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# Millennial scale impact on the marine biogeochemical cycle of mercury from early mining on the Iberian Peninsula

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## Millennial scale impact on the marine biogeochemical cycle of mercury from early mining on the Iberian Peninsula

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[1] The high-resolution mercury record of a *Posidonia oceanica* mat in the northwest Mediterranean provides an unprecedented testimony of changes in environmental mercury (Hg) loading to the coastal marine environment over the past 4315 yr BP. The period reconstructed made it possible to establish tentative preanthropogenic background Hg levels for the area ( $6.8 \pm 1.5 \text{ ng g}^{-1}$  in bulk sediments). A small, but significant, anthropogenic Hg increase was identifiable by  $\sim 2500$  yr BP, in agreement with the beginning of intense mining in Spain. Changes in the record suggest four major periods of anthropogenic Hg pollution inputs to the Mediterranean: first, during the Roman Empire (2100–1800 yr BP); second, in the Late Middle Ages (970–650 yr BP); third, in the modern historical era (530–380 yr BP); and fourth, in the industrial period (last 250 years), with Hg concentrations two-, four-, five-, and tenfold higher than background concentrations, respectively. Hg from anthropogenic sources has dominated during the last millennium (increase from  $\sim 12$  to  $\sim 100 \text{ ng g}^{-1}$ ), which can be related to the widespread historical exploitation of ore resources on the Iberian Peninsula. The chronology of Hg concentrations in the mat archive, together with other Hg pollution records from the Iberian Peninsula, suggests regional-scale Hg transport and deposition and shows earlier marine Hg pollution than elsewhere in Europe. Moreover, the mat also records a higher number of historic contamination phases, in comparison with other natural archives, probably due to the fact that the bioaccumulating capacity of *P. oceanica* magnify environmental changes in Hg concentrations. In this study, we demonstrate the uniqueness of *P. oceanica* meadows as a long-term archive recording trends in Hg abundance in the marine coastal environment, as well as its potential role in the Mediterranean as a long-term Hg sink.

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### 1. Introduction

[2] There is a general consensus that natural archives provide a means to reconstruct mercury (Hg) fluxes and trends at local, regional, and even global scales [Fitzgerald *et al.*, 1998, 2005]. Many advances have been made in recent years in the understanding of past deposition of Hg using continental natural archives [e.g., Biester *et al.*,

2007]. Previous studies have focused on estimating the natural and anthropogenic contribution of past Hg inputs based on the analysis of natural environmental archives, such as peat [Pheiffer-Madsen, 1981; Martínez-Cortizas *et al.*, 1999; Bindler, 2003], lake sediments [Aston *et al.*, 1973; Swain *et al.*, 1992], glacial ice [Vandal *et al.*, 1993; Schuster *et al.*, 2002], and marine sediments [Buckley *et al.*, 1995; Gobeil *et al.*, 1999]. While most studies regarding marine environments emphasize Hg contamination patterns in offshore areas and over the last few centuries at most [Aston *et al.*, 1973; Gobeil *et al.*, 1999; Di Leonardo *et al.*, 2009], few studies for coastal areas that span longer timescales exist because of the unstable nature of sedimentary processes and the low resolution of most marine records. However, studies of river sediments from Rio Tinto [Leblanc *et al.*, 2000] and lagoon sediments from southern France, also receiving riverine inputs [Elbaz-Poulichet *et al.*, 2011], showed clearly that historical mining and metallurgy introduced Hg to the marine environment surrounding coastal areas of the Iberian Peninsula and southern France.

[3] The mat deposits built by the seagrass *Posidonia oceanica* constitute a remarkable archive in coastal

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Mediterranean areas. This endemic angiosperm forms a biogenic reef of senescent plant tissues and sediments stored under anoxic conditions that can reach 8 m in thickness and 6000 years in age, and presents a high-chronostratigraphic coherence [Boudouresque et al., 1980; Mateo et al., 1997; Lo Iacono et al., 2008]. According to the curve of the Holocene sea-level change predicted along the Mediterranean French coasts by Lambeck and Bard [2000], by 10,000 yr BP the sea was 40 m below the present-day level. Thus, knowing that the distribution of *P. oceanica* is limited to ~40 m depth due to the insufficient irradiance at higher depths [Pasqualini et al., 1998], the natural archives formed by *P. oceanica* during the Holocene can potentially reach up to ~10,000 yr BP. These mat deposits have proven to be valuable for obtaining unprecedented paleoecological, biogeochemical, and environmental information of marine coastal ecosystems for the Late Holocene [Romero et al., 1994; Mateo et al., 1997, 2002, 2010; Lo Iacono et al., 2008; López-Sáez et al., 2009; Serrano et al., 2011, 2012]. Moreover, it has been recognized that heavy-metal concentrations in senescent *P. oceanica* tissues can be used as a proxy for short- (ca. 30 years [e.g., Tovar-Sánchez et al., 2010]) and long-term (ca. 5000 years [Serrano et al., 2011]) variations in metal fluxes to the sea.

[4] It is well recognized that atmospheric deposition is the primary source of Hg to the oceans [Mason and Sheu, 2002], while biotic and abiotic production, oxidation, and sea-air exchange of Hg dominate the transport and deposition of Hg on local, regional, and global scales [e.g., Mason et al., 1994; Lamborg et al., 2002; Amyot et al., 2005]. The Hg gas present in the atmosphere (typically as elemental Hg ( $\text{Hg}^0$ ) and divalent ionic Hg ( $\text{Hg(II)}$ ) chemical forms) can experience biotic and abiotic reactions and transformations that allow for deposition in the ocean [Fitzgerald et al., 2007]. In the coastal zone, Hg(II) from, for example, mining activities is delivered via runoff and/or atmospheric deposition and can either be reduced to  $\text{Hg}^0$ , with possible return to the atmosphere, or buried in sediments (i.e., scavenged, absorbed, or adsorbed), or converted to methylated species by both biological and chemical mechanisms [Fitzgerald et al., 2007].

