The influence of natural vs anthropogenic factors on trace metal(loid) levels in the Mussel Watch programme: two decades of monitoring in the Spanish Mediterranean Sea

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Abstract.

The spatial distribution and temporal trends of trace metals (i.e. Cd, Cu, Hg, Pb and Zn) and a metalloid (i.e. As) along the Spanish Mediterranean coast from 1993 to 2013 are presented with a new estimation of their background levels monitored using wild mussels. Over a 20 years period, yearly mussel monitoring was undertaken with a rigorous field sampling protocol using 3 pooled samples strategy (3 x n=80, with 8 mussels in the 3.0 to 3.9 size categories at each site), obtained in the pre-spawning period (May-June) to minimize biological factors and seasonal variability, which is a fundamental element of the international programme. Spatial distribution was characterized every 5 years and temporal trends were determined in 11 locations. The main aims of the present long term study are to evaluate the environmental status of different coastal locations regarding trace metal levels and follow the evolution of these levels over time after the implementation of regulatory measures. Regarding spatial distribution, the highest values for Cd, Cu, Hg and Pb were found close to known highly anthropogenic cities or shipyard areas. However, As and Zn did not strictly follow this pattern, showing natural increased concentrations in the Levantine Balearic and Strait of Gibraltar-Alboran Sea demarcations respectively. These distributions are associated with the conjunction of two geological formation inputs (Massif Central in France and Iberian Pyritic Belt in Spain) and the oceanographic conditions in the adjacent coastal area. In the case of temporal trends, metal concentrations decreased significantly over time in most stations, confirming the effectiveness of the regulatory measures and prohibitions established under European legislation. Concentrations of Pb were above the established thresholds for human consumption in only 12-14% of the sampling areas. With the information obtained for this study, we estimate background concentrations and propose new Background Assessment Criteria (BAC) for the Spanish Mediterranean coast as a threshold criterion: 1.62 mg/kg d.w. for Cd, 8.75 mg/kg d.w. for Cu, 0.202 mg/kg d.w. for Hg and 2.83 mg/kg d.w. for Pb.

Exceptions should exist for As and Zn, for which there should be different levels in each demarcation, due to the geological, hydrological and oceanographic peculiarities of the Spanish coast. For the Levantine-Balearic demarcation, the proposed background concentrations are 117 mg/kg d.w. for As and 200 mg/kg d.w. for Zn., whereas in the Strait of Gibraltar-Alboran Sea demarcation, they are 27.5 mg/kg d.w. for As, and 471 mg/kg d.w. for Zn. This work demonstrates the vital importance of defining the background levels of metal(loid)s at a regional or subregional level because, for areas not affected by anthropogenic causes which have high values as the result of natural processes, this would avoid the risk of constantly surpassing the levels proposed in directives.

Keywords: metal(loid)s, mussels , monitoring, Spain, Mediterranean.

1. Introduction

Metal(loid)s are ubiquitous elements in the environment and occur naturally as they are part of the Earth's crust (Wedepohl 1995). These elements are redistributed among the different environmental compartments resulting from physical (i.e. erosion), geological (i.e. vulcanism and hydrothermal waters), geochemical (i.e. dissolution) or biological (i.e. bioturbation and microbial activity) processes. However, this dispersion among environmental compartments has accelerated due to the human need to exploit the geological formations where these metal(loid)s have the highest concentrations in confined conditions. Mismanagement of the waste derived from mining extraction (Conesa and Schulin., 2010), together with the lack of control over domestic and industrial waste (Belcheva et al., 2015) accounts for part of the dispersion. This is compounded by other sources of pollution such as river inputs or atmospheric deposition (Jickells, 1995), shipyard areas or eventual spills from ships (Santos-Echeandía et al., 2005) or industries, leading to an increase of metal(loid) concentrations in the different marine environmental matrices (i.e. water, sediments and biota). The marine environment represents the final destination of all this waste. At very low concentrations, some metals are essential to maintain crucial biochemical and physiological functions in living organisms. However, they become harmful when they exceed certain threshold levels (Ansari et al., 2004). Both the toxic effects and the potential for bioaccumulation of metals in marine biota exposed via water, sediment or the food chain are therefore of particular concern as the ultimate consequence is the serious deterioration of marine ecosystems and an increased risk to human health from seafood consumption.

Although the main input of contaminants to coastal waters comes from the atmosphere and through water (rivers and submarine groundwater discharge) (Trezzi et al., 2016a), the concentration of these substances in the waters of a certain area is highly variable over time. Therefore, it is necessary to define an integrating matrix for contamination over time, mainly sediment or biota as proposed by international monitoring programmes (UNEP/FAO/IOC/IAEA, 1993; OSPAR, 2010). Given their trophic ecology and benthic characteristics, bivalve molluscs, in particular mussels of the genus *Mytilus*, have been used and are particularly suitable for purposes of monitoring the chemical environmental state of coastal and open-sea marine areas.(Ifremer, 2006; Kimbrough et al., 2008; Benedicto et al., 2011; León et al., 2013; Besada et al., 2014; Campillo et al., 2017; Beyer et al., 2017). International organizations and conventions (OSPAR, 2010; UNEP/FAO/IOC/IAEA, 1993) also recommend their use in this context. The wild mussel (*Mytilus galloprovincialis*) found along the coasts of Spain is

considered a good biological indicator of coastal pollution because it is a widely-distributed sedentary species, is easy to sample, and is resilient to changing environmental conditions. More importantly, thanks to its low detoxification capacity, it accumulates organic and inorganic pollutants to reflect environmental conditions (Rainbow, 1995; León et al., 2013; Campillo et al., 2017). Mussels can accumulate metal(loid)s to concentrations several orders of magnitude higher than levels in the surrounding aquatic media (Casas et al., 2008; Benedicto et al., 2010) making them excellent tracers for monitoring coastal water quality (Catsiki and Florou, 2006; Rainbow and Phillips, 1993).

The Spanish Institute of Oceanography initiated the mussel monitoring programme, which evolved as a response to the Coordinated Environmental Monitoring Programme (CEMP, OSPAR "Convention for the Protection of the Marine Environment of the North East Atlantic") on the north Atlantic and Cantabrian coasts (Besada et al., 2002), and the Programme for the Assessment and Control of Pollution in the Mediterranean region (MEDPOL, Land-based sources Protocol of the UN MAP-Barcelona Convention) (Rodríguez et al., 1995; León et al., 2013). Currently, the Programme has the main purpose of monitoring selected chemical pollutants and contaminant-related biomarkers in Spain's coastal zones to identify geographical distributions and temporal changes in contaminant concentrations and biological responses (Martínez-Gómez et al., 2008; León et al., 2013; Campillo et al., 2017). This information also serves to evaluate the environmental protection activities enforced in Spain within the European Union Marine Strategy Framework Directive, which requires that EU Member States take action to achieve or maintain a good environmental status (GES) in their coastal marine regions. The detection of hot-spots or consistent increases over years in a certain area will support policy makers in establishing regional strategies or a more restrictive legislation regarding waste disposal.

However, there are a number of natural environmental variables (i.e. geology, hydrology, biogeochemistry and oceanography), that cause some metal(loid)s to concentrate in mussels from certain areas (Leonzio 198; Bargagli et al., 1996; Campillo et al., 2019). As these inputs are not anthropogenic, it is not possible to reduce their concentrations even if a mitigation strategy was applied. In these cases, it is vitally important to define the background levels of metals, taking into account the special casuistry of the regions or subregions (Santos-Echeandia et al., 2012) that, in the absence of the specific basal concentrations, might seem to suffer a high impact of anthropogenic pressures. In addition, the fact of having basal concentrations at the regional or subregional level of contaminants other than those that appear in European directives as priority substances, can help better assess the impact and consequences of specific accidents (i.e. the Prestige oil spill, Santos-Echeandia et al., 2005; Soriano et al., 2006). Besides, it would be interesting to establish background values for the contaminants of emerging concern (Cobelo-García et al., 2015; Romero-Freire et al., 2019) in order to evaluate whether these substances are spreading through the environment and increasing their concentrations in the different marine matrices (Neira et al., 2015; Almécija et al., 2016).

Biological factors (i.e. reproductive status, nutritional condition) are also relevant and could affect concentration of pollutants, and in particular to biomarker responses, as has been confirmed both in field and laboratory experiments (Fattorini et al., 2008, Bellas et al., 2014; González-Fernández et al., 2015a,b). In this sense, the accumulation of metals and organic

contaminants in mussel tissues is dependent on reproductive status, with higher internal concentrations during resting than reproductive period (Fattorinini et al., 2008; González-Fernández et al., 2016). Previous studies (Bellas et al., 2014; González-Fernández et al., 2015a) also highlighted the influence of the nutritional condition of mussels on antioxidant and physiological biomarker responses. For this reason international monitoring programmes recommend always sampling mussels in the same period of the year to obtain comparable data for each area thus reducing as far as possible biological (i.e. reproductive status, food availability, etc) and environmental variability (i.e. temperature, salinity).

This study presents an assessment of the geographical distribution and temporal trends of target trace metal(loid)s after two decades of monitoring wild mussels (*M. galloprovincialis*) from the Spanish Mediterranean coast. The Mediterranean Sea presents contamination concerns due to the combined action of anthropogenic pressures (urban development, tourism, industrial and transport activities) from a large number of countries and the low rate of renewal limited to its exchange of water with the Atlantic Ocean through the Strait of Gibraltar. To the best of our knowledge, this is the first long-term study of metal(loid) pollution monitoring using wild mussels in this area. Only three previous studies exist in the literature, however, they do not cover the whole Spanish Mediterranean coastal area (Benedicto et al., 2003), or consider a shorter time series (Guitart et al., 2012) or employ caged mussels in specific places (Benedicto et al., 2010). The evaluation of risk assessment and GES requires not only environmental assessment criteria (EACs) to identify impacts on the ecosystem but also to discriminate between impacted and non-impacted areas with background levels in each subregion. This information is in the context of EU regulation (Marine Strategy Framework Directive) for the measures required to obtain GES, as well as under the Integrated Monitoring and Assessment Programme (IMAP) of the MAP-Barcelona Convention system.

