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Angel Pérez-Ruzafa, Laurent Dezileau, María José Martínez-Sánchez, Carmen Pérez-Sirvent, María Pérez-Marcos, et al.. Long-term sediment records reveal over three thousand years of heavy metal inputs in the Mar Menor coastal lagoon (SE Spain). *Science of the Total Environment*, 2023, 902, pp.166417. 10.1016/j.scitotenv.2023.166417 . hal-04184941

**HAL Id: hal-04184941**

**<https://hal.science/hal-04184941>**

Submitted on 22 Aug 2023

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## Journal Pre-proof

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PII: S0048-9697(23)05042-8

DOI: <https://doi.org/10.1016/j.scitotenv.2023.166417>

Reference: STOTEN 166417

To appear in: *Science of the Total Environment*

Received date: 10 May 2023

Revised date: 16 August 2023

Accepted date: 17 August 2023

Please cite this article as: A. Pérez-Ruzafa, L. Dezileau, M.J. Martínez-Sánchez, et al., Long-term sediment records reveal over three thousand years of heavy metal inputs in the Mar Menor coastal lagoon (SE Spain), *Science of the Total Environment* (2023), <https://doi.org/10.1016/j.scitotenv.2023.166417>

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## Long-term sediment records reveal over three thousand years of heavy metal inputs in the Mar Menor coastal lagoon (SE Spain)

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### Abstract

The Mar Menor lagoon combined high biological production and environmental quality, making it an important economic engine. However, the pressure of human activities put its ecological integrity at risk, the oldest environmental impact being mining activity recorded since Roman times, about 3,500 years ago, reaching its maximum intensity in the 20th century, contributing heavy metals to the lagoon sediments for almost 30 centuries.

This work reviews the spatiotemporal evolution of the main heavy metals in this coastal lagoon using data from 272 surface sediment samples obtained during the last 40 years and two deep cores covering the total history of the lagoon (c. 6,500 yrs BP), so as their incidence in the lagoon trophic web.

The observed patterns in sedimentation, sediment characteristics and heavy metal content respond to the complex interaction, sometimes synergistic and sometimes opposing, between climatic conditions, biological production and human activities, with mining being mainly responsible for Pb, Zn and Cd inputs and port activities for Cu. High Fe/Al, Ti/Al and Zr/Al ratios identify periods of mining activity, while periods of arid climatic conditions and deforestation

that increase erosion processes in the drainage basin and silt concentration in the lagoon sediments are determined by high Zr/Rb and, to a lesser extent, Zr/Al and Si/Al ratios. After the cessation of direct discharges into the lagoon in the 1950s, the recent evolution of heavy metals concentration and its spatial redistribution would be determined by hydrographic and biogeochemical processes, solubility of different elements, and coastal works in harbours and on beaches. The bioconcentration factor decreases along the trophic levels of the food web, suggesting that the lagoon ecosystem provides an important service by retaining heavy metals in the sediment, largely preventing their bioavailability, but actions involving resuspension or changes in sediment conditions would pose a risk to organisms.

Keywords: Coastal lagoon; Heavy metals; Mar Menor; Marine Pollution; Sediments; Mining activity.

## 1. Introduction

Coastal lagoons constitute ecosystems of high biological and socioeconomic value (Anthony et al., 2016; Newton et al., 2018; Pérez-Ruzafa et al., 2019a), but at the same time, human impacts, including heavy metal pollution, are a growing threat to them and to the goods and services they provide to human societies. The Mar Menor, one of the largest coastal lagoons in Europe, also had the uniqueness of combining high biological productivity and high environmental and water quality (Pérez-Ruzafa et al., 2020), which has made it an important socio-economic engine based on the quality and quantity of its fishing production, salt mining, tourism activities, water sports, nature observation and thalassotherapy or as a residential area. However, the increasing pressure of human activities carried out in its watershed and in its coastline and basin has produced many changes and impacts that have put its ecological integrity at risk (Pérez-Ruzafa et al., 2019b).

Detecting and assessing the effects of pollution in this type of environment is complex, as coastal lagoons are naturally stressed systems as a consequence of their high spatiotemporal and physicochemical variability (Barnes, 1980; UNESCO, 1981; Kjerfve, 1994; Elliott & Quintino, 2007; Pérez-Ruzafa et al., 2007). The species living in them are tolerant to this stress, adapting their physiology and behaviour to a wide range of fluctuations. Thus, by assuming that lagoon communities have similar characteristics to those of polluted areas that suffer from anthropic stress, the consequence is that it is very difficult to find biological indicators

for them capable of differentiating between natural and culturally stressed states (Pérez-Ruzafa et al., 2018). This fact, which has been called the “estuarine quality paradox” (Dauvin, 2007; Elliot & Quintino, 2007; Dauvin & Ruellet, 2009), insists on the need to precisely know the elements and processes that govern the functioning of coastal lagoons, the cause-effect relationships that are established and the factors and actions that produce environmental stress and pollution in them. At the same time, it should be noted that among the ecosystem services provided by coastal lagoons is the ability to remove or reduce many of these pollutants from circulation in food webs, mainly by retaining them in the sediment in insoluble or non-bioavailable forms (Pérez-Ruzafa et al., 2019a; Vazquez-Botello et al., 2020).

The impacts suffered by the Mar Menor are not recent and, although with varying intensity and consequences, date back to more than 3,000 years ago, when the first human settlements of any importance appeared on its shores (Lillo, 1978; Pérez-Ruzafa et al., 1987). Since then, human pressures have been overlapping and added their effects on an ecosystem that, due to its semi-enclosed, shallow, and transitional nature, is particularly fragile and vulnerable (Pérez-Ruzafa & Marcos, 2019).

The oldest major environmental impact was due to mining activity in the surrounding mountains of Cartagena-La Unión, which began with the first Phoenician colonies about 3,500 years ago, and developed under Carthaginian and Roman rule, mainly with the exploitation of copper (Cu), tin (Sn), zinc (Zn), silver (Ag), lead (Pb), iron (Fe), and manganese (Mn) (Eiroa, 1986; Fernández Gutiérrez, 1985; Manteca et al., 2005). This activity reached its maximum intensity in the first half of the 20<sup>th</sup> century, contributing heavy metals to the lagoon and its sediments for almost 30 centuries.

In parallel, changes in land use and vegetation since the early stages of human colonisation (Azuara et al., 2020) and, above all, the deforestation that occurred during the High Middle Ages throughout the lagoon’s surrounding, determined a significant destructuring of the soil reflected in an increase in erosion and sedimentation rates, mainly of fine materials, towards the bottom of the Mar Menor. This effect of pollution and clogging accelerated remarkably at the beginning of the 20<sup>th</sup> century, mainly due to the intense mining of the Cartagena Mountain range at that time (García Dory & Maldonado, 1980), finally causing a decrease in the surface and bathymetry of the lagoon (Pérez-Ruzafa et al., 1987, 1991).

Mining discharges into the lagoon reached a turning point when, in the 1950s, the inhabitants and holidaymakers of the coastal village of Los Urrutias mobilised against them (Pérez-Ruzafa & Marcos, 2019). In parallel, this period saw a major transformation of the mining sector, with the beginning of large-scale open-pit mining and the centralisation of the activity on the Mediterranean Sea side, with the diversion of tailings discharges to Portmán Bay, with important and well-known consequences for the bay (Pérez-Sirvent et al., 2018; Baza-Varas et al., 2021; Bourrin et al., 2021).

However, although direct discharges ceased in the lagoon, the levels of heavy metals accumulated in its sediments reached such high concentrations that, in the 1970s, the Peñarroya mining company considered its re-exploitation (Simonneau, 1973), although this initiative was not finally carried out. Simonneau (1973) estimated that there were some 25 million tonnes of mining sediments at the bottom of the lagoon. She estimated that the metal content of the Mar Menor seabed could reach up to 2000 mg/kg of Pb, 3000 mg/kg of Zn and 5% of Fe in the most superficial fine sediments of the northern basin, while in the southern part, where the main sporadic watercourses carrying mineral waste in their avenues are located, these values could exceed 5000 mg/kg of Pb and Zn, and above 10% of Fe in the vicinity of the inner shore of the lagoon (Simonneau, 1973). In the last decade of the 20<sup>th</sup> century, 25 years after the cessation of mining, it was estimated that there were still 26,080, 1202, 1328 and 1.48 kt of Fe, Pb, Zn and Ag, respectively, in the form of mineral residues (including gossan) (Manteca & Ovejero, 1992). Currently, some studies show that these concentrations persist in the soils and sediments, and erosion and the contributions of the sporadic watercourses that tribute to the lagoon, facilitated by a climate of typically torrential rains, continue to incorporate these compounds to a greater or lesser extent into the aquatic environment (Conesa et al., 2010; Martínez-López, 2021).

The increasing level of heavy metals in sediments and ecosystems, especially in estuarine and semi-enclosed areas, is considered one of the most serious and global problems due to their toxicity and persistence (Varol & Şen, 2012). However, in the Mar Menor, they are not found in relevant quantities in the water column or at the highest levels of the trophic web and so far, no health problems have been detected. Nevertheless, the threat is real and, in recent years, probably due to the increase in coastal activities and beach maintenance works, as well

as the availability of more local studies, social activism has refocused attention on the risks of heavy metal pollution in the lagoon.

The aim of this work is to review the distribution and spatio-temporal evolution of the main heavy metals present in this coastal lagoon and to analyse the environmental and human factors that determine them and their bioaccumulation in the trophic web.

## 2. Material and methods

The analysis of the evolution and incidence of heavy metals in the coastal lagoon of the Mar Menor has been carried out at three levels: 1) the temporal evolution over the last 6500 years, based on two cores taken inside the lagoon, 2) the recent evolution of the concentration and spatial distribution over the last 40 years, based on extensive sampling of surface sediments carried out over the last 40 years, and 3) their potential impact on the trophic webs.

The respective datasets have been statistically analysed to describe the temporal and/or spatial patterns found and the relationship of these variations with human activities in the lagoon and the bioconcentration factor found in the organisms. Data sources and statistical methods are described in the respective sections.

### 2.1 Study area

The Mar Menor, a hypersaline coastal lagoon located in the SE of the Spanish coast (37°38'-37°50' N, 0°42'-0°52' W), has a surface area of 136 km<sup>2</sup> and an average depth of 4.4 m, making it one of the largest lagoons in the Mediterranean (Fig. 1). During the sampling period (1980s to 2021), the salinity of its waters showed very heterogeneous temporal dynamic and its seasonal averages fluctuated between 39.2 and 45.2. Water temperature showed a fairly regular pattern, with seasonal averages ranging between 10.0°C and 30.2°C (Pérez-Ruzafa et al., 2019b; Fernández-Álías et al., 2022). The lagoon is isolated from the Mediterranean Sea by a sand bar (La Manga), which is crossed by two artificial channels and a natural inlet complex. The substrates of the lagoon are predominantly muddy and sandy, with some areas of natural rocky bottoms around the three islands within the lagoon. The muddy bottoms, which are mainly in the central area, are usually covered by a dense meadow of algae *Caulerpa prolifera* (Forsskål) J.V.Lamouroux, 1809. Sandy bottoms (with sand contents up to 89%) are located at the margins of the basin and in the small bays surrounding the islands, and are usually covered with scattered patches of the phanerogam *Cymodocea nodosa* (Ucria) Asch.

(Pérez-Ruzafa et al., 1989, 2012). Natural rocky bottoms and rock blocks of artificial hard substrates (harbour jetties and dykes designed to retain sediment on artificial beaches) are covered by photophilic algal assemblages showing vertical zonation patterns (Pérez-Ruzafa et al., 2008).

## 2.2 Long-term evolution of sediment structure and sedimentation rates and heavy metal concentration over the last 6500 years

### 2.2.1 Sampling stations and protocols

in September 2011, two 4 m long sediment cores (MM1 and MM2) were collected at 5 and 4 m below sea level respectively, from the bottom of the lagoon (Fig. 1), using the UWITEC® gravity coring platform (Laboratoire des Sciences du Climat et de l'Environnement and University of Chambéry) (Dezileau et al., 2011). Core MM1 was collected in the center of the lagoon basin, in the deepest zone (5 m deep), and core MM2 was collected at 800 m from the sandy barrier at 4 m deep and more than 8,500 m away from the different watercourse mouths (Fig. 1). Each 4 m core was composed of two consecutive units of 2 m length and 83 mm inner diameter. The two consecutive sections were cored from a first position followed by a third section (1 to 3 m) from a position approximately 1 m away to cover the technical hiatus between the first two sections. The detailed methodology for the collection and analysis of these samples can be found in Dezileau et al. (2016).

### 2.2.2 Geochronology of core analyses

The chronology of core MM1 has been established for the last 6500 years using  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$ , and (AMS)  $^{14}\text{C}$  dates on monospecific shell samples, geochemical analyses of mining-contaminated lagoonal sediments, and palaeomagnetism (see Dezileau et al., 2016 for details). We assessed the modern reservoir  $^{14}\text{C}$  age by comparing an age derived from  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  data and geochemical analysis of mining-contaminated lagoonal sediments with an AMS  $^{14}\text{C}$  age of a pre-bomb mollusc shell (see Sabatier et al., 2010, for method). The age model using  $^{137}\text{Cs}$ ,  $^{210}\text{Pb}$ , and (AMS)  $^{14}\text{C}$  was calculated using OxCal 4 (with 17  $^{14}\text{C}$  dates). In the Mar Menor, the linear sedimentation rate (LSR) obtained for the MM2 core suggests a low mean accumulation rate of 0.6 mm/yr, from the base to the top of the core. The activities of the nuclides of interest were determined using a Canberra Ge well detector and compared with the known activities of an in-house standard (volcanic rock, Condomines et al., 1995). For



each sediment sample, the ( $^{210}\text{Pb}$  unsupported) excess activities were calculated by subtracting the ( $^{226}\text{Ra}$  supported) activity from the total ( $^{210}\text{Pb}$ ) activity. To date the  $^{210}\text{Pb}$  chronology we use the CFCS model (Golberg, 1963; Krishnaswami et al., 1971). The CFCS model can be applied when typical lagoonal conditions prevail (Sabatier et al., 2008). The error bars on ( $^{210}\text{Pb}_{\text{ex}}$ ) and ( $^{137}\text{Cs}$ ) do not exceed 6% (+/- 20 years).

$^{14}\text{C}$  analyses were performed on *Cerastoderma glaucum* (Bruguère, 1789) mollusc shells in each contiguous 1 cm sediment section with the ARTEMIS accelerator mass spectrometer at the Laboratoire des Sciences du Climat et de l'Environnement-CNRS at Saclay (France). As the radiocarbon age of lagoon and marine organisms is usually older than the atmospheric  $^{14}\text{C}$  age (Siani et al., 2001; Reimer & McCormac, 2002; Sabatier et al., 2010),  $^{14}\text{C}$  ages were corrected for reservoir age following Sabatier et al. (2010) and converted to calendar years using OxCal v4.2 software (Bronk Ramsey, 2001, 2008) (see Dezileau et al., 2016 for details). For core MM1, we have no absolute age constraints. The proposed age scale for MM1 was developed by graphically comparing the lead profile between the two sediment cores. The correlation is similar for the first meter. It is possible to observe a slight shift of 15 cm from the second meter on. In these two archives close to each other, we assume that this discrepancy is small and that the chronology established in MM2 can be used as a good approximation for MM1.

### 2.2.3 Geochemical analyses of core samples

X-ray fluorescence spectrometry (XRF) analyses were performed on the split sediment surface of cores MM1 and MM2 every 0.5 cm using a non-destructive Avaatech core scanner (EPOC, Université Bordeaux 1). The split core was covered with a 4  $\mu\text{m}$  thin Ultralene to avoid contamination. Geochemical data were obtained at different tube voltage, 10 kV for Al, Si, S, Cl, K, Ca, Ti, Mn, and Fe, and 30 kV for Zn, Br, Sr, Rb, and Zr (Richter et al., 2006). This was complemented by granulometric analyses on contiguous 1 cm samples using a Beckman-Coulter LS13320 laser diffraction particle size analyser (Géosciences Montpellier) (Dezileau et al., 2016).

### 2.2.4 Data analyses of core samples

To detect temporal patterns in the input of heavy metals into the lagoon, the nature of the sediments and the associated environmental conditions, data from consecutive sequential cores, obtained every cm, have been analysed.

#### 2.2.4.1 Long term changes in element association and their relationship with sediment structure

The correlation between the different variables, irrespective of their magnitude, along the chronological sequence of cores MM1 and MM2, has been calculated by Spearman's Rank correlations using Primer 7. The obtained distance matrix was represented by a cluster. Associations that resulted in a correlation greater than 0.5 and  $p < 0.05$  are shown.

#### 2.2.4.2 Multivariable patterns in the relationships between sediment characteristics and heavy metal contents over the last 6500 years

Furthermore, to explore the patterns of the relationships between sediment characteristics and heavy metal contents over the last 6500 years in a multivariate perspective, we performed a Principal Component analysis (PCA) on the square root transformed data matrix of the two cores, using CANOCO v.5.15 software (Ter Braak & Šmilauer, 2018). Since the differences between the two cores appeared to absorb most of the variation along the first axis and the apparent influence of time sequence on axis 2, the analysis was repeated for each core separately using the chronological sequence as a covariate to remove this effect from the ordination.

#### 2.2.4.3 Effect of human activities and climatic conditions on long-term evolution of heavy metals concentration in lagoon sediments

Likewise, in order to analyse whether there were significant differences between predefined periods according to the intensity of human activities and the geomorphological, physiographic, or climatic conditions of the area, we have analysed the data matrix using multivariate analysis of variance.

To do this, we have defined two factors, "core" with two levels (MM1 and MM2), and "environment" defined with 5 levels, mining, vegetation degradation, vegetation recovery, sand bar closure and undefined (for periods without clear climatic conditions or notable activities), based on the available historical information and previous works (García Dory & Maldonado, 1980; Eiroa, 1986; Manteca et al., 2005; Dezileau et al., 2016; Azuara et al., 2020) (Fig. 2). The "mining" and "vegetation degradation" levels are considered distinct. Although it could be assumed that the exploitation of mines generates at the same time a degradation of vegetation (use of wood by miners or heating of furnaces), however, it has been proved by

Azuara et al. (2020) that the important development of agriculture and mining activities around Carthago Nova has been detrimental to the shrublands of the Thermo-Mediterranean belt and not to the Meso-Mediterranean forests. Therefore, these two levels are differentiated. The process of “*sand bar closure*” and isolation of the lagoon from a semi-protected bay to a leaky lagoon began around 3200 BC and continued progressively until 2600 BC according to the chronology obtained in core MM2 (Dezileau et al., 2016). Between 300 BC and 100 AD the lagoon became restricted and choked, and has remained so until the present day (Dezileau et al., 2016; Pérez-Ruzafa et al., 2019b).

As each level corresponds to a different number of core units, significant differences have been analysed by a permutational multivariate analysis of variance (PERMANOVA) using the Primer 7 package (Anderson, 2005), after square root transformation and standardisation of the data and using Euclidean distances matrix of the sampling units and a random subset of 9999 permutations. Significant terms were investigated by a posteriori pairwise comparison with the PERMANOVA t-statistic and 9999 permutations. The contribution of each variable to mean differences between factor levels was examined using Similarity percentage analysis (SIMPER) (Clarke et al., 2014).

## 2.3 Recent evolution and spatial distribution of heavy metal concentration on surface sediments

### 2.3.1. Sampling stations and protocols

Over the last four decades, the spatial and temporal variations in the surface sediment characteristics of the Mar Menor lagoon have been analysed through various research projects and monitoring programs on the ecological quality of the lagoon carried out by our research group “Ecology and Management of Coastal Marine Ecosystems”, which has allowed us to compile an extensive series of water and sediment data from the 1980s to 2021. Over the last 25 years, a network of sampling stations spatially covering the lagoon basin has been used following the same sampling and analysis protocols (Fig. 1). The sampling stations were grouped into five zones according to the terrestrial and marine influence of each area (Pérez-Ruzafa et al., 2005). The heavy metal analyzes carried out throughout these campaigns have not yet been published.

Surface sediment samples were taken by hand with a small shovel in shallow areas, or with a van Veen grab from the boat at deeper stations. The top 5 cm of substrate was stored and transported in darkness and cooled in polyurethane bags to the laboratory, where they were dried at room temperature. During this process they were stirred to break up the lumps before being sifted to a size of 2 mm. The granulometric distribution in surface sediments was determined in subsamples, after dispersion by mechanical agitation in a solution of sodic-hexametaphosphate and  $\text{Na}_2\text{CO}_3$ , using the Bouyoucos hydrometer method (Soil Conservation Service, 1973) until 2010, and since then using a battery of sieves and mechanical agitation on even more recent samples. Prior to this, salts were removed by washing and centrifugation, and organic matter was removed by hydrogen peroxide treatment or calcination at  $435^\circ\text{C}$ . Grain size classification was carried out according to the International Association for Soil Science (Duchaufour, 1975). Organic matter (om) was determined by the Walkley-Black method (Buchanan, 1984) or by calcination (Loss on Ignition) of a subsample in a muffle at  $435^\circ\text{C}$  for 48 hours to avoid calcination of carbonates. The sample was previously dried at  $110^\circ\text{C}$  in an oven for 24 hours to completely remove humidity (Nelson & Sommers, 1996; Schumacher, 2002). The complete methodology is described in Pérez-Ruzafa et al. (2004, 2005, 2012). In total, 272 sediment samples were taken during this period.

### 2.3.2 Determination of heavy metals in surface sediments

Total Pb, total Zn, total Cd, total Cu, total As, total Hg and total Fe were determined in the fine fraction (<2mm) of the sediments after a preliminary digestion of 15 minutes using a Milestone ETHOS PLUS microwave carried out on 100 mg of sample, ground in a ball mill and placed in Teflon tubes containing 5 ml concentrated hydrofluoric acid, 200  $\mu\text{l}$  concentrated nitric acid and 5 ml milliQ  $\text{H}_2\text{O}$ . The microwave heating programme consisted of a 7-minute ramp up to 1,000 W and then held at 1,000 W for 8 minutes. Finally, the samples were transferred to an ice bath and stored in the refrigerator for analysis. Closed digestion systems were used to avoid losses in the determination of volatile elements such as As and Hg. In addition, the use of closed containers allows higher temperatures to be reached by increasing the pressure, which is particularly suitable for samples with complex matrices (Sastre et al., 2002).

