

# Comparing spatial and temporal changes in metal trends (Cr, Ni, Pb and Zn) on the Portuguese shelf since the 1970s

Mário Mil-Homens · Rodney L. Stevens ·  
Ingemar Cato · Fátima Abrantes

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**Abstract** Comparison between an archive dataset, collected during the 1970s (1974–1977), and samples taken during the PALEO1 cruise (2002) enabled evaluation of large-scale and long-term spatiotemporal changes in Al, Cr, Ni, Pb and Zn contents in bulk surface sediments in four areas of the Portuguese shelf. The so-called gradient method (GM) with normalisation to Al, a proxy for terrigenous clay content, was applied. The studied areas are distributed from north to south along the western margin, with the northernmost located off shore the Ave and Douro rivers, a central one located off shore the Lis River and a southern one located off shore the Mira River. One-way ANOVA and Kruskal-Wallis tests were

used to identify differences among study areas and periods of sample collection. A comparison of metal contents in 2002 samples with the Portuguese classification scheme regulation for deposition of dredged materials in coastal areas indicates good environmental quality in terms of Cr, Ni, Pb and Zn levels. Nevertheless, the GM results suggest an increase in metal loadings relative to Al from the 1970s to the 2002 samples (except for Pb). The Algarve area on the southern shelf is characterised by having high number of sites with metal level on class 2. These high values have traditionally been explained by a substantial supply of natural metals from the Guadiana, Tinto and Odiel rivers that drain areas Iberian Pyrite Belt formations. This supply has probably been magnified by present and past mining activities. For quality evaluation of marine sediments, especially when using total metal contents, this study shows the importance of considering all possible sources of metal loading. The natural grain size and composition variability have also a crucial influence on the metal content, and the combined evaluation allows a more holistic perspective.

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M. Mil-Homens (✉)  
Divisão de Oceanografia Ambiental e Bioprospeção, Instituto  
Português do Mar e da Atmosfera, I.P.,  
Avenida de Brasília, 1449-006 Lisboa, Portugal  
e-mail: mario.milhomens@ipma.pt

R. L. Stevens  
Department of Earth Sciences, University of Gothenburg,  
P.O. Box 460, 405 30 Gothenburg, Sweden

I. Cato  
Division of Geophysics and Marine Geology, Geological  
Survey of Sweden,  
P.O. Box 670, 75 128 Uppsala, Sweden

F. Abrantes  
Divisão de Geologia Marinha e Georrecursos, Instituto  
Português do Mar e da Atmosfera, I.P.,  
Avenida de Brasília s/n, 1449-006 Lisboa, Portugal

M. Mil-Homens  
CIIMAR, Marine and Environmental Research Center,  
Rua dos Bragas, 289, 4050-123 Porto, Portugal

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## Introduction

The growth of environmental concern in modern societies has motivated national and local authorities to monitor environmental status (e.g., O'Connor 1990) and to

implement new environmental policies. Numerous investigations have demonstrated the occurrence of metal contamination in shallow marine environments such as in Sydney's estuaries and adjacent offshore areas (Birch 1996) and Gulf of Lions (Roussiez et al. 2006). Previous studies on shallow marine environment/riverine systems off western Iberia indicated anthropogenic influences responsible for local and confined contamination areas of the inner and middle part of the Galician rias (Prego and Cobelo-Garcia 2003), estuaries (e.g., Bilbao estuary (Cearreta et al. 2000), Huelva estuary (Nieto et al. 2007)) and Gulf of Cadiz (Palanques et al. 1995). In Portugal, previous studies documented high levels of metal contamination in the Ave River (Gonçalves et al. 1992), the Cávado River (Gonçalves et al. 1994), the Aveiro lagoon (e.g., Ramalhosa et al. 2005), the Tagus (Canário et al. 2005; Vale et al. 2008) and the Sado (Cortês and Vale 1995) estuaries. The contaminants may further be transferred to the adjacent shelf area (e.g., Jouanneau et al. 1998; Mil-Homens et al. 2009) and partially to deeper parts of the Portuguese Margin through submarine canyons (Richter et al. 2009; Costa et al. 2011; Mil-Homens et al. 2013). According to Machado et al. (2005) the southwestern Iberian sediments are geochemically characterised by the occurrence of trace element (Pb and Zn) enrichments relative to the average shale levels. Mil-Homens et al. (2007) has defined for the Portuguese coast two distinct regional geochemical baselines for Cr, Ni, Pb and Zn related to the differences in the oceanographic and sedimentological settings between the western and Algarve coasts in the archive dataset collected during the 1970s by the Geology and Marine Georesources Division (DivGM-IPMA) (former Marine Geology Department of the Portuguese Geological Survey), with the latter characterised by high metal enrichments. These enrichments are interpreted as reflecting the drainage of Iberian Pyrite Belt (a sedimentary volcanic complex) and the mining activity that for nearly 5,000 years have targeted the metal-enriched formations (Davis Jr. et al. 2000). Mil-Homens et al. (2006) studied the down-core distributions of metal concentrations in the three areas of the Portuguese western coast using the northwestern (off shore the Ave and Douro rivers), central (off shore the Lis River) and southwestern (off shore the Mira River) shelf sectors in the present study. The results obtained show slight anthropogenic enrichments for Pb and Zn in the Lis samples (central shelf) since the beginning of the twentieth century, with the highest levels from the 1950s until the present. In the Ave-Douro cores, the

signal of anthropogenic enrichment was not identified, due in part to the dispersive effect of both bioturbation and the regional strong hydrodynamic processes occurring at shallow (<100 m) water depths. These processes can be responsible for masking or making the anthropogenic signal recorded in sediments weaker. Metal enrichments found down-core in some areas (e.g., Mira area) are probably the result of early diagenetic remobilisation and reprecipitation.

