



## Recent and historical pollution legacy in high altitude Lake Marboré (Central Pyrenees): A record of mining and smelting since pre-Roman times in the Iberian Peninsula

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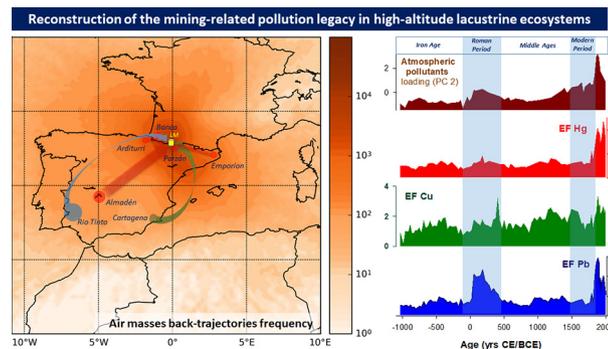
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### HIGHLIGHTS

- Atmospheric Hg deposition in Central Pyrenees mostly reflects emissions from Almadén mine (central Spain).
- Roman silver and lead mining in Iberian Peninsula is recorded in the Pyrenean summit.
- Regional atmospheric pollution during the Roman times rivalled the Industrial Period.
- Complex interplay between local and regional trace metal pollution sources.
- The pollution legacy in alpine lakes needs to be considered in management plans.

### GRAPHICAL ABSTRACT



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### ABSTRACT

We have analyzed potential harmful trace elements (PHTE; Pb, Hg, Zn, As and Cu) on sediment cores retrieved from lake Marboré (LM) (2612 m a.s.l, 42°41' N; 0° 2' E). PHTE variability allowed us to reconstruct the timing and magnitude of trace metal pollutants fluxes over the last 3000 years in the Central Pyrenees. A statistical treatment of the dataset (PCA) enabled us to discern the depositional processes of PHTE, that reach the lake via direct atmospheric deposition. Indeed, the location of LM above the atmospheric boundary layer makes this lake an exceptional site to record the long-range transport of atmospheric pollutants in the free troposphere. Air masses back-trajectories analyses enabled us to understand the transport pathways of atmospheric pollutants while lead isotopic analyses contributed to evaluate the source areas of metal pollution in SW Europe during the Late Holocene. PHTE variability, shows a clear agreement with the main exploitation phases of metal resources in Southern Europe during the Pre-Industrial Period. We observed an abrupt lead enrichment from 20 to 375 yrs CE mostly associated to silver and lead mining and smelting practices in Southern Iberia during the Roman Empire.

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Historical mining  
Pyrenees

This geochemical data suggests that regional atmospheric metal pollution during the Roman times rivalled the Industrial Period. PHTE also increased during the High and Late Middle Ages (10–15<sup>th</sup> centuries) associated to a reactivation of mining and metallurgy activities in high altitude Pyrenean mining sites during climate amelioration phases. Atmospheric mercury deposition in the Lake Marboré record mostly reflects global emissions, particularly from Almadén mines (central Spain) and slightly fluctuates during the last three millennia with a significant increase during the last five centuries. Our findings reveal a strong mining-related pollution legacy in alpine lakes and watersheds that needs to be considered in management plans for mountain ecosystems as global warming and human pressure effects may contribute to their future degradation.

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## 1. Introduction

Metallurgy has been key for the development of human society during Pre-industrial times (Killick and Fenn, 2012). The Iberian Peninsula is particularly rich in mineral resources and has a long history of mining and smelting activities with several of the world's most representative historical mining districts. Almadén mines, located in Central Spain, has been the World's largest mercury (Hg) mine until its closure at the turn of this century. This mine has been actively exploited during two millennia producing 30% of the globally mined Hg with an accumulated historic Hg emission estimate of 10,000 tons (Hylander and Meili, 2003). Southern Iberia is also very rich in mineral resources hosting important silver (Ag) and lead (Pb) mining hotspots. These resources have been exploited for several millennia, with more than 10,000 tons of Pb produced contributing to 40% of the World's total lead production between 1200 yrs BCE (before Common Era) and 500 yrs CE (Common Era). Most of the Iberian Ag and Pb mining located in Rio Tinto and Mazarrón-Cartagena mining districts were intensively exploited by Phoenicians, Carthaginians and Romans.

In NW Iberia, mining and metallurgy started in the Chalcolithic–Early Bronze Age 4500 years ago according to archaeological information (de Blas, 1996, 2005) although the first atmospheric pollution signal related to these human activities has been dated 500 years before (~5 kyrs ago) (Martínez-Cortizas et al., 2016). To a lesser extent, the Pyrenees has also been largely exploited during the last centuries for Ag and Pb production (e.g. Arditurri mines in Western Pyrenees (Thalacker, 1804), Emporion mines in Catalonia (Montero-Ruiz et al., 2007)). Southern Central Pyrenees also have local rich deposits of metals including copper (Cu), Pb, Ag and iron (Fe), many of them historically mined and processed at high elevation emplacements (>2000 m a.s.l.) (e.g. Bielsa-Parzán mining district (Calvo, 2008; Nieto-Callen, 1996)), although the timeline of their activities is not well constrained prior to the last 500 years.

Unfortunately, historical mining and metalworking activities have left a long-lasting imprint on the environment (Hansson et al., 2019). Indeed, although numerous natural and anthropogenic activities can increase contaminant levels in the environment, mining operations are notable regarding the number of particulates generated, the global impact, and the trace metals' toxicity associated with atmospheric pollutant emissions (Csavina et al., 2012). Thus, large quantities of PHTE such as Pb, Hg, Cu, zinc (Zn) or arsenic (As) have been released to the regional atmosphere during the last millennia and subsequently deposited and stored in the Iberian Peninsula (Gallego et al., 2019; Hanebuth et al., 2018; Kylander et al., 2005; Leblanc et al., 2000; Manteca et al., 2017; Martínez-Cortizas et al., 1999, 2002, 2012, 2013, 2016; Mil-Homens et al., 2017; Serrano et al., 2013) among others, and elsewhere in the Northern Hemisphere even in remote, pristine glacier ice in the Alps and the Arctic (Hong et al., 1994, 1996; McConnell et al., 2018, 2019; Preunkert et al., 2019; Rosman et al., 1997), regions located far away from the pollution source. Understanding this environmental legacy, i.e. the persistence of PHTE pollution overtime from past anthropogenic emissions, and the fluxes from terrestrial to aquatic ecosystems (Bacardit and Camarero, 2010) should help environmental policy

makers to design future and sustainable environmental management plans and monitoring programs. Indeed, as recently highlighted by Camarero (2017) and Le Roux et al. (2019), the long-term PHTE monitoring provided by natural archives is particularly needed in mountain environments such as the Pyrenees in order to assess the response of mountain critical zones to Global Change.

Among natural archives, lake sediments have been widely used to reconstruct past mining and metalworking activities as well as other anthropogenic sources, e.g. (Cooke et al., 2011, 2020; Díez et al., 2017; Elbaz-Poulichet et al., 2020; Mariet et al., 2018; Renberg et al., 1994; Thevenon et al., 2011; Wilhelm et al., 2017). These continuous sedimentary records allow us to understand the variability of different mining-related pollution sources through time as well as to assess their environmental legacy. Surprisingly, yet relatively few pollution records from lacustrine sediments exist in the Iberian Peninsula (Camarero, 2017; Camarero et al., 1998; Corella et al., 2017, 2018; García-Alix et al., 2013; Hillman et al., 2017; Martín-Puertas et al., 2010). High-altitude mountain lakes record most efficiently past atmospheric pollution phases due to enhanced atmospheric precipitation and the "cold trapping" effect caused by elevation making these locations regional convergence areas of atmospheric pollutants (Camarero, 2017). Recent depositional patterns based on lake surface sediments show a W-E distribution with higher trace metal concentrations in the eastern Pyrenees lakes (Bacardit and Camarero, 2009; Camarero, 2003, 2017). Inventories of trace metals in soils and sediments in several lake catchments in the central Pyrenees have shown a large anthropogenic component (Bacardit and Camarero, 2010; Bacardit et al., 2012). High levels of pre-industrial pollutants have been reported in several Pyrenean lakes (Camarero et al., 1998; Lavilla et al., 2006), but millennial-long, well-dated records are scarce (Hansson et al., 2017). Recent research in several well-dated records from mountain lakes across an altitudinal transect in the Southern Central Pyrenees (NE Spain) assessed the variable pollutant loading in these ecosystems during the Industrial period (Corella et al., 2018). This study highlighted that among all studied lakes, high-altitude, pristine Lake Marboré (LM), located at the Pyrenean summit (>2600 m. a.s.l.) records most efficiently past regional atmospheric deposition of PHTE. LM has provided the sedimentary record at the highest altitude in the Pyrenees (Leunda et al., 2017; Oliva-Urcia et al., 2018) in a privileged location in the free troposphere. Therefore, LM record can be considered as representative of background, global atmospheric pollution since long-range transport of atmospheric pollutants mostly takes place above the atmospheric boundary layer.

This study aims to reconstruct the atmospheric pollution in the Pyrenees related to mining and metalworking activities in the Iberian Peninsula during the main historic periods of the last three millennia (namely Iron Age (IA; 1000 yrs BCE–218 yrs BCE), Roman Period (RP; 218 yrs BCE–476 yrs CE), Early Middle Ages (EMA; 476–1000 yrs CE), High Middle Ages (HMA; 1000–1300 yrs CE), and Late Middle Ages (LMA; 1300–1492 yrs CE), Modern Period and beginning of Contemporary Age (MP; 1492–1850 yrs CE) and the Industrial Period (IP; 1850 yrs CE–Present day). To achieve this goal, we have carried out a multi-proxy research strategy on the first 175 cm of a sediment core retrieved in the distal area of LM that comprises the last 3000 years. The

multidisciplinary analyses included i) the determination of major, minor and trace metals that allowed us to quantify the geochemical composition of the sediments down-core; ii) lead isotopic analyses to evaluate the possible sources of metal pollution during the different historical phases of mining production in the Iberian Peninsula; iii) multivariate statistical modelling to discern the depositional processes of each geochemical element and; iv) air masses back-trajectories computation to evaluate the atmospheric transport pathways of major pollutants.

