



Anthropogenic impact and lead pollution throughout the Holocene in Southern Iberia

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HIGHLIGHTS

- ▶ Holocene paleoenvironmental records have been studied and reviewed in South Iberia
- ▶ A multidisciplinary approach unravels the past metal pollution in this region.
- ▶ Evidence of anthropogenic impacts has been recognized in diverse environments.
- ▶ Activities related with metallurgy boosted the anthropogenic environmental impact.
- ▶ The oldest anthropogenic lead pollution signal has been identified in Western Europe.

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ABSTRACT

Present day lead pollution is an environmental hazard of global proportions. A correct determination of natural lead levels is very important in order to evaluate anthropogenic lead contributions. In this paper, the anthropogenic signature of early metallurgy in Southern Iberia during the Holocene, more specifically during the Late Prehistory, was assessed by mean of a multiproxy approach: comparison of atmospheric lead pollution, fire regimes, deforestation, mass sediment transport, and archeological data. Although the onset of metallurgy in Southern Iberia is a matter of controversy, here we show the oldest lead pollution record from Western Europe in a continuous paleoenvironmental sequence, which suggests clear lead pollution caused by metallurgical activities since ~3900 cal BP (Early Bronze Age). This lead pollution was especially important during Late Bronze and Early Iron ages. At the same time, since ~4000 cal BP, an increase in fire activity is observed in this area, which is also coupled with deforestation and increased erosion rates. This study also shows that the lead pollution record locally reached near present-day values many times in the past, suggesting intensive use and manipulation of lead during those periods in this area.

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1. Introduction

Lead poisoning is an environmental and public health hazard on a global scale (e.g., Rabinowitz and Needleman, 1982; Finster et al., 2004). Until recently leaded gasoline has been the major source of dispersion of this element into the environment (USEPA, 1998). Nevertheless, lead also occurs naturally in the earth's crust. The lead contribution derived from anthropogenic activities should be differentiated from the natural baseline to better understand the spatial and temporal distributions of lead (e.g., Mielke et al., 2010) and to identify the severity of lead pollution in the landscape. The environmental, geographical and

historical contexts of Southern Iberia offer an excellent opportunity to approach these goals. Southern Iberian marine and continental paleoclimatic records are very sensitive to abrupt climate changes due to their latitudinal location, where African, Atlantic and Mediterranean climate realms meet (Bard et al., 2000; Shackleton et al., 2003; Martrat et al., 2007; Martín-Puertas et al., 2010; among others). In addition, the Iberian Peninsula has been continuously populated during the last 1.3 Ma and therefore has a long history of human settlement (Finlayson et al., 2006; Oms et al., 2000; Duval et al., 2011; among others). Relevant to the purpose of this paper is also the relative abundance of mineral resources in Southern Iberia, which, coupled with its geographical location, has historically acted as a strategic resource for local and foreign civilizations, whether it be the Phoenician, Carthaginian or Roman empires. For these reasons, Iberia is a region very well suited to study

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both the role of climate changes in human societies and early anthropic impact in the environment (Jiménez-Espejo et al., 2007; González Sampérez et al., 2009; Cortés Sánchez et al., 2012).

With the beginning of agriculture in the Holocene, human activities have had an increasing influence on the environment, whether terrestrial, marine or atmospheric. The systematic application of fire technologies for specific economic activities, such as slash-and-burn agriculture, animal husbandry or metallurgy produced certain environmental signatures that can be recognized today in the sedimentary records (Nriagu, 1983; Martínez Cortizas et al., 1997; Brännvall et al., 1997; Whitlock and Anderson, 2003; Carrión et al., 2007; among others). In particular, metallurgical production has been shown to release heavy metal airborne pollution to the atmosphere (Renberg et al., 2001). The chronology and diachronic change of atmospheric pollution during the late Holocene can be identified in different types of environments showing a hemispheric distribution scale (Weiss et al., 1999 and references therein; Renberg et al., 2001; Alfonso et al., 2001; among others).

Lead has been an important raw material for humans (Patterson, 1972; Nriagu, 1983). It has been widely used in ancient times in processes aimed at the recovery of silver from ores with low silver content (a procedure termed *cupellation*) (Rothemberg et al., 1989) and is also often associated with other metal-ore outcrops and used in different metal alloys. Lead records in lacustrine and marine sediments can be used to identify the time period in which extraction and/or manipulation of this metal took place, causing atmospheric or runoff pollution (Renberg et al., 2001). Identifying the origin of this signal can be confusing in low-altitude environments, where a mixture of inputs from atmospheric deposition, human settlements (Martín-Puertas et al., 2010), fluvial deposition or natural contamination by weathering of lead outcrops (Weiss et al., 1999) can occur. However, in remote high-altitude lakes without lead influence from the catchment basin, the main source of lead input is atmospheric deposition.

In this paper we show that the lead signature in the alpine Laguna de Río Seco (Sierra Nevada, Spain) during the Holocene can be explained as an atmospheric deposition record from Southeastern Iberia, caused by both natural and anthropogenic factors, the latter of them including, significantly, mining and metallurgy. This record features a marked pattern, with significant increases in lead content in certain time periods in the past. These patterns are then compared to the archeological record of the region in order to explore the causes, timing and intensity of the activities responsible for the lead variations. We focus on Late Prehistory because the studied lead pollution record shows that important anthropogenic environmental impacts, less known than the present ones, occurred during this period. Nevertheless more recent history, from the Roman Empire onwards, will be also included in the general discussion.

2. Regional setting

2.1. Metal-ore outcrops in Southeastern Iberia

Important metal-ore outcrops occur in two different geological contexts from Southeastern Iberia: the Betic mountain range and the easternmost sector of the Iberian Massif (Sierra Morena) (Fig. 1). A detailed review of lead outcrops and other associated metal-ores is represented in a metallogenetic map (Fig. 1; Sierra López et al., 1972a, 1972b, 1972c, 1972d), which includes review information from the Geological and Mining Institute of Spain (IGME).