Thus, the objectives of this study are: a) Characterize the geographical distribution of metal(loid)s in mussels from the Spanish Mediterranean coast. b) Evaluate the temporal trends of metal(loid) levels in mussels over a 20 year period. c) Recommend new regional or subregional background levels for metal(loid)s in mussels from the Spanish Mediterranean coast. d) Study the naturally occurring processes or factors that foster high metal(loid) levels in the mussels of certain areas, which are assumed to be moderate to low anthropogenically impacted.

2. Material and methods

2.1. Sampling

Wild mussels (*Mytilus galloprovincialis*) were collected in 31 locations which constitute part of the Spanish “Mussel Watch” Network, located along 2000 km of the Western Mediterranean coast, from the Gulf of Lion (Spain–France border) to the Strait of Gibraltar (Figure 1; Table 1). These locations comprehend two of the five demarcations defined in the Marine Strategy Framework Directive for Spain, the Strait of Gibraltar-Alborán Sea and the Levantine-Balearic demarcations (Figure 1). The sites were selected considering the natural population density of mussels, accessibility to the sampling sites, and representativeness of the surrounding areas, and defined, three typologies: i) Vulnerable sites (V), that are close to large urban, port or industrial locations (some of which are considered hotspots in the MED POL programme such as Barcelona and Tarragona) (UNEP/MAP/MED POL 2005). ii) Reference sites (R), which

correspond to areas of high ecological interest could potentially show baseline levels because they are far from significant direct discharges. iii) Coastal sites (C), which may be located close to medium-sized urban locations or not close to the main sources of pollution (Table 1). The locations were sampled by hand with a scraping tool at an approximate depth of 0.3 m on a yearly basis (from 1993 to 2013) when mussels were in their pre-spawning period (May-June) to standardize and minimize the variability of results caused by biological factors (age, sexual maturity, food availability) (Cossa et al., 1980; Campillo et al., 2017) and physicochemical variability (temperature and salinity) (Cáceres-Martínez and Figueras., 1998; Carro et al., 2004). Overall, the field sampling strategy followed the guidelines proposed by the MEDPOL Biomonitoring Programme (UNEP/FAO/IOC/IAEA, 1984, 1993; UNEP/RAMOGÉ, 1999), but also considered the guidelines for integrated chemical and biological effects monitoring in coastal areas proposed by the International Council for the Exploration of the Sea (ICES) (Davies and Vethaak., 2012). The stations and sampling protocols did not change over the 20-year period, providing coherent and reproducible field sampling conditions (Benedicto et al., 2010; Guitart et al., 2012). The salinity and temperature of the seawater were also determined in situ for all of the sampling campaigns using a portable multiparametric meter (WTW, model Multi 340i/SET*) (Table 1). Not all sampling sites (31) were sampled every year because two different objectives were pursued. In this way, the whole spatial distribution was characterized every 4-5 years (23-29 sampling areas depending on accessibility and mussel presence) and selections of 11 sites were sampled yearly for temporal trends characterization (Table 1). At each station, around 250 specimens (3-4 cm length) were collected. Following collection, mussels were gently cleaned to remove shell adherences. The mussel samples were stored at 4°C and transported to the laboratory where they were frozen until preparation of the sample. The soft tissues were separated from the shells and three composite samples (n=3) of the flesh (n=80 individuals equally distributed within the size interval 3.0-3.9 cm) were made from each site to reduce inter-individual variability and to obtain an environmentally representative sample for all required analyses. Every pooled sample was freeze-dried, homogenized and powdered with a centrifugal ball mill (Fritsch 06102), and stored in acid washed glass vials until analysis. The sampling procedure applied is in line with the proposals of the Joint Monitoring Programme (2003) of the OSPAR Commission (1992), and the MEDPOL Programme, Barcelona Convention (1996).

2.2. Analytical procedure

Analytical procedures were kept similar during the two decades of the study (Rodríguez et al., 1995; Benedicto et al., 2004, 2010; Guitart et al., 2012). Tissue samples were processed with nitric acid in Teflon digestion bombs placed in conventional or microwave ovens. Briefly, 0.3-1 g of the freeze-dried mussel sample was placed in a Teflon reactor and, after the addition of 1 ml of Milli-Q water and 6 ml of concentrated Merck Suprapur nitric acid, the reactor was heated with an appropriate temperature ramp. Target metal(loid)s, were analyzed either by flame AAS (F-AAS, AAAnalyst 100) for As, Cu and Zn, while Cd and Pb were determined by graphite furnace with Zeeman background correction (ZGF-AAS, 4110 ZL, Perkin-Elmer). For Hg determined cold vapor generation using a flow injection mercury system (CV-AAS, FIMS 400, Perkin Elmer) was employed. Detection limits were 0.30, 0.005, 0.50, 0.50, 0.003 and 0.30 mg/kg dry weight (mg/kg d.w.) for As, Cd, Cu, Pb, Hg and Zn, respectively.

Validation of the analytical methods included rigorous Quality Assurance/Quality Control (QA/QC) samples (i.e., procedural blanks, duplicated samples, and certified reference materials) to ensure that the data produced were accurate and reproducible. Three successive certified reference materials, CRM 278, CRM 278R, and ERM 278, were employed within batches of analyzed samples as internal laboratory quality assurance procedures and were purchased from the European BCR Office and the Institute of Reference Materials and Measurements (IRMM, Belgium, Europe). In addition, the laboratory external quality assurance included twice-yearly the participation in European round robin tests for trace metal determination in marine matrices through QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe). Since 1992, our laboratory has accounted for 94.7% satisfactory results ($Z\text{-Score} < \pm 2$). Moreover, our laboratory has also participated in the several Worldwide Interlaboratory Exercises and the MEDPOL regional round tests for the determination of trace metals in several marine matrices organized by the IAEA for the same purpose (Azemard et al., 2006).

2.3. Flow calculation

Hydrodynamic flows were computed from the current velocity fields provided by the Mediterranean Sea Physical Reanalysis Product MEDSEA_REANALYSIS_PHYS_006_004 (MEDre hereafter), in the framework of the Copernicus Marine Environment Monitoring System (CMEMS; <http://marine.copernicus.eu/>). MEDre is based on numerical simulations provided by the Nucleus for European Modelling of the Ocean (NEMO), forced by the ERAInterim atmospheric reanalysis fields of the European Centre for Medium-Range Weather Forecasts (ECMWF), with a variational data assimilation scheme (OceanVAR) for temperature and salinity, vertical profiles, and satellite Sea Level Anomaly along track data. The grid domain covers the entire Mediterranean Sea basin, with a regular horizontal resolution of 1/16 degree and 72 unevenly-spaced vertical levels, and provides daily- and monthly-averaged data of potential temperature, salinity, sea surface height, and horizontal current velocity from 1987 to the present.

The net flows through the Strait of Gibraltar were computed by lateral and vertical integration of the zonal component of current velocities (positive eastwards), along a meridional transect ($E -5^{\circ} 45'$) from Cape Malabata (Morocco, $N 35^{\circ} 49'$) to Point La Morena (Spain, $N 36^{\circ} 4'$) (Figure 1). Daily-averaged currents were time-filtered by a successive moving-average $A_{21}A_{21}A_{22}$ Godin filter (see, e.g. Thomson and Emery, 2014) in order to remove the subinertial variability of periods shorter than 21 days, as established by Soto-Navarro et al. (2010) for computing exchange flows through the Strait of Gibraltar.

Similarly, to estimate input flows from the Gulf of Lion, the meridional component of the monthly-averaged current velocity (in this case, considering the southward direction positive in order to define positive inflows) was laterally- and vertically-integrated (to a depth of 200 m) along a zonal transect ($N 42^{\circ} 19'$) from Cap de Creus on the Spanish coast ($E 3^{\circ} 30'$) to the 1000 m isobath ($E 3^{\circ} 56'$), and then yearly time-averaged. This transect was defined according to the incoming pattern of flow lines from the Gulf of Lion shelf, computed from the 2001-2013 time-averaged current fields (Figure 1).

2.4. Statistical analysis

The significance of temporal trends for each metal(loid) concentrations in mussel tissues was tested using Kendall's Tau-b correlation coefficient at both 0.01 and 0.05 significance levels, reporting the *p*-values in each case. This coefficient represents the degree of concordance in paired observations (Hollander and Wolfe, 1999). In our context, the Tau-b correlation coefficient measures the association between concentrations and time (i.e., attempts to find significant temporal patterns), and is robust in the presence of outliers. This test is recommended by the ICES (ICES, 1996, 2000) for this kind of study. The Tau-b correlation tests were performed using R software (R Core Team, 2019). The parametric correlation was determined by using the Pearson test.

3. Results and Discussion

3.1. Trace metal(loid) levels in mussels: geographical features.

Apart from the metals considered as priority pollutants in the Marine Strategy Framework Directive (i.e. Cd, Hg, Pb), a highly toxic metalloid (As) (Crespo-López et al., 2009; Gaudet et al., 2018) and two essential metals that can produce toxic effects above threshold concentrations (i.e. Cu and Zn) (Morel and Prince, 2003) were determined in wild mussels. Table 2 presents a summary of the metal concentrations found in the mussels of this-long term study. The spatial distribution for all sampling points was characterized every 4-5 years, and temporary trends were characterized for 20 years in the most relevant areas. The median, mean $\pm$ standard deviation and range of concentrations for each metal analyzed in mussels collected in 4-5 years intervals (1993, 1998, 2003, 2007 and 2011) are shown for long-term comparison. In addition, we include the historical information for each trace metal, based on the twenty-year series. After five quinquennial sampling efforts, the general geographical distributions of target metal concentrations along the Mediterranean Spanish Coast are well defined and show mostly comparable values over time.