## 2. Study site

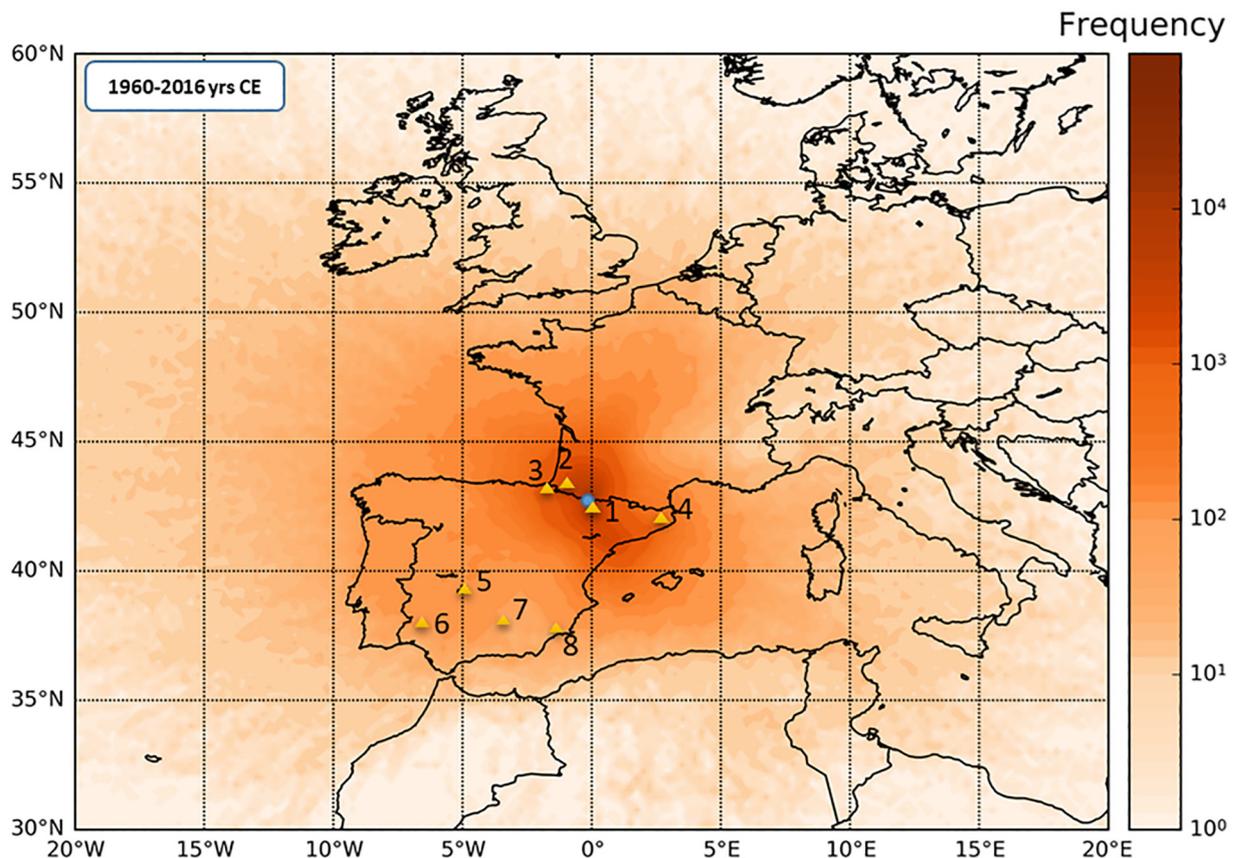
LM (42°41' N; 0°2' E, Fig. 1) is a lake emplaced at 2612 m a.s.l. within a glacier cirque located in the Spanish Central Pyrenees. The lake has a surface area of 14.3 ha and it is emplaced in a watershed of 137 ha (Valero-Garcés et al., 2013), lying on Cretaceous-Tertiary carbonated rocks (Pujalte et al., 2016; Samsó Escolá and Robador, 2018). Mean annual temperature and precipitation at the nearest meteorological station (Góriz station, located at 2220 m a.s.l.) are 4.9 °C and ~2000 mm (Leunda et al., 2017). The vegetation cover around the lake is very scarce with only a few patches of alpine herbs (Leunda et al., 2017). The lake has a maximum depth of 30 m and an elongated morphology with ~500 m along the WNW-ESE axis and ~200 m across (Sánchez-España et al., 2018). Since there is no direct connection with the nearby Monte Perdido and Marboré glaciers (García-Ruiz et al., 2014), lake level is controlled mostly by precipitation/evaporation balance (Nicolás-Martínez, 2013; Valero-Garcés et al., 2013) with small ephemeral inlets and outlets located in the lake's western and southern shores respectively. The lake was dammed in the 1940s but the dam was never completely functional and it has been decommissioned. LM is a cold

dimictic and ultra-oligotrophic lake which surface is covered by ice and snow from December to July (Sánchez-España et al., 2018).

## 3. Material and methods

### 3.1. Back-trajectories analyses

To estimate the atmospheric transport pathways to LM, the back trajectories of air masses were computed using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model developed by NOAA's Air Resources Laboratory (ARL) (Draxler et al., 2009). The HYSPLIT model is a complete software for computing simple air parcel trajectories as well as complex transport, dispersion, chemical transformation and deposition simulations (Draxler et al., 2009). It is often used for forward and back-trajectory air masses analysis, and to establish source-receptor relationships (Stein et al., 2015). The calculation method is a hybrid method between the Lagrangian approach, using a moving frame of reference for advection and diffusion calculations as the trajectories on air parcels move from their origin, and the Eulerian methodology using a fixed three-dimensional grid as a frame of reference to compute pollutant air concentrations (Stein et al., 2015). Three-dimensional kinematic trajectories were computed daily at 12:00 UTC, with a 72-hour runtime at 100m above ground level (agl), considering as arrival point the LM location. The back trajectories were calculated using the meteorological fields of the global meteorological model ECMWF (European Centre for Medium Range Weather Forecasts). In order to cover the entire studied period, we used ERA40 and ERA-Interim data reanalysis with similar spatial and temporal resolutions. The data reanalysis used has a spatial resolution of 0.5° (latitude x longitude), 22 vertical levels from the surface to 250 mb and a



**Fig. 1.** Frequency map of air masses back trajectories arriving to Lake Marboré (LM, blue circle). Yellow triangles indicate the location of historical mining sites mentioned in the text (1 - Parzán; 2 - Banca; 3 - Arditurri; 4 - Emporion; 5 - Almadén; 6 - Río Tinto; 7 - La Carolina-Linares; 8 - Mazarrón-Cartagena). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

temporal resolution of 6 h. The back trajectories were calculated every 6 h during the period 1960–2016 yrs CE. Although climate variability has caused changes in weather conditions and extreme events at local and regional scales affecting the intensity of atmospheric circulation dynamics during the Late Holocene (Sánchez-López et al., 2016), we assumed that general atmospheric circulation patterns has remained similar. Therefore, the 20–21<sup>st</sup> century air masses back trajectories are representative of the studied period (i.e. last 3000 years). ERA40 data reanalysis were used for the computation of back trajectories for the period 1960–1993 yrs CE, while ERA-Interim for the period 1994–2016 yrs CE (Dee et al., 2011). These meteorological fields were converted into the ARL standard format using the HYSPLIT model. Back-trajectories from 1960 to 2016 yrs CE have been added on a  $0.25^\circ \times 0.25^\circ$  grid to visualize air masses sources (frequency map shown in Fig. 1). Frequency map represents the number of back-trajectories passing above every location before arriving to LM in the 1960–2016 yrs CE time period. To estimate the main source areas of these trajectories arriving to LM we have defined several regions and calculated the number of trajectories passing through those regions before arriving to LM (Table 1). Note that since back-trajectories pass above more than one region before arriving to LM, the sum of all percentages does not equal 100%. For calculation of specific emission sources (i.e. mining districts) we have considered for each site an area equal to its location  $\pm 2^\circ$  (latitude and longitude).

### 3.2. Sediment cores and age-depth model

A long (~7 m) sediment core (MAR11-1U) and a short (0.2 m) gravity core (MAR11-1G-1U) were retrieved in august 2011 from the deepest part of LM using an UWITEC floating platform and coring equipment from the Pyrenean Institute of Ecology (IPE-CSIC) (Oliva-Urcia et al., 2018). Core correlation between the short and the long core was carried out using the Pb concentration profiles (Oliva-Urcia et al., 2018). For the development of the composite UWITEC sedimentary sequence we used consecutive sections since the recovery factor was excellent. Sediment cores were split lengthwise for sedimentary facies description and discrete sampling. A continuous sampling was carried out every 2 cm out for geochemical analyses. LM sediments during the Late Holocene mainly consists of laminated siliciclastic mud with very low Total Organic Carbon content (TOC ranging from 0.1 to 1.1%) (Corella et al., 2018; Oliva-Urcia et al., 2018; Valero-Garcés et al., 2013). Recent sedimentation has been characterized with sediment traps located in the deeper areas of the lake since 2017. Annual surveys include water sampling and temperature, pH, conductivity and oxygen depth profiles.

The chronology for the Late Holocene sediment sequence in LM was developed using five Accelerator Mass Spectrometry (AMS)  $^{14}\text{C}$  radiometric dates from long core MAR11-1-U and  $^{137}\text{Cs}/^{210}\text{Pb}$  dating performed from the gravity core MAR11-1G-1U.  $^{210}\text{Pb}$  dating in the short core was obtained by gamma ray spectrometry. Excess (unsupported)  $^{210}\text{Pb}$  was calculated by the difference between total  $^{210}\text{Pb}$  and  $^{214}\text{Pb}$  for individual core intervals.  $^{210}\text{Pb}$  chronology was determined using

the constant rate of supply (CRS) model (Appleby, 2001). The  $^{210}\text{Pb}$  age model is supported by the presence of a  $^{137}\text{Cs}$  peak at 6 cm (1963 yr CE) in agreement with the  $^{210}\text{Pb}$  chronology (Leunda et al., 2017; Oliva-Urcia et al., 2018). The age-depth model has been constructed by linear interpolation between the median ages of the probability distribution of adjacent calibrated dates (see Leunda et al. (2017) and Oliva-Urcia et al. (2018) for a complete description and information of the LM age-depth model). In this study we have focused in the upper 175 cm of the studied sedimentary sequence that comprises the period 1032 yrs BCE– 2010 yrs CE with mean sedimentation rates of  $0.06 \text{ mm yr}^{-1}$ .

### 3.3. Geochemical and geophysical analyses

Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, P, Pb, Si, Sr, Ti, Zn, and Zr concentration were analyzed in 91 samples by optical emission spectrometry using inductively coupled plasma-atomic emission spectroscopy (ICP-OES; Thermo ICP-OES iCAP 6300 DUO-Thermo Fisher Scientific, Waltham, MA, USA) at the IPE-CSIC laboratories. Samples were previously digested with  $\text{HNO}_3$  (9 ml) and  $\text{HCl}$  (3 ml) in a microwave oven 'BERGHOF MWS'. Total Hg concentration measurements were carried out by Atomic Absorption Spectrophotometry using an Advance Mercury Analyzer (AMA 254, LECO Company). This equipment is specifically designed for the direct mercury determination in solid and liquid samples without a need of sample chemical pre-treatment. Certified reference material (CRM) were used to determine the accuracy and precision of the Hg measurements (NCS DC87103, soil,  $[\text{Hg}] = 0.017 \pm 0.003 \text{ mg kg}^{-1}$ ). The repeatability was  $S_r \leq 15\%$  and the relative uncertainty associated with the method ( $k = 2$ ) was  $\pm 20\%$ . All analyses were run at least in triplicate. Total Carbon (TC), Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC) had been previously determined with a LECO SC 144 DR elemental analyzer (Oliva-Urcia et al., 2018). TIC values were obtained by subtracting TOC from TC (Fig. 2).

