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The *Posidonia oceanica* marine sedimentary record: A Holocene archive of heavy metal pollution

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ABSTRACT

The study of a *Posidonia oceanica* mat (a peat-like marine sediment) core has provided a record of changes in heavy metal abundances (Fe, Mn, Ni, Cr, Cu, Pb, Cd, Zn, As and Al) since the Mid-Holocene (last 4470 yr) in Portlligat Bay (NW Mediterranean). Metal contents were determined in *P. oceanica*. Both, the concentration records and the results of principal components analysis showed that metal pollution in the studied bay started ca. 2800 yr BP and steadily increased until present. The increase in Fe, Cu, Pb, Cd, Zn and As concentrations since ca. 2800 yr BP and in particular during Greek (ca. 2680–2465 cal BP) and Roman (ca. 2150–1740 cal BP) times shows an early anthropogenic pollution rise in the bay, which might be associated with large- and short-scale cultural and technological development. In the last ca. 1000 yr the concentrations of heavy metals, mainly derived from anthropogenic activities, have significantly increased (e.g. from ~15 to 47 μg g^{-1} for Pb, ~23 to 95 μg g^{-1} for Zn and ~8 to 228 μg g^{-1} for As). Our study demonstrates for the first time the uniqueness of *P. oceanica* meadows as long-term archives of abundances, patterns, and trends of heavy metals during the Late Holocene in Mediterranean coastal ecosystems.

1. Introduction

Heavy metals occur naturally in the environment and some play a key biological role in plants (Cu, Zn, Fe, Mn, and Ni), while others such as Pb, Al, As, Cd and Cr are highly toxic non-essential elements (e.g. Delhaize and Ryan, 1995; Shanker et al., 2005). Heavy metals are regarded as dangerous pollutants in the aquatic ecosystems because of their toxicity, their persistence in the environment, and their ability to accumulate in living organisms (Schüürmann and Markert, 1998). They tend to accumulate in ecosystems such as mangroves and wetlands (Harbison, 1986; Weis and Weis, 2004), and their bioaccumulation into the different trophic levels may have damaging effects on humans and important economic consequences (e.g. ecosystem remediation).

Heavy metals can enter marine ecosystems from natural (e.g. mineral weathering, volcanic eruptions and dust deposition) and/or anthropogenic sources (e.g. mining, fossil fuel combustion, agriculture, industry, marine traffic, urban development and sewage). While some metals are primarily mobilized by human activities (Pb, Cd, Zn, Cr, Cu, As and Ni), others like Al, Fe and Mn have a mainly lithogenic origin (Druguet et al., 1995; Fishbein, 1981; Nriagu, 1990).

Anthropogenic environmental pollution caused by heavy metals began with the domestication of fire; later, the industrial revolution led to an unprecedented demand for metals and an exponential increase in the intensity of metal emissions (Nriagu, 1996). The fluxes of these metals into the environment (air, water, soils, and sediments) can derive from diffuse or point sources, and the spatial scale of the resulting contamination can range from local to global. The comparison of the different heavy metals inputs to the NW Mediterranean clearly indicates the predominance of the atmospheric deposition pathway over run-off (Guieu et al., 1991).

The adverse effects of anthropogenic fluxes of metals on marine ecosystems are of concern due to the continuous decline in seagrasses (Orth et al., 2006). Determining the fate and toxic effects of chemicals on seagrass condition and associated food webs has not been yet a priority research issue (Lewis and Devereux, 2009). However, it is thought that potentially phytotoxic, non-nutrient chemicals may be a contributing factor to seagrass losses because their habitat is restricted to shallow areas where exposure is greatest (Bester, 2000; Schlacher-Hoenlinger and Schlacher, 1998a). There are some reviews that summarize the fate and effects of anthropogenic chemicals on seagrass ecosystems, though critical tissue concentrations for the most common near-shore chemicals and seagrass species are unknown (Lewis and Devereux, 2009; Ralph et al., 2006).

Posidonia oceanica is the most abundant seagrass in the Mediterranean Sea. This endemic species forms topographically complex biogenic

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reefs of senescent plant tissues and sediments under anoxic conditions, generating a peat-like deposit known as 'mat' (e.g. Boudouresque et al., 1980). These deposits can reach up to 8 m in thickness and up to 6000 yr in age and their stratigraphy reflects the chronology of formation (Boudouresque et al., 1980; Lo Iacono et al., 2008; Mateo et al., 1997). To guarantee reliable reconstructions, the vertical structure of a natural archive must be as undisturbed as possible, accretion rates should allow adequate time resolution, and preservation conditions should minimize the long-term diagenetic effects on the stored materials (e.g. Valette-Silver, 1993). These requirements are met by *P. oceanica* mat, which opens exciting possibilities for obtaining unprecedented paleoecological, paleobiogeochemical, and paleoenvironmental information of *P. oceanica*-dominated ecosystems over the Mid and Late Holocene (López-Sáez et al., 2009; Mateo and Romero, 1997; Mateo et al., 1997, 2002, 2006, 2010; Romero et al., 1994).

It has been recognized that heavy metal concentrations in senescent *P. oceanica* tissues can be used as a proxy of trace metal concentrations for short-term periods (ca. 30 yr) using retrospective techniques (Pergent-Martini and Pergent, 2000; Roméo et al., 1995; Tovar-Sánchez et al., 2010). While several studies have explored trace metal concentrations over the last decades in seagrass ecosystems, there is still no detailed information on changes in heavy metal abundances over long-term periods. In addition, seagrasses have been shown to act as a sink for biogenic elements (e.g. C, N and P; Mateo et al., 1997; Romero et al., 1994), and to concentrate and accumulate chemicals in their tissues (Schlacher-Hoenlinger and Schlacher, 1998b). In seagrass meadows, the precipitation of heavy metals at the sediment–water interface may be enhanced by the high pH values caused by intense photosynthesis. Moreover, sulfate reduction in anaerobic sub-surface sediments may contribute to the retention of heavy metals as sulfides, as demonstrated for mangrove ecosystems (Harbison, 1986).

In this work we present the first attempt at describing millennial scale trends and patterns in heavy metal abundances in a *P. oceanica*-dominated Mediterranean bay in NE Iberian Peninsula. We also provide some preliminary evidence on the potential role of *P. oceanica* meadows as significant long-term heavy metal sinks at the Mediterranean scale. We argue that it is essential to discriminate between natural and anthropogenic sources of heavy metals that reach the sea in order to correctly evaluate the effects of human activities on the health of coastal ecosystems and develop policies to minimize them.

2. Study area

The Portlligat Bay (42°17′32″N; 3°17′28″E) is a small inlet located in the NE coast of the Iberian Peninsula, in the province of Girona, oriented to the NE towards the Mediterranean Sea (Fig. 1). This is a shallow bay (<10 m deep) located at Cape Creus, which is the last outlet of the Pyrenees, and at the same time the most easterly point of the Iberian Peninsula. Portlligat Bay is connected to the sea through a wide opening to the NW of 213 m. *P. oceanica* meadows cover 94,315 m^2 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). In some areas, the bottom is irregular and shows several forms of erosion revealing thick *P. oceanica* mats. The bay receives episodic freshwater inputs from a typical Mediterranean temporary stream that flows into it from its NE shore. The annual mean precipitation ranges between 500 and 800 mm, and mainly occurs from October through to December (average range for the period 2000–2006, as recorded by the meteorological station of Roses, Servei Meteorològic de Catalunya).

