700 years reconstruction of mercury and lead atmospheric deposition in the Pyrenees (NE Spain)

J.P. Corella ^{a,*}, B.L. Valero-Garcés ^b, F. Wang ^c, A. Martínez-Cortizas ^d, C.A. Cuevas ^a,
A. Saiz-Lopez ^a

^a Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Rocasolano, CSIC, Serrano 119, 28006, Madrid, Spain

^b Pyrenean Institute of Ecology, CSIC, Zaragoza, Spain, Avda Montañana 1005, 50059, Zaragoza, Spain

^c Centre for Earth Observation Science, Department of Environment and Geography, University of Manitoba, Winnipeg, MB R3T 2N2, Canada

^d Departamento de Edafología y Química Agrícola, Facultad de Biología, Universidad de Santiago de Compostela, Campus Sur E-15706, Santiago de Compostela, Spain

HIGHLIGHTS

- Atmospheric Hg and Pb depositional history is reconstructed for the last 700 yrs.
- Atmospheric vs. run-off mercury input are detangled by microfacies analyses.
- Highest mercury accumulation occurred during World War II.
- Mercury fluxes are in agreement with those estimated by global inventories.
- Mining activities were the main contributors to Hg and Pb atmospheric fluxes.

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ABSTRACT

Geochemical analyses in varved lake sediment cores (Lake Montcortès, Pre-Pyrenees) allowed reconstruction of mercury (Hg) and lead (Pb) atmospheric deposition over the past seven centuries in the Pyrenees (NE Spain). Accumulation Rates (AR) from the Middle Ages to the Industrial Period ranged from 2500 to 26130 $\mu\text{g m}^{-2}\text{y}^{-1}$ and 15–152 $\mu\text{g m}^{-2}\text{y}^{-1}$ for Pb and Hg respectively. Significant metal pollution started ca CE 1550 during a period of increased exploitation of ore resources in Spain. Colder and humid conditions in the Pyrenees during the Little Ice Age may have also favoured Hg and Pb atmospheric deposition in the lake. Therefore, the interplay between increased rainfall (wet deposition) and mining activities in the Iberian Peninsula has driven Hg and Pb AR during the Pre-industrial Period. More recently, the use of leaded gasoline in Europe in the mid-20th century may explain the highest Pb AR between CE 1953 and 1971. The highest Hg AR occurred in CE 1940 synchronous with the highest Hg production peak in Almadén mining district (southern Spain) and the Second World War. The record of Hg enrichment in Lake Montcortès shows a decrease during the last decades in Western Europe similar to other regional records and global emission models. This study highlights the exceptional quality of varved sequences to tease apart pollutants depositional mechanisms, identify historical periods of increased atmospheric pollution and provide a historical context for pollutant baseline values to make correct assessments of recent (atmospheric) pollution in lake ecosystems.

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1. Introduction

The contribution of atmospheric deposition on trace metal concentrations in soils and sediments is controlled by both the

hydrological cycle and atmospheric patterns (Blais et al., 2015; Salomons and Förstner, 1984). Mercury (Hg) and lead (Pb) are major global pollutants subject to long-range transport, posing a threat for both human and environmental health at a global scale. During the last decade, both elements have been given priority attention by international programs aiming to reduce environmental and human exposure to them (AMAP/UNEP, 2013; Pacyna

* Corresponding author.

E-mail address: pcorella@iqfr.csic.es (J.P. Corella).

et al., 2009; Selin, 2009). Mercury and Pb are emitted to the atmosphere from both anthropogenic and natural sources. Nevertheless anthropogenic emissions have greatly exceeded natural release to the atmosphere over historical times (Amos et al., 2013; Engstrom et al., 2014; Martínez-Cortizas et al., 1999; Martínez Cortizas et al., 2012; Schwikowski et al., 2004), even at remote locations far from emission sources (Bindler et al., 2001; Fitzgerald et al., 1998; Lindeberg et al., 2006; Weiss et al., 1971). These anthropogenic emissions before the Industrial Period are mostly related to historical mining (Allan et al., 2013; Martínez-Cortizas et al., 1999, 2002). The Mediterranean has a long history of mining activities with the two world's largest Hg mines located in southern Spain (Almadén mining district) and Slovenia (Idrija mine). Almadén mines (Fig. 1), have alone contributed approximately one third of the globally mined Hg, with an accumulated historic Hg emission estimate of 10000 tons (Hylander and Meili, 2003). 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) and marine sediments in the Western Mediterranean (Portlligat Bay, Fig. 1) (Serrano et al., 2013). One decade after the closure of the mines in the early 2000s, total gaseous Hg concentrations in the air still exceeded the Hg World Health Organization (WHO) air quality standards (maximum recommended levels at 1000 ng m^{-3}) for nearby urban areas (WHO, 2000; Tejero et al., 2015). In Idrija, more than 34 000 tons of Hg were dissipated to the environment during five centuries of mining and significant mercury concentrations in the air are still present near the major sources of mercury vapour (Gosar et al., 1997). More locally, in the Pyrenees, the presence of ore deposits in the Bielsa-Parzán mining district (Fig. 1) may have been known since pre-Roman times (Calvo, 2008). In Lake Redó, for example, Camarero et al. (1998) detected a large increase in Pb concentrations in sediments dating to circa CE 500–700, that were attributed to, non-historically documented, mining activities in the area. However, Pb galena was not largely exploited until the 16th century. Galena was subsequently smelted in local kilns. More than 15000 kg of lead were produced by the end of the 16th century (Nieto-Callen, 1996). The onset of large-scale Pb production started by the end of the 19th century lasting until CE 1928, when the closure of the mines due to the decrease in Pb prices ended with the historical metal mining in this area (Calvo, 2008; Fanlo et al., 1998).