Principal Component Analyses (PCA) were applied to reduce the large geochemical dataset into a smaller number of variables (i.e. principal components (PC)) helping to interpret environmental and depositional processes. PCA was carried out including all the elements (Cu, Zn, Cd, Mn, Ca, Fe, P, As, Hg, Pb, Sr, Zr, Si, Cr, Mg, Ti, B, K, Al and Ba) using trace metals' concentrations (Fig. 3) and accumulation rates (Fig. S1). The PCA was performed with varimax rotation over the geochemical dataset using the SPSS 23.0 software. To calculate Enrichment Factors (EFs), firstly, all the PTHE have been normalized to aluminum (Al) in order to confirm that the changes in metals concentrations are not related to detrital input variability. Al has been selected for normalization since this lithogenic element is immobile (i.e. geochemically stable) in the sediments and it is abundant in carbonated watersheds (Boës et al., 2011; Tylmann, 2005). Later, EFs have been calculated using the average element concentrations before 1000 BCE as baseline conditions which may differ from natural background values. EFs have been estimated to identify and quantify anthropogenic interferences in natural element cycles (Amos et al., 2015; Biester et al., 2007; Weiss et al., 1999).

$$EF = \frac{\frac{[M_{cm}]}{[Al_{cm}]}}{\frac{[M_{bottom}]}{[Al_{bottom}]}}$$

$[M_{cm}]$  and  $[Al_{cm}]$  represent the metal and aluminum fluxes at the same depths of the sediment cores while  $[M_{bottom}]$  and  $[Al_{bottom}]$  are the metal and aluminum fluxes in the basal sediments of the sediment cores in LM. Hg EF has been calculated as the ratio between the  $[\text{Hg}]$  in a given sample by the average  $[\text{Hg}]$  in the section below 1000 BCE following Biester et al. (2007).

**Table 1**  
Back trajectories percentages passing over different regions and arriving Lake Marboré area.

Region	Longitude	Latitude	Percentage of back-trajectories/%
SW France	42.83N–45.83N	1.83W–0.83E	51.9
Ebro valley	40.00N–42.50E	1.83W–2.83E	52.1
Central and western Spain	40.00N–42.00N	10.00W–2.5W	16.4
Southern Spain	36.00N–40.00N	10.00W–1.00E	17.4
Northern Africa	30.00N–36.00N	10.00W–5.00E	3.0

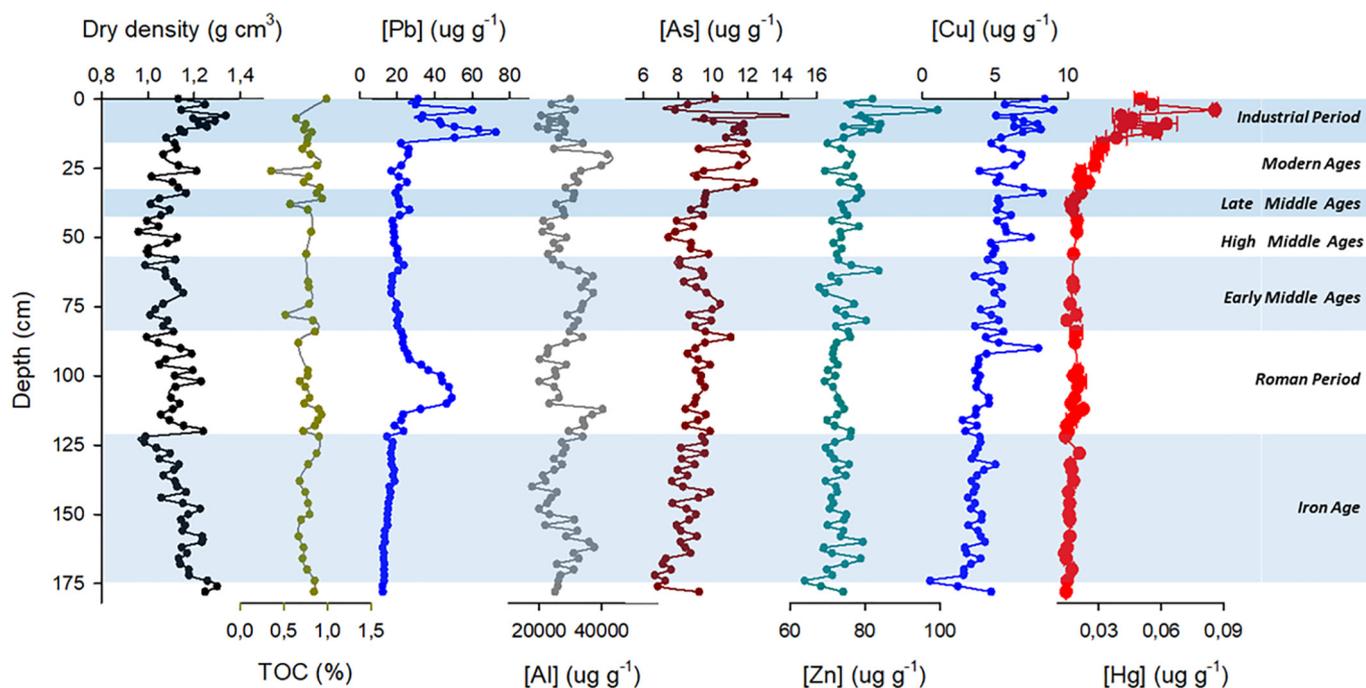


Fig. 2. LM down-core evolution of Potential Harmful Trace Metal (PHTM) and aluminum concentrations, Organic Matter Content (TOC) and sediment density values.

### 3.4. Pb isotopic analyses

Pb isotope ratios are commonly used as tracers of both natural and anthropogenic sources of metals recorded in natural archives (Komárek et al., 2008). In order to shed light on the origin of Pb pollution found in the LM record, 45 samples were collected for Pb isotopic analyses. A 0.1 g of powdered rock was digested overnight in  $\text{HNO}_3$  and evaporated to dryness. The residue is dissolved in 0.5 M ammonium acetate, and Pb separated of the major cations by conventional ion-exchange chromatography (DigiSEP Blue, SCP Science). The recovered Pb is evaporated to dryness, dissolved in 0.5 M  $\text{HNO}_3$  and diluted to a final concentration of 100–200 ppb. The samples were measured using the standard bracketing method. ICP-MS measurements were carried out with an Element 2 SF-ICP-MS (Thermo Finnigan, Bremen, Germany) equipped with a guard electrode to eliminate secondary discharge in the plasma and to enhance overall sensitivity. The high resolution double focusing (reverse Niers–Johnson geometry) single collector ICP-MS instrument provides flat top peaks in the low resolution mode ( $m/\Delta m$  300) which was used for the analysis of  $^{202}\text{Pb}$ ,  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ . A micro volume autosampler (SC-2 DX FAST Autosampler, ESI Inc., Omaha, NE, USA) and a sample introduction kit consisting of a PFA microflow nebulizer, a Peltier-cooled spray cyclonic chamber and a sapphire injector tube (ESI Inc., Omaha, NE, USA) were employed to transport the samples into the plasma of the ICP-MS. This configuration increases the sensitivity and stability of the conventional sample introduction setup. Samples were diluted ten times with 2% (v/v) high purity  $\text{HNO}_3$  to reduce the risk of clogging. The solutions were introduced into the plasma using a PFA nebulizer, operating in self-aspiration mode at a flow rate of 50 ml/min. Regarding reagents and standards, all the solutions were prepared with high purity water (18.2 MV cm) from Milli-Q element system designed for ultra-trace analysis (Millipore, Milford, MA, USA). Nitric acid (65%, analytical-reagent grade, Scharlab, Barcelona, Spain) was further purified by sub-boiling distillation (DST-1000 Sub-Boiling Distillation System, Savillex Corporation, USA). Standard calibration solutions were prepared by appropriate dilution of a dissolved amount of NIST 981 certified standard (Inorganic Ventures) with 2% high-purity nitric acid.

## 4. Results and discussion

### 4.1. Concentrations and depositional processes of trace metals in LM

#### 4.1.1. Recent depositional processes: ice phenology, run-off and lake processes

Recent sediments in the deeper areas of LM characterized with sediment traps consist of siliciclastic silt, with about 1.1% TOC, no carbonate and 0.05% TS. Although carbonate-bearing formations occur in the watershed and the moraine deposits, the sediments in the lake are mostly devoid of carbonates (Oliva-Urcia et al., 2018). Mineral composition of the sediments is dominated by quartz, micas and detrital clay minerals, with presence of minor sulfides and other heavy minerals (mainly titanium oxides and zircon), all more resistant to weathering processes. Based on sediment traps data, the calculated sediment fluxes range between  $390 \text{ g m}^{-2} \text{ yr}^{-1}$  in the more proximal zones closer to the NW inlet to  $250 \text{ g m}^{-2} \text{ yr}^{-1}$  in the more distal areas. Microscope smear slide observations of recent sediments show the sporadic presence of heavy minerals in the sediments (pyrite, galena, sphalerite and barite) indicative of occasional contributions from the watershed. High Fe and Zn values have been found in the water column analysis in the thermocline in the ice-free period, being interpreted as a result of weathering reactions involving sulfides in the watershed (Sánchez-España et al., 2018). However, the influx of heavy metals into the lake due to run-off processes is expected to be small and likely constant during the last millennia as the composition of the surface sediment in LM drainage remained the same in spite of glacier advances and retreats outside the watershed retreat (García-Ruiz et al., 2015).

The Iberian Peninsula has experienced different climatic periods during the Late Holocene (namely the Ibero-Roman Humid Period (IRHP), Dark Ages Cold Period (DACP), Medieval Climate Anomaly (MCA), Little Ice Age (LIA) and Recent Warming) that most likely affected the annual duration of ice cover (i.e. ice phenology) in Spanish alpine lakes as it has been shown for the most recent phases (Sánchez-López et al., 2015). Ice phenology variability might have influenced differently the trace metal concentrations in LM sediments since the lake remains frozen about eight months per year (Sánchez-España et al.,

2018). Direct atmospheric deposition of trace metals to the lake surface is hindered during cold periods when the lake is frozen and deposited metals would accumulate in the ice layer until discharged into the lake following ice melting. A similar process has been interpreted for pollen rain content during the Late Glacial and beginning of the Holocene (Leunda et al., 2017) as well as in other lakes in polar regions (Pérez-Rodríguez et al., 2019). In the case of mercury deposited on the ice and snow, it could also undergo re-emission to the atmosphere following heterogeneous photochemistry on the ice surface and/or snowpack (Angot et al., 2016). This process would release a fraction of the ice-trapped Hg back into the atmosphere contributing to lower atmospheric deposition of Hg to the lake. On the contrary, large re-emission of other trace metals such as Pb, Cu, As and Zn from ice lake surface is not expected since these elements are largely immobile and would be remobilized during ice-melting and stored in the natural sink (i.e. the lake). Additionally, trace metals deposition in the Southern Pyrenees mainly occurs during the warm season when inland air masses enriched in trace elements and a thicker atmospheric mixed layer occurs (Bacardit and Camarero, 2009). Ice phenology would also affect the lake's annual stratification patterns and thus trace metals mobility in the water column. This process would affect Zn and, to a lesser extent, Cu and As (Sánchez-España et al., 2018). Nevertheless, we do not expect that this seasonal process would affect the annual depositional fluxes of these elements.

