary study (Chapter 4). The second core was immediately frozen and shipped to the lab where it was sectioned into 1 cm slices with a stainless steel band saw. The edges of each slice were removed, the residual peat dried at 105° C in Teflon bowls, and milled with a Titanium centrifugal mill equipped with 0.25 mm sieve. This core was used for detailed studies presented in Chapter 5 and Appendix 3. The depth of peat samples is given in centimetre below the layer of the living vegetation, which is 8 (HIJ), 2 (OUT) and 3 (HAR) cm.

The sampling collection and preparation protocol for the 1 cm-sliced core was developed and established by our own working group (Appendix 1) to obtain uncontaminated peat samples with high spatial resolution. The slicing of frozen cores using a band saw was a considerable improvement to the earlier method of cutting fresh cores at ambient temperatures using a knife. The subsequent SEM/EDX analyses of peat samples showed that thin plates of pure

**Table 1.** Summary on site characteristics.

| site | Hietajärvi | Outokumpu | Harjavalta | Alkkia |
|---|---|---|---|---|
| Location | 63°09′N, 30°40′E | 62°40′N, 28°5′E | 61°21′N, 22°11′E | 62°11′N, 22°48′E |
| Climatic zone | Middle boreal | Southern boreal | Southern boreal | Southern boreal |
| Annual mean temperature (°C) | 1.5 | 2.3 | 4.1 | 3.0 |
| Annual precipitation sum (mm)[a] | 616 | 615 | 571 | 612 |
| Altitude (m a.s.l.) | 168 | 108 | 40 | 160 |
| Bog conditions | ombrotrophic | ombrotrophic | ombrotrophic | vegetation damaged |
| Samples collected[b] | 2 Peat cores (September 2001)<br>Porewater samples (August 2003) | 2 Peat cores (September 2001)<br>Porewater samples (August 2003) | 2 Peat cores (September 2001)<br>Porewater samples (August 2003) | 3 Peat cores (September 2001)<br>Porewater samples (August 2003) |
| Depth of peat | >2 m | <6 m[c] | >2 m | 1.60 m |
| Main atmospheric metal sources | Long-range transport | Cu-Ni mine (1910-1989)<br>Pilot Cu plant (1913-1929) | Cu smelter (since 1945)<br>Ni smelter (since 1959) | Experimental Cu/Ni application (1962) |
| Mean annual metal deposition[d] [mg $m^{-2}$ $a^{-1}$] | Cd 0.019 ± 0.004<br>Cu 0.5 ± 0.1<br>Ni 0.15 ± 0.03<br>Zn 2.0 ± 0.9<br>bulk deposition, unfiltered, 1992-2000 | | Cd: not available<br>Cu 8 ± 2<br>Ni 1.2 ± 0.2<br>Zn 3.2 ± 0.5<br>bulk deposition, filtered, 4 km SE of smelter, 1993-1996 | |

[a] For the period 1950-1999, see Table 14.
[b] At HIJ, OUT, HAR: One high-resolution core, sliced frozen in 1 cm intervals, and one core sliced in the field in 5 cm intervals; at ALK: one high-resolution core taken at the Ni-treated site, and two cores sliced in the field in 5 cm intervals (taken at the untreated control site and the Cu-treated site).
[c] See Table 14.
[d] Deposition at HIJ: see Chapter 5; at HAR: see Chapter 6.

Ni-Cr (up to 6 µm length) were present in almost all samples, probably originating from the degeneration of the band saw (see chapter 1-4.2.1.3). However, there are several indications showing that this potential contamination from the sample preparation is negligible for the establishment of Ni concentration profiles even in peat at low-background sites (Chapter 5, Fig. 22): (1) The comparison of Ni concentrations in peat samples obtained from slicing frozen cores (this study) with those from gentle cutting at ambient temperatures (Krachler et al. 2003) showed negligible differences in background concentrations (0.62 ± 0.07 µg $g^{-1}$, n=16 and 0.46 ± 0.09 µg $g^{-1}$, n=18, respectively). (2) The concentration of the HIJ top sample (living vegetation) is at present-day background levels of mosses collected by hand (Poikolainen et al. 2004). (3) Well-defined Ni concentration peaks are found even in pre-industrial layers of the HIJ site.

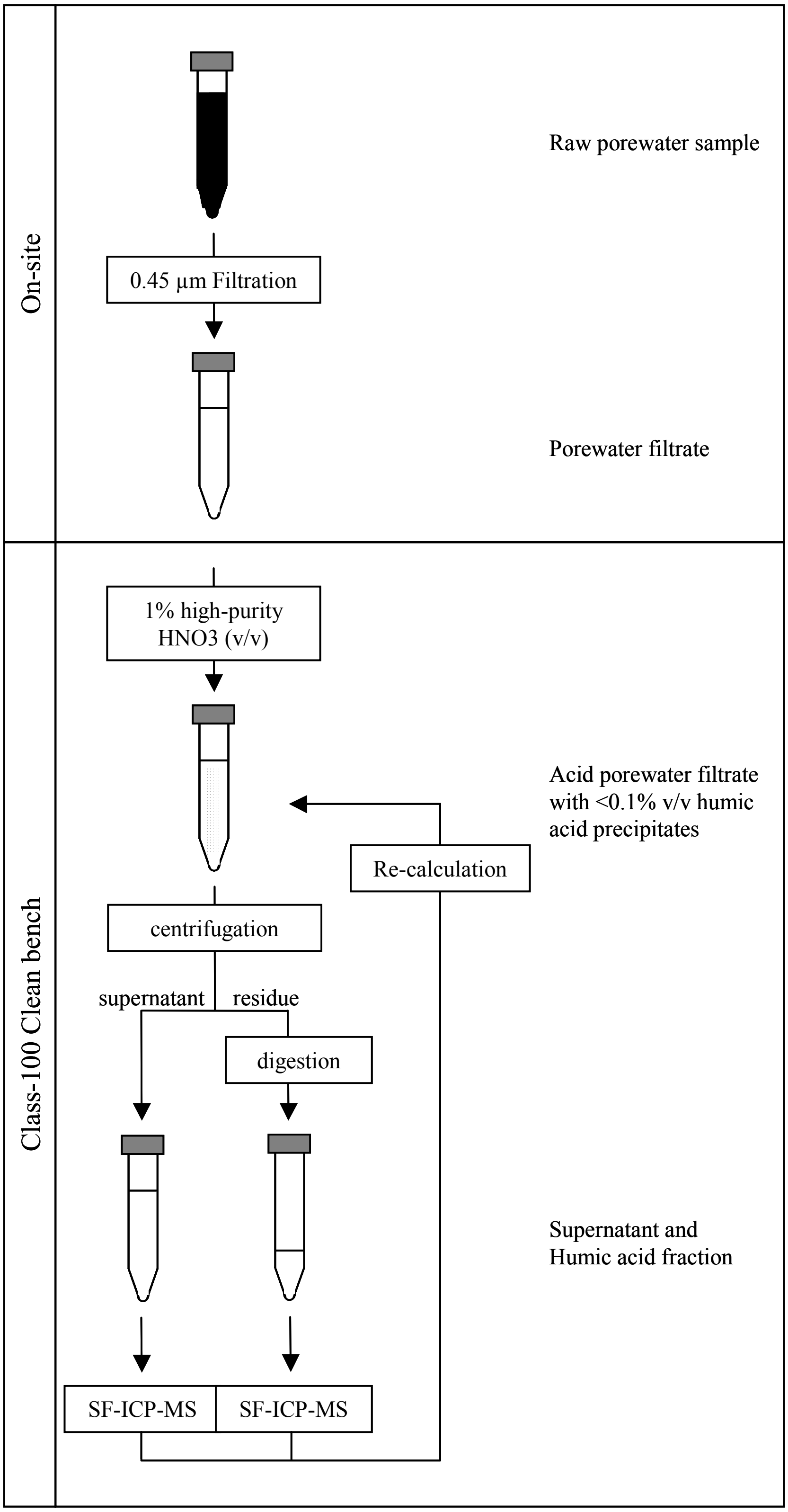


**Fig. 5.** Scheme of the porewater sampling protocol.

#### 1-3.2.2 Porewater samples

Porewater samples were collected in August 2003 using a new porewater sampler designed by the author for sampling ombrotrophic peat bogs and yielding low blank values for trace metals. The sampler consisted of a Plexiglas syringe (80 cm length) containing a 15 ml polypropylene (PP) sample bottle. Holes (3 mm diameter) allowed the raw porewater to flow directly into the sampling tubes. A scheme of the subsequent sample treatment is presented in Fig. 5. All steps were optimized to reduce potential contamination of samples, and followed strict quality control procedures in accordance with the guidelines of the Natural Resources of Canada for the collection of natural water samples (McQuaker 1999).

Blank values of the sampling device (including syringe filter, Plexiglas sampler, sampling tubes and the amount of $HNO_3$ used for sample stabilisation) as well as of field blanks representing the atmospheric input during the on-site filtration are given in Chapter 2, Table 10. The contamination of Cu, Mn and in particular of Zn by atmospheric dust during filtration might be overestimated at HIJ, as only one of the two field blanks was contaminated by these elements (as shown by high standard deviations), and Zn concentrations of most HIJ porewater samples were 60% of the field blank. Porewater concentrations of Co, Cr, Cu, Mo, Ni, Sc and Zn in some of the HIJ or OUT samples were at the level of blanks (sampling device and atmospheric dust).

In addition, a Hesslein-type *in-situ* porewater sampler (Hesslein 1976) also called a "peeper", was used to collect porewater from HIJ and OUT *via* dialysis. The peeper was carefully leached prior to use and peeper preparations were done in a glove bag. Despite this, the blank levels of all elements are higher for the peeper method than for the syringe-type sampler except for Sc and Mn, which have similar blank levels (Chapter 2, Table 7 and 8).

A detailed description of the sampler designs, the sampling protocols and the evaluation of both sampling methods is given in Chapter 2. The depth of porewater samples are given in centimetres below the surface (living vegetation).

### 1-3.3 ANALYTICAL TECHNIQUES

A summary of the analytical techniques used in this study as well as the parameters analysed and their importance is given in Table 2. All methods and analytical techniques are described in Chapters 2 to 6, and Appendix 1 and 3. The author is responsible for all analyses except where other persons are indicated.

**Table 2.** Objectives, parameter and analytical techniques performed on peat and porewater samples.

| Objectives | Parameter analysed | Analytical techniques[a] / models | Peat samples | Porewater samples |
|---|---|---|---|---|
| Metal concentrations | Cd[b], Co | ICP-SF-MS (GF-AAS[b])<br>ICP-OES | HIJ, OUT<br>HAR | HIJ, OUT, HAR, ALK |
| | Cu, Ni[b] | ICP-SF-MS (GF-AAS[b])<br>ICP-OES<br>XRF (EMMA) | HIJ, OUT<br>HAR<br>ALK | HIJ, OUT, HAR, ALK |
| | Zn | XRF (EMMA) | HIJ, OUT, HAR, ALK | HIJ, OUT, HAR, ALK |
| Age dating | $^{210}$Pb | LB γ-spec / $^{210}$Pb CRS model | HIJ, top 25 cm<br>OUT, top 39 cm<br>HAR, top 14 cm | |
| | $^{14}$C | AMS / $^{14}$C bomb pulse curve<br>AMS /$^{14}$C conventional | HIJ, OUT, HAR (sel)[c]<br>HIJ, OUT, HAR (sel)[c] | |
| Characterization of solid particles | bulk composition | SEM/EDX | OUT (14, 34 cm)<br>HAR (13, 17 cm) | |
| Characterization of humification / peat accumulation | Humification | Light Absorbance | HIJ, OUT, HAR, ALK | |
| | Density | Density calculation | HIJ, OUT, HAR, ALK | |
| | C | CS-Analyzer | HIJ, OUT, HAR | |
| Indicator of ombrotrophic conditions | Sr, Ca | XRF (EMMA, TITAN) | HIJ, OUT, HAR | |
| | | ICP-SF-MS | | HIJ, OUT, HAR, ALK |
| | ash | Combustion at 550 °C | HIJ, OUT, HAR (sel)[c] | |
| | pH | pH electrode | | HIJ, OUT, HAR, ALK |
| Indicator of natural dust deposition | Sc | ICP-SF-MS<br>ICP-OES | HIJ, OUT<br>HAR | HIJ, OUT, HAR, ALK |
| | Ti | XRF (TITAN) | HIJ, OUT, HAR | |
| | | ICP-SF-MS | | HIJ, OUT, HAR, ALK |
| | ash | Combustion | HIJ, OUT, HAR (sel)[d] | |
| Influence of S-Fe cycle on trace metal distribution | S | CS-Analyzer | HIJ, OUT, HAR | |
| | | Ion chromatography | | HIJ, OUT, HAR, ALK |
| | Fe | XRF (EMMA) | HIJ, OUT, HAR, ALK | |
| | | ICP-SF-MS | | HIJ, OUT, HAR, ALK |
| pH | pH | pH electrode | HIJ, OUT, HAR | HIJ, OUT, HAR, ALK |

[a] ICP-SF-MS: Inductively coupled plasma sector-field mass spectrometry. GF-AAS: Graphite furnace atomic absorption analysis. ICP-OES: Inductively coupled plasma optical emission spectrometry; XRF: X-Ray fluorescence spectrometry. EMMA: Energy-dispersive miniprobe multielement analyzer. LB γ-spec: Low background gamma-spectrometry; CRS model: Constant rate of supply; AMS: Accelerator mass spectrometry; SEM/EDX: Scanning electron microscopy with energy-dispersive X-ray microanalysis; TITAN: Energy-dispersive XRF spectrometer for Ti determination.

[b] Before the ICP-SF-MS was installed at the Institute, Cd and Ni concentrations in the OUT core had been determined using GF-AAS.

[c] sel: Selected samples only; macrofossils of *Sphagnum* species separated from 5 samples of both the upper section of the cores ($^{14}$C bomb pulse curve age dating) and the deeper part of the core (conventional $^{14}$C age dating).

[d] sel: Selected samples only.

### 1-3.3.1 ICP sector-field MS

Metals at the low concentration range (ng L-1 level and max. 50 µg g-1, respectively) were determined using an Element2 (Thermo Electron, Germany) ICP sector-field MS (ICP-SF-MS). Powdered peat samples and certified plant reference materials were digested in duplicate using a microwave-heated high-pressure autoclave (ultraCLAVE II, MLS) employing high-purity reagents (subboiled HNO3, H2O2 and HBF4) as described elsewhere (Krachler et al. 2003). Acidified porewater filtrates were treated as shown in Fig. 5 and analyzed together with certified River Water reference materials (Table 3).

Table 3 summarizes the general performance of the ICP-SF-MS for the trace metal determinations, and the improvements for blank reduction required for porewater analyses. The complete protocols are described in Chapter 5 (peat samples) and Chapters 2 and 6 (porewater samples). Limits of detection (LODs) obtained for the porewater analyses are given in Table 10. Concentrations of elements in the reference materials were within the certified range or differed less than 9% from the certified value except of SLRS-2, where sub-samples were stored in polypropylene sampling tubes (Falcon, Becton Dickinson) before the analyses were performed.

In a second run, Fe as well as major cations were determined using a prototype of a HF-resistant tandem spray chamber. It consisted of a cyclonic and a Scott-type spray chamber made from PFA and PEEK. Details are found in Chapter 3.

### 1-3.3.2 ICP-OES and graphite furnace AAS

Trace metal concentrations of the HAR core containing up to 600 µg $g^{-1}$ Cu were determined using ICP-OES (Vista MPX, Varian). Peat digests performed as described in 1-3.3.1 were analyzed without dilution using an inert Sturman-Masters cyclone spray chamber and V-slit nebulizer. For Cu, Ni, Co and Cd determinations, Sc was used as internal standard. The LODs of the ICP-OES analysis, referring to solid samples, were as follows (in µg $g^{-1}$): Cd 0.006, Co 0.05, Cr 0.05, Cu 0.03, Ni 0.05, Sc 0.001, V 0.04. The certified reference material CTA-VTL-1 Virginia Tobacco Leaves was digested and analyzed twice per batch. Concentrations determined were within the certified range or deviate less than 12% from the certified value.

Before the ICP-SF-MS was installed at the Institute, Cd and Ni concentrations in the OUT core were determined on separate digests using graphite furnace atomic absorption spectrometry (GF-AAS) (Analytik Jena). The general performances were given in Table 4.

**Table 3.** Summary on the general performance of the SF-ICP-MS analyses of trace metals.

| | |
|---|---|
| Equipment | ELEMENT2 (Thermo Electron, Germany),<br>Guard electrode,<br>Sapphire injector tube<br>Ni-cones, coated for 10 min with sample matrix |
| Working conditions | Sample preparation in Class-100 clean benches<br>Sample introduction system and plasma region hosted in Class-100 clean benches |
| Reagents | $H_2O$, Milli-Q-Element system (Millipore, USA)<br>65% $HNO_3$ p.a., purified by sub-boiling (MLS, Germany) |
| Element masses | $^{111}$Cd, $^{59}$Co, $^{52}$Cr, $^{63}$Cu, $^{56}$Fe, $^{55}$Mn, $^{95}$Mo, $^{60}$Ni, $^{208}$Pb, $^{45}$Sc, $^{51}$V, $^{66}$Zn |
| Resolution (m/Δm) | 300 Cd, Mo, Pb<br>4000 Co, Cr, Cu, Fe, Mn, Mo, Ni, Sc, V, Zn |
| Sample introduction system | Micro-Flow PFA-100 nebulizer<br>PFA Scott-type spray chamber<br>Self-aspirating mode |
| Internal Standard | In, ~1 µg $L^{-1}$ |
| Certified Reference Materials | Peat: NIST SRM 1573 A Tomato Leaves;<br>CTA-OTL-1 Oriental Tobacco Leaves<br>Porewater: NRCC SLRS-2 River Water<br>NRCC SLRS-4 River Water |
| Improvements for porewater analyses (blank reduction) | Acid leaching of Teflon sample cups (40% $HNO_3$, 50°C, 10 hours)<br>Pre-rinsing of pipette tips (5% v/v $HNO_3$ – 1% v/v $HNO_3$ – $H_2O$)<br>2-fold purification of $HNO_3$ (MLS, Germany)<br>Wash solution with additive (Krachler et al. 2005) |

#### 1-3.3.3 X-Ray fluorescence and neutron activation analysis

Determination of Zn and Sr concentrations, as well as of high Cu and Ni concentrations (up to 1 mg g-1) in powdered peat samples were performed using a X-ray fluorescence analyser (XRF) optimized for transition elements (EMMA) as described elsewhere (Cheburkin and Shotyk 1996). The LODs were as follows (µg g-1): Cu 2, Ni 2.5, Zn 1.5, Sr 1. The TITAN XRF analyser (Cheburkin and Shotyk 2005) optimized for Ti, was used for the determination of Ti, Ca and Cl concentrations. The following LODs were obtained (µg g-1): Ti 1.5, Ca 10, and Cl 100. All XRF analyses were performed by A. K. Cheburkin (University of Heidelberg) using various certified plant reference materials for calibration.

Concentrations of Sc in samples of the HAR core as well as two unlabeled reference materials were determined using neutron activation analysis (NAA) at ACTLABS (Ancaster, Ontario, Canada). Results of the reference materials were not in the certified range (GBW 07602, Bush Branches and Leaves: 0.13 vs. certified 0.31 ± 0.02 µg $g^{-1}$ Sc; CTA-OTL-1, Oriental Tobacco Leaves: 0.55 vs. ~0.38 µg $g^{-1}$ Sc).

**Table 4.** Performances of the GF-AAS analyses of Cd and Ni.

| | Wave length [nm] | Injection volume [µL] | modifier | Pyrolysis temperature [°C] | Atomization temperature [°C] |
|---|---|---|---|---|---|
| Cd | 228.8 | 20 | Pd-Nitrate | 650 | 1500 |
| Ni | 232.0 | 20 | - | 900 | 2200 |

### 1-3.3.4 Low-background γ-spectrometry and $^{210}$Pb age dating

Activities of $^{210}$Pb were determined in bulk samples of peat powder using low-background γ-spectrometry (GCW 4028 HPGE, Canberra). Ages were calculated using the constant rate of supply (CRS) model as described elsewhere (Appleby 2004). Data were provided by G. Le Roux and A. K. Cheburkin (University of Heidelberg). More details are given in Chapter 5. All age dates of peat samples given in the text are expressed in ages A.D. and refer to $^{210}$Pb age dates unless other methods are indicated.

### 1-3.3.5 Accelerator mass spectrometry and $^{14}$C age dating

Macrofossils selected from wet peat slices were age dated using accelerator mass spectrometry (AMS). The conventional (calibrated) radiocarbon age dates were provided by D. G. Bonani (ETH Zürich). Details are described in Chapter 5. For dating macrofossil samples accumulated within the last 50 years using the bomb pulse curve method (b.p.c.), the calibrated ages were graphically evaluated using the general-purpose curve derived from annually averaged atmospheric $^{14}$CO2 values in the northernmost northern hemisphere; this curve reflects the elevated $^{14}$C concentrations in the atmosphere due to nuclear weapons testing (Fig. 6). This method has been successfully used to date peat accumulation with an accuracy of ±2 years (Goodsite et al. 2001; Goslar et al. 2005).

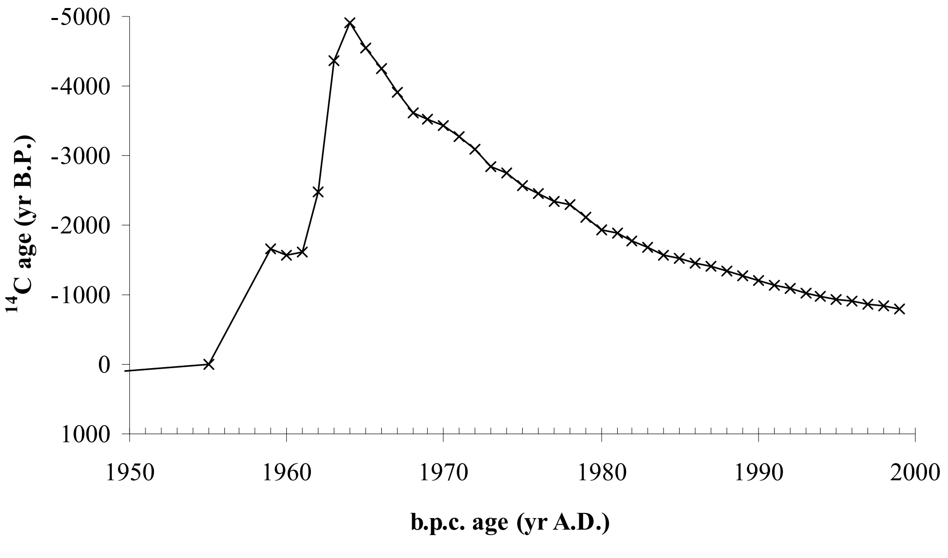


**Fig. 6.** The bomb pulse curve (calculated by Jan Heinemeier 2002).

### 1-3.3.6 Scanning electron microscopy

Particle analysis was performed using a Leo 440 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray micro-analysis unit (EDX) (Zeiss, Germany, and Link-Isis, Oxford Instruments, UK), operated at an acceleration voltage of 20 kV and a beam current of 0.5 to 2 nA. Two samples containing maximum Cu concentrations at OUT and HAR (depths of 14 cm and 13 cm), and two samples of elevated Cu concentrations of pre-industrial ages (determined using $^{210}$Pb) were prepared using size-fractionation in order to separate the organic matter and to enrich solid particles in smaller fractions. Frozen peat samples were thawed and size-fractioned inside a protective Plexiglas chamber using sieves of 2 mm, 200 µm, 63µm and 2 µm mesh size. Each fraction was rinsed until the rinse solution was clear. The fraction < 2µm consisting of approx. 1 L of rinsing solution was filtered until clogging using a 0.45 µm syringe filter (polycarbonate). Samples of the fractions > 200 µm, > 63 µm, > 20 µm and < 20 µm were oven-dried at 30° C on filter paper. Filters were glued on a sample plate and coated with carbon. In order to identify metal-rich phases among the abundance of organic particles, backscatter mapping was used.

### 1-3.3.7 UV-VIS spectrometry, CS-analyzer and density

Powdered peat samples (0.02 g) were extracted at approx. 90°C using 10 ml of 8% NaOH solution (1 hour). The solution is made up to 20 ml with deionised water, shaken and filtered through filter papers (Schleicher & Schuell). Samples were diluted (1:1) using deionised water directly before colorimetric measurements using a UV-VIS spectrometer ($\lambda$=550 nm). Details are found elsewhere (Blackford and Chambers 1993; Roos-Barraclough et al. 2004). The humification data were provided by H. Wild (University of Heidelberg). Carbon and S concentrations of powdered peat samples were determined using a Leco SC-144 analyzer (Leco, USA). Density was calculated after determining the thickness (± 0.1 mm) as well as the wet and dry weight of three single plugs with defined area, obtained from the inner part of each frozen peat slice.

### 1-3.3.8 TOC analyzer, ion chromatography and pH measurements

Dissolved organic carbon (DOC) was measured in filtered and acidified porewater samples (3% $H_2SO_4$ v/v) using a TOC analyzer (TOC-5000, Shimadzu, Japan).

The analysis of inorganic S (as determined as sulfate) was performed on filtered porewater samples using a Dionex DX-120 ion chromatograph (Dionex, USA) equipped with an AS14A column, AS RS suppressor and a conductivity detector.

The pH was measured on fresh, unfiltered porewater samples immediately after the collection using a pH electrode (Inlab 412, Ingold, Switzerland).

## 1-4 Results and Discussion

### 1-4.1 ANALYTICAL SECTION

### 1-4.1.1 Syringe-type porewater sampler vs. the peeper method (Chapter 2)

The major advantages of the syringe-type sampler were its low metal blank values and its speed and simplicity. However, there are two drawbacks of the syringe-type sampler: The macroporosity of peat may cause preferential flow during suction, obscuring concentration patterns (Blodau and Moore 2002). Further, filtration artefacts due to filter clogging and/or the interference between colloidally associated metals and the membrane occurred (see Chapter 1-4.2.2.2). Although the peeper method would be less affected by preferential flow and filtration artefacts (Blodau and Moore 2002; Buffle et al. 1992), it was not possible to establish reliable concentration profiles at these concentration levels with the exception of Co and Mn.

### 1-4.1.2 Inter-method comparison of trace metal analysis (Appendix 2)

Although maximum metal concentrations considerably differ between HIJ, OUT, HAR and ALK, deeper layers of each core were found to have similar low concentrations (e.g. Cu ~1 µg $g^{-1}$) (Chapter 5, Fig. 22). However, for direct comparison of concentrations performed with ICP-SF-MS (HIJ, OUT) and ICP-OES (HAR), respectively, the concentration bias resulting from systematic errors of the analyses had to be quantified.

An inter-method comparison based on regression analysis of 11 HAR peat digests (Appendix 2) showed statistically significant correlations between ICP-SF-MS and ICP-OES data for all elements ($r \geq 0.99$; n=11; $p < 0.01$). Relative systematic errors were ≤ 4% for Cd, Co, Cu and Ni concentrations, and 7% and 14% for Cr and V, respectively. The constant systematic errors were as follows (in µg $g^{-1}$): ≤ 0.02 (Cd and Co), 0.06 (Ni), 0.07 (Cr), 0.48 (Cu) and 22 (V). Although the constant systematic error of Cu and Cd analyses between SF-ICP-MS and ICP-OES accounts for approx. 50% of mean concentrations in deep layers, it is within the natural variation of Cu and Cd concentrations in deeper peat layers of the HAR core.

The comparison between metal (Cd and Ni, respectively) concentrations obtained using ICP-SF-MS and GF-AAS was based on regression analysis of 80 samples of the OUT core, each of them analyzed in duplicate digestions (separate digestions for ICP-SF-MS and GF-

AAS). The correlations were statistically significant ($r \geq 0.81$; $n \geq 77$; $p < 0.01$). The relative systematic errors were 14% (Cd) and 5% (Ni), and the constant systematic errors 0.03 (Cd) and 0.23 (Ni) µg $g^{-1}$.

Although Sc concentrations were determined without using an internal standard for the ICP-OES analyses, the correlation between ICP-SF-MS and ICP-OES was better than that between ICP-SF-MS and NAA (r=0.99 and 0.86, respectively), and systematic errors were lower (13% and 0.010 µg $g^{-1}$, and 300% and 0.055 µg $g^{-1}$, respectively).

## 1-4.2 PEAT BOGS AS ARCHIVES

### 1-4.2.1 Characterization of bulk peat samples

#### *1-4.2.1.1 General description (Chapter 5, Appendix 3, 4)*

The HIJ core (80 cm long) covered a much longer time period (until ~630 B.C.) than the OUT core (85 cm, until ~600 A.D.) and the HAR core (70 cm, until ~1100/1200 A.D.). The increasing degree of decomposition with depth (Chapter 5, Fig. 21) was consistent with the increasing ages of the peat layers in HIJ and OUT. In contrast, except for a highly decomposed zone from 14 to 30 cm which was dominated by *Eriophorum* species, the HAR core was generally less decomposed despite growth increments similar to OUT (0.08 cm $yr^{-1}$). However, peat accumulation rates were non-linear, and considering only the last 100 years, average growth increments at HAR (0.15 cm $yr^{-1}$) were considerably lower than at HIJ (0.22 cm $yr^{-1}$) and OUT (0.32 cm $yr^{-1}$) (Chapter 5). Further studies showed that these differences were related to climatic factors (Appendix 3): primarily temperature at OUT and precipitation at OUT, HAR and HIJ; in addition however, emissions from the Harjavalta smelter might have impacted the peat accumulation at HAR. Density profiles reflected the degree of decomposition very well, whereas they were independent of ash content (~ 1% at HIJ and OUT, and 0.3% to 2% at HAR).

Several parameters indicated that all cores were taken from the ombrotrophic layers of the bogs: the Ca profiles of both bulk samples (Chapter 5) and porewater samples (Appendix 4), the low ash contents of ≤ 2% and pH values of porewaters ≤ 4.

Scandium concentrations as an indicator of mineral dust input varied between 30 and 250 ng $g^{-1}$ at all sites (Chapter 5, Fig. 21), which was low compared to other continental ombrotrophic bogs (Shotyk et al. 2001).

### *1-4.2.1.2 Bulk concentrations of trace metals (Chapters 4, 5, Appendix 5)*

‘Background’ concentrations for metals in peat were calculated using the deep layers of HIJ as a reference (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) (Chapter 5, Fig. 22). At all sites and for all elements, the concentrations in deeper layers were at these background values or below the detection limit of the instrument (XRF, ICP-OES). In contrast, metal concentrations were elevated in upper layers, in particular those of Cu with up to 10,000 (ALK), 440 (HAR), 35 (OUT) and 2 (HIJ) times compared to background values (Chapter 4, Fig. 18; Appendix 5). The concentration differences were much less distinct for the other metals (Ni > Co > Cd > Zn).

At OUT and HAR the zone of elevated metal concentrations was characterized by sharp, distinct Cu and Co peaks and broad Ni peaks, and corresponded to periods of mining and smelting activity (Chapter 5, Fig. 22). In contrast, elevated Cd and Zn concentrations were found even in deeper layers. Maximum Zn concentrations were similar at all sites as well as the shape of the Zn profiles at ALK and HIJ (Chapter 5, Fig. 22; Appendix 5).

The distribution of all metals of interest, at all sites, was independent of the input of mineral dust (as indicated in the vertical Sc distribution), the degree of decomposition, and the distribution of S and Fe (Chapter 5, Fig. 21, 22; Appendix 5). There was no evidence of an influence of the underlying sediment on the metal concentrations in overlying layers.

### *1-4.2.1.3 Mineral particles in peat (Chapter 6, Appendix 6)*

The main minerals and other inorganic phases found in selected OUT and HAR peat samples were biogenic and detrital Si-oxides as well as various silicates and aluminosilicates, often Fe- and Ti-rich. They were unsorted (2 to 90 microns) and present as angular to rounded plates. There were small spheres of Ti-oxides present also. At HAR, Si-oxides and Fe-aluminosilicates were additionally present as spheres, and Ti-rich phases were more frequent than at OUT.

Although a few particles were found containing the metals of interest, it was not possible to unequivocally identify the dominant mineral phases. Total metal concentrations in peat were generally low; in order to obtain sufficient counting statistics the amount of sample investigated would have had to be considerably increased. It was not possible to enrich the samples as both particles were still associated with organic structures (e.g. *Sphagnum* leaves) and these broke down during wet sieving. While particles of interest were between ≤ 2 and 25 microns, the presence of large, uneven organic structures obstructed the electron beam as well as the emitted fluorescence. Moreover, they hindered the proper coating of the sample with conductive C leading to SEM images of poor quality (e.g. stripes). Even if single grains were present, the scattering of the electron beam excited the surrounding filter paper if particles are small in size (e.g. < 10 micron). Due to the small size and low number of particles the preparation of thin sections would be questionable unless the organic matter is removed. The destruction of organic matter using oxidizing chemicals or combustion was not possible as this would simultaneously affect the metal particles present in lower oxidation states (e.g. sulfides). A selection of SEM images and EDX spectra is given in Appendix 6.

Copper-containing particles in the layer corresponding to peaks in Cu concentrations (OUT 13, HAR 11) consisted of Cu-Fe-S with varying amounts of C-O. In HAR 11, Cu-S-C-O phases are present. Some particles might be identified either by shape or by the absence of a significant O signal as chalcopyrite. Copper-containing particles at OUT 13 were rather coarse grains (10 to 20 micron), while those at HAR 11 were smaller (≤ 10 micron) and rather thin plates. Three Ni-containing particles were found at OUT 13. The strong Ni-Cr-Fe-association suggested that particles probably originate from the sample preparation (stainless steel band saw, see chapter 1-3.2.1). At HAR 11, two groups of Ni phases were found: thin plates of Ni or Ni-Cr associations, some of them clearly without significant amounts of O and C content and mostly present as thin plates; and a few Ni-(Fe)- containing phases with distinct O-C contents and partially with traces of other metals (Cu, Zn, Co). One Zn-S-C-O containing particle was also found. The lack of the typical stainless steel association (Ni-Cr-Fe), the detectable amounts of Cu, Zn and Co as well as the presence of a metal-rich sphere suggested that at least some of the particles were related to smelter emissions.

In contrast, in layers pre-dating the mining and smelting period (OUT 33, HAR 15), Cu, Ni and Zn predominantly occurred as metal-rich phases, either separately or joint together, with varying amounts of C and mostly insignificant contents of O. In most cases, these metal-rich phases were not well-shaped and were adhering to or coating organic matter. In one case, the organic matter surrounding a Cu-Zn-Ni-rich particle contained detectable amounts of Cu, Zn, Ni and S. One particle at OUT 33 consisted of a Na-Cl-K-Ca-O association with distinct zones of elevated Zn-S contents. At HAR 15, one additional Cu-Al-Cl-O-Ca association with variable S contents was found. In some cases, Ni at HAR was associated with traces of Si.

### 1-4.2.2 Characterization of porewater samples

#### *1-4.2.2.1 General description (Chapter 6)*

The pH values at HIJ and OUT were between 3.6 and 4.0, and < 3.4 at HAR (Chapter 6, Fig. 27). Concentrations of S were highest in the top layers of HAR (25 µM), with values exceeding average rainwater concentrations at this site by 40%. Elevated concentrations were found in the intermediate layers of the OUT profile (approx. 8 µM), while S concentrations were below the LOD at HIJ. Porewaters at HAR were also rich in Fe, with concentrations in the subsurface layers seven times higher that at OUT and HIJ. Concentrations of DOC decreased downwards with values between 40 and 60 mg $L^{-1}$ at all sites.

#### *1-4.2.2.2 Effect of humic substances on the metal determination (Chapter 2)*

In general, the “dissolved metal concentrations” in water are operationally defined by a 0.45 µm filtration (Buffle et al. 1992). However, a laboratory experiment on four different filter membranes of similar filter design (0.45 µm syringe filter, 25 mm diameter) showed that concentrations strongly depend on the filter membrane used: Mean concentrations (n=3) in differently processed filtrates varied between minimum and maximum by a factor of 1.16 (Pb), 1.24 (Sc), 1.33 (Ni), 1.34 (Cd), 1.39 (Zn), 1.44 (Co), 1.62 (Mn), 2.0 (Mo) and 5.0 (Cu), while this feature was negligible for Cr and V. In natural aquatic systems, approx. 50% of the DOC content consists of humic substances (Keskitalo and Eloranta 1999). These are organic macromolecules which tend to coagulate at the filter surfaces, especially at high filtration flow rates typical for 0.45 µm filtrations (Buffle et al. 1992). Considering the high DOC content in these samples, and the high potential of the humic substances for complexing Cu and other heavy metals in water (Thurman 1985), the differences in metal (and in particular in Cu) concentrations most likely originated from the differences in agglomeration on the membranes and/or the ability of the membranes to exclude these coagulates. Similar conclusions were drawn by (Horowitz et al. 1996) who found considerable filtration artefacts for river waters, but not for a surface bog water.

Humic acids precipitated after samples were acidified for trace metal analysis. These precipitates accounted for < 0.1% v/v of the sample volume, but contained approx. 12% of the total Cu concentrations in subsurface porewater samples. In contrast, they contained 4% in the uppermost porewater sample (depth of 10 cm). Although the total contents of Cu in the humic acid fraction could not explain the high variation (factor of 5) between different filter membranes, the different proportions between the surface and subsurface layers demonstrated that significant changes in the amount and/or the composition of humic acids occurred with depth. This might explain why strong filtration artefacts occurred in the bulk porewater sample of this study (representing the depth interval of 10 to 60 cm) but not in the study of Horowitz et al (1996) performed on bog surface samples.

#### *1-4.2.2.3 Concentrations of dissolved Cu, Ni, Co, Zn and Cd (Chapter 6)*

At HIJ and OUT, porewater concentrations were in a similar range, with values of <8 nM of Cu and Ni, <1.4 nM of Co, <250 nM of Zn, and for most samples <0.3 nM Cd (Chapter 6, Fig. 28). Despite the generally low concentrations, the porewater profiles indicated a limited release of Ni and Co from solid phases in the upper layers, and of Zn and in particular Cd (10 nM of Cd) in the surface layer at OUT. In contrast, at HIJ concentrations of all metals increased downwards. Porewater concentrations at HAR exceeded those at HIJ and OUT by a factor of 2 (Zn), 10 (Cd), 20 (Co) and 100 (Cu and Ni), with high concentrations throughout the upper part of the profile (10-40 cm).

### 1-4.2.3 Metal retention and post-depositional processes

#### *1-4.2.3.1 Metal accumulation in peat vs. atmospheric deposition records (Chapter 5)*

In order to estimate the extent of metal retention in the peat layers, metal accumulation rates (ARs) were calculated as described elsewhere (Appleby 2004). Using $^{210}$Pb a continuous record for the last 100 years was obtained for HIJ, OUT and HAR (Chapter 5, Fig. 23, 24, 25). At HIJ and OUT, the $^{210}$Pb age dates were in excellent agreement with those obtained using the $^{14}$C b.p.c. method. Due to the lower activity of unsupported $^{210}$Pb and subsampling difficulties at HAR, the age uncertainty is comparatively high at HAR.

At HIJ wet and dry deposition has been continuously monitored since 1992 using bulk deposition collectors situated in an open area (Leinonen 1993; Leinonen 1994; Leinonen 1996; Leinonen 1997; Leinonen 1998; Leinonen 1999a; Leinonen 1999b; Leinonen 2000; Leinonen 2001; Leinonen and Juntto 1992). Due to the limited data set (4 peat samples within the monitoring period) and the lack of significant changes in the deposition rates, the long-term trend of metal accumulation in peat could not be evaluated. However, the HIJ site was used as a reference site and to quantify the extent of metal retention. At OUT and HAR, the trend in atmospheric metal deposition was estimated on the basis of ore production rates at the Outokumpu mines, and the emissions at the Harjavalta smelter, respectively. However, changes in the production processes (e.g. changes in grinding technologies at OUT and the increase in stack height at HAR) could have affected the net emission (and therefore also deposition) of metals at these sites.

Despite these uncertainties, Cu ARs provided an accurate reflection of the local deposition history at HIJ and OUT, suggesting quantitative retention of Cu at HIJ. Deposition data for Co was not available at HIJ. At OUT, ARs reflected the Cu mining history. Small differences between the Cu and Co concentration profiles could be explained by changes in the ore production processes. Although Ni ARs were elevated at OUT and exceeded monitoring data at HIJ, they provided a poorer reflection of the local Ni deposition histories. At HAR, Cu, Ni and Co ARs corresponded to the general trends in metal emission history. Metal inventories exceeded those at HIJ by 60 (Cu), 30 (Ni) and 7 (Co) times, respectively (Chapter 5, Table 19). However, the uncertainties of the $^{210}$Pb age dates and the poor time-resolution between adjacent samples made interpretations on the mobility of these metals at HAR difficult. A limited downward migration of Cu, Ni and Co, with vertical shifts of a few centimetres, could not be excluded at HAR.

The interpretation of Cd ARs at HIJ was difficult, as long-range atmospheric transport and emissions from forest fires must be considered. In contrast to the other elements, the significance of Cd deposition related to the mining of Cu-Ni ores at OUT is unknown. The elevated Cd ARs at HIJ compared to OUT could therefore be consistent with the deposition history, whereas the comparatively low Cd ARs at HAR suggested significant mobilisation of Cd at HAR. Zinc ARs at HIJ, OUT and HAR increased from 3 to 30 mg m$^{-2}$ yr$^{-1}$ during the past century, independent of local emission histories, suggesting that the distribution of Zn was mainly controlled by post-depositional processes.

#### *1-4.2.3.2 Metal accumulation in peat vs. porewater concentrations (Chapter 6)*

At HIJ, porewater concentrations of all metals increased downwards (Chapter 6, Fig. 28), with dissolved Zn representing up to 8% to bulk concentrations (Fig. 29). The elevated concentrations below 40 cm corresponded to highly decomposed peat layers (H7-H8 van Post scale), where the hydraulic conductivity is drastically reduced due to the breakdown of inter-connected pores and the formation of dead-end and closed pores (Baden and Eggelsmann 1963; Hoag and Price 1997). The extended equilibration time of porewaters with the solid phase might result in greater porewater concentrations compared to upper layers (H3-H6) where comparably fast advective flow dominates.

At OUT, porewater Cu concentrations were not significantly greater than at HIJ, although bulk Cu concentrations exceeded background levels up to 35 times in upper layers. Concentrations of the other metals exceeded those at HIJ by a factor of 2 (Ni), 2.5 (Zn), 7 (Co) and 25 (Cd) in corresponding layers. The strong Cd release within the surface layers and the constantly low concentrations in deeper layers suggested post-depositional redistribution. In contrast, Ni and Zn concentrations were comparatively low considering that the broad zone of elevated peat concentrations indicated post-depositional processes. The release of dissolved

Co was also inconsistent with the sharp, distinct peak in the bulk concentration profile, similar to that of Cu.

The high porewater concentrations at HAR indicated post-depositional mobilization of all metals from solid particles in the upper, contaminated layers. This was consistent with the peat profile which shows elevated metal concentrations extending into peat layers which pre-date the smelting period.

#### *1-4.2.3.3 Potential mechanisms of retention and mobilization (Chapter 6, Appendix 6, 7)*

Chalcopyrite was the dominant Cu-bearing ore at Outokumpu, and this is most likely the dominant form of Cu which was supplied to the bog in the form of dust. The same mineral was found in the peat layers accumulated during the main phase of Cu mining, where Cu concentrations were greatest. In the acid surface water of the bog, chalcopyrite might be dissolved by oxidative acid dissolution. However, the weathering of chalcopyrite is generally slow due to the formation of a Fe-depleted, Cu-S rich surface layer (Abraitis et al. 2004; Gleisner 2005), and dissolved humic matter could further protect the particles. With subsequent peat accumulation these particles became buried in the permanently anoxic waters where chalcopyrite should be thermodynamically stable in a broad pH range (Shotyk 1996). The porewater analyses confirmed that chalcopyrite dissolution was not a significant process (Chapter 6, Fig. 28). Furthermore, the SEM images showed that the mineral particles adhered to the Sphagnum leaves even after careful rinsing (Appendix 6). The thermodynamic and kinetic stability of chalcopyrite and the specific structure and "filter" capacities of the Sphagnum peat (Chapter 1-1.3) might explain the accurate reflection of mining history in peat layers (Fig. 24), and the presence of sharp and distinct peaks in Cu concentrations (Fig. 22).

Assuming that the Cu retained at OUT consisted of chalcopyrite, the corresponding Co and Ni concentrations could be estimated from the average composition of the Outokumpu ores (Table 18) and the Cu peat concentrations. This theoretical, ore-related Co concentration profile (Appendix 7) was consistent with the true Co concentration profile, indicating that Co was retained to the same extent, and probably by the same process. The Ni content of the Outokumpu ores was low, but so is the lithogenic components supplied by dusts natural (Fig. 21). The comparison of calculated ore-related inputs with the Ni concentrations in peat showed that an additional Ni source must be present (Appendix 7). Nickel was only mined during a brief period (Vuonos open pit mining, 1972-1977), and Ni concentrations in the Vuonos Ni-ore exceeded those in the Outokumpu Cu-ore by a factor of 3. Nevertheless, the total amount of ore mined at Vuonos was huge (10 Mt, compared to 5 Mt at Outokumpu) and should have resulted in a distinct Ni peak in peat layers, similar to that of Cu as long as Ni is immobile in peat. The main Ni ores were pyrrhotite and pentlandite, the former one thought to be readily attacked by oxidative dissolution (Jambor 1994; Nicholson 1994). The presence of a broad Ni peak in the peat layers (Fig. 22), together with the low release of Ni to the porewater today (Fig. 28) suggested that Ni was mobilized and redistributed during an early stage of deposition. The release of Co to the porewater could be related to this redistribution, as it was present in low amounts in the Ni-ores. The low porewater concentrations of Zn indicated that dissolution also occurs predominantly at an early stage of deposition, whereas the mobilization of Cd seemed to be more dynamic.

In contrast to OUT, at HAR the deposited particles were thought to be mainly oxides, which should readily dissolve in acid conditions. This could explain the greater porewater concentrations of all metals at HAR than at OUT. As peat layers at HAR were poorly decomposed, advective flow of the porewaters would transport dissolved metals into deeper layers. This was consistent with the elevated bulk concentrations of all metals in layers of pre-dating the smelting period.

## 1-5 Conclusions

At OUT, where Cu is predominantly deposited as chalcopyrite, both approaches – the comparison of the peat core record with the deposition history as well as porewater concentrations – indicate that Cu is well retained, together with Co. Small differences between the Co and the Cu bulk concentration profile could be either explained by differences in the deposition history or by a limited release of Co to the porewater. In contrast, Ni, Zn and Cd, also thought be deposited in form of sulfides, are most likely affected by dissolution and transport, subsequent to deposition. Further studies are needed to establish the mechanisms of retention and mobilisation, and the effect of humic substances on metal mobility. However, the results of this study suggest that the crucial point for the retention of deposited sulfides might be the oxidation of particles in the aerated surface layer of the bog.

At HAR, where metals are presumably deposited in form of oxides, all metals are affected by post-depositional mobilisation. The lower pH values here promote the dissolution of these particles. The low degree of peat decomposition at this bog might promote the transport of metals into deeper layers by advective flow of porewaters.

In respect to the use of peat bogs as archives, the following general conclusions can be drawn:

(1) Metal ARs can provide accurate records of atmospheric Cu and Co deposition related to Cu mining activities. The quality of these records is mainly dependent on the accuracy and

precision of the age dating, as well as the peat accumulation rate. Faster peat accumulation rates promote high-resolution records and reduce the residence time of particles in the acid, oxidising surface. (2) Accurate records of atmospheric metal deposition related to smelting activities are less likely. In the long-term, the bulk of deposited particles will dissolve. The dissolved metals might be subsequently removed by either the organic matter (complex formation, ion exchange) or by precipitation of stable particles (sulfides, metals). However, the extent of this redistribution will be strongly dependent on the pH and redox potential of the pore fluids, the flow velocities of the porewater, and the availability of dissolved sulphide. The reliability of chronological records of atmospheric metal deposition will probably increase with increasing distance from a given smelter.

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# ANALYTICAL SECTION

# CHAPTER 2

Rausch, N., L. Ukonmaanaho, T.M. Nieminen, M. Krachler, G. Le Roux, W. Shotyk. A syringe-type sampler for obtaining porewaters from ombrotrophic bogs, and application to trace metal (µg $L^{-1}$ to sub-µg $L^{-1}$) determinations.

*Limnology and Oceanography. Methods* (submitted 2005)

# A syringe-type sampler for obtaining porewaters from ombrotrophic bogs, and application to trace metal ($\mu g\ L^{-1}$ to sub-$\mu g\ L^{-1}$) determinations

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**Abstract.** A new sampling device was developed which is suitable for allowing trace metals to be determined in humic-rich porewaters from ombrotrophic peat bogs. The porewater sampler consists of a sampling tube with Plexiglas tube with small holes at the lower end and an internal plunger. By lifting the plunger, the raw porewater sample is collected into the sampling tube. Immediately after collection, samples were filtered through 0.45 µm syringe filters. Inductively coupled plasma sector field mass spectrometry was used for the determination of Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sc, V and Zn concentrations. Four different 0.45 µm syringe filters were tested: The degree of filtration artefacts is dependent on the element; relative standard deviations in elemental concentration across the 4 filter types range from 2% (Cr) to 72% (Cu). The lowest blank values together with sufficiently low filtration artefacts were obtained with unwashed Whatman GD/XP filters. Blank values of the sampling and filtration devices are as follows (in $\mu g\ L^{-1}$): Cd 0.001, Co 0.009, Cr 0.05, Cu 0.07, Mn 0.2, Mo 0.02, Ni 0.10, Pb 0.004, Sc 0.011, V 0.01, Zn 1; additional contamination by atmospheric dust during the filtration is significant for Cr, Cu and Zn. Natural background concentrations of investigated elements were at ng $L^{-1}$ levels except for Zn (lower $\mu g\ L^{-1}$). A peeper was also evaluated but, with the exception of Co and Mn, the peeper is not suitable for sampling porewaters at these concentration levels.

*Keywords:* peatlands; sampling method; trace metals

## Introduction

Ombrotrophic peat cores have recently proved to be meaningful archives of recent as well as ancient atmospheric Pb and Hg deposition (Benoit et al. 1998; Pheiffer-Madsen 1981; Shotyk et al. 2001; Vile et al. 1999; Weiss et al. 1999). To function as an archive, the metals must be immobile in the peat layers. Studies to date have shown that Cu, Ni, Co and Cd might be immobile in peat layers (Kempter and Frenzel 2000; Krachler et al. 2003; Mackenzie et al. 1998; Mighall et al. 2002; Shotyk et al. 2002), but this remains to be confirmed. One way to independently evaluate the potential mobilization of these metals is to establish porewater concentration profiles.

The porewaters in the saturated zone of peat bogs are anoxic, rich in colloidal humic substances as well as in particles of plant residues originating from the decomposition of organic matter. Moreover, because bog waters receive metals by atmospheric deposition only, metal concentrations are extremely low (Shotyk 1989; Steinmann and Shotyk 1997). Whereas some procedures have been successfully developed to obtain surface waters or porewater from peatlands for the determination of major ions as well as Al and Fe (Bendell-Young 2003; Blodau et al. 2002; Gorham et al. 1985; Shotyk 1989; Steinmann and Shotyk 1997; Urban et al. 1987; Urban et al. 1989), no procedure exists to establish porewater profiles of transition metals.

In this study, we developed a new sampling device suitable for collecting porewaters from ombrotrophic peat bogs for the determination of Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sc, V and Zn concentrations at ultratrace levels. It consists of a sampling tube with Plexiglas tube with small holes at the lower end and an internal plunger. By lifting the plunger, the raw porewater sample is collected into the sampling tube and can be immediately filtered at the sampling site. This procedure is inexpensive, rapid, easy-to-use and results in low blank values. In addition, we used a peeper (Hesslein 1976) to simultaneously collect porewater samples via dialysis. The goal of this study is to establish a reliable procedure for collecting porewater samples from ombrotrophic peat bogs of remote and contaminated sites and to establish concentration ranges of Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sc, V and Zn at these sites.

