

# ATMOSPHERIC Pb DEPOSITION DURING THE LAST 4,600 YEARS RECORDED BY TWO OMBROTROPHIC PEAT BOGS IN NW SPAIN

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## ABSTRACT

Two ombrotrophic peat bogs in Northwestern Spain provided a history of 4,600 years of Pb accumulation. Highest Pb concentrations (84-87  $\mu\text{g g}^{-1}$ ) are found near the bogs surface but there are also other subsuperficial peaks (6-14  $\mu\text{g g}^{-1}$ ) indicating preindustrial atmospheric pollution. The enrichment factors (EFs) show in both cores a remarkably similar record. Atmospheric Pb pollution dates back to approximately 2,500 years ago, reaching a first maximum during the Roman Period. For the last 300 years, Pb EFs increase significantly due to industrial development but the uppermost sample of the bogs show decreasing Pb EFs, probably due to the phasing out of leaded gasoline. These results are also supported by  $^{206}\text{Pb}/^{207}\text{Pb}$  isotope ratio: it continuously decreases until 2,000 BP (from 1.275 at 4,070  $^{14}\text{C}$  yrs BP to 1.182), indicating the growing importance of Pb released from Iberian ores by ancient mining. Peat samples at 2-4 cm depth shows unradiogenic Pb ( $^{206}\text{Pb}/^{107}\text{Pb} = 1.157$ ), indicating the strong influence of leaded gasoline.

## INTRODUCTION

Penido Vello (PVO) and Pena da Cadela (PDC) bogs are ombrotrophic bogs located in the Xistral Mountains in Northwestern Spain, at elevations of 780 m and 970 m a.s.l. respectively, separated only 5 km and 20-25 km south of the coast. The mean annual temperature in the area ranges from 10 °C to 7.5 °C, and annual precipitation from 1400 to 1800 mm.

The present day vegetation is represented by *Sphagnum papillosum*, *Eriophorum angustifolium*, *Molina caerulea*, *Carex durieui*, *Erica mackaiana* and *Calluna vulgaris*. The bogs microtopography is very smooth.

The main characteristics of both bogs, as well as growth rates and some elements fluxes are given in Martínez Cortizas *et al.* (2000). The accumulation patterns of Pb, Cd and Zn extracted in KCl were previously studied (Martínez Cortizas *et al.*, 1997). Since the 1970s, a coal-fired power station approximately 25 km east of the bogs has been in operation.

Radiocarbon age dating of the basal samples of the cores indicated that they represent 4,000 and 4,600 years of peat accumulation. The maximum depths of the bogs is 3.5 m in PVO and 5 m in PDC, although with did not sampled them to the bottom.

## METHODS

The PVO and PDC bogs were sampled by cutting cores of 25 x 25 cm to a depth of 250 cm and 185 cm respectively in recent exposures. The cores were wrapped in plastic bags then aluminium foil, and brought to the laboratory. The fresh cores were immediately sliced into 2 cm slices (the upper meter of PVO and the whole PDC core) or into 5 cm slices (the rest of the PVO core). Peat samples were dried at 105 °C, milled to very fine powder and homogenized.

Lead and Ti concentrations were analyzed using the Energy-dispersive Miniprobe Multielement Analyzer (EMMA) at EMMA Analytical Inc. (Canada). This equipment is described elsewhere (Cheburkin *et al.*, 1997) as well as its application to trace element analysis of peats (Cheburkin & Shotykh, 1996). Detection limit for Pb is  $0.4 \mu\text{g g}^{-1}$  and for Ti  $30 \mu\text{g g}^{-1}$ . The instrument was calibrated using reference materials: NIST 1515, 1541, 1547, 1575 and BCR-60, BCR-62 and V-1. Lead isotope analysis were done by thermal ionisation mass spectrometry (TIMS) using a VG Sector mass spectrometer at the University of Berne (Switzerland). Peat samples from selected depths were sent for radiocarbon age dating .

Age models were obtained by calculating non-linear polynomial equations. Enrichment factors for Pb were also calculated by normalizing the Pb/Ti ratios of the peat samples to the Pb/Ti ratio of the upper continental crust after Wedepohl (1995).