Geologically, Cape Creus and Portlligat Bay are old formations that originated ca. 400 million years ago along with the Pyrenees. The Cape Creus (eastern Pyrenees) migmatitic complex consists of an association of sillimanite schists, granitoids, quartz-gabbros and pegmatites. The substrate of Cape Creus is of igneous and sedimentary origin, later transformed through metamorphism and faulting, particularly during the Hercynian period (Druguet et al., 1995).

The most traditional activities in the Portlligat Bay area such as dry land agriculture (mainly grape and olive trees) and fisheries have been gradually replaced by others related to the tourist and

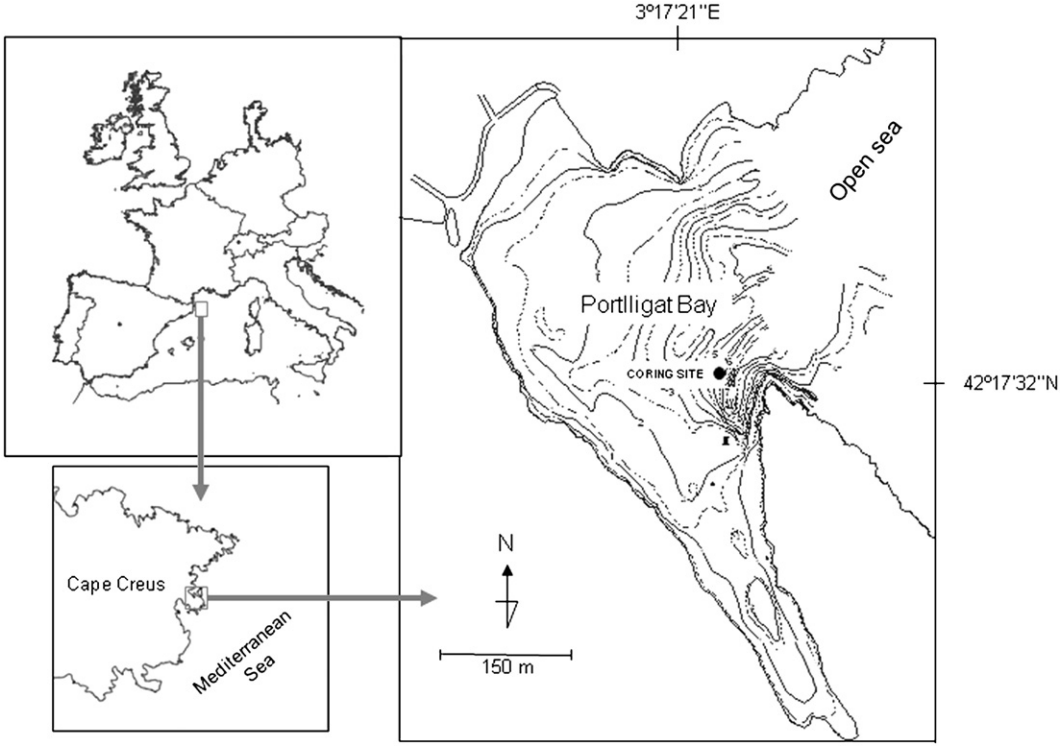

Fig. 1. Location of the study site, Portlligat Bay, Girona, northwestern Mediterranean.

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development sectors that are today the main economic activities in the area.

3. Materials and methods

3.1. Field and laboratory procedures

A 5 m long core of *P. oceanica* mat was sampled in 2000 in Portlligat Bay (NW Mediterranean, Girona, Spain). Coring was carried out on a meadow at 3 m depth, using a floating drilling platform that combined pneumatic percussion and rotation. The effective size of the mat core obtained was 475 × 8.5 cm (length × diameter of PVC pipe). The core was cut into 1 cm slices and oven-dried at 70 °C until a constant weight was reached. About half of the slices (every second one) were then wet-sieved (1 mm mesh) in order to remove coarse plant debris.

From each sample, *P. oceanica* sheaths were separated under a stereomicroscope and cleaned first with seawater and then rinsed quickly with ultrapure water (Millipore Milli-Q system) to remove exogenous particles and salts adhered to the surface. The use of sheaths to reconstruct paleopollution is justified because they can give an indication of metal abundance over a known period.

Sheath samples were dried at 60 °C until constant weight and ground using an agate mortar. From each core slice, 0.1 g of sheath was digested in an acidic solution (Mateo and Sabaté, 1993). A second set of sheath samples was digested using HNO_3 (Suprapure, Merck) to perform arsenic analyses. The glassware was cleaned prior to the analyses by rinsing it with 10% HNO_3 and MQ ultrapure water. All manipulations were performed with non-metal instruments. The accuracy of the digestion and the analytical procedures was checked by analyzing standard reference materials (SMR 279, *Ulva lactuca*) and reagent blanks in each digestion batch (Table 1).

The heavy metal content was determined by mass and optical spectrometry (ICP-MS, Perkin Elmer, Elan 6000 and ICP-OES, Thermo Jarrell Ash, ICAP 61E, respectively) at the Scientific-Technical Services of the University of Barcelona. ICP-MS was used for measuring cadmium (Cd), lead (Pb), copper (Cu), nickel (Ni), chromium (Cr), zinc (Zn), manganese (Mn), and arsenic (As). Iron (Fe) and aluminum (Al) were measured with ICP-OES. All values reported here are expressed in micrograms of metals per gram ($\mu g\ g^{-1}$) of sheath dry tissue.

3.2. Radiocarbon dates and age model

Fourteen samples of *P. oceanica* sheath debris were radiocarbon dated at the National Ocean Sciences AMS Facility-NOSAMS (Woods Hole Oceanographic Institution, Woods Hole, MA) following standard procedures (Karlen et al., 1968; Stuiver and Pollack, 1977; Table 2). Sheaths were rinsed in ultrapure MQ water in order to remove fine sediment particles, inspected under a stereomicroscope for attached allochthonous materials, and dried at 60 °C to a constant weight before radiocarbon dating.

All dates reported in this paper are expressed as radiocarbon dendrocalibrated years determined with CALIB software v.4.4 (Stuiver et al., 1998). The marine reservoir effect due to the carbon dissolved in marine water was corrected considering the point of intersection of the fitted linear function and the x-axis of the uncorrected age vs. depth plot as the regionally-specific age offset, e.g. by subtracting 353 yr from the raw laboratory radiocarbon ages. This correction agrees well with the reservoir effect determined for the Mediterranean Sea (390 ± 85 yr; Siani et al., 2000) and fits the assumption that the age of the core top (living seagrass) is recent (a few years at most).

The corrected ages for the marine reservoir effect (Table 2) were used to produce an age–depth model using the Clam.R software (Blaauw, 2010). The best fit was obtained with a smooth-spline model, and is represented in Fig. 2. According to this model, accretion rates ranged from 8.1 to 476 mm yr^{-1}, and the mean resolution was 9.4 yr cm^{-1}. The core studied was 475 cm and covers the last 4470 cal yr BP.