Important ore outcrops are present in the Betic mountain range, especially in its Internal Zones, where three main geological units can be distinguished: the Nevadofilabride, the Alpujárride and the Maláguide complexes. All of them show mineralization of lead, silver and copper, among others (Fig. 1; Sierra López et al., 1972a, 1972b, 1972c, 1972d). Seam deposits of lead occur in the Nevadofilabride complex, sometimes associated with silver and copper. Azurite and

malachite (copper minerals) can be associated with this mineralization. Some areas are also rich in gold. Lead mineralizations, sometimes associated with copper or zinc, are very frequent in the Alpujárride complex and common in the Maláguide one (Fig. 1; Sierra López et al., 1972a, 1972b, 1972c, 1972d).

In addition, lead, silver and zinc can be found in the volcanic area of Cabo de Gata-Mazarrón. These metal ores are located in fractured seams, and frequently associated with gold, among other ores (Fig. 1). The eastern sector of the Iberian Massif is mainly characterized by mineralizations of silver, lead, copper and zinc (Sierra López et al., 1972a, 1972b, 1972c, 1972d).

2.2. Lacustrine lead sedimentary records in Southeastern Iberia. Zoñar Lake and Laguna de Río Seco (LdRS)

The lead pollution continental record of Southeastern Iberia is based on data from two lakes: Zoñar (Martín-Puertas et al., 2010), and Laguna de Río Seco (this study). Zoñar Lake (37°28.997' N, 4°41.245' W; 300 m above sea level (MASL)) is a large, permanent lake located in Córdoba (central Andalusia) (Fig. 1). This lake bears a very complete record of the late Holocene and Martín-Puertas et al. (2010) were able to correlate its high-resolution lead pollution data with different prehistoric and historic periods. This lead record shows higher values when archeological settlements were located on the margins of the lake (Ortiz, unpub. data).

High mountain lakes and wetlands, specifically from Southern Iberia, have been shown to be ideal locations for recovering high-resolution paleoenvironmental information (Anderson et al., 2011; Jiménez-Moreno and Anderson, 2012; García-Alix et al., 2012; Jiménez-Moreno et al., in press). Laguna de Río Seco (37°02.43' N, 3°20.57' W) is a small oligotrophic lake (Pulido-Villena et al., 2005) from Sierra Nevada (Southern Iberia) (Fig. 1). This lake, originating from a south-facing glacial cirque at ~3020 masl, has a surface of 0.42 ha and a maximum depth of ~2 m (Morales-Baquero et al., 1999). This small depression was excavated on the metamorphic basement (mainly schist) of Sierra Nevada by cirque glaciers during the late Pleistocene, and a small lake developed after the last deglaciation (Schulte, 2002). Its catchment basin does not show any lead occurrences (Sierra López et al., 1972b). Its sedimentary record covers the entire Holocene (Anderson et al., 2011). High aeolian dust inputs have been documented recently (Pulido-Villena et al., 2005; Morales-Baquero et al., 2006; Reche et al., 2009; among others). This aeolian influence can also be recognized in its Holocene record (Jiménez Espejo et al., 2011).

2.3. Westernmost Mediterranean marine record

The Alboran Sea is located in the westernmost Mediterranean Sea. It is a semi-enclosed basin surrounded by the Iberian Peninsula to the North and the North Africa margin to the South. High sedimentation rates and its latitudinal position make sediments from the Alboran Sea a key location for paleoclimate studies (e.g., Martrat et al., 2007). For this study we selected the core ODP 976C-1H-1 for comparison with the continental data studied in this paper (see above).

Site ODP 976 (36°12' N, 4°18' W, 1108 m below sea level) is located in the Alboran Basin, off the coast of the city of Malaga (Fig. 1). A high-resolution lead record for the Late Holocene is preserved in this core (Martín-Puertas et al., 2010).

2.4. Sedimentary charcoal records from Southeastern Iberia

Holocene charcoal records, a proxy of fire activity, from SE Iberia have been previously described in lacustrine or peat environments from this region at different elevations (Carrión et al., 2007; Gil-Romera et al., 2010; Anderson et al., 2011; among others). We selected a suite of these records that are in close proximity to our study area in order to compare with the lead record from the Southeastern

