Enrichment and contamination level of trace metals in the Mediterranean marine sediments of Spain

Remedios Martínez-Guijarro*[a], Maria Paches[b], Inmaculada Romero[a], Daniel Aguado[b]

a. 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.

b. 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.

*Corresponding author: mmarting@hma.upv.es

Abstract

These pollutants reach the aquatic environment and accumulate in the sediment. Among the chemical pollutants, metals represent a notable hazard since they are not biodegradable and have the capability to bioaccumulate, resulting in toxic effects in both the short and long term. In this study, the content of metals and As in marine sediments of the Spanish Mediterranean coast was determined. A total of four annual sampling campaigns were carried out along the Valencian Community coastline, where the presence of eight trace elements (Cr, Cd, Ni, Pb, Cu, Hg, Zn and As) was determined. In this area, the presence of the contaminants is due to both natural and anthropogenic sources. The results obtained allowed, first, to establish nearness Reference Values of the area under study, second, to use several pollution indices (Contamination Factor, Enrichment Factor, Geoaccumulation Factor, Nemerow Pollution Index, and Modified Pollution Index) to determine contamination levels in the area, and finally to select the best index to apply in this coastal zone. The best indices to use in this region are EF and MPI since both take into consideration the natural contributions of the elements studied. The results revealed that according to the index used only two studied zones are classified as Heavily and Severely polluted. The

remaining zones (between 25-29%) were classified as Moderately or Moderately to Heavily polluted and most of the zones (63% to 100%) were classified as Unpolluted / Low Polluted and Unpolluted / Slightly Polluted. The outcomes obtained with this work indicate that in general, the Valencian coast does not present significant levels of pollution due to the studied trace elements.

1. Introduction

Coastal ecosystems have changed drastically due to human activity in a short period of time, creating immense ecological impacts. A significant quantity of chemical contaminants is released every day into the waterways and the marine environment (Lloyd-Smith and Immig, 2018). Thus, chemical pollution poses a threat to the aquatic environment, both in the short and long term, with toxic and chronic effects for aquatic organisms, which can result in biodiversity loss, deleterious effects on wildlife habitats, degradation of the ecosystem, and possible poisoning of humans (Morton and Blackmore, 2001; Fung et al., 2004; Ip et al., 2004; Johnston and Roberts, 2009). Among the chemical pollutants, metals represent a notable hazard since they are not biodegradable and have the capability to bioaccumulate in aquatic ecosystems (Censi et al., 2006). However, metals are present in natural systems and may be of natural origin. Therefore, the presence of metals in the sediments of aquatic ecosystems can originate from both the Earth's crust and anthropogenic sources. These pollutants accumulate in the sediments in the same manner, irrespective of their source. Consequently, the straightforward determination of metals in sediments is an inappropriate way to assess whether or not they are polluted (Idris, 2008). Thus, since the origin of metal may also be natural, the environmental impact of metals and the pollution level in the sediments should be determined with the aid of a diverse range of pollution indices. For these

indices to be useful, they should compare different geographical zones, provide information about natural or anthropogenic sources, or even relate metal concentration with the toxic effects on organisms living close to the affected areas.

To this end, a pollution index represents a powerful tool for processing, analysing, and conveying raw environmental information to decision-makers, managers, technicians, and the public (Ramos et al., 2004).

Several indices have been developed to evaluate metal pollution, which have been classified in various manners by different authors. Caeiro et al. (2005) classified pollution indices into three types: *contamination indices*, which compare the contaminants with clean and/or polluted stations measured in the study area; *background enrichment indices*, which compare the results for the contaminants with different baseline or background levels; and *ecological risk indices*, which compare the results for the contaminants with Sediment Quality Guidelines (SQG) or Values. Qingjie et al. (2008) classified the commonly used pollution indices into two types, *single indices* and *integrated indices,* which are used to calculate contamination with only one metal or with more than one metal, respectively.

Extensive research has been carried out on the content of metals in the marine and estuarine sediments of the coastal areas of north-western Spain (Carral et al., 1995, Rubio et al., 2000, Cobelo-García and Prego, 2003) and the Atlantic south-west (Ligero et al., 2002; Borrego et al., 2002; Morillo et al., 2004). However, very few studies have focused on metal pollution in sediments of the Spanish Mediterranean coast, which have been affected by historical pressures and are threatened by current ones (Lejeusne et al., 2010); moreover, these studies mainly correspond to the north-east littoral (Cataluña) (López-Sánchez et al., 1996; Guevara-Riba et al., 2004).

The human activities carried out in the narrow coastal strip produce pollutants that may generate negative impacts in the receiving environment (water, air, soil and/or sediments) when certain thresholds are exceeded. In fact, the Valencian coastline is a high-density population zone, featuring industrialised areas, a strong tourism sector, and a significant agricultural sector (GVA, 2018). Therefore, it is necessary to recognise and properly manage the levels of metals present in order to avoid or mitigate these impacts on the aquatic environment.

The present study was implemented to meet the following objectives: (1) to establish the average content of metals (Cr, Cd, Ni, Pb, Cu, Hg, Zn) and As in the Valencian Community (VC) coastal sediments, to be used as a proxy for baseline concentration or reference levels and to assess their spatial variability; (2) to evaluate the relationship between metals and As and their possible natural or anthropogenic sources by using multivariate analysis; (3) to evaluate the pollution levels of elements by using different types of pollution index (single and integrated indices); (4) to select the index that best determines the polluting element level in the sediments of the VC coast, in order to propose a valuable tool to improve environmental management.

