

## **Assessment of the impact of heavy metals in sediments along the Spanish Mediterranean coastline: Pollution Indices.**

Maria Paches<sup>1</sup>, Remedios Martínez-Guijarro<sup>\*2</sup>, Daniel Aguado<sup>1</sup>, Jose Ferrer<sup>1</sup>

1. CALAGUA – Unidad Mixta UV-UPV, Institut Universitari d'Investigació d'Enginyeria de l'Aigua i Medi Ambient – IIAMA, Universitat Politècnica de València, Camí de Vera s/n, 46022 Valencia, Spain.

2. GEIA - Institut Universitari d'Investigació d'Enginyeria de l'Aigua i Medi Ambient – IIAMA, Universitat Politècnica de València, Camí de Vera s/n, 46022 Valencia, Spain.

\*Corresponding author: mmarting@hma.upv.es

### **Abstract**

A comprehensive study was carried out to evaluate the occurrence, significance of concentrations and spatial distribution of heavy metals (Cr, Cd, Ni, Cu, Pb, Hg, Zn and As) in sediments along the Valencia coastline (Spain). The sampling campaign covered 476 km of the coastline in a 4-year period. The highest concentrations of metals in the sediments were mainly Cr, Ni, Zn and Cd (up to 28.93 mg Cr kg<sup>-1</sup> dw, 15.80 mg Ni kg<sup>-1</sup> dw, 57.13 mg Zn kg<sup>-1</sup> dw and 0.293 mg Cd kg<sup>-1</sup> dw), obtained in the northern areas, some central areas and in an isolated area on the southern coastline. The Sediment Quality Guidelines applied reveal that for all metals studied, none of them reached, or exceed, the “effects of median range” or the “probable effect level”. The Pollution index reveals that 75% of the stretch coastline has a low priority risk level and the rest “medium-low priority risk level”. And, lastly Potential Ecological Risk index shows that all but one zone have low ecological risk.

### **Keywords**

Heavy metals; Sediment pollution; Risk assessment; Ecological Risk Indices; Background Enrichment Indices; Environmental impact; Pollution effects

## **Introduction**

The presence of heavy metals in the environment is attracting growing interest from researches and the community because of the toxicity, persistence and accumulation of these metals in the environment and aquatic habitats (Fachinelli et al. 2001; Loska and Wiechula 2003; Upadhyay et al. 2006; Zhou et al. 2008). Heavy metals represent a threat to natural habitats, in both the long and short term, with toxic and chronic effects on organisms that can lead to loss of biodiversity in the ecosystems affected (Johnston and Roberts 2009).

The presence of these pollutants in aquatic ecosystems is due to both natural processes (i.e. rock weathering coastal and seabed erosion) and human activities, like population growth, industrial developments, harbour expansions, tourism-related activities on the coast, discharge of inadequately treated municipal and industrial wastewater, and numerous recreational and commercial activities (Yalcin et al. 2009; Hosono et al. 2010).

Heavy metals enter aquatic systems by natural and anthropogenic pathways such as rivers, urban and industrial waste dumping, atmospheric particulate deposition, coastal and seafloor erosion, after which the sediments act as a metal accumulation repository (Leivouri 1998; Ip et al. 2007; Li et al. 2013).

The low solubility metals transported into aquatic ecosystems are quickly fixed on the solid material in suspension, (Förstner and Wittman 1981) which is ultimately deposited in the sediments, which thus act as a store of metals with concentrations of several orders of magnitude higher than those of the adjacent interstitial and overlying waters.

The release of heavy metals into the environment has a great impact on aquatic systems and affects the entire food chain from the producer to the consumer (Badri and Aston 1983; Luoma 1990; Christophorides et al. 2009).

Several heavy metals have been assigned to the priority list in European legislation, and limit values have been proposed for the protection of endangered habitats. The first Priority Substances Directive (Directive 2008/105/EC) set environmental quality standards (EQS) for substances in surface waters and made it possible to apply EQS to sediment and biota instead of those for water. A later proposal (Directive 2013/39/EU) recognised the need to improve the efficiency of monitoring campaigns. Monitoring of sediment has thus become essential for environmental assessment of heavy metal pollution. This

assessment requires data from the sediments themselves, since the low metal concentrations and high salinity values in the water column could interfere with analytical methods (Rainbow 1995).

As the accumulation of metals in the sediment poses a long term threat to water bodies and other areas of the environment, there is a need for sediment quality indicators to assess the risks of contamination and toxicity by metals in the aquatic environment. Numerous Sediment Quality Guidelines (SQGs) have been compiled to assess metal contamination and deal with environmental concerns. SQGs are useful for screening sediment contamination by comparing contaminant concentrations with the appropriate quality guideline. The guidelines evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality (Wenning and Ingersoll 2002).

Heavy metal pollution in a given area can also be assessed by tools such as pollution indices (Pejman et al. 2010). Caeiro et al. 2005, classified pollution indices into three types: Contamination Indices, Background Enrichment Indices and Ecological Risk Indices. *Contamination indices* compare the contaminants with clean and/or polluted stations measured in the study area or simply add the total metal concentrations, *Background Enrichment Indices* compare the results for the contaminants with different baseline or background levels, and *Ecological Risk Indices* compare the results for the contaminants with SQGs or Values.

The use of these SQG is world widely applied. In the Mediterranean systems the SQGs have been used to assess the ecotoxicological sense of metal concentration in sediments for example in The Bahiret el Bibane lagoon in Tunisia (Barhoumi et al. 2017), in the Bay and the Gulf of Thessaloniki, Northwester part of the Aegean Sea, (Christophoridis et al. 2009), or in the Tigris River (Turkey) (Varol 2011). In Spain, SQGs have been applied to identify zones according to their sediment quality in the Bay of Santander (north of Spain) (Alvarez-Guerra 2007) or in the Atlantic coast (Riba et al. 2009).

In the Valencia coastal region previous research on chemical composition or heavy metal contents on sediments had been carried out (Lopez 1986; Sanchiz et al. 2000). Although the researches are valuable none of them taken into account the whole stretch coastline nor apply SQG to predict adverse biological effects in contaminated sediments. In addition, heavy metals levels in commercial ports located along the Spanish coast have also been studied but none of those ports are from Valencia region (Casado-Martínez 2009).

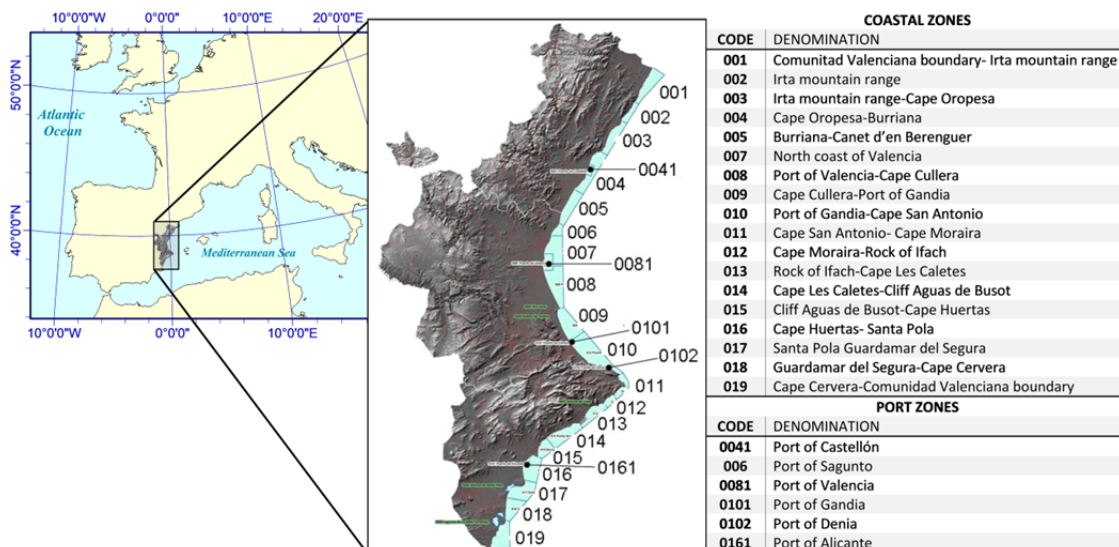
As to our knowledge there has not yet been a prior exhaustive impact assessment of heavy metals in the sediments along the Spanish Mediterranean coastline in Valencia. The objectives of this study were: (1) to analyse the heavy metal content (Cr, Cd, Ni, Pb, Cu, Hg, Zn and a metalloid As) in Valencia coastal sediments; (2) to identify the source of the anthropogenic impact; (3) to assess the contamination of heavy metals in surface sediments in the area according to the Sediment Quality Guidelines (SQGs) and two Ecological Risk Indices (Mean Effects Range Median quotient (MERMQ) and three Background Enrichment Indices (Potential Ecological Risk Index, Pollution Load Index, modified Degree of Contamination).

## Material and Methods

### Study area

The study was carried out along the Valencia coastline, which is 476 km long (Fig 1). The study area includes leisure areas, which bear intensive maritime traffic, and popular tourist areas. The coastline is also affected by the large agriculture and industrial sectors in the region.

