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Baseline

Geographical distribution of metals and metalloids along the estuary of the Oka River in the biosphere reserve of Urdaibai, Spain

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ABSTRACT

Sediments sampled at the estuary of the Oka River in the biosphere reserve of Urdaibai, Spain were analyzed for trace elements. Sediments were collected at 45 points of the estuary and the concentration of 14 elements was measured. The geoaccumulation indexes (I_{geo}), Normalized Average Weighted Concentrations (NAWC) and mean Effect Range-Median quotients (mERMq) were calculated. The results obtained were complementary and allowed intra- and inter-estuary comparison. According to the present findings, the estuary was classified as healthy, since the anthropogenic contribution of metals and metalloids was generally small. However, shipping and fishing activities at the ports of Bermeo and Mundaka and urban and industrial wastes from Gernika were regarded as the major pollution sources. Nevertheless, only slightly contaminated and toxic sediments, especially related to Ni and Cu, were found in the towns of Gernika and Mundaka.

The estuary of the Oka River is in the Basque Country, in the north of the Iberian Peninsula, northern Spain. The territory of this river, which flows into the Bay of Biscay, is one of the most important natural areas of the Basque Country, where we can find many animal species and many ecosystems. Owing to its biodiversity and unique ecological conditions, UNESCO designated the natural area of Urdaibai *Biosphere Natural Reserve* in 1984. Consequently, it can be supposed that the environment under study is, in general, a clean area. However, there are some potential contamination sources, such as the waste coming from the urban activity, and the agriculture and animal husbandry that take place in the area and ends up in the estuary, which should not be overlooked. Tourism is also important in this region and is becoming another important contamination source, especially in the summer (Rodriguez-Iruretagoiena et al., 2016). The impact coming from the ports of Mundaka or Bermeo, which are located in the mouth of the estuary, must also be taken into account.

Among the different contaminants, metals are one of the groups having the greatest risk to cause adverse effects in aquatic environments (Kim and Hong, 2023). The pollutant nature of metals, their long survival and bioaccumulation, can determine the ecosystem health of an estuary. Above a certain concentration level, these elements in question are very dangerous for living beings and can even become a risk for human health. In the Water Framework Directive of the European Union (WFD, 2000) some metals are included in the list of priority substances. Moreover, Cd, Hg, Pb and Ni are classified as preference substances in the Directive 2013/19/EU of the European Parliament and of the Council of 12 August 2013 in the field of water policy (EU, 2013).

This work assessed the contamination level in the estuary of the Oka River regarding metals and metalloids. Many variables have an effect on the natural cycle of metals and metalloids in estuaries, including water pH, salinity, redox potential, the amount of dissolved oxygen and the presence of organic binders (van Ryssen et al., 1999). Furthermore, different biochemical processes can modify the fate and bioavailability of metals and metalloids on these transitional areas.

Once in the estuary, most metals and metalloids accumulate in sediments in a more conservative way than in water (Dekov et al., 1998; Franco et al., 2002). Metals are usually found in solid state in sediments. The concentration of metals and metalloids accumulated on this matrix depends on the physico-chemical and hydrodynamic conditions of the estuary. In fact, owing to different biochemical processes, metals previously accumulated in the sediments can pass to the water phase and become a second source of contamination along the estuary (Kennish, 1998). For all these reasons, sediments have often been used to investigate the history of chemical contamination in aquatic environments

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(Zwolsman et al., 1996).

The source of the Oka River is at the foot of the Oiz Mountain, in Bizkaia, Spain (Fig. 1), right at the junction of the nearby mountain streams. The river basin irrigates a land area of 149 km^2 (Irabien and Velasco, 1999) and is 25 km long until it reaches the Cantabrian Sea. On average, the Oka River has a depth of 3 m, running between not very populated towns and reaching its maximum depth of 4 m at 1.5 km from the sea (Raposo et al., 2009). The volume of the sea tide is greater than

