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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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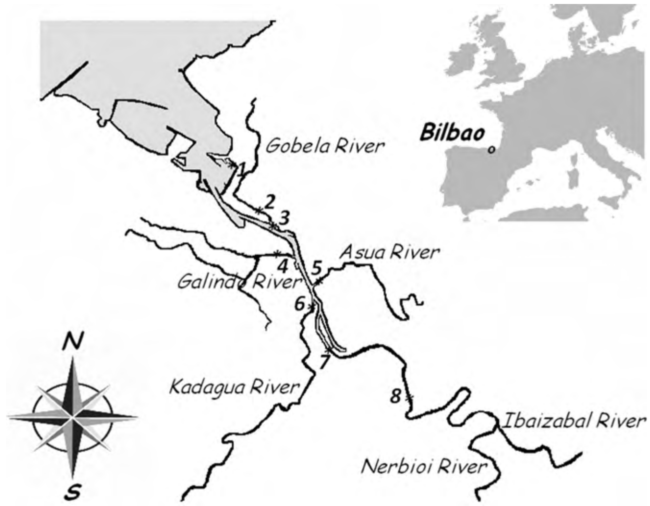

Fig. 1. Geographical location of the estuary of the Nerbioi–Ibaizabal River and the location of the sampling stations: 1. ARriluze, 2. GObela, 3. UDondo, 4. GAlindo, 5. ASua, 6. KAdagua, 7. ZOrrotza and 8. Alde Zaharra.

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 ($\kappa < 0.2\ \mu S\ cm^{-1}$, Millipore), and left in a 10% nitric acid (Panreac) bath for 24 h. Afterwards, it was thoroughly rinsed with Ellix and MilliQ water ($\kappa < 0.05\ \mu S\ cm^{-1}$, 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.