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Heavy metals, especially lead, deposition recorded in an ombrotrophic peat bog near Manchester, United Kingdom

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Abstract. A peat monolith representing up to 4,000 years of peat accumulation near Manchester, England, was collected. Major and trace elements were analysed with XRF and for Cd and Pb in the deeper samples with GF-AAS following acid digestion. Pb isotopic composition was measured with TIMS and ICP-MS. The results show a pollution since the Roman Period due to local lead sources and an increase in lead pollution in the last century due to leaded gasoline as fingerprinted by Pb isotopic signatures.

1. INTRODUCTION

England has a rich mining and industrial history. For example, Lee and Tallis investigated Pb pollution history in peat bogs in Britain [1]. They assumed that the sources of Pb were regional due to lead extraction and industries in the area since Roman Period.

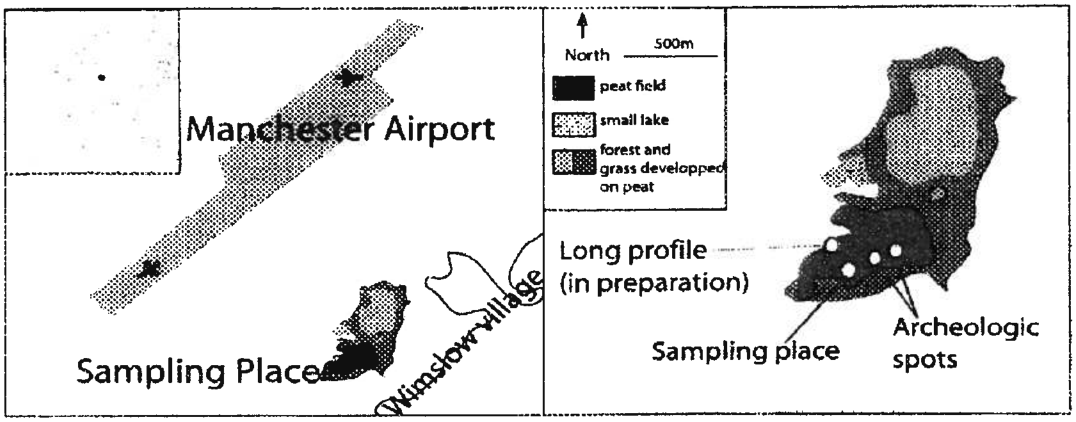


Figure 1. Map of Lindow Moss

With a view to determine the sources of Pb (i.e. local sources versus long range atmospheric transport) in England, we studied the geochemistry of a peat monolith from the

Lindow bog, and analysed the isotopic composition of Pb. Lindow Moss is a famous ombrotrophic peat bog in the South of Manchester [2, 3] (cf. Figure 1) not far from the Pennine peat bogs investigated by Lee and Tallis. Ombrotrophic peat bogs can be used as archives of atmospheric metal deposition [4, 5], especially for lead [6, 7] because the inorganic constituents are only supplied by atmospheric deposition [8].

2. MATERIAL AND METHODS

2.1 Material

A monolith of peat (220cm) was sampled at Lindow Moss, a former raised bog, located to the South of Manchester, Cheshire, England. Lindow Moss is well known due to the extensive palaeoecological and archaeological researches prompted by the discoveries of bog bodies dating from the Iron Age or the Roman Period [2, 3, 9]. Because of the long history of peat cutting at the bog, the top of the core had no living moss and it is not known how much of the peat surface is missing.

2.2 Methods

The peat monolith was sectioned in 2cm slices, dried and milled. Metals (Cu, Zn, Pb in the top of the core, Ti) and Sr concentrations were measured using X-ray fluorescence analysers [10, 11]. Because of the relatively high limit of detection of XRF (0,6ppm), Pb was also analysed with Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) following acid HNO_3-HBF_4-H_2O_2 microwave digestion [12]. Cd concentrations were measured following a similar procedure.

The same liquid aliquots obtained after digestion were measured for Pb isotopes on TIMS at the Institute of Environmental Geochemistry, Heidelberg and with the Micromass Isoprobe ICP-MS at the Imperial College/Natural History Museum joint analytical facility, London, using standard procedures for Pb isotopes geochemistry [13-15].

The bottom of the core was ^{14}C age dated: 2033 (±14) B.C.