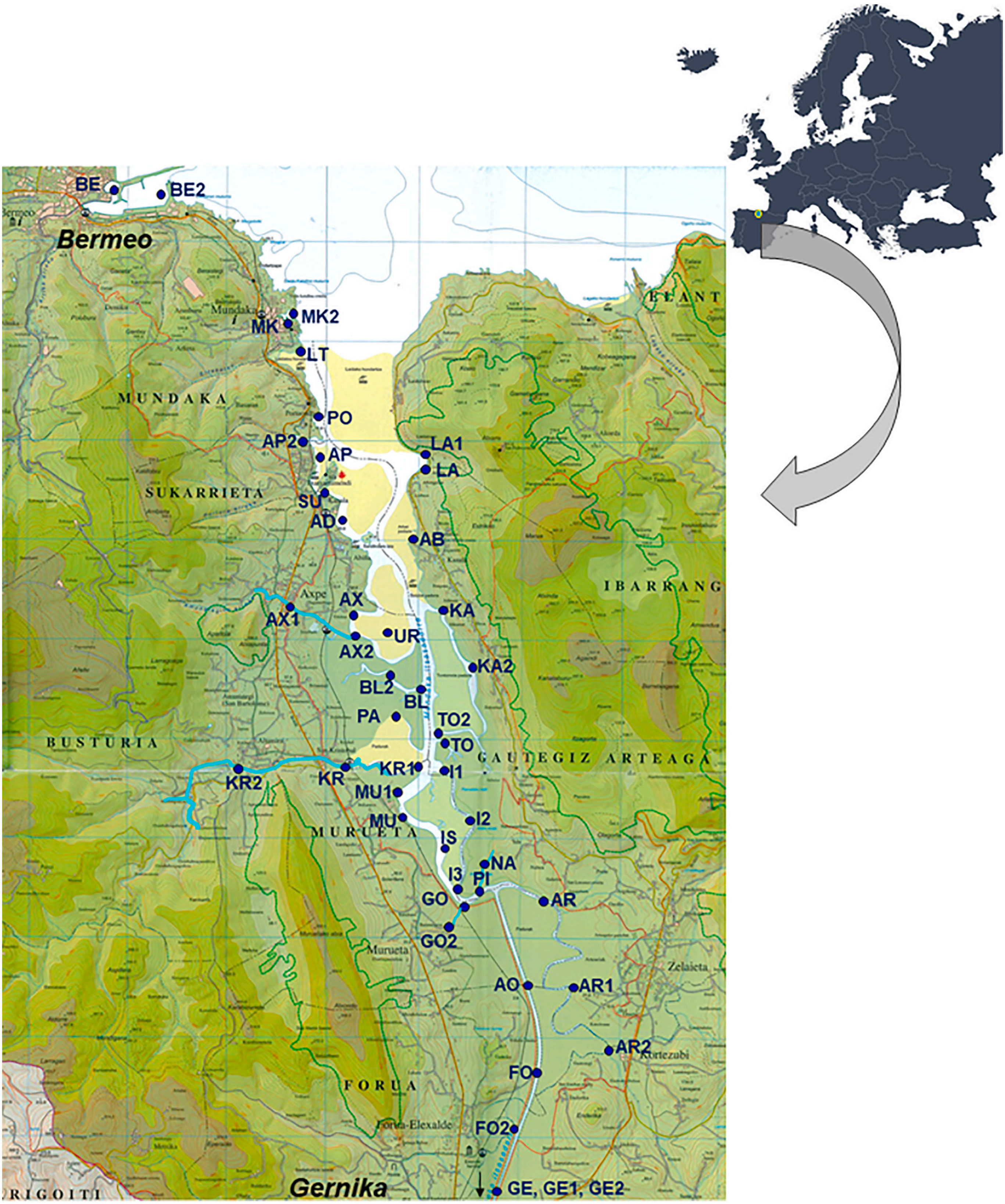

Fig. 1. Geographical location of the Urdaibai Biosphere Natural Reserve and the 45 sampling points in this study.

the volume of the river, and when saltwater and fresh water meet in the estuary, they form a homogeneous mixture.

The population living around the Oka River is 45,000. It is mostly surrounded by small towns and the most populated one is Gernika, with 17,000 residents (Raposo et al., 2009), where there is an ongoing industrial activity. In summer, there is a significant increase in traffic due to the beaches of Laida (on the right bank) and Sukarrieta (on the left bank), which receive visitors from all over the Basque Country. In the estuary, various recreational sports and activities are carried out, such as sailing and sport fishing. There are two ports along the estuary; the port of Bermeo (17,000 inhabitants) has a great inshore fishing activity and Mundaka (2,000 inhabitants) has a port that accommodates medium-sized fishing boats. The main channel of the estuary has been slightly modified with an artificial channel along the first 5 km after the town of Gernika.

In the estuary of the Oka River, metal and metalloid concentrations have been measured in other studies (Irabien and Velasco, 1999; Soto et al., 2003; Bartolomé et al., 2006). However, this type of research is not very often found in the bibliography. Different studies have been carried out analyzing sediments, fish and mollusks and the harmful effects that these toxics can have on organisms. The evolution of metals and metalloids over time has also been analyzed using oysters and sediments collected in the natural reserve (Raposo et al., 2009; Rodriguez-Iruretagoiena et al., 2016). The lithogenic or anthropogenic origin of heavy metals in sediments has also been investigated (Irabien and Velasco, 1999).

The aim of this work was to analyze the concentration of metals and metalloids in the sediments collected in the course of the Oka River in order to determine the geographical distribution of the contamination and assess the potential toxicological risk of the sediments. For this purpose, forty-five sites were strategically selected along the estuary in order to carry out a representative sampling in the studied area (Fig. 1).

Surface sediments (0–2 cm) were collected in January of 2011 using latex gloves from riverbanks at low tide. A boat and a stainless van Veen dredge (capacity: 2 L; sampling area: 260 cm^2; weight: 10.42 kg; dimensions: 55 cm × 30 cm × 15 cm) were used for the collection of samples sited in the main channel. In all the cases, samples were transported to the laboratory in plastic bags at 4 °C to reduce the microbiological activity. Before analysis, the sediments were frozen at −20 °C and lyophilised at 150 mTorr and −52 °C in a Cryodos apparatus (Telslar, Spain) for 48 h. The dry samples were sieved and the fraction <63 μm was retained for analysis. After placing about 0.5 g of dry sediment in an extraction vessel and adding 20 mL HNO_3/HCl 3:1 (Tracepur, Meck) acid mixture, focused ultrasonic energy (HD2070 Sonopulus Ultrasonic Homogenizer, Bandelín) was applied for 6 min. The extracts were passed through a 0.45 μm filter and diluted in water down to a concentration of 1 % HNO_3. Finally the concentration of Al, As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sn, V and Zn was measured in the samples by inductively coupled plasma mass spectrometry (ICP/MS) (Perkin-Elmer, NexION 300). The analysis were carried out inside a 100 Class clean room. The external calibration method with internal correction was used. Standard solutions of the analytes and the internal standards (^{45}Sc, ^{115}In, ^{209}Bi, ^{9}Be and ^{74}Ge) were obtained from Alfa Aesar (SpecpureR, Plasma standard solution, Karlsruhe, Germany). The calibrants were prepared in 1 % subboiled HNO_3. The detection limits and reproducibility estimated for each element are summarized in Table 1. More details about the analytical procedure and quality assurance and quality control (QA/QC) procedures can be found elsewhere (Fdez-Ortiz de Vallejuelo et al., 2009).