This coastline, which combines areas of great ecological value with highly anthropized areas (GVA, 2009), was divided into several zones on a holistic basis (coastal water zones and port zones, Fig. 1). Annual mean salinity value, coastal geomorphology, coastal transport services, prevailing winds, rainfall, fluvial areas, continental inputs and wetland zones were taken into account (Romero et al. 2013).



**Fig. 1** Study area (Valencia Community, Spain)

### Sample collection

In each zone 4 simple samples were taken to mix into a composite sample per zone from 2010 to 2015 yielding a total of 96 integrated samples.

The upper layer of collected sediment was approximately 6 to 10 cm thick. Sampling was carried out by trained personnel by means of 20 mL methacrylate corers. The corers were then placed in portable refrigerator, taken to the laboratory as quickly as possible and stored at -20°C until analysed.

### **Analytical techniques**

The sediments were freeze dried (ilShin FD5510 freeze dryer) and dry sieved. The heavy metals were determined using acid digestion with nitric acid (65% Merck, Suprapur) and hydrogen peroxide (30% Merck, Suprapur) in a Milestone Ethos 1 microwave according to the EPA 3051 method to obtain the solution of the total metal content.

Analyses of cadmium (Cd), copper (Cu), lead (Pb), chromium (Cr), nickel (Ni), zinc (Zn) and metalloid arsenic (As) were performed by Graphite Furnace Atomic Absorption Spectrometry or Flame Atomic Absorption Spectrometry (AAAnalyst 800 Perkin Elmer with Zeeman correction), according to the metal concentration. Mercury (Hg) was determined by the cold vapour technique on an Atomic Absorption Spectrometer with autosampler (AS 90) and a flow injection system (FIAS 100). All the processes were performed in accordance with the APHA (2012).

Data were analysed as total metal concentrations on a dry weight basis and are expressed in acid soluble  $\text{mg kg}^{-1}$  dry weight ( $\text{mg kg}^{-1}$  dw). The detection limits (LOD) and quantification limits (LOQ) expressed in acid soluble  $\mu\text{g kg}^{-1}$  dw were: LOD, Cr 5.57; Cd 1.23; Ni 10.55; Pb 11.61; Hg 13.21; Cu 15.92; As 14.94 and Zn expressed in  $\text{mg kg}^{-1}$  dw 1.02. The LOQ determined were Cr 18.56; Cd 4.08; Ni 35.16; Pb 38.70; Hg 44.02; Cu 53.07; As 49.79 and Zn expressed in  $\text{mg kg}^{-1}$  dw 3.41.

The routine procedure involves duplicate digestion and metal measurement to test analytical reproducibility. To prevent contamination, all glassware, plasticware and equipment used were washed prior to use by soaking in 20%  $\text{HNO}_3$  for 24 h and rinsed with Milli-Q water. To identify background contamination, procedural blanks were analysed for every ten samples.

### **Statistical analysis**

The data were subjected to a multivariate statistical cluster analysis. Statistical analyses were applied to experimental data transformed by  $\text{Ln}(x)$  to achieve normally distributed data. A cluster analysis (CA) was performed on the transformed data set using Ward's method with squared Euclidean distances as a

measure of similarity. This technique was used to find any similarities between the sampling zones and identify relatively homogeneous groups of samples with similar properties.

A Pearson correlation test was applied to examine the relationship between the measured variables (i.e. the different heavy metals measured). The statistical analyses were conducted on SPSS 16.0.

### Assessing sediment contamination

Numerical sediment quality assessment guidelines may be used to identify and designate sediments with high, moderate, and low probabilities of being associated with adverse effects on aquatic organisms. Of the numerous Sediment Quality Guidelines (SQGs) available, two (Long et al. 1995 and Macdonald et al. 1996) were used in this study in addition to five others to assess the degree of heavy metal contamination and ecological risks.

#### a) Sediment Quality Guidelines (SQGs)

The sediment quality assessment guidelines provide two guideline values for several contaminant substances (trace metals, total polychlorinated biphenyls PCBs, pesticides, polynuclear aromatic hydrocarbons PAHs). These two values define concentration ranges that are rarely, occasionally, or frequently associated with adverse effects. Sediment Quality Guideline values (Table 1) were established by Long et al. (1995) to estimate the biological effects of sediments for the protection of organism living in or near sediments (Zhao et al. 2014; Pejman et al. 2015). This SQG involves ELR (effects of low range) and ERM (effects of median range) values. Other SQGs values (Table 1) set by Macdonald et al. (1996) contain the TEL (threshold effect level) and PEL (probable effect level) values. ERL and TEL (low range values) are concentrations below which adverse effects are not expected, while ERM and PEL are concentrations above which adverse effects can be expected more often than not.

**Table 1** Sediment Quality Guideline values (mg kg<sup>-1</sup>, dry weight). (ERL) Effects of Low Range and (ERM) Effects of Median Range; (TEL) Threshold Effect Level and (PEL) Probable Effect Level [\*] Long et al. (1995); [\*\*] Macdonald et al. (1996)

	Cr	Cd	Ni	Pb	Hg	Cu	Zn	As	
<b>ERL</b>	8.1	1.2	20.9	46.7	0.150	34.0	150.0	8.2	[*]
<b>ERM</b>	370.0	9.6	51.6	218.0	0.710	270.0	410.0	70.0	
<b>TEL</b>	52.3	0.68	15.9	30.2	0.13	18.7	124.0	7.24	[**]
<b>PEL</b>	160.0	4.21	42.8	112.0	0.70	108.0	271.0	41.6	

## b) Pollution Index

The sediment pollution indices applied in this work were the **Ecological Risk Indices** (Mean Effects Range Median quotient (MERMQ), mean PEL quotients (m-PEL-Q)) and **Background Enrichment Indices** (Potential Ecological Risk Index (RI), Pollution Load Index (PLI), modified Degree of Contamination (mCd) (Christophoridis et al. 2009; Gao et al. 2012; Li et al. 2013; Zhao et al. 2014; Pejman et al. 2015).

### – Mean Effects Range Median quotient (MERMQ)

The MERMQ was calculated (Eq. 1) by dividing each chemical concentration by its respective ERM and averaging the individual quotients (Long et al. 2000).

$$MERMQ = \frac{\sum_{i=1}^n C_i/ERM_i}{n} \quad (1)$$

Where  $C_i$  is the concentration of metal  $i$  in analysed sediments,  $ERM_i$  (Effects Range Median) is the guideline values reported by Long et al. (1995) (Table 1) for the metal  $i$  and  $n$  is the number of metals. In this index all the contaminants were combined in a single value for four risk levels of the MERMQ index:  $MERMQ \leq 0.1$  (low priority risk level and 9% probability of being toxic);  $0.1 < MERMQ \leq 0.5$  (medium-low priority risk level and 21% probability of being toxic);  $0.5 < MERMQ \leq 1.5$  (high-medium priority risk level and 49% probability of being toxic);  $MERMQ > 0.5$  (high priority risk level and 76% probability of being toxic).

### – mean PEL quotients (m-PEL-Q)

This index combines metal content and PEL-SQG values for the measured heavy metals (As, Cr, Ni Cd, Cu, Zn, Hg and Pb). The m-PEL-Q index was calculated by Eq.(2) (Long et al. 1998):

$$m - PEL - Q = \frac{\sum_{i=1}^n (C_i/PEL_i)}{n} \quad (2)$$

Where  $C_i$  is the measured metal concentration ( $i$ ),  $PEL_i$  is the PEL value of metal ( $i$ ), and  $n$  is the number of metals. Several toxicity probability classes were defined for biota: mPEL quotients  $\leq 0.1$  with 8% probability of being toxic, 0.11–1.5 with 21% probability of being toxic, 1.51–2.3 with 49% probability of being toxic, and  $\geq 2.3$  with 73% probability of being toxic.

### – Potential Ecological Risk Index (RI)

The potential ecological risk index (RI) (Hakanson 1980) was used to analyse the ecological risk of heavy metals in the study zone (Pejman et al. 2015) by Eqs.(3) and (4):

$$RI = \sum_{i=1}^n E_r^i = \sum_{i=1}^n T_r^i \times C_f^i \quad (3)$$

$$C_f^i = \frac{C_s^i}{C_n^i} \quad (4)$$

where  $E_r^i$  is the potential ecological risk factor of each heavy metal,  $T_r^i$  is the toxic response factor of heavy metal  $i$  (e.g., Cd= 30, Hg=40, Cu =Pb = Ni= 5, Cr = 2, Zn =1, As=10),  $C_f^i$  is the contamination factor of heavy metal  $i$ ,  $C_s^i$  is the concentration of heavy metal  $i$  in the sediment,  $C_n^i$  is the background value of heavy metal  $i$ . Following Hakanson (1980), the following tiers were used for the RI value: i)  $RI < 150$  (*low ecological risk*); ii)  $150 \leq RI < 300$  (*moderate ecological risk*); iii)  $300 \leq RI < 600$  (*considerable ecological risk*); iv)  $RI > 600$  (*very high ecological risk*).

