Science of the Total Environment 645 (2018) 761–772

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Trace metal enrichment during the Industrial Period recorded across an altitudinal transect in the Southern Central Pyrenees

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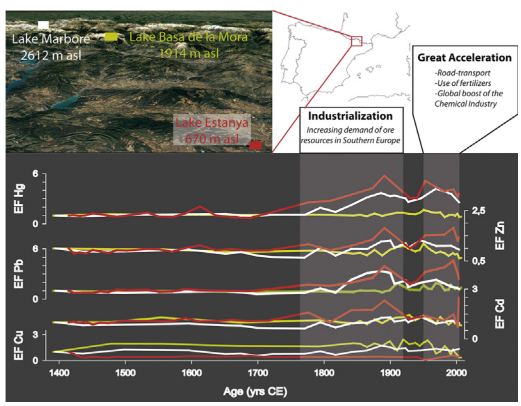
HIGHLIGHTS

- Significant enrichments of Hg, Pb, Cd and Zn in NE Spain during the Industrial period
- Site-specific processes and geographical location may affect metals enrichment factors
- High-altitude alpine lakes record more efficiently regional pollution
- Highest trace metal accumulation between 1840 and 1920 CE due to local mining activities
- Secondary increase in anthropogenic trace metals EFs during the Great Acceleration

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 December 2017
Received in revised form 3 July 2018
Accepted 12 July 2018
Available online xxxx

Keywords:
Atmospheric pollution
Lakes
Altitudinal gradient
Trace metals
Industrial Period
Pyrenees

ABSTRACT

The study of three lacustrine sedimentary archives along an altitudinal transect in the Southern Central Pyrenees - lakes Estanya, Basa and Marboré- has provided a unique record of changes in anthropogenic trace metal concentrations over the last six centuries in NE Iberian Peninsula. Although site-specific processes influence metals enrichments in each lacustrine system, significant enrichments of Hg and Pb and minor to moderate enrichments of Cu, Cd, and Zn with respect to baseline (Pre-industrial) concentrations highlight intensive release of anthropogenic trace metals with the advent of the Industrial Revolution leading to maximum values during the 20th century. The largest trace metal pollution occurred between 1840s and 1920s CE mainly derived from the increasing demand of ore resources in Southern Europe during the Industrialization. A second, less distinct pollution phase occurred between 1950s and 1990s, associated with the "Great Acceleration" and increased trace metal emissions related to road-transport, use of fertilizers in agriculture and the global boost of the Chemical Industry. Enrichment of mercury during the Industrial Period correlates well with Hg production in Spanish Almadén mines and global emission inventories. Local mining in the Pyrenees and regional smelting activities in Spain and Southern France may explain the enrichment of lead (and associated by-products cadmium and zinc) during the first pollution phase while the use of leaded gasoline since the mid-20th century drives the higher Pb enrichment

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https://doi.org/10.1016/j.scitotenv.2018.07.160

factor found till the late 20th century. This investigation demonstrates that environmental regulations controlling emissions of hazardous metals during the last decades have greatly contributed to a significant reduction of these anthropogenic trace metals enrichments in natural ecosystems although they still double pre-industrial levels. This study also exemplifies the different sensitiveness of lacustrine systems to record past atmospheric pollution phases and highlights the need of multi-archive studies to conduct regional (rather than local) pollution reconstructions.

1. Introduction

The atmospheric release of trace metal pollutants is a major problem that threatens living organisms and human population at a global scale. An increasing awareness in the emission trends of mercury, lead and cadmium is developing during the last decades since they are priority contaminants within various international programs aiming at the reduction of environmental and human exposure to air pollution (Pacyna et al., 2009). Although these trace metals are also released to the atmosphere from natural sources (soil and rock dust, natural forest fires, sea spray, volcanism), anthropogenic emissions such as fossil fuel combustion, waste incineration and metallurgy and/or industrial processes are by far the primary pollution source since historical times (Amos et al., 2013, 2015; Martinez-Cortizas et al., 1999; Nriagu, 1996; Gascón-Díez et al., 2017). Mining and smelting activities have been the main anthropogenic sources of atmospheric emissions of trace metals -including Cu, Pb, Hg, Cd and Zn - at a global scale (Dudka and Adriano, 1997; Hylander and Meili, 2003). The release of toxic heavy metals during (pre)historic mining and metallurgy activities – particularly since Roman times- also constitute one of the oldest, large-scale anthropogenic impact on the environment (Hillman et al., 2015; Martínez-Cortizas et al., 1997; Nriagu, 1996; West et al., 1997). Nevertheless, it was not until the Industrial Revolution when trace metal releases to the atmosphere became a global concern. Industrialization brought an unprecedented demand for metals and an exponential increase in the intensity of mining, smelting and roasting activities (Nriagu, 1996). As a consequence, the input of these anthropogenic metals into the Earth's surface has greatly exceeded those in the lithosphere (Han et al., 2002).