The average concentrations and the maximum and minimum values obtained in the sediments of the Oka river estuary are summarized in Table 1. The highest concentrations obtained along the course of the river were those of Fe, Mg and Al, probably because of their lithogenic origin. The sediments of the Oka River are the result of the erosion of the surrounding sedimentary rocks (Irabien and Velasco, 1999). In fact, high concentrations of Fe, Mn, Cr, Ni and Co were measured in the volcanic rocks studied around Gernika (Rossy, 1988).

On the other hand, in the case of Ni, Cr, Cu and Zn, for example, the maximum values deviated significantly from the average value. This may be an indicator of marginal or extreme points, meaning that there was significantly more Ni, Cr, Cu and Zn in the sediments collected at some sampling points than in most of the others. Regarding the rest of the elements, the differences between the average and the maximum or minimum values was not so obvious, but since the identification of these outlying data was important for the analysis, the distribution of the concentrations corresponding to each element was represented in Box-Whisker type graphs (Fig. 2). These graphs allowed the identification of the outlier concentration values collected in Table 1.

The identified high outlier values (mg kg^{-1}) for each element were as follows: Al (3.23 × 10^3, 3.24 × 10^3, 2.87 × 10^3), Cd (0.212, 0.210), Co (8.18), Cr (90.0, 34.6, 33.1, 31.0), Cu (82.1, 50.1, 36.3, 34.8, 33.3), Fe (1.30 × 10^4, 1.27 × 10^4, 1.09 × 10^4, 1.07 × 10^4), Mn (618), Ni (105, 36.2, 23.8), Pb (50.0), Sn (3.08, 2.86, 2.66) and Zn (154, 118, 116). As depicted in Fig. S1, these representative points appeared to be related to activities of the towns located in the estuary. In fact, the areas associated with the most populated areas showed the highest metal presence. In Bermeo, high concentrations of Al, Cu, Fe and Zn were measured near the dock (BE2) and in the dam of the seaport (BE). Even in the first, high values of Cd and Sn were obtained, which might be the result of accumulation of such metals caused by the coming and going of ships over the years (Ruiz et al., 1996). High concentrations of Cr and Ni were measured near Gernika (GE and GE2 sampling sites) and at the beginning (FO2) and end (I3, PI) of the artificial channel located in the highest part of the estuary. In this area, some industrial activities that use galvanizing processes are carried out. The reason for the high Co and Mn concentrations measured at point AX1 was not easily explained. It could be the result of the degradation of volcanic rocks of basaltic origin (Rossy, 1988; Irabien and Velasco, 1999). Sediments with excessively high Fe concentrations may have a lithogenic origin. In all the analyzed sediments, the concentration level of Fe was higher than the levels obtained for the other metals. However, apart from lithogenic origin, the potential impact of the anthropogenic contribution must be taken into

Table 1
Values corresponding to the maximum (max.), minimum (min), average (in mg·kg^{-1}) and the 25th and 75th percentiles of the concentrations obtained in the sediments collected at 45 sampling points in the estuary of the Oka River. The procedural Limit of detection (LOD, mg kg^{-1}), the relative standard deviation (RSD, n = 5) and the number of high and low outliers corresponding to each element are indicated.

	Al	As	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sn	V	Zn
LOD	0.8	0.4	0.1	0.1	0.7	0.1	0.2	0.9	0.6	0.3	0.2	0.1	0.1	1
RSD (%)	3	5	4	2	4	1	4	0.5	2	2	2	5	2	2
Min.	911	0.200	0.0500	3.13	4.50	5.56	4.39 × 10^3	814	29.5	4.72	14.3	0.0500	0.0500	32.7
Q_{25}	1.51 × 10^3	2.23	0.0500	3.67	15.4	11.9	5.98 × 10^3	2.08 × 10^3	88.8	8.28	18.8	1.11	8.23	50.8
Average	1.80 × 10^3	4.43	0.0571	4.41	19.3	18.1	7.16 × 10^3	2.63 × 10^3	156	13.5	24.1	1.35	10.6	4.43
Q_{75}	1.95 × 10^3	6.51	0.0500	5.08	21.6	17.9	7.76 × 10^3	3.26 × 10^3	202	14.0	28.1	1.68	13.6	69.1
Max.	3.24 × 10^3	9.47	0.212	8.18	90.0	82.1	1.30 × 10^4	4.78 × 10^3	618	105	50.0	3.08	19.8	154
High outliers	3	0	2	1	4	4	4	0	1	3	1	3	0	3
Low outliers	0	0	0	0	2	0	0	0	0	0	0	1	2	0

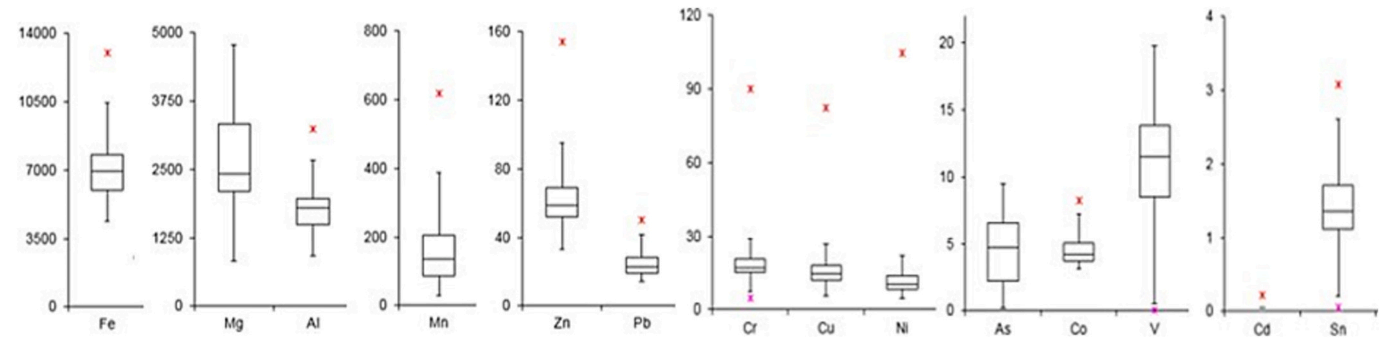

Fig. 2. Distribution of the concentrations of the different elements measured in the sediments (mg kg^{-1}) in Box-Whisker graph format. The box shows the 25th and 75th percentiles, the middle line the 50th percentile, and the stars the presence of high outlier data (purple star) or low outlier data (red star). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

account to explain the high concentration found in some elements in the sediments under study.

