Atmospheric Pb pollution in N Iberia during the late Iron Age/Roman times reconstructed using the high-resolution record of La Molina mire (Asturias, Spain)

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Abstract Extensive mining took place in Spain during the Iron Age and Roman times, although a detailed chronology is still lacking due to the inherent difficulties in dating mining structures. In this study we sampled and analyzed a core from La Molina mire in the Asturias region, northern Spain. Because more than 100 Roman mines have thus far been found within 20 km of the mire, our aim was to shed light on local mining history, which we can then compare to the wider narrative of early mining pollution in Spain. We focus on the section from ~500 BC to AD ~600, which has a high temporal resolution of 6–15 year per sample. Geochemical analyses included the determination of major, minor and trace lithogenic elements (Si, Al, Fe, Ti, Ga, Rb, Y, Zr, Th) as markers of mineral content of the peat, and trace metals/metalloids (Mn, Cu, Ni, As, Pb) as well stable Pb isotopes, as potential markers of atmospheric metal pollution. The use of principal components analysis enabled the identification of a dominant geogenic component and a secondary pollution component. The earliest pollution signal of the covered period was recorded by ~300 BC, coinciding with the late local Iron Age. Average $^{206}Pb/^{207}Pb$ ratios of samples with ages older than this date was 1.204 ± 0.002, while all samples with a younger age had a less radiogenic ratio. Based on the metal pollution component four phases were identified: I, ~500 to 300 BC; II, ~300 to 20 BC; III, ~20 BC–AD 480; IV, AD ~480 to 600. The lowest isotopic ratio and highest proportion of

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pollution Pb (^{206}Pb/^{207}Pb ratio of 1.157 and 89 % of total accumulated Pb) was reached at peak Pb production during Roman times (AD ∼180 to 340), indicating that this was the period of most intense metal contamination in the area over the studied period. It is remarkable that the La Molina record shows a more extended period (two centuries) of active mining in comparison with other areas in Iberia, and a pattern of repeated shifts in Pb pollution of short duration, which is likely related to the local history of exploitation and exhaustion of mines within the area.

Introduction

The evidence for long-range preindustrial atmospheric metal pollution was first established by analyzing Pb in an ice core from Greenland (Murozomi et al. 1969). Later studies confirmed and extended the metal pollution record to ancient times (Ng and Patterson 1981; Boutron and Patterson 1983; Hong et al. 1994, 1996; Rosman et al. 1997). The increased metal concentrations detected in the ice were related to the pace of historical global Pb production due to mining and metallurgical activities (Patterson 1971; Nriagu 1980, 1983, 1998). Only a few years after the first discovery of Pb pollution signals in the Greenland ice, studies from the British Isles demonstrated that peatlands also recorded prehistoric Pb pollution (Lee and Tallis 1973; Livett et al. 1979; Martin et al. 1979), but in contrast to the Greenland record this pollution was connected to historical Pb production on the British Isles. Since then, the type and number of archives used to trace past pollution has expanded to include lake sediments (Renberg et al. 1994), river sediments (Matschullat et al. 1997), estuarine sediments and coastal marshes (Leblanc et al. 2000; Alfonso et al. 2001), mine sediments (Mighall et al. 2002a), complex soils (Kylander et al. 2008), mussel shells (Labonne et al. 1998), human bones (Drasch 1982) and marine plant remains (Serrano et al. 2011).

Across much of Europe, these natural archives have shown that the start of atmospheric metal pollution can be traced back to the Bronze Age, to as early as ∼2530 BC in Spain (Leblanc et al. 2000) and ∼2400 BC in

Britain (Mighall et al. 2002b). Taken together, ice, peat and sediment archives have shown that the most widespread pollution phase in ancient times was the one starting in the late Iron Age and peaking in Roman times. This signal is related to mining and metallurgy by Iron Age cultures such as the Phoenicians, Carthaginians and the Greek and Roman Empires and it has been detected in almost all studied records in western, central and northern Europe spanning at least the last 3000 years. The general trend shows a start ∼1000 to 500 BC, peaking by the first and second centuries AD and collapsing by ∼AD 400. This is the case for Sweden (Renberg et al. 1994, 2001; Brännvall et al. 1997, 2001; Bindler 2011), Britain (Lee and Tallis 1973; West et al. 1997; Mighall et al. 2002a, 2002b, 2002c, 2009; Le Roux et al. 2004), Germany (Matschullat et al. 1997; Hettwer et al. 2003), France (Alfonso et al. 2001; Négrel et al. 2004), and Switzerland (Shotyk et al. 1996, 1998; Weiss et al. 1997; Zaccone et al. 2007). In some regions, this chronology is so consistent that it has been suggested that Pb can be used as a chronological marker (Renberg et al. 2001).

Although there is a common narrative of historical Pb and metal pollution across much of Europe, there are, nevertheless, local histories showing important differences, which can be of particular interest for historical and archaeological studies and studies of regional environmental changes. In Sweden, for example, the early signal has been attributed to long-range transport of pollution (Brännvall et al. 1997; Klaminder et al. 2003). No Iron Age phase was detected in records from the Eifel area in Germany (Schettler and Romer 1998), Southern France (Labonne et al. 1998) and Ireland (Schettler and Romer 2006). No Roman peak occurred in records from Bavaria (Küster and Rehfuess 1997) and Central and South-eastern France (Monna et al. 2004a, 2004b; Baron et al. 2005). Evidence for only a weak pollution signal in the Roman period was found in Finland (Meriläinen et al. 2010). All these examples suggest specific regional variations in the evolution of mining and metallurgy in prehistoric and ancient times across Europe.

