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Risk assessment of trace elements in sediments: The case of the estuary of the Nerbioi–Ibaizabal River (Basque Country)

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ABSTRACT

Long term (January 2005–January 2008) monitoring of sediments was used to investigate metal pollution in the estuary of the Nerbioi–Ibaizabal River (Bilbao, Basque Country). Sediments were collected from eight representative locations of the estuary approximately every three months. The concentration of fourteen elements was measured in sediment extracts. Different graphical representations of the data set, simple statistical methods and sediment quality guidelines were combined to investigate trends in space and time, identify pollution sources, and assess sediment quality from a toxicological point of view. In general terms, the main trend reveals a significant fall in metal concentration over the period investigated. There are still certain points of the estuary with relatively high concentration of toxic metals, but the toxicological approach suggests that the risk for living organisms is not important.

1. Introduction

Pollution of the natural environment by trace metals is a worldwide problem. Trace elements from natural and anthropogenic sources continuously enter the aquatic ecosystem where they pose a serious threat because of their toxicity, long time persistence and bioaccumulation [1]. The impact of anthropogenic perturbation is most strongly felt by estuaries which drain densely populated and industrialized areas. Metals enter estuaries both from tributary rivers and from direct discharges. Atmospheric deposition is another important pathway to be considered. When particle-reactive pollutants, such as trace elements, enter estuarine waters, many are quickly adsorbed on suspended matter and removed to bottom sediments [2]. Sediment as a compartment is more conservative than water, as it accumulates historical data on processes within water bodies and the effect of anthropogenic factors on these processes. For these reasons, sediment quality parameters have been used as environmental indicators and their ability to trace and monitor contamination sources is largely recognised. Sediments show a high capacity to accumulate and eventually integrate the low concentrations of trace elements usually found in water. In order to better interpret the results of any contaminant analysis some concepts have been suggested, such as the study of spatial and temporal variance in the objective area using multiple repeated sampling over an extended period of time [3].

The European Water Framework Directive (WFD) [4] is a legislative basis for the maintenance and recovery of water quality. Although the WFD does not refer to sediments as a body to be specifically investigated, sediments play an important role in the good ecological and chemical status of water [5]. A number of methods (contamination indexes, background enrichment indexes or ecological risk indexes) are available for assessing sediment quality, and each has its pros and cons. Only a few have been specifically developed for estuarine environments [6]. For example, enrichment indexes like the enrichment factor, E_f [7] and the geoaccumulation index, I_{geo} [8], provide a simple way of comparing the extent of metal pollution at different sites within the estuary.

This work is centred on the sediments of the estuary of the Nerbioi–Ibaizabal River (Metropolitan Bilbao, Bay of Biscay, Basque Country), which have been affected by industrial activities (especially primary iron and steel production and transformation) since the 19th century. The Metropolitan area of Bilbao, with a total of 17 towns, is the largest concentration of inhabitants (about 1 million) in the south-eastern corner of the Bay of Biscay, generating urban wastewaters [9] and effluents from more than 2700 industrial facilities [10]. The physical nature of the estuary has been highly modified since the end of the XIX century, mainly by means of canalization, dredging and construction of dykes [11]. Since the early 1980s there has been a decrease in pollution on the estuary, due to (a) recession in the overall primary industrial activities, (b) closure of mine workings, (c) treatment of domestic and industrial sewage and (d) political environmental protection policies and actions [12,13]. Nevertheless, the estuary still presents high levels of contamination in both the water column and sediments [14,15].

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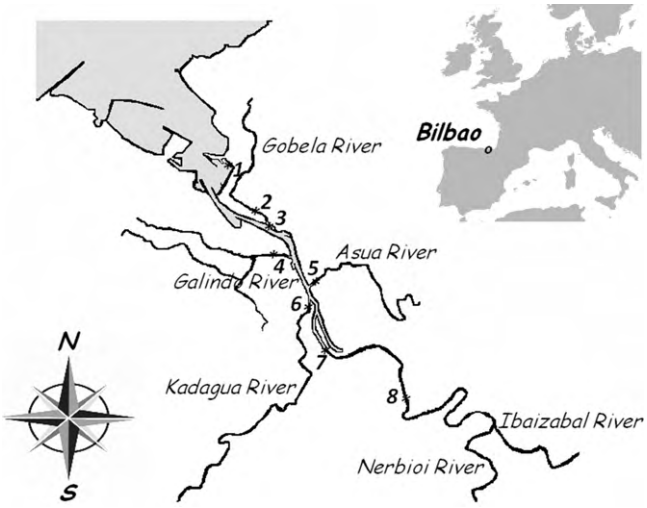

Fig. 1. Geographical location of the estuary of the Nerbioi–Ibaizabal River and the location of the sampling stations: 1. ARriluze, 2. GObela, 3. UDondo, 4. GAlindo, 5. ASua, 6. KAdagua, 7. ZOrrotza and 8. Alde Zaharra.

Previous works have investigated the metallic content of sediments from the estuary [9,11,15–26], but to our knowledge in none of them have sediments been collected seasonally.

A programme of regular monitoring of sediments has enabled us to investigate (i) the spatial, temporal and seasonal variations in trace element concentrations along the estuary of the Nerbioi–Ibaizabal River, (ii) the origin of trace elements and their path of entry into the estuary, (iii) the environmental risk associated with the metallic content of sediments using available Sediment Quality Guides (SQGs) and, finally, (iv) the efficiency of the wastewater treatment systems as part of the Revitalization Strategic Plan for the Metropolitan area of Bilbao.

2. Materials and methods

2.1. Study area and sampling procedures

The estuary of the Nerbioi–Ibaizabal River (N43°19′, W3°00′, Fig. 1) is located on the continental shelf of the Cantabrian coastline in the northern coast of the Iberian Peninsula. The main fresh water input comes from the Nerbioi and Ibaizabal rivers (68%), while the rest comes from the smaller tributaries Kadagua (27%), Galindo (4%), Asua (0.7%) and Gobela (0.3%) [22]. Further details about its physical and hydrodynamic characteristics can be found elsewhere [20,27].

Approximately 500 g of surface sediment samples (~2 cm depth) were collected at low tide from eight stations strategically distributed along the estuary, with an average distance between samples of 11 km (see Fig. 1). GO, GA, AS and KA are in the tidal part of the main tributaries. UD is in a semi-closed dock and AR is in the mouth of the estuary. Both ZO and AZ are in the upper part of the main channel.

Sampling was carried out approximately every three months from January 2005 to January 2008 (12 sampling campaigns). Sediments were collected using plastic sampling utensils and latex gloves to avoid sample contamination with metals, put into clean plastic bags and taken to the laboratory in portable cooler boxes at 4 °C to reduce the effects of microbiological activity.

Once in the laboratory, the sediment samples were frozen and then lyophilized in a Cryodos apparatus from Telstar. Finally, samples were sieved to assure a maximum particle size of 65 μm and kept in the refrigerator at 4 °C until analysis.

Table 1
Experimental conditions used in the analysis by ICP/MS.