To analyze the correlations between the concentrations of the 14 elements that were measured, a Pearson's correlation matrix was built with the data from the 45 sampling points and the results are shown in Table 2. The values with a Pearson's correlation coefficient greater than $r > 0.56$ were considered statistically significant at a 95 % of confidence level. Representative correlations were obtained between Al-Cd, Al-Fe, Co-Mn, Cr-Ni, Cu-Sn, Cu-Zn, Pb-Zn, Pb-V, V-Mg, V-As and Sn-Zn (Table 2).

The concentration values measured in the sediments at the 45 sampling points were also analyzed by Principal Component Analysis (PCA). Data were mean centered and scaled to unit standard deviation in the variables direction before analysis. Results showed that 77 % of the total data variance can be explained using four PCs (PC1: 30 %, PC2: 22 %, PC3: 15 %, PC4: 10 %). The obtained PC1-PC2 and PC4-PC3 score and loading plots are depicted in Fig. 3. Sampling points LT, SU, AP, MK2, BE and BE2, located closest to the sea, were distinguished from other sampling points along PC1, and such separation was related principally to higher levels of Al, Pb, Zn, Sn, Fe, Cd, Cu, V and Mg (Fig. 3a). KR2 was also separated from other sampling points along PC1, showing positive score values for Cr and Ni. GE2, located at the upstream river source, was also separated from the other sampling points along PC2, and this was related to higher levels of Co, Cr, Ni and Mn (Fig. 3a). Similarly, sampling points BE2, AP and GE were distinguished from other sampling locations along PC3, and for BE2 and AP, this was related to higher levels of Fe, Cd, Al and Mg, whereas for GE, this was related to higher levels of Ni, Sn and Cr (Fig. 3b). The sampling sites AX1 and MK2 were also separated from other sampling points along PC4, and for AX1, this was related to higher levels of Co and Mn, whereas for MK2, this was related to a higher level of Cu (Fig. 3b).

In order to measure the magnitude of the anthropogenic contribution and, consequently, to estimate the contamination level of sediments, geoaccumulation indices were calculated. Geoaccumulation indices (I_{geos}), were calculated following Müller's (1981) equation for each sample and each element, as follows:

$$I_{geo} = log_2 \frac{c}{1.5\ c_{bg}}$$

where c is the concentration of each element measured on each sample, and c_{bg} is the concentration that can be considered natural for each element in the studied area. The I_{geo} can be used to estimate the magnitude of the anthropogenic contribution in the area under study. According to the scale established by Müller (1981) the following classification can be used according to the I_{geo} values obtained: the sediment is not contaminated (Igeo < 1), very slightly contaminated ($1 < I_{geo} < 2$), slightly contaminated ($2 < I_{geo} < 3$), contaminated ($3 < I_{geo} < 4$), significantly contaminated ($4 < I_{geo} < 5$) and highly contaminated (I_{geo}

Table 2
Correlation matrix. Correlations statistically significant (r > 0.56) are marked in grey.

	Al	*As*	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Mg*	*Mn*	*Ni*	*Pb*	*Sn*	*V*	*Zn*
Al	1.000													
As	-0.037	1.000												
Cd	0.684	-0.058	1.000											
Co	0.294	-0.148	0.023	1.000										
Cr	-0.095	-0.261	-0.101	-0.039	1.000									
Cu	0.090	-0.073	0.155	-0.017	0.301	1.000								
Fe	0.673	0.112	0.386	0.213	0.005	0.038	1.000							
Mg	0.454	0.262	0.357	-0.250	-0.258	-0.069	0.302	1.000						
Mn	0.291	-0.064	0.243	0.759	0.050	0.182	0.056	-0.112	1.000					
Ni	-0.021	-0.361	-0.021	0.163	0.912	0.394	-0.008	-0.289	0.275	1.000				
Pb	0.392	0.305	0.202	0.061	-0.296	0.514	0.099	0.397	0.203	-0.214	1.000			
Sn	0.421	-0.046	0.323	-0.042	0.374	0.588	0.325	0.313	0.017	0.358	0.511	1.000		
V	0.374	0.563	0.232	-0.342	-0.324	0.013	0.219	0.642	-0.279	-0.473	0.577	0.307	1.000	
Zn	0.493	-0.093	0.223	-0.001	-0.017	0.617	0.391	0.344	-0.033	0.051	0.730	0.745	0.336	1.000