Figures 2a and 2b show the variability of historical data (i.e., the average of the twenty-year sampling) associated with each sampling location for Cd and Hg respectively. As observed by Besada et al. (2012) for the mussels of the N-NW Spanish Coast, Hg, Cd, and Pb presented the largest ranges of average concentrations, while Cu, Zn, and As had average concentrations with smaller ranges. However, our study found a ratio between the highest and lowest values of each range that were higher than in the previously cited study, and reached approximately 2400 for the first group of metal(loid)s, whereas the second group had an average concentration within a factor not larger than 60 over the entire area of study. These differences may be associated to the longer period of our study and to higher anthropogenic or natural sources of metals along the Mediterranean coast because the lower value range is similar in both Spanish coastal areas (the N-NW Spanish Coast and Mediterranean Sea).

As Figure 2a illustrates, some locations showed Cd levels above the historical mean value of 0.592 mg/kg d.w. (Table 2). The highest values were observed in mussels from Cartagena and Portmán, with a mean value four times higher (2.75 mg/kg d.w.) or that triplicates (2.08 mg/kg d.w.) the historical one. Portmán is a semienclosed bay, where already non-active mine (Cartagena-La Unión mining district) released its residue for three decades until the end of its exploitation in the 1990s. The geological complex of this area is formed of minerals rich in Cd, Fe, Pb and Zn (Oen et al., 1975). In spite of being currently inactive, the large number of remnant water ponds and waste deposited as waste dumps in the old plants, currently cause

continuous metal inputs to the bay at present, either through runoff. As an example, recent studies have shown an enrichment of the adjacent waters to Portman Bay in Cd, Fe, Ni, Pb or Zn (Trezzi et al., 2016b; Alorda-Kleinglass et al., 2019). Thus, these metals continue to be bioavailable for the mussels that filter huge liters of these metal rich waters and bioaccumulate them in their tissues. Only after 2015, did rehabilitation work begin on the bay to remove mining waste and prevent the arrival of contaminated runoff waters into the marine environment. In addition to the influence of the mining complex, Cartagena is one of the Iberian Peninsula's important port areas. Tabarca (1.28 mg/kg d.w.) and I. Columbretes (1.17 mg/kg d.w.) also have higher values than the historical mean for Cd. The former station is very close to the area of influence of the Cartagena-La Union mining district and its high values may be associated with this fact. However, I. Columbretes station was intended to be a reference due to its location far from any anthropogenic input (Figure 1, Table S1). The high Cd values found in mussels from this station could be associated with the oceanography, as major upwelling events are recurrent in this area, and on the other hand is geology because the island has a volcanic origin. In fact, previous works (Benedicto et al., 2011) have already shown these high values of Cd in mussels from I. Columbretes. Finally, two other stations whose Cd values fall above the mean historical value are La Herradura (1.06 mg/kg d.w.) and Calahonda (1.10 mg/kg d.w.) representing an increase of approximately 35%. These stations were considered as reference site and coastal area with low anthropogenic pressure, as supported by the low concentrations of polycyclic aromatic hydrocarbons and organochlorine contaminants found in mussels from these locations (León et al., 2013; Campillo et al., 2017). However, cadmium inputs at these sites may indicate some influence from domestic inputs (Benedicto et al., 2011).

The lowest levels of Cd in mussels were found in Vallcarca (0.374 mg/kg d.w.) and Cullera (0.384 mg/kg d.w.) which were considered coastal areas (Table S1) with low to moderate anthropogenic pressure, respectively. In general, the coastline covering the stations from Vallcarca to Cullera (with the exception of Delta del Ebro) presented the lowest Cd levels (0.430 ± 0.047 mg/kg d.w.). The high Cd levels found in mussels from the Delta del Ebro station are associated with the River Ebro water discharge. This river has the third largest basin in the Mediterranean Sea, draining an area of approximately 85.000 km² (UNEP/MAP/MED POL, 2003). The Ebro and Rhône rivers are the main ones that discharge into the western Mediterranean Sea and represent more than the 70% of the total riverine discharge (Ludwig et al., 2009). Chemical and radiochemical industries are also important in the Ebro river basin, as in the case of the town of Flix, where large quantities of non-treated waste have been accumulated for decades in the sediments of a nearby reservoir (Terrado et al., 2006). These activities have resulted in the presence of high levels of pollutants (i.e. Cd and Hg) in the river water and sediments, and of some of its tributaries (Schuhmacher et al., 1995; Carrasco et al., 2010), which pose a risk for the biota and wildlife inhabiting the river (Soto et al., 2011; Carrasco et al., 2011; Roig et al., 2016). During heavy rain bouts, the river discharges high volumes of water to the coastal area and contaminated river sediments as suspended particulate matter. The bioaccumulation effect of the contaminants transported by the river during high flow events has been detected in mussels collected close to the Ebro river mouth (Campillo et al., 2019). Cadmium concentrations were similar to those measured in the western Mediterranean Sea (0.46-2.89 mg/kg d.w., Benedicto et al 2011), including the Balearic Islands (0.25-1.70 mg/kg d.w., Deudero et al., 2007). Values were also in the range of

those reported for the Greek coast (0.262-5.43 mg/kg d.w., Sakellari et al., 2013), Turkish coast (0.09-3.32 mg/kg d.w., Belivermis et al., 2016) and Lybian coast (1.19-2.41 mg/kg d.w., Galgani et al., 2014). However, the Cd concentrations in mussels found in this study were higher than those measured in previous studies of the Spanish Mediterranean coast (0.20-1.25 mg/kg d.w., Benedicto et al., 2003; 0.30-1.70 mg/kg d.w., Fernández et al., 2012), the Adriatic Sea (0.51-1.24 mg/kg d.w., Kristan et al., 2014; 0.4-0.6 mg/kg d.w., Kanduc et al., 2016), the Algerian coast (0.50-0.82 mg/kg d.w. Rouane-Hacene et al., 2015) and the N-NW Spanish coast (0.357-2.01 mg/kg d.w., Besada et al., 2014). However, they were lower than the concentrations reported for the French Mediterranean coast (0.20-10.0 mg/kg d.w., Ifremer, 2006).

Regarding Hg, mussels sampled within the transect between Barcelona and Peñíscola reported the highest values of the Spanish Mediterranean Iberian coast (0.233-0.463 mg kg d.w.) (Fig. 2a) with the exception of Cartagena (0.629 mg kg d.w.), exceeding the mean historical value of 0.148 mg/kg d.w. (Table 2). Two of the sampling locations in this transect (i.e. Barcelona, Tarragona) are in highly populated, industrialized areas considered as vulnerable sites. Our results support this as does the concentration of PAHs and organochlorine contaminants and contaminant-related responses in mussels found in previous studies from these sampling sites (Martínez-Gómez et al., 2008; León et al., 2013; Campillo et al., 2017). In the case of mussels from Delta del Ebro, the explanation for the high levels is the same as previously explained above for Cd. The contaminated sediments located in the Flix area upstream of the River Ebro are the main source of Hg when the water flows of the rivers increase. Due to the winds and regional oceanic circulation, the plume of this river occasionally flows north (30%) but is mainly southwards (70%) (Fernández-Novoa et al., 2015) reaching a maximum distance of 80 km from the river mouth (Palanques and Drake, 1990). Thus, the high Hg levels found in the mussels from stations located to the north (Salou) and south (Peñíscola) would be associated with the Ebro River plume and the transported contaminants. Finally, the Vallcarca station is located close to a cement plant that extracts its raw material from the rocks that form the Macizo del Garraf, located 15 kms south of Barcelona. This geologic structure mainly consists of carbonaceous rocks (Keil et al., 1986) that easily dissolve and whose associated elements finally reach the adjacent coast. Thus, the elevated levels found in Vallcarca may be associated with both land-based sources and atmospheric inputs that come from the concrete industry. In addition, the influence of the Llobregat River, which crosses the industrial area located south of Barcelona city (Pinedo et al., 2014) and flows southwards due to the regional current conditions, would contribute to an increase in Hg levels found in the mussels of Vallcarca. In fact, these authors found relevant enrichment factors of Cd, Hg, Pb and Zn in the coastline between Badalona and Sitges (located south of Vallcarca). Cartagena shows the highest value along the whole coast (0.629 mg kg d.w.). As with cadmium, the importance of the port area and its related activities is a key factor to explain the high Hg values. The lowest levels of Hg were found in Cadaqués, I. Medas, Blanes, Sta. Pola, Almuñecar, Torrox and Marbella, with values below 0.120 mg/kg d.w. All these stations are reference sites or coastal areas with low anthropogenic pressure, supporting our results and the organic contaminant bioaccumulation results observed in previous studies (León et al., 2013, Campillo et al., 2017). The highest value of the range measured in our study for Hg (0.847 mg/kg d.w.) was the highest of all the values reported in the studies shown in Table 3., The only exceptions are the values reported by Benedicto et al., (2003) for the Andalusian coast in Spain (1.80 mg/kg d.w.) and Deudero et al., (2007) for the Balearic Islands (2.21 mg/kg d.w.). Like the Hg results, the Pb concentrations in

mussels found in our study comprised the highest reported values of the studies conducted in Spanish and Mediterranean waters, with values two and three orders of magnitude above those found in mussels from other Mediterranean coasts (Galgani et al., 2014; Adriatic Sea, Kristan et al., 2014; Kanduc et al., 2016, Lybian coast,) (Table 3).