## Materials and Procedures

### SAMPLE COLLECTION USING THE POREWATER SAMPLER

The porewater sampler consists of a Plexiglas tube with screw thread at the bottom end which fits to 15 ml polypropylene (PP) conical centrifuge tubes (Greiner Bio-One, Frickenhausen, Germany) (Fig. 7). The interior of the Plexiglas tube is capped by a sealed, movable plunger with a nylon head. Above the screw thread, holes (3 mm diameter) allow the porewater to flow into the sampling tubes. Assuming an average water content of 75% v/v in peat, a final volume of 10 ml porewater sample corresponds to a catchment of a theoretical sphere of 1.5 cm radius; this allows sampling intervals of > 3 cm.

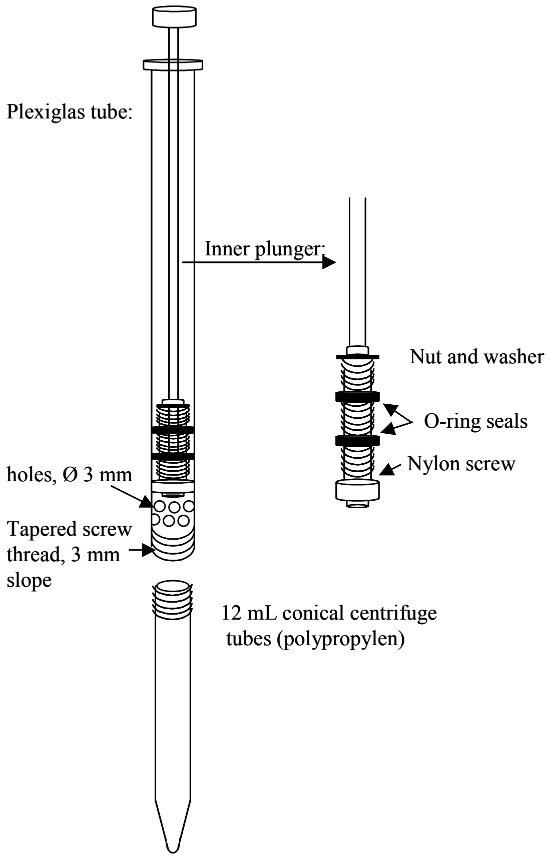

**Fig. 7.** The syringe-type sampler consists of a Plexiglas tube with screw thread at the bottom end, fitting to 15 ml PP conical centrifuge tubes. The interior of the Plexiglas tube is caped by a sealed, movable plunger with nylon head. Above the screw thread, small holes are drilled through which the porewater flows into the sampling tubes when moving the plunger upwards.

For the collection of a porewater sample, a new PP sampling tube is fixed at the bottom end of the Plexiglas tube and capped by pushing down the inner plunger. The sampling device is slowly pushed down until the holes reach the desired depth. A slight vacuum is applied by carefully pulling the inner plunger in the range of one to several cm; the necessary vacuum depends on the water holding capacity and density of the peat. Within 5 to 10 min, the raw porewater drops into the sampling tube. The plunger is pushed down to close the sampling tube and the bog porewater sampler is lifted to surface. In order to obtain the dissolved fraction, the raw porewater sample (~ 10 ml) is immediately filtered into a new PP sampling tube using a 0.45 µm GD/XP PVDF 25 mm syringe filter (Whatman, Brentford, United Kingdom) and a 10 ml plastic syringe (Discardit$^{TM}$ II, Becton Dickinson & Co, Franklin Lakes, NJ, USA). Contact of samples with the atmosphere could be minimized by rapidly decanting into plastic syringes and capping the second sampling tube by the filter device during the filtration. Gloves made of latex or polyethylene (PE) were used during all steps. A sample volume of 10 ml allows sampling in 3 cm intervals. In order to avoid disturbance of the porewater profile, the sampling device should be pushed slowly downwards into the peat, without using the same sample hole twice. In this study, samples were collected in 5 cm intervals in triplicate representing a total area of approximately 16 m$^2$. Field blanks (n=2 or 3) were established by processing high-purity water through GD/XP filters in the field (without using the sampling device) at each sampling site. Filtered samples and blanks were packed into plastic bags and kept as cool as possible until arrival in the laboratory. In the case of the Finnish samples, the porewaters were maintained between 6-13°C for a maximum of nine days.

### SAMPLE COLLECTION USING THE PEEPER

A Hesslein-type in-situ porewater sampler (Hesslein 1976), also called a "peeper", was used to collect porewater from ombrotrophic peat bogs via dialysis. Sample chambers were arranged at 1 cm intervals, in two columns which allows sampling in duplicate. Each chamber has a volume of approximately 4 ml. The peeper body and the membrane-fixing cover are made of Plexiglas; nylon screws fix the cover with the peeper body.

Before use, the peeper body, the Plexiglas cover and the Nylon screws were leached in 10% HNO3 for two weeks then carefully rinsed with water and dried in a class-100 clean bench. The cleaned peeper was wrapped with PE foil and packed into a plastic bag to prevent re-contamination by dust. At the sampling site, peeper chambers were filled with water which was deaerated at the sampling site by flushing with N2 (instrumental-grade) in order to avoid metal losses due to oxidation of reduced metal species (Bufflap and Allen 1995). Subsequently chambers were covered with a carefully pre-cleaned Nuclepore Polycarbonate membrane of 0.45 µm pore size (Whatman) using PE gloves and plastic tweezers. In order to avoid metal contamination by atmospheric dust, the whole preparation should be performed either in a clean room facility or in a N2-flushed glove bag in the field. Using a clean room facility, the prepared peeper must be stored in a N2 filled glove bag until its installation at the sampling site in order to avoid contamination as well as re-aeration of the sample chambers. In both cases, contamination by atmospheric dust must be controlled by subsampling field blanks of the water used for the replenishment of peeper chambers (n=2 to 3) at the end of the peeper preparation at the sampling site.

Peepers installed in the peat bog were removed after six weeks of equilibration time. The membrane surface was briefly rinsed with water and the peeper put immediately into a N2-flushed PE glove bag. Within this glove bag, a 10 ml multipipette with exchangeable PE dispenser tips (Eppendorf, Hamburg, Germany) were used to pierce the membrane and transfer the porewater samples from the peeper chambers into PP tubes. Sample handling and storage during the field trip was done as described above.

### SAMPLE TREATMENT AFTER COLLECTION

Upon arrival in the laboratory, samples were acidified to 1% v/v in a class 100 laminar flow bench using $HNO_3$ (see below); they were stored at -18°C until the analyses in order to reduce potential leaching of trace metals from the sample tubes. In cases where humic acids (HAs) precipitated in the filtrate, samples are centrifuged for 10 min at 3000 rpm after recording the volume of the filtrate. The supernatant was decanted, and the residue covered with 25 µL of concentrated $HNO_3$. After 30 min, 2.48 mL $H_2O$ was added to obtain a final "digestion" solution of 1% v/v $HNO_3$. Metal concentrations of this digested final solution were re-calculated to the original concentration in the filtrate. Total metal concentrations were then calculated by summing the concentrations of metals in both the residue and the supernatant fraction.

### INSTRUMENTATION AND REAGENTS FOR METAL ANALYSIS

Measurements were carried out with an ICP-sector-field-MS (ICP-SF-MS) (Element2, Thermo Electron, Bremen, Germany) equipped with a guard electrode to eliminate secondary discharge in the plasma and to enhance overall sensitivity. A sample introduction kit consisting of a microflow PFA nebulizer, a Scott-type PFA spray chamber and a sapphire injector tube were used to reduce blank levels. The entire sample introduction system, including the autosampler and the plasma region of the ICP-SF-MS, is hosted in a class 100 laminar flow bench. All sample handling and the preparation of all standards were performed in clean rooms under laminar flow clean air benches of class 100 to minimize the potential risk of contamination. For the preparation of all solutions, water from the Milli-Q-Element system (Millipore, Milford, Massachusetts, USA) is used. This high-purity water is used throughout the experiments. Nitric acid (65%, analytical-reagent grade) is further purified twice by distillation, using a quartz unit for sub-boiling of acids (MLS GmbH, Leutkirch, Germany). Both the water and the acid purification system are operated in a clean room. All calibration standards and all samples were acidified using this high-purity $HNO_3$ (1% v/v). Pipette tips were pre-cleaned before use employing three subsequent rinse solutions (5% v/v $HNO_3$ – 1% v/v $HNO_3$ – $H_2O$). To correct for instrumental drifts and plasma fluctuations, all analyte solutions were spiked with an indium standard solution to a final concentration of 1.3 $\mu g\ L^{-1}$. Blank values of the untreated PP sampling tubes are below the limit of quantitation with the exception of Co (0.006 $\mu g\ L^{-1}$) and Cr (0.03 $\mu g\ L^{-1}$). Operating conditions of the ICP-SF-MS are given in Table 5. The protocol and reagents employed here have been used to successfully measure trace elements in polar ice (Krachler et al. 2005).

**Table 5**. Operating parameters of the ICP-SF-MS using a self-aspirating microflow sample introduction system.

| | | |
|---|---|---|
| Tune parameters | | |
| Gas flows [L min$^{-1}$] | | |
| Sample | 1.0 | |
| Additional | 0.07 | |
| Auxilliary | 0.6 | |
| Cool | 16 | |
| Sample uptake [s] | 130 | |
| Sample wash [s] | 60 | |
| Sample flow rate [μL min$^{-1}$] | 50 | |
| RF power [W] | 1270 | |
| | | |
| Acquisition parameters | $m/\Delta m \sim 300$ | $m/\Delta m \sim 4000$ |
| Mass window (%) | 90 | 85 |
| Samples/peak | 20 (Cd: 35) | 20-30 |
| Sample time [ms] | 0.01 | 0.015 |
| Runs | 5 | 6 |
| Passes | 5 | 6 |
| | | |
| Evaluation parameters | Low Resolution | Medium Resolution |
| Search window [%] | 75 | 60 |
| Integration window [%] | 60-80 | 50-80 |
| Integration type | average | average |

## Assessment

### QUALITY CONTROL

The reliable determination of metal concentrations at sub-μg L$^{-1}$ levels required a rigid quality control protocol. Two river water reference materials with certified elemental concentrations, SLRS-2 and SLRS-4 (National Research Council Canada, Ottawa, Canada) were analyzed twice with every batch of samples to ensure the accuracy of the measurements. Comparison of the measured values with certified values in the reference materials showed excellent to good agreement for all elements except for Zn in SLRS-2 (Table 6). Additionally, a composite porewater reference sample (PW sample), mixed from filtered, acidified and centrifuged porewater samples of different sample depths, collected at the Outokumpu site in Finland (see below), was also analyzed twice per batch to evaluate the influence of sample matrix on the precision of the measurements. With the exception of Mo and Sc, the relative standard deviations (RSDs) of the bulk porewater sample ranged between 7% and 14% (n=2 measurements on m=10 days), which is similar or even better than the corresponding RSD of the standard reference material with similar concentrations (data not shown). In cases where total RSDs were considerably higher for the porewater sample than for the reference materials (i.e. 39% for Mo and 69% for Sc), the corresponding elemental concentrations in the porewater sample were at the limit of quantitation. Therefore, we conclude that the determination of elemental concentrations in porewater samples is not affected by sample matrix effects. All potential contamination sources were carefully controlled by processing blank values similar to the sample treatment (see below).

### TEST SITES

For preliminary experiments, two sampling sites in rural areas at the Black Forest, SW Germany were chosen: BF1, the ombrotrophic peat bog “Kaltenbronn” near Gernspach, was used to collect porewater samples from different depths to finally obtain a bulk porewater sample used for a laboratory filtration experiment for the syringe-type sampler method; BF2, the ombrotrophic peat bog “Kohlhüttenmoor” near St. Blasien, was used to install a peeper to test two different membranes regarding their metal permeability. Following the experiences gained by these pilot studies, three sites in Finland with different levels of atmospheric metal contamination were sampled: site HIJ, near the lake Hietajärvi in the Patvinsuo National Park, Eastern Finland, where the level of atmospheric deposition is at background values (Ilyin et al. 2002; Poikolainen et al. 2004); OUT, near the small town Outokumpu, Eastern Finland where Cu-Ni ores have been mined in former days; and HAR, near the town Harjavalta, located in the populated and strongly industrialized southwestern part of Finland.

### SELECTION OF FILTERS FOR THE BOG POREWATER SAMPLER

The operational definition for dissolved constituents is based on processing whole-water samples through a 0.45 µm membrane filter. However, some studies have shown that a number of factors associated with filtration, other than just pore size (e.g. diameter, manufacturer, volume of sample processed, amount of suspended particles in the sample), can produce substantial variations in the ‘dissolved’ concentrations of e.g. Cu, Zn, Pb, Co, and Ni (Hall et al. 1996; Horowitz et al. 1996); these variations result from the inclusion/exclusion of colloidally-associated trace elements. Due to the continuous decay of organic material in peat bogs, water samples taken from peat bogs are rich in humic substances, which range from colloidal, higher molecular weight humic acids to lower molecular weight fulvic acids. Furthermore, the ‘raw’ porewater of an ombrotrophic peat bog is usually dark brown and opaque due to a high particle load (mainly pieces of plants, but also humic colloids), which

**Table 6**. Accuracy of SLRS-4 and SLRS-2 and precision of the measurements, as well as of GD/XP filtrates and of real samples. Concentrations given in µg $L^{-1}$.

| | Concentrations [µg $L^{-1}$] | | | | | RSDs [%] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SLRS-4 | | SLRS-2 | | PW sample | measurement (within-run)[a] | | | Filtrates[b] | Samples[c] |
| | found (n=20) | certified | found (n=20) | certified | (n=18) | SLRS-4 | SLRS-2 | PW | GD/XP | |
| Cd | 0.014 ± 0.001 | 0.012 ± 0.002 | 0.037 ± 0.004 | 0.028 ± 0.004 | 0.030 ± 0.002 | 3.6 | 6.2 | 2.9 | 28 | 12-20 |
| Co | 0.035 ± 0.003 | 0.033 ± 0.006 | 0.083 ± 0.007 | 0.063 ± 0.012 | 0.058 ± 0.004 | 3.7 | 1.8 | 2.5 | 27 | 22-24 |
| Cr | 0.31 ± 0.03 | 0.33 ± 0.02 | 0.44 ± 0.04 | 0.45 ± 0.07 | 0.13 ± 0.01 | 1.7 | 2.1 | 4.4 | 8.9 | 17-24 |
| Cu | 1.84 ± 0.19 | 1.81 ± 0.08 | 3.10 ± 0.30 | 2.76 ± 0.17 | 0.29 ± 0.03 | 1.9 | 2.1 | 9.3 | 88 | 16-27 |
| Mn | 3.39 ± 0.34 | 3.37 ± 0.18 | 10.3 ± 1.0 | 10.1 ± 0.3 | 2.1 ± 0.2 | 1.4 | 1.6 | 2.1 | 45 | 20-30 |
| Mo | 0.20 ± 0.04 | 0.21 ± 0.02 | 0.17 ± 0.02 | 0.16 ± 0.02 | 0.013 ± 0.004 | 1.9 | 6.0 | 6.8 | 82 | 16-36 |
| Ni | 0.71 ± 0.07 | 0.67 ± 0.08 | 1.08 ± 0.09 | 1.03 ± 0.10 | 0.32 ± 0.03 | 1.5 | 1.9 | 4.2 | 20 | 21-24 |
| Pb | 0.082 ± 0.018 | 0.086 ± 0.007 | 0.149 ± 0.028 | 0.129 ± 0.011 | 0.212 ± 0.011 | 12.6 | 3.6 | 2.3 | 13 | 19-27 |
| Sc | 0.015 ± 0.003 | - [d] | 0.013 ± 0.003 | - [d] | 0.005 ± 0.003 | 10.2 | 8.3 | 6.0 | 8.3 | 15 |
| V | 0.35 ± 0.03 | 0.32 ± 0.03 | 0.26 ± 0.02 | 0.25 ± 0.06 | 0.15 ± 0.01 | 2.2 | 1.8 | 2.7 | 5.8 | 17 |
| Zn | 1.26 ± 0.32 | 0.93 ± 0.10 | 4.31 ± 0.45 | 3.33 ± 0.15 | 5.6 ± 0.5 | 11.7 | 3.1 | 5.7 | 31 | 25 |

[a] average precision of the analysis of SLRS-4, SLRS-2 and of a filtered and centrifuged porewater sample for a single run (i.e. on one day), determined using statistical analysis on n= 2 determinations on m= 10 days

[b] precision of the analysis of n=3 filtrates of the pre-cleaned GD/XP filter, determined within one single run (i.e. on one day)

[c] precisions of the analysis of n=3 samples taken from the same depth and analysed within one single run, averaged for n=9 to 12 different depths of each the HIJ, OUT and HAR site; given are the range between lowest and highest average precision of the three sites

[d] not certified

easily leads to a decrease in effective pore size during the filtration due to filter clogging. Moreover, metals which tend to be present in the dissolved fraction in anoxic environments like peat bogs could be oxidized during the sampling, potentially leading to precipitation and retention by the filter membrane. As the porewater concentrations of the investigated metals are expected to be in the ng $L^{-1}$ range, the filtration step is therefore a crucial point for the determination of the dissolved metal concentrations. We designed a laboratory experiment to test the following disposable syringe filters of 0.45 µm pore size and 25 mm diameter under controlled and constant conditions for their suitability for bog porewater samples: (1) Aquatron 30/CA, a cellulose acetate membrane with 30 µm pre-filter (Schleicher and Schuell, Dassel, Germany); (2) GD/XP, a polyvinylidendifluorid (PVDF) membrane with 10 and 5 µm polypropylene pre-filters (Whatman); (3) Millex HA MCE, a mixed cellulose ester membrane (Millipore, Billerica, MA, USA); and (4) Minsart RC25, a regenerated cellulose membrane (Sartorius AG, Göttingen, Germany). The testing criteria were (1) throughput – limited by the extremely high particle load; and more importantly, (2) blank levels and (3) filtration artefacts, on the basis of mean concentrations and RSDs of triplicate filtrates. To obtain a bulk sample, porewater samples were collected from different depths at the sampling site BF1. To prevent oxidation and subsequent precipitation of iron oxides, the sampling tubes were pre-flushed with $N_2$ (in the laboratory), filled up to the top with raw porewater sample during sample collection and stored cold until the arrival in the laboratory (within 4 hours after sampling). All subsequent sample processing was performed in a $N_2$-flushed Glove Bag™ (Instruments for Research and Industry, Cheltenham, PA, USA): Raw porewater samples (dark brown, opaque) were mixed together in a clean 1 L PP bottle resulting in a bulk sample for the filter experiment. The following procedure was adopted using 10 ml plastic syringes (see above) and investigated syringe filters: (1) processing of 10 ml water through unwashed filter in order to obtain the blank values of untreated filters ($\text{Blank}_F$); (2) a harsh cleaning procedure using 10 ml 0.5% $HNO_3$ and 3 × 10 ml water; (3) processing of 10 ml water in order to get blanks of pre-cleaned filters ($\text{Blank}_{F,\text{clean}}$); (4) filtration of 2.5 ml of the bulk sample through the pre-cleaned filter after discarding the first five drops (first filtrate, F1); and (5) further filtration of the bulk sample through the same filter until complete filter clogging (second filtrate, F2). Each type of filter was processed in triplicate, and processing of single filters was random in order to exclude variations due to a temporal trend (e.g. a depletion of dense particles in the bulk sample due to settling, an increasing agglomeration of colloids in the raw bulk sample, as well as potential oxidation followed by precipitation and

**Table 7.** Blank values [µg $L^{-1}$] of the investigated metals for the sampling of porewaters using the syringe-type sampler (± 1 s).

| | $Blk_F$ [a] (n=3) | | | | $Blk_{sampling\ device}$ [b] | $Blk_{F,GDXP}$ + $Blk_{sampling\ device}$ [c] | $Blk_{atm}$ [d] | | |
|---|---|---|---|---|---|---|---|---|---|
| | Aquatron | GD/XP | Minisart | Millex | (n=3) | | HIJ (n=2) | OUT (n=3) | HAR (n=2) |
| Cd | 0.0005 ± 0.0007 | <0.0002 | <0.0002 | 0.007 ± 0.006 | 0.001 ± 0.001 | 0.001 ± 0.001 | 0.0010 ± 0.001 | 0.0012 ± 0.0001 | 0.0043 ± 0.003 |
| Co | <0.0003 | 0.0005 ± 0.0007 | <0.0003 | 0.003 ± 0.001 | 0.008 ± 0.003 | 0.009 ± 0.003 | <0.0003 | 0.001 ± 0.0002 | 0.007 ± 0.007 |
| Cr | 0.04 ± 0.01 | <0.006 | 0.010 ± 0.001 | 0.10 ± 0.02 | 0.05 ± 0.03 | 0.05 ± 0.03 | 0.124 ± 0.001 | 0.010 ± 0.0004 | 0.03 ± 0.03 |
| Cu | 0.5 ± 0.5 | 0.013 ± 0.003 | 0.176 ± 0.002 | 0.18 ± 0.04 | 0.06 ± 0.04 | 0.07 ± 0.04 | 0.10 ± 0.06 | 0.03 ± 0.02 | 0.608 ± 0.07 |
| Mn | 0.05 ± 0.06 | <0.007 | <0.007 | 0.08 ± 0.04 | 0.2 ± 0.1 | 0.2 ± 0.1 | 0.04 ± 0.05 | 0.018 ± 0.001 | 0.35 ± 0.17 |
| Mo | 0.06 ± 0.05 | 0.009 ± 0.006 | 0.03 ± 0.01 | 0.012 ± 0.005 | 0.008 ± 0.007 | 0.02 ± 0.01 | <0.003 | 0.005 ± 0.001 | 0.008 ± 0.002 |
| Ni | 0.02± 0.02 | 0.01 ± 0.02 | <0.014 | 0.13 ± 0.01 | 0.09 ± 0.03 | 0.10 ± 0.04 | <0.014 | <0.014 | 0.23 ± 0.27 |
| Pb | 0.03 ± 0.03 | 0.004 ± 0.003 | 0.01 ± 0.01 | 0.11 ± 0.01 | <0.002 | 0.004 ± 0.003 | <0.002 | <0.002 | 0.083 ± 0.05 |
| Sc | 0.010 ± 0.001 | 0.011 ± 0.001 | 0.010 ± 0.001 | 0.010±0.001 | <0.002 | 0.011 ± 0.001 | <0.002 | 0.010 ± 0.001 | 0.003 ± 0.002 |
| V | <0.001 | <0.001 | <0.001 | 0.006 ± 0.002 | 0.01 ± 0.01 | 0.01 ± 0.01 | 0.002 ± 0.003 | 0.002 ± 0.0002 | 0.008 ± 0.006 |
| Zn | <0.7 | <0.7 | <0.7 | 11 ± 8 | 1 ± 1 | 1 ± 1 | 9 ± 7 | 0.9 ± 0.3 | 5 ± 5 |

[a] Laboratory blanks of the filter device, including the syringe filter and PE syringes as well as the leaching of the sampling tubes (1% $HNO_3$, without pre-treatment)

[b] Laboratory blanks of the sampling device, including the contamination from short-time contact with the syringe-type sampler and from leaching of the sampling tubes (1% $HNO_3$, without pre-treatment)

[c] Sum of the GD/XP filter device and the sampling device with s obtained from error propagation: $s^2_{sum\ Blks} = s^2_{PC\ leached} + s^2_{Peeper\ 10\ days} + s^2_{field\ water}$

[d] Field blanks corresponding to the contamination by dust from the atmosphere during the filtration; includes also the leaching of the sampling tubes for the same period than for samples

**Table 8**. Blank values [µg $L^{-1}$] of the investigated metals for the sampling of porewaters using the peeper (± 1 s).

| | Blks of membrane (n=3) | | | Blks of peeper (n=3) | | Blks of field water (n=2) | Sum Blks[a] |
|---|---|---|---|---|---|---|---|
| | GHP | PC | $PC_{leached}$ | 24 hrs | 10 days | | ($PC_{leached}$ + $Peeper_{10d}$ + field water) |
| Cd | 0.010 ± 0.001 | 0.010 ± 0.003 | 0.002 ± 0.0001 | 0.012 ± 0.002 | 0.008 ± 0.001 | <0.0002 | 0.010 ± 0.001 |
| Co | 0.012 ± 0.005 | 0.002 ± 0.001 | 0.0008 ± 0.0001 | 0.013 ± 0.001 | 0.017 ± 0.005 | <0.0003 | 0.02 ± 0.005 |
| Cr | 0.11 ± 0.04 | 0.3 ± 0.1 | 0.21 ± 0.02 | 0.11 ± 0.02 | 0.12 ± 0.02 | 0.011 ± 0.005 | 0.34 ± 0.03 |
| Cu | 0.6 ± 0.3 | 0.28 ± 0.06 | 0.037 ± 0.002 | 0.61 ± 0.3 | 1.5 ± 0.7 | <0.012 | 1.5 ± 0.7 |
| Mn | 0.5 ± 0.2 | 0.3 ± 0.2 | 0.06 ± 0.03 | 0.22 ± 0.03 | 0.24 ± 0.01 | 0.012 ± 0.005 | 0.3 ± 0.03 |
| Mo | 0.17 ± 0.02 | 0.014 ± 0.006 | <0.003 | 0.028 ± 0.012 | 0.036 ± 0.001 | <0.003 | 0.036 ± 0.001 |
| Ni | 0.26 ± 0.03 | 0.30 ± 0.06 | 0.12 ± 0.08 | 0.7 ± 0.1 | 0.72 ± 0.06 | 0.017 ± 0.002 | 0.9 ± 0.1 |
| Pb | 0.04 ± 0.01 | 0.06 ± 0.03 | 0.054 ± 0.05 | 0.11 ± 0.01 | 0.10 ± 0.06 | 0.018 ± 0.002 | 0.17 ± 0.08 |
| Sc | <0.002 | <0.002 | <0.002 | 0.005 ± 0.004 | <0.002 | <0.002 | 0.005 ± 0.002 |
| V | 0.101 ± 0.007 | 0.006 ± 0.001 | 0.005 ± 0.003 | 0.015 ± 0.004 | 0.019 ± 0.005 | <0.001 | 0.024 ± 0.006 |
| Zn | 29 ± 4 | 21 ± 10 | 16 ± 2 | 5 ± 1 | 6 ± 1 | 1.4 ± 0.1 | 23 ± 2 |

[a] Standard deviation calculated after error propagation: $s^2_{\text{sum Blks}} = s^2_{\text{PC leached}} + s^2_{\text{Peeper 10 days}} + s^2_{\text{field water}}$

sedimentation of inorganic compounds); moreover, the chronological order of filtration was also evaluated to ensure that there were no temporal trends. All filtrates (blanks and samples) were acidified to 1% v/v in a class 100 clean bench using $HNO_3$.

Due to the high particle load, throughput was very low for all filter types. Higher throughputs were found for the filters containing internal pre-filters (GD/XP and Aquatron filter: 2.5 mL) compared to the others (Minisart 1 mL, Millex 0.5 mL). Regarding Millex filters, a second filtrate could not be obtained as the filter clogged completely within the first 3 ml. Flow rates of all filters dropped rapidly, indicating a decrease in effective pore size due to clogging. The GD/XP filter suffered from the 40 mL–cleaning procedure, as indicated by a decelerating passage of the rinsing solution.

Blank values of Cd, Co, V and Zn of unwashed filters ($Blk_F$) were at or close to the limit of detection (LOD) except of Millex filters which were considerably higher (Table 7). Regarding Cr, Cu and Pb, $Blk_F$ were at or near the LOD for the GD/XP filter only. Regarding Mn, Mo and Ni, the GD/XP showed similarily low $Blk_F$ values as the Minisart and Millex filter, respectively. After applying the harsh cleaning procedure, blank values ($Blk_{F,clean}$) of all elements were below the LOD for all filters.

Filtration artefacts were studied on the basis of elemental concentrations and RSDs in the two filtrates F1 and F2 (Fig. 8). As the concentrations in the F1 and the F2 filtrate were similar, neither sorption processes at the filter surface nor filter clogging (occurring after 2.5 mL latest) affect the metal concentrations significantly. For samples taken in Finland (see below), the particle load of porewater samples was found to vary with the degree of peat decomposition; therefore, the amount of processed sample until the filter clogged differed between samples. In order to eliminate concentration variations due to different particle loads of samples, we recommend filtering samples until the filter clogs to dripping rather than processing a defined sample volume. A striking feature of the filtration experiment is the high RSD obtained for triplicates of each single filter type ($RSD_{filter}$), but also across different filter types ($RSD_{across}$). The concentrations in both filtrates (F1 and F2) have been determined within one single run of ICP-SF-MS measurements (i.e. on one single day). Considering the (average) RSDs of ICP-SF-MS measurements obtained for a porewater sample within one single run (2% to 9%), the $RSDs_{filter}$ and $RSD_{across}$ were considerably greater, even though the concentrations of filtrates exceed those of the in-house-reference porewater by a factor of 2 to 10 (Table 6, Fig. 8). The high RSDs could not be explained by potential signal suppression due to different amounts of humic substances and/or filter extractables in the filtrate, as the RSD of the internal standard was 5.8% for the complete ICP-SF-MS run; as mentioned above, any temporal trend during the sequence of filtration could also be excluded. Therefore, the filtration step alone was responsible for the negative influence on the precision of the determination of porewater concentrations for all investigated elements, especially when using a $HNO_3$-treated GD/XP filter ($RSDs_{filter}$ mainly between 6 to 30%). The least variations *between* different filters were found for Cr and V, with $RSDs_{across} \leq 3\%$. However, standard deviations were significantly lower with the Minisart filter than with the Aquatron and GD/XP filter (Cr: $F_{2,2}$, p=0.01; V: $F_{2,2}$, p=0.05). Considerable variations were found for (1) Pb ($RSDs_{across}$: ±7%), Co (±14%), Cd (±16%) and Mn (±23%). These elements correlate significantly with each other (r>0.82; df=16, p=0.01), indicating similar retention mechanisms at each single filter. Highest concentrations were obtained with the Aquatron filter, together with low standard deviations. (2) Considerable variations were also found for Sc ($RSDs_{across}$ ±10%), Ni (±11%), and Zn (±15%). However, these elements did not correlate with each other. Standard deviations of Sc of different filter types significantly differed from each other ($F_{2,2}$, p=0.05); a high Sc concentration together with a low $RSDs_{filter}$ was obtained with the Minisart filter. In contrast, $RSDs_{filter}$ of Ni were 14% for each filter type. Therefore, filtration artefacts for Ni seem to occur across all types of filter, and in a similar range. Standard deviations of Zn were significantly lower for the Aquatron filter than for the other filters ($F_{2,2}$, p=0.01). Strongest filtration artefacts were found for Cu (72% $RSD_{across}$) and Mo (33%), and even within one filter type, RSDs were high (e.g. 90% $RSD_{filter}$ for Cu using the GD/XP filter). Using the Aquatron filter, lowest concentrations but smallest RSDs were obtained. In contrast, using the Minisart filter, highest concentrations were accompanied by high RSDs.

In summary, the Millex filter is in general not appropriate due to its low sample throughput (complete clogging after the filtration of 2.5 ml of bulk sample). For Cr and Sc, the Minisart filter is most suitable due to the low RSDs, whereas for Cd, Co, Mn, Zn, Pb and V, high yields together with low RSDs are obtained with the Aquatron filter. Using the GD/XP filter, slightly lower metal concentrations and higher RSDs are obtained compared to the Aquatron filter. However, only the $Blk_F$ of this filter type were sufficiently low to process samples even from very remote sites without pre-cleaning (Table 7); moreover, $RSDs_{filter}$ of the GD/XP could be reduced by avoiding the harsh cleaning procedure, as indicated by the lower RSDs of real samples collected in Finland, which include the natural inhomogenity of metal concentrations within a certain depth in the peat bog (Table 6). Therefore, for the filtration of porewater samples from ombrotrophic peat bogs, we recommend the use of the GD/XP filters.

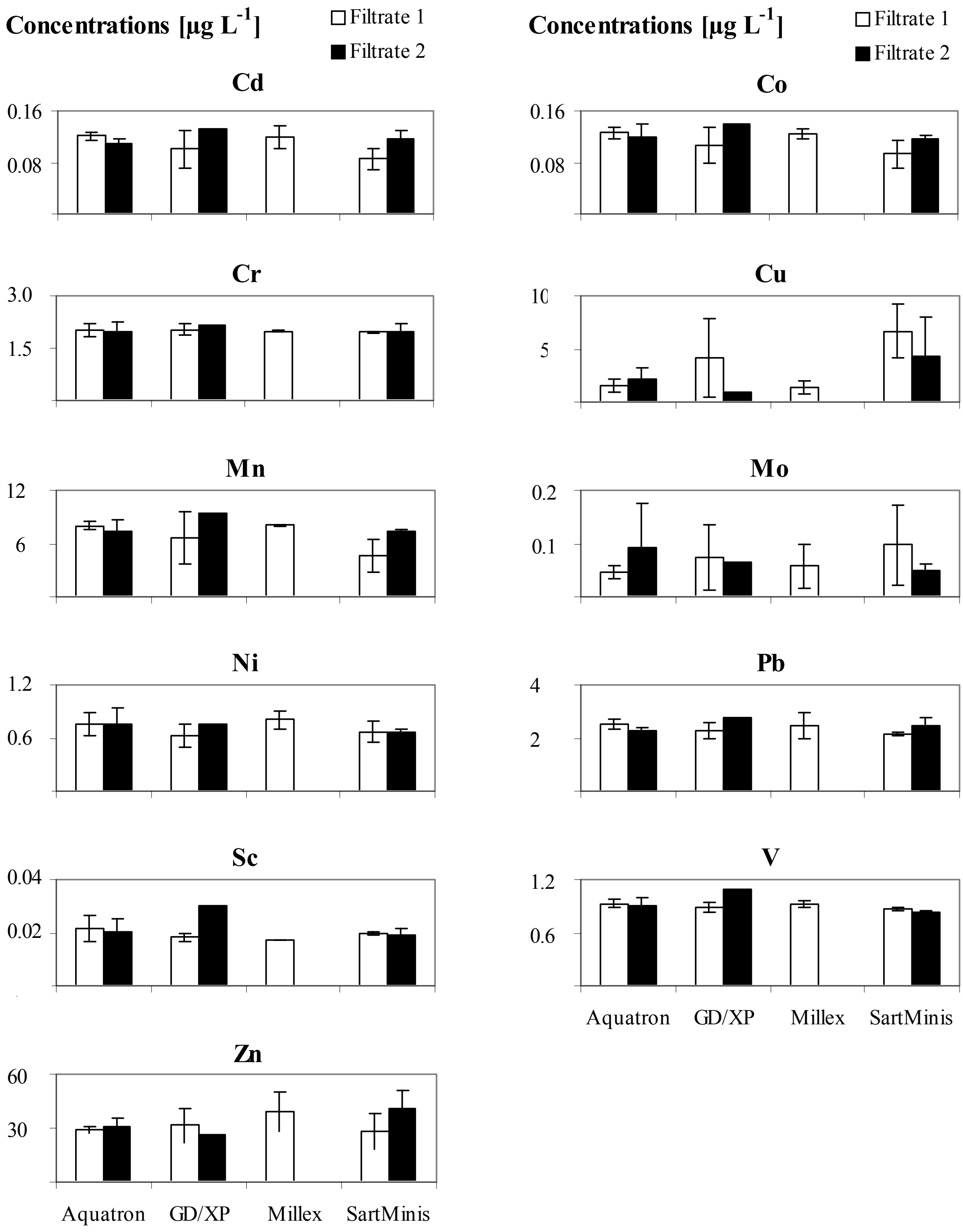

**Fig. 8.** Concentrations [µg $L^{-1}$] of investigated metals in the first and second filtrate of a porewater bulk sample from BF1. Error bars represent the standard deviations of triplicate filtrates with the exception of the second filtrate of GD/XP where two filters clogged completely; with the Millex filter, no second filtrates could be obtained due to complete filter clogging.

### EFFECT OF OXIDATION

Redox-sensitive elements such as Mn could precipitate after oxidation; a potential underestimation of Mn concentrations in filtrates due to the retention of Mn oxides at the filter must therefore be evaluated. The raw bulk porewater sample was removed from the glove bag subsequent to the filtration experiment, and exposed in open vessels to ambient air in a class 100 clean bench. After both 5 min and 20 min, subsamples were filtered in duplicates using the Millex filter, and concentrations were determined within the same ICP-SF-MS run. Manganese concentrations in the filtrates processed in the clean bench were not significantly lower than those processed in the $N_2$-flushed glove bag. We conclude that potential oxidation artefacts during the filtration of a porewater sample (which takes approx. 10 min) at ambient air is negligible within this time scale. This feature can be explained by the typically low pH of porewater samples (pH ~ 4) from ombrotrophic peat bogs, at which oxidation rates are reduced (Eary and Schramke 1990).

### SELECTION OF MEMBRANES FOR THE PEEPER METHOD

In contrast to the manual filtration of porewater samples, the peeper method allows ‘dissolved’ metals to diffuse freely through the pores of the membrane, which reduces the sensitivity for membrane clogging. Nevertheless, sorption processes at the membrane could reduce the concentrations of the investigated metals, especially for metals associated with organic molecules. Two 0.45 µm-membranes with low protein-binding properties were tested for their handling capacities, blank levels and metal permeability: PC, a Nuclepore polycarbonate membrane (Whatman); and GHP, a hydrophilic polypropylene membrane (Pall Life Sciences, East Hills, NY, USA). Laboratory blanks of the PC and GHP membranes ($Blk_{PC}$, $Blk_{GHP}$) were obtained in a class 100 clean bench by covering a piece of membrane (0.08 x 0.03 m) with $H_2O$ (i.e. 14 mL) for a period of six weeks (i.e. the equilibration time for the peeper; see below) after pre-rinsing the membrane. Membranes were trenched by hand using PE gloves and plastic tweezers. The blank values obtained by this procedure correspond to a leaching volume of 6 L $m^{-2}$ membrane, whereas the ratio of membrane area to chamber volume corresponds to a leaching volume of 11 L $m^{-2}$ membrane. Therefore, membrane blanks might overestimate the true contamination of samples due to the membrane, especially when considering that the membranes were on both sides in contact with water (i.e. peeper chambers and porewater).

Laboratory blanks of the peeper ($Blk_{peep}$) were prepared by leaching the peeper chambers with $H_2O$ for both 24 hours or ten days in a class 100 clean bench; even though the peeper had been wrapped with plastic foil, the loss of $H_2O$ due to evaporation was approx. 1 mL per day per chamber, and had to be compensated for by adding water. Due to the high rate of evaporation, we decided to not extend the leaching experiment to six weeks (i.e. the equilibration time). Therefore, $Blks_{peep}$ might underestimate the true contamination by metal leaching from the Plexiglas for the period of installation. Peeper blanks were processed in triplicate, each of them consisting of the sample of four individual chambers.

A peeper with GHP and PC membrane covering the depth interval of 15 to 30 cm on any column was installed at the BF2 site as described above, but without using a glove bag during peeper preparation and sample collection. Several studies which evaluated the necessary equilibration time in sediment porewaters and the importance of membrane type can be found in the literature (Brandl and Hanselmann 1991; Carignan et al. 1985; Hesslein 1976; Steinmann and Shotyk 1996). Equilibration times have varied anywhere from 3 to 20 days for sediments. In contrast to sediments, porewater of ombrotrophic peat bogs generally have lower metal concentrations, which reduces the concentration gradient between the porewater and the pure water; furthermore, metals could be associated with organic molecules which might lower diffusion rates. For these reasons, we increased the equilibration time to a period of six weeks, as suggested by Steinmann and Shotyk (1996).

Due to the greater thickness (GHP: 101 µm, PC: 6-11 µm) and breaking strength, the GHP membranes were easier to handle than PC membranes. Blank levels of investigated metals were up to 90% lower for the PC membrane than for GHP membrane, except for the blank of Cr which was three times higher using the PC membrane (Table 8). As a rough estimation of the contribution of the leaching from the membrane and the peeper to the total concentrations in the porewater sample, the sum of these blanks, together with the porewater concentrations of investigated metals are indicated for both membranes in Fig. 9. For the GHP membrane, the concentrations of Cr, Cu, Ni and Zn in most of the porewater samples are at the level of estimated blanks. Higher concentrations of Cd, Co, Cr, Cu, Ni, Pb and Zn, together with steeper concentration gradients in the porewater profiles, were found in samples covered by the PC membrane than in samples covered by the GHP membrane (Fig. 9). The differences in concentrations obtained using GHP and PC membrane exceed the differences in blank levels of the two membranes. Furthermore, average RSDs of 30% to 60% for GHP–PC duplicates of a given depth exceed the maximum RSDs for chamber duplicates (22%; see below). Therefore, the higher concentrations found with the PC membrane was indeed due to an enhanced permeability for metals in the given equilibration period. Similar Mn, V and Sc concentrations were found for both membranes. The higher concentrations of Mo in samples covered by the GHP membrane were due to contamination of the membrane with Mo. With blank values generally lower and yields higher, we recommend the use of PC membranes.

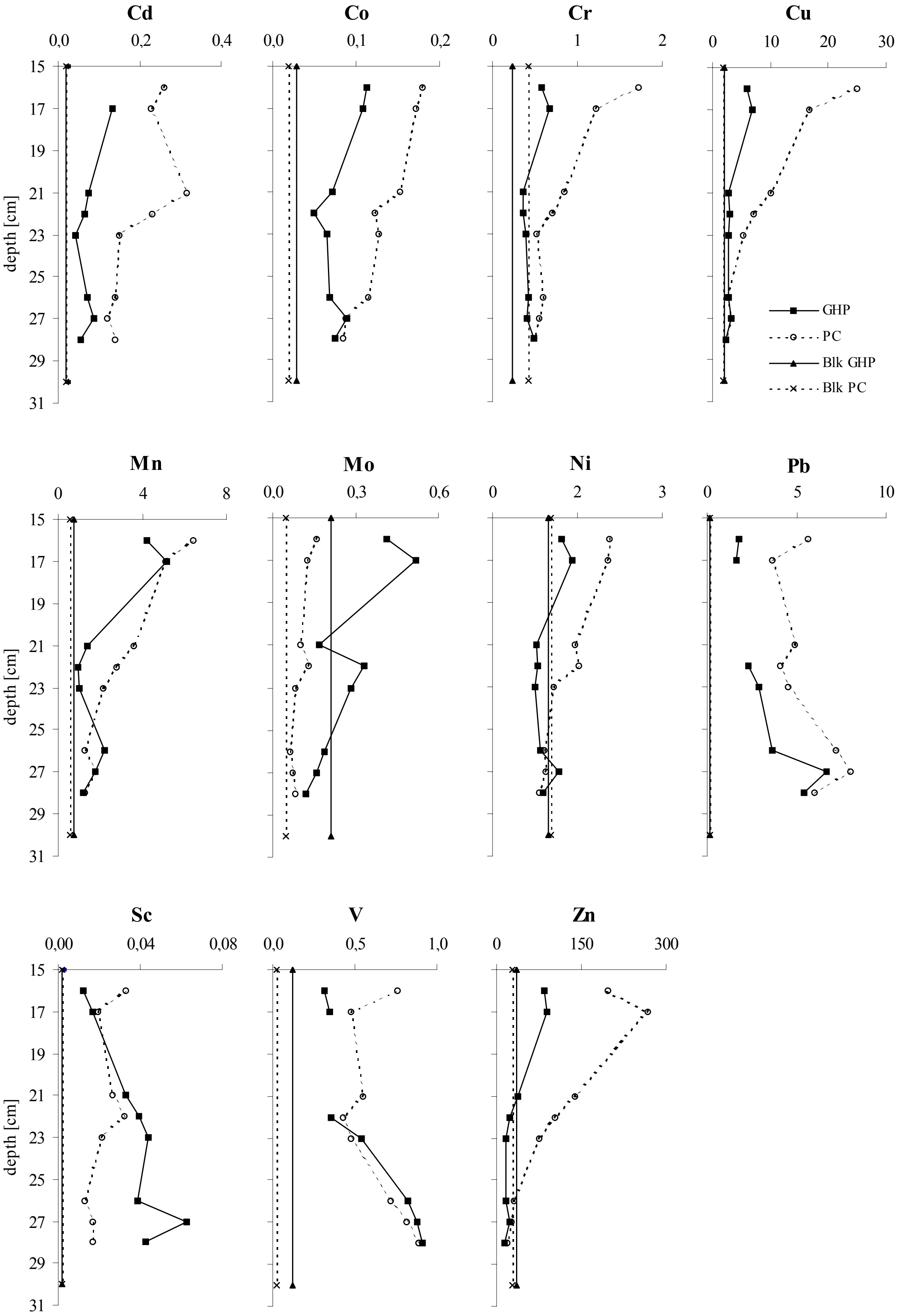

**Fig. 9.** Comparison of porewater concentrations [µg $L^{-1}$] using two different 0.45 µm membranes (GHP and PC) on a peeper. Estimations of the blank levels from membrane and Plexiglas leaching are indicated as vertical lines (Blk GHP, Blk PC).

### POREWATER SAMPLES OBTAINED WITH THE SYRINGE-TYPE SAMPLER

A laboratory study was used to evaluate blank levels obtainable using the bog porewater sampler. Additionally, a field study was undertaken at the HIJ, OUT and HAR sites in Finland to (1) evaluate the extent of contamination by atmospheric dust during the filtration in the field; (2) assess the natural range of elemental concentrations in porewater samples; (3) to evaluate blank levels at the remote site; and (4) compare variations due to the sampling technique with the natural variations of metal concentrations within a certain depth.

Laboratory blanks of the sampling device were prepared in triplicate in a class 100 clean bench by collecting water in PP sampling tubes with the porewater sampler. Before blanks were processed, the sampler was carefully rinsed with 2% $HNO_3$ and water, whereas the PP sampling tubes were used without pre-treatment, as used in the field. Therefore, the blank of the sampling device included not only the contamination by the short-term contact of samples with the sampler, but also the contamination from the leaching of the PP sampling tubes by the 1% $HNO_3$ (v/v). The sum of laboratory blank levels of the sampler and the unwashed GD/XP syringe filter obtained from the filtration experiment is given in Table 7, together with standard deviations calculated by error propagation of each laboratory blank.

In the field study, raw porewater samples were filtered through (unwashed) GD/XP syringe filters into unwashed PP sampling tubes in the field, immediately after the extraction. Field blanks (n=2 or 3) were taken by processing water through GD/XP filters in the field (without using the sampling device), at each sampling site. As contamination by the filter employed is insignificant ($Blk_F$ of GD/XP, Table 7), the field blanks represent the contamination of samples by atmospheric dust during the filtration of the sample in the field ($Blk_{atm}$).

As humic acids (HAs) precipitated in the filtrates after acidification, samples were centrifuged, and trace metal concentrations were determined in both the residue and the supernatant. In this paragraph, results for the supernatant fraction are considered, whereas the determination of metals in the residue is discussed below.

The results of blank levels show that the limiting factor for the determination of the investigated metals in porewater samples is the sampling device itself, whereas $Blk_F$ values of the GD/XP filters are negligible (Table 7). Blank values of Cd, Pb, Sc, V and Zn are at the limit of detection or $\leq$ 20% compared to the lowermost concentrations found in samples of the remote site (Table 9). Regarding Co, Cr, Mo and Ni, the contribution of the contamination from the sampling device to the lowermost concentrations in porewater samples was 50% to 95%. However, regarding most samples, the porewater concentrations were well above the blank values, especially in samples taken from populated areas (BF1 and BF2, HAR).

**Table 9.** Concentration ranges [µg $L^{-1}$] of samples from Finland using the syringe-type sampler.

| | HIJ | OUT | HAR |
|---|---|---|---|
| Cd | 0.005-0.04 | 0.01-1.2 | 0.04-0.4 |
| Co | 0.01-0.03 | 0.02-0.08 | 0.07-1 |
| Cr | 0.10- 0.23 | 0.12-0.16 | 0.2-0.5 |
| Cu | 0.2-0.4 | 0.2-0.4 | 5-44 |
| Mn | 0.6-3 | 1-3 | 3-21 |
| Mo | 0.01-0.04 | ≤ 0.025 | 0.02-0.06 |
| Ni | 0.10-0.33 | 0.1-0.3 | 0.7-20 |
| Pb | 0.11-0.53 | 0.1-0.3 | 0.7-5 |
| Sc | <0.002–0.01 | 0.01-0.02 | <0.002 |
| V | 0.11-0.4 | 0.08-0.17 | 0.1-1 |
| Zn | 4-22 | 3-11 | 8-34 |

HIJ: the low-background site Hietajärvi
OUT: the site of former mining activity
HAR: the site of present smelting activity

The extent of additional contamination of samples during the filtration step related to atmospheric dust particles ($Blk_{atm}$) is strongly site-dependent. The $Blk_{atm}$ of Cd, Cr, Mo, V, Zn, Cu, Mn, Ni and Pb are four to 40 times higher at the industrialized HAR site compared to the OUT and HIJ site (Table 7). However, the lowermost porewater concentrations found at HAR still exceed the $Blk_{atm}$ by a factor of 8 to 13 times. Compared to the contamination caused by the sampling device, the additional contamination during the filtration step of Cr, Cu and Zn at the remote site is significant. A random contamination of one of the field blank sampling tubes might be responsible for the elevated $Blk_{atm}$ of Cu and Zn at the HIJ site, as shown in the high standard deviations. Nevertheless, we strongly recommend to filter porewater samples within a $N_2$-flushed glove bag in order to reduce overall blank levels.

The elemental concentrations ranges in samples taken from the industrialized area (HAR) were similar to concentrations found in central Europe (BF1, Table 6), but considerably higher than in samples from the more remote sites in Eastern Finland. Overall concentration ranges were small for Cr, Mo, Sc, V and Zn (factor 5 to 10 between minimum and maximum concentrations of all samples), but high for the other elements (up to a factor of 220 for Cu). Average RSDs obtained for triplicates taken at a given depth varied between 15% and 24% for most of the elements (Table 6). For Cr, Ni, Pb, Sc and V, these RSDs were clearly higher than RSDs obtained for the filtration step alone (n=3) – even in the HAR samples where the concentration ranges are high compared to the BF1 sample of the filtration experiment. For this reason, we conclude that the RSDs of sample triplicates for these elements reflect the natural variation of porewater concentrations in ombrotrophic peat bogs. For the other elements, RSDs are considerably lower for real samples (which include the natural variation) than for the GD/XP filtrate of the filtration experiment where the filters were pre-cleaned before use. The implication is that the precision of the filtration step could be improved by avoiding the cleaning procedure; however, it is not possible to determine whether the RSDs of porewater concentrations of these elements reflect the natural variations of porewater concentrations at a certain depth or the variations due to filtration artefacts.

### STUDY ON HUMIC ACID PRECIPITATES

In order to determine metal concentrations using ICP-SF-MS, samples must be acidified to pH 1. At this pH, the humic acid fraction (HA) of the humic substances precipitates(Aiken 1985). The HAs were separated by centrifuging the samples for 10 min at 3000 rpm. The supernatant is colored, but clear, indicating the presence of dissolved fulvic acids; the residues consisted of small amounts (1 to 6 $mm^{-3}$ for an original filtrate volume of 10 ml) of gelatinous HA precipitates adhering at the conical end of the PP tube; this makes a quantitative transfer into digestion vessels difficult. For this reason, precipitates were digested within the sample tube: The residues were dried within the opened PP sample tubes in a class 100 laminar flow bench and covered by a minimum amount of 25 µL concentrated $HNO_3$. After 30 min, 2.48 ml of water was added to obtain a final $HNO_3$ concentration of 1% v/v. As the concentrated $HNO_3$ might leach significant amounts of metals from the plastic tubes, the limit of detection in these diluted digestions using the $HNO_3$ treatment in PP tubes ($LOD_{res,digest}$) was calculated from 3-times the standard deviation of 10 blanks of diluted digests, and of the limit of quantification ($LOQ_{res,digest}$) from 10-times the standard deviation. Limits of detection and of quantification as well as sample concentrations in diluted digests were re-calculated to concentrations of the original filtrate ($LOD_{res,filtrate}$, $LOQ_{res,filtrate}$) (i.e. before the HAs precipitated) by multiplying the metal concentrations in the diluted digest with the volume of the diluted digests (2.50 ml), divided by the original volume of each filtrate (between 6 and 11 mL).