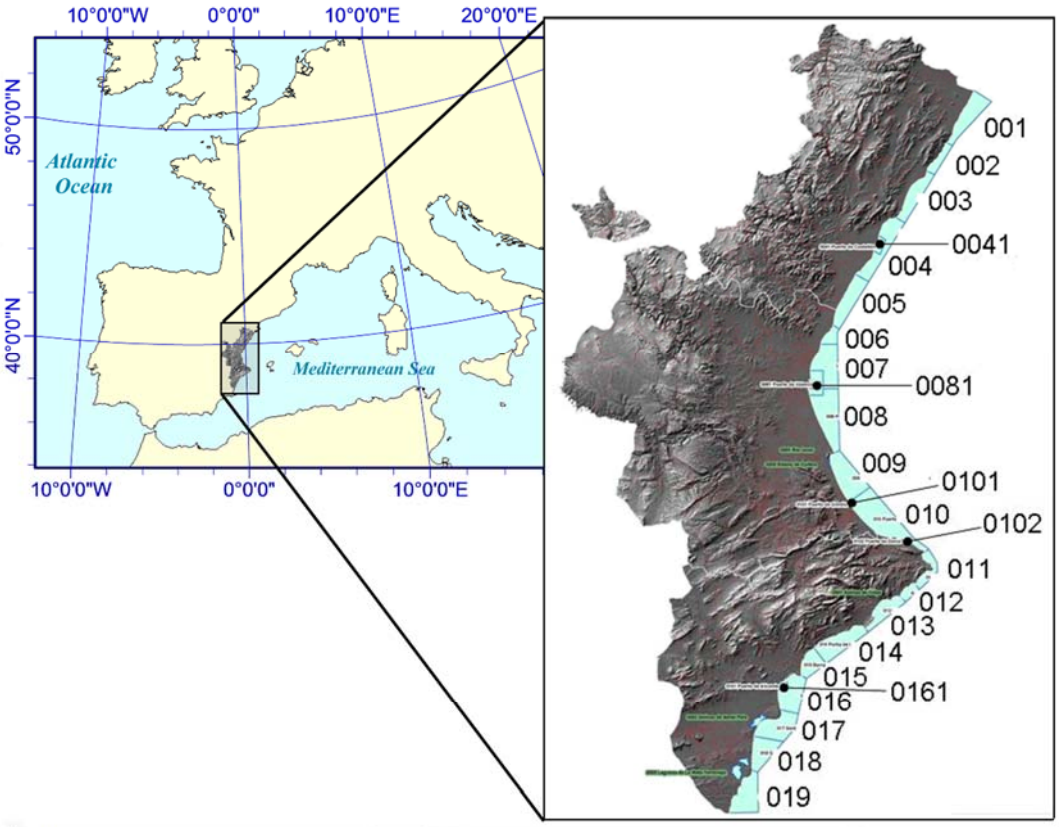
2. Material and Methods

2.1. Study area and sampling

The study was carried out along the Valencian Community coastline, which is 476 km long (Fig 1) and features leisure areas that bear intensive maritime traffic, along with popular tourist areas. This coastline is also affected by the significant agricultural and industrial sectors in the region (Ramos et al., 2002). The study area, which combines areas of great ecological value with highly anthropised areas (Muñoz and Domenech, 2012), was divided into several zones based on a holistic approach (coastal water zones and port zones, Fig. 1). For this categorisation, 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).

Figure 1. Study area and location of sampling zones in the Valencian Community, Spain



Code zone	Denomination	Code zone	Denomination	Code zone	Denomination
001	Comunidad Valenciana boundary-Irta mountain range	010	Port of Gandia-Cape San Antonio	0041	Port of Castellón
002	Irta mountain range	011	Cape San Antonio-Cape Moraira	006	Port of Sagunto
003	Irta mountain range-Cape Oropesa	012	Cape Moraira-Rock of Ifach	0081	Port of Valencia
004	Cape Oropesa-Burriana	013	Rock of Ifach-Cape les Caletes	0101	Port of Gandia
005	Burriana-Canet d'en Berenguer	014	Cape les Caletes-Cliff Aguas de Busot	0102	Port of Denia
007	North coast of Valencia	015	Cliff Aguas de Busot-Cape Huertas	0161	Port of Alicante
008	Port of Valencia-Cape of Cullera	016	Cape Huertas-Santa Pola		
009	Cape of Cullera-Port of Gandia	017	Santa Pola-Guardamar del Segura		
		018	Guardamar del Segura-Cape Cervera		
		019	Cape Cervera-Comunidad Valenciana boundary		

The sampling campaigns were performed annually for 4 years (2010, 2011, 2012, and 2015). In each sampling zone, two to four replicates were taken from surface sediments, which were then mixed into a composite sample for each zone. The upper layer of collected sediment was approximately 6 to 10 cm thick.

Sampling was performed by trained personnel by means of 20 mL methacrylate corers. The corers were then placed in a portable refrigerator, taken to the laboratory as quickly as possible, and stored at -20ºC until analysed.

2.2. Analytical techniques

The sediments were freeze dried (freeze dryer ilShin, model FD5510, ilShin Biobase Europe, Netherlands) and dry sieved through a <1mm mesh. The trace elements were determined using acid digestion with nitric acid (65% Merck, Suprapur) and hydrogen peroxide (30% Merck, Suprapur) in a microwave oven (Milestone, model Ethos 1, Milestone Srl, Italy), according to the EPA method (EPA 3051A, 2010) to obtain the solution of the pseudo-total metal content. Analyses of cadmium (Cd), copper (Cu), lead (Pb), chromium (Cr), nickel (Ni), zinc (Zn), iron (Fe), and metalloid arsenic (As) were performed by Flame or Furnace Atomic Absorption Spectrometry (Atomic Absorption Spectrophotometer with Zeeman correction, Model AAnalyst 800, Perkinelmer España, SL, Madrid), according to the metal concentration. Mercury (Hg) was determined by the cold vapour technique on an Atomic Absorption Spectrometer with autosampler and a flow injection system (Autosampler model AS 90 and Flow Injection System model FIAS 100, Perkinelmer España, SL, Madrid). All the processes were performed in accordance with the APHA (2012).

Data were analysed as pseudo-total metal concentrations on a dry weight basis and are expressed in acid soluble mg kg^{-1}dry weight (mg kg^{-1}dw). The LOD of this analytical procedure was established by analysing 10 repetitions of the "analytical blanks" (dissolution with reagents in the quantities used in the samples) through the entire analytical process. The LOD corresponding to instrumental signal has been calculated as three times the standard deviation (SD), according to the equation: LOD=3 SD. The

LOQ corresponding to instrumental signal was studied in the same way as LOD being set as ten times the SD, according to the equation: LOQ=10 SD. The procedure for calculating the LOD and LOQ are based on ISO 17025 standard (Sagrado et al., 2005). The detection limits (LOD) and quantification limits (LOQ) expressed in acid soluble μg kg^{-1} dw, were: LOD, Cr 5.6; Cd 1.2; Ni 10.6; Pb 11.6; Hg 13.2; Cu 15.9; As 14.9; Zn and Fe, both of which are expressed in mg kg^{-1} dw, were 1.0 and 50.0, respectively. The LOQ determined were: Cr 18.6; Cd 4.1; Ni 35.2; Pb 38.7; Hg 44.0; Cu 53.1; As 49.8; Zn and Fe, both of which are expressed in mg kg^{-1} dw, were 3.4 and 166.6, respectively. To evaluate the performance of the total analytical process, the reference sediment samples spiked with target analytes and duplicates unspiked samples have been analysed in exactly the same manner as actual samples. The recovery percentages are 80.3–105.2 for Cr, 88.8–108.0 for Cd, 84.9–103.4 for Ni, 95.5–106.7 for Pb,100.9–107.9 for Hg, 86.6–98.1 for Cu, 88.1–101.8 for As, 82.9–100.2 for Zn and 95.0–105.1 for Fe.

