Marine Chemistry 117 (2009) 77–87

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Porewater geochemistry in a Galician Ria (NW Iberian Peninsula): Implications for benthic fluxes of dissolved trace elements (Co, Cu, Ni, Pb, V, Zn)

J. Santos-Echeandia [a,*], R. Prego [a], A. Cobelo-García [a], G.E. Millward [b]

[a] Marine Research Institute (CSIC), C/Eduardo Cabello, No. 6, Vigo 36208, Spain
[b] University of Plymouth. PL4 8AA Plymouth, UK

ARTICLE INFO

Article history:
Received 30 October 2008
Received in revised form 30 April 2009
Accepted 1 May 2009
Available online 8 May 2009

Keywords:
Dissolved metals
Vigo Ria
Metal fluxes
Trace elements
Pore water geochemistry
Benthic fluxes

ABSTRACT

The geochemical behaviour of dissolved trace elements in sediment interstitial waters from the Vigo Ria (Galicia, Spain) has been determined. Dissolved concentrations in the pore waters ranged between 1.7–23.2 nM for Co, 1.5–131 nM for Cu, 19.5–159 nM for Ni, 0.02–19.3 nM for Pb, 5.4–260 nM for V and 0.2–241 nM for Zn. Values for Cu, Pb and Zn were highest along the axis of the ria, whereas Co, Ni, V and Zn were more abundant in the area of the industrialised shipyards. The metal profiles were affected by sedimentary redox processes, which were monitored by means of Mn and Fe concentrations and pore water pH. Dissolved Cu and V had relatively high concentrations in the oxic surface layer and their concentrations decreased with depth, although in deeper layers concentrations of V increased in association with the presence of dissolved organic ligands. Cobalt and Ni followed the behaviour of Mn, although they were depleted in surface oxic layers their concentrations increased in the Mn reduction zone. Lead and Zn had highly irregular profiles because of their lower redox-sensitivity and their complexation with organic material is not as pronounced as that for Cu. Dissolved metal concentrations in overlying waters oscillated between 0.7–2.1 nM for Co, 5.5–50.5 nM for Cu, 4.6–10.0 nM for Ni, 1.4–9.1 for Pb, 5.7–28.5 nM for V and 14.6–66.5 nM for Zn. Using Fick's first law of diffusion, the benthic fluxes of the elements varied between 0.03–0.24 nmol cm^{-2} y^{-1} for Co, (−0.02)–1.11 nmol cm^{-2} y^{-1} for Cu, 0.16–1.70 nmol cm^{-2} y^{-1} for Ni, (−0.14)–0.03 nmol cm^{-2} y^{-1} for Pb, 1.52–4.35 nmol cm^{-2} y^{-1} for V and (−0.37)–0.90 nmol cm^{-2} y^{-1} for Zn. Fluxes were higher in the ria axis for Cu, Ni, V and Zn and in the shipyard area for Co, while Pb fluxes were negligible at all the stations. This work has demonstrated that the redox geochemistry and diagenetic processes of the sediments and pore waters control the benthic fluxes in the Vigo Ria. When the upper layer of the sediment is oxic a high exportation of Cu and V to the overlying waters occurs and during less oxidizing conditions of this layer, Ni and Co exportation from the pore water increases. Dissolved trace metal benthic fluxes to the Vigo Ria were significant for most of the metals (Cu, Ni and V) and were of the same order of magnitude to the riverine inputs.

1. Introduction

Sediments play a major role in the overall fluxes of trace elements in coastal systems, acting as a source and/or sink to/from the water column. Metal accumulation in sediments depends on the flux of biogenic and lithogenic material to the seabed (e.g. Boyle et al., 1976; Bruland, 1980; Jeandel et al., 1987) and the scavenging of dissolved metals by suspended particulate phases (oxides, organic particle coatings, clay particles, etc.; e.g. Goldberg, 1954; Craig, 1974; Balistrieri et al., 1981). Deposited particulate material undergoes diagenetic changes, involving partitioning trace elements between particles and interstitial waters. These processes depend upon several factors including pH, occurrence of complexants, salt concentrations, changing redox conditions, and decomposing organic matter (Forstner and Kersten, 1989; Carignan and Nriagu, 1985; Boudreau, 1987, 1991; Boudreau and Canfield, 1988; Jorgensen and Revsbech, 1983). The geochemical processes controlling the partitioning and recycling of metals in sediments have significant implications in regulating their sediment–water exchange. Recycling occurs, predominantly, at or near the sediment–water interface where pore water metal concentrations are typically in excess of those in bottom waters (Emerson et al., 1984; Hines et al., 1984; Heggie et al., 1987; Widerlund, 1996; Skrabal et al., 1997; Monterroso et al., 2007) resulting in net benthic fluxes of dissolved metals to the water column.

