

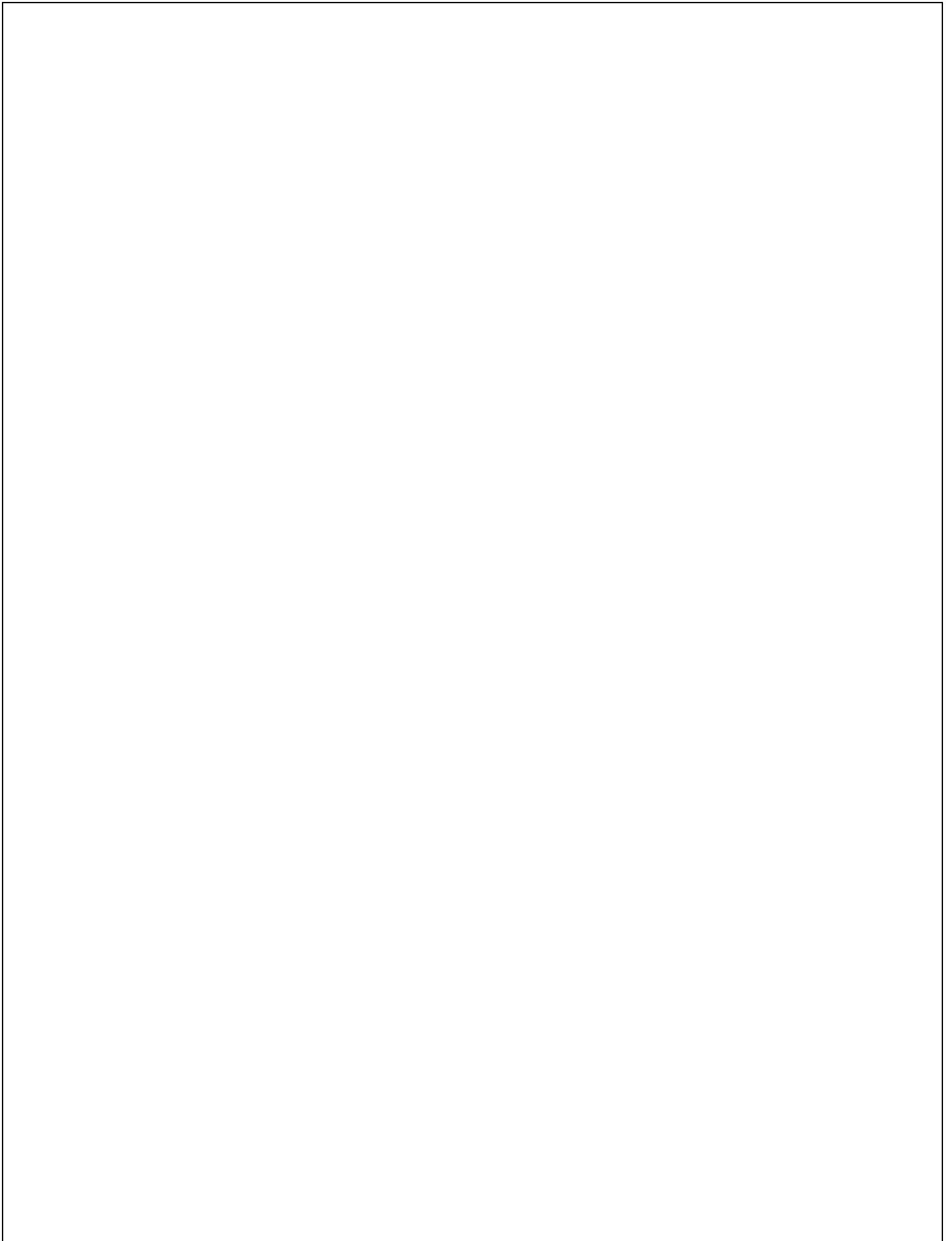
POST EXPEDITION FIELD and STATUS REPORT

Identifying the predominant sources of
Cu, Zn and Pb to a peat profile
At a Lindow Moss near Manchester, England

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View of the Lindow Moss on the on the 22nd August



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PREFACE

The report primarily provides a public record of the field work, detailing how and where peat and other environmental samples as well as plant samples were taken for later analysis and dating. Additionally, the present status of the samples is given.

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Dr. John Prag (The Manchester Museum, Manchester, England),
Ms. Clare Pye (The Manchester Museum, Manchester, England),
Mr. Michael Goodsite (University of Odense, Denmark).

DISCLAIMER

The ideas and opinions expressed in this report are the authors alone. They do not necessarily reflect the opinions or ideas of the funding agencies, employers, or corporate sponsors.