Natural archives (mostly peat and lacustrine sediments) have been widely used to reconstruct atmospheric depositional histories of pollutants - see Amos et al. (2015); Biester et al. (2007); Blais et al. (2015); Cloy et al. (2008); Engstrom et al. (2014) and references therein - since instrumental measurements of these atmospheric pollutants are scarce and barely span the last decades. Unfortunately there is an uneven distribution of atmospheric pollutants natural archives. Surprisingly, there is only a few reconstructions of Hg pollution during the last millennium in the Iberian Peninsula, where Almadén mines are located (Martínez-Cortizas et al., 1999, 2012; Serrano et al., 2011).

The quantification of atmospheric deposition using natural archives is not straightforward. In lake sediments it is often difficult to disentangle run-off inputs vs atmospheric deposition of pollutants. Besides, metal remobilization in the sediment/water interphase caused by bioturbation and redox changes may affect some elements concentrations (Biester et al., 2007; Outridge and Wang, 2015). However, no apparent losses of total Hg seem to occur in lake sediments (Rydberg et al., 2008). On the other hand, ombrotrophic mires receive pollutants solely via atmospheric deposition (Martínez Cortizas et al., 2012; Shotyk et al., 1996). As a result, these records may suffer long periods of aerial exposure and inner diagenetic processes that tend to distort metal accumulation

(Biester et al., 2007; Enrico et al., 2016).

Annually laminated (i.e. varved) lake sediments located in small mountain catchments overcome these limitations since anoxic conditions in the lake's hypolimnion impede the alteration of surface sediments by bioturbation (Brauer, 2004). Their high chronological resolution, annual to seasonal, also provides a unique opportunity to quantify trace metals loads and to evaluate the long and short-term ecosystem's responses to the implementation of environmental policies. Unfortunately, studies on varved sediments are scarce and in some cases barely spanning a few decades (see for example Rydberg et al., 2008), mostly due to limnological changes caused by human-induced eutrophication processes (Hollander et al., 1992; Lotter et al., 1997). The varved Lake Montcortès is an annually-laminated record in the NE Iberian Peninsula with preservation of biogenic varves for the last millennia (Corella et al., 2011b, 2012). In this study we describe the trace metal record from this lake, which represents one of the few high-resolution reconstructions of Hg and Pb depositional history in southern Europe for the last 700 years. In addition, this study builds on previous investigations where endogenic and allochthonous sediments were well characterized (Corella et al., 2012, 2014, 2016). This detailed understanding of the lake's sedimentary microfacies and depositional processes has allowed us to discriminate the Hg and Pb inputs from the lake watershed (delivered to the lake via run-off) that may introduce noise to the atmospheric signal. We also provide an evaluation of the possible natural and anthropogenic sources of these metals, as well as the depositional processes operating at local and regional scales since the Middle Ages.

2. Materials and methods

2.1. Study site

Lake Montcortès is located in the southern Pre-Pyrenees ($42^\circ 19' \text{ N}$, $0^\circ 59' \text{ E}$, 1031 m a.s.l.), within the sub-Mediterranean bioclimatic domain, between the Mediterranean lowlands and the Middle Mountain belt (Rull et al., 2011). The lake was formed by karstic processes on Triassic evaporite-bearing formations (Corella et al., 2011b). The lake's watershed is relatively small (1.39 km^2 surface area) and composed of carbonates and evaporites (Triassic) and conglomerates (Oligocene) (Fig. 1B). Meadows and pastures dominate in the watershed lowlands while deciduous and conifer forests cover the elevated areas (Corella et al., 2014). The morphology of the lake is almost circular, with a surface area of 0.14 km^2 , a maximum water depth of ~30 m and steep margins. There is no permanent inlet (only an ephemeral stream located in the southern area of the lake) and the lake level is controlled by an outlet stream located in the northern shore and the groundwater inflow/outflow balance (Fig. 1B). A permanently anoxic monimolimnion is well developed below 18–20 m depth (Corella et al., 2012). Anoxic bottom conditions prevailed in the lake during the Late Holocene and enabled the preservation of biogenic varves punctuated by detrital layers related to run-off processes.

