



Occurrence and geographical distribution of metals and metalloids in sediments of the Nerbioi-Ibaizabal estuary (Bilbao, Basque Country)



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ABSTRACT

Pollution in estuaries is an issue of high concern for scientists, local stakeholders and authorities. Sediments have been frequently used as sentinels of chemical pollution, including metals and metalloids. The estuary of the Nerbioi-Ibaizabal River was subjected to an important input of metals since the late XIXth century until about 1975. Afterwards, a significant decrease in chemical pollution has occurred due to a progressive closure of the most polluting activities and the pre-treatment of waste waters. However, a large scale civil engineering work, including a large movement of highly polluted sediments, has recently started in order to reduce the effects of floods and improve the urban image of the city. A precise description of the magnitude and geographical distribution of chemical pollution in the estuary nowadays would make feasible a future quantification of the effects derived from the above-mentioned work. With this aim, we collected sediments at about 50 sites in the inter-tidal part of the estuary in January 2009, 2010, 2011 and 2014, and the concentration of fourteen elements (Al, As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sn, V and Zn) in the acidic extract of the samples was simultaneously measured by ICP/MS. Afterwards, geoaccumulation indexes were calculated in order to estimate the metal fraction of anthropogenic origin. The Normalized and Weighed Average Concentrations (NWAC's) were also calculated to identify areas of higher concern. Finally, the mean Effect-Range-Median quotients (mERMq's) allowed us to estimate the toxicity associated to the sediments. The results show that: *i*) the geographical distribution of metals is rather heterogeneous within the estuary and changes from sampling campaign to sampling campaign, *ii*) hotspots of metal pollution are concentrated in a few points (the surroundings of the Gobela and Galindo tributary rivers and the closed dock of Deusto in 2009, 2010 and 2011, and the Abra Bay, the dock of Portu and the point where the effluent of the biggest waste water treatment plant of the area is released into the river in 2014), and *iii*) most of the sediments collected in those hotspots of pollution are highly toxic, mainly due to the presence of Pb, Cd, Zn, Cu and As of anthropogenic origin.

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1. Introduction

Estuaries are very sensitive areas susceptible to be affected by contamination inputs of different origin, such as industry, domestic sources, agriculture, traffic road run-offs, shipping and atmospheric deposition (Spencer, 2002). Pollutants can enter in the estuary from tributary rivers and direct discharges. The impact of anthropogenic perturbation is more important in estuaries which drain densely populated and industrialized areas.

Trace elements are important pollutants that threaten the equilibrium of estuaries due to their toxicity, long persistence and bioaccumulation (Chon et al., 2010; Kumar et al., 2008). In extreme situations, they may represent a serious risk for living organisms and even for human health (Farias et al., 2007). Some metals are included in the list of the

main pollutants of the Water Framework Directive (2000/60/EC, WFD) of the European Union; furthermore, Cd, Hg, Pb and Ni are classified as priority substances in the Directive 2013/39/EU.

The fate of metals and metalloids in estuaries depends on the pH, salinity, redox potential, dissolved oxygen and the concentration of organic chelators in the water column (Ahdy and Khaled, 2009; Del Valls et al., 2004). Furthermore, estuaries are very dynamic systems in which different biogeochemical processes can affect the fate and bioavailability of metals and metalloids. In water, they are frequently associated to organic matter and/or suspended particles (Alomary and Belhadj, 2007; Filgueiras et al., 2004; Moor et al., 2001). In sediments, metals appear more or less tightly associated to the solid phase, which determines their availability to biota and their tendency to get re-dissolved in water (Caccia Valentina et al., 2003). Under certain physico-chemical conditions, metals previously trapped in the sediments may be remobilised to the water phase and consequently act as a secondary source of contamination to the estuary (Kennish, 1998).

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Sediment is more conservative than water and most of the metals and metalloids are finally stored in the sediments. Consequently, sediment cores can be used to reconstruct the history of metal pollution within the area under study (Birch et al., 2001; Christophoridis et al., 2009). Sediments have been used as environmental indicators and their ability to trace and monitor contamination sources is widely recognised (Lipnick et al., 2002). Sediments are not specifically mentioned in the WFD but, as they also play an important role in the chemical and ecological state of the water due to the interactions between both mediums (Borja and Heinrich, 2005), the WFD establishes a guideline for sediments, which is just to avoid an increase in pollutant concentrations with time.

The estuary of the Nerbioi-Ibaizabal River (Bilbao, Basque Country) was strongly impacted by industrial activities, such as iron and steel production and transformation, untreated domestic sewage and mining activities since the late 19th century (García-Barcina et al., 2006; Jesus Belzunce et al., 2001). The gradual implementation of a system to collect and treat most of the sewage waters of industrial and urban origin, together with the closure of the most polluting companies, have resulted in an evident improvement of the environmental quality of the estuary (García-Barcina et al., 2006). The image of the city in the surroundings of the estuary has been completely renewed in a process that continues nowadays. One of the civil engineering works that has recently started (beginning of 2015) consists in the transformation of an isthmus in an island in the area of Zorrozaurre, with an important movement of highly polluted sediments. This actuation represents an evident threat due to a possible mobilisation of pollutants to the water layer that may affect the ecological and chemical status of the estuary.