3.3. Numerical procedures

Pearson correlation analysis was used to test for significant relationships among metals. Patterns were explored using regression analysis. The magnitude of changes in heavy metal concentrations over the period reconstructed was quantified using the coefficient of variation (CV).

In order to obtain an integrated perspective of metal content and compare its evolution throughout the core, a Metal Abundance Index (MAI) similar to that used in Usero et al. (1997) was calculated as follows:

$$MAI = (Cf_1 \times Cf_2 \ldots Cf_n)^{1/n}$$

where Cf_n is the log-transformed [$y = \log(x+1)$] concentration of the metal *n* in the sample. The index was calculated with normalized data in order to eliminate the dependence of the variance on the mean. The aluminum was not included in the MAI index because measurements were not available for the upper 160 cm of the core. Core sections with missing data for some metals were not taken into account when calculating MAI. Pearson correlation analyses were performed between MAI values and metal concentrations to assess the weight of each metal in the index.

We used principal component analysis (PCA) on metal concentrations (Fe, Mn, Ni, Cu, Pb, Cd, Zn and Cr) in order to provide insights into the structure of the variance (Jolliffe, 2002) and identify underlying factors accounting for their distribution. Data were transformed to Z-scores (calculated as: $[X_i - X_{avg}]/SD$, were X_i is the percentage of a given type in a given sample, X_{avg} is the average of the population and SD is the standard deviation) to avoid the scaling effect and obtain average-centered distributions.

Table 1
Summary of measurements of trace elements in the certified material *Ulva lactuca* (SRM 279) and blanks. Mean ± standard deviation ($\mu g\ g^{-1}$); *n* = number of analyses.

	Fe	Mn	Ni	Cr	Cu
Certified value	2300 ± 100	2030 ± 30	15.9 ± 0.4	9.7 ± 0.9	13.1 ± 0.4
Measured value	2840 ± 60	2540 ± 70	13.3 ± 0.6	11.1 ± 0.4	13.8 ± 0.5
	n = 6	*n* = 6	*n* = 7	*n* = 7	*n* = 7
Blanks	0.17 ± 0.17	0.04 ± 0.01	0.008 ± 0.003	0.43 ± 0.07	0.04 ± 0.02
	n = 12	*n* = 12	*n* = 12	*n* = 12	*n* = 12
	Pb	Cd	Zn	As	Al
Certified value	13.5 ± 0.4	0.3 ± 0.02	51.3 ± 1.2	3.1 ± 0.2	–
Measured value	15.6 ± 0.5	0.1 ± 0.01	57.1 ± 2.2	3.5 ± 0.1	–
	n = 7	*n* = 7	*n* = 7	*n* = 6	–
Blanks	0.006 ± 0.000.1	0003 ± 0.0001	0.44 ± 0.11	0.11 ± 0.0004	0.24 ± 0.09
	n = 12	*n* = 12	*n* = 12	*n* = 6	*n* = 12

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Table 2
Details of radiocarbon dating of the *Posidonia oceanica* sheath samples from the core. The accession laboratory sample number assigned by NOSAMS is indicated. The reservoir effect (RE) affecting the ages was estimated as 353 years. BP stands for 'before the present' (the core was sampled in 2000).

Depth (cm)	NOSAMS #	Raw age (yr BP)	Age error (+/−)	Corrected age (yr BP-RE)
41	OS-29665	710	45	357
62	OS-29666	895	45	542
77	OS-29667	975	40	622
110	OS-29668	1430	40	1077
145	OS-29651	1600	45	1247
213	OS-44491	1710	25	1357
255	OS-44492	2120	30	1767
287	OS-44493	2270	30	1917
307	OS-44494	2500	30	2147
326	OS-44497	2560	25	2207
355	OS-44498	3130	25	2777
386	OS-44499	3320	30	2967
415	OS-44502	3500	35	3147
437	OS-44504	3850	30	3497

The numerical procedures were performed using the statistics software package STATISTICA 7.1 (StatSoft, Okla.) and the PCA using the SPSS statistical software package.

3.4. Baseline heavy metal concentrations

Mean metal concentrations in samples older than 2800 yr BP (351–475 cm) were considered as baseline concentrations for Portlligat Bay (BL) based on the PCA results (see below) and because they predate extensive mining activities. Therefore, the mean concentrations of heavy metals mainly derived from anthropogenic activities (those associated to the first principal component of the PCA; see below), As and MAI were used to estimate enrichment factors (EF, %) for four subsequent periods: EPP (early pollution period, 243–351 cm, 1600–2800 yr BP); PRE (post-Roman Empire, 47–243 cm, 500–1600 yr BP); ME (modern era, 17–47 cm, 200–500 yr BP) and IR (industrial revolution, 1–17 cm, <200 yr BP) as follows:

$$\textit{Enrichment Factor}\ (\%) = ((X_i / X_{BL})*100)-100$$

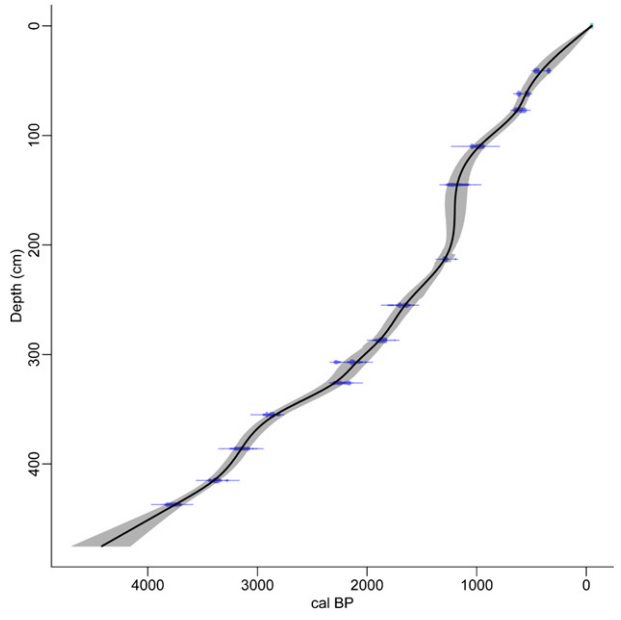

Fig. 2. Time-stratigraphic framework for the studied core. The solid line represents a best fit (a smooth-spline model; Blaauw, 2010) through 14 radiocarbon dates calibrated with the program "CALIB 4.4" and corrected for the reservoir effect.

where X_i is the metal content at each core level, and X_{BL} is the average baseline metal concentration (4470–2800 ^{14}C yr BP). Then, the average ± standard error of mean (S.E.M.) metal EF was calculated for each period and each metal.

4. Results

4.1. Metal records

Concentrations of major elements such as Fe and Al ranged between 1243 and 17,166 μg g^{-1} and 583 and 2162 μg g^{-1} respectively, while trace elements such as Cd ranged between 0.2 and 0.7 μg g^{-1} (Table 3). Variability in heavy metal concentrations during the Mid and Late Holocene in Portlligat Bay ranged between 22 and 56% (CV); Ni, Cr, Cu, Cd and Al showed lower variation than Fe, Mn, Pb, Zn and As (Table 3).