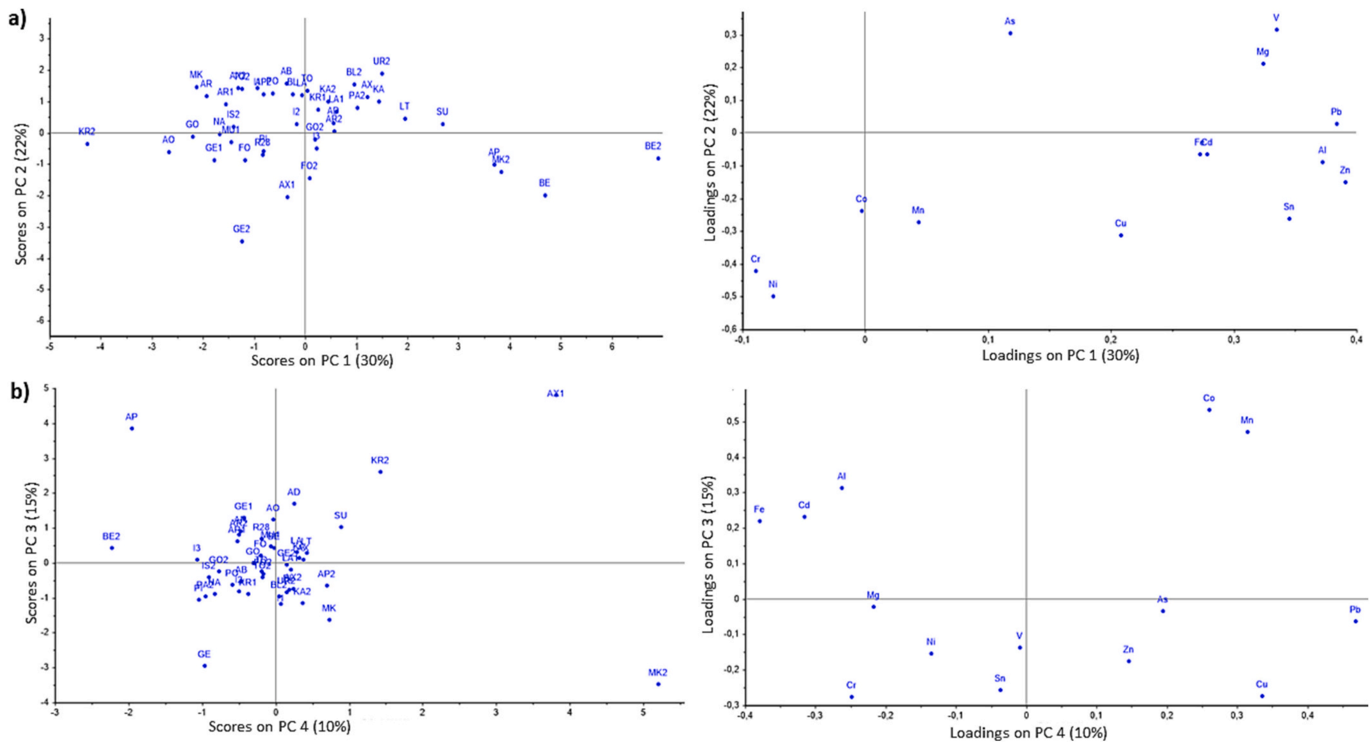

Fig. 3. Scores and loadings plots of PC1-PC2 (a) and PC4-PC3 (b) obtained by analyzing the metal concentrations measured at 45 sampling points in this study.

> 5).

The concentration values that can be considered natural around Urdaibai (c_{bg}) are those proposed by Cearreta et al. (2000), except in the case of Cd. In this case, the value estimated by Rodríguez et al. (2006) was used. The values used (in mg kg $^{-1}$) were as follows: As, 16.0; Cd, 0.24; Cr, 85.0; Cu, 20.0; Fe, 25,000; Mn, 300; Ni, 23.0; Pb, 21.0; and Zn, 63.0. For elements not mentioned, we did not find a c_{bg} value in the bibliography.

The geoaccumulation indices obtained indicated that the impact of the anthropogenic contribution in the Oka river estuary was small, because most of them were below 1 (the limit indicating the absence of contamination). Two very slightly contaminated points (1 < Igeo < 2) were found, one in Mundaka port (MK) for Cu and the other for Ni in Gernika (GE). Fig. 4 reflects the possible anthropogenic contribution of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. Looking at the Box-Whisker distribution (Fig. 4), it can be seen that the main part of the boxes and percentiles are below zero. The maximum values above zero are those of Cu (1.45), Mn (0.46), Ni (1.60), Pb (0.67) and Zn (0.71).

With the aim to identify the most significant sources of metals and metalloids, the NWAC (Normalized and Weighed Average Concentration) scores were calculated. For the calculation of NWACs, a score between 0 and 10 was given firstly to each sediment (sampling point)

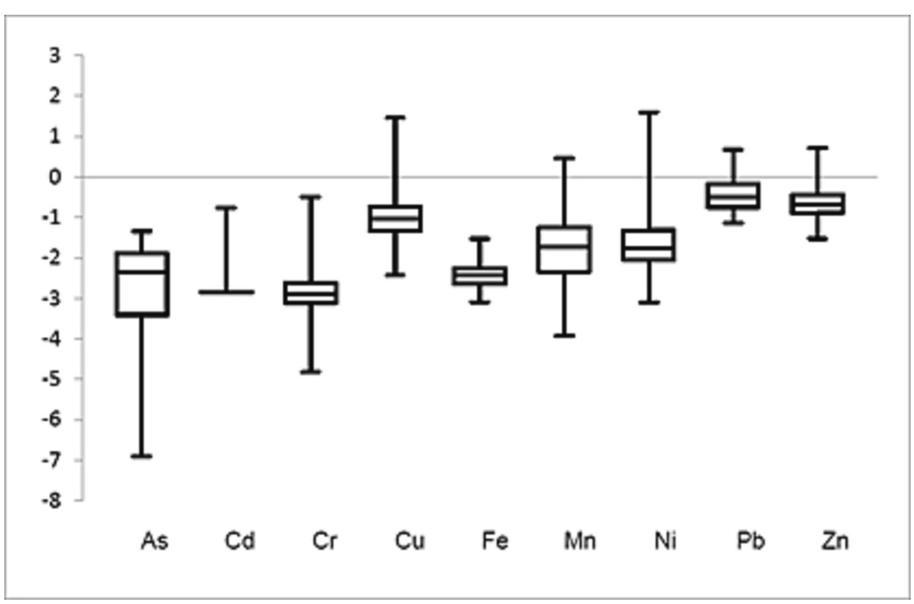

Fig. 4. Box-Whisker plots of calculated geoaccumulation indices in sediments for As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The box shows the 25th and 75th percentiles and the center line of the box shows the 50th percentile.