Nriagu (1980) estimated that the peak in production during the Roman Empire was about 50,000 tons of Pb. Iberia was one of the main mining areas during this period, and mining here accounted for about 40 % of the global production (Nriagu 1983). Large-scale mining took place in SE (near Cartagena and Mazarrón), SW (Río Tinto) and NW Spain (Lewis and

Jones 1970; Flores 1981; Rosman et al. 1997). In this study we present the results of a high-resolution analysis of a peat core from La Molina, a bog located in Asturias (NW Spain), an area that was intensely mined for gold during Roman times. Within 20 km of the mire there are more than 100 known mining sites connected to the Roman period (Perea and Sánchez-Palencia 1995). The analyses include major, minor and trace lithogenic elements (Si, Al, Fe, Ti, Ga, Rb, Y, Zr, Th), Pb and Pb isotopes, and other trace metals/metalloids (Mn, Cu, Ni, As). In contrast to previous work on peat records from the mountains in NW Spain (Martínez Cortizas et al. 1997, 2002, Kylander et al. 2005), La Molina has an exceptionally good resolution for the Late Iron Age/Roman period ($\sim$500 BC–AD $\sim$500), providing a detailed reconstruction of the chronology of local/regional atmospheric metal pollution from $\sim$500 BC to the present. Comparison with records available for N Spain also enabled us to detect differences in the history of mining and metallurgy during the Roman period.

Site description

La Molina is a mire macrotope located in the Alto de La Espina range at 650 m a.s.l. (Concejo de Salas, Asturias, NW Spain) (43°22′52.2″N, 6°19′38.4″W; Fig. 1). It is dominated by acid *Sphagnum* bogs, and was declared a Site of Community Importance in the Natura 2000 network. Other taxa present are *Scirpus* sp., *Festuca* sp., *Polygonum amphibium* L, *Menyanthes trifoliata* L, *Molinia caerulea* (L) Moench, *Potentilla* sp., *Dactylorhiza maculata* (L) Soó, *Digitalis purpurea* L., *Mentha rotundifolia* (L) Huds and Ericaceae (*Erica tetralix* L, *E. mackaiana* Bab and *Calluna vulgaris* (L) Hull). Present-day forests are remnants of the original deciduous species that once were abundant, mainly oak (*Quercus robur* L), beech (*Fagus sylvatica* L), birch (*Betula alba* L), and chestnut (*Castanea sativa* Mill). Forest crops of pine species and *Eucalyptus globulus* Labill dominate, together with fields of cereal crops and pasture.

The area belongs to the Narcea Antiform that was raised during the Tertiary and modified by differential erosion, forming a system of ridges of moderate elevation (600–800 m a.s.l.). The lithology is comprised of quartzite and slates. The La Molina mire complex is close (4 km NW) to the Narcea and Pigüeña basins, where many gold deposits have been found, which belonged to the Roman *Conventus Asturum* (Perea and Sánchez-Palencia 1995). In Roman times the common way to extract the gold was through hydraulic force with water-canalization systems (*corrugi*) and water deposits (*piscinae* or *stagna*). Remains of these Roman hydraulic infrastructures with canals having secondary branches fed with water from the mountains still exist in the Narcea-Pigüeña area (Fernández Mier 1999).

Materials and methods

Sampling

A 215-cm-deep peat core was collected on July 2005 using a Russian peat corer (50-cm-long and 5 cm in diameter). Peat sections were placed in PVC tubes, protected in plastic guttering and stored under cold conditions (4 °C) prior to laboratory sub-sampling and analysis. The core was sectioned into continuous 1-cm-thick slices. From each section, a sub-sample was taken and stored for later microfossil analysis, while the rest was dried at 105 °C and ground to fine powder (<50 μm) using an automatic agate mortar (pre-cleaned with diluted HCl and MilliQ water). Here we only present data for the section between 115 and 45 cm of depth, which spans from $\sim$500 cal BC to AD $\sim$600.

Two units could be distinguished in the stratigraphy of this part of the core, Unit I (115–87 cm) consists of brown peat rich in mineral matter, and Unit II (87–43 cm) is black peat with four layers rich in mineral matter.

Bulk density

Bulk density was determined by taking three plugs 1-cm-thick with a cylinder of 2 cm in diameter. The peat was then dried at 105°C until constant weight and the density expressed as the average dry mass per cubic centimetre of the three plugs.

Elemental composition of the peat

The elemental composition of the peat was determined in the dried, milled and homogenized samples. Carbon content was determined using a Leco-Truspec CHNS analyzer. Concentrations of major, minor and trace
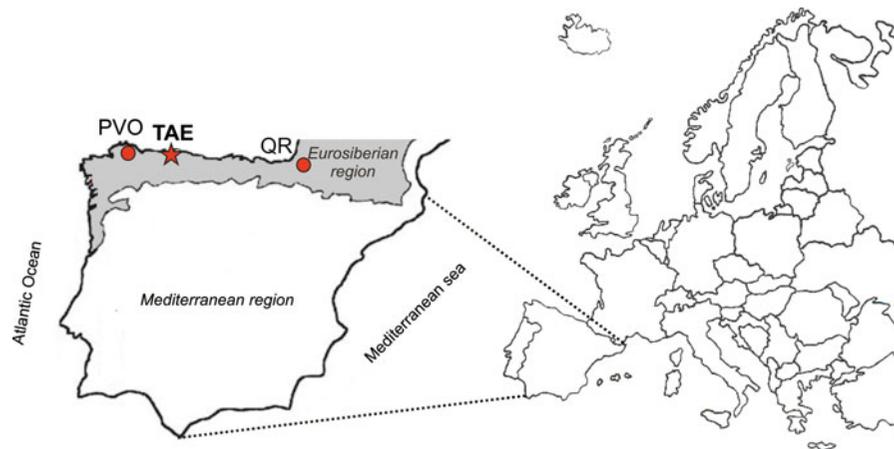
Fig. 1 Location of La Molina mire (TAE, *red star*), Penido Vello bog (PVO) and Quinto Real mire (QR) (*red circles*). (Color figure online)

lithogenic elements (Si, Al, Fe, Ti, Ga, Rb, Y, Zr, Th) and trace metals and metalloids (Pb, Mn, Ni, Cu and As) were obtained by X-ray fluorescence dispersive EMMA-XRF analysis (Cheburkin and Shotyk 1996; Weiss and Shotyk 1998). The instruments are hosted at the RIAIDT (Infrastructure Network for the Support of Research and Technological Development) facility of the University of Santiago de Compostela (Spain). Standard reference materials were used for the calibration of the instruments. Quantification limits were 0.01 % for Al, Fe, Ti, 0.05 % for Si, 0.5 $\mu g\ g^{-1}$ for Pb and Th, and 1 $\mu g\ g^{-1}$ for the other trace elements. Replicate measurements were done on one of every five samples in order to account for reproducibility; all replicates agreed within a 5 %.