The metal content found in marine sediments reflects a diversified set of natural processes (e.g., source erosion, early diagenesis) and anthropogenic influences. Variations in metal levels of marine deposits do not automatically imply changes in contaminant load from land sources but may rather be related to variable amounts of metal-carrying components of sediments. Since both the minerogenic fine fraction and organic matter are predominantly involved in the inclusion and adsorption of heavy metals, their natural variability with increasing distance from land and under different environmental conditions will strongly affect metal enrichment levels. The distinction between metals with an anthropogenic origin from those occurring naturally must be considered in order to fully evaluate contamination. The accumulation of both natural and anthropogenic components of the sediments occurs simultaneously, complicating their distinction and characterisation. Several procedures have been developed to compensate for these effects of variable grain size and organic matter. Geochemical normalisation involves metal ratios using a reference element, such as Al, Fe, Li or Sc (e.g., Windom et al. 1989; Loring 1990; Loring and Rantala 1992; Grousset et al. 1995), with Al being a reliable indicator of terrigenous alumino-silicate detritus (e.g., Canfield et al. 1996). The so-called gradient method (Cato 1977, 1989) is one of these procedures and consists on a graphic approach that attempts to compensate for natural variability in sediment grain size and organic matter by considering the gradient (slope) between a given metal and the organic carbon, clay or a reference element (e.g., Al) used as a proxy for terrigenous clay minerals. This technique has previously been tested mainly with relatively fine-grained coastal marine and estuarine sediments. In the present work, we apply the gradient method to the predominantly sandy sediments with variable mud (silt + clay) contents of the four areas of the Portuguese continental shelf. Our main aim is to characterise and interpret spatial changes of Cr, Ni, Pb and Zn levels in four areas of the Portuguese shelf, while temporal changes (the

Algarve area was not sampled in 2002) were assessed on the three areas of the western shelf, in order to assess metal contamination. Additionally, in the absence of national sediment quality guidelines, metal contents are classified according to the classification scheme used to regulate dredged materials deposition in coastal areas (Portaria no. 1450/2007), with the aim to demonstrate the importance of accounting the sediment natural variability in the evaluation of sediment quality.

## Regional setting

The wave regime along the Portuguese shelf shows strong seasonal variability (Costa 1992). In summer, the NW swells have wave heights lower than 2 m along the entire west coast; in winter, the northern and southern sectors are characterised by NW swells with wave heights of about 3–4 and 2 m, respectively. Strong storm events with wave heights greater than 9 m only occur along the northern coast during southerly wind periods (Vitorino et al. 2002). The southern Portuguese coast has a lower wave energy regime, and swells are predominantly from the SW–S and SE, with average wave heights of 1 m, while during storms (also from the SW and SE), the wave heights do not reach 5 m (Costa 1992).

Onshore, the region north of Nazaré is characterised by rough relief, with several mountains exceeding 1,000 m. This facilitates orographic precipitation ( $>1,000$  mm year<sup>-1</sup>) and greater river discharges than in the south (Fig. 1b). Several rivers (e.g., Minho, Lima, Ave, Cávado, Douro) debouch directly into the sea, draining mainly granite, greywacke and schist formations. The Douro River has one of the most extensive drainage basins (Fig. 1a), extending into Spain, and the highest river discharge of all Portuguese rivers (average annual river flux of about  $11.14 \times 10^9$  m<sup>3</sup> years<sup>-1</sup>; APA 2012). Further south, the smaller Lis River drains mainly clastic sedimentary and carbonate formations.

South of Nazaré, the continental morphology is much flatter and the climate is drier. Two major rivers (Tagus and Sado) have large estuaries that would trap most material in transport (Postma 1980). Both rivers drain mainly clastic sediment formations. Compared to these, the Mira River has a limited discharge. The Guadiana is the only major river draining directly in to the southern Algarve coast. The main lithology in both the Mira and Guadiana drainage basins are greywacke, schist and a volcano-sedimentary complex with polymetallic

sulphide complexes of Cu, Pb, Zn and Fe–Mn. The Algarve coast lithology is dominated by carbonate rock cliffs and sandy beaches.

The northern part of the country is both more industrialised and populated than the southern part, with the exception of the Lisboa and Setúbal areas (Fig. 1a). The main industries in the north developed strongly during the 1960s, comprising textile, leather tanning, rubber manufacturing, food processing (olive oil refineries, slaughter houses and cattle breeding areas), galvanisation, electroplating and cement, glass, plastic and paper production industries. In comparison, the southern part generally has a very limited industrial development, associated mainly with old mines within the Iberian Pyrite Belt and with tourism along the Algarve coast. However, agricultural activities are important throughout the country. In Portugal, environmental policies to improve industrial and domestic effluent treatment have been implemented in the late 1980s.

## Materials and methods

### Sediment sampling

Two sets of sediment samples from the Portuguese continental shelf have been used, together extending over ca. 340 km of coastline. One set, the 1977 archive dataset held by the Geology and Marine Georesources Division (DivGM-IPMA), had been collected using Van Veen or Shipeck grabs at 267 sampling sites along the entire Portuguese shelf during several oceanographic cruises in the period 1974–1977. Of these, 155 samples were used in the present study (cf. open and closed circles in Fig. 1a; also, see below). The main goal of this earlier extensive sampling programme was to obtain a general textural and geochemical characterisation of the Portuguese shelf surface sediments.

The second set of samples was taken during the PALEO1 cruise aboard the FS *Poseidon* in May 2002, when 29 Oktopus box-cores were collected in three areas along the western Portuguese shelf (cf. squares in Fig. 1a; Monteiro et al. 2002), which is from north to south, off shore the Ave and Douro rivers ( $n=9$ ) in an area known as Douro Mud Complex, a fine-grained sedimentary body generally having mud contents of more than 50 % (e.g., Dias 1987), the Lis River ( $n=9$ ) and the Mira River ( $n=11$ ) and is the same set published in Mil-Homens et al. (2006). These sampling areas

were selected to represent key environmental settings (oceanography, climate, geology, industrial activity and land use) for specific shelf and adjacent land areas. The 2002 sampling areas are also known to have recent accumulation of relatively fine-grained sediments (Mil-Homens et al. 2006). From the 1977 archive dataset, we selected the three areas that overlapped with the 2002 sampling zones. These were the western shelf areas offshore of (from north to south) the Ave and Douro rivers ( $n=43$ ), the Lis River ( $n=34$ ) and the Mira River ( $n=43$ ) cf. closed circles in Fig. 1a). A fourth area covered by the 1977 archive dataset (albeit not by the 2002 dataset) was selected along the southern continental shelf, off shore the Algarve region ( $n=35$ ).

### Laboratory analyses

#### 1977 archive samples

Surface samples (upper 2 cm) from the archive dataset were prepared and analysed for grain-size distributions and organic carbon, carbonate and metal levels of bulk sediments (<2-mm fractions) during the 1980s. Prior to grain-size analysis, organic matter was removed with  $H_2O_2$ , and water-soluble salts by washing with distilled water. Gravel, sand (63–2,000  $\mu\text{m}$ ) and mud (<63  $\mu\text{m}$ ; silt (63–4  $\mu\text{m}$ ) + clay (<4  $\mu\text{m}$ )) fractions were separated by wet sieving. After drying at 40 °C into an oven, carbonate and metal levels were determined on the fractions less than 2 mm. Carbonate determinations were obtained by means of a gasometric (Hulseman) method. Subsamples analysed for metals were powdered in an agate mortar before digestion. Major (Al) and trace element (Cr, Ni, Pb and Zn) concentrations were determined using 0.1 g after total dissolution in HCl,  $HNO_3$ ,  $HClO_4$  and HF, by means of inductively coupled plasma optical emission spectrometry (ICP-OES) in 1987, following the procedure described in Miranda (1987).