[5] Over the last few centuries or longer, anthropogenic contributions, such as from mining and metallurgy [Hylander and Meili, 2003], have come to dominate the global cycling of Hg [Fitzgerald et al., 1998]. In Spain, the Iberian pyrite belt has been exploited since the Copper Age [Leblanc et al., 2000]; these ores are rich in iron, lead, and copper as well as gold, silver, tin, and Hg. In addition to the release of metals to watercourses [Leblanc et al., 2000; Elbaz-Poulichet et al., 2011], peat cores from northwestern Spain recorded increases in the atmospheric deposition of Hg that parallel increasing human activities during the last millennia in the Iberian Peninsula and, in particular, the influence of historical mining and metallurgy on regional atmospheric metal pollution deposition [Martínez-Cortizas et al., 1997, 1999].

[6] The Mediterranean Sea has received the imprint of a very complex history due to early and intense human activities. The absence of adequate paleorecords to document the relevant spatial and timescales of human activities in the area have resulted in a concomitant lack of information on long-term changes in environmental and biological

features of Mediterranean ecosystems. The wide distribution of *P. oceanica* meadows around coastal Mediterranean areas and the stable paleorecord they generate open exciting opportunities for developing environmental reconstructions.

[7] In this article, we present the first reconstruction of changes in Hg at a millennial scale using the *P. oceanica* mat under a meadow growing in a small bay in the northwest Mediterranean (Portlligat, Girona, Spain). We also review Hg data from *P. oceanica* meadows and from a range of peat, lagoon, and estuarine sediment studies that have recorded past atmospheric deposition and accumulation rates of Hg in westernmost Europe. We discuss the reliability of *P. oceanica* mat deposits as paleorecords of changes in Hg fluxes to the marine environment and summarize the impact of Hg pollution in the Iberian region over the past 4300 yr BP showing earlier marine Hg pollution than anywhere else in Europe. The results obtained also provide evidence for a possible key role of seagrass meadows as a long-term pollutant filter and sink.

## 2. Methods and Field Description

### 2.1. Study Site

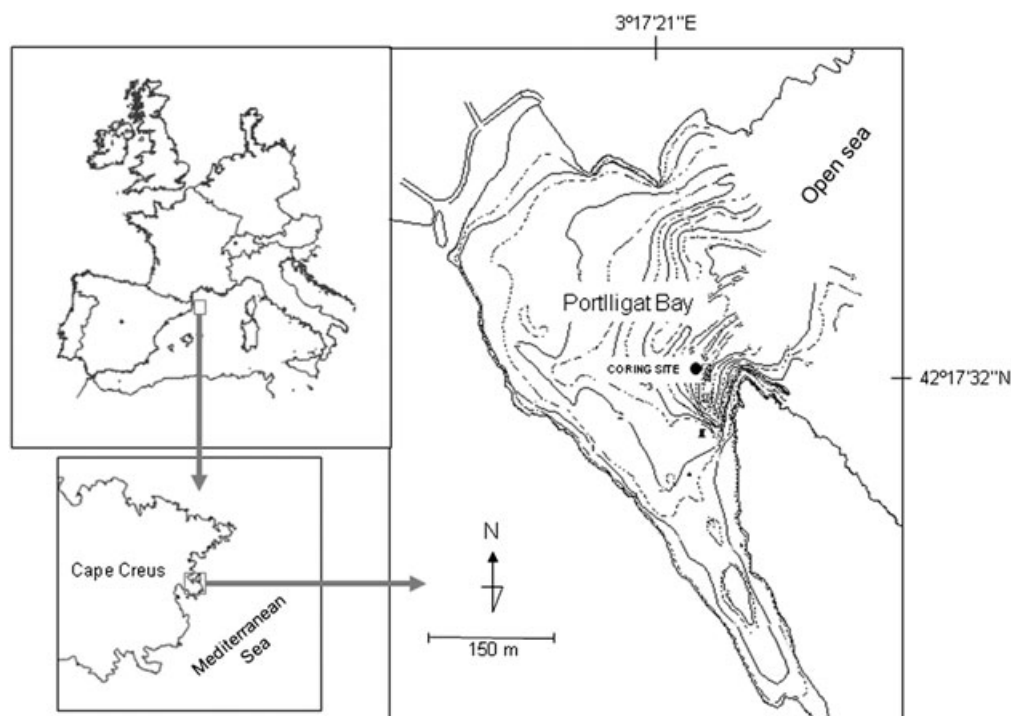
[8] The Portlligat Bay ( $42^{\circ}17'32''\text{N}$ ;  $3^{\circ}17'28''\text{E}$ ) is a small (0.14 km<sup>2</sup>) and shallow (<10 m deep) inlet located along the northeast coast of the Iberian Peninsula and connected to the sea through a 213 m wide opening to the NW (Figure 1). Geologically, the Cape Creus (eastern Pyrenees) and Portlligat Bay are old formations that originated ca. 400 million years ago along with the Pyrenees. The Cape Creus migmatitic complex consists of an association of sillimanite schists, granitoids, quartz gabbros, and pegmatites.