Nebulisation flow	0.94 L min^{-1}
Plasma flow	15 L min^{-1}
Auxiliary flow	1.2 L min^{-1}
Sample flow	1 mL min^{-1}
Measured isotopes	^{27}Al, ^{75}As, ^{111}Cd, ^{59}Co, ^{52}Cr, ^{63}Cu, ^{57}Fe, ^{24}Mg, ^{55}Mn, ^{60}Ni, ^{208}Pb, ^{120}Sn, ^{51}V, ^{66}Zn
Radiofrequency power	1000 W
Integration time	1000 ms
Replicates	3–4

2.2. Analytical methods

All plastic and crystal material was firstly washed with soap and water, rinsed with Ellix quality water (κ < 0.2 μS cm^{-1}, Millipore), and left in a 10% nitric acid (Panreac) bath for 24 h. Afterwards, it was thoroughly rinsed with Ellix and MilliQ water (κ < 0.05 μS cm^{-1}, Millipore) before use.

Chemical analysis for trace element determination (Al, As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sn, V and Zn) was performed by inductively coupled plasma/mass spectrometry (ICP/MS) on the fine fraction (<65 μm) of the sediments after acid extraction assisted by ultrasound focused energy [28]. Briefly, 0.5 g of dried sediment (weighted to the fifth decimal position by a balance from Mettler) was transferred to an extraction vessel with 20 mL of HNO_3/HCl (Tracepur, Meck) acid mix. Ultrasound energy was applied for 6 min by means of a HD 2070 Sonopuls Ultrasonic Homogenizer from Bandelin, equipped with a 6 mm glass probe. The extract was filtered through a 0.45 μm filter and diluted in water. Before analysis by ICP/MS (Elan 9000 from PerkinElmer), internal standards (Be, Sc, In and Bi) were added to the diluted samples. Calibrant solutions and internal standards were purchased from Alfa Aesar. Blanks were processed in a similar way. All the aliquots were stored at 4 °C and analysed within 24 h in a Class 100 clean room. The argon (99.999%) used in the ICP/MS measurements was supplied by Praxair. The operating conditions used in the ICP/MS measurements are summarised in Table 1.

Accuracy of the method was checked by analysis of the NIST-1646a certified reference material (estuary sediment, National Institute of Standards and Technology) with satisfactory results.

3. Results and discussion

3.1. Concentrations found and possible origin of the elements

The whole concentration data set is available on request. It is summarised in Fig. 2 in the form of Box–Whisker plots.

Correlation analysis of all data was performed in order to find possible connections between element concentrations. Those connections could indicate a similar origin of certain elements in the estuary or the existence of interactions, synergistic or antagonistic, among elements, resulting in mutually changing concentrations in the sediment. The correlation matrix obtained is shown in Table 2. For clarity, statistically significant correlation coefficients at a 95% confidence level (r > 0.56) are presented in bold. Cd, As, Fe, Pb, Sn, V, Zn, and Cu are significantly and positively correlated all together, which reveals a common, and probably anthropogenic, origin of all of them in the estuary of the Nerbioi–Ibaizabal River. Chromium is also highly correlated with most of them. There are also clear connections between the concentration of Al and Mg in sediments. This is probably related to their common, natural and oceanic origin. Correlations have also been found between cobalt and nickel, as well as between chromium and nickel. Cobalt is frequently associated with nickel as impurity in electroplating industry. Chromium is also often used in metal coating activities, abundant in the area.

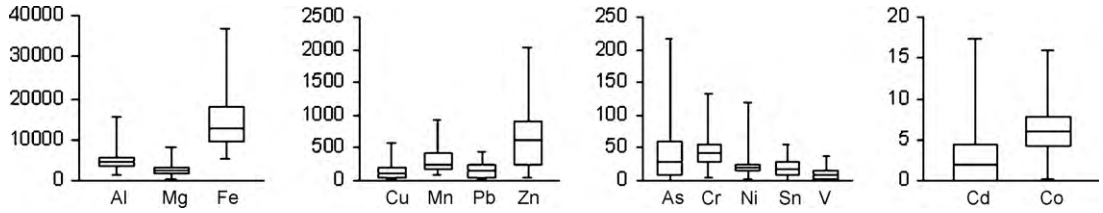

Fig. 2. Box–Whisker plots of the element concentrations (mg kg^{-1}) found in all the sediments considered in this work. The box shows the 25th percentile and the 75th percentile, and the whiskers represent the smallest and largest concentrations, while the line inside the box is the median of the population.

Manganese is the only element which shows no significant correlation with any other and, to our knowledge, it is not used in the surrounding industries [29].

3.2. Comparison with data reported for the estuary and other estuaries throughout the world: pollution level

Comparison with concentrations found in this work and those published previously for the area [9,11,15–26] is not easy due to differences in sampling points and methodology of analysis. The most comprehensive series in time is probably that reported by Leorri et al. [15], who report data on the concentration of As, Cr, Cu, Ni, Pb and Zn in sediments collected at 14 locations along the estuary in October 1997, 2000, 2003 and 2006. Additional information (concentrations of Al, Fe, Mn, S, Si and Ti, also in UD sampling point) is also available for the 1997 campaign of Cearreta et al. [20]. Six of their sampling points almost coincide with our locations in AZ, ZO, KA, AS, GA and AR. It should be noted that they measured the metal content of sediments by X-ray fluorescence spectroscopy, a non-destructive optical technique which provides the determination of the total concentration of elements, rather than only the acidic extractable fraction. Concentrations reported by Cearreta's group and some of those measured in this work are plotted in Fig. 3 for comparison.

As can be observed in Fig. 3, for most of the elements considered, our results fit fairly well with the long term falling trend described by Cearreta's data set, and concentrations found in October 2006 are of the same order. Cr constitutes the only clear exception to this rule, with concentrations significantly lower than those reported by Cearreta's group, probably due to a poor recovery of this metal during ultrasound assisted acid leaching of the sediments. The oldest available data [16] also confirm the higher metallic content of the sediments in the early 80s.

Comparison with the concentrations found in sediments of other estuaries provides a preliminary and relative estimation of the pollution level of the sediments in the Nerbioi–Ibaizabal River estuary. Table 3 summarizes the concentrations found in the bibliography for other similar environments. From the table it can be concluded that, in general, the metal content of sediments from the Nerbioi–Ibaizabal cannot be considered alarming in comparison with other estuaries. The maximum values found for Mn and Ni, however, are over those measured in the rest of estuaries considered, and values for As, Cu, Pb and Zn are only below the concentrations of the estuary of the Odiel-Tinto River, well known for its high metallic content due to the special geochemical characteristics of the lands it drains. For Cd, only one estuary (St. Lucie in Florida, USA) shows higher concentrations than the Nerbioi–Ibaizabal.