Isotopic analyses

Lead stable isotopes were determined using Quadrupole ICP-MS (Perkin-Elmer ELAN 6100; Umeå University, Sweden) after strong acid digestion ($HNO_3 + HClO_4$, 10:1 at 130 °C) of $\sim$0.15–0.25 g of dried (105 °C) peat in open Teflon vessels (Renberg et al. 2002). Dwell times of 50 ms were used and isotopic values were corrected empirically for fractionation by repeated analysis of NIST SMR 981 reference Pb material (1.081 ± 0.0033 per a.m.u.). Within-run accuracy was confirmed by analysis of a reference lake sediment, IAEA SL-1 (Bindler et al. 2004), and was $\pm$ 0.0025.

To estimate the concentration of pollution Pb to the total Pb accumulated in the peat samples, we have used a simple binary mixing model (Kylander et al. 2005):

$$Pb_P = \frac{^{206}Pb/^{207}Pb_{peatsample} - ^{206}Pb/^{207}Pb_{prepoll}}{^{206}Pb/^{207}Pb_{pollution} - ^{206}Pb/^{207}Pb_{prepoll}} \times Total\ Pb$$

where Pb_P is the proportion of Pb originating from pollution sources, $^{206}Pb/^{207}Pb_{peat\ sample}$ is the isotopic ratio of the peat sample, $^{206}Pb/^{207}Pb_{pollution}$ is the ratio of atmospheric Pb pollution and $^{206}Pb/^{207}Pb_{prepoll}$ is the ratio for samples older than 2300 cal BP.

Radiocarbon dating and chronology

Six peat samples from the upper 131 cm of the core were selected for ^{14}C and sent to the Ångstrom Laboratory at the Uppsala University (Sweden) and the Centro Nacional de Aceleradores (CSIC, Spain), where the AMS technique was applied. The ^{14}C dates (Electronic Supplementary Material, ESM 1) were calibrated using the IntCaL09.14C calibration curve (Reimer et al. 2009), and they were used to produce an age-depth model. We also constrained the age model by assigning an age of AD 1975 to the near-surface peat section showing the largest Pb concentration and the recent lowest $^{206}Pb/^{207}Pb$ ratio as found in previous investigations in NW Spain (Kylander et al. 2005; Martínez Cortizas et al. 2012), although reconstructing recent atmospheric metal pollution is not the objective of this research. The age/depth model (Electronic Supplementary Material, ESM 2) was obtained using

the Clam program developed by Blaauw (2010; http://chrono.qub.ac.uk/blaauw/wiggles/). The best fit was obtained with a fourth order polynomial. According to this model, the 115-cm section represents the last ∼2500 years and the time resolution is particularly good (15–6 years per sample) for the period 2100–1760 cal BP. All dates provided are in calibrated years unless specified otherwise.

Statistical analysis

We performed a factor analysis by principal components (PCA, correlation mode and varimax rotation) on the chemical composition of the peat, using the lithogenic and metal tracers. Before analysis, the data were standardized (Z-scores calculated as: $[X_i - X_{avg}]$/STD, where X_i is the concentration of a given element in a given sample, X_{avg} is the average of the population and STD is the standard deviation) to avoid the scaling effect and obtain average-centered distributions (Eriksson et al. 1999). PCA analysis was done using the SPSS 15.0 software package.

A varimax rotation solution was applied to maximize the loadings of the variables on the components. In practice, this rotation allocates into the components variables that are highly correlated (i.e. sharing a large proportion of their variance). Because we deal with records of chemical elements, this means that the components will contain elements showing very similar records. In this way, the chemical signals tend to be more clear and helpful to identify and interpret the underlying (latent) factors affecting them.

Results

Bulk density and carbon content

The bulk density variations (Fig. 2) in the section of interest for this research can be divided into three main sections: from 115 to 103 cm bulk density shows the largest values, 0.36–0.51 g cm^{-3}; values decrease almost steadily from 0.3 to 0.14 g cm^{-3} until 85 cm, and then remain almost constant (0.10–0.13 g cm^{-3}) until 45 cm.

Carbon content is lower below 85 cm (Fig. 2), with values ranging from 10 to 20 %. Above 85 cm the content rises abruptly, varying between 25 and 45 %

(most samples between 35 and 40 %). Peaks in concentration occur at 81 cm, 71–68, 63–60 and 54–51 cm. A sharp decrease is noticeable at 51–49 cm, with values comparable to the lower section.

Lithogenic elements

The depth records of lithogenic elements (Fig. 2), except for Fe, show an opposite variation to that of the carbon content (R = −0.92 to −0.95). Concentrations are highest below 87–85 cm, are almost constant for Si, Ti, Zr and Th, and show a two stepped decrease (with a local minimum at 97 cm) for Al, Ga, Rb and Y. Above 87–85 cm a well-defined pattern of peaks is shared by all elements, including Fe, with local maxima at 75 cm, 66 cm, 57 cm, and 51–49 cm (the largest of this section of the core).

Iron concentrations are fairly constant, with most samples showing values between 0.6 and 1.6 %, apart from the peaks already mentioned (1.7–4.0 %). The largest concentrations were found at 51–49 cm (Fig. 2).

Metals and Pb isotope ratios

Lead concentrations show little variation below 72 cm (Fig. 3) with values mostly around 15–19 µg g^{-1}, although small peaks can be identified at 100, 89, 83, and 75–72 cm. Between 72 and 47 cm concentrations initially drop to show a local minimum (6 µg g^{-1}) at 69 cm and increase abruptly after that peaking at 64, 56–54 and 51 cm, the latter peak having the highest Pb concentration (34 µg g^{-1}). After the last peak, Pb concentrations abruptly decrease to minimum values (4–5 µg g^{-1}) until 45 cm.

Lead enrichment factors (EF), calculated by normalizing to Al and using the average Pb/Al ratio of the base of the core (samples older than 8000 yr cal BP) as reference material, show background values below 106 cm (Fig. 3; note that we represented the inverse of the EF for the sake of comparison to the isotope ratios), increasing values between 106–100 cm, remain almost constant until 87 cm, show an increasing trend until 52 cm (with local minima at 79, 72, 64, and 55 cm) and decrease sharply above 52 cm. Lead accumulation rates show an average value of 3.2 ± 0.4 mg m^{-2} year^{-1} below 72 cm (which is 3.4-fold the average background accumulation rate). Above this depth, values continuously decrease to reach background values from 52 cm upwards.