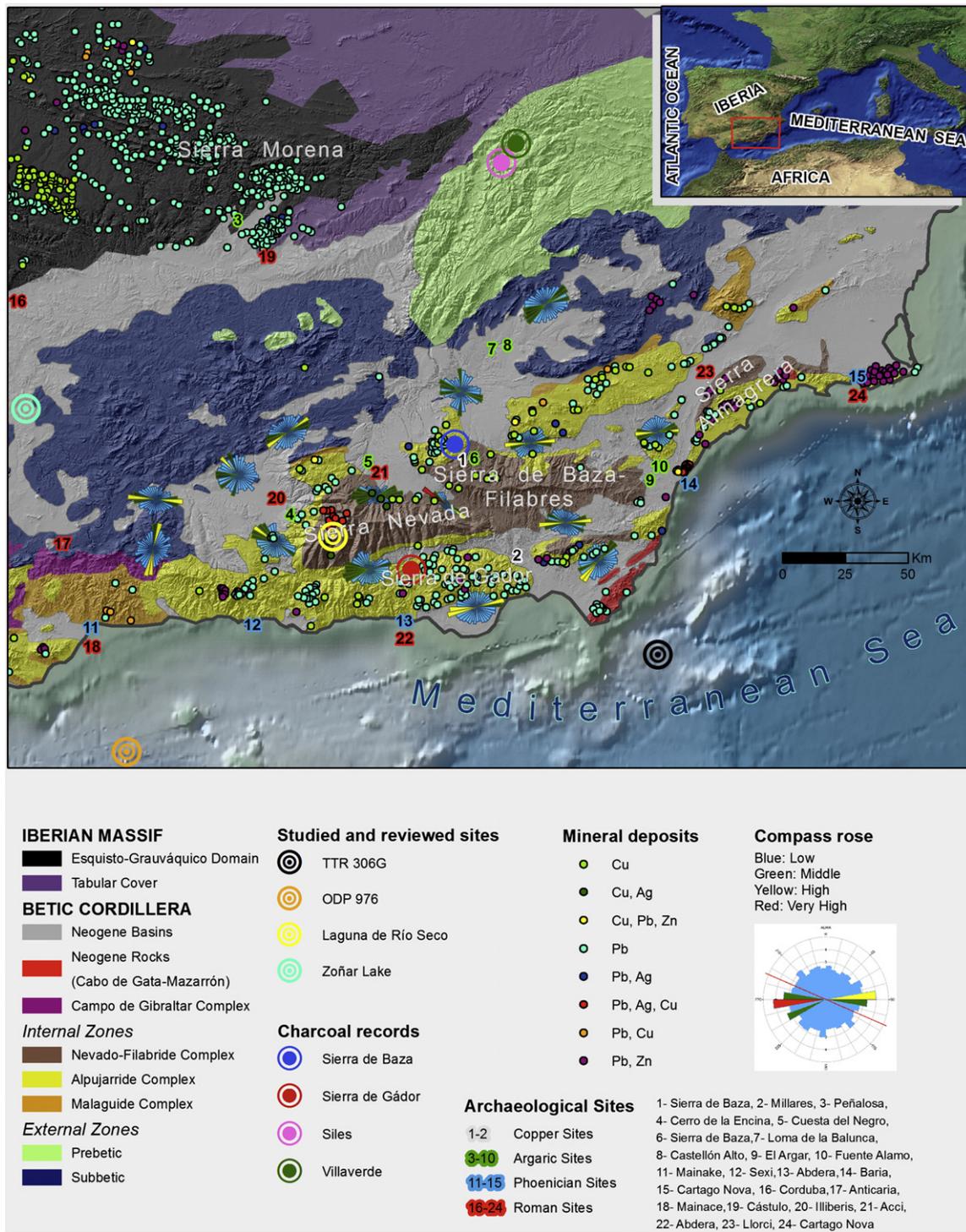


Fig. 1. Regional geologic and geographic map of the studied area. 1) Studied and compared environmental records. 2) Metal-ore outcrops. 3) Settlements of different cultures. 4) Recent wind pattern for Southeastern Iberia.

Iberia sites. These sedimentary charcoal records are: Laguna de Río Seco, Villaverde, Siles, Sierra de Baza and Sierra de Gádor (Fig. 1).

3. Material and methods

3.1. Lead and aluminum records from Laguna de Río Seco

A 137.5 cm-long sediment core (LdRS 06-01) was collected from the center of Laguna de Río Seco in 2006 (Anderson et al., 2011). Lead and

aluminum contents were analyzed from 64 sediment samples taken at ~2 cm intervals throughout the sediment core. The age model for the studied core is based on 9 AMS radiocarbon dates that were calibrated using CALIB 5.0.2 (Stuiver et al., 1998), and a series of ²¹⁰Pb and ¹³⁷Cs data (Anderson et al., 2011).

Lead analysis was performed using inductively coupled plasma-mass spectrometry (ICP-MS) previous to HNO₃ and HF digestion. Measurements were taken in triplicate through spectrometry (Perkin Elmer Sciex Elan 5000) using rhenium and rhodium as internal standards. The

instrumental error is $\pm 2\%$ and $\pm 5\%$ for elemental concentrations of 50 mg kg^{-1} and 5 mg kg^{-1} respectively (Bea et al., 1996). Results are expressed in mg kg^{-1} .

Aluminum measurements were obtained by X-Ray Fluorescence (XRF) using a Bruker AXS S4 Pioneer. Samples were prepared as fused beads using glass discs prepared by melting about 0.3 g of ground bulk sediment with lithium tetra borate flux. The quality of the analysis was monitored with reference materials showing high precision with 1 sigma 1.0–3.4% on 16 data-sets at the 95% confidence level. Results are expressed in mg kg^{-1} .

3.2. Recent wind pattern data sources

Daily wind directions of 19 weather stations from Southeastern Iberia were collected for the last 11-year period from the Environmental Agency of the Andalusian Regional Government (<http://www.juntadeandalucia.es/medioambiente/site/porta/web/>). They have been summarized in compass roses showing the main wind directions in this area. Red and yellow colors represent the most frequent wind directions, and green and blue colors, the least ones. Closed stations with similar wind directions were summarized in the same compass rose in order to simplify the map (Fig. 1).

4. Results

4.1. Laguna de Río Seco lead record

The lead record during the past 10,000 calibrated years before the present (cal BP) from the Laguna de Río Seco is shown in Fig. 2. A mean background value of $28 \pm 2 \text{ mg kg}^{-1}$ of lead content is found in the sediments previous to ~ 4500 cal BP. There are no previous intensive metallurgical evidences in the archeological record from Southeastern Iberia, and the small lead variations from $\sim 10,000$ to 4500 cal BP could be associated to climate oscillations, related with humid and arid periods in this area. In this sense lead content shows slight variations associated to the end of the African Humid Period around 7000 cal BP (Rodrigo Gámiz et al., 2011). Since ~ 4500 years; an increasing trend in lead content is observed. During the Copper Age (~ 4500 to ~ 4200 cal BP) slightly higher values were reached but they cannot be distinguished from the natural background in lead atmospheric input. However, the first clear increase in lead occurred from ~ 3900 to 3500 cal BP (1950–1550 calibrated years before Christ (cal BC)), during the Early Bronze Age, reaching a peak value of 37 mg kg^{-1} . A large increase in lead content, with a maximum value of 93 mg kg^{-1} is reached later on, between ~ 3200 and ~ 2500 cal BP (1250–550 cal BC or Late Bronze Age and Early Iron Age). Another peak is recorded between ~ 2100 and ~ 1700 cal BP, with a lead value around 66 mg kg^{-1} corresponding to Roman-time emissions. A smaller peak, with a value of 55 mg kg^{-1} , is recorded at ~ 1300 cal BP. A sharp increase occurred in the last 300 years, reaching values of 111 mg kg^{-1} , consistent with the Industrial Revolution and the subsequently the use of leaded fuels.