A better approach to the pollution level of the sediments in the Nerbioi–Ibaizabal River estuary may be to use the so-called geoaccumulation index (I_{geo}), which can be calculated by Eq. (1) [8].

$$I_{geo} = \log_2 \frac{c}{1.5 \cdot c_{bg}} \quad (1)$$

where c is the concentration of the metal in the sediment and c_{bg} is the estimated background value for the area. According to the geoaccumulation index sediments can be classified as non-polluted ($I_{geo} < 1$), very slightly polluted ($1 < I_{geo} < 2$), slightly polluted ($2 < I_{geo} < 3$), moderately polluted ($3 < I_{geo} < 4$), highly polluted ($4 < I_{geo} < 5$) and very highly polluted ($I_{geo} > 5$). The geoaccumulation indexes calculated for the sediments are summarized in Fig. 4 in the form of Box–Whiskers plot. The background values used have been estimated by Cearreta et al. [20], except for Cd which was estimated by Rodriguez et al. [46] because Cearreta does not give a reference for this metal. Cd exhibits the highest geoaccumulation indexes, with values even over 5 (all of them in 2005). The other problematic elements are Cu, Pb, Zn and, to a lesser extent, As, with quite a lot of sediments lying in the moderately polluted range and some of them close to or even within the highly polluted range (always sediments from UD, GO, GA or AS). For Mn and Ni, however, although the concentrations found in the Nerbioi–Ibaizabal are higher than those measured in other similar environments, the

Table 2
Correlation matrix obtained after analysis of the concentrations measured in all the sediments considered in this work. Figures in bold show correlation coefficients which are significant at a 95% confidence level ($r > 0.56$).

	Al	As	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sn	V	Zn
Al	**1.00**													
As	0.07	**1.00**												
Cd	−0.01	**0.60**	**1.00**											
Co	0.32	0.24	0.21	**1.00**										
Cr	0.14	0.52	0.55	0.46	**1.00**									
Cu	0.00	**0.66**	**0.70**	0.15	0.38	**1.00**								
Fe	0.12	**0.68**	0.54	0.28	**0.56**	**0.71**	**1.00**							
Mg	**0.66**	0.24	0.20	0.25	0.16	0.22	0.33	**1.00**						
Mn	0.34	−0.04	0.13	0.24	0.13	0.27	0.47	0.40	**1.00**					
Ni	0.11	0.05	0.13	**0.58**	**0.57**	0.12	0.35	0.03	0.28	**1.00**				
Pb	0.07	**0.76**	**0.83**	0.36	**0.64**	**0.74**	**0.73**	0.25	0.19	0.31	**1.00**			
Sn	0.14	**0.85**	**0.60**	0.39	**0.69**	**0.73**	**0.83**	0.33	0.22	0.37	**0.82**	**1.00**		
V	0.24	**0.91**	**0.58**	0.37	0.47	**0.69**	**0.66**	0.42	0.10	0.02	**0.70**	**0.82**	**1.00**	
Zn	0.12	**0.64**	**0.74**	0.31	0.53	**0.65**	**0.61**	0.34	0.21	0.23	**0.79**	**0.70**	**0.60**	**1.00**

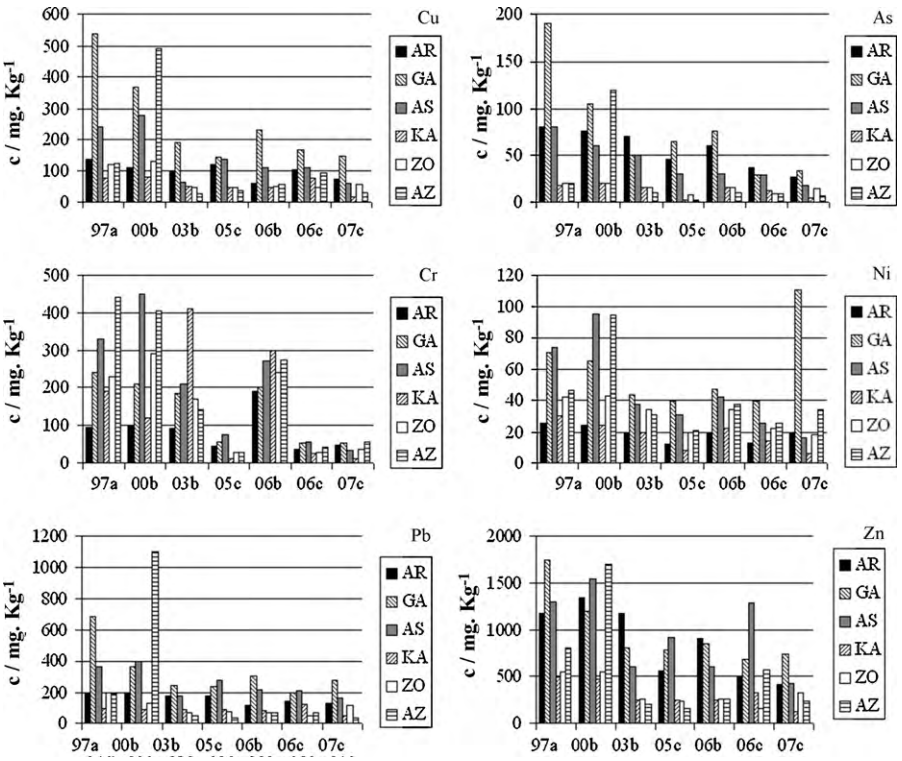

Fig. 3. Concentration of elements (mg kg^{-1}) found in sediments from different sampling locations of the estuary of the Nerbioi–Ibaizabal River collected in October (different years). (a) [20]; (b) [15]; (c) this work.

geoaccumulation indexes give no cause for concern, due to the relatively high background values estimated for the area. It is to be highlighted that, although still indicating slight pollution, geoaccumulation indexes that increase over time (reaching values of 1.80) have been calculated for Ni in sediments from GA. Again, the high background values reported for Fe result in negative geoaccumulation indexes. A poor recovery in the extraction process during the analysis of the sediments (corroborated when comparing our data with that of Leorri et al., Fig. 3) could be responsible for the low indexes calculated for Cr as well.

3.3. Toxicity assessment

The sediment quality guide (SQG) most widely used to assess the toxicity of sediments is probably that proposed by Long et al. [47]. This approach is based on the relation between measured concentrations of chemicals and observed biological effects, such as mortality, growth or reproduction of living organisms. Effects range low (ERL) are defined as concentrations below which effects are expected to be rare, and effects range medium (ERM) as concentrations above which effects are expected to be frequent. Details on how these criteria have been estimated can be found elsewhere [48]. ERL and ERM values have been proposed, among other pollutants, for As (8.2/70), Cd (1.2/9.6), Cr (81/370), Cu (34/270), Ni (20.9/51.6), Pb (46.7/218) and Zn (150/410), all of them in mg kg^{-1}. ERM's and ERL's have not been reported for Al, Mg, Fe Mn, Sn, V and Co because, in general terms, they are not considered toxic. The ERM value for Zn is exceeded in sediments from AR, GO, UD, GA and AS in most of the sampling campaigns considered here. Only a few sediments collected in AZ and KA are below the ERL concen-

Table 3
Concentration of several elements (mg kg^{-1}) found in sediments collected in different estuaries of the world.