Due to the leaching of metals from the sampling tube during the treatment of the residue with concentrated $HNO_3$, the $LODs_{res,digest}$ of Cd, Co, Cr, Cu, Mn, Ni, Pb and Sc in a final concentration of 1% v/v $HNO_3$ were higher by a factor of 4 to 25 than the LODs obtained for the supernatant fraction ($LOD_{meas}$), i.e. for aqueous samples of the same acid concentration (Table 10). However, after re-calculation of the $LOD_{res,digest}$ to concentrations in the original filtrate, previous to the precipitation, the LODs for the determination of HA-bound metals were in the same range as that of the dissolved fraction.

**Table 10.** Limits of detection [µg $L^{-1}$] for the super natant fraction ($LOD_{meas}$), the residue digests ($LOD_{res,digest}$) and for the HA-bound fraction, re-calculated for the original porewater filtrate ($LOD_{res,filtrate}$). These limitations arise from random contamination of vessels, not from the sensitivity of the instrument

| | $LOD_{meas}$ [a] (1%v/v $HNO_3$) | $LOD_{res,digest}$ [b] (1%v/v $HNO_3$) | $LOD_{res,filtrate}$ [c] (1%v/v $HNO_3$) |
|---|---|---|---|
| Cd | 0.0002 | 0.002 | 0.0005 |
| Co | 0.0003 | 0.001 | 0.0003 |
| Cr | 0.006 | 0.02 | 0.004 |
| Cu | 0.012 | 0.08 | 0.02 |
| Mn | 0.007 | 0.03 | 0.008 |
| Mo | 0.003 | 0.003 | 0.001 |
| Ni | 0.014 | 0.05 | 0.014 |
| Pb | 0.002 | 0.05 | 0.01 |
| Sc | 0.002 | 0.001 | 0.0003 |
| V | 0.001 | 0.001 | 0.0004 |
| Zn | 0.7 | 1.7 | 0.4 |

[a] Limit of detection for the supernatant fraction of filtered porewater sample (1%v/v $HNO_3$).

[b] Limit of detection for diluted digests of the residue (HA) fraction (1%v/v $HNO_3$ after dilution).

[c] Limit of detection for the concentration of the HA-bound fraction, back-calculated to concentrations of the original porewater filtrate (1% v/v $HNO_3$)

The concentrations of Mo, Sc and Zn in the HA-fraction were at or below the $LOQ_{res,filtrate}$ in all investigated profiles. Cadmium, Pb, Cr, Ni and Cu concentrations of the HA-fraction could be determined with sufficient precision ($>LOQ_{res,filtrate}$) in HAR samples only. Cobalt and Mn concentrations in the HA-fraction could be quantified in HAR and OUT samples, whereas V concentrations exceed the $LOQ_{res,filtrate}$ by far in all samples.

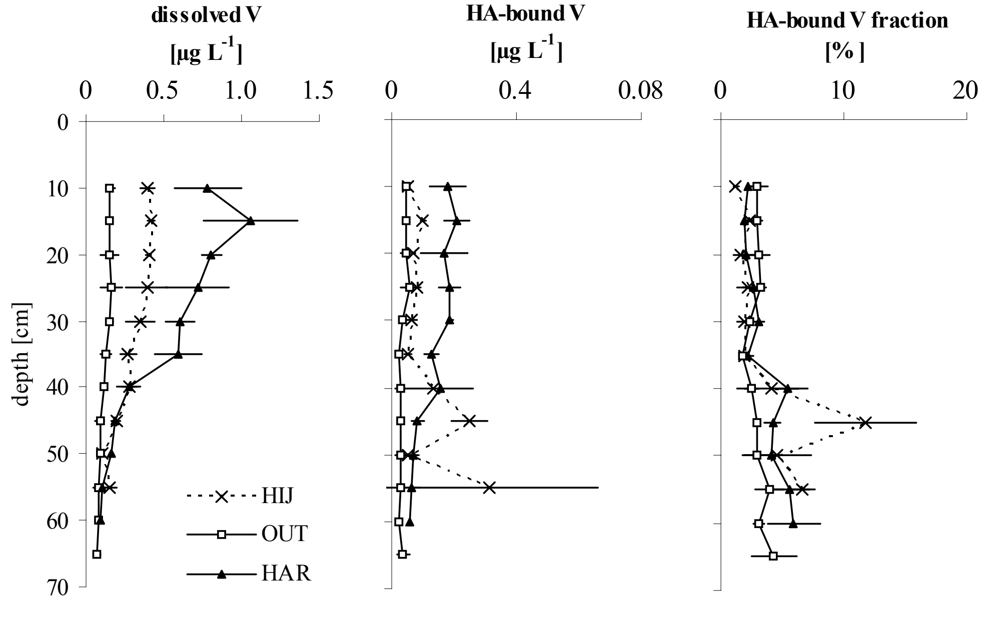

**Fig. 10.** The concentration of dissolved V (as measured in the supernatant), of humic-acid bound V (re-calculated for concentrations in the original filtrate) and the percentage fraction of humic-acid bound V to total concentrations in the original filtrate. Error bars represent the standard deviation of triplicates.

For Cd, Pb, Cr and Mn, the concentrations in the HA-bound fraction were dependent on the total metal concentrations in the filtrate, with relative contributions to the total concentrations between 2% and 5% throughout the profile (data not shown). In contrast, the fractionation of Co, Ni and V between dissolved and HA-fraction was dependent on depth: in the upper layers, the HA-fractions contribute to 1% (Ni) to max. 3% (V) to the total concentrations, whereas they increase up to 3% (Ni) and max. 7% (V) at greater depths; a characteristic profile is highlighted in Fig. 10. The increase in HA-bound metals might be explained by the slightly increasing abundance of HA-precipitates with increasing depth at HIJ, OUT and HAR, and/or by a change in the structure of the HAs. The relative contribution of HA-bound Cu was approximately 12%, but was considerably lower in the uppermost sample (4%). Therefore, we strongly recommend to calculate total Cu concentrations by considering both the HA-bound and dissolved fraction. As the HA-bound fraction of the remaining elements could either not be determined or contributed less than 5% to the total concentrations, we suggest to disregard this fraction for the determination of porewater concentrations.

### POREWATER SAMPLES OBTAINED WITH THE PEEPER

The purpose of the comparative laboratory and field study was to (1) determine blank levels for the peeper sampling method; (2) evaluate whether they are sufficiently low for sampling bogs of remote sites; (3) evaluate the variations due the natural variations of metal concentrations at different depths, and (4) compare both sampling methods.

A peeper was installed at the HIJ and OUT site in Finland as described above, but with the following improvements for blank reduction: the PC membrane was leached for one week using three consecutive acid leaching solutions ($HNO_3$, pH 3.5); the peeper preparation (filling of chambers, membrane installation) as well as the sample collection after the equilibration period was performed in a $N_2$-flushed glove bag (and in a clean room at OUT, respectively). Peeper samples were collected on the same day as those of the syringe-type sampler. For each sample, the contents of two underlying chambers were combined in order to obtain a sample volume of 8 mL. Water which was used to fill the peeper chambers was sampled from the material in duplicate when the second peeper was installed at the OUT site. In a laboratory study, blanks of the leached membrane were processed as described for untreated membranes.

As discussed above, the determination of blank levels was subject to various errors, and therefore these values are a rough estimation of potential contamination only. Blank values of the field water were at or below the LOD (Table 8), indicating that the water carried in a PE

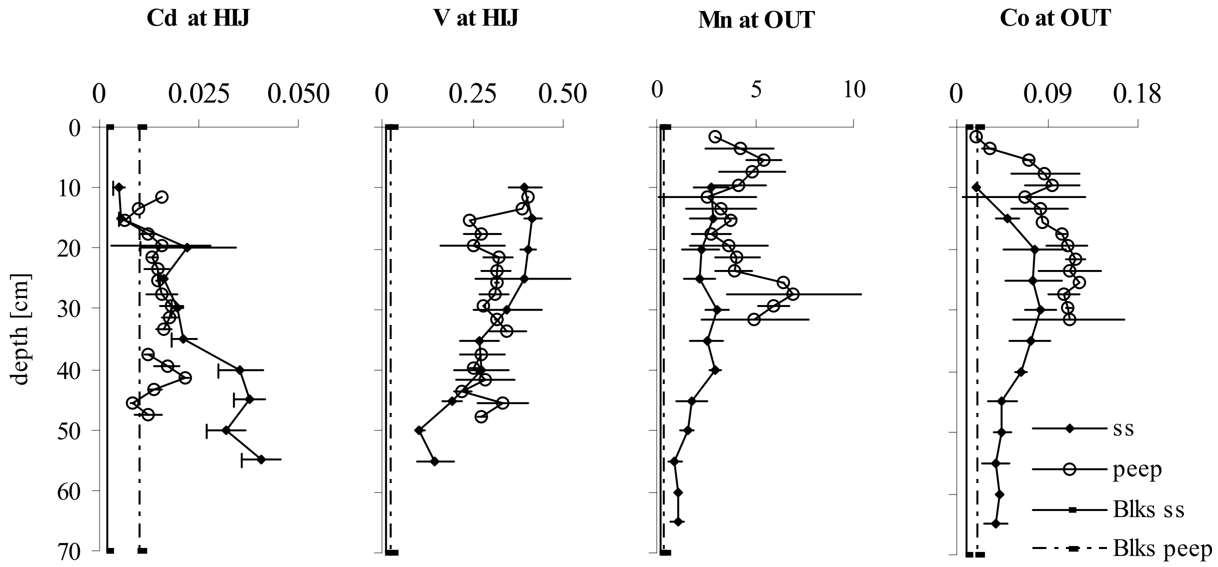

**Fig. 11.** Comparison of porewater concentrations obtained from the syringe-type sampler (ss, solid lines) and from peepers (peep, dotted lines), together with the corresponding sum of blank levels (selected elements only). Error bars represent the standard deviation of triplicates (ss) and duplicates (peep), respectively.

container (which had been acid leached prior to use) had not been contaminated significantly during the sampling trip and the preparation of peepers. Membrane blanks could be considerably lowered for all elements except Cr and Pb by using the leaching procedure. Therefore, the limiting contamination source was the metal leaching from the Plexiglas chambers.

The sum of peeper blank values of Cr, Cu, Mo, Ni, Pb and Zn exceeded the concentrations in HIJ and OUT samples taken with the porewater sampler by a factor of up to 6 (Table 9). Therefore, the peeper method was not suitable for sampling porewaters at natural concentration levels of these elements. Even though peeper blank levels of Cd and V are sufficiently low, the porewater profiles hardly reflect the concentration gradient shown by samples obtained with the porewater sampler (Fig. 11). The peeper concentration profiles of Mn and Co traced those of the porewater sample quite well, with higher concentrations in peeper samples. Relative SDs of chamber duplicates averaged 17% for Co and 24% (HIJ) to 34% (OUT) for Mn.

### SAMPLE STORAGE

For the period between sample collection and arrival in the laboratory (nine days at maximum), samples had to be stored at outdoor temperatures (6°C to 13°C). After acidification to 1% v/v $HNO_3$ in the laboratory, samples were kept frozen at -18°C, defrosted overnight and centrifuged; then metal concentrations were determined. A second series of measurements was performed after keeping the samples for 4 months in the fridge at 6°C. Results of these two data sets were subjected to a paired t-test to assess potential leaching of metals from the sampling tubes. For Cd, Co, Mn, Mo, Ni, V and Zn, the pre-requisite of the t-test (independence of differences from concentrations) were not fulfilled. Concentrations of Sc did not differ significantly between the two series. In contrast, the t-test showed a statistically significant positive concentration difference of Cr, Cu and Pb concentrations in porewater samples after the 4-months period of cold storage: Cr: 0.09 ± 0.08 µg $L^{-1}$ (t=11, df=91, $p<0.01$); Cu: 0.3 ± 0.1 µg $L^{-1}$ (t=19, df=57, $p<0.01$); Pb: 0.08 ± 0.06 µg $L^{-1}$ (t=10, fd=60, $p<0.01$). As this increase in concentrations due to the leaching from the sample tubes were in the range of lowermost sample concentrations, we strongly recommend performing measurements as soon as possible as well as storing samples frozen.

## Discussion

With the exception of Zn, metal concentrations of porewater samples taken from ombrotrophic peat bogs at low-background sites were found to be at sub-µg $L^{-1}$ levels. Using clean laboratory facilities, pure reagents and ICP-SF-MS instrumentation, the determination of metal concentrations at these levels is reliable, accurate and precise. However, the collection of such samples, i.e. working under field conditions, without clean laboratory devices, is not trivial, and all potential contamination sources must be well under control and precisely determined (McQuaker 1999). Using the bog porewater sampling method, both the contamination of porewater samples by the sampling device (including the GD/XP filter and the PP sampling tubes) as well as the random contamination by atmospheric dust during the filtration step can be determined precisely. In contrast, the determination of possible contamination sources for the peeper method is subjected to high errors: Metals leaching from the membrane are released from both sides of the membrane; however, the water column at the “bog” site could move in vertical and horizontal directions, and concentrations may change after rainfall or periods of high evaporation. Therefore, the amount of metals which are truly released to the sample chamber cannot be reliably determined. Nevertheless, the blank levels of all elements are higher for the peeper method than for the porewater sampler except for Sc and Mn, which have similar blank levels. The improved blank levels of the bog porewater sampler, however, are necessary for the establishment of concentration profiles of ombrotrophic peat bogs from remote sites, i.e. when natural processes are of interest. In this study, where no glove bag was used for filtration, even with the bog porewater sampler, Cr, Mo and Sc (probably also Zn) could not be reliably determined in the HIJ site as the blanks reflecting atmospheric contamination of samples considerably increased the overall blank levels. In peat bogs of rather populated or industrialized areas such as in central Europe (BF1, BF2) or the southwestern part of Finland (HAR), where porewater concentrations of all metals were found to be higher than at the HIJ and OUT sites, the peeper method might work as well as the syringe-type sampler method.

A further advantage of the syringe-type sampler is its speed and simplicity. The collection of one single sample, inclusive filtration, takes less than 20 min. This allows collecting several samples from each depth across a given area of the bog, on one single day. By increasing the number of subsamples, information about the homogeneity of metal concentrations in the bog can be obtained. Furthermore, complete transects across the bog, representative for one single day, can be obtained. The collection of samples on different days would allow studies on short-time or seasonal variations in the movement of dissolved metals; e.g. the influence of water table movements – which occur after strong rainfall or periods of high evaporation – to the mobility of metals. In contrast, sampling using the peeper needs two field trips, one for the installation and one for the sample collection; the most time-consuming step is the installation of the membrane, which is laborious and takes a few hours and requires working in a glove bag at the field. Short-term variations can not be obtained, as diffusion processes need time for equilibration.

However, there are two drawback of the syringe-type sampler: (1) The macroporosity of peat may cause preferential flow during suction (Blodau and Moore 2002). (2) Our experiments show that filtration artefacts due to filter clogging and/or the interference between colloidally associated metals and the membrane occur. There are a lot of commercial filters available by many manufactures, of which we selected four filters with low-protein binding capacities. There might be other filters available with higher yields for colloidally-associated metals (like Cu and Mo) than obtained with the GD/XP and the Minisart filters.

After the PP sampling tube is fixed at the bottom end of the bog porewater sampler, the sampling holes are 13 cm above the bottom end. Even though the peat tightly encloses the sampling device when inserted into the bog, the sampling tube might displace the surrounding porewater upwards, leading to a potential admixing of underlying porewater to the requested sample (up to 13 cm). As ICP-SF-MS measurements require sample volumes of one mL only, there is no need to use a 10 mL sampling tube; nevertheless, we decided to use these PP tubes because they were found to be sufficiently clean for the determination of investigated metals at sub-µg $L^{-1}$ levels. A conversion to smaller sampling tubes with similar blank levels might improve the resolution of the sampling method.

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# CHAPTER 3

Krachler, M., N. Rausch, H. Feuerbacher, P. Klemens. 2005. A new HF-resistant tandem spray chamber for improved determination of trace elements and Pb isotopes using inductively coupled plasma - mass spectrometry.

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# A new HF-resistant tandem spray chamber for improved determination of trace elements and Pb isotopes using inductively coupled plasma - mass spectrometry

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**Abstract.** The use of a new HF-resistant tandem spray chamber arrangement consisting of a cyclonic spray chamber and a Scott-type spray chamber made from PFA and PEEK provides a straightforward approach for improving the performance of inductively coupled-mass spectrometry (ICP-MS). The characteristics of the tandem spray chamber were critically evaluated against a PEEK cyclonic and a PFA Scott-type spray chamber, respectively. Sensitivity across the entire mass range was increased by about three times compared to the conventional setup utilizing only one spray chamber. Precision of the results, especially at low signal intensities, improved by 160% and 31% compared to the cyclonic and Scott-type spray chamber, respectively. Using the tandem spray chamber, the oxide formation rate was lowered by about 50%. Signals as low as 30 counts could be determined under routine measurement conditions with a RSD of 2.4% thus allowing to precisely quantify small concentration differences at the ng L$^{-1}$ concentration level. The excellent precision (0.02-0.07%) of $^{206}$Pb/$^{207}$Pb and $^{206}$Pb/$^{208}$Pb ratios determined in pore water samples was rather limited by the instrumental capabilities of the single collector ICP-MS instrument than by the performance of the tandem spray chamber.

*Keywords:* ICP-MS, tandem spray chamber, lead isotope ratios, trace elements, pore waters

## Introduction

The stability and efficiency of the sample introduction system is one of the limiting factors for the precision achievable using ICP-MS. The smoother the sample is introduced into the mass spectrometer, i.e. the more homogeneous the droplet size distribution of the sample aerosol, the better the precision of the analytical results.

In this respect, the two most frequently employed types of spray chambers used in ICP-MS, cyclonic and Scott-type spray chambers, respectively, offer different performance characteristics. Cyclonic spray chambers provide higher sensitivity, whereas Scott-type spray chambers generally help to produce a more stable sample aerosol. Assembling both spray chamber designs in series yielding a single tandem spray chamber arrangement can potentially combine the advantages of both ways of aerosol processing. A similar tandem spray chamber made from quartz glass and introduced several years ago already demonstrated improved performance, but suffers from some drawbacks which have restricted its use so far (Olofsson et al. 2000; Krystek and Ritsema 2002; Thermo Electron Co.). For example, additional heating of the cyclonic spray chamber with an IR lamp and cooling the Scott-type spray chamber was required to improve sensitivities by about 3-times (Olofsson et al. 2000) compared to one spray chamber. Moreover, this tandem spray chamber is made from quartz glass and thus has another two major disadvantages: 1) analyte solutions containing HF or $HBF_4$ cannot be analyzed and 2) even though quartz glass will provide blank contributions that are acceptably low for many applications, contaminations originating from chemically inert materials such as PFA and PEEK are much smaller and thus these materials are nowadays preferred for low level (ng $L^{-1}$ or below) determinations.

The aim of this study is to critically evaluate the performance characteristics of the prototype of a new HF-resistant tandem spray chamber by the determination of 24 trace elements (Ag, Al, Ba, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Mg, Mn, Ni, Pb, Rb, Sb, Sc, Sr, Tl, Ti, U, V, Zn) and Pb isotope ratios in small volumes of humic-rich pore water samples from peat bogs using clean room facilities and an inductively coupled plasma-sector field mass spectrometer (ICP-SF-MS).

## Experimental

### LABORATORIES AND INSTRUMENTATION

All sample handling in the laboratory and the preparation of all standards were performed in clean rooms under laminar flow clean air benches of class 100 to minimize the potential risk of contamination.

The ICP-MS used in this study was an Element2 ICP-SF-MS (Thermo Electron, Bremen, Germany) equipped with a guard electrode to eliminate secondary discharge in the plasma and to enhance overall sensitivity. A micro volume autosampler (ASX 100, Cetac Technologies, Omaha, NE, USA) and a HF resistant sample introduction kit consisting of a microflow PFA nebulizer (Elemental Scientific Inc., Omaha, NE, USA), a PEEK cyclonic spray chamber (internal volume: 40 mL) or a PFA double pass Scott-type spray chamber (internal volume: 100 ml) and a sapphire injector tube served as the standard configuration. In the tandem spray chamber arrangement, a prototype consisting of the PEEK cyclonic spray chamber mentioned above was directly connected to a Scott-type spray chamber made from PFA (internal volume: 100 mL) (electronic supplementary information – ESI 1). Both spray chambers were drained using a peristaltic pump operated at 2 rpm. At the low sample uptake used in this study (< 100 µL min$^{-1}$), however, no liquid was drained from the Scott-type spray chamber.

The PFA nebulizer was operated in the self-aspirating mode (~75 µL min$^{-1}$) to avoid potential contamination from the peristaltic pump tubing and to allow a smooth introduction of the sample aerosol into the ICP-SF-MS. The optimum nebulizer gas flow was slightly higher for the tandem spray chamber compared to that needed when the ICP-SF-MS was operated with only one spray chamber. Further details of the ICP-SMS operating conditions and the data acquisition parameters for both concentration and Pb isotope determinations have been reported previously (Krachler et al. 2005; Krachler et al. 2004a-c). The entire sample introduction system was hosted in a class 100 laminar flow bench.

### REAGENTS AND STANDARDS

For the preparation of all solutions, high purity water (18.2 MΩ cm) from a MilliQ-Element system designed for ultra trace analysis (Millipore, Milford, MA, USA) was used. Nitric acid (65%, analytical-reagent grade, Merck, Darmstadt, Germany) was further purified twice by distillation, using a high purity quartz unit for sub-boiling of acids (MLS GmbH, Leutkirch, Germany). Both the water purification system and the sub-boiling distillation unit were operated in clean rooms.

Calibration solutions for the 24 elements considered (Ag, Al, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Rb, Sr, Tl, Ti, U, V, Zn) were prepared daily by appropriate dilution of a multi element stock standard solution (Merck) and single element standard solutions (Cs, Sb, Sc; Merck) with 1% (v/v) high purity nitric acid. Quantification of trace element concentrations was performed establishing calibration curves by linear regression. For daily mass calibration of the ICP-SMS, a multi element solution containing 10 mg L$^{-1}$ of each Ba, B, Co, Fe, Ga, In, K, Li, Lu, Na, Rh, Sc, Tl, U and Y was diluted with 1% $HNO_3$ to a concentration level of 1 µg L$^{-1}$. Indium at a concentration of 1 µg L$^{-1}$ was used for internal standardization of the measurements. A 0.05% detergent (Klarin®, Reinelt, Friedberg, Germany) solution, used for rinsing in between the analyte solutions, was prepared by diluting appropriate amounts of the detergent with 1% high purity nitric acid.

### SAMPLE COLLECTION AND PROCESSING

Samples (volume: 10 mL) were collected from specific depths using a pre-cleaned, home-made pore water extraction device constructed from plexiglass. Immediately after collection, the pore water samples were filtered on-site through 0.45 µm high purity filters (GD/XP, Whatman) into 15 ml-Falcon® tubes. Following US EPA Method 1669 (Telliard 1996), pore water samples were acidified with double sub boiled nitric acid to 1% (v/v) in a class 100 clean bench upon arrival in the laboratory. After some days of storage at 4°C in the refrigerator, a precipitate of humic acids was visible in the pore water solutions. This precipitate, developing at low pH values, was subjected to centrifugation at 3000 rpm for 10 min. The supernatant was analyzed for trace elements and Pb isotopes in this study. Detailed investigations on the trace element content of the precipitate revealed that generally the precipitate contains only a very small amount (from 2 to 4% of the total metal concentration of the filtered pore water sample) of trace elements with a maximum of 10% for Cu and Cr in the worst case. Thus it is well justified to consider only the supernatant for analyses.

All pore water samples were collected in triplicate at each specific depth. The results presented for Pb isotope ratios are the mean of the analyses of the three pore water samples.

### QUALITY CONTROL

For the assessment of the accuracy of elemental concentrations determined in the pore water samples, the riverine water reference material (SLRS-4, National Research Council Canada, Ottawa, Canada) was used for quality control purposes. Good agreement between the experimentally established and certified concentrations within their analytical uncertainties could be established (Krachler et al. 2005; Krachler et al. 2004a-c).

The accuracy of Pb isotope ratio measurements was ascertained by the analyses of the certified Pb isotope standard NIST SRM-981. In agreement with our previous work (Krachler et al. 2005; Krachler et al. 2004c), replicate measurements on different days demonstrated that the experimental and certified $^{206}$Pb/$^{207}$Pb and $^{206}$Pb/$^{208}$Pb ratios agreed to within 0.06% (Table 11).

**Table 11**. Experimentally established (average ± □[a]) and certified (average ± 2 □[a]) Pb isotope ratios in the isotopic reference material NIST SRM-981.

| NIST SRM-981 | Found, N=2 | Certified | Deviation from certificate |
|---|---|---|---|
| $^{207}$Pb/$^{206}$Pb | 0.9141 ± 0.0003 | 0.91464 ± 0.00033 | 0.06% |
| $^{208}$Pb/$^{206}$Pb | 2.1673 ± 0.0006 | 2.1681 ± 0.00033 | 0.04% |

[a] ± …standard deviation

## Results and discussion

All performance characteristics described in this study are compared to our standard sample introduction configuration (same sample capillary and low flow PFA nebulizer, PEEK cyclonic spray chamber, guard electrode) used previously for the determination of trace elements and Pb isotopes in ice and water samples (Krachler et al. 2005; Krachler et al. 2004a-c). Additionally, the features of the PFA Scott-type spray chamber are included for a comparison.

### SENSITIVITY AND SIGNAL STABILITY

Using the tandem spray chamber, the $^{115}$In response of the ICP-SF-MS increased by 280% compared to the conventional setup utilizing only one spray chamber. It should be noted, however, that actual signal intensities vary with sample uptake rate, i.e. increased sample uptake rates provide higher signal intensities and vice versa.

The observed enhancement of signal intensities was mass dependent with lower masses gaining less signal enhancement (2.5 times), while the benefit for higher masses (> m/z 115) approached an improvement factor of three (Fig. 12).

**Table 12.** Comparison of performance characteristics of various spray chambers.

| | Spray chamber | | |
|---|---|---|---|
| | PEEK/PFA tandem | PEEK cyclonic | PFA Scott-type |
| Precision, % (N=55)[a] | | | |
| *Mean* ± | 1.05 ± 0.57 | 2.46 ± 0.79 | 1.53 ± 0.98 |
| *Median* | 0.90 | 2.37 | 1.18 |
| Matrix tolerance | + | − | + |
| Sensitivity | ++ | + | − |
| Oxide formation rate, %[b] | 4 - 5 | 6 - 12 | 6 - 12 |

[a] obtained for ~ 20 000 cps measured at m/z 115 in the medium resolution mode (m/Δm 4000).
[b] based on UO/U ratio

In addition to the signal enhancement for all masses, the tandem spray chamber markedly increased the stability of the signals. Compared to the performance of the cyclonic spray chamber, the within-run precision for comparable signal intensities and identical acquisition parameters was improved by a factor of ~3 (Table 12). Adopting the data acquisition parameters given elsewhere Krachler et al. 2005; Krachler et al. 2004b), relative standard deviations for the determination of elemental concentrations were generally between 0.5 and 1%. As an example, Fig. 13 highlights the relative standard deviation (RSD) of the $^{115}$In signal (≈ 20 000 cps) measured in the medium resolution mode (m/Δm 4000) of the ICP-SMS during the course of 8 hours. Precisions of the $^{115}$In signal were at or above 2% using the cyclonic spray chamber. In contrast, the superior aerosol quality produced with the help of the tandem spray chamber decreased RSDs of the $^{115}$In signal to < 2%, and frequently below 1%

(Fig. 13). In that context the Scott-type spray chamber (2nd spray chamber) acts like a buffering volume that stabilizes the aerosol generated by the nebulizer and the cyclonic spray chamber (1st spray chamber).

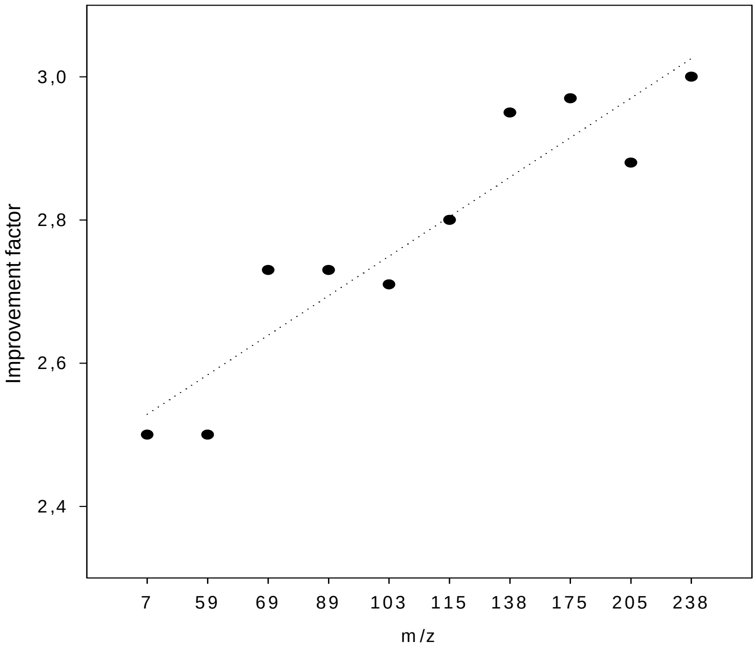

**Fig. 12.** Enhancement of signal intensities (n=3, precisions of single data points ≤ 5%) across the entire mass range obtained with the HF-resistant tandem spray chamber compared to a PEEK cyclone spray chamber. Note: The dotted regression line indicates a hypothetical linear relationship between improvement of sensitivity and m/z.

For the evaluation of the precision and accuracy of Pb isotope ratio measurements, we adopted an analytical protocol developed recently by our group (Krachler et al. 2004a,c). The precision (0.02-0.07%) of $^{206}$Pb/$^{207}$Pb and $^{206}$Pb/$^{208}$Pb ratios (n=72) determined in the pore water samples was similar to that obtained previously using only one spray chamber (Krachler et al. 2004a,c) and was limited by the instrumental capabilities (single collector, counting statistics) of the ICP-SF-MS itself, rather than by the performance of the tandem spray chamber. It is additionally important to note here that natural variations in the samples themselves, i.e. the average of the analyses of pore water samples collected in triplicate from the same depth, revealed higher relative standard deviations (generally 0.1-0.3%) than did the ICP-SF-MS measurements (Fig. 14). For complex samples such as pore waters, therefore, the precision offered by the instrumental setup described here is excellent.

### OXIDE FORMATION

The formation of element oxides and other polyatomic species is a well recognized drawback of ICP-MS. To help overcome this problem, ICP-SF-MS is gaining popularity. Many of these polyatomic interferences can be separated from the analyte signal using the medium (m/Δm 4000) or the high resolution mode (m/Δm 10 000) of the ICP-SF-MS employed. Nevertheless, for many applications it is essential to minimize the formation of oxides and other interfering

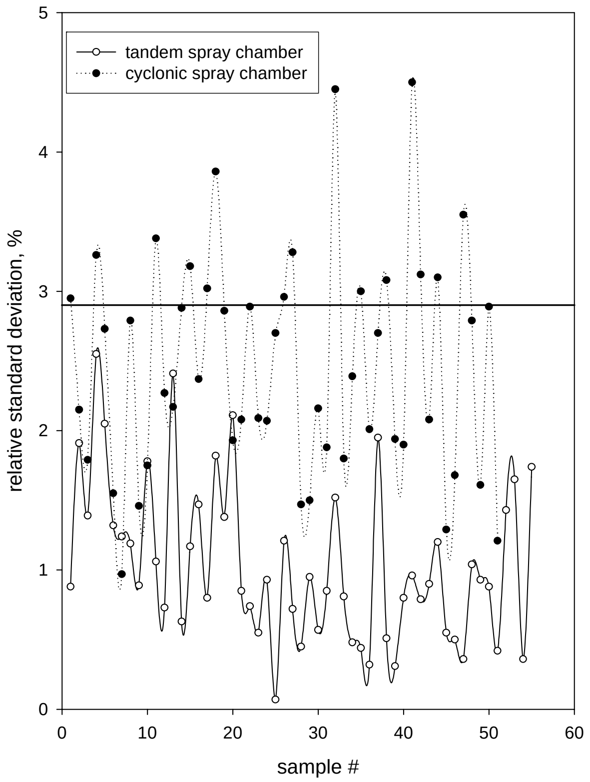

**Fig. 13.** Comparison of signal stabilities of the $^{115}$In signal monitored in the medium resolution mode (m/Δm 4000) using either the tandem spray chamber or a PEEK cyclonic spray chamber analyzing organic-rich pore water samples during the course of 8 hours. Each data point represents the average of 3 x 8 individual scans across the mass range.

species in order to gain maximum sensitivity and to allow accurate determinations of elemental concentrations and isotope ratios in the low resolution mode (m/Δm 300). Using a low flow nebulizer, one spray chamber and the guard electrode, the formation of oxides is relatively high for the employed ICP-SF-MS and amounts to a minimum value of 6-12% based on the UO/U ratio (Krachler et al. 2004a). In turn, the tandem spray chamber produces a slightly dryer aerosol yielding an UO/U ratio ranging from 4% to 5%, respectively. This feature, however, is certainly only a marginal advantage, and if lower oxide formation rates are needed, another sample introduction system consisting of an aerosol desolvation device is required.

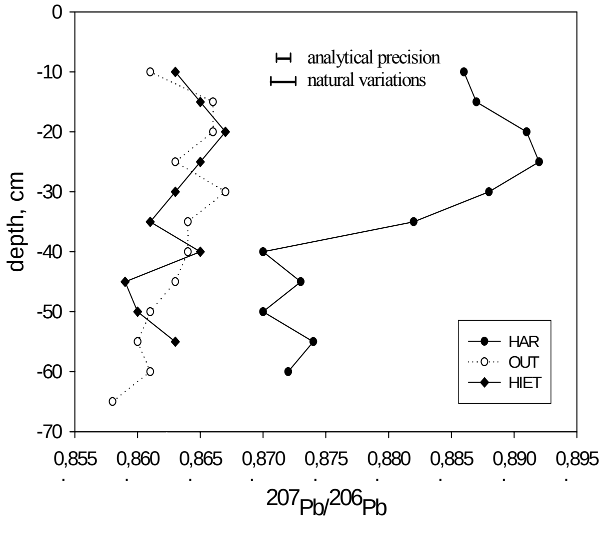

**Fig. 14.** Isotopic composition ($^{207}$Pb/$^{206}$Pb) of the pore water profiles collected at three peat bogs in Finland. Note that the analytical precision (i.e. instrumental capabilities, ~0.05%) of Pb isotope analyses using ICP-SF-MS is approximately 3-times better than natural variations of isotopic ratios as evident through triplicate sampling at the same depth.

### MATRIX TOLERANCE

The employed guard electrode enhances sensitivity by several times, but, at the cost of loss of matrix tolerance of the ICP-SF-MS. In a previous study we found signal suppressions of up to 50% when analyzing an undiluted riverine water reference material (SLRS-4) using the PEEK cyclonic spray chamber alone (Krachler et al. 2004b). This huge signal suppression was not evident during the determination of trace elements in SLRS-4 and pore water samples using the tandem spray chamber, suggesting a higher matrix tolerance than the cyclonic spray chamber. It should be noted, however, that the Scott-type spray chamber also produces stable signals during the analyses of SLRS-4, indicating that internal standardization becomes very important when the cyclonic spray chamber is employed, even when only water samples are to be analyzed.

### PORE WATER ANALYSES

Pore water samples were collected from three Finnish bogs: near Harjavalta (HAR), close to a Cu-Ni smelter in southwestern Finland; Outokumpu (OUT) which is the location of a famous Cu-Ni mine, and Hietajärvi (HIJ) which is a low-background site, remote from any point sources of atmospheric trace metals. Pore water samples analyzed in this study are a part of an ongoing study aiming to evaluate the use of the chemical composition of pore waters as a sensitive indicator of the release of trace metals from atmospheric particles to the pore fluids, as well as the potential of these metals to migrate subsequent to their deposition. Here we want to present preliminary concentration data from an industrial site (OUT) and a control site which is remote from industrial activity (HIJ). As many of the elements under investigation may be fixed in the peat column, their concentrations in the pore water samples can be very low (Table 13).

Concentrations as low as a few ng $L^{-1}$ need to be precisely determined in the pore water samples to establish useful depth profiles. Uranium and Sc concentrations, for example, vary only within a few ng $L^{-1}$). These low concentrations correspond to a few thousand counts $s^{-1}$ for U determined in the low resolution mode and ~30 counts for Sc monitored in the medium resolution mode. Given the stable performance of the tandem spray chamber, these low concentrations can be determined with relative standard deviations of 1.4% (U) and 2.4% (Sc), respectively, allowing precise quantifications of elemental concentrations at ultra low concentration levels.

**Table 13.** Summary of statistics of elemental concentrations (µg $L^{-1}$) of selected trace elements in the pore water samples from two different peat bogs (A…Outokumpu; B…Hietajärvi) in Finland.

| | Peat Bog A, (n=36) | | | Peat Bog B, (n=24) | | | |
|---|---|---|---|---|---|---|---|
| Element | Min. | Max. | Median | Min. | Max. | Median | Ratio A/B* |
| Ag | 0.001 | 0.008 | 0.003 | 0.001 | 0.008 | 0.003 | 1 |
| Al | 18 | 48 | 29 | 21 | 89 | 33 | 0.9 |
| Ba | 0.29 | 2.8 | 1.1 | 0.26 | 1.7 | 0.49 | 2.2 |
| Bi | 0.003 | 0.017 | 0.006 | 0.004 | 0.013 | 0.006 | 1 |
| Ca | 89 | 620 | 260 | 180 | 410 | 240 | 1.1 |
| Cd | 0.007 | 1.17 | 0.015 | 0.016 | 0.149 | 0.034 | 0.4 |
| Co | 0.024 | 0.119 | 0.055 | 0.022 | 0.060 | 0.029 | 1.9 |
| Cr | 0.11 | 0.34 | 0.17 | 0.13 | 0.47 | 0.27 | 0.6 |
| Cs | 0.009 | 0.089 | 0.019 | 0.022 | 0.167 | 0.053 | 0.4 |
| Cu | 0.24 | 0.96 | 0.37 | 0.24 | 2.5 | 0.50 | 0.7 |
| Fe | 28 | 240 | 103 | 25 | 125 | 43 | 2.4 |
| Mg | 40 | 130 | 87 | 44 | 89 | 59 | 1.5 |
| Mn | 0.90 | 6.5 | 3.4 | 0.69 | 2.4 | 0.96 | 3.5 |
| Ni | 0.39 | 14 | 0.51 | 0.46 | 0.89 | 0.57 | 0.9 |
| Pb | 0.15 | 0.65 | 0.28 | 0.22 | 0.91 | 0.35 | 0.8 |
| Rb | 0.20 | 5.7 | 0.59 | 0.53 | 7.3 | 1.7 | 0.4 |
| Sb | 0.021 | 0.091 | 0.035 | 0.043 | 0.102 | 0.062 | 0.6 |
| Sc | 0.002 | 0.021 | 0.004 | 0.002 | 0.014 | 0.003 | 1.3 |
| Sr | 0.32 | 2.2 | 1.0 | 0.85 | 2.9 | 1.3 | 0.8 |
| Tl | 0.001 | 0.009 | 0.004 | 0.011 | 0.050 | 0.017 | 0.2 |
| Ti | 0.62 | 2.0 | 1.1 | 0.84 | 7.3 | 1.2 | 0.9 |
| U | 0.002 | 0.006 | 0.004 | 0.003 | 0.014 | 0.006 | 0.7 |
| V | 0.04 | 0.23 | 0.10 | 0.10 | 0.59 | 0.28 | 0.4 |
| Zn | 3.9 | 15 | 6.8 | 8.5 | 36 | 13 | 0.5 |

## Conclusions

The prototype of the tandem spray chamber evaluated in this study is made from chemically inert materials (PFA and PEEK), does not require any heating and/or cooling of the spray chambers employed and distinctly improves instrumental performance (mainly ~3-times improvement of sensitivity and high stability of ICP-MS signals). Therefore this “plug in and measure” tandem spray chamber is a straightforward, HF-resistant and cost-effective tool to improve the performance of any ICP-MS. The tandem spray chamber that can be easily adopted for routine analyses, will become commercially available in the very near future.

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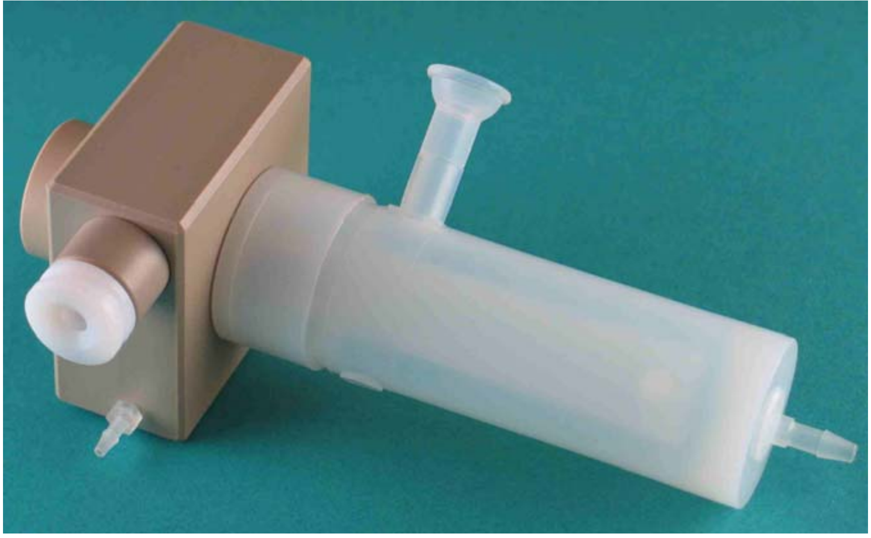
## Electronic Supplementary Information

**ESI 1:** Photo of the tandem spray chamber arrangement consisting of a PEEK cylonic spray chamber and a PFA Scott-type double-pass spray chamber.



# PEAT BOGS AS ARCHIVES

# CHAPTER 4

Ukonmaanaho, L., T.M. Nieminen, N. Rausch, W. Shotyk. Heavy metal and arsenic profiles in ombrogenous peat cores from four differently loaded areas in Finland.

*Water, Air, and Soil Pollution* **158***: 277-294, 2004*

# Heavy metal and arsenic profiles in ombrogenous peat cores from four differently loaded areas in Finland

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*Water, Air, and Soil Pollution* **158***: 277-294, 2004*

**Abstract.** The concentrations and vertical distribution of Cu, Ni, Zn, Pb and As were studied in four different ombrotrophic peat bogs with varying heavy metal loads at Hietajärvi, Outokumpu, Harjavalta and Alkkia in Finland. At each site a peat sample (15x15x100cm) was taken using a Titanium Wardenaar corer, and the samples were cut into 5 cm slices. Dried and milled samples were determined by X-ray-fluorescence (XRF). The mean concentrations of the elements were at their highest at Harjavalta (the most polluted area), apart from Cu which had the highest value at the Cu-treated site at Alkkia. Cu concentrations were above 'the lowest effective limit' (LOEL) on all the plots except for the background plot at Hietajärvi. The maximum Cu values were reached in the topmost 20 cm layer, indicating the effects of mining and smelting activities. The highest Zn and Ni concentrations occurred in the 0-40 cm layer. At all sites the maximum Pb concentrations were located between 10-50 cm. However, the Pb concentrations were higher at Alkkia and Harjavalta than at Outokumpu and Hietajärvi, indicating anthropogenic sources of Pb at the former sites. The As concentration was also the highest in the uppermost peat layers. The mean concentrations were markedly lower in the deeper layers (40-80 cm) than in the upper layers

*Keywords*: deposition, distribution, heavy metals, peat, pollution factor

## Introduction

Peat consists of organic deposited matter produced by vegetation. In ombrotrophic peat bogs the only source of water and nutrients is atmospheric deposition, because the 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 in peat under the acrotelm limit metal mobility through adsorption and sulphide formation (Wilkin and Barnes, 1997). The capacity of ombrotrophic peat bogs to accumulate elements makes them useful tools to assess contamination levels in terrestrial ecosystems.

In Finland, heavy metal concentrations in the surface layers of ombrotrophic peat bogs have been used to estimate heavy metal deposition at a regional scale since the early 1970's

(Pakarinen 1981; Pakarinen and Tolonen, 1976). Some of these trace metal studies have determined the vertical distribution of copper, lead and zinc (Kaunisto and Paavilainen, 1988). However, fewer studies have examined the distribution of arsenic and nickel. In organic soils the mobility of zinc and nickel is strongly related to pH, while lead and copper fluxes tend to be more determined by organic matter (Bergkvist *et al.,* 1989). Field experiments have shown that arsenic can be mobilized and transported from contaminated soils to groundwater or surrounding lakes (Räisänen *et al.,* 1997; Kalbitz and Wennrich, 1998).

Forest mosses are widely used as air pollution bioindicators (e.g. Rühling and Tyler 1968; Tyler 1970, Poikolainen *et al.,* 2004), although they usually indicate only the current situation. The vertical distribution of elements in peat could provide information about recent trace element deposition, as well as about temporal trends (e.g. Shotyk, 1996; Shotyk *et al.,* 1997, Steinnes, 1997). Especially *Sphagnum* peat from ombrotrophic peat bogs provides significant information about temporal and spatial trends of air-pollution-derived trace elements (Steinnes, 1997). Heavy metal distribution in age-dated peat cores by depth has been used to determine the deposition history of heavy metals: for example, long chronologies of lead deposition have been obtained in Switzerland (Shotyk *et al.,* 1997; Shotyk *et al.,* 1998) and in Spain (Martínez-Cortizas *et al.,* 1997). For peat cores to be used as archives, however, it is necessary to verify that the investigated element is permanently immobilised in the peat and cannot migrate after the decomposition process has started.

In a previous paper we studied the enrichment of trace elements in the upper 15 cm layer of a polluted and an unpolluted peat bog (Nieminen *et al.,* 2002). In the present study, we have taken deeper (c. 100 cm) peat cores from four peat bogs with known metal deposition history loads in the central part of Finland. The aim was to study the compatibility of the vertical distributions of copper (Cu), lead (Pb), nickel (Ni), zinc (Zn) and arsenic (As) concentrations in the uppermost layer of the ombrotrophic peat bogs and the recent pollution history of the site, as well as regional differences between the sites in heavy metal concentrations.

## Material and methods

### SITE DESCRIPTION

The concentrations and vertical distribution of Cu, Ni, Zn, Pb and As were studied at four *Sphagnum*-dominated, undrained, ombrotrophic peat bogs at Hietajärvi, Outokumpu, Alkkia and Harjavalta (Fig. 15, Table 14).

The Hietajärvi site is located in Patvinsuo National Park, Eastern Finland (63°09’N, 30°40’E), where the peatland area is in a natural condition (Tuominen and Mäkelä, 1995). As there are no agricultural activities or roads in the vicinity, and no point sources of heavy-metal air pollution within a radius of tens of kilometres, the only source of air pollution is from long-range, transported emissions (Ukonmaanaho *et al.,* 1998; 2001). This site is used here to provide a record of 'background' deposition for comparison with the other sites. The Hietajärvi catchment has been systematically monitored since 1989 as a part of the UN-ECE International Cooperative Programme on Integrated Monitoring in order to monitor the effects of long-range transboundary air pollution on forest ecosystems (Manual... 1999).

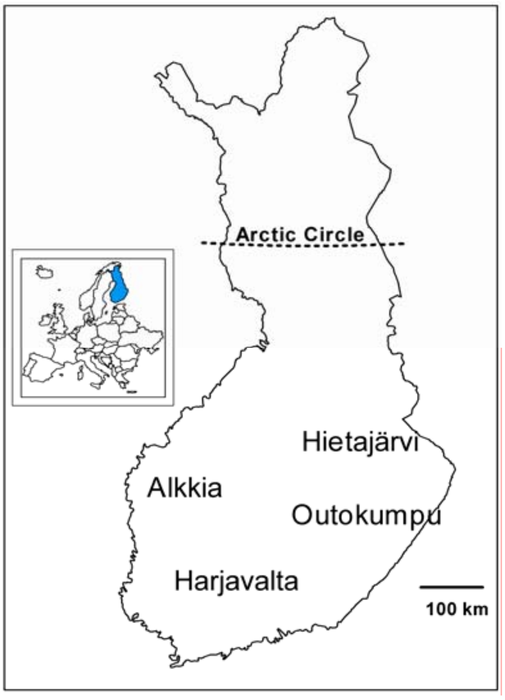

**Fig. 15.** Location of the study sites.

The Outokumpu sampling site is located in a pristine peat bog of the Viurusuo mire complex in Eastern Finland, 8 km SW of the town of Outokumpu (62°40'N, 28°51'E). A Cu-Ni mine and concentration plant operated at Outokumpu from 1910 until the 1980's, and a small smelter from 1913 until 1929 (Kuisma, 1985). Although the prevailing wind direction in southern Finland is SW, the effect of particulate emissions from the mining area should be detectable in the peat bog. Furthermore, the wind direction in this region frequently changes to the NE because of the meteorological effects of the numerous nearby lakes.

The Alkkia sampling site is located in SW Finland (62°11', 22°48'E). In July 1962, an ore-prospecting simulation experiment was carried out at the Tunkiosalonneva mire (at Alkkia) by applying Cu, Ni and Zn sulphate on 20 x 20 m test areas in a peat bog. The plot sampled in this study was treated with 200 kg Cu ha$^{-1}$ (Veijalainen, 1998). As the surface vegetation is severely damaged on some of the plots, the distribution and mobility of these elements may be drastically different compared to the situation in naturally growing peat.

**Table 14.** General features of the study areas.

| Site | Hietajärvi | Outokumpu | Harjavalta | Alkkia |
|---|---|---|---|---|
| Climatic zone | Middle boreal | Southern boreal | Southern boreal | Southern boreal |
| Annual mean temperature, °C [a] | 1.5 | 2.3 | 4.1 | 3.0 |
| Annual temperature sum, °C [a] | 1064 | 1188 | 1268 | 1110 |
| Annual precipitation sum, mm [a] | 616 | 615 | 571 | 612 |
| Altitude m a.s.l. | 168 | 108 | 40 | 160 |
| Peat type | Cottongrass-pine bog [b] | Cottongrass-pine bog [b] | Cottongrass pine bog [b] | Cottongrass-dwarf-shrub pine bog [c] |
| Depth of peat | >2 m | > 6 m [d] | >2 m | 1.60m |
| $pH_{(H_2O)}$ of surface peat layer | 4.09 | 4.02 | 3.83 | 3.86 |
| Decomposition of peat, (after von Post) | H3-H8 | H1-H5 | H1-H8 | H1-H8 |
| Name of the mire complex | Patvinsuo | Viurusuo | Pyhäsuo | Tunkiosalonneva |

[a] for period 1950-1999, estimated using the method described in Ojansuu and Henttonen, 1983.
[b] Laine and Vasander, 1996
[c] Huikari, 1952
[d] Leino and Saarelainen 1990

At the Harjavalta site, peat samples were taken from a pristine peat bog in the Pyhäsuo mire complex, 6 km northeast of Harjavalta, SW Finland (61°21'N, 22°11'E), where a copper smelter has been operating since 1945 and a nickel smelter since 1959 (Kuisma, 1985). Emissions from the smelter have severely affected the forest vegetation in the immediate vicinity of the stack. The slag produced during smelting is stored in land basins at the plant site. The Cu slag is pumped into the tailing area as sludge, and the granulated Ni-slag is piled in heaps and landscaped. During piling the uncovered Ni-slag heaps are an additional source of dust emissions (Nieminen *et al.*, 2002).

