J. Phys. IV France 107 (2003)
© EDP Sciences, Les Ulis
DOI: 10.1051/jp4:20030499

Retention of atmospheric Cu, Ni, Cd and Zn in an ombrotrophic peat profile near the Outokumpu Cu-Ni mine, SE-Finland

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Abstract. Peat cores taken from ombrotrophic bogs are widely used to reconstruct historical records of atmospheric lead and mercury deposition [1, 2]. In this study, the retention of copper, nickel, cadmium and zinc in peat bogs are studied by comparing high resolution, age dated concentration profiles with emissions from the main local source, the Outokumpu copper-nickel mine. An ombrotrophic peat core was taken from the vicinity of Outokumpu, E Finland. Copper and zinc concentrations of dry peat were measured by XRF, cadmium and nickel by GF-AAS, and sample ages by 210Pb. Only copper and nickel show enhanced concentrations in layers covering the mining period, indicating a retention of these elements. However, the more detailed comparison of ore production rates and concentrations in age-dated samples show clearly that only copper is likely to be permanently fixed, while nickel doesn't reflect the mining activity. Even though copper is retained in the upper part of the profile, a possible re-deposition of this element by secondary processes (e.g., water table fluctuations) can not be excluded. This question will be resolved by further investigations, e.g. by pore water profiles.

1. INTRODUCTION

Peat cores taken from ombrotrophic bogs are widely used to reconstruct historical records of atmospheric lead and mercury deposition [1, 2]. As a pre-condition, particles which were originally deposited at the surface of the bog must be permanently fixed in these layers. In this study, the retention of copper, nickel, and zinc in peat bogs are studied by comparing high resolution, age dated concentration profiles with emissions from local sources. The discovery of the Outokumpu deposit in 1910 was the beginning of modern mining industry in Finland, and it developed rapidly to one of the world's major copper deposit [3, 4]. Hence, the mining activity should be the main source of copper and nickel within the last century in this sparsely populated area, and main emissions of these metals should be proportional to ore production rates.

2. METHODS

A peat core was collected from an ombrotrophic peat bog 9 km far from Outokumpu, Eastern Finland, where the copper-nickel mine operated from 1913 to 1989. The core was subsampled in 1 cm slices to get trace metal concentrations and 210Pb age dates in high resolution. Copper and zinc were measured in dried and milled samples by X-ray fluorescence (XRF). Nickel and cadmium were measured by graphite furnace AAS (GF-AAS) after $HNO_3/HBF_4/H_2O_2$ microwave digestion, with RSDs of double-digestions mostly below 5%. Accuracy was evaluated by analysis of international reference materials. The element profiles were compared with the chronology of mining activity at Outokumpu, which could be reconstructed out in detail from various descriptions in literature.

3. RESULTS

High copper concentrations are found in a short zone at the upper part of the core, with 2 distinct peaks at the depths of 11,5 cm (69 mg/kg) and 14,5 cm (53 mg/kg), respectively, and a smaller one at 8,5 cm. Below this zone, the concentrations decrease within 20 cm, until they reach constantly low values of 3 mg/kg (below 41 cm). Nickel is also enriched in the upper layers, but this zone is more extended than the copper one (6,5 to 25,5 cm), and with only one distinct peak in 11,5 cm, which corresponds with the main copper peak. A sharp nickel peak occurs in the depth of 45,5 cm, together with a corresponding silicon peak, indicating an enhanced input of natural nickel minerals by soil dust. In contrast to copper, the concentrations increase constantly with depth in the deeper part of the profile.