Estuary	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Ref.
Krka (Croatia)	–	–	0.75	11	16	–	232	5.7	11	10	[30]
St Lucie (Florida)	–	5–23	7.8–29	5.2–91	3.1–72	–	–	13–55	2.8–23	3.4–127	[31]
Vigo (Spain)	–	–	–	33	26	23,500	–	23	57	96	[32]
Medway (UK)	14	–	–	76	42	30,282	315	28	67	138	[33]
Mersey (UK)	–	–	5.7	36	40	–	–	–	65	242	[34]
Hudson (New York)	–	–	–	–	78	34,000	–	–	81	182	[35]
Pearl River (China)	–	–	7.4–24	34–135	6.2–100	–	–	11–54	16–93.3	55–268	[36]
Severn (UK)	–	0.05–0.9	–	43–80	24–46	–	–	19–27	50–68	148–237	[37]
Tagus (Portugal)	–	1.7–5.9	–	–	28–89	–	–	–	65–200	–	[38]
Ulla (Spain)	–	–	14–16	191–438	96–135	30,900–42,100	495–521	69–91	57–58	134–190	[39]
Thames (UK)	15	–	–	36	24	21,711	328	21	63	115	[40]
Marabasco (Mexico)		0.05–0.3	6–95	–	0.7–31	–	–	9–26	2–18	53–179	[41]
Pontevedra (Spain)	–	–	–	30–280	6–227	–	–	3–21	37–144	38–243	[42]
Odiel-Tinto (Spain)	278	–	–	66	1051	–	-	30	523	1574	[43]
Ennore Creek (India)	–	0.5	6.95	49	22	2023	226	18	32	97	[44]
Tamaki (New Zeeland)		0.11–1.0	–	–	21–47	–	–	–	51–122	138–272	[45]
Nerbioi–Ibaizabal (Basque Country)	0.6–220	0.01 –17	0.3–16	5.0–134	15–571	5230–36,715	66–935	3.4–120	21–445	41–1260	This study

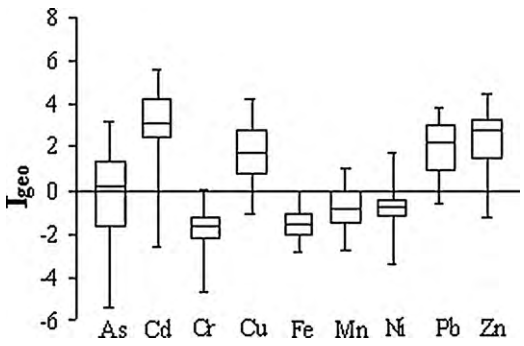

Fig. 4. Box–Whisker plots of the geoaccumulation indexes calculated for the sediments considered in this work. The box shows the 25th percentile and the 75th percentile, and the whiskers represent the smallest and largest indexes, while the line inside the box is the median of the population.

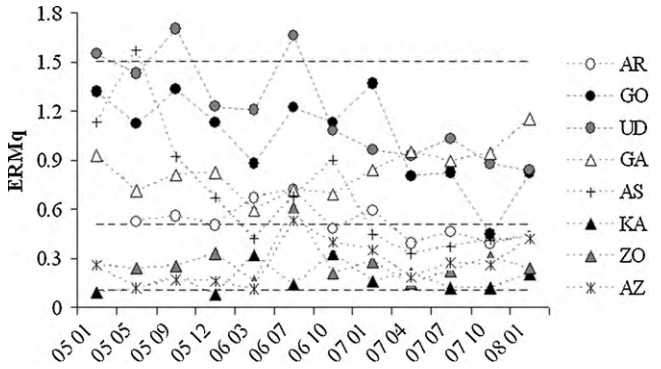

Fig. 5. ERMq values calculated for the sediments considered in this work. ERMq < 0.1, non-toxic; 0.1 < ERMq < 0.5, slightly toxic; 0.5 < ERMq < 1.5, moderately toxic; ERMq > 1.5, highly toxic.

tration. The estimated background value for the area is well below the ERL, e.g., 63 mg kg^{-1} [20]. Lead (estimated background value, 21 mg kg^{-1}) also shows concentrations which frequently exceed the ERM value calculated for this trace element, specially in GO and UD and, to a lesser extent, in AS and GA. Concentrations for Pb in KA, ZO and AZ are generally below or close to the ERL value. Ni concentrations above the ERM value were only found in sediments collected in GA in five of the sampling campaigns. In addition, Ni concentration seems to have increased over time in this location. It should be noted, however, that the estimated background value for Ni in the area (23 mg kg^{-1}) is close to, but above, the ERL concentration defined for this element. The concentrations found for Cr are nearly always below the ERL value. In this case, surprisingly, the estimated background is quite high (85 mg kg^{-1}). For Cd, only in the first three campaigns were concentrations above the ERM value obtained at the AS location, together with a couple of samples from GO and another one from UD. Finally, Cu (background, 20 mg kg^{-1}) and As exhibit similar behaviour, with concentrations systematically over the ERM value in GO and UD locations. In the case of As, its background value (16 mg kg^{-1}) is also well over the ERL concentration.

In an attempt to assign each sediment with a unique factor describing its overall toxicity concerning metals and As, ERM quotients (ERLq's) have also been calculated as the average of each of the ratios between the concentration measured for an element and its corresponding ERM value [49]. ERMq factors allow us to easily compare with other areas or different historical episodes, facilitate decision maker's work in sediment quality assessment, and have frequently been used in these kinds of works [15,50]. They can be used to describe the sediment as non-toxic (ERMq < 0.1), slightly toxic (0.1 < ERMq < 0.5), moderately toxic (0.5 < ERMq < 1.5) and highly toxic (ERMq > 1.5). The ERMq values calculated are summarized in Table 4, and their trend over time is shown in Fig. 5. As observed, only four sediments are catalogued as highly toxic, three of them collected in UD and one in AS, all of them before summer 2006. The rest of the sediments, nearly in the same proportion, are catalogued as slightly toxic (those of KA, ZO and AZ) and moderately toxic (those of GO, UD and GA). Only a couple of sediments could be considered as non-toxic, both of them coming from KA. The case of AS is to be highlighted, with ERMq values well over 0.5 until autumn 2006 and clearly lower from then on, a fact that undoubtedly indicates a recovery of the location in terms of metal pollution over the period of the survey. ERMq values for GO and UD also show a significant decrease over time, while GA exhibits the opposite trend (Fig. 5), probably due to the presence of a large wastewater plant in the area.

3.4. Time distribution

Fig. 6 shows the trends over time of the concentrations (overall, minimum and maximum among sampling points) of the different elements considered in this work. As observed, concentrations of Al, Co, Mg, Ni and V increase over time and those of As, Cd, Cu, Pb, Sn and Zn exhibit the opposite behaviour. The situation of Cr, Fe and Mg is not so clear. This suggests that the estuary sediments have undergone an overall recovery over the period studied regarding the most toxic elements, except Ni.