Fig. 2 Records of bulk density (g cm^{-3}), carbon (%), major, minor (%) and trace lithogenic elements (µg g^{-1}) in the core sampled at La Molina mire (Asturias, Spain)
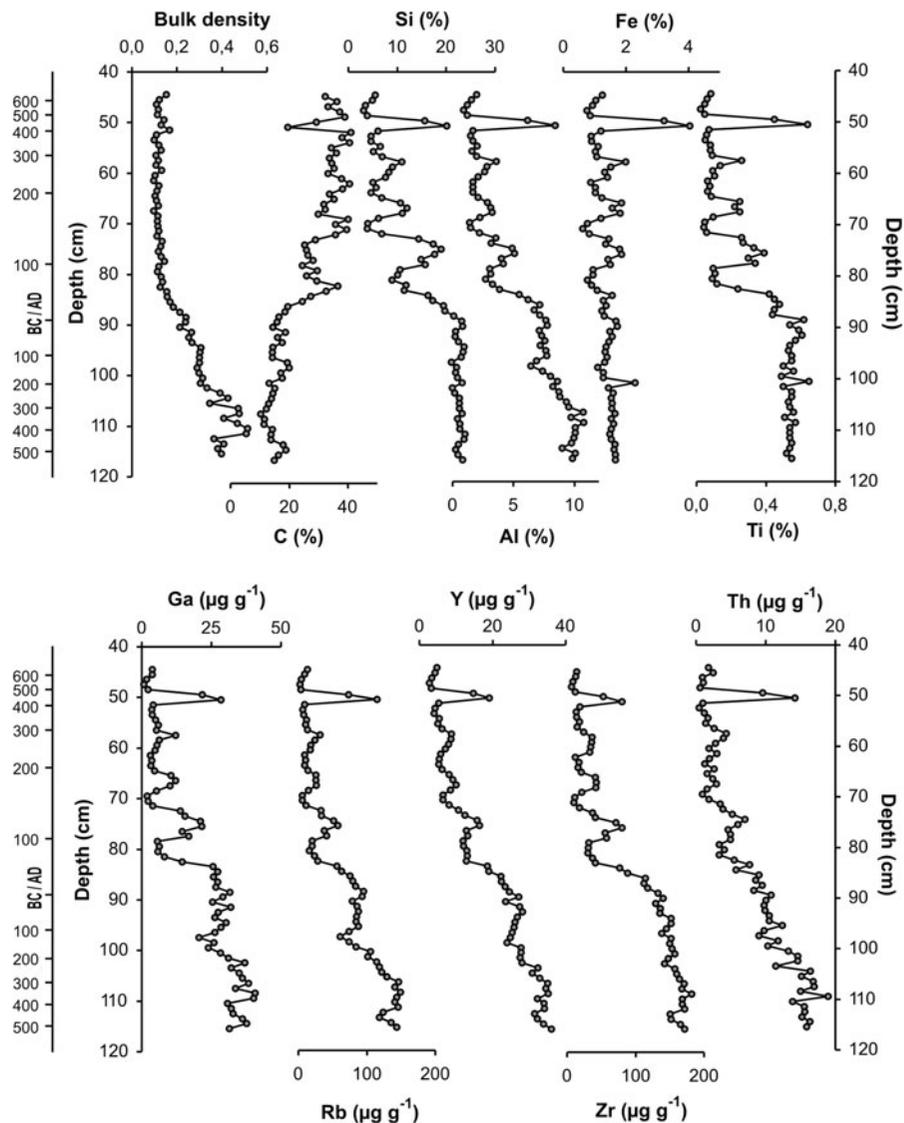
Lead isotopes, expressed as ^{206}Pb/^{207}Pb ratios, show the highest values (1.209–1.203) in samples below 106 cm, comparable to the average ratio (1.204 ± 0.002) found for samples older than 8000 cal yr BP (Fig. 3). From 106 to 52 cm the isotopic ratio decreases to reach a minimum value of 1.157. Within this decreasing trend local shifts to lower ^{206}Pb/^{207}Pb ratios are found at 100, 89, 79, 72, 64 and 55 cm. The isotope ratio shows a highly significant correlation to the inverse of the enrichment factor (Pearson correlation coefficient R = 0.95), but only moderate correlation with Pb accumulation rates (Pearson correlation coefficient R = 0.62).

The other metals analyzed show more irregular records (Fig. 3) that broadly coincide with that of the lithogenic elements: lower variation below 85 cm and a similar pattern of elevated concentrations between 85 and 45 cm.