In order to correct for dilution by variable biogenic sediments we normalized Pb to Al content, assuming that Al concentrations in lake and marine sediments come from alumina-silicates (e.g., Brumsack, 1989; Piper and Perkins, 2004). Normalized Pb/Al values show a similar trend to the lead content (Fig. 3), increasing drastically since ~ 3900 cal BP.

4.2. Recent wind patterns

There is a long wind pattern record from Southern Iberia, allowing us to construct a robust model of regional wind distribution. The main wind directions in Southern Iberia are E-W, NE-SW, and to a lesser degree N-S and SE-NW (Fig. 1). Winds in this region show a marked seasonality with wind direction driven primarily by topography near

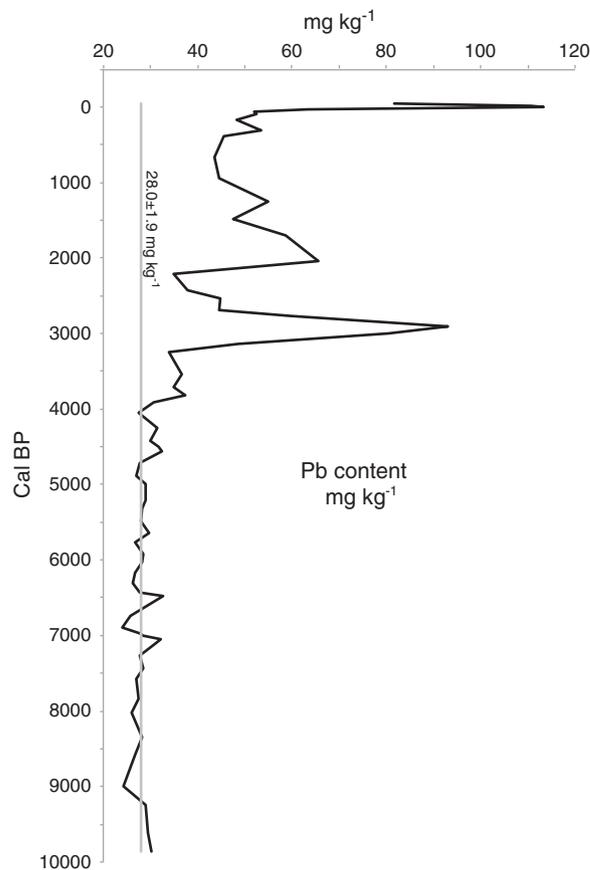


Fig. 2. Lead content (mg kg^{-1}) from the Laguna de Río Seco record during the Holocene (core LdRS 06-01). The gray straight line marks the pre-mining background.

to the coast, where mountains and valleys strongly influence the wind directions (Viedma Muñoz, 1998).

5. Natural vs. anthropogenic signals: heavy metals, fires and environmental change

5.1. Heavy metal atmospheric pollution

Our ability to differentiate between natural and anthropogenic pollution in some sedimentary records is complicated by variability in local bedrock concentration, and by exogenous (natural or anthropogenic) heavy metals inputs. The lithology of the catchment basin around the Laguna de Río Seco is characterized by mica-schist without any evidences of lead mineralization (Sierra López et al., 1972b), which probably has little influence in the lead record.

Several studies have demonstrated a correlation between the production or utilization of a specific heavy metal, emission to the atmosphere, and its deposition in lakes, peat bogs, ice, or oceanic basins (Nriagu, 1983; Martínez Cortizas et al., 1997; Brännvall et al., 1997; among others). Lead is not a redox sensitive element and relative recent lead enrichments do not usually develop diagenetic alterations or dissolution in lacustrine environments, especially in short time intervals, such as the studied record (e.g., Pearson et al., 2010). In addition the correlation between our record with other European ones from recent to the Roman period indicate that downward diffusion of recent lead deposits did not occur. Fast diagenetic remobilization mainly affects redox-sensitive elements (manganese, iron, nickel, copper, among others) (Tribovillard et al., 2006). These elements form oxides (solid phase electron acceptors) and/or changes in oxidation states that promote variations from soluble to immobile forms allowing migration along the sedimentary column and developing