Rias are estuarine-coastal systems formed by flooding of river valleys in the Pleistocene–Holocene in regions of high relief during the last interglacial transgression, and are typical of world areas such as NW Iberia, SW England or SE Asia (Bianchi, 2007). Several of the Galician Rias (NW Iberian Peninsula) are under significant anthropogenic influence due to the population and industry settled on their margins (Prego et al., 2008), thereby altering the natural distribution and processes of trace metals. The Vigo Ria occupies an area of 156 km^2 with a volume of 3275 km^3 of water; the main tributary is the Oitaven River, located at the head of the ria (Fig. 1) and oriented approximately parallel

---

* Corresponding author. Tel.: +34986231930; fax: +34986292762.
E-mail address: jusae@iim.csic.es (J. Santos-Echeandia).

0304-4203/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.marchem.2009.05.001

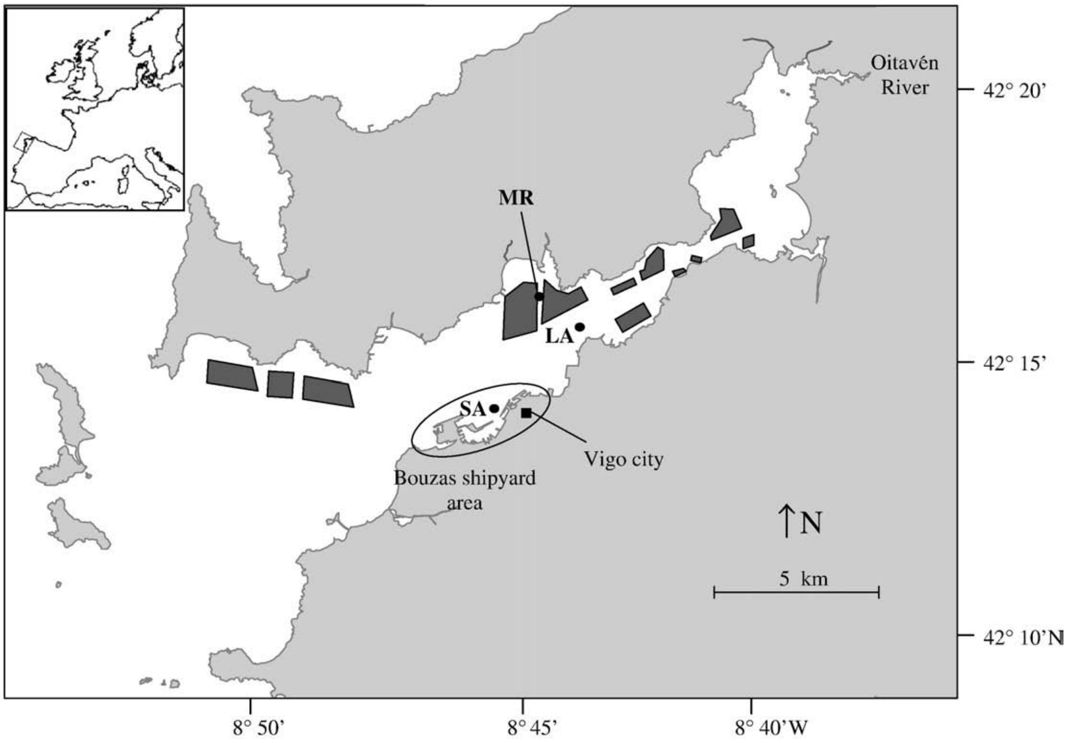

Fig. 1. Vigo Ria map with the three sampling stations: mussel rafts (MR), longitudinal axis of the ria (LA) and shipyard area (SA).

to its longitudinal axis. It is the most industrialised and populated ria in Galicia with approximately 400,000 inhabitants, 80% of which are based at the southern margin (city of Vigo; Fig. 1). Industrial and port activities have occupied the banks of this ria for decades, especially the Bouzas shipyard (Fig. 1). In addition, and due to the high biological productivity of the Iberian Atlantic coastal margin, Galician Rias produce 250,000 ton of mussels per year, representing about 50% of the European production (Smaal, 2002). Accordingly, the Vigo Ria is covered by a great number of mussel rafts (Fig. 1).