3. RESULTS AND DISCUSSION

3.1 Metals concentration profiles

The Sr, metals concentrations and metal enrichment factors (EF):

$$EF = \frac{[Me]_{peat} / [Ti]_{peat}}{[Me]_{crust} / [Ti]_{crust}} \qquad (1)$$

are shown on Figure 2.

The Sr concentration profile suggests two distinct depositional environments: the deeper part (-220cm, -130cm) with high concentrations influenced by mineral dissolution and the upper part (-130cm,surface) with low Sr concentrations only influenced by atmospheric inputs.

Pb and Cu profiles show similar features with a very high peak (>500ppm for Pb) in the top of the profile. However, lower in the monolith, while the concentrations of Pb are remarkable, Cu concentrations are less prominent and approach the limit of detection for XRF (1,5ppm). In the same way, Cd and Zn profiles show similar features, which suggests they have identical sources and the same chemical behaviour in peat.

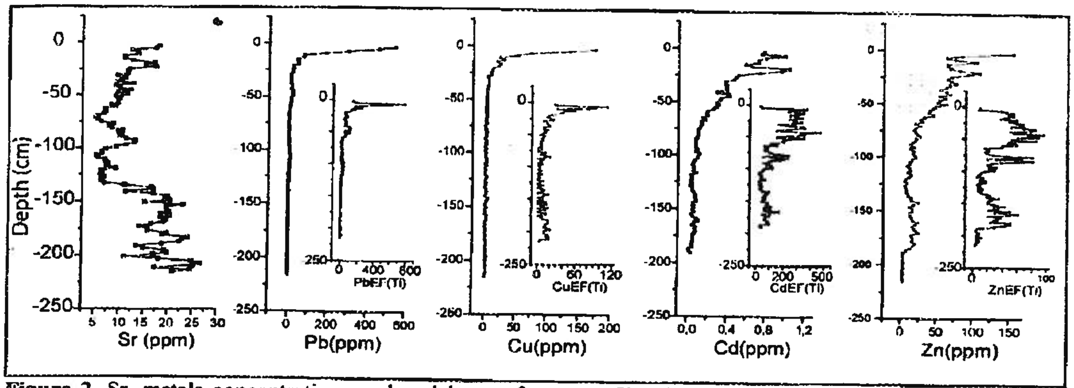


Figure 2. Sr, metals concentrations and enrichment factor profiles from Lindow Moss, the crustal ratios are taken from [16].

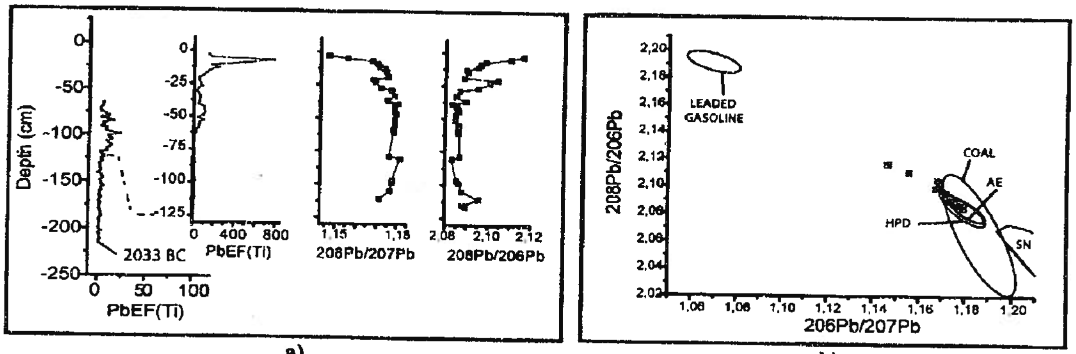
Unfortunately, up to now, no clear evidences of the immobility of Zn, Cd and Cu in peat has been demonstrated and we may interpret the Pb record with any confidence [4].

We will then focus the rest of the discussion on Pb concentration and isotopic composition.

3.2 Pb Enrichment Factor and Pb isotopic signatures

Pb EF and $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$ ratios profiles are shown on figure 3a). There are three periods of pronounced Pb enrichment:

- One around 100cm depth
- The second around 50cm depth
- The bigger one in the top of the profile.



a) b)

Figure 3. a) Pb concentration and isotopes profiles, b) Pb isotopes ratios on a $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ diagram (squares: peat samples, COAL data from [17], HPD: "High Peak district ores" and AE: "Alderley Edge ores" from [18] and leaded gasoline (1994) from[19], also included SN: natural, background Pb (preanthropogenic) from [6, 20, 21]).