2.2. Sediment cores and age model

Two UWITEC gravity cores (MON12-3A-1G, 78 cm length, and MON12-2A-1G, 106 cm length) were retrieved at the deepest distal lake basin (~30 m water depth) (Fig. 1C). The sediment cores were split lengthwise and high resolution images were obtained by the AVATECH core scanner coupled camera. The sediment sequence was sampled in 26 cm-long plastic holders for thin-section preparation following the methodology described by Brauer and Casanova (2001). Sedimentary facies characterization was performed by optical inspection of thin sections. A composite

Fig. 1. A) Map of the Iberian Peninsula with the location of Lake Montcortès and the main sites mentioned in the text; B) Lake Montcortès sketch geological map with location of the ephemeral inlet (dotted line) and the main outlet in the southern and northern areas of the lake respectively; C) Bathymetric map of the lake and location of the coring sites.

sedimentary sequence of ~1 m in length was obtained by detailed facies correlation using marker layers – mostly detrital layers – unequivocally identified in both sediment cores (Corella et al., 2014).

The age-depth model is based on two independent dating techniques: i) varve counting performed on calcite layers and ii) radiometric dating by ^{210}Pb and ^{14}C . Previous studies in Lake Montcortès documented a nonlinear varve counting error with a mean between 0 and 3%. Less than 1% of varves were interpolated due to poor varve preservation in selected intervals (Corella et al., 2012, 2014). Constant rate of supply (CRS) modeling of the ^{210}Pb activities was applied to obtain the ^{210}Pb chronology (Corella et al., 2014). The good agreement between both chronologies supports the robustness of Lake Montcortès age-depth model. The upper 1 m of sediment spans from CE 1386 to Present – see Corella et al. (2014) for further description of the age depth model –.

2.3. Sediment sampling procedure

Since the aim of this study is the reconstruction of atmospheric pollutants deposited in the lake sediments, sediment-laden deposits (i.e. detrital layers) from watershed runoff have to be considered. These detrital layers represent allocthonous material eroded from the lake catchment. Mass wasting events involving littoral material from the steep slopes of the lake are also recorded in the distal area of the lake sediments as mass movement turbidites –see Corella et al. (2014) for further details of sedimentary facies– which may contain metal concentrations that do not reflect direct atmospheric deposition. Both, detrital layers and mass wasting events are affected by lake's internal reworking processes and watershed hydrology, obscuring the atmospheric signal preserved in the lake sediments. Therefore, sediment samples from thinly laminated varved intervals were obtained after a detailed inspection of the sedimentary facies using a binocular scope ($\times 5$ magnification) in order to avoid cm-thick detrital layers and turbidites that punctuate the sedimentary record.

2.4. Geochemical analyses

A suite of major and minor elements (e.g. Zr, Ti, Zn, Rb, K, S, As, Al, Fe, Br, Cr, Ca, Sr and Si) were analyzed in the composite sedimentary sequence, at a vertical resolution of 0.2 mm, using an X-ray fluorescence (XRF) AVAATECH core scanner (2000 A, 10–30 kV and 20–50 s measuring time). The results are given as counts per second (cps), providing high-resolution semi-quantitative information of the geochemical composition of the sediment down-core that was compared to microfacies.

A total of 87 discrete samples at a vertical resolution of 0.5–1 cm were analyzed quantitatively for Hg and Pb. The samples were weighed before and after drying to estimate the sediment bulk density. The dried samples were acid digested on a microwave digestion system (MARS V of CEM). The digestant was then analyzed for Pb by inductively coupled plasma mass spectrometry (ICP-MS) on a PerkinElmer DRC II instrument, and for Hg by cold vapor atomic fluorescence spectroscopy (CVAFS) on a Tekran Model 2600 Mercury Analyzer. QA/QC for sediment core analysis was carried out using replicates, method blanks, field blanks, and a certified reference material (CRM, Buffalo River Sediment 8704 from NIST, USA). All measured samples showed less than 15% deviation from CRM. Lead and Hg concentrations are expressed in $\mu\text{g g}^{-1}$ of dry weight sediment. Mass accumulation rates were calculated as the product of their concentration in the sediment, the dry bulk density of the sediment, and sedimentation rates according to Givélet et al. (2003). Enrichment factors (EFs) of these two elements

are commonly used to identify and quantify anthropogenic interferences in natural element cycles (Amos et al., 2015; Biester et al., 2007; Weiss et al., 1999). In this study, EFs have been calculated using the average element fluxes during the pre-medieval period –before CE 1550, following Amos et al. (2015), as baseline conditions which may differ from natural background values –:

$$EF = \frac{\text{Hg flux}_{\text{cm}}}{\text{Hg flux}_{\text{baseline}}}$$

2.5. Statistical analysis

Principal Component Analyses (PCA) was applied to reduce the large geochemical dataset into a smaller number of variables (i.e. principal components (PC). PCA was carried out including all the elements (Zr, Ti, Zn, Rb, K, S, As, Al, Fe, Br, Cr, Ca, Sr, Pb, Hg and Si). The XRF dataset was re-sampled every centimeter to obtain a homogeneous database. The PCA was performed with varimax rotation over the geochemical dataset using the SPSS 23.0 software. PCs were then be interpreted in terms of environmental and depositional processes (Giralt et al., 2008).