The mean historical concentration value for Pb (5.05 mg/kg d.w., Table 2) was only exceeded in 5 of the 31 stations (i.e. Portman, Cartagena, Barcelona, Vallcarca and Almería). The historical mining activities and the remaining tailings in Portman Bay are the likely reason for these enhanced levels of Pb in mussels (72.18 mg/kg d.w.) for Portman and Cartagena, as already observed and explained previously for Cd. Barcelona (10.57 mg/kg d.w.), is one of the Spain's major Mediterranean ports, in addition to being a highly populated (3.3 million inhabitants, INE 2020) and industrialized area. Vallcarca (7.24 mg/kg d.w.), as explained above, is influenced by the concrete industry and the waters coming from the Llobregat river (Pinedo et al., 2014). In fact, Benedicto et al. (2011) showed high levels of Pb in the mouth of the Llobregat River in a caged mussels experiment. Finally, Almería (7.45 mg/kg d.w.) is also an important port area, and our sampling point is very close to the old ore loading lock built in the early 20th century, which was used until recently. Despite not exceeding the historical mean values, other notable stations for Pb levels were Málaga, Alicante and Castellón. The common characteristic of all of them is the high population and major ports and industries, as in the case of Barcelona reported above. In addition to the mining activities mentioned, the use of tetraethyl lead as gasoline additive (antiknock) for decades was also a relevant source of Pb, particularly in main urban nuclei and terrestrial transport routes, until its use was banned in 2001 (RD 785/2001). The lowest values for this metal were measured in Manilva, I. Medas, La Herradura, Marbella, Cadaqués and Cullera (<2.20 mg/kg d.w.), all of which are reference stations or coastal areas with a low anthropogenic influence (León et al., 2013).

Copper is the element that shows the most similar concentrations along the entire coast, with values in the range of 4.78-10.29 mg/kg d.w. and a mean historical value of 5.30 mg/kg d.w. (Fig. 2b). This was not surprising since this metal is a well-known essential element for mussels, which have biological mechanisms (i.e. metallothioneins) to regulate the concentrations of essential metals in their tissues (Swaileh and Adelung, 1994). Background levels of copper in NW Mediterranean mussels have been found around 7-8 mg/kg d.w. (RNO 2005; Marchand et al., 2009). In our study, the only copper value that stands out above the rest is for Barcelona (10.29 mg/kg d.w.), which represents an excess approximately 30% higher than the mean historical value, indicating a notable contamination of copper in the area. Copper is a common element found in the antifouling paints of boats (Turner, A. 2010), thus, the concentration of this element in port areas, both in the water (Santos-Echeandia et al., 2008) and sediments (Prego et al., 2008; Singh, N. and Turner, A. 2009) is usually higher than in other coastal areas. In fact, after Barcelona, other locations with high levels of Cu in mussels are the ports of Valencia (7.35 mg/kg d.w.), Alicante (7.33 mg/kg d.w.), Cartagena (7.50 mg/kg d.w.), Málaga (7.86 mg/kg d.w.) and Algeciras (7.55 mg/kg d.w.). We found the lowest copper values (<6.00 mg/kg d.w.) in the mussels collected in Cadaqués, I. Medas, Blanes, I. Columbretes, Cullera, Cabo de la Nao, Herradura and Manilva. All these stations are reference locations or close to medium-sized urban nuclei or not close to the main pollution sources (León et al., 2013). Despite several studies that indicate mussels are not a good bioindicator for copper pollution (RNO 2005; Besada et al., 2014; Guendouzi et al., 2017) our data reflect the differences in anthropogenic pressure between areas for this element. Copper concentrations were higher

than those reported in all the studies shown in Table 3 with the exception of the Balearic Islands (5.90-58.3 mg/kg d.w.) (Deudero et al., 2007), the French Mediterranean coast (3.8-67 mg/kg d.w.) (Ifremer, 2006) and the Turkish coast (3.9-173 mg/kg d.w.) (Belivermis et al., 2016).

With respect to As, the stations located in the north of the Spanish Mediterranean coast (i.e. Cadaqués, I. Medas, Blanes and Barcelona) exceeded the mean historical value (16.8 mg/kg d.w., Table 2) with levels oscillating between 27.33 and 43.72 mg/kg d.w. (Fig. 2b) and Águilas (28.19 mg/kg d.w.). However, Zn showed the highest values along the south coast, from Estrecho to Portman. The mean historical value of this element is 146 mg/kg d.w., and the levels found in the stations located in the Strait of Gibraltar-Alboran Sea demarcation oscillated between 212-357 mg/kg d.w. (Fig. 2b). Two geological complexes control these trends and behavior: the Iberian Pyritic Belt in the case of Zn (Leistel et al., 1998) and the French Central Massif in the case of As (Elbaz-Poulichet et al., 2017). Due to the complexity and length of the explanation of the various processes involved in the behaviour of these two elements, we devote a complete section (3.3.) to the As and Zn in the mussels of the Spanish Mediterranean coast.

To put the present data into perspective, we compared it to trace metal(oid) concentrations in mussels found in similar monitoring studies, carried out mainly in the Mediterranean Sea (Table 3). However, complications involved in the comparison of data from different studies include the substantial changes implemented in analytical methods, the seasonality of sampling, and the type of monitoring (i.e. native or caged mussels) (Andral et al., 2010). Regarding the latter, monitoring programmes that use indigenous populations of wild mussels “passive biomonitoring” have better sensitivity to tissue contaminant accumulation, due to long-term exposure (Martínez-Gómez et al. 2017). Arsenic concentrations were comparable to another study carried out in the Spanish Mediterranean coast (13-83 mg/kg d.w., Fernández et al., 2012). However, the highest value of the range for As (112 mg/kg d.w.) was well above the other studies conducted in the Mediterranean Sea or the N-NW Spanish coast (Besada et al., 2014). Levels of Zn reported in our study were similar to those found along the French coast (43-357 mg/kg d.w., Ifremer, 2006), the Turkish coast (16-441 mg/kg d.w., Belivermis et al., 2016) and the N-NW Spanish coast (141-361 mg/kg d.w., Besada et al., 2014). However, concentrations were higher than those measured in the Balearic Islands (48.9-317 mg/kg d.w., Deudero et al., 2007), the Adriatic Sea (51.7-194 mg/kg d.w., Kritan et al., 2014; Kanduc et al., 2016) the Algerian coast (71.6-154 mg/kg d.w., Rouane-Hacene et al., 2015) or the Lybian coast (141-197 mg/kg d.w., Galgani et al., 2014) and lower than levels reported for the Greek coast (33-804 mg/kg d.w., Sakellari et al., 2013) (Table 3).

3.2. Temporal trends over two decades.

The temporal trends of metal(loid) concentrations in mussel tissues were tested for significance using the Kendall's Tau-b correlation coefficient at significance levels of both 0.01 and 0.05. We only considered the stations sampled in more than 15 of the 20 years (I. Medas, Barcelona, Tarragona Delta del Ebro, Peñíscola, Valencia, Portmán, La Herradura, Manilva and Algeciras). Table 4 shows the coefficients obtained and the level of significance for each metal(loid). Fig. 3a–c shows the trends observed for Hg, Cd and Pb at these 10 locations. Overall, we observed a generally decreasing trend over time for most target metal(loid)s and

areas (Figure 3a-c). Furthermore, these decreases were particularly relevant before the year 2000 at several sites and for some metals (i.e. Hg in Tarragona, Delta del Ebro, Portman, La Herradura, Manilva and Algeciras; Cd in Tarragona and Valencia; Pb in Tarragona and Peñíscola) (Figure 3a-c). Despite the decrease in concentrations not being equally evident in all of the stations and for all of the metal(loid)s, approximately 90% of the paired observations (metal(loid)-location) indicated decreasing trends, 45% of which were statistically significant, after two decades of study (Table 4). These trends clearly respond to the implementation of measures to regulate discharges of metal from domestic and industrial sources and atmospheric emissions into the marine environment in order to reduce pollution in the marine environment following EU policies and directives. For example, the effectiveness of the restrictions implemented in the EU has been reflected in the declines of the air emissions recorded from 1990 to 2016 for Pb, Cd, Hg, As, Cu and Zn by 93, 65, 71, 67, 65 and 36%, respectively (EEA, 2018). Regarding industrial and domestic waste, several studies have revealed that environmental remediation actions have led to a reduction of metal levels in mussels (Besada et al., 2014; Belcheva et al., 2015). This is particularly relevant for Pb due to the gradual reduction of the maximum content in gasoline during study period (0.4 g/L in 1987, 0.15 g/L in 1988 and 0.005 g/L in 1999) (RD 1485/1987; RD 1728/1999) until its complete ban in 2001 (RD 785/2001). Although the general trend the series was to decrease, there were puntual increments or periods in which concentration remained constant. Guitart et al. (2012) recently studied this phenomenon, known as “temporal trend breaks”.

With the exception of the mussels from Barcelona and Fuengirola, and to a lesser extent Manilva, Cd levels showed slight and moderate trends to decrease (Kendall τ -b coefficient < -0.4 and < -0.7 , respectively) in all stations (Fig. 3a), reaching statistical significance in Tarragona, Peñíscola, Castellón and Portmán (Table 4). The main inputs of Cd to the marine environment may be of natural (i.e. upwelling events) or anthropogenic (i.e. domestic and industrial inputs) origin, with the former more common along the Atlantic Spanish coast (Santos-Echeandía et al., 2009; Prego et al., 2013; Besada et al., 2014). Thus, the decrease in Cd concentration may be associated with a reduction in domestic and industrial waste as a result of the new limits established by national and EU regulations.