– *Pollution Load Index (PLI)*

This index was used to assess the degree of anthropogenic metal contamination as calculated by Eqs.(5), (6):

$$PLI = \sqrt[n]{C_f^1 \times C_f^2 \times C_f^3 \times \dots \times C_f^n} \quad (5)$$

$$C_f^i = \frac{C_s^i}{C_n^i} \quad (6)$$

where  $C_s^i$  and  $C_n^i$  are concentration of metal and background content, respectively, of metal  $i$ .

$PLI > 1$  signifies contamination and  $PLI < 1$  absence of pollution.

– *Degree of Contamination*

Introduced by Hakanson (1980), this index was originally a method of calculating an overall pollution factor based on seven metals and one organic contaminant (PCB). Individual Contamination Factors were based on the following formula, Eq.(7):

$$C_f^i = \frac{C_s^i}{C_n^i} \quad (7)$$

where  $C_s^i$  is the concentration of metal in at least five sub-samples and  $C_n^i$  is the concentration of metal in the selected reference background. The overall degree of contamination is given by Eq.(8):



$$C_d = \sum_{i=1}^8 C_f^i \quad (8)$$

Since it is not always feasible to analyse all the components in this index, a generalized index was proposed in Abraham and Parker (2008) to provide the modified degree of contamination as calculated by Eq.(9):

$$mC_d = \frac{\sum_{i=1}^{i=n} C_f^i}{n} \quad (9)$$

where  $C_f^i$  is contamination factor,  $n$  = number of analysed elements and  $i = i^{\text{th}}$  element. According to the modified degree of contamination values, each sample falls into one of the seven tiers: i)  $mC_d < 1.5$  (*nil to very low degree of contamination*); ii)  $1.5 \leq mC_d < 2$  (*low degree of contamination*); iii)  $2 \leq mC_d < 4$  (*moderate*); iv)  $4 \leq mC_d < 8$  (*high*); v)  $8 \leq mC_d < 16$  (*very high*); vi)  $16 \leq mC_d < 32$  (*extremely high*); vii)  $mC_d \geq 32$  (*ultra-high degree of contamination*).

## Results

### Heavy metal content in surface sediment

The heavy metal contents analysed in the sediments from the Valencia coastline are summarized in Table 2. The average concentration range in all the study zones were: 4.64-28.97 mg kg<sup>-1</sup> for Cr, 0.11-0.29 mg kg<sup>-1</sup> for Cd, 1.92-17.01 mg kg<sup>-1</sup> for Ni, 8.72-57.13 mg kg<sup>-1</sup> for Zn, 2.19-9.33 mg kg<sup>-1</sup> for Pb, 0.01-0.18 mg kg<sup>-1</sup> for Hg, 1.18-6.53 mg kg<sup>-1</sup> for Cu and 2.71-36.21 mg kg<sup>-1</sup> for As. The order of the average sediment metal content (highest to lowest) is as follows: Zn>As>Cr>Ni>Pb>Cu>Cd>Hg.

There was a large spatial and temporal dispersion in the metal concentration data. In the norther coast concentration values were higher than in the south. For example, zones 001 to 003 exhibited greater Ni and As values of up to 80-86% larger than in the southern areas such as 013 to 016. For other metals this variation is up to 75% for Zn and Cr, 60% for Cu, and 40% for Pb and Cd.

In the remaining southern zones (017 to 019), almost all the metals registered higher concentrations, although these were still lower than those obtained in the northern areas (001 to 003).

Zones 016 and 017 exhibit larger Hg concentration with values of 0.145 and 0.182 mg kg<sup>-1</sup> dw, respectively. Spatial differences for this metal were also established between northern areas 001 to 010, with values 77% higher than southern areas, 011 to 015. As with the other metals, the Hg values were highest in the two southernmost zones 018 and 019.

The values obtained for port areas reveal a spatial distribution similar to the coastal zones. The northernmost port areas (Castellón, Sagunto, Valencia and Gandia) exhibit higher concentrations than the ports of Denia and Alicante in the south, although the concentrations in these port areas in no case exceeded the values of northern coast zones 001 to 003.

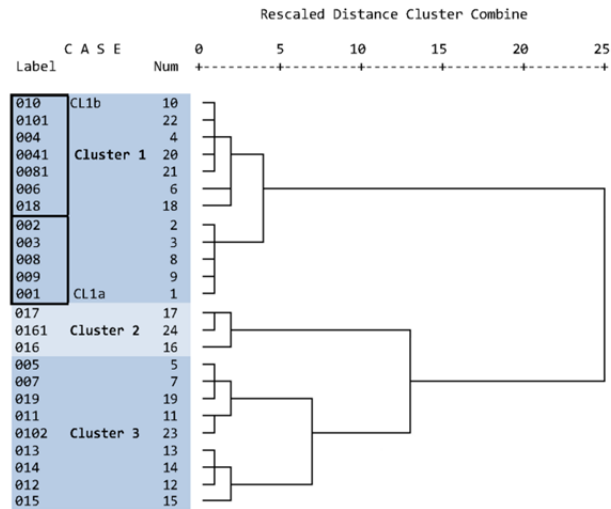
The temporal dispersion of the concentrations throughout the 4-year study period showed high Variation Coefficients (data not shown) around 30-50%, in most areas. Some zones (015, 018, 019, 0041 and 0081) had Hg standard deviation values equal to or greater than the average value because the value in one of the 4 years studied was noticeably higher than the other three (e.g. in zone 019, 0.022, 0.074, 0.005 and 0.007 mg kg<sup>-1</sup> for 2010, 2011, 2012 and 2015, respectively).

**Table 2** Summary of heavy metal concentration in surface sediment at the study zone (2010, 2011, 2012 and 2015 years).  
The concentrations are given as Mean±Standard Deviation (SD).

Zones	Cr (mg kg <sup>-1</sup> dw)	Cd (mg kg <sup>-1</sup> dw)	Ni (mg kg <sup>-1</sup> dw)	Pb (mg kg <sup>-1</sup> dw)	Hg (mg kg <sup>-1</sup> dw)	Cu (mg kg <sup>-1</sup> dw)	Zn (mg kg <sup>-1</sup> dw)	As (mg kg <sup>-1</sup> dw)	
Coastal Zones	001	28.93±8.91	0.239±0.049	15.80±1.84	8.83±3.76	0.043±0.010	5.32±1.09	56.47±4.81	27.55±7.32
	002	26.46±7.62	0.248±0.032	14.48±1.27	6.13±2.43	0.026±0.014	4.66±1.07	52.05±5.78	26.27±7.07
	003	28.97±7.87	0.293±0.045	17.01±1.20	5.73±2.83	0.032±0.017	4.58±0.98	57.13±7.38	36.21±12.26
	004	20.09±7.33	0.190±0.016	10.60±2.59	4.98±1.33	0.025±0.013	2.78±0.93	35.71±0.32	23.35±10.26
	005	13.34±4.33	0.164±0.037	6.46±0.83	3.83±1.10	0.027±0.007	1.96±0.38	32.71±5.04	13.49±4.24
	007	11.50±3.97	0.116±0.027	5.96±1.09	3.65±1.44	0.031±0.007	1.84±0.44	25.03±2.41	12.87±2.62
	008	25.79±10.11	0.287±0.056	13.38±1.87	8.02±2.72	0.042±0.023	3.81±0.78	48.71±9.86	29.68±12.04
	009	24.70±9.49	0.278±0.059	12.53±2.25	7.26±3.24	0.060±0.025	3.53±0.92	42.23±7.90	27.20±8.04
	010	16.88±4.28	0.232±0.024	8.37±1.53	5.57±2.67	0.034±0.018	3.88±1.96	32.85±11.14	19.08±7.05
	011	11.82±4.05	0.246±0.028	4.44±1.22	4.78±1.76	0.014±0.003	2.44±0.38	18.99±5.15	18.83±5.55
	012	11.97±6.80	0.183±0.019	2.74±0.44	5.75±2.50	0.009±0.002	1.45±0.22	13.35±2.89	9.48±5.37
	013	9.21±3.07	0.165±0.023	4.54±1.05	3.38±1.33	0.008±0.002	2.48±0.7	16.54±4.44	6.12±1.60
	014	5.97±2.15	0.153±0.026	3.03±0.28	3.50±0.92	0.008±0.002	1.98±0.23	14.14±5.85	4.42±0.81
	015	4.64±1.92	0.149±0.018	1.92±0.68	2.19±0.70	0.013±0.012	1.18±0.07	8.72±2.59	2.71±0.60
	016	5.23±1.83	0.120±0.006	2.00±0.51	6.48±2.49	0.145±0.040	1.73±0.22	13.77±3.04	3.44±0.96
	017	10.76±2.81	0.165±0.028	4.87±0.75	9.33±3.27	0.182±0.060	5.01±1.3	31.67±10.87	5.07±1.71
	018	16.39±4.37	0.149±0.016	10.12±2.55	4.04±1.95	0.041±0.039	6.53±1.62	29.05±6.01	6.32±2.91
	019	8.10±2.83	0.126±0.012	4.52±0.85	3.76±1.60	0.038±0.046	1.69±0.22	18.98±6.20	10.95±5.36
	Port Zones	0041	16.70±5.72	0.205±0.020	9.20±1.10	5.28±2.85	0.060±0.075	3.20±0.3	37.66±6.50
006		15.70±5.77	0.128±0.009	10.32±7.52	5.10±2.06	0.158±0.128	5.08±4.6	37.98±21.28	18.05±5.37
0081		13.98±2.37	0.140±0.036	6.82±1.18	7.24±1.41	0.047±0.059	3.46±0.96	30.83±11.14	19.98±5.73
0101		17.31±7.15	0.202±0.009	9.07±2.57	7.05±2.70	0.038±0.027	4.63±1.59	36.01±4.97	17.72±5.42
0102		9.30±3.44	0.113±0.029	3.90±0.67	6.11±1.51	0.027±0.020	1.84±0.56	21.86±5.23	27.21±16.22
0161		7.90±3.50	0.176±0.016	3.43±1.33	8.71±3.75	0.076±0.032	3.79±1.32	21.86±1.58	4.01±1.35

## Multivariate statistical analyses

A cluster analysis was carried out to study the spatial variation of the heavy metal concentrations in depth. Figure 2 shows the dendrogram of the cluster analysis obtained.