## RESULTS AND DISCUSSION

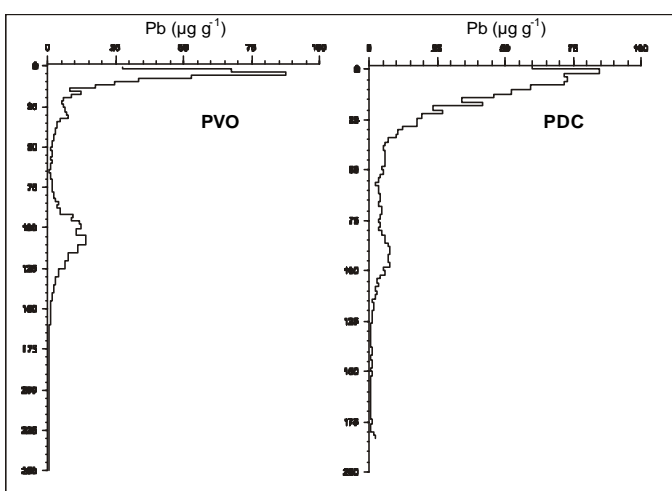


Fig. 1. Pb concentration profiles at the PVO and PDC bogs (Xistral Mountains, Northwestern Spain)

Table 1. Average and standard deviations of Pb fluxes for different periods in the PVO and PDC ombrotrophic peat bogs (in  $\mu\text{g m}^{-2} \text{y}^{-1}$ ).

Period	PVO	PDC
Last 300 years	$4575.0 \pm 2705.3$	$4530.0 \pm 1153.0$
Last 500 years	$3370.0 \pm 2918.5$	$3391.7 \pm 1744.2$
Middle Ages (500-1500 BP)	$186.1 \pm 125.1$	$307.1 \pm 193.0$
Roman period (1500-2100 BP)	$589.3 \pm 402.7$	$261.6 \pm 70.0$
Metal Ages (2100-2500 BP)	$98.0 \pm 80.3$	$94.3 \pm 31.2$
Background flux (>2500 BP)	$31.1 \pm 16.3$	$24.7 \pm 15.0$

Figure 1 shows the concentration profiles of PVO and PDC bogs. Highest Pb concentrations are found at depths of 3 cm (PDC) and 5 cm (PVO) and are remarkably similar, with  $84$  and  $87 \mu\text{g g}^{-1}$  respectively. Both cores also show a subsuperficial peak, at depths of 85-100 cm (PDC,  $6-7.5 \mu\text{g g}^{-1}$ ) and 90-115 cm (PVO,  $9-14 \mu\text{g g}^{-1}$ ). The variations of the concentrations of Pb can not be explained in terms of the ash content profiles or other properties of the peat and suggest they are related to variations on the deposition of Pb due to atmospheric pollution by mining and industrial activities since prehistoric times.

For peats older than 2,500 years Pb fluxes are similar in both bogs,  $25-30 \mu\text{g m}^{-2} \text{y}^{-1}$  and can be considered as background fluxes (Table 1). Since 2,500 years ago Pb fluxes increased continuously until the Roman period, although at this time the flux in PVO is more than 2-fold as compared with PDC. With the fall of the Roman Empire and during the Middle Ages the flux decreased, but the average Pb flux in PVO was 1.5-fold lower than in PDC. For peats younger than 500 years (since the discovery of America and after the Industrial Revolution) the average fluxes are again in good agreement for both bogs.

The chronology of the enrichment factors (EFs), calculated by normalising

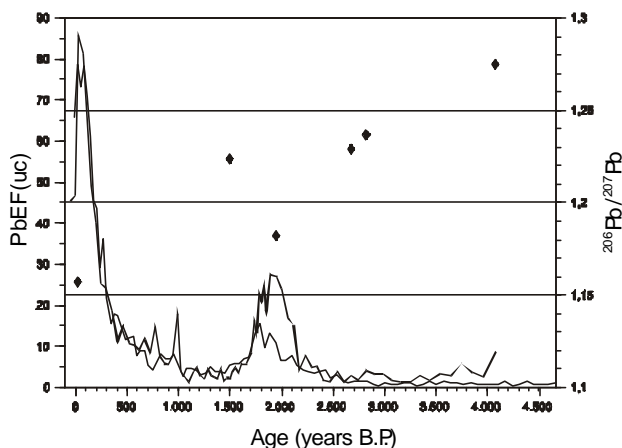


Fig. 2. Chronology of PbEFs in PVO (bold line) and PDC and  $^{206}\text{Pb}/^{207}\text{Pb}$  isotope ratios (diamonds) for selected PVO peat samples.

This ratio continuously decreases until 2,000 BP ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.182$ ), indicating the growing importance of Pb released from Iberian ores by ancient mining. The medieval times show again more radiogenic Pb, correlating with the decline of the Roman empire and its mining activity. Peat samples at 2-4 cm depth show unradiogenic Pb ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.157$ ), indicating the strong influence of leaded gasoline. This ratio agrees with measurements of Mediterranean trade winds ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.154 \pm 0.002$ ) at that time.