depending on the concentration of contaminants determined. If the concentrations were low, the score was close to zero and vice versa (Gredilla et al., 2014). However, this does not necessarily mean that a sediment with a low concentration of elements is not toxic and inversely. In this work, the concentrations of the 14 measured elements were used in the calculation of the NWAC scores (see Fig. S2). The two sampling points with the highest concentrations of metals and metalloids were BE2 (NWAC score 10.00) and AP (NWAC score 9.76). Among all the sampling points, only AP and BE2 showed Cd concentrations above the detection limit. The sampling point AP is located in Sukarrieta and contained high concentrations of Al, Fe and Cd. The sampling point BE2, on the other hand, is located in the dock of the port of Bermeo, with the highest concentrations of all metals and metalloids. In particular, the concentrations of Al, Cd, Cu, Fe, Mg, Sn, V and Zn recorded at BE2 were the highest with respect to the average concentrations obtained for these elements along the estuary. While high concentrations of Cr, Cu, Ni and Sn were recorded at the sampling point GE, located downstream of the town Gernika, its NWAC score assigned was only 2.0 (Fig. S2). Such a lower score was due to the concentrations of As, Cd and V being below the limit of detection. From Fig. S2, sampling points with the lowest NWAC scores included KR2 (0.00), AO (1.3), NA (2.3), MK (1.6), GO (2.5) and IS (2.9). With the exception of KR2 and MK, these sampling points are located in the central part of the estuary, whereas KR2 is located in Busturia, at the upstream of a tributary river joining the estuary, and MK in the port of Mundaka.

Sediment Quality Guidelines (SQGs), which express the relation between chemicals available in the sediment and the adverse effects they cause on benthic communities, were further used to classify the sampling points. As the SQGs refer to individual pollutants, the use of mean Sediment Quality Guidelines quotients (mSQGqs) has been proposed to account simultaneously for the combined effect of different pollutants present in the sediment (Garmendia et al., 2019). The mSQGqs have been broadly used in different parts of the world (Apitz et al., 2007; Chen et al., 2007; Stuart and Graeme, 2007; Balthis et al., 2009), and are calculated by dividing the pollutant concentration measured in sediment by its respective SQG to obtain the corresponding SQGq. Based on the number of pollutants under study, these individual SQGs are summed and divided by the number of pollutants considered. Under the concept of SQGs, the effects range-median (ERM) has been the most widely used to calculate the corresponding mERMq of sediments (Long et al., 1995; Jeffrey et al., 1999; Hyland et al., 2003; Fulton et al., 2006; Long, 2006; Alvarez-Guerra et al., 2009). The ERMs represent mid-range concentrations of chemicals above which adverse effects on a wide variety of benthic organisms are likely to occur (MacDonald et al., 1996). ERM values have been reported for only 7 of the 14 elements considered in this work (As, Cd, Cr, Cu, Pb, Ni and Zn). The other elements are considered to be non-toxic, or toxic only at extremely high concentrations. Based on the analyses of matching chemical and toxicity data from over 1000 sediment samples from the USA estuaries (Long et al., 2000), the mERMq of <0.1 have a 9 % probability of being toxic, the mERMq of 0.11–0.5 have a 21 % probability of being toxic, the mERMq of 0.51–1.5 have a 49 % probability of being toxic, and the mERMq of >1.50 have a 76 % probability of being toxic (Gredilla et al., 2013).

According to the mERMq values obtained (Fig. 5), only sediments coming from 15 of the 45 sampling points showed a probability of being slightly toxic (mERMq = 0.1–0.5), suggesting that the impact of anthropogenic activities were relatively small in the study area. The highest mERMq value were observed at GE (0.39), followed by GE2 and MK (0.17).

The information obtained by NWAC and mERMq was found to complementary. According to the NWAC scores, the highest metal presence was found at sampling points BE2, AP, GE, MK, BE and SU. However, regarding mERMq values, FO2, AR2, LT, KA, AP and I3 should also be considered toxicologically relevant.

This study provided information on the environmental conditions around the Oka river estuary located in the Urbaibai Biosphere Natural Reserve in Spain. In general, the estuary of the Oka River can be divided into four areas according to the level of metal contamination: i) the town of Gernika, ii) the artificial channel, iii) the area from Murueta (MU) to Sukarrieta (SU) and, iv) the lower left end of the estuary. Significantly, high concentrations of Ni and Cr were measured around the town of Gernika, possibly as the result of the town's industrial activities (Irabien and Velasco, 1999). Similar situation occurred in the main channel, with high concentrations of Ni and Cr being measured at the beginning and end of the artificial channel possibly due to accumulation of such elements there. In the area that goes from Murueta to Sukarriera, the area where the majority of sampling points were located, no significant sources of metal pollution was found. The last mentioned area (the lower left end of the estuary) was the area with the most significant pollution, including the sampling points of Sukarrieta (SU), Mundaka (MK and MK2) and Bermeo (BE and BE2) with high concentrations of Cu, Pb, Sn and Zn. Sukarrieta, Mundaka and Bermeo are the towns that showed the highest anthropogenic activities in the estuary and the shipping and transport movements associated with the local ports may be responsible for such high metal concentrations found.