The routine procedure involves duplicate digestion and metal measurement to test analytical reproducibility. To identify background contamination, procedural blanks were analysed for every ten samples.

2.3. Statistical analysis

The element data were transformed to achieve normality (ln [metal]) and different statistical analyses were applied to experimental data. One-way analysis of variance (ANOVA) was used to test spatial differences on ln-transformed data for the 24 studied zones. If a significant F-ratio (significance $\leq \alpha = 0.05$) was found, post-hoc multiple comparison testing was performed using Scheffé and Bonferroni procedures.

To examine the relationship between all the elements measured, the Pearson correlation test and the Factor Analysis (FA) were applied. The FA was accomplished by applying the Varimax rotational technique to facilitate the interpretation. Varimax rotation was applied because orthogonal rotation minimises the number of variables with high loading on each component and facilitates the interpretation of the results. The purpose of this statistical technique is to obtain a small number of factors which account for most of the variability in the variables set (element concentrations). Kaiser-Meyer-Olkin (KMO) and Bartlett's tests were used to verify whether it was appropriate to implement the FA on the dataset. The statistical analyses were conducted with SPSS 16.0.

2.4 Metal reference levels

The baseline concentration, as reference values of the study area, must first be determined in order to use any pollution index. When the metal reference values are not available, some authors take reference values from the Earth's average values found in clay in sedimentary rocks, as reported by Turekian and Wedepohl (1961) (Rubio et al. 2000; Loska and Wiechula, 2003; Christophoridis et al. 2009; Ghrefat et al. 2011; Chabukdhara and Nema, 2012; Mashiatullah et al. 2013; Nowrouzi and Pourkhabbaz, 2014; Saher and Siddiqui. 2016; Delshab et al. 2017). However, as these values are much higher than those found in this study area, statistical methods were used to determine the baseline concentration or reference levels (Reimann et al., 2005). The statistical methods selected require first, to remove the outlier values and then, in a "clean" data set, (assumed to be anthropogenically undisturbed) determine the essential statistical parameters. These extreme values have been identified and eliminated using boxplot (Tukey, 1977). The baseline was determined as the median value plus twice the absolute median deviation (Median+2DMA) of the values. According to Matschullat et

al. (2000) and Reimann et al. (2005), it is strongly recommended to use median and median absolute deviation (MAD) instead of arithmetic mean and standard deviation.

2.5 Evaluation of metal contamination: geochemical approach

In this study, several indices were used to evaluate the pollution levels of sediments. These indices, described in Qingjie et al. (2008), are classified into two types: (i) single indices, and (ii) multiple-element indices based on an algorithm.

2.5.1. Single indices: These indices determine the contamination level due to one element.

(i) Contamination factor (CF)

The CF index is the ratio between element concentration at the sampling site (C_{site}) and the concentration of the same element at a background or reference level ($C_{background}$).

$$CF = \frac{C_{site}}{C_{background}} \qquad \text{Eq (1)}$$

This factor can be easily determined and provides information on the concentration of an element at the study site, and the same element at a background or reference level. Nevertheless, this index does not take into consideration lithogenic and sedimentary inputs of the element of interest (Brady et al., 2015).

The terminologies that are used to describe the CF are the following: CF<1, *low contamination factor*; 1≤CF<3, *moderate contamination factors*; 3≤CF<6, *considerable contamination factors*; and CF≥6, *very high contamination factor* (Qingjie et al., 2008).

(ii) Geoaccumulation index (I_{geo})

The geoaccumulation index was proposed by Müller (1969) in order to determine and define metal contamination in sediments (Banat et al., 2005). I_{geo} enables the assessment of contamination by comparing current and preindustrial concentrations. It can be calculated by the following equation:

$$I_{geo} = log\left(\frac{C_i}{1.5 \times C_b}\right) \qquad \text{Eq (2)}$$

where C_i is the measured concentration of the element *i* in the sediment, Cb is the geochemical background concentration or reference value of the element *i*. Factor 1.5 is used because of possible variations in the background or reference values for a given element in the environment as well as very small anthropogenic influences. The geo-accumulation index classifies the sediments into seven classes according to Müller (Buccolieri et al., 2006; Qingjie et al., 2008): <0 *practically unpolluted*; 0–1 *unpolluted to moderately polluted*; 1–2 *moderately polluted*; 2–3 *moderately to strongly polluted*; 3–4 *strongly polluted*: 4–5 *strongly to extremely polluted*; >6 *extremely polluted*.

(iii) Enrichment Factor (EF)

EF is a geochemical index based on the assumption that, under the natural sedimentation conditions, there is a linear relationship between a reference element (RE) and other elements. This index makes it possible to identify whether the enrichment in the sediments of an element is caused by anthropogenic or natural sources by normalising the element of interest against an element that has no anthropogenic source (Brady et al., 2015). The elements used as reference must fulfil a variety of criteria, such as: having no anthropogenic source, being present in sufficiently high concentrations so that anthropogenic sources have little effect, and having minimal natural variations in the sediment (Brady et al., 2015). Elements which are most often used as references are aluminium (Al) and iron (Fe), because these elements are abundant in the natural environment, to the extent that anthropic contributions do not produce significant variations in their concentration.

In this study, Fe was used as a conservative tracer to differentiate natural from anthropogenic components. In fact, several authors have successfully used the iron to

normalise polluting elements (Mucha et al., 2003; Meza-Figueroa et al., 2009; Bhuiyan et al., 2010; Esen et al., 2010; Seshan et al., 2010).

The Enrichment Factor (EF) for sediment samples was calculated using the following equation (Loska et al., 2004):

$$EF = \frac{\left(\frac{C_i}{C_{ref}}\right)_{sample}}{\left(\frac{C_i}{C_{ref}}\right)_{Background}} \qquad \text{Eq (3)}$$

Where C_i and C_{ref} refer to the concentration of element *i* and Fe in the sediment samples and background or reference level respectively.