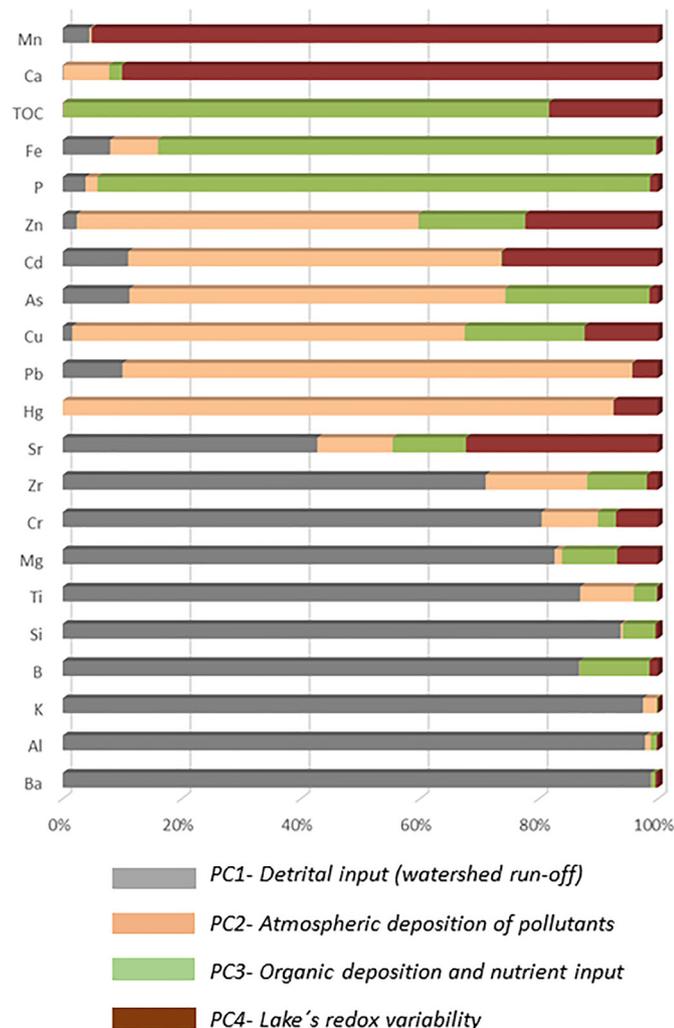


Fig. 3. Communalities of the geochemical elements obtained from Principal Component Analyses (PCA).

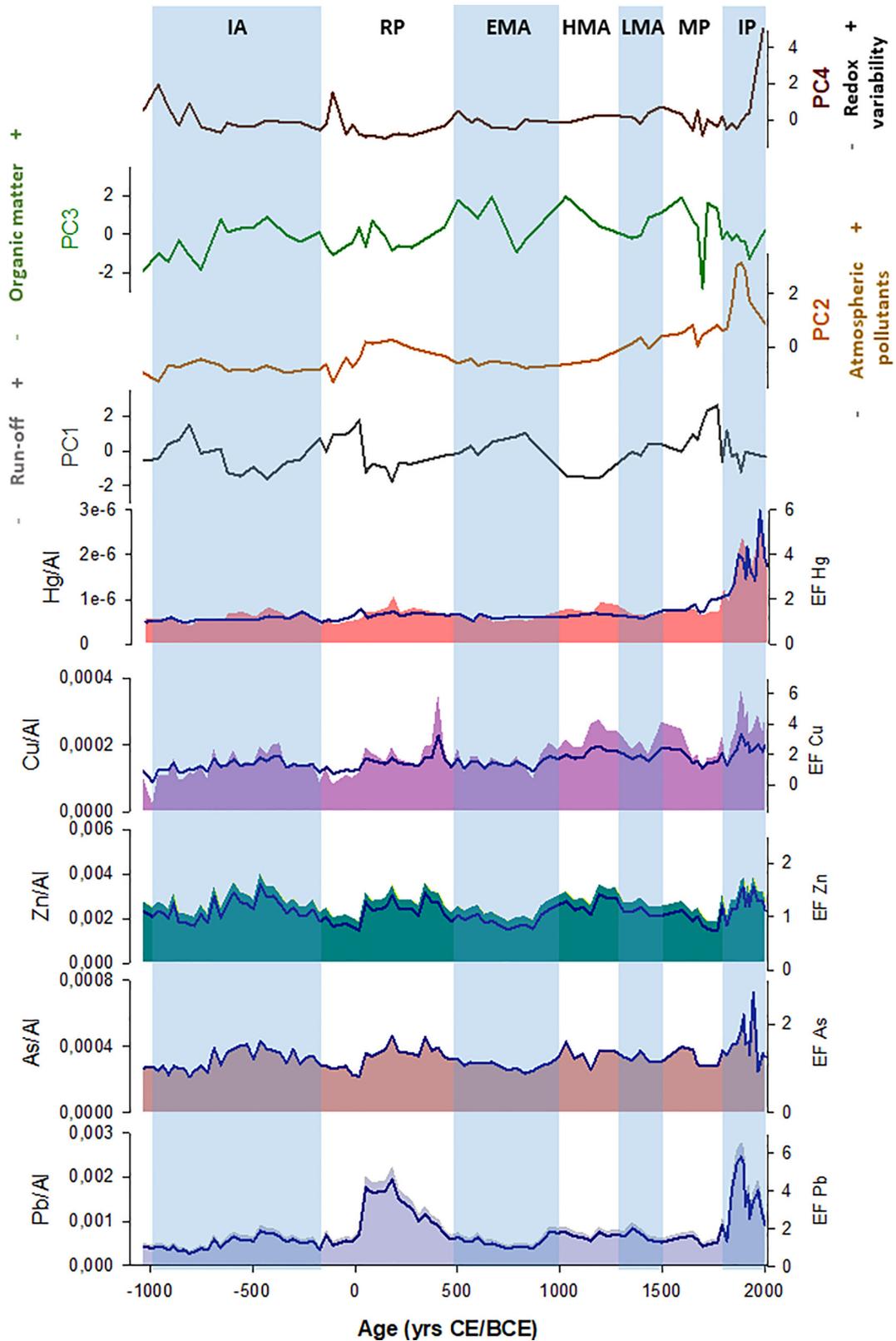
#### 4.1.2. Principal component analyses of the geochemical dataset

PCA was applied over the geochemical dataset (both in trace metal concentration and accumulation rates). PCA on trace metal concentrations shows four main eigenvectors representing 81.84% of the matrix variance (Table 2). These eigenvectors explain the main environmental factors controlling sediment deposition and lake's endogenic and allochthonous processes. Factor loadings of each element in the extracted eigenvectors (PCs) and PCs variability are shown in Figs. 3 and 4 and Fig. S1 highlighting the fractionation of the communalities. Both PCA using trace metal concentration and accumulation rates show similar variances and grouping of geochemical elements (Figs. 3 and S1; Tables 2 and S1).

The first component (PC1 46.7% of the variance) is related to lithogenic elements (Zr, Sr, Si, Cr, Mg, Ti, B, K, Al and Ba) and represents the delivery of allochthonous material to the lake via watershed run-off. Periods of increased run-off occurred between 910 and 650 BCE, 160 BCE–30 CE, 660–830 CE and 1650–1770 CE most likely related to periods with higher snow cover in winter and/or increase snowmelt in summer. The second component PC2 (19.57% of the total variance) is characterized by large positive loadings of Hg (0.90) and Pb (0.77), and moderate positive loadings of Cu (0.73), As (0.71), Cd (0.64) and Zn (0.59). PC2 suggest atmospheric deposition as the main process controlling the sediment enrichment of PHTE. PC2 show relatively low values during the IA while reached high values during the RP particularly between 60 and 200 yrs CE. PC2 strongly decreased during the EMA and progressively increased since the onset of the HMA reaching maximum values at the end of the 19<sup>th</sup> century (Fig. 4). PC2 progressively increased during the Little Ice Age when colder conditions occurred in the Pyrenees (Morellón et al., 2012) suggesting climate influence on Hg deposition since PC2 is dominated by Hg. Thus, increased Hg levels during the LIA could result from lower re-emission of the Hg deposited on the snow/ice covering the lake surface and the catchment and enhanced transfer to the sediment during thawing events. Major increases in PC 1 and 2 show large temporal dissimilarities suggesting that the main trace metal pollutants input by weathering and run-off are not the main environmental processes driving hazardous trace metal pollutants content in the lake.

The third component (PC3, 8.69% of the variance) is mainly characterized by positive loadings of TOC, Fe and P and reflects the accumulation of organic matter in the lake's bottom and nutrients input. Recent limnological surveys in the lake documented some variability in the biological activity in LM waters, although TOC values in the water column are extremely low (ranging from 0.3 mg/l to 1.2 mg/l (Sánchez-España et al., 2018)). Therefore, PC3 fluctuating values during the last 3000 years would therefore reflect the variability in lacustrine primary production. PC4 (6.88% of the variance) is related to large positive loading of Ca, Mn and Cd. No carbonate precipitates in the lake as the water column is undersaturated in calcite (Oliva-Urcia et al., 2018; Sánchez-España et al., 2018). Therefore, PC4 may reflect carbonate fluxes in the lake conditioned by the variable dissolution rate of carbonate particles from the watershed, controlled by water temperatures during the summer (Oliva-Urcia et al., 2018). Redox variability in the hypolimnion could also affect Mn and Cd as they are sensitive to redox-driven cycling in lacustrine systems (Hamilton-Taylor and Davison, 1995). PC4 shows relatively stable values suggesting that the lake has been well oxygenated during the last 3 millennia, similarly to recent years when limnological surveys have documented a well oxygenation of the lake's water column throughout the annual cycle (Sánchez-España et al., 2018). PC4 peaks at 950 yrs BCE, 100 yrs BCE and 2000 yrs CE are more likely to respond to detrital carbonate accumulation in the lake since Mn is mostly linked to Ca-rich laminae in the Marboré sediments (Oliva-Urcia et al., 2018).

The moderate loadings of As and Zn in PCs 3 and 4 suggest that these elements can be either i) mobilized and re-precipitated in the sediment



**Fig. 4.** Principal Components eigenvectors (PC) and Enrichment Factors (EF) and normalization (coloured area) of PHTM recorded in LM during the last 3000 years. Main historical periods are also indicated; Iron Age (IA), Roman Period (RP); Early, High and Late Middle Ages (EMA, HMA and LMA respectively); Modern Period and beginning of Contemporary Age (MP); Industrial Period (IP).

under anoxic/oxic changes in the hypolimnion and/or ii) fixed in organic compounds. Nevertheless, the continuous oxygenation of the hypolimnion and the very reduced biological activity (TOC in the sediment

<1%) in this lake suggest that both factors do not have a significant influence on these elements variability during the Late Holocene. The lack of correlation between Hg and Pb with lithogenic and redox-

**Table 2**

Results of the Principal Component Analyses using the scores (loading factors) of the extracted principal components obtained for the geochemical datasets.