The vegetation on each bog was characterised by a sparse tree (*Pinus sylvestris*) cover. Most of the ground layer in all the sites consisted of *Sphagnum* species e.g. *Sphagnum fuscum*, *S. balticum*, *S. angustifolium* or *S. magellanicum*, all of which more or less indicate ombrotrophy. In addition, some dwarf shrubs (e.g. *Andromeda polifolia, Empetrum nigrum, Ledum palustre* and *Vaccinium* species) and a few herbs such as *Carex globularis* and *Rubus chamaemorus* are found in varying amounts at each site.

The major sources of Cu, Pb and Zn pollution in Finland are metallurgical processes, and of Ni pollution energy production and the use of oil fuel in industry (Jalkanen, 2000). Most of the As derived from anthropogenic sources is released as a by-product of mining, metal-refining processes, the burning of fossil fuels, and agricultural use (Cullen and Reimer, 1989;

Nriagu, 1994; Cai *et al.,* 2002). According to Melanen *et al.* (1999), emissions of heavy metal particulates in 1997 in Finland were one third of the level in the early 1990s due to the installation of sulphur-removal systems; some metal-containing particles, e.g. Pb, Cu and Ni, are often associated with $SO_2$ emissions. Heavy metal emissions in Finland during 1990–2001 are shown in Fig. 16, and emissions from the Harjavalta Cu-Ni smelter in Fig. 17.

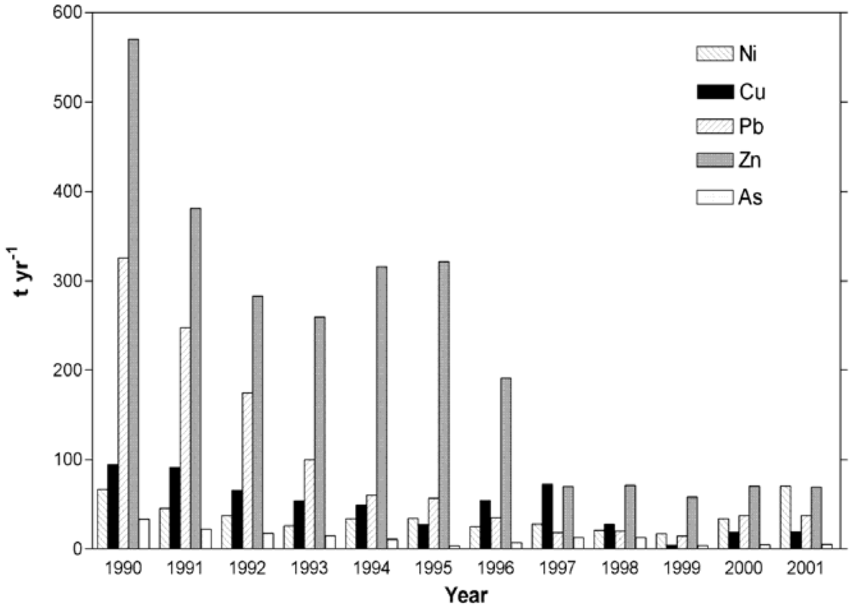

**Fig. 16.** Finnish emissions of Zn, Pb, Ni, Cu and As during 1990-2001.

## SAMPLING AND ANALYSIS

The criteria applied in choosing the sites were firstly that the sampling sites should be exposed to heavy metal deposition (in the vicinity of a smelter, mine, heavy metal application), and secondly that the sites should represent as homogeneous ombrotrophic peat bogs as possible. Samples were taken from the lawn (surface layer between hummocks and hollows) near the central part of each bog. The peat sample (15 x 15 x 100 cm) was taken using a Titanium Wardenaar corer in September 2001. The living *Sphagnum* moss layer was removed from the top of the samples and the samples were cut into 5 cm slices with a titanium knife, and then packed in plastic bags. The species composition of the living vegetation was recorded at each site. 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 using an Energy-dispersive Miniprobe X-ray fluorescence-Multielement analyzer (EMMA-XRF) (Cheburkin and Shotyk, 1996) at EMMA Analytical Inc., Elmvale, Ontario, Canada.

Bonferroni tests (Sokal and Rohlf, 2000) were applied to the data to test for differences in mean concentrations between sites and two depth classes: upper layer (0-40 cm) and deeper layer (40-80 cm). Because of non-normal distribution, logarithm-transformed data were used.

The pollution factor (PF) was calculated in order to make comparisons between the reference site (Hietajärvi) and the other sites in two depth classes: upper (0-40 cm) and deeper layer (40-80 cm). The average element concentrations of the Outokumpu, Harjavalta, and Alkkia cores were divided by the corresponding concentrations of the Hietajärvi core as follows:

$$PF = \bar{x}_{\text{polluted}} / \bar{x}_{\text{Hietajärvi}}$$

The PF values thus merely provide a rough estimate of the extent of pollution at these sites compared to the Hietajärvi background site.

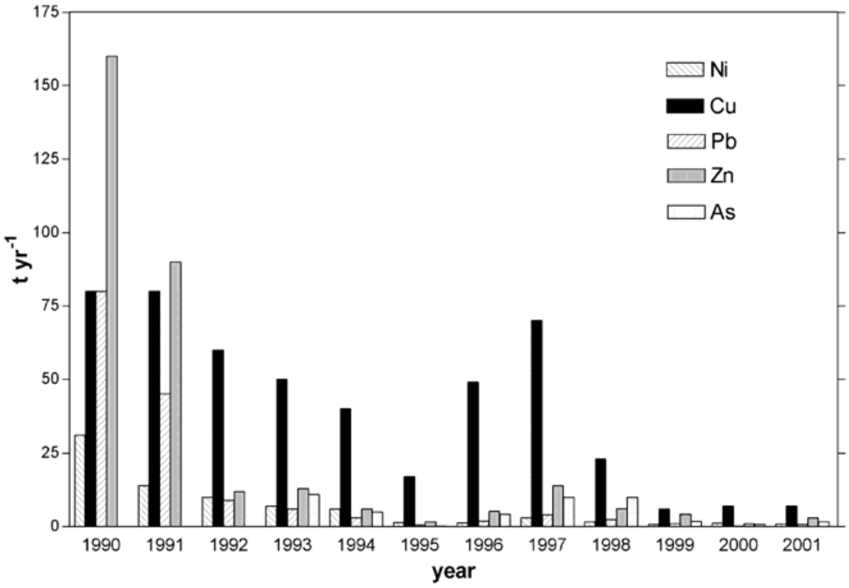

**Fig. 17.** Emissions of Zn, Pb, Ni, Cu and As from the Harjavalta Cu-Ni smelter during 1990-2001. Arsenic monitoring started in 1993.

## Results

### CONCENTRATIONS

The average total concentrations of As, Cu, Ni, Pb, and Zn in the peat cores are shown in Table 15. Overall, the concentrations in the upper layer (0-40 cm) of the peat cores were at their highest at Harjavalta and their lowest at Hietajärvi, apart from Cu which had the highest value (2731 µg g$^{-1}$) at the Cu-treated Alkkia site. The mean Cu concentration at Harjavalta was approximately 12% of the corresponding Cu concentration at Alkkia. The mean Zn concentration was lowest at Alkkia (27 µg g$^{-1}$), and slightly higher at Hietajärvi (32 µg g$^{-1}$). The differences in concentrations showed a strong regional pattern and a relationship with local pollution sources and depth.

The mean concentrations were markedly lower in the deeper layer (40-80 cm) than in the upper layer, and the differences in concentrations between plots were often non-significant.

**Table 15.** Average concentration ($\mu g\ g^{-1}$) and standard deviation (italics in parentheses) of Cu, Pb, and Ni in the surface layer (0-40 cm) and bottom layer (40-80 cm) of the peat in each site (n=8). Means within columns followed by same letter (lower case for 0-40 cm depth, and upper case for 40-80 cm depth) are significantly different from each other according to Bonferroni tests ($p < 0.05$).

| Site | Layer | Cu | Pb | Ni | Zn | As |
|---|---|---|---|---|---|---|
| Hietajärvi | 0-40 cm | 3.3 *(1.05)*ab | 11.3 *(4.55)* | 2.5 *(1.31)*a | 32.4*(13.01)* | 2.6*(1.63)*a |
| Outokumpu | | 21.4*(15.93)*c | 12.0 *(6.11)* | 6.1*(1.44)* | 52.5*(11.93)* | 3.4*(2.18)*b |
| Harjavalta | | 333.4 *(338.20)*a | 28.9 *(17.90)* | 83.9 *(81.32)*ab | 92.2*(57.61)* | 11.1*(6.71)*ab |
| Alkkia | | 2731.4 *(10.08)*bc | 20.3*(15.88)* | 7.7*(10.08)*b | 26.8*(21.22)* | 4.2*(2.94)* |
| Hietajärvi | 40-80 cm | 1.9*(0.65)* | 5.3 *(4.13)*A | 1.2 *(0.94)* | 4.7*(2.04)*AB | 0.6*(1.19)*AB |
| Outokumpu | | 2.8 *(1.66)* | 7.5 *(3.76)*B | 2.5*(1.02)* | 13.6*(11.99)*ACD | 2.3*(0.61)*AC |
| Harjavalta | | 3.9 *(1.11)* | 5.7 *(0.54)*C | 3.4*(3.58)* | 4.2*(0.84)*C | 1.9*(1.08)*BD |
| Alkkia | | 3.1*(2.82)* | 0.2*(0.37)*ABC | 1.6*(1.08)* | 1.8*(1.15)*BD | 0*(0)*CD |

## DISTRIBUTION

The distributions of all the elements were characterised by the highest concentrations occurring in the topmost 40 cm, with a rapid decrease on moving to deeper layers (Fig. 18). There was not much variation in the vertical distribution of Cu at the Hietajärvi background site, but at all the other sites the values started to increase towards the surface layer at the depth of 45-20 cm. The maximum Cu values were reached in the topmost 20 cm layer, while the highest Zn and Ni concentrations occurred in the top 40 cm layer. With respect to Pb there was no clear decrease on moving downwards in the profile, apart from at Harjavalta and Alkkia. At all sites the highest Pb concentrations were between 10-50 cm. The concentration of As was also the highest in the uppermost layers, decreasing in deeper depths to the detection limit of the analytical equipment used.

## POLLUTION FACTORS

In general, the other sites were more polluted (i.e. pollution factor > 1) than the Hietajärvi reference site (Table 16), especially in the case of Cu, which is logical because all the sites except Hietajärvi have been exposed to high Cu deposition or treatment. The exceptionally high Cu PF value in the upper layer (0-40 cm) at Alkkia (PF value = 828, i.e. the Cu concentration at Alkkia was over 800 times higher than at the Hietajärvi background site) is due to the Cu treatment. However, the PF values for Zn (upper and deeper layers) and for As and Pb (deeper layer) at Alkkia were similar or less than those at Hietajärvi. The PF values for Pb, Ni, Zn and As were highest at Harjavalta in the upper layer, while in the deeper layer the highest PF values were found at the Harjavalta or Outokumpu sites.

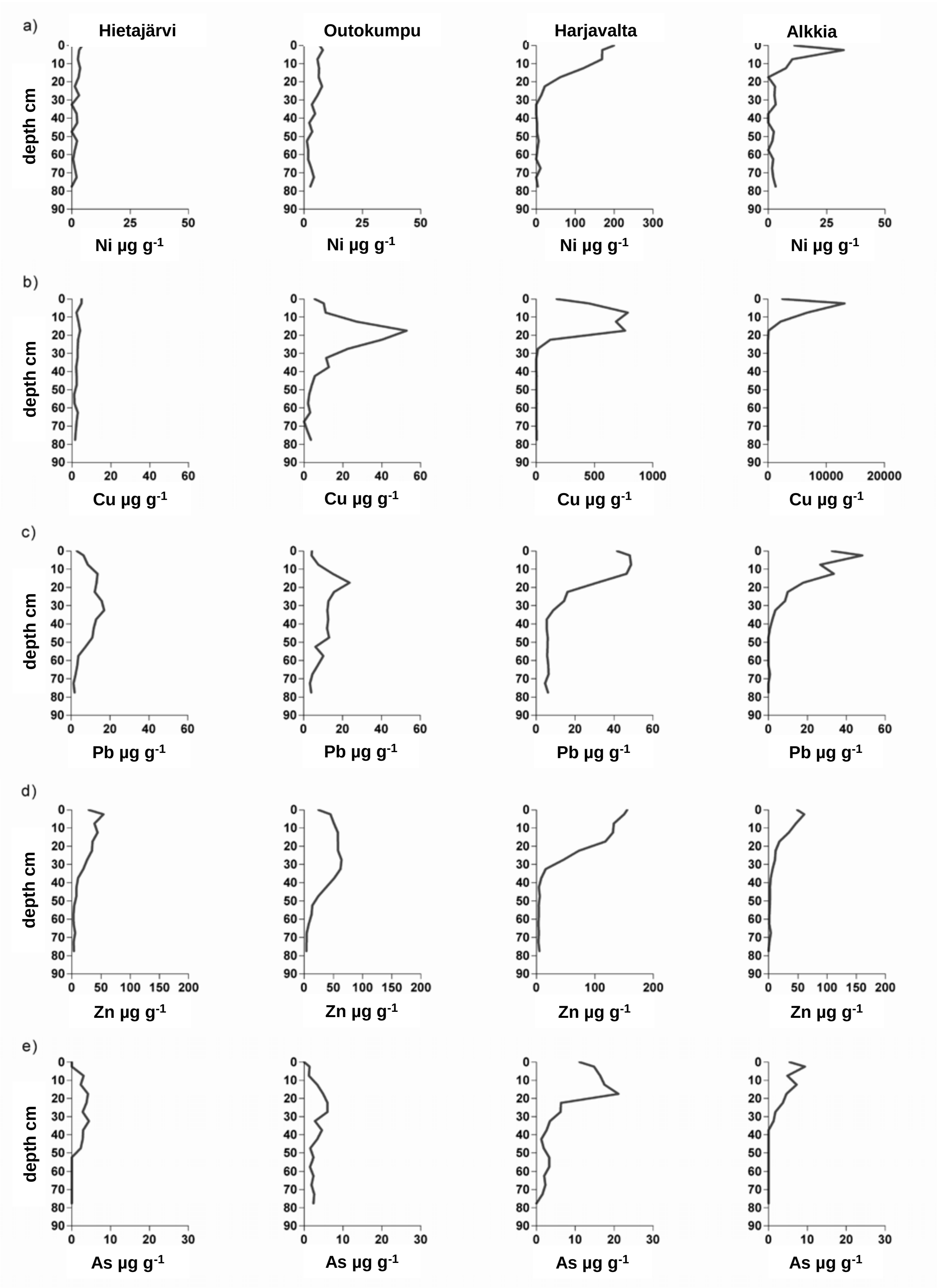

**Fig. 18.** Concentrations and distribution of a) Ni, b) Cu, c) Pb, d) Zn and e) As, in peat cores taken from the Hietajärvi, Outokumpu, Harjavalta and Alkkia sites. Samples were taken in September 2001. Note the different scales.

**Table 16.** Pollution factors (PF) for the different sites and two depth classes: surface (0-40 cm) and bottom layer (40-80 cm) using Hietajärvi as a reference site. The values used were mean concentrations of the whole profile.

| Site | Cu | Pb | Ni | Zn | As |
|---|---|---|---|---|---|
| *0-40 cm* | | | | | |
| Hietajärvi | 1 | 1 | 1 | 1 | 1 |
| Outokumpu | 6 | 1 | 2 | 2 | 1 |
| Harjavalta | 101 | 3 | 34 | 3 | 4 |
| Alkkia | 828 | 2 | 3 | 1 | 2 |
| *40-80 cm* | | | | | |
| Hietajärvi | 1 | 1 | 1 | 1 | 1 |
| Outokumpu | 1 | 1 | 2 | 3 | 4 |
| Harjavalta | 2 | 1 | 3 | 1 | 3 |
| Alkkia | 2 | 0 | 1 | 0 | 0 |

## Discussion

Previous studies in the Nordic countries have shown that heavy metal concentrations in deposition, mosses, needles, litterfall, soil etc. are generally relatively low compared to those found in temperate forest ecosystems (Bergkvist *et al.,* 1989; Ukonmaanaho *et al.,* 1998; Poikolainen *et al.,* 2004). In this study there were significant differences between sites and elements in heavy metal concentrations in peat. Local emissions at all the sites have decreased during the past decades, which was also reflected in the vertical distribution and concentration of the elements in peat. At Hietajärvi, which is a background area, the decrease in the concentration of elements reflected more the reduction in the long-range transport of heavy metal deposition into Finland than local sources. According to Poikolainen *et al.,* (2004), local emissions have the clearest effect on Cu and Ni deposition, which is also supported by the results of our study. The mean concentrations of the elements were at their highest in the Harjavalta peat, apart from Cu which had the highest value at the Cu-treated site at Alkkia. The PF values indicated that the other sites were more polluted than the Hietajärvi reference site. This was especially true for Cu, due to the fact that all the sites except Hietajärvi have been exposed to high Cu deposition or treatment. According to the critical concentration values for heavy metals in humus presented by Tyler (1992), the Cu concentrations were above ‘the lowest effective limit’ (LOEL, >20 mg kg$^{-1}$) on all the plots except for Hietajärvi. This suggests that Cu may have had ecotoxicological effects on the organisms in these areas.

In addition, the Ni concentration was above LOEL (20 µg $g^{-1}$; calculated for lichens and mosses) at Harjavalta.

### NICKEL

The Harjavalta site, which is located at a distance of 6 km from the Harjavalta Cu-Ni smelter, was clearly affected by the smelter. The highest Ni concentrations occurred in the surface peat (199.7 µg $g^{-1}$) and were well above the maximum Ni value (69 µg $g^{-1}$) recorded in 2000 in a national forest moss survey (Poikolainen *et al.,* 2004). The Ni concentrations decreased sharply on moving down to the deeper peat layers. However, the concentration at a depth of 25 cm was still 12.6 µg $g^{-1}$, after which the concentrations were small and inconsistent. Although Ni can form relatively weak complexes with organic matter, it is a rather mobile element that can be leached to some extent from the upper soil layers (Bergkvist *et al.,* 1989; Kabata-Pendias, 2001). At Harjavalta (Derome and Nieminen, 1998) and at Hietajärvi (Ukonmaanaho *et al.,* 2001) Ni has been reported to be relatively mobile in forest soil. The Ni smelter at Harjavalta has been operating since 1959 (Kuisma, 1985) and production has increased up until the present day. Although the measured Ni emissions from the stack have decreased, some additional Ni may be released during the nickel-refining process. According to the air particle measurements carried out in the vicinity of the Harjavalta smelter (distance between 0.8–1.5 km) in 1992 and in 1997, the concentrations of Cu- and Ni-containing particles (ng $m^{-3}$) have increased since 1992, while those of Zn and Pb have decreased (Saari *et al.,* 1998). In addition, the Ni concentrations in forest moss in the surroundings of the Harjavalta smelter increased from 1995 to 2000 (Poikolainen *et al.,* 2004). Our study site at Harjavalta is located downwind from the smelter.

The Ni concentrations in the upper peat layer at Alkkia were about 10% of those at Harjavalta; the Ni concentration in the topmost peat layer at Alkkia was as high as 32.3 µg $g^{-1}$. Because atmospheric deposition is not likely to be the cause of the relatively high Ni concentration in the surface layer at Alkkia, horizontal leaching from a nearby Ni-treated plot has probably contaminated the Cu-treated site sampled in this study. According to Veijalainen (1998), the peat (0-20 cm) at Alkkia has retained 63 % of the Ni dose applied, which was much lower than the corresponding 93% for Cu.

At the Outokumpu site, which is near the disused Cu-Ni mine, the Ni concentrations were less than 10 µg $g^{-1}$ throughout the whole peat profile. The Ni concentration decreased uniformly with increasing depth, although there was a slight increase at a depth of 70 cm. This might be due to Ni migration from the bedrock up into the overlying peat layer. Relatively low Ni concentrations in the Outokumpu peat profile, despite the vicinity of the Cu-Ni mine, indicate that the disused mine has had only a slight effect on the Ni concentration in the peat. On the other hand, most of the added Ni may have already leached out from the studied profile to the lower peat layers, as has earlier been noted (Bergkvist, 1989; Kabata-Pendias, 2001). At the Hietajärvi site the Ni concentrations were low (<5 µg $g^{-1}$) compared to the other sites, and decreased relatively evenly on moving down the profile.

## COPPER

The Cu concentrations in the Alkkia peat bog (Cu trial) were extremely high (maximum 13 000 µg $g^{-1}$) in the upper 15 cm layer. In this site the vegetation was severely damaged; only some liverworts were growing in the hollows, and *Eriophorum vaginatum, Calluna vulgaris*, and *Vaccinium sp*. on the hummocks. The litter layer was 5 cm thick and primarily consisted of undecomposed needles. It is clear that the extremely high Cu treatment has affected peat accumulation during the past few decades. *Sphagnum* mosses usually contribute most of the new organic matter to the surface peat (Clymo, 1983; Tolonen and Vasander, 1992; Paavilainen and Päivänen, 1995), but at Alkkia *Sphagnum* mosses had completely disappeared. However, some vascular plants such as *Arctostaphylos uva-ursi, Calluna vulgaris* and *Eriophorum vaginatum* were still present, and these probably have added organic matter also in the deeper layers of the peat through rhizomes and roots (Saarinen *et al.,* 1992). Veijalainen (1998) reported that stand mortality at Alkkia had increased on almost all the treated plots during 1964-1990. The Cu concentrations deeper in the peat profile were not markedly higher than the corresponding values at the other sites, suggesting that there has been insignificant vertical migration of Cu during the 40-year period.

At Harjavalta the highest Cu concentration occurred at a depth of 5-10 cm: 786 µg $g^{-1}$. In a peat profile taken earlier in the immediate vicinity of the Harjavalta Cu-Ni smelter (2 km), the average Cu concentration for the whole profile was 994 µg $g^{-1}$ (Nieminen *et al.,* 2002), while the Cu concentration in the upper 5 cm layer was over 4000 µg $g^{-1}$. According to Saari *et al.* (1998), 60 % of the Cu emissions are released from the low stack (70 m) at Harjavalta, and the rest from the taller stack (140 m). The dominance of the low stack emissions should theoretically cause a sharp decline in Cu deposition with increasing distance. However, at a distance of 6 km from the smelter the smelter derived pollutants seem to have caused elevated Cu concentrations in the surface layer of this peat.

At the Outokumpu site, which has been affected by earlier mining activities, the Cu concentrations in the upper 40 cm layer were high, with a peak value at a depth of 15-20 cm

(52.8 µg g$^{-1}$). However, this peak value is below the maximum value (260 µg g$^{-1}$) found in the national forest moss survey in 1990 (Poikolainen *et al.,* 2004). The Cu concentrations in Outokumpu were significantly higher than at corresponding depths in the Hietajärvi background area, clearly indicating the influence of the Cu-Ni mine in the vicinity of this peat bog. According to a lake sediment study carried out near Outokumpu, Cu and Ni accumulation was also clearly evident in lake Laukunlampi, which is located 10 km SE from Outokumpu mine (Verta *et al.,* 1989).

The Cu concentrations in a previous study on the same Hietajärvi plot were approximately the same as those obtained in this study (Nieminen *et al.,* 2002). At all of the studied sites, especially those that were exposed to a high Cu load, the highest Cu concentrations occurred in the upper 20 cm of the peat profile, indicating increased atmospheric deposition in recent years.

### LEAD

In contrast to Cu and Ni, the concentration of Pb showed only small differences between the sites. Surprisingly, there were more significant differences between the sites in the lower peat layer than in the upper peat layer, even though the average Pb concentration in the lower layer was relatively low. At all sites, the highest Pb concentrations occurred in the layers between 10-50 cm. The Pb concentrations obtained in the present study (on average 0.2-28.9 µg g$^{-1}$) were slightly higher than the background values of 3.8-8.3 µg g$^{-1}$ reported by Pakarinen (1981). However, Pakarinen's results were based on deeper peat layers (total depth 4.0-6.7 m) and the Pb concentrations obtained in our study were relatively small compared, for example, to the results of Shotyk (1996). Shotyk studied two mires in the Jura Mountains, where the maximum Pb peaks were over 80 µg g$^{-1}$. Jensen (1997) reported Pb concentrations ranging from 0.59 to 227 µg g$^{-1}$ in the uppermost 35-cm layer of six ombrotrophic mires located at considerable distances from distinct local sources in Sweden and Norway. According to Poikolainen *et al.,* (2004), on the other hand, the maximum Pb concentrations in forest mosses in Finland in 1995 were 50 µg g$^{-1}$.

The Pb concentration is obviously related to the overall pollution gradient in space and time. Maximum Pb deposition values were reached around 1975, after which they started to decrease (Farmer *et al.,* 1996). The gasoline use by cars has earlier been the primary source of Pb but, since 1993, only unleaded gasoline has been used in Finland (Jalkanen, 2000); in Europe and North America the reduction in the use of leaded gasoline started in the beginning of the 1970s (Farmer *et al.,* 1996). The shape of the distribution of Pb down the peat profile was different from that of the other elements; the highest value occurred in the middle of the profile, most clearly at the Hietajärvi site. A similar kind of distribution has been found in an age-dated lake sediment profile at Hietajärvi, and it was suggested that the increase in Pb started during the 18th century and may be attributed to atmospheric deposition (Simola *et al.,* 1991). Correspondingly, Renberg *et al.* (2002) considered that the high Pb concentration in Swedish lake sediments is due to the Industrial Revolution, which caused increased atmospheric Pb pollution beginning in the end of the 18th century. Many studies have shown that the Pb deposited on the surface of ombrotrophic bogs is effectively immobilized (Vile *et al.,* 1995; Shotyk, 1996; Shotyk *et al*., 1998), and this is suggested by our results, because the highest concentrations were restricted to the middle of the profile. However, when examining these results it should be kept in mind that although peat age increases with depth, the depth is not a reliable indicator of age because of local variations in production and decay (Tolonen, 1971; Wallén *et al.,* 1988, Johnson and Damman, 1993; Damman *et al.,* 1992).

### ZINC

On the average, the Zn concentrations in the upper layer of the Harjavalta peat bog were almost double or more compared to the other sites. This is obviously due to the influence of the smelter. However the Zn concentrations at all the sites were below the maximum value (137 µg $g^{-1}$) found in 1995 in the national forest moss survey (Poikolainen *et al.,* 2004). All the plots were characterized by the highest Zn concentration occurring in the surface layer, the concentrations decreasing with increasing depth, and the greatest decrease taking place at depths greater than 40 cm. Similar results have also been found by Espi *et al.* (1997), who attributed the phenomenon to bioaccumulation; both Zn and Cu are essential nutrients for plants and therefore subject to nutrient uptake and nutrient cycling (Andersson *et al*., 1991). Other studies on Zn in soils have shown weak depth gradients and weak correlation with deposition (Andersson *et al.,* 1991; Ukonmaanaho *et al.,* 2001; Nieminen *et al.,* 2002). The Zn concentrations in the deeper layer (40-80 cm) of the peat at all the sites were more alike, which confirms the above assumption.

### ARSENIC

The As concentrations were at a similar level on all the plots (on average 3-4 µg $g^{-1}$ in the upper layer, less than 3 µg $g^{-1}$ in the deeper layer), apart from the upper layer at Harjavalta where the average value was 11.1 µg $g^{-1}$, which was fourfold higher compared to the Hietajärvi background area. The maximum As concentration in forest moss in Finland in 1995 and 2000 was approximately 1 µg $g^{-1}$ (Poikolainen *et al.*, 2004). The higher As concentration in the Harjavalta peat profile is undoubtedly due to emissions from the Harjavalta Cu-Ni smelter. On the other hand, extensive agricultural areas are located close to the Harjavalta site, and As-containing agrochemicals, e.g. fungicides, have probably been applied there (Kauranne and Sillanpää 1992). Hence the agricultural area might be a source of additional As. The As concentrations at all the sites were at their highest in the uppermost layers, and decreased at greater depths to below the detection limit of the analytical equipment. The fate and transport of As in the environment are strongly dependent on the chemical form (e.g. arsenate, arsenite) of As in the soil (Cai *et al.,* 2002). However, we determined only total As in this study.

## Conclusions

The aim of our study was to determine whether the vertical distribution of elements in *Sphagnum* peat profiles of ombrotrophic peat bogs could help to indicate the effect of local deposition. This was indicated by the vertical distributions of all the elements (Cu, Ni, Pb, Zn, As), which were characterised by the highest concentrations occurring in the topmost 40-cm, with a rapid decrease on moving down the profile. The results also showed a strong regional pattern and relationship with local pollution sources. Concentrations of As, Ni, Pb and Zn were at their highest at Harjavalta, which is also the most polluted area according to the existing emission data, while the highest Cu value occurred at the Cu-treated Alkkia site. Pollution factor values indicated that the other sites were more polluted than the Hietajärvi reference site. This was especially the case for Cu because all the sites, except for Hietajärvi, have been exposed to high Cu deposition or treatment. The Cu concentration was above the critical concentration level at all the sites except Hietajärvi, indicating that Cu may have ecotoxicological effects on soil organisms in these areas. The distribution of Cu and Pb in the peat profiles suggests that they were less mobile than Ni, Zn and As, which is in agreement with earlier studies on the mobility of these elements. The highest Pb concentration occurred at a depth of between 10-50 cm. Lower Pb concentrations in the uppermost surface peat could 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 elsewhere in Europe and in North America, has significantly decreased in recent decades.

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# CHAPTER 5

Rausch, N., T.M. Nieminen, L. Ukonmaanaho, G. Le Roux, M. Krachler, A.K. Cheburkin, G. Bonani, W. Shotyk. 2005. Comparison of atmospheric deposition of copper, nickel, cobalt, zinc and cadmium recorded by Finnish peat cores with monitoring data and emission records.

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# Comparison of atmospheric deposition of copper, nickel, cobalt, zinc and cadmium recorded by Finnish peat cores with monitoring data and emission records

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**Abstract.** 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 sector field inductively coupled plasma-mass spectrometry. Samples were age-dated using both $^{210}$Pb and $^{14}$C (bomb pulse curve). At the Outokumpu (OUT) site as well as the low-background site Hietajärvi (HIJ), $^{210}$Pb age dates are in excellent agreement with the $^{14}$C bomb pulse curve method, and the precision is between one and ten years for most of the samples; at the Harjavalta (HAR) site, precision is greater than 6 years. Mean regional "background" concentrations have been calculated from deeper peat layers of the HIJ site (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). For layers accumulated within the last 100 years, accumulation rates (ARs) have been calculated. At sites with < 0.06 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 three and 30 mg m$^{-2}$ yr$^{-1}$, and of Cd between 24 and 140 µg m$^{-2}$ yr$^{-1}$ at all sites, and are independent of the chronology of their inputs from the atmosphere.

*Keywords:* Cu; Ni; Co; Zn; Cd; atmospheric deposition; peatlands; mining; smelting

## Introduction

Ombrotrophic peat cores have recently proved to be meaningful archives of recent as well as ancient atmospheric metal deposition, especially for Pb (Shotyk et al. 2001; Vile et al. 1999; Weiss et al. 1999) and Hg (Benoit et al. 1998; Givelet et al. 2003; Pheiffer Madsen 1981; Roos-Barraclough and Shotyk 2003). In contrast, there are far fewer studies on the distribution and fate of Cu (Holynska et al. 1998; Kettles and Bonham-Carter 2002; Livett et al. 1979; Mackenzie et al. 1998; Mighall et al. 2002; Monna et al. 2004; Shotyk et al. 2002), Ni (Holynska et al. 1998; Krachler et al. 2003), Co (MacKenzie et al. 1998), Cd (Monna et al. 2004; Shotyk et al. 2002) or Zn (Espi et al. 1997; Kempter and Frenzel 2000; Kettles and

Bonham-Carter 2002; Livett et al. 1979; Mackenzie et al. 1998; Monna et al. 2004; Shotyk et al. 2002; Sugden et al. 1993) in ombrotrophic peat bogs. While some studies have provided evidence that Cu concentrations may reflect the history of ancient mining and smelting (Kempter and Frenzel 2000; Mighall et al. 2002), Zn is thought to be rather mobile in peat and to be readily redistributed by plants (Espi et al. 1997; Kempter and Frenzel 2000; Livett et al. 1979; Mackenzie et al. 1998; Monna et al. 2004; Shotyk et al. 2002; Sugden et al. 1993). In general, however, previous work on these trace metals in ombrotrophic peat tends to suffer either from poor temporal resolution, uncertain analytical data, a lack of characterisation 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 which had already been subjected to preliminary study (Nieminen et al. 2002; Ukonmaanaho et al. 2004). Replicate cores were frozen and precisely cut into 1 cm slices, and age dated using both $^{210}$Pb and $^{14}$C (including the atmospheric “bomb pulse curve”(Jungner et al. 1995). This approach has been used successfully for atmospheric deposition of Pb and Hg (Shotyk et al. 2003; Shotyk et al. 2005) 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, nearby a Cu-Ni smelter, Outokumpu, near the famous Cu-Ni mine, and Hietajärvi, a “low background” control site which 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, subsequent to 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) (Fig. 19). The surface waters have a pH of ~ 4 which is typical of ombrotrophic bogs. A detailed description of the sampling sites is given elsewhere (Nieminen et al. 2002; Ukonmaanaho et al. 2004) 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 (Ukonmaanaho et al. 2001). The OUT sampling site is located in the Viurusuo mire complex in eastern Finland, 8 km SW 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 from 1913 until 1929 (Kuisma 1985). At the HAR site, peat samples were taken from a peat bog in the Pyhäsuo mire complex, 6 km northeast of Harjavalta, SW Finland, where a Cu smelter has operated since 1945 and a Ni smelter since 1959 (Kuisma 1985).

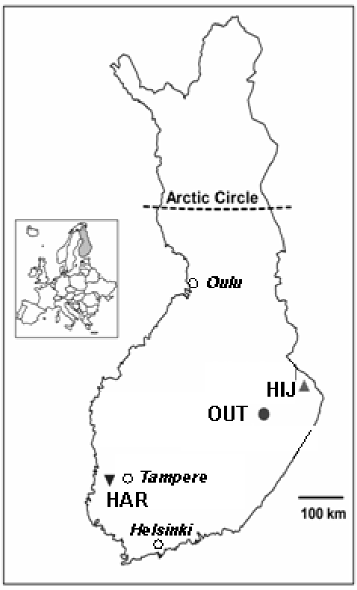


**Fig. 19.** Map of Finland with the location of the sampling sites indicated. HIJ: Hietajärvi; OUT: Outokumpu; HAR: Harjavalta.

### SAMPLING.

Each site was sampled using a titanium Wardenaar corer. The cores were immediately frozen and shipped to the lab where they were sectioned into 1 cm slices with a stainless steel band saw. The edges of each slice were removed, the residual peat dried at 105° C in Teflon bowls, and milled with a Titanium centrifugal mill equipped with 0.25 mm sieve. Details of the sample collection and preparation protocol are given elsewhere (Givelet et al. 2004).

### 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 (Ukonmaanaho et al. 2004). Other studies also found replicate cores recording similar metal concentrations (Benoit et al. 1998; Kempter and Frenzel 1997; Kempter and Frenzel 2000; Kettles and Bonham-Carter 2002; Mighall et al. 2002)

### AGE DATING.

Recent peat samples were age dated using $^{210}$Pb (CRS model) (Appleby and Oldfield 1978). The activities of $^{210}$Pb were determined in bulk samples of peat powder using low background gamma spectrometry (GCW 4028, HPGE, Canberra). 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 AD 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 (Shore et al. 1995) and then age dated ($^{14}$C) using accelerator mass spectrometry (AMS) at the ETH Zürich. In two highly decomposed samples where no *Sphagnum* could be identified, *Carex* fibres were selected (**Table 17**). For dating using the bomb pulse curve (b.p.c.), ages were graphically evaluated using the calibrated $^{14}$C b.p.c. of the northernmost northern hemisphere (Goodsite et al. 2001). For samples older than 1800, calibrated (bomb-corrected) radiocarbon ages were presented as 2σ-ranges (95% confidence limit) and calculated using the program CalibETH (Niklaus et al. 1992).

### 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 (Krachler et al. 2003). 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 core, while 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 µg $L^{-1}$ 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 analysed using an inert Sturman-Masters cyclone spray chamber and V-slit nebulizer using Sc as internal standard element for the Cu, Ni, Co and Cd determination. Method detection limits for ICP-OES analysis, referring to solid samples, were as follows: Cu 0.03 µg $g^{-1}$, Ni 0.05 µg $g^{-1}$, Co 0.05 µg $g^{-1}$, Cd 0.006 µg $g^{-1}$. Cobalt concentrations approached the limit of detection of ICP-OES in the HAR samples below of 30 cm.

### QUALITY CONTROL AND INTER-METHOD 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 inter-method comparison based on regression analysis of ten 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 ≤ 3% for Cd, Co, Cu and Ni and 13% for Sc concentrations.

### FURTHER ANALYSES.

Zinc and Sr were determined using an energy-dispersive miniprobe X-ray fluorescence multi-element analyzer as described elsewhere (Cheburkin and Shotyk 1996). For Ca, a new X-ray fluorescence spectrometer was used (Cheburkin and Shotyk 2005). Percentage light absorption of NaOH extracts (8%) of peat samples was determined using a UV-VIS spectrometer ($\lambda$=550 nm) as a proxy of peat decomposition as described elsewhere (Blackford and Chambers 1993). Density was calculated after determining the thickness (± 0.1 mm) and dry weight of three single plugs with defined area.

## 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 at HAR and HIJ core, respectively (Fig. 20). In HAR, the lower $^{210}$Pb inventory (Fig. 21) is due to the proximity to the Baltic Sea and not due to differences in precipitation (approx. 600 mm at all sites). Due to the lower activity of unsupported $^{210}$Pb the age uncertainty calculated by error propagation (Appleby 2004) is higher for the HAR samples (± 6 to 75 years for the last century) than for the OUT (± 3 to 30 years) and HIJ (± 1 to 8 years) samples. The $^{210}$Pb activities were determined in bulk peat samples which are representative of the entire peat slice which is 1 cm thick (Givelet et al. 2004). In contrast, the age dates obtained using the b.p.c. of $^{14}$C requires a measurement of the percent modern carbon (PMC), relative to A.D. 1950, in a single plant macrofossil which has been removed from the peat slice and weighs but a few mg. A plant macrofossil which 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 centre of the plug removed from the slice for subsampling. Good agreement is found in the HIJ and OUT samples (Table 17). Due to the greater error of the $^{210}$Pb dating of the HAR samples, the $^{14}$C AMS b.p.c. age dates generally fall within the range of $^{210}$Pb dates, too, although some samples show a high bias to the $^{14}$C b.p.c. age. However, the samples in ten and eleven cm depth have similar $^{14}$C b.p.c. age dates, suggesting that macrofossils may not have originated from the centre of these slices. Additionally, the $^{14}$C b.p.c. 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 b.p.c. dates do not constrain the $^{210}$Pb ages, this reflects sub-sampling difficulties rather than a problem with the age dates themselves. Because the $^{210}$Pb age dates are consistent with the $^{14}$C b.p.c. (HIJ, 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 last 150 years thereby allowing the age-depth-relationship of the core to be reconstructed (Fig. 20) and yielding the accumulation rates of the elements of interest. The age-depth models show that peat accumulation is non-linear. Moreover, bogs which are situated close together, such as HIJ and OUT may exhibit very different growth rates. Regarding the last 100 years, growth rates are low at HAR (0.15 cm yr$^{-1}$), compared to OUT (0.32 cm yr$^{-1}$) and HIJ (0.22 cm yr$^{-1}$). If the last 1000 years are considered using calibrated $^{14}$C age dates), greater growth rates are found at HAR and OUT (0.080 cm yr$^{-1}$) than at HIJ (0.057 cm yr$^{-1}$). 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.).

*Following page:*

**Table 17.** Age dates of $^{210}$Pb, $^{14}$C bomb pulse curve and conventional $^{14}$C of the HIJ, OUT and HAR core obtained from bulk peat samples and macrofossils. *Sph*: *Sphagnum* species

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

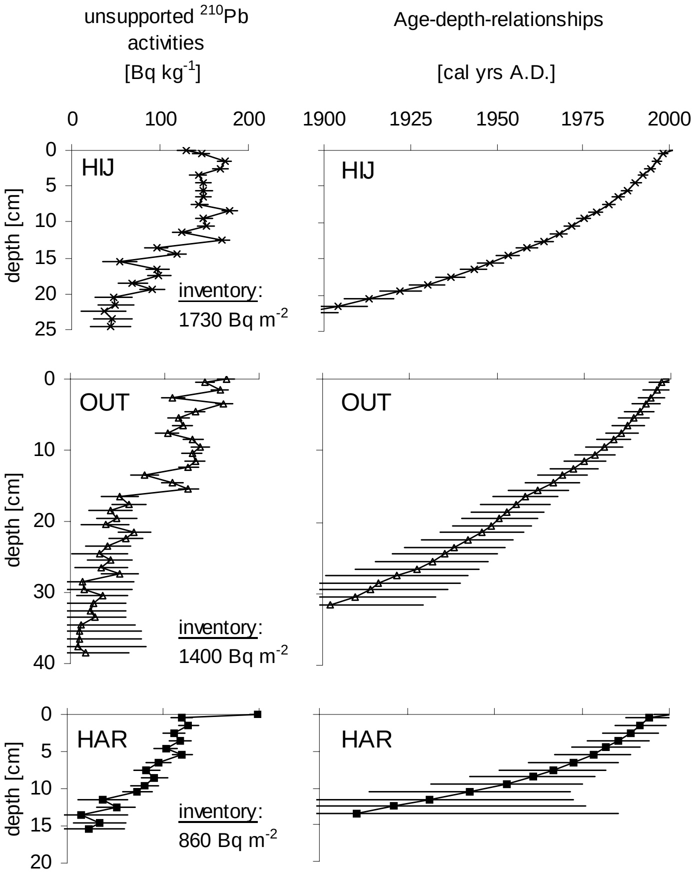


**Fig. 20.** Age dating using $^{210}$Pb: Unsupported $^{210}$Pb activities and age-depth-relationships of the HIJ, Out and Har cores.

### 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. Calcium 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 (Shotyk et al. 2001; Steinmann and Shotyk 1997). The concentrations of Ca found in all three peat cores are well within the range reported for continental ombrotrophic peat bogs (see ESI 2). 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) (Fig. 21). 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 (ESI 2).

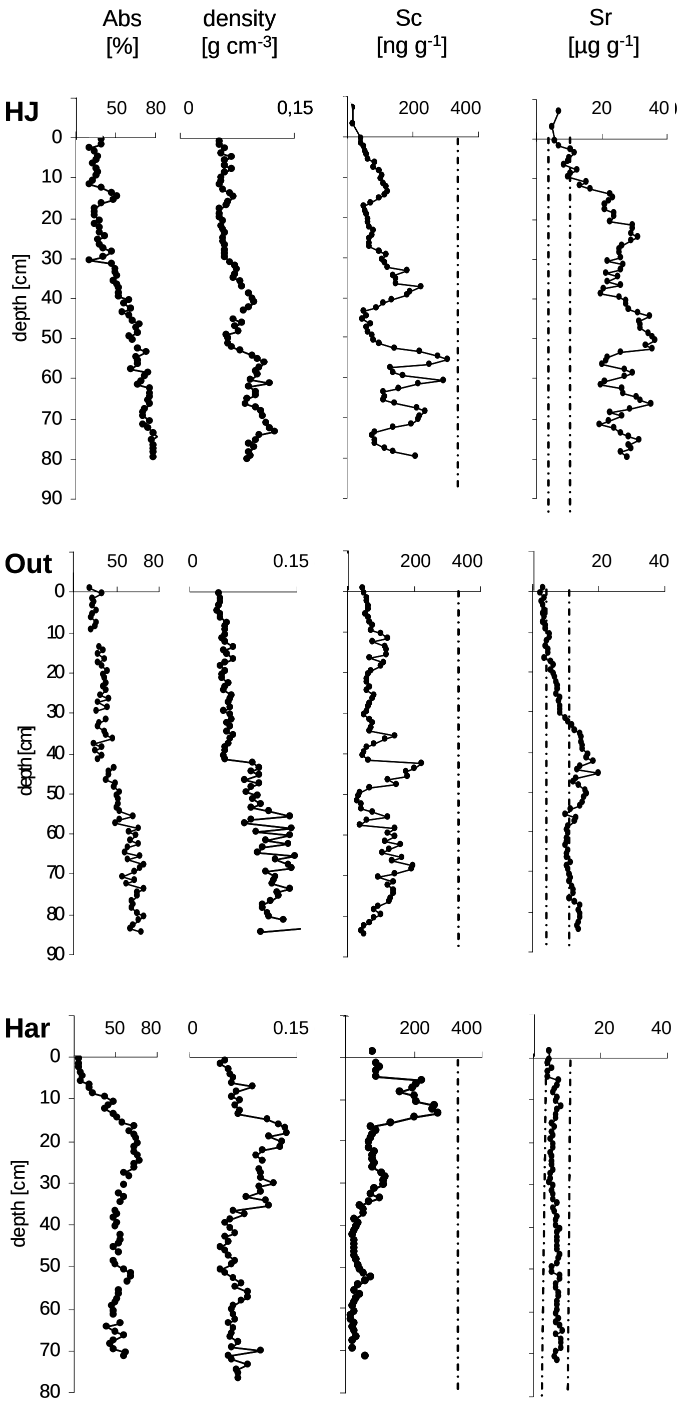


**Fig. 21.** Depth profiles of absorption, density, Sc and Sr concentrations for HIJ, OUT and HAR. Dashed lines indicate typical values of ombrotrophic bogs from Switzerland.

## PRE-INDUSTRIAL "BACKGROUND" CONCENTRATIONS

The HIJ site is situated within a National Park in an area which 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. $^{14}$C yrs), which pre-date 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 (Shotyk et al. 2002), 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) (Koljonen 1992; Steinmann and Shotyk 1997). In contrast, Ni concentrations slightly increase downwards in the HIJ profile, so that reliable MRBs could not be calculated. However, the lowest Ni concentrations found in very old (> 5320 $^{14}$C yr B.P.) layers of the Swiss peat bog average 0.46 ± 0.09 µg $g^{-1}$ Ni (n=18) (Krachler et al. 2003). 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 (Fig. 22). Peaks of Cu and Cd concentrations occur in layers slightly below those of Ni, Co and Zn, corresponding to the different onset 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, while Cd and Zn are enriched up to 7 and 28 times in the upper part of the core.

### INFLUENCE OF MINERAL MATTER ABUNDANCE ON THE 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 (Shotyk et al. 2001).

Assuming that for pre-industrial 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

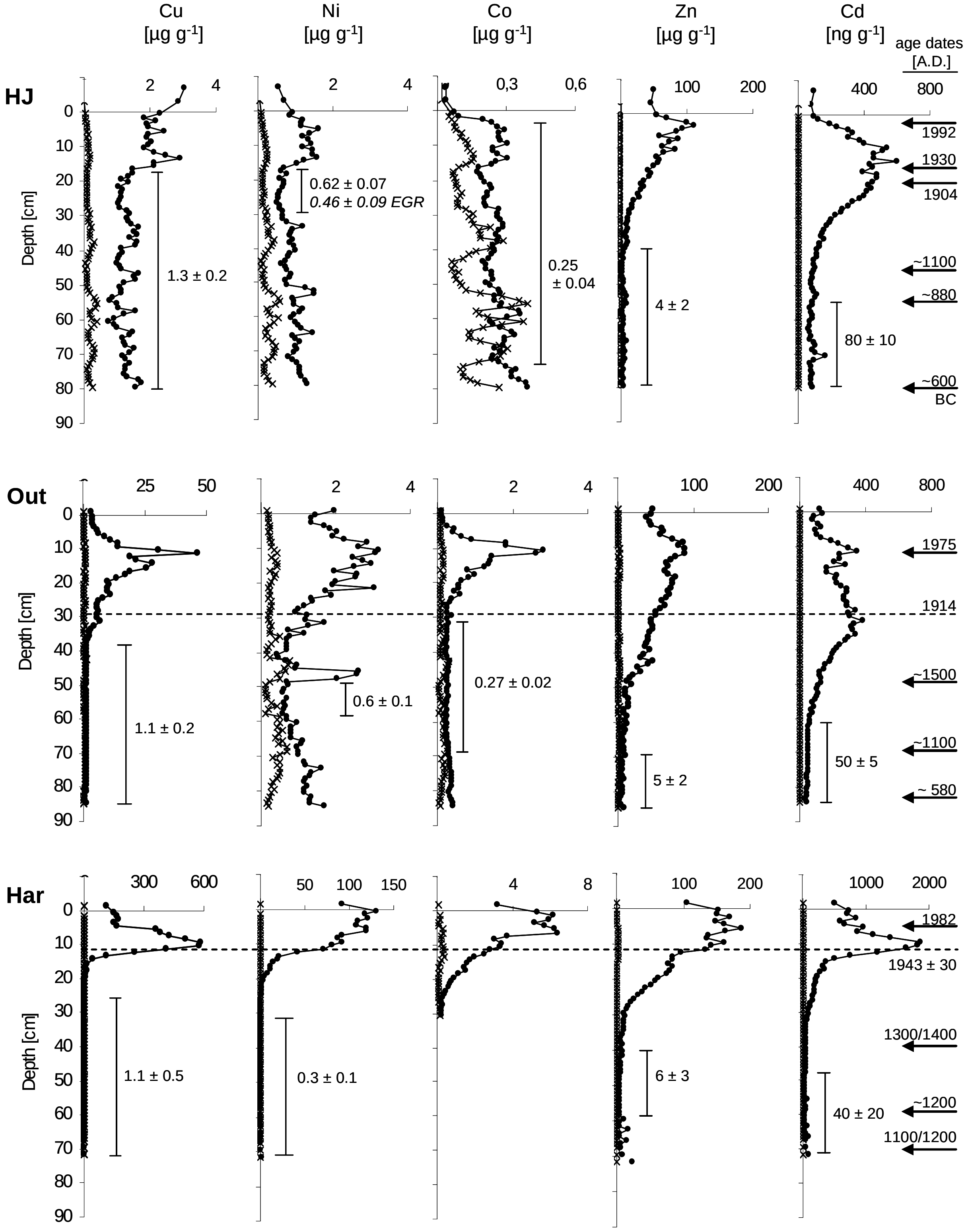


**Fig. 22.** Concentrations of Cu, Ni, Co, Zn and Cd (solid dots), and calculated concentrations of lithogenic Cu, Ni, Co, Zn and Cd concentrations (crosses) at the HIJ, OUT and HAR cores. For layers of constant metal concentrations, mean values are given. The horizontal dashed line refers to the onset of mining (OUT) and smelting (HAR), as derived from the $^{210}$Pb chronologies.

product of Sc concentrations and the metal/Sc ratio of the natural dust. As there are strong regional differences in the "soil dust" composition between the three sites, the metal/Sc ratios of local tills (Koljonen 1992) 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 pre-industrial layers of the HIJ core (Fig. 22); 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 (Monna et al. 2004; Shotyk et al. 2002). 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 (Fig. 22), the influence of local bedrock composition is negligible (see above). Further studies are necessary to determine weather 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 THE TRACE METAL DISTRIBUTION

In the cores from HIJ and OUT, the peat layers where trace metals are most enriched (Fig. 22) are poorly decomposed (Fig. 21). At HAR, too, the greatest absorbance values clearly underly 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 compensates for variations in the degree of humification of the peats when calculating metal accumulation rates.