**Fig. 2** Dendrogram of cluster analysis for all zones of the study area

Three main different clusters, each with different subgroups, can be seen. The first cluster (CL1) contains the sites with the highest heavy metal concentration. This cluster may be divided into two subgroups (CL1a and CL1b). Subgroup CL1a contains the northern areas (001,002 and 003) and some central areas, such as 008 and 009. The second subgroup, CL1b, contains mainly harbour areas (0041, 006, 0081, 0101). Zone 018 had high metal concentrations and is also part of this cluster (CL1b), despite being in the south.

The second (CL2) and third cluster (CL3) contain the moderate and low concentration sites, respectively. CL2 is formed by coastal zones 016, 017 and the port area 0161. CL3 contains zones 005, 007, 011 to 015, 019 and the port area 0102. These sites are mostly in the south of the study area.

The Pearson correlation coefficient was calculated to determine the correlation between the heavy metal concentrations. The correlation matrix for the variables measured is shown in Table 3.

**Table 3** Correlations coefficients of heavy metals in surface sediments

		<b>Cr</b>	<b>Cd</b>	<b>Ni</b>	<b>Pb</b>	<b>Hg</b>	<b>Cu</b>	<b>Zn</b>	<b>As</b>
<b>Cr</b>	Correlation	1.000							
	Sig.(bilateral)								
<b>Cd</b>	Correlation	<b>0.713**</b>	1.000						
	Sig.(bilateral)	<b>0.000</b>							
<b>Ni</b>	Correlation	<b>0.955**</b>	<b>0.610**</b>	1.000					
	Sig.(bilateral)	<b>0.000</b>	<b>0.002</b>						
<b>Pb</b>	Correlation	0.475*	0.383	0.374	1.000				
	Sig.(bilateral)	0.019	0.064	0.072					
<b>Hg</b>	Correlation	0.147	-0.113	0.229	<b>0.582**</b>	1.000			
	Sig.(bilateral)	0.494	0.598	0.281	<b>0.003</b>				
<b>Cu</b>	Correlation	<b>0.701**</b>	0.459*	<b>0.765**</b>	<b>0.581**</b>	0.493*	1.000		
	Sig.(bilateral)	<b>0.000</b>	0.024	<b>0.000</b>	<b>0.003</b>	0.014			
<b>Zn</b>	Correlation	<b>0.922**</b>	<b>0.576**</b>	<b>0.953**</b>	<b>0.568**</b>	0.408*	<b>0.789**</b>	1.000	
	Sig.(bilateral)	<b>0.000</b>	<b>0.003</b>	<b>0.000</b>	<b>0.004</b>	0.048	<b>0.000</b>		
<b>As</b>	Correlation	<b>0.841**</b>	<b>0.525**</b>	<b>0.793**</b>	0.375	0.033	0.385	<b>0.780**</b>	1.000
	Sig.(bilateral)	<b>0.000</b>	<b>0.008</b>	<b>0.000</b>	0.071	0.878	0.063	<b>0.000</b>	

\*\* . Correlation is significant at  $p < 0.01$

\* . Correlation is significant at  $p < 0.05$

High positive correlations ( $p < 0.01$ ) were found for Cr-Ni, Cr-Zn and Ni-Zn with a Pearson Coefficient higher than 0.922. Moderately positive correlations ( $p < 0.01$ ) were obtained for As, Cu and Cd with the first three metals ((As-Cr(0.841), As-Ni(0.793); As-Zn (0.780) and Cu-Ni(0.765), Cu-Zn(0.789) and Cu-Cr(0.701), Cd-Cr(0.713) and Cd-Ni(0.610)).

A statistically significant correlation was also obtained ( $p < 0.01$ ) for Pb with the metals Hg, Cu and Zn, although in these cases the Pearson coefficients are lower (Pb-Hg(0.582), Pb-Cu(0.581), Pb-Zn(0.568)).

### **Adverse effects associated with heavy metal pollution: Sediment Quality Guidelines and Pollution Indices**

The adverse effects of heavy metal levels on biological organisms in the sediments were evaluated by comparison with the available benchmark sediment quality guidelines and applying the different ecological pollution indices.

#### a) Comparison *Sediment Quality Guidelines (SQGs)* with sediment samples studied

Firstly, the values obtained for the Valencia coast (Table 2) are compared with SQG values proposed in Long et al. 1995 (Table 1). As can be seen in Figures 3a and 3b, the values for Ni, Pb, Cu, Zn, Cd and Hg are lower than the ERL values, so that no adverse effects can be expected on aquatic organisms due to the metal concentration found in the study.

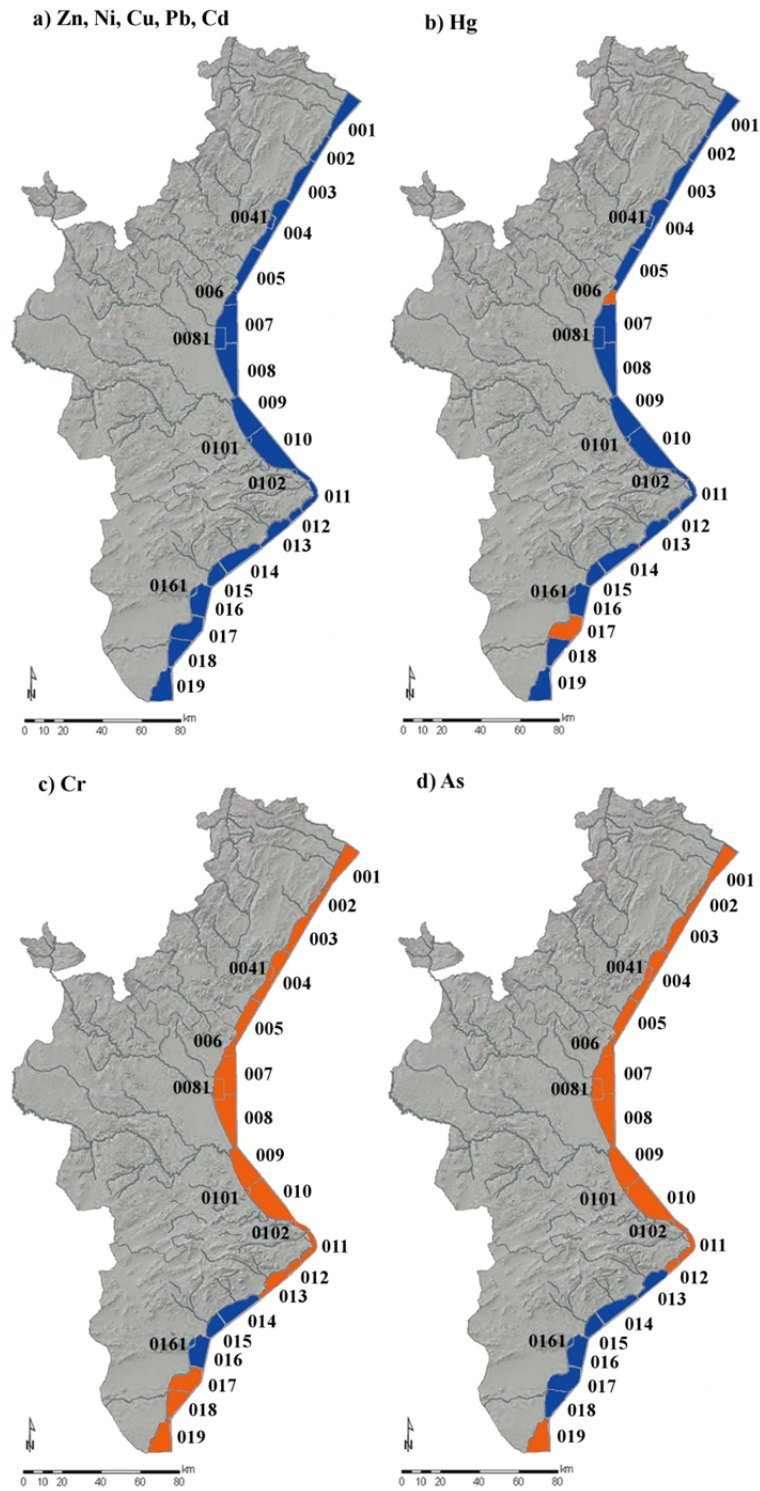
In zones 006 and 017 the Hg concentration is within the range defined by ERL-ERM ( $ERL < [Hg] < ERM$ ), showing that the sediments in both zones can be associated with occasional adverse effects on benthic organisms (Fig. 3b).