Element	PC1	PC2	PC3	PC4
Ba	0.98	-0.03	0.08	0.06
Al	0.97	-0.10	0.10	0.04
K	0.95	-0.14	0.04	0.01
B	0.91	0.03	0.33	0.12
Si	0.89	-0.06	-0.22	0.06
Ti	0.88	0.28	0.19	0.03
Mg	0.85	0.10	0.29	0.25
Cr	0.85	0.29	0.16	0.25
Zr	0.81	0.39	0.30	0.13
Sr	0.63	0.34	0.34	0.54
Hg	-0.01	0.90	-0.02	0.26
Pb	-0.26	0.77	-0.02	-0.17
Cu	0.12	0.73	0.41	0.32
As	0.30	0.71	0.44	-0.10
Cd	0.27	0.64	-0.03	0.41
Zn	0.12	0.59	0.33	0.37
P	0.18	0.13	0.88	-0.10
Fe	0.26	0.26	0.83	0.05
TOC	0.03	-0.02	0.72	0.34
Ca	0.03	0.25	0.13	0.85
Mn	0.15	0.04	0.00	0.68
PCA variance	46.70	19.57	8.69	6.88
Accumulated variance	46.70	66.27	74.96	81.84

sensitive elements and TOC also suggests that watershed runoff, redox variability and biological activity are not the main contributors to these major pollutant contents and fixation in the sediment. Therefore, although it may be a baseline deposition of some trace metals due to the weathering in the basin and run-off processes, the increase in PHTE would be mainly related to higher atmospheric deposition due to human activities at a local to sub-continental scale.

#### 4.1.3. Temporal trace metal's concentration evolution

Hazardous trace metals follow different down-core concentration evolutions in the upper 175 cm of the analyzed sediment cores (Fig. 2). Pb concentration increased progressively during the IA with mean [Pb] of 14.8 mg kg<sup>-1</sup>. [Pb] abruptly increased at the onset of the RP reaching maximum values between 50 and 210 yrs CE. During this period mean [Pb] of 46 mg kg<sup>-1</sup> are above the Pb TEC (Threshold Effect Concentration) guidelines in freshwater sediments (MacDonald et al., 2000), i.e. above the threshold from which harmful effects on ecosystems are likely to be observed. Low [Pb] values were recorded during the EMA and the HMA, with values of 19.6 mg kg<sup>-1</sup> and 18.6 mg kg<sup>-1</sup> respectively, although [Pb] did not return to pre-roman values. Higher [Pb] occurred during the LMA ([Pb] of 21.7 mg kg<sup>-1</sup>) and the MP ([Pb] of 25.6 mg kg<sup>-1</sup>) reaching the highest values during the IP, when [Pb] of 46 mg kg<sup>-1</sup> resemble the Pb values recorded during the RP. Arsenic showed increasing concentration values from the onset of IA to the end of the RP reaching a maximum concentration peak of 11 mg kg<sup>-1</sup>. Then it progressively decreased until the end of the HMA and showed elevated and fluctuating values during the MP and the IP with mean [As] of 10.8 mg kg<sup>-1</sup> (above [As] TEC values). Zn and Cu concentration progressively increased during the last 3000 years with mean values of 74.2 and 4.7 mg kg<sup>-1</sup>, respectively. Mercury concentrations remained low until the end of the Middle Ages (0.018 mg kg<sup>-1</sup>), increased during the MP (0.027 mg kg<sup>-1</sup>) and doubled during the IP (0.054 mg kg<sup>-1</sup>).

#### 4.2. Atmospheric transport of major pollutants

Air masses back trajectories reaching LM were computed to investigate the atmospheric transport of main pollutants from the

main mining districts in the Iberian Peninsula (Fig. 1). The analyses of back trajectories reaching LM reveal that 50% of air masses come from SW France and the Ebro valley (Table 1). Air masses sources progressively decrease southward with Central and Western Spain contributing to 16.4% of total air masses in the region, Southern Spain (17.4%) and Northern Africa (3%). Air masses from the Atlantic Ocean or emitted in the Central Iberian Peninsula are usually displaced to the Western Mediterranean Sea due to the westerlies flows. Once in this region, air masses can be trapped and funneled through the Ebro valley impacting in the Pyrenean mountain range. Likewise, Northern African air masses reach the Western Mediterranean basin and subsequently transported to the Pyrenees funneled through the Ebro valley. Other pathways are possible, such as the direct arrival through the Iberian Peninsula or, indirectly, through the Atlantic Ocean eventually reaching the Pyrenees from the south. Air masses back trajectories indicate that the transport from emission sources in central and southern Iberian Peninsula (e.g. Almadén, Río Tinto, Cartagena, Linares) is not direct and would follow the Western Mediterranean route.

On the other hand, changes in atmospheric patterns, particularly related to the intensity of winds could have played an effect on delivery of trace metals from southern Spain during past climate phases in the Late Holocene (Le Roux et al., 2012; Martínez Cortizas et al., 2020; Sánchez-López et al., 2016). Indeed, the Roman Period experienced an E-W humidity gradient marked by an interplay between negative North Atlantic Oscillation (NAO) and positive East Atlantic (EA) phases. These changes in the atmospheric teleconnection patterns might resulted in different air masses trajectories making different sources areas of metal pollution possible. Therefore, changes in the provenance of air masses is likely making alternative sources areas of metal pollution plausible. Inter-annual and multiannual variations in North Africa dust emissions have been extensively related to variability in atmospheric modes, such as the NAO and the ENSO (El Niño–Southern Oscillation) (Pey et al., 2013; Rodríguez et al., 2015; Salvador et al., 2014) when NAO positive phase occurs, the probability of transporting air masses from North Africa towards the IP is higher. Nevertheless, air masses travelling long distances usually move in upper layers, i.e. emissions from surface in the atmospheric boundary layer reach the free troposphere and then are transported by the westerlies flows. High altitude LM would therefore record the impact of long-range transport of trace metals-bearing air masses travelling in the free troposphere from southwestern Europe.

Global atmospheric Hg lifetime against surface deposition is estimated to be in the range of 3 to 6 months (Horowitz et al., 2017). Therefore, it is very likely that major Hg extractive episodes in Almadén resulted in high deposition in LM area. Indeed, 9.5% of the total back-trajectories arriving to LM pass over Almadén region (Table 1). Regarding other more immobile elements such as Pb, Zn, As or Cu, several studies have quantified the modern atmospheric transport of PHTE related to mining operations to determine how far the pollutants could travel from the emission sources (Asif et al., 2018; Csavina et al., 2012). These investigations documented the exponential fall of As, Zn and Pb concentration values with the distance from the mining site. Residence times of mining related-atmospheric particles might be limited to hours when PHTE would travel hardly beyond a few dozens of km except for minimum quantities. Several ore deposits are located within this distance to LM, as the Spanish Ag, Pb and Cu mines from Bielsa and Benasque and the French Montaignu mines, where Ag and Pb have been exploited in ancient times (Calvo, 2008; Girard et al., 2010; Pérez et al., 2008). Ore extraction in larger Ag-Pb and Cu Pyrenean mines such as Arditurri or Banca, in the Basque Country and Southwestern France respectively has also been documented since Roman times (Ancel et al., 2001; Thalacker, 1804). Nevertheless, back trajectories results demonstrate that the emissions from large-scale mining districts located

in Southern Spain can easily reach LM in less than three days (Fig. 1) depositing PHTE in the lake. Indeed, La Carolina-Linares, Mazarrón-Cartagena and Río Tinto mines source areas represent 8.5, 8.4 and 7% respectively. Therefore, the few air masses from the southern mining districts could rapidly transport the metals emitted during metal extraction activities and being eventually recorded in LM sedimentary archive.

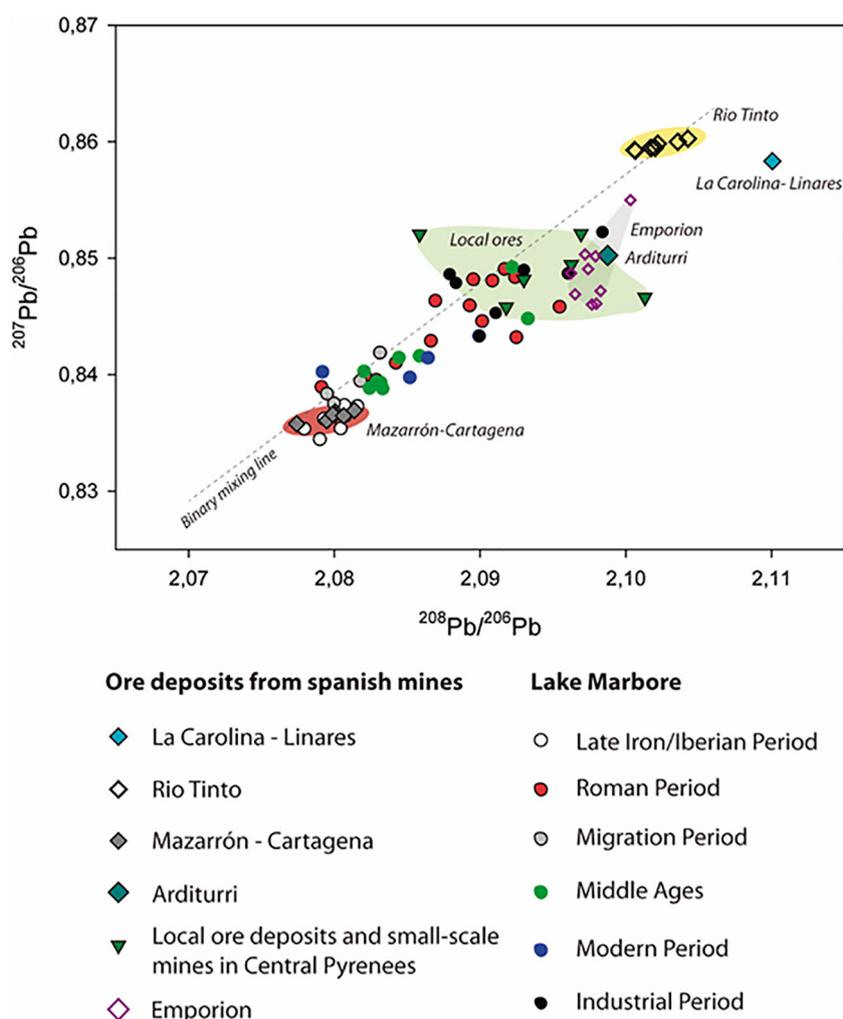
#### 4.3. Sources and environmental impact variability of mercury, silver, lead and copper mining

##### 4.3.1. Lead

Positive Pb EF was found during several periods of the last 3000 years (Fig. 4). Pb EF and  $Pb_{flux}$  remained low until 700 BCE and progressively increased since then until a maximum in 460 yrs BCE (Pb EF 2, Pb MAR  $12.7 \times 10^3 \mu g m^2 yr^{-1}$ ) and progressively decrease afterwards. Pb EF peaked again at 140 BCE (Pb EF 1.8, Pb MAR  $20.6 \times 10^3 \mu g m^2 yr^{-1}$ ). Maximum Pb EF was found during the RP between 20 and 375 yrs CE (Pb EF 3.5, Pb MAR  $31 \times 10^3 \mu g m^2 yr^{-1}$ ). Maximum peaks occurred at 50 yrs CE (Pb EF 4.5, Pb MAR  $37.5 \times 10^3 \mu g m^2 yr^{-1}$ ) and 180 yrs CE (Pb EF 5, Pb MAR  $38.5 \times 10^3 \mu g m^2 yr^{-1}$ ). Pb EF progressively decreased since the end of the RP reaching minimum values similar to natural baseline conditions between 750 and 870 yrs CE. Pb EF increased at

the onset of HMA at 950 yrs CE and remained high (mean values of 1.6) until 1350 yrs CE (Pb EF 1.8, Pb MAR  $15 \times 10^3 \mu g m^2 yr^{-1}$ ). Low Pb levels occurred between 1500 and 1820 yrs CE (Pb EF 1.5, Pb MAR  $17.5 \times 10^3 \mu g m^2 yr^{-1}$ ) reaching minimum enrichment (1.1) at 1700 yrs CE that resembles natural background values. During the IP Pb EF was very high (Pb EF 4.1, Pb MAR  $39.3 \times 10^3 \mu g m^2 yr^{-1}$ ) with maximum values at 1880 yrs CE (Pb EF 6.3, Pb MAR  $51.2 \times 10^3 \mu g m^2 yr^{-1}$ ). As and Zn follows the same trend than Pb suggesting a common source since both elements are by-products of ore exploitations from local veins enriched in galena, fluorite and sphalerite minerals.