[9] *P. oceanica* meadows cover 94,315 m<sup>2</sup> in Portlligat Bay, which represents 69% of the total area. Most of the seafloor in the bay is dominated by a consistent meadow with some interspersed sandy bioclastic areas [Lo Iacono et al., 2008]. The bay receives episodic freshwater inputs from a typical Mediterranean temporary stream that flows into it from its northeast shore. The most traditional activities in the Portlligat Bay area, such as dry-land agriculture and fisheries, have been gradually replaced by others related to tourism and development sectors.

### 2.2. Sampling and Age Model

[10] A 5 m long core of *P. oceanica* mat was collected from a 3 m deep meadow in 2000 in Portlligat Bay using a floating drilling platform that combined pneumatic percussion and rotation. All manipulations were performed with nonmetal instruments.

[11] Twelve samples of *P. oceanica* sheath debris were radiocarbon dated at the National Ocean Sciences AMS Facility (Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA), following standard procedures [Stoddart, 1969; Stuiver and Pollack, 1977]. Sheaths were rinsed in ultrapure Milli-Q water (Millipore, Billerica, Massachusetts, USA) and inspected under a stereomicroscope for attached reworked materials. Samples were dried at 60°C to a constant weight before radiocarbon dating. All dates reported in this article are expressed as radiocarbon dendrocalibrated years determined with CALIB software v.4.4 [Stuiver et al., 1998]. The corrected ages for the marine



**Figure 1.** Location of the study site, Portlligat Bay, Girona (northwest Mediterranean) and position of the drilling point in the *P. oceanica* bed.

reservoir effect were used to produce an age-depth model (i.e., smooth-spline model) using Clam software ([Blaauw, 2010] see Supporting Information, hereinafter SI). According to this model, accretion rates ranged from 0.7 to 2.7 mm yr<sup>-1</sup>, and the time resolution ranged from 4 to 15 yr cm<sup>-1</sup>. The core studied was 475 cm long and covers 4315 cal yr BP. For further description, see Serrano *et al.* [2012] and SI.

### 2.3. Biogeochemical Analyses

[12] The core was cut into 1 cm slices, and then each slice was weighed before and after oven-drying at 60°C until constant weight (dry weight; DW). Samples were subsequently subdivided by quartering. The organic matter (OM) and the carbonate content (CaCO<sub>3</sub>) were then measured in aliquots from about half of the slices (every second one). The OM was determined by measuring the weight loss on ignition at 450°C for 5 hours. The CaCO<sub>3</sub> was determined using a Scheibler calcimeter [Nelson, 1982]. Five milliliters of 10% HCl were added to 0.4 g DW milled sediment, and the volume of CO<sub>2</sub> evolved was recorded and compared to a standard of 0.2 g of pure carbonate (dry CaCO<sub>3</sub> powder, BAKER ANALYZED<sup>®</sup>).

### 2.4. Hg Analyses

[13] For about half of the core slices (every second one), the dried bulk sediment was milled and homogenized and then approximately 0.05–0.075 g were analyzed for Hg content using thermal decomposition atomic absorption spectrometry (Umeå University, SMS100; PerkinElmer, Boston, Massachusetts, USA; Technische Universität Braunschweig, DMA-80; Milestone Inc., Shelton,

Connecticut, CT), which eliminates the need for further sample pretreatment (cf. USEPA method 7473). Each lab analyzed 76 alternate samples. At both laboratories, measured concentrations of standard reference materials included in the analyses were within their certified ranges and all relative standard deviation (SD) of all replicate analyses (approximately every 10th sample) were ≤9%, and in all but two cases <6%. Comparative analyses between the labs are within the analytical uncertainty.

### 2.5. Numerical Procedures

[14] The Hg accumulation (ng cm<sup>-3</sup>) was calculated by multiplying the soil bulk density (g cm<sup>-3</sup>) by the Hg concentration (ng g<sup>-1</sup>). Accumulation rates (μg m<sup>-2</sup> yr<sup>-1</sup>) were obtained by dividing total Hg accumulation (μg m<sup>-2</sup>) by the time span represented by each cm section (yr cm<sup>-1</sup>). It is important to note that the changes in soil density along the archive influence the Hg accumulation (e.g., lower soil density yields lower Hg accumulation). The changes in mat accretion rates (cm yr<sup>-1</sup>) also influence the Hg accumulation rates (e.g., higher mat accretion rates lead to lower estimated Hg accumulation rates).

[15] Mean Hg concentrations in samples older than 2800 yr BP (352–475 cm) were considered as background concentrations (BG) for Portlligat Bay based on the results obtained for Hg and those previously found in the same core for other metals [Serrano *et al.*, 2011], and because these depths predate extensive mining activities. Therefore, the mean Hg concentrations (ng g<sup>-1</sup>), accumulation (ng cm<sup>-3</sup>), and accumulation rates (μg m<sup>-2</sup> yr<sup>-1</sup>) in samples older than 2800 yr BP were used to estimate enrichment factors (EFs) as follows:



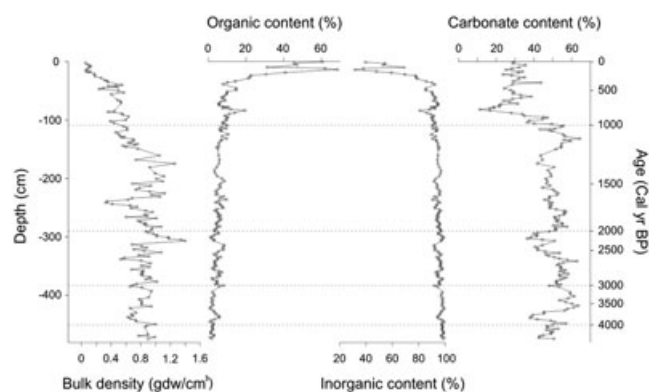
$$EF = (X_i/X_{BG}), \quad (1)$$

where  $X_i$  is the Hg content (concentration, accumulation, or accumulation rate) in each sample and  $X_{BG}$  is the average background Hg content between 2800 and 4315 cal yr BP.

