



Methodology to assess the mobility of trace elements between water and contaminated estuarine sediments as a function of the site physico-chemical characteristics



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HIGHLIGHTS

- Innovative methodology to have a rapid diagnosis about the mobility of metals
- Real simulation of the estuarine conditions
- New tool using estuarine water at low and high tides as extractant of trace elements
- Possibility to understand the main trends in mobility from sediments to the water
- Identification of the factors governing mobility processes

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ABSTRACT

This work presents an innovative methodology to have a rapid diagnosis about the mobility of selected trace elements of known toxicity and biological risk (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn and Zn) present in contaminated sediments. The novel strategy presented in this work uses, therefore, the own estuarine water in contact with sediments as the extracting agent to perform the mobility tests, simulating the real situation of the estuary. This water suffers from different physico-chemical conditions (low and high tides) and gives consequently, rather better information than the one obtained by the routine sequential extraction procedures. The final step of this methodology was the use of spatial modelling by kriging method and multivariate chemometric analysis, both for a better interpretation of the results.

To achieve this goal, sediment and water samples were strategically collected at eight different points (four in tributary rivers, one in a closed dock, two in the main channel and another one in the mouth) along the Nervión-Ibaizabal River estuary (Metropolitan Bilbao, Basque Country) approximately every three months (summer, autumn, winter and spring) during a whole year.

Physico-chemical changes, such as pH, carbonate content and organic matter of the sediments, together with variations in water salinity appear to be responsible for metal mobility from the sediment to the water layer. The influence of these variables was higher in the sites located close to the sea. Moreover, the mobility of trace elements was even higher at high tide in sediments with lower metal content.

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1. Introduction

Trace metal contamination has become a serious problem in many coastal areas of the world. The possible toxic effect that the bioavailable metal part loaded in sediments of these environments may have in living organisms contributes principally to this fact (Kress et al., 2004).

Until some years ago most of the environmental studies carried out in aquatic environments were only focused in the measurements of the total metal concentration. This fact is clearly not enough, because it only allows a short-term environmental assessment of the area under study.

The study of processes governing the occurrence of metals in both sediment and water is of outstanding importance to understand the mobility, reactivity and consequently, the availability of toxic trace elements (Du Laing et al., 2009b). Although the free metal ions are the most mobile and bioavailable forms (Prokop et al., 2003), metals in more complicated molecular forms may also be remobilized. These last compounds could be the result of natural processes, such as weathering and/or erosion of geological formations, but anthropogenic activities can also be responsible of their formation and occurrence. Both natural and anthropogenic purposes could change drastically the environmental conditions of an area (e.g. redox, conductivity, pH, and organic matter), which may cause remobilisation of trace elements previously accumulated in sediments. Decreases in pH of the water, for example, might

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induce the oxidation of organic matter or sulphides, and promote the liberation of metals to the water layer from metallic complexes and solid suspended matter (Markiewicz-Patkowska et al., 2004; Zoumis et al., 2001; Silva et al., 2013). The salinity, on the other hand, can also induce the mobility of trace metals to water column as soluble chloride complexes (Hahne and Kroontje, 1973; Zhao et al., 2013).

Understanding all these processes is not easy, but it is important for environmental studies and risk assessment of any aquatic environment. Numerous studies have been carried out with this objective. For instance, Du Laing et al. (2009a) used pore water to study metal mobility between sediment and water in estuaries. Different sequential extraction procedures have been used to investigate the mobility of heavy metals from sediment to water in different aquatic environments, like in rivers or coastal areas (Kersten and Forstner, 1986; Kiratli and Ergin, 1996; Tessier et al., 1979; Ure et al., 1993; Usero et al., 1998). The Bureau Communautaire de Référence (BCR) proposed a sequential extraction procedure with 3 steps: in the first one, acetic acid as extractant to determine the acid soluble metal fraction, in the second one hydroxylamine hydrochloride to detect the reducible fraction, and in the third one, hydrogen peroxide and ammonium acetate are combined to extract the oxidisable metal fraction (Quevauviller, 1998). Previous to this BCR methodology, the German national standard DIN 19730 suggested the use of ammonium nitrate solution for total extraction in mobilisation studies of soils (Deutsche-Norm DIN, 19730, 1997). Simpson et al. (2004) and Villanueva et al. (2012) carried out different laboratory experiments on metal behaviour in sediments and showed changes that external parameters may cause in the mobilisation of the accumulated metals.