Respectfully submitted by

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ABSTRACT

This field report describes the field expedition undertaken on Thursday the 22nd August to Lindow Moss near Manchester, England.

Four meters of peat cores were collected with Ti Wardnaar and Belarus corers. They will provide a record of natural Cu, Zn and Pb sources to the peat profile. We hope that the data will help to assess why the Cu and Zn concentrations in the skin of the Lindow Man are anomalous (*Pyatt et al., 1991*).

Subsamples will be analysed for major elements, trace elements, Pb and Sr isotopes and macrofossils.

Plants samples (*Sphagnum* moss) were collected providing a record of actual atmospheric deposition.

I. GENERAL INFORMATION

CONTACT INFORMATION

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Peat coring, photography

TRAVEL

On Wednesday 21st August 2002, William Shotyk and G. Le Roux drove with William Shotyk's private car from Reading to Manchester university near the site.

ACCOMMODATION

The team slept in the student residence of the Manchester University.

LOGISTICS

All equipment was shipped from Heidelberg to Manchester and received by the museum staff. Samples were frozen immediately after collection at -18°C . Later, they were kindly wrapped by the museum staff, packed with the coring equipment, and sent back to Heidelberg.

II. PEAT CORE SAMPLING

Mid-west England is an ideal area to find ombrotrophic peat blanket and raised bogs which could be used as an archive of past environments (Livett et al., 1979). The average annual precipitation is very high (>1000mm/y, see fig 1) and the average annual temperature is around 5°C. The snow cover days are less than 10 in the year (NationalGeographic, 2002).



fig 1: Precipitations Map

SITE LOCATION

Lindow bog is 13km far from the South of Manchester and 2,5 km South from Manchester Airport . The coordinates of Lindow Moss sampling site are **Z=71m; N:53°19'17,2''; W:002°16'18,4''**.

The mire has a long history of peat cutting and there is always a peat farm near the bog. As a result of this exploitation, the bog is devastated and there are no intact remnants of the original surface.



fig 2: entrance to the peat farm



fig 3: general view of the exploited part of Lindow Moss, note the abundance of indigenous wood, which represents a subfossil pine woodland (see text for explanation).



fig 4: Aerial photo of the area, note: the brown part in the north of the peat site is now a artificial pond. The other brown parts are peat-harvesting areas.

RECONNAISSANCE AND SURVEY

Survey was conducted with a Global Positioning System (GPS), handheld receiver.

EQUIPMENT

All the equipment as well for the transport as for the sampling was provided by Prof. Dr. William Shotyk, shotyk@ugc.uni-heidelberg.de, Director of the Institute of Environmental Geochemistry, University of Heidelberg in Germany.

List of the equipment:

- 1 Wooden core boxes
- Ti Wardenaar corer
- Ti pry bar and 2 Ti lifting rods
- Ti Belarus borer,
- Ti extension of the Belarus corer,
- Sledgehammer
- Tool kit (wrenches, screwdrivers, knives, nails, screws)
- Set of knives
- Hatchet, shovel
- Polyethylene film
- Plastic bags

Garbage bags
Aluminium foil
25 ml plastic bottles for water sample
PET gloves
Emergency kit
Permanent markers

EXPEDITION PLAN

The primary goals of the expedition can be summarised as follow:

- to see the famous Lindow moss where Lindow Man was found, to help us better understand the site.
- to obtain Wardenaar cores and Belarus cores as archives of atmospheric and aquatic input of Cu, Zn and Pb.
- to collect plant samples, surface water samples and make observations at the coring site.

GENERAL NOTES

Permissions: John Prag had secured the permission of the peat farm people for taking cores and samples at Lindow Moss.

Route Planning and Navigation: John Prag guided the expedition team.

Method: Cores were removed using a 15 x 15 cm Ti Wardenaar corer (first meter, dried peat) and then with the Belarus corer for the next 4 meters until a wood layer (see description of the site) which made the sampling difficult. Belarus cores (length c.a.:50cm) were alternatively taken in 2 holes dug by hand. Short descriptions of the cores were done (ca. length, different layers and colours). Cores photographed and wrapped with polyethylene film, then plastic, and sealed in core boxes. Cores were frozen at -18°C for storage at the Manchester University Museum and then sent on the 9th September to the institute of Environmental Geochemistry of the Heidelberg University for storage .



fig 5: A remnant of the uppermost section of the bog. The wardenaar core was collected here, to have some recent peat for comparison with deeper, older samples.



fig 6: The Ti wardnaar corer could only be driven into the peat using a sledgehammer; the peat surrounding the corer had to be partially excavated to allow the corer to be removed.



fig 7: Length of the total Belarus cores indicates the depth of peat coring.