### 3. Results

#### 3.1. The *P. oceanica* Archive

[16] The sediments beneath *P. oceanica* meadows (often referred to as mat or matte) are mainly composed of siliciclastic (46%) and biogenic carbonate (46%) fine-grained materials and, to a lesser degree, by organic matter (8% [Serrano *et al.*, 2012]; Figure 2). Bulk density values range from 0.05 to 1.40 g DW cm<sup>-3</sup>, while the inorganic and carbonate contents range from 31 to 99% and 11 to 64% respectively (Figure 2).



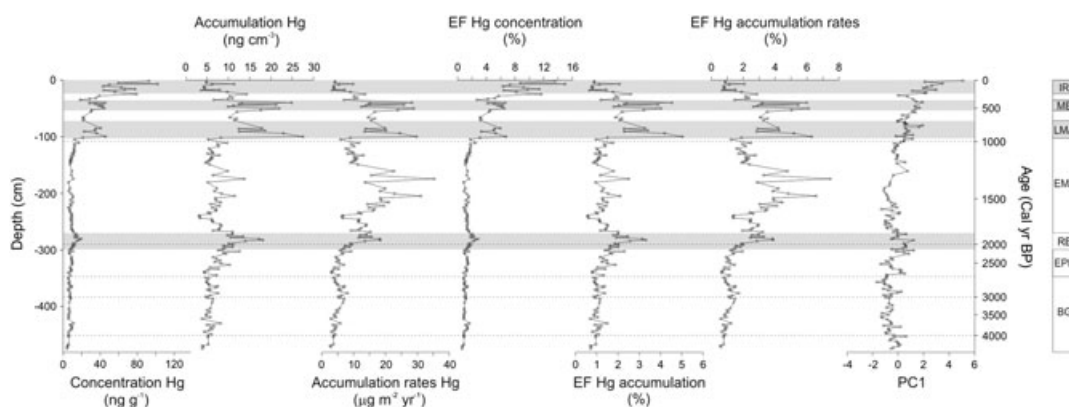
**Figure 2.** Changes in the main components along the *P. oceanica* mat core from Portlligat. Inorganic content and carbonate content are expressed as percentage of the total sample DW.

[17] The *P. oceanica* mat is not homogeneous and changes greatly with aging, mainly in relation to the decrease in the organic matter content. The organic content is higher in the upper layers (average of 32% in the top 50 cm, within ca. 500 years of burial), below which the mat becomes increasingly dominated by the inorganic fraction (ranging from 80 to 99% in 50–475 cm, ca. 4315–500 yr BP). Similarly, the mat starts as low compacted sediments (average 0.2 g DW cm<sup>-3</sup> in the top 39 cm, <420 yr BP), then becomes increasingly denser until 150 cm depth (~1 g DW cm<sup>-3</sup> after ca. 1300 years of burial). Thereafter, the mat density oscillates around an average value of 0.85 g DW cm<sup>-3</sup> until the core bottom (Figure 2).

#### 3.2. Hg Record

[18] Concentrations of Hg range from 4 to 102 ng g<sup>-1</sup> (measured at 472 and 7 cm, respectively; Figure 3). The Hg record shows lower concentrations between 352 and 475 cm (6.8 ± 1.5 ng g<sup>-1</sup>), which have been defined as the BG for this study area. The sections between 266 and 299, 71 and 105, 35 and 53, and <21 cm depth show higher Hg concentrations of 9–20, 12–46, 18–45, and 43–102 ng g<sup>-1</sup>, respectively. In the top 105 cm of the core, Hg concentrations largely oscillate, but increase exponentially until the surface.

[19] Hg accumulation ranges from 3 to 28 ng cm<sup>-3</sup>, with the calculated Hg accumulation rates from 3 to 35 μg m<sup>-2</sup> yr<sup>-1</sup> (Figure 3). Average background Hg accumulation and accumulation rates (i.e., in samples older than 2800 <sup>14</sup>C yr BP) are 5.5 ± 1.0 ng cm<sup>-3</sup> and 4.8 ± 1.3 μg m<sup>-2</sup> yr<sup>-1</sup>, respectively. As is the case for Hg concentrations, the sections between 266 and 299, 71 and 105, and 35 and 53 cm show higher Hg accumulation (8–28 ng cm<sup>-3</sup>) and accumulation rates (7–30 μg m<sup>-2</sup> yr<sup>-1</sup>). In addition, the section between 106 and 268 cm also shows high Hg accumulation rates (6–35 μg m<sup>-2</sup> yr<sup>-1</sup>), although the Hg concentrations are relatively low. On the contrary, in the upper 21



**Figure 3.** Changes in Hg concentrations (ng g<sup>-1</sup>), accumulation (ng cm<sup>-3</sup>), and accumulation rates (μg m<sup>-2</sup> yr<sup>-1</sup>) of *P. oceanica* bulk sediments during the Late Holocene. Changes in enrichment factors for Hg concentration, accumulation, and accumulation rates through the period reconstructed. Anthropogenic metal pollution is represented by the scores of the first principal component (PC1) (dominated by the high positive loadings of metals associated with anthropogenic activities: Zn, Pb, Cd, Cu, and Fe) obtained for the same core by Serrano *et al.* [2011]. Hg record periods: BG, 4315–2800 cal yr BP; EPP, 2800–2100 cal yr BP; RE, 2100–1800 cal yr BP; EMA, 1800–970 cal yr BP; LMA, 970–650 cal yr BP; ME, 530–380 cal yr BP; and IR, last 250 cal yr BP).

cm, Hg accumulation and accumulation rates are relatively low ( $4\text{--}11\text{ ng cm}^{-3}$  and  $3\text{--}10\text{ }\mu\text{g m}^{-2}\text{ yr}^{-1}$ , respectively), despite the higher concentrations.