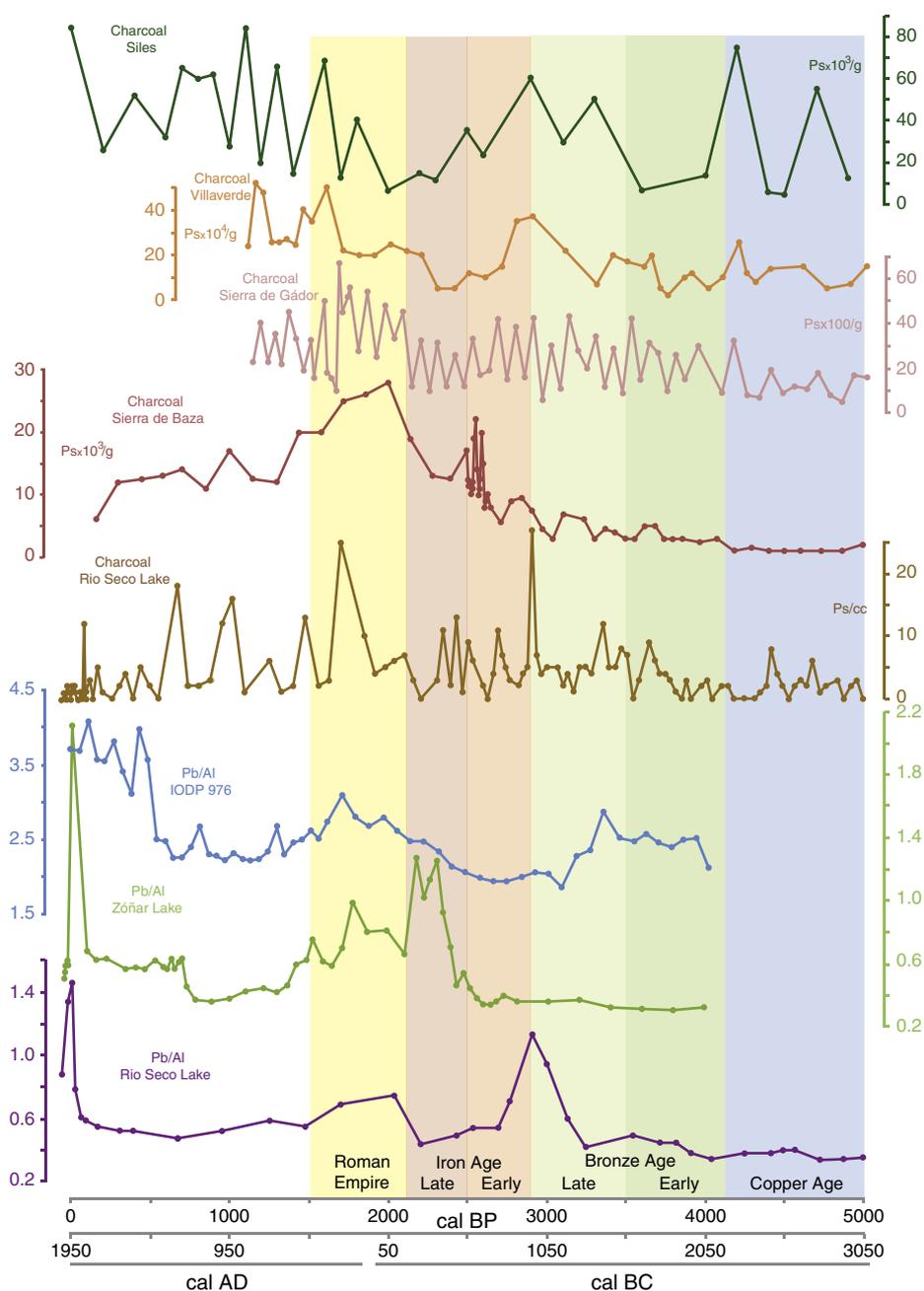


Fig. 3. Comparison between Pb/Al rate from the Laguna de Río Seco (core LdRS 06-01), Zóñar Lake (Martín-Puertas et al., 2010), and site ODP 976 (Martín-Puertas et al., 2010), and charcoal records from the Laguna de Río Seco (core LdRS 06-01) (Anderson et al., 2011), the Sierra de Baza (Carrión et al., 2007); Villaverde (Carrión et al., 2001), the Sierra de Gádor (Carrión et al., 2003), and Siles (Carrión, 2002). Charcoal content is expressed in: particles/gram or particles/cm³. Calibrated years before the present (cal BP), calibrated years before Christ (cal BC), and calibrated years Anno Domini (cal AD).

diagenetic enrichments. For this reason we suggest caution in interpretation of single peak enrichment of redox sensitive elements as the proposed anthropogenic nature for the so-called “nickel event” (Pontevedra-Pombal et al., 2013).

Today, the sources of atmospheric lead are mainly smelter, fuel combustion and incineration of solid waste (Settle and Patterson, 1980; Nriagu and Pacyna, 1988; Nriagu, 1989; Pacyna et al., 1995). Anthropogenic pre-industrial lead pollution was mainly due to mining and smelting (mainly of sulfide ores) (Hong et al., 1994, 1996), although soil erosion related with extreme deforestation and intensive agriculture could slightly increase the lead content before the development of mining activities at ~6000 cal BP (Weiss et al., 1999). The record of the pre-anthropogenic signal provides the natural background of lead aerosols (Weiss et al., 1999), very useful in differentiating between

natural and anthropogenic signals. Smelting of lead–silver alloys from sulfide ores was developed at least 5000 years ago in Europe, increasing greatly the lead atmospheric production from 4000 to 2700 cal BP (Settle and Patterson, 1980).

The pre-metallurgical background of lead content in sediments varied depending on the local mining influence. In Central Europe it is established previous to ~3000 cal BP (Weiss et al., 1999), in Southern France, previous to ~2300 cal BP (in some marshes located in Southern France) (Alfonso et al., 2001), and in the northeastern coast of Iberia previous to ~2800 cal BP (Serrano et al., 2011). Our record from Río Seco shows that background values are slightly outrange at ~4500 cal BP, which could be interpreted as the beginning of the anthropogenic influence. However, clear evidence of the anthropogenic signal in the Río Seco record has not been registered until ~3900 cal BP (~1950 cal BC), with

the intensification of Early Bronze Age metallurgy (see discussion below for further details).

5.2. Fire regime

The existence of past fires can be registered in the sedimentary record of the surrounding sedimentary basins as the occurrence of charcoal remains, which were transported by wind and water during and following a fire event (Whitlock and Anderson, 2003). Generally there is a link between fire frequency and climate. For example, many studies show enhanced fire frequency associated with increased warmth and/or drought (Whitlock and Anderson, 2003; Jiménez-Moreno et al., 2008; Swetnam et al., 2010; Marlon et al., 2012). However, an increase in fire activity during the late Holocene could also be due to enhanced human influence on the landscape from pasturing, forest clearance, mining, and agriculture (Carrion et al., 2007, 2010; Anderson et al., 2011). In fact, greater-than-present fire activity during the late Holocene has been interpreted as human-induced in many sites in central Asia and central North America (Power et al., 2008).

There is evidence of many metal-ore extractive techniques used in Southeastern Iberia that involve fire. For example, burning the superficial metal outcrops (Blázquez, 2005), smelting activities, forest clearance to locate metal outcrops, or the “fire-setting” techniques used during the Bronze Age where the metal-ore outcrops were burned in order to facilitate the metal extraction (Moreno Onorato et al., 2010).