In a further study, the Mann–Kendall test [51] was applied to each element at each sampling point, in order to get further information on the spatial and time distribution of the metals. The Mann–Kendall test detects, with a given confidence level, falling or rising trends in time series with at least four sampling campaigns, and it has already been used when dealing with metals and sediments [52]. Calculations were made by means of the Excel template MAKESENS (freely available from http://projects.dnmi.no/~emep/assessment/MAKESENS_1_0.xls). The results obtained are summarized in Table 5. The most outstanding feature of the results is that for AZ, ZO and KA, any significant trend detected (Al, As, Co, Cr, Mg and V) is positive, that is, a trend rising over time, whereas any trend exhibited (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn) by the rest of the sampling points, e.g., AS, UD, GO and AR, is always negative. This suggests

Table 4
ERMq values calculated for the sediments considered in this work. ERMq < 0.1, non toxic; 0.1 < ERMq < 0.5, slightly toxic; 0.5 < ERMq < 1.5, moderately toxic; ERMq > 1.5, highly toxic. NC: not calculated. In bold underlined, sediments cataloged as highly toxic; in bold, sediments cataloged as moderately toxic.

	05 01	05 05	05 09	05 12	06 03	06 07	06 10	07 01	07 04	07 07	07 10	08 01
AR	NC	**0.52**	**0.56**	**0.50**	**0.67**	**0.72**	0.48	**0.59**	0.39	0.46	0.39	0.43
GO	**1.32**	**1.12**	**1.33**	**1.13**	**0.88**	**1.22**	**1.13**	**1.37**	**0.80**	**0.82**	0.45	**0.82**
UD	**1.55**	**1.43**	**1.70**	**1.23**	**1.21**	**1.66**	**1.08**	**0.96**	**0.93**	**1.03**	**0.88**	**0.84**
GA	**0.93**	**0.71**	**0.81**	**0.82**	**0.59**	**0.72**	**0.69**	**0.84**	**0.95**	**0.89**	**0.94**	**1.15**
AS	**1.13**	**1.57**	**0.92**	**0.67**	0.42	**0.68**	**0.90**	0.45	0.33	0.37	0.41	0.42
KA	0.09	0.11	0.19	0.08	0.32	0.14	0.33	0.16	0.21	0.12	0.12	0.20
ZO	0.26	0.24	0.25	0.33	0.16	**0.61**	0.21	0.28	0.15	0.22	0.31	0.24
AZ	0.26	0.12	0.17	0.16	0.11	**0.53**	0.40	0.35	0.18	0.27	0.26	0.42

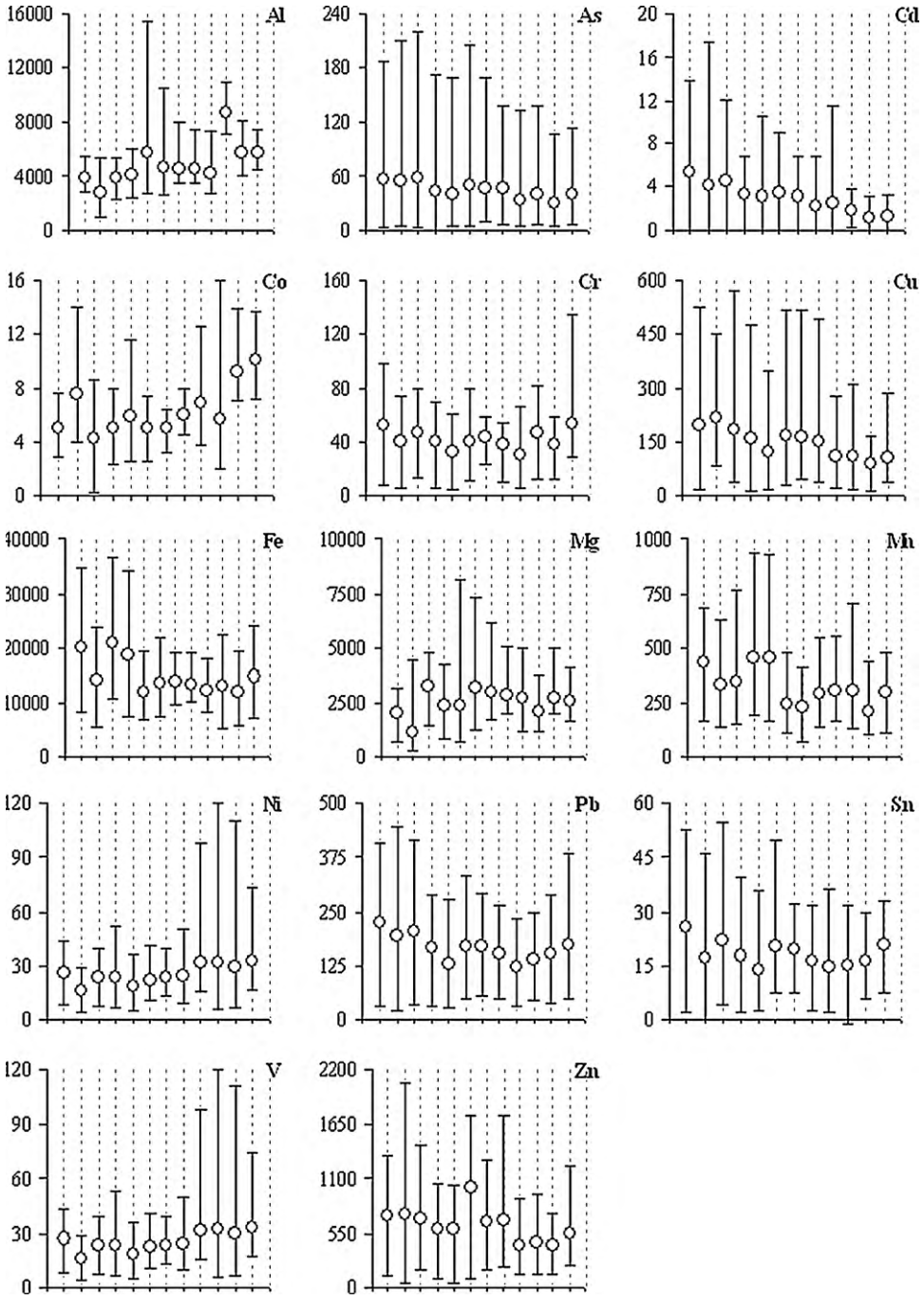

Fig. 6. Average (white circle), minimum and maximum (whiskers) concentrations (mg kg^{-1}) measured in each sampling campaign, in the next order starting from the left side of the *X* axis: January 05, May 05, September 05, December 05, March 06, July 06, October 06, January 07, April 07, July 07, October 07 and January 08.

that the most heavily polluted sediments could be acting as a metal pollution source, with highly toxic elements redissolving into the water layer and later being expelled from the estuary into the ocean. Sediments with an overall lower metal content act as receivers of elements of natural origin, such as Al and Mg, and maybe also others like Cr and V, all of which converge in a general process of metal redistribution and homogenization throughout the estuary. The exception to this rule is GA, with significant increases in only Co and Ni concentrations. This fact suggests a possible malfunctioning, regarding Ni and Co, of the wastewater treatment plant (WWTP) located on the banks of the Galindo tributary, about 200 m upstream from our GA sampling point. The potential problems related to the presence of the WWTP have been already reported [15]. These observations are in good agreement with the trends observed in the ERMq values (Fig. 5).