Five contamination categories were established in this index (Sutherland, 2000): EF<2, *depletion to mineral enrichment*; 2≤EF<5, *moderate enrichment*; 5≤EF<20, *significant enrichment*; 20≤EF<40, *very high enrichment*; and EF>40, *extremely high enrichment*.

2.5.2. Multiple-element indices (integrated indices): Integrated indices are indicators used to calculate sediment contamination due to more than one pollutant element, and are based on the single indices. These integrated indices are the result obtained from an algorithm applied to a set of single indices (Qingjie et al., 2008).

(iv) Nemerow Pollution Index ($PI_{Nemerow}$)

The Nemerow Pollution index (Nemerow, 1991) is based on the mean of the Contamination Factors of the set of elements studied ($CF_{average}$). It also incorporates into its calculation the impact that may be caused by the maximum Contamination Factor (CF_{max}), which is obtained from a single pollutant, from among all those considered (Brady et al., 2015). $PI_{Nemerow}$ is defined by Eq (4),

$$PI_{Nemerow} = \sqrt{\frac{(CF_{average})^2 + (CF_{max})^2}{2}} \qquad \text{Eq (4)}$$

This index classifies the sediments into 5 grades (Cheng et al., 2007): $PI_{Nemerow}$<0.7, *safety domain*; 0.7≤$PI_{Nemerow}$<1.0, *precaution domain*; 1.0≤$PI_{Nemerow}$< 2.0, *slightly polluted domain*; 2.0 ≤$PI_{Nemerow}$<3.0, *moderately polluted domain*; and $PI_{Nemerow}$>3.0, *seriously polluted domain*.

(v) Modified Pollution Index (MPI)

This index was developed by Brady et al. (2015), and is calculated using Enrichment Factors according to Eq (5).

$$MPI = \sqrt{\frac{(EF_{average})^2 + (EF_{max})^2}{2}} \qquad \text{Eq (5)}$$

Where $EF_{average}$ is the average Enrichment Factor for the whole set of elements in the sediment studied, and the EF_{max} is the maximum value of Enrichment Factor for a single element in the sediment.

This index makes it possible to determine a non-conservative behaviour of the elements in the sediments due to the normalisation with an element such as Al or Fe.

The following classes are established in Brady *et al.* (2015) for MPI index: MPI<1, *Unpolluted*; 1<MPI<2, *Slightly polluted*; 2<MPI<3, *Moderately polluted*; 3<MPI<5, *Moderately polluted-heavily polluted*; 5<MPI<10, *Heavily polluted*; 10<MPI, *Severely polluted*.

2.6 Comparison of qualification sediment for the pollution index

The indices used (single and integrated) classify the contamination into different levels. In order to enable a comparison between them, some authors have proposed common terminologies between the indices. By applying the equivalences of Qingjie et al. (2008) for single indices, and Brady et al. (2015) for integrated indices, sediments are qualified according to the levels of contamination listed in Table 1.

Table 1 Common terminologies between indices. Pollution classes for single indices (Qingjie et al., 2008) and integrated indices (Brady et al., 2015).

Single indices				**Integrated indices**		
Qualification	**CF**	**EF**	**Igeo**	**Qualification**	**PI $_{Nemerow}$**	**MPI**
Unpolluted	**<2**	**<2**	**<0.42**	**Unpolluted**	**<0.7**	**MPI<1**
Low polluted	**2-4**	**2-4**	**0.42-1.42**	**Slightly polluted**	**0.7<PI$_{Nem}$<1**	**1<MPI<2**
Moderatelly polluted	**4-16**	**4-16**	**1.42-3.42**	**Moderatelly polluted**	**1<PI$_{Nem}$<2**	**2<MPI<3**
Strongly polluted	**16-32**	**16-32**	**3.42-4.42**	**Moderatelly-heavily polluted**	**----------**	**3<MPI<5**
Extremely polluted	**>32**	**>32**	**>4.42**	**Heavily polluted**	**2<PI$_{Nem}$<3**	**5<MPI<10**
				Severely polluted	**PI$_{Nem}$>3**	**10<MPI**

3. Results

3.1. Reference concentrations of metals and As

The calculated baseline concentrations at the studied zone were: Cr 22.5 mg·kg^{-1}; Cd 0.24 mg·kg^{-1}; Ni 13.3 mg·kg^{-1}; Pb 8.6 mg·kg^{-1}; Hg 0.06 mg·kg^{-1}; Cu 5.9 mg·kg^{-1}; Zn 50.0 mg·kg^{-1}; As 35.6 mg·kg^{-1}; and Fe 23.3 g·kg^{-1}.

3.2. Metal and As concentrations of sediments

The statistical description of trace element concentrations in the sediments of all sampling zones along the coast are shown in Table 2.

Table 2. Statistical description of metals and As concentrations in surface sediment at the study zone (2010, 2011, 2012 and 2015 years).

Trace element		**Cr**	**Cd**	**Ni**	**Pb**	**Hg**	**Cu**	**Zn**	**As**	**Fe**
Units		**mg kg^{-1} dw**								**g kg^{-1} dw**
Coastal Zones	Maximum	37.5	0.36	18.3	12.6	0.27	7.9	66.7	47.1	36.7
	Minimum	2.4	0.10	1.3	1.7	0.01	1.1	6.8	1.8	2.9
	Mean	15.6	0.19	8.0	5.4	0.04	3.2	30.5	15.7	14.8
	SD	9.6	0.06	5.1	2.8	0.05	1.7	16.3	11.8	10.5
	Median	13.0	0.18	6.2	4.8	0.03	2.4	27.5	12.2	10.4
Port Zones	Max	23.6	0.23	21.6	11.4	0.34	12.0	69.7	51.0	45.8
	Min	2.8	0.08	1.8	2.3	0.01	1.2	16.6	2.0	4.6
	Mean	13.5	0.16	7.1	6.6	0.07	3.7	31.0	17.7	14.6
	SD	5.7	0.04	4.0	2.6	0.07	2.2	11.7	10.1	8.0
	Median	12.0	0.16	6.2	6.8	0.05	3.1	28.5	18.5	14.7

SD standard deviation

The element concentration values exhibit high variability between sampling campaigns, with a variation coefficient greater than 30% for Hg, Cr, Pb, and As, between 20-30% for Zn and Cu, and less than 20% for Ni and Cd. The Fe content exhibited homogeneous values with variation coefficient values below 12%.