3. Results and discussion

3.1. Lake sedimentary facies and geochemistry

Annually-resolved biogenic varves characterize Lake Montcortès sedimentary sequence (Corella et al., 2011b). These varves are composed of calcite layers that precipitate due to enhanced bioproductivity during summer algal blooms, and organic detritus deposited throughout the year (Corella et al., 2012). Thin clastic laminae also occur within the carbonate and organic couplets and they record seasonal deposition by heavy storm events (Corella et al., 2016). Dry bulk densities of the biogenic varves show average values of $\sim 0.5 \text{ g cm}^{-3}$ for the upper 10 cm, and 0.7 g cm^{-3} for deeper sediments (Fig. 2). Turbidite layers punctuate the sedimentary record and are the result of sediment delivery to the lake during watershed run-off events. They display higher dry bulk densities ($\sim 1 \text{ g cm}^{-3}$) than biogenic varves. Three lithostratigraphic units have been defined according to the frequency of turbidites. The top (youngest) unit I (0–11.5 cm, 1902–2012 CE; AR = 0.13 cm yr^{-1}) and bottom (oldest) unit III (49–100 cm, 1386–1844 CE; AR = 0.11 cm yr^{-1}) are mostly dominated by biogenic varves. Unit II (11.5–49 cm, 1902–1844 CE) shows the highest turbidite frequency and thickness and the highest accumulation rates (AR = 0.64 cm yr^{-1} , Fig. 2). Turbidites were removed from the age-depth profile in order to calculate sediment fluxes.

The μ -XRF downcore geochemical record shows a clear correspondence with the sedimentary facies. We have selected two elements (Ca and Zr) to illustrate the geochemical variability of the Montcortès record. The endogenic carbonate precipitation enrichment in units I and III is well defined by the calcium record, while the increase of turbidite frequencies and fining upwards texture is well-represented by the Zr record (Fig. 2). The total metal concentrations in Lake Montcortès sediment before the onset of the Industrial Period (lithostratigraphic unit III, 1386–1844 CE) range from 0.03 to $0.11 \mu\text{g g}^{-1}$ (mean values of $0.054 \mu\text{g g}^{-1}$; sd = 0.01) for Hg and 6.9 – $23 \mu\text{g g}^{-1}$ (mean values of $11.8 \mu\text{g g}^{-1}$; sd = 2.9) for Pb. Since 1844 CE, metals concentrations in the sediment range between 0.05 and $0.2 \mu\text{g g}^{-1}$ (mean values of $0.11 \mu\text{g g}^{-1}$; sd = 0.03) and 14.1 – $36.4 \mu\text{g g}^{-1}$ (mean values of $25.1 \mu\text{g g}^{-1}$; sd = 5.8) for Hg and Pb respectively (Fig. 2).

Fig. 2. From left to right: Core image of the studied Lake Montcortès sedimentary sequence; U X-ray fluorescence (XRF) profiles for calcium (Ca) and zirconium (Zr). Variation of scores of PC1, PC2, PC3 and PC4 against depth; lead (Pb) (black) and mercury (Hg) (red) concentration in the sediment. Dashed lines represent the Threshold Effect Concentrations (TEC) values in dry sediment for Hg and Pb according to MacDonald et al. (2000); age depth model based on varve counting (Corella et al., 2014) and bulk density profile. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Environmental and depositional processes of trace metals in the lake

PCA results show that multi-element relationships are related to the main environmental processes controlling sediment deposition in the lake. The four main eigenvectors account for 81.5% of the matrix variance (Table 1). The results of the PCA are presented in terms of factor loadings of each element in the extracted eigenvectors (PCs) highlighting the fractionation of the communalities (Fig. 3).