Data accuracy and precision were checked by analysing 17 replicate samples of the reference material (MESS-1) and 28 samples prepared in duplicate and analysed at random positions within a batch. Analytical precision was assessed using the Thompson and Howarth (1976) method modified by Li et al. (1995). Modelled precision for the duplicate samples at  $1\sigma$  is approximately 2 % for Al, 3 % for Cu, 9 % for Ni, Pb and Zn and 20 % for Cr. Based on mean values of replicate samples, accuracy was within 7 % of certified

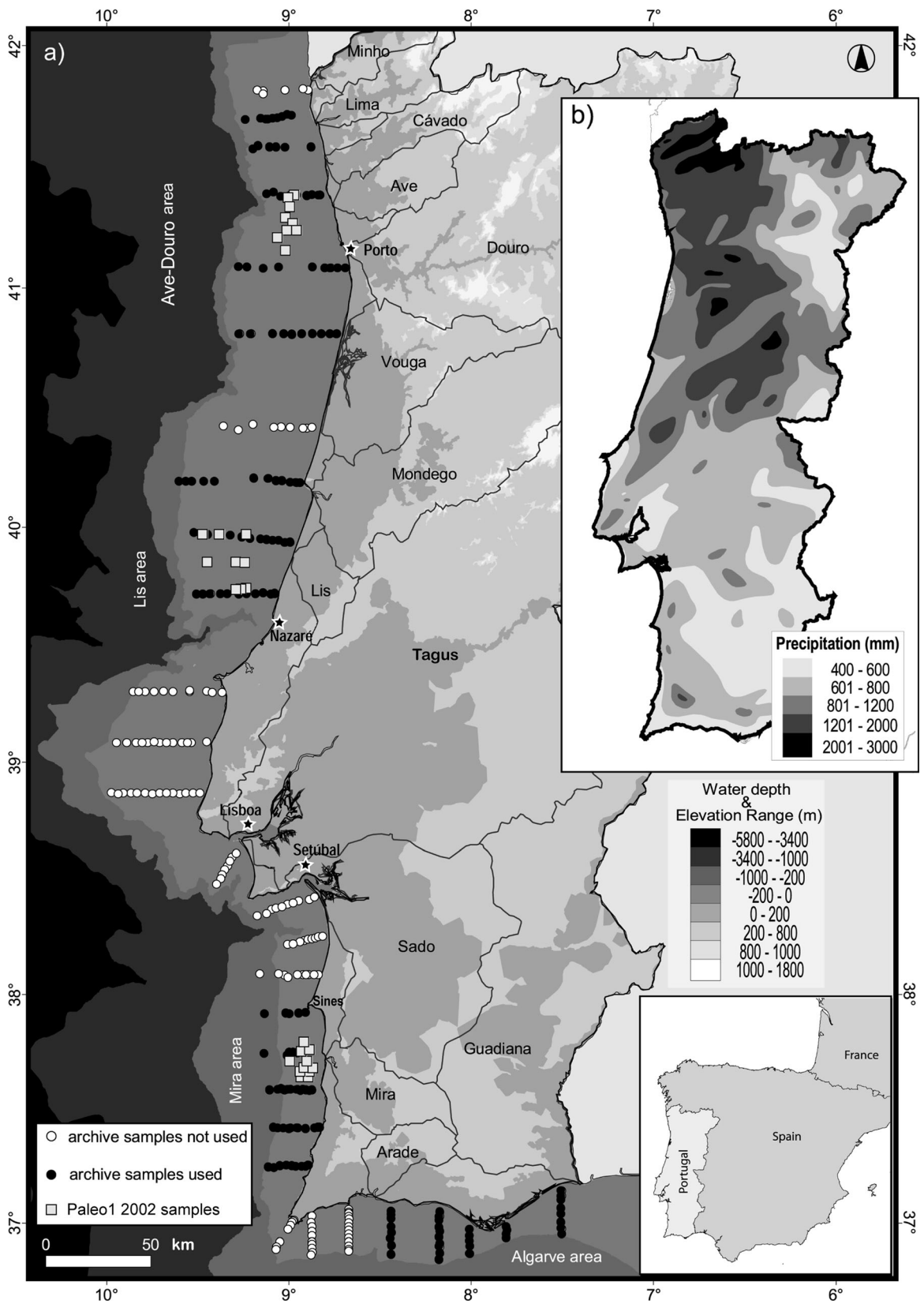
values for Al and Cu, 12 % for Ni and Pb, 19 % for Zn and 38 % for Cr. The low recovery obtained especially for Cr in the archive dataset was probably associated with the presence of refractory minerals (such as chromite) that are partly resistant to chemical attack.

#### 2002 samples

In the PALEO1 2002 surface samples (upper 1 cm layer), the coarsest fraction (>2 mm) was removed by wet sieving after dispersion with Calgon and organic matter destruction with  $H_2O_2$ . One subsample of this material was used for grain-size determinations, which were performed with a Coulter LS230, a laser-based instrument that measures particles between 4 and 2,000  $\mu\text{m}$ . Sand, silt and clay contents were derived from these data. A second subsample was oven-dried at 60 °C and powdered and homogenised in an electrical agate mortar (Fritsch model Pulverisette 7). Organic carbon ( $C_{org}$ ) contents were determined by LECO CHNS 932 based on the difference of the total carbon (TC) measured in the dried sample and the same sample after being combusted for organic carbon ( $C_{org}$ ) destruction during 8 h through a predefined three-stepwise increase in temperature up to 400 °C. Calcium carbonate ( $CaCO_3$ ) contents were then calculated through the formula  $CaCO_3 (\%) = 8.33 \times (C_{inorg})$ , being  $C_{inorg}$  (inorganic carbon) and assuming that all carbonate present as calcium carbonate. Metal levels (Al, Cr, Ni, Pb and Zn) were determined using 0.2 g of this homogenised “bulk” sediment, after total dissolution in a three-step acid treatment (Aqua Regia 3:1  $HCl:HNO_3$ ,  $HClO_4$  and HF). Elemental data were obtained by ICP-OES.

Quality control was assessed by analysis of blank reagents, duplicates and a standard reference material (MAG-1). Based on the model described above for the 1977 dataset, analytical precision at  $1\sigma$  was approximately 2 % for Al, Cr and Ni, 4 % for Zn and 7 % for Pb. Based on mean values, accuracy was in good agreement with certified values for all elements studied. Al and Ni had accuracy better than 4 %, while for Cr, Pb and Zn values are 4–10 %.