Unfortunately, atmospheric emission inventories of trace metals are scarce and restricted to the last decades (Horowitz et al., 2014; Nriagu, 1979; Nriagu, 1989; Olendrzyński et al., 1996; Pacyna et al., 2007; Pacyna and Pacyna, 2001; Streets et al., 2017; Zhang et al., 2016). In this line, natural archives have been widely used to reconstruct the long-term pollution history related to human activities to contextualize current atmospheric pollution changes. These sedimentary records also allow us: i) to understand the variability of different pollution sources through time and; ii) to evaluate the different ecosystem's response to enhanced pollution in terms of contaminant's burden and residence time in sediments and soils prior to their release back to the surface environment. This paleoenvironmental information can support policy makers to develop strategies and policies to reduce their emissions and impact in fragile ecosystems.

In the Iberian Peninsula, which has a long tradition of mining and smelting activities since Roman times, primarily focused upon the exploitation of mercury, gold, silver and lead, the anthropogenic release of trace metal to the environment has been continuously preserved in peatbogs (Martinez-Cortizas et al., 1999; Martínez Cortizas et al., 2012), marine and coastal sediments (Leorri et al., 2014; Martín-Puertas et al., 2010; Rubio et al., 2000; Serrano et al., 2011) and lacustrine sediments (Camarero et al., 1998; Corella et al., 2017; García-Alix et al., 2013; Hillman et al., 2017; Martín-Puertas et al., 2010). Indeed, mining during Roman times at the Iberian Peninsula and other Roman provinces led to large-scale trace metals atmospheric pollution even recorded in Greenland ice core records (Rosman et al., 1997). Among natural archives, mountain lakes record most efficiently past atmospheric pollution phases since: i) their sediments accumulate continuously and, therefore, the pollution chronicle can be precisely dated using radiometric techniques; ii) the enrichments of trace metals are not overestimated as occurs in peatbogs and/or marine sediments (Biester et al., 2007; Serrano et al., 2011); iii) the "cold trapping" effect caused by elevation that make these locations regional convergence areas of atmospheric pollutants (Camarero, 2017); iv) their location in remote areas that may not be greatly affected by local activities thus recording the long-range transport of atmospheric pollutants (Bacardit et al., 2012; Camarero et al., 2009; Catalan, 2015; Thevenon et al., 2011) and v) their reduced catchments make them more sensitive to direct atmospheric deposition of pollutants. Nevertheless, trace metal's biogeochemical cycles are intrinsic to each individual alpine lake. Therefore, a site-specific detailed understanding of trace metal depositional processes should be achieved before using these natural archives as proxies for past regional atmospheric pollution.

The main objective of this study is to evaluate the anthropogenic trace metal enrichment and depositional patterns in the Southern Central Pyrenees since the onset of the Industrial Period. In this aim, a comparative study has been undertaken in three contrasting lacustrine environments across an altitudinal gradient from Lake Estanya (located in the lowland close to the Ebro Basin) and the alpine lakes Basa de la Mora and Marboré, located in high-elevation areas of the South Central Pyrenees. The trace metal distribution in each lake, as well as the intercomparison of the different metal concentration and enrichments among the studied lakes allow us: i) to understand the different lake's ability to preserve the pollution signal according to their intrinsic limnological and morphometric characteristics; ii) to reconstruct the atmospheric contamination in the Southern Pyrenees for the last six centuries and iii) to elucidate possible sources controlling the enrichment of the anthropogenic trace metals (Cu, Cd, Hg, Zn and Pb) at a local Vs regional scale.

2. Study site

The three studied lakes are located in a N-S altitudinal transect - Lake Estanya (LE), 670 m a.sl; Lake Basa de la Mora (LB), 1914 m a.s.l. and Lake Marboré (LM); 2612 m a.s.l.; Fig. 1, across the Southern Central Pyrenees. The area is characterized by south verging thrust and folds, mainly composed of Mesozoic and Early Cenozoic rocks (Vera, 2004). LM and LB are located in the Inner Mountain Range while LE is located in the Southern External Ranges, close to the northern boundary of the Ebro River Basin. The three lakes have relatively small lake's surface area (ranging from 5.5 to 18.8 ha) and small to middle sized watersheds (ranging from 106 to 462 ha) composed mostly of carbonated bedrock (Leunda et al., 2017; Morellón et al., 2009a; Oliva-Urcia et al., 2018; Pérez-Sanz et al., 2014; Valero-Garcés et al., 2013).

The Southern Central Pyrenees are located in a transitional area between the Eurosiberian and Mediterranean bioclimatic regions (Peinado Lorca and Rivas-Martínez, 1987) which are mainly different in terms of precipitation amount and seasonality. Mean annual temperatures and precipitation across the altitudinal gradient ranges from ~5 °C and 2000 mm close to LM to 14 °C and 470 mm in LE (Morellón et al., 2009b). The elevational gradient across the three lakes results in an altitudinal distribution of vegetation where lowlands are occupied by crops and riparian corridors while forest composed of *Pinus unciata*