The first two components (PC1 and PC2, 48.7% of accumulated variance) are related to lithogenic elements. Both PCs represent the delivery of allochthonous material to the lake via watershed run-off. PC1 is tied mainly to Zr, Ti, Rb and K. On the other hand, PC2 is dominated by S and As with high positive loadings, and Al and Fe to a lesser extent. PC1 could represent material eroded from Oligocene conglomerates that outcrop in the northern area of the watershed (Fig. 1). PC2 may explain the input from Triassic evaporites and shales located in the southwestern area of the watershed. These facies are enriched in gypsum and arsenic (Heinrichs and Udluft, 1999). PC2 may also reflect redox variability in the hypolimnion since both elements (S and As) are sensitive to redox-driven cycling in lacustrine systems (Hamilton-Taylor and Davison, 1995). The

Table 1

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
Zr	0.87	0.12	-0.29	0.16
Ti	0.84	0.32	0.27	0.20
Zn	0.84	0.26	-0.33	-0.07
Rb	0.83	0.27	-0.34	0.16
K	0.72	0.55	-0.13	0.30
S	0.37	0.75	0.02	-0.03
As	0.11	0.74	-0.23	0.05
Al	0.55	0.66	-0.07	0.25
Fe	0.54	0.58	-0.35	0.22
Br	-0.15	-0.58	0.22	-0.04
Cr	-0.10	-0.12	0.93	-0.13
Ca	-0.23	-0.17	0.91	-0.05
Sr	-0.14	-0.27	0.71	0.41
Si	0.52	0.41	-0.04	0.54
Hg	-0.24	-0.22	-0.04	-0.85
Pb	-0.06	0.05	0.03	-0.93
PCA variance	28.8	19.8	17.9	15.0
Accumulated variance	28.8	48.7	66.5	81.5

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

correlation between Fe and S also suggest early diagenetic precipitation of pyrite under strong anoxic conditions (Corella et al., 2011b). PC1 and PC2 scores remained low and fairly constant during deposition of units I and III, but showed high scores in lithostratigraphic unit II (CE, 1844–1902). The period corresponding to Unit II (late 19th century) witnessed large regional floods (Barriendos and Llasat, 2003; Corella et al., 2014) and intense local land use (Rull et al., 2011) that may have led to an increased sediment delivery to the lake.

The third component (PC3, 17.9% of the variance) is mainly characterized by positive loadings of Ca, Sr and Cr. The positive association of Ca and Sr suggests that PC3 reflects endogenic carbonate production in the lake - i.e. calcite layers deposition during spring-summer algal blooms (Corella et al., 2012) -. Thus, PC3 remained fairly constant down-core. Chromium mostly occurs in the Triassic shales from the watershed. Nevertheless, this element can be easily mobilized and re-precipitated with endogenic carbonates and fixed in the sediment under strong anoxic conditions in lake's hypolimnion (Nriagu et al., 1993).

The fourth component PC4 (15% of the total variance) is characterized by large negative loadings of Hg (−0.85) and Pb (−0.93), suggesting atmospheric deposition as the main process controlling the sediment enrichment of these two major pollutants. The lack of correlation with lithogenic elements confirms that erosion and watershed runoff are minor contributors to Hg and Pb content and distribution in the sediment. PC4 scores show an increasing trend

(i.e. Hg and Pb enrichment) since the onset of the Pre-Industrial period (Figs. 2 and 4). Strontium and Si show moderate positive loadings on PC4 (0.42 and 0.55 respectively). Both elements are largely linked to bioproductivity processes in the lake: Si is also related to biogenic Si associated to diatom blooms (Melles et al., 2012; Pellicer et al., 2016), while Sr can be associated to biogenic carbonates (Corella et al., 2011a) (bivalve shells and charophytes' stems; Anadón et al., 2002; Dodd and Crisp, 1982). The anti-correlation between Hg-Pb and Si-Sr may suggest a "biodilution effect" when enhanced algal blooms would result in lower biological concentration of pollutants (Pickhardt et al., 2002), which should be further investigated.

3.3. Mercury and Pb atmospheric deposition since the 14th century

The annually-resolved sediment record from Lake Montcortès allows us to reconstruct the Hg and Pb depositional evolution since CE 1386 with a sub-decadal resolution. As shown in Fig. 4, three main periods can be distinguished according to the changes in atmospheric metal deposition (PC4 scores): Pre-Colonial, Pre-Industrial and Industrial periods:

3.3.1. Pre-Colonial period (CE 1386–1550)

Atmospheric metal deposition shows the lowest values of the last 700 years during Medieval times. The average Hg concentration during this period is $0.054 \mu\text{g g}^{-1}$, representing the baseline conditions that may differ from natural background values since the anthropogenic contribution during the Medieval Period cannot be entirely ruled out. Lake Montcortès record shows two relative Hg AR peaks dated at CE 1454 ($48 \mu\text{g.m}^{-2}.\text{y}^{-1}$) and CE 1488 ($42 \mu\text{g.m}^{-2}.\text{y}^{-1}$). These peaks occurred during a period of reduced precipitation (Corella et al., 2014, 2016, Fig. 4) and, therefore, an increase in Hg AR is unlikely. Furthermore, sedimentation rate is rather constant during this period ruling out intrinsic depositional processes that may explain these peaks. Therefore, the discrete nature of the Hg peaks points to two singular events. Interestingly, they correspond (based on temporal correlation) with two major volcanic eruptions – Kuwae (Vanuatu, Southern Pacific) and St Helens (EEUU) at 1452–1453 CE and 1480–1482 respectively (Yamaguchi, 1983; Gao et al., 2006). In particular Kuwae volcano delivered to the atmosphere some of the largest aerosol fluxes in the past 700 years (Gao et al., 2006). Enhanced Hg deposition during major eruptions has been reported in other remote locations (Daga et al., 2016; Ribeiro Guevara et al., 2010; Roos-Barraclough et al., 2002; Schuster et al., 2002). Volcanic eruptions are a major natural source of gaseous Hg emissions to the atmosphere (Nriagu and Becker, 2003), as large explosive eruption can release >1000 Mg of Hg per event (Pyle and Mather, 2003). If the Hg peaks recorded in Lake Montcortès are related to these volcanic events, it would suggest that Hg emissions from major volcanic eruptions can be transported inter-hemispherically and reach the western Mediterranean.