Separating lithogenic and pollution components

Successful separation of chemical and biological signals in environmental archives has been obtained by other authors using PCA (Koinig et al. 2003; Muller et al. 2008; López-Merino et al. 2010, 2011; Martín-Puertas et al. 2011; Serrano et al. 2011). To separate
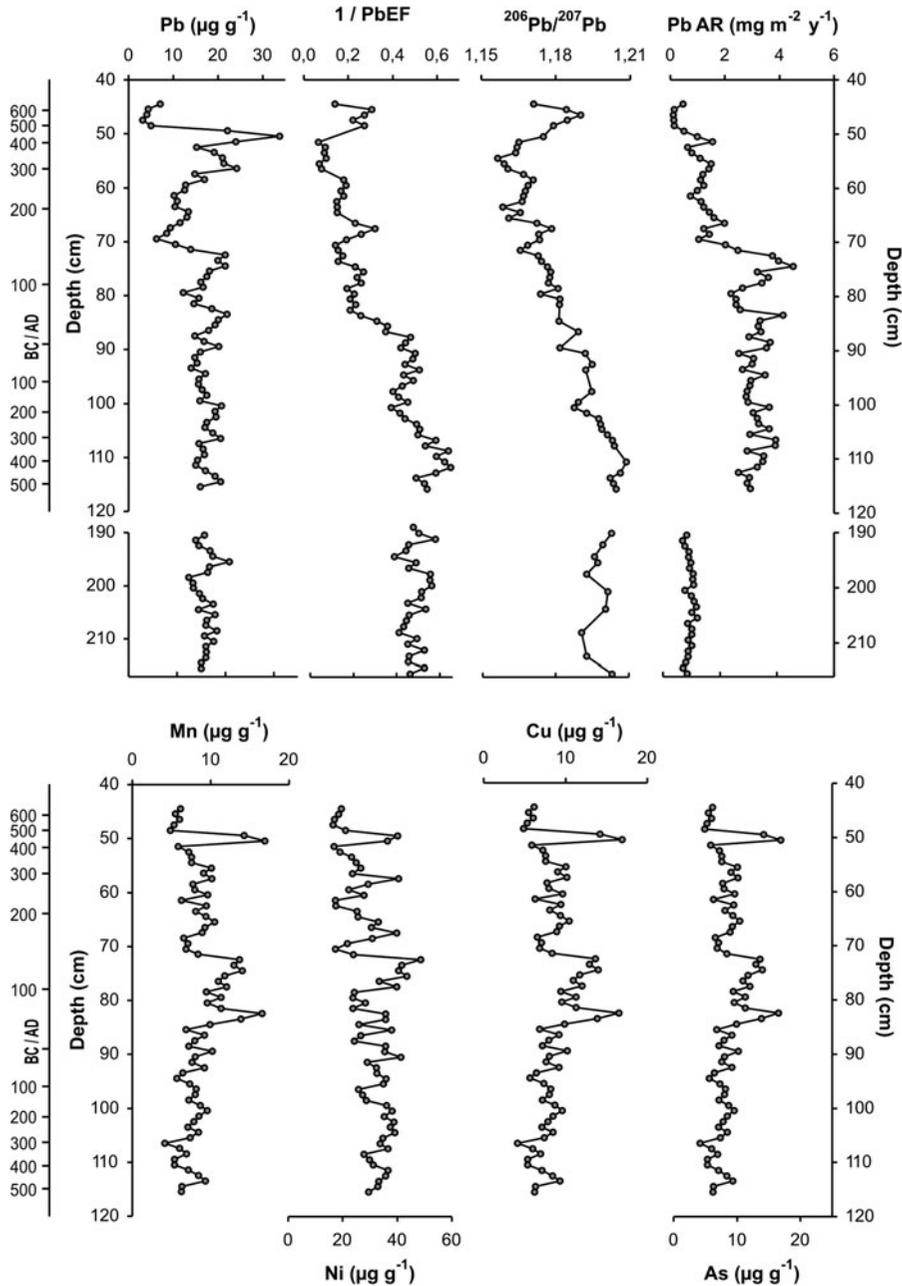
Fig. 3 Record of lead concentrations (μg g^{-1}), lead enrichment factors (note that we represented the inverse of the EF for the sake of comparison to the isotope ratios), lead isotope ratios (^{206}Pb/^{207}Pb), lead accumulation rates (mg m^{-2} year^{-1}), trace metals/metalloids (Mn, Ni, Cu, As; μg g^{-1}) in the core sampled at La Molina mire (Asturias, Spain). Error bars were not included because they are smaller or similar in size to the sample symbols

the possible contribution of lithogenic (soil dust) and pollution sources of Pb and other metals in La Molina mire, we have also performed a PCA that included lithogenic tracers, metals and ^{206}Pb/^{207}Pb ratios for samples below 45 cm (from $\sim$500 BC to AD $\sim$600).

Two principal components accounted for 85 % of the total variance of this set of elements. The first principal component, PC1, explained 74 % and the second principal component, PC2, explained 11 % of the total variance. PC1 is characterized by very large

positive loadings (0.91–0.98, Table 1) of the litho-genic elements, and also high loadings (0.73–0.87) of the trace metals. Thus, this component seems to account for the mineral content of the peat, and the underlying factor is the geogenic contribution to the peat. PC2 is characterized by a large positive loading (0.95, Table 1) of the $^{206}Pb/^{207}Pb$ ratio and we can safely interpret it as indicating metal (Pb) pollution. This is also supported by the highly significant correlation (R = 0.97) between the PC2 scores and the inverse of the Pb enrichment factors.

For all lithogenic elements, more than 80 % of their variance is explained by the geogenic contribution (PC1), which would be derived from sources such as soil erosion. For the trace metals the largest contribution (53–75 %) to their variance is also related to geogenic sources. But part of the variation in Pb concentrations (22 %) is explained by the pollution component (PC2). The negative factor loading of Pb in PC2 (Table 1) indicates that its concentration increases with decreasing isotopic ratios, as expected if it was associated with pollution (pollution sources have lower $^{206}Pb/^{207}Pb$ ratios, Rosman et al. 1997; Kylander et al. 2005). Part of the variance of Fe and Mn is also allocated to this component, but being redox-sensitive elements subject to post-depositional

Table 1 Factor loadings of the variables used in the PCA analysis (because the PCA was performed on the correlation mode, the square of the factor loadings accounts for the proportion of variance of each element associated to the principal components)

	PC1	PC2
Ti	0.98	0.06
Al	0.97	0.11
Ga	0.97	0.11
Rb	0.97	0.05
Si	0.96	0.13
Th	0.93	0.07
Zr	0.91	0.24
Y	0.91	0.26
Cu	0.87	0.01
Ni	0.82	−0.08
As	0.81	−0.21
Fe	0.79	−0.32
Mn	0.78	−0.45
Pb	0.73	−0.47
$^{206}Pb/^{207}Pb$	0.23	0.95

remobilization a direct link to pollution is difficult to assess.

Figure 4 represents the records of factor scores for the two principal components. Factor scores are non-dimensional, average-centered values that measure the intensity of each factor. Positive scores in PC1 indicate increased mineral dust content in the peat, while larger negative scores in PC2 indicate increased atmospheric metal pollution. Based on the pollution signal (PC2 scores; note that the X-axis has been inverted in Fig. 4), the peat record can be divided into four main sections: (I) below 106 cm the largest positive values are observed; (II) 106–89 cm, decreasing positive values in two steps (IIa and IIb); (III) 89–49 cm, a see-saw pattern of progressively more negative scores with local largest negative values between 57–49 cm (IIIb); and (IV) 49–45 cm, an abrupt change to positive values.