When the element concentrations were analysed, the ANOVA results revealed statistically significant spatial differences (significance level <0.05) in the content of Cr, Cd, Ni, Cu, Zn, As, and Fe. Subsequent statistical analyses, through the post hoc tests, verified that the differences corresponded to the zones from the north-central (zones 001 to 010) and those of the south (zones 011 to 019). These differences were especially evident in the north-central areas for elements Cr, Ni, Zn, As, and Fe with values between 55–70% higher than those in the south, and 30% for Cd. In the case of Cu, significant differences in concentration only occurred between the northern (001 to 005) and southern areas, with an average value 30% higher in the northern areas. For the levels of Pb and Hg, no statistically significant differences were found between the studied zones.

Table 3 shows the Pearson correlation coefficients obtained between the trace element contents. High correlation coefficients were obtained for several elements. Some metals that were strongly correlated at 0.01 significant levels were: Ni-Cr (r=0.87), Ni-Zn (r=0.82), Ni-As (r = 0.75), Ni-Fe (r =0.94), Cr-As (r =0.82), Cr-Fe (r = 0.79), As-Fe (r = 0.79), and finally Zn-Fe (r = 0.89).

Table 3. Pearson correlation coefficients of the trace elements

		Cr	Cd	Ni	Pb	Hg	Cu	Zn	As	Fe
Cr	Correlation	1.00								
	Sig.(bilateral)									
Cd	Correlation	0.40**	1.00							
	Sig.(bilateral)	0.00								
Ni	Correlation	0.87**	0.49**	1.00						
	Sig.(bilateral)	0.00	0.00							
Pb	Correlation	0.45**	0.14	0.28**	1.00					
	Sig.(bilateral)	0.00	0.17	0.01						
Hg	Correlation	0.08	-0.05	0.18	0.24*	1.00				
	Sig.(bilateral)	0.42	0.65	0.07	0.02					
Cu	Correlation	0.68**	0.34**	0.74**	0.48**	0.34**	1.00			
	Sig.(bilateral)	0.00	0.00	0.00	0.00	0.00				
Zn	Correlation	0.61**	0.58**	0.82**	0.29**	0.35**	0.64**	1.00		
	Sig.(bilateral)	0.00	0.00	0.00	0.00	0.00	0.00			
As	Correlation	0.82**	0.32**	0.75**	0.36**	-0.00	0.34**	0.57**	1.00	
	Sig.(bilateral)	0.00	0.00	0.00	0.00	0.97	0.00	0.00		
Fe	Correlation	0.79**	0.52**	0.94**	0.26*	0.21	0.63**	0.89**	0.79**	1.00
	Sig.(bilateral)	0.00	0.00	0.00	0.01	0.04	0.00	0.00	0.00	

** Correlation is significant at p<0.01
* Correlation is significant at p<0.05

The results obtained with the application of the Factor Analysis (FA) are displayed in Table 4 (KMO 0.78; Bartlett's test p-value < 0.05). FA performed on the element dataset revealed two factors with eigenvalues > 1 that explained 71.6% of the variability of the data. The first factor (F1) explained 57.9% of the total variance and is positively related mainly to Cr, Ni, Zn, As, Fe, and also to Cd that has less factor loading.

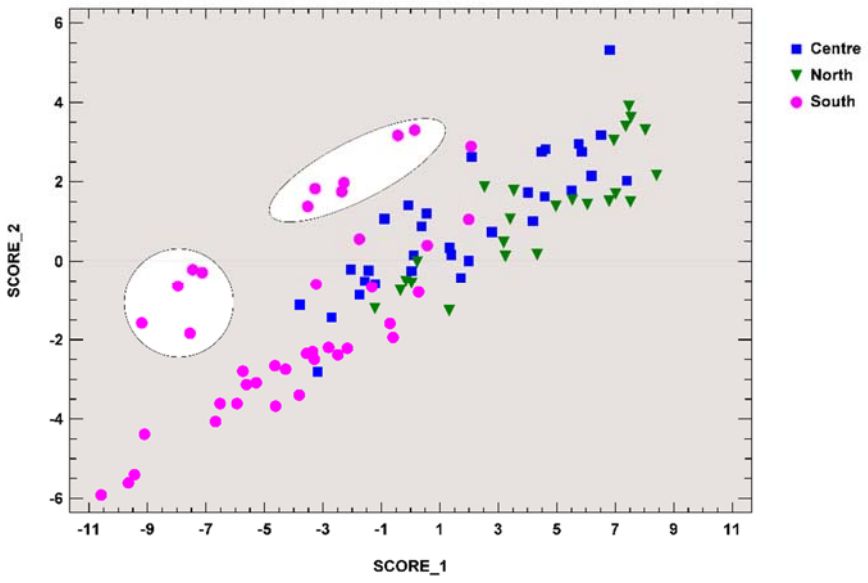
The second factor was mainly related to Hg and Pb. Lastly, the Cu had similar loading values in both factors (F1 0.59; F2 0.60).

Table 4: Factor matrix loading after Varimax rotation.

	Factor 1	***Factor 2***
Ln Cr	0.86	0.26
Ln Cd	0.66	-0.10
Ln Ni	0.92	0.28
Ln Pb	0.24	0.62
Ln Hg	-0.08	0.86
Ln Cu	0.59	0.60
Ln Zn	0.79	0.38
Ln As	0.83	0.07
Ln Fe	0.92	0.25
Eigenvalue	5.21	1.24
%Variance	57.9	13.8
%Cumulative Var.	57.9	71.6

Figure 2 shows the factor scores for each sample. As can be seen in this Figure, samples from the north to the central areas are aligned in positive F1 and F2 axes. Meanwhile, those corresponding to the southern zones are lining up in negative values on both axes. Samples from zone 016, 017, and 0161 are outside this trend (these samples are circled in Figure 2).

Figure 2. Factor scores for each sediment sample.



3.3. Contamination Indices

3.3.1. Single indices

Analysing the outcomes of the evaluations using CF, I_{geo} and EF revealed that:

Contamination Factor (Figure 3a)

In over 75% of the zones, and for all elements analysed, the values obtained for the CF were below 1, reflecting *low contamination*. CF values between 1–3 with a classification of *moderate contamination*, were obtained in 11 zones mainly due to metals Cr, Ni, Zn, Cd and Hg. Only in zone 017, and due to Hg, was the value of CF greater than 3 (CF=3.1); therefore, the sediment was classified at the level of *considerable contamination*.