Lead accumulation rates in the Lake Montcortès sediment follow the same trend as that of the regional (paleo) precipitation reconstruction (Corella et al., 2014) (Fig. 4). The lowest Pb AR occurred between CE 1467 and 1498 ($2500 \mu\text{g.m}^{-2}.\text{yr}^{-1}$), agreeing very well with the largest aridity crises (i.e. reduced rainfall) of the last 700 years in NE Spain. Accumulation rates increased significantly again during a period of increasing precipitation between CE 1521 and 1557. This agreement between Pb accumulation and rainfall variability suggests that wet deposition controlled natural Pb atmospheric deposition in NE Iberian Peninsula during the Middle Ages. Increased rainfall may also increase the Pb fluxes to the lake from catchment soils via run-off, although this argument is less plausible since Pb does not correlate with run-off related

Fig. 4. Atmospheric metal deposition in southern Europe during the last 700 years based on varved lacustrine records. From top to bottom: Global volcanic activity index (Crowley, 2000); Reconstruction of heavy rainfalls in Lake Montcortès for the last 700 years (Corella et al., 2014); Pb mass accumulation rates in Lake Montcortès; PCA4 representing the atmospheric metal deposition; Lake Montcortès enrichment factors for mercury (red) and lead (black) and mercury enrichment factor from Charo de Lamoso peatbog (Martínez Cortizas et al., 2012) (NW Spain); mercury mass accumulation rates in Lake Montcortès and reconstruction of mercury production from Almadén mines (Hylander and Meili, 2003). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

elements (Fig. 3) and sediment detrital layers were not considered in this study.

3.3.2. Pre-industrial period (CE 1550–1840)

The Montcortès record shows a progressive increase in atmospheric pollutants deposition since CE 1536 (negative PC4 scores, Figs. 2 and 4). A similar pattern has been documented in marine sediments (*Posidonia oceanica* mats) from Portlligat Bay (NE Spain, Fig. 1A) (Serrano et al., 2011) and the Chao de Lamoso peat record from NW Spain that showed a clear increase by that time (Martínez-Cortizas et al., 1999). Almadén Hg production and shipping for silver mining in the Spanish colonies greatly increased since CE 1555 and lasted for more than 250 years (Hylander and Meili, 2003). In addition, the increase in Hg mining in Idrija in the 16th century - estimated in 6380 tons, Hylander and Meili (2003) - most likely resulted in large amounts of Hg dissipated to the environment. Therefore, the increase in Hg release to the atmosphere related to Hg mining, storage and transport could explain the increase in Hg AR in Lake Montcortès sediments between CE 1536 and 1771 (mean Hg AR of $38.4 \mu\text{g.m}^{-2}.\text{yr}^{-1}$). This period also coincides with the coldest and most humid conditions of the last millennium in the Southern Pyrenees (Morellón et al., 2012) that would have favoured Hg deposition in Lake Montcortès since Hg accumulation is also controlled by temperature and humidity variations (Martínez-Cortizas et al., 1999). The decline of Hg AR in the lake since CE 1771 could also reflect the decrease in precipitation that experienced the area at the end of the 18th century (Rull et al., 2011; Morellón et al., 2012; Corella et al., 2016). Therefore, we consider that the interplay between climate variability and anthropogenic mercury emissions from Hg mining in the Mediterranean area has driven Hg atmospheric deposition in Lake Montcortès during the Pre-Industrial Period.

Regional/continental increase in Pb mining and smelting in Europe may explain the Pb atmospheric contamination recorded in Lake Montcortès during the pre-industrial period. The increase in Pb AR between CE 1531 and 1546 may respond to the increase in Pb mining in the nearby Royal Mines of Parzán (Nieto Callen, 1996). The development of new techniques for silver production required large amounts of Pb in Europe during the 16th century. In addition, the widespread use of Pb-laden ammunition since the 15th century also led to higher Pb production in several European mining areas (Molenda et al., 1976). The CE 1531–1546 peak in Pb AR observed in Lake Montcortès also coincides with an abrupt increase in Pb deposition in lakes from northern Europe (Brännvall et al., 2001). Lead mining in Europe and the Pyrenees largely occurred during the Pre-industrial period, suggesting local and regional Pb mining and smelting activities as the most likely source of Pb atmospheric contamination in the lake during this period. These mining and roasting activities increased local Pb atmospheric emissions while increased rainfall contributed to increased Pb wet deposition into the lake (Fig. 4). Lead deposition reached the highest value ($\sim 4000 \mu\text{g.m}^{-2}.\text{yr}^{-1}$) of this period between 1735 and 1758 with a two-fold increase in the EF.