Discussion

Sourcing the metal (Pb) pollution

A thorough review of the isotopic composition of possible Pb sources in NW Spain was done by Kylander et al. (2005). Figure 5 summarizes some of the most important sources in a three-isotopes plot. The $^{206}Pb/^{207}Pb$ ratio of samples of section I (1.204 ± 0.002, n = 9) is identical to the pre-pollution aerosol (PPA; estimated as the average of samples with ages older than 8000 yr cal BP—Fig. 3). This ratio is lower than that found in other peat records from NW Spain (Martínez Cortizas et al. 2002; Kylander et al. 2005) but comparable to those found in other areas of Europe (Kylander et al. 2010). In sections II and III the trend shows a continuous change from these values that suggests a mixing of two components (Fig. 5), but at least five of the sources identified by Kylander et al. (2005), Saharan dust, and ores from N, NW and SW Spain, fit within the field of variation of the $^{208}Pb-^{206}Pb-^{206}Pb/^{207}Pb$ ratios of samples from the La Molina mire older than AD ~600. The effect of Saharan dust may have been significant only in pre- and early-pollution times, because its isotopic composition is quite similar to that of samples of section II. The ores from N and SW Spain cannot be discarded as possible sources, but some samples of the upper part of section IIIa and those of section IIIb show isotopic

Fig. 5 Three-isotope plot with identification of possible Pb
sources. NWSp PPA: NW Spain pre-pollution aerosol; NSp-or
and SWSp-or: N and SW Spain ores; NWSp-or1 and or2: NW
Spain ores; NWSp-sl: NW Spain soils; SD: Saharan dust. Phase
I: *black circles*; phase II: *open circles* (IIa) and *shaded circles*
(IIb); phase III: *open diamonds* (IIIa), *shaded diamonds* (IIIb);
phase IV: *open squares*

ratios that fall beyond the field of these ores (particu-
larly the N Spain ore), pointing to a different end-
member source. Thus, the ores from NW Spain are the
more likely sources of pollution Pb. These sources
have an average $^{206}Pb/^{207}Pb$ ratio of 1.153, which is
lower than ores of SW Spain (Stos-Gale et al. 1995; we
used this value as the reference to calculate the
contribution of pollution Pb). A similar result was
obtained by Monna et al. (2004a) in the analysis of a
peat record (Quinto Real) from the Pyrenees, in which
no inputs of Pb from SW Spain were detected possibly
due to masking by the local inputs.

In section IV (after AD ∼480), the isotopic
composition shows a return to more radiogenic
signatures similar to those of section II (up to 1.190).

Chronology of atmospheric metal pollution in late
Iron Age and Roman times

In Figure 6 we have represented the chronology of the
changes in metal pollution (record of PC2 scores)
based on the age/depth model, and the main features of
the sections defined previously are synthesized in
Table 2. As indicated in the introduction, generalized
atmospheric metal pollution in Europe had started by

∼1000 to 500 BC, peaked during the first and second
century AD and collapsed by AD ∼400. The record
from La Molina mire is similar to this overall
chronology, confirming the general pattern. However,
because La Molina peat record contains a much higher

level of detail during this early pollution period than previous studies (Martínez Cortizas et al. 2002; Kylander et al. 2005), we see not only this common European narrative of long-term atmospheric metal pollution but also changing patterns of prehistoric and ancient mining and metallurgy within Spain that reflect a local/regional history. The main difference is the relatively later start, because the data suggest that no significant mining activity took place in the early and middle Iron Age (until ~300 BC, Table 2) in the surroundings of La Molina.

The metal record of Penido Vello (PVO), a mountain blanket bog (780 m a.s.l.) located 100 km west of La Molina, suggests that atmospheric pollution in NW Spain started by ~1250 BC (Kylander et al. 2005). In contrast, the first signs of metal pollution in the last ~2500 years in La Molina mire do not occur until ~300 BC (section IIa, Fig. 6B, D), during the late local Iron Age, with an increasing trend until ~180 BC, when it reached a local maximum, and then stabilized for a short period until ~20 BC. This first pollution signal in La Molina coincides approximately with a prominent increase in Pb and decrease in the isotopic ratio ($^{206}Pb/^{207}Pb$) in the PVO record from ~570 BC and a decrease in the isotopic ratio in the Quinto Real mire (located 400 km to the east of La Molina; Monna et al. 2004a) (Fig. 6C). Although no variations were found in La Molina for Pb accumulation with regard to the previous phase, average Pb isotopic ratios changed from 1.198 to 1.192 and the proportion of pollution Pb increased from about 6 % to stabilize around 20 %, notwithstanding the maximum (32 %) at ~180 BC (Table 2). For this period, total Pb accumulation rates in La Molina (Table 2) were more than three times greater than those recorded in PVO (Kylander et al. 2005), but the accumulation rate of pollution Pb was quite similar (0.89 ± 0.31 mg m^{-2} year^{-1} in La Molina and 0.85 mg m^{-2} year^{-1} in PVO).

From ~20 BC Pb pollution continuously increased to peak by AD ~180 (phase IIIa, Fig. 6B, D). Relatively high levels of pollution were maintained until AD ~480 (phase IIIb, Fig. 6B, D), encompassing the whole Roman period. The average Pb isotopic ratio decreased to 1.174 and 1.165 (phases IIIa and IIIb respectively), and pollution Pb represented between a minimum of 20 % at the beginning of the phase and maximum of 89 % by AD ~180 (Table 2). Contrary to this evidence, total Pb accumulation rates decreased (Table 2). This was due to a dramatic reduction in Pb

fluxes from geogenic sources, as indicated by the negative correlation between Pb accumulation and isotopic composition mentioned above. Pollution Pb accumulation rates increased slightly in phase IIIa (1.05 ± 0.33 mg m^{-2} year^{-1}) but more than doubled in phase IIIb (2.24 ± 0.68 mg m^{-2} year^{-1}) when the lowest $^{206}Pb/^{207}Pb$ ratio (1.159, Fig. 3) of the whole record occurred (Fig. 6C).