### INFLUENCE OF DEPOSITION HISTORY ON THE TRACE METAL DISTRIBUTION

If the elements are retained by the peat column, subsequent to 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 Harjavalta 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 $^{210}$Pb CRS age model as described elsewhere (Appleby 2004). 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.

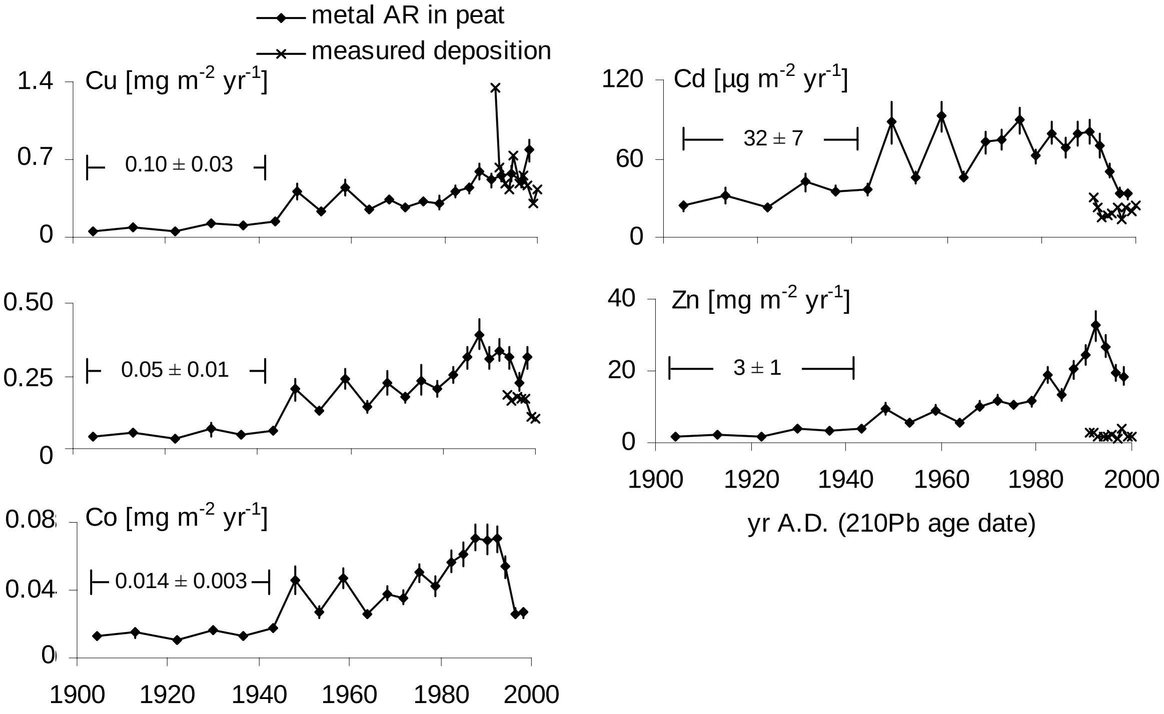
**Metal accumulation rate vs. deposition history at Hietajärvi.**

Copper, Ni, and Co ARs were low at the beginning of the 19th century, and increased considerably from ~1945 onwards (Fig. 23). 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 only started in 1990 in the vicinity of the coring site (Leinonen 1993; Leinonen 1994; Leinonen 1996; Leinonen 1997; Leinonen 1998; Leinonen 1999a; Leinonen 1999b; Leinonen 2000; Leinonen 2001; Leinonen and Juntto 1992). Prior to this, there were various possible trace metal sources for this area (including settlement, forest fires, 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 $m^{-2}$ $yr^{-1}$, 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 $m^{-2}$ $yr^{-1}$ in 1991) which doesn't 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 Erisman et al. (Erisman et al. 1998) showed that the *effective* atmospheric deposition to a given ecosystem is strongly dependent on 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 (Jalkanen 2000). Alternatively, the elevated Ni accumulation rate could be lead back to post-depositional processes. The retention of Co in the peat layers cannot be assessed, as monitoring data for Co is lacking.

Zinc ARs are decoupled from true deposition. This is consistent with some studies suggesting that Zn might be recycled by higher plants (Espi et al. 1997; Livett et al. 1979). 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 ca. 3 times higher in 1985 than in 2000 (Poikolainen et al. 2004); the decline in Cd AR at HIJ is consistent with this trend.

**Fig. 23.** ARs of Cu, Ni, Co, Zn and Cd in peat (HIJ) and atmospheric bulk deposition (wet+dry) at open area as monitored at HIJ.



## Metal accumulation rate vs. emission history at Outokumpu

The area was fairly inaccessible until the discovery of the ore deposit lead 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 a underground mine from 1912 to 1989, and the "Vuonos" ore body with two different ore types, mined between 1972 and 1982, both underground and by open pit (Laznicka 1993; Parkkinen and Reino 1985). These ore bodies not only differ from each other in their chemical composition (Table 18), 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 (Kuisma 1985). All things considered, the ore production rate (Fig. 24) is only an approximate guide to local metal emissions.

**Table 18.** Characterization of the Upper Continental Crust (UCC) and of 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 | n.a. |
| Cd | 0.1 | n.a. | n.a. | n.a. | 0.02-7.1 |
| Zn | 65 | 0.8 | 1.6 | 0.06 | 0.9-232 |

[a] After (Wedepohl 1995)

[b] After (Mäkinen 1938)

[c] After (Parkkinen and Reino 1985)

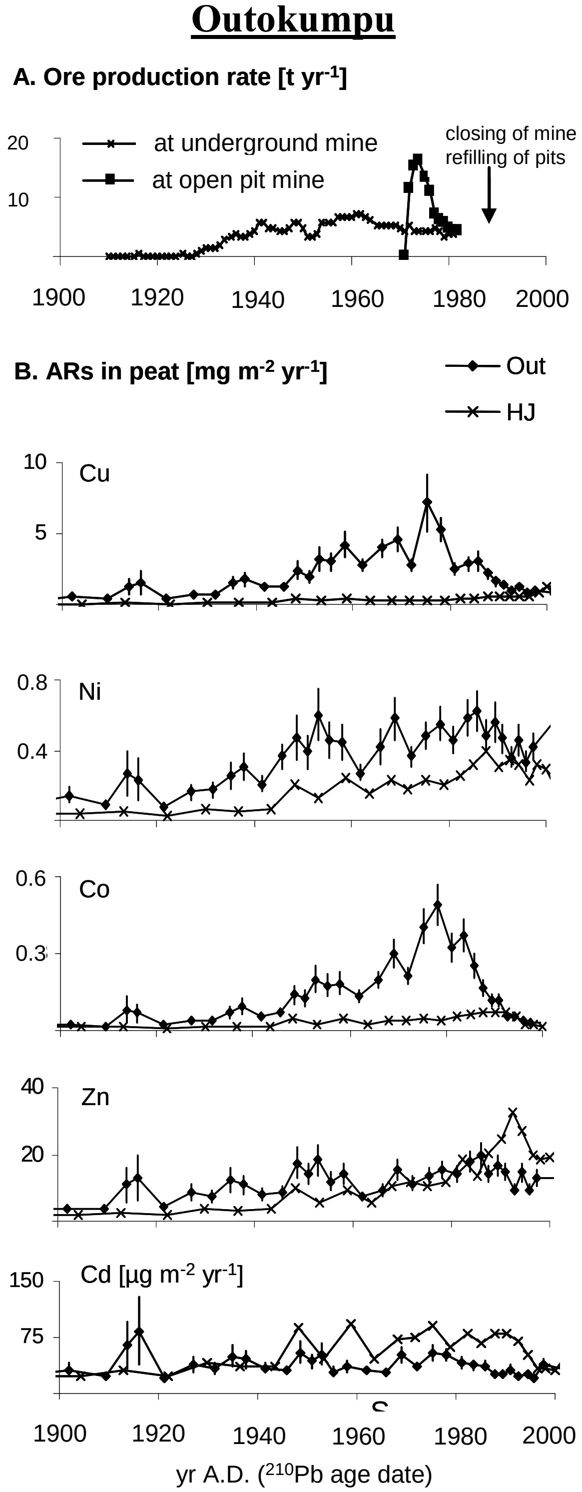
[d] Range of annual emissions for the period 1985 to 1999 (Nieminen et al. 2002); n.a. no data available

During the early years of the 20th century, ARs of Cu and Ni slightly exceed the ARs at HIJ, while ARs of Co and Cd are similar to the low-background site (Figure 6). From 1931 ± 17 onwards, 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 (1975/78). The continuously decreasing Cu and Co ARs since 1986 ± 5 coincide with the decline of mining industry since 1983, and subsequent re-filling 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 onwards could be due to the changeover to separate grinding grades for different ore types in 1977 (Kauppinen 1978). 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 open pit at Vuonos. This is even more remarkable considering that the ore of Vuonos contains three times more Ni than the OUT ore. In addition, Ni ARs recorded by the OUT core are twice that of the low-background site, while Cu and Co ARs are up to 23 and 10 times higher. Clearly, the Ni ARs obtained using the peat core are not an accurate reflection of the local Ni emission history and this reflects post-depositional mobility. Zinc ARs are very similar to ARs at HIJ, 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 vs. 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 (Nieminen et al. 2002); since 1985, the company has monitored the emissions of Cu, Ni, Zn and Cd (Fig. 25). 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 (Nieminen et al. 2002; Ukonmaanaho et al. 2004).

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 $^{210}$Pb 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 (Fig. 25). However, considering only the average values of $^{210}$Pb age dates, the increase in Cu AR in “1931” pre-dates the true beginning of Cu smelting at HAR in 1945 by approximately 14 years. However, the spatial difference between the sample accumulated in “1931” and the overlying sample accumulated in “1943” is only one centimeter. Therefore, the difference (14 yrs) between the increase in Cu ARs (peat) and the known beginning of smelting activity is a consequence of the great uncertainties in the $^{210}$Pb 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 (Pongrácz 2004). 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 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.



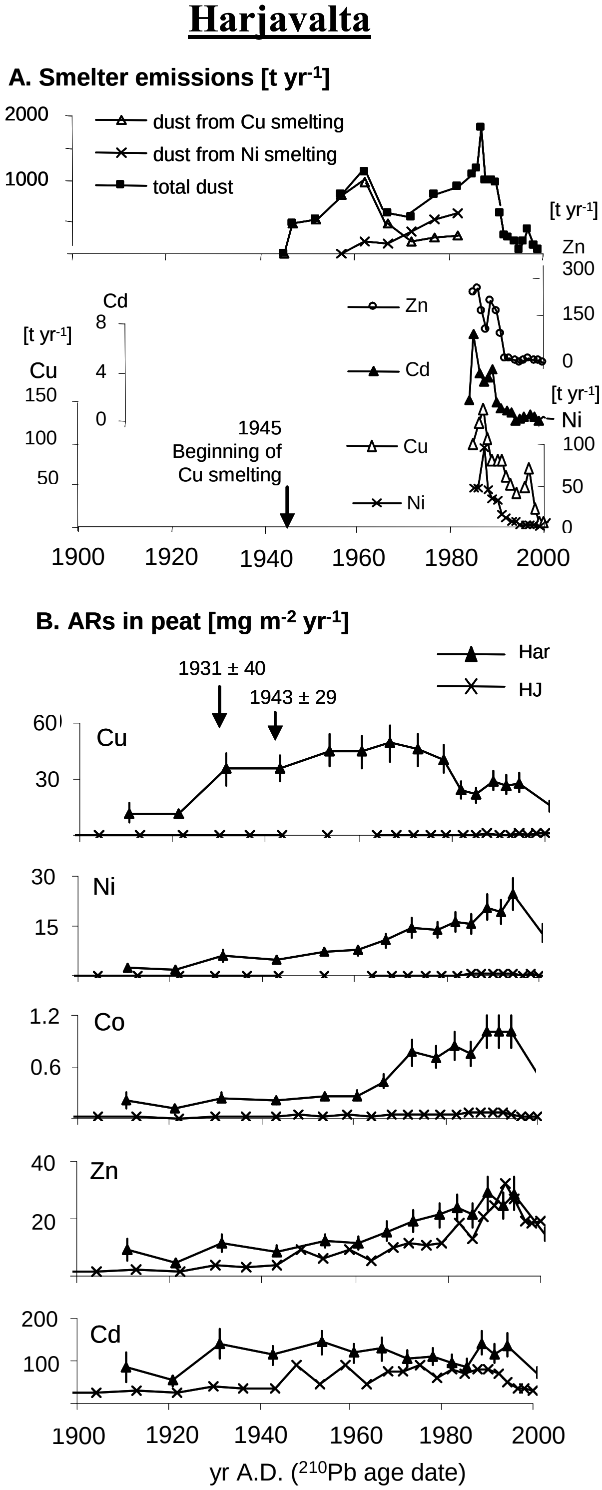


**Fig. 24.** A. Ore production rates at the Outokumpu mines. B. Accumulation rates of Cu, Ni, Co, Zn and Cd in peat

**Fig. 25.** A. Emissions at the smelter. B. Accumulation rates of Cu, Ni, Co, Zn and Cd in peat. See text for explanations.

### POST-DEPOSITIONAL MOBILITY

Cumulative metal inventories (Table 19) show that the peat bog at HAR has been severely impacted 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). Regarding peat samples pre-dating 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 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 pre-dating the installation of air filters. The most likely reason for the elevated ARs are therefore downward migration of these metals, subsequent to their release from the smelter and deposition on the bog surface, on the order of a few centimeters (Fig. 22). 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 18**). Inventories of Zn and Cd at HAR are only twice those of HIJ, although up to 230 t yr$^{-1}$ Zn and 7 t yr$^{-1}$ Cd are released at the smelter (**Table 18**). Long-range transport contributes significantly to the atmospheric deposition of these elements in Finland (Ilyin et al. 2002; Rühling et al. 1987). 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.

**Table 19.** 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 |

## Acknowledgments

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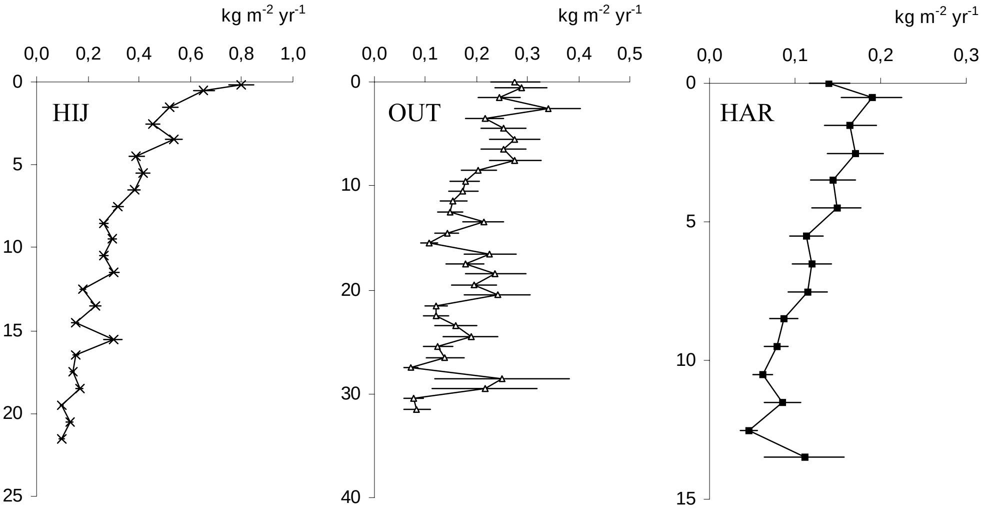
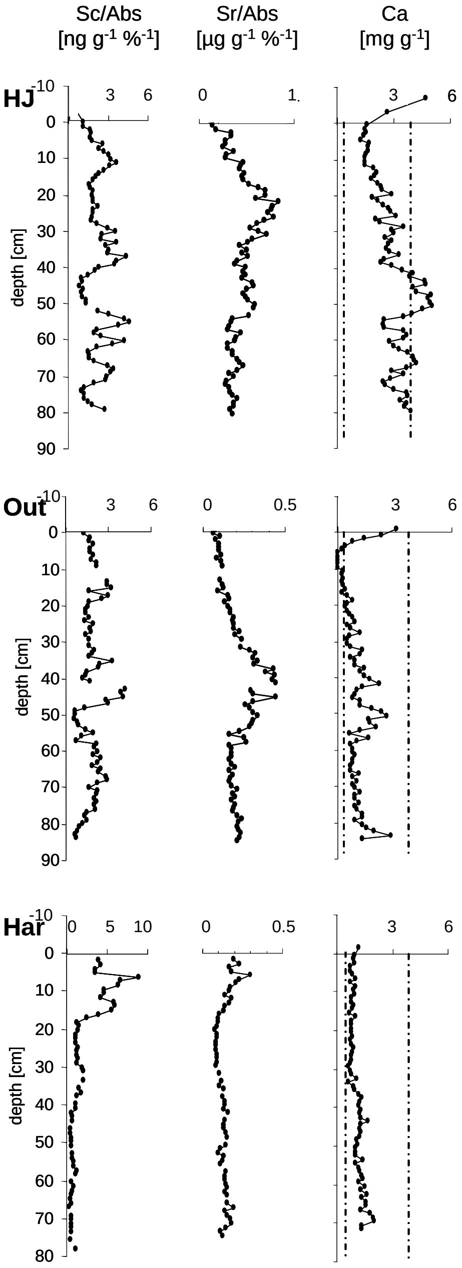
# Electronic Supporting Information (ESI)

Supporting Information contains mass accumulation rates (ESI1), and Sc and Sr concentrations normalized to absorbance as well as Ca concentrations (ESI2) of HIJ, OUT and HAR.



**ESI1.** Mass accumulation rates [kg $m^{-2}$ $yr^{-1}$]



**ESI2.** Sc/Absorbance and Sr/Absorbance ratios, and Ca concentrations. Dashed lines indicate typical values of ombrotrophic bogs from Switzerland

# CHAPTER 6

Rausch, N., T.M. Nieminen, L. Ukonmaanaho, M. Krachler, W. Shotyk. Porewater evidence of metal (Cu, Ni, Co, Zn, Cd) mobilization in an acidic, ombrotrophic bog impacted by a smelter, Harjavalta, Finland and comparison with reference sites.

*Environmental Science and Technology* in review (2005)

# Porewater evidence of metal (Cu, Ni, Co, Zn, Cd) mobilization in an acidic, ombrotrophic bog impacted by a smelter, Harjavalta, Finland and comparison with reference sites

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*Environmental Science and Technology* in review (2005)

**Abstract.** Porewaters were collected from three Finnish peat bogs subjected to varying inputs of atmospheric trace metals: Harjavalta (HAR), near a Cu-Ni smelter, Outokumpu (OUT), near a Cu-Ni mine, and Hietajaervi (HIJ), a low background site. Metals were collected using a purpose built pore water sampler and determined using sector field inductively coupled plasma-mass spectrometry (SF-ICP-MS). Porewater concentrations at HIJ and OUT (Cd <0.3 nM, Co <1.4 nM, Cu, Ni <8 nM, Zn <250 nM) are independent of metal concentrations in the solid phase (peat). At OUT there is a limited release of Ni to the porewaters, but concentrations in the aqueous phase are generally below 0.3% of the total concentration in any given peat sample. These data are consistent with the immobility of these metals subsequent to deposition from the air. In contrast, porewaters at HAR are enriched in trace metals compared to the other sites by a factor of 2 (Zn), 10 (Cd), 20 (Co) and 100 (Cu and Ni) with dissolved fractions of Cu and Ni accounting for ca. 20 % of the metal inventories in the cores. The elevated release of metals from solid phases at HAR is consistent with the post-depositional migration of metals at this site and reflects the predominance of oxide phases supplied to the bog surface and the much lower pH values (<3.4). The elevated proton concentrations not only promote mineral dissolution, but also compete with cation exchange processes and hinder the formation of metal complexes with organic ligands.

*Keywords*: Cu; Ni; Co; Zn; Cd; porewater; mobility; peatlands

## Introduction

Ombrotrophic peat cores have recently proved to be meaningful archives of recent as well as ancient atmospheric metal deposition, especially for Pb (Shotyk et al. 2001; Vile et al. 1999; Weiss et al. 1999) and Hg (Benoit et al. 1998; Givelet et al. 2003; Pheiffer Madsen 1981; Roos-Barraclough and Shotyk 2003). In contrast, there are far fewer studies on the distribution and fate of Cu (Holynska et al. 1998; Kettles and Bonham-Carter 2002; Livett et al. 1979; MacKenzie et al. 1998; Mighall et al. 2002; Monna et al. 2004; Shotyk et al. 2002), Ni (Holynska et al. 1998; Krachler et al. 2003), Co(MacKenzie et al. 1998), Cd (Monna et al. 2004; Shotyk et al. 2002) or Zn (Espi et al. 1997; Kempter and Frenzel 2000; Kettles and Bonham-Carter 2002; Livett et al. 1979; MacKenzie et al. 1998; Monna et al. 2004; Shotyk et al. 2002; Sugden et al. 1993). In a previous study (Rausch et al. 2005) we compared high resolution reconstructions of atmospheric metal deposition with the known metal emission histories at three sites in Finland. Nickel, Zn and Cd accumulation rates did not reflect the chronology of their atmospheric inputs. In contrast, Cu and Co accumulation rates reflect the known metal deposition histories very well, except for the site of greatest metal loading. As an independent check on the interpretation of the previous study, trace metals were also measured in the porewaters, and these data are the subject of the present paper.

To date, porewater analyses from ombrotrophic peat bogs have been restricted to gaseous compounds, anions, major element cations as well as Fe and Mn (Blodau et al. 2002; Steinmann and Shotyk 1997; Urban et al. 1989). A few studies have been published which report concentrations of trace elements in bog surface waters (Bendell-Young 2003; Gorham et al. 1985; Shotyk 1989). The porewaters in ombrotrophic bogs represent a unique natural water system. Because metals are supplied only by the atmosphere (precipitation and dust), the concentrations of major elements such as Ca are comparable to rainwater values. Although Ca can be added to the porewaters by dissolution of calcite or apatite in dust at the bog surface (Le Roux 2005), or removed in deeper layers by ion exchange (Shotyk and Steinmann 1994), in general these waters are dilute. Below the living vegetation layer, the decomposition of plant matter results in the formation of peat and consumes dissolved oxygen. Conceptually, the bog surface can be viewed as consisting of an aerated ‘acrotelm’ where decay is comparatively rapid, overlying a ‘catotelm’ which is permanently anoxic. Despite the popular use of these terms, there have been few quantitative studies of the redox chemistry of bog porewaters (Blodau et al. 2002; Steinmann and Shotyk 1997). Peat in the acrotelm tends generally to be poorly decomposed and therefore has a relatively high hydraulic conductivity; during seasonal water table draw down, oxygen may penetrate these surface layers. All of the porewaters are rich in dissolved organic matter, and contain elevated partial pressures of $CO_2$.

In this study, we used a purpose-built sampler to study the mobility of Cu, Ni, Co, Zn and Cd in the porewaters of ombrotrophic peat bogs. Samples were collected from ombrotrophic peat bogs in Finland which had already been subjected to preliminary studies (Nieminen et al. 2002; Ukonmaanaho et al. 2004): Harjavalta, nearby a Cu-Ni smelter, Outokumpu, near the famous Cu-Ni mine, and Hietajärvi, a “low background” control site which receives atmospheric trace metals predominantly from long range transport. In selected peat layers, metal-containing particles were identified using SEM/EDX analysis.

The main goal of the study is to determine the extent of Cu, Ni, Co, Zn and Cd mobility in ombrotrophic peat bogs of varying metal loads and to discuss possible mechanisms of metal release from the solid phase.

## Materials and Methods

### STUDY SITES AND HYDROLOGICAL CONDITIONS

Porewater samples were collected in undisturbed, *Sphagnum*-dominated ombrotrophic peat bogs at Hietajärvi (HJ), Outokumpu (OUT) and Harjavalta (HAR) (Fig. 26). A detailed description of the sampling sites is given elsewhere (Nieminen et al. 2002; Ukonmaanaho et al. 2004) but summarized here. The HIJ site is located in the Patvinsuo National Park, Eastern Finland, where the peatland area remains in a natural condition (Tuominen and Mäkelä 1995). 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 (Ukonmaanaho 2001). The OUT sampling site is located in the Viurusuo mire complex in eastern Finland, 8 km SW of the town of Outokumpu. A Cu-Ni mine and concentration plant operated at Outokumpu from 1910 until the 1980s, and a small smelter from 1913 until 1929 (Kuisma 1985). At the HAR site, porewater samples were taken from a peat bog in the Pyhäsuo mire complex, 6 km northeast of Harjavalta, SW Finland, where a Cu smelter has been operating since 1945 and a Ni smelter since 1959 (Kuisma 1985).

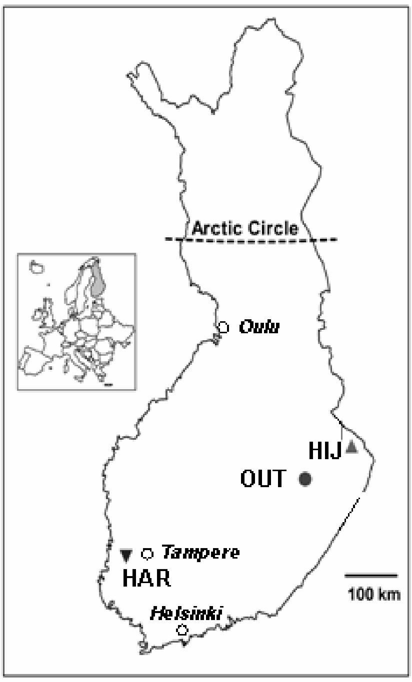

**Fig. 26.** Map of Finland with the location of the sampling sites indicated. HIJ: Hietajärvi, OUT: Outokumpu, HAR: Harjavalta

At the HIJ site, an intense rain event occurred on the day before sampling; the surface peat was not water-saturated during sampling. Continuous rainfall at the OUT site and showers at the HAR site led to water-saturated conditions at the time of sampling.

### POREWATER SAMPLING

Porewater samples were collected using a new porewater sampler designed specifically for sampling ombrotrophic peat bogs and yielding low blank values for trace metals. The new porewater sampler consists of a Plexiglas syringe (80 cm long) containing a 15 ml polypropylene (PP) sample bottle. Holes (3 mm diameter) allow the porewater to flow directly into the sampling tubes. The sampling device was pushed slowly downwards into the peat and a slight vacuum was applied by carefully pulling the inner plunger. Within 5 to 10 min, the raw porewater entered the sampling tube. Raw porewater samples (~ 10 ml) were immediately filtered into a new sampling tube using a 25 mm 0.45 µm GD/XP polyvinylidendifluoride (PVDF) syringe filter (Whatman, Brentford, United Kingdom) and a 10 ml plastic syringe (Discardit$^{TM}$ II, Becton Dickinson, Franklin Lakes, NJ, USA). Contact of samples with the atmosphere was minimized by rapid decanting into plastic syringes and capping the second sampling tube. Gloves made of latex or polyethylene (PE) were used during all steps. Samples were collected in 5 cm intervals in triplicate, with each depth being sampled using a different point of entry on the bog surface. Field blanks (n=2 or 3) were established by processing high-purity water through GD/XP filters in the field (without using the sampling device) at each sampling site in order to estimate the importance of atmospheric contamination of samples during the filtration step. Separate porewater samples were collected for both the determination of S and Cl concentrations (no acidification after filtration) and of dissolved organic carbon (DOC) (filtered into glass vessels containing diluted $H_2SO_4$ leading to a final acid concentration of 3% v/v). All told, water samples were taken from ca. 16 $m^2$ of each bog surface. All samples and blanks were packed into plastic bags and stored in the dark at 6°C to 13°C for up to nine days until they arrived in the laboratory.

### SAMPLE TREATMENT

For trace metal analysis, filtered porewater samples were acidified to 1% v/v in a class 100 laminar flow bench using $HNO_3$ (see below) and stored at -18°C until the analyses could be performed. As humic acids (HAs) precipitated in the acidified filtrate, samples were centrifuged for 10 min at 3000 rpm after recording the volume of the filtrate. The supernatant was decanted, and the residue covered by 25 µL conc. $HNO_3$. After 30 min, 2.5 mL of water was added to obtain a final "digestion" solution of 1% v/v $HNO_3$. Metal concentrations in these residues were re-calculated to the original concentration in the filtrate. As Zn could not be determined in the HA fraction and HA-bound Cd, Co and Ni contributed less than 5% to the total concentrations in the original filtrate, the HA fraction of these metals was not considered for the determination of porewater concentrations. The relative contribution of HA-bound Cu however was between 4% and 12%, and porewater concentrations of Cu were calculated by summarizing the concentrations of both fractions.

### INSTRUMENTATION AND REAGENTS FOR TRACE METAL ANALYSIS

Measurements were carried out with an ICP-sector field MS (ICP-SF-MS) (Element2, Thermo Electron, Bremen, Germany) equipped with a guard electrode to eliminate secondary discharge in the plasma and to enhance overall sensitivity. A sample introduction kit consisting of a microflow PFA nebulizer, a Scott-type PFA spray chamber and a sapphire injector tube was used to reduce blank levels. The entire sample introduction system, including the autosampler and the plasma region of the ICP-SF-MS, is hosted in a class 100 laminar flow bench. All sample handling and the preparation of all standards were performed in clean rooms under laminar flow clean air benches of class 100 to minimize the potential risk of contamination. For the preparation of all solutions, water from a Milli-Q-Element system (Millipore, Milford, Massachusetts, USA) was used. Nitric acid was obtained by purifying nitric acid (65%, analytical-reagent grade) twice by distillation using a quartz unit for sub-boiling of acids (MLS GmbH, Leutkirch, Germany). Both the water and the acid purification system are operated in a clean room which has also been used to successfully measure trace metals in polar ice (Krachler et al. 2005). The Milli-Q-water and the purified nitric acid were used throughout the sampling and measurement procedure. All calibration standards and all samples are acidified using this $HNO_3$ (1% v/v). Pipette tips were pre-cleaned before use employing three subsequent rinse solutions (5% v/v $HNO_3$ – 1% v/v $HNO_3$ – $H_2O$). To correct for instrumental drifts and plasma fluctuations, all analyte solutions were spiked with an indium standard solution to a final concentration of 1.3 $\mu g\ L^{-1}$.

### QUALITY CONTROL

Two river water standard reference materials with certified elemental concentrations were analyzed twice with every batch of samples to ensure the accuracy of the measurements: SLRS-2 and SLRS-4 (National Research Council Canada, Ottawa, Canada). Comparison of the measured values with certified values showed good to excellent agreement for all elements except Zn in SLRS-2 (4.31 ± 0.45 instead of 3.33 ± 0.15 µg $L^{-1}$). Average RSDs for a single run of measurements (n=18) were between 2.5% and 9.3%, whereas average RSDs of triplicate samples from a single depth were considerably higher (12% to 27%). Blank values of the complete sampling device (including GD/XP filter, plexiglas sampler, sampling tubes and the 1% $HNO_3$) were as follows (in µg $L^{-1}$): Cu 0.07 ± 0.03, Ni 0.10 ± 0.04, Co 0.009 ± 0.003, Zn 1 ± 1 and Cd 0.001 ± 0.001.

### SCANNING ELECTRON MICROSCOPY (SEM)

In two peat samples (OUT and HAR at the depth of approx. 10 cm), the morphology and chemical composition of individual mineral particles was studied using a SEM Leo 440 (Zeiss, Jena, Germany) equipped with an energy-dispersive X-ray microanalysis (EDX) unit (Link-Isis, Oxford Instruments, Witney, UK). The instrument was operated at an acceleration voltage of 20 kV and a beam current of 0.5 to 2 nA. The EDX analysis allowed semi-quantitative estimations of the particle composition and was used to identify minerals in the peat, which had been emitted by the mine and smelter. In order to identify metal-rich phases among the abundance of organic particles, backscatter mapping was used. Sample preparation was as follows: Peat cores were collected using a Ti Wardenaar core, immediately frozen and shipped to the lab where they were sectioned into 1 cm slices with a stainless steel band saw (Givelet et al. 2004). Subsamples (with an area of approx. 6 $cm^2$) of the inner part of the slice were thawed within a plastic bag and size-fractioned inside a protective Plexiglas chamber using sieves of 2 mm, 200 µm and 2 µm mesh size. Each fraction was rinsed until the rinse solution was clear. Samples were oven-dried at 30° C, glued to a sample plate and coated with carbon prior to analysis.

### FURTHER ANALYSES

The pH was measured on fresh, unfiltered samples immediately after the collection using a pH electrode (Inlab 412, Ingold, Urdorf, Switzerland). The analysis of inorganic S (as determined as sulfate) was performed on filtered porewater samples using a Dionex DX-120 ion chromatograph (Dionex, Sunnyvale, CA, USA) equipped with an AS14A column, AS RS suppressor and a conductivity detector. As the oxidation of the porewater sample was not prevented, the determined sulfate concentrations might include reduced sulfur species (e.g. $H_2S$, $HS^-$) which were oxidized during filtration. The limits of detection were 2.0 µM S.

Dissolved organic carbon (DOC) was measured in filtered and acidified porewater samples (3% $H_2SO_4$ v/v) using a TOC analyzer (TOC-5000, Shimadzu, Kyoto, Japan).

## Results and Discussion

### POREWATER PROFILES OF PH, S, FE AND DOC

At HIJ and OUT, the pH values are between 3.6 and 4.0 (Fig. 27), which is within the typical range of ombrotrophic peat bogs (Shotyk 1988; Steinmann and Shotyk 1997). In contrast, the pH values of the HAR site are considerably lower than HIJ and OUT at all depths; the lowest pH values are found in the upper layers where concentrations of dissolved inorganic S are at least nine times higher than at the other sites. The elevated S concentrations in the peats and the depressed pH values of the porewaters are probably the result of the earlier $SO_2$ emissions from the smelter at Harjavalta. In contrast, at OUT inorganic S concentrations exceed the limit of detection only at intermediate depths (Fig. 27). In addition to the enrichments of dissolved S, the porewaters at HAR are also rich in Fe, with concentrations in the subsurface layers seven times higher that at OUT. Concentrations of DOC decrease from 60 to 40 mg $L^{-1}$ with depth at HIJ and HAR.

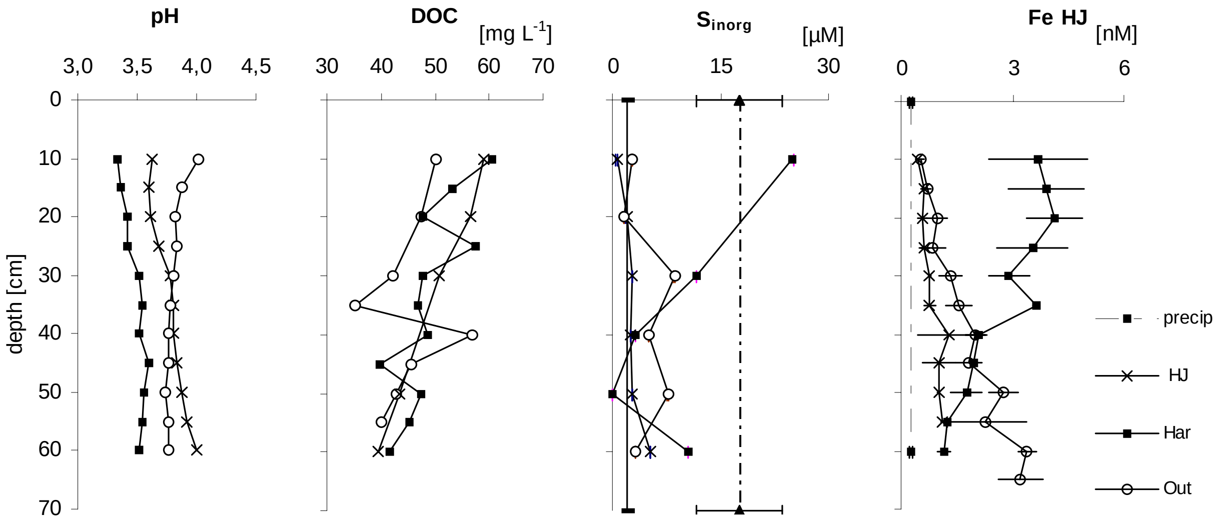

**Fig. 27.** Profiles of pH, DOC, inorganic S and total Fe. Dotted vertical lines represent mean annual inorganic S concentrations in (wet and dry) deposition at HIJ for the period 1989-1995 as reported elsewhere (Ukonmaanaho et al. 1998), and are similar to average annual rainwater concentrations in 4 km distance to the HAR smelter as calculated from mean annual wet deposition for the period 1993-1996 (Derome and Nieminen 1998) (see text); no deposition data available for Fe at HAR. The solid vertical line represents the limit of detection of S.

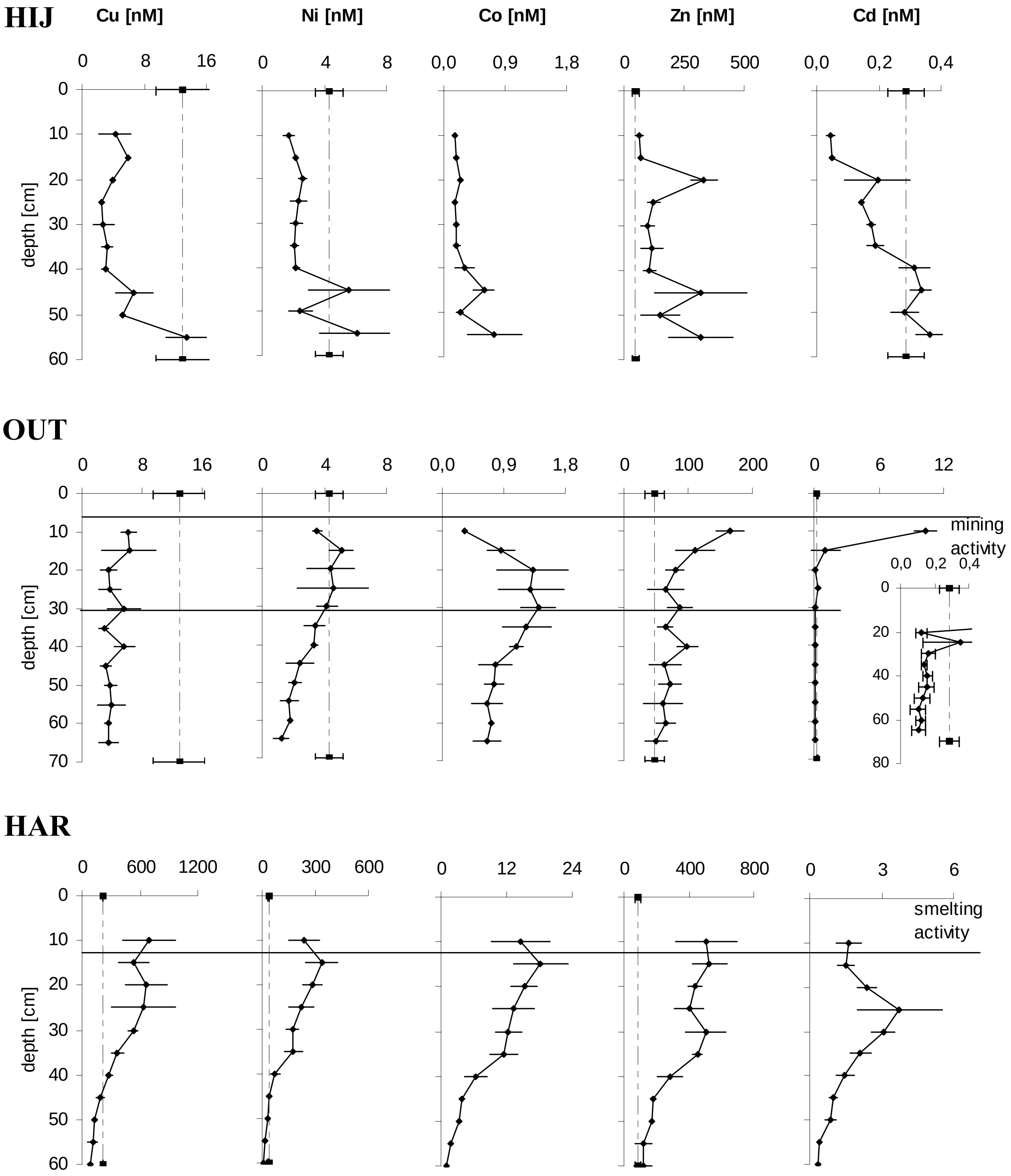

**Fig. 28.** Porewater concentration profiles of Cu, Ni, Co, Zn and Cd at HIJ, OUT and HAR. Periods of mining and smelting activities after $^{210}$Pb age dating are indicated. Vertical lines at OUT and HIJ represent average mean annual concentrations in (wet and dry) deposition monitored at HIJ (1992-2000) (Leinonen 1993; Leinonen 1994; Leinonen 1996; Leinonen 1997; Leinonen 1998; Leinonen 1999a; Leinonen 1999b; Leinonen 2000; Leinonen 2001), and at HAR those in 4 km distance of the Harjavalta smelter as calculated from bulk deposition fluxes (filtered samples) (Derome and Nieminen 1998) (see text).

### TRACE METAL CONCENTRATIONS AT THE LOW-BACKGROUND (HIJ) AND MINING SITE (OUT)

At HIJ and OUT, porewater concentrations are in a similar range, with values of <8 nM of Cu and Ni, <1.4 nM of Co, <250 nM of Zn, and for most samples <0.3 nM Cd (Fig. 28). Compared to the average bulk precipitation concentrations at these sites, which have been continuously monitored at HIJ during the last decade by the Finnish Meteorological Institute (Fig. 28) (Leinonen 1993; Leinonen 1994; Leinonen 1996; Leinonen 1997; Leinonen 1998; Leinonen 1999a; Leinonen 1999b; Leinonen 2000; Leinonen 2001), the porewater concentrations are clearly depleted in Cu (70%), Ni (60% at least) and Cd (85% in upper layers at HIJ). For most samples at HIJ and OUT, Zn concentrations are a factor of 1.3 higher than those of bulk precipitation. Whereas at HIJ the Ni concentrations in porewaters are below precipitation values, at OUT they are comparable to the reported values for precipitation. Cobalt and Cd are also elevated, probably reflecting the partial dissolution of metal-bearing particles emitted by mining activities (1912 to 1989 A.D.). Previous studies have shown that these layers have been strongly affected by the mining industry, with bulk metal concentrations up to 50 times higher than in layers pre-dating the mining period (Rausch et al. 2005; Ukonmaanaho et al. 2004).

### TRACE METAL CONCENTRATIONS AT THE SMELTER SITE (HAR)

Porewater concentrations at HAR exceed those at HIJ and OUT by a factor of 2 (Zn), 10 (Cd), 20 (Co) and 100 (Cu and Ni). Although the maximum metal concentrations occur in the upper part of the profile, strongly elevated metal concentrations are also found in layers pre-dating the smelting period.

### COMPARISON OF SOLID AND AQUEOUS PHASE CONCENTRATIONS

In order to estimate the extent of metal releases, the dissolved fractions are compared to total concentrations in the solid phase (peat). In its natural state, the (wet) peat samples taken at HIJ, OUT and HAR have water contents between 88 wt-% to 94 wt-%. Therefore, “wet peat” can be regarded as an organic-rich natural water system. Bulk metal concentrations (including solid and dissolved fractions) are obtained for the water column using the bulk density, water content and metal concentrations of the peat. The average relative contribution of the dissolved fraction to the total concentrations of single layers is given for upper (contaminated) and deeper (uncontaminated) layers.

At HIJ and OUT dissolved fractions of Cu, Ni and Co account for only 0.2% of the metal inventories in both upper and deeper layers (Fig. 29), in contrast to Zn at HIJ and Cd at OUT (up to 9%). The strong concentration gradient of Cd in the porewater profile together with the low concentrations in deeper layers shows that dissolved Cd is effectively removed in deeper, more reducing peat layers. The results from HIJ and OUT porewater analyses are generally consistent with the previous study showing that Cd, Zn and Ni are rather affected by post-depositional processes, whereas Cu is immobile (Rausch et al. 2005). The elevated Co concentrations in the porewaters at OUT are inconsistent with the immobility of this element in that profile.

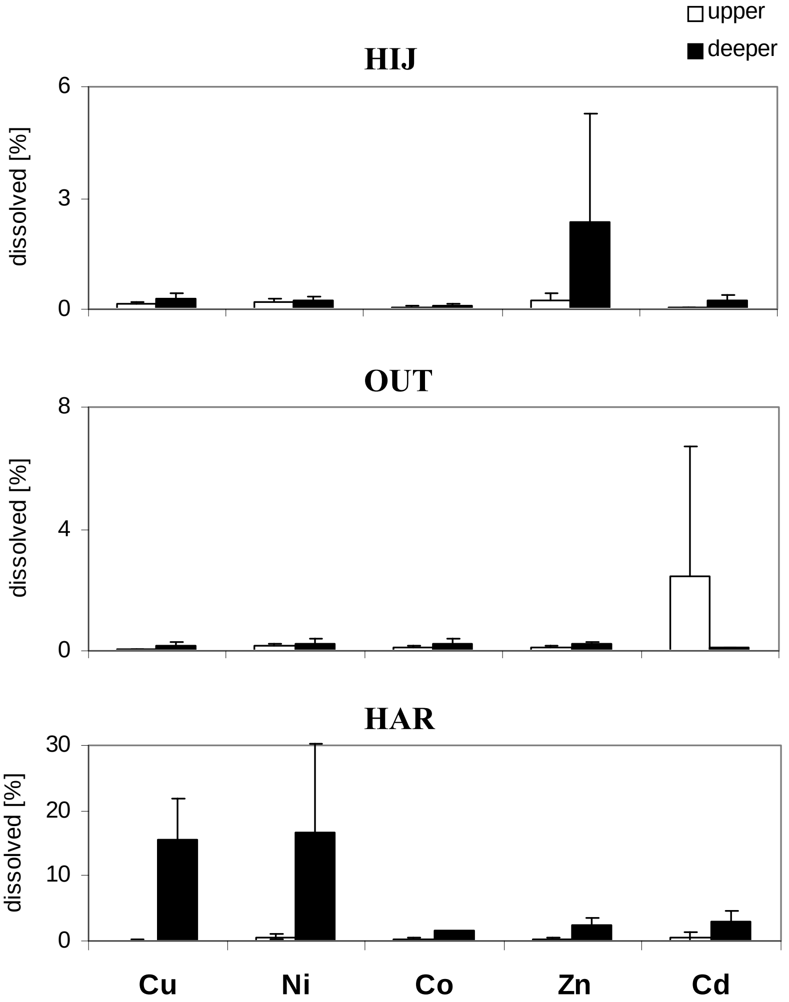

**Fig. 29.** Percentage of the dissolved fractions of investigated trace metals to total concentrations in the peat-containing water column, for both upper (0-25cm) and deeper (<25 cm) peat layers. Maximum total concentrations for HIJ-OUT-HAR are as follows (µM): Cu: 3.1-32-650; Ni: 1.8-4-180; Co: 0.3-2.4-10; Zn: 100-70-230; Cd: 0.3-0.2-1.2 and are calculated from bulk concentrations given elsewhere (Rausch et al. submitted)

The greatest proportion of dissolved metals by far is found in the HAR profile, with considerable differences seen between upper and lower layers. In the uppermost layers, a much lower percentage of the metals are found in the dissolved fraction. This is somewhat misleading, however, because the total concentrations of the metals are so high, relative to 'background' values. For example, in the uppermost layers of the HAR profile, Cu concentrations in the peat are up to 600 times greater than the 'background' values found in the deeper peat layers at HIJ (Rausch et al. 2005). In the deeper peat layers at HAR, the metal concentrations in the solid phase are comparable to the 'background' values for the deeper, uncontaminated peat layers at HIJ. However, the porewater metal concentrations are elevated at these depths (Fig. 28). As a result, the percentage of total metal which is in the aqueous phase is greatest in the deeper section, with ca. 15 % of the total Cu and Ni in the porewaters. All trace metals in the deeper layers, especially Cu and Ni, show a high percentage in the aqueous phase, and this is a clear indication that the metals in the HAR core have been mobilized from the solid phase.

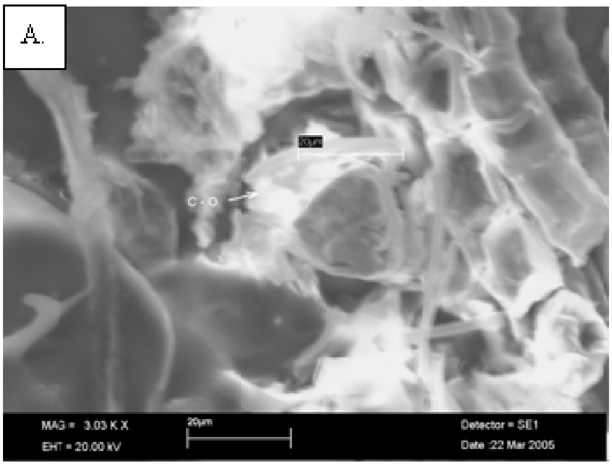

**Fig. 30.** SEM image of a single, angular plate of the composition Cu-Fe-S adhering to organic material; this is the predominant Cu-bearing particle in the OUT peat layer of maximum bulk metal concentration (13 cm). At HAR, particles of similar composition are found, but smaller and less common, and a few particles of the composition Cu-S.

### POSSIBLE MECHANISMS OF IMMOBILISATION OF CU AT OUT

The peat core at OUT contains elevated concentrations of Cu which reflect inputs to the surface layers from the mining activities (Rausch et al. 2005). Despite the elevated concentrations in the solid phase, the porewaters show no response, with Cu concentrations not significantly greater than at HIJ. Analyses of selected samples using the SEM revealed Cu-bearing particles, primarily chalcopyrite ($CuFeS_2$) up to ca. 25 microns (Fig. 30). Chalcopyrite was the dominant Cu-bearing ore at Outokumpu, and this is most likely the dominant form of Cu which was supplied to the bog in the form of dust. In the acidic bog waters, chalcopyrite should dissolve under oxidising conditions, releasing Cu, Fe, and S to the pore fluids. The porewater analyses, however, show that the pore fluids contain no more Cu, Fe, or S than the background site. The porewater analyses, therefore, indicate that the oxidative dissolution of chalcopyrite is not significant. The dissolution of chalcopyrite can be written

$$CuFeS_2 + 4\ O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2\ SO_4^{2-} \quad (1)$$

There are several possible reasons for the preservation of chalcopyrite grains in the waters of the bog at OUT. First, with up to 60 mg $L^{-1}$ DOC, the surface layers may have become coated with organic ligands (dissolved humic matter) and protected from dissolution. Second, the rate of dissolution might be slow relative to the rate of peat accumulation (0.62 cm $yr^{-1}$ for the upper 10 cm at OUT), such that the grains became incorporated in anoxic peat before there was an opportunity for them to dissolve. Third, it might be that the surface of the bog is effectively anoxic, despite the widely held view of an aerobic acrotelm. A simple calculation of the solubility of chalcopyrite as a function of redox potential shows that it should react under oxidising conditions, but not under reducing conditions (Fig. 31). The porewater data suggests that the redox potential at HIJ is reducing with respect to chalcopyrite. We argue that Cu is well preserved in the OUT profile because it has been supplied *via* the atmosphere mainly as chalcopyrite, and that this phase is thermodynamically stable in the anoxic peat.