Arsenic content was determined by Hydride Generation Atomic Fluorescence Spectrometry (GH-AFS) using a PSA Millennium Excalibur 10055 equipment. Samples were prepared in 30%

HCl and 2% I-/AA (ascorbic acid).  $\text{NaBH}_4$  was used as reducing agent and Ar as carrier gas. Fe and Zn were determined by FAAS (Perkin-Elmer 1100B Flame Atomic Absorption Spectrophotometer) and the rest by ETAAS (Unicam 929 AASpectrometer with FS90 plus autosampler) when the analyte is at trace level as it uses a more efficient atomization system. To determine the total content of heavy metals, QA/QC procedures (Quevauviller, 2002) were followed, using different reference materials: NIST SRM 2711 Montana Soil, NIST SRM 2709 San Joaquin Soil, NCS DC 73319, NCS DC 73320, NCS DC 73321, NCS DC 73323, NCS DC 73324, NCS DC 73325. The Zeta- scores calculated for the CRM were in the -0.2 to +0.3 range. Coefficients of variation (five replicates) were in the 1.5-2.5 range, depending of the element and sample. The experimental conditions are included in supplementary material appendix A.

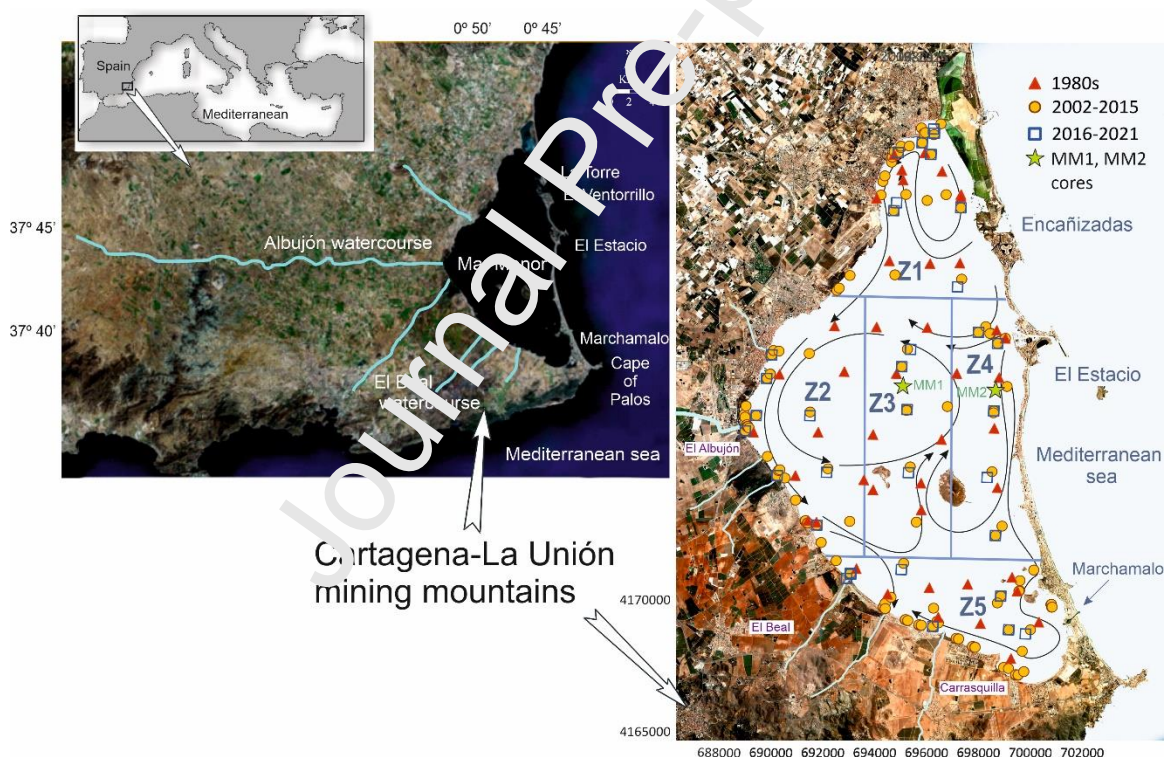


Figure 1.- Left: Location of the Mar Menor showing its drainage basin and the main watercourses; Right: Stations sampled in the different periods and zones (Z1-Z5) into which the lagoon has been divided for the spatial and temporal analyses. The arrows indicate the main circulatory currents in the lagoon.

### 2.3.3 Data analyses of surface sediments

To explore the relationship between the concentration of heavy metals and sediment characteristics, the best linear model accounting for the observed variation of each metal and sediment granulometric fractions and organic matter content was analysed using multiple linear regression models (GLM) with forward and backward stepwise variable selection (using Systat package v. 13 and  $p < 0.05$  as inclusion criterion).

#### 2.4 Heavy metals in organisms and bioaccumulation rates

Previous or simultaneous works by other authors on the incidence of heavy metals in the waters, sediments and organisms of the Mar Menor has also been reviewed (Simonneau, 1973; De León et al., 1982; Auernheimer et al., 1984, 1996; Sanchez et al., 2000; Marín-Guirao et al., 2005a, 2005b, 2007, 2008; Conesa & Jimenez-Cárceles, 2007; Albadalejo et al., 2009; María-Cervantes et al., 2009; Conesa et al., 2010; Dasserakis et al., 2010; Navarro et al., 2010; Tsakovski et al., 2012; García & Muñoz-Vera, 2015; Muñoz-Vera et al., 2015, 2016; Martínez-López et al., 2019; Serrano et al., 2019; Romero et al., 2020; León et al., 2021). This joint data compilation, although relatively heterogeneous, allows us to analyse the global state of heavy metals in the ecosystem, the main sources of contamination, its pathways through the food web and their trends.

To this end, each species was assigned the trophic level that corresponds to it according to its feeding habits and the results obtained in the previous analysis of the lagoon's food web carried out with Ecopath (Pérez-Ruzafa et al., 2020). For each species in each reviewed paper, the bioconcentration factor (BCF), defined as the ratio between concentration of each metal in an organism and the concentration in the environment (Kanazawa, 1983), was calculated for each heavy metal, taking the mean concentration of the metal in the surface sediment as a reference. The average BCF values obtained for the different metals in each species were plotted against the trophic level and the best fit regression was estimated using Excel.

### 3. Results

#### 3.1 Long-term evolution of sediment structure and sedimentation rates and heavy metal concentration over the last 6500 years

The evolution of sediment structure, sedimentation rates and heavy metal concentrations in the Mar Menor during the last 6550 years were studied using the two 4 m long cores taken in the deepest areas of the lagoon. The highest values and the largest fluctuations of the

biogeochemical indicators are found in the MM1 core. The higher amplitude of the oscillations in this core can be explained by its hydrodynamic conditions with respect to the MM2 core. The location of MM1, in the central and deepest part of the basin, currently coincides with the centre of the main gyre of the lagoon circulatory system, while MM2 is closer to the sandbar and more exposed, both to peripheral circulatory currents (García-Oliva et al., 2018), and to storms that have frequently broken the sand bar (Dezileau et al., 2011). Accordingly, the MM1 core was considered to better represent the internal conditions of the lagoon and the relationship with terrestrial inputs, which are the main source of the fine sediment fraction and heavy metals. For this reason, it was used to analyse the relationship and dynamics of the different variables.

### 3.1.1 Long-term evolution of sediment structure

In the upper layers of the cores, the percentage of sand decreases from the vicinity of the lagoon barrier to the centre of the lagoon according to a gradient of marine influence. However, this situation has been different throughout the history of the Mar Menor. The MM1 core is dominated by the sandy fraction in the first thousand years of the sequence (between 5,200 and 4,300 yrs BP), after the closure and stabilisation of the sandy bar that separates the lagoon from the Mediterranean. The MM2 core has followed the opposite evolution, being of a muddy nature (silty clay loam or silt loam) during the first two thousand years, indicating a main sedimentation zone with low hydrodynamics in the area closest to the present sandy bar and probably a washing area in the inner part (terrestrial boundary) of the lagoon.

After that period, MM1 progressively evolved towards muddier textures, showing strongly muddy periods between 3,950-3,100 yrs BP and 950-150 yrs BP (Figs. 3-4). In contrast, MM2 began to increase in the sandy fraction three thousand years BP, which has intensified in the last thousand years BP, with fluctuations associated with storms in the Mediterranean that broke the sand bar increasing the communication between the lagoon and the sea. The main peaks of coarse sands occur around 290, 255, 210, 170, 150, 60, 40, and 5 cm, with values above 20% of sand, which, together with high values of Si/Al (>12) and Zr/Al (>2.5) ratios, is interpreted as a significant contribution of sand of marine origin. MM1 and MM2 showed a more balanced granulometry between 2,750 and 3,000 yrs BP and in the last 150 years.

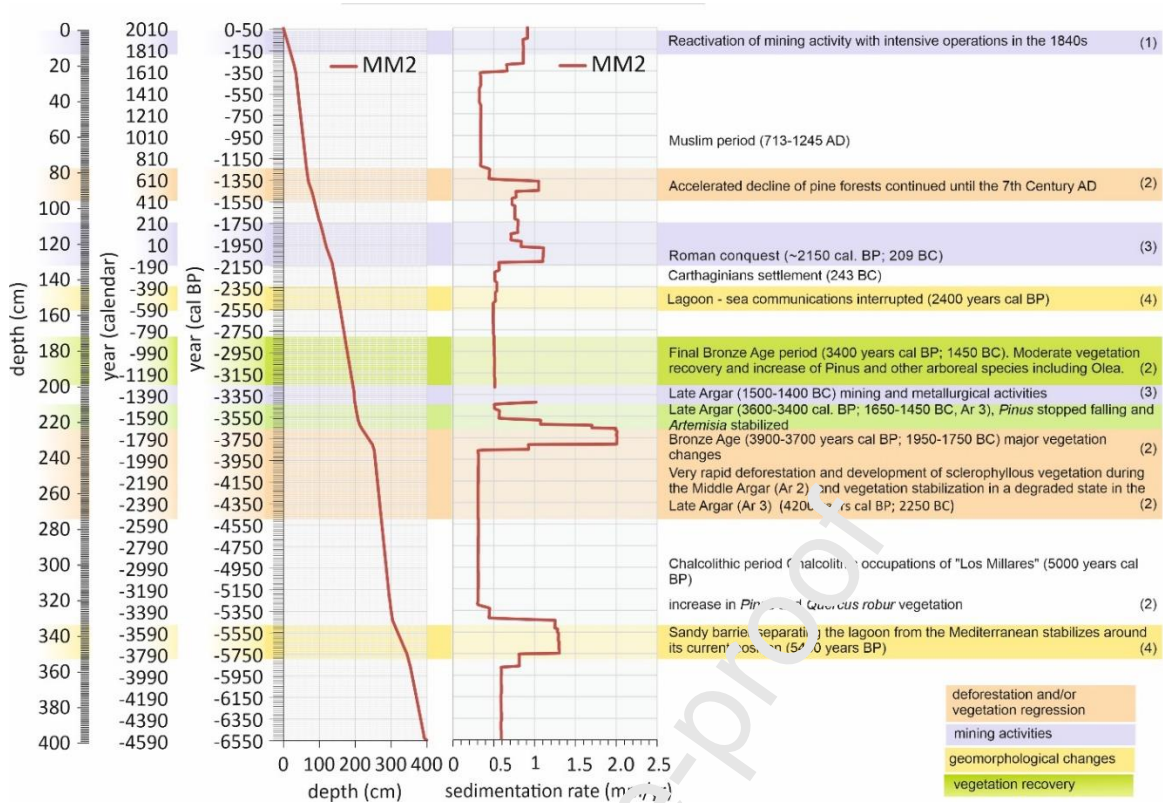


Figure 2.- Age vs. depth for the MM2 core (Dezileau et al., 2016) and sedimentation rates estimated from these data. The ordinate axis shows the relationship of the core layers to calendar year and years Before Present (BP). The horizontal coloured bands represent the main historical and environmental features, including the periods of most intensive mining activity over the period covered by the sediment layers. These periods have been used as levels for the Environment factor in the statistical analyses. References for the defined periods are included in figure (1) García Dory & Maldonado, 1980; (2) Azuara et al., 2020; (3) Eiroa, 1985; Fernández Gutiérrez, 1986; Manteca et al., 2005; (4) Dezileau et al., 2016.



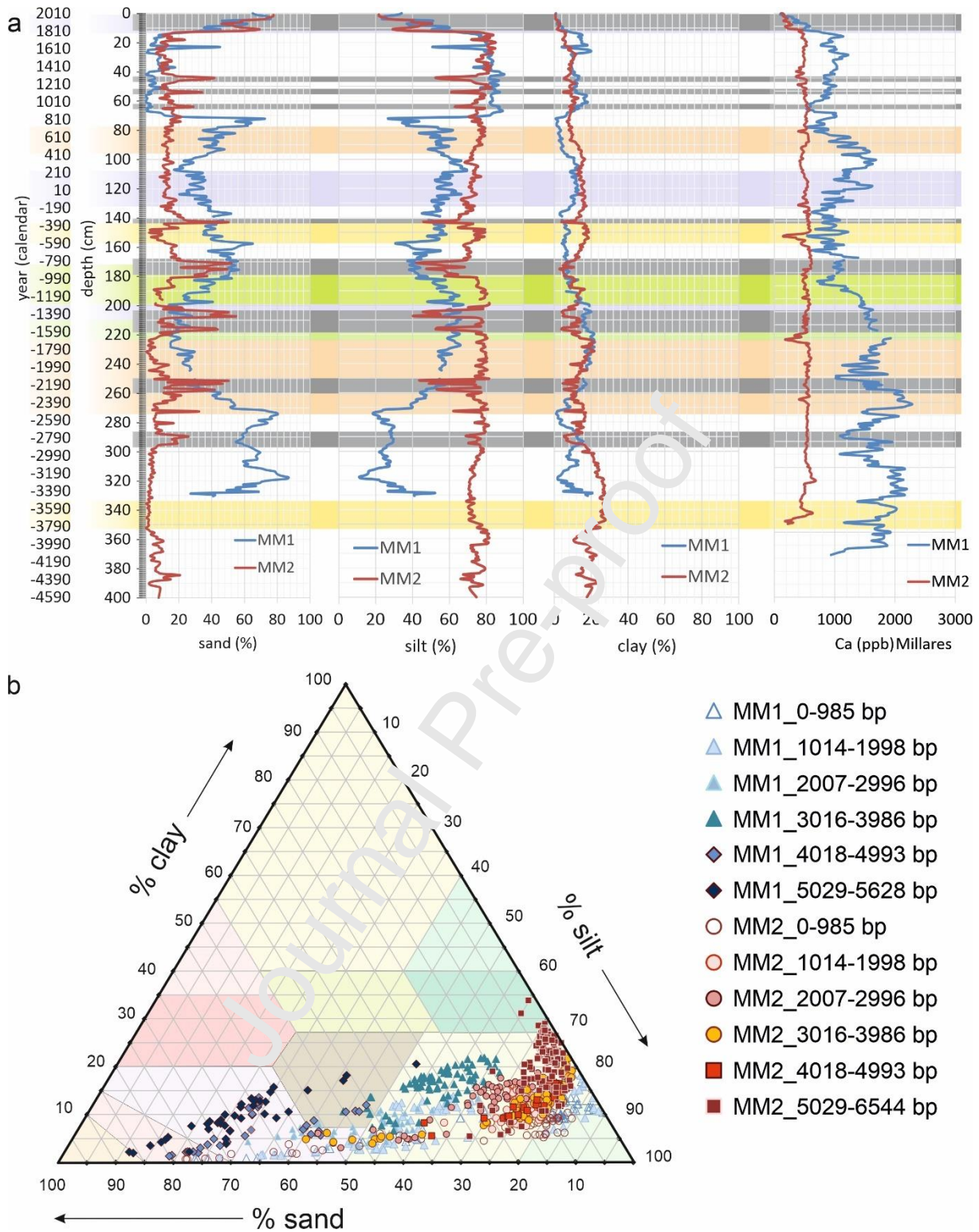


Figure 3.- a) Vertical profiles for sand, silt, clay, and Ca contents in cores MM1 and MM2. The estimated age of the sediments is also stated. The horizontal coloured bands correspond to the main environmental conditions related to climate and human activities or the geomorphological state of the lagoon according to Figure 2. The grey bands mark the main variations of the sand fraction in core MM2; b) Textural triangle showing the temporal evolution of the sediment textures in cores MM1 and MM2.

### 3.1.2 Sedimentation rates

Sedimentation rates in core MM2 have also fluctuated over time (Fig. 2), with peaks of 2 mm/yr at 3,750 yrs BP, and other peaks between 1-1.5 mm/yr in the periods 5,750-5,500 yrs BP, 2,150-1,950 yrs BP and 1,500-1,350 yrs BP. During the last 150 years they show a further increase, approaching 0.9 mm/yr.

These peaks in sedimentation rates coincide chronologically with the closure of the sand bar that separated the inner basin of the Mediterranean and with periods of deforestation in the Bronze Age during the Argar period, the beginning of Roman colonisation, the intensification of mining exploitations and a new period of deforestation, which mainly affected pine forests, and the reactivation of mining in the 17<sup>th</sup> and 19<sup>th</sup> centuries and, subsequently, coastal works with sand dumping on the beaches from the end of the 20<sup>th</sup> century.

### 3.1.3 Historical evolution of the element composition and concentration of heavy metals

#### 3.1.3.1 Long term variability in element association and their relationship with sediment structure

The results of the Spearman's Rank correlation analysis in the MM1 core showed two main clusters of variables, negatively correlated with each other ( $\rho = -0.37$ ;  $p = 0.0001$ ), and with only eight pairs of highly correlated and significant variables ( $p < 0.05$ ) (Fig. 4). All variables within each of the respective main clusters showed a positive correlation. The first cluster consists of Ca levels and the variables with significant correlation, Sand vs Si/Al ratio ( $\rho = 0.74$ ;  $p < 0.05$ ), Zr/Al vs Zr/Rb ratios ( $\rho = 0.72$ ;  $p < 0.05$ ), the second cluster consist of two others, one being the variables Br and Sr along with the significant pairwise correlations, S vs Cl ( $\rho = 0.66$ ;  $p < 0.05$ ), Ti/Al vs Fe/Al ( $\rho = 0.92$ ;  $p < 0.05$ ), and the other includes the sedimentation rates, Zr, silt, Nb, Y, Rb and the significant pairwise correlations clay vs Si ( $\rho = 0.67$ ;  $p < 0.05$ ), Ti vs Fe ( $\rho = 0.97$ ;  $p < 0.05$ ), Zn vs Pb ( $\rho = 0.84$ ;  $p < 0.05$ ), and Al vs K ( $\rho = 0.96$ ;  $p < 0.05$ ).

The inclusion of Ca and sand in the same main cluster can be explained by the fact that the granulometric fraction consists mainly of foraminifera shells, however, the low correlation and lack of significance may be because other sources of calcium carbonate through runoff and in situ precipitation during warm periods also contribute to the Ca concentration in the sediments.

Analyses performed on the MM2 core data maintains the two main clusters and the significant correlations between Zn vs Pb ( $\rho = 0.85$ ;  $p < 0.05$ ) and Zr/Al vs Zr/Rb ( $\rho = 0.87$ ;  $p < 0.05$ ) and Ti/Al vs Fe/Al ratios ( $\rho = 0.91$ ;  $p < 0.05$ ), but include some differences, for example Ca, which is included in the same cluster as sedimentation rates, clay and heavy metals and the correlations between Al vs Si ( $\rho = 0.98$ ;  $p < 0.05$ ), Fe vs Rb ( $\rho = 0.90$ ;  $p < 0.05$ ) and S vs Br ( $\rho = 0.49$ ;  $p < 0.05$ ) are significant here (results are shown in supplementary material Appendix B, Figure B.1).