In the PVO record, Kylander et al. (2005) divided the Roman period into two pollution phases, one until AD ~190 and a second one until AD ~510, similar to that proposed by Monna et al. (2004a) for Quinto Real; which are congruent with the general pollution pattern found at La Molina. This suggests the same overall chronology for the Roman mining/metallurgy period across N Spain. A significant difference is that since AD ~190 Pb accumulation rates decreased (to 0.16 ± 0.13 mg m^{-2} year^{-1}) and the isotopic ratio increased in the Galician area (represented by the PVO record, a bog located in the *C. Lucensis*) while accumulation rates remained high (Fig. 6C) in the Asturian area (represented by La Molina mire, located in the *C. Asturum*) and in the Pyrenees (Quinto Real), being up to 14-fold greater at La Molina than at PVO. Thus, after AD ~180 a period of intense mining and metallurgy may have been maintained for more than two centuries in the Asturian and Pyrenean areas, but finally ended synchronously with NW Spain.

One interesting feature of the record of La Molina for the Roman period is the see-saw pattern shown by pollution (Fig. 6D). At least six local maxima are identifiable, centred at ~20 BC, AD ~65, AD ~140, AD ~180, AD ~320 and AD ~440, pointing to changes in the intensity of mining and metallurgy in the area. This pattern is also followed by Pb enrichment factors (Fig. 3), the mineral matter content of the peat (PC1 scores, Fig. 6D) and the total tree pollen influx (Fig. 6E). Peaks in atmospheric metal pollution were accompanied by increases in dust load to the mire and by reductions of tree pollen influx (forest cover). At the beginning of the Roman period recoveries of the forest occurred during phases of low metal atmospheric pollution, but since AD ~180 almost no recovery took place, which may indicate that the forests reached a no-return state due to the intense anthropogenic impact. The scale of transformations linked to the intensification of ore exploitation was also reflected in other areas by a dramatic decline in forest cover and increased soil erosion during the
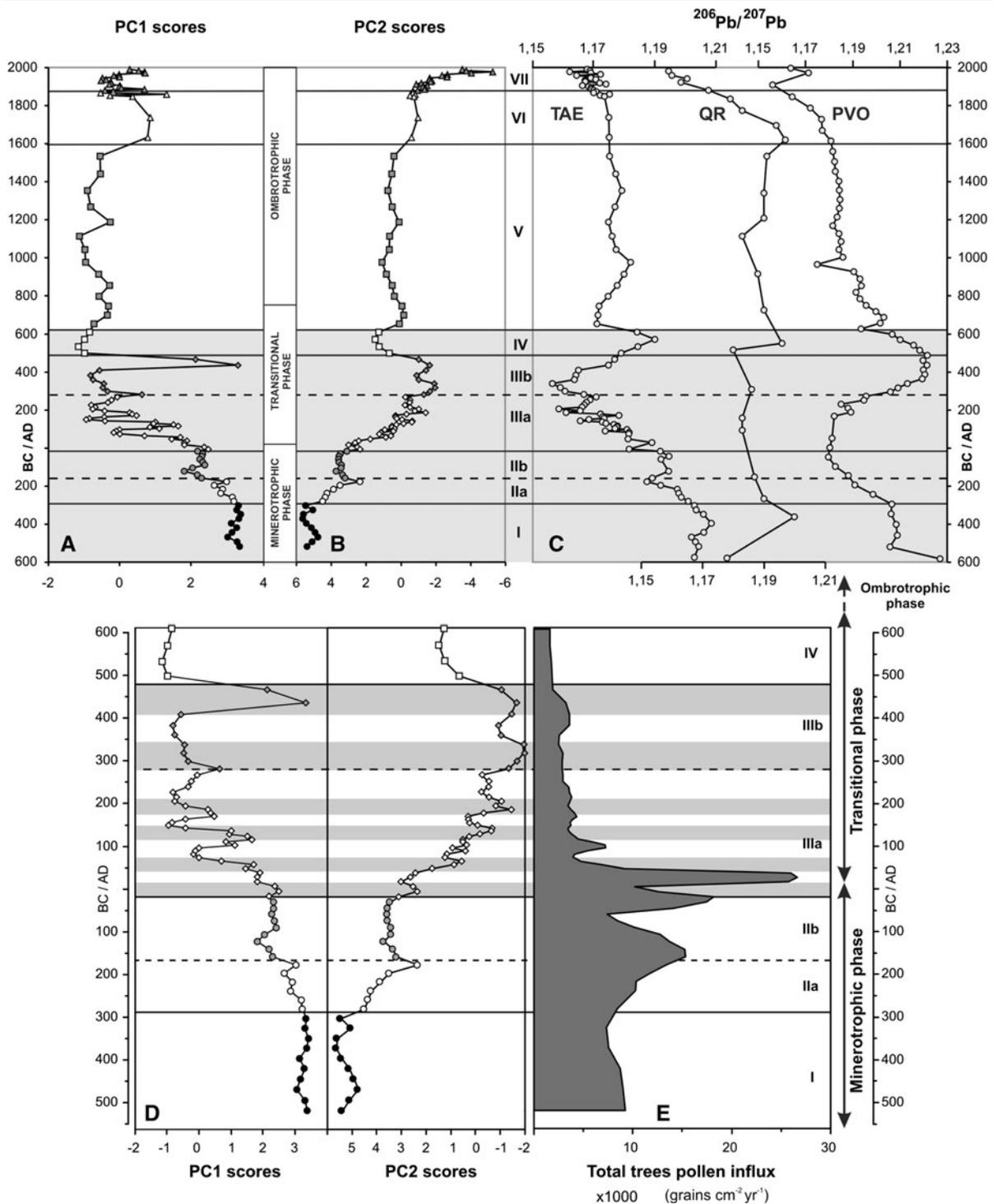
Fig. 6 Chronology of the changes in **A** fluxes of inorganic matter (PC1 scores) and **B** atmospheric metal pollution (PC2 scores) in La Molina from ∼500 BC to present; **C** changes in Pb isotopic signature during the last 2500 years in La Molina (TAE), Quinto Real (QR, data from Monna et al. 2004a) and Penido Vello (PVO; data from Kylander et al. 2005); **D** detailed record of PC1 and PC2 scores and **E** total tree pollen influx in La Molina for the Late Iron Age/Roman phase (concentration data extracted from López-Merino (2009) and pollen influx calculated using the age model). The age model for QR has been obtained with the radiocarbon ages provided in Monna et. al (2004a), using the Clam software (Blaauw 2010). Symbols as in Fig. 5