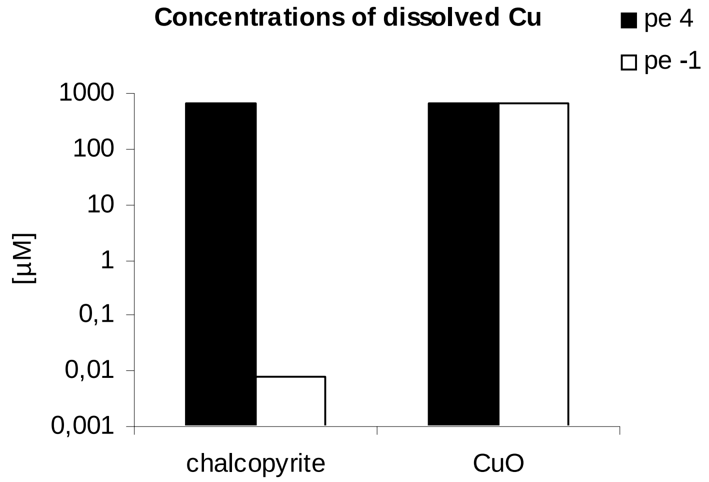

**Fig. 31.** Concentrations of dissolved Cu (µM) after oxidative and reductive dissolution of chalcopyrite ($CuFeS_2$) and an oxidized Cu phase ($\log_K$ (CuO) = 7.64, corresponding to cristalline tenorite); total Cu concentrations 650 µM, temperature 10°C.

### COMPARISON OF DISSOLVED AND SOLID METAL INPUT AT HAR

In general, elevated metal concentrations at upper peat layers could be either the result of a high input of dissolved metals *via* the percolating rainwater, or that of a release of formerly deposited solid particles. In order to estimate the relative contributions at HAR, we compared the Cu accumulation rates in peat samples accumulated in 1994 (mg $m^{-2}$ $yr^{-1}$) (Rausch et al. 2005) with mean annual Cu fluxes from filtered bulk deposition as monitored during 1993-1996 at a distance of 4 km from the Harjavalta smelter (Derome and Nieminen 1998). Although Cu was not perfectly retained in the HAR peat layers, the Cu accumulation rate exceed the rainwater fluxes by a factor of 3.5, indicating that the deposition of particulate Cu is more important than dissolved Cu. As an independent check, we calculated Cu concentrations in rainwater from these deposition rates as follows (Fig. 28):

$$[\text{Me}_{\text{rainwater}}] = [\text{Me deposition}] \times 1000 \times [\text{precip sum}]^{-1} \qquad (1)$$

where [Me $_{\text{rainwater}}$] is the metal concentration in rainwater (nM), [Me deposition] the mean annual Cu deposition rate from rainwater for the period 1993-1996 (µmol $m^{-2}$ $yr^{-1}$) (Derome and Nieminen 1998) and [precip sum] the annual precipitation sum for the period 1950-1999 at the HAR area (mm) (Ukonmaanaho et al. 2004). These data too demonstrate that the HAR porewater profile mainly reflects the release of metals from solid phases to the porewaters, and not because of their supply from precipitation.

### POSSIBLE MECHANISMS OF MOBILISATION OF CU AT HAR

Compared to OUT and HIJ, porewater concentrations at HAR are up to 100 times greater. Despite the fact that both OUT and HAR have been impacted by atmospheric Cu contamination, Cu is mobilised from the solid phase only at HAR. The smelting of Cu and Ni ores at HAR would have supplied the bog with metals mainly in the form of oxides. Chalcopyrite grains were found in the peat layer at HAR, but were much less common than at OUT, and much smaller. Although oxidized Cu phases were not found in the peat using SEM/EDX, we assume that most of the Cu and Ni deposited on the bog surface at HAR was originally in the form of oxides. The dissolution of copper oxide can be written

$$CuO + 2\,H^+ \rightarrow Cu^{2+} + H_2O \qquad (2)$$

In contrast to the dissolution of chalcopyrite, this reaction is not only independent of redox potential (Fig. 31), it is dependent on pH. The much lower pH at HAR (3.3) would promote this reaction, relative to OUT which is less acidic (pH 3.9). The much lower pH at HAR has two further ramifications. First, it would hinder the complexation of Cu by organic matter by promoting the dissociation of Cu-organic complexes.

$$CuL + 2\,H^+ \rightarrow Cu^{2+} + 2\,H_2L \qquad (3)$$

The formation of complexes with organic matter, both in the solid phase as well as the aqueous phase, has traditionally been thought to be the dominant mechanism by which peat bogs retain atmospheric Cu (Jones 1987; Livett 1988; Livett et al. 1979; Stewart and Fergusson 1994). Second, the low pH of the solution would also increase the competition between protons and Cu ions for exchange sites on the solid phase (peat)

$$\mathrm{Cu\text{-}R} + 2\,\mathrm{H}^+ \rightarrow \mathrm{Cu}^{2+} + 2\,\mathrm{H_2\text{-}R} \qquad (4)$$

where R refers to the organic substrate. The net effect of the low pH on both of these reactions would be to maintain elevated concentrations of Cu in the pore fluids. Advective flow of the porewaters near the surface of the bog, and bulk diffusion in deeper layers, would transport Cu away from the zone into which it was deposited originally. The final result would be a chronology of atmospheric Cu deposition which was inconsistent with the historical records of smelting and refining .

The mechanism of Cu immobilisation at OUT and mobilisation at HAR proposed here would also explain the trends seen for the other transition metals supplied to OUT primarily as sulphides, and at HAR as oxides.

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# Appendices

### Appendix 1

Givelet, N., G. Le Roux, A. K. Cheburkin, B. Chen, J. Frank, M. E. Goodsite, H. Kempter, M. Krachler, T. Noernberg, N. Rausch, S. Rheinberger, F. Roos-Barraclough, A. Sapkota, C. Scholz, W. Shotyk. 2004. Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical mineralogical and isotopic analyses. *Journal of Environmental Monitoring* **6**: 481-482.

### Appendix 2

Inter-method comparison of trace metal determinations

### Appendix 3

Ukonmaanaho, L., T. Nieminen, N. Rausch, A. Cheburkin, G. Le Roux, W. Shotyk. 2005. Recent organic matter accumulation related to some climatic factors in ombrotrophic peat bogs near heavy metal emission sources in Finland. *Global and Planetary Changes* in review

### Appendix 4

Porewater concentration profiles of various metals at HIJ, OUT and HAR

### Appendix 5

Bulk peat concentrations: of Cu, Ni and Zn at Alkkia
of S and Fe at HIJ, OUT and HAR

### Appendix 6

SEM/EDX analysis of OUT 13, 33 and HAR 11, 15

### Appendix 7

Ore-related Ni and Co imput at OUT

## 7-1 Appendix 1

# Suggested protocol for collecting, handling and preparing peat cores and peat samples for physical, chemical, mineralogical and isotopic analyses

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**Abstract.** For detailed reconstructions of atmospheric metal deposition using peat cores from bogs, a comprehensive protocol for working with peat cores is proposed. The first step is to locate and determine suitable sampling sites in accordance with the principal goal of the study, the period of time of interest and the precision required. Using the state of the art procedures and field equipment, peat cores are collected in such a way as to provide high quality records for paleoenvironmental study. Pertinent field observations gathered during the fieldwork are recorded in a field report. Cores are kept frozen at -18 °C until they can be prepared in the laboratory. Frozen peat cores are precisely cut into 1 cm slices using a stainless steel band saw with stainless steel blades. The outside edges of each slice are removed using a titanium knife to avoid any possible contamination which might have occurred during the sampling and handling stage. Each slice is split, with one-half kept frozen for future studies (archived), and the other half further subdivided for physical, chemical, and mineralogical analyses. Physical parameters such as ash and water contents, the bulk density and the degree of decomposition of the peat are determined using established methods. A subsample is dried overnight at 105 °C in a drying oven and milled in a centrifugal mill with titanium sieve. Prior to any expensive and time consuming chemical procedures and analyses, the resulting powdered samples, after manual homogenisation, are measured for more than twenty-two major and trace elements using non-destructive X-Ray fluorescence (XRF) methods. This approach provides lots of valuable geochemical data which documents the natural geochemical processes which occur in the peat profiles and their possible effect on the trace metal profiles. The development, evaluation and use of peat cores from bogs as archives of high-resolution records of atmospheric deposition of mineral dust and trace elements have led to the development of many analytical procedures which now permit the measurement of a wide range of elements in peat samples such as lead and lead isotopes ratios, mercury, arsenic, antimony, silver, molybdenum, thorium, uranium, rare earth elements. Radiometric methods (the carbon bomb pulse of $^{14}C$, $^{210}Pb$ and conventional $^{14}C$ dating) are combined to allow reliable age-depth models to be reconstructed for each peat profile.

## Introduction

The use of peat cores from bogs in paleoenvironmental studies has increased dramatically during the last decade.(Farmer et al. 1997; Mackenzie et al. 1988; Martínez Cortizas et al. 1999; Monna et al. 2004; Novak et al. 2003; Vile et al. 1995) The reasons for this are not only that peat cores from ombrotrophic bogs are excellent archives of many kinds of atmospheric particles: soil dust, volcanic ash, phytoliths, anthropogenic aerosols, and many trace elements but peat bogs are also economically attractive archives because the concentrations of trace elements such as mercury (Hg) and lead (Pb), are sufficiently high that they are much more accessible by conventional methods of analysis than other archives of atmospheric deposition such as ice cores. Unlike glacial ice which is restricted to Alpine and Polar regions, peatlands are widely distributed across the globe, accounting perhaps 5% of the land area of the Earth.(Charman 2002) There is growing evidence that undisturbed bogs have faithfully preserved the historical records of a wide range of trace metals, despite the low pH and abundance of dissolved organic acids in the waters, and the seasonal variations in water table (and impact which this may have on redox state). In the case of a metal such as lead, for example, the historical record of atmospheric Pb deposition is so well preserved in undisturbed bogs(Shotyk et al. 1998) that our ability to read and interpret the peat bog records is largely independent of chemical processes taking place within the bog itself, but can depend to a large extent on the methods used to collect, handle, and prepare the samples for analysis.(Shotyk et al. 2002) Moreover, the lack of a commonly used, validated protocol has hindered the interpretation and comparison of peat core metal profiles from different laboratories within the international community. Therefore, to compare the published peat bog records with one another or to other archives (e.g. lake sediments, ice cores, tree rings), and for detailed reconstructions of atmospheric metal deposition, a comprehensive protocol for working with peat cores is warranted.

Since the first cores for chemical analysis were collected at Etang de la Gruère in the Jura Mountains, Switzerland, in the autumn of 1990, (Shotyk and Steinmann 1994) many changes and developments have been made with respect to the practical aspects of this work. The present paper shows that the effects of core compression during sampling, the spatial resolution obtained by core cutting, as well as the accuracy and precision of peat core slicing can very much affect the measured record of trace element concentrations and enrichment factors (EF). Moreover, in this paper we have summarized the refinements made to the methodological procedures and analyses which have been developed by our research group over the years, to share these with the international community. We hope that the protocol described here can serve as a guideline for future paleoenvironmental studies using peat cores from bogs. Improvements to the description of the coring sites and the cores themselves, the accuracy and precision of slicing techniques and sub-sampling, as well as the physical and chemical analytical methods employed and the dating methods used to model the age-depth relationship, will help to ensure that the results obtained by different research teams are directly comparable.

## Background to the problem

Comparison of two peat bog records of atmospheric lead pollution from Etang de la Gruère in Switzerland (EGR) have shown that while the general agreement between the two cores (EGR, cores 2F and 2K) is very good, there are also some differences. (Shotyk et al. 2002) One difference is revealed by the concentration profiles of anthropogenic Pb. The 2F core reveals two pronounced peaks of nearly identical Pb EF during the 20th century, but in the 2K core the more recent of these two is less pronounced (Fig. A1-1). Here, possible reasons for this difference are explored: differential core compression during sample collection, the relative thick peat slices (3 cm) used to represent the individual samples, and from the imprecision of the cutting technique used to section the cores.

### EFFECTS OF CORE COMPRESSION ON ANTHROPOGENIC PB CONCENTRATIONS

A summary of some physical and chemical properties of the two peat cores is given in Figure 1. In general, both profiles contain a zone of enhanced peat humification from ca. 20 to 60 cm which is visible upon inspection of the cores in the field (darker colour, finer texture, fewer visible plant remains). This zone is also revealed in each core by the elevated bulk density values at these depths, as well as reduced pH values and lower yields of extractable porewater (Fig. A1-2). However, there are some discernible differences between the two cores. First, the ash content profile shows significantly higher maximum ash content in the 2F core (8.6 %) compared with 2K (6.9 %). Second, the maximum bulk density in the 2F core (0.15 g $cm^{-3}$) exceeds that of 2K (0.13 g $cm^{-3}$). Both of these changes suggest that the 2F core experienced compression in the vertical direction, relative to the 2K core. At the time which core 2F was collected (26. August, 1991), the bog surface was very dry; with the depth to water table approximately 70 cm below the peat surface. During these conditions, it is very difficult to obtain a peat monolith without compressing the core, especially with the abundance of roots of *Ericaceous* shrubs and *Eriphorum* fibres which dominate the near surface layers of the peat profile. Comparison of the ash content and bulk density profiles introduces (Fig. A1-1) the suspicion that the 2F core was compressed, relative to 2K, during core retrieval.

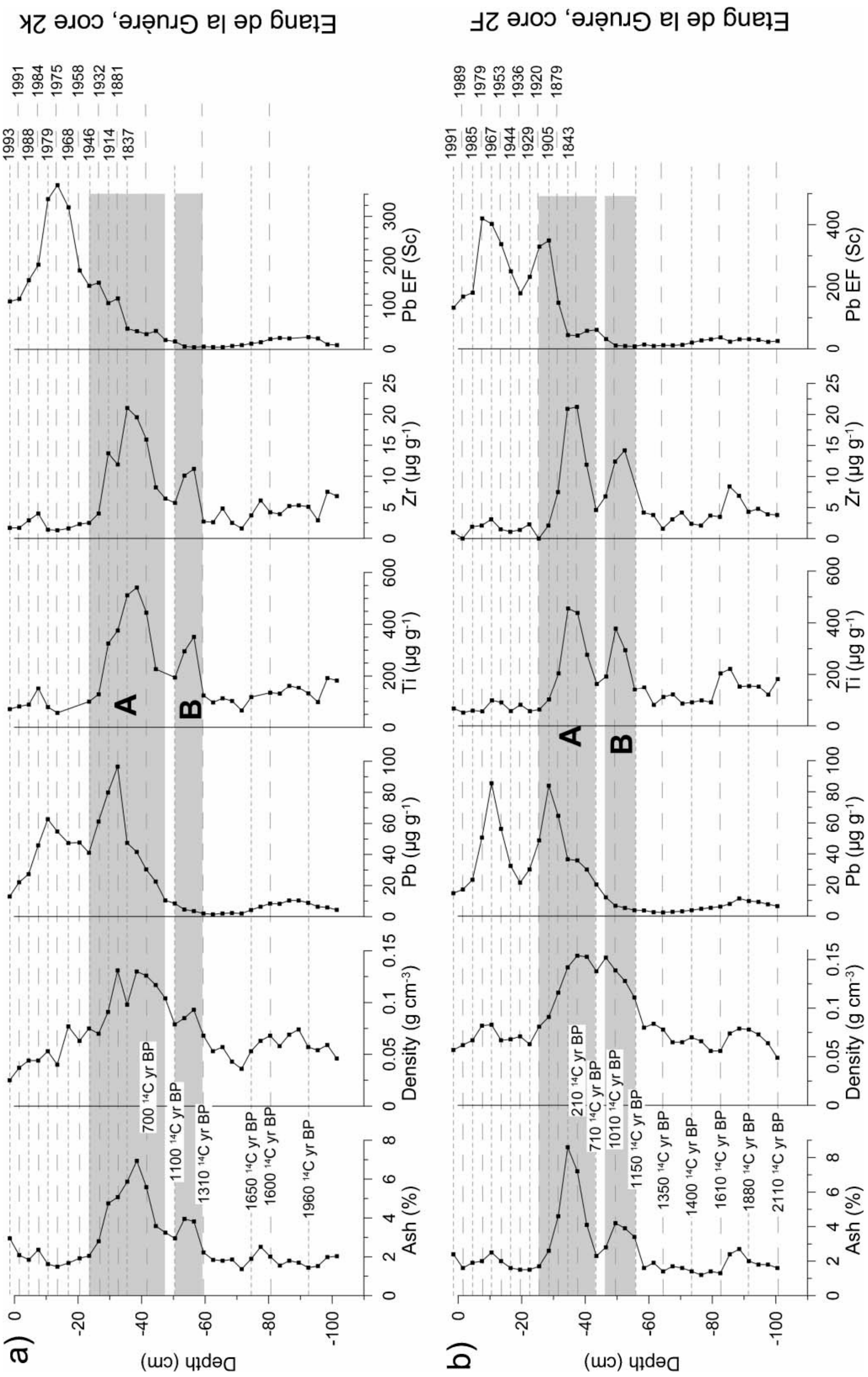

**Fig. A1-1. a)** Ash content, bulk density, concentrations of Pb, Ti, Zr, and Pb EF in the 2K core. **b)** ash content, bulk density, concentrations of Pb, Ti, Zr, and Pb EF in the 2F core. Maximum concentrations of Ti and Zr are indicated beside the peaks identified by the shaded bars. Pb EF calculated using Sc (relative to Earth's Crust). Age dates shown on the right hand side of box b) were obtained using $^{210}$Pb, age dates within box b) are radiocarbon ages, expressed as conventional radiocarbon years Before Present.

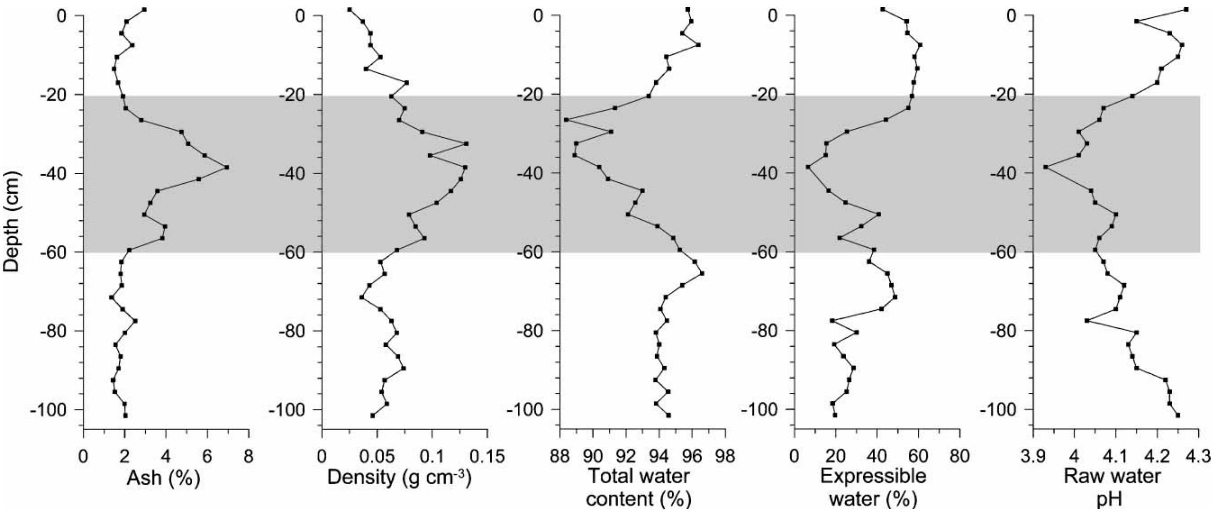

**Fig. A1-2.** Ash concentration, bulk density, total water content, expressible water, and raw water pH, 2K core

The abundance and distribution of total Pb concentrations exhibit striking differences: in 2F, there are two nearly identical peaks in Pb concentration, whereas in the 2K core the deeper, older peak is clearly superior (Fig. A1-1). The concentrations of Pb at these depths exceed the LLD (0.4 µg $g^{-1}$) by more than two orders of magnitude, and in this concentration range the accuracy and precision of the Pb measurements using EMMA XRF are better than 5% (Cheburkin and Shotyk 1996). Thus, the difference in the abundance and distribution of Pb cannot be explained in terms of analytical error. Titanium and Zr both show two pronounced peaks in each core, but the ratios between the two peaks differ (Fig. A1-1): in the 2K core, the ratio of Ti and Zr in peak A to peak B are 1.5 and 1.9, respectively; the corresponding ratios in 2F are 1.2 and 1.5, respectively. Thus, soil-derived mineral material is relatively more abundant in the A peak of the 2K core than the A peak of the 2F core. To say it another way, Pb, Ti, and Zr are relatively more abundant in the B peak of core 2F compared with core 2K. This difference may simply reflect the extent of natural variation with a given area at a given time, as observed previously using *Sphagnum* mosses collected from a given bog during a single year.(Weiss et al. 1999) However, if both Pb and Ti have been accidentally increased at any point in the 2F peat core by vertical compression while coring, then both elements would increase in concentration to the same extent, and this would have no net effect on anthropogenic Pb calculated as described earlier. Thus, the direct effect of compression in the 2F peat core on the concentrations of Pb and Ti cannot explain the differences in the relative abundance of anthropogenic Pb between the two cores.

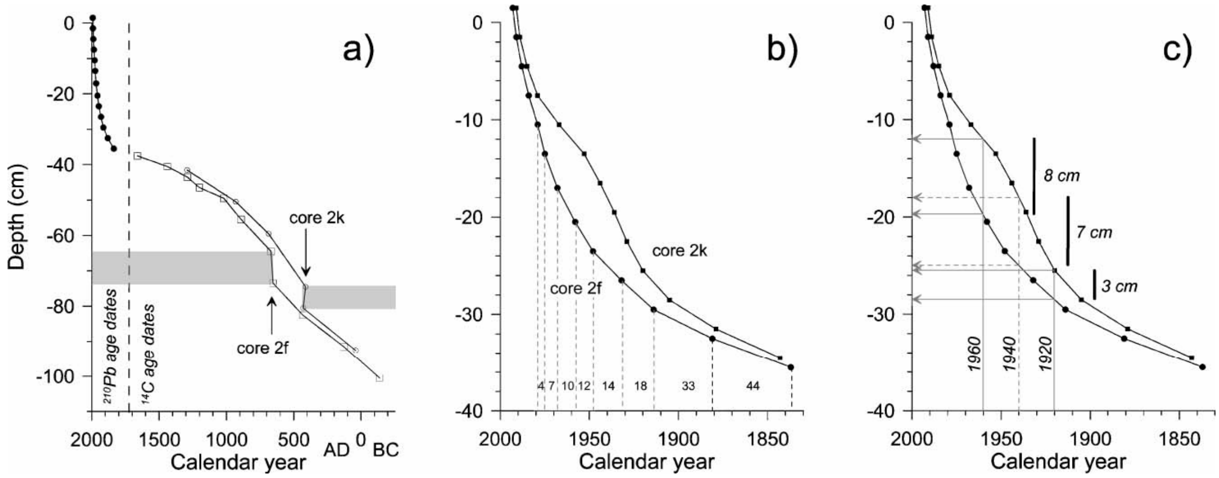

**Fig. A1-3. a)** Age-depth relationship in the two peat cores. Vertical dashed line distinguishes $^{210}$Pb from $^{14}$C age dates. Notice that both $^{14}$C curves show an inflection, indicated by the arrows, but that this section is deeper in the 2K core (shaded bar on right) compared to 2F (shaded bar on left). **b)** $^{210}$Pb age dates of the two peat profiles. Numerical values between vertical dotted lines indicate the number of calendar years represented by each slice. **c)** Assuming that the $^{210}$Pb age should represent the same depth in each peat core, the dotted line indicates the vertical displacement (cm) between the two cores at AD 1920, the dashed line at AD 1940, and the solid line at AD 1960.

## EFFECTS OF CORE COMPRESSION ON THE AGE-DEPTH RELATIONSHIP

To further evaluate the possibility that the 2F core may have been compressed and to try to understand the possible importance of this process, the age depth relationship has been plotted for the entire length of both cores (Fig. A1-3a) and for only the uppermost layers which were dated using $^{210}$Pb (Fig. A1-3b). Both graphics show clearly that there has been some vertical displacement of the 2F core, relative to 2K. First, the arrows in Fig. A1-3a show an inflection point where age does not measurably change with depth; in the 2F core, this is found between 64 and 74 cm, but in the 2K core from 74 to 81 cm. The change in $^{210}$Pb age with depth shows that the 2F core has certainly been compressed, relative to 2K, in particular in the range ca. 10 to 30 cm (Fig. A1-3b).

Also shown in Fig. A1-3c is the incremental age, in calendar years, for the individual slices of 2K samples pre-dating ca. 1980. This information is included to emphasize the increase in age of each peat slice with increasing depth. In the range where the 2F core was compressed, the individual peat slices represent from 4 to 33 years of peat accumulation. The effect of compression on age therefore becomes increasingly important with depth, as a greater proportion of older material becomes compressed into a given volume. The extent of compression can be estimated by assuming that any given $^{210}$Pb age should be found at the same depth in each core. Assuming this ideal case, the vertical difference between the two cores is approximately 3 cm at 1920, 6 cm at 1940, 12 cm at 1960, and 4 cm at 1980 (Fig. A1-3c).

Despite these differences and the causes to which they are due, compression of the peat core will affect the activity of $^{210}$Pb and the concentrations of Pb and Sc. Compression of the peat core alone, therefore will not affect the chronology or intensity of the changes in anthropogenic Pb concentrations.

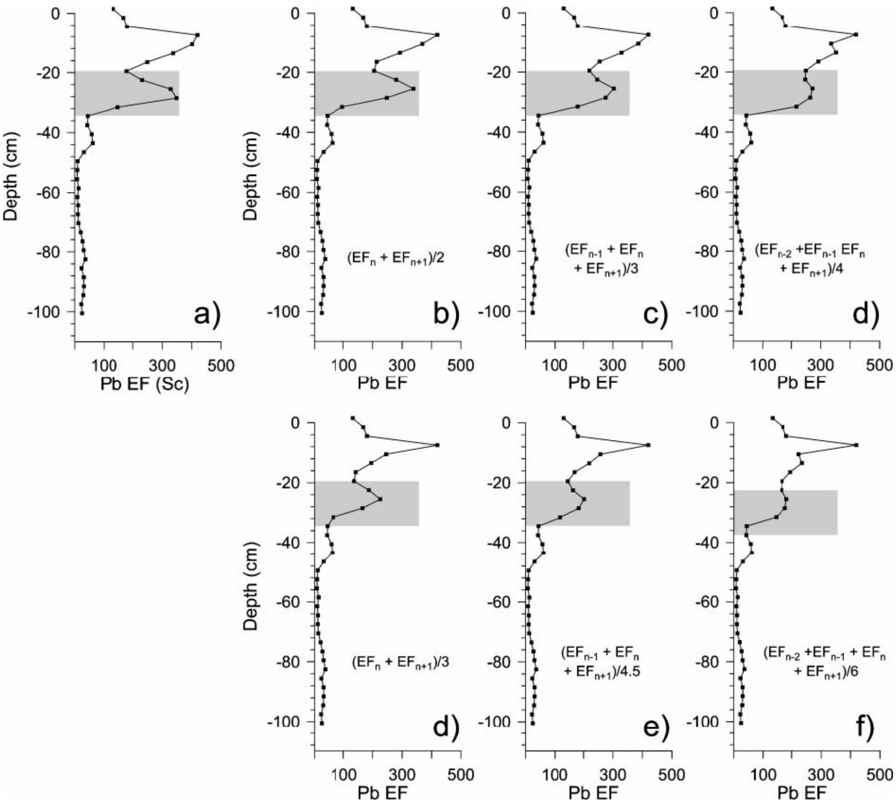

**Fig. A1-4.** Modelling the effects of varying the thickness of the peat slices and the position of the cut on the vertical distribution of Pb EF, from 10.5 cm to 32.5 cm in the EGR 2F core. The original data set is given in a) where the Pb EF (calculated using Sc as the reference element and the Earth's Crust as reference point) is plotted versus depth. b) to d) simulate the effect of varying the position of the cut, but not the thickness of the peat slice. e) to g) simulate the effect of varying both the position of the cut and the thickness of the slice.

## EFFECTS OF HAND SLICING OF PEAT CORES ON THE CHRONOLOGY OF ANTHROPOGENIC PB

When the two peat cores were sectioned, they had been removed from the bog and were cut fresh, at ambient temperature, by hand using a bread knife. A measuring tape was attached to the cutting board and used to guide the eye while positioning the knife blade. While the intended thickness of each slice was 3 cm, no effort was made to determine the accuracy or precision of the cuts. Using the green plant material as a guide to the location of the living, biologically active layer, this section was cut away first, and is the first sample of each core. Strictly speaking, however, this material is living plant matter, and not peat. After cutting away the living layer, the top of the core became the "zero" depth, and all subsequent cuts, in increments of ca. 3 cm, were made relative to this point. Given the differential compression between the two cores and the differences in age-depth relationship, modelling of curve smoothing and combined smoothing plus compression scenarios indicates that the thickness and position of peat core slicing can significantly affect the intensity of a peak in anthropogenic Pb (Fig. A1-4.) by incorporating overlying and underlying material of lower anthropogenic Pb concentration. Not only could this process affect the calculated concentration of anthropogenic Pb per slice, but also the chronology of the enrichment, as determined using $^{210}$Pb, as material of younger and older age becomes incorporated into any given slice.

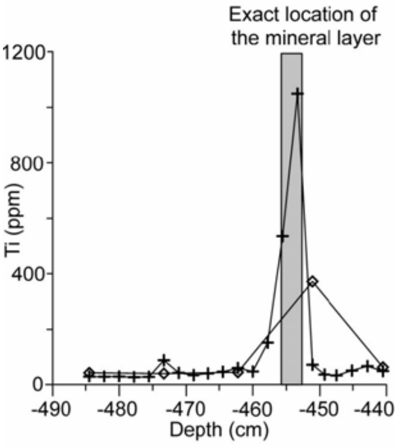

**Fig. A1-5.** Concentration of Ti (ppm) between 440 and 490 cm depth from a peat core from the Black Forest, Germany. Titanium concentrations were measured in every second sample, cut into 1 cm slices; those are reported as crosses (+) whereas average Ti concentrations for five samples (10 cm peat section) are indicated by diamonds (◇).

### EFFECT OF THE THICKNESS OF A PEAT SLICE ON THE SIGNAL RESOLUTION

The resolution and magnitude of any given peak depends on the thickness of the slice. The thinner the slice is, the better will be the resolution of the record. Moreover, as shown in Fig. A1-1, over a small vertical distance (ca. 50 cm), there are extreme changes in Pb concentration, as well as significant changes in ash content and bulk density. Therefore the thickness of the slices is of greatest importance in the uppermost peat layers which represent the most critical time period in terms of pollution reconstruction (i.e. the past two centuries since the start of industrialisation). However, even in the lower peat layers, the thickness of the slices is also important. For example, short-lived events such as the deposition of volcanic ash can be clearly resolved using 1 cm slices (Fig. A1-5). Thicker slices, however, not only provide poorer resolution (Fig. A1-5), but they also prevent the event from being accurately age-dated. Taken together, the available evidence suggested that the protocol used during the past decade had to be improved. Specifically, cutting the cores very precisely into 1 cm slices will maximize the signal/noise ratio of the peaks in metal concentration and therefore greatly contribute to improving the accuracy, reproducibility and reliability of peat bog archives (Fig. A1-6).

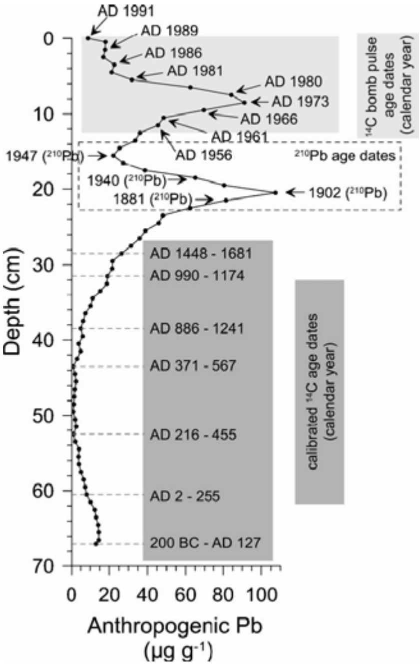

**Fig. A1-6.** Concentration of Pb (ppm) for the Wardenaar peat profile 2G from Étang de la Gruère, Switzerland (Shotyk, unpublished). This core was collected the same year as the EGR 2F core (i.e. 1991). It shows the kind of resolution, which can be obtained using 1 cm slices (compare the 2F and 2K cores (Fig. A1-1) which were cut into 3 cm slices) and accurate age dating. The upper layer age dates have been calculated using the $^{14}$C "atmospheric bomb pulse curve" (Goodsite et al. 2001).

## Improvements and proposed protocol

Since EGR 2F and 2K cores were collected in 1991 and 1993, respectively, several changes have been made in the collection, handling and preparation of peat cores to improve the accuracy and precision of peat bog records of atmospheric dust and trace metal deposition. The most important changes are summarised below.

### FIELD SAMPLING STRATEGY

The success of paleoenvironmental studies using peat cores as archives largely depends on the ability to select appropriate peatlands which have preserved high-quality paleoenvironmental records. Therefore careful selection of sites and coring locations within the sites are critical elements of field research. Although, the strategy will vary depending on the purpose of the study and the site itself, several general considerations can be helpful to design suitable field sampling strategies and for retrieving peat cores. Since comprehensive field observations are a very valuable aspect of the survey, pertinent information that should be recorded are listed and discussed below.

## SITE SELECTION

To reconstruct the deposition history of atmospheric particles using peat cores, selection criteria should include the morphology of the peatland (topography and depth of peat accumulation), character of peat (visual inspection of the botanical composition, degree of decomposition, moisture content and abundance of mineral matter), possible damages to the peatland and to the peatland hydrology (peat cutting, drainage, dams), possible use of the peatland for forestry or agriculture, and distance from human activities.

Not all peatlands are appropriate for the reconstruction of the changing rates of atmospheric metal deposition and it is worthwhile to pay particular attention on the selection of the peatland. The quality of the paleoenvironmental record for many trace elements is mainly controlled by the trophic status of the peatland as revealed by e.g. the botanical composition and abundances of mineral matter. Ombrotrophic ("rain-fed") bogs should be favored over other types of peatlands, as they receive water solely from atmospheric precipitation (rain, snow) falling onto their surface. Ideally, the most valuable part of a bog is the raised dome. Neither groundwater nor surface water runoff from other areas can reach the raised part of the bog, as it is above the level of the local groundwater table. Moreover, ombrotrophic bogs provide records with better time resolution than minerotrophic deposits, mainly due to the lower degree of organic decomposition. Both biological and chemical characteristics that can be used in the field and in the lab to establish the existence of an ombrotrophic zone are presented elsewhere in detail (Shotyk 1996). The mineralogical and chemical composition of the basal sediment on which the peatland is resting should be also considered. Weathering of minerals from the underlying rocks and sediments could be an important source of ions which migrate upward into the peat by diffusion (Shotyk and Steinmann 1994). There is a great difference between the trophic status of peat profile in a bog forming on calcareous versus granitic substratum, with carbonate weathering clearly supplying more metals to the basal peat layers. Therefore, ombrotrophic bogs underlain by granites are chemically less affected by upward diffusion of ions and should be favoured over bogs growing on carbonate rocks.

If ombrotrophic bogs are common in temperate and boreal latitudes, they are scarce in sub-Arctic and Arctic latitudes (Charman 2002). Therefore at high latitudes, minerotrophic peat deposits may have to be used as archives of atmospheric metals even though they are fed both by atmospheric and terrestrial inputs. Recent studies have shown that at some predominantly minerotrophic peatlands, mercury and lead may be supplied exclusively by the atmosphere and therefore can still provide a record of the changing rates of atmospheric deposition of those elements (Givelet et al. ; Roos-Barraclough and Shotyk 2003; Shotyk 2002; Shotyk et al. 2003). Such reconstructions, however, must be interpreted with great caution and on an element by element basis because some metals of interest e.g. nickel (Krachler et al. 2003) and uranium (Krachler and Shotyk) are certainly enriched in minerotrophic peat due to weathering inputs.

Before selecting the exact site for collecting peat profiles at a peatland, the site morphology must be known. If this is not the case, it could be established by depth profiling at least two transects at 90°. This process will help selecting the deepest ombrotrophic part of a bog or the deepest organic accumulation of a minerotrophic peat deposit. Comparison of mercury and lead fluxes to hummocks and hollows of ombrotrophic bogs suggest that cores from both locations are recording trends in atmospheric deposition of Hg and Pb, but that hollow cores are recording lower input values than hummock cores, apparently due to a larger component of dry and occult (fog) deposition at hummocks than at hollows (Norton et al. 1997). Therefore sampling sites located in “lawns”, or at the transition between hollow and hummock are considered to be optimal and therefore recommended.

Prior to peat core collection, permission to retrieve geologic and environmental samples should be secured from the owner of the land if necessary. This is especially important in the case of nature reserves and other protected areas where many of the remaining central European raised bogs are found.

## CORE COLLECTION

The low density and the unsaturated environment of the topmost layers of a peat bog make the collection of good quality peat cores challenging. It is difficult to cut these layers as they are easily trampled and compressed. Moreover, the upper layers of a peat bog represent the past decades which is the most critical and interesting period in terms of atmospheric pollution, not only for trace metals and organic contaminants, but also for fallout radionuclides. The main concern about this section is to collect surface layers as an undisturbed continuous peat profile extending as far back in time as possible in an effort to reach “natural background” values. By using procedures developed by our research group, all fieldwork is completed in such a way as to minimize the impact on the environment, utilizing the latest techniques and best available technology for sampling, handling and preparing the materials.

### Modified Wardenaar corer

The topmost layers of peat can be collected using a 10 cm × 10 × 100 cm Wardenaar peat profile cutter(Belokopytov and Beresnevich 1955) which is commercially available. Our 1 m

Wardenaar corer with XY dimensions 15 cm × 15 cm, was home-made using a Ti-Al-Mn alloy and includes a serrated cutting edge; this new cutting edge cuts more easily through dwarf shrubs (e.g. *Ericaceous* shrubs) and *Eriphorum* root fibres. This feature, combined with the larger cross sectional area means that any given slice undergoes less compression in the Z (vertical) dimension. Moreover, the enlargement of the XY dimensions to 15 cm of the new Wardenaar corer compared to the older version (10 cm) provides enough peat sample material to conduct a wide range of analyses and still to be able to preserve part of the material as an archive for futures work, even using thin slices (i.e. 1 cm). The state of the art of the modified Wardenaar corer and the best way to collect a good quality peat core from the surface layers of a bog are described in detail elsewhere (Noernberg et al. ).

During extraction, some compression of the peat core is unavoidable. However, the compression can be measured, using the bog surface as a reference. After extraction, the Wardenaar corer is laid horizontally on the bog surface, on a large sheet of plastic; the top half of the Wardenaar corer is removed, exposing the peat monolith. This core is described visually in the field (length, colour, texture, plant remains, moisture, special layers) and photographed. The core is inspected for modern plants of the bog surface which may have "contaminated" the outside of the core; these are carefully removed using a small knife. The exposed surface and two sides of the core are wrapped in polyethylene cling film. A wooden core box built specifically for the Wardenaar core is lined with plastic (a large sheet, or two large sheets, is made using plastic garbage bags). The plastic-lined wooden core box is placed over the peat core. Two people lift the bottom half of the Wardenaar corer, flip it carefully backward 180°, allowing the peat core to slide down into the box. The surface of the core is wrapped in polyethylene cling film, with the film pressed down around the sides of the core and ends using a plastic spatula. The core is covered with plastic, labelled and the lid attached using screws. In this way, handling of the core in the field is kept to a minimum.

### Belarus corer

A Belarus (Macaulay) peat sampler is used for deeper peat layers (Belokopytov and Beresnevich 1955). Two versions of this corer are actually used: stainless steel and titanium (Ti). The titanium corer, which is much lighter, was constructed using the same alloy as for the Wardenaar corer.

Cores are removed from two holes adjacent to the hole from the Wardenaar core, approximately 20 cm apart, in parallel overlapping design. Peat cores are carefully packed onto plastic-semi tubes which are lined with polyethylene cling film: while still in the peat corer, the peat sample (a semi-cylinder ca. 50 cm long and 10 cm wide) is wrapped with polyethylene cling film and a plastic semi-tube is placed on top; the corer is gently flipped backwards 180°, and holding the semi-tube, the core is carefully slid away from the corer. Again, the cores are described and photographed without touching them. The core is wrapped with polyethylene cling film, labelled, and packed in rows in a transport aluminium box.

### Motorized corer for frozen peat

A unique peat sampler was designed and built by Mr. Tommy Nørnberg for obtaining continuous samples of frozen peat in the Arctic. Up to 10 meters of frozen peat in 70 cm sections can be removed using this corer. The sampler and the coring technique is described in detail elsewhere (Noernberg et al. ).

Cores are kept cool until they can be frozen: this is done soon as possible after collection, and kept frozen at -18 °C until they can be prepared in the laboratory. Cores collected from frozen peat deposits are shipped frozen back to the laboratory.

## FIELD OBSERVATIONS

Pertinent field observations that should be gathered during the fieldwork include sampling date and time, sampling site significance and location. The precise location of the core collection should be indicated on a topographical map and the GPS coordinates recorded. Because it may be very useful to return to the coring site at some future date, burying a plastic soda pop bottle containing a handful of steel just below the surface of the coring site will allow the exact site of core collection to be found later, using a metal detector. This also helps to avoid possible further peat collection at the same location, as the peat stratigraphy may have been affected by the coring session. Notes on colour, component, length, depth, core compression and other details (e.g. layers of wood, charcoal) are also information that should be recorded. As noted earlier, core compression during sample collection can be a problem, because of secondary effects on the metal concentration profiles and/or the age-depth relationship. Therefore, coring in spring or early summer when the peatland is at its wettest is recommended. Additional pertinent information that should be recorded includes maximum depth of peat accumulation at the collection site and possible disturbance. Collection of representative surface plant species may serve as a valuable reference for the plant material which constitutes the fossil botanical assemblage of the peat cores.

In order to achieve consistency in recording such data, a field report should be written. This primarily provides a public report of the fieldwork, detailing how and where peat and other geologic or environmental samples were taken for subsequent dating and analysis. The Field Report format developed by M.E. Goodsite is highly recommended (Goodsite and Shotyk 2001) and is available for downloading for free use at http://www.rzuser.uni-heidelberg.de/~i12/eergebnisse.htm.

## SAMPLES PREPARATION

To have a rapid, approximate description of the geochemistry of a peat core, a sacrificial core may be sliced immediately in the field using a serrated stainless steel knife into 3 cm slices. Using plastic gloves, each slice is placed in a plastic bag and the bag squeezed by hand to express the pore water. The pore waters may be analyzed for pH, major element cations and anions, and DOC (Shotyk and Steinmann 1994). Slicing the core by hand with a knife has some advantages, as it can provide a rapid survey of the geochemistry of the peat profile if the pore waters are analysed. However it only provides an approximate description of the geochemistry, and this preparation procedure is not suitable to reconstruct high-resolution records of atmospheric metal contamination.

### Slicing the cores

With respect to high-resolution records, Wardenaar, Belarus and Nørnberg peat cores are cut frozen in the lab into 1 cm increments using a stainless steel band saw with stainless steel blades. The width of the blade is 1 mm, so ca. 10% of each slice is lost during cutting. The accuracy of the thickness of theses slices is better than ± 1 mm. For Belarus and Nørnberg cores, a slicing system was designed and constructed as described elsewhere (Noernberg et al. ). A similar system made of an Omega SO 200a band saw and a precision cutting table is used to slice the Wardenaar cores. Because the cores are large and long, they are heavy (~23 kg) and the cutting table is necessary for precise cutting. The individual slices are subsequently placed on a polyethylene cutting board and the outer 1 cm of each slice is trimmed away using a 13 × 13 cm polyethylene plate and either an acid rinsed ceramic knife or a Ti knife (Fig. A1-7). The outside edges are systematically discarded, as those could have been contaminated during the sampling and preparation procedures by layers enriched in mineral matter such as tephra layers (e.g. Faroe Island cores), or where there are very high metal concentrations (due to intense atmospheric pollution). The cutting board and knife are rinsed with deionised water three times between each slice. Then slices are packed into labelled zip-lock plastic bags for storage and further preparation.

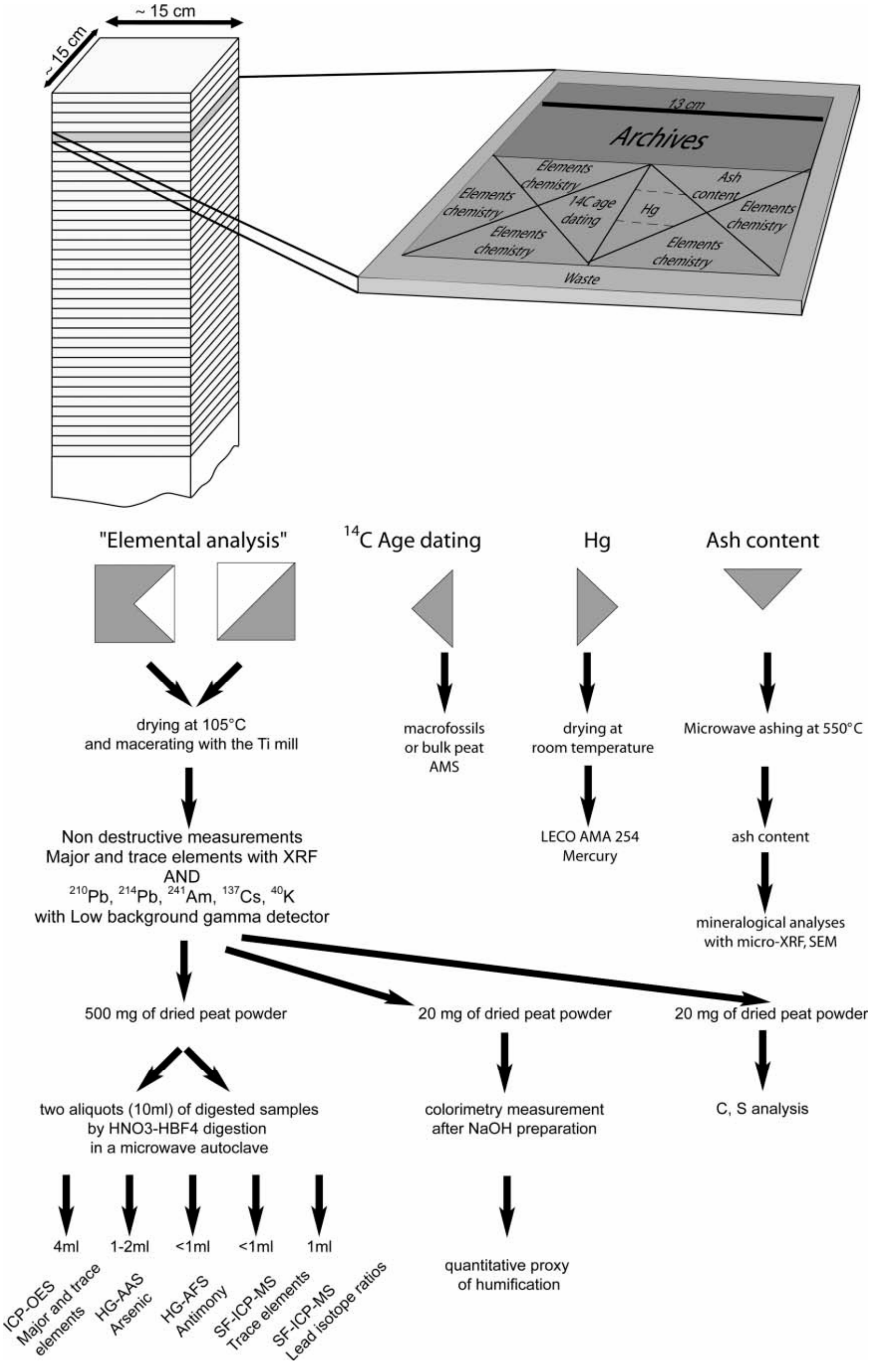

**Fig. A1-7.** Analytical flow chart and sub-sampling strategy for a peat slice from a Wardenaar core. The outside edges of the slices are systematically removed to waste to ensure that only the uncontaminated part of each sample is used for study. Part of the slice is archived for possible future studies. Peat triangles are sub-sampled, oriented to ensure that, for any given analysis, the sub-samples are taken from the same position in each slice.

## Sub-sampling Strategy

Great care has to be focused on the orientation of each slice during the slicing session with respect to its original position when it was in the peat monolith. To guarantee the reconstruction of high-resolution records, peat material for a given analysis should be sub-sampled along a conceptual micro-core within the Wardenaar core and therefore at a similar location within the oriented slices.

A sub-sampling strategy is defined for each individual core depending of the main objective of the study. An example of the approach we use is shown in Fig. A1-7. Two 6 × 6 cm squares are removed using a polyethylene plate. The squares are divided into four triangles by cutting each square along its diagonal. Each triangle is identified with respect to its position within the peat slice, packed into labeled bags and reserved for previously defined analyses (Fig. A1-7). Part of the material is archived at -18 °C for possible future studies, and the remainder of the sub-samples will be processed for physical, chemical, mineralogical and isotopic analyses.

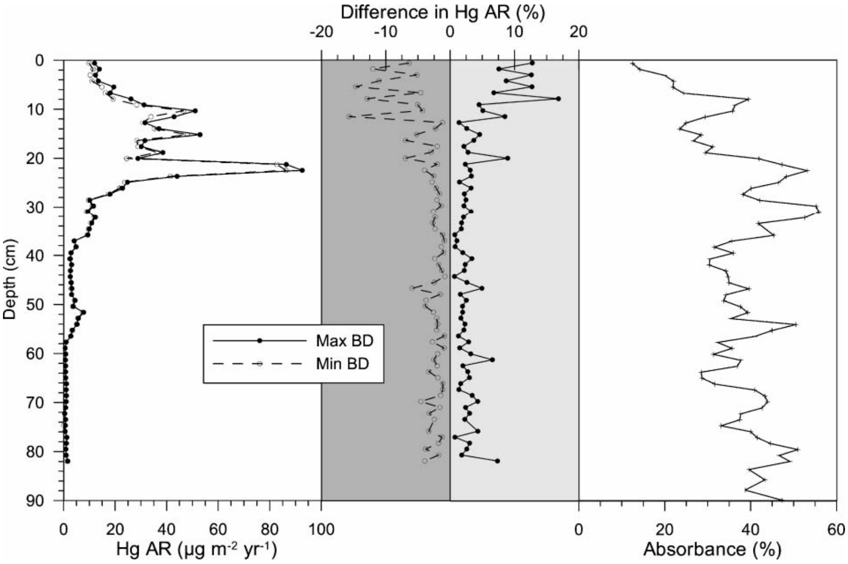

**Fig. A1-8.** Comparison of mercury accumulation rate profiles calculated using a) minimum bulk density value and b) maximum bulk density value for a peat core from southern Ontario, Canada. The corrected absorbance is an indicator of the degree of peat humification.

### Drying and milling

The peat samples are dried at 105 °C in acid-washed Teflon bowls, and macerated in a centrifugal mill equipped with a Ti rotor and 0.25 mm Ti sieve (Ultra centrifugal Mill ZM 1-T, F.K. Retsch GmbH and Co., Haan, Germany). This yields a very fine, homogeneous powder with average particle size of ca. 100 µm (and Gaussian particle size distribution). For finer powder (e.g. for slurry sampling AAS), the direction of the sieve can be reversed. For samples rich in mineral matter (e.g. tephra layers) and for organic-rich sediments, an agate ball mill is used instead. The powdered samples are manually homogenised and stored in airtight plastic beakers. The milling is carried out in a Class 100 laminar flow clean air cabinet to prevent possible contamination of the peat samples by lab dust. In the laboratory, all of the sample handling and preparation is carried out using clean laboratory techniques. Peat powder stored for longer than one year in humid conditions should be re-dried prior to analysis following similar procedures for certified standard reference materials (e.g. plant SRMS from NIST, BCR, or IAEA).