Regarding Hg, mussels from all of the stations showed decreasing trends, in particular Algeciras (Kendall τ -b coefficient = -0.811), and with statistical significance over 70% of stations (Table 4), except for Barcelona that had stable concentrations. The levels of this element in the early 90s were in the range of 0.200-0.700 mg/kg d.w., and most of the stations were below 0.200 mg/kg d.w. in 2013 (Fig. 3b). This general decrease indicates the effectiveness of the actions implemented by the European Union and Spain to reduce the anthropogenic emission of this element into the environment (Guieu et al., 1997). In addition, Hg levels decreased both in stations close to hotspots and those far away from such anthropogenic pressures. This indicates that the main Hg input in the Mediterranean area (i.e. atmosphere) is decreasing. Mussels from all the stations except Malaga and Fuengirola showed significant decreasing trends for Pb concentrations, in particular those from Castellón (Kendall τ -b coefficient = -0.886) (Table 4). Only the slow increasing trend in Malaga was statistically significant. The decrease in concentrations for almost 70% of the stations is statistically significant (Table 4; Fig. 3c). The concentration and distribution of Pb in the oceans is mainly driven by human activities (Villares et al., 2005) and, historically, anthropogenic emissions of Pb were related to the consumption of leaded gasoline as well as to the low or nonexistent treatment of urban

and industrial sewage (Stephenson and Leonard, 1994). An example of this is the different rate of decrease (slope of the equation) observed in Tarragona and Valencia after the total ban of leaded gasoline in 2001 (RD 785/2001) (Fig. S1). We observe similar decrease for Hg and Pb along the French Atlantic and Mediterranean coast (RNO, 2000) and for the N-NW coast of Spain (Besada et al., 2014). In the case of Cu, all stations except Tarragona and Valencia showed decreasing trends, but less than 30% of these were statistically significant (Table 4). This is not surprising because, as previously mentioned, Cu is an essential element and mussels can modulate its concentration in their tissues, which explains the lower significant trends our study found for this metal. In addition, during the last decades, Cu has been widely used in antifouling paints, which are the main source of this element in ports and shipyard areas (Turner, 2010). Regarding As concentrations, mussels from most of the stations showed slow and moderate decreasing trends, 40% of which were statistically significant, mainly in mussels sampled from the central stations of the Spanish Mediterranean coast (Valencia Cullera and Portman). Finally, Zn showed decreasing trends in all stations except Fuengirola. The decrease was statistically significant in half of the stations (Table 4) and the result of the adoption of regulatory measures.

It is worth noting that La Herradura was the only station that showed no statistically significant trends (neither an increase nor a decrease). This fact indicates the great success to having chosen this station as one of the reference sites for the Strait of Gibraltar-Alborán Sea demarcation from the start of the monitoring programme in the early 90s.

3.3. The influence of “natural” processes on the metal(oid) levels in mussels: As and Zn as a case of study

Arsenic concentrations in mussels from the stations located along the north Spanish Mediterranean coast (i.e. Cadaqués, I. Medas, Blanes and Barcelona), showed higher mean concentrations (36 ± 7 mg/kg d.w.) than the stations southwards (18 ± 4 mg/kg d.w.) (section 3.1. and Fig 2), similar to those found by Andral et al. (2004) along the adjacent French coast (29 ± 3 mg/kg d.w.). In addition, and to the best of our knowledge, the As levels found in mussels from the northern stations of our study are the highest reported for the western Mediterranean coasts (Table 3). Not only the concentrations, but also the temporal trends of As in these stations are similar (Figure 4a), pointing to a common source of this element in mussels.

Arsenic is a minor but ubiquitous element in the Earth’s crust with an average concentration between 1-1.8 mg/kg (Wedephol 1995). There are three major natural sources of arsenic contamination: hydrothermal activity, ore deposits, and Cenozoic sediments (Masuda 2018). This element has many applications, but its use has been especially common in pesticides and wood preservation. Although anthropogenic contamination due to the application of arsenic compounds in agricultural fields is decreasing, activities to exploit natural resources, such as mining, are a continuing cause of environmental arsenic contamination. Ore deposits are the second main source of arsenic worldwide. Although the distribution of naturally occurring arsenic contamination around ore bodies is generally localized, anthropogenic materials associated with the mining of ore bodies, such as tailings and sludge, expand the area of contamination into the hydrosphere, pedosphere and atmosphere of the surrounding area. The excavated ore bodies and the ensuing chemical weathering produce sediments highly contaminated with arsenic that become sources of potential arsenic contamination (Masuda,

2018). In southern France, the border of the Massif Central has been an important mining area of non-ferrous (Pb-Zn-Ag-Au) metals, with byproducts like As or Cd, since at least the medieval period and probably even earlier (the Roman era). Arsenic concentrations in mine sediments can reach up to 3800 mg/kg (Leblanc et al., 1996) and up to 250 mg/L in acidic waters (Casiot et al., 2003). Mining activity intensified at the end of the nineteenth century, then declined in the second half of the twentieth century. The vast majority of metal mines closed in the 1960s except the Salsigne gold mine, which closed in 2004, and had produced 25% of As in the world. Although most of the mines are now abandoned, they still present a threat to the environment and human health (Doumas et al., 2016). In fact, Tarvainen et al. (2013) showed that the average As concentration in topsoils for agricultural or grazing use in the area between the Massif Central and the French coast is higher than 20 mg/kg whereas the mean value in Europe is around 5.7 mg/kg. The major rivers that discharge into the Mediterranean Sea along the French Coast (the Aude, the Orb and the Herault) and the right bank tributaries of the Rhône River such as the Gardon River have former metal(loid) mining sites in their watersheds. Several authors (Casiot et al., 2005; Elbaz-Poulichet et al., 2017) have reported high As concentrations both for dissolved (189 µg/L) and particulate (19 mg/g) fractions in the water of these watercourses.

The predominant species of dissolved As present in mine tailings is As (III) due to the acidic conditions of these environments. However, when these waters reach the river courses, As (III) is oxidized to As (V), which tends to be sorbed to suspended particles by co-precipitation with Fe oxo-hydroxides, and most of it ends up in the sediments of the rivers. Consequently, As concentrations decrease in the Rhône river water mouth reaching values around 2 µg/L of dissolved and 73 µg/g of particulate As (Elbaz-Poulichet et al., 1996; Elbaz-Poulichet et al., 2017) but riverbed sediments are enriched in As.

With an average water discharge of $52 \cdot 10^9 \text{ m}^3$ per year and a solid discharge in the order of $4.6 \cdot 10^6$ tonnes per year, the Rhône River represents the major riverine source of water and particles to the western Mediterranean Sea (Elbaz-Poulichet et al., 1996). During high flooding events, sediment particles from the Rhône River and its tributaries are resuspended (Poulier et al., 2019) and transported long distances from the mouth of the rivers to the Gulf of Lion waters. Guieu *et al.* (1993) have estimated that about two-thirds of the solid discharge accumulates over an area of 4000 km², representing 17% of the total surface of the continental shelf in the Gulf of Lion. About 10% of the Rhône's solid discharge may cross the shelf as suspended matter (SM). In general terms, it is expected that metal(loid) concentrations in the water column would decrease as a consequence of the dilution effect after a flooding event; however, some elements are the exception. During a three-year study of metal(loid) concentrations in the Rhône river under different hydrological conditions, Ollivier et al., (2006) showed that As, Sb and Ni increased their concentrations in the water column of the Rhône River following flooding events, to reach values of 6 µg/L of dissolved As (3 times the mean annual concentration). This fact is related to a higher contribution of waters enriched in the elements issuing from the western tributaries of the Rhône River, which drain old mine tailings and the run-off of the soils of this basin enriched in As as explained above. Guieu et al. (1993) estimated a mean input of 132 tons per year of As from the Rhône river to the Gulf of Lion waters, 72% in dissolved fraction and 28% as particulate material that would be enhanced after flooding events. Once in the Gulf of Lions waters, dissolved arsenic in the form of arsenate, can be incorporated by phytoplanktonic species when phosphate is a limitant

nutrient, thus bioaccumulating this element. In fact, microalgae represent one of the main sources of the biotransformation of inorganic arsenic into organic compounds such as arsenobetaine, arsenocholin and arsenosugars. In this sense, it is known that the main factors that determine the variability of arsenic levels in mussels, at least within a certain range of concentrations around 10-50 mg/kg (dw), are natural and/or of trophic origin (Fattorini et al., 2008). Thus, the concentrations of As higher than these levels (up to 112 mg/kg d.w.) found in the northernmost stations of the Spanish Mediterranean Coast may reflect an anthropogenic source, probably associated with the French Massif Central and its related fluvial inputs along the French Coast. Pujo-Pay et al. (2011) showed that the Gulf of Lion waters are depleted in phosphate in comparison with other Mediterranean areas, thus phytoplankton uses nitrate and arsenate to compensate the lack of available phosphate. Likewise, Minas and Minas (1989) showed an increase in phytoplanktonic productivity in the Gulf of Lions associated to the Rhone river discharges.

The predominant current in the Gulf of Lion is westwards, showing its highest speed in the known as Liguro-Provençal-Catalan current that comes from the Ligurian Sea, reaches the Gulf of Lion and goes southwards parallel to the Spanish Mediterranean coast (Milot, 1991). This current transports the waters from the mouth of the Rhône river (and other minor streams) enriched in As due to the As-rich lithogenic suspended particulate matter and phytoplanktonic cells that have previously accumulated dissolved As in the form of arsenate. Mussels from the north Mediterranean Spanish coast would filter these waters to get their food, mainly phytoplankton, and accumulate As in their tissues. This would be a credible hypothesis to explain the high values of this element in mussel tissues and further research on this item would benefit the establishment of background levels of this metalloid in mussels from the NW Mediterranean subregion.