Table 2 Chronology of the phases of Pb pollution detected in La Molina (Asturias, Spain) record between $\sim$500 BC and AD $\sim$600

Phase	Age (cal BC/AD)	Pb ($\mu g\ g^{-1}$)	Pb AR (mg m^{-2} year^{-1})	^{206}Pb/^{207}Pb	Poll Pb
IV	500–600 AD	4 (1)	0.2 (0.1)	1.185 (0.005)	27–49
IIIb	280–500 AD	22 (6)	1.2 (0.3)	1.164 (0.006)	72–82
IIIa	20 BC–280 AD	15 (4)	2.5 (1.1)	1.174 (0.007)	20–89
IIb	180–20 BC	16 (1)	3.0 (0.3)	1.192 (0.003)	18–28
IIa	300–180 BC	18 (1)	3.3 (0.4)	1.198 (0.001)	6–32
I	500–300 BC	17 (2)	3.1 (0.4)	1.204 (0.002)	0–4

Average Pb concentrations in $\mu g\ g^{-1}$, average lead accumulation rates (PbAR) in mg m^{-2} year^{-1}, average lead isotope ratios (^{206}Pb/^{207}Pb), and percentage of pollution Pb (Poll Pb)

period, which closely paralleled the increase in atmospheric pollution (Martínez Cortizas et al. 2005; Mighall et al. 2006; Mohamed et al. 2010; Constante et al. 2010; Kaal et al. 2011). At the same time, there is evidence of a change in the hydrological regime of the mire (higher water table during the transitional phase; Fig. 6E) starting by AD $\sim$20, that was interpreted as the result of intentional flooding due to its use as a water reservoir for Roman mining practices (López-Merino et al. 2011) and was probably responsible for the decrease in the mineral matter fluxes from the mire's catchment. Remains of complex Roman hydraulic infrastructures that fed on water from the mountains have been found in the nearby areas of the Narcea-Pigüeña basins (Fernández Mier 1999). In phase IIIb (Fig. 6E) total tree pollen influx remained low, without showing any relationship to Pb pollution, reflecting more regional activities. The end of this subphase is marked by a sharp, short-lived increase in mineral dust (PC1, Fig. 6D).

The extensive decline of the forest was not solely exclusive to N Iberia, as it also occurred in other parts of Spain (Monna et al. 2004a; Martín-Puertas et al. 2011; Gil-Romera et al. 2010; Currás et al., 2012) and almost all major areas of Europe that were mined during this period (Küster and Rehfuess 1997; Labonne et al. 1998; Kempter and Franzel 1999; Lang 2003; Oldfield et al. 2003; Baron et al. 2005; Schmidt et al. 2008; Cruise et al. 2009; Giguet-Covex et al. 2011). Modelling of prehistoric deforestation also suggests a dramatic increase in forest decline in Western and Central Europe between 350 BC and AD 350 (Kaplan et al. 2009).

The see-saw pattern for pollution is also somewhat reflected in the chronologies of Pb enrichment in other peat records from NW Spain (Martínez Cortizas et al. 2002; Kylander et al. 2005), although their much lower time resolution does not enable a proper comparison. Large decadal variations in Pb accumulation were also detected in a high-resolution study of a lake sediment record from Ireland (Schettler and Romer 2006), and were attributed to possible changes in the wind regime and thus on atmospheric deposition. But Lewis and Jones (1970) described that Roman mining in NW Spain involved a sequence of phases of extraction and eventual exhaustions of the mines, meaning that operations at individual mines lasted from a few years to decades whilst regionally mining continued over several centuries as new sources were continually exploited. Thus, without discarding the possible influence of other processes (changes in wind direction and strength, processes affecting the growth of the mire, etc.), the pattern seen in La Molina may in fact reflect the history of mining exploitation and economic development in NW Spain.

The Romans had conquered NW Spain by 19 BC, with the prospect of ore exploitation being a major driving force stimulated by smaller scale mining in prehistoric times (Lewis and Jones 1970). The chronological continuity in the La Molina record supports the idea that Romans may have initially focused their interest on already known (at least since late Iron Age) mining areas across Europe, reflecting the widespread consequences of the intensive and spatially extensive mining and metallurgical activity during Roman times. A fact that is also supported by Pb records from other areas of Europe (Le Roux et al. 2004; Cloy et al. 2008; Mighall et al. 2009).

By AD $\sim$480 Roman mining and metallurgy seem to have collapsed. Lead concentrations attained the minimum values observed in the record, accumulation rates decreased sixfold compared to the previous period, the average isotopic ratio increased significantly and

pollution Pb dropped to a minimum relative contribution of 27 % (phase IV, Fig. 6B, D; Table 2).

Conclusions

Geochemical characterization by analyzing major, minor and trace elements (lithogenic elements and metals), as well as the isotopic composition of the accumulated Pb, in combination with the exceptional location in an area extensively mined in Roman times and good temporal resolution, enabled a detailed reconstruction of the chronology of atmospheric metal pollution of the La Molina mire record from $\sim$500 BC to AD $\sim$600. Despite the predominance of geogenic sources, the statistical analysis (PCA) helped to discriminate between geogenic and anthropogenic contributions to the mire.

We have found a general agreement with previous work done in N Spain and other areas of Europe, particularly those that were major mining Roman centres (Britain, Germany, France) or those where the low local inputs (Greenland) or high background isotopic signatures (Sweden) enhanced the detection of pollution, even from long-range transport. More significantly, La Molina mire also recorded specific phases within the long-term historical record, which can be linked to local/regional activities.

Four phases of pollution could be identified, related to late Iron Age and Roman mining. Pollution in Roman times was the largest experienced in La Molina mire for the whole studied period, with maximum pollution-Pb contributions close to 90 % of the total accumulated Pb. Compared to other areas in NW Spain, La Molina showed an extended period of exploitation for more than two centuries (from AD $\sim$240 to AD $\sim$480), although mining collapsed synchronously with the fall of Roman Empire. Also interesting is the see-saw pattern shown during the whole Roman period ($\sim$20 BC to AD $\sim$480), which suggests sub-phases of mining and metallurgy, accompanied by forest decline, probably related to local exhaustion and mining operations. Other unrelated factors, like those affecting transport and deposition of Pb, however, cannot be discounted.

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