**Fig. 1** **a** Locations of 1974–1977 and 2002 sediment sampling sites along the Portuguese shelf, also showing water depth and elevation as well as the main drainage basins. **b** Precipitation map of Portugal. Elevation and precipitation data are from the Atlas do Ambiente Digital (Agência Portuguesa do Ambiente, Alfragide), water depth (bathymetry) data from the DivGM-IPMA (former UGM-LNEG)



## Gradient method

Usually, the most important carriers of contaminants, organic matter and fine-grained minerogenic particles have large specific surface areas available for different types of sorption processes. On that basis, Cato (1977) has proposed a gradient method (GM) based on the relationship between metal contents and a proxy for fine sediments ( $<63 \mu\text{m}$ ), which is organic matter, clay content or a reference element (e.g., Al). When a relationship between metal and Al with a steep gradient (slopes of the equation  $y = a x + b$ , where  $b$  represents the  $y$  intercept) is found, the high level of metal loading can be associated with high levels of contamination. Note that low variability in either the metal-carrier substances or in metal levels constitutes a limiting factor for GM application. The GM approach provides an interpretative tool complementary to other normalisation techniques that can be used in environmental monitoring studies allowing the characterisation of both spatial and temporal evolution trends of metal contents in the marine and estuarine environments.

## Statistical analyses

Box-and-whisker plots were computed for each study area, showing the minimum, maximum, median and lower and upper quartiles for each variable. The box represents the interquartile range that contains 50 % of values. The whiskers are lines that extend from the box to the highest and lowest values. The line across the box indicates the median. The median value was selected as a measure of the central tendency, rather than the mean, because it is not as ambiguous as the mean in skewed populations, which are common in such settings.

The Shapiro-Wilk's test was used to assess the normality of Al, Cr, Ni, Pb and Zn distributions in each study area for both the 1977 and 2002 datasets. Differences among study areas and periods of sample collections were tested using one-way ANOVA (for normally distributed elements) and the Kruskal-Wallis test (for non-normally distributed elements). In order to identify population differences, the data were then analysed using the Dunnett's T3 post hoc test (which does not assume equal variances and accommodates unequal group size and multiple comparisons) for a significance level of 0.05.

## Results

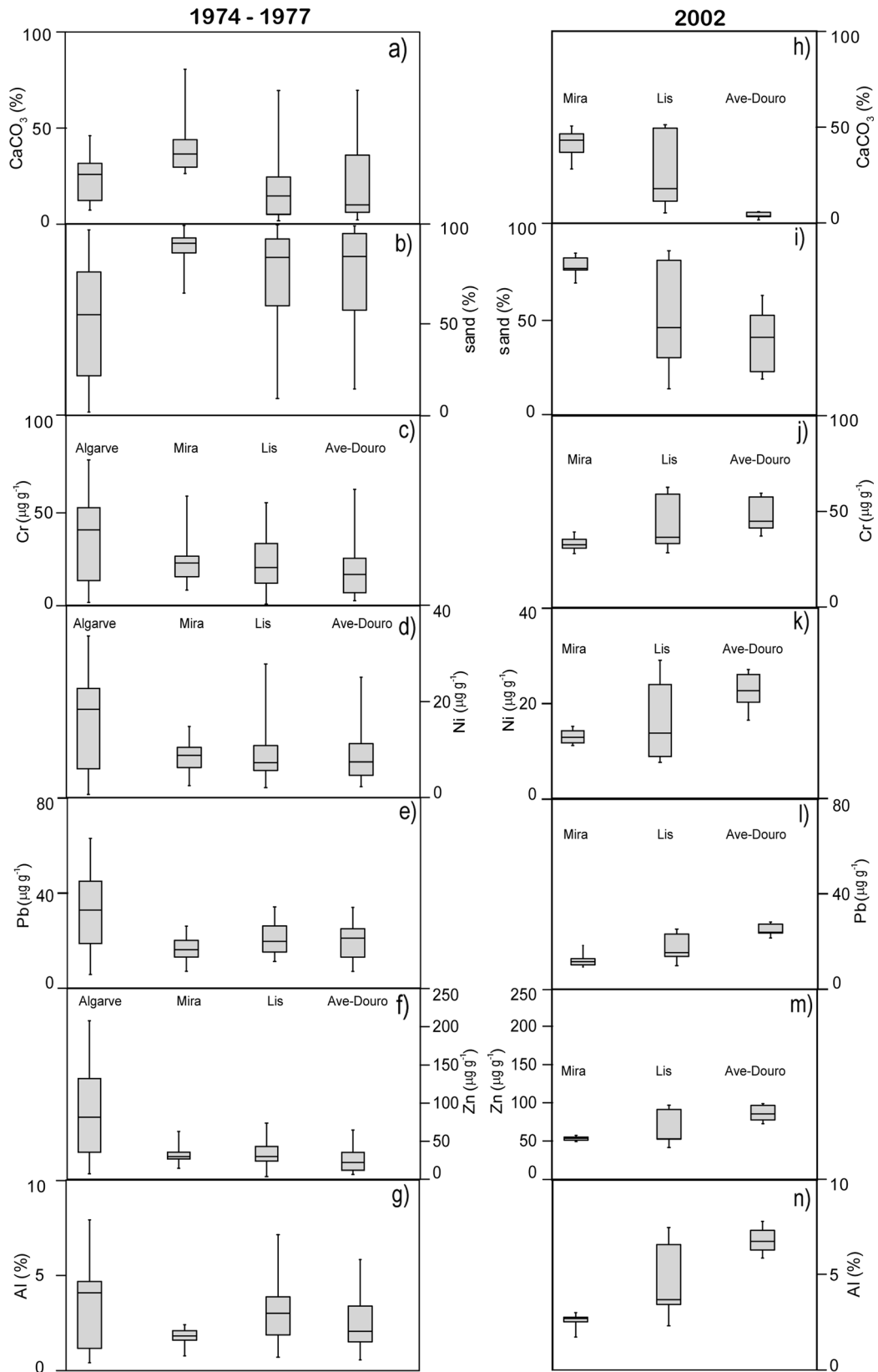
### 1977 archive dataset

In the period 1974–1977, carbonate contents were highest on the southern shelf (Algarve area, median of 26 %) and particularly on the adjacent southwestern shelf (Mira area, median of 36 %; Fig. 2a). The western shelf surface sediments (Ave-Douro 1977, Lis 1977 and Mira 1977 areas) had higher sand contents (median values of 83, 83 and 90 %, respectively; Fig. 2b) than did the southern shelf (Algarve 1977 area; median value of 53 %). Thus, the southern shelf was characterised by higher contents of mud and, as shown more fully below, also the studied heavy metals. The sediments from the Algarve 1977 area were characterised by both high metal and Al values and variability (Fig. 2c–g).