### 3.3. Enrichment Factors

[20] Mean Hg concentrations in samples older than 2800 yr BP (352–475 cm) were used as the background reference to estimate enrichment factors for six subsequent periods based on temporal changes in the Hg record: early pollution period (EPP; 300–349 cm, 2800–2100 yr BP); Roman Empire (RE; 269–299 cm, 2100–1800 yr BP); Early Middle Ages (EMA; 106–268 cm, 1800–970 yr BP); Late Middle Ages (LMA; 71–105 cm, 970–650 yr BP); modern era (ME; 35–53 cm, 530–380 yr BP); and Industrial Revolution (IR; 1–21 cm, <250 yr BP). Mercury concentrations in all periods considered (from 2800 yr BP until present) are higher than background levels, with metal EF values ranging from 1.2 to 9.6 (Figure 4).

## 4. Discussion

### 4.1. The *P. oceanica* Mat: A Natural Archive and Sink of Pollution Hg

[21] Several authors have shown that the different compartments of *P. oceanica* meadows (i.e., living and dead plant matter and sediment) are accurate archives of past and present mercury contamination [e.g., Pergent-Martini, 1998; Lafabrie et al., 2007a, 2007b, 2008b]. Thus, each mat sample analyzed (encompassing ca. 10 years per sample) may provide a valid average value of past metal concentrations [Serrano et al., 2011].

[22] The bioaccumulation capacity of the seagrass *P. oceanica* (the concentration factor for Hg has been estimated to be 3200 [Pergent-Martini, 1998]) leads to higher concentrations in seagrass tissues with respect to the dissolved gaseous mercury concentration in coastal seawater of the Mediterranean basin ( $18\text{--}47\text{ }\mu\text{g/L}$  [Lanzillotta and Ferrara, 2001]). Therefore, the Hg signal in the *P. oceanica* mat deposits may have been mainly formed by the active absorption of Hg from the sediment and the water column during plant growth [Pergent-Martini, 1998] and the subsequent adsorption of Hg in the senescent plant tissues and

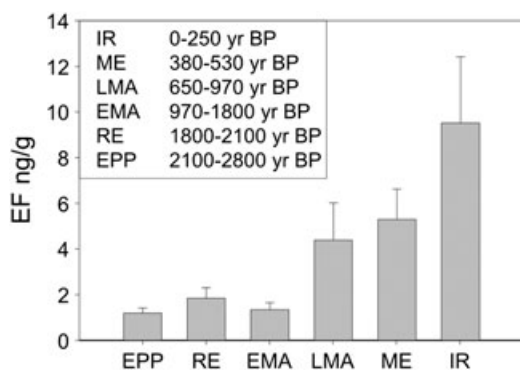
particles before and after burial in the sediment [Breteler et al., 1981; Yin et al., 1997]. In addition, a large proportion of Hg in natural waters is complexed with dissolved organic matter [Lamborg et al., 2003; Fitzgerald et al., 2007], and therefore other sources of detrital organic matter (i.e., seston) entering the mat [Papadimitriou et al., 2005] may also have contributed to the Hg signal.

[23] To interpret past changes in metal abundances using natural archives, some debate exists as to whether it is best to use metal concentrations, metal accumulation, or metal accumulation rates [e.g., Biester et al., 2007]. Each of these three data presentations are provided and compared here, but for modeling the past deposition of metals using the *P. oceanica* mat archive, it seems more accurate and faithful to base the interpretation of changes using the metal concentration record, because both Hg accumulation and accumulation rates are largely influenced by changes in bulk density in the top ~300 cm and, in particular, by the low-density values in the top ~100 cm (Figures 2 and 3). In addition, Hg accumulation rates are influenced by changes in mat accretion rates, in particular, during a period of high accumulation (between 124 and 264 cm, average accretion rates  $0.21\text{ cm yr}^{-1}$ ; SI) that leads to an increase in Hg accumulation rates, although concentrations are at background values (Figure 3). Changes in *P. oceanica* mat bulk density and accretion rates were related to ecological or environmental processes [Serrano et al., 2012] and are thus not related to metal fluxes. Therefore, the interpretation of both the Hg accumulation and the Hg accumulation rates in *P. oceanica* records as faithful proxies of past metal abundances can lead to potentially erroneous conclusions.

[24] A positive correlation between the organic matter content in sediments and Hg concentrations has been reported [e.g., Yin et al., 1997; Sunderland et al., 2006], thus the high organic content in the upper 40 cm (<430 yr BP) might have influenced Hg accumulation in the mat. However, the correlation between C and Hg is relatively low ( $R^2 = 0.31$ ;  $P = 0.03$ ; results not shown) and seems not to reflect a causal relationship, because the Hg/C molar ratio faithfully reflects the same changes in total Hg concentrations along the record (SI).

[25] Large differences in the carbonate content can increase or decrease the Hg concentration, accumulation, and accumulation rates. Thus, the lower carbonate content in the upper 100 cm (<950 yr BP) might have increased the Hg content in the mat, but both variables are not correlated during this period ( $P = 0.73$ ).