Detailed Description of the site:

The site was a very extensive post-glacial lowland peat bog (600ha) (Turner and Scaife, 1995) dominated by *Sphagnum* species and cotton sedges (*Eriophorum Angustifolium*) (Stead et al., 1986) developed on a pine woodland, “forest layer” according to Turner and Scaife; this phase dates between 4343 and 3803 B.C. (first phase) and between 2563 and 2139 B.C. (second phase)(Lageard et al., 2000). The development of the bog is explained in detail in a PhD thesis no (Roberts, 1998).

The chemistry of a peat monolith taken previously is described in a paper given in Appendix.

The extension of Lindow Moss in the past was very vast as indicated on the old maps, traces of peat cutting parcels on aerial maps and the artefacts of peat cutting around the modern site. On the surface of the peatland which remains today, much if not most is covered by the woody remains of one of the forested phases. Difficulties in coring were due to the presence of trees on the trajectory of the Belarus corer.

Fortunately, we found a place where the bog is regrowing indicated by the presence of living *Sphagnum*, following what must have been only irregular cutting of peat by hand. Moreover there is a small remnant uppermost section of the bog, which was cored with the Wardnaar Ti corer. The top of this core will be analysed for ^{210}Pb , too see how much, if any, modern peat accumulation it may contain.

But unfortunately, to investigate deposition of elements to the bog from the atmosphere, we have to be careful because of the clearly modified hydrology by drainage and the great disturbance of the bog by peat cutting (Turner and Scaife, 1995).



fig 8: Tree fossils are now found at the modern surface because of peat cutting.



fig 9: Belarus core (last Belarus core, 4th meter) with piece of wood (will be identified and age dated using ¹⁴C).

STATUS OF STUDY

The present status of our study as of the 15th September, 2002 is briefly as follows:

All samples are archived at the Institute of Environmental Geochemistry, University of Heidelberg in Germany.

- **Wardnaar core** was precisely cutted in 1cm slice.
- **Belarus cores** will be cut into 1 cm slices using a stainless steel electric saw.
- All slices (every second centimetre for Belarus peat cores) will be subsampled and analysed for major elements chemistry (XRF, ICP-OES), trace elements (XRF, ICPMS, GFAAS, IDMS), isotope chemistry (TIMS, ICPMS).
 - **Water samples** will be measured with ICP-OES.
 - **Plant samples** collected during this trip will be measured for major elements, trace elements using XRF and for ⁷Be, ²¹⁰Pb using gamma spectrometry.

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ANNEXE:
Paper submitted to Journal de physique IV

**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.

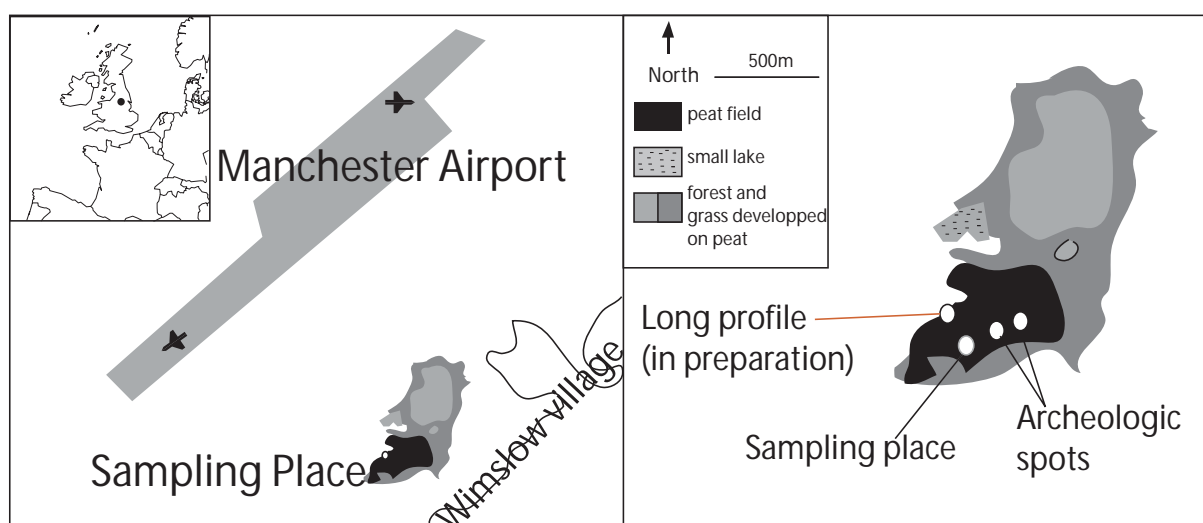


Figure 1. Map of Lindow Moss

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 HNO₃-HBF₄-H₂O₂ 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 ¹⁴C age dated: 2033 (±14) B.C.