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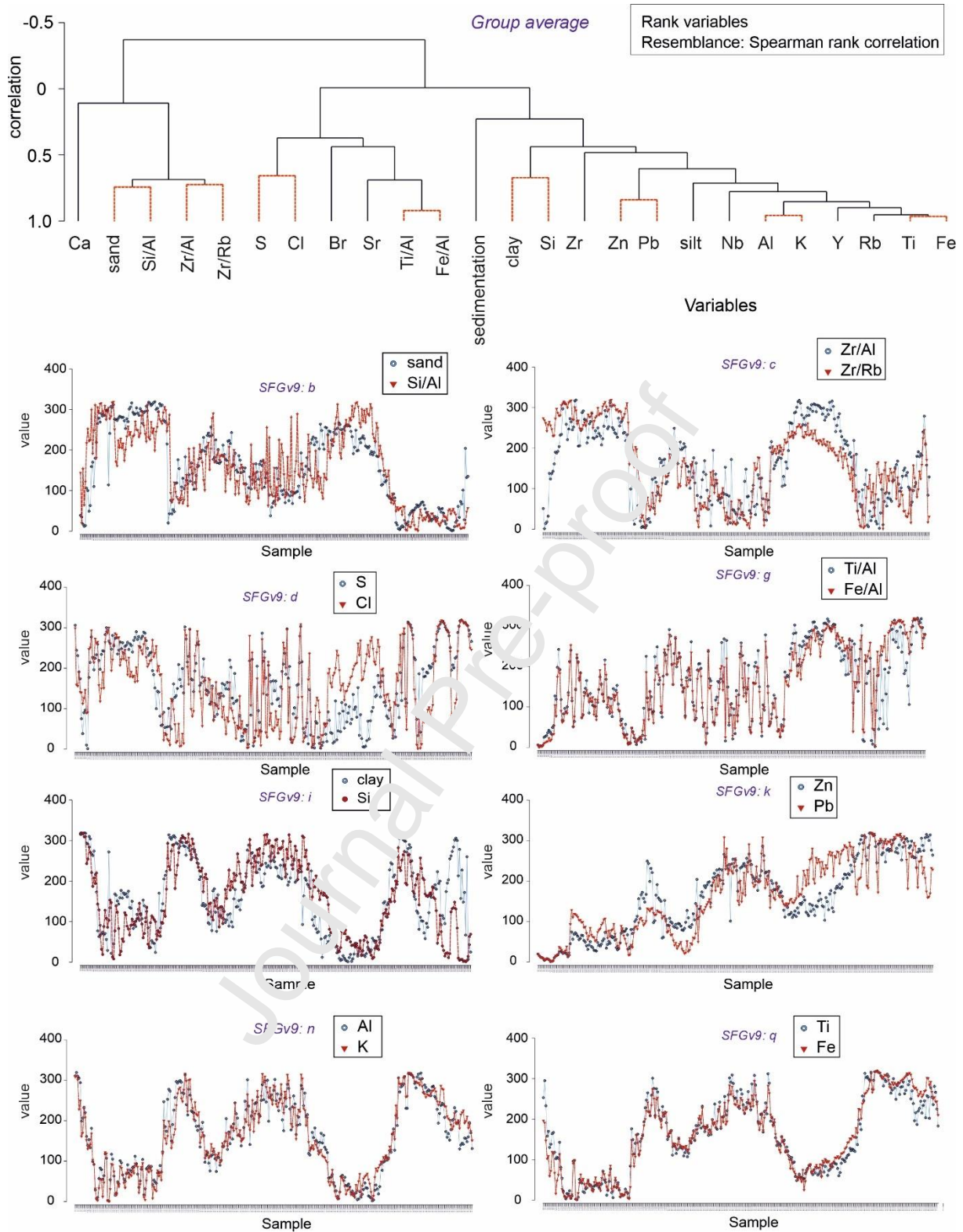


Figure 4.- Cluster analysis of the geochemical variables considered from the Spearman Rank correlation matrix performed on the MM1 core, and correlograms of the pairs of variables with correlations higher than 0.5 and significance level  $p < 0.05$ . Samples on the x-axis are ordered chronologically from left (present) to right (6,500 yrs BP).

Figures 5 and 6 show the XRF records of the MM1 and MM2 cores with down-core variations of the main metals and elemental ratios (variation in concentration of Nb, Ti, Y and Rb, used as indicators of terrestrial inputs under aridic warm conditions, are shown in supplementary material appendix B, Figure B.2; all them show similar behaviour than Al and Fe). The MM1 core, located in the centre of the lagoon, is more sensitive to changes in the composition of the different elements and ratios. The Ti/Al ratio (Fig. 5) shows two main peaks, the first, chronologically, with a value of 14.33, occurs on centimetre 289.5 (4,961 yrs. BP), and the second, and highest, with a value of 26.7 in the upper layer. A notable but much smaller peak, with a maximum value of 6.25, occurred between centimetres 37 and 71 (1,550 and 1,372 yrs BP). This pattern coincides with the Fe/Al index (Spearman correlation rank  $r = 0.92$ , Fig. 4), with a first peak value of 122.43 on centimetre 289.5, a second peak of 83.36 between centimetres 91 and 66 cm, and a maximum value of 590.77 on centimetre 1 (Fig. 5a).

The variation of Zr/Al ratio also shows a first relevant maximum at centimeter 289.5, with a value of 58.02, two periods of maximums between 200 and 72 cm with a featured value of 26.5 at centimeter 84, and finally its highest peak of 86.98 at centimeter 1.

The Si/Al ratio also had maxima in the same periods, but with a different pattern of intensities. Between centimetres 334.5 and 269.5 there was a period of high values with a maximum of 149.27 on centimetre 289.5. The last period with a notable maximum also took place on cm 1, reaching 40.73.

The pattern shown by Zr/Rb ratio was more variable, with periods of high and low mean values much longer in time, affecting both cores, but mainly MM1.

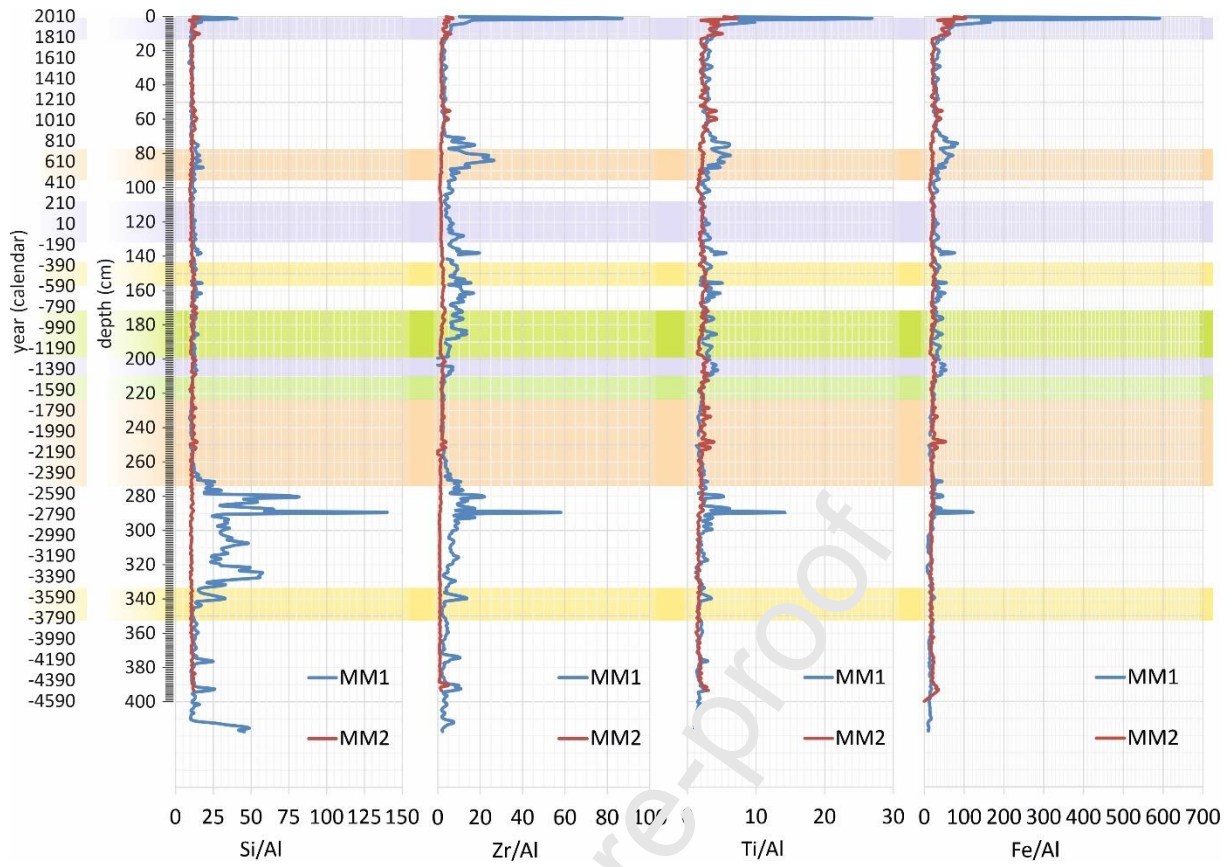


Figure 5. XRF records of MM1 and MM2 cores with down-core variations of the ratios Si/Al, Zr/Al, Ti/Al and Fe/Al.

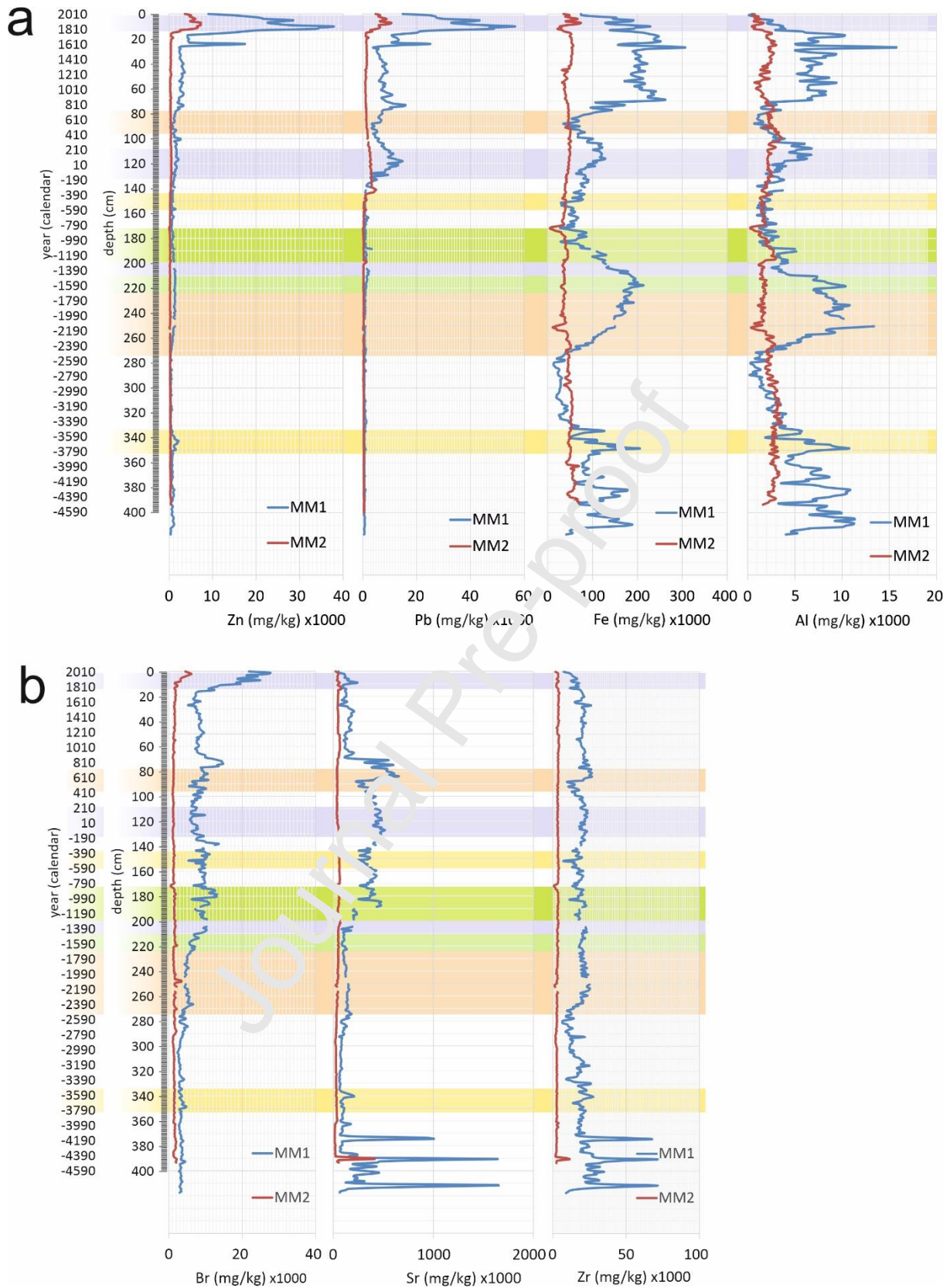


Figure 6. XRF records of MM1 and MM2 cores with down-core variations of a: Zn, Pb, Fe and Al concentration, b: Br, Sr and Zr concentrations.

### 3.1.3.2 Multivariable patterns in the relationships between sediment characteristics and heavy metal contents over the last 6500 years

The first two axes of the PCA analysis performed on the MM1 and MM2 matrix of sedimentological and element concentrations (Fig. 7a), including elemental ratios and sedimentation rates, explains 60.64% of the total variance. It discriminates both cores along axis 1, which explains 36.63% of the variance, with core MM1 in the positive part, determined by a higher concentration of all the elements analysed, mainly Zr, S, Br and Cl, and MM2 in the negative part, determined by a lower elemental concentration and higher silt and clay contents. The second axis explains an additional 24.02% of the variance and is determined in the positive part by higher sand contents and higher values of Zr/Rb, Zr/Al, Ti/Al, Si/Al, and Fe/Al ratios, and in the negative part by higher silt, clay, Al and K contents and sedimentation rates. The arrangement of the samples suggests some chronological influence on the gradient of axis 2, with more recent levels in the positive part.

Figure 7b-e shows the results of the PCA analyses performed for both cores separately and using the chronological sequence as a covariate. The first two axes of these analyses explain 59.84% and 56.74 % of the variance of cores MM1 and MM2, respectively. The chronology of the samples alone would explain an additional 1.29% and 2.12% of the variance respectively, indicating the existence of an increasing temporal trend in most of the main variables.

The MM1 core sections showed segregation along axis 1 (44.21% of the explained variance), determined by high values of sand content and elemental ratios in the positive part, and by a high content of clay and silt fractions, Al, K, Ti, Si and Fe in the negative part. Element ratios (Fe/Al, Si/Al, Ti/Al), Zn and Pb concentrations mark the segregation along the positive part of axis 2 (15.63%), and Zr/Rb, Sr, Zr, Cl and S along the negative part. This axis segregates mainly the periods of highest mining activity.

The PCA analysis performed on the MM2 core shows similar results (Fig. 7d-e), with a clearer differentiation between inputs due to mining activities and vegetation degradation. Segregation of samples is observed along axis 1 (39.36%), dominated by Zr/Al and Si/Al ratios in the positive part. The second axis (17.38%) is mainly determined by Zn, Br, Fe and Pb in the positive part and silt and clay composition in the negative part. Zr/Rb and silt content are mainly linked to vegetation degradation of the in the lagoon watershed and Fe/Al and Ti/Al to



mining activities. Sedimentation rates show little influence in both analyses, especially in MM2, indicating the similar influence of both processes.

### 3.1.3.3 Effect of human activities and climatic conditions on long-term evolution of heavy metals concentration in lagoon sediments

The PERMANOVA analyses showed significant differences between both cores and for the Environment factor and their interaction, indicating that each core performed differently under the different environmental conditions. Pairwise comparison indicates that there are significant differences between all environmental conditions and human activities defined on the stratigraphic sequence except for the levels degraded vegetation vs. vegetation recovery in core MM1 (Table 1).

Table 1. PERMANOVA table of results of the analyses performed on the MM1 and MM2 core sequences for sedimentological variables. Bold characters indicate significant differences.

Source	df	SS	MS	Pseudo-F	P(perm)
Core (Co)	1	3041	3041	219.35	<b>0.0001</b>
Environment (En)	4	740.45	185.11	13	<b>0.0001</b>
CoxEn	4	507.77	126.94	9	<b>0.0001</b>
Residual	694	9621.7	14		
Total	703	16169			
PAIR-WISE TESTS					
Within level 'MM1' of factor 'Core'					
Groups	t	P(perm)			
undefined vs. mining	3.831	<b>0.0001</b>			
undefined vs. degraded vegetation	2.451	<b>0.0017</b>			
undefined vs. sand bar closure	2.647	<b>0.0007</b>			
undefined vs. vegetation recovery	1.975	<b>0.0118</b>			
mining vs. degraded vegetation	3.748	<b>0.0001</b>			
mining vs. sand bar closure	2.36	<b>0.0028</b>			
mining vs. vegetation recovery	2.693	<b>0.0003</b>			
degraded vegetation vs. sand bar closure	3.339	<b>0.0004</b>			
degraded vegetation vs. vegetation recovery	1.336	0.1577			
sand bar closure vs. vegetation recovery	3.318	<b>0.0005</b>			
Within level 'MM2' of factor 'Core'					
Groups	t	P(perm)			
undefined vs. mining	6.064	<b>0.0001</b>			
undefined vs. degraded vegetation	4.463	<b>0.0001</b>			

undefined vs. sand bar closure	4.516	<b>0.0001</b>
undefined vs. vegetation recovery	4.497	<b>0.0001</b>
mining vs. degraded vegetation	4.137	<b>0.0001</b>
mining vs. sand bar closure	5.431	<b>0.0001</b>
mining vs. vegetation recovery	2.353	<b>0.0045</b>
degraded vegetation vs. sand bar closure	4.333	<b>0.0001</b>
degraded vegetation vs. vegetation recovery	2.649	<b>0.0014</b>
sand bar closure vs. vegetation recovery	6.074	<b>0.0001</b>

The Simper analysis performed on the normalised matrix of elements concentration, elemental ratios and sedimentation rates (Supplementary material, Appendix C Table C.1), shows that the periods with mining activity are the most different from the rest of periods (average squared distance=39.04), characterised by Zn (14.35%), Pb (11.22%) contents, and the Ti/Al (11.1%) and Zr/Al (7.63%) ratios.

Mining activities differ from the other periods by higher concentrations of Zn, Fe/Al, Pb, Ti/Al and Zr/Al, these variables explain more than 40% of the cumulative variance in the differences with the other periods with small fluctuations depending on the period considered. Periods of degraded vegetation coincide with the highest mean sedimentation rates ( $10.99 \pm 0.61$  mm/yr), differentiating these periods from those with vegetation recovery ( $9.74 \pm 0.74$  mm/yr) and sand bar closure ( $8.36 \pm 0.12$  mm/yr) or undefined periods, which showed the lowest sedimentation rates ( $6.61 \pm 0.16$  mm/yr).

The period after sand bar closure is characterised by the highest levels of clay and Cl, high levels of Zr/Rb ( $3.39 \pm 0.18$ ), and the lowest values of Rb ( $3081.55 \pm 279.73$ ), Pb ( $635.70 \pm 37.86$ ), Nb ( $1290.41 \pm 45.19$ ), S ( $11,635.53 \pm 602.29$ ), Fe ( $66,202.72 \pm 4556.00$ ) and Fe/Al ( $22.07 \pm 0.91$ ).

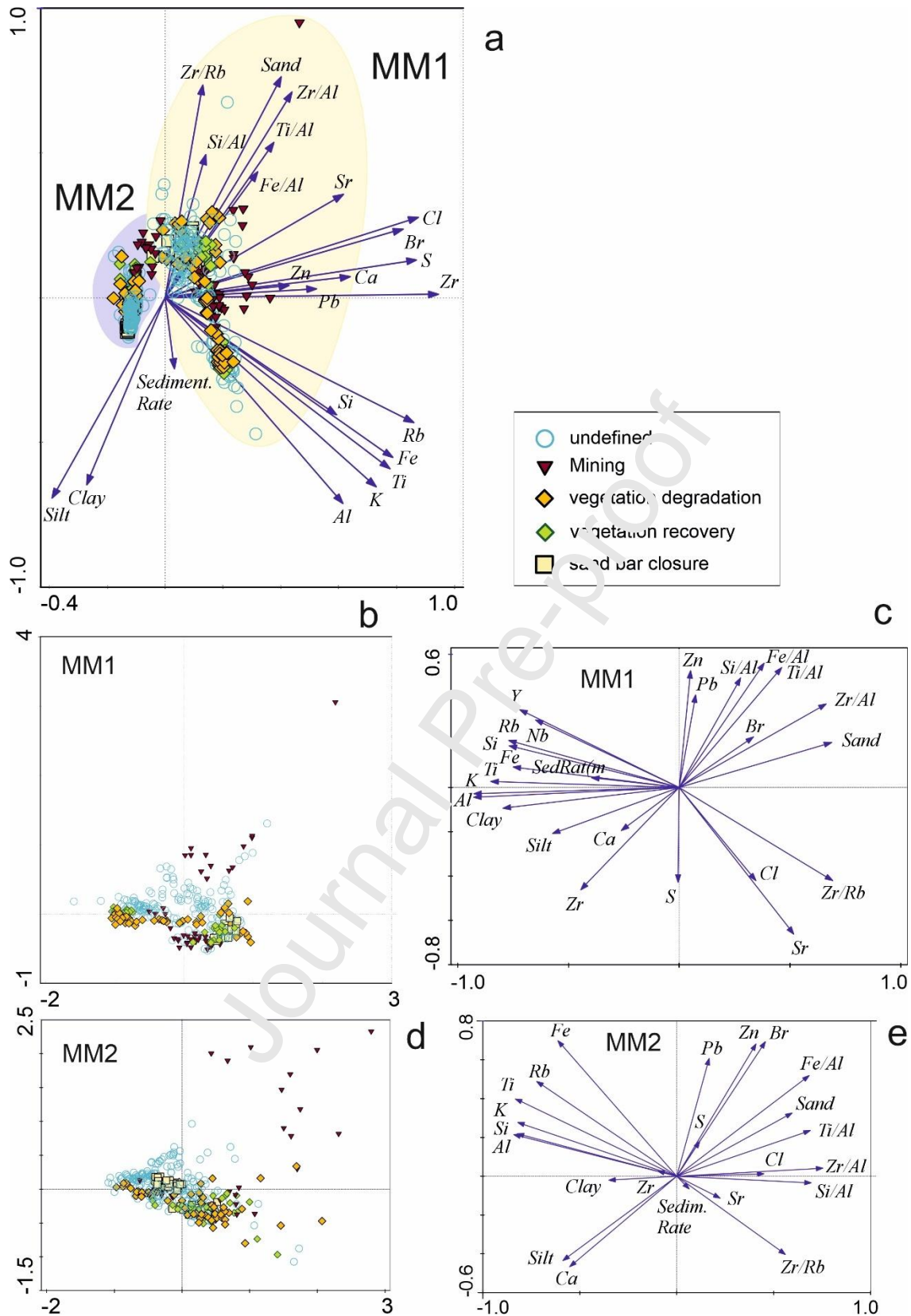


Figure 7. Ordination diagrams of the PCA analysis performed on the MM1 and MM2 matrix of sedimentological and element concentrations, including elemental ratios and sedimentation rates. a: joint analyses; b-e: results of the PCA analyses performed for both cores separately and using chronological sequence as a covariate.

### 3.2. Recent evolution and spatial distribution of heavy metal concentration on surface sediments

The compilation of data and samples analysed during the last 40 years shows a large spatiotemporal variability of the surface sediments of the Mar Menor lagoon. PERMANOVA analysis showed significant differences in metal contents between periods, zones, and their interaction ( $p < 0.05$ ) (Figs. 8-10 and Supplementary material, Appendix C, Table C.2).