## Analyses

### PHYSICAL ANALYSES

The precision of the bulk density measurements is of great importance for the reconstruction of records of metal contamination as the bulk density data is used to calculate the rates of metal accumulation. Until recently, the centers of the peat slices were sub-sampled using a sharpened stainless steel tube (16 mm diameter) and these plugs used to determine the dry bulk density. The height of each plug was measured to an accuracy of 0.1 mm and the volume calculated. After recording wet weights, plugs were dried at 105 °C overnight and the dry mass was weighed to 1 mg. Later, in order to decrease the discrepancy of the diameter of the plugs induced by the operator, a hand-operated stainless steel press was used to recover plugs of 20 mm diameter with an accuracy of 0.1 mm.(Noernberg et al. ) However, with respect to the heterogeneity of peat material within a slice, especially the upper layers of modern accumulation, and the unknown, possibly important uncertainties in the measurement of the volume and weight of a small plug of peat material, we found that the determination of bulk density was an important source of error in the calculation of rates of metal accumulation. For example, the calculation of Hg accumulation rates in a peat core from southern Ontario using the minimum and the maximum value of bulk density determined using four plugs for each slice show the calculated Hg accumulation rates of mercury may be ± 10 % of the accumulation rate value calculated using the average bulk density value of the four plugs (Fig. A1-8). This is mainly explained by the heterogeneity of the peat material within a given slice, especially in the surface peat layers which are poorly decomposed. Therefore the use of larger volume samples, such as the 6 × 6 cm rectangle as recommended in the previous section, should improve the quality of the bulk density measurement because they are more representative of the slice, thereby also improving the accuracy of the rate of metal accumulation calculation.

The degree of decomposition of the peat is measured by colorimetry on alkaline peat extracts at 550 nm using a Cary 50 UV-visible spectrophotometer. The powdered peat samples (0.02g) are placed in test tubes and 8 % NaOH soln. (10 ml) is added. The samples are shaken then heated 95 ± 5 °C for 1 hour, then made up to 20 ml with deionised water, shaken and left to stand for 1 hour before being re-shaken and filtered through Whatman no. 1 filter papers. Samples are diluted with an equal quantity of deionised water directly before colorimetric measurement. The percentage of light absorption (% absorbance) in these extracts may be used as a proxy of peat humification.(Caseldine et al. 2000).

## CHEMICAL ANALYSES

The development, evaluation and use of peat cores from ombrotrophic bogs as archives of high-resolution reconstructions of atmospheric deposition of mineral dust and trace elements have led to the development of many analytical procedures which now permit the measurement of a wide range of elements in peat samples.

Prior to any expensive and time consuming chemical procedure and analysis, measurement of major and trace elements in peat samples using the non-destructive and relatively inexpensive X-Ray Fluorescence (XRF) method is performed on all peat samples first. This method provides invaluable geochemical data that helps to document the natural geochemical processes which occur in the peat profiles and their possible effect on the distribution of trace elements. Calcium (Ca) and strontium (Sr), for example, can be used to identify mineral weathering reactions in peat profiles, manganese (Mn) and iron (Fe) redox processes, bromine (Br) and selenium (Se) atmospheric aerosols of marine origin. Titanium (Ti) and zirconium (Zr) are conservative, lithogenic elements whose abundance and distribution reflects the variation in mineral matter concentration in the peat core.(Shotyk et al. 2001) One gram of dried, milled peat may be analysed for these and other major and trace elements simultaneously (Y, K, Rb, Cr, Ni, Cu, Zn, As and Pb) using the EMMA XRF.(Cheburkin and Shotyk 1996; Cheburkin and Shotyk 1999) Titanium (Ti) may be analysed precisely using the new TITAN XRF spectrometer which provides a lower limit of detection for Ti of only 1 $\mu g\ g^{-1}$. Both instruments measure the sample in powder form. Because the method is non-destructive, these same samples can be used again for other measurements (Fig. A1-7). Complete details about the design and construction of this instrument are presented in a separate publication.(Cheburkin and Shotyk)

### Mercury

Solid peat samples can be analysed for Hg using a direct mercury analyser (LECO AMA 254).(Roos-Barraclough et al. 2002) The main advantage of this approach is that no acid digestion of the peat sample is necessary. After air-drying overnight in a Class 100 laminar flow clean air cabinet, three subsamples, previously removed from a pre-selected, fresh portion of each slice, are analysed for total Hg, and the results of the three subsamples are averaged (Fig. A1-7). The detection limit of the instrument is 0.01 ng Hg and the working range is 0.05 to 600 ng Hg, with reproducibility better than 1.5%.

## Acid digestion procedures

Other elements in solid peat samples can be quantified for a wide selection of trace elements using instrumental neutron activation analysis (INAA). As no certified reference material for trace elements in ombrotrophic peat was available until recently, INAA data served as a reasonable benchmark for the development of other analytical procedures requiring dissolution of peat samples. In this context, several digestion procedures for the acid dissolution of peat have been developed and evaluated using open vessel digestion as well as closed vessel digestion procedures on a hot plate or using microwave energy. No matter which digestion approach is considered, it is essential to completely destroy the silicate fraction of peat in order to release the trace elements that are hosted in the silicates. This can be achieved by the addition of HF or $HBF_4$ to the acid mixture, whereas the use of $HBF_4$ provides many advantages in that context and thus is highly recommended (Krachler et al. 2002; Krachler et al. 2002).

## Quantification of trace elements

Trace elements in these digestion solutions have been determined using ICP-MS, ICP-OES, HG-AAS and HG-AFS (Chen et al. 2003; Krachler et al. 1999; Krachler et al. 1999; Krachler et al. 1999; Krachler et al. 2002; Krachler et al. 2001). The large variety of analytical instruments available allowed several inter-method comparisons which greatly benefit the quality of the analytical results (Fig. A1-7). Both ICP-MS and ICP-OES were used to analyse more than 25 elements, whereas work to date with HG-AAS and HG-AFS mainly focused on the determination of low concentrations of arsenic and antimony in peat.(Chen et al. 2003; Shotyk et al. 2004) Using ICP-MS, a powerful multi-element technique with low detection limits, it has been possible to establish complete chronologies of Ag, Tl, Pb, Cd;(Shotyk and Krachler) Mo, U, Th (Krachler and Shotyk), the REE (Krachler et al. 2002) and V, Cr, Ni (Krachler et al. 2003). A method has also been developed to determine major elements in acid digested peat samples using ICP-OES and this has been successfully applied to the determination of Al, Ca, K, Mn, Ti, Fe, Na, Sr, Mg concentrations. Again, measurements of international, certified, standard reference materials yielded results which are in good agreement with the certified values.

## Lead isotope measurements

Lead isotope ratios in peat can largely help to identify the predominant anthropogenic sources of Pb. Lead isotopes measurements can be performed using ICP-MS. We recently developed a method using sector field inductively coupled mass spectrometry (ICP-SF-MS) after acid digestion of peat powders using a high-pressure and high-temperature microwave autoclave.(Krachler et al. ) The accuracy and precision of the ICP-SMS protocol was further evaluated using thermal ionisation mass spectrometry (TIMS) of selected samples and an in-house peat reference material. In general, the Pb isotope ratios determined using ICP-SMS deviated from the TIMS values by less than < 0.1%. Given the throughput of the ICP-SMS compared to the TIMS (which requires chemical separation of Pb), the ICP-SMS approach offers great promise for environmental studies to fingerprint the predominant sources of anthropogenic Pb. In a few cases when improved accuracy and precision are needed, the Pb isotopes ratios in these selected samples may also be measured using thermal ionisation mass spectrometry (TIMS).

### Quality control

Decreasing limits and thresholds require accuracy, comparability and traceability of analytical measurements for the determination of elemental content in peat material. Certified Standard Reference Materials of coals and plants from the National Institute of Science and Technology (USA), the International Atomic Energy Agency (Vienna), South Africa, the European Community, Poland, the Czech Republic, and China are analysed in triplicate as blind standards. However, to guarantee accuracy, quality control, quality assurance or validation of a measurement by means of certified reference material, the assessment of analytical results in certified reference materials must be as accurate as possible and every single step has to be fully evaluated. To date, the lack of a common certified peat reference material has hindered the quality assurance of the generated analytical data from different laboratories in the international community. There are ongoing efforts to fill the lack of a common certified peat reference material for working with peat material by developing a multi-element reference material for low-ash peat to be used by the international community.(Barbante et al. 2000; Yafa et al. 2003)

### Mineralogical analyses

Mineralogical analyses of the inorganic fraction could be of particular importance to identify the origin and type of anthropogenic and natural particles deposited on the surface of the peat bog. However because of the very low inorganic content in ombrotrophic peat, it is very difficult to extract the deposited atmospheric particles. Moreover in the case of a general study also including bulk peat geochemistry, there may be only a small quantity of peat available for mineralogical analyses. Finally the extraction method used is dependent on the type of mineral investigated because the reagents and temperature used could modify the minerals by oxidation (e.g. sulphides) or dehydration (e.g. clays). However, prior to mineralogical analyses, samples should not be milled. Many methods for extracting minerals grains from the bulk peat matrix are available from the literature, some of them designed for the extraction of specific fractions such as tephra glasses(Dugmore et al. 1992; Persson 1971) or recent anthropogenic particles.

One method used in our laboratory and proposed by Steinman and Shotyk (1997) is to ash the peat at 550 °C, remove the carbonates and other inorganic components formed during the ashing process using dilute HCl. These samples are then ready for optical microscopy and could also be analysed after preparation using Scanning Electron Microscope (SEM w/EDAX). Another approach is to digest the peat with 65% $H_2O_2$ in a Teflon beaker on a hot plate. Every ca. three days, the reagents are poured off and a new solution of 65% $H_2O_2$ is added until there is no visible trace of organic matter. However, this procedure is time-consuming and could last more than two weeks. It is possible to use an ultrasonic bath to mechanically extract the minerals before and after each $H_2O_2$ attack. Individual mineral grains which are large enough could be also directly analysed by microscopic techniques such as microbeam XRF (Cheburkin et al. 1997).

**Age dating**

Establishing high quality chronologies is a critical feature of paleoenvironmental studies, especially for the last few hundred years which have witnessed so many changes. A reliable and detailed chronology is essential if peat bogs are to be compared with other high-resolution archives such as polar ice, laminated lake sediments, tree rings, bryophytes, including herbarium specimens. Multiple techniques can be used to develop peat chronologies including analyses of short-lived radioisotopes ($^{210}$Pb, $^{137}$Cs, $^{241}$Am, $^{14}$C bomb pulse), historical pollen, chronostratigraphic markers, tephra layers, and fly-ash particles (Renberg et al. 2001).

**Radiocarbon age dating**

It should be relatively straightforward to establish radiocarbon-based chronologies for most Holocene peats used for paleoenvironmental reconstructions. However, there are a number of problems to be considered in radiocarbon dating peat. In the past, $^{14}$C age dating was typically done using the decay counting method on bulk samples. This method had the disadvantage of wasting a large amount of material, because several grams of dry peat was needed. Moreover, radiocarbon age dating of bulk samples can be problematic as it may lead to $^{14}$C age inversions in cases where older peat layers have been penetrated by younger plant roots.(Weiss et al. 2002) Therefore macrofossils of *Sphagnum* moss, specifically selected and cleaned are ideal for radiocarbon dating as mosses have no root systems and therefore cannot introduce younger carbon to lower layers. Careful sample selection and cleaning (removing roots of other plants), pre-treatment (washed water followed by an acid-base-acid treatment) circumvents other potential problems such as the mobility of carbon in the peat profiles. However some movements of carbon can occur, especially of dissolved organic carbon; the translocation of younger carbon to deeper horizons by vascular plant roots or the possible "reservoir" effect involving translocation of older carbon to contemporary vegetation also are real concerns.

Age dates of plant macrofossils younger than AD 1950 can be obtained using $^{14}$C by directly comparing the absolute concentration of $^{14}$C in the sample to the general-purpose curve derived from annually averaged atmospheric $^{14}CO_2$ values in the northernmost northern hemisphere: post-1950 $^{14}$C concentrations in the atmosphere are elevated compared to natural levels due to atomic weapons testing. This approach which effectively matches the $^{14}$C concentrations (percent modern carbon, or PMC) in successive plant macrofossils to the increase (since AD 1950) and subsequent decrease (since AD 1963) in $^{14}$C concentrations is the so called "bomb pulse curve of $^{14}$C" and has been successfully used to date peat accumulation in Denmark and in southern Greenland. (Goodsite et al. 2002) This comparatively new dating method has been found to provide high-resolution age dates which are accurate to ± 2 years.

## Radiometric age dating

$^{210}$Pb is widely used for dating environmental records in natural archives such as lake sediments, peat bogs and marine sediments spanning the last 130 years or so.(Appleby et al. 1988) Assessing $^{210}$Pb dates in conjunction with dates from longer time-scale dating methods such as $^{14}$C can be beneficial in a number of respects. Age dating peat profiles by combining independent dating methods helps to provide a reliable long time-scale chronology. The main advantage of $^{210}$Pb age dating is that it can be done in-house using low background gamma spectrometry and therefore eventually reduces the cost of age dating. In contrast, $^{14}$C age dating of plant macrofossils can be done only at those labs with Acceleration Mass Spectrometry (AMS) facilities.

When building up an age dating strategy, an important question is what are we trying to date? The age dating strategy will be different if we try to provide dates for a few events such as the concentration peaks in a record or if we establish a chronology for an entire record. In the case of dating specific events, the optimum strategy would be to direct all the effort at these particular periods.(Mauquoy et al. 2002) Therefore great attention is required in selecting material sent to the laboratory, to be sure that the most important events are dated. To establish a precise chronology for the entire peat profile, a regular interval of sample selection will guarantee the generation of an accurate age-depth model and therefore of a reliable peat chronology.

### Modelling the age-depth relationship

Chronology reconstruction is based on a series of radiometric dates, sometimes supplemented by other markers (e.g. tephra layers…). As independent check, various models can be applied, all of which have underlying assumptions, even if they are not explicitly stated. The choice of model varies but is most often subjective, favouring linear model based on $R^2$ values, using central calibrated dates, and assuming continuous peat accumulation often without evaluating this assumption.

Without a large number of dates there is no convincing reason for preferring one regression to another or for using the same regression for all profiles.(Telford et al. ) We are forced to return to a subjective evaluation of curve fitting as well as our knowledge of peatland system. If we want to estimate maximum possible error then we should perhaps evaluate the age-depth function obtained from a range of models which would give us an error range. Of course, this still excludes the error ranges on the calibrated ages used to generate the age-depth relationship. As far we are aware, there is no available method to deal with these errors, because the probability distribution of calibrated ages is non-normal.(Bennet 1994)

## Conclusion

The protocol described here is time consuming and expensive. There is no need to apply it to poor quality cores. We recommend that for the study of the uppermost layers a peat bog, three Wardenaar cores should to be collected. The first one could be used to investigate the quality and the suitability of the peat deposit for paleoenvironmental purposes. This core could be visually inspected, described, and cut by hand in the field. Measurement of the pH and the calcium concentration in the porewater can be used to determine the trophic status of the peat profile, and the chlorine concentration to reveal the influence of marine aerosols. As first approximation of the chronology, Pb could be measured using XRF which would clearly indicate the beginning of industrialisation. In Europe, this approach would also identify the Roman period, if this is present in the peat core. If the core is in good agreement with the selection criteria define during the first step of the study (ombrotrophic peat deposit, time period of interest), then the second core should be cut into 1 cm slices and the protocol proposed in this paper could be followed. The third core should be storage intact at -18 °C as an "archive" which could be used in future studies.

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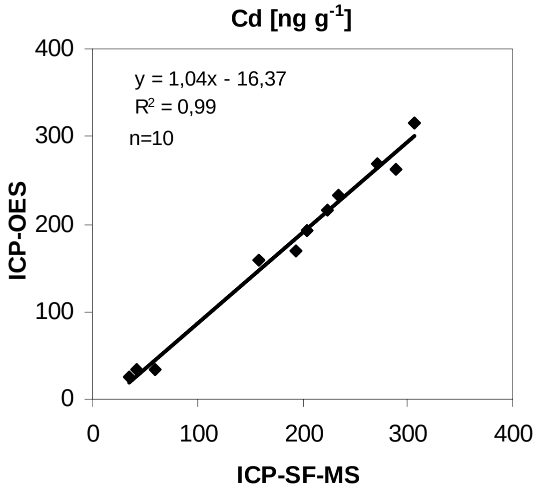
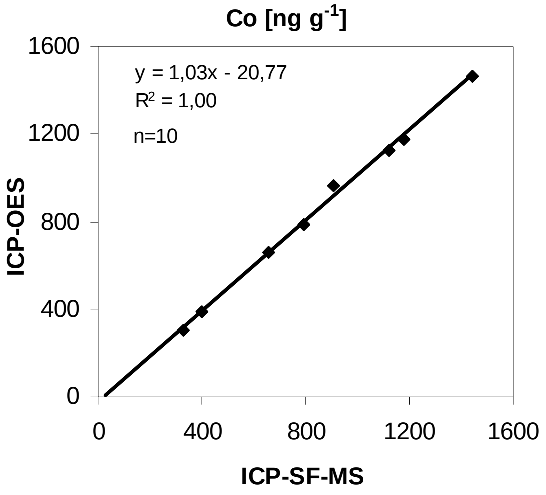
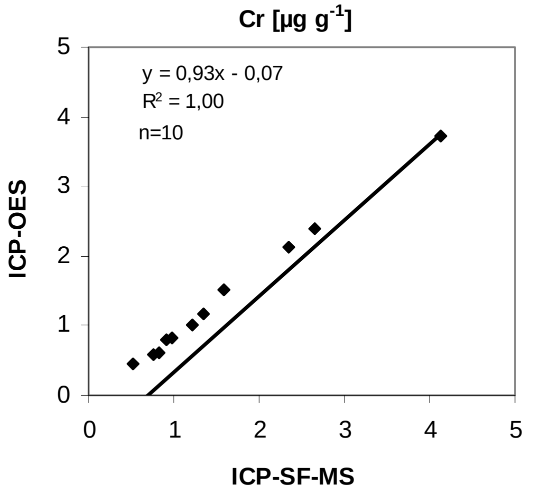
# 7-2 Appendix 2

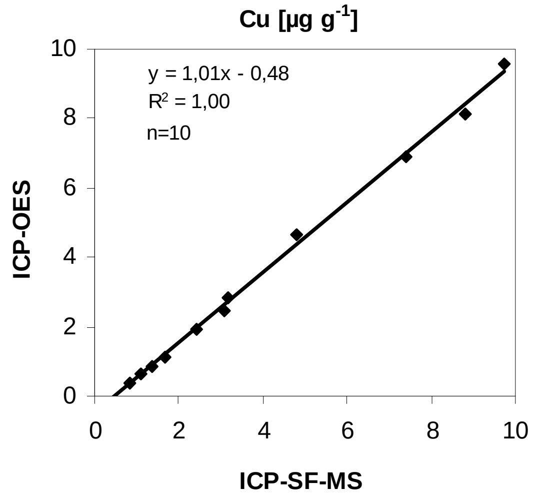
## Inter-method comparison of trace metal determinations

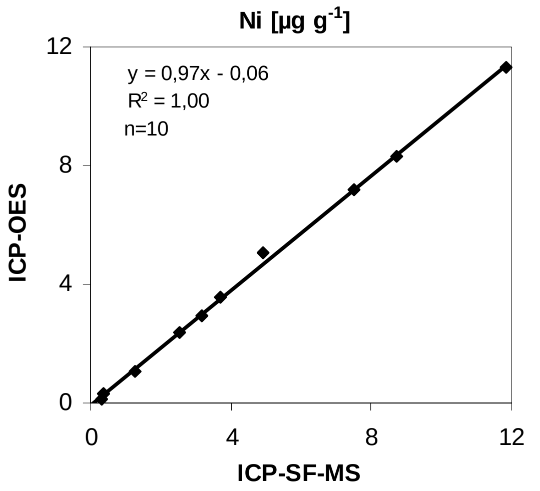
Cd-Co-Cr-Cu-Ni-V: ICP-SF-MS *vs.* ICP-OES analysis

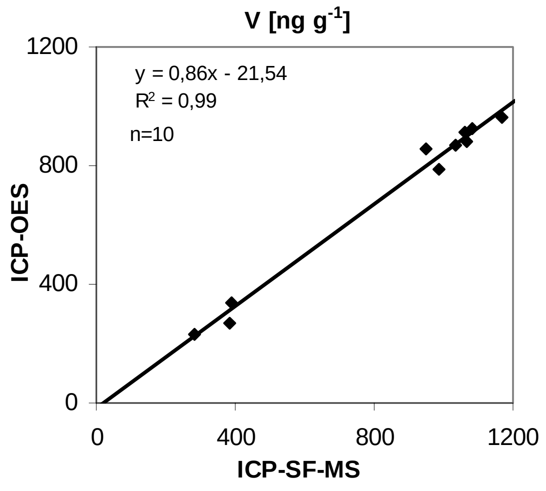




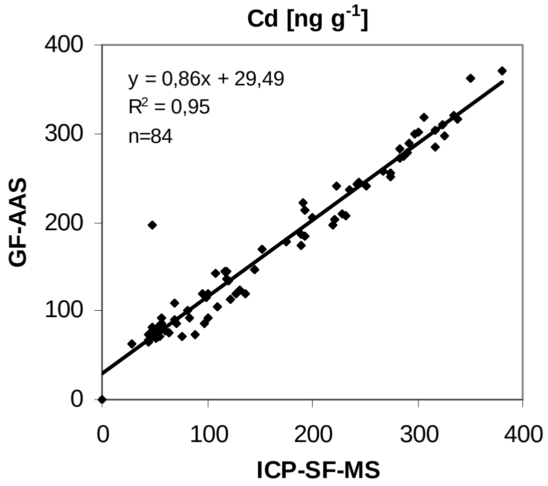


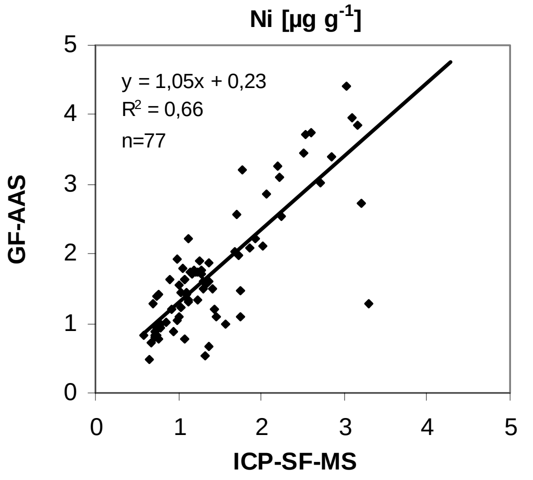




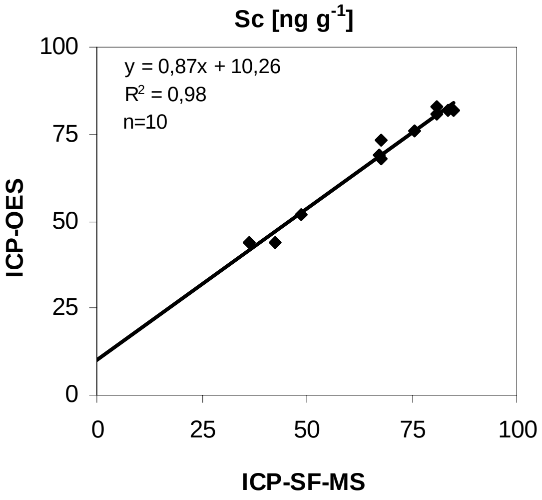


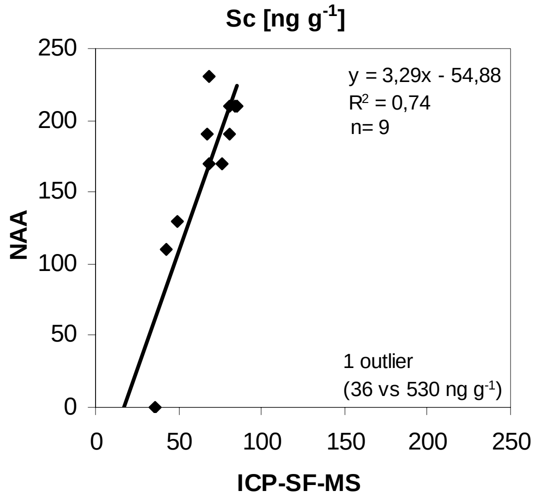
## Cd-Ni: ICP-SF-MS *vs.* GF-AAS

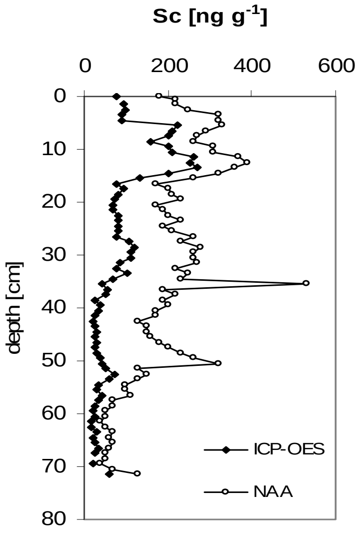




## Sc: ICP-SF-MS *vs.* ICP-OES / NAA







Sc concentrations in the HAR peat profile using ICP-OES and NAA, respectively

## 7-3 Appendix 3

# Recent organic matter accumulation in relation to some climatic factors in ombrotrophic peat bogs near heavy metal emission sources in Finland

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*Global and Planetary Changes* in review (2005)

**Abstract.** Accumulation of organic matter (OM) was studied in four ombrotrophic peat bogs in Finland: Harjavalta (vicinity of a Cu-Ni smelter), Outokumpu (near a closed Cu-Ni mine), Alkkia (Ni treated site) and Hietajärvi (a background). At each sampling site two peat cores (15x15x100cm) were taken. Age-dating of peat was determined using $^{210}$Pb method (CRS model). The local annual temperature sum and precipitation for the past 125 years were modeled. The objective was to compare recent net accumulation rates of heavy metal polluted ombrotrophic peat bogs with those of a pristine bog, and to study the relationship between weather and net accumulation rates. Based on $^{210}$Pb age-dating, the upper 16cm peat layer at Harjavalta, 35cm at Outokumpu and 25cm at Hietajärvi represents 125 years of peat formation, yielding the following average peat accumulation rates: Harjavalta 1.3 mm $a^{-1}$, Outokumpu 2.8 mm $a^{-1}$ and Hietajärvi 2.0 mm $a^{-1}$. At the Alkkia site, the Ni treatment in 1962 had completely stopped the peat accumulation. Net accumulation rates were related to precipitation at Outokumpu, Harjavalta and Hietajärvi sites. In addition emissions released from the nearby located Cu-Ni smelter could have affected negatively OM accumulation at Harjavalta site.

*Keywords*: carbon accumulation, emissions, evaporation index, $^{210}$Pb age-dating, peat accumulation

## Introduction

Current concern about greenhouse gases and the global carbon (C) balance has raised great interest about the role of peatlands. Due to their massive accumulation of organic matter, peatlands form an enormous reservoir of terrestrial carbon by removing carbon dioxide ($CO_2$) from the atmosphere (Bellisario et al. 1998). In Finland, the total carbon storage in peatlands is estimated to be 5000 Tg (Tg $=10^{12}$ g) (Laine and Minkkinen 1996). However, we still have a quite limited understanding about the impacts of many environmental factors on the peat formation.

The accumulating of organic matter is determined by the balance between net primary production (NPP) and decomposition rate, which are controlled by climate, the type of vegetation, water table level and soil nutrient status and acidity (Clymo 1984; Trettin et al.1995; Davidson et al. 2000). Cool temperatures and poor aeration retard decomposition, and consequently, soil carbon stocks are highest in cool and moist biomes and lowest in hot and dry biomes. In peatlands the reason for constant organic matter accumulation is merely the slow rate of decomposition and not the rate of net primary production (Clymo 1965; Thormann et al. 2002). However decomposition in the aerobic acrotelm results in significant losses of carbon. According to Francez and Vasander (1975) 90-97 % of the carbon fixed by living plants is typically lost by decomposition before the remaining proportion is transferred to long-term storage in the catotelm. Below the first few centimeters of peatland surface, decomposition is mainly hindered by a lack of oxygen. The highest long-term rates of peat accumulation are associated with raised ombrotrophic bogs in which *Sphagnum* species are dominant (Tolonen and Vasander 1992; Laine and Vasander 1996). However, even in ombrotrophic bogs great temporal variation in carbon accumulation have been observed. In some years, even net carbon losses can occur, which are considered to be related to fluctuations of the water table (Alm et al. 1999). According to number of studies (Shurpali et al. 1995; Waddington and Roulet 1996; Alm et al. 1999) peatlands can change from carbon sinks to carbon sources in years when the summertime watertable is below the long-term average level.

Besides to the climatic factors both the net primary production and the decomposition processes can be affected by various other causes. It has been indicated that plant tissues with higher initial concentrations of nitrogen and phosphorus decompose faster than those with lower tissue nutrient concentrations (Bartsch and Moore 1985; Szumigalski and Bayley 1996; Thormann et al. 2002). Many heavy metals are known to be highly toxic to organic matter decomposing soil microbiota (Adriano 2001; Kabata-Pendias 2001), and a severely retarded decomposition of organic matter is a widely reported phenomenon in heavy metal impacted environments (Tyler 1975; Strojan 1978; Freedman and Hutchinson 1980; Berg et al. 1991). This interference in the decomposition processes enhances organic matter accumulation. On the other hand, mosses are known to be sensitive to high metal deposition loads (Brown and Wells 1990; Tyler 1990; Guschina and Hardwood 2002). Since the *Sphagnum*–mosses are the most important net primary producers of ombrotrophic bogs, toxic amounts of metal deposition could have a mitigating effect on organic matter accumulation. It is therefore difficult to predict the effects of heavy metal pollution on the accumulation of organic matter in peatlands.

Although metal contents of age-dated peat cores from ombrotrophic peat bogs, which get water inputs solely through precipitation, have successfully been used to establish records of atmospheric heavy metal pollution in the past (Shotyk 1996; Shotyk et al. 1997; 1998;

Martinez-Cortizas et al. 1997), the impact of metal pollution itself on the net organic matter accumulation in peatlands has not earlier been subject to study. Our objective was to compare recent (last 125 years) net organic matter accumulation rates of heavy metal polluted ombrotrophic peat bogs with those of a pristine bog and to study the relationship between net organic matter accumulations rate and climate related factors.

## Material and methods

### SITE DESCRIPTION

The study relates to four *Sphagnum* dominated ombrotrophic peat bogs in Finland (Table A3-1). The Harjavalta site is located 6 km northeast of a large copper-nickel smelter. The Outokumpu site is located 8 km southeast from a copper-nickel mine, which operated until the end of the 1980s. The Alkkia site is located in southwest Finland, where an ore-prospecting simulation experiment was carried out in 1962 by applying nickel (Ni), copper (Cu) and zinc (Zn) sulphate to 20 x 20 m test areas (Veijalainen, 1998). The plot treated with 200 kg Ni ha$^{-1}$ was used in this study. The fourth site, Hietajärvi, is located in the Patvinsuo National Park, Eastern Finland. It is a background site with no significant point sources of air pollution nearby, which has therefore had a minimal human interference (Tuominen and Mäkelä, 1995).

**Table A3-1.** Characteristics of the study sites (BP= before present).

| Site | Annual temperature sum, °C[a] | Annual precipitation sum, mm[a] | Humification[b] | Thickness of peat, m | Age of peat, years[d] |
|---|---|---|---|---|---|
| Harjavalta<br>(61°21’N,22°11’E) | 1264 | 567 | H1 to H8 | > 2 | 350 BP<br>(depth of 195-200 cm) |
| Outokumpu<br>(62°40’N,28°51’E) | 1196 | 603 | H1 to H5 | 6[c] | 1500 BP<br>(depth of 240-245 cm) |
| Hietajärvi<br>(63°09’N,30°40’E) | 1079 | 616 | H3 to H8 | > 2 | 2600 BP<br>(depth of 195-200cm) |
| Alkkia_Ni<br>(62°11’N,22°48’E) | 1110 | 612 | H1 to H9 | 1.6 | 4250 BP<br>(depth of 175-180cm) |

[a] For period 1880-1999 estimated using the method described in Ojansuu and Henttonen (1983)
[b] After von Post (1922)
[c] Leino and Saarelainen (1990)
[d] Conventional $^{14}$C age dating, determined at the University of Heidelberg

Study sites were located at pristine ombrotrophic bogs (cotton grass pine bog) with a sparse tree (*Pinus sylvestris*) cover. Most of the ground layer at Harjavalta, Outokumpu and Hietajärvi sites consisted of *Sphagnum* species, including *S. fuscum*, *S. balticum*, *S. angustifolium* and *S. magellanicum*, all of which more or less indicate ombrotrophy. In addition, some dwarf shrubs (e.g. *Andromeda polifolia, Empetrum nigrum, Ledum palustre* and *Vaccinium* species), herbs such as *Rubus chamaemorus* and sedges such as *Eriophorum vaginatum* were found in varying amounts at each site. The vegetation at the Alkkia site was severely damaged; with only some liverworts and few patches of S*phagnum fuscum* moss in the hollows and mainly *Eriophorum vaginatum* on the hummocks exist.

Average arsenic (As), Cu, lead (Pb), Ni and Zn emissions during 1990's in Finland were As 14.5 t $a^{-1}$, Cu 59.4 t $a^{-1}$, Ni 35.1 t $a^{-1}$, for Pb 115.4 t $a^{-1}$ and Zn 274 t $a^{-1}$ (Finnish Environment 2004). Bulk deposition in background areas in Finland ranged from 0.05-0.09 mg $m^{-2}$ for As, 0.30-0.38 mg $m^{-2}$ for Cu, 0.08-0.14 mg $m^{-2}$ for Ni, 0.22-0.69 mg $m^{-2}$ for Pb and 0.58-3.23 mg $m^{-2}$ for Zn in 1999 (Leinonen 2000). In contrast the site located next to the Harjavalta Cu-Ni smelter, the mean annual (1993-1998) deposition of Cu was 149 mg $m^{-2}$, Ni 64 mg $m^{-2}$ and Zn 17 mg $m^{-2}$ (Derome 2000).

## METHODS AND ANALYSIS

At each sampling site two peat cores ($15x15x100cm^3$) were taken from lawn near the central part of each bog using a titanium Wardenaar corer in September 2001. From the first core the degree of humification was determined in the field (for 1 m) after von Post (1922) (Table A3-1). The second core was wrapped in a plastic foil and transported to the laboratory where it was frozen and later cut into 1 cm slices with stainless steel band saw. Samples were dried at 105 ºC in acid-washed Teflon bowls and macerated in a centrifugal mill fitted with a Ti rotor and 0.25 mm sieve. Concentrations of As, Cu, Ni, Pb and Zn were measured by X-ray fluorescence (XRF). Carbon concentration of each slice was determined with a LECO-CS analyser (not for Alkkia). Accuracy was evaluated by analysis of international reference materials. All results are expressed on an oven-dry (105 °C) weight basis. The bulk density (g $cm^{-3}$) was determined by weighing a smaller volumetric sub-sample of each slice after drying.

The mean annual net organic matter (OM) accumulation was calculated by dividing the product of the slice volume and bulk density by the number of the years corresponding to each slices. The net carbon accumulation was derived multiplying net OM accumulation (g $m^{-2}$ $yr^{-1}$) by carbon concentration. Age dating of peat slices was done using $^{210}Pb$ dating constant rate of supply (CRS) model (Appleby and Oldfield, 1978). The activities of $^{210}Pb$ were determined on bulk samples of peat powder using low background gamma spectroscopy (GWC 4028, HPGE, Canberra). Estimated errors in $^{210}Pb$ age dates are based on error propagation of $^{210}Pb$ counting errors and density variability (Rausch et al. 2005). 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 AD 1950 selected from each peat core, except at Alkkia. In addition, a Russian corer was used to obtain a half-cylinder 50 cm long, 12 cm wide sample from the borehole left by the Wardenaar corer, starting at least 50 cm below the bottom of the hole. Ages of older peat samples were obtained using conventional $^{14}$C age dating (Table A3-1).

Because weather observations close to the study sites were not available, we decided to use as an alternative 'surface fitting weather model' developed by Ojansuu and Henttonen (1983). Model is based on measurements of monthly mean temperature and precipitation made at Finnish Meteorological Institute weather stations. Used parameters were longitude, latitude and elevation (m a.s.l.). With this model local annual temperature and precipitation sum were estimated to each site back to the year 1880. Average of temperature and precipitation sum was calculated for the years corresponding to each slice. Evapotranspiration index was calculated as ratio between precipitation and temperature sum.

In addition macrofossiles were identified from each slices to approximately depth of 30 cm depending on site (exluding Alkkia). Identifying was performed from thawed sub-sample using optical microscopy.

Pearson product-moment correlations and the paired t-test with a probability of Bonferroni's inequality were used to examine relationship between precipitation, temperature sums and evapotranspiration index and organic matter accumulation. GraphPad Prism (4.0) was used for performing all the statistical analyses. From Hietajärvi site the highest value (net OM accumulation rate 501.5 g m$^{-2}$ yr$^{-1}$) was omitted from correlation analyses.

## Results and discussion

### PEAT ACCUMULATION

The results presented in this paper concern peat accumulation during the last 125 years (i.e dating starts approximately from 1880), if not otherwise stated. The peat was $^{210}$Pb age-dated at 1 cm intervals to the depth in which the age of 125 years was obtained. The upper 16 cm of peat at Harjavalta, 35 cm at Outokumpu and 25 cm at Hietajärvi and less than 1 cm at Alkkia represents the remains of 125 years peat formation (Table A3-2). The core consists of ombrotrophic *Sphagnum* peat in all sites. At Harjavalta mostly *Sphagnum balticum* and *S. sectio cuspidata* mosses were found between bands of *Eriophorum vaginatum* down to the depth of 17 cm, degree of humification increased downwards from $H_1$-$H_3$. At Outokumpu *S. fuscum* was prevailing species in whole age-dated core, the degree of humification increased downwards from $H_1$-$H_3$. At Hietajärvi *S. angustifolim* and *S. fuscum* dominated the core down to the depth of 23 cm. Peat was more humificated at Hietajärvi than other sites, being in surface layer $H_3$ and deeper $H_4$. At Alkkia species from the peat core were not identified. Mathematical error in the $^{210}$Pb ages was higher for the Harjavalta samples (6 to 75 years for the last century) than for the Outokumpu (± 3 to 30 years) and Hietajärvi (± 1 to 8 years). Greater error in Harjavalta was due to greater variations in density (see below) and lower activities of unsupported $^{210}$Pb. Evaluation of $^{210}$Pb age dating is expanded upon Rausch et al. 2005. At Alkkia $^{210}$Pb age dating results could not be interpreted due to Ni treatment.

**Table A3-2.** OM accumulation, peat increment, carbon accumulation, annual temperature and precipitation sum at Harjavalta during past 125 years.

| Period | cm from surface | OM g $m^{-2}$ $a^{-1}$ | Peat increment mm $a^{-1}$ | Carbon g $m^{-2}$ $a^{-1}$ | Annual Temperature sum, ºC | Annual Precipitation sum, mm |
|---|---|---|---|---|---|---|
| 1994-1999 | 0.5 | 72.2 | 1.4 | 35.0 | 1321 | 636 |
| 1992-1993 | 1.5 | 217.2 | 5.0 | 105.0 | *1221* | 615 |
| 1989-1991 | 2.5 | 183.6 | 3.3 | 89.1 | 1295 | 605 |
| 1985-1988 | 3.5 | 142.1 | 2.5 | 69.5 | *1238* | 640 |
| 1982-1984 | 4.5 | 204.3 | 3.3 | 100.6 | 1307 | 624 |
| 1978-1981 | 5.5 | 147.5 | 2.5 | 74.2 | *1253* | 617 |
| 1973-1977 | 6.5 | 178.8 | 2.0 | 88.8 | *1231* | *560* |
| 1967-1972 | 7.5 | 109.1 | 1.7 | 54.7 | 1310 | *504* |
| 1961-1966 | 8.5 | 99.9 | 1.7 | 50.7 | 1264 | *526* |
| 1954-1960 | 9.5 | 100.6 | 1.4 | 50.9 | *1244* | *525* |
| 1943-1953 | 10.5 | 58.0 | 0.9 | 30.0 | 1276 | *558* |
| 1931-1942 | 11.5 | 59.5 | 0.8 | 30.6 | 1278 | *525* |
| 1921-1930 | 12.5 | 68.9 | 1.0 | 35.9 | *1216* | 572 |
| 1911-1920 | 13.5 | 110.0 | 1.0 | 58.4 | *1249* | *542* |
| 1899-1910 | 14.5 | 103.9 | 0.8 | 55.2 | *1196* | *520* |
| 1877-1898 | 15.5 | 61.3 | 0.5 | 32.7 | 1323 | *507* |

Over the age-dated period peat average annual increment was 1.3 mm $yr^{-1}$ at Harjavalta, 2.8 mm $yr^{-1}$ at Outokumpu and 2.0 mm $yr^{-1}$ at Hietajärvi (Table A3-2,3,4). Peat increment in these bogs is well in line with long-term accumulation rates of peat in Finland, which have been calculated to vary from 0.2 to 4.0 mm $yr^{-1}$, with an average value of 0.5 mm (Korhola and Tolonen 1996). At Alkkia, it was impossible to estimate the corresponding average annual accumulation rate because peat accumulation ceased in 1962 due to the Ni treatment. At the other sites the mean annual increment in the upper layers was greater than in the lower layers, and conversely the bulk density was lower in upper layers and the highest in lower

**Table A3-3.** OM accumulation, peat increment, carbon accumulation, annual temperature and precipitation sum at Outokumpu during past 125 years.

| Period | cm from surface | OM g $m^{-2}$ $a^{-1}$ | Peat increment mm $a^{-1}$ | Carbon g $m^{-2}$ $a^{-1}$ | Annual Temperature sum, ºC | Annual Precipitation sum, mm |
|---|---|---|---|---|---|---|
| 1997-1999 | 0.5 | 137.7 | 3.3 | 68,1 | 1300 | 615 |
| 1996 | 1.5 | 435.6 | 10.0 | 217,4 | *1147* | 651 |
| 1994-1995 | 2.5 | 221.5 | 5.0 | 110,5 | 1238 | 681 |
| 1993 | 3.5 | 415.6 | 10.0 | 203,8 | *1002* | *598* |
| 1991-1992 | 4.5 | 198.0 | 5.0 | 97,6 | 1201 | 721 |
| 1989-1990 | 5.5 | 221.2 | 5.0 | 108,5 | 1228 | 606 |
| 1988 | 6.5 | 443.0 | 10.0 | 215,5 | 1384 | 738 |
| 1986-1987 | 7.5 | 261.8 | 5.0 | 131,1 | *1084* | 689 |
| 1984-1985 | 8.5 | 250.9 | 5.0 | 123,4 | 1222 | 661 |
| 1981-1983 | 9.5 | 170.3 | 3.3 | 84,6 | *1181* | 712 |
| 1978-1980 | 10.5 | 165.8 | 3.3 | 82,6 | *1176* | *555* |
| 1975-1977 | 11.5 | 148.1 | 3.3 | 72,6 | *1089* | *553* |
| 1972-1974 | 12.5 | 165.9 | 3.3 | 82,1 | 1281 | 672 |
| 1969-1971 | 13.5 | 203.1 | 3.3 | 101,6 | *1149* | *553* |
| 1966-1968 | 14.5 | 156.8 | 3.3 | 76,8 | *1183* | 660 |
| 1962-1965 | 15.5 | 130.8 | 2.5 | 64,6 | *1141* | *568* |
| 1958-1961 | 16.5 | 152.6 | 2.5 | 77,7 | 1231 | *537* |
| 1955-1957 | 17.5 | 167.4 | 3.3 | 83,5 | *1139* | *583* |
| 1953-1954 | 18.5 | 216.0 | 5.0 | n.d | 1263 | 647 |
| 1951-1952 | 19.5 | 250.3 | 5.0 | 124,5 | *1109* | *557* |
| 1949-1950 | 20.5 | 226.0 | 5.0 | 112,8 | *1189* | *569* |
| 1946-1948 | 21.5 | 155.2 | 3.3 | 76,8 | 1288 | *535* |
| 1942-1945 | 22.5 | 134.0 | 2.5 | 67,7 | *1180* | 641 |
| 1938-1941 | 23.5 | 122.2 | 2.5 | 61,3 | 1260 | *492* |
| 1935-1937 | 24.5 | 158.5 | 3.3 | 79,7 | 1329 | 649 |
| 1931-1934 | 25.5 | 145.6 | 2.5 | 72,8 | 1229 | *587* |
| 1927-1930 | 26.5 | 141.4 | 2.5 | 70,6 | *1120* | 648 |
| 1921-1926 | 27.5 | 92.1 | 1.7 | 44,9 | *1191* | 655 |
| 1916-1920 | 28.5 | 111.5 | 2.0 | 54,6 | 1274 | 600 |
| 1914-1915 | 29.5 | 241.1 | 5.0 | 117,8 | *1173* | *465* |
| 1909-1913 | 30.5 | 112.8 | 2.0 | 56,4 | 1218 | *563* |
| 1902-1908 | 31.5 | 84.4 | 1.4 | 43,0 | *1113* | *544* |
| 1895-1901 | 32.5 | 74.8 | 1.4 | 36,7 | 1271 | *590* |
| 1886-1894 | 33.5 | 64.1 | 1.1 | 32,2 | *1141* | *542* |
| 1881-1885 | 34.5 | 103.3 | 2.0 | 50,5 | *1138* | *466* |

n.d = no data, *italics < average*

**Table A3-4.** OM accumulation, peat increment, carbon accumulation, annual temperature and precipitation sum at Hietajärvi during past 125 years.

| Period | cm from surface | OM g $m^{-2}$ $a^{-1}$ | Peat increment mm $a^{-1}$ | Carbon g $m^{-2}$ $a^{-1}$ | Annual Temperature sum, ºC | Annual Precipitation sum, mm |
|---|---|---|---|---|---|---|
| 1998-2000 | 0.5 | 175.7 | 3.3 | 82.8 | 1131 | 672 |
| 1997 | 1.5 | 531.5 | 10.0 | 250.2 | 1168 | *589* |
| 1994-1996 | 2.5 | 195.5 | 3.3 | 93.9 | *1053* | 677 |
| 1992-1993 | 3.5 | 274.9 | 5.0 | 128.8 | *987* | 678 |
| 1990-1991 | 4.5 | 339.0 | 5.0 | 162.7 | *982* | 652 |
| 1988-1989 | 5.5 | 290.9 | 5.0 | 139.4 | 1245 | 698 |
| 1985-1987 | 6.5 | 198.1 | 3.3 | 94.1 | *990* | 674 |
| 1982-1984 | 7.5 | 224.1 | 3.3 | 106.0 | 1084 | 673 |
| 1979-1981 | 8.5 | 196.6 | 3.3 | 93.9 | 1096 | 650 |
| 1975-1978 | 9.5 | 138.5 | 2.5 | 64.3 | *973* | *551* |
| 1972-1974 | 10.5 | 138.4 | 2.5 | 64.9 | 1191 | 646 |
| 1968-1971 | 11.5 | 130.5 | 2.5 | 61.6 | *1028* | *571* |
| 1964-1967 | 12.5 | 140.4 | 2.5 | 68.1 | *1061* | *581* |
| 1959-1963 | 13.5 | 133.6 | 2.0 | 65.8 | 1118 | *576* |
| 1953-1958 | 14.5 | 115.8 | 1.7 | 56.4 | *1056* | *577* |
| 1948-1952 | 15.5 | 129.5 | 2.0 | 65.5 | *1006* | *589* |
| 1943-1947 | 16.5 | 121.9 | 2.0 | 57.0 | 1113 | 633 |
| 1937-1942 | 17.5 | 88.7 | 1.7 | 41.4 | 1151 | *560* |
| 1930-1936 | 18.5 | 74.0 | 1.4 | 33.6 | *1074* | 637 |
| 1922-1929 | 19.5 | 66.1 | 1.3 | 31.4 | *1045* | 687 |
| 1913-1921 | 20.5 | 70.6 | 1.3 | 33.8 | 1195 | *569* |
| 1904-1912 | 21.5 | 60.3 | 1.1 | 28.2 | *1025* | *557* |
| 1894-1903 | 22.5 | 57.2 | 1.0 | 27.2 | 1103 | *577* |
| 1879-1893 | 23.5 | 39.5 | 0.7 | 19.1 | *1032* | *505* |

layers excluding Alkkia (Fig. A3-1), where the lack of new peat formation after Ni-treatment has lead to a compaction of the uppermost peat layers. The bulk density is expected to generally increase with depth because of the greater pressure and compaction at depth and also because of increasing decomposition rate of peat.

The net OM accumulation rate as an annual average over the 125 years period was 96 g $m^{-2}$ $yr^{-1}$ at Harjavalta, 140 g $m^{-2}$ $a^{-1}$ at Outokumpu and 115 g $m^{-2}$ $a^{-1}$ at Hietajärvi (Table A3-2,3,4). Pakarinen et al. (1983) reported OM accumulation rates of 202 to 309 g $m^{-2}$ $yr^{-1}$ in the surface layer (top 10 cm) of the peat at five ombrotrophic peat bogs in Finland. However those results were only from aerobic layer (acrotelm) of the peat, our peat profiles contain in addition of aerobic layer also part of anaerobic peat layer (catotelm). Alm et al. (1992)

reported peat accumulation rates ranging from 39.8 to 80.7 g C $m^2$ $yr^{-1}$ during the last 212-147 years at different peatland site types in a mire complex in central Finland, which was quite comparable to the recent carbon accumulation rates of our study (Table A3-2,3,4). The net carbon accumulation rate of the Harjavalta peat samples varied from 30.0 to 105.0 g $m^2$ $yr^{-1}$, those of Outokumpu from 32.2 to 215.5 and those of Hietajärvi from 19.1-250.2.

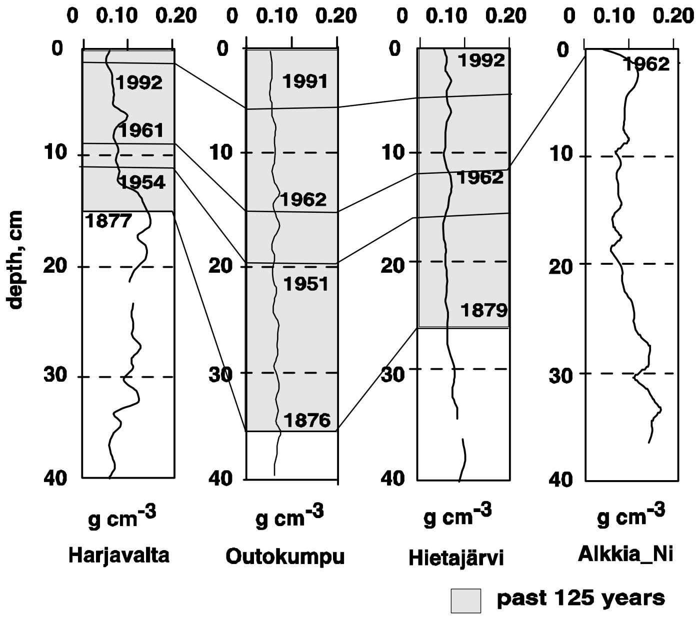

**Fig. A3-1.** Bulk density of peat from surface layer to the depth of 40 cm at Harjavalta, Outokumpu, Hietajärvi and Alkkia sites. Connecting line between cores indicates peat of same age.

### PEAT ACCUMULATION RATE VS. PRECIPITATION AND TEMPERATURE SUM

Estimated annual temperature and precipitation sum had no correlation with each other. At Harjavalta annual temperature sum ranged between 1196-1323 ºC (Table A3-2,3,4), at Outokumpu 1002-1384 ºC and at Hietajärvi 973-1245 ºC. Temperature was the lowest at Hietajärvi, which was expected due to the most eastern and northern location. No increasing or decreasing trend was observed in temperature at any of the sites. Estimated precipitation sum ranged at Harjavalta between 504-640 mm, at Outokumpu 465-738 mm and at Hietajärvi 505-698 mm. Precipitation showed slightly increasing trend at all sites.