Charcoal records from Southern Iberia (Fig. 3) document an increasing fire activity since 4100 cal BP (see Anderson et al., 2011 for synthesis), agreeing with an expanded human influence on the landscape (Carrion et al., 2007, 2010; Anderson et al., 2011), and therefore, with an intensification of mining, agriculture and pasturing. In particular, the Río Seco record shows increases in lead deposition during peaks of fire activity in the area around that time (Fig. 3). Co-variation of the two proxies, especially at ~2900 cal BP, evidences that mining and metallurgy could have played a locally important role in the fires regimes of Southern Iberia.

5.3. Deforestation and erosion

Metallurgy during the Copper and Bronze Age was mainly based on copper, and the smelting processes required important amounts of fuel (wood) (Constantinou, 1982, 1992; Stöllner, 2003). Intensification of this activity could lead to deforestation, vegetal cover loss, triggering erosion and desertification of the landscape, although the impact of intensive agriculture and pasturing cannot be ruled out. In Mediterranean areas, such as Cyprus, this kind of process has been described and important alluvial deposits related with enormous erosion during this period have been described (Weisgerber, 1982).

High slopes and semi-arid conditions from Southern Iberia contributed to the early impact of human activities in deforestation and erosion processes. Extremely high erosion rates have been described during historical periods with important development of deltaic systems (Jabaloy-Sánchez et al., 2010). Nevertheless, during the Late Prehistory the only indirect evidence of deforestation in Southeastern Iberia is the presence of a turbiditic layer in core TTR 306G, located in the westernmost Mediterranean region (Fig. 1) (Nieto-Moreno et al., 2011). The deposition of this turbiditic event, dated for this study, took place between ~3800 and 3000 cal BP. This turbidite could have then been triggered by the first large anthropic impact in the vegetation in Southeastern Iberia pointed by this study (i.e., fires or fuel needed), that drove to slope instability and favoring erosive processes in bare well-developed primal soils. However, turbidites from marine records have been related with different processes, such as sea level changes, earthquakes, fluvial detrital supply and so on (Vizcaino et al., 2006) making the interpretation of this kind of deposits very complex.

6. Human activity and lead atmospheric pollution records

6.1. Pre-metallurgical Late Prehistory (~10,150–5150 cal BP)

Although lead content slightly increased from ~4500 cal BP in the Río Seco record, prior to ~3900 cal BP there is no clear evidence to suggest human-caused lead atmospheric pollution. The copper slags recorded at Cerro Virtud (Almería, SE Iberia), dated to the late 5th millennium BC, are the earliest evidence of copper smelting so far recorded in Iberia – and indeed in Western Europe (Ruiz Taboada and Montero Ruiz, 1999). Although there is ample evidence of the quarrying and mining of non-metallic minerals in the Iberian Neolithic (~7550–5150 cal BP), and it is probable that Cerro Virtud might represent some form of early experimentation with copper smelting, it is generally agreed that in Southern Iberia systematic metallurgy did not start until the late 4th millennium BC (~5150 cal BP).

6.2. Copper Age (~5150–4150 cal BP)

Although Southern Iberian Copper Age metallurgy, which basically involves copper smelting and the working (hammering) of native gold, has been well studied in the last 50 years, there is an on-going controversy concerning the scale of metallurgical production and its environmental effects. According to Murillo-Barroso and Montero-Ruiz (2012) Southern Iberian early copper metallurgy differs from that of the rest of the Old World in a number of aspects: (1) common pottery used for smelting in Iberia is different from smelting crucibles elsewhere both in shape and fabric; (2) melting crucibles with handles, common in Central and Southern Europe, have not been found in Iberia; (3) although lead ores are abundant in southern Iberia, especially in the Southeast, and lead appears naturally with copper minerals, lead is absent in Iberian Copper Age copper metallurgy, which is the opposite of what happens in France and some other places in Europe and the Near East; (4) annealing was hardly used in the Iberian Chalcolithic to recover some ductility lost by cold working, something well known in the Old World. In addition to these differences, it must be noted that in Southern Iberia, Copper Age copper mining and smelting was carried out on a scale much lower than that found in south-east Europe or the Near East.

Recent studies have claimed that the copper metallurgy conducted during the Copper Age at sites located in Southwestern Spain, such as Cabezo Juré (Huelva) and Valencina de la Concepción (Seville), would have entailed a significant environmental impact including deforestation and pollution with heavy metals at both local and regional levels (Nocete et al., 2005, 2007). However, Montero Ruiz et al. (2007) suggested that these authors could have attributed to human action what is, in fact, sedimentation caused by undetermined circumstances. The lead record in Copper Age sediments from Sierra Nevada shows values hardly distinguishable from those of natural background (Figs. 2, 3), and therefore, do not register the deep anthropogenic environmental impact suggested by Nocete et al. (2005, 2007) in Southwestern Spain. During this period the low scale of productivity (mainly of local scope) and the specific nature of the Copper Age copper metallurgy in Southern Iberia (Montero Ruiz, 1994; Hunt Ortiz, 2003; Costa Caramé et al., 2010), would have caused low heavy metal emissions, and the record of Laguna de Río Seco reflects this scenario. In agreement, other sedimentary records from Southeastern Iberia, such as Zoñar Lake (Cordoba) or ODP 976 core in the Alboran Sea (Martín-Puertas et al., 2010) do not show evidence of lead pollution for this time period.

6.3. Early Bronze Age (EBA) (~4150–3500 cal BP)

Around 4150 cal BP important changes occurred among the prehistoric communities of Southeastern Iberia. The appearance of Argaric societies (the local name of the EBA) involved a significant increase in the

social and cultural complexity in which metallurgy has been traditionally considered as a key factor (Montero Ruiz, 1994; Montero Ruiz and Murillo-Barroso, 2010; Lull et al., 2010). Compared to the Copper Age, metallurgical production in the Iberian South-East was intensified with a production increase up to five-fold (Montero Ruiz, 1993). Copper, usually with high percentages of arsenic was the mineral used from the beginning of the Argaric time, although gold and, very specially, silver reached significant importance in the manufacture of ornaments. In contrast, the tin-bronze alloy is only widely used during a later period, around 3750 cal BP (Montero Ruiz, 1993, 1994; Montero Ruiz and Murillo-Barroso, 2010; Lull et al., 2010). Lead isotope analyses of archeological artifacts and ores show a picture characterized by the great mobility of metal objects and the exploitation of resources located on different mining areas throughout Southern Iberia (Montero Ruiz and Murillo-Barroso, 2010).