3.3.3. Industrial period (CE 1840–present)

The abrupt increase in industrial activities since the mid 19th century led to a significant increase in the deposition of atmospheric pollutants, reaching maximum values between CE 1940s and 1960s (Fig. 4). After a several decade-long period (ca. CE 1780–1842) of low Hg deposition ($\sim 30 \mu\text{g.m}^{-2}.\text{yr}^{-1}$), values progressively increased since the mid 19th century (ca. CE 1842) peaking during the mid 20th century (mean AR $109 \mu\text{g.m}^{-2}.\text{yr}^{-1}$). Two major Hg deposition events occurred at CE 1930 and 1940, synchronous with two major Hg production maxima in Almadén mine (Hylander and Meili, 2003) (Fig. 4). Increasing demand of the

weaponry industry for the production of Hg fulminates for explosive detonators and pharmaceutical needs may be responsible for the largest Hg deposition fluxes of more than 2830 tons in CE 1941 (Hernández et al., 1999). Both measurements and estimates performed at Almadén, suggest that roasting processes would have released up to 10 tons of Hg per year at a production up to 1500 tons of Hg per year (Ferrara et al., 1998). According to these estimates, 19 tons of Hg would have been released in CE 1941 in southern Spain solely in the Almadén mining district. Such large Hg emissions were likely responsible for the five-fold increase in Hg EF recorded in Lake Montcortès sediments. Higher Hg emissions during WWII not only occurred in Almadén as other mining district worldwide experienced a similar surge in production. Several sites in remote regions from South and North America have also shown high Hg accumulation rates around CE 1940 (Beal et al., 2015; Biester et al., 2002; Schuster et al., 2002). Coral skeletons from the South China Sea and North Atlantic myctophids, have also revealed the highest Hg concentrations in the marine realm during the WWII (Martins et al., 2006; Sun et al., 2016). This global increase in Hg deposition highlights the long-range atmospheric transport of gaseous Hg, from anthropogenic emission sources to remote areas where atmospheric Hg can be oxidized to divalent Hg (Hg^{II}), and deposited onto terrestrial and marine ecosystems (Wang et al., 2014).

The Hg record of Lake Montcortès shows a decreasing trend since WWII, which does not match the Hg global production or the anthropogenic Hg emissions to the atmosphere related to widespread industrial uses of Hg (Fig. 4) (Horowitz et al., 2014; Hylander and Meili, 2003). Global reconstructions show the highest Hg AR between CE 1960 and 1980, while Montcortès record presents a progressive decrease after WWII, although accumulation rates remained high for the period CE 1945–1981 (mean $103 \mu\text{g.m}^{-2}.\text{yr}^{-1}$). This earlier late-industrial decline in Hg AR from Lake Montcortès is not observed in other Hg reconstructions from northern Europe or North America (Bindler et al., 2001; Engstrom and Swain, 1997; Lindeberg et al., 2007; Schuster et al., 2002), and thus appear to reflect more local factors (i.e. the reduction in Almadén Hg mining). In fact, a decreasing trend in mercury production in Almadén occurred since the 1960s (with up to 5200 flasks production per month) until the closure of the mines during the last decade (Tejero et al., 2015), which is in well agreement with the Lake Montcortès record. The reduction in Hg accumulation rates in Lake Montcortès has been estimated to be $\sim 40\%$ since CE 1990, in agreement with global emissions inventories that account for a reduction of 2.2% yr^{-1} in Western Europe (Zhang et al., 2016). This decrease in Hg depositional fluxes is most probably a consequence of the decline in Hg anthropogenic emissions in Europe related to; i) the closure of Almadén mines, ii) the phasing out of Hg for industrial uses (reduced use of Hg in products and their waste), iii) the marked reduction of Hg consumption in Western Europe chlor-alkali plants and iv) the emission decrease from coal-fired power plants (Horowitz et al., 2014; Zhang et al., 2016).