Cr and As (Fig. 3c and Fig. 3d, respectively) in most areas show values within the ERL and ERM ( $ERL < [Cr, As] < ERM$ ) range. Only zones 014 to 016 and 0161 for Cr and zones 013 to 018 and 0161 for As have concentrations lower than the ERL.

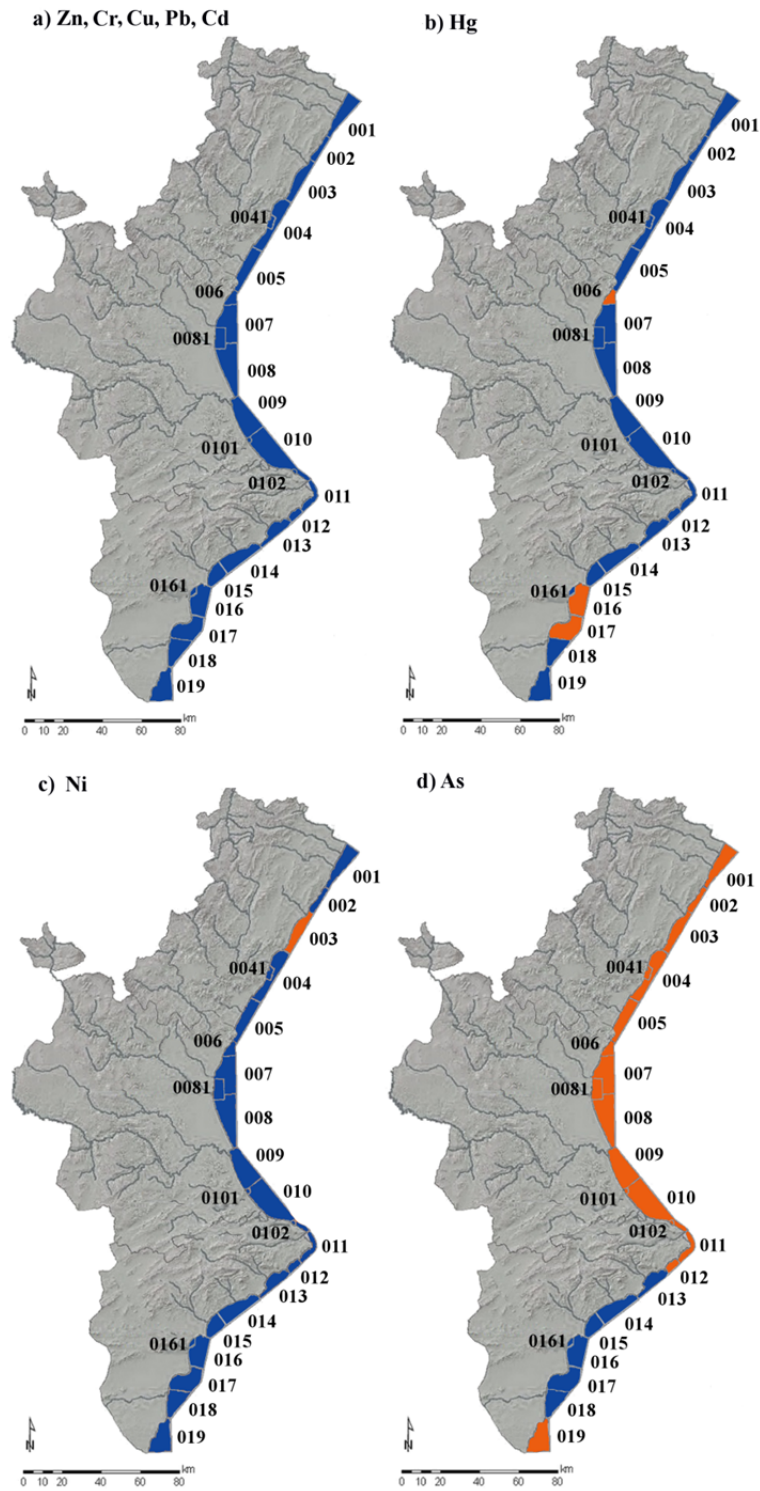
Comparing the measured concentrations of metals with the SQGs values (TEL and PEL) proposed by Macdonald et al. 1996 (Table 1), Cr, Cd, Pb, Cu and Zn metal concentrations are below the TEL (Fig. 4a).

Hg and Ni exhibit for almost all zones, concentration values lower the TEL, excepted in zones 006, 016 and 017 for Hg (Fig. 4b) and zone 003 for Ni (Fig. 4d). In these areas values are within the range of  $TEL < [Hg, Ni] < PEL$ . This also occurs for As (Fig. 4d), that shows 17 of 24 zones in the range defined by TEL and PEL values.

It should be noted that the concentration of all the metals studied in no case reached or exceeded the ERM and PEL.



**Fig. 3** Evaluation of the studied areas applying Sediment Quality Guidelines (SQGs) developed by Long et al. (1995). **a)** Zn, Ni, Cu, Pb and Cd; **b)** Hg; **c)** Cr; **d)** As  
 (Blue zones=[metal]<ERL; Orange zones=ERL<[metal]<ERM)



**Fig. 4** Evaluation of the studied areas applying Sediment Quality Guidelines (SQGs) developed by Macdonald et al. (1996). **a)** Zn, Cr, Cu, Pb and Cd; **b)** Hg; **c)** Ni; **d)** As (Blue zones= [metal]<TEL; Orange zones= TEL<[metal]<PEL)



## b) Pollution Indices

Following the usual research practice (Gao et al. 2012; Pejman et al. 2015; Zhang et al. 2016) a series of indices based on the concentration of the measured metal were applied to determine any possible effects on aquatic organisms living in the sediments. The results can be seen in Fig. 5 and Table 4.

The background values of the study area must be known in order to apply these indexes. Most of the studies consulted use the average shale value as background values (Turekian and Weipohl 1961).

However, as these values are much higher than the metal concentrations in the study area, statistical methods (Reimann et al. 2005) were used to determine the chemical backgrounds, consisting of the median value plus twice the absolute median deviation (Median+2DMA) of the values obtained for the sediments analysed. The calculated background values were: Cr 22.47 mg·kg<sup>-1</sup>; Cd 0.24 mg·kg<sup>-1</sup>; Ni 13.33 mg·kg<sup>-1</sup>; Pb 8.64 mg·kg<sup>-1</sup>; Hg 0.06 mg·kg<sup>-1</sup>; Cu 5.89 mg·kg<sup>-1</sup>; Zn 50.04 mg·kg<sup>-1</sup>; As 35.61 mg·kg<sup>-1</sup>.

The zones were classified after applying the pollution indexes as follows:

### – Mean ERM quotient (MERMQ):

According to the classification established for MERMQ, 75% of the zones have an index of  $\leq 0.1$ , which indicates a *low priority risk level* with toxicity probability of only 9%. However, zones 001 to 003, 006, 008 and 009 were between 0.1 and 0.5 ( $0.1 < \text{MERMQ} \leq 0.5$ ), giving a *medium-low priority risk level* with a toxicity probability of 21%.

### – Mean PEL quotients (mPELq)

Ten of the 24 areas studied (005, 007, 012 to 016, 018, 019 and 0161) have a mPELq index of  $< 0.1$ , giving a low toxicity probability of 8% for aquatic organisms, due to the levels of metals present in the sediment. The remaining 14 zones (001 to 004, 006, 008 to 011, 017, 0041, 0081, 0101 and 0102) have a value for this index in the range of 0.11-1.5, giving a toxicity probability of 49%.