The frequency of the sampling campaigns (every three months) has enabled us to search for seasonal trends in the time series. In the sampling points with higher metal content no significant trend has been observed. In locations with concentrations close to the estimated background values, data suggests the possibility of seasonal trends for some elements, with higher concentrations at the end of summer time and lower ones in winter. The time series, however, are not long enough to make a firm conclusion about the significance of that trend and, in addition, its existence is not systematic for all the elements considered. This issue undoubtedly calls for further investigation if consistent conclusions are to be obtained.

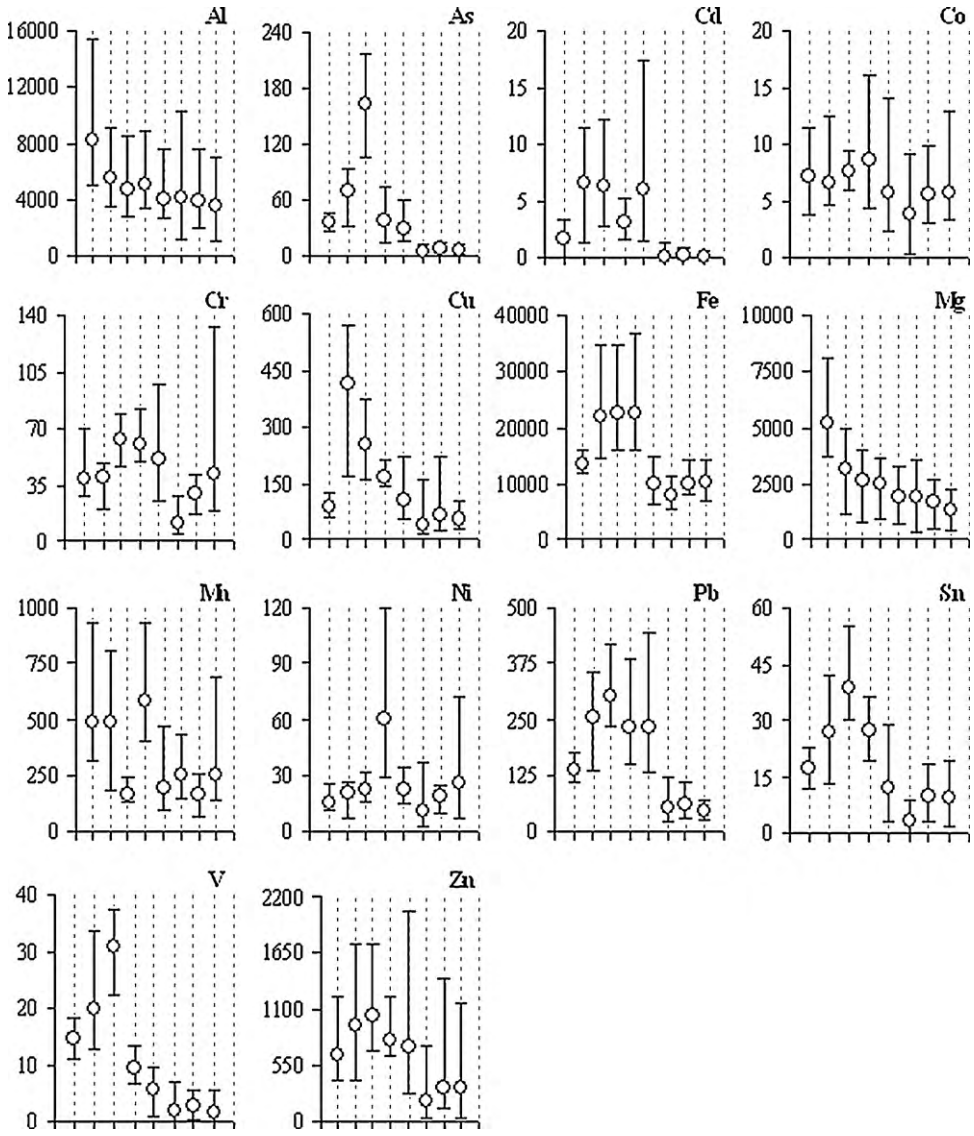

Fig. 7. Average (white circle), minimum and maximum (whiskers) concentrations (mg kg^{-1}) measured in each sampling point, in the next order starting from the left side of the *X* axis: AR, GO, UD, AS, GA, KA, ZO and AZ.

Table 5
Results of the Mann–Kendall test applied to check the evolution with time of each element concentration at each sampling point. 95, 99 and 99.9 figures indicate, respectively, positive (+) or negative (−) trends identified at a 95, 99 or 99.9% significance level.

	AZ	ZO	KA	AS	GA	UD	GO	AR
Al	+99	+95	+99	+95				
As			+95	−99.9		−99.9	−95	−95
Cd				−99		−99.9		−95
Co		+95			+99			
Cr	+95			−95		−99		
Cu				−95		−99.9	−95	
Fe				−99		−99		
Mg	+95							
Mn				−95				−99
Ni				−99	+95		−90	
Pb				−99		−95	−95	
Sn						−99	−95	
V	+95					−95		
Zn						−95	−95	

3.5. Spatial distribution

Fig. 7 shows the average, minimum and maximum concentrations of each metal at each sampling point. The spatial distribution of Al and Mg is similar, with the highest values close to the sea and ever lower values the more upstream the sampling point is, a fact that confirms the oceanic, and probably natural, origin of both elements. As and V also show similar trends regarding their spatial distribution in the estuary. The most problematic location for those two elements is clearly UD, whilst AR, GO, AS and GA have intermediate concentrations and KA, ZO and AZ significantly lower concentrations. The high correlation coefficients found for Al–Mg and As–V (Table 2) are in good agreement with the observed trends. It is also to be highlighted that similar profiles have been detected for Cd, Pb and Zn. Chromium could also be included in this group, but the similarities among sampling points are not so marked. The profile of Cu differs slightly, because it exhibits notably higher concentrations in GO, which confirms this tributary river as the most probable input of this metal into the system. Sn and Fe show similar distribution to Cd, Pb and Zn. The distribution of Ni and Co in the estuary is quite homogeneous, with the exception of AS, where the highest concentrations of Ni have been measured. The input of

this element into the estuary is clearly related to the Asua tributary River. Finally Mn, compared to the rest of elements, exhibits a different spatial distribution, which is in good agreement with the lack of significant correlations with other metals previously found (Table 2).

4. Conclusions

In general terms, the Nerbioi–Ibaizabal River estuary's current situation regarding metal pollution in sediments cannot be described as alarming. It is true, however, that, especially in the case of some very toxic elements, such as As, Cd, Cu, Pb and Zn, there are still some locations with relatively high concentration values, sometimes one hundred times higher than the estimated background values for the area. This is especially true for locations such as UD, GO, GA and AS (in the first sampling campaigns), which form the "high metal content" group. These concentrations, however, do not seem to be high enough to become a toxicological risk, as the calculated ERM values confirm. In contrast we have identified other points with a low metal content, KA in the most important tributary river on the West bank of the estuary, and ZO and AZ, both of them in the main channel and the upmost part of the estuary. The characteristics of AR are clearly different, probably due to the influence of the ocean on this location.