3. RESULTS AND DISCUSSION

3.1 Metals concentration profiles

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

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

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.

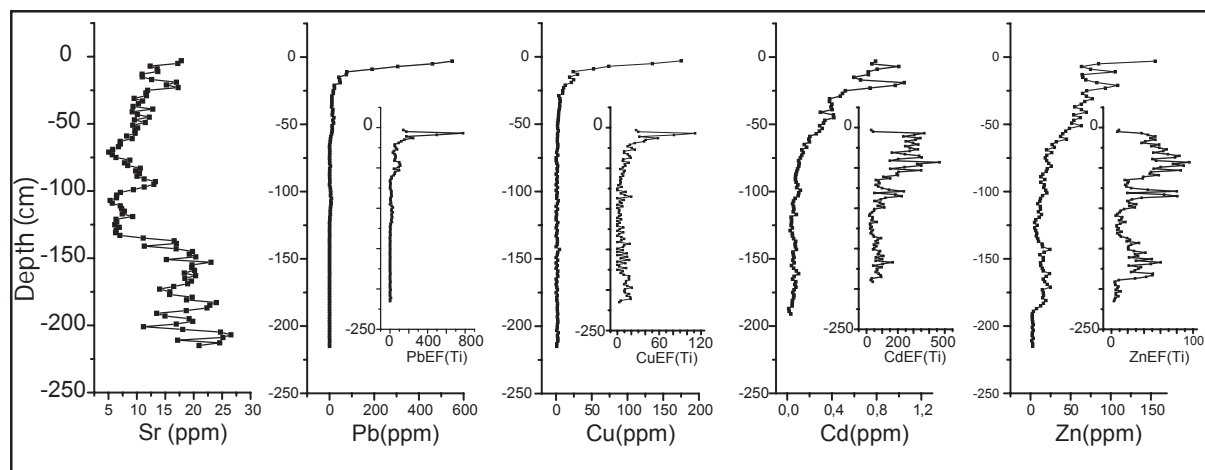


Figure 2. Sr, metals concentrations and enrichment factor profiles from Lindow Moss, the crustal ratios are taken from [16].

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 $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$ 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.

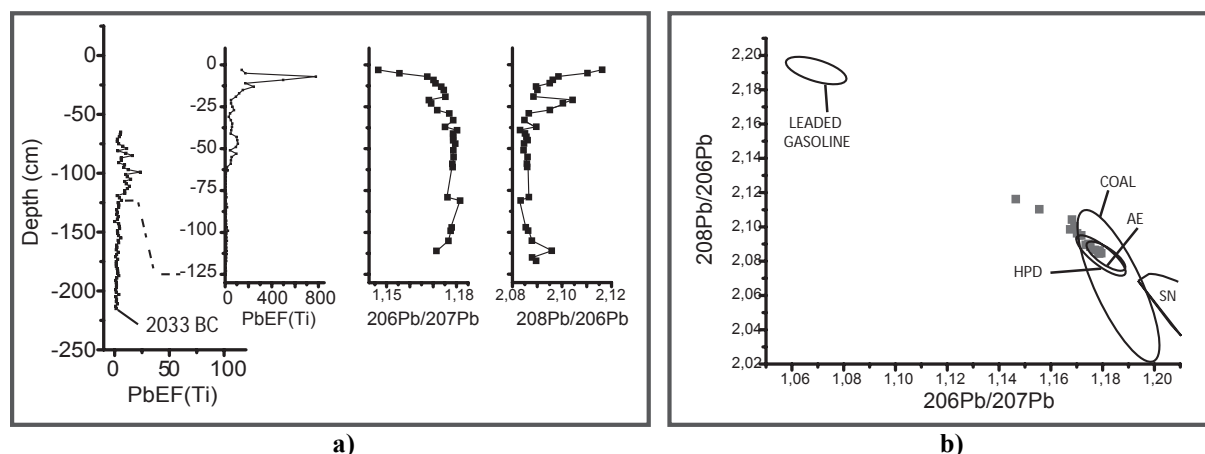


Figure 3. a) Pb concentration and isotopes profiles, b) Pb isotopes ratios on a $^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$ diagram (squares: peat samples, COAL data from [17], HPD: “High Peak district ores” and AE: “Alderley Edge ores” from [18] and leaded gasoline (1994) 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 Grenzhorizont) 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 $^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{206}\text{Pb}/^{207}\text{Pb}$ 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 $^{206}\text{Pb}/^{207}\text{Pb}$. 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.

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