Minimum heavy metal concentrations were measured in samples older than 1000 yr BP (108–475 cm) and maximum heavy metal concentrations were found during the last 860 yr BP (0–95 cm), except for Mn and Ni (ca. 2500 yr BP in both cases; Table 3). Iron and Cu were positively correlated with all metals studied along the mat core, with the exception of Mn and Cu (Table 4). In addition, we identified two groups of heavy metals which correlated positively with each other: (i) Cr, Mn, Ni and Al; and (ii) Pb, Cd, Zn and As. Manganese was negatively correlated with As.

The concentration records for Pb, Cd, Cu, Zn and Fe (Fig. 3) have similar trends. All elements were at baseline concentrations between 350 and 475 cm (Table 5). The intervals between 325 and 357 cm, and 268 and 317 cm show high concentrations of 12–33 μg g^{-1} for Pb, 0.3–0.6 μg g^{-1} for Cd, 12–22 μg g^{-1} for Cu, 19–48 μg g^{-1} for Zn, and 3888–11,578 μg g^{-1} for Fe. In the top 118 cm of the core Pb, Cd, Cu, Zn and Fe concentrations increase steadily until the surface. The As record has similar trends to those of the above described metals (Fig. 3), but the low number of analyses between 161 and 475 cm does not allow further detailed interpretations. In a similar way, Al was not analyzed in the upper 145 cm and temporal trends for this element are not further discussed.

The Mn, Ni and Cr records have similar trends (Fig. 3). Large deviations from baseline concentrations (up to 140 μg g^{-1}) for Mn are observed between 355 and 386 cm. The sediment sections between 325–357 cm, 268–317 cm and 64–219 cm also show high concentrations for Mn (70–191 μg g^{-1}), Ni (11–26 μg g^{-1}), and Cr (10–18 μg g^{-1}). In the top 64 cm of the core the concentrations of these metals decrease steadily to the surface.

The average MAI was 1.17 ± 0.01 and the maximum and minimum values were 1.41 and 1.01 at 80 and 279 cm respectively (Table 3). Overall, the MAI significantly increased from the bottom to the top of the core (linear regression, $r = -0.69$, $P<0.0001$). All heavy metals included in the MAI were positively correlated with it along the core

Table 3
Descriptive statistics of metal concentrations in *Posidonia oceanica* sheaths and MAI values in the *Posidonia oceanica* mat deposit. Units are in μg metal g^{-1} dry weight sample. S.E.M., standard error of mean; CV, coefficient of variance (%).

Variable	Mean	S.E.M.	N	Minimum	yr BP	Maximum	yr BP	CV (%)
Fe	7618.7	255.0	170	1242.6	1459	17,165.7	860	44
Mn	79.3	2.7	166	13.3	4469	191.0	2334	45
Ni	14.9	0.3	171	7.2	1459	26.3	2541	26
Cu	14.6	0.3	169	6.6	1459	30.6	13	26
Pb	16.4	0.6	171	5.7	4381	47.3	13	47
Cd	0.4	0.0	169	0.2	1258	0.7	208	29
Zn	34.6	1.2	157	10.7	1654	95.1	75	42
Cr	12.8	0.2	139	7.7	1581	21.6	704	22
As	89.1	6.2	66	3.3	1073	228.0	124	56
Al[a]	1364.8	32.5	102	582.8	4469	2162.1	3835	24
MAI	1.2	0.0	120	1.0	1671	1.4	704	9

[a] Data from 1250 yr BP until 4469 yr BP.

Table 4
Pearson correlation coefficients between metal concentrations along the mat core. Levels of significance: $^{*}P \leq 0.05$, $^{**}P \leq 0.01$, $^{***}P \leq 0.001$; NS, $P \geq 0.05$; significant correlations in bold (r value). Number of cases in parentheses.

	Fe	Mn	Ni	Cr	Cu	Pb	Cd	Zn	As	Al
Fe		***	***	***	***	***	***	***	***	***
Mn	**0.34** (162)		***	***	NS	NS	NS	NS	**	***
Ni	**0.56** (169)	**0.27** (164)		***	***	NS	NS	NS	NS	***
Cr	**0.60** (136)	**0.40** (137)	**0.59** (138)		***	NS	NS	NS	NS	***
Cu	**0.61** (165)	0.06 (162)	**0.47** (167)	**0.38** (137)		***	**	***	***	***
Pb	**0.46** (169)	0.02 (164)	0.01 (170)	0.05 (138)	**0.45** (167)		***	***	***	NS
Cd	**0.28** (165)	−0.13 (162)	0.04 (167)	0.00 (135)	**0.24** (165)	**0.42** (167)		***	***	NS
Zn	**0.51** (154)	−0.05 (153)	0.00 (156)	0.14 (130)	**0.69** (154)	**0.53** (156)	**0.44** (153)		***	NS
As	**0.45** (66)	−**0.39** (63)	−0.17 (66)	−0.08 (64)	**0.40** (65)	**0.70** (66)	**0.44** (62)	**0.71** (64)		NS
Al	**0.59** (99)	**0.41** (97)	**0.56** (101)	**0.51** (76)	**0.33** (99)	0.11 (101)	−0.11 (101)	0.04 (92)	−0.01 (6)	

record ($P<0.001$ in all cases, with the exception of Mn and Ni, with $P>0.05$). Higher MAI values in the upper core levels can to a major extent be explained by the high concentrations of Fe, Cu, Pb, Cd, Zn and As recorded in these levels.

4.2. Principal component analysis

Two principal components had eigenvalues greater than 1 and explained a 62% of the total variance. The first principal component (PC1) accounts for 40% of the explained variance and is dominated by the high positive loadings (0.68–0.82) of metals associated with anthropogenic activities (Zn, Pb, Cd and Cu); Fe has a moderate positive loading (0.58) in this component. The second principal component, PC2, explains a 22% of total variance and large positive loadings (>0.68) were found for Ni, Cr and Fe; Mn and Cu showed moderate positive loadings (0.60 and 0.49 respectively). PC1 and PC2 are highly negatively correlated in the upper 107 cm of the core. Fig. 4a shows the records of score elements associated to the two factors. Almost all elements have high communalities (>0.60) except Cd and Mn (≈0.40), as expressed by the total length of the bars in Fig. 5, hence most of the variations in metal concentrations in the mat deposit are dominated by processes/factors involving these two principal components, while a significant part (38%) remains unexplained. As an example, the unexplained variation in Ni concentrations (after detrending from PC2) points to Ni enrichment (i.e. pollution; Fig. 4b) in some sections having positive loadings for PC1, in particular between 325 and 345 cm and 268 and 317 cm.

4.3. Enrichment factors

EF ranged between −20% and +1073% (Fig. 6). Lead and Cd concentrations in all periods after extensive mining activities started (i.e. 2800 yr BP until present) were higher than baseline levels (metal EF values ranged between +72 and +255% for Pb and +24 and +82%, for Cd). In addition, positive metal EF were measured for As, Zn and Fe in the PRE, ME and IR periods (+347 to +1073%, +27 to +132% and +13 to +51%, respectively) and for Cu in the ME and IR periods (+20 to +31%). In contrast, negative metal EF were found for Zn and Fe in the EPP period (−15% and −11% respectively), and Cu in the EPP and PRE periods (−8% and −4% respectively). In summary, the MAI showed higher average metal EF in the IR and ME (+21% and +19% respectively) than in the PRE and EPP (+12% and +5% respectively).