### – Potential ecological Risk (RI):

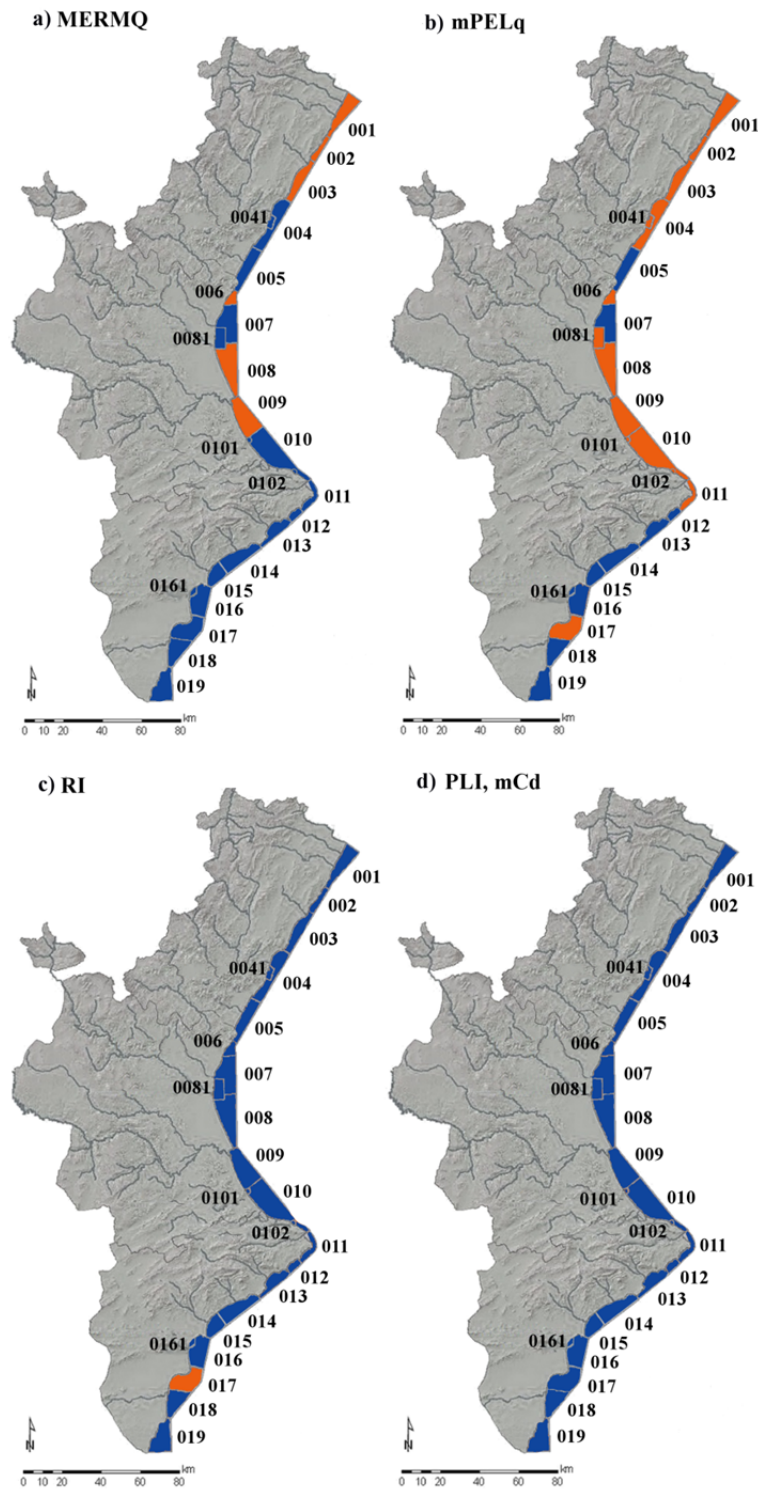
All the zones have an index of  $RI < 150$ , which indicates that the set of metals measured in the sediments in the study area represent a low ecological risk. Within them the higher values of this index are presented in zones 016 and 006 (122.4, 142.4, respectively). Only the zone 017 is classified as a *moderate ecological risk* since the RI values is  $> 150$  (159.6).

### – Pollution Load Index (PLI):

The values of the PLI index in all the zones scored a PLI value lower than 1, indicating the absence of contamination. However, it should be noted that zones 001 to 003, 008 and 009 gave a PLI index close to 1 (0.98, 0.94, 0.90 and 0.88, respectively).

– Modified Degree of Contamination (mCd)

The value obtained for the mCd index in the 24 zones was below 1.5, indicating little or no contamination. Once again, areas 001 to 003, 006, 008, 009 and 017 had the highest pollution index values.



**Fig. 5** Distribution of pollution index in the surface sediments of the Valencian coastline. **a) MERQ index** (blue zones=MERQ index $\leq$ 0.1; orange zones= $0.1 < \text{MERQ} < 0.5$ ); **b) mPELq index** (blue zones=mPELq $<$ 0.1; orange zones=mPELq between 0.11-1.5); **c) RI index** (blue zones=RI $<$ 150; orange zones= $150 < \text{RI} < 300$ ); **d) PLI, mCd indices** (blue zones= PLI $<$ 1 and mCd $<$ 1.5)

**Table 4** Pollution index values in Valencia coastal sediments

ZONE	MERMQ	mPELq	RI	PLI	mCd	
COASTAL ZONES	001	0.13	0.21	85.1	0.97	0.99
	002	0.12	0.19	71.5	0.83	0.87
	003	0.15	0.23	85.1	0.94	0.98
	004	0.10	0.15	58.3	0.64	0.66
	005	0.06	0.10	50.5	0.48	0.50
	007	0.06	0.09	46.7	0.43	0.44
	008	0.13	0.20	88.1	0.90	0.92
	009	0.12	0.19	97.7	0.88	0.90
	010	0.08	0.13	68.3	0.66	0.67
	011	0.06	0.11	53.2	0.46	0.49
	012	0.04	0.07	37.9	0.33	0.38
	013	0.04	0.06	34.5	0.32	0.36
	014	0.03	0.05	31.3	0.27	0.30
	015	0.02	0.03	31.2	0.20	0.23
	016	0.05	0.07	122.4	0.35	0.59
	017	0.08	0.11	159.6	0.64	0.91
	018	0.06	0.10	61.1	0.57	0.63
	019	0.05	0.08	51.1	0.39	0.41
	PORT ZONES	0041	0.09	0.14	82.8	0.70
006		0.11	0.16	142.4	0.78	0.92
0081		0.08	0.13	67.0	0.63	0.63
0101		0.09	0.14	68.0	0.70	0.71
0102		0.08	0.13	46.7	0.45	0.47
0161		0.05	0.07	85.0	0.47	0.60

## Discussion

Most of Valencia's population and industries are concentrated along its coastline. The human activity in this narrow strip produces contaminants that have an impact on the different compartments (water, sediment, air) of the coastal system from urban and industrial discharges, fish farms, sea traffic in and out of large commercial ports, nautical sports, etc. In addition, the entire coastal area receives agricultural run-off containing a high proportion of micronutrients, pesticides, herbicides, etc.

Heavy metals are included in these pollutants that eventually reach the aquatic ecosystems. These elements due to their low solubility are quickly fixed on the solid material in suspension (Förstner and Wittmann 1981) that ultimately will be deposit on the sediments.

In some coastal zones studied (003, 006, 010, 011, 014, 016 and 017) the concentrations of the heavy metals found are in agreement with those reported in 1991 by Sanchiz et al. 2000.

These authors also detected high concentrations of Hg and Pb in the sediments in the south of Valencia Community, as in zone 017, where the highest Pb and Hg values were obtained.

Other studies carried out in the Mediterranean also reported noticeably higher metal concentrations than those obtained in the present study since their sampling station gather point sources of contamination such as the mouths of rivers (Palanques and Díaz 1990) or dredged sediment from ports areas (Casado-Martínez et al. 2009).

Our results reveal that the north of Valencia has higher concentrations of Cr, Ni, Zn and Cd than the other areas. These particular metals are characterized by their lithogenic origin, so that their presence in zones 001, 002 and 003 could be attributed to the nearby mountain ranges. It must be kept in mind that some heavy metals (unlike other priority substances or specific pollutants like pesticides, DDT, etc.), can have a natural origin and the existence of certain levels of heavy metals in an aquatic ecosystem does not necessarily imply anthropogenic pollution.

Other heavily concentrated sites are zones 008 and 009, which receive pressures from densely populated areas with many industrial and agricultural activities.

Urban and industrial waste and wastewater management are the main sources in these areas of As, Cr, Ni, Pb and Hg (PRTR-España 2016). Furthermore, Hg is also released into the environment through the combustion of fossil fuels and from various industrial activities (Donze et al. 1990). In addition, Zn comes from the production and transformation of metals, the chemical industry and the food and beverage industry in the area. The coastline also receives the agricultural runoff with fertilizers that increase the Cd levels (Adriano 2001), as well as herbicides and pesticides that contain arsenic (Donze et al. 1990).

High metal contents were also found in areas 0041, 006, 0081 and 0101, which are near ports with intense maritime traffic. These zones are also influenced by the nearby industrial areas, so that the origin of these metals can be mostly considered as anthropic.

In areas near sea ports with commercial shipping activities and nautical sports activities, different hydrophobic complexes of Cu and Zn are commonly used in biocidal paints for boat maintenance (Turley et al. 2000; Parks et al. 2010). This indicated that residues of these compounds are detected with increasing frequency in coastal environments near ports (Pynaert and Speleers 2005) as it is showed in the studied port zones which reveal rises of 14% for Cu.

Other anthropogenic pressure may come from river basin discharge. In fact, zone 018 which is located at the south exhibits high concentrations of metals, possibly due to the influence of the Segura river basin.