From a technological point of view, the minerals used in metal production were mainly oxide ores, carbonates – such as malachite and azurite – and sulfides like chalcopyrite or chalcocite. Arsenic, tin, lead and others appear as trace elements in these minerals (Moreno Onorato, 2000; Rovira Llorens, 2005), as well as in finished objects (Hook et al., 1987; Montero Ruiz, 1994; Moreno Onorato et al., 2010). Even in Herrerías (Sierra Almagrera, Almería) and Peñalosa (Jaén), the largest mining centers of the Iberian Southeast documented to date, copper ores contain large amounts of lead, which is in accordance with the composition of the finished artifacts that have been analyzed (Montero Ruiz, 1993; Moreno Onorato et al., 2010).

Therefore, there is no evidence to assert that lead was the main target for mining activities during the EBA. But these archeo-metallurgical data together with the plausible manipulation of minerals with some lead content, support the evidence of atmospheric lead pollution detected in the Laguna de Río Seco during this period. The first lead increase from the Laguna de Río Seco record (although slight: $\sim 9 \text{ mg kg}^{-1}$ from the long-standing natural average) can be dated at around ~ 3900 cal BP (Figs. 2, 3), which coincides with the first stages of the EBA period in Southern Iberia. The lead record from ODP 976 site (Fig. 3) also registered this slight increase. A careful analysis of this record shows a strong correlation with the archeological data. From ~ 3800 to 3500 cal BP the scale of metallurgical production increased notably, agreeing with the high lead content in the Río Seco record for this period, when important mining sites like Peñalosa (Jaén) began to be exploited (Moreno Onorato, 2000). New metallic objects like axes, swords and diadems were also produced for the first time. Tin-bronze alloy, previously unknown, was introduced, thus expanding metallurgical complexity (Montero Ruiz and Murillo-Barroso, 2010).

Around ~ 3500 cal BP, the lead record from the Laguna de Río Seco shows an important decrease, which is again very consistent with archeological data, pointing to a discontinuity (perhaps a collapse) of Argaric communities (Castro et al., 1996) and, most importantly for the aim of this paper, the metallurgical activity just around ~ 3500 cal BP (Lull et al., 2010).

6.4. Late Bronze Age (LBA) (~ 3500 – 2800 cal BP) and Early Iron Age (EIA) (~ 2800 – 2500 cal BP)

During the LBA and EIA two major mining and metallurgical regions can be identified in Southern Iberia: one in the Huelva region (Southwestern Spain), related with metal extraction in the Iberian Pyritic Belt and the presence of a natural harbor (Ría de Huelva) (Hunt Ortiz, 2003), and another one in Southeastern Iberia with disperse mining sites (Molina Fernández, 1978; García Alfonso, 2000; Lorrio, 2008). Although the metals used during the first stages of the LBA were the same as in the EBA, an important change in the metallurgical technology occurred around ~ 3200 cal BP. The production of tin-bronze alloys greatly intensified, and trade networks expanded, even through the Atlantic area, due to the importance of the Atlantic tin outcrops (Hunt Ortiz, 2003).

During this period, silver production was very important in Southwestern Iberia (Aubert, 2001). In this area, after the EBA, native silver was scarce and the use of argentiferous galena, a lead sulfur, was more common. In some outcrops the lead content is sufficient for silver extraction without addition of external lead (Hunt Ortiz, 2003), but in others the addition of external lead (cupellation) was necessary (especially in some jarosites). The lead addition to raw materials was very usual during the EIA period, even where the outcrops had enough lead content (Anguilano et al., 2010).

The origin of cupellation in Southern Iberia is a matter of controversy; it probably appeared during the LBA, prior to the start of Phoenician influence (Hunt Ortiz, 2003). In some cases, lead for cupellation was imported from other regions (Hunt Ortiz, 1995; 2003; Murillo-Barroso, in press; among others). Although the main source area of imported lead for cupellation in the Pyrite Belt is still unknown, some evidence points to a plausible massive lead extraction in Southeastern Iberia, which is justified by: 1) the significant lead content of the Alpujarride materials from Southeastern Iberia, 2) the isotopic lead evidences (Renzi et al., 2009; Murillo-Barroso, in press) and 3) the importance of local metallurgical settlements in Southeastern Iberia since ~ 3050 cal BP (Blázquez et al., 1984).

Lead was also progressively used in bronze metallurgy during the LBA and EIA for ternary alloys (lead, tin and copper) in Southern Iberia (Rovira Llorens, 1993, 1995). The use of lead in these alloys was due to the natural presence of lead in copper-tin metal-ores, the use of lead as tin substitute, and mainly the proprieties of lead that improve the handling of the metal-mixture. The expansion of lead-bronze in Southern Iberia was due to the availability of this metal-ore, such as Alpujarride outcrops.

The increase of lead pollution detected in the Río Seco record from ~ 3100 to ~ 2500 cal BP is synchronic with evidence of strong deforestation detected in Southwestern Spain (Stevenson and Moore, 1988) attributed to the intense mining and metallurgical activity that took place in the Huelva region between the LBA and EIA (Stevenson and Harrison, 1992). The lead increase during this period is detected slightly earlier in the Alboran Sea ODP 976 core (~ 3350 cal BP), and subsequently it decreases to minimum values. These differences between the records can be explained by the local-regional origin of lead pollution that can be registered with different values depending on environment and/or proximity to the source area (Martínez Cortizas et al., 1997).