In the 1980s, the only zone that showed significant differences with all others was Z5 ( $p < 0.0001$ ). The metals that reached the highest concentrations at this time were Fe, Zn and Pb, with mean values above 66,988, 4833 and 4438 mg/kg, respectively, all in the southern basin. All three showed a significant decrease in the periods 2002-2015 and 2016-2021, mainly in the southern basin. Regarding these same heavy metals, in the periods 2002-2015 and 2016-2021, the southern basin (Z5) only showed significant differences with the northern basin (Z1,  $p = 0.005$ ) and the western part of the lagoon (Z2,  $p = 0.007$ ). Z2, in 2002-2015, also differs from zones 3 and 4 ( $p < 0.005$ ). Finally, in the last period studied, the northern and western zones (Z1 and Z2) differ significantly from the central and southern zones ( $p = 0.0001$ ), with the eastern zone (Z4) being indistinguishable from all the other zones.

There are no data for other trace elements such as Hg and As, potentially very toxic, in the 1980s, but in the period 2002-2015, they are present, although in very low concentrations. Arsenic reached its highest concentrations in 2009, with a maximum value of 128.4 mg/kg in the Carrasquilla watercourse, and Hg reached its highest value in 2017, with 0.46 mg/kg in El Ciervo island, both in the southern basin (CARM, 2019).

In the 1980s period, Cu reached its highest average value in zone Z5 ( $60.40 \pm 3.47$  mg/kg). In the period 2002-2015, it was reached in zone Z4 ( $87.82 \pm 31.64$  mg/kg). In this period, the maximum point values of this metal were reached in the areas under the influence of sport harbours, as they are 211.77 mg/kg in zone 4, close to El Estacio channel which houses the main marina of the Mar Menor, and 75.32 mg/kg, in Z1, close to the fishing and sport port of Lo Pagán. In the period 2016-2021, their concentrations decreased to a maximum mean value in the lagoon of  $19.53 \pm 9.32$  mg/kg in zone 4, close to El Estacio marina.

In general, the areas with the highest metal concentrations are in the inner southern shore, where are the main contributing watercourses (especially El Beal watercourse which is the main entry for mining waste since Phoenician times) and in the sedimentation areas in the centre of the southern basin, south from the Perdiguera and El Barón islands. The only exceptions are Cd, which tends to accumulate only in the deepest areas of the lagoon, in the centre of the main circulatory gyres, and Cu, mainly associated with the channel and the marina of El Estacio. This may be due to the relative mobility of Cd in the marine environment (Neff, 2002) and the relationship of Cu with port activities and the use of antifouling paints (Drude De Lacerda, 1994).

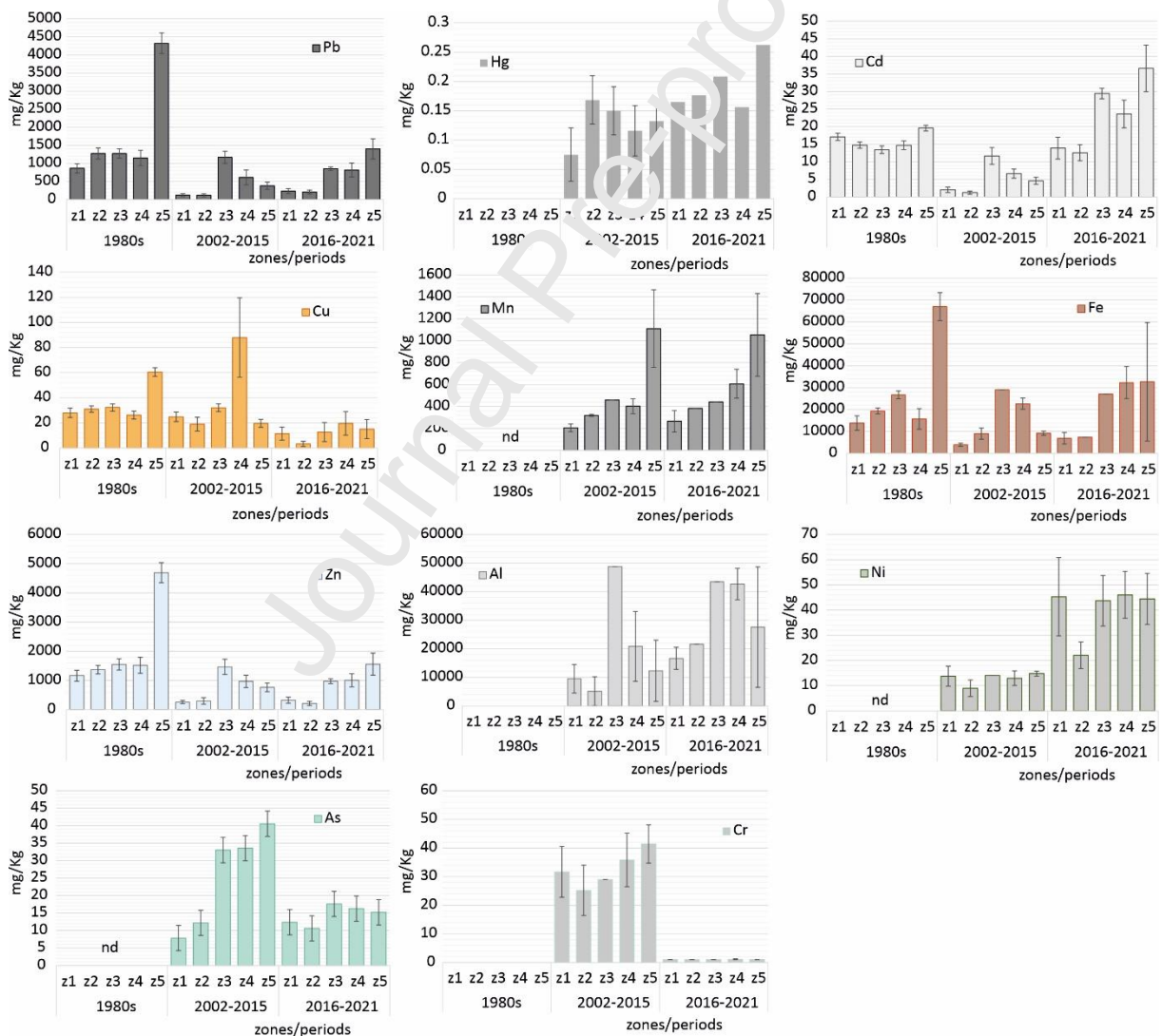


Figure 8. Mean values and standard errors of the heavy metal concentrations in the five zones into which the Mar Menor has been divided for study between the 1980s and 2021.

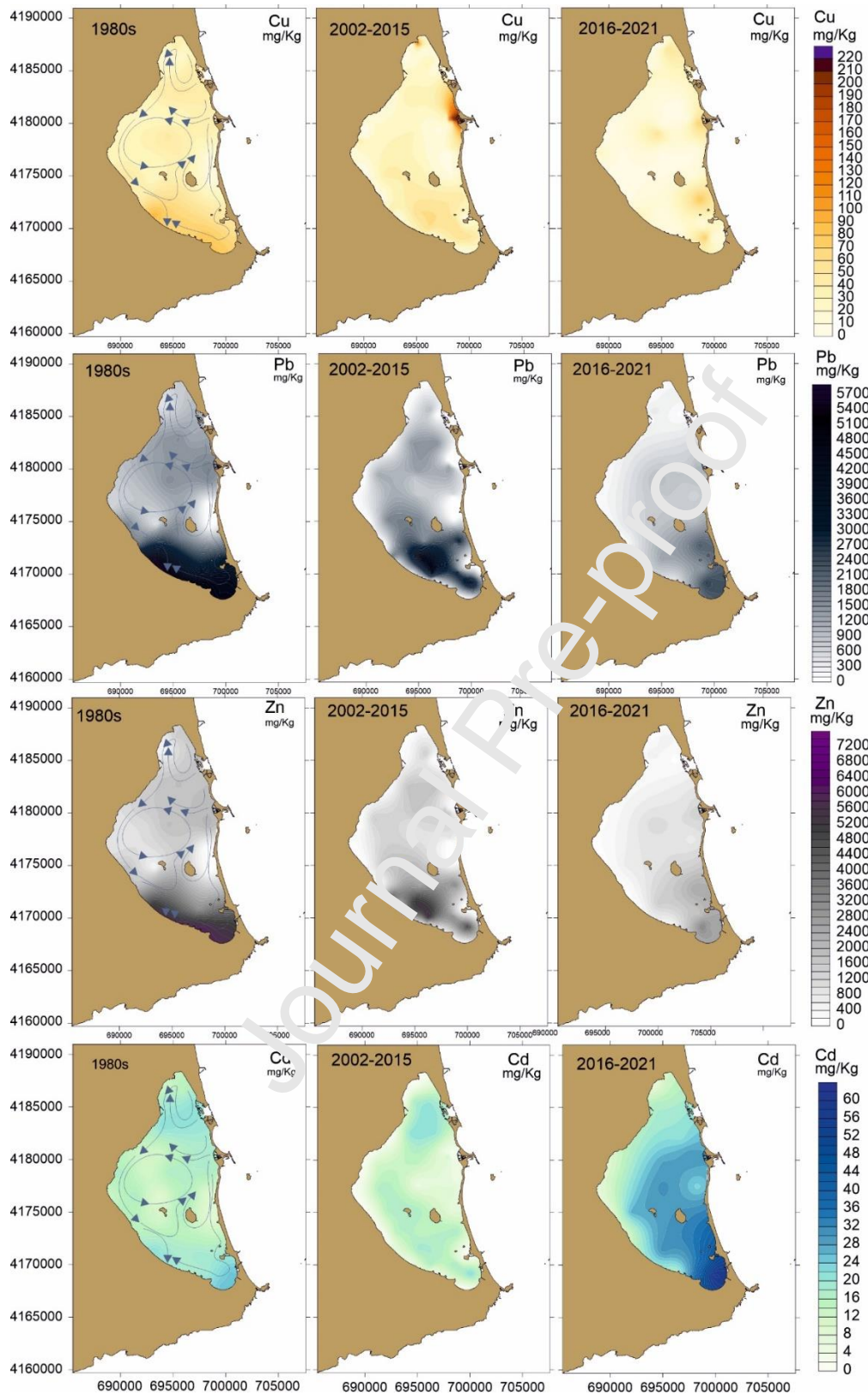


Figure 9. Evolution of the spatial distribution of some of the main heavy metals (Cu, Pb, Zn and Cd) present in the sediments of the Mar Menor, from the period 1980s to 2016-2021.

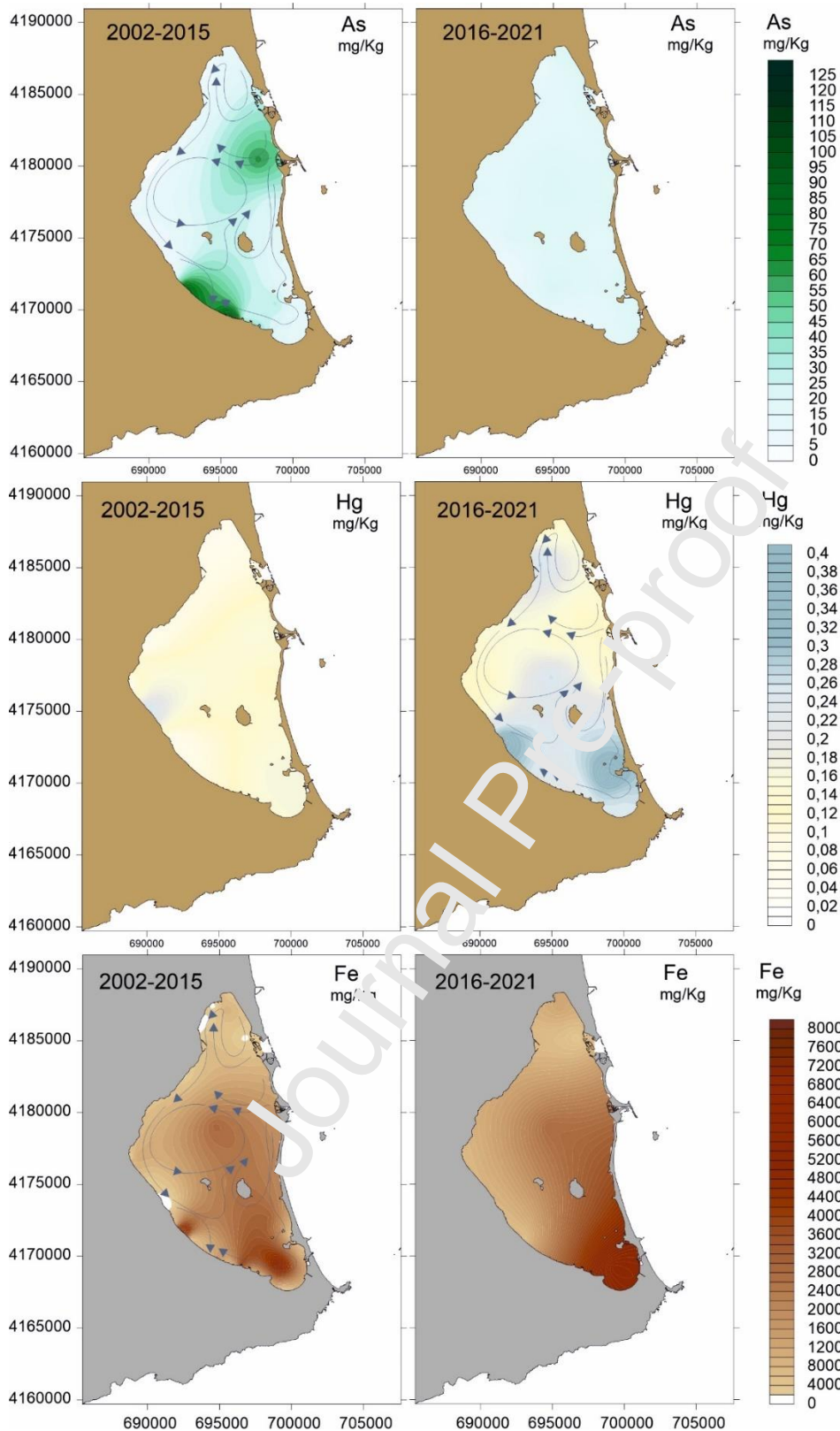


Figure 10. Evolution of the spatial distribution of some of the main heavy metals (As, Hg and Fe) present in the sediments of the Mar Menor, for the periods 2002-2015 and 2016-2021.

Since mining discharges into the lagoon ceased in the 1950s, no significant increases in the levels of heavy metal related to this activity could be expected in subsequent years, although in practice variations are observed depending on the metal considered. Thus, while most of the main metals (Pb, Zn, Fe) and As tend to see their maximum concentrations reduced, Cd shows a clear increase in the deepest areas and in the southern basin, coinciding with the centre of the great circulatory gyres. The differential increase of some metals compared to others in the last period considered could be related to the fact that in the last decade large areas in the southern part of the Mar Menor, close to the former mining areas, have been ploughed and put under agricultural cultivation. The more soluble elements, or those bound to the finer fractions of the soil, would be more easily transported towards the lagoon by winds and runoff water.

For its part, in the period 2002-2015, Hg reached its maximum mean concentration in Z2 ( $0.17 \pm 0.08$  mg/kg), with a maximum local concentration ( $0.59$  mg/kg) to the south of El Albuji3n water course. In 2016-2019, although the maximum value in the lagoon was lower ( $0.35$  mg/kg; also in Z2), this metal appears more distributed throughout the entire basin, reaching mean values of  $0.26 \pm 0.03$  and  $0.21 \pm 0.01$  mg/kg in zones Z5 and Z3, respectively (Fig. 8).

The PCA carried out on the mean values in the 5 zones during the three periods studied clearly shows the spatiotemporal evolution of the main metals analysed (Fig. 11). The first two axes explain 91.42% of the variability of the data. Axis 1, with 69.5% of the variance explained, clearly separates the three metals especially linked to mining activity and concentrated mainly in the southern part of the lagoon in the 1980s, when the direct discharges into the lagoon had already ceased, but mining was still active. Concentrations have been decreasing and becoming homogeneous throughout the lagoon over the following three decades. For its part, axis 2, which explains an additional 24.47% of the variance, clearly discriminates the behaviour of Cu, especially present in zone 4 during the period 2002-2015, at the positive end, and that of Cd, with very low values in the 1980s, but whose presence increases drastically in the period 2016-2021, in a clear spatial gradient, from zone Z5, where it reaches the maximum concentration, towards zones Z3, Z4, Z2, and Z1.



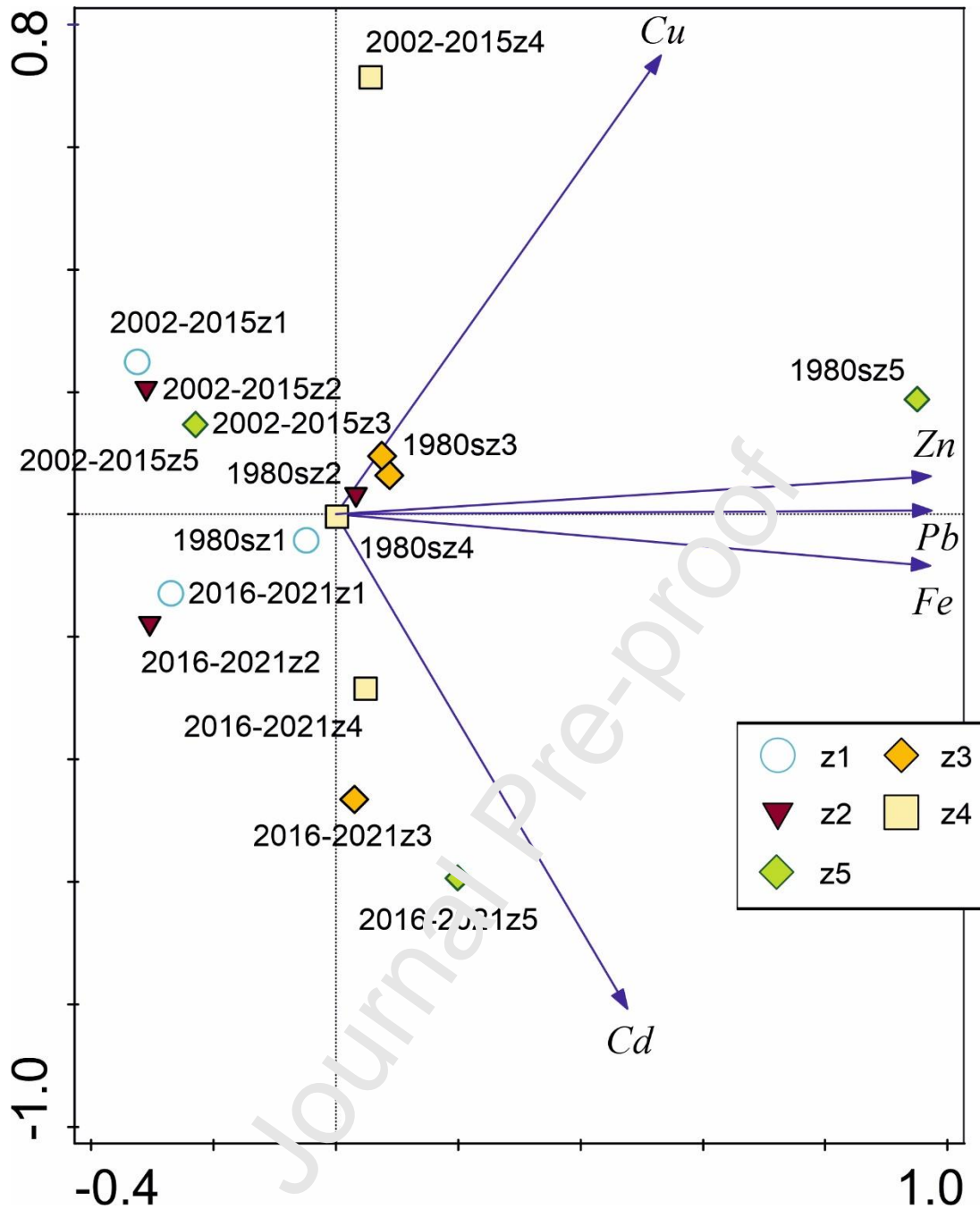


Figure 11. Representation of the mean average values of heavy metal concentration in the five zones defined for the Mar Menor lagoon in the three study periods on the space defined by the two first axes of the PCA carried out.

The linear regression models with forward and backward variable selection performed for each metal using sediment texture and organic matter content show a positive relationship of fine sediment fractions with most metals (Table 2). Organic matter content is only selected, with a negative coefficient, in the explanatory model for Pb concentrations. Coarser sediment

fractions, such as fine sands, only appear selected, with positive coefficients, in the models for Cu and Cd. In addition, Fe does not show a significant relationship with any of the sediment variables.

The analysis of these relationships requires further studies. On the one hand, some metals such as As or Cr show few cases where their concentration has been measured at the same time as the sediment characteristics. On the other hand, there is an important covariation between the spatial distribution of the samples and the contents of organic matter and fine fraction of the sediments.

Table 2. Coefficients and significance value of the explanatory variables selected by linear regression models with forward and backward variables selection performed for each metal using the texture and organic matter content of the sediments. Bold characters indicate significant differences.