The study of metal mobility is even more important in estuaries, as they suffer extreme physico-chemical changes caused mainly by tidal variations. The use of standard extraction procedures, using model extractants such as acetic acid, hydroxylamine hydrochloride or similar is not, however, the best approach to investigate the mobility of metals between sediments and water, since the real conditions of the estuary are not certainly attached. In order to solve this problem, a new methodology is proposed in this paper. This study is focused on several locations of the estuary of the Nerbioi-Ibaizabal River (Metropolitan Bilbao, Bay of Biscay, Basque Country), an area that has been affected by industrial activities (specially local iron and steel foundry) since the 19th century. This estuary is one of the most important urban areas of the Cantabric coast, having the Metropolitan area of Bilbao, a total of 17 villages and about 1 million of habitants generating urban wastewaters. The morphology of the Nerbioi-Ibaizabal estuary has been highly modified since the end of the last century, mainly by means of canalisation and dredging (Gredilla et al., 2012). Since the early 1980s a clear decrease in contamination has been observed in the estuary, due to a recession of the industrial activity, the closure of mine workings, the treatment of domestic and industrial sewage and the implementation of environmental policies (Barreiro and Aguirre, 2005). Nevertheless, the estuary still presents high levels of contamination in both water column and sediments (Moros et al., 2009; Amigo et al., 2012; Fdez-Ortiz de Vallejuelo et al., 2010; Landajo et al., 2004; Tueros et al., 2009). Therefore, to identify specific associations between metals and their mobilisation, sediments and water samples collected in the Nerbioi-Ibaizabal estuary with different pollution levels and physico-chemical conditions were used to investigate metal mobility between sediments and water. This methodology makes use of kriging interpolation and multivariate chemometric analysis for the better interpretation of the experimental results.

2. Materials and methods

2.1. Study area

The estuary of the Nerbioi-Ibaizabal River, Metropolitan Bilbao (Fig. 1) is located on the continental shelf of the Cantabrian coastline

in the northern coast of the Iberian Peninsula. Its moderate freshwater inflow is of 25 m³/s and the predicted suspended sediment load ranges from 143 to 1043 tonnes/year (Arias et al., 2008; Belzunce et al., 2001). The current estuary is 15 km long, with an average width of 100 m, the channel depth ranging from 2 m in the upper estuary to 9 m at the mouth and a mean tide level variation is ranging from 1 to 4.5 m (Cearreta et al., 2000). 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%) (Leorri et al., 2008). After a deep study of the area the next sampling points were chosen: Asua (AS), Gobela (GO), Kadagua (KA) and Galindo (GA), which are located in tributary rivers, Alde Zaharra (AZ) and Zorrotza (ZO) that are in the main channel, Udondo (UD), which is a closed dock, and Arriluze (AR) that is in the mouth of the estuary.

2.2. Sampling procedures

Deep water (in contact with the sediment, both at low and high tides) and surface sediment (~500 g, ~2 cm depth, at low tide) were collected approximately every three months during a year (four different campaigns, practically every season), at eight points of the estuary (Fig. 1). For water sampling a 2 L Van Dorm type all-plastic water sampler (KD Denmark, Research Equipment, Silkeborg, Denmark) was employed (Fernández et al., 2008).

Water temperature, conductivity, salinity, pH, redox potential and dissolved oxygen were measured in situ by means of a precalibrated YSI 556 multiparametric probe (YSI Environmental, Yellow Springs, Ohio). Waters samples were after transported to the laboratory and stored at 4 °C and protected against light until analysis.

Sediment samples were collected from river banks at low tide using plastic utensils and latex gloves to avoid sample contamination with metals. They were after put into cleaned plastic bags and they were finally transported to the laboratory in portable cooler boxes at 4 °C to reduce the effects of microbiological activity. Once in the laboratory they were frozen in the refrigerator at –20 °C, and then lyophilized at 150 mTorr and –52 °C in a Cryodos apparatus (Telstar, Spain) for 48 h. After this, samples were sieved to assure a maximum particle size of 65 µm, fraction usually used in mobilisation tests (Che et al., 2003; Warren et al., 2012), and kept in the refrigerator at 4 °C until analysis.

2.3. Samples characterisation

2.3.1. Granulometric analysis

In order to study the effect of sediment texture in the mobilisation of trace elements, a granulometric analysis of some sediment samples was done. For this, the granulometric fractions of the sediments, such as contents of sand, silt and clay were considered. The separation of the particle-size fractions was achieved by a vibrator system (Endecotts Octagon Digital, England) supplied with a column of sieves of 2, 0.25 and 0.0065 mm. The weight of each the fraction was determined by a balance (Mettler Toledo AE2000, with an accuracy of ±0.0001 g). The grain size separation analysis was carried out by classification proposed by Shepard and Folk (Folk and Ward, 1957; Shepard, 1954).

2.3.2. Physico-chemical properties of sediment samples

The pH of the sediments was measured in a 1/5 sediment/distilled water suspension of the sample after equilibrium for 18 h, and the conductivity was measured in the filtrate of a similar shaken for 1/2 h (Ranzt et al., 1999). The carbonate content was determined by back-titration of 1 g of sediment in an excess of 0.25 M H₂SO₄ (Du Laing et al., 2007). The organic matter content was measured by weight loss after incineration of oven-dried samples (2 h at 450 °C) (Tack et al., 2006).

2.3.3. C, H, O and N contents of the sediments

The elemental analysis of sediments was realised using a EuroEA Elemental Analyser. The analytical procedure consists on: a) the

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