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

O. Serrano [a,*], M.A. Mateo [a], A. Dueñas-Bohórquez [b], P. Renom [a], J.A. López-Sáez [c], A. Martínez Cortizas [d]

[a] Centro de Estudios Avanzados de Blanes (CEAB), c/Accés a la Cala St. Francesc, 14. 17300 Blanes, Girona, Spain
[b] Faculty of Geosciences, Utrecht University, Postbus 80.021, 3508 TA Utrecht, The Netherlands
[c] G.I. Arqueobiología, Instituto de Historia, Centro de Ciencias Humanas y Sociales, CSIC, c/Albasanz 26-28, Madrid, Spain
[d] Departamento Edafologia y Quimica Agricola, Facultad de Biologia, Campus Sur s/n, 15782 Santiago, Spain

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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 $\mu g\ g^{-1}$ for Pb, ~23 to 95 $\mu g\ g^{-1}$ for Zn and ~8 to 228 $\mu g\ g^{-1}$ 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

* Corresponding author. Tel.: +34 972 336101; fax: +34 972 337806.
E-mail address: oserrano@ceab.csic.es (O. Serrano).

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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

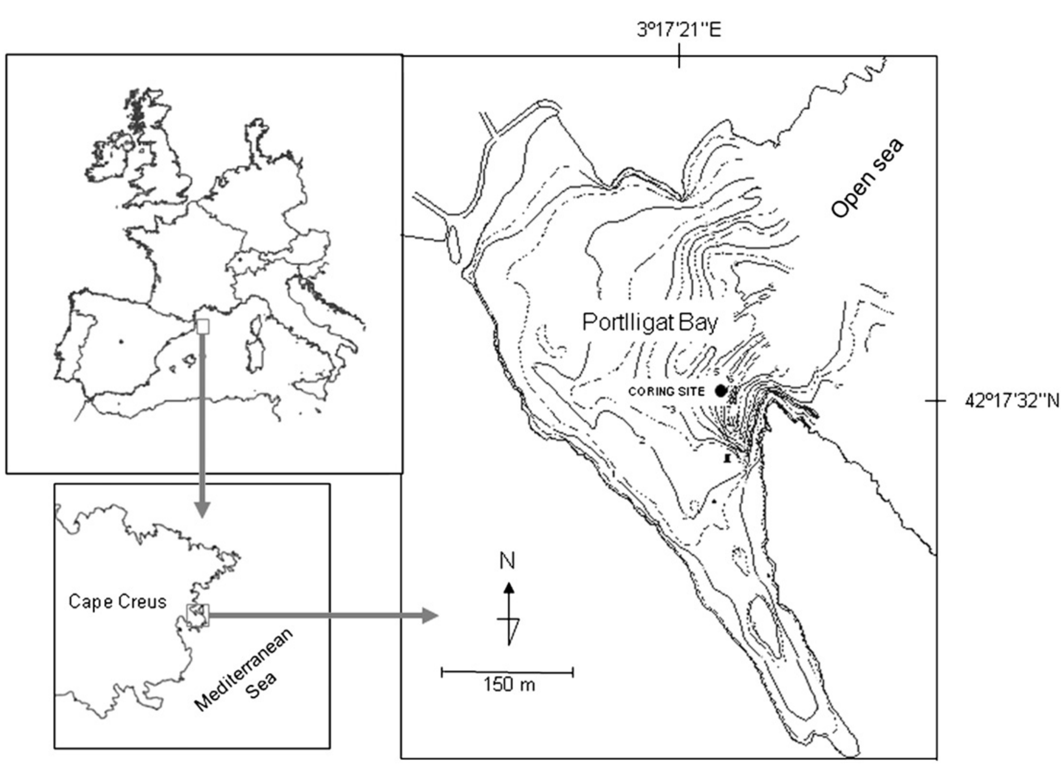

Fig. 1. Location of the study site, Portlligat Bay, Girona, northwestern Mediterranean.