**4.3.1.1. Iron Age.** The Pb isotopic dataset show a large variability across a well-defined mixing line (Fig. 5).  $^{208}Pb/^{206}Pb$  and  $^{207}Pb/^{206}Pb$  ratios show the lowest (geogenic) values during the IA thus suggesting that Pb concentrations during this interval may reflect natural sources. Small increases in Pb EF during the 6<sup>th</sup> and 3<sup>rd</sup> centuries BCE may reflect ore extraction from the region of Murcia in Spain (Cartagena/Mazarrón mines) in agreement with previous archaeological and paleolimnological findings from coastal lagoons in Western Mediterranean that recorded the environmental impact related to the intense mining activities in the Cartagena mining district (Elbaz-Poulichet et al., 2011; Manteca et al., 2017).



**Fig. 5.** Changes in  $^{208}Pb/^{206}Pb$  and  $^{207}Pb/^{206}Pb$  isotopic ratio in LM compared with other natural and anthropogenic (mining) sources. Different Pb isotopic values have been obtained from: Oxford archaeological lead isotope database (OXALID) (Stos-Gale and Gale, 2009) for the Linares, Río Tinto and Cartagena mines, Arditurri mines (Velasco et al., 1996), local galena mines from Emporion (NE Spain) (Montero-Ruiz et al., 2007), ore deposits and local mines from Southern Central Pyrenees (Camarero et al., 1998; Girard et al., 2010; Subías et al., 2015).

**4.3.1.2. Roman Period.** The large increase in Pb during the Roman Empire also coincides with the highest (anthropogenic)  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  isotopic ratios. The agreement of the isotopic values between 50 and 375 yrs CE and the isotopic Pb signature from local high-altitude ore deposits from nearby mines (i.e. Parzán, Bizielle, Cierco, Palouma) might suggest the exploitation of Pb and Ag in high alpine environments in the Central Pyrenees during the Roman Period.  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  isotopic ratios during the RP are similar to those during the turn of the last century when Parzán mines were largely exploited (Fanlo et al., 1998; Nieto-Callen, 1996), suggesting a plausible Roman exploitation of these mines. Nevertheless, in spite of the geochemical similarities of LM signatures for Roman and recent mining compared to regional sites, the LM isotopic results do not allow a clear adscription to local PHTM mining sources since we cannot disentangle local and regional mining from other regional pollution sources.

In our opinion, the anomalously high Pb levels during the Roman Empire imply that most of the trace metal pollution came from large-scale regional mining rather than local sources. Several indicators suggest that the exploitation of ore resources in high alpine areas from the Southern Central Pyrenees would have remained very local (if any) resulting in very reduced metal smelting and associated pollution during this period:

- i) The absence of historical records documenting Roman mining in this region. Indeed, Roman mining is often associated to the development of large infrastructures to favor transport of metal resources which are not known in the area. As an example, Arditurri silver mines exploitation during roman times came with the development of large associated infrastructures for trading (Irabien et al., 2012; Urteaga, 2014).
- ii) Mining procedures used in these exploitations required a continuous supply of goods for metal roasting and smelting which frequently results in large regional environmental impacts (i.e. deforestation and fires) (Pèlachs et al., 2009). Such environmental impacts (i.e. pollen indicators of deforestation, major increases in charcoal as indicator of biomass burning) have not been documented in regional and local paleoenvironmental reconstructions (González-Sampériz et al., 2017; Leunda et al., 2017, 2020) (Fig. 6). Additionally, studies in charcoal kilns from high altitude areas of the Pyrenees documented that charcoal production for ore smelting was likely very localized in time and space (Pèlachs et al., 2009).

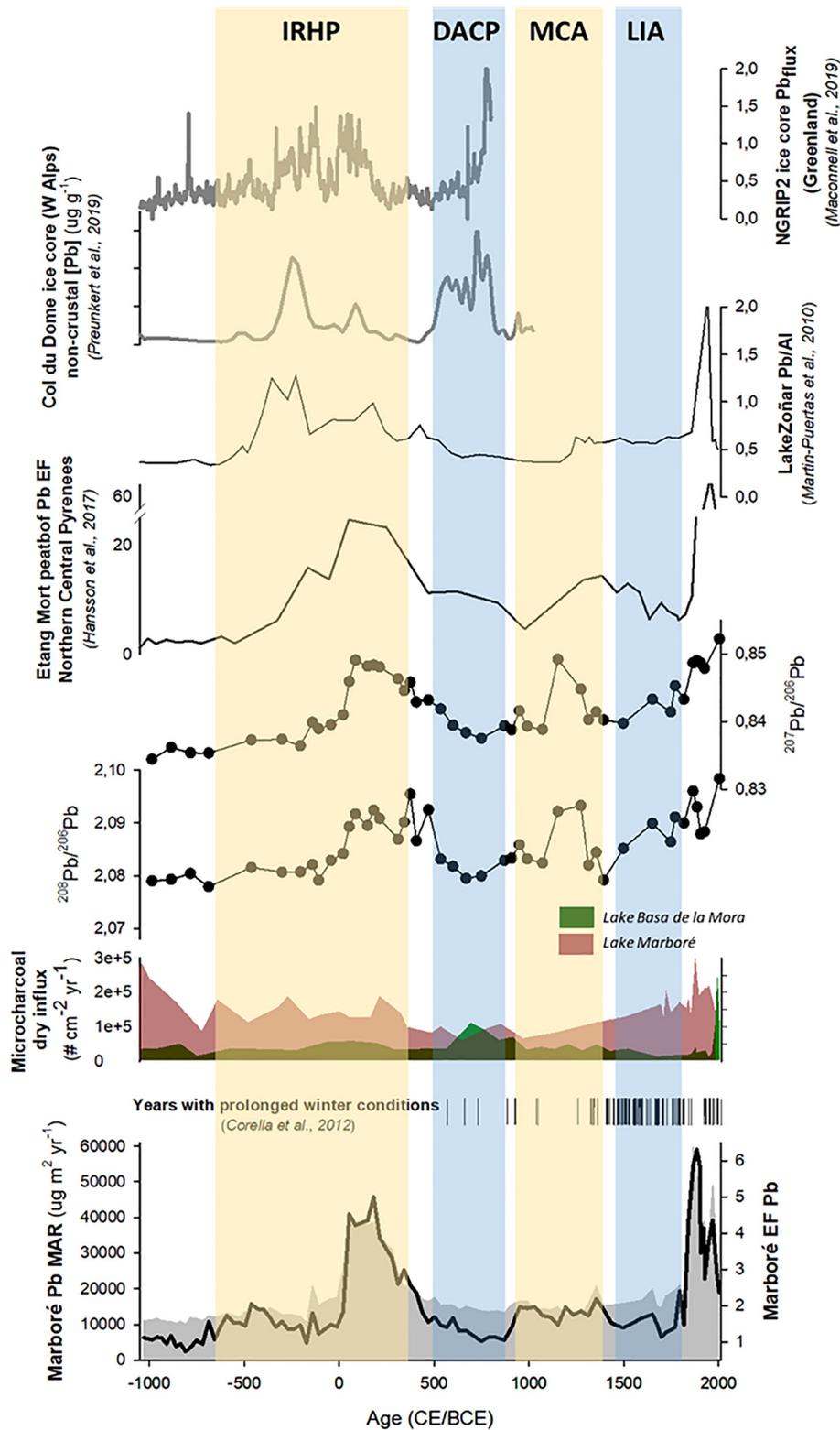
A unique feature of the LM Pb record compared to other Pyrenean records is that the maximum pre-industrial Pb levels occurred during the Roman period, synchronous to an alpine peatbog record from Northern Central Pyrenees (Hansson et al., 2017), but not with other sites in Eastern and Western Pyrenees, where maximum Pb levels appeared later at 660–680 yrs CE (Camarero et al., 1998; Irabien et al., 2012). The anomalously high Pb concentration in LM and the absence of large mining operations in the Central Pyrenees suggest that most of the trace metal pollution came from other large-scale regional mining sources. Southern Spain hosts the most important Ag and Pb mines from the Ancient World. It has been calculated that about 70% of the total atmospheric Pb released to the environment during Roman times worldwide could be assigned to the Rio Tinto and Mazarrón source areas (Rosman et al., 1997). Therefore, increased Pb fluxes during the RP might reflect the signal of large-scale mining in southern Spain. Indeed, the isotope values of LM samples for the last 3000 years fall along a mixing line between two main end-members defined by Mazarrón-Cartagena and Rio Tinto mining districts. Those LM samples from the IA show mostly a composition similar to Mazarrón-Cartagena mining district, while isotopic values during the RP have a larger range that could be an indication of more varied sources during that time, including a higher influence of Rio Tinto as well as higher input of lead from the lake's watershed via run-off. Northwestern Spain would also constitute

alternative metal pollution sources since mining activities have been well documented in the area (Martínez-Cortizas et al., 2013). Nevertheless, their contribution to the Lake Marboré Pb record are expected to be very reduced.