We do not yet have ^{14}C ages of these three peaks, but there is good stratigraphic evidence (known as Grenzenhorizont) compared to other dated profiles in the bog [3] that they could be respectively assigned to the Roman Period, Medieval Period and Recent Period. This is in good agreement with other archives in Europe [22] and with the study of Lee and Tallis [1]. But what are the main sources of atmospheric Pb in England? This could be answered by study of Pb isotopes measured in the samples compared to the possible sources of lead in England [17-19].

Figure 3b) is a diagram $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ representing Pb isotopes ratios measured in peat samples, and in three of the major sources of Pb in the atmosphere: coals, Pb ores and leaded gasoline. In Figure 3b), we can see how it is difficult to distinguish coals and lead ores signatures. During the Roman Period, coal was surely not the most important source of atmospheric lead, but during the Medieval Period and moreover during the Industrial Revolution, Pb emitted by coal combustion was probably significant. However, in this case there are two mines within 30km, which produce Pb and which have been in near continuous production since ancient times, which must be a major source of Pb identified in this study.

In the top of the core, the decrease in Pb is correlated with a decrease in $^{206}Pb/^{207}Pb$. The shift in Pb isotope ratios to less radiogenic values probably reflects not only the declining importance of Pb emissions from coal burning and industry (since 1900 for coal, since 1940 for Pb ores [23]), but also the increasing emissions of gasoline Pb compounds manufactured using Australian Pb ores. Thus locally, the Pb pollution due to mining and industrial activities was more important than pollution due to leaded gasoline.

References

[1] Lee, J.A. and J.H. Tallis, *Nature*, **245** (1973) 216-218.
[2] Stead, I.M., J.B. Bourke, and D. Brothwell Eds., Lindow Man, the body in the bog. (British Museum London,London,1986).pp. 206
[3] Turner, R.C. and R.G. Scaife Eds., Bog bodies, new discoveries and perspectives. (British Museum,London,1995).pp. 256
[4] Shotyk, W., et al., *EPSL*, **145 E** (1996) 1-7.
[5] Martinez-Cortizas, A., et al., *Science*, **284** (1999) 939-942.
[6] Shotyk, W., et al., *Science*, **281** (1998) 1635-1640.
[7] Vile, M.A., R.K. Wieder, and M.J.V. Novák, *Biogeochem.*, **45** (1999) 35-52.
[8] Shotyk, W., *Earth Science Reviews*, **(25)** (1988) 95-176.
[9] Pyatt, F.B., et al., *Oxford Journal of Archeology*, **10 (1)** (1991).
[10] Cheburkin, A.K. and W. Shotyk, *Fresenius J. Anal.Chem.*, **354** (1996) 688-691.
[11] Shotyk, W., et al., *EPSL*, **199** (2002) 21-37.
[12] Krachler, M., et al., *Spectrochim. Acta Part B*, **57** (2002).
[13] Hamelin, B., F. Grousset, and E.R. Sholkovitz, *Geochim. Cosmochim. Acta*, **54** (1990) 37-47.
[14] Rehkaemper, M. and A.M. Halliday, *Int. J.Mass Spectrometry*, **58** (1998) 123-133.
[15] Longerich, H.P., B.J. Fryer, and D.F. Strong, *Spectrochim. Acta Part B*, **42** (1987) 39-48.
[16] Wedepohl, K.H., *Geochim. Cosmochim. Acta*, **59** (1995) 1217-1232.
[17] Farmer, J.G., L.J. Eades, and M.C. Graham, *Environmental Geochemistry and Health*, **21** (1999) 257-272.
[18] Rohl, B.M., *Archeometry*, **38 (1)** (1996) 165-180.
[19] Monna, F., et al., *ES&T*, **31** (1997) 2277-2286.
[20] Sun, S.S., *Phil.Trans.R.Soc.Lond.*, **A 297** (1980) 409-445.
[21] Ferrand, J.-L., B. Hamelin, and A. Monaco, *Continental Shelf Research*, **19** (1999) 23-47.
[22] Renberg, I., R. Bindler, and M.-L. Brännvall, *The Holocene*, **11 (07)** (2001) 511-516.
[23] Smith, J. and C. Phillips. The Lancashire/Cheshire Region from AD 1540. (Longman,London,1994).pp.