As it is pointed out by Micó et al. (2006) pollutants from the industry around this basin have been discharged indiscriminately easing the bottom accumulation level.

In general, the southern areas of Valencia have lower concentrations of almost all metals than northern areas. Taking into account the significant statistical correlations among the metals studied, three groups of metals can be identified. The first group is formed by Cr, Ni, As, and Cd. All these metals were found in the same proportions in the sediments throughout the coastline. As Suresh et al. (2011) suggest, if the correlation coefficient between the metals is high, they have common sources, mutual dependence and identical behaviour during their transport, as occurred in Cr and Ni, which may share lithogenic origin.

The second group is formed by Cu and Zn, whose origin could be attributed to shipping and yachting activities, fishing harbours and fish-farming installations, which employ antifouling paints with active biocide zinc products, including zinc pyrithione, which is known to undergo transchelation with copper, depending on their relative concentrations in the water or sediment (Konstantinou et al. 2004). These biocides show a relatively high octanol/water partition coefficient, which could justify the enrichment of the antifouling compound in the sediment (Konstantinou et al. 2004).

Finally, Pb and Hg are joined, probably due to their lower concentration range and atmospheric origin. These aerosol-particles containing Pb are atmospherically transported (Cochran et al. 1998, Li et al. 2000) and may increase the sediment concentration. Although Pb has been removed from petrol, the historic contamination could affect the coastal sediments in many areas and its effects may last for decades. On the other hand, Hg can be released into the atmosphere by many processes, both natural and anthropogenic, with long residence times (about 0.5-2 yr) (Rada et al. 1989). The precipitation of this metal and oxidation processes can make it take on a water-soluble ionic form that may enter into aquatic systems. The atmospheric deposition of Hg (gas or particles) represents a major input of this element into the surface environment (Mason and Sheu 2002; Amos et al. 2012). Since the Hg species have a high affinity with particle surfaces and form insoluble precipitates, this metal is easily transported from the water column to the sediment (Kuwabara et al. 2003).

The evaluation of the sediments by the SQGs proposed by Long et al. 1995 and Macdonald et al. 1996, resulted in little or no adverse effects on aquatic organisms in the study area for Ni, Pb, Cu, Zn and Cd. However, for Cr and according to the SQGs of Long et al. (1995) there are 20 zones that have a Cr concentration within the ERL-ERM range, ( $ERL < [Cr] < ERM$ ), which indicates that adverse effects may

occasionally occur in benthic organisms. This effect was not found when applying Macdonald et al.'s SQG since the Cr (TEL) value is 6.5- fold higher than ERL.

For As both SQGs applied yield 17 zones within the range (ERL<[metal]<ERM; TEL<[metal]<PEL). The Hg gives 2 zones within the range of ERL<[metal]<ERM. Nevertheless, when other limits are applied (TEL-PEL) the number of zones increases, and zone 016 changes from “not expected effect” to “occasionally occurrence adverse effect”. It is important to highlight that none of the metals studied exhibit concentration equal or higher to ERM or PEL values, suggesting that the whole stretch coastline studied evidence no potential risk to aquatic organism.

According to the MERMQ and mPELq Ecological Risk Indices, 75% of the zones in the first index and 42% of those in the second do not present any risk of toxicity or have a very low risk. This difference between the results of both indexes is due to the fact that the guide values for the mPELq index are lower (e.g. 56-60 % Cr, Cd, Cu; 40-48% Pb, As; and 33.9% in the case of Zn, etc.), thus resulting in a greater number of areas with a higher probability of toxicity and a higher level of risk.

The results obtained from the RI index determine that the 23 out of 24 areas have low ecological risk, and only zone 017 have moderate ecological risk. The areas that show the highest values are the southern 016 and 017 and the port area 006, due to the Hg concentrations, since this index incorporates a toxic response factor for each metal. Since Hg is very toxic, those areas that have the highest Hg values also have the highest RI index values.

According to the results of the PLI and mCd indices, the 24 zones studied either do not have any metal contamination or the levels are very low. However, due to the values of these indexes in the northern areas 001 to 003 and the central areas 008 and 009, which are approaching the limit for adverse effects, it would be advisable to monitor these zones on a regular basis.

## **Conclusions**

The most polluted areas were found in the northern areas (001, 002 and 003), in some central areas (008, 009 and 010) and in two zones in the south of the Valencia coastline (017 and 018).

Cr, Ni, As, and Cd were found in the same proportions in the sediments throughout the coastline, reflecting a similar origin (lithogenic, urban and industrial waste, wastewater...) and transport processes.

The presence and correlation between Cu and Zn in the sediments was attributed to shipping and yachting activities and the use of antifouling paints with active biocide zinc products.

The conclusion drawn from the assessment, based on the application of guide levels with two SQGs, two Ecological Risk Indices and the three Background Enrichment Indices, is that the sediments in this area do not present contamination from the metals studied. The risk of sediment contamination is quite low and neither are there any adverse effects on aquatic organisms.

## **Acknowledgements**

This research work has been supported by the *Generalitat Valenciana* as part of the studies involved in the Water Framework Directive.

## **References**

- Abraham GMS, Parker RJ (2008) Assessment of heavy metal enrichment factor and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environ Monit Assess* 136:227–238. <https://doi.org/10.1007/s10661-007-9678-2>
- Adriano D (2001) Trace elements in terrestrial environments: biogeo- chemistry, bioavailability and risks of metals. Springer-Verlag, New York 866 pp
- Alvarez-Guerra M, Viguri J, Casado-Martinez MC, Angel DelValls T (2007) Sediment quality assessment and dredged material management in Spain: part I, application of sediment quality guidelines in the Bay of Santander. *Integr Environ Assess Manag* 3:529–538
- Amos HM, Jacob DJ, Holmes CD, Fisher JA, Wang Q, Yantosca RM, Corbitt ES, Galarneau E, Rutter A, Gustin MS, Steffen A, Schauer JJ, Graydon JA, St. Louis VL, Talbot RW, Edgerton ES, Zhang Y, Sunderland EM (2012) Gas-particle partitioning of atmospheric Hg (II) and its effect on global mercury deposition. *Atmos Chem Phys* 12:591–603. <https://doi.org/10.5194/acp-12-591-2012>
- APHA (2012) Standard methods for the examination of water and wastewater, 21th. American Public Health Association, American Water Works Association, Water Environment Federation, Washington
- Badri MA, Aston SR (1983) Observation on heavy metals geochemical associations in polluted and nonpolluted estuarine sediments. *Environ Pollut (Ser B)* 6:181–193
- Barhoumi B, Jouili S, Derouiche A, Elbarhoumi A, Mahfoudhi G, Atyaoui A, Bouabdallah S, Touil S, Ridha Driss M (2017) Sediment baseline study of levels, distributions and potential ecological risks of heavy metals in Bahiret El Bibane Lagoon (Tunisia, southwestern Mediterranean Sea). *GERF Bull Biosci* 8:1–14
- Caeiro S, Costa MH, Ramos TB, Fernandes F, Silveira N, Coimbra A, Medeiros G, Painho M (2005) Assessing heavy metal contamination in Sado Estuary sediment, an index analysis approach. *Ecol Indic* 5: 151–169. <https://doi.org/10.1016/j.ecolind.2005.02.001>



- Casado-Martínez MC, Forja JM, DelValls TA (2009) A multivariate assessment of sediment contamination in dredged materials from Spanish ports. *J Hazard Mater* 163:1353–1359. <https://doi.org/10.1016/j.jhazmat.2008.07.106>
- Christophoridis C, Dedepsidis D, Fytianos K (2009) Occurrence and distribution of selected heavy metals in the surface sediments of Thermaikos Gulf, N. Greece. Assessment using pollution indicators. *J Hazard Mater* 168:1082–1091. <https://doi.org/10.1016/j.jhazmat.2009.02.154>
- Cochran JK, Frignani M, Salamanca M, Bellucci LG, Guerzoni S (1998) Lead-210 as a tracer of atmospheric input of heavy metals in the northern Venice Lagoon. *Mar Chem* 62:15–29
- Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council
- Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy text with EEA relevance
- Donze M, Nieuwendijk C, Boxtel A, Quaak M (1990) Shaping the environment: aquatic pollution and dredging in the European community. Delwel Publishers, Hague 184 pp
- EPA Method 3051A (2007) Microwave assisted acid digestion of sediments, sludges, soils, and oils. Washington, DC. <https://www.epa.gov/sites/production/files/2015-12/documents/3051a.pdf>. Accessed May 2017
- Facchinelli A, Sacchi E, Mallen L (2001) Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. *Environ Pollut* 114:313–324. [https://doi.org/10.1016/S0269-7491\(00\)00243-8](https://doi.org/10.1016/S0269-7491(00)00243-8)
- Förstner U, Wittmann GT (1981) Metal pollution in the aquatic environment. Springer-Verlag, London
- Gao X, Chen CTA (2012) Heavy metal pollution status in surface sediments of the coastal Bohai Bay. *Water Res* 46:1901–1911. <https://doi.org/10.1016/j.watres.2012.01.007>
- GVA (2009) IMPRESS Document. Article 5 of the Water Framework Directive
- Hakanson L (1980) An ecological risk index for aquatic pollution control, a sedimentological approach. *Water Res* 14:975–1001
- Hosono T, Su CC, Siringan F, Amano A, Onodera S (2010) Effects of environmental regulations on heavy metal pollution decline in core sediments from Manila Bay. *Mar Pollut Bull* 60:780–785. <https://doi.org/10.1016/j.marpolbul.2010.03.005>
- Ip CCM, Li XD, Zhang G, Wai OWH, Li YS (2007) Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. *Environ Pollut* 147:311–323. <https://doi.org/10.1016/j.envpol.2006.06.028>