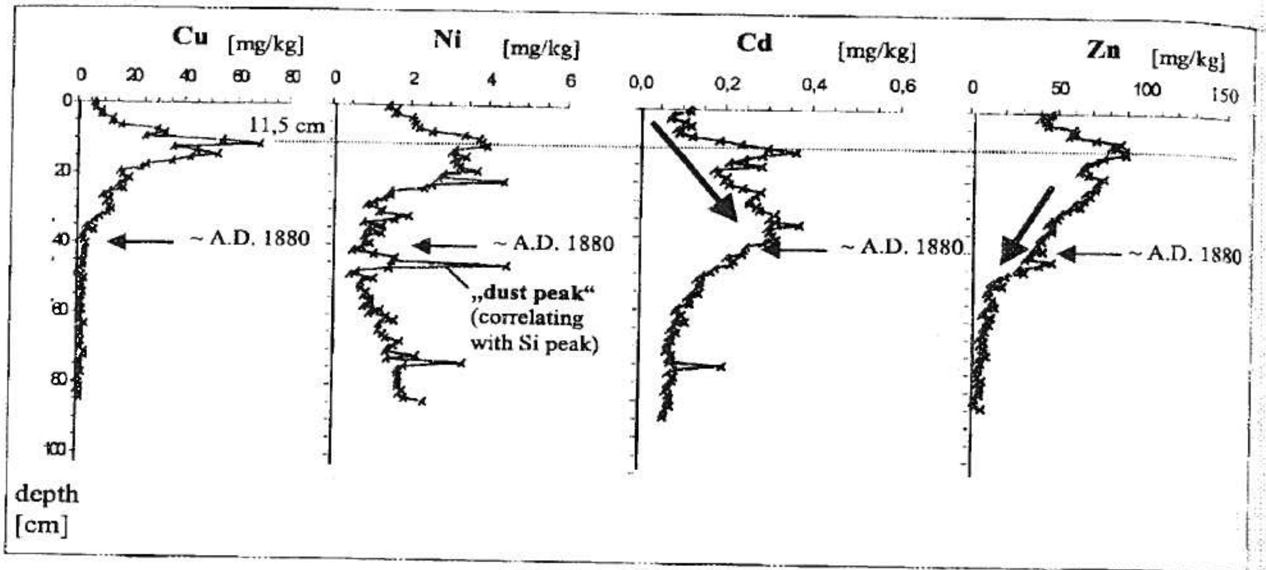


Figure 1. Concentrations of copper, nickel, cadmium, and zinc in dry peat, plotted against depth. The elements show only one common feature, the concentration peak in the depth of 11,5 cm. High enrichments in the layers of the last century are only shown by copper and nickel.

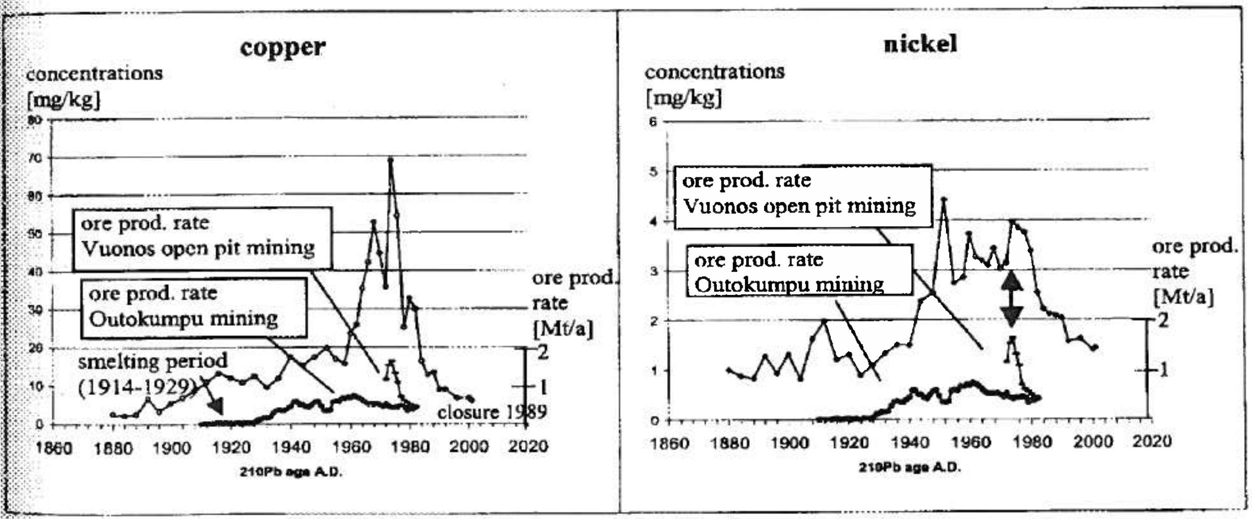
There is a general tendency for cadmium to increase in concentrations from the surface down to 36 cm, with a pronounced peak at 11,5 cm (which corresponds with the peaks of copper and nickel). In contrast, except for the peak at 11,5 cm, zinc tends generally to decrease downward.

As sharp changes in concentrations are lacking in both cadmium and zinc profiles, and high concentrations occur in samples older than A.D. 1880 ± 10, these elements appear not to reflect recent emissions of local mining activity, even though they are present in the Outokumpu ores as impurities (1% zinc [5]). Hence, mobilization of these elements during diagenesis is the most likely explanation of the concentration profile. In contrast, copper and nickel, which are enriched in these ores up to 3,8% (copper) and 0,33% (nickel) [5], seem to be retained in samples covering the mining period.