Results from correlation analyses (Table A3-5) indicated that the net OM accumulation rate correlated positively with the annual precipitation at all sites, while there was no correlation between the net OM accumulation rate and the annual temperature sum. Instead evapotranspiration index and net OM accumulation rate had significant positive relationship. The Alkkia site was excluded from these calculations because of the cessation of the peat growth.

**Table A3-5.** Pearson correlation coefficient and p values ($p < 0.05$) between net OM accumulation rate in each site and temperature and precipitation sum and evapotranspiration index. (n=17-35).

| | Temperature sum | | Precipitation sum | | Evapotranspiration index | |
|---|---|---|---|---|---|---|
| | r | p | r | p | r | p |
| Harjavalta, *net OM accumulation* | -0.111 | ns | 0.605 | * | 0.612 | * |
| Outokumpu, *net OM accumulation* | -0.082 | ns | 0.367 | * | 0.414 | * |
| Hietajärvi, *net OM accumulation* | -0.083 | ns | 0.656 | * | 0.627 | ** |

ns= not significant

Precipitation was positively correlated with net OM accumulation at the Outokumpu, Hietajärvi and Harjavalta sites (Table A3-5). We tested also so-called 'lag-effect' (one period lag in precipitation sum vs. net OM accumulation), correlation was significant in all sites. Because both precipitation sum and net OM accumulation had increasing trend toward present, the correlation was expected and cannot be directly interpreted as a causal relationship between these two factors. However a positive correlation between net OM accumulation rate and precipitation may also reflect the relationship between high water table levels and anaerobic conditions that reduce peat decomposition. In fact, during the last 20 years period the estimated precipitation sum exceeded the average precipitation sum at all sites, which would suggest that water table has been higher than normally and would explain the relatively high net OM accumulation rate.

As expected, we got result that there was no significant correlation between net OM accumulation rate and temperature sum (Table A3-5). However there was observed a slight negative trend between temperature sum and net OM accumulation rate at all sites inferring that at cold temperature peat accumulation is greater than in warm temperature. Such a relationship was expected because the cool conditions retard decomposition process and hence promote peat accumulation, whereas in warmer conditions decomposition is faster and peat accumulation rates lower (Davidson et al. 2000). Interestingly, Thorman (2002) has reported somewhat controversial results about mass loss of *Sphagnum* and *Carex* peat in different temperatures in laboratory conditions. He noticed that mass losses of *Sphagnum* peat by fungi and bacteria alone or together was greater at 14 ºC than at 20 ºC. In contrast *Carex* peat lost more mass in 20 ºC. This could indicate that nutrient-rich plants have higher temperature optimal for decomposition rates. Our peat consist mostly of *Sphagnum* species.

Evapotranspiration index, which combines effect of precipitation and temperature, correlated significantly with net OM accumulation rate at all sites (Table A3-5). According to Richard (2002) climate has overall controlling mechanism in net OM accumulation rate. Summer temperatures may account for latitudinal changes, but it is probably water balance that is the key factor. It is also important to keep in mind that climatic factors can affect the continuous decomposition of the entire peat profile. However the climatic influence is strongest in the peat layers near the surface. They are the first to intercept precipitation, and also the most susceptible to evaporative losses.

Although the observed correlations are not very strong, they suggest that warmer and wetter climate as predicted for the northern boreal regions in the future, peatlands may have a greater rate of organic matter turnover in the top layers (Räisänen 1997; Wieder 2002).

### PEAT ACCUMULATION RATE VS. HEAVY METALS

The average total concentrations of As, Cu, Ni, Pb and Zn in the peat cores are shown in Table A3-6. There are large differences between sites, especially in the case of Cu and Ni. The Cu concentrations were the highest at Harjavalta, maximum concentrations being as high as 1268 µg $g^{-1}$, which is far in excess of the averaged measured concentrations of surface peat in a background site in southern Finland (4.1-7.1 µg $g^{-1}$, Starr and Ukonmaanaho 2001); correspondingly Jensen (1997) reported Cu concentrations changing from 0.1 to 18.7 µg $g^{-1}$ in the uppermost 35-cm-layers of six ombrotrophic mires located far from distinct local sources in Sweden and Norway. The emissions from the Cu-Ni smelter at Harjavalta have clearly had an effect on deposition in the surrounding peat bogs, as has already been reported in previous studies (Nieminen et al. 2002, Ukonmaanaho et al. 2004). The Cu concentration of the other sites was less than 3% of those at the Harjavalta site. The most dramatic effect on net OM accumulation rate was caused by the Ni treatment at Alkkia. The nearly complete absence of vegetation and the consequent lack of any NPP, had lead to a complete cessation in net OM accumulation.

As already noted, the peat increment at Harjavalta was less than at Hietajärvi and Outokumpu sites, being only 16 cm during the last 125 years. The peat increment at Harjavalta was only 1 mm or less before 1953, which was noticeably less than at the other sites. However, the $^{14}$C-dated peat at 150 cm depth at Harjavalta was only 350 years old reflecting earlier high accumulation rates, while at Outokumpu it was 1500 years and at Hietajärvi 2600 years (Table A3-1). The younger age of the peat at Harjavalta was reflected in the lower degree of humification at the bottom of the studied profile being only $H_3$ at ca. 100 cm depth (Table A3-1). The corresponding value at Outokumpu was $H_6$ and at Hietajärvi $H_8$. This suggests that some local environmental factor has disturbed the most recent development of peat at Harjavalta in surface layers, e.g. local drought or wet periods. However, the estimated temperature and precipitation data is insufficient to describe in detail all local variations in the weather conditions. However, the lower organic matter accumulation rate in recent peat layers at Harjavalta compared to the other study sites gives some support to the hypothesis of retarded NPP due to the moss growth interference by metal toxicity. Hence smelter derived pollutants, especially of Cu, Ni and $SO_2$, might have caused reduced NPP, even in case where no visible changes in the vegetation have been detected. On the other hand the factors related to natural peat bog development can explain the observed peat growth decline as well.

Table A3-6. As, Cu, Ni, Pb and Zn average concentrations (mg $kg^{-1}$) in the 125-year-old peat layer.

| Element | | Harjavalta | Outokumpu | Alkkia | Hietajärvi |
|---|---|---|---|---|---|
| As | Average | 5.9 | 2.6 | 4.0 | 4.1 |
| | min-max | 3.4-8.5 | 0-4.4 | 1.9-128.4 | 0-6.3 |
| Cu | Average | 280 | 21 | 17 | 3 |
| | min-max | 18-1268 | 5.5-68.8 | 13.5-21.9 | 0-5.6 |
| Ni | Average | 152 | 6 | 717 | 2 |
| | min-max | 31-278 | 0-20.8 | 268-1043 | 0-6.1 |
| Pb | Average | 40 | 13 | 56 | 17 |
| | min-max | 21.4-59.8 | 3.2-24.3 | 31.5-70.9 | 2.3-27.0 |
| Zn | Average | 136 | 62 | 104 | 60 |
| | min-max | 76.8-187.5 | 38.8-89.3 | 67.9-128.4 | 27-110.8 |

At Outokumpu, which is located near a Cu-Ni mine, the maximum Cu concentration in the peat was 68.8 µg $g^{-1}$, which is well beyond background concentrations. The ore extraction rates of the mine peaked in the 1970s (Kuisma 1985). However, no relationship between ore extraction and the peat accumulation rate was observed. On the contrary, the peat accumulation rates were the greatest at the Outokumpu site, even exceeding those at the background site Hietajärvi.

The Ni concentrations were the greatest at the Alkkia Ni-treated site. The Ni concentration in the upper 5 cm averaged 717 µg $g^{-1}$. For comparison, the average Ni concentration in the topmost 10 cm of peat was only 5.81 µg $g^{-1}$ in Finnish Lapland (Ukonmaanaho & Nieminen 2005). The extreme Ni concentration was caused by the Ni sulphate application (200 kg $ha^{-1}$), which was delivered to the Alkkia site in 1962. Although Ni is generally known to be a mobile element in organic substrates (Kabata-Pendias 2001), 200 kg $ha^{-1}$of Ni applied has remained in the uppermost 100 cm layer. This might be a consequence of sulfate reduction and the precipitation of Ni. According to a survey, which was conducted two years after the Ni application in 1964, 16 % of the trees had died (Paavilainen 1969), and when the study was repeated in 1990 the figure had risen to 39% (Veijalainen 1998). Clearly, the extremely high

Ni treatment had a major detrimental, even toxic, effect on vegetation and subsequently on the peat accumulation. Indeed, the peat growth has practically ceased and *Sphagnum* mosses have almost completely disappeared from the site. However, some *Eriophorum* covered hummocks still exist. A high dose of Cu at Alkkia has had similar effect (Ukonmaanaho et al. 2004). Vegetation at the Alkkia Cu treated site was nearly as damaged as Ni treated site, but the peat core from the Cu site has not yet been age dated, the impact of Cu cannot yet be compared to that of Ni. This result however shows that high Ni dose is extremely damaging to the vegetation and hence prevents virtually all new peat accumulation.

The Ni concentrations at Harjavalta were also high, averaging 153 µg $g^{-1}$, but remarkably less than at Alkkia. In addition to high Cu concentration, elevated Ni concentrations might have had an effect on the peat accumulation at Harjavalta site. The average Ni concentration at the Outokumpu and Hietajärvi sites was less than 0.1 % of the value of Alkkia's.

Concentrations of As, Zn and Pb in the peat were low at all four sites. Background concentrations of the Pb at the peatlands have been reported to range between 3.8 and 19.3 µg $g^{-1}$ in Finland (Pakarinen et al 1981; Ukonmaanaho & Nieminen 2005). 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 µg $g^{-1}$. Jensen (1997) reported Pb concentrations changing from 0.59 to 227 µg $g^{-1}$ in background sites in Sweden and Norway. Concentrations of As, Pb and Zn were much greater at Harjavalta and Alkkia sites than at the eastern and more remote sites Outokumpu and Hietajärvi. The lower traffic volume and population density in eastern Finland presumably result in lower deposition loads of the heavy metals in the regional compared to southern and western Finland. Because concentrations of As, Pb and Zn were not elevated we conclude that these elements have not had any impact on peat accumulation at the studied sites.

## Conclusions

Organic matter and carbon accumulation rates during the last 125 years were found to be related precipitation sum and evapotranspiration index at Outokumpu, Hietajärvi and Harjavalta sites. This would suggest that, climate has a controlling mechanism in net OM accumulation rate. In a warmer and wetter climate, which may occur in the future, peatlands in northern boreal regions of the world may become even more important sinks for atmospheric $CO_2$. At the Ni treated site at Alkkia, it was not possible to estimate OM accumulation rates because of the apparent cessation in peat growth after the treatment in

1962 due to Ni toxicity. In addition differences in net OM accumulation rates between the sites were related to the specific local conditions. This was especially the case at the Harjavalta site, where the net OM accumulation rate was considerable less than at the other sites. One explanation for this difference might be the emissions released from the nearby Cu-Ni smelter which appears to have reduced the net OM and peat accumulation rates at the Harjavalta site. In contrast at the Outokumpu site, even though it is in the vicinity of an old Cu-Ni mine, such a effect could not observed. There was not remarkable difference in peat accumulation rates between Outokumpu and background site Hietajärvi.

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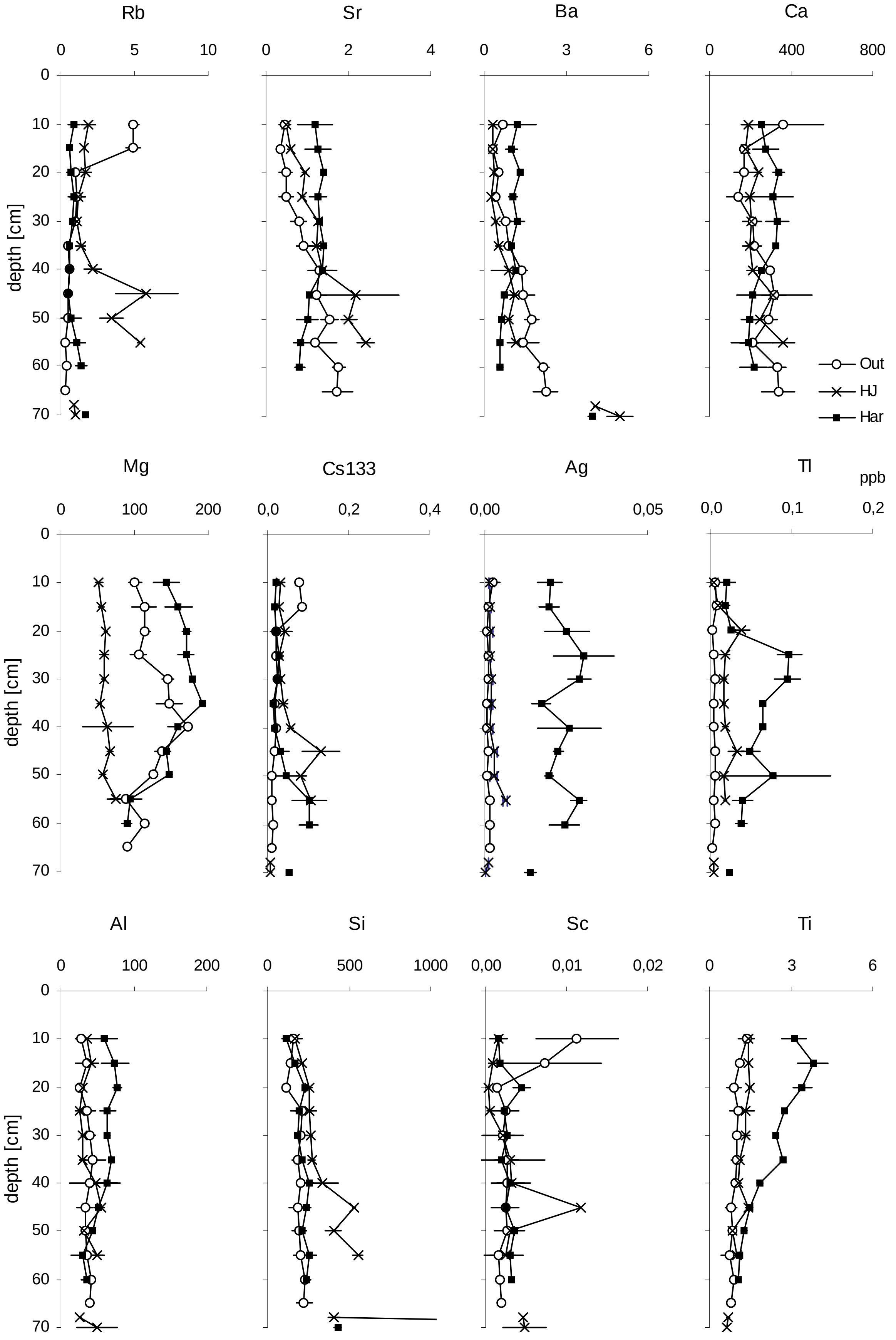
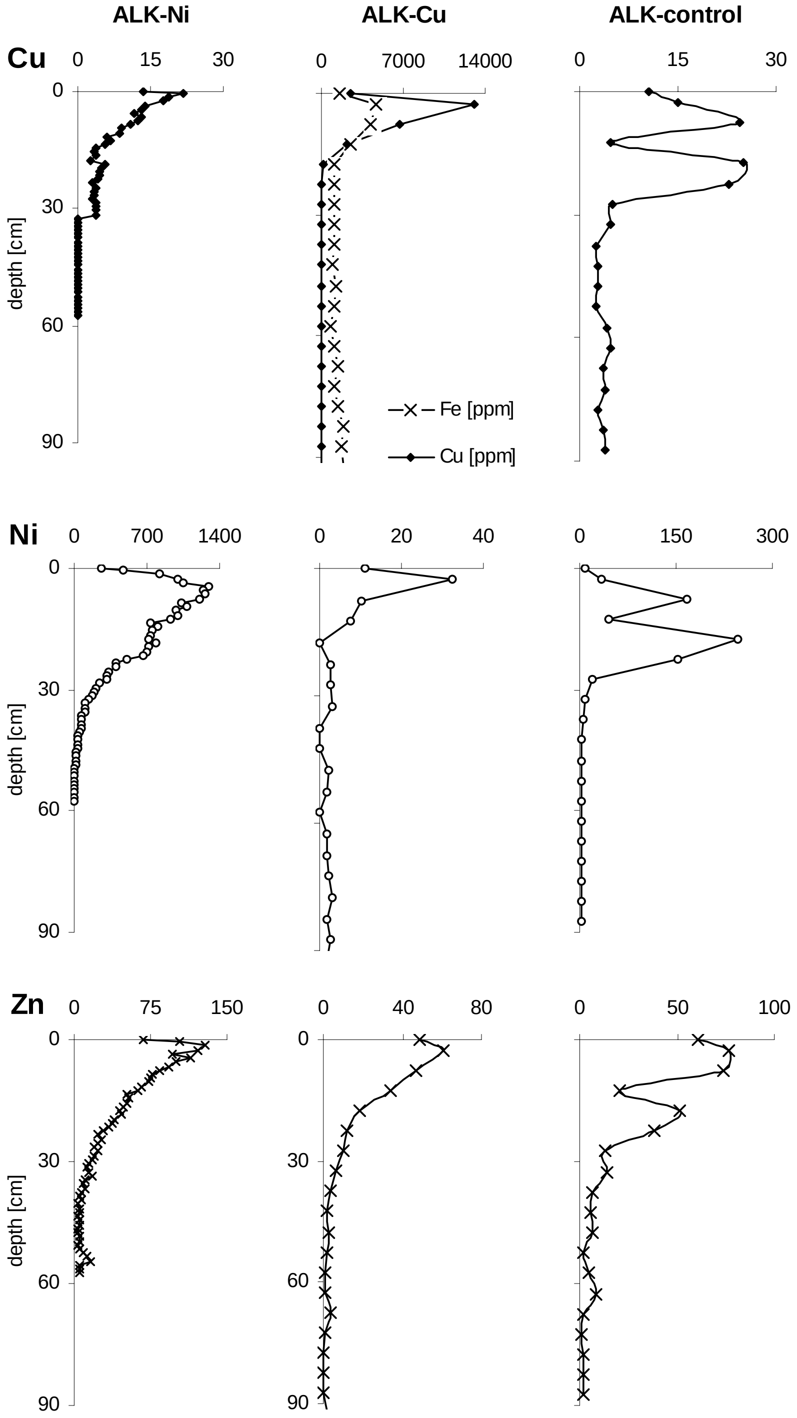
# 7-4 Appendix 4

## Porewater concentrations of various metals at HIJ, OUT and HAR



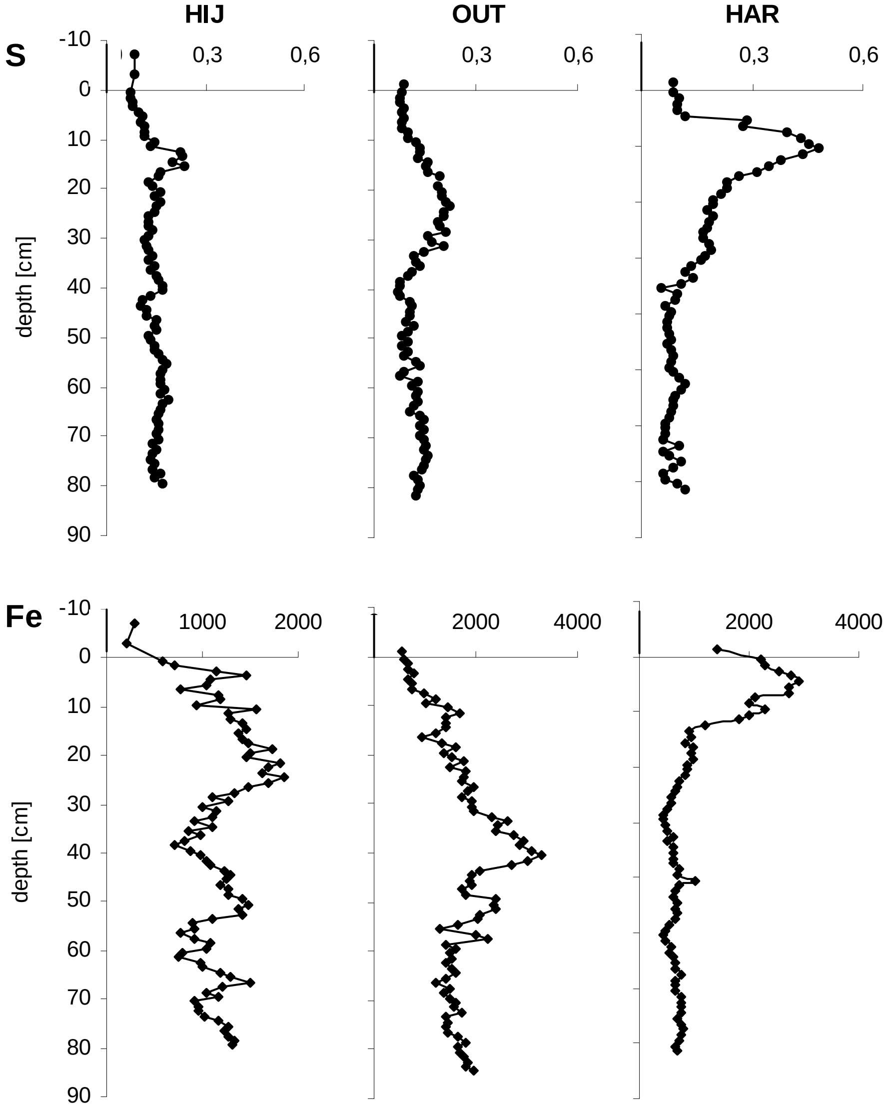
# 7-5 Appendix 5

## Bulk concentrations of Cu, Ni and Zn [$\mu g\ g^{-1}$] at Alkkia



ALK-Ni: Ni-treated site at Alkkia
ALK-Cu: Cu-treated site at Alkkia
ALK-control: untreated site at Alkkia

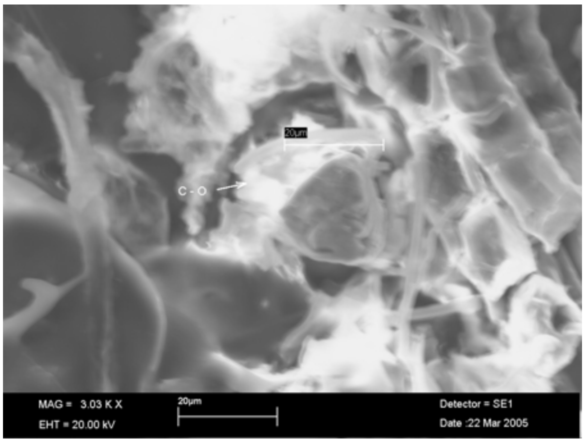
## Bulk concentrations of S and Fe at HIJ, OUT and HAR



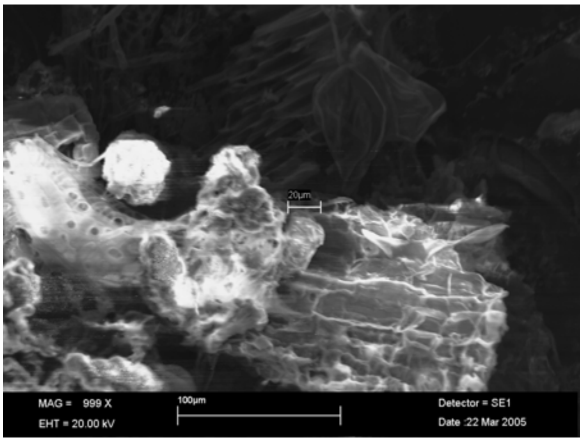
# 7-6 Appendix 6

## SEM Images of Cu and Ni containing particles in OUT 13, 33 and HAR 11, 15

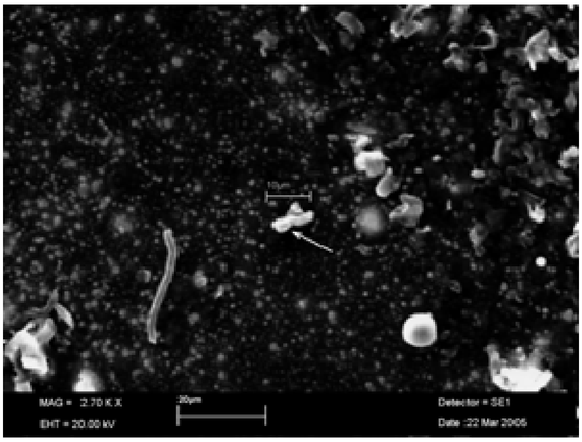
## OUT 13



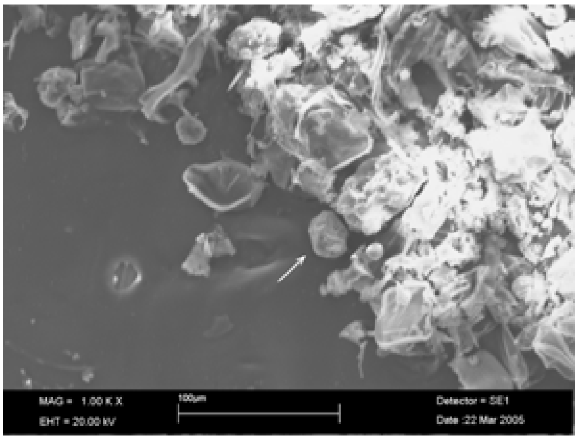
Cu-Fe-S (C,O)



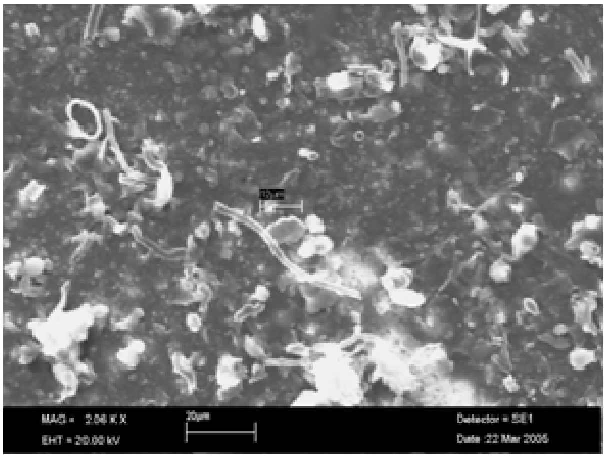
Cu-Fe-S (C,O)



Cr-Fe-C (+Ni, Mn)

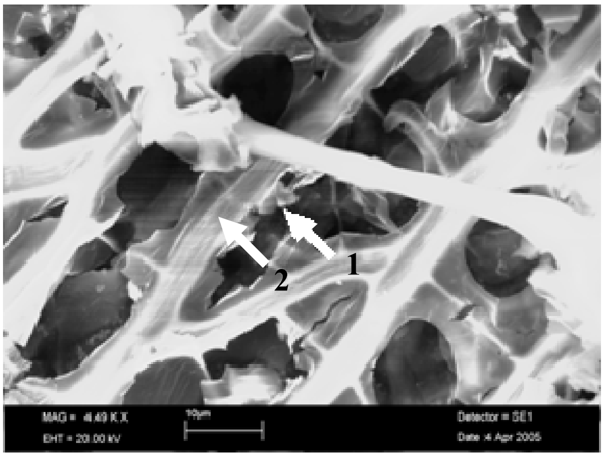


Fe-S-O?-C

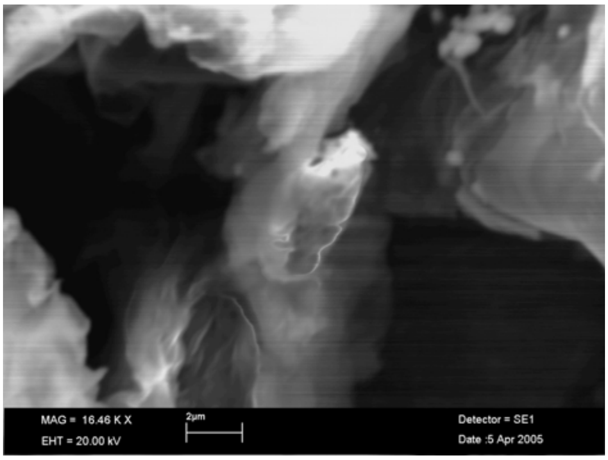


Fe-S (C) (no O)

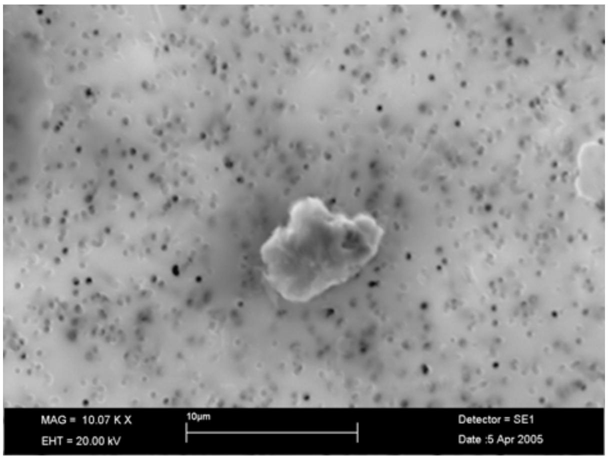
# OUT 33



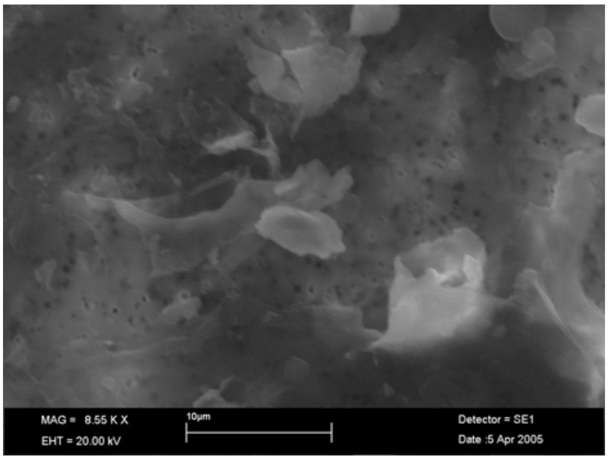
1: Cu-(Zn-Ni) particle containing few C, O
2: Organic structure containing Cu,Zn,Ni (+S)



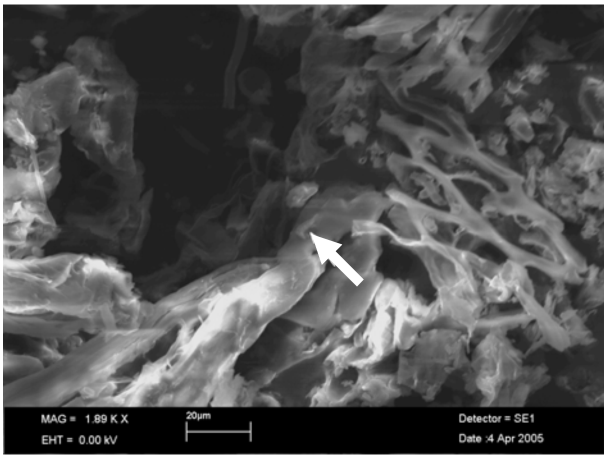
Cu + few Zn (C,O)



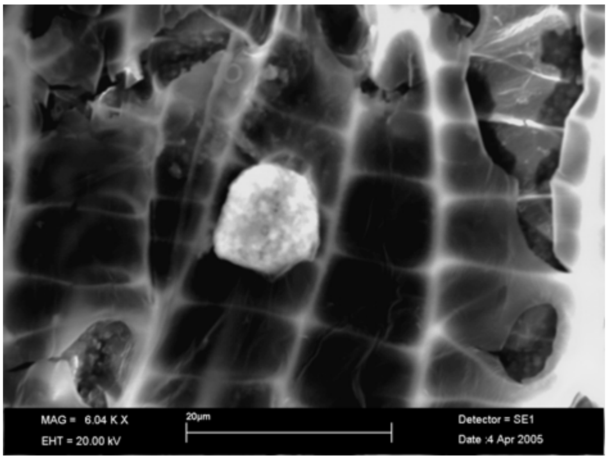
Cu-C see spectrum C (below)



Cr-Ni-C (O)

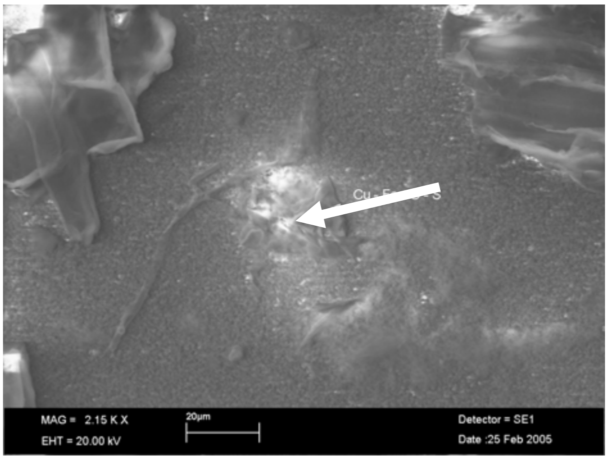


Zn (C,O)

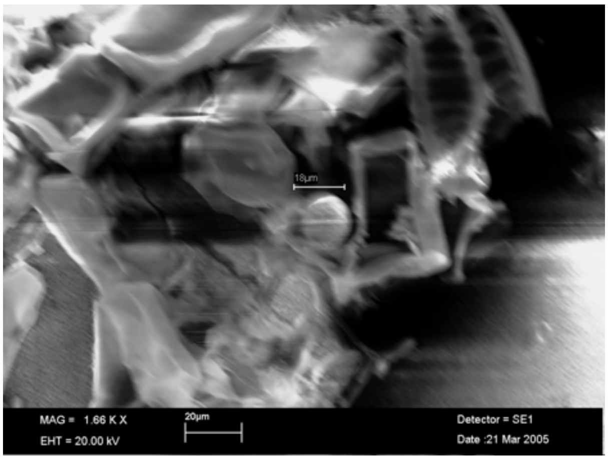


Na-Cl-K-Ca-O (Zn,S) + C,O

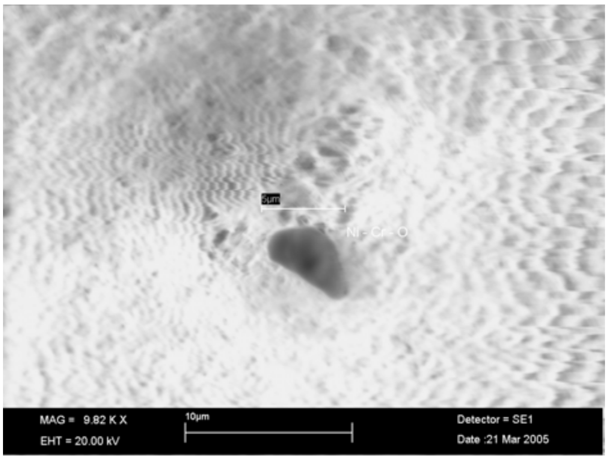
# HAR 11



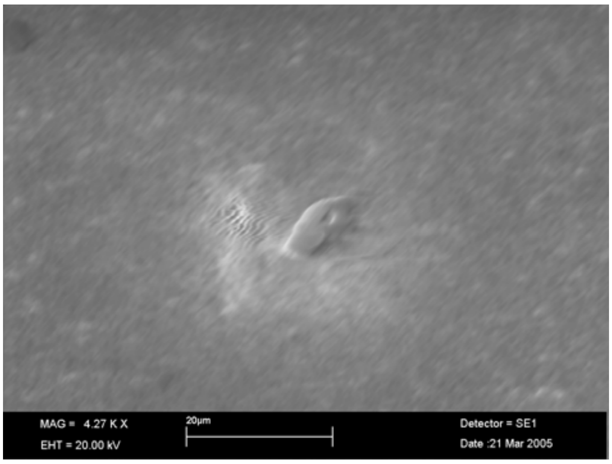
Cu-Fe-S (C,O) (< 5 micron)



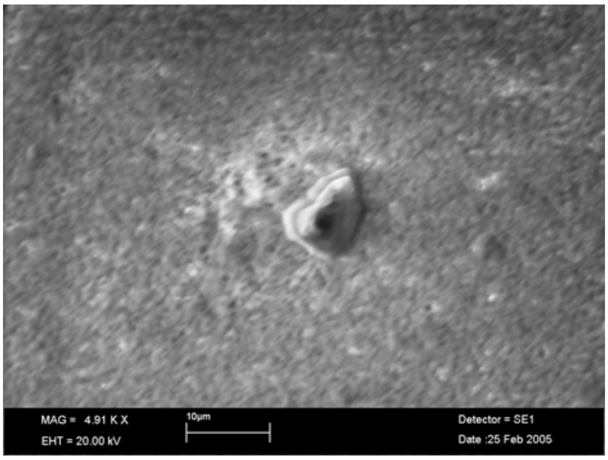
Ni-Fe-O (C?) + Cu, Zn (Ni-rich!)



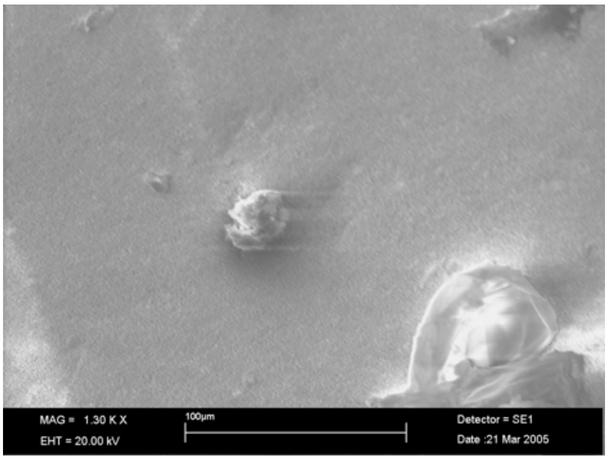
Ni-Cr



Ni

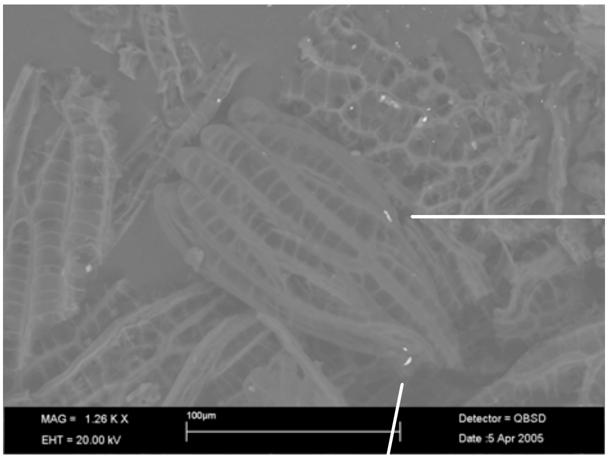


Fe-C-O

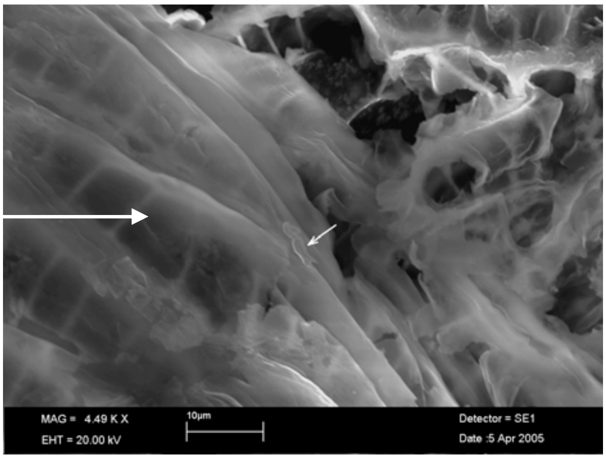


Fe-Si-O (Fe-poor, Si-rich)

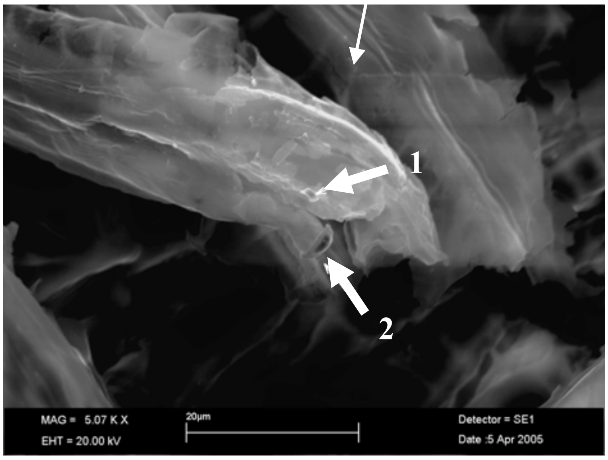
# HAR 15



Backscatter image: Organic structure with metal-rich precipitates (light spots)

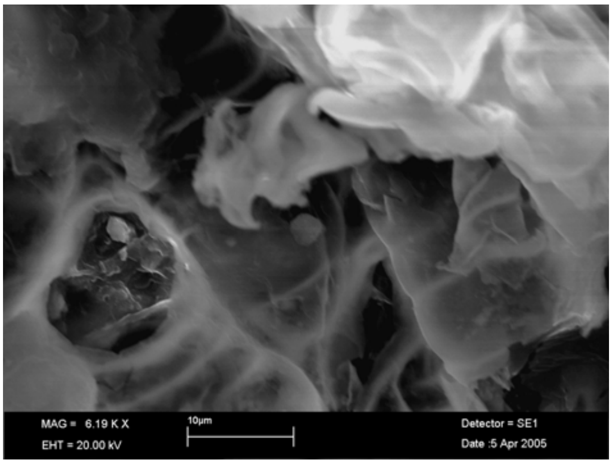


Cu-Zn-Ni-C (O) (Cu:Zn:Ni ~ 3:1:0.5)

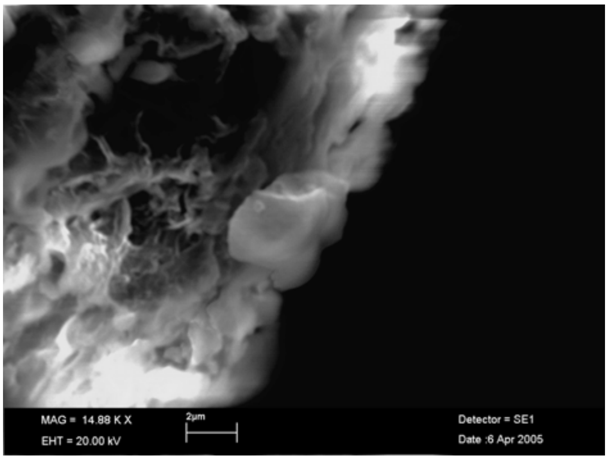


1: Fe-C; 2: Ni-C (O)

Ni-C (few O)

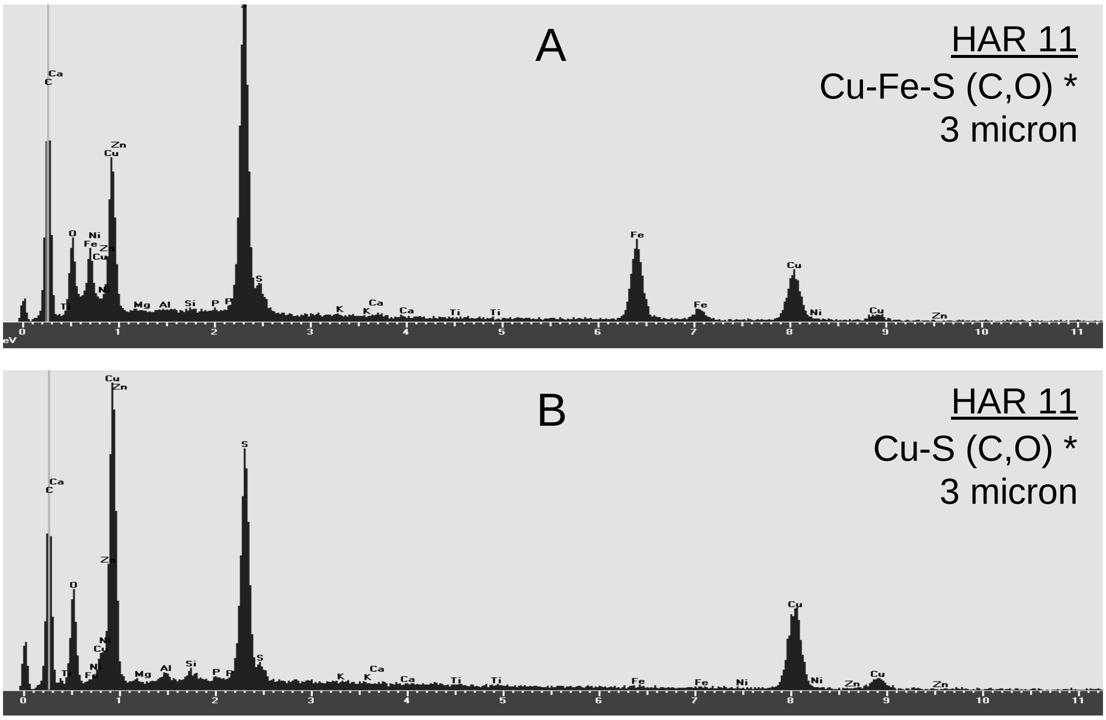


Zn-C + few Fe (few O)

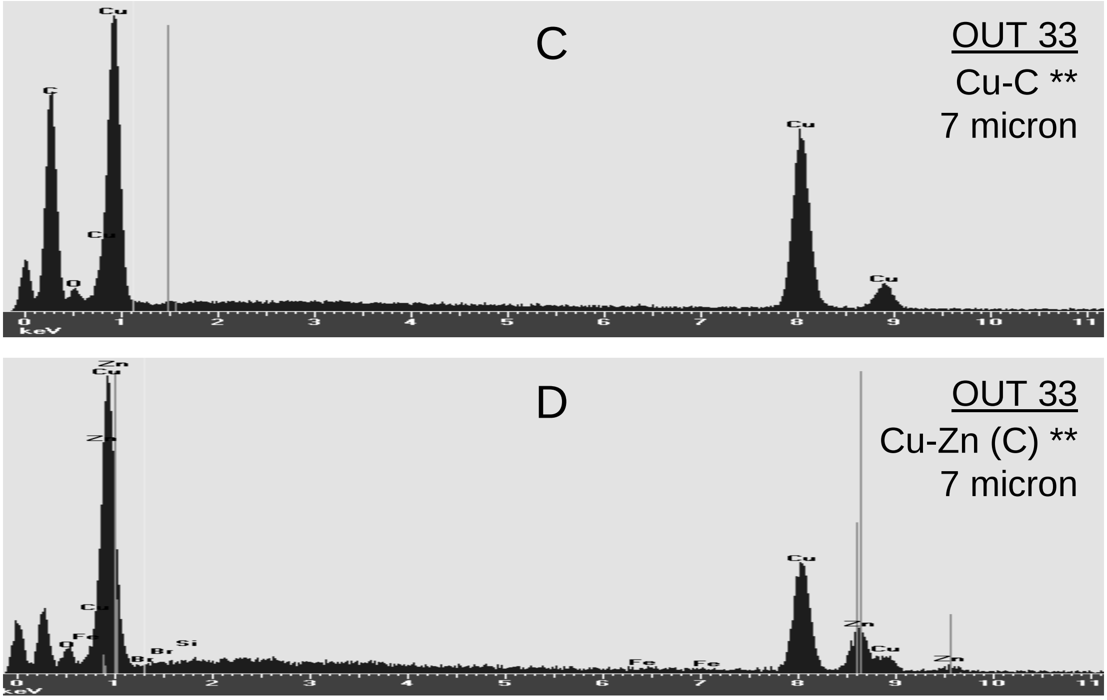


Cu-Al-Cl-O-Ca (K) and variable S

## Typical spectra of Cu-containing particles in peat layers corresponding to peaks in Cu concentrations (A, B) and in deeper peat layers (C, D)



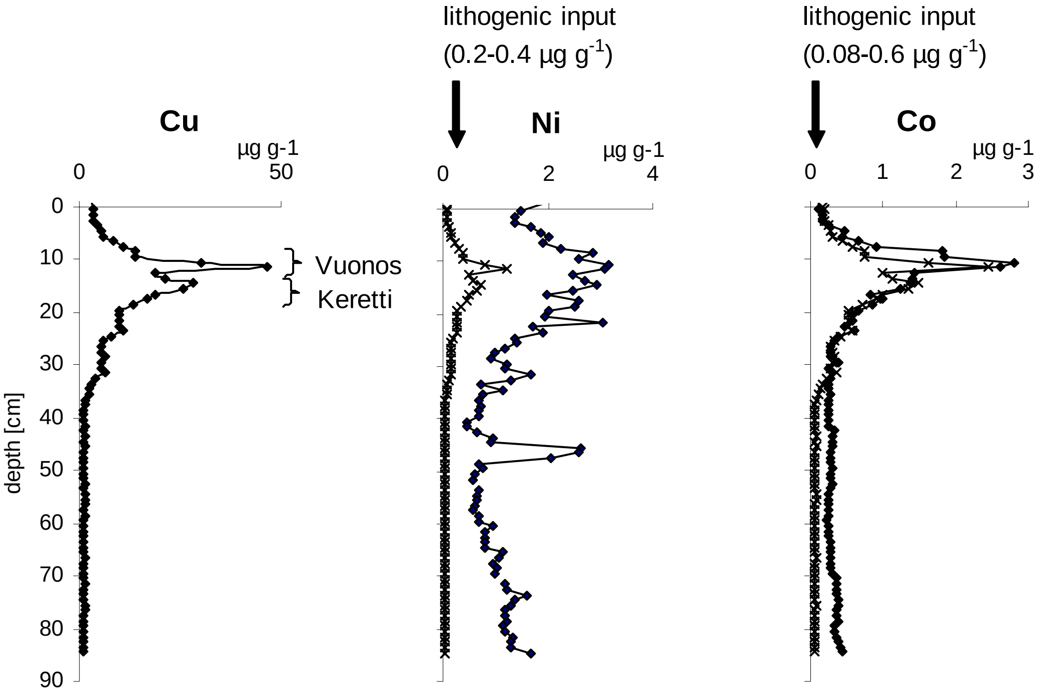
* C,O: signal is most likely originating from the excitation of the surrounding filter paper and/or the surrounding organic matter; no C,O signal found in particles > 10 µm



** all metal-containing particles in OUT 33 and HAR 15 are metal-rich and contain more or less C

# 7-7 Appendix 7

## Estimations of ore-related Ni and Co input at OUT



**Left:** Bulk concentration profile of Cu with main ore production periods indicated (Vuonos: huge amounts of Cu-poor, Ni-rich ores; Keretti: main shaft at the Outokumpu Cu-rich ore body). **Middle**: Bulk concentration profile of Ni (solid dots) and theoretical Ni concentrations calculated from Cu bulk concentrations and the average Ni content of the Outokumpu ores (crosses). **Right:** Bulk concentration profile of Co (solid dots) and theoretical Co concentrations calculated from Cu bulk concentrations and the average Co content of the Outokumpu ores (crosses). In addition, the lithogenic input of Ni and Co is given.

# Erklärung

Hiermit erkläre ich, Nicole Rausch, geb. 17.10.1969 in Karlsruhe, Baden-Württemberg, an Eides statt, dass ich die vorgelegte Dissertation selbst verfasst und mich dabei keiner anderen als der von mir ausdrücklich bezeichneten Quellen und Hilfen bedient habe.

Ich, Nicole Rausch, geb. 17.10.1969 in Karlsruhe, Baden-Württemberg, erkläre zudem an Eides statt, dass ich an keiner anderen Stelle ein Prüfungsverfahren beantragt habe, dass ich die Dissertation nicht in dieser oder anderer Form bereits anderweitig als Prüfungsarbeit verwendet habe und dass ich sie an keiner anderen Fakultät als Dissertation vorgelegt habe.

Heidelberg, 2. Juni 2005