In the 1977 archive dataset, the three study areas on the western shelf (Ave-Douro (A–D), Lis (L) and Mira (M)) had very similar median values for Cr, Ni, Pb and Zn levels, but these were only about half those observed in the Algarve (Alg) study area on the southern shelf (Fig. 2).

Population differences in elemental contents between the 4 studied areas were tested using one-way ANOVA and Kruskal–Wallis test for normally and non-normally distributed metals, respectively. Significant differences in metal contents ( $p < 0.05$ ) among the 4 study areas was determined using the Dunnett's T3 post-hoc tests. Aluminium and metal (Cr, Ni, Pb and Zn) contents in the Alg1977 study area are significantly different from the A-D11977 and M1977 areas and from the 3 areas located on the western shelf, respectively. Significantly positive correlation coefficients ( $r$ ) between mud contents and bulk Al contents were found along the Portuguese shelf ( $0.76 < r < 0.93$ ;  $p < 0.01$ ), except for the M1977 area where  $r = 0.37$  ( $p = 0.14$ ). Furthermore, Cr, Ni, Pb and Zn were correlated with Al in all four study areas ( $r \geq 0.60$ ;  $p < 0.01$ ), except for Pb in the Mira 1977 ( $r = 0.18$   $p = 0.25$ ).

**Fig. 2 a–n** Box-and-whisker plots of  $\text{CaCO}_3$ , sand, Cr, Ni, Pb, Zn and Al in the study areas for the 1977 archive and the PALEO1 2002 datasets. The plot shows the minimum, maximum, median and lower and upper quartiles. The *box* represents the interquartile range that contains 50 % of the values. The *whiskers* are the lines that extend from the box to the highest and lowest values. The *line* across the box indicates the median



## 2002 dataset

Surface sediments from the northwestern Ave-Douro (A-D2002) and southwestern Mira (M2002) areas are characterised by the lowest and highest sand (median values of 41 and 77 %) and carbonate contents (median values of 4 and 43 %), respectively (Fig. 2h, i). The A-D2002 shows higher mud contents (median value of 59 %) and higher contents of the elements Al, Cr, Ni, Pb and Zn than those recorded at M2002 area (Fig. 2j–n).

For the 2002 dataset, after determining significant differences among the three study areas in the elemental concentrations ( $p < 0.05$ ), Dunnett's T3 post hoc tests were applied to specify which areas differ. The results indicate that A-D2002 is significantly different than M2002 for all elements, while L2002 is only significantly different than A-D2002 for Pb and Zn. Al is significantly different in the three study areas. Chromium, Ni, Pb and Zn in the L2002 area are not significantly different than M2002 area. The  $r$  in the Mira area ( $r = 0.70$ ,  $p < 0.05$ ) between mud contents and bulk Al contents is lower than in the other two studied areas (A-D2002,  $r = 0.82$ , and L2002,  $r = 0.93$ ,  $p < 0.01$ ). Chromium, Ni, Pb and Zn were significantly and strongly correlated with Al in the A-D2002 and L2002 areas ( $r \geq 0.81$ ,  $p < 0.01$ ), except for Pb in the A-D2002 area ( $r = 0.62$ ,  $p = 0.08$ ). In the Mira area, the low variability for the 2002 dataset of the studied elements may limit the significance of the calculated regression lines.

## Differences between the two times (1970s vs. 2002)

Comparison of Cr, Ni, Pb and Zn levels between the 1977 archive and the 2002 datasets indicate the possible changes among areas and an increase in content over the 25 years that separates the two sampling periods. The statistical differences, based on one-way ANOVA and Kruskal-Wallis tests, show that Al, Cr, Ni and Zn levels are significantly different between datasets in the western areas, while Pb is not significantly different in the A-D and L.

## Discussion

### 1977 archive dataset vs. 2002 dataset

The high-energy dynamic processes created by both NW swells and northern winds existing along the

western shelf leads to an efficient removal of fine-grained materials from the bottom sediment cover and can thereby explain the low metal contents of the western coast surface sediments. Lower carbonate contents on the A-D shelf, the northernmost study area, are consistent with a large supply of terrigenous, siliciclastic materials from major northern rivers (e.g., Douro, Minho). In contrast, in the Mira area, the highest median carbonate and sand contents (Fig. 2a, b) and the lowest Al range variability are likely to reflect both morphologic characteristics, small rivers with unimportant input of terrigenous material and a narrow shelf, and circulation, where turbulent bottom currents may well induce an efficient transfer of fine material to deeper areas. Additionally, the sand fraction is characterised by abundant biogenic debris. In the Algarve coast area, the relative higher median carbonate contents (median  $\text{CaCO}_3 = 26\%$ , Fig. 2a) are interpreted as a reflection of the occurrence biogenic debris together with the input into the area of the particles generated by the erosion of carbonate rock cliffs. The presence in the marine sediments of these coarse-grained particles and inert substances are responsible for metal dilution.

Organic carbon is not considered in this study because there were insufficient organic carbon measurements for the archive samples from the western shelf. Furthermore, in the 2002 surface sediments, organic carbon is interpreted to be predominantly of marine origin, based on low C/N ratios ( $< 11$ ) and stable carbon isotope signatures of  $-25\text{‰} < \delta^{13}\text{C} < -21\text{‰}$  (Alt-Epping et al. 2009). Thus, it would not necessarily be involved in contaminant transport from land, although organic matter is involved in latter aggregation, sedimentation and consolidation processes of fine-grained particles. Rather, minerogenic particles in the fine fraction, especially clay minerals, are commonly considered to be a main carrier of contaminants from onshore/nearshore to offshore areas along the Portuguese coast. In order to compensate for grain-size and sediment composition effects on metal contents, the latter were normalised against Al levels (e.g., Windom et al. 1989). The use of Al as a proxy for minerogenic fine particles, especially clay minerals, is supported by the moderately strong correlations recorded between mud contents and bulk Al contents for the 1977 archive ( $r = 0.79$ ,  $p < 0.01$  for Ave-Douro;  $r = 0.76$ ,  $p < 0.01$  for Lis;  $r = 0.93$ ,  $p < 0.01$  for Algarve) and 2002 ( $r = 0.82$ ,  $p < 0.01$  for Ave-Douro;  $r = 0.93$ ,  $p < 0.01$  for Lis;  $r = 0.79$ ,  $p < 0.01$  for Mira) datasets. The highest coefficients of