4. DISCUSSION

To estimate the retention of copper in the peat, copper concentrations were plotted against the ^{210}Pb age dates of the samples, together with the ore production rates at Outokumpu (Fig. 2 a). Two different ore bodies have been exploited there, the "Outokumpu ore body" (3,8% copper, 0,1% nickel) by drilling, and the "Vuonos ore body" (2,5% copper, 0,3% nickel) by both open pit mining and drilling [5, 6]. From

1914 to 1929, the ores were also processed by roasting, leaching and electrowinning, but only in a small test plant (6550 t Cu in total [7]). The increasing copper concentrations in samples dating A.D. 1913 to 1962, as well as the "Vuonos peak" (A.D. 1972 to 1982) and the final decline (closure A.D. 1989), fit very well with the ore production of the two mines. This reflection, together with the constantly low copper content of the deeper samples (< 2 mg/kg below 47 cm; see Fig. 1) implies that copper is not migrating downwards. However, the peaks before and after the Vuonos peak (dated for 1962 to 1972 and 1978 to 1974, respectively) as well as the early beginning of copper increase (18 ± 10 ^{210}Pb years before the first test drillings at Outokumpu) could not be explained by emissions of this local source. Secondary local sources (e.g., traffic and waste disposal by inhabitants, local industry) could only be of minor importance, as this part of Finland is only sparsely populated and as the mined ore was transported away [3, 8]. Enhanced input of soil dust can be excluded, because there is no simultaneous enrichment of silicon in these samples. Hence, for the early increase of copper concentrations it is possible that from 1892 onwards long-range transport of copper-containing particles from the more industrialized southern or south-western part of Finland (e.g. Nokia pulp and paper mill, built in 1865), or even central and eastern Europe may have contributed to the early enrichment of copper. Although, a possible downward shift of copper in the range of 5 to 6 cm can not be excluded. In contrast, there is no evidence in literature to explain the high copper concentration peak of samples from A.D. 1964 ± 2 to 1972 ± 2. The mining history of Outokumpu is very well reported, and no changes in mining techniques, new shafts or placement of waste took place at this time, which could have led to over-proportional emissions compared to ore production rate. Emissions by secondary sources which are in the range of dust emissions of Vuonos open-pit mining, as well as such a big influence of long-range transported aerosols, are also unlikely. Therefore, re-deposition of copper particles in the range of a few centimetres is the most possible explanation for the peak in around A.D. 1968, e.g. by water table fluctuations or humification reactions. As copper is stable in different oxidation states (+I and +II), and forms strong complexes with organic acids, deposited particles can be dissolved and again precipitated, or adsorbed or complexed by organic matter, depending on Eh/pH conditions.



a) b)

Figure 2: Metal concentrations (-o-) against ^{210}Pb age dates of dry peat samples, together with ore production rate of the Outokumpu mine (- for Vuonos opern pit mining, -*- for mining by drillings) after Kuisma [7]; a) copper b) nickel.

In contrast to copper, nickel concentrations seem to reflect not only the local mining activity, but also other processes (Fig. 2 b). Even though highest nickel concentrations are found in samples accumulated during the nickel open pit mining in Vuonos, the values are only 3,3 times higher than that ones of samples older than A.D. 1913 ± 10, and barely higher than that of samples formed during copper mining. However, nickel concentrations in the local bedrock vary from 74 mg/kg in the widespread mica schists to 1200 and 1700 mg/kg in quartzites and serpentinites [8], respectively, which are relatively high compared to the proper nickel ore with 3300 mg/kg nickel. Hence, local dust must be considered as a notable source for nickel, whereas it could be neglected for copper because of its low content in local bedrock (< 100 mg/kg in all local rocks compared to at least 24500 mg/kg in copper ore). While there is a small peak in nickel concentrations in the peat profile (11,5 cm) corresponding to open-pit copper-nickel mining, there is a number of other peaks in nickel concentrations which do not correspond to local mining activities. Thus, nickel appears to be mobile to some extent, and this mobility may depend on the size, mineralogy, and solubility of the nickel-bearing particles at the time of deposition. Alternatively, the anomalous nickel concentration peaks in the peat profile may simply reflect periods of enhanced deposition of local, nickel-rich soil dust.

5. CONCLUSION

This preliminary study shows that neither cadmium nor zinc is likely to be permanently fixed in the peat layers. The mobility of nickel seems to depend on the kind of compound which is originally deposited, while copper is likely to be retained in the peat profile, perhaps because of its well-known strong affinity to organic material. Further investigations (e.g., pore water profiles, leaching experiments and X-ray diffractometry) are needed to study dissolution/fixation processes during peat diagenesis and water table fluctuations, to exclude re-distribution of copper and nickel. Age-dating by 14C AMS bomb pulse curve [9] will evaluate accuracy of the presented 210Pb age dates.

Acknowledgements

The authors are grateful to William Roberts, Kari Lyytikäinen, and Lauri Hirvisaari for their help during field trip.

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