Going back to the temporal trend of As (Fig 4a), the stations located along the north Mediterranean Spanish coast follow a similar pattern with a remarkable peak in 2003, and to a lesser extent in 2005 and 2007, that we do not observe in the central or southern coast areas. The I. Medas station also experienced important peaks in 2008-2009-2010, as did Barcelona in 2009 and 2010. In order to confirm our previous hypothesis, we conducted a study about current fields in the Gulf of Lion and Spanish continental shelves between 2001 and 2013 (Figure 4b) placing a transect at Cap de Creus as shown in Fig. 4b, where the annual mean currents coming from the Gulf of Lion area were calculated. The mean annual flow plotted in Fig 4a for the period 2001-2013 shows three main peaks during the years 2003, 2005 and 2008-2010. With the exception of 2007, these high flow values match with the higher As concentrations in mussels, supporting our theory about the origin of the As found in mussels from the Spanish north Mediterranean coast. It is important to highlight that flow is not the only factor influencing As concentrations in mussels. Apart from this variable, water discharge and suspended particulate matter concentrations from the Rhône River and smaller rivers (the Aude, the Orb and the Hérault) play an important role. In this way, Poulier et al. (2019) conducted a sixteen-year monitoring study (2000-2016) to evaluate annual water discharge and suspended particulate matter (SPM) from the Rhône River to the Gulf of Lion. Regarding SPM fluxes, Poulier et al. (2019) observed an important increase in 2002 and 2008 associated with heavy rains and water discharges from the Rhône River during winter. Ollivier et al. (2006) also reported the 2002 event in their study about As fluxes from the Rhône River to the Gulf of Lion during flooding events. Additionally, Juza et al. (2013) confirmed that the transports of

the Ligurian-Provençal-Catalan current were higher in winter (1.5-2 Sverdrups) than in summer (1 Sverdrup). Slight increases in SPM flow were observed in 2006 and 2010. This is likely associated with the maximums of As found in mussel tissues in 2003, 2007 and 2009 as these filter-feeding organisms integrate the concentrations of metal(loid)s accumulated during the previous 12-18 months. The As peak observed in Barcelona in 2010 is singular because, due to the lack of mussels, the location of the sampling point had to be changed that year. Although there was an important water flow across the Cap de Creus in 2005, the low water discharge and SPM flux from the Rhône River during the previous winter (Poulier et al., 2019) caused the concentrations of As in mussels tissue to show an increase compared to 2004 or 2006 levels. However, this increase was, not as great as one might expect if only considering the flow. Another interesting aspect is the fact that As concentrations decrease consistently each year as we move south in the Spanish coast (Figure 4a). This supports our theory that the source of As comes from the north, specifically from the rivers discharging into the Gulf of Lion, and that the effect of the discharge on As accumulation is diluted as the current flows southwards.

It might seem improbable that As from the Rhône and smaller rivers could reach a region 200-300 kms away. However, several studies have already reported similar behaviours. Rivers can transport mining contaminants great distances from their source regions, mainly in particulate form (Macklin et al., 2006). For example, Cd originating from a former Zn refining plant in the Lot River basin (France) is transported along the Garonne-Gironde river-estuary system (Audry et al. 2004) and from there by coastal currents along the Atlantic coast, where the contamination of oysters has been reported more than 400 km from the source (Baudrimont et al. 2005). In the Danube River, the dispersal of sediment-associated metals occurs hundreds of kilometers downstream from past or present mines, resulting in the transfer of contaminants across international borders (Bird et al. 2010). Finally, metal(loid) contamination of the Tinto and Odiel Rivers that drain the former mines in the Iberian Pyrite Belt is transferred by marine currents to the Mediterranean Sea through the Strait of Gibraltar (Elbaz-Poulichet et al. 2001).

It is precisely this inflow of Atlantic water through the Strait of Gibraltar towards the Mediterranean Sea that could be the reason for the high Zn levels found in the Strait of Gibraltar-Alboran Sea demarcation compared to the Levantine-Balearic one (Fig. 2b). In fact, the Zn values in mussels from this area of the Spanish coast are one of the highest measured in the Mediterranean Sea (Table 3). Although most of these values can be associated with domestic or industrial areas (i.e. Algeciras and Malaga), levels were similar in locations considered low-impacted coastal areas (i.e. Estrecho, Marbella, Fuengirola, Almuñecar and Calahonda) as well as in reference stations (i.e. Manilva and Herradura). Therefore, in addition to the anthropogenic factor, another Zn input may exist. The western area of the Strait of Gibraltar, the Gulf of Cadiz, has historically been identified as an area affected by the input of metal-rich rivers (Guadiana, Tinto-Odiel and Guadalquivir) (Van Geen et al., 1997). The elevated concentrations in these rivers (Delgado et al., 2009; Laiz et al., 2020) resulted from their passage through the Iberian Pyritic Belt (Munha et al., 1986). This geological formation recognised as the largest area of sulphide mineralization in the world, hosting great quantities of ores, including 14.6 Mt of Cu, 13.0 Mt of Pb, 34.9 Mt of Zn or 46,100 t of Ag (Leistel et al., 1998). As a consequence, studies have observed high metal concentrations of Zn (up to 10.4 ug/L) (van Geen et al., 1991, Laiz et al., 2020) in the Gulf of Cádiz compared to the 0.01-0.2 ug/l typical in Atlantic waters (Landing et al., 1995; Ellwood and van den Berg, 2000). However,

these high values are not restricted to this area since they are transported by the coastal currents towards Portuguese coasts (Santos-Echeandia et al., 2012) or through the Strait of Gibraltar to the Mediterranean Sea (van Geen et al., 1988; Elbaz-Poulichet et al., 2001). With the aim of confirming our hypothesis, we conducted a study of the fluxes through the Strait of Gibraltar between 1993 and 2013 in a virtual transect located near Tarifa. The net flow, resulting from the inputs to and outputs from the Mediterranean Sea was calculated and integrated for the two years previous to the mussels sampling date (around 15 May). Andrisoa et al. (2019) showed that the age of 3-4 cm mussels in this area may be around 2 years. Although 2 years may seem a long time, some authors (Wang et al., 1996) have reported low decontamination kinetics in mussels. Net inflows to the Mediterranean Sea and mean Zn concentrations in mussels for all the stations in the Strait of Gibraltar Strait-Alboran Sea (n=10) by year were plotted (Fig. 5). The pattern of both variables (net flow and Zn concentrations) was very similar showing the possibility of being statistically significant. This circumstance was confirmed after application of a Pearson correlation test (n=21, R=0.61, p<0.01). Therefore, it can be concluded that Zn levels in the mussels from this demarcation are strongly influenced by the Atlantic waters enriched in Zn from the Gulf of Cadiz.

3.4.A proposal for subregional trace metal(loid) background concentrations (BC) in the Mediterranean Iberian coast mussels

To date, baseline metal(loid) values have been reported for the whole western Mediterranean basin (Andral et al., 2010; Benedicto et al., 2011), with background concentrations (BC) and background assesment criteria (BAC) proposed for the whole Spanish Mediterranean coast (Marine Strategy Framework Directive in Spain) (Table 5). BACs are derived mathematically from BCs to enable the robust analysis of monitoring data in relation to the objective that concentrations should be “near background”.

After understanding both the natural and anthropogenic pressures and hydrological, biogeochemical and oceanographic processes that may occur along the Spanish Mediterranean coast, our aim is to establish updated subregional BCs and BACs for some metals that Marine Strategy Framework Directive (i.e. Cd, Hg and Pb) considers priority pollutants. In addition, we intend to set new concentrations and criteria for other metals in mussels in this area, which are not currently included but could be of future interest (i.e. As, Cu and Zn). In fact, such BACs values for the Atlantic area already exist (OSPAR 2008) (Table 5). The existence of baseline values for a high number of elements, despite such elements not being current priority substances has proven to be of great help when evaluating the impact of environmental catastrophes (i.e. the Prestige oil tanker accident; Soriano et al., 2006) or in view of the imminent entry into the environment of emerging pollutants (i.e. Platinum Group Elements; Neira et al., 2015).

Different BCs should be proposed for each demarcation along the Spanish Mediterranean coast for As and Zn due to the own singularities of each demarcation (i.e. geology, hydrology and oceanography). For this purpose, the 90th percentile of the reference areas (i.e. I. Medas, I. Columbretes, Tabarca, Herradura and Manilva, Table S1) in the last six years of the study (2008-2013) has been applied (León et al., 2013). For the Levantine-Balearic demarcation, BCs would be 78.2 mg/kg d.w. for As, and 133 mg/kg d.w. for Zn. In the case of the Strait of Gibraltar-Alboran Sea demarcation, BCs would be 18.3 mg/kg d.w. for As and 314 mg/kg d.w. for Zn (Table 5). For the other elements, BCs along the Spanish Mediterranean coast would be

1.08 mg/kg d.w. for Cd, 5.83 mg/kg d.w. for Cu, 0.134 mg/kg d.w. for Hg and 1.89 mg/kg d.w. for Pb (Table 5). Although the general temporal trend along the Spanish Mediterranean coast was a decrease in metal(loid) concentrations as a result of the actions taken and directives implemented, levels of As in the north and Zn in the south derive from a “natural geologic” source and their levels seem to have reached a minimum. The case of As must be taken with caution since one of the two reference stations in the Levantine-Balearic demarcation presents historical maximums for this element (i.e. I. Medas). Therefore, if this station were excluded, the baseline value would be 3.1 mg/kg d.w. This is not the case for Zn, since both reference stations present similar values. The new proposed BACs, obtained as a result of multiplying the BCs by 1.5 (OSPAR REF), for the Levantine-Balearic demarcation are 117 mg/kg d.w. for As and 200 mg/kg d.w. for Zn. In the case of the Strait of Gibraltar-Alboran Sea demarcation, BAC values would be 27.5 mg/kg d.w. for As and 471 mg/kg d.w. for Zn. For other elements, BACs would be common for both demarcations: 1.62 mg/kg d.w. for Cd, 8.75 mg/kg d.w. for Cu, 0.202 mg/kg d.w. for Hg and 2.83 mg/kg d.w. for Pb (Table 5).