5. Discussion

Heavy metal analyses of *P. oceanica* mat have provided an unprecedented vista of the abundances, patterns, and trends of heavy metals during the Late Holocene in Mediterranean coastal ecosystems. The concentration records and the PCA results show that metal pollution in the studied bay started ca. 2800 yr BP. The increase in Fe, Cu, Pb, Cd, Zn and As concentrations since ca. 2500 yr BP and in particular during Roman times shows an early anthropogenic pollution rise in the Portlligat Bay, which might be associated with large- and short-scale cultural and technological development. After ca. 1200 yr BP, metal pollution steadily increased, with an acceleration

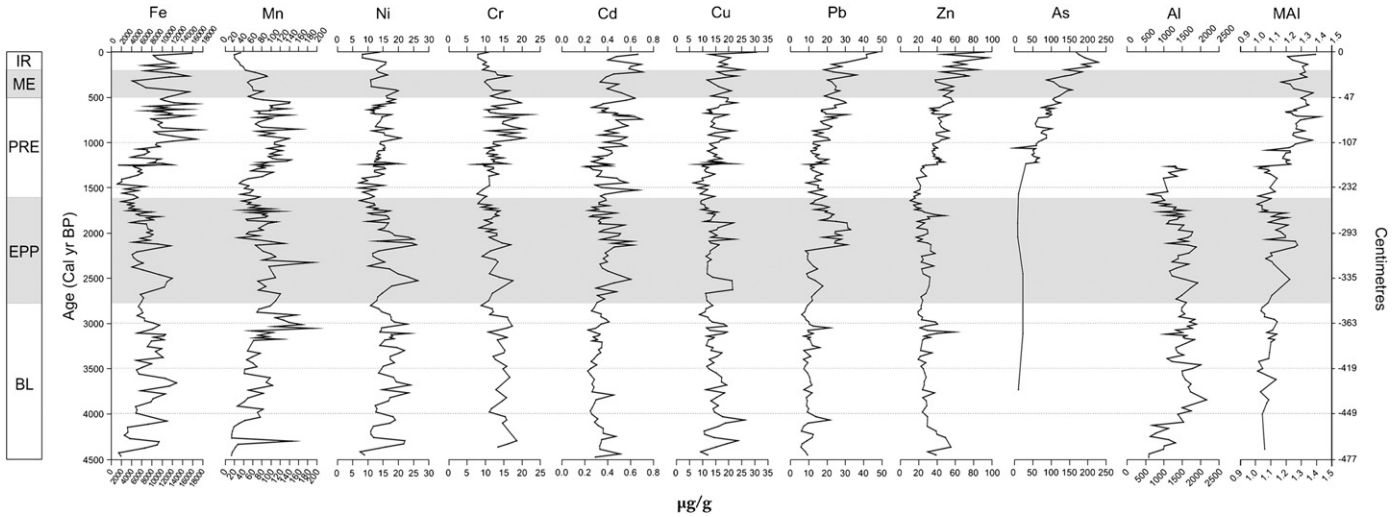

Fig. 3. Changes in metal concentrations of *Posidonia oceanica* sheaths and in the Metal Abundance Index (MAI) during the Late Holocene. IR, Industrial Revolution, 0–200 yr BP; ME, Modern Era, 200–500 yr BP; PRE, Post-Roman Empire, 500–1600 yr BP; EPP, early pollution period, 1600–2800 yr BP; and PRM: Pre-Mining (baseline).

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Table 5
Review of the range of metal concentrations of senescent *P. oceanica* sheaths reported by other authors around the Mediterranean Sea. Total average metal concentrations, average baseline metal concentrations (BL, samples older than 2800 ^{14}C yr BP) and minimum values measured in this study. BL values in *italic* cannot be considered as really BL metal concentrations (see text). Units are in μg metal g^{-1} dry sample weight. S.E.M., standard error of mean.

Fe	Mn	Ni	Cr	Cu	Pb	Cd	Zn	As	Al	References
		2–223	6–207	4–26	1–135	0.1–5.6	8–51	6–44		Gosselin et al.(2006)
110–2870				6.2–46.3	1.6–54.7	0.3–1.5	13–147			Roméo et al.(1995)
60–3380				3.2–57.9	1.2–36.6	0.1–3.9				Baroli et al.(2001)
					8.5–18.5					Tranchina et al.(2005)
250–7250	7–207			6–12	2–21	0.4–0.9	18–107			Ancora et al.(2004)
44–226.7				22.2–58.1	5.2–1088.4	0.3–20.5	109.2–3191.5			Caredda et al.(1999)
1000–2250	50–75	2–15	4–7	15–20	2–8			2–16		Romero et al.(2003)
1243–17,166	13.3–191	7.2–26.3	7.7–21.6	6.6–30.6	5.7–47.3	0.2–0.7	10.7–95.1	3.3–228	583–2162	This study (range)
7257.5 (375)	*71.6 (6)*	*16.5 (0.5)*	*14.5 (0.3)*	14.8 (0.5)	9.9 (0.4)	0.3 (0.0)	30.4 (1.4)	16.5 (6.5)	1416.6 (55)	This study (BL ± S.E.M.)
1242.6	13.3	7.2	7.7	6.6	5.7	0.2	10.7	3.3	582.8	This study (minimum)

in the last 350 yr (Fig. 4a). It was also possible to establish baseline metal abundances and natural ranges for the study site.

5.1. Organo-metal complexes: reliability of *P. oceanica* sheaths as an indicator of past heavy metal abundances

Many authors have shown a positive correlation between heavy metal concentrations in senescent *P. oceanica* sheaths and environmental metal pollution (e.g. Tranchina et al., 2005); however, these studies are indirect approaches (e.g. without monitoring ambient water concentrations) that have not yet been shown to hold true. The lack of information about (i) the relation between ambient and tissue metal concentrations, (ii) the effects of weight loss during decomposition on heavy metal concentrations (e.g. Capiomont et al., 2000), and (iii) post-mortem exchange including adsorption/desorption processes between senescent plant tissues and the chemicals in the surrounding water and sediments (Lyngby and Brix, 1989; Wahbeh and Mahasneh, 1984), puts into question the assumption that the heavy metal content of senescent sheaths reliably reflects ambient paleoconcentrations.

We have recently investigated the dynamics of various heavy metals during anaerobic decomposition of *P. oceanica* sheaths (*unpublished data* of the authors and Haller, 2009). While Cr, Cu, Cd and Zn showed no significant changes during 1-yr of decomposition, Mn and Ni significantly decreased and Pb, Fe and Al significantly increased. All the heavy metals studied reached a plateau (i.e. no significant differences with respect to 2–3 previous sampling events) after ca. 200 days, with the exception of Al, which continued to increase exponentially.