[26] The mat-sediment record shows a pattern of Hg enrichment that matches well with historical events and does not seem to respond to diagenetic processes or to be affected by local geological inputs. In superficial sections, Hg is mainly associated to organic-rich sediments, but during early diagenesis, organic matter is mineralized, potentially releasing Hg. However, the concomitant reduction of sulphate limits the mobility of Hg in pore water by adsorption and coprecipitation onto acid-volatile sulfide and pyrite [e.g., Gagnon et al., 1997], as well as the fact that in annually laminated lake sediments, it has been shown the total Hg concentrations are not influenced by diagenetic losses of carbon [Rydberg et al., 2008]. In addition, the Hg concentration record is positively correlated ( $R^2 = 0.69$ ; Figure 3) with the record of metal (Zn, Pb, Cd, Cu, and Fe) pollution obtained from the same mat core



**Figure 4.** Average enrichment factors  $\pm$  SD with respect to background levels (BG, samples older than 2800 cal yr BP) for six contamination periods: EPP, RE, EMA, LMA, ME, and IR. See Figure 3 for the chronology of the phases.

[Serrano *et al.*, 2011]. Although the biogeochemistry and the specific pollution history are not the same for all metals, it seems probable that the correlation found is a consequence of the fact that these metals are coemitted during mining and metallurgy.

[27] The long-term Hg sink (i.e., cumulative mass) in the 475 cm *P. oceanica* mat studied was estimated to be 38.7 mg m<sup>-2</sup>, accumulated at an average rate of 10 µg m<sup>-2</sup> yr<sup>-1</sup>. The bioaccumulator nature of *P. oceanica* [Pergent-Martini, 1998; Sanz-Lázaro *et al.*, 2012] and the characteristics of the mat (i.e., high content of plant debris, sediment organic matter, and muddy sediments [Serrano *et al.*, 2012]) can confer an unusual ability to accumulate metals in marine coastal areas. The sheltered environment of *P. oceanica* meadows allows deposition of the finest clay, silt, and detrital particles, which provide optimum surfaces for Hg transport. Also, the high organic content in the mat, which strongly complex heavy metals [Al-Farawati and van den Berg, 2001], points to a possible key role of seagrass meadows as a long-term Hg filter and sink. There is growing interest in the fate of pollutant metals in the ocean, but not much is currently known [Fitzgerald *et al.*, 2007]. Further studies are needed to adequately assess the relevance of the mat as a pollutant sink.

#### 4.2. History of Hg in the Northwest Mediterranean: Natural vs. Anthropogenic Contributions

[28] Analyses of *P. oceanica* mat provide a unique record of long-term changes in Hg (this study) and other metals (i.e., Fe, Mn, Ni, Cr, Cu, Pb, Cd, Zn, As, and Al [Serrano

*et al.*, 2011]) during the Late Holocene in Mediterranean coastal ecosystems. The period covered by the *P. oceanica* mat provides initial evidence of what can be considered as a tentative preanthropogenic BG Hg concentration in the northwest Mediterranean (6.8 ± 1.5 ng g<sup>-1</sup>; Table 1). This BG value is the lowest reported for bulk *P. oceanica* sediments or plant tissues (i.e., for leaves, sheaths, rhizomes, roots, and superficial mat sediments) in the western Mediterranean (Table 1).

[29] Previous studies reported that Hg concentrations in recent *P. oceanica* tissues from low impacted areas may reflect the “background noise” of the Mediterranean [e.g., Lafabrie *et al.*, 2008a, 2008b]. Indeed, the use of this expression might be inappropriate because atmospheric and also waterborne Hg pollution in this part of Europe has been extensive over the last millennium or longer [e.g., Martinez-Cortizas *et al.*, 1999; Elbaz-Poulichet *et al.*, 2011]. Therefore, the preanthropogenic Hg concentrations measured in this study may represent a more realistic natural background value for the area of study.

[30] The *P. oceanica* mat record reflects a higher number of historic Hg contamination phases, in comparison with other natural archives from this region. Features in the Hg concentration record of the mat partially overlap the chronology of other records in coastal lagoon sediments from France [Elbaz-Poulichet *et al.*, 2011], estuarine sediments from southwest Spain [Leblanc *et al.*, 2000], and in atmospheric Hg deposition records in peat from northwest Spain [Martinez-Cortizas *et al.*, 1999] (Figure 5). But the

**Table 1.** Review of Available Data for Hg Concentrations on *P. oceanica* Tissues (Living and Dead Sheaths, Roots, and Rhizomes) and Superficial *P. oceanica* Sediments Reported by Other Authors Around the Mediterranean Sea

Plant tissue	Hg (ng g <sup>-1</sup> )	Hg (ng g <sup>-1</sup> )	Location	Source
	range	mean ± SD		
Living leaf	20–630	236 ± 158	Italian coast	3, 4, 5, 6, 8, 12
	NR	34 ± 8	Ischia (Italy)	15
	NR	60 ± <5	Sardinia (Italy)	8
	50–176	115 ± 45	French coast	2, 6, 14, 15, 17
	10–71	45 ± 19	Corsica (France)	3, 6, 8, 10, 11, 13, 14, 15, 16, 17
	18–450	169 ± 91	Spanish coast	18, 19
	NR	289 ± 11	Italian coast	9
Living sheath	NR	39 ± 7	Ischia (Italy)	15
	NR	92 ± 5	French coast	15
	10–55	36 ± 12	Corsica (France)	9, 11, 15, 16
	43–91	66 ± 5	Italian coast	1
Living rhizome	26–142	48 ± 14	Ischia (Italy)	15
	31–150	52 ± 10	French coast	15
	23–89	65 ± 22	Corsica (France)	7, 15, 16
	NR	75 ± 35	Spanish coast	18
	29–280	127 ± 39	Spanish coast	18, 19
Sheath remains	17–407	249 ± 143	Italian coast	1, 9
	15–113	25 ± 4	Ischia (Italy)	15
	70–705	127 ± 15	French coast	15
	9–100	55 ± 12	Corsica (France)	7, 9, 15, 16
Sediment	NR	560 ± 140	Italian coast	8
	NR	70 ± 40	Sardinia (Italy)	8
	NR	20 ± 10	Corsica (France)	8
	NR	48 ± 30	Spanish coast	18
	<b>Sediment Background</b>	<b>4–102</b>	<b>17 ± 18</b>	<b>Spanish coast</b>
	<b>4–11</b>	<b>7 ± 1</b>	<b>Spanish coast</b>	<b>This study</b>