The record obtained for these two bogs is remarkably similar with that of world lead production during the last 5,500 years given by Settle and Patterson (1979) or by Nriagu (1996). The chronology has many features in common with the record showed by other peat cores from Europe (Lee & Tallis, 1973; Shotyk, 1996, 1998), ice cores from the Arctic (Hong et al., 1994) and extensive studies on atmospheric lead pollution using peat cores, lake sediments and boreal forest soils (Renberg et al., 2000). It also is in good agreement with previous studies in NW Spain and with the archaeological and historical records of Pb production in Spain (Martínez Cortizas *et al.*, 1997).

Nevertheless, despite the consistency in the history of Pb atmospheric pollution showed by the two bogs and shared with other records in Europe, it is worth mentioning that there are some striking differences in the enrichments, particularly when considering the bogs are separated by a short distance (5 km). The Pb EFs for PVO are greater than those of PDC until the II<sup>nd</sup> century AD. For peat samples older than 2,500 years EFs are up to 5 times, and for the Roman period are 2-3 times higher in PVO. This can not be explained by the differential growth of the bogs as the same feature is shown by the average Pb flux during the Roman period (also 2-fold in PVO, see Table 1). Nor it can be explained in terms of differences in the peat forming vegetation composition or other peat properties (ash content, degree of decomposition, ...).

At least for the Roman Period it is obvious from Figure 1 that Pb concentrations are higher at PVO, indicating a greater deposition at lower elevations (PVO, 780 m a.s.l.). This would imply an increased dry deposition since the present gradient of precipitation (Martínez Cortizas & Pérez Alberti, 2000) suggests a higher wet deposition at PDC, and there is no evidence of a change of the gradient during Roman times.

More interesting is the fact that Ti concentrations of PVO have been lower than those of PDC for the last 4,000 years (data not shown): minimum observed values for PVO are 30-50  $\mu\text{g g}^{-1}$  while for PDC they are not lower than 100  $\mu\text{g g}^{-1}$ , indicating a greater Ti accumulation at higher altitude (PDC, 970 m a.s.l.). It may be the result of a chemical fractionation of the element

to the Pb/Ti ratio of the upper continental crust, show a consistent history of Pb pollution.

Since 2,500 years ago until the II<sup>nd</sup> century AD Pb EFs increase to reach a maximum at the I<sup>st</sup> century AD (30 times the natural background value in PVO and 15 times in PDC). After that the Pb EFs decrease to almost background values. Since 1,000 BP the EFs increase again but after 500 BP it rises abruptly to EFs values indicating fluxes 75 to 85 fold the natural background fluxes. In recent times Pb pollution seems to have decreased again.

This interpretation is also supported by the Pb isotope ratios of a selected set of samples of the PVO bog. The preanthropogenic Pb shows a strongly radiogenic signature with a  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of 1.275 at 4,070  $^{14}\text{C}$  yrs BP.

caused by a physical fractionation during dust transport. This is in agreement with results obtained in studies on atmospheric mineral dust. Schuetz (1989) indicates that size, mass and concentration of most elements change drastically during transport, and some of them (i.e. Ti, Hf, ...) are strongly enriched in the 10-20 $\mu$ m fraction; while for particles with sizes <5 $\mu$ m most elements are found in crustal proportions. As the coarse components of the dust settle during transport the concentration of the elements also changes. This effect seems to be more intense at transport distances very close to the source area and attenuates during long range transport since the grain size of the dust decreases and homogenizes. In our bogs, the Pb EFs for peat samples older than 2,500, assume to represent natural background variations, also support this idea: average Pb EF for PDC is  $0.91 \pm 0.41$  and for PVO  $3.12 \pm 1.79$ , suggesting that the difference in altitude is playing an important role on element fractionation.

We sampled and analysed a set of 20 soils of the area to see whether the local source of dust has the potential to contribute to the fractionation. We found that Ti in the clay is enriched 2 times in comparison to the silt. So it is reasonable to assume that the physical fractionation of dust during transport may contribute to a chemical fractionation of the element. At the lowest elevation (PVO) the dust load seems to be enriched in coarser particles and depleted in Ti and at the higher elevation (PDC) it seems to be enriched in finer particles and, thus, in Ti.

It can be concluded, that the enrichment factors calculated using lithogenic elements, like Ti, which are subject to fractionation by the atmospheric processes that control dust deposition and transport, have to be carefully considered when comparing the results obtained for different bogs.

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