The existing literature on heavy metal fluxes during organic matter diagenesis is unspecific and in many cases previous findings are in disagreement with our observations. It is generally accepted for Fe, Pb and Al that their concentrations are higher in senescent than in living tissues as these metals are easily adsorbed by organic detritus (e.g. Ragsdale and Thorhaug, 1980; Wahbeh and Mahasneh, 1984).

Several authors reported that Cr, Cu, Mn, Ni and Zn are also adsorbed during diagenesis (Lyngby and Brix, 1989; Misra and Prande, 1974; Ragsdale and Thorhaug, 1980; Wahbeh and Mahasneh, 1984), while others reported desorption or stability for Cr, Cu, Mn, Ni, Zn, Cd and As (Lee et al., 1991; Lyngby and Brix, 1989; Misra and Prande, 1974; Wahbeh and Mahasneh, 1984; Weis and Weis, 2004). Therefore, although heavy metal exchange may have taken place during diagenesis, this may have ceased after an initial rapid decay of labile organic matter within the first 3–5 yr after plant death (Lafabrie et al., 2007; Romero et al., 1992).

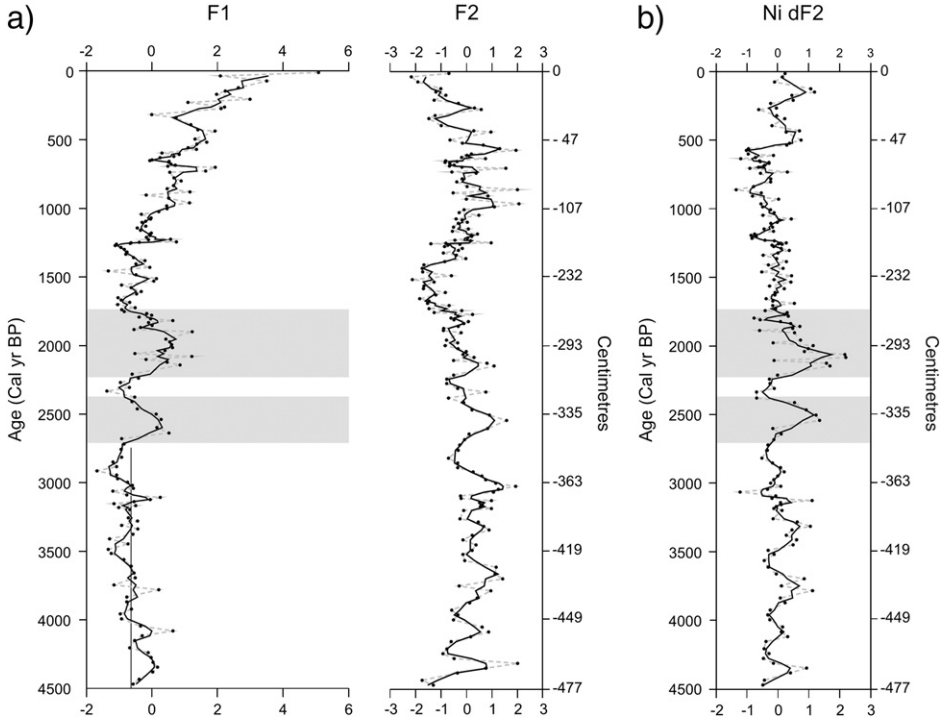

Fig. 4. a) Variations of factor scores (F1 and F2) against depth in the *Posidonia oceanica* mat deposit. The vertical line indicates the baseline period. b) Variations in detrended F2 for Ni concentration profile (Ni dF2) against depth.

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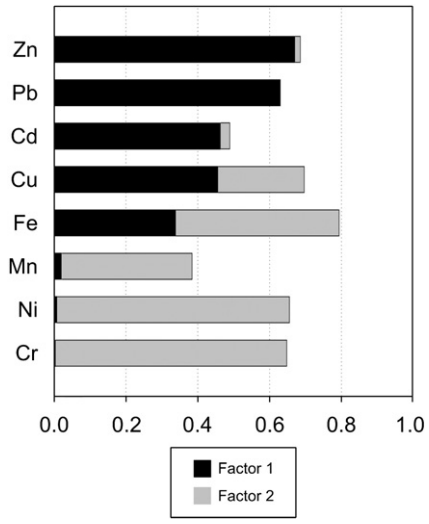

Fig. 5. Communalities (total length of the bars) of the elements and their association with the two factors for concentrations.

Consequently, the heavy metal concentrations in each mat sample analyzed (encompassing ca. 8 yr as derived from the accretion rate of the mat) may provide a valid average value of the changes in heavy metal abundances in the paleoenvironment, and reflect the dynamics of metal inputs to the system. In addition, a unique feature of the present case is the early burial of sheaths under stable and high anoxic conditions within the first top mat centimeters, remaining stored for millennia (Mateo et al., 2006).

5.2. Natural versus anthropogenic contributions

Although changes in metal concentrations in Portlligat Bay can be attributed to both natural and anthropogenic sources, our results are strongly consistent with an increasing importance of anthropogenic inputs of Pb, As, Cd, Zn, Cu and Fe from 2800 yr BP onwards (0–351 cm), mainly due to socio-cultural changes and mining activities (Figs. 3 and 4). In particular, in the last 1200 yr BP (0–243 cm) the concentrations of almost all heavy metals have significantly increased (e.g. from ~15 to 47 μg g^{-1} for Pb, from ~23 to 95 μg g^{-1} for Zn and from ~8 to 228 μg g^{-1} for As; Fig. 3). This was also reflected by a particularly steep increase (21%) in MAI values (Fig. 6). In addition, the simultaneous increasing trends of the Pb, Cd, Zn, As, Fe and Cu concentrations until the present (heavy metals mainly derived from anthropogenic activities), strongly suggest that heavy metal inputs were concentrated in time and space and related to anthropogenic sources. The negative EF values for Fe and Zn in the EPP period, and for Cu in the EPP and PRE periods may be due to the fact that other factors than anthropogenic pollution controlled their fluxes in the area of study, such as the nature of the inorganic mineral matter.

5.2.1. Anthropogenic pollution (Zn, Pb, Cd, Cu, Fe, As and Ni)

The first principal component is positively correlated to heavy metals mainly deriving from anthropogenic activities (e.g. Nriagu, 1990). The concentration of Zn, Pb, Cd, Cu, Fe and As, the MAI values and PC1 scores follow baseline values between 351 and 475 cm (i.e. in sheaths older than 2800 yr BP), which is consistent with the low population density during the Bronze and Iron Ages in the region under study (e.g. Riera and Esteban-Amat, 1994; Fig. 3). However, heavy metals have been exploited since the Bronze Age in Western Europe (Bartelheim et al., 2002; Craddock, 1995) and, therefore, changes in metal concentrations in samples older than 2800 yr BP (i.e. in Fe, Ni, Cu and Pb profiles, and PC1) may have also been affected by anthropogenic activities (e.g. Pb pollution for at least the last 4000 yr in Europe; Renberg et al., 2000).