- Johnston EL, Roberts DA (2009) Contaminants reduce the richness and evenness of marine communities: a review and meta-analysis. *Environ Pollut* 157(6):1745–1752. <https://doi.org/10.1016/j.envpol.2009.02.017>
- Konstantinou IK, Albanis TA (2004) Worldwide occurrence and effects of antifouling paint booster biocides in the aquatic environment: a review. *Environ Int* 30:235–248. [https://doi.org/10.1016/S0160-4120\(03\)00176-4](https://doi.org/10.1016/S0160-4120(03)00176-4)
- Kuwabara JS, Alpers CN, Marvin-Di Pasquale M, Topping BR, Carter JL, Stewart AR, Fend SV, Parchaso F, Moon GE, Krabbenhoft DP (2003) Sediment-water interactions affecting dissolved-mercury distributions in Camp Far West Reservoir, California. *Publications of the US Geological Survey* 53. <http://digitalcommons.unl.edu/usgpsubs/53>. Accessed Feb 2018
- Leivouri M (1998) Heavy metal contamination in surface sediments in the Gulf of Finland and comparison with the Gulf of Bothnia. *Chemosphere* 36(1):43–59
- Li XD, Wai OWH, Li YS, Coles BJ, Ramsey MH, Thornton I (2000) Heavy metal distribution in sediment profiles of the Pearl River estuary, South China. *Appl Geochem* 15:567–581
- Li F, Huang J, Zeng G, Yuan X, Li X, Liang J, Wang X, Tang X, Bai B (2013) Spatial risk assessment and sources identification of heavy metals in surface sediments from the Dongting Lake, Middle China. *J Geochem Explor* 132:75–83. <https://doi.org/10.1016/j.gexplo.2013.05.007>
- Long ER, MacDonald DD, Smith SL, Calder FD (1995) Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environ Manag* 19:81–97
- Long ER, Field LJ, Macdonald DD (1998) Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environ Toxicol Chem* 17(4):714–727
- Long ER, MacDonald DD, Severn CG, Hong CB (2000) Classifying the probabilities of acute toxicity in marine sediments with empirically derived sediment quality guidelines. *Environ Toxicol Chem* 19: 2598–2601
- López P (1986) Composición del sedimento en sistemas acuáticos del litoral Mediterráneo Español. *Limnética* 2:11–18
- Loska K, Wiechula D (2003) Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. *Chemosphere* 51: 723–733. [https://doi.org/10.1016/S0045-6535\(03\)00187-5](https://doi.org/10.1016/S0045-6535(03)00187-5)
- Luoma SN (1990) Processes affecting metal concentrations in estuarine and coastal marine sediments. In: Furness RW, Rainbow PS (eds) *Heavy metals in the marine environment*. CRC Press, Boca Raton, pp 51–66
- Macdonald DD, Carr RS, Calder FD, Long ER, Ingersoll CG (1996) Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology* 5:253–278
- Mason RP, Sheu GR (2002) Role of the ocean in the global mercury cycle. *Glob Biogeochem Cycles* 16(4):1–14. <https://doi.org/10.1029/2001GB001440>

- Micó C, Peris M, Sánchez J, Recatalá L (2006) Heavy metal content of agricultural soils in a Mediterranean semiarid area: the Segura River Valley (Alicante, Spain). *Span J Agric Res* 4(4):363–372
- Palanques A, Díaz JI (1990) Contaminación de metales pesados en los sedimentos superficiales de la plataforma continental de Barcelona (Mediterráneo Noroccidental). *Rev Soc Geol Esp* 3(3–4):357–371
- Parks R, Donnier-Marechal M, Frickers P, Turner A, Readman J (2010) Antifouling biocides in discarded marine paint particles. *Mar Pollut Bull* 60:1226–1230. <https://doi.org/10.1016/j.marpolbul.2010.03.022>
- Pejman A, Bidhendi GN, Ardestani M, Mohsen Saedi M, Akbar Baghvand A (2015) A new index for assessing heavy metals contamination in sediments: a case study. *Ecol Indic* 58:365–373. <https://doi.org/10.1016/j.ecolind.2015.06.012>
- PRTR-España (2016) Spanish Register of Emissions and Pollutant Sources. <http://www.prtr-es.es/>. Accessed December 2017
- Pynaert K, Speleers L (2005) Development of an integrated approach for the removal of tributyltin (TBT) from waterways and harbours: prevention, treatment and reuse of TBT contaminated sediments. Report by the Environmental Research Center, Hofstade-Aalst, Belgium, 52 pp
- Rada RG, Wiener JG, Winfrey MR, Powel DE (1989) Recent increase in atmospheric deposition of mercury to North Central Wisconsin lakes from sediment analyses. *Arch Environ Contam Toxicol* 18:175–181. <https://doi.org/10.1007/BF01056202>
- Rainbow PS (1995) Biomonitoring of heavy metal availability in the marine environment. *Mar Pollut Bull* 31(4–12):183–192. [https://doi.org/10.1016/0025-326X\(95\)00116-5](https://doi.org/10.1016/0025-326X(95)00116-5)
- Reimann C, Filzmoser P, Garrett RG (2005) Background and threshold: critical comparison of methods of determination. *Sci Total Environ* 346(1–3):1–16. <https://doi.org/10.1016/j.scitotenv.2004.11.023>
- Riba I, Casado-Martínez C, Forja JM, Del Vall A (2004) Sediment quality in the Atlantic coast of Spain. *Environ Toxicol Chem* 23:271–282
- Romero I, Pachés M, Martínez-Guijarro R, Ferrer J (2013) Glophymed: an index to establish the ecological status for the Water Framework Directive based on phytoplankton in coastal waters. *Mar Pollut Bull* 75:218–223. <https://doi.org/10.1016/j.marpolbul.2013.07.028>
- Sanchiz C, García-Carrascosa A, Pastor A (2000) Heavy metal contents in soft-bottom marine macrophytes and sediments along the Mediterranean coast of Spain. *Mar Ecol* 21(1):1–16
- Suresh G, Ramasamy V, Meenakshisundaram V, Venkatachalapathy R, Ponnusamy V (2011) Influence of mineralogical and heavy metal composition on natural radionuclide contents in the river sediments. *Appl Radiat Isot* 69:1466–1474. <https://doi.org/10.1016/j.apradiso.2011.05.020>
- Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the earth's crust. *Geol Soc Am Bull* 72:175–192
- Turley PA, Fern RJ, Ritter JC (2000) Pyrithione as antifoulants: environmental chemistry and preliminary risk assessment. *Biofouling* 15: 175–182. <https://doi.org/10.1080/08927010009386308>

Upadhyay AK, Gupta KK, Sircar JK (2006) Heavy metals in freshly deposited sediments of the river Subernarekha, India: an example of lithogenic and anthropogenic effects. *Environ Geol* 50:397–403. <https://doi.org/10.1007/s00254-006-0218-0>

Varol M (2011) Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *J Hazard Mater* 195:355–364. <https://doi.org/10.1016/j.jhazmat.2011.08.051>

Wenning RJ, Ingersoll CG (eds) (2002) Executive summary of the SETAC Pellston workshop on use of sediment quality guidelines and related tools for the assessment of contaminated sediments. Society of Environmental Toxicology and Chemistry (SETAC), Pensacola

Yalcin MG, Tumuklu A, Sonmez M, Erdag DS (2010) Application of multivariate statistical approach to identify heavy metal sources in bottom soil of the Seyhan River (Adana), Turkey. *Environ Monit Assess* 164(1–4):311–322. <https://doi.org/10.1007/s10661-009-0894-9>

Zhang Z, Juying L, Mamat Z, QingFu Y (2016) Sources identification and pollution evaluation of heavy metals in the surface sediments of Bortala River, Northwest China. *Ecotoxicol Environ Saf* 126:94–101. <https://doi.org/10.1016/j.ecoenv.2015.12.025>

Zhao S, Feng C, Wang D, Tian C, Shen Z (2014) Relationship of metal enrichment with adverse biological effect in the Yangtze Estuary sediments: role of metal background values. *Environ Sci Pollut Res* 21:464–472. <https://doi.org/10.1007/s11356-013-1856-x>

Zhou J, Ma D, Pan J, Nie W, Wu K (2008) Application of multivariate statistical approach to identify heavy metal sources in sediment and waters: a case study in Yangzhong, China. *Environ Geol* 54:373–380. <https://doi.org/10.1007/s00254-007-0824-5>