In order to assess the relative magnitude of benthic fluxes of dissolved trace elements (Cu, V, Ni, Co, Pb and Zn) to the Vigo Ria compared to other major sources (e.g. freshwater discharge), we conducted a seasonal geochemical study using short cores (≤10 cm) taken in representative zones of the Vigo Ria. The aim was to assess the influence of the redox conditions (based on pH and dissolved Fe and Mn profiles) on the distribution of dissolved trace elements in interstitial waters.

2. Materials and methods

2.1. Sample collection and pre-treatment

Cores (approx. 10 cm) of undisturbed sediment and approximately 100 mL of the overlying waters were taken with a 'Rouvillois' box-corer fitted with Plexiglas tubes (length 20 cm, diameter 5.4 cm) at three stations in winter, spring and summer 2005 onboard the *R/V* Mytilus (IIM-CSIC). The station locations were chosen to be representative of the different environments within the longitudinal axis (LA) of the ria, the shipyard area (SA), and below the mussel rafts (MR; Fig. 1) (water depth 22, 15 and 15 m respectively). Acid-washed Plexiglas tubes were placed inside a *Rouvilloise* grab sampler to obtain the sediment cores. The tubes were sealed at the top and bottom with rubber bungs immediately after collection to maintain anoxic conditions (Dale and Prego, 2002) and inspected for trapped air pockets and to verify that the collection process had not disturbed the sediment structure. At the onshore lab, sediment cores were stored in plastic bags at −18 °C.

The main characteristics of the Vigo Ria sediments, such as grain size distribution, organic matter and calcium carbonate, presence of bioturbation and porosity have been previously described (Rubio et al., 2000; Bernardez et al., 2005; Vilas et al., 2005; Diz and Frances, 2008; Ysebaert et al., 2009) and showed almost invariant composition between sampling locations. All the samples were generally muddy (70–80%) with a small percentage of sand or gravel of bioclastic origin and dispersed shells especially below the mussel rafts. The percentage of organic matter was similar among the sampling points, ranging from 6 to 8% of the sediment, whereas the percentages of calcium carbonate were low in the middle section of the Ria (0–10%) and higher (10–15%) below mussel rafts (Rubio et al., 2000). With respect to bioturbation, low macroorganism activity in the sediments is indicated by the lack of in-fauna soft-bodied organisms and the scarcity of bioclasts in the cores. Bioturbation is more pronounced in sediments in the outer ria, mainly due to higher oxygen levels in the pore waters and lower organic matter concentrations (Rubio et al., 2000; Diz and Frances, 2008).

Preservation of redox conditions during core sectioning was achieved by using a glove-box filled with N_2 (815-PGB, Plas-Labs). Frozen cores were extruded from the tube and the overlying water was placed into acid-cleaned plastic bottles. The sediment cores were sliced into 2–3 cm thick layers and allowed to thaw inside acid-cleaned polyethylene centrifuge tubes. The pH was then measured using a microelectrode (Unisense, Denmark). In order to extract the pore water, the centrifuge tubes, containing the sediment sections, were filled with N_2 and centrifuged at 3000 rpm for 40 min, after which the tubes were then returned to the N_2-filled glove-box and opened. The supernatant was then passed through acid-washed 0.45 µm pore size acetate cellulose syringe filters and collected in acid-washed 50 mL polyethylene bottles and acidified (pH 2) with concentrated HNO_3 (Merck Suprapur$^{®}$). The overlying waters were filtered and acidified as above.

2.2. Pore water analysis

Total dissolved metals were determined by means of stripping voltammetry using a Metrohm VA-694 equipped with a hanging mercury drop electrode (HMDE) as the working electrode, Ag/AgCl as the reference electrode, and a Pt wire as the counter-electrode. Prior to