In the absence of a level for Environmental Assessment Criteria (EACs) derived from ecotoxicological tests, such as the ones of organic pollutants (OSPAR Commission; Law et al. 2010), the decision taken was to adopt the contaminant concentrations in fish and shellfish for human health risk, and the use of Commission Regulation (EC) No 1881/2006 (and subsequent additions and amendments) to protect public health (European Commission, 2006). This regulation includes maximum levels for Pb (7.5 mg/kg d.w.), Hg (2.5 mg/kg d.w.), and Cd (5.0 mg/kg d.w.) (Table 5), in bivalve molluscs but not for the other elements presented in this study, although recent updates of the regulation have included As in rice. However, at least in the case of Hg (2.5 mg/kg d.w.), the value requires readjustment, with some exceptions (i.e. the Tyrrhenian Sea; Leonzio et al., 1981). This is because, to the best of our knowledge, environmental levels in mussels from different world coastal areas are well below (at least one order of magnitude) these concentrations (Besada et al., 2012; Table 3 of this study). It would be worth addressing this topic in the future to obtain ECs for metal(loid)s from ecotoxicological test data as already happens with organic pollutants.

If we consider all the samples measured during the 20-year series, 31%, 5%, 44%, 12%, 5% and 16% of them had concentrations above the BAC values for Hg, Cd, Pb, Cu, Zn and As respectively in the Levantine-Balearic demarcation and 13%, 1%, 30%, 1%, 3% and 0% for the same elements in the Strait of Gibraltar-Alboran Sea demarcation. However, if only the last two years of sampling (2012-2013) were taken into account, the percentages decrease to 14%, 0%, 24%, 10%, 2%, 0% for Hg, Cd, Pb, Cu, Zn and As respectively in the Levantine Balearic demarcation and 0%, 0%, 24%, 0%, 5% and 0% for the same elements in the Strait of Gibraltar-Alboran Sea demarcation. This marked decrease in all the elements confirms the data presented in section 3.2. (Temporal trends) resulting from the implementation of new regulatory measures to protect the coastal environment. Nevertheless, the data clearly show that, for metal(loid) pollution, the environmental status of the Strait of Gibraltar-Alboran Sea demarcation waters was better than those of the Levantine-Balearic ones. With the exception of the high Pb concentrations consistently measured in bivalves from Barcelona, Vallcarca, Castellón, Portmán, Almuñecar and Málaga, none of the other paired observations (location/metal(loid)) represent a risk for human consumption as their values are below the ECs. However, it is important to highlight that the percentage of the stations that do not meet the EC value for Pb has not decreased over time. If we consider all the samples measured

during the 20-years series, 12% of them exceeded the value. If only using data from the last 5 years, 14% of them exceed the value, compromising the GES of certain areas of the Spanish Mediterranean coast.

4. Conclusions and Future work

The present study provides an overview of the state of contamination and evolution over time of metal(loid)s in coastal waters of the Spanish Mediterranean through monitoring of wild mussels. In most of the cases, the decreasing temporal trends were statistically significant, mainly for Pb and Hg. This evolution is probably the consequence of the regulatory measurements adopted and decision-making by policy makers, through implementation of European directives and restrictions on discharges into the marine environment. Regarding the spatial distribution, data analysis has demonstrated a proper selection of reference areas and hot-spots in the Iberian mussel network. However, in the case of As and Zn concentrations in mussels, we observed marked geographical distribution differences that were not always associated with potential anthropogenic pressures. It has been shown that natural factors such as hydrology, oceanography and biogeochemistry have to be taken into account when evaluating the data obtained in monitoring programmes since such factors can cause high concentrations of metal(loid)s in areas far from sources of contamination. Despite the implementation of different regulatory measures over the years in the form of directives, levels of these two metal(loid)s continue to be high in mussels as a result of natural factors and processes such as those already mentioned. Therefore, this work demonstrates that it is vitally important to define the background levels of metal(loid)s at the regional or subregional scale so that areas not affected by anthropogenic causes but with high values as a result of natural processes do not constantly breach directives.

Despite this extensive study, and others conducted in the past, much work still remains to be done in monitoring pollution as programmes are in continuously evolving. It would also be of great interest to analyze a greater number of metal(loid)s apart from those the directives indicate as priority substances. These would include those associated with new technologies, the emerging Technology Critical Elements (TCEs), which could pose a risk to the environment in the near future. It would also be important to establish BCs and ECs for more metal(loid)s, including those of emerging concern, since they point the likely impact of pollutants on the environment.

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Figure captions:

Figure 1. Location of sampling sites along the Spanish Mediterranean coast.

Figure 2. a) Average Hg, Cd and Pb concentrations in mussel tissues from the Spanish Mediterranean coast over the 20-years sampling period. **b)** Average Cu, Zn and As concentrations in mussel tissues from the Spanish Mediterranean coast over the 20-years sampling period.

Figure 3. a–c: Temporal variations of Hg, Cd and Pb (mg/kg dry weight) in mussel tissues from the Spanish Mediterranean coast during the period 1993–2013.

Figure 4. a) Arsenic concentration in seven different locations on the north area of the Spanish Mediterranean coast and water flow (dotted line) at the Cap de Creus during the period 2001-2013. **b)** Location of the transect where water flows towards the Spanish coast were calculated.

Figure 5. Mean concentration of Zn in mussels from the Strait of Gibraltar-Alboran Sea demarcation and net water flow towards the Mediterranean Sea in a transect located in Tarifa during the period 1993-2013.

Figure 1

Figure 2

b

C

Figure 4

Figure 5

Table 1. Information about the mussel sampling sites (31) along the Iberian Mediterranean coast, indicating mean temperature and salinity values, description, sampling years, and a purpose of each one

		Temperature (°C)	Salinity (‰)	Description	Sampling Years	Type
1	Cadaqués	17,1±1,1	37,5±0,4	C	1993-1999;2002-2007;2011	S
2	I. Medas	17,6±1,6	37,4±0,4	R	1993-2013	T
3	Blanes	17,7±1,1	37,6±0,3	C	1993-1999;2002-2007;2011	S
4	Barcelona	17,8±1,4	37,6±0,3	V	1993-2013	T
5	Vallcarca	18,2±1,6	37,4±0,4	C	1993-1999;2001-2007;2011	S
6	Tarragona	19,4±1,5	37,1±0,5	V	1993-2013	T
7	Salou	18,0±1,8	37,6±0,3	V	1993-1999	S
8	Delta del Ebro	19,2±1,7	34,5±2,8	C	1993-2002;2004-2013	T
9	Peñíscola	19,2±1,6	35,9±1,1	C	1993-1999;2003-2013	T
10	I. Columbretes	17,6±0,9	37,9±0,6	R	1993-1997;2002-2003;2005-2008;2010	S
11	Castellón	18,9±1,2	37,5±0,9	V	1993-1999;2005-2013	S
12	Valencia	19,4±1,8	37,4±0,4	V	1993-2013	T
13	Cullera	19,1±1,1	37,2±0,4	C	1993-1999;2001-2012	S
14	C. Nao	19,1±2,0	37,7±0,2	C	1993-2000	S
15	Alicante	20,1±1,3	37,6±0,1	V	1993-1999	S
16	Santa Pola	19,9±0,9	37,3±0,8	C	2004-2013	S
17	Tabarca	19,6±1,1	37,4±0,7	R	1993-1999;2002-2004	S
18	Portmán	21,6±0,9	37,0±0,4	C	1993-1995;1997-2003; 2005-2013	T
19	Cartagena	20,7±1,2	36,9±0,5	C	1993-2013	T
20	Águilas	19,2±0,6	37,0±0,7	C	1993-1996;1998-1999;2002-2003	S
21	Almería	18,7±1,4	37,1±0,5	V	1993-1998	S
22	Calahonda	18,1±2,0	37,0±0,4	C	1993-1999;2001-2006;2011	S
23	Almuñecar	17,9±2,1	37,0±0,6	C	1993-1999;2001-2007;2011	S
24	La Herradura	18,3±1,8	37,0±0,6	R	1993-1999;2001-2012	T
25	Torrox	18,8±1,6	36,8±0,5	C	1993-1999;2003-2007;2011	S
26	Málaga	18,1±1,8	37,3±0,4	C	1993-1999;2004-2013	S
27	Fuengirola	18,3±1,6	37,1±0,4	C	1993-1999;2001-2007;2011	S
28	Marbella	19,0±1,2	36,6±0,5	C	1993-1999;2003-2006;2011	S
29	Manilva	17,0±1,2	37,0±0,4	R	1993-2013	T
30	Algeciras	19,5±2,1	36,1±1,3	V	1994-2013	T
31	Estrecho	17,1±1,2	36,9±0,3	C	1993-2007	S

C: Coastal Site; R: Reference Site; V: Vulnerable Site

S: Spatial study; T: Temporal trend

Table 2. Summary of the concentrations of trace metals (mg/kg dry weight) in wild mussels for the five sampling surveys (Std = standard deviation).