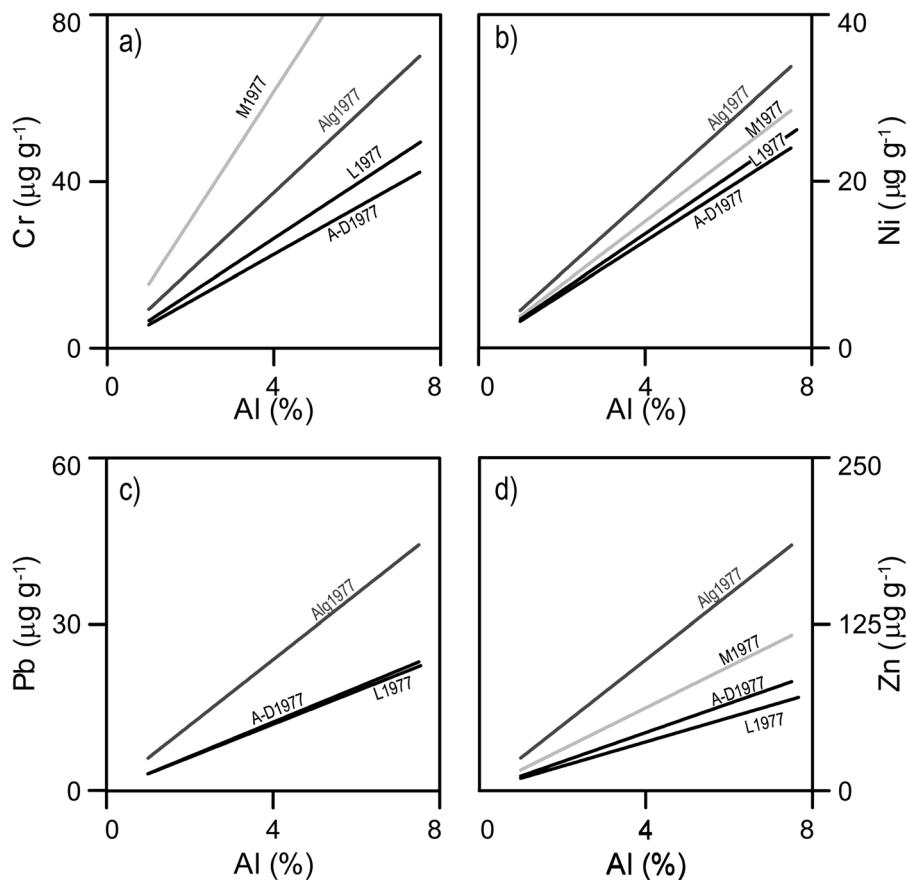


determination ( $R^2$ ) obtained for sediments from the Alg1977 area indicate that most of the metal content variability (between 88 and 98 % for Pb and Ni, respectively) is explained by Al (proxy for fine-grained particles). The decrease of metal variability explained by Al on the three western coast areas may suggest the influence of other sediment components as carriers for them (e.g., organic matter, amorphous silica, Fe oxyhydroxides). This can also be reflected by the occurrence of intercepts different from zero in Figs. 3 and 5.

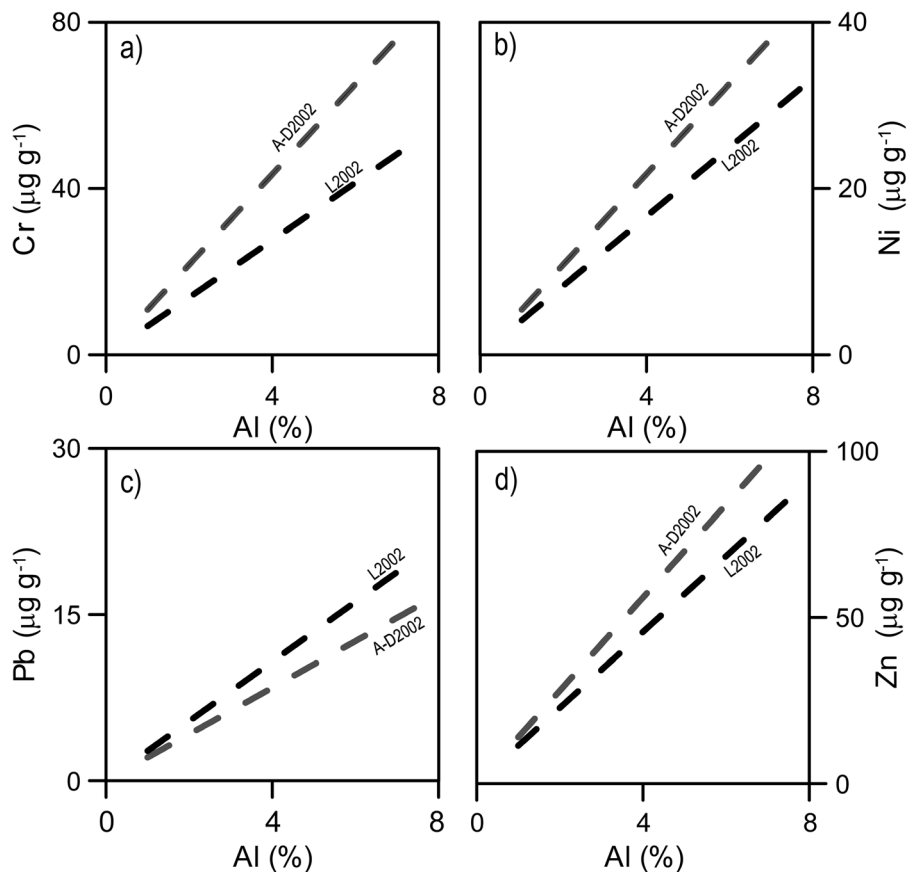
The gradients (slopes) of heavy metal (Cr, Ni, Pb and Zn) vs. Al contents in the four areas for the two datasets are plotted in Figs. 3, 4 and 5. In these figures, only selected metals vs. Al relationships that are judged suitable for comparing between the four study areas are presented. Additionally, only the gradients as such (no data points) are shown for Cr, Ni, Pb and Zn; for purposes of comparison, the trends were “forced” to converge at the origin. The low variability of Al contents

in the Mira area limits the significance of the calculated regression lines, constraining the application of the GM, as previously indicated. Additionally, the relatively low  $r$  ( $0.60 < r < 0.62$ ) obtained for the metal vs. Al relationships (e.g., Pb in A-D1977, L1977 and A-D2002) may also affect the comparison between the two datasets.