Metal	n	Organic matter	fine_sand	gross_silt	fine_silt	clay	adj.mult. R <sup>2</sup>
Pb	61	-122.72; p= <b>0.002</b>	-	-	70.48; p= <b>0</b>	32.75; p= <b>0.01</b>	0.658
As	7	-	-	-	1.01; p= <b>0.001</b>	-	0.868
Cd	47	-	0.16; p= <b>0</b>	-	-	0.34; p= <b>0</b>	0.738
Cr	4	-	-	-	-	0.61; p= <b>0.009</b>	0.925
Cu	46	-	0.56; p= <b>0.035</b>	3.79; p= <b>0</b>	-	-	0.579
Fe	21	-	-	-	-	1634; p=0.09	0.134
Zn	64	-	-	-	68.89; p= <b>0</b>	-	0.598

### 3.3. Heavy metals in organisms and bioaccumulation rates

Bioaccumulation of different heavy metals in organisms tends to be different in different parts of the body. Navarro et al. (2010) found a higher concentration of Cu and Zn in the liver of 8 cormorants found dead in the sand barrier of the lagoon ( $30.33 \pm 10.16 \mu\text{g/g}$  and  $105.56 \pm 23.10 \mu\text{g/g}$ , respectively), while Pb was preferentially concentrated in the feathers ( $22.51 \pm 20.07 \mu\text{g/g}$ ) and Cd in the kidney ( $0.70 \pm 0.51 \mu\text{g/g}$ ). The levels of Pb found in the main accumulating organs (kidney, liver, and feather) exceeded those found in individuals of the same genus, or even of the same species, from other geographic locations.

Values may also show differences between different species, both at the level of bioconcentration (considered here as the average concentration in a given species or trophic level versus the average concentration in the sediments of the Mar Menor), and at the metal that preferentially bioaccumulates, although regularities can be found depending on the trophic level.

Primary producers, at trophic level 1, tend to accumulate mainly Pb (Fig. 12). The biofilm on *Cymodocea nodosa* presented the maximum Zn ( $7047 \pm 99 \mu\text{g/g dw}$ ), Pb ( $8972 \pm 84.9 \mu\text{g/g dw}$ ), Cu ( $130.1 \pm 9.4 \mu\text{g/g dw}$ ) and Cd ( $12.49 \pm 2.59 \mu\text{g/g dw}$ ) in the mouth areas of El Beal and Ponce watercourses in the south of the lagoon (Marín Guirao et al., 2005b, 2008), although there are unexplained differences between the data from both studies.

In the case of benthic invertebrates in the lagoon, Cu is the metal that tends to accumulate the most, multiplying by 16 times the concentration found in the sediment in the case of the gasteropod *Hexaplex trunculus* ( $358.21 \pm 50.79 \mu\text{g/g ww}$ ). The highest local concentration values for other metals have been described for the filter feeder bivalves *Ostrea edulis* ( $9441.4 \pm 46.5 \mu\text{g/g dw}$  of Zn) and *Venerupis aurea* ( $886.5 \pm 29.0 \mu\text{g/g dw}$  of Pb), and the annelid *Sipunculus nudus* ( $24.03 \pm 0.1 \mu\text{g/g dw}$  of Cd) (Marín-Guirao et al., 2008; Albaladejo et al., 2009). In any case, comparisons between publications cannot be direct as the concentrations measured by the different authors are referred in some cases to wet weight (ww) and in others to dry weight (dw) (Cresson et al., 2017).

In fish, the highest values have been cited in *Salaria pavo* ( $88.8 \pm 0.9 \mu\text{g/g dw}$  of Zn), *Syngnathus abaster* ( $43.5 \pm 0.1 \mu\text{g/g dw}$  of Pb) and  $21.0 \pm 0.2 \mu\text{g/g dw}$  of Cu), *Mullus barbatus* ( $1.12 \pm 0.05 \mu\text{g/g ww}$  of Cd), *Lythognathus mormyrus* ( $61 \mu\text{g/g ww}$  of Fe) and *Anguilla anguilla* ( $6.6 \mu\text{g/g ww}$  of Mn) (Marín-Guirao et al., 2008; Albaladejo et al., 2009). It is worth adding the data of  $5.00 \pm 0.34 \mu\text{g/g ww}$  of Se measured by Romero et al. (2020) in the liver of *Anguilla anguilla*.

In general, the maximum concentrations of Cd and Pb found in organisms have remained relatively constant, or even lower, in the different studies during the last decades, except in the case of As which showed some increase (María-Cervantes et al., 2008; Marín-Guirao et al., 2008; León et al., 2021). However, these data are not always comparable due to the heterogeneity in the distribution of the elements and the non-coincidence of the sampling sites.

There is no constant and defined spatial pattern in the concentration of heavy metals in organisms, beyond the observation that values are generally higher in the southern area of the Mar Menor, particularly in the areas of influence of watercourses that sporadically discharge water and sediments into the lagoon (León et al., 2021). Absolute values should be

analysed with caution, as the different published works do not sample randomly but tend to concentrate where highest concentrations are expected to be found. Analysis of all published data against mean sediment values shows that the bioconcentration factor tends to be higher for Pb in primary producers (including biofilm) than in the other trophic levels. Cd, Cu, and Zn tend to be bioconcentrated by herbivores and filter feeders. In contrast, higher trophic levels, including gastropods, crustaceans, and fish, tend to show low bioconcentration factors (Fig. 12).

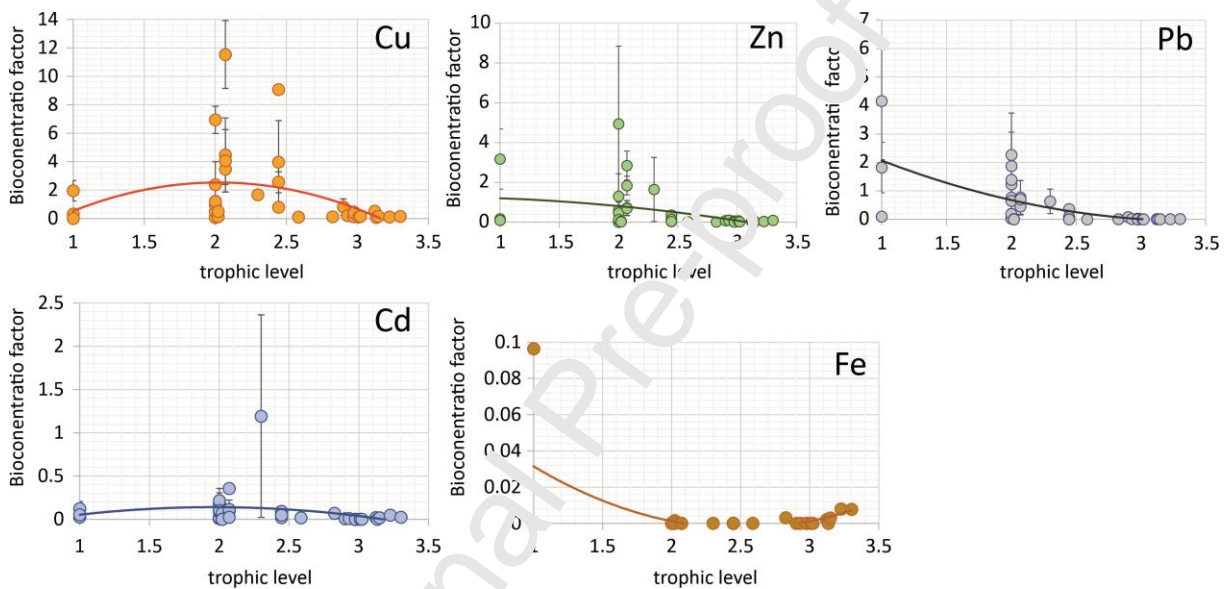


Figure 12. Mean bioconcentration factor of the main heavy metals analysed in the species of the Mar Menor in relation to the trophic level they occupy in the food web. This factor has been obtained from data published in the scientific literature and refers to the mean values measured in the sediments of the entire Mar Menor in the period 2002-2017.

## 4. Discussion

### 4.1 Environmental conditions, sedimentation processes and historical evolution of heavy metals in the Mar Menor in relation to climatic changes and human activities

The Mar Menor has been undergoing a complex process of transformation for more than 5,500 years, following the last desiccation around about 6,500 yrs BP and the last consolidation of the current sand bar that isolates it from the Mediterranean. Such transformations have intensified and accelerated in more recent times, along the same lines as other human-caused impacts on natural ecosystems. Ecosystem functioning has been

compromised by the risk of its homeostatic and regulatory capacities, and environmental parameters and biological communities have undergone changes that affect their environmental heterogeneity (Pérez-Ruzafa et al., 2018, 2019b). In this context, there has been a change in substrate properties and composition.

The main forces shaping the nature of the sediments and their distribution in the lagoon have been its isolation-connection with the Mediterranean Sea, the climatic regime (rainfall and wind erosion), the vegetation cover of the catchment basin and human activities, mainly those involving deforestation, land clearing and mining. Together, they produce a complex scenario, especially notable when there are synergies between several factors.

The changes in sediment structure found in cores MM1 and MM2, and the alternation between the predominance of fine or sandy fractions in each one of them, depending on the period considered, are determined by the marine influence, which has changed depending on the formation of the sand bar and the opening of the communication channels with the open sea. This is reinforced by the changes also shown in the mollusc species richness observed in cores, with an impoverished malacological fauna, indicating a low marine influence that progressively increased reaching a maximum in species richness around 4,250 yrs BP, when the exchange between the lagoon and sea reached a new maximum probably due to the opening of inlets (Dezileau et al., 2016).

The concentration of heavy metals in sediments is the result of the balance between input and deposition rates and the flux of detrital metals, the latter depending on changes in redox conditions and bottom water and sediment oxygen concentration (Shaw et al., 1990). In some studies, in lagoon and estuarine environments, variations in the downcore solid phase of Mn, Ni, and Cu have been attributed to changes in redox conditions accompanying changes in surface water palaeoproductivity (Finney et al., 1988).

Titanium is considered representative of the terrigenous detrital fraction of sediments and an indicator of the relative dilution of biogenic material by terrigenous debris (Shaw et al., 1990). In the eastern Mediterranean basin, in coastal waters, high values of Ti/Al index have been associated with Ti-rich North Africa (Saharan) aeolian dust, generally from marls (Lourens et al., 2001; Larrasoña et al., 2003), while low values would be determined by the predominance of Al inputs, associated with terrigenous aluminosilicate minerals, and therefore generally also

linked to surface fluvial or runoff sources of terrigenous origin, masking the aeolian dust inputs (Köhler et al., 2008). As in the case of the Ti/Al ratio, the maximum values of the Fe/Al ratio are up to 4 orders of magnitude higher than those observed in other areas of the Mediterranean and those reported for African dust (Köhler et al., 2008). In the Mar Menor, the main source of Fe is the terrigenous red clay that constitutes the soils of the catchment basin.

In the same way, Nb is usually positively correlated with elements representing clay substances ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ), and negatively correlated with  $\text{SiO}_2$ , which comprises aeolian sand (Liu et al., 2022), and Rb in oceanic sediments is also linked to inputs of terrigenous detritus-clay erosion materials (Slukovskii & Svetov, 2016).

In this context, the drastic decline that followed the high peaks in Si/Al, Zr/Al, Ti/Al or Fe/Al ratios that occurred between 5500 and 4550 yr BP coincided with climatic changes, a significant lack of rainfall and an aridity crisis in the mid-Holocene in southwestern Europe (Navarro-Hervás et al., 2012) that led to a rapid deforestation process during the Bronze Age that probably increased the erosion of native soils during sporadic torrential rains. This is in agreement with the negative correlations that these indices show with Nb, Y, and Rb, as indicators of terrestrial inputs under arid conditions. However, in our study area, the interpretations are complex since the absence of permanent watercourses, the proximity to North Africa and the influence of winds from the Sahara, and the torrential water regime typical of semi-arid areas mean that some factors show synergies on some occasions and antagonistic effects on others. At the same time, climatic processes interact with biological processes in the lagoon waters so that increases in primary production, which may coincide with higher temperatures and nutrient inputs from wind erosion, would also increase sediment organic matter, while proliferations of siliceous valved diatoms and foraminifera, with their carbonate shells would increase sandy fractions, so as Si and Ca contents in the sediments. In fact, there is a significant correlation between Ti/Al and Fe/Al indices and, in general, these changes also coincide with a drastic decrease in the sandy fraction of the sediments in the centre of the lagoon and with the increase of elements such as Fe, Al, Nb, Ti, Y, Rb and Zr. During this period, the maximum concentration of Ca in the sediment is also reached, probably also influenced by spontaneous precipitation in shallow and warm water conditions. Today, submarine outcrops with flat rock formations of limestone crust and

aggregates of rubble welded together by calcium carbonate can be observed in the Mar Menor.

Si/Al and Fe/Al ratios, which would represent variations of hematite and goethite, are usually considered as indicators of terrigenous inputs (Köeler et al., 2008). However, even assuming that the silicon input could also be mostly of terrigenous origin in some geographical areas, its fluctuations in the lagoon ecosystem could be determined by its use by diatoms, so that the changes in this relationship and its comparison with Ti/Al patterns could suggest changes in lagoon trophic conditions leading to phytoplankton proliferation. Thus, Si/Al and Zr/Al ratios are considered in lagoon areas as those that best discriminate between marine vs. drainage basin source areas (Dezileau et al., 2011; Sabatier et al., 2012; Raj et al., 2015). The high Zr/Al ratio value could be explained by the presence of heavy minerals (such as zircon) from the marine sand, and the high Si/Al ratio may also be due to quartz minerals in the marine sand. In the Mar Menor, Si/Al and Zr/Al ratios have the same evolution with depth, especially in the first three metres of sediment cores (Dezileau et al., 2016).

In fact, the correlations between the clusters including Ca, sand and the Si/Al ratio and the Ti/Al and Fe/Al ratios are negative, suggesting that they may be indicators of alternating periods, with greater runoff and terrigenous contributions or with dominance of biological production and high temperatures in a context where the low human population in the area in those periods made anthropogenic eutrophication virtually non-existent.

The pattern followed by the increase in Zn and Pb concentration is clearly different from that of Al and Fe. Although there are some overlapping peaks once mining started, these are possibly because of surface runoff or wind deposition, which affects both mining waste and soil erosion, especially in arid periods, with possible occasional torrential rainfall. These coincidences are non-existent prior to the start of mining operations.

The start of mining is usually dated to the middle of the 2nd century BC (Mangas & Orejas, 1999; Bellón Aguilera, 2009) and is clearly observed in the increase of Pb and Zn in the core segment dated to -190 BC. However, the sedimentological records in the MM1 core show small increases in Zn as early as around 3600 BC and again at the beginning of the Bronze age, around 2300 BC, which would last until 1000 BC.

4.2 Current spatiotemporal variation of heavy metals in the surface sediments of the lagoon

In the Mar Menor, the changes in surface sediments in the last three decades, mainly in the coastal fringe but also in deeper areas due to the effect of waves and currents, also have a lot to do with the dredging and sand deposition carried out, mainly for the regeneration and maintenance of the beaches. Those coastal works have the dual effect of redistributing sands and increasing the content of fine clay-sized particles and organic matter in both dredged and pumped areas, altering biogeochemical processes (Pérez-Ruzafa et al., 2006). In this context, the lagoon basin has been affected by sediment movements in the deeper areas depending on currents, with areas that have been eroded, increasing their depth and others where accumulations have occurred, becoming shallower (Erena et al., 2020).

Our data on the spatial distribution of the maximum values of heavy metals concentration in the lagoon are in agreement and consistent with those provided by Sanchiz et al. (2000), Marín-Guirao et al. (2005a, 2008) or Albaladejo et al. (2002). However, the fact that our data have been obtained in different projects, with different objectives over several decades, introduces heterogeneity in the sampling, both spatially and in the metals analysed and the environmental variables measured on each occasion, which prevents more robust experimental approaches. This heterogeneity is also found in the bibliographic data both in the publications carried out in the Mar Menor and in other lagoons, which makes it difficult to carry out a more in-depth review based on meta-analyses.

The distribution of the heavy metals analysed depends on anthropogenic activity and the way they are transported by hydrodynamic currents, depending on their solubility or their binding to suspended particles. Thus, Cu shows spatial and temporal patterns linked to its use in antifouling paints, and therefore, to the location of the main port areas and the administrative policies that have regulated its use. Pb and Zn are related to mining activity. Fe and Al are more related to the nature of soil materials and erosion processes linked to climatic conditions and agricultural or deforestation activities. In addition, the change of uses in the Mar Menor environment, such as the introduction of irrigated crops mainly in the southern basin, has induced new soil movements and, quite possibly, the use of new substances such as fertilizers or pesticides that may contain a different composition of elements (Pérez-Ruzafa, Cartagena city council report).

The main watercourses with mining influence affecting the Mar Menor, such as El Beal, Ponce and La Carrasquilla, continue to be areas particularly affected by the accumulation of



sediments rich in mining waste, which reach the shore of the lagoon, providing sediments with high total Pb contents (200-4016 mg/kg) with an average value of bioassimilable Pb of 7.3% of the total, Zn (200-6000 mg/kg) with a mean concentration reaching 4604 mg/kg, and a bioassimilable fraction of 2.7% on average, Cu (50-300 mg/kg), with an average concentration of 55 mg/kg and an average bioassimilable value of 2.2%; and Cd with maximum values reaching 30 mg/kg and a mean value of 4.4 mg/kg, although the authors point out that this last metal presented an average assimilability value between 7% and 48% of the total, highlighting the environmental risk of this element (García-García, 2004; Navarro et al., 2008; García-Lorenzo et al., 2014). Subsequently, Conesa et al. (2011) in the soils of the alluvial plain of El Beal watercourse, less than 700 metres from the shore of the Mar Menor, obtained even higher average concentrations, reaching 7655 mg/kg of Pb, 3205 mg/kg of Zn, 106 mg/kg of Cu, 23.5 mg/kg of Cd and 2639 mg/kg of Mn (see also Navarro et al., 2012; García-Lorenzo et al., 2012).

More recently, Martínez-López et al. (2019) analysed the values and interactions of As, Fe and Mn in the streams that flow into the lagoon, highlighting the importance of the mineralogical composition of the soils as a determining factor in the mobility of the studied trace metals. Soil acidity can mobilise As associated with carbonates and that retained by insoluble minerals such as sulphides and jarosites. According to this work, particulate arsenic entering the Mar Menor lagoon through watercourses would be susceptible to mobilization when the organic matter content is high (Martínez-López et al., 2019). In this context, the marked dispersion observed towards the north of the lagoon from El Beal watercourse in the period 2002 to 2017 would coincide with the critical years of the eutrophication process, while in 2018 these values were significantly lower, coinciding with the year in which the Mar Menor showed a sensitive recovery after the temporary reduction of the contributions of nutrient-laden water from the watershed (Pérez-Ruzafa et al., 2019b). The disappearance of the macrophyte meadows dominated by *Caulerpa prolifera* due to the first dystrophic crisis (Belando et al., 2017) exposed the sediments, with a high load of organic matter, anoxic and with hydrogen sulphide content, to mobilisation, while the oxygenation of the sediment surface layer and the decrease in hydrogen sulphide production, which would cause colonization by faunal communities in the following two years, would favour their retention.

In addition, the deposition and accumulation of metals will be strongly affected by the characteristics of the sediments, mainly by their granulometry. Fine sediments, with a higher surface/volume ratio, will have a greater retention capacity than sands and, therefore, the accumulation of metals at the bottom of the lagoons may also be a consequence of the distribution and movements of fine sediments (Drude de Lacerda, 1994).

In our work, regression models show that the finest sediment fractions, such as fine silts and clays, best explain the concentration of most of the heavy metals, such as Pb, As, Cd, Fe and Zn. Only in the case of Cu and Cd do middle fractions, such as coarse silts or fine sands, play a relevant role. The dispersion capacity of the different metals probably responds to a complex relationship between their solubility and their binding to the fine fractions of the sediment and the washing and dragging capacity of the different granulometric fractions by the waters depending on the intensity of the currents and runoff in periods of torrential rains. This could explain why more soluble elements such as Cd show some association with moderately coarse granulometries. The organic matter content is not related to the concentration of any metal, except in the case of Pb, with which there is a strong negative relationship.

Furthermore, the high content of organic matter in the sediments in the central basin of the Mar Menor leads to anoxic conditions and sulphide production, mainly linked to the *Caulerpa prolifera*-*Cymodocea nodosa* mixed meadows, dominated by *C. prolifera* which has a very low contribution to the trophic web (Pérez-Ruzafa et al., 2012, 2020). Under these conditions Cd, Hg and Pb may tend to form poorly soluble metal sulphides, contributing to their retention in sediments as observed in the Scheldt estuary (Millward & Turner, 2009), and precluding their incorporation into the trophic webs.

In this sense, the Mar Menor provides one of its great ecosystem services by retaining these metals in the silts and clays of the sediment, largely preventing them from being bioavailable.

However, it should be noted that, in general, when fine sediment particles are resuspended, they could disperse metals into the water column with potential availability for uptake by biota, for example, metals such as Cu, Cd or Pb were found in tropical coastal ecosystems interacting with organic matter and other geochemical supports increasing their bioavailability (Beraldi et al., 2019). This is precisely one of the main risks of inadequate

dredging or sediment resuspension, being essential not to alter the conditions that allow the low solubility and bioavailability of metals in the lagoon (Pérez-Ruzafa & Marcos, 2019).

The chemical behaviour of the different elements and their solubility in water, their specific adsorption constant with floating and sediment particles or the solubility constant of the new metal complexes formed with the chemical species present in the lagoon water must also be considered. The fraction of a given metal in the dissolved phase relative to its suspended particulate concentration decrease according to its partition coefficient ( $K_D$ ), from Cd ( $K_D \approx 10^3$ ) > Zn ( $K_D \approx 10^4$ ) > Cu ( $K_D \approx 10^6$ ) > Hg and Pb ( $K_D \approx 10^7$ ) (Millward & Turner, 2009). Furthermore, the high specificity of Cu for carboxyl and polyphenolic functional groups and the high stability constant of Cd and chlorine complexes will favour the permanence of these metals in solution over metals such as Fe and Cr with high affinity for inorganic particles with fast sedimentation rates (Drude de Lacerda, 1994). Therefore, when measured in the water column in coastal waters, Hg and Pb show a non-conservative behaviour by rapidly decreasing in concentration from the point source (Millward & Turner, 2009). This means that surface distribution maps in sediments, in the case of metals such as Pb, Hg, Fe and Cr will also be more concentrated near the input sources, and the dispersion gradient will be sharper. However, for metals such as Cd it will be more difficult to determine as it is mainly in the dissolved phase and will disperse rapidly. The fact that Cu showed a high concentration very close to the harbours in the period 2002-2015, probably indicates that its main input took place within the harbours, limiting its dispersal.