Continuous scattered human activity and the establishment of commercial enclaves on the coast near the study area between 1600 and 2800 yr BP (EPP, 243–351 cm) (Delibes and Montero, 1999; Martin, 1986; Riera and Esteban-Amat, 1994; Ruiz de Arbulo, 1991; Sanmartí and Santacana, 2005) may have lead to a slight increase in heavy metal pollution in Portlligat Bay during this period (MAI Enrichment Factor = 5.1%). In fact the results of the PCA analyses suggest that significant anthropogenic metal pollution started ca. 2800 yr BP, and peaked at 335 cm (ca. 2500 yr BP) and at 299 cm (ca. 2061 yr BP), in agreement with the golden age of Greek and Roman empires, respectively (Fig. 4a). Iron, Ni, Cr, Cd, Cu and Pb concentrations significantly increased with respect to baseline concentrations during both periods, in which large quantities of heavy metals were required to sustain the high standard of living (Healy, 1978; Hong et al., 1994). In addition, although mines were operated on a small scale, uncontrolled smelting of large quantities of ores in open fires resulted in substantial

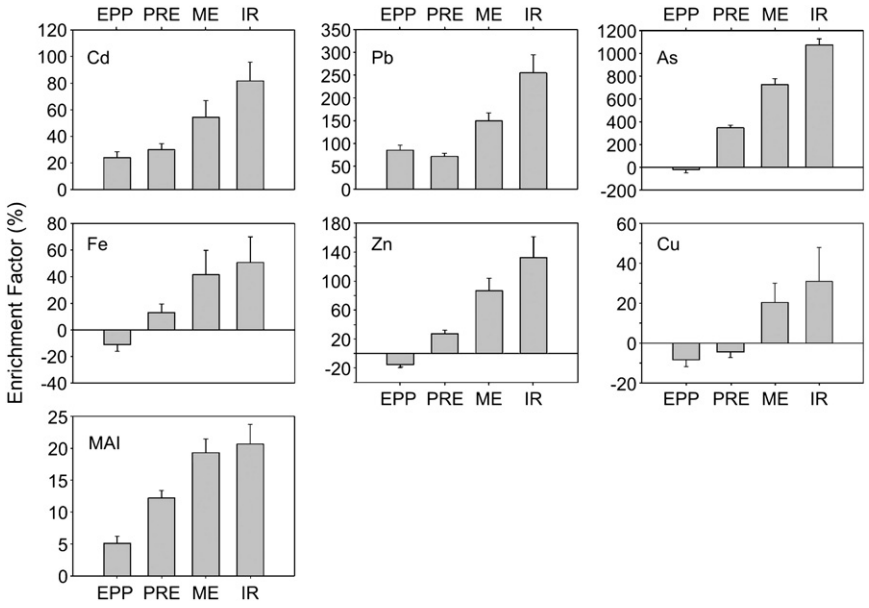

Fig. 6. Average Enrichment Factors (%) ± standard error of mean with respect to baseline levels (BL, samples older than 2800 yr BP) for 4 post-anthropogenic periods. IR, Industrial Revolution, 0–200 yr BP; ME, Modern Era, 200–500 yr BP; PRE, Post-Roman Empire, 500–1600 yr BP; and EPP, early pollution period, 1600–2800 yr BP.

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emissions of trace metals to the atmosphere on a global scale (e.g. Jouffroy et al., 2007; Nriagu, 1996) also reaching Portlligat Bay. The results of the Ni residual variation (after detrending from PC2) strongly suggest that Ni concentrations were also above baseline concentrations during Greek and Roman times in the area of study, in agreement with the hypothesis of higher pollution during both periods (Fig. 4b). However, over the last millennium Ni record did not follow the same pattern of variation as those elements associated to PC1. Thus the different patterns observed can be related to high natural Ni inputs in the area of study in relation to anthropogenic inputs (further discussed below).

In particular Cd and Pb show a much larger increase during Greek and Roman periods (2 to 3-fold baseline concentrations, respectively; EF during EPP = +24% and +85% respectively; Fig. 6). Changes in Cd concentrations along the core may be mainly related to natural phenomena such as upwelling of deep waters rich in Cd or river inputs, at least until the industrial revolution when anthropogenic sources began to be relevant (Bruland, 1980; Fowler, 1990). However, the consistent rise in Pb concentrations (up to 34 $\mu g\ g^{-1}$ ca. 2000 yr BP) matches with the early large-scale atmospheric pollution by this toxic heavy metal found in ice layers deposited in Greenland between 2500 and 1700 yr BP (Hong et al., 1994) and in European lake sediments and bogs during Greek and Roman times (e.g. Jouffroy et al., 2007; Kylander et al., 2005; Martínez Cortizas et al., 2002; Renberg et al., 1994; Shotyk et al., 1998), providing quantitative evidence of the importance of mining and smelting in the south of Spain for the Carthaginian and Roman civilizations (e.g. Rosman et al., 1997; Martínez Cortizas et al., 1997).

The rising concentrations of heavy metals of a largely anthropogenic origin (As, Pb, Zn, Cd, and Fe) during PRE (500–1600 yr BP, 47–243 cm) is in accordance with previous findings of a relatively important anthropization process during the last 1600 yr BP, with particular emphasis on cattle raising, agriculture (chestnut, vineyards and olive trees), mining and smelting, development of cities and roads, increased anthropogenic fires and woodland clearance in Catalonia (Bonnassie, 1988; López-Sáez et al., 2009; Riera and Esteban-Amat, 1994). From a historical point of view, this period (PRE) should mark an inflexion regarding anthropogenic pollution in coastal ecosystems, as was shown by both the highly positive EF measured for heavy metals mainly derived from anthropogenic activities (ranging between −4% and +347%) and the MAI EF (+12%; Fig. 6).

The results of the PCA analysis show that Zn, Pb, Cd, Cu, Fe, As and Ni concentrations synchronically and steadily increased ca. 1200 yr BP onwards (e.g. from 13 to 47 $\mu g\ g^{-1}$ for Pb, 35 to 92 $\mu g\ g^{-1}$ for Zn and 64 to 168 $\mu g\ g^{-1}$ for As; Fig. 3). Several events may have induced the change in the heavy metal budget in the environment during the last millennium, such as the development of intense anthropogenic activities in the area (e.g. several shipwrecks dated within the last 1000 yr BP were found in Cape Creus; e.g. Romero et al., 1994) and to the fact that many ancient mines in Central Europe were reopened around 1000 yr BP (Nriagu, 1979). The steady increase in Pb concentrations found after ca. 1200 yr BP (0–108 cm) is in agreement with studies on other types of natural archives that have confirmed the global nature of Pb pollution (e.g. Renberg et al., 1994).

The results strongly suggest that human activities have continued to increase pollution levels in Portlligat Bay within the modern era (ME, 200–500 yr BP, 17–47 cm), and in particular within the industrial revolution (IR, last 200 yr BP, 1–17 cm; Fig. 3). Of special relevance are the very high pollution levels of As and Pb (values higher than 200 and 40 $\mu g\ g^{-1}$ respectively), as they are recognized as two of the more dangerous environmental pollutants due to their implications for human health (e.g. Craig et al., 2003). This higher concentration of heavy metals in the environment agrees with other regional records that demonstrate how during the modern era the coastal and Pyrenean areas of NE Spain underwent increasing anthropization and contamination (i.e. agricultural expansions, forest exploitation and high grazing pressure; Bonnassie, 1988; Galop, 1998; López-Sáez et al., 2009; Pèlachs, 2004; Riera and Esteban-Amat, 1994), with the development of coal mines (Miras et al., 2007; Pèlachs, 2004) and large furnaces with tall stacks (around 500 yr BP; Nriagu, 1979). These factors may have contributed and drastically extended the sphere of influence of smelters and industrial installations, and thereby increased heavy metal pollution elsewhere due to long-range dispersal through atmospheric deposition and run-off. The industrial revolution led to an unprecedented demand for heavy metals and an exponential increase in the population density in Europe and in the intensity of heavy metal emissions, both in absolute masses and in the number and type of toxic metal compounds released (in particular for Cu, Pb and Zn; Nriagu, 1996) and this is reflected in the *P. oceanica* mat core.