The Alg1977 and M1977 areas have the steepest metal vs. Al gradients (Fig. 3), which is interpreted as a result of the accumulation of sediment resultant from the weathering and erosion of the metal-enriched Iberian Pyrite Belt geological formations. Despite the relatively low Mira River discharge and consequently low sediment transport to the adjacent shelf area, the existence in the drainage area of basic rocks formations and doleritic veins together with the erosion of Sines Intrusive Massif (see Fig. 1), composed by basic and intermediate igneous rocks (gabbros, diorites and syenites) whose weathering typically provides detrital material enriched



**Fig. 3** a–d Significant gradients for bulk metal contents (Cr, Ni, Pb and Zn) relative to Al for the 1977 archive dataset along the western and southern Portuguese shelf (see text for further explanation). **a** Cr, **b** Ni, **c** Pb and **d** Zn



**Fig. 4** a–d Significant gradients for bulk metal contents (Cr, Ni, Pb and Zn) relative to Al for the 2002 dataset along the western Portuguese shelf (see text for further explanation). a Cr, b Ni, c Pb and d Zn

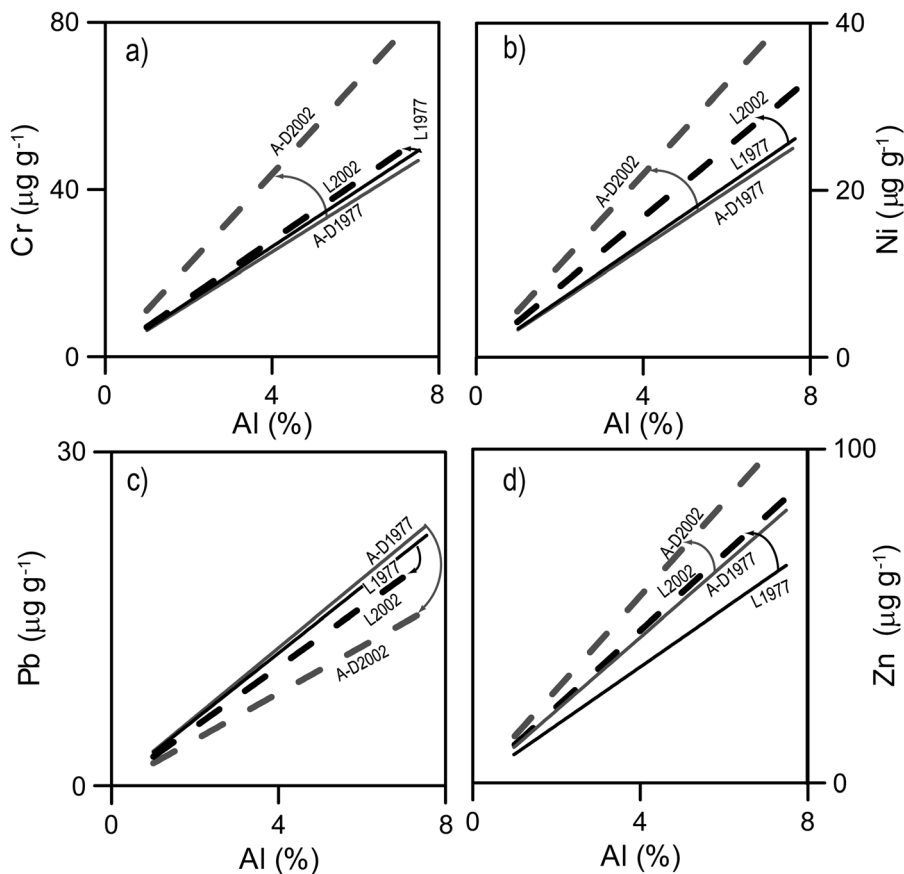
in Ni and Cr (e.g., Forstner and Wittmann 1981)), may explain the relatively high Ni and Cr loadings in the M1977 area relative to Al.

The gradients for Cr, Ni and Zn relative to Al in the A-D2002 area are steeper than in the L2002 area (Fig. 4) which is consistent with a significant anthropogenic contribution from the major rivers draining into the Ave-Douro shelf, compared to the relatively low Lis River discharge. However, Pb has lower loadings relative to Al in the recent samples from the Lis and Ave-Douro areas (Fig. 5). Compared to the 1977 archive dataset, this decrease can be attributed to a decrease of the importance of diffuse (atmospheric) sources associated with lower Pb emissions derived from combustion of unleaded fuel. Portugal banned leaded fuel at the end of the 1990s (Roma-Torres et al. 2007). Further evidence for such a decrease in Pb has been published by Mil-Homens et al. (2006). This work results show that although no natural Pb sources exist in the Lis catchment area, continuous sediment sequences from the

shelf that covers approximately the last 150 years and reveals an increase in Pb/Al between the 1950s and the 1980s, followed by a slightly decrease Pb/Al. The atmosphere represents the most important pathway for Pb transportation to the ocean (Nriagu 1989). The main anthropogenic carriers of Pb in the atmosphere are aerosols formed by fossil-fuel burning and industrial processes, which may be transported long distances and account for global contamination levels (Nriagu 1978). The low discharge of the Lis River would explain why atmospheric supply seems to be “better represented” in Lis shelf sediments than on the Ave-Douro shelf, where higher terrigenous sediment input by major rivers (such as Douro) presumably masks Pb atmospheric supply.

Sediment quality criteria and comparison to the gradient method

National sediment quality guidelines (SQGs) have been drawn up by many environmental protection agencies