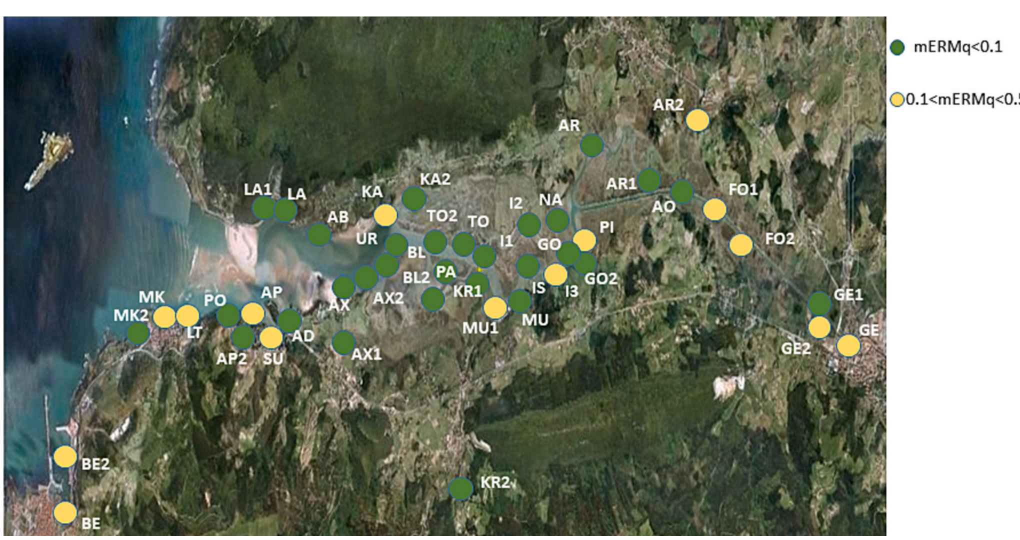

Fig. 5. Geographical distribution of sampling points according to mERMq values. Points between 0.1 and 0.5 have been designated and marked in yellow. Sites with mERMq $<$ 0.1 are shown in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In summary, the estuary was generally found to be healthy, and the high concentrations observed for various metal elements were related to lithogenic origin, except for the impact of human activities at specific towns that caused relatively higher concentrations of various toxic elements. However, further studies should be focused on the potential pollution from Ni and Pb, as these elements are included in the list of priority substances within the European Water framework Directive (WFD, 2000).

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CRediT authorship contribution statement

X. Alberdi Igartua: Investigation, Formal analysis. **A. Rodriguez-Iruretagoiena:** Methodology, Investigation, Data curation. **A. Gredilla:** Writing – review & editing, Writing – original draft, Investigation, Conceptualization. **S. Fdez-Ortiz de Vallejuelo:** Validation, Supervision, Software. **G. Arana:** Writing – review & editing, Visualization, Project administration. **A. de Diego:** Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **J.M. Madariaga:** Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

Alvarez-Guerra, M., Viguri, J.R., Casado-Martinez, M.C., DelValls, T.A., 2009. Sediment quality assessment and dredged material management in Spain: part I, application of sediment quality guidelines in the bay of Santander. Integr. Environ. Aseess. Manag. 3, 529–538.

Apitz, S., Barbanti, A., Giulio Bernstein, A., Bocci, M., Delaney, E., Montobbio, L., 2007. The assessment of sediment screening risk in Venice Lagoon and other coastal areas using international sediment quality guidelines. J. Soils Sediments 7, 326–341.

Balthis, W., Hyland, J., Fulton, M., Pennington, P., Cooksey, C., Key, P., DeLorenzo, M., Wirth, E., 2009. Effects of chemically spiked sediments on estuarine benthic communities: a controlled mesocosm study. Environ. Monit. Assess. 161, 191–203.

Bartolomé, L., Tueros, I., Cortazar, E., Raposo, J., Sanz-Landaluze, J., Zuloaga, O., de Diego, A., Etxebarria, N., Fernández, L., Madariaga, J.M., 2006. Distribution of trace organic contaminants and total mercury in sediments from the Bilbao and Urdaibai Estuaries (Bay of Biscay). Mar. Pollut. Bull. 52, 1111–1117.

Cearreta, A., Irabien, M.J., Leorri, E., Yusta, I., Croudace, I.W., Cundy, A.B., 2000. Recent anthropogenic impacts on the Bilbao estuary, northern Spain: geochemical and microfaunal evidence. Estuar. Coast. Shelf Sci. 50, 571–592.

Chen, Y.-Z., Yang, H., Zhang, Z.-K., Qin, M.-Z., Jin, F., LÜ, J.-J., 2007. Application of equilibrium partitioning approach to the derivation of sediment quality guidelines for metals in Dianchi lake. Pedosphere 17, 284–294.

Dekov, V.M., Araujo, F., van Grieken, R., Subramanian, V., 1998. Chemical composition of sediments and suspended matter from the Cauvery and Brahmaputra rivers (India). Sci. Total Environ. 212 (2–3), 89–105.

EU, 2013. Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 on Priority Substances in the Field of Water Policy.

Fdez-Ortiz de Vallejuelo, S., Barrena, A., Arana, G., de Diego, A., Madariaga, J.M., 2009. Ultrasound energy focused in a glass probe: an approach to the simultaneous and fast extraction of trace elements from sediments. Talanta 80 (2), 434–439.

Franco, J., Borja, A., Solaun, O., Perez, V., 2002. Heavy metals in mollucs from the Basque Coast (Nothern Spain): results from an 11-year monitoring programme. Mar. Pollut. Bull. 44 (9), 973–976.

Fulton, M., Key, P., Wirth, E., Leight, A., Daugomah, J., Bearden, D., Sivertsen, S., Scott, G., 2006. An evaluation of contaminated estuarine sites using sediment quality guidelines and ecological assessment methodologies. Ecotoxicology 15, 573–581.