The aim of this work was to characterise the estuary of the Nerbioi-Ibaizabal River in terms of metal pollution, in order to make feasible a future quantification of the effects derived from the Zorrozaurre island actuation. To this end, four sampling campaigns were conducted in 2009, 2010, 2011 and 2014 to collect surface sediments in about 50 points throughout the tidal part of the estuary. The concentration of fourteen metals and metalloids was measured in all the samples and the results were statistically investigated to: *i*) define the geographical distribution of the analytes in the estuary, *ii*) identify hotspots of contamination, *iii*) estimate the toxicity associated to the sediments and *iv*) check if there is any significant change in metal and metalloid concentration with time.

2. Materials and methods

2.1. Study area and sampling procedures

The estuary of the Nerbioi-Ibaizabal River is located in the continental shelf of the Cantabrian coastline in the northern coast of the Iberian Peninsula (Fig. 1). It crosses the city of Bilbao, one of the most important urban areas in the Cantabrian coast. The main fresh water input comes from the Nerbioi and Ibaizabal rivers (68%), while the rest comes from the smaller tributaries as Kadagua (27%), Galindo (4%), Asua (0.7%) and Gobela (0.3%) (Landajo et al., 2004).

At the end of the XIXth century, Bilbao city experienced a dramatic increase in population due to the exploitation of the local iron and the beginning of industrial activity (manufacture of steel, electroplating, ship construction). All the wastewaters from urban and industrial origin were directly dumped into the estuary in that period, which led to an environmental collapse of the Nerbioi-Ibaizabal estuary by the middle of the XXth century (Cearreta et al., 2002; Jesus Belzunce et al., 2001; Saiz-Salinas, 1997). However, the situation of the estuary improved significantly at the end of the XXth century due to the closure of the most polluting industries and mine activities, and to the implementation of the so-called “strategy for the integral recovery of the estuary of Bilbao” (García-Barcina et al., 2006). The estuary still suffers nowadays, however, the pressure coming from a million people living around it (Leorri et al., 2008). Several works have investigated the occurrence and

distribution of metals and metalloids in the estuary with different objectives and using a variety of approaches (Bartolome et al., 2006; Fdez-Ortiz de Vallejuelo et al., 2010, 2014; Gredilla et al., 2014; Leorri et al., 2008; Sanz Landaluze et al., 2004).

Forty nine sites were strategically selected in order to carry out a representative sampling in the Nerbioi-Ibaizabal estuary (Fig. 1). The samples were collected in January 2009, January 2010, January 2011 and January of 2014. Surface sediments (0–2 cm) were collected by hand using latex gloves from the river bank at low tide. In the sampling points 1 to 11 sediments were collected from a boat using a VanVeen type grab (capacity: 2 L; sampling surface: 260 cm²; weight: 10.42 kg; dimensions: 55 cm × 30 cm × 15 cm). In all cases, samples were transported to the laboratory in cleaned plastic bags at 4 °C.

2.2. Sample preparation and analysis

Once in the laboratory, sediment samples were frozen at –20 °C and lyophilised at 150 mTorr and –52 °C in Cryodos apparatus (Telslar, Spain) for 48 h. The dry samples were sieved to assure a maximum particle size of 63 µm and kept in the refrigerator at 4 °C in dark until analysis.

About 0.5 g of dried sediment was transferred to an extraction vessel with 20 mL of HNO₃/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 to 1% acid before the analysis. The concentration of Al, As, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sn, V and Zn was measured in the samples by ICP/MS (Perkin-Elmer, NexION 300) in a Class 100 clean room. The experimental conditions are summarised in Table 1. More details about the analytical procedure can be found elsewhere (Fdez-Ortiz de Vallejuelo et al., 2009).

The detection limits (LOD) were estimated by replicate analysis of procedural blanks ($n = 8$). The certified reference material NIST 1646a (estuary sediment, National Institute of Standards and Technology) was used to check the accuracy and repeatability of the method ($n = 5$). The results expressed as LOD (in mg·Kg⁻¹), percent of recovery (accuracy) and relative standard deviation (RSD, reproducibility) are summarised in Table 2. The recoveries in Table 2 were estimated using the concentrations experimentally measured after acid extraction of the sample and the total concentrations certified for the NIST 1646a.

Among other statistical treatments, Principal Component Analysis (PCA) of the datasets was separately performed for each sampling campaign by means of The Unscrambler Program (v. 9.2 Camo, Oslo, Norway). Each dataset consisted on a matrix with n rows (number of sampling sites) depending on the sampling campaign ($n = 49$: in 2009; 47: in 2010; 47: in 2011 and 49: in 2014) and 14 columns (number of measurement elements in each sample) which was centred and scaled before PCA. Concentrations below the detection limit were replaced by half of the detection limit estimated for each element.

3. Results and discussion

3.1. Element concentrations in sediments: geographical distribution and trends in time

The concentrations found in the sediment samples are shown as supplementary material in Tables S1 to S4. Samples from BE2 and BEK (in 2010) and 5 and BE2 (in 2011) were accidentally lost. We considered the possibility to work with Al-normalised concentrations in order to verify if grain size variability in the fine fraction might be partially behind the variability in metal concentration between sites and/or sampling campaigns. However, as the general trends observed in raw data and Al-normalised data were similar, probably because trace metal concentrations were measured after aqua regia extraction instead

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