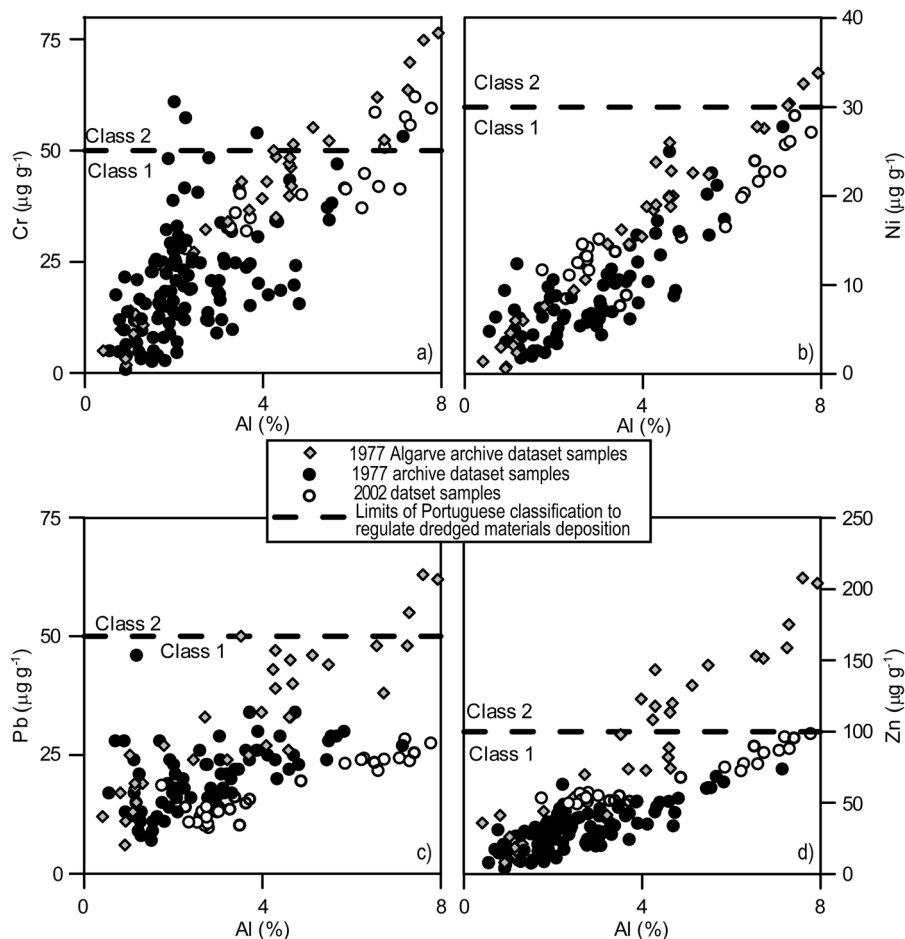
**Fig. 5** a–d Temporal variations in gradients for bulk metal contents (Cr, Ni, Pb and Zn) relative to Al in surface sediments of the Ave-Douro and Lis areas on the western Portuguese shelf between 1974–1977 and 2002 (see text for further explanation). **a** Cr, **b** Ni, **c** Pb and **d** Zn

worldwide to aid in comparative assessments of the environmental status of marine and estuarine sediments for management purposes. Such reference values need to be used with caution, since they often do not adequately account for regional variability, particularly if extrapolated to other countries with different environmental settings. In Portugal, national sediment quality guidelines are not defined, with exception for the classification scheme used to regulate deposition of dredged materials in coastal areas (heavy metal contents regulated by the Portuguese state through legislation published in 2007; Portaria no. 1450/2007). Therefore, this Portuguese classification scheme is used below to “classify” metal contamination for the 1974–1977 and 2002 sediment datasets from the Portuguese shelf.

Based on Ni, Pb and Zn contents of bulk surface sediments (<2-mm fraction), surface sediments from the Ave-Douro, Lis and Mira shelf areas sampled in 2002 are generally within class 1 (clean dredged materials that can

be deposited in the aquatic environment or as replacement in locations subject to erosion without restrictive rules, such as beaches; Fig. 6). Chromium is the single element that causes some samples of both 1977 and 2002 datasets, to be classified as class 2 (trace-contaminated dredged material that can be deposited in water, with consideration for the ecological characteristics of the receiving environment and the legitimate use of these materials; Fig. 6a). For the 1977 archive dataset, Ni, Pb and Zn contents are within class 1 for all three western study areas (Fig. 6b–d). Algarve area on the southern shelf is characterised by having high number of sites (15, 9, 4 and 3 sites for Zn, Cr, Ni and Pb, respectively) with metal contents corresponding to class 2 (Fig. 6 a–d). For Zn, 43 % ( $n=15$ ) of the sites investigated have Zn contents corresponding to class 2 (Fig. 6d).

Based on this Portuguese classification scheme, sediment environmental quality on the western Portuguese shelf had evidently deteriorated in terms of Pb by the



**Fig. 6** a–d Comparison of the Portuguese classification to regulate dredged materials deposition in coastal areas (Portaria no. 1450/2007) with metal loadings for Cr, Ni, Pb and Zn relative to

Al in surface sediments of the 1977 and 2002 Ave-Douro and Lis areas. *Horizontal dashed lines* represent class 1 limits. **a** Cr, **b** Ni, **c** Pb and **d** Zn

1970s but had markedly improved by the turn of the century. This can be confirmed by the results obtained above when applying the GM in the formerly more heavily contaminated Ave-Douro and Lis areas. In contrast, steepening gradients for Cr, Ni and Zn suggest caution against in misinterpreting the western shelf as being of good environmental quality in terms of the Portuguese Classification of dredge material in coastal zones.

To date, the lack of data from 2002 as well as the limited historical data for the Algarve region prevents precise assessment of long-term trends in sediment quality for the southern Portuguese shelf. Substantial natural metal enrichment from the Iberian Pyrite Belt formations resulting from drainage by the Guadiana, Tinto and Odiel rivers (Spanish rivers) of the Iberian Pyrite Belt formations, probably magnified by present and past mining activities, would classify this sector as a

“hotspot” in terms of any environmental quality criteria. Evidently, any future Portuguese sediment quality guidelines would have to carefully accommodate the strong regional variability and strictly distinguish between anthropogenic and natural “contamination” along the Portuguese continental shelf.

## Conclusions

In the present study, the GM and SQGs have been applied to surface samples collected along the Portuguese shelf, in part to compare the level of relative metal loading between different regions (study areas) and 25 years apart (the 1977 archive dataset and 2002 samples). The Alg1977 and M1977 areas had the steepest metal vs. Al gradients, interpreted to be due to weathering and erosion of the

metal-enriched geological formations of the Iberian Pyrite Belt. From the set of studied metals, Ni shows small differences in gradients between the four study areas, suggesting relatively similar Ni loadings on the entire Portuguese shelf. The overall Ni, Pb and Zn to Al gradients have increased further in the central (Lis) and northwestern (Ave-Douro) shelf areas. This may reflect enhanced anthropogenic input, despite improved treatment of industrial and domestic effluents in these highly industrialised and urbanised, more northern coastal regions. The Ave-Douro 2002 samples had gradients for Cr, Ni and Zn (relative to Al) higher than those recorded in the Lis samples, a result that can be explained by an important contribution from the major northern rivers, especially the Douro. Nevertheless, Pb to Al gradient in 2002 became less pronounced in both the central (Lis) and northwestern (Ave-Douro) shelf areas. This may reflect a decrease in the use of leaded fuel in motor vehicles that ended at the end of the 1990s and/or a decrease of Pb emissions derived from industrial sources.

Quality evaluation of these marine sediments is especially important when using total metal contents. This study shows how important it is to consider all the possible metal sources as well as the natural grain size and composition of the sediments, to better understand to which extent is the metal content related to the sediment characteristics. The definition of any future sediment quality guidelines for Portugal should carefully accommodate for the strong regional variability between western and southern continental shelf areas.

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