Therefore, the risks to ecosystem integrity, organism survival and human health depend on the toxicity of metals and their concentration in the environment, solubility, and bioavailability, that can be regulated by the physicochemical conditions of sediments and water. Some metals such as Cr, Mn, Fe and Se are essential trace elements, necessary in adequate concentrations, although some of them may be toxic in high concentrations. Concern about the content of heavy metals in the lagoon's sediments and their potential incorporation into the trophic web has been increasing in the Mar Menor up to the present day and has been the subject of numerous research studies on the organisms that inhabit the lagoon (De León et al., 1982; Auernheimer et al., 1984, 1996; Sanchiz et al., 2000; Marín-Guirao et al., 2005a, 2005b, 2007, 2008; Conesa & Jimenez-Cárceles, 2007; Albadalejo et al., 2009; María-Cervantes et al., 2009; Conesa et al., 2010; Dassenakis et al., 2010; Navarro et al.,

2010; Tsakovski et al., 2012; García & Muñoz-Vera, 2015; Muñoz-Vera et al., 2015, 2016; Serrano et al., 2019; Romero et al., 2020).

When comparing the levels of heavy metals with those of other coastal lagoons, a great variability of situations is found, depending on the characteristics and human activities developed in each geographical area. Studies on heavy metal pollution in coastal lagoons and estuaries are abundant and many of them establish comparisons between ecosystems (Pavoni et al., 1987; Matteucci et al., 2005; Accornero et al., 2007; Bloundi et al., 2008; Arienzo et al., 2013; Signa et al., 2013; Maanan et al., 2015; Liang et al., 2018; Leone et al., 2020; Yu et al., 2020; Zoidou & Sylaios, 2021; El Zrelli et al., 2021; Ben Mna et al., 2021; Chouikh et al., 2021; Reyes-Márquez et al., 2023; Yapi et al., 2023). In this context, compared to other lagoons and estuaries in the literature, the data from our study show that the Mar Menor stands out mainly for its Pb levels. With an estimated mean of 538.67 mg/kg, it is the lagoon with the highest concentration of this metal, only comparable to the industrial area of the Venice Lagoon, which reach 401.0 mg/kg (Accornero et al., 2008). Other lagoons with high levels of this metal are Thau (88.0 mg/kg) or Berre-Vaine (61 mg/kg) (Accornero et al., 2008) in the south of France, on the Mediterranean coast. Venice lagoon also stands out for high concentrations of Cd (20.34 mg/kg) and Zn (2940.0 mg/kg) (Accornero et al., 2008).

The Mar Menor also stands out for its concentration of Mn (509.4 mg/kg), higher than those of the Bay of Cadiz and surrounding areas (330.3-448.0 mg/kg) (Rodríguez-Barroso et al., 2010). The Zn levels of the Mar Menor (786.2 mg/kg) are below those of Venice, but far exceed those of other lagoons such as Pialassa Baiona (352.7 mg/kg) (Arienzo et al., 2013) or the five lagoons that make up the Po delta where the maximum value reaches 152 mg/kg (Zonta et al., 2019). In contrast, Cr levels in the Mar Menor (11.42 mg/kg) are well below those of most of the lagoons such as Berre (147.0 mg/kg), Berre Vaine (112.0 mg/kg) (Accornero et al., 2008), those of the Po delta (104 mg/kg) (Zonta et al., 2019), Vistula (91 mg/kg), Nador (55 mg/kg) or Venice (25.8 mg/kg) (Accornero et al., 2008). Also, Ni concentrations in the Mar Menor (29.7 mg/kg) are relatively low compared to those of the Po delta (89 mg/kg), Vistula (39 mg/kg), Berre (36 mg/kg) or Venice (33.4 mg/kg) (Accornero et al., 2008; Zonta et al., 2019). Hg levels (0.2 mg/kg), are among the lowest in all lagoons, being Pialassa Baiona, with 56.3 mg/kg (Matteucci et al. 2005), or the industrial zone of Venice with 13.07 mg/kg (Accornero et al., 2008), the lagoons that present the highest concentrations. Despite the large number

of marinas built in the Mar Menor, the levels of Cu in sediments (26.4 mg/kg), are also relatively low compared to Thau (173 mg/kg), Venice (129.4 mg/kg), Prevost (80 mg/kg), Maugio (70 mg/kg), Po Delta (54 mg/kg), Bages (36 mg/kg), Sidi Moussa, (37 mg/kg), Berre Veine (37 mg/kg), Manzalah (34.4 mg/kg), Berre (31.04 mg/kg), Baccares (30 mg/kg) or Leucate (29 mg/kg), (Accornero et al., 2008; Arienzo et al., 2013; Zonta et al., 2019). And they are even lower than those of some protected areas such as the coastal protected area of Essaouira on the Atlantic coast of Morocco (29.5 µg/g dw) (Chouikh et al., 2021). The concentration of Fe in the sediments of the Mar Menor, although very high (12,617.9 mg/kg), is nevertheless much lower than in Venice (77,390.0 mg/kg) (Pavoni et al., 1987), this being a metal that has been little analysed in other lagoons.

#### 4.3 Heavy metals in the Mar Menor biota and its comparison with other lagoons

In the case of biota, it is more difficult to find works with which comparisons can be made. However, the concentration of some metals found in some organisms in the Mar Menor can be considered high, such as the averaged concentration of As found by León et al. (2021) in *Hexaplex trunculus trunculus* (544.8 mg/kg dw). Arsenic, which is considered carcinogenic, mutagenic and teratogenic and which can cause health problems, is found in high concentrations on the slopes of the mining mountain range and in the soils of the southern shore of the Mar Menor, where up to 5000 mg/kg of As have been measured (Martínez-López et al., 2020).

Cd levels found by Marin-Guirao et al. (2008) in *Sipunculus (Sipunculus) nudus* (24.03 mg/kg dw) are also high, but only in specimens taken at the mouth of the wadi that discharges mining wastes, while in other localities they barely reach 0.2 mg/kg dw. In other species, the mean concentration remains below 2 mg/kg dw, with the highest levels in filter-feeding molluscs such as *Venerupis aurea* (2.2 mg/kg dw; Marin-Guirao et al., 2008), *Ostrea edulis* (1.9 ± 0.5 mg/kg dw; De León et al., 1982; Marín-Guirao et al., 2008; Benedicto et al., 2009), *Pinna nobilis* (1.7 mg/kg fw; Rodríguez-Puente et al., 2001), or *Ruditapes decussatus* (1.1 mg/kg dw; María-Cervantes et al., 2009). These values are in the same order of magnitude as those found for *Venerupis* sp. in the small lagoon of Fondo Porto in Sicily (1.4 mg/kg dw; Signa et al., 2013).

The mean Cu concentration is also high in the molluscs *Hexaplex trunculus* (319.6 ± 33.7 mg/kg dw, De León et al., 1982), *Ostrea edulis* (106.2 ± 14.6 mg/kg dw; De León et al., 1982; Marín-

Guirao et al., 2008; Benedicto et al., 2009), and to a lesser extent, in the decapod *Palaemon serratus* ( $61.3 \pm 10.8 \text{ mg/kg dw}$ ; De León et al., 1982; Marín-Guirao et al., 2008) and the fish *Syngnathus abaster* ( $12.4 \text{ mg/kg dw}$ ; De León et al., 1982; Marín-Guirao et al., 2008). These high mean concentrations are all determined by the higher values in individuals sampled close to the wadi that discharges mining wastes, although in our work Cu is at present more related to the proximity to marinas. However, it is remarkable that Cu shows very low values in a very active sediment-eating detritivore like *Holothuria poli*, in which it only reaches concentrations of  $1.1 \pm 0.1 \text{ mg/kg dw}$  (León et al., 2021). In fish, in general, the mean value for Cu is  $4.3 \pm 0.7 \text{ mg/kg ww}$ . In the Mar Menor, the mugilid *Chelon auratus*, for example, reached  $2.8 \pm 4.9 \text{ } \mu\text{g/g dw}$  (De León et al., 1982; Fernández et al., unpublished data), a value lower than the maximum measured in this group of fish in the Manzala lagoon, in Egypt ( $5.4 \text{ mg/kg dw}$ ), Fogliano ( $4.5 \text{ mg/kg ww}$ ) or the Gulf of Gabes in Tunisia ( $6.3 \text{ mg/kg dw}$ ), but higher than in Caprolace ( $0.7 \text{ mg/kg ww}$ ) (Leone et al., 2020).

Hg levels are much lower than those detected in most other lagoons. The highest value in the Mar Menor is found again in *Hexaplex trunculus* ( $0.1 \text{ mg/kg dw}$ , De León et al., 1982), and in the grey mullet *Chelon auratus* ( $0.01 \text{ mg/kg dw}$ ), while, in Sicilian lagoons the same species (named as *Liza aurata*) reaches  $4.1 \text{ mg/kg ww}$ , and in Ghar El Melh in Tunisia *Mugil cephalus* reaches  $0.3 \text{ mg/kg dw}$  (Leone et al., 2020).

Pb also reaches high levels in filter-feeding molluscs with an average for the different species studied in the Mar Menor of  $572.2 \pm 318.7 \text{ mg/kg dw}$  (De León et al., 1982; Rodríguez\_Puente, 2001; Marín-Guirao et al., 2008; Benedicto et al., 2009). However, this value is significantly lower in fishes in general ( $5.4 \pm 1.4 \text{ mg/kg dw}$ ), being  $2.3 \pm 2.6 \text{ mg/kg dw}$  in *Chelon auratus* and  $3.5 \pm 0.5 \text{ mg/kg dw}$  in *Mugil cephalus* (De León et al., 1982; Sánchez Bassols, 2008; Fernández et al., unpublished), values lower than or similar to those found in the grey mullet *Liza ramada* from El Serv lagoon ( $5.0 \pm 6.2 \text{ mg/kg dw}$ ), and to those found in *L. ramada* and *Mugil cephalus* in Manzala in Egypt ( $4.6 \pm 6.2 \text{ mg/kg dw}$  and  $3.15 \text{ mg/kg dw}$ , respectively) (Leone et al., 2020).

In the Mar Menor, benthic macrophytes appear to have a high capacity to accumulate metals. Pb concentrations in *Cymododea nodosa* reaches on average  $1348.24 \text{ mg/kg dw}$ , Zn can reach up to  $7047 \text{ mg/kg dw}$ , and Cd up to  $9.4 \text{ mg/kg dw}$  (Sanchiz et al., 2000; Marín-Guirao et al., 2005b, 2008; Serrano et al., 2019). These levels are much higher than the maximum levels

found, for example, in *C. nodosa* in the Tunisian waters or in the Bizerte lagoon, where 190 µg/g dw of Pb and 257 µg/g dw of Zn are reached, and in Ghar El Melh lagoon reaching 123 µg/g dw of Pb and 240 µg/g dw of Zn, or in the Thesalonika Gulf, where 561.9 µg/g dw dw of Mn, 342.7 µg/g dw of Zn, 44.9 µg/g dw of Cu, 18.24 µg/g dw of Pb or 0.86 µg/g dw of Cd are reached (Malea et al., 2013). However, the concentration of Cd in the same species reaches 12 mg/kg dw in Bizerte (Zakhama-Sraieb et al., 2019), with this lagoon having similar concentrations of this metal in sediments as the Mar Menor. In fact, unlike Pb, despite the high concentration found in this plant, Cd shows a very low bioconcentration factor in *Cymodocea nodosa* in the Mar Menor (0.12). For other metals, the bioconcentration factors reported also for this species in the Thesalonika Gulf by Malea et al. (2013), up to 3.4 for Mn, 2.85 for Zn, 2.6 for Cu, 0.92 for Pb, 0.95 for Co and between 17.4 and 78 for Cd, except for Cd, are similar to those calculated in our work for this species in the Mar Menor.

Mn levels (1186.75 mg/kg) found in the phanerogam *Cymodocea nodosa* in the Mar Menor are also high, but lower than those found in other macrophytes in Brazilian lagoons such as Piratininga and Itaipu, the first one receives large amounts of untreated organic wastes and suffer frequent episodes of anoxia and high concentrations of H<sub>2</sub>S, while the second is better connected to the sea and only suffer anoxia in the deepest area (Drude de Lacerda et al., 1992). In Piratininga, *Ruppia maritima* reached concentrations of 1800 mg/kg and *Cladophora* sp. of 2900 mg/kg, while in Itaipu, *Chara* sp. reached Mn concentrations of up to 10,400 µg/g. In fact, in general, the highest concentrations of heavy metals in macrophytes were observed in Itaipu, a lagoon that presented the lowest total metal content but a higher fraction of metals weakly bound to sediments, showing that low redox potential was the main variable that maintains metals in non-bioavailable forms, possibly as refractory sulfides and metal-organic complexes (Drude de Lacerda et al., 1992).

Regarding the Cu, it has been detected in concentrations of 30.20 mg/kg dw in *C. nodosa* in the Mar Menor, having found values of 22 mg/kg dw in Bizerte and Ghar El Melh lagoons, although this metal can reach concentrations in the same species of 193.5 mg/kg dw in harbour areas (Zakhama-Sraieb et al., 2019).

In the case of the benthic algae *Caulerpa prolifera*, the idea of the high capacity of macrophytes to accumulate Pb is reinforced, having provided data of Pb in average of 526.5 ± 257.4 mg/kg dw for this species in the Mar Menor (Sanchiz et al., 2000; Benedicto et al., 2009).

In general, despite the high values found in the sediments, it is not easy to find a pattern in the comparisons of the concentrations of Cd, Cu, Pb and Zn in the biota of the Mar Menor, with respect to those reported in other areas.

In fact, such comparisons should be taken with caution. For example, the highest values given for *C. nodosa* by Marín-Guirao et al. (2008) in the Mar Menor correspond to the biofilm, not the plant itself, which has values one order of magnitude lower, and most papers in the literature do not usually specify the degree of epiphytism found in their specimens or whether epiphytes are removed prior to analysis. Furthermore, in the Mar Menor studies there is a marked tendency to sample at the mouth of the watercourse through which the mining waste entered directly and which continues to transport heavy metals during heavy rainfall events. But these data cannot be generalised to the whole lagoon. Finally, some works express the metal content of the fauna without specifying whether the individuals have been previously eviscerated and the remains of sediment in the digestive tract removed.

In any case, the detection of elevated concentrations in organisms should be a warning of potential risks, but these should be considered with due caution. In general, as expected, in contaminated areas the Cu concentration in species such as *Capitulum mitella*, *Balanus amphitrite* or *Semibalanus balanoides* can reach values of 545 µg/g dw, 3472 µg/g dw and 3750 µg/g dw, respectively, but in supposedly uncontaminated regions Cu levels can also be relatively high, for example, in the copepod *Anomalocera patersoni*, it can also reach high values, such as 41.9 µg/g dw. Similarly, the amphipod *Orchestia gammarellus* can reach concentrations of 397 µg/g dw and 139 µg/g dw of Zn and Cu respectively, in heavily polluted areas such as Restrongue Creek, England, but in remote, sparsely populated and supposedly uncontaminated areas such as Millport, Scotland, values of 188 µg/g dw and 77.5 µg/g dw in *Orchestia gammarellus*, or 80.6 µg/g dw and 110 µg/g dw in *Palaemon elegans* (Rainbow, 2002), have also been detected, respectively for the same metals.

Therefore, an important consideration could be that toxicity is related to a threshold concentration of metabolically available metal and not to the total concentration of accumulated metal (Rainbow, 2002). Thus, the transfer of trace metals in the food chain can be significant for aquatic invertebrates, but this transfer is controlled not only by the amount of accumulated metal in the prey, but also by its physicochemical form, which in turns results from the physiological detoxification process favoured by the prey species (Rainbow, 2002).



This could explain the general decreasing trend of the bioconcentration factor in the Mar Menor at the higher trophic levels of the food web.

In addition, metal uptake by organisms can be very different depending on substrate or water column conditions, independently of the concentration of metals. In fact, laboratory experiments on the passive assimilation of Cu and Zn by dead *C. nodosa* plants have showed that metal uptake can be very different depending on the environment conditions, independently of the concentration in the water solution (Sánchez et al., 1999). The results showed that the pH of the solution significantly affected the uptake, increasing as pH decrease and being maximum at a pH value of 4.5. In addition, competitive uptake takes place, with Cu absorbing preferentially to Zn (Sánchez et al., 1999).

In this context, the behaviour of each metal can be different. It has also been shown that the formation of metal sulphides and complexation by organic complexes are very important aspects in terms of toxicity reduction. Cu is mainly associated with the oxidisable phase while Zn and Pb are mainly associated with the reducible phase (Fernandes, 1997). Kouassi et al. (2018) also observed that Cu, Pb, Co, and Ni mainly formed inert complexes in sediments, while Zn formed labile complexes. Because of this, both works consider Zn as the element with a higher risk to biota in their respective studies (Fernandes, 1997; Kouassi et al. 2018). Kouassi, et al. (2018) also considered Co and Ni to pose a medium risk, and Cu and Pb a low risk in Ebrie Lagoon in Côte d'Ivoire.

Low redox potential has also been considered the main variable maintaining metals in non-bioavailable forms, possibly as refractory sulphides and metal-organic complexes in sediments from two coastal lagoons in Rio de Janeiro, Brazil (Drude de Lacerda et al, 1992).

Similarly, within the Antinioti lagoon on the island of Corfu in Greece, it was found that Cd and Zn bound to large particles were less prone to desorption than smaller ones, and so were effectively captured. In sediments, diagenetic processes were responsible for post-depositional changes in the forms of metals (particularly Fe, Mn, and Cd). Thus, any interventions introducing changes in the physico-chemical conditions may result in the release of metals, with negative implications on the ecological quality of the lagoon (Botsou et al., 2019).

The importance of sediment structure has also been shown in the Po Delta lagoons, where the percentage of fine particles ( $d < 16 \mu\text{m}$ ), strongly influenced the concentrations of some trace elements (Cu, Pb, Zn), while others such as As, Cr, Hg or Ni, were less dependent on grain-size distribution. In this case, it was considered that Ni may be of ecotoxicological concern due to its potential mobility and that, therefore, changes in redox conditions because of hypoxia/anoxia episodes may induce release of Ni from sediments (Zonta et al., 2019).

The high concentrations of the different elements in the sediments after more than 3500 years of continuous inputs of heavy metals from mining in the Mar Menor contrast with their low impact on the food web, which shows decreasing BCFs as one moves up the trophic level. This highlights the extraordinary ecosystem service provided by the lagoon ecosystem, retaining heavy metals in the sediments and preventing their transmission and bioaccumulation through organisms, preserving human health and allowing the exploitation of fisheries, fish being the main resource exploited.

Despite the fundamental role of the processes involved in this service, the mechanisms by which it takes place are insufficiently studied. It would be very important to know in greater detail the biogeochemical processes that determine the biosolubility of metals in a complex environment involving the differential uptake of vegetation, from microphytobenthos to macroalgae and phanerogams, the differential role played by organic matter at different levels of oxygen or sulfide concentration and redox conditions, and their interaction with carbonates and iron present in the sediments.

Many of these components operate synergistically, but others are antagonistic and the predominance of one over the other can be a determinant of potential risks to organisms and human health. Only with a detailed understanding of these processes can the real risk of sediment dredging and coastal works for the maintenance of beaches or port infrastructures be assessed.

Despite the social denunciation of the effects of mining activity on the quality of life in the lagoon in the 1950s (Pérez-Beltrán, 1953; Pérez-Ródenas, 1953; Lozano, 1953), this concern was diluted after the dumping stopped in the Mar Menor in the 1960s and after the cessation of mining activity in the 1970s. Indeed, in the work of Velasco et al. (2016) it does not appear

among the risks to the ecological integrity of the ecosystem and the goods and services it provides, considered by stakeholders.

However, as shown in this paper, scientific concern about the effect of accumulated waste on soils and sediments has remained present, and possible remediation measures have even been analysed, such as the possibility of using microalgae consortia in photobioreactors for the removal of heavy metals (Gil-Izquierdo et al., 2021).

Although in the process of building governance plans, mining wastes are among the environmental pressures to consider and measures for environmental recovery of ancient mining areas and forestation of mountain ranges against erosion are mentioned (García-Ayllón, 2018), the priority of actions is mainly focused on agricultural uses due to the problems of eutrophication that became socially visible in 2016. The practically inexistent incidence of harmful effects derived from heavy metals among the residents and visitors of the Mar Menor has most probably influenced the fact that since the direct discharges into the lagoon ceased, during many years there have been no claims or relevant social issues and that potential risks have not been seriously considered in the management policies of the Mar Menor. However, scientific interest has been maintained over the years and recently, with the change in the trophic status of the lagoon, social concern has been revived, although health concern has focused more on the effect of mining waste soils on the populations settled on the slopes of the mining mountain range. As a result, some actions have started to be considered, and the Law 3/2020, on the “Recovery and protection of the Mar Menor” (LRPMM, 2020) includes an article on “mining ordination and management” (Art. 75) which provides for the identification, decommissioning and restoration of abandoned mining facilities and sites affected by metallic mining with potential environmental impact for the Mar Menor, with three lines of action, on mining structures and facilities, on soils contaminated by mining in the vicinity of population centres, and on runoff of heavy metals in wadis discharging into the Mar Menor. In addition, the law establishes surveillance, control and monitoring networks, including control of the presence of heavy metals in fish. However, until now, the various regulations and tools of environmental protection that exist have not worked properly to avoid the increasing impacts on this enclosed coastal lagoon, where the pressures that it has been suffering from human activity throughout its history (mining, mass tourism, construction of ports and coastal infrastructures, dredging of sediments and sand dumping, enlargement of communication

channels with the open sea, agriculture) have added to the previous ones, rather than replacing each other. In this context, some years ago it was developed an Integrated Territorial Investment (ITI) of the Mar Menor, as an innovative model of integrated strategy for coastal zone management (ICZM) to overcome the shortcomings of previous management systems and a new model of comprehensive governance of the lagoon and its watershed (García-Ayllón, 2018), but not much progress has been made since then, in an environment more concerned with ideologies and political interests than with management.