	1993 (n=28)			1998 (n=29)			2003 (n=23)			2007 (n=24)			2011 (n=23)			Historical (1993-2013) ^a		
	Median	Mean±Std	Range	Median	Mean±Std	Range	Median	Mean±Std	Range	Median	Mean±Std	Range	Median	Mean±Std	Range	Median	Mean±Std	Range
As	-	-	-	-	-	-	16.5	21.3±19.1	3.05-86.0	22.2	23.5±15.3	2.25-75.7	14.2	14.5±5.96	2.01-26.1	14.9	16.8±13.9	1.76-112
Cd	0.557	0.649±0.460	0.111-2.99	0.527	0.592±0.374	0.064-1.97	0.489	0.553±0.363	0.109-1.74	0.750	0.756±0.392	0.140-1.68	0.504	0.571±0.271	0.130-1.15	0.505	0.592±0.428	0.045-3.41
Cu	6.33	5.91±2.55	0.793-11.2	5.87	5.03±2.67	0.551-10.7	6.45	5.42±2.86	0.766-11.5	5.42	5.42±2.54	0.700-12.3	6.04	5.94±2.00	0.818-10.8	5.86	5.30±3.02	0.287-16.6
Hg	0.172	0.215±0.153	0.012-0.656	0.180	0.185±0.117	0.031-0.493	0.106	0.112±0.071	0.017-0.299	0.109	0.108±0.049	0.015-0.197	0.093	0.112±0.060	0.013-0.295	0.120	0.148±0.126	0.002-0.847
Pb	2.88	7.63±25.1	0.357-181	2.41	3.41±5.29	0.310-49.0	2.45	4.20±6.92	0.279-39.6	2.33	4.24±6.29	0.223-32.4	1.79	2.79±2.54	0.163-11.3	2.24	5.05±17.2	0.115-271
Zn	130	149±85.7	18.4-389	111	146±107	15.5-429	151	164±115	16.9-444	121	151±102	14.6-388	129	142±64.7	21.7-2.87	119	146±107	13.7-584

^a Calculated considering all sampling sites (31) and years (20) for each trace metal.

Table 3. Trace metal concentrations in mussels from similar monitoring studies (values in mg/kg dry weight).

Location	As	Cd	Cu	Hg	Pb	Zn	Reference
Mediterranean coast (Spain)	1.76-112	0.045-3.41	0.287-16.6	0.002-0.847	0.115-271	13.7-584	<i>This work</i>
Western Mediterranean	-	0.46-2.89	-	0.04-0.33	0.5-8.3	-	Benedicto et al., 2011*
Balearic Islands (Spain)	0.80-11.0	0.25-1.70	5.90-58.3	0.13-2.21	3.3-18.6	48.9-317	Deudero et al., 2007
Mediterranean coast (France)	-	0.20-10.0	3.8-67	0.04-0.68	0.10-27.7	43-357	Ifremer, 2006
Tyrrhenian Sea (Italy)	-	1.08-1.89	-	0.09-0.13	0.98-1.62	-	Lafabrie et al., 2007
Adriatic Sea (Italy)	8.00-42.0	0.40-1.90	1.50-10.0	0.02-0.22	0.30-3.20	15.0-160	Fattorini et al., 2008
Adriatic Sea (Gulf of Trieste, Italy)	14.7-29.9	0.51-1.24	3.46-11.3	-	0.76-2.16	73.4-172	Kristan et al., 2014
Adriatic Sea (Croatia)	18.1-22.1	0.4-0.6	2.3-11.8	-	0.5-6.2	51.7-194	Kanduc et al., 2016
Adriatic Sea (Croatia)	-	0.48-1.72	5.92-369	0.12-10.30	0.99-14.79	93-536	Kljakovic-Gaspic et al., 2010
Adriatic Sea (Montenegro)	-	-	4.6-17.2	-	-	132-280	Joksimovic et al., 2011
Mediterranean Sea (Greece)	-	0.262-5.43	0.9-11	-	-	33-804	Sakellari et al., 2013
Mediterranean Sea (Turkish coastline)	5.3-18.3	0.09-3.32	3.9-173	-	bdl-22.9	16-441	Belivermis et al. 2016
Mediterranean Sea (Algerian West Coast)	-	0.50-0.82	1.0-15.7	-	3.10-15.5	71.6-154	Rouane-Hacene et al., 2015
Mediterranean Sea (Lybian coastline)	-	1.19-2.41	3.56-5.32	-	0.41-0.71	141-197	Galgani et al., 2014*
Galicia and Cantabrian coast (NW Spain)	6.39-13.3	0.357-2.01	3.94-9.92	0.055-0.623	0.658-28.1	141-361	Besada et al., 2014

bdl.

Below detection limit

*Caged mussels

Table 4. Kendall τ -b correlations for the different metals at the different sites.

Site		As	Cd	Cu	Hg	Pb	Zn	Period
Medas Islands	Kendall τ -b	-0.128	-0.076	-0.438**	-0.339*	-0.429**	-0.057	1993-2013
	Significance level τ -b	0.295	0.327	0.003	0.016	0.003	0.371	n=21
Barcelona	Kendall τ -b	-0.205	0.352*	-0.076	0.019	-0.247	-0.267*	1993-2013
	Significance level τ -b	0.183	0.013	0.327	0.464	0.062	0.049	n=21
Tarragona	Kendall τ -b	-0.333	-0.486**	0.352*	-0.638**	-0.514**	-0.362*	1993-2013
	Significance level τ -b	0.064	0.001	0.013	0.000	0.000	0.011	n=21
Delta del Ebro	Kendall τ -b	-0.412*	-0.074	-0.021	-0.684**	-0.274*	-0.190	1993-2013
	Significance level τ -b	0.032	0.339	0.462	0.000	0.049	0.130	n=20
Peñíscola	Kendall τ -b	-0.200	-0.451**	-0.190	-0.307*	-0.621**	-0.569**	1993-2013
	Significance level τ -b	0.223	0.004	0.147	0.041	0.000	0.000	n=18
Castellón	Kendall τ -b	-0.276	-0.505**	-0.276	-0.510**	-0.886**	-0.391*	1993-2013
	Significance level τ -b	0.084	0.004	0.084	0.004	0.000	0.023	n=15
Valencia	Kendall τ -b	-0.590**	-0.133	0.152	-0.320*	-0.219	-0.248	1993-2013
	Significance level τ -b	0.002	0.210	0.177	0.022	0.088	0.062	n=21
Cullera	Kendall τ -b	-0.636**	-0.137	-0.085	-0.197	-0.425**	-0.163	1993-2012
	Significance level τ -b	0.002	0.227	0.327	0.128	0.007	0.184	n=18
Portman	Kendall τ -b	-0.485*	-0.567**	-0.216	-0.328*	-0.602**	-0.567**	1993-2013
	Significance level τ -b	0.016	0.000	0.106	0.025	0.000	0.000	n=19
La Herradura	Kendall τ -b	-0.333	-0.041	-0.298	-0.265	-0.252	-0.111	1993-2012
	Significance level τ -b	0.076	0.418	0.040	0.058	0.072	0.267	n=19
Málaga	Kendall τ -b	0.200	-0.044	-0.471**	-0.177	0.338*	-0.206	1993-2013
	Significance level τ -b	0.242	0.420	0.004	0.174	0.032	0.135	n=17
Fuengirola	Kendall τ -b	-0.286	0.295	-0.105	-0.505**	0.200	0.010	1993-2011
	Significance level τ -b	0.199	0.070	0.313	0.004	0.164	0.500	n=15
Manilva	Kendall τ -b	-0.026	0.019	-0.305*	-0.501**	-0.533**	-0.371**	1993-2013
	Significance level τ -b	0.476	0.464	0.028	0.001	0.000	0.009	n=21
Algeciras	Kendall τ -b	-0.382*	-0.358*	-0.211	-0.811**	-0.190	-0.574**	1994-2013
	Significance level τ -b	0.043	0.014	0.104	0.000	0.130	0.000	n=20

* Correlation is significant at the 0.05 level (1-tailed).

* * Correlation is significant at the 0.01 level (1-tailed).

Table 5. Proposed baseline concentrations and assessment criteria in the Western Mediterranean and subregional scales

	As (mg/kg d.w.)	Cd (mg/kg d.w.)	Cu (mg/kg d.w.)	Hg (mg/kg d.w.)	Pb (mg/kg d.w.)	Zn (mg/kg d.w.)	Reference
Background concentration levels (BCs)							
West Mediterranean coast (caged mussels)	-	1.29	-	0.090	1.17	-	Andral et al., 2010
West Mediterranean coast (caged mussels)	-	1.33	-	0.100	1.40	-	Benedicto et al., 2011
Iberian Mediterranean Coast	-	0.725	-	0.125	2.50	-	IEO datasets (2015)
Western Mediterranean region	-	0.660	-	0.109	1.58	-	UNEP/MAP/MEDPOL 2016 (MEDPOL Database)
Alboran Sea	-	0.607	-	0.103	1.51	-	
North Western Mediterranean	-	0.690	-	0.110	1.59	-	
Western Islands and Archipelagos		1.330	-	0.111	1.70	-	
Levantine-Balearic (L-B)	78.2	1.08	5.83	0.134	1.89	133	<i>This study</i>
Strait of Gibraltar-Alboran Sea (SG-AS)	18.3	1.08	5.83	0.134	1.89	314	<i>This study</i>
Background Assessment Criteria (BACs) and Environmental Criteria (ECs)							
BAC Iberian Mediterranean Coast*	-	1.08	-	0.188	3.80	-	IEO datasets (2015)
BAC NW Mediterranean Sea	-	1.09	-	0.188	3.80		UNEP/MAP/MEDPOL 2015
BAC Mediterranean Sea (Med BACs)		1.09		0.173	2.31		UNEP/MAP/MEDPOL 2016 (MEDPOL Database)
BAC proposed value L-B	117	1.62	8.75	0.202	2.83	200	<i>This study</i>
BAC proposed value SG-AS	27.5	1.62	8.75	0.202	2.83	471	<i>This study</i>
BAC OSPAR	-	0.96^^	5.5^	0.09^^	1.30^^	150^	OSPAR 2008^/OSPAR2009^^ CE 2006**
EC	-	5	-	2.5	7.5	-	

* applied under the EU Marine Strategy Framework Directive (EU MSFD) in Spain
**Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in food stuffs.

Author declaration

1. Conflict of Interest

Potential conflict of interest exists: No

We wish to draw the attention of the Editor to the following facts, which may be considered as potential conflicts of interest, and to significant financial contributions to this work: Not applicable

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Credit author statement

Juan Santos-Echeandia, writing of the manuscript.

Juan A. Campillo, conceptual design and revision of the manuscript.

Jose A. Egea, statistics.

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