Hg concentrations and background metal concentrations (BG, in samples older than 2800 <sup>14</sup>C yr BP) ± SD from bulk *P. oceanica* mat sediments measured in this study. Units are in ng Hg g<sup>-1</sup> dry sample weight. NR, not reported. Source: 1. Ancora *et al.* [2004]; 2. Augier *et al.* [1980]; 3. Capiomont *et al.* [2000]; 4. Costantini *et al.* [1991]; 5. Ferrara *et al.* [1989]; 6. Ferrat *et al.* [2003]; 7. Lafabrie *et al.* [2003]; 8. Lafabrie *et al.* [2007a]; 9. Lafabrie *et al.* [2007b]; 10. Lafabrie *et al.* [2008a]; 11. Lafabrie *et al.* [2008b]; 12. Lafabrie *et al.* [2009]; 13. Maserti *et al.* [1988]; 14. Pergent-Martini [1994]; 15. Pergent-Martini [1998]; 16. Pergent-Martini and Pergent [2000]; 17. Pergent *et al.* [2011]; 18. Sanchiz *et al.* [1999]; 19. Sanchiz *et al.* [2001]



bioaccumulation nature of the seagrass *P. oceanica* [Pergent-Martini, 1998] magnifies the changes in environmental Hg concentrations and therefore seems to provide a clearer image of the anthropogenic impacts than other natural archives, especially as it pertains to the coastal environment.

[31] A small, but significant, anthropogenic Hg increase began ~2500 yr BP (in the EPP, Hg EF = 1.2), which is consistent with the beginning of intense mining in Spain in the Celtic period [Flores, 1981; Hernández-Sobrino, 1993]. The precise origin of the additional Hg entering Portlligat Bay during the EPP is unknown, but we can reasonably speculate that it is likely associated with large-scale cultural and technological development and with continuous scattered human activities on the coast near the study area [Martin, 1986; Ruiz de Arbulo, 1991; Riera and Esteban-Amat, 1994; Delibes and Montero, 1999; Sanmartí and Santacana, 2005].

[32] The *P. oceanica* mat record can be divided into four major periods of anthropogenic Hg pollution: 1) the RE period (2100–1800 cal yr BP); 2) the LMA (970–650 cal yr BP); 3) the recent historical era (530–380 cal yr BP); and 4) the modern industrial period (last 250 cal yr BP). Mercury concentrations are 2, 4, 5, and 10 times higher in these four periods, respectively, than in sample levels predating extensive anthropogenic metal pollution.

[33] A pronounced increase from an average  $8 \text{ ng g}^{-1}$  in the EPP to  $13 \text{ ng g}^{-1}$  occurred in Roman times, which is temporally consistent with the period in which cinnabar refining and the greatest mining activities took place in Iberia [Goldwater, 1972; Flores, 1981; Domergue, 1990]. The impact of Hg pollution around the Iberian region during

Roman times is registered not only in these mat sediments from an embayment on the Catalonia coast (northeast Spain), but also downstream of rivers in Cadiz (draining mines in the Rio Tinto basin, southern Spain) [Leblanc et al., 2000] and in atmospheric deposition records in Galicia (northwest Spain) [Martínez-Cortizas et al., 1999]. Taken together, these results show quite early regional pollution emissions of Hg both to surface waters and to the atmosphere that can be clearly related to the widespread historical exploitation of ore resources on the Iberian Peninsula. This is much earlier than has been thus far observed elsewhere in Europe (Figure 5).

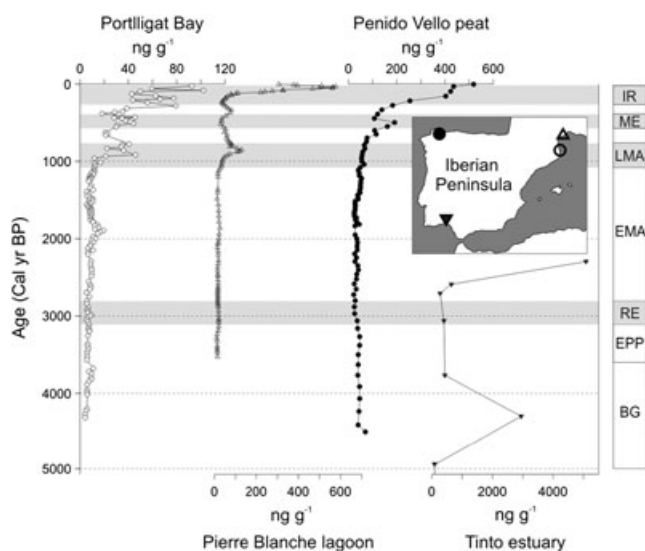
[34] Large quantities of heavy metals were required, and uncontrolled smelting of large amounts of ores resulted in substantial emissions of metals to the atmosphere on a regional and even hemispheric scale [Healy, 1978; Jouffroy et al., 2007; Nriagu, 1996]. At a regional scale, the use of the red-colored ore (cinnabar) as a pigment in paints and dyes by Romans, and mercury gilding for, for example, amphora decoration [e.g., Baylley and Russel, 2008], would have increased Hg emissions to the environment. A proof of this is that several wrecks loaded with archaeological remains (e.g., amphora) dated to Roman times and earlier were found buried in mat sediments in the area under study [Nieto, 1986; Romero et al., 1994], which demonstrates the intensity of maritime activities with the coves as strategic places of refuge and commercial exchange.