The large increase in Pb accumulation rates in Lake Montcortès between CE 1841 and 1970 is similar to other western Mediterranean and Pyrenean records and shows the massive rise in Pb pollution since the onset of the Industrial Revolution (Camarero et al., 1998; Elbaz-Poulichet et al., 2011; Martínez Cortizas et al., 2012; Rosman et al., 2000; Schwikowski et al., 2004; Shotyk et al., 1998; von Gunten et al., 1997). The first phase of atmospheric fallout of anthropogenic Pb before CE 1930 (mean Pb AR $2150 \mu\text{g.m}^{-2}.\text{yr}^{-1}$) is the synergistic response of i) an increase in the frequency of rainfall events in the Central Pyrenees (Corella et al., 2014) enhancing Pb wet deposition; ii) increasing Pb regional emissions caused by higher production and advances in smelting techniques during the Second Industrial Revolution in Europe (CE 1870–1914) (Shotyk et al., 1998); and iii) renewed Pb mining in the

Parzán area at the turn of the century (Fanlo et al., 1998). Lead isotopic studies conducted in the western Alps showed that regional and local mining, as well as smelting activities, were the dominant source of Pb pollution during this period (Rosman et al., 2000). The combined effect of local (closure of the Parzán mines in the early CE 1930s) and global (the worldwide economic recession during the 1930s) factors resulted in reduced Pb emissions and a decrease of Pb AR to almost Pre-industrial levels (Fig. 4). The onset of WWII caused a marked new increase in Pb AR that peaked between CE 1953 and 1971 (mean Pb AR $5920 \mu\text{g.m}^{-2}.\text{yr}^{-1}$), in agreement with other Pyrenean lake records (Camarero et al., 1998) and coastal lagoons from southwestern Mediterranean (Elbaz-Poulichet et al., 2011). These maxima Pb depositional fluxes are most likely due to the use of leaded gasoline, which greatly increased since 1950 and contributed to more than 60% of total emitted Pb (Schwikowski et al., 2004). The significant decline in Pb emissions in Western Europe since CE 1970 led to a progressive reduction in Pb deposition. Finally, the significant reduction of Pb deposition after CE 2003 to current levels is related to the total ban of leaded gasoline in Spain in CE 2001.

3.4. Environmental implications

The three to four-fold increase of Hg and Pb EF in Lake Montcortès sediments during the 20th century is in agreement with previous studies in ombrotrophic mires from NW Spain (Fig. 4) (Martínez Cortizas et al., 2012), but differs greatly with estimates from marine records in NE Spain (Portillag Bay, Fig. 1), where estimated EF for Pb and Hg were >10 (Serrano et al., 2013; Serrano et al., 2011). As the authors identified, the higher accumulation in the marine records is most likely due to the bioaccumulating capacity of *Posidonia oceanica*. This bioaccumulation may result in a magnification of trace metal concentrations as the plant acts as a pollutant sink. Lake Montcortès EF of Hg and Pb are consistent with global values of other peat records and lacustrine sequences - see review in Amos et al. (2015); Biester et al. (2007); Engstrom et al. (2014) - supporting that lake Montcortès varved sediments are a good archive of Pb and Hg atmospheric pollution in NE Spain.

Both Hg and Pb concentrations reached the Threshold Effect Concentration (TEC) in CE 1939 and 1956 respectively. TEC is a consensus-based sediment quality guideline that represents the pollutant concentrations above which adverse effects in freshwater ecosystems may occur (MacDonald et al., 2000). Although Hg and Pb levels have been significantly reduced in the last decades, this study suggests that atmospheric deposition of pollutants may reach significant levels that should be considered in lake's restoration strategies.

4. Conclusions

Geochemical analyses performed in sediment cores from varved Lake Montcortès, provide a high-resolution reconstruction of the Hg and Pb pollution history in Western Mediterranean since CE 1386. Low regional and global mining activity during medieval times was responsible for the low Hg values during this period. Volcanic eruptions may have been responsible for some Hg flux peaks recorded in sediments from Medieval times. During the Pre-industrial period (CE 1550–1840) the interplay between i) Hg production from the two largest mercury mines (Almadén and Idrija) and ii) climate (colder and wetter conditions) may have controlled Hg deposition in the lake. Mercury accumulation rates experienced a significant increase during the Industrial period (after 1840 CE) with a five-fold increase during the WWII related to intense Hg mining in Almadén, coal burning and enhanced global mercury production. The decrease in Hg accumulation rates during

the last decades is coherent with the observed trends in Hg emission inventories from Western Mediterranean, that account for a reduction of ~2% per year since CE 1990.

Local and regional mining and smelting practices controlled the Lake Montcortès Pb depositional fluxes during the Pre-industrial period. The use of leaded gasoline in Europe most likely triggered the highest Pb accumulation rates in the lake during the mid-20th century. The good correlation between periods of increased Pb deposition and higher rainfall favors wet deposition as an intensifier of Pb deposition.

The concentration of Hg and Pb in the sediments reached maximum values (exceeding TEC) in the mid 20th century. Trace metal concentrations decreased since then as a consequence of reduced mining activities in the Iberian Peninsula and the implementation of environmental regulations during the last decades. This study helps to target limnological conditions and management strategies in aquatic ecosystems, and shows the need for high-resolution (varved) records and multiproxy studies to make sound assessments of (atmospheric) pollution in lake ecosystems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2017.02.018>.

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