Garmendia, M., Fdez-Ortiz de Vallejuelo, S., Liñero, O., Gredilla, A., Arana, G., Soto, M., de Diego, A., 2019. Long term monitoring of metal pollution in sediments as a tool to investigate the effects of engineering works in estuaries. A case study, the Nerbioi-Ibaizabal estuary (Bilbao, Basque Country). Mar. Pollut. Bull. 145, 555–563.

Gredilla, A., Fdez-Ortiz de Vallejuelo, S., Arana, G., de Diego, A., Madariaga, J.M., 2013. Long-term monitoring of metal pollution in sediments from the estuary of the Nerbioi-Ibaizabal River (2005–2010). Estuar. Coast. Shelf Sci. 131, 129–139.

Gredilla, A., Fdez-Ortiz de Vallejuelo, S., de Diego, A., Arana, G., Madariaga, J.M., 2014. A new index to sort estuarine sediments according to their contaminant content. Ecol. Indic. 45, 364–370.

Hyland, J.L., Balthis, W.L., Engle, V.D., Long, E.R., Paul, J.F., Summers, J.K., Van Dolah, R.F., 2003. Incidence of stress in benthic communities along the U.S. Atlantic and Gulf of Mexico Coasts within different ranges of sediment contamination from chemical mixtures. Environ. Monit. Assess. 81, 149–161.

Irabien, M.J., Velasco, F., 1999. Heavy metals in Oka river sediments (Urdaibai National Biosphere Reserve, nothern Spain): lithogenic and anthropogenic effects. Environ. Geol. 37, 54–63.

Jeffrey, L.H., Robert, F.V.D., Timothy, R.S., 1999. Predicting stress in benthic communities of southeastern U.S. estuaries in relation to chemical contamination of sediments. Environ. Toxicol. Chem. 18, 2557–2564.

Kennish, M.J., 1998. Trace metal-sediment dynamics in estuaries: pollution assesment. Rev. Environ. Contam. Toxicol. 155, 69–110.

Kim, H.G., Hong, S., 2023. Influence of land cover, point source pollution, and granularity on the distribution of metals, metalloids, and organic matter in the river and stream sediments in the Republic of Korea. Environ. Sci. Pollut. Res. 30, 65129–65140.

Long, E.R., 2006. Calculation and uses of mean sediment quality guideline quotients: a critical review. Environ. Sci. Technol. 40, 1726–1736.

Long, E.R., MacDonald, S.L., Smith, F.D., 1995. Calder, incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manag. 19, 81–97.

Long, E.R., MacDonald, D.D., Severn, G.C., Hong, C.B., 2000. Classifying probabilities of acute toxicity in marine sediments with empirically derived sediment quality guidelines. Environ. Toxicol. Chem. 19, 2598–2601.

MacDonald, D.D., Carr, R.S., Clader, F.D., Long, E.R., Ingersoll, C.G., 1996. Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology 5 (4), 253–278.

Müller, G., 1981. The heavy metal pollution of the sediments of Neckars and its tributary: a stocktaking. Chem. Zeit. 105, 157–164.

Raposo, J.C., Bartolomé, L., Arana, G., Zabaljauregui, M., de Diego, A., Zuloaga, O., Madariaga, J.M., Etxeberria, N., 2009. Trace metals in oysters, Crassotrea sps., from UNESCO protected natural reserve of Urdaibai: space-time observations and source identification. Bull. Environ. Contam. Toxicol. 83, 223–229.

Rodríguez, J.G., Tueros, I., Borja, A., Belzunce, M.J., Franco, J., Solaun, O., Valencia, V., Zuazo, A., 2006. Maximum likelihood mixture estimation to determine metal background values in estuarine and coastal sediments within the European Water Framework Directive. Sci. Total Environ. 370, 278–293.

Rodriguez-Iruretagoiena, A., Rementeria, A., Zaldibar, B., Fdez-Ortiz de Vallejuelo, S., Gredilla, A., Arana, G., de Diego, A., 2016. Is there a direct relationship between stress biomarkers in oysters and the amount of metals in the sediments where they inhabit? Mar. Pollut. Bull. 111, 95–105.

Rossy, M., 1988. Contribution à l'étude du magmatisme mesoique du omain pyreneen (Ph D Thesis).. Univ. Franche, Comte.

Ruiz, J.M., Bachelet, G., Caumette, P., Donard, O.F.X., 1996. Three decades of Tributyltin in the coastal environment with emphasis on Arcachon Bay, France. Environ. Pollut. 93, 195–203.

Soto, J., Soto, J.A., Corral, D., Gelen, A., Diaz, O., Navas, A., 2003. Heavy metal pollution evolution in sediments from Urdaibai Bay (Spain). In: Proceedings of Fourth International Symposium on Nuclear and Related Techniques NURT 2003 VIII Workshop on Nuclear Physics WONP 2003. Cubaenergia, Cuba (pp. CD-ROM).

Stuart, L.S., Graeme, E.B., 2007. Predicting metal toxicity in sediments: a critique of current approaches. Integr. Environ. Assess. Manag. 3, 18–31.

van Ryssen, R., Leermakers, M., Baeyens, W., 1999. The mobilisation potential of trace metals in aquatic sediments as a tool for sediment quality classification. Environ. Sci. 2 (1), 75–86.

WFD, 2000. Directive of the European Parliament and of the Council 2000/60/EC Establishing a Framework for Community Action in the Field of Water Policy. European Commission Environment, Luxembourg.

Zwolsman, J.J.G., van EcK, G.T.M., Burger, G., 1996. Spatial and temporal distribution of trace metals in sediments from the Scheldt Estuary, south-west Netherlands. Estuar. Coast. Shelf Sci. 43, 55–79.