[35] Mercury concentrations in mat sediments decreased by 1700 cal yr BP with the fall of the RE and remained almost stable during the EMA period ( $\sim 9 \text{ ng g}^{-1}$ ), being similar to those of the EPP.

[36] Anthropogenic Hg has dominated the concentration record during the last millennium after the establishment of the Islamic kingdom, when Hg metallurgy was first introduced [Domergue, 1989]. From a historical point of view, the last millennium marked an inflexion regarding Hg pollution in the Portlligat Bay, with an increase in Hg concentrations from  $\sim 12$  to  $\sim 100 \text{ ng g}^{-1}$ . Previous studies also showed substantial and continuous impact around the Iberian region from 1000 yr ago to present in atmospheric deposition records, such as peat [Martínez-Cortizas et al., 1999], river sediments [Leblanc et al., 2000], and in a French coastal lagoon receiving both atmospheric and riverine inputs [Elbaz-Poulichet et al., 2011]. Together, these demonstrate an important regional impact, both in terms of direct emissions to waters and emissions to the atmosphere (Figure 5), because about half of the registered global Hg production has been extracted in Europe, where Spanish mines alone constituted one third of the world's mined Hg [Hylander and Meili, 2003].

[37] A range of activities may have contributed to Hg contamination during the last millennium, such as the development of intense anthropogenic activities in the area, such as agriculture, development of cities and roads, and increased anthropogenic fires and woodland clearance in Catalonia [Bonnassie, 1988; Riera and Esteban-Amat, 1994; López-Sáez et al., 2009], but most important is the fact that many ancient mines in Central Europe were reopened around 1000 yr BP [Nriagu, 1979].

[38] In particular, Hg concentrations peaked by 920–780 cal yr BP during the LMA period, 510–430 cal yr BP during the ME period, 280, 180, and 80 cal yr BP and at present



**Figure 5.** Chronology of Hg pollution in southern France and the Iberian Peninsula. Data for the Spanish records included in this figure were obtained from Martínez-Cortizas et al. [1999] (Penido Vello peat), Leblanc et al. [2000] (Tinto estuary), and this study (Portlligat Bay); data for France were obtained from Elbaz-Poulichet et al. [2011] (Pierre Blanche Lagoon). Year 2000 is considered to be the present. See Figure 3 for the identification and the chronology of the phases.



during the IR period. The higher Hg concentrations during the LMA period (EF = 4) is in agreement with the intense metallurgy during the Islamic period [Hernández-Sobriano 1993], the widespread use of Hg salts as medication against leprosy and plague [Rasmussen et al., 2008], and the deforestation reported for the area under study [López-Sáez et al., 2009]. A global Hg emission peak during the 18th century was reported by Hylander and Meili [2003], which is also recorded in the *P. oceanica* mat of Portlligat.

[39] Hg contamination decreased between 650 and 550 cal yr BP, which is correlated in time with deep economic depression and diseases in Western Europe. Hg concentrations decreased again around ca. 300 cal yr BP. These periods with lower Hg contamination could also be attributed to variations in Hg mining activity and amalgamation processes in Europe [Fitzgerald et al., 1998; Martínez-Cortizas et al., 1999; Hylander and Meili, 2003].

[40] During the last 250 years, Hg concentrations increased exponentially until recent decades, reaching values 10 times higher than background levels. This higher concentration of Hg in the marine environment agrees with terrestrial records that demonstrate how in recent times northeast Spain experienced increasing anthropogenic impact (i.e., agricultural expansion, forest exploitation, and high grazing pressure [Bonnassie, 1988; Riera and Esteban-Amat, 1994; Galop, 1998; Pèlachs, 2004; López-Sáez et al., 2009]) and contamination attributed to the burning of coal [Pèlachs, 2004; Miras et al., 2007], intense mining activities in the Iberian pyrite belt in southwest Spain [Leblanc et al., 2000], metallurgical activities, gold and silver extraction from sediments through amalgamation in Europe [Nriagu, 1979], and the utilization of Hg-based pesticides. The impact of intensive anthropogenic activities that started ~150 yr ago correlates well with records from other areas [e.g., van Geen et al., 1997] Figure 5).

[41] Unequivocally, regional or long-distance transport of anthropogenic Hg is the cause of increasing Hg concentrations in marine sediments near regions not impacted by localized human-related sources of Hg [e.g., Fitzgerald et al., 1998], such as the Portlligat Bay in our study. Thus, furthermore, more geographically extensive sampling of *P. oceanica* mats may enable a reconstruction of the complex history of metal contamination in the Mediterranean region, as well as the spatial variation of this pollution, especially in the marine environment.

[42] In this study, we demonstrated the uniqueness of *P. oceanica* meadows as a long-term archive for records of trends in Hg abundance in the marine coastal environment. In addition, we show its potential role in the Mediterranean as a millenary pollution filter and sink.

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