The large increase in As and Pb concentrations (EF of +1073% and +255% respectively; Fig. 6) matched with anthropogenic point sources such as smelting, combustion of fossil fuels, runoff, wastewater inputs, use of antifouling agents, application of pesticides and fertilizers (e.g. Morel and Price, 2003). Run-off from a temporary stream and atmospheric deposition seem to be the most probable transport mechanisms for As into the bay (Elbaz-Poulichet et al., 2001; Fishbein, 1981).

5.2.2. Other sources of metals (Mn, Fe, Cr and Ni)

The second principal component accounts for most of the variation of metals which mainly have a lithogenic origin (Mn, Fe and Cr), but also part of the changes in Ni. Thus the results suggest the input of inorganic mineral matter due to soil erosion (surface run-off) and atmospheric deposition of soil dust particles, as the main mechanisms controlling the fluxes of these elements to the bay. Studies on the composition of present bulk atmospheric deposition in the Pyrenees also found that Fe and Mn had a lithogenic origin, while Ni showed intermediate properties (Bacardit and Camarero, 2009). However, their distribution may also be affected by a combination of other factors such as anthropogenic activities, local natural phenomena, long distance metal transport, climatic variability, and competence for binding sites and/or diagenetic processes.

The concentration records of elements associated to PC2 show similar patterns than those associated to PC1 between 4500 and 2500 yr BP, but the PC2 scores steadily increased from ca. 1500 yr BP until ca. 500 yr BP and afterwards decreased until present (Fig. 4). Assuming that PC2 represents lithogenic mineral inputs (i.e. run-off and atmospheric soil dust deposition which have long been considered the major dispersion pathways of trace elements in the ocean; e.g. Guieu et al., 1991), the record of scores suggests an overall decrease in moisture availability after ca. 4000 yr BP in the Iberian Peninsula, and in particular over the last millennium, in agreement with records of lakes (Pérez-Obiol and Julià, 1994), rivers (Magny et al., 2003), speleothems (Drysdale et al., 2006), marine sediments (Ariztegui et al., 2000), soils (Araus et al., 1997; Carrión et al., 2010) and peat bogs (e.g. Martínez Cortizas et al., 1999, 2005).

5.3. Mediterranean baseline heavy metal concentrations

The time window encompassed by the sampled core made it possible for the first time to set what can be considered as the pre-anthropogenic baseline (BL) metal abundances for *P. oceanica* sheaths in the NW Mediterranean (Table 5). Only BL values for heavy metals positively correlated with PC1, As and Al can be considered as pre-anthropogenic metal concentrations in the area under study.

Several investigations reported metal concentrations in recently dead *P. oceanica* sheaths from the western Mediterranean basin (maximum 30 yr ago; Table 5). Heavy metal concentrations measured in millenary mat sheaths were similar to data reported for recently dead sheaths. Iron and As concentrations, conversely, were one order of magnitude higher. The lowest metal concentrations measured in this study were found, as it was expected, in sheaths corresponding to

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periods with low anthropogenic pressure (before ca. 1200 yr BP, 110–475 cm). Although it seems that many factors (i.e. natural sources, post-mortem exchange including adsorption/desorption processes, and the effects of weight loss during decomposition on heavy metal concentrations) should have led to higher concentrations of some heavy metals in the millenary sheaths (this study) compared to metal concentrations in recent *P. oceanica* sheaths reported for other areas with lower terrigenous inputs (e.g. offshore islands; Gosselin et al., 2006), this does not explain the higher minimum concentrations found for all metals in our study (Table 5).

Anyway, the expression 'Mediterranean baseline metal contamination levels', used for the last 30 yr (e.g. Baroli et al., 2001; Conti et al., 2010), might be inappropriate. Since the industrial revolution and due to atmospheric dispersion of heavy metals, no water mass in the Mediterranean can be considered free from anthropogenic metal inputs. Nevertheless, heavy metal concentrations at the bottom of the core generally fell within the range of the lowest values published so far (Table 5) and therefore, the average metal concentrations recorded along the 'pre-anthropogenic section' of the core could be considered as plausible reference metal baseline values for *P. oceanica* meadows, in geological settings similar to those of the study site.

The fluctuations in the abundance of heavy metals found during the last 4470 yr at Portlligat Bay (CV range between 22 and 56%) were lower than the values reported for the Balearic Archipelago in the last 3 decades, according to lepidochronological analyses (CV range between 6 and 258%; Tovar-Sánchez et al., 2010). This may be because each mat sample analyzed integrated ca. 8 yr of heavy metal abundance history, and therefore the inter-annual variations in metal abundances were smoothed. In addition, large heavy metal fluxes during the decay of *P. oceanica* sheaths and/or changes in natural and/or anthropogenic inputs may account for large changes in heavy metal concentrations in short-term studies (e.g. lepidochronological studies, ca. 30 yr). Thus, retrospective geochemical monitoring studying *P. oceanica* mat deposits represents a potential tool for evaluating historical developments in mining technology, patterns of dispersion and deposition of heavy metals at local, regional and global scales over the Late Holocene in Mediterranean coastal ecosystems.

6. Final comments

The extent to which the heavy metal concentrations determined in the old plant detritus can be considered faithful proxies of paleopollution is still difficult to establish. Additional studies of other Mediterranean *P. oceanica* mats are needed to fully evaluate some of the hypotheses generated by the Portlligat Bay mat core and discriminate between local and general processes over the Holocene. Factors such as local geology and climatic processes, as well as the behavior of organo-metal complexes in different sedimentary systems may hinder paleoreconstructions. Also, further studies should aim at elaborating adequate correction factors or transfer functions to infer paleopollution based on old organic samples.

Our results suggest that these problems may not be critical for many anthropogenic heavy metals (such as Pb, As, Zn and Cd), because the magnitude of their increase at least for the last 500 yr BP appears to be far larger than natural contributions. For all of the above, it seems indisputable that the *P. oceanica* mat is a meaningful record of anthropogenic heavy metal inputs.

The bio-accumulator nature of *P. oceanica* debris points to a possible key role of seagrass meadows as a long-term pollutant filter and sink, by storing large amounts of organo-metal complexes in the mat for millennia. However, further studies are needed to adequately assess the relevance of the mat as a pollutant sink. In addition, the implications of using *P. oceanica* debris for manufacturing agriculture compost or food for ruminant animals (Cocozza et al., 2011; Serio et al., 2004; Torbatinejad et al., 2007) still need to be adequately addressed.

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