There is no evidence of lead pollution from Zoñar Lake record, near Córdoba (central Andalusia) (Martín-Puertas et al., 2010). The progressive decrease of lead content in the Río Seco record at the end of the Early Iron Age, around ~ 2500 cal BP, may be associated with the decline of traditional mining areas of Southern Iberia (Hunt Ortiz, 2003), related to a possible depletion of surface metal outcrops, or the exploration of more productive outcrops farther away, such as those from Alpujarride complex in Murcia.

6.5. Missing record of late prehistory and historical periods of lead pollution in the Laguna de Río Seco

Although the lead record from Laguna de Río Seco is a good proxy for metallurgy development in Southeastern Iberia, sources of lead pollution originating at sites distant from this lake were not registered. The Zoñar Lake record shows a Pb/Al deposition increase from ~ 2400 to 2100 cal BP, agreeing with the period of Late Iron Age, related to Iberian mining smelting activity and trading with Greeks and Phoenicians (Martín-Puertas et al., 2010). There is no record of this activity in the Laguna de Río Seco or in the marine ODP 976 record. Only Pb/Al increase is recognized in the Zoñar record and was interpreted by Martín-Puertas et al. (2010) as a local contamination in the lake due to the presence of a settlement located on the lake banks. All these observations indicate an important feature of lead records that can be applied to other proxies: the distance

to the sources significantly controls the intensity of the contamination signal.

According to isotopic analyses, one of the main sources of Roman metals was Southern Iberia (Rosman et al., 1997; Alfonso et al., 2001). Although it is not the scope of our paper – we have focused in late prehistory – it should be noted that one of the main lead pollution periods recorded in the Northern Hemisphere is the Roman period (~2150 and 1500 cal BP), when the maximum lead production before the industrial period was recorded (Settle and Patterson, 1980). This lead pollution peak is also identified in the Laguna de Río Seco (from ~2100 to ~1700 cal BP) showing a decline during the late Roman period.

6.6. Late Prehistory vs. recent atmospheric lead pollution record

The comparison between different lead records from Southeastern Iberia demonstrates that significant lead pollution occurred during the Late Prehistory, Roman Empire and medieval times. However, the maximum values of lead pollution are reached in the last decades, since the Industrial Revolution. This increasing trend is recorded earlier in the Alborán Sea than in Zoñar Lake and Laguna de Río Seco, where it is evident in the past ~300 cal BP, registering the new development of lead mining and metallurgy in Southern Iberia (González Portilla, 1998). The maximum values of lead pollution in Zoñar Lake and Laguna de Río Seco occurred between the 1950s to the 1970s, consistent with the major use of leaded-fuel. Subsequently, the increase in unleaded-fuels, and the environmental awareness about lead emissions allowed a reduction in lead pollution (USEPA, 1998), which has been documented in Zoñar Lake and Laguna de Río Seco records. In general, past lead pollution values are lower than the ones of the last decade, except for those from Late Bronze and Early Iron Ages, in Laguna de Río Seco, and those from Late Iron Age and Roman Empire in Zoñar Lake. These data suggest that during these periods, a high atmospheric lead pollution was recorded in these areas, pointing to a large use of smelting and manipulation of lead. Despite the intense mining and metallurgy that can be inferred during these periods, the technologies and demand could not have allowed the volume of lead manipulation involved during recent periods. These considerations point to the location and proximity of the smelting and manipulation centers as major factors in metal content increase in the past records, as can be observed in present days (e.g., Lee et al., 2006).

7. Conclusions

The Holocene lead record from a remote alpine lake at 3020 masl helped us in distinguishing human from the natural baseline (pre-anthropogenic background) lead pollution throughout a long period of the Southern Iberian Late Prehistory (the so-called 'age of metals'). It provided extraordinary information about trends and human behavior when there is no record from written sources. Lead pollution seems to occur since ~3900 cal BP, which can be correlated with the start and gradual expansion of lead-using metallurgy by local communities. This dust pollution was generated in the extraction or smelting areas, surrounding Sierra Nevada, and transported by winds to the Laguna de Río Seco at higher elevation. The beginning of these activities is coeval with the increase in fire activity in Southeastern Iberia. Although it can be expected that these fire regimes were coupled with increases in deforestation and high erosion rates, only indirect evidences of these processes have been recognized. All these independent proxies together with the archeological evidence suggest that the human impact on the landscape due to the development of metallurgy was very intense.

The comparison with other lead records allowed us to recognize that lead pollution is spatially variable, and depends mainly on the proximity of the source of emissions, and of the scope of the metallurgical

activities. Four main periods of different lead pollution can be identified in the Laguna de Río Seco record.

During the Copper Age (~5150–4150 cal BP/~3200–2200 cal BC) metallurgy in Southern Iberia was low-scale and low-intensity and mainly dedicated to copper extraction. The lead pollution during this time period in the Río Seco record is hardly distinguishable from those of pre-metallurgical times.

During the Early Bronze Age (~4150–3500 cal BP/~2200–1550 cal BC), metallurgy intensified greatly, especially in Southeastern Iberia. Copper, silver, and gold were the most important metal-ores. Although lead was a trace metal, the manipulation of minerals with lead content caused the slightly atmospheric lead pollution detected in the Laguna de Río Seco during this period.

During the Late Bronze and Early Iron ages (~3500–2500 cal BP/~1550–550 cal BC) there was an important change in the metallurgical technology. Lead was intensively extracted, and used in ternary alloys (lead, tin and copper) and in cupellation processes. The development of cupellation processes in the pyritic belt (Southwestern Iberia) in order to extract silver led to an intensive exploitation of Southeastern Iberia lead outcrops. Intensive metallurgical activities were reflected in the atmospheric lead pollution record from the close site of Laguna de Río Seco.

Finally, most recent contamination signals, such as the Roman Empire pollution (~2100 and ~1700 cal BP), were also identified in the Río Seco record, being coherent with data from historical sources.

Our study also demonstrates that the measures developed in order to reduce lead emissions to the atmosphere during the last decades have worked, and a decreasing trend has been observed in the lead pollution record from Southern Iberia, reaching locally values previous to the Industrial Revolution, as in the case of Zoñar Lake.

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Appendix A. Supplementary data

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