In addition, observations derived from sediments quality guides (SQGs) based on ecotoxicological essays, tell us that, nowadays, only sediments from UD, GO and GA can still be defined as moderately toxic, while the rest fall into in the slightly toxic category. This includes AS, which has undergone a rapid recovery in the quality of its sediments, probably related to the presence of a wastewater collector which started operating in the area in 2005. This collector (which conducts sewage water from industries located on the banks of the Asua River to the wastewater treatment plant at Galindo), together with a possible deficient operation of the WWTP, should also explain the increase in Ni and Co concentration detected in sediments from the GA sampling point.

For several elements, specific paths of entry into the estuary have been identified (As, Cu and V seem to flow down the Gobela River and Ni down the Asua River, for instance), which calls for special action in these areas.

Nevertheless, taking into account the general trends shown over time by metal concentrations in most of the locations considered, it can be said that steps taken within the framework of the Plan for the Integral Recovery of the Bilbao Estuary, which started in 1984 and have recently finished [12], have resulted in a slow but continuous reduction in metal content of the sediments. On the other hand, the possibility that sediments from the most polluted locations are currently acting as a pollution source in the estuary themselves should not be ruled out, as has already been pointed out elsewhere [15]. What it is not so clear is whether metals resulting from this source are actually being expelled from the estuary or simply redistributed all over the estuary, thereby forcing a slight but constant improvement in metal content of sediments from the less polluted locations.

Finally, data obtained during this three year period from the "low metal content" locations, e.g., KA, ZO and AZ, suggests that when concentrations are close to those of the background values a seasonal trend may be happening, with higher concentrations in summer and lower concentrations in winter. This fact, however, requires further investigation and should be studied in the future.

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References

[1] H.S. Chon, D.G. Ohandja, N. Voulvoulis, Implementation of U.E. water framework directive: source assessment of metallic substances at catchment levels, J. Environ. Monitor. 12 (2010) 36–47.
[2] V.G. Caccia, F.J. Millero, A. Palanques, The distribution of trace metals in Florida Bay sediments, Mar. Pollut. Bull. 46 (2003) 1420–1433.
[3] G.F. Birch, S.E. Taylor, C. Matthai, Small-scale spatial and temporal variance in the concentration of heavy metals in aquatic sediments: a review and some new concepts, Environ. Pollut. 113 (2001) 357–372.
[4] Directive 200/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, OJEC L 327 (2000), 1–72.
[5] A. Borja, H. Heinrich, Implementing the European Water Framework Directive: the debate continues . . ., Mar. Pollut. Bull. 50 (2005) 486–488.
[6] T.A. DelValls, A. Andres, M.J. Belzunce, J.L. Buceta, M.C. Casado-Martinez, R. Castro, I. Riba, J.R. Viguri, J. Blasco, Chemical and ecotoxicological guidelines for managing disposal of gredged material, Trends Anal. Chem. 23 (2004) 819–828.
[7] S.A. Sinex, G.R. Helz, Regional geochemistry of trace elements in Chesapeake Bay sediments, Environ. Geol. 3 (1981) 315–323.
[8] F. Ruiz, Trace metals in estuarine sediments from the southwestern Spanish coast, Mar. Pollut. 42 (2001) 482–490.
[9] M.J. Belzunce, O. Solaun, J. Franco, V. Valencia, A. Borja, Accumulation of organic matter, heavy metals and organic compounds in surface sediments along the Nervión Estuary (Northern Spain), Mar. Pollut. Bull. 42 (2001) 1407–1411.
[10] J.M. García-Barcina, M. Oteiza, A. de la Sota, Modelling the faecal coliform concentration in the Bilbao estuary, Hidrobiology 475 (2002) 213–219.
[11] J.I. Saiz-Salinas, Evaluation of adverse biological effects induced by pollution in the Bilbao estuary (Spain), Environ. Pollut. 96 (1997) 351–359.
[12] P.M. Barreiro, J.J. Aguirre, 25 años del plan integral de saneamiento de la ría de Bilbao, Dyna (2005) 25–30.
[13] J.M. García-Barcina, J.A. González-Oreja, A. de la Sota, Assessing the improvement of the Bilbao estuary water quality in response to pollution abatement measures, Water Res. 40 (2006) 951–960.
[14] S. Fernández, U. Villanueva, A. de Diego, G. Arana, J.M. Madariaga, Monitoring trace elements (Al, As, Cr, Cu, Fe, Mn, Ni and Zn) in deep and surface waters of the estuary of the Nerbioi–Ibaizabal River (Bay of Biscay, Basque Country), J. Mar. Syst. 72 (2008) 332–341.
[15] E. Leorri, A. Cearreta, M.J. Irabien, I. Yusta, Geochemical and microfaunal proxies to assess environmental quality conditions during the recovery process of a heavily polluted estuary: the Bilbao estuary case (N. Spain), Sci. Total Environ. 396 (2008) 12–27.
[16] I. Seebold, C. Labarta, J.M. Amigó, Heavy metals in the sediments of the Bilbao estuary, Pergamon Ser. Environ. Sci. 7 (1982) 459–463.
[17] J.I. Saiz-Salinas, G. Francés-Zubillaga, Nereis diversicolor: an unreliable biomonitor of metal contamination in the "Ria de Bilbao" (Spain), Mar. Ecol. 18 (1997) 113–125.
[18] J.I. Saiz-Salinas, Evaluation of adverse biological effects induced by pollution in the Bibao estuary (Spain), Environ. Pollut. 96 (1997) 351–359.
[19] J.M. Ruiz, J.I. Saiz-Salinas, Extreme variation in the concentration of trace metals in sediments and bivalves from the Bilbao estuary (Spain) caused by the 1989–90 drought, Mar. Environ. Res. 49 (2000) 307–317.
[20] A. Cearreta, M.J. Irabien, E. Leorri, I. Yusta, I.W. Croudace, A.B. Cundy, Recent anthropogenic impacts on the Bilbao estuary, Northern Spain: geochemical and microfaunal evidence, Estuar. Coast. Shelf Sci. 50 (2000) 571–592.
[21] A. Cearreta, M.J. Irabien, E. Leorri, I. Yusta, A. Quintanilla, A. Zabaleta, Environmental transformation of the Bilbao estuary, N. Spain: microfaunal and geochemical proxies in the recent sedimentary record, Mar. Pollut. Bull. 44 (2002) 487–503.
[22] A. Landajo, G. Arana, A. de Diego, N. Etxebarria, O. Zuloaga, D. Amouroux, Analysis of heavy metal distribution in superficial estuarine sediments (estuary of Bilbao, Basque Country) by open-focused microwave-assisted extraction and ICP-OES, Chemosphere 56 (2004) 1033–1041.
[23] J.S. Landaluze, A. de Diego, J.C. Raposo, J.M. Madariaga, Methylmercury determination in sediments and fish tissues from the Nerbioi–Ibaizabal estuary (Basque Country, Spain), Anal. Chim. Acta 508 (2004) 107–117.
[24] L. Bartolomé, I. Tueros, E. Cortazar, J.C. Raposo, J. Sanz, O. Zuloaga, A. de Diego, N. Etxebarria, L.A. Fernández, J.M. Madariaga, Distribution of trace organic contaminants and total Mercury in sediments from the Bilbao and Urdaibai Estuaries (Bay of Biscay), Mar. Pollut. Bull. 52 (2006) 1111–1117.
[25] M.L. Martínez-Díaz, J. Blasco, D. Sales, T.A. DelValls, Biomarkers study for sediment quality assessment in Spanish ports using the crab *Carcinus maenas* and the clam *Ruditapes philippinarum*, Arch. Environ. Contam. Toxicol. 53 (2007) 66–76.
[26] J. Moros, S. Fdez-Ortiz de Vallejuelo, A. Gredilla, A. de Diego, J.M. Madariaga, S. Garrigues, M. de la Guardia, Use of reflectance infrared spectroscopy for monitoring the metal content of the estuarine sediments of the Nerbioi–Ibaizabal River (Metropolitan Bilbao, Bay of Biscay, Basque Country), Environ. Sci. Technol. 43 (2009) 9314–9320.
[27] A. Uriarte, M. Collins, A. Cearreta, J. Bald, G. Evans, Sediment supply transport and deposition: contemporary and late quaternary evolution, in: Oceanogra-