## 5. Conclusions

The current configuration of the Mar Menor coastal lagoon began after a process of drying 6500 years ago and went through a first phase of increased currents or runoff in the inner area of the lagoon and increased sedimentation in the area close to the sea. This period lasted until 4300 years BP, once the formation of the sandy bar that separates it from the Mediterranean were completed. From then on, there was a progressive increase in marine influence, which culminated around 4200 years BP. Since then, a lagoon configuration like the present one can be assumed, with different degrees of marine influence and alternating periods of greater sedimentation of fine materials with peaks in the periods 3,950-3,100 yrs BP and 950-150 yrs BP. The marine influence, associated with storms, has been increasing in the last thousand years, and in particular in the last 200 years, where human interventions on the sand bar, creating or enlarging communications channels with the open sea, have been added.

Sedimentation rates are associated, throughout the history of the lagoon, with Al and Fe inputs, as well as other indicators of terrigenous inputs (Ti, Nb, Si/Al, Fe/Al) and coincide with the isolation of the lagoon from the open sea and periods of deforestation in the Argaric period and the beginning of Roman colonisation, and the intensification of mining activity in the 17th and 19th centuries. A recent peak in sedimentation rates, no longer associated with terrigenous inputs, is related to sand dumping works on the beaches during the last 30 years.

High Fe/Al, Ti/Al and Zr/Al ratios identify periods of mining activity, being related to high concentrations of Pb and Zn, while periods of arid climatic conditions and deforestation that would increase erosion processes in the drainage basin are determined by high Zr/Rb and, at a lesser extent Zr/Al and Si/Al ratios and to increased concentrations of silt. Inputs of Pb, Zn

and Cd originate from mining activity and their highest concentrations are located in the vicinity of the wadis coming from the mining mountain range. The higher solubility of Cd makes it the heavy metal associated with mining with the highest recent dispersion throughout the lagoon and the only one that continues to increase in concentration, due to the continuous scouring of soils in the mining basin.

The first increases in Pb levels in the sediments, which would be linked to the first intensive mining operations, are detected as early as 1460 BC, in the late Argar period, and are consolidated around 1380 BC, then decrease to increase significantly again towards 290 BC after the Roman conquest of Cartago Nova, with intensive activity between 275 BC and 50 BC. Finally, the maximum levels are reached with the mining exploitations of the industrial era between 1855 and 1967 and, since then, they have been decreasing to the present day. However, sedimentological data show increases in Zn levels as early as 3600 BC and in the Early Bronze Age, around 2300 BC and continuing until 1500 BC, which could indicate incipient mining activity earlier than previously assumed.

Cu appears to be closely linked to nautical ports activity and its use in antifouling paints. This explains its remarkable increase and distribution in the period 2002-2015 and its decrease in 2016-2021 following the ban on its use for this purpose. As and Hg are pollutants without a clear origin and with a different time pattern, which need special monitoring because of the health risks they may pose.

The dynamics and distribution of heavy metals in the lagoon sediments is the result of inputs associated with human activities that generate them (mining and port activity), climatology (which determines surface dragging by runoff during episodes of rain), coastal works (with the contribution of the dredging of mud and sand, which mobilise metals from the lower strata or bury the upper layers of sediment), and the redistribution within the lagoon due to hydrodynamics. Changes in bathymetry detected in recent surveys also suggest erosion and redistribution of surface sediments. Sediments inputs for beaches regeneration or increased sedimentation rates due to rainfall since the cessation of mining activity explain the progressive decline in metals concentration such as Pb in the upper sediment layer, even though there are still inputs of mining metals due to the entrainment of minerals from tailings remaining in the bed of the wadis in the south of the lagoon, increased by the clearing of land for agricultural use in recent years in an area relatively affected by former mining.

Eutrophication process, and the associated dynamics of macrophyte meadows with the increase of organic matter in the sediments, or the recovery of ecological balances and re-oxygenation of the sediment surface layer and recolonisation of the bottom by fauna, may influence the mobility of some metals, such as As, favouring their dispersion or retention, respectively.

The relatively low bioconcentration factor found across the trophic levels of the Mar Menor lagoon food web suggests that the lagoon provides an important ecosystem service by retaining heavy metals in the sediment, largely preventing their bioavailability, but the high concentration accumulated in the sediments and found in some specimens in the literature, especially in individuals collected in the vicinity of the main source of mining waste input, shows that there is a real risk. The behaviour and bioavailability of metals is highly dependent on the redox conditions, pH, organic matter content and grain size structure of the sediment, and these effects may be different depending on the metals. Therefore, inadequate beach management and dredging or resuspension of sediment indiscriminately or with inappropriate methods or timing can have significant consequences. The consideration of biogeochemical processes in management decisions is essential to not alter the conditions that allow the low solubility and bioavailability of metals.

There is still much work to be done to understand the biogeochemical processes that determine the bioavailability and bioconcentration or detoxification mechanisms of metals in a complex environment in which many factors operate synergistically, but others are antagonistic. Part of this knowledge could be obtained from the meta-analysis of the numerous works published in different coastal lagoons, estuaries and marine environments but, given the large number of factors involved, studies will also be necessary in mesocosms where the different environmental conditions of the water column and the sediment, or the very biological communities that contribute to the bioturbation of the sediments or to the assimilation processes, can be controlled in experimental designs. Only with detailed knowledge of these processes will it be possible to assess the real risk of human interventions in areas sensitive to heavy metal contamination and design adequate prevention or restoration measures.

## Acknowledgements

This work is a tribute to Professor Alberto Barba Navarro, active researcher in many of the projects that have made possible our studies on pollutants in the Mar Menor lagoon, as well as Juan Pérez Ródenas, Angel Pérez Beltrán and Juan José Lozano, for their defense of the Mar Menor against mining spills in the 1950s.

The sediment collection and lab work has been supported by different projects over the years, including “Mar Menor Coastal Monitoring System” (Science and Technology Plan of the Region of Murcia 2007-2010), “Ecological status and vulnerability of aquatic ecosystems to climate change: biological, ecological and functional indicators for monitoring the adaptation of macrophytes to stress, ECOLIFE” (CGL2008-05407-CO3-01, R+D+I Spanish National Plan 2008-2011), “Response of the trophic web of a coastal lagoon to nutrient inputs, EUTROCOST” (CGL2004-06891/BOS), “The role of connectivity in maintaining the genetic structure and trophic web of coastal marine populations and communities, CONNECTMAR” (CTM2014-56458-R, R+D+I Spanish National Plan, “Erosion/Submersion during Storm Events in the Western Mediterranean Coastal Region” (MISTRALS PALEOMEX project), “Mobile Oceanographic Observatory of the Region of Murcia, OOMUR” (2I18SAE00056 RIS3Mur Strategy of the Region of Murcia and the European Union, and “Monitoring and predictive analysis of the ecological state evolution of the Mar Menor lagoon ecosystem and prevention of impacts 2020-2022” financed by the General Directorate of the Mar Menor of the Region of Murcia. We thank Philippe Martinez from the Laboratoire Environnements et Paléoenvironnements Océaniques et Continentaux at the University of Bordeaux for the XRF analyses (PACS platform). We also acknowledge the Club Náutico de Lo Pagán for their harbour facilities. We express our gratitude to all members, current and former, of the University of Murcia ECOSISTCOST research group who collaborated in the data collection over the last 25 years, and to the participants of the coring expedition, particularly E. Regnier (Technician, LSCE – IPSL, Paris).

## Authors contribution statement

**Angel Pérez-Ruzafa:** Conceptualization, Investigation, Formal analysis, Data Curation, Supervision, Writing Original draft, Projects management and administration, Funding

acquisition, Review, Editing & Validation. **Concepción Marcos:** Formal analysis, Supervision, Writing Original draft, Projects administration, Funding acquisition, Validation, Writing, Review & Editing; **Laurent Dezileau:** MISTRALS PALEOMEX project funding acquisition and administration, Review, Editing & Validation; **María José Martínez-Sánchez:** Investigation, heavy metal analyses and validation; **Carmen Pérez-Sirvent:** Investigation, heavy metal analyses and validation; **María Pérez-Marcos:** Bibliographic data collection, curation and analyses, Review & Editing; **Ulrich von Grafenstein:** Investigation, MISTRALS PALEOMEX cores analyses.

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Supplementary material

## Appendix A

Experimental conditions and instrumental parameters for the samples analysed by FAAS, ETAAS and HG-AFS

Table A.1. Experimental conditions and instrumental parameters for the samples analysed by FAAS.

Parameter and/or condition	Zn	Cd	Pb	Cu	Fe
wavelength (nm)	213.9	228.8	217.0	324.8	248.3
Slit width (nm)	0.7	0.7	0.7	0.7	0.2
Calibration (mg l <sup>-1</sup> )	0.5-2	0.5-2	5-20	1-5	1-5
Air-Acetylene Flow	7.9- 1.2	5.4-1.9	5.4-1.9	6.3-1.3	6.3-1.8

Table A.2. Experimental conditions and instrumental parameters for the samples analysed by ETAAS.

Parameter and/or condition	Cd	Pb	Cu
wavelength (nm)	228.8	217.0	324.8
Slit width (nm)	0.5	0.5	0.5
background correction	D2	D2	D2
Atomizer	Platform	Platform	Wall
Injection volume (μl)	10	10	10
Calibration (μg l <sup>-1</sup> )	0.5-5	10-100	10-100

Table A.3. Heating program for Cd, Pb and Cu in ETAAS

	Stage	Temperature (°C)	Ramp (°C s <sup>-1</sup> )	Hold time (s)
Cd	1	300	20	15
	2	1700	4	4
	3	2700	3	3
Pb	1	300	20	15
	2	1700	4	4
	3	2700	3	3
Cu	1	400	20	8
	2	800	20	15
	3	2100	0	3
	4	2300	0	3

Experimental conditions and instrumental parameters for the determination of As by GH-AFS

Parameter and/or condition	
wavelength (nm)	197.3
Current intensity (primary) (mA)	27.5
Current intensity (Boost) (mA)	35
Injection volume (ml)	2
Waiting time (s)	15
Measurement time (s)	30
Memory time (s)	30
Measurement mode	peak height
Ar flow (ml min <sup>-1</sup> )	300

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Calibration ( $\mu\text{g l}^{-1}$ )	50-300
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Detection limits (DL) for the samples analysed by FAAS, ETAAS and HG-AFS.

	DL	Units
Fe	0.3	ppm
Cu	10.00	ppb
Cd	0.20	ppb
Pb	10.00	ppb
Zn	0.05	ppm
As	0.30	ppb

Quantification limits (QI) for microwave digestion samples analysed by FAAS, ETAAS

	QI	Units
Fe	150	ppm
Cu	5000	ppb
Cd	100	ppb
Pb	5000	ppb
Zn	25	ppm
As	150	ppb

## Appendix B

Figure B.1. Cluster analysis of the geochemical variables considered from the Spearman Rank correlation matrix performed on the MM2 core, and correlograms of the pairs of variables with correlations higher than 0.5 and significance level  $p < 0.05$ . Samples on the x-axis are ordered chronologically from left (present) to right (6,500 yrs BP).

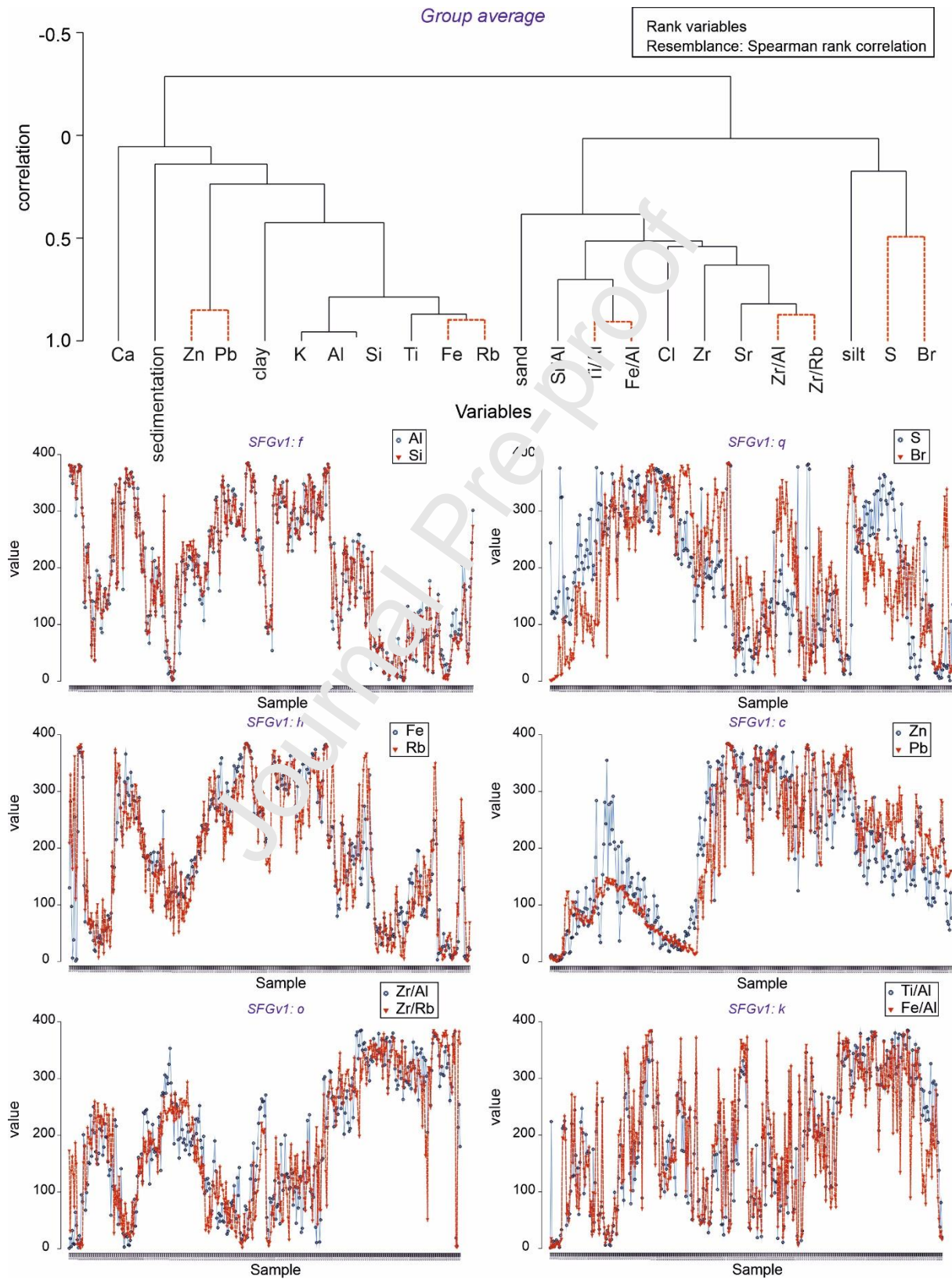
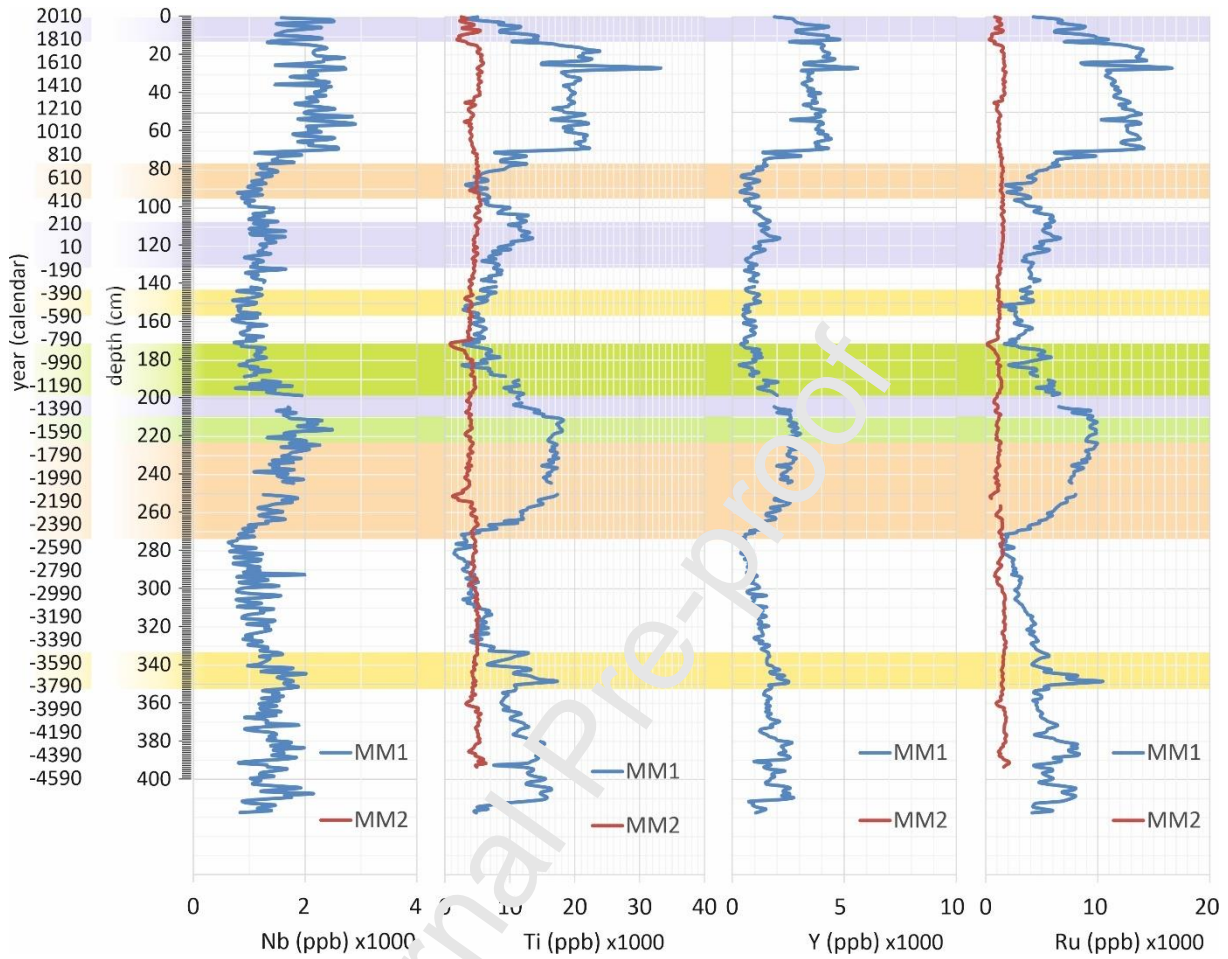


Figure B.2. Down-core variations in concentration of Nb, Ti, Y and Rb, used as indicators of terrestrial inputs under aridic warm conditions.



## Appendix C

Table C.1. Results of the Simper analyses performed on the normalized data matrix of elements concentration, elemental ratios and sedimentation rates, showing the variables that most contribute to the differentiation in sediment characteristics between environmental conditions.