The environmental impact of Roman mining has also been detected in other natural archives in the French Pyrenees, and Northwestern and Southern Spain (e.g. García-Alix et al., 2013; Hanebuth et al., 2018; Hansson et al., 2017; Hillman et al., 2017; Kylander et al., 2005; Manteca et al., 2017; Martín-Puertas et al., 2010; Martínez-Cortizas et al., 1997, 2013; Pontevedra-Pombal et al., 2013)). Nevertheless, those records show variable timing and magnitude due to their location with respect to the emission sources. Thus, while LM Pb record agrees very well with Pb levels recorded in peatbogs from the Northern Central Pyrenees (Hansson et al., 2017) (Fig. 6) as well as with Pb levels recorded in coastal sediments from NW Mediterranean (Portlligat bay, 270 km east from LM) (Serrano et al., 2011). On the other hand, Pb levels in Lake Zoñar (Southern Spain) showed maximum values between 500 and 100 yrs BCE due to extensive mining in Southern Iberian Peninsula by Iberians, already influenced by Greeks and Phoenicians (Fig. 6) (Martín-Puertas et al., 2010). Further timing discrepancies have been found with other high-altitude pollution and remote records in the Alps (Cold du Dome ice core Western Alps (Preunkert et al., 2019)) and Greenland (NGRIP2 (McConnell et al., 2018)) (Fig. 6). This asynchrony in maximum Pb levels underlines the variable influence of diverse emission sources in each location. Greenland ice core records would represent the whole European emissions and Western Alps ice cores would record mostly emissions from France and Northern Mediterranean. On the other hand, LM would record PHTM emissions mostly from the main mining districts from Southwestern Europe representing the atmospheric Pb levels during the RP at a regional to sub-continental scale because of the privilege location of LM in the free troposphere. Indeed, the high Pb content in the atmosphere was a major health concern in the Iberian Peninsula during Roman times affecting Iberian population as recorded in the Pb isotopic composition of human bones from living individuals in NW Iberian Peninsula (López-Costas et al., 2020).

Pb concentrations and  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  isotopic ratios progressively declined since the end of the 2<sup>nd</sup> century CE coinciding with the decrease of Roman mining in the Iberian Peninsula, largely attributed to the socio-economic crises of the Roman Empire. These economic crises started with the Antonine plague that disrupted mining through high mortality and decreased demand as well as with the reduced silver content used in coinage in the 3<sup>rd</sup> century CE (McConnell et al., 2018). During EMA, the proximity of the mines to population settlements was a significant factor for mine abandonment due to the transportation costs and because local miners adopted methods and infrastructure less efficient than those of Roman times (Martinon-Torres and Rehren, 2011).

**4.3.1.3. Last millennium.** An increase in Pb EF and MAR and a shift towards more radiogenic values occurred during the HMA and LMA most likely related to the renew mining activities and the exploitation of more local mines as Parzán (Fig. 1). This period coincides with widespread innovations in mining and refining processes in Europe to reach the high demands of the increasing European population between 11–13<sup>th</sup> centuries. The Pb peak at the second half of the 12<sup>th</sup> century coincides with the first historical evidences of local mining in Parzán when Aragonese King Alfonso II conceded official privileges of exploitation of the Bielsa mines to the local people (Bielza de Ory, 1983). The decline of Pb levels since 1350 yrs CE recorded in LM sediments coincides with the interrupted metal production in Europe during the Black Death Pandemic (1349–1353 yrs CE) that dropped atmospheric Pb to undetectable levels (More et al., 2017). Pb levels recovered afterwards, but remained low during the following centuries that might be related to the onset of large-scale silver mining in South America. In this context, high alpine, small-scale silver mines such as the ones in the Axial Pyrenees were less profitable and probably intermittently abandoned.



**Fig. 6.** From bottom to top: Lead enrichment factor (EF), Pb Mass Accumulation Rates (MAR) during the last 3000 years; Calcite sublayering in Lake Montcortès as a proxy of prolonged winter conditions in Southern Central Pyrenees (Corella et al., 2012); Charcoal fluxes in LM and Lake Basa de la Mora sediment records as proxies of fires and human activities in the area (Leunda et al., 2020); Pb isotopic ratios in LM; Etant Mort Pb EF (redrawn from Hansson et al. (2017)); Lead content in western Alps (Col du Dome ice core (Preunkert et al., 2019)) and Greenland ice cores (McConnell et al., 2019). Coloured vertical bars represent the main climatic phases during the Late Holocene.

However, historical archives documented that more than 15,000 kg of Pb were produced (and smelted in local kilns) in Parzán by the end of the 16<sup>th</sup> century (Nieto-Callen, 1996). Only at the end of the 19<sup>th</sup> century, Pb levels increased exponentially in LM (Fig. 6) and other Pyrenean

lakes (Corella et al., 2017, 2018) due to large-scale exploitation of Parzán mines (Fanlo et al., 1998; Nieto-Callen, 1996).

The correspondence between atmospheric Pb levels and warmer climate phases during the last millennium suggests a connection

between source availability (i.e. ore extraction and smelting) and depositional processes with climate. Thus, the Pb and Ag mining extractive period in the Pyrenees during the HMA and LMA coincided with the MCA, a warm and arid period in the Iberian Peninsula between 950 and 1350 yr CE (Moreno et al., 2012). Prolonged snow-free periods at the mining sites would have favoured ore resources exploitation in mountain areas. On the other hand, a return to almost baseline natural backgrounds of atmospheric Pb levels that occurred between the EMA and the MP coincided with the DACP and the LIA, known as cold periods in NE Iberian Peninsula (Corella et al., 2012, 2013; Morellón et al., 2012) and Iberian mountains (Oliva et al., 2018). Atmospheric pollution levels were particularly low during the Maunder Minimum (1645–1715 yrs CE) when trace metals accumulation fluxes were greatly reduced (Fig. 4). Therefore, climate variability has been likely also a determinant factor controlling mining in high-alpine environments (e.g. Parzán mines located at >2300 m a.s.l.) during the last centuries. The relation between past warmer climate phases and mining activities in high alpine environments was also observed in the western Alps (Guyard et al., 2007) where ore extraction became possible because of glaciers retreated in the region when temperature increased.

#### 4.3.2. Copper

Cu EF increased progressively reaching the highest values at the end of the IA at 360 yrs BCE (Cu EF 2) (Fig. 4). Cu EF decreased during the first phase of the RP until 50 yrs CE. Cu EF started to increase during the mid 4<sup>th</sup> century and peaked at the onset of the 5<sup>th</sup> century CE (410 yrs CE, Cu EF 3.2). Cu EF reduced during the EMA and increased during the HMA and LMA (Cu EF 2) with maximum Cu enrichment at 1200 yrs CE (Cu EF 2.7). Cu EF remained high during the 16<sup>th</sup> century with mean Cu enrichment of 2.4. Cu EF decreased during the 18<sup>th</sup> century and increased again during the IP (Cu EF 2.6) peaking at the turn of the 19<sup>th</sup> century (Cu EF 3.4).

The first documented increase in copper concentrations in Greenland exceeding the natural levels occurred about 2500 years ago (Hong et al., 1996) and provides evidence for widespread copper mining during the Iron Age. The oldest presence of copper miners and metalworkers in the region was documented in the Montpellier region (Southern France) in the 3<sup>rd</sup> millennium BCE (Ambert et al., 2002) while large copper mines were in operation in N Iberia since the Chalcolithic (de Blas, 2005; Vidal, 2012; Martínez-Cortizas et al., 2016).

The Cu enrichment in LM during the 4<sup>th</sup> century BCE agrees well with an enrichment in Cu recorded in peatbogs sediments from Northern Central Pyrenees between 480 and 180 yrs BCE (Hansson et al., 2017) suggesting copper mining from the abundant Cu-rich ore deposits in the region (Calvo, 2008). The high Cu levels since 50 yrs CE remained elevated during almost all Roman Empire most likely due to the highly polluting smelting technologies used for copper production during Roman times in Europe (Hong et al., 1996). This is in agreement with the roman exploitation of Banca mines (French Western Pyrenees), the largest roman copper mines in France, between the 1<sup>st</sup> century BCE and the 4<sup>th</sup> century CE (Ancel et al., 2012; Urteaga, 2014). Nevertheless, the highest copper production in the Iberian Peninsula occurred in the Río Tinto region (SW Iberia) as well in other copper mines from NW Iberia (Wilson, 2002). Maximum atmospheric Cu levels between the mid 4<sup>th</sup> century and the early 5<sup>th</sup> century might reflect the increase in copper demand for coinage when Roman monetary system shifted to a bimetallic currency composed of a gold and copper alloy (McConnell et al., 2018; Wilson, 2002).

Copper levels increased again in LM record at around 1200 yrs CE and persisted high for almost five centuries. The enrichment in the early 13<sup>th</sup> century occurred almost one century before the first historical documents of copper mining in the area when kings Alfonso II and Jaime II conceded privileges for mineral extraction to local noblemen in the Pyrenean surrounding valleys as well as from Santa Eulalia la Mayor (60 km south of LM) in 1277 and 1293 yrs CE, respectively. The use of

local kilns for Cu, Ag, Pb and Fe smelting practices were also documented during this time (Nieto-Callen, 1996). Cu levels decreased during the 18<sup>th</sup> century and peaked again in the 19<sup>th</sup> century. This variability is in agreement with the historical local mining activities of the area that derived, on the one hand, in unsuccessful copper resources prospection during the 18<sup>th</sup> century and, on the other hand, the boost of copper mines in the region during the 19<sup>th</sup> century (Nieto-Callen, 1996).

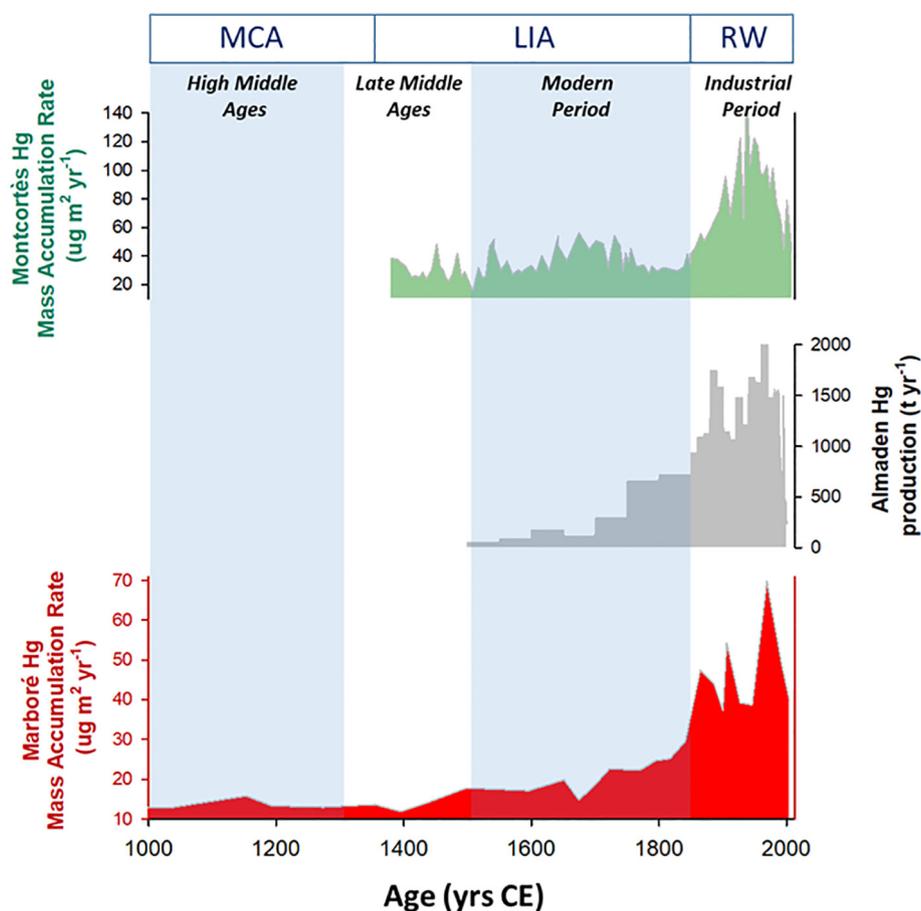
#### 4.3.3. Mercury

Hg levels in LM showed a significant variability during the Late Holocene. Mercury EF and Hg<sub>flux</sub> were at the lowest levels until 620 yrs BCE (EF <1, 12.8 µg m<sup>2</sup> yr<sup>-1</sup>) and remained high between 620 and 270 yrs BCE (Hg EF = 1.2, Hg MAR = 13.4 µg m<sup>2</sup> yr<sup>-1</sup>). Low values were found until 20 yrs CE and then increased slightly during the RP. Hg EF remained stable until the MP, when Hg EF progressively increased with mean Hg EF values of 1.9 (Hg MAR = 18.4 µg m<sup>2</sup> yr<sup>-1</sup>) reaching maximum values during the IP (Hg EF = 3.7, Hg MAR = 40 µg m<sup>2</sup> yr<sup>-1</sup>).