phy and Marine Environment of the Basque Country, Elsevier, Amsterdam, 2004, pp. 97–131.
[28] S. Fdez-Ortiz de Vallejuelo, A. Barrena, G. Arana, A. de Diego, J.M. Madariaga, Ultrasound energy focused in a glass probe: an approach to the simultaneous and fast extraction of trace elements from sediments, Talanta 80 (2009) 434–439.
[29] S. Fdez-Ortiz de Vallejuelo, Diagnóstico, evolución y predicción de la concentración metálica en el estuario del río Nerbioi–Ibaizabal, PhD Thesis, University of the Basque Country, 2008.
[30] E. Prohic, G. Kniewald, Heavy metal distribution in recent sediments of the Krka River Estuary—an example of sequential extraction analysis, Mar. Chem. 22 (1987) 279–297.
[31] M. Zhang, Z. He, P. Stoffella, D. Calvert, X. Yang, P. Sime, Concentrations and solubility of heavy metals in muck sediments from the St. Lucie Estuary, U.S.A., Environ. Geol. 44 (2003) 1–7.
[32] B. Rubio, M.A. Nombela, F. Vilas, Geochemistry of major and trace elements in sediments of the Ria de Vigo (NW Spain): an assessment of metal pollution, Mar. Pollut. Bull. 40 (2000) 968–980.
[33] K.L. Spencer, Spatial variability of metals in the inter-tidal sediments of the Medway Estuary, Kent, UK, Mar. Pollut. Bull. 44 (2002) 933–944.
[34] B.J. Harland, D. Taylor, A. Wither, The distribution of mercury and other trace metals in the sediments of the Mersey Estuary over 25 years 1974–1998, Sci. Total Environ. 253 (2000) 45–62.
[35] H. Feng, J. Kirk Cochran, H. Lwiza, B.J. Brownawell, D.J. Hirschberg, Distribution of heavy metal and PCB contaminants in the sediments of an urban estuary: the Hudson River, Mar. Environ. Res. 45 (1998) 69–88.
[36] I. Carman, L. Xiang-Dong, Z. Gan, W. Onyx, L. Yok-Sheung, Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China, Environ. Pollut. 147 (2007) 311–323.
[37] S. Duquesne, L.C. Newton, L. Giusti, S.B. Marriott, H.J. Stärk, D.J. Bird, Evidence for declining levels of heavy-metals in the Severn Estuary and Bristol Channel U.K. and their spatial distribution in sediments, Environ. Pollut. 143 (2006) 187–196.
[38] S. França, C. Vinagre, I. Caçador, H.N. Cabral, Heavy metal concentrations in sediment, benthic invertebrates and fish in three salt marsh areas subjected to different pollution loads in the Tagus Estuary (Portugal), Mar. Pollut. Bull. 50 (2005) 998–1003.
[39] R. Prego, A. Cobelo-García, Twentieth century overview of heavy metals in the Galician Rias (NW Iberian Peninsula), Environ. Pollut. 121 (2003) 425–452.
[40] M.J. Attrill, R.M. Thomes, Heavy metal concentrations in sediment from the Thames Estuary, UK, Mar. Pollut. Bull. 30 (1995) 742–744.
[41] A.J. Marmolejo-Rodriguez, R. Prego, A. Meyer-Willerer, E. Shumilin, A. Cobelo-Garcia, Total and labile metals in surface sediments of the tropical river-estuary system of Marabasco (Pacific coast of Mexico): Influence of an iron mine, Mar. Pollut. Bull. 55 (2007) 459–468.
[42] N. Fernández, J. Bellas, J. Lorenzo, R. Beiras, Complementary Approaches to Assess the Environmental Quality of Estuarine Sediments, Water Air Soil Pollut. 189 (2008) 163–177.
[43] J. González-Pérez, J. de Andrés, L. Clemente, J. Martín, F. González-Vila, Organic carbon and environmental quality of riverine and off-shore sediments from the Gulf of Cádiz, Spain, Environ. Chem. Lett. 6 (2008) 41–46.
[44] M. Jayaprakash, M.P. Jonathan, S. Srinivasalu, S. Muthuraj, V. Ram-Mohan, N. Rajeshwara-Rao, Acid-leachable trace metals in sediments from an industrialized region (Ennore Creek) of Chennai City, SE coast of India: an approach towards regular monitoring, Estuarine Coast. Shelf Sci. 76 (2008) 692–703.
[45] G. Abrahim, R. Parker, Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand, Environ. Monit. Assess. 136 (2008) 227–238.
[46] J.G. Rodriguez, I. Tueros, A. Borja, M.J. Belzunce, J. Franco, O. Solaun, V. Valencia, A. Zuazo, Maximum likelihood mixture estimation to determine metal background values in estuarine and coastal sediments within the European Water Framework Directive, Sci. Total Environ. 370 (2006) 278–293.
[47] E. Long, D. Macdonald, S. Smith, F. Calder, Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments, Environ. Manage. 19 (1995) 81–97.
[48] E.R. Long, L.G. Morgan, The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program, National Oceanic and Atmospheric Administration (NOAA), Technical Memorandum NOS OMA 62, 1990.
[49] E.R. Long, L.J. Field, D.D. McDonald, Predicting toxicity in marine sediments with numerical sediment quality quidelines, Environ. Toxicol. Chem. 17 (1998) 714–727.
[50] M. Álvarez-Guerra, J.R. Viguri, M.C. Casado-Martínez, T.A. DelValls, Sediment quality assessment and dredged material management in Spain: Part I, Application of sediment quality guidelines in the Bay of Santander, Integr. Environ. Assess. Manage. 3 (2007) 529–538.
[51] D. Helsel, R. Hirsch, Statistical Methods in Water Resources: Studies in Environmental Science, Elsevier, New York, 1992, pp. 323–355.
[52] F.M. Conly, R.W. Crosley, J.V. Headley, E.K. Quagraine, Assessment of metal in bed and suspended sediments in tributaries of the Lower Athabasca River, J. Environ. Sci. Health 42 (2007) 1021–1028.