Group Undefined					
Average squared distance = 20.75					
Species	Av.Value	Av.Sq.Distance	Sq.Distance/SD	Contrib%	Cum.%
Fe/Al	-0.0911	0.2	0.19	0.96	0.96
Zn	-0.0995	0.246	0.15	1.19	2.15
Pb	-0.0759	0.39	0.29	1.88	4.03
Sedimentation rate	-0.289	0.542	0.43	2.61	6.64
Ti/Al	-0.0589	0.563	0.14	2.71	9.35
Br	-0.0965	0.741	0.35	3.57	12.92
Sr	-0.134	0.745	0.35	3.59	16.51
Zr/Al	-0.0449	0.746	0.13	3.59	20.1
S	-0.163	0.757	0.46	3.65	23.75
Al	0.0074	0.83	0.32	4	27.75
clay	0.0192	0.922	0.45	4.44	32.19
Zr	-0.0547	0.927	0.53	4.46	36.65
Cl	-0.106	0.94	0.49	4.55	41.21
K	0.0205	0.978	0.38	4.71	45.92
Ca	0.0155	1.02	0.41	4.93	50.85
Zr/Rb	-0.133	1.1	0.4	5.31	56.16
Si	0.121	1.15	0.29	5.56	61.72
sand	-0.0734	1.17	0.45	5.65	67.37
Fe	0.0205	1.22	0.4	5.87	73.24
Group Mining					
Average squared distance = 39.04					
Species	Av.Value	Av.Sq.Distance	Sq.Distance/SD	Contrib%	Cum.%
Si/Al	0.195	0.124	0.13	0.32	0.32
Sedimentation rate	0.149	0.158	0.5	0.4	0.72
Si	-0.316	0.333	0.45	0.85	1.58
Al	-0.232	0.404	0.43	1.04	2.61
K	-0.128	0.496	0.48	1.27	3.88
Ti	-0.013	0.525	0.5	1.34	5.23
Rb	0.0106	0.679	0.49	1.74	6.97
silt	-0.35	0.751	0.46	1.92	8.89
Fe	0.142	0.773	0.46	1.98	10.87
clay	-0.372	0.812	0.52	2.08	12.95
Zr/Rb	0.131	0.876	0.42	2.24	15.19
sand	0.398	0.894	0.47	2.29	17.48
Ca	-0.264	0.985	0.49	2.52	20
Zr	0.124	1.1	0.56	2.81	22.81
Cl	0.227	1.13	0.56	2.88	25.7
S	0.205	1.26	0.55	3.22	28.91
Sr	0.363	1.65	0.5	4.22	33.13

Br	0.524	2.63	0.38	6.75	39.88
Zr/Al	0.209	2.98	0.12	7.63	47.51
Ti/Al	0.547	4.33	0.13	11.1	58.61
Pb	1.16	4.38	0.35	11.22	69.83
Zn	0.987	5.6	0.34	14.35	84.18

## Group vegetation degradation

Average squared distance = 19.66

Species	Av.Value	Av.Sq.Dist	Sq.Dist/SD	Contrib%	Cum.%
Zn	-0.207	0.0135	0.52	0.07	0.07
Si/Al	-0.195	0.0717	0.24	0.36	0.43
Pb	-0.268	0.0929	0.35	0.47	0.91
Fe/Al	-0.0988	0.182	0.33	0.92	1.83
Ti/Al	-0.107	0.391	0.31	1.99	3.82
Br	-0.147	0.431	0.46	2.19	6.01
Rb	-0.041	0.661	0.43	3.36	9.37
Fe	-0.017	0.711	0.46	3.61	12.98
silt	-0.00543	0.72	0.45	3.66	16.64
sand	0.00369	0.74	0.44	3.76	20.41
Zr/Rb	0.129	0.759	0.4	3.86	24.27
Zr/Al	-0.00306	0.808	0.28	4.11	28.37
clay	0.00274	0.855	0.51	4.35	32.73
Cl	0.104	0.901	0.52	4.58	37.31
Ti	0.054	0.902	0.49	4.59	41.89
Sr	0.0204	1.06	0.34	5.4	47.29
Si	0.0861	1.19	0.47	6.04	53.33
S	0.232	1.2	0.55	6.11	59.44
Zr	0.142	1.21	0.54	6.14	65.58
Ca	0.281	1.27	0.53	6.44	72.02

## Group sand bar closure

Average squared distance = 10.71

Species	Av.Value	Av.Sq.Dist	Sq.Dist/SD	Contrib%	Cum.%
Pb	-0.397	0.0033	0.5	0.03	0.03
Zn	-0.262	0.00441	0.32	0.04	0.07
Si/Al	-0.223	0.02	0.29	0.19	0.26
Ti	-0.52	0.035	0.37	0.33	0.59
Si	-0.505	0.0419	0.53	0.39	0.98
Fe	-0.473	0.0438	0.41	0.41	1.39
K	-0.465	0.0512	0.46	0.48	1.86
Rb	-0.491	0.0676	0.42	0.63	2.5
Al	-0.436	0.077	0.53	0.72	3.21
Fe/Al	-0.108	0.0894	0.32	0.83	4.05
Ca	-0.395	0.184	0.38	1.72	5.76
Ti/Al	-0.184	0.258	0.33	2.41	8.18
silt	0.148	0.389	0.42	3.63	11.81
Sedimentation rate	-0.107	0.474	0.5	4.43	16.24
Zr/Al	-0.0385	0.5	0.42	4.67	20.91
Zr	-0.385	0.571	0.49	5.34	26.24



sand	-0.371	0.753	0.48	7.03	33.27
Br	-0.117	0.85	0.51	7.94	41.21
Sr	0.00964	0.94	0.51	8.78	49.99
S	-0.234	0.961	0.47	8.97	58.96
Cl	-0.124	1.17	0.49	10.97	69.93
Zr/Rb	0.145	1.31	0.49	12.24	82.17

Group vegetation recovery

Average squared distance = 17.82

Species	Av.Value	Av.Sq.Dist	Sq.Dist/SD	Contrib%	Cum.%
Pb	-0.385	0.00875	0.31	0.05	0.05
Si/Al	-0.23	0.0123	0.41	0.07	0.12
Zn	-0.217	0.015	0.52	0.08	0.2
Fe/Al	-0.0842	0.0623	0.36	0.35	0.55
Ti/Al	-0.0851	0.146	0.38	0.82	1.37
Zr/Al	-0.00078	0.407	0.47	2.28	3.65
silt	-0.0773	0.503	0.51	2.82	6.48
sand	0.123	0.514	0.52	2.88	9.36
Ca	-0.00176	0.603	0.51	3.38	12.74
clay	-0.203	0.665	0.49	3.73	16.47
Zr/Rb	0.229	0.672	0.43	3.77	20.25
Rb	0.0442	0.945	0.5	5.31	25.56
Si	-0.073	0.971	0.46	5.45	31.01
Br	0.204	0.989	0.52	5.55	36.56
Zr	0.133	1.03	0.57	5.8	42.35
Cl	0.179	1.08	0.54	6.07	48.42
Ti	0.0365	1.1	0.47	6.19	54.6
Fe	0.0536	1.17	0.47	6.58	61.19
Sr	0.22	1.22	0.48	6.86	68.05
S	0.36	1.25	0.56	7.03	75.08

Undefined & mining

Average squared distance = 65.21

Variable	Average squared distance = 65.21		Av.Sq.Dis t	Sq.Dist/SD	Contri b%	Cum. %
	undefined	mining				
Zn	-0.0995	0.987	6.97	0.38	10.68	10.68
Fe/Al	-0.0911	0.628	6.82	0.13	10.46	21.15
Pb	-0.0759	1.16	6.25	0.41	9.59	30.73
Ti/Al	-0.0589	0.547	5.21	0.15	8	38.73
Zr/Al	-0.0449	0.209	3.75	0.14	5.76	44.49
Br	-0.0965	0.524	3.73	0.5	5.72	50.2
Sr	-0.134	0.363	2.62	0.7	4.02	54.22
sand	-0.0734	0.398	2.28	0.79	3.49	57.71
silt	0.0819	-0.35	2.21	0.81	3.39	61.1
Cl	-0.106	0.227	2.17	0.9	3.32	64.42
S	-0.163	0.205	2.13	0.87	3.27	67.69
Ca	0.0155	-0.264	2.07	0.66	3.18	70.87

undefined & degraded vegetation

Average squared distance = 41.69

Variable	Average squared distance = 41.69		Av.Sq.Dis t	Sq.Dist/SD	Contri b%	Cum. %
	undefined	degraded vegetation				

Variable	Av.Value	Av.Value	Av.Sq.Dis t	Sq.Distance/SD	Contri b%	Cum. %
Sedimentation rate (mm/yr)	-0.289	0.589	3.5	0.81	8.39	8.39
Al	0.0074	0.263	2.77	0.61	6.65	15.04
K	0.0205	0.157	2.39	0.69	5.73	20.77
Ca	0.0155	0.281	2.35	0.77	5.63	26.4
Si	0.121	0.0861	2.33	0.52	5.59	31.98
Zr	-0.0547	0.142	2.16	0.9	5.18	37.17
Ti	0.0422	0.054	2.11	0.63	5.07	42.24
S	-0.163	0.232	2.1	0.89	5.04	47.28
silt	0.0819	-0.00543	2	0.73	4.8	52.09
Si/Al	0.181	-0.195	1.96	0.18	4.71	56.79
Rb	0.0646	-0.041	1.96	0.62	4.69	61.48
Fe	0.0205	-0.017	1.92	0.63	4.61	66.09
Zr/Rb	-0.133	0.129	1.92	0.64	4.61	70.7

mining & degraded vegetation

Average squared distance = 64.60

Variable	Av.Value	Av.Value	Av.Sq.Dis t	Sq.Distance/SD	Contri b%	Cum. %
Zn	0.987	-0.207	6.98	0.37	10.8	10.8
Fe/Al	0.628	-0.0988	6.82	0.13	10.55	21.36
Pb	1.16	-0.268	6.47	0.41	10.01	31.37
Ti/Al	0.547	-0.107	5.1	0.15	7.9	39.26
Zr/Al	0.209	-0.00306	3.79	0.15	5.87	45.13
Br	0.524	-0.147	3.48	0.47	5.39	50.52
Sr	0.363	0.0204	2.8	0.68	4.33	54.86
Sedimentation rate (mm/yr)	0.119	0.589	2.54	0.92	3.93	58.78
Ca	-0.264	0.281	2.53	0.82	3.91	62.7
Al	0.232	0.263	2.52	0.59	3.91	66.6
S	0.205	0.232	2.44	0.92	3.77	70.37

undefined & sand bar closure

Average squared distance = 74.57

Variable	Av.Value	Av.Value	Av.Sq.Dis t	Sq.Distance/SD	Contri b%	Cum. %
clay	0.0192	0.851	3.48	0.9	10.12	10.12
Zr/Rb	-0.133	0.145	2.46	0.71	7.15	17.27
Cl	-0.106	-0.124	2.09	0.79	6.09	23.36
sand	-0.0734	-0.371	1.99	0.68	5.8	29.16
Si/Al	0.181	-0.223	1.93	0.18	5.62	34.78
S	-0.163	-0.234	1.7	0.75	4.94	39.73
Sr	-0.134	0.00964	1.68	0.68	4.9	44.63
silt	0.0819	0.148	1.67	0.68	4.84	49.47
Rb	0.0646	-0.491	1.66	0.47	4.84	54.31
Zr	-0.0547	-0.385	1.59	0.84	4.63	58.94
Si	0.121	-0.505	1.58	0.34	4.61	63.55
Br	-0.0965	-0.117	1.57	0.7	4.57	68.12
Ti	0.0422	-0.52	1.57	0.44	4.56	72.68

mining & sand bar closure						
Average squared distance = 58.82		mining	sand bar closure			
Variable	Av.Value	Av.Value	Av.Sq.Dis t	Sq.Distance/SD	Contri b%	Cum. %
Zn	0.987	-0.262	7.1	0.38	12.08	12.08
Pb	1.16	-0.397	6.76	0.42	11.5	23.58
Fe/Al	0.628	-0.108	6.74	0.13	11.45	35.03
Ti/Al	0.547	-0.184	5.07	0.15	8.63	43.66
clay	-0.372	0.851	4.17	0.86	7.08	50.74
Br	0.524	-0.117	3.85	0.51	6.54	57.28
Zr/Al	0.209	-0.0385	3.5	0.14	5.94	63.23
Sr	0.363	0.00964	2.67	0.76	4.55	67.77
Cl	0.227	-0.124	2.38	0.92	4.05	71.83
degraded vegetation & sand bar closure						
Average squared distance = 34.35		degraded vegetation	sand bar closure			
Variable	Av.Value	Av.Value	Av.Sq.Dis t	Sq.Distance/SD	Contri b%	Cum. %
clay	0.00274	0.251	3.44	0.87	10	10
Sedimentation rate (mm/yr)	0.589	-0.107	3.14	0.83	9.13	19.13
Al	0.263	0.436	2.44	0.54	7.11	26.24
S	0.232	-0.234	2.35	0.91	6.84	33.08
Cl	0.104	-0.124	2.09	0.86	6.1	39.18
Zr	0.142	-0.385	2.04	0.86	5.93	45.1
Zr/Rb	0.129	0.145	2.03	0.73	5.92	51.03
Sr	0.020	0.00964	1.97	0.59	5.74	56.77
Ca	0.281	-0.395	1.89	0.76	5.51	62.28
K	0.157	-0.465	1.83	0.59	5.33	67.61
sand	0.00369	-0.371	1.61	0.73	4.69	72.3
undefined & vegetation recovery						
Average squared distance = 39.4		undefined	vegetation recovery			
Variable	Av.Value	Av.Value	Av.Sq.Dis t	Sq.Distance/SD	Contri b%	Cum. %
K	0.0205	0.0778	2.48	0.67	6.24	6.24
Sedimentation rate (mm/yr)	-0.289	0.362	2.46	0.73	6.17	12.4
Fe	0.0205	0.0536	2.37	0.67	5.95	18.35
Ti	0.0422	0.0365	2.3	0.64	5.78	24.14
S	-0.163	0.365	2.27	0.89	5.69	29.83
Rb	0.0646	0.0442	2.22	0.67	5.57	35.4
Al	0.0074	0.0669	2.2	0.6	5.53	40.93
Si	0.121	-0.073	2.14	0.48	5.38	46.31
Cl	-0.106	0.179	2.09	0.87	5.24	51.55
Sr	-0.134	0.22	2.07	0.67	5.2	56.75
Zr	-0.0547	0.133	1.98	0.95	4.96	61.71
Si/Al	0.181	-0.23	1.93	0.18	4.85	66.56
Zr/Rb	-0.133	0.229	1.89	0.69	4.75	71.3

mining & vegetation recovery

Average squared distance = 61.60		mining	vegetation recovery			Contri	Cum.
Variable	Av.Value	Av.Value	Av.Sq.Dis t	Sq.Distance/SD	b%	%	
Zn	0.987	-0.217	7	0.38	11.37	11.37	
Pb	1.16	-0.385	6.73	0.42	10.93	22.3	
Fe/Al	0.628	-0.0842	6.68	0.13	10.84	33.14	
Ti/Al	0.547	-0.0851	4.83	0.14	7.84	40.98	
Br	0.524	0.204	3.68	0.53	5.97	46.95	
Zr/Al	0.209	-0.00078	3.39	0.13	5.5	52.46	
Sr	0.363	0.22	2.85	0.78	4.63	57.09	
S	0.205	0.365	2.5	0.93	4.06	61.15	
Cl	0.227	0.179	2.18	0.93	3.54	64.69	
Zr	0.124	0.133	2.1	0.95	3.41	68.1	
K	-0.128	0.0778	2.04	0.68	3.31	71.41	

degraded vegetation & vegetation recovery

Average squared distance = 37.54		degraded vegetation	vegetation recovery			Contri	Cum.
Variable	Av.Value	Av.Value	Av.Sq.Dis t	Sq.Distance/SD	b%	%	
Sedimentation rate (mm/yr)	0.589	0.362	3.73	0.89	9.94	9.94	
Al	0.263	0.0669	3.29	0.69	8.76	18.7	
K	0.157	0.0778	2.91	0.75	7.74	26.44	
S	0.232	0.365	2.44	0.93	6.51	32.95	
Sr	0.0204	0.22	2.3	0.63	6.12	39.07	
Zr	0.142	0.133	2.21	0.94	5.9	44.97	
Si	0.0861	-0.073	2.16	0.73	5.75	50.72	
Ti	0.051	0.0365	1.98	0.76	5.27	55.99	
Cl	0.104	0.179	1.96	0.89	5.23	61.22	
Ca	0.281	-0.00176	1.93	0.84	5.14	66.37	
Fe	-0.017	0.0536	1.86	0.73	4.97	71.33	

sand bar closure & vegetation recovery

Average squared distance = 32.29		sand bar closure	vegetation recovery			Contri	Cum.
Variable	Av.Value	Av.Value	Av.Sq.Dis t	Sq.Distance/SD	b%	%	
clay	0.851	-0.203	3.63	0.93	11.25	11.25	
S	-0.234	0.365	2.53	0.91	7.84	19.09	
Cl	-0.124	0.179	2.3	0.88	7.14	26.23	
Sedimentation rate (mm/yr)	-0.107	0.362	2.18	0.75	6.74	32.97	
Sr	0.00964	0.22	2.17	0.75	6.71	39.69	
Zr/Rb	0.145	0.229	1.95	0.77	6.04	45.73	
Br	-0.117	0.204	1.91	0.83	5.91	51.64	
K	-0.465	0.0778	1.85	0.56	5.73	57.37	
Zr	-0.385	0.133	1.84	0.94	5.71	63.08	
Al	-0.436	0.0669	1.7	0.53	5.26	68.34	

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sand	-0.371	0.123	1.49	0.87	4.6	72.95
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Table C.2. Results of the Permanova performed on the surface sediments on the matrix of heavy metals (Cd, Cu, Pb, Zn) using the factors Period (Pe) and zone (zo). Bold figures indicate significant differences ( $p < 0.05$ ). In pairwise tests, only significant and marginally significant (\*) results are showed.

Source	df	SS	MS	Pseudo-F	P(MC)
Pe	2	109.4	54.702	23.762	<b>0.0001</b>
zo	4	72.425	18.106	7.8652	<b>0.0001</b>
Pexzo	8	39.913	4.9892	2.1673	<b>0.0121</b>
Res	132	303.87	2.3021		
Total	146	611.46			

PAIR-WISE TESTS

Term 'Pexzo' for pairs of levels of factor 'zone'

Within level '1980s' of factor 'Period'

Groups	t	P(MC)
z1, z5	8.5072	<b>0.0001</b>
z2, z5	8.3616	<b>0.0001</b>
z3, z5	7.8838	<b>0.0001</b>
z4, z5	5.9635	<b>0.0001</b>

Within level '2002-2015' of factor 'Period'

Groups	t	P(MC)
z1, z3	2.761	<b>0.0025</b>
z1, z4	2.1413	<b>0.0013</b>
z1, z5	2.6681	<b>0.0048</b>
z2, z3	2.8077	<b>0.0037</b>
z2, z4	2.4968	<b>0.0043</b>
z2, z5	2.6765	<b>0.0071</b>

Within level '2016-2021' of factor 'Period'

Groups	t	P(MC)
z1, z3	2.7488	<b>0.0354</b>
z1, z5	2.3799	0.0535*
z2, z3	3.3865	<b>0.0106</b>
z2, z5	3.1753	<b>0.011</b>

Table C.3. Results of the SIMPER analyses performed on matrix of heavy metals (Cd, Cu, Pb, Zn) content in surface sediments, considering the factors Period x zone.

Groups 1980s & 2002-2015

Average squared distance = 9.74

Variable	1980s	2002-2015		Contrib%	Cum. %
	Av. Value	Av. Value	Sq. Dist/SD		
Pb	0.856	-0.321	3.16	0.9	32.4
Zn	0.736	-0.157	2.65	0.86	59.64
Cd	0.669	-0.571	2.38	1.2	84.08

Groups 1980s & 2016-2021

Average squared distance = 8.27

Variable	1980s	2016-2021		Contrib%	Cum. %
	Av. Value	Av. Value	Sq. Dist/SD		
Cu	0.391	-1.28	3.26	1.38	39.11
Zn	0.736	-0.262	2.23	0.78	66.41
Pb	0.856	-0.0612	2.01	0.75	90.71

Groups 2002-2015 & 2016-2021

Average squared distance = 9.53

Variable	2002-2015	2016-2021		Contrib%	Cum. %
	Av. Value	Av. Value	Sq. Dist/SD		
Cd	-0.571	0.954	3.7	0.99	38.8
Cu	0.0391	-1.28	2.96	0.62	69.9
Zn	-0.157	-0.262	1.49	0.63	85.52

Groups z1 & z2

Average squared distance = 4.61

Variable	z1	z2		Contrib%	Cum. %
	Av. Value	Av. Value	Sq. Dist/SD		
Cu	-0.122	-0.134	1.51	0.58	32.74
Cd	-0.303	-0.417	1.16	0.64	57.85
Zn	-0.377	-0.383	1.12	0.39	82.07

Groups z1 & z3

Average squared distance = 4.91

Variable	z1	z3		Contrib%	Cum. %
	Av. Value	Av. Value	Sq. Dist/SD		
Cd	-0.303	0.667	1.44	0.83	29.96
Pb	-0.402	0.599	1.35	0.97	58.13
Zn	-0.377	0.488	1.24	0.99	84.02

Groups z2 & z3

Average squared distance = 5.17

Variable	z2	z3		Contrib%	Cum. %
	Av. Value	Av. Value	Sq. Dist/SD		
Zn	-0.383	0.488	1.52	0.9	29.31
Cd	-0.417	0.667	1.51	0.95	58.56
Pb	-0.368	0.599	1.44	0.96	86.44

Groups z1 & z4

Average squared distance = 7.06

z1	z4
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Variable	Av.Value	Av.Value	Av.Sq.Dist	Sq.Dist/SD	Contrib%	Cum.%
Cu	-0.122	0.208	3.07	0.53	43.52	43.52
Cd	-0.303	0.318	1.46	0.98	20.73	64.25
Pb	-0.402	-0.014	1.34	0.71	19.03	83.28

Groups z2 & z4

Average squared distance = 7.74

	z2	z4				
Variable	Av.Value	Av.Value	Av.Sq.Dist	Sq.Dist/SD	Contrib%	Cum.%
Cu	-0.434	0.208	3.36	0.51	43.37	43.37
Zn	-0.383	0.0311	1.61	0.63	20.78	64.15
Pb	-0.368	-0.014	1.46	0.73	18.89	83.04

Groups z3 & z4

Average squared distance = 3.83

	z3	z4				
Variable	Av.Value	Av.Value	Av.Sq.Dist	Sq.Dist/SD	Contrib%	Cum.%
Cu	0.063	0.208	1.23	0.39	32.25	32.25
Pb	0.599	-0.014	1.19	0.87	31.06	63.31
Zn	0.488	0.0311	1	0.79	26.16	89.47

Groups z1 & z5

Average squared distance = 9.75

	z1	z5				
Variable	Av.Value	Av.Value	Av.Sq.Dist	Sq.Dist/SD	Contrib%	Cum.%
Zn	-0.377	1.05	3.34	0.98	34.26	34.26
Pb	-0.402	0.902	2.11	0.84	31.87	66.13
Cu	-0.122	0.266	1.71	0.76	17.57	83.7

Groups z2 & z5

Average squared distance = 9.31

	z2	z5				
Variable	Av.Value	Av.Value	Av.Sq.Dist	Sq.Dist/SD	Contrib%	Cum.%
Zn	-0.383	1.05	3.53	0.93	37.94	37.94
Pb	-0.368	0.902	2.9	0.78	31.18	69.11
Cd	-0.417	0.336	1.48	0.8	15.85	84.96

Groups z3 & z5

Average squared distance = 6.04

Variable	Av.Value	Av.Value	Av.Sq.Dist	Sq.Dist/SD	Contrib%	Cum.%
Pb	0.599	0.902	2.29	1.44	37.92	37.92
Zn	0.488	1.05	2.1	1.19	34.75	72.66

Groups z4 & z5

Average squared distance = 10.00

	z4	z5				
Variable	Av.Value	Av.Value	Av.Sq.Dist	Sq.Dist/SD	Contrib%	Cum.%
Pb	-0.014	0.902	3.17	0.84	31.68	31.68
Cu	0.208	0.266	2.96	0.55	29.6	61.28
Zn	0.0311	1.05	2.9	0.89	28.97	90.25



## Highlights

Increase in sediments Pb and Zn, linked to mining, are detected as early as 1460 BC

Cu appears to be linked to nautical ports activity

Eutrophication and macrophyte meadows dynamic may influence the metals mobility

The relatively low bioconcentration factor suggests an important ecosystem service

Inadequate beach management and dredging can increase the bioavailability of metals

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