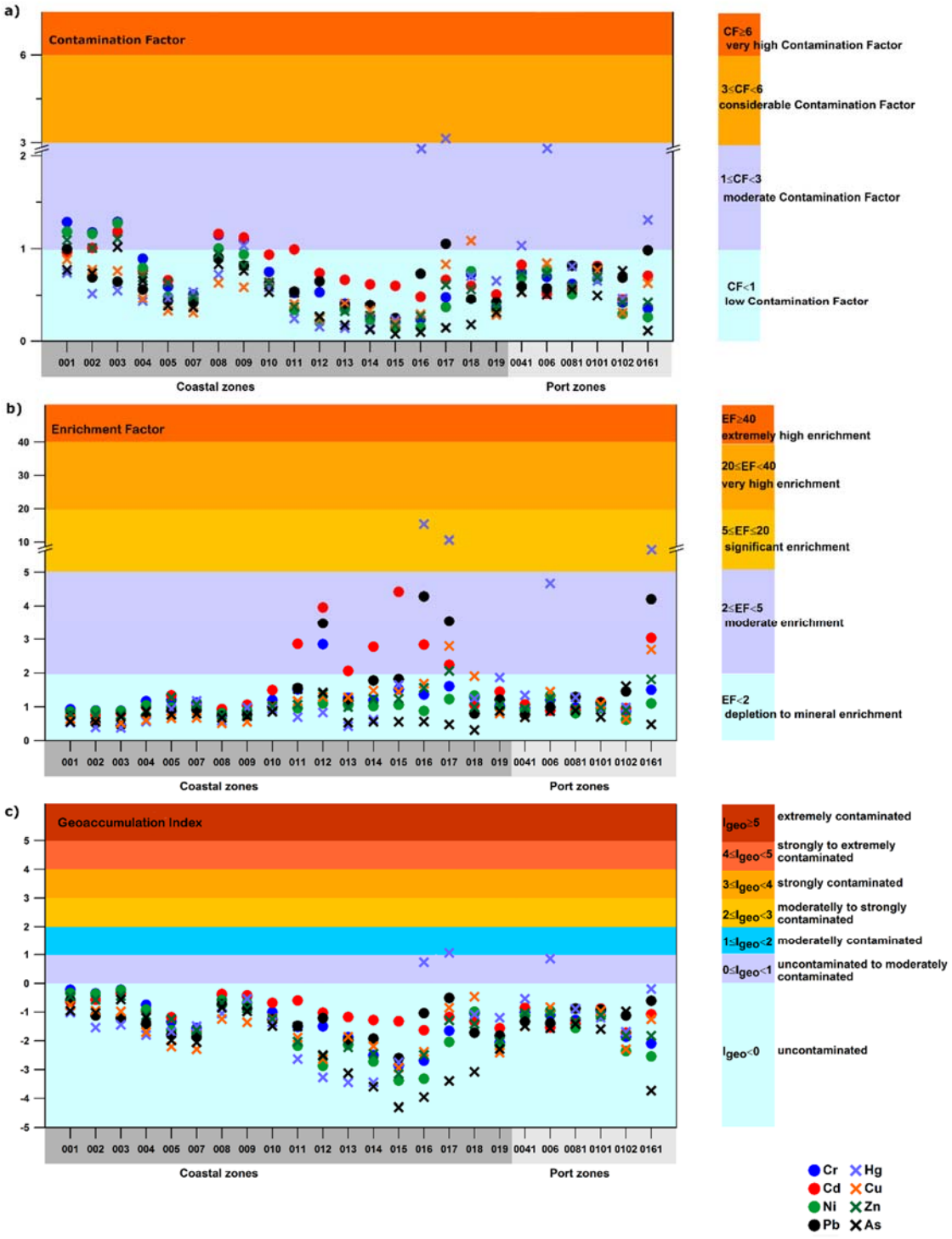
EF index (Figure 3b)

The analysis of the EF index for the individual elements revealed that in most of the areas studied and in almost all elements, there was no enrichment (EF<2). Only in some areas and due mainly to the metals Cd (7 zones), Pb (4 zones), and Hg (1 zone), the EF index exhibited values between 2 and 5, thus indicating *moderate enrichment*. In the coastal zones 016, 017, as well as in the port 0161, due to Hg, the highest values of EF occurred (between 5 and 20) resulting in these areas being classified as *significant enrichment*.

I_{geo} index (Figure 3c)

The values of I_{geo} were below 0 in nearly all the zones and, therefore, according to this index, the sediments did not present metal pollution. Only in zones 006 and 016, due to Hg, the values of this index indicate that the sediments exhibit a level of contamination that ranges from *uncontaminated* to *moderately contaminated*. In addition, the zone 017 that resulted classified as *moderately polluted.*

Figure 3. Single pollution indices: a) Contamination Factor, b) Enrichment Factor and c) Geoaccumulation index



3.3.2. Integrated indices

The outcomes using $PI_{Nemerow}$ and MPI, are presented in the following paragraphs:

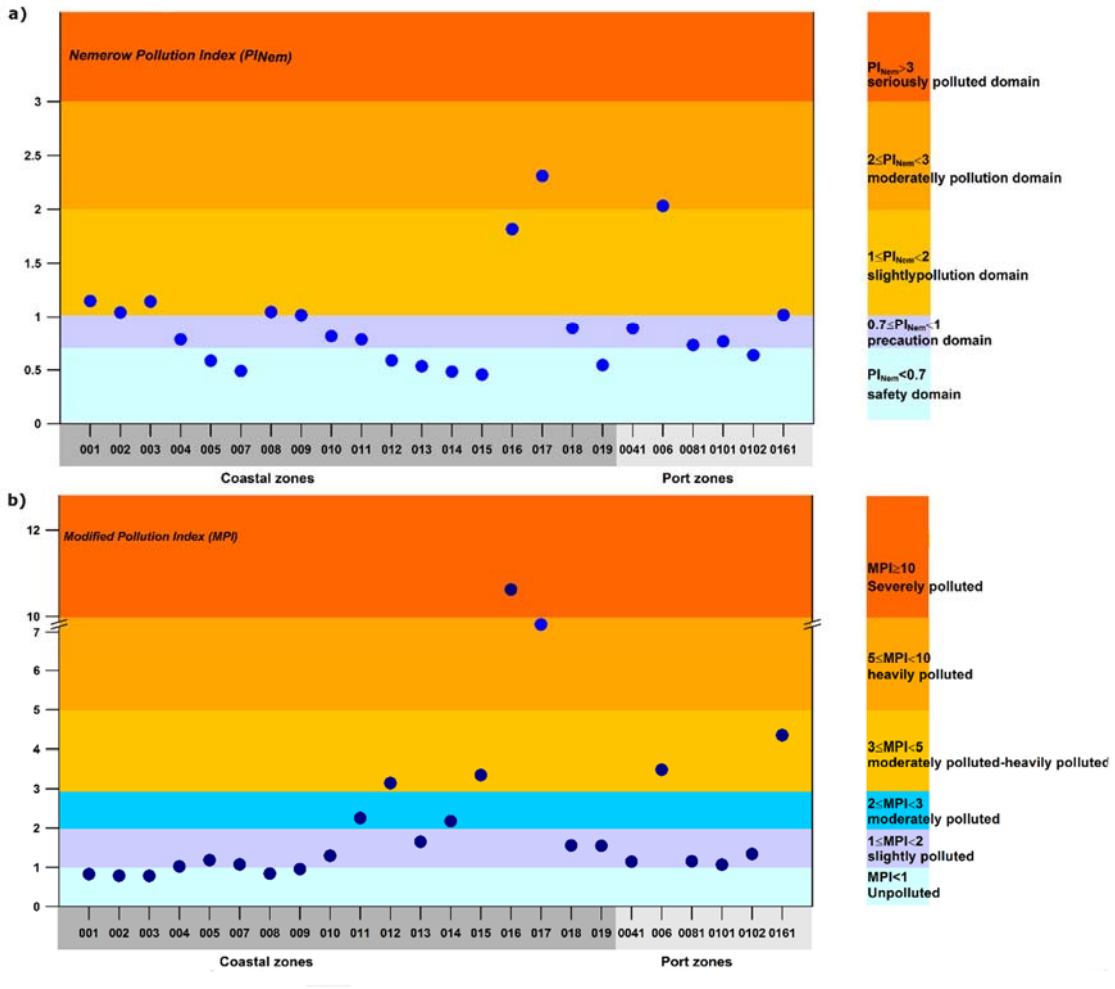
$PI_{Nemerow}$ *index* (Figure 4a)

Taking into account the values of this index, the zones were grouped into four groups. A first group formed by eight zones, all but one located in the south of the VC, with a $PI_{Nemerow}$ *index* <0.7, thus classified as *safety domain*. A second group formed by seven zones placed mainly in the north-central areas of the coast studied with a $PI_{Nemerow}$ *index* in the range 0.7–1, classified as a *precaution domain*. The third group also formed by seven zones with a $PI_{Nemerow}$ *index* in the range 1-2, classified as a *slightly polluted domain*. Finally, only two zones exhibited the highest value of the $PI_{Nemerow}$ *index* (range 2-3) thus, belonging to the category of a *moderately polluted domain*.

MPI index (Figure 4b)

Applying this index, the studied coastal zones were classified into six contamination levels. The first group (*unpolluted*) with values of MPI < 1 was formed by five zones of the northern and central littoral areas. Another group (*slightly polluted*) consisted of eight coastal zones and three port areas with MPI values in the range 1–2. The third group (*moderately polluted*) was formed only by two zones with MPI values within the range 2–3. Two coastal zones and two port zones were integrated into a fourth group (*moderately polluted* to *heavily polluted*) with MPI values in the range of 3-5. The highest values of the MPI index correspond to the zones 016 and 017, resulting in classifications of *severely polluted* and *heavily polluted* respectively.

Figure 4. Integrated Pollution indices: a) Nemerow Pollution Index and b) Modified Pollution Index



According to the common terminologies listed in Table 1, only two studied zones are classified as *Heavily* and *Severely polluted.* The remaining zones (between 25-29%) were classified as *Moderately* or *Moderately to Heavily polluted* and the most zones (63% to 100%) were classified as *Unpolluted / Low Polluted* and *Unpolluted / Slightly Polluted*.

4.- Discussion

The results show different trends in metal and As concentrations along the coast of Valencia. Statistically significant spatial differences were revealed with the ANOVA for Cr, Cd, Ni, Cu, Zn, As, and Fe between the north-central areas (zones 001 to 010) and the southern areas (zones 011 to 019). These differences may be due to the fact that the

sediments of the north-central zones receive greater contributions of these elements from natural origin, due to the proximity of mountain systems and sedimentary inputs from terrestrial waterways. However, there were no statistically significant differences in Pb and Hg concentrations between the zones, maybe because both metals, can reach the coastal ecosystem through atmospheric transport, and the entire study area was affected in a similar way (Martinčič et al., 1989). The concentrations of the metals found in the present work were in agreement with those reported in 1991 by Sanchiz et al. (2000) from the littoral stretch, corresponding to zones 003, 006, 010, 011, 014, 016, and 017. These authors also detected high concentrations of Hg and Pb, especially the first metal, in southern areas, as well as in zones 016 and 017.

It is important to highlight that the data obtained in this study allowed, for the first time in the VC, the statistical determination of baseline or reference concentrations for each of the eight elements studied, since preindustrial values of these elements could not be found for the sediments in the study area. Without reference values, many indices used to evaluate polluting elements cannot be applied.

The high correlations found between the metals Fe, Ni, Cr, and Zn suggest that the presence of these metals in the study area was strongly governed by natural processes. In contrast to this group, the other metals may have reached sediments due to multiple anthropogenic sources of pollution. On the littoral, activities and actions such as urban and industrial discharges, aquaculture installations, sea traffic in and out of large commercial ports, nautical sports, etc., affect the metal content in the sediments (Integrated coastal zone management in Spain, 2019). In addition, the entire coastal area receives agricultural run-off with a high content of micronutrients, metals, pesticides, and herbicides (Rico Amorós, 2002).

This was also suggested by the factor analysis results, which revealed that the elements studied could be grouped into two factors, explaining most of the variability of the data. Factor 1 represents the "metals of natural origin" (Zn, Cr, Ni, Fe), inferred by their high correlation with Fe. The zones located to the very north (001, 002, and 003) exhibit high F1 scores, suggesting that the metals from these stretches of the coast were mainly of lithogenic origin since the Irta Mountain range with geochemical composition with high metal contents is close to the coast (IGME, 2018). The presence in this first factor of elements of non-natural origin, such as As and Cd, can be attributed to their relationship with metals of natural origin. Although Cd is a rare element, it is nevertheless ubiquitous in the Earth's crust, appearing in sediments linked to deposits of zinc sulphide (Boluda and Egea, 2017). Furthermore, Arsenic is highly correlated with Fe because it is strongly adsorbed by iron and manganese oxyhydroxides (Rodriguez, 2001; Wauchope and Mcdowell, 1984).