Hg emissions before the Industrial Period have been mostly attributed to historical mining, volcanic activity and coal burning (Cooke et al. (2020) and references therein). Periods of Hg levels in LM are not coherent with the impact of the main volcanic eruptions in the Northern Hemisphere, although the decadal chronological resolution of LM might have hindered the identification of volcanic episodes with large Hg emissions to the atmosphere (e.g. Vesubio volcanic eruption in 79 yr CE coinciding with the higher Hg EF during the 1<sup>st</sup> century CE). Recent studies in the French Pyrenees and Southeastern France have suggested that atmospheric Hg deposition increase during the Medieval and the Modern Period was mostly caused by enhanced Hg emissions from biomass burning (Elbaz-Poulichet et al., 2011; Enrico et al., 2017). Nevertheless, Hg MAR and EF in LM does not coincide with major deforestation and burning episodes in alpine environments from the Southern Central Pyrenees (González-Sampérez et al., 2017, 2019; Leunda et al., 2017, 2020) (Fig. 6). Therefore, Hg net fluxes recorded in LM would most likely be related to Hg emissions caused by local and/or regional mining activities.

Hg EF for the period 1000 yrs BCE–1500 yrs CE correlates well with Zn EF ( $\sigma = 0,81$ ) and, to a lesser extent, with Cu ( $\sigma = 0,65$ ). This correlation suggests that Hg enrichments before the Modern Period might be related to the exploitation of i) local Pb (Ag)-Zn veins which are dominated by galena and sphalerite deposits (Subías et al., 2015) and/or ii) chalcopyrite exploited in local fire settings for copper extraction since these minerals can host significant Hg concentrations (George et al., 2018; Rytuba, 2003) which can eventually result in increased Hg emissions (as by-products) to the local atmosphere. Recent paleolimnological studies in the Alps have also highlighted the influence of local Cu and Pb-Ag ore exploitations controlling Hg enrichment in high alpine environments in ancient times (Elbaz-Poulichet et al., 2020). Nevertheless, we cannot exclude Hg emissions from regional sources (i.e. Almadén mines, Central Spain) since large-scale cinnabar mining in Almadén has been carried out during the last 2500 years (Hernández, 2007). Considering back trajectories analyses and atmospheric Hg residence times it is very likely that major Hg extractive episodes in Almadén resulted in an increase Hg accumulation in LM. Almadén's mining exploitation by Romans and Arabs resulted in large Hg release to the atmosphere. Indeed, the Roman writer Pliny the Elder wrote about the extraction of Hg (and its distillation in marmites) and its trade between Spain and Rome in the 1<sup>st</sup> century CE, while the Arabs intensified Hg production in Almadén with more than 1000 laborers working in the mines during the 11<sup>th</sup> century (Goldwater, 1972).

The progressive increase in Hg EF and MAR that occurred in LM during the last 500 years greatly differs from the other metal EFs evolution (Fig. 7) and follows the Hg historical production in Almadén documented during the last five centuries (Hylander and Meili, 2003). Hg production significantly increased in the 16<sup>th</sup> century due to the need for Hg amalgamation in silver mining in the Spanish colonies. As a result, large amounts of Hg dissipated to the environment. As an example,



**Fig. 7.** Atmospheric mercury (Hg) deposition in the Central Pyrenees over the last millennium from LM (this study) and Montcortès (Corella et al., 2017) as well as estimations of mercury production in Spanish mines (Hylander and Meili, 2003). Main historical and climatic phases are also indicated.

between 1571 and 1660 yrs CE approximately 25,000 tons of Hg were produced in the mines (Hylander and Meili, 2003). This likely resulted in a 30% increase in Hg MAR during this period ( $18.2 \mu\text{g m}^{-2} \text{yr}^{-1}$ ) from the stable Hg MAR before the Modern Period ( $13.7 \mu\text{g m}^{-2} \text{yr}^{-1}$ ). A 25% decrease in Hg MAR at 1675 yrs CE could be explained by the drastic decrease in Hg Almadén production during the second half of the 17<sup>th</sup> century due to the exhaustion of Hg resources in Almadén (Bethell, 1984) and the reduction of Hg shipping to South America. Nevertheless, the discovery of new veins in Almadén at the turn of the century most likely explains the abrupt increase in Hg MAR during the early 18<sup>th</sup> century ( $22.6 \mu\text{g m}^{-2} \text{yr}^{-1}$ ). Hg levels progressively increased during the Industrial Period peaking at the turn of the 20<sup>th</sup> century (EF of  $\sim 4$  and MAR of  $\sim 40 \mu\text{g m}^{-2} \text{yr}^{-1}$ ) and between 1960 and 1970 yrs CE (EF of 4.8 and MAR  $70 \mu\text{g m}^{-2} \text{yr}^{-1}$ ) when Hg production peaked at 10000 tons per year (Hylander and Meili, 2003). The Hg variability pattern recorded in LM during the 20<sup>th</sup> century is similar to the recent Hg variability highlighted in multi-short cores studies in Southern Sweden and NW Spain (Bindler et al., 2004; Martínez Cortizas et al., 2012).

The 2-fold decline in Hg MAR since 1970 yrs CE coincides with a decreasing trend in Hg production in Almadén during the last decades (Fig. 7) until its closure in the 2000s. This 2-fold decrease in atmospheric Hg concentrations since the 1970s is in agreement with direct atmospheric monitoring and glacier firn records (EMEP; Faïn et al., 2009).

In the Iberian Peninsula, anthropogenic Hg release to the atmosphere due to mining activities in Almadén ca. 2500 years before present was first documented in peat cores from NW Spain (Martínez-Cortizas et al., 1999), estuarine sediments from Southwestern Spain (Leblanc et al., 2000) and marine sediments in the Western

Mediterranean (Portlligat Bay) (Serrano et al., 2013). In the Pyrenees, atmospheric Hg fluxes have been previously reported in peat sediments from the French Pyrenees (Enrico et al., 2017) as well as in lake Montcortès in the Pre-Pyrenees located at 1031 m a.s.l. (Corella et al., 2017). LM Hg concentration and fluxes agree well with atmospheric Hg fluxes previously reported in peat sediments from the French Pyrenees (Enrico et al., 2017) as well as in low-elevation lake Montcortès sediments in the Pre-Pyrenees (Corella et al., 2017) highlighting the regional to sub-continental scale pollution recorded in these natural archives.

## 5. Summary and conclusions

The geochemical Lake Marboré record allowed us to understand the atmospheric variability of hazardous trace metals related to historical mining and metalworking activities in the Iberian Peninsula during the Late Holocene. The location of the lake at  $>2600$  m a.s.l. makes it particularly sensitive to tropospheric transport of trace metals. Historical metallurgy has derived in a significant increase in Hg, Pb and, to a lesser extent, Zn, Cu and As during the Pre-Industrial Period constituting one of the oldest, large-scale anthropogenic impact on the environment. This historical atmospheric pollution has left a profound geochemical signature in the lake where several trace metals reach concentration levels that might have had ecotoxicological implications in these high-mountain ecosystems.

The multidisciplinary approach involving statistical, isotopic and meteorological re-analyses have also enabled the reconstruction of the history and sources of hazardous trace metal pollutions over the last 3000 years. Back trajectories analyses show that air masses capable of

transporting atmospheric pollutants to Lake Marboré may come from almost all southwestern Europe and northern Africa in less than 3 days highlighting the sensitiveness of the lake to track environmental pollution sources at a local to sub-continental scale. Pb isotopic analyses suggest that Ag and Pb mining in south-eastern Spain might have been responsible for subtle trace metal enrichments during the Late Iron Age. Very high atmospheric Pb fluxes were found during the Roman Empire most likely related to the global rise of atmospheric Pb emission from Río Tinto and Mazarrón mines emplaced in southern Iberia Peninsula. Isotope analyses suggest a contribution of small-scale ore exploitation from local, high-altitude mines but more archaeological surveys are needed as the assessment of all local sources is a critical issue when reconstructing the history of pollution using natural archives. Independently of the source we find evidence that atmospheric Pb levels were of the same magnitude that the ones found during the Industrial Period. Local Ag, Pb and Cu mining reactivated in the Central Pyrenees during the High Middle Ages when socio-economic conditions and mild-climates allowed ore extraction in high-alpine environments and all over the Iberian Peninsula. These local mining activities significantly decreased during the harsh climate conditions documented at the onset of the Little Ice Age. Contrarily, atmospheric Hg progressively increased during the Modern Period due to the large-scale production in Almadén mines in Central Spain, leading to high loads of Hg burden in Pyrenean sedimentary environments.

Lake Marboré record of past emissions related to mining and metalworking activities shows a common pattern with other European pollution records showing a climax during the Roman period, Medieval times and since the Industrial Revolution. This agreement could be partly explained by the location of the lake above the mixing atmospheric boundary layer, therefore, recording long-range (inter-hemispheric) atmospheric pollutants transport. The lake's location in a high elevation area, as well as the watershed and limnological characteristics of Lake Marboré makes this site a unique record of past atmospheric contamination that highlights the usefulness of long-term pollution archives to contextualize current atmospheric pollution levels. Indeed, the environmental consequences and atmospheric Pb pollution in Antiquity are substantial and could even exceed present-day levels.

This study provides a further understanding of the pollution burden legacy in lacustrine sediments constituting a significant environmental hazard for high-mountain ecosystems that should be adequately quantified and monitored. Our findings also contribute to the contextualization of current air metal pollution by reconstructing long-term (centennial to millennial-scales) atmospheric trace metal levels beyond the very few instrumental measurements that barely spans the last decades. Nevertheless, the determination of pollution sources presented in this study are not entirely conclusive. Follow-up studies on Lake Marboré focussed on Hg, Pb, Nd and Sr isotopes will shed more light on the provenance and biogeochemical cycling of the main pollutants deposited in the lake.

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### Credit authorship contribution statement

J.P.C and B.V.G devised the research. J.P.C wrote the manuscript. J.P.C, M.J.S, R.M, J.R-A, performed the elemental geochemistry analyses. A.G carried out the isotopic analyses. P.G.S provided the pollen data. J.A.A and C.A.C computed the air masses back-trajectories analyses; All co-authors helped in the data interpretation and manuscript writing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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