Factor 2 denotes those metals (Pb and Hg) in the aquatic environment mainly due to anthropogenic sources. In addition to the source, these elements display similar behaviour since both elements in the aquatic system can be methylated and can access the system through atmospheric transport (Cochran et al., 1998, Li et al. 2000; Mason and Sheu, 2002; Amos et al., 2012). Lastly, Cu appears in both factors suggesting that the variability the Cu concentration was due to other factors not taken into account in this statistical analysis.

Therefore, the metals present in the studied coastal ecosystem may be of mixed origin, both anthropogenic and natural. This highlights the need to apply indices not only to assess metal but also to discern their source, which may improve the procedures employed to reduce or control these pollutants.

When single indices are applied, the results may vary depending on which one is used. For example, according to the Contamination Factor (CF) assessment, the southern zones (011 to 015, and 018 to 019) did not present contamination or were very low in nearly all the elements analysed. However, the northern zones (001 to 003, 008, and 009) which showed large element values, resulted in moderate pollution caused by the metals Cr, Cd, Ni, Zn, and Hg. This may be because this index does not consider the lithogenic and sedimentary contributions (Brady et al., 2015), but the raw value.

As pointed out before, the northern areas (001 to 003) directly collect lithogenic contributions from the Irta mountain range, whereas the zones located in the centre of VC (008 and 009) receive metals (Cr, Ni, Cu, etc.) indirectly from natural processes, as these areas accumulate sediments transported by freshwater outlets to the coast, such as the mouths of the Júcar and Turia rivers, the Albufera lake, etc.

Contrary to the CF index, the results with the Enrichment Factor (EF) show that southern areas (011 to 017) were classified as moderately polluted due to the presence of toxic metals such as Cd, and in some areas Pb and Hg. Particularly, Hg presented significant enrichment in two southern zones (016 and 017). The EF index does take into account the lithogenic contributions since it incorporates the reference element (Fe) in its determination. For this reason, the three northern areas with the highest concentrations of metals Cr, Zn, and Ni were classified as uncontaminated.

According to Zhang and Liu (2002), EF values between 0.5 and 1.5 indicate that the presence of the metal was entirely from materials from the Earth's crust or natural processes, whereas EF values greater than 1.5 suggest the contribution of anthropogenic sources. Since in the southern areas (011 to 017), and mainly in zones 016, 017, and the port areas (006 and 0161), the value of EF for Cd, Pb, and Hg exceeded 1.5, it could be concluded that these metals were generated by anthropic processes.

Finally, in all but 3 zones (016, 017 and 006), the Geoaccumulation Index (I_{geo}) was always negative, thus, all the remaining zones were classified as uncontaminated for all metals. These low values can be yielded because this index reduces its sensitivity in low concentrations. Note that it is a logarithmic index and its assessment tends to be more accurate when there is a significant enrichment due to more intense anthropic activity (Brady et al., 2015).

Comparing the results of these 3 indices, the EF index identifies a greater number of polluted areas. Nevertheless, the EF index seems to be stricter than I_{geo} and not only takes into account the proportion of elements of natural origin (as opposed to CF) but also determines the zones that receive elements that are more associated with anthropic sources.

In general, and according to the results of these three single indices (CF, EF and I_{geo}) considerable and intense pollution of metals and As in the sediments of the study area was not found. Almost all the stretch (coastal and port) was classified in the lowest levels of pollution (*uncontaminated/low contamination*). Only 3 zones (016, 017, and port 006) were classified in the levels of *moderate contamination*/*significant enrichment*.

Nevertheless, when integrated indices are applied, the results may differ slightly. The two integrated indices (PI_{Nem} and MPI) used in this study also presented differences in the yielded results. This could be expected as in their estimation they apply different single indices; i.e., PI_{Nem} uses Contamination Factor, while the MPI index uses Enrichment Factor.

Integrated indices (PI_{Nem} and MPI), indicated that several zones have considerable pollution levels. These indices classified several of the southern zones and some port zones as heavily polluted and severely polluted, due to the high content of Cd, Hg and

Pb. Although the high content of Cd, Hg, and Pb may affect aquatic organisms living in or near sediments, when the effects and risk level for these areas are analysed using *Sediment Quality Guidelines, SQG* (Long et al. 1995; Macdonald et al. 1996) and *Ecological Risk Indices* (MERMQ and mPELq), only occasional adverse effects for organisms and a low-medium risk level are obtained (Paches et al., 2019). Therefore, the Cd, Hg, and Pb levels detected in the VC coast do not in any way constitute a potential risk to aquatic organisms.

In many zones, the classification according to single indices was not consistent with the integrated indices. The single indices evaluating each element separately do not consider the complex nature of the metals that mainly occur in urban and industrial environments when they are generated by the same source (Brady et al., 2015). Therefore, using integrated indices that take a set of metals into account can be considered a good starting point for assessing the contamination of sediments.

According to the results of this study, the indices that best reflect the contamination by metals and As in the sediments of the VC are EF and MPI, since both indices are the most restrictive and reveal the most polluted areas due to elements of anthropogenic origin. Between these two indices, the most suitable for environmental management is probably the MPI index. The joint assessment of metal pollution in this coastal region is appropriate, given that the polluting elements share a common origin. Therefore, in those areas that the MPI index determines some kind of pollution, the same corrective action may reduce the levels of contamination and enhance the environmental quality of the coast.

5.- Conclusions

The study conducted through 476 km of the Valencian Community coastline evidence that there are spatial differences for Cr, Cd, Ni, Cu, Zn, As and Fe concentrations,

between the sediments of the north-central areas and the southern areas. These differences may be due to the sediments of the north-central zones receive greater contributions of these elements from natural origin.

The Pb and Hg levels have no statistically significant differences between zones since the sources of these elements are of anthropogenic origin

In addition, a valuable contribution of the study is to determine for the first time an approximation of a reference or background levels for elements studied.

According to the results of the three single indices applied (CF, EF and Igeo) there are not any zones classify as considerable and intense pollution of metals. However, with integrated indices (PI_{Nem} and MPI) several zones (006, 016 and 017) have considerable pollution levels.

The indices that best reflect the contamination by metals and As are EF and MPI, since both indices reveal the most polluted areas due to metals of anthropogenic origin. Between these two indices, the most suitable for environmental management of coastal sediments studied is the MPI index, because the joint assessment of metal and As pollution in this coastal region is appropriate due to a common origin of these metals.

Conflict of interest

The authors declare no conflict of interest.

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