



Prevalence of tide-induced transport over other metal sources in a geologically enriched temperate estuarine zone (NW Iberian Peninsula)



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ABSTRACT

Tide-induced transport, diffuse fluxes and river inputs of arsenic, cobalt, chromium, manganese and nickel were studied in an estuarine zone located at the Ria of Ortigueira in the Galician coast of NW Spain to evaluate comparatively the magnitude of trace-element inputs in the estuarine ecosystem. Short-sediment cores and flooding water were collected at the intertidal area of La-Caleira Inlet in spring and summer 2008 during the first 50 min of tidal inundation. High concentrations of dissolved chromium (up to 23 nM) and nickel (256 nM) were found in waters of the Lourido River during 2008. Chromium (up to 795 mg·kg⁻¹) and nickel (up to 533 mg·kg⁻¹) in surface sediments of the study area were also high, pointing to natural geological sources (Cape Ortegal Complex). Fluxes associated with molecular diffusion and tide-induced transport across the sediment–water interface were quantified and compared to the river contribution. Mean fluxes from the Lourido River were 0.03 μmol·m⁻²·d⁻¹ for As, 0.02 μmol·m⁻²·d⁻¹ for Co, 0.43 μmol·m⁻²·d⁻¹ for Cr, 0.72 μmol·m⁻²·d⁻¹ for Mn and 5.98 μmol·m⁻²·d⁻¹ for Ni. Diffusive fluxes were negative which indicates the flow of trace elements towards the sediment –0.47 ± 0.12 μmol·m⁻²·d⁻¹ for As; –0.007 ± 0.001 μmol·m⁻²·d⁻¹ for Co; –0.003 ± 0.009 μmol·m⁻²·d⁻¹ for Cr; –5.44 ± 1.65 μmol·m⁻²·d⁻¹ for Mn; and –0.02 ± 0.05 μmol·m⁻²·d⁻¹ for Ni. Tide-induced transport of trace metals was up to four orders of magnitude greater than diffusive fluxes. The contributions of trace elements to the estuarine zone from fluvial and benthic origin were quantified, emphasizing the importance of tide-induced transport in estuarine systems.

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1. Introduction

Rivers are considered one of the main sources of trace elements from land to the coastal environments. This transport depends on the nature of the river basins and physical and chemical characteristics of water. Weathering, anthropogenic materials and atmospheric deposits are the main sources of dissolved and particulate trace elements to estuaries (Martin et al., 1980; Viers et al., 2007). During weathering, mineral constituents are released to natural waters and metals may be transported in a dissolved form or adsorbed on suspended material, incorporated in the lattice of freshly formed inorganic compounds such as Al, Fe and Mn (oxy)hydroxides or sorbed in organic matter. Particles originating in the catchments settle in margins, flood plains and other low hydrodynamic sites.

Besides rivers, bottom sediments of estuaries and rias may also act as a source or a sink of trace elements to the water column. In subtidal sediments it has been recognized that bioirrigation/bioturbation (Cardoso

et al., 2008; Meysman et al., 2006) and molecular diffusion (Man et al., 2004; Ospina-Alvarez et al., 2014; Zabel et al., 1998) are known to promote the exchange of solutes across the sediment–water interface. However, most of the estuaries and rias are characterized by extensive intertidal areas. These sediments are subjected to changes of pressure, temperature, light exposure and solute concentration (Hammond, 2001) every tidal cycle. The periodic inundation of sediments induces the export of nutrients and trace elements to the water column (Caetano et al., 2007; Huettel et al., 1998), the supply of oxygen to deeper sediment layers (Kener and Wallmann, 1992) and the removal of solutes to the solid fraction (Falção and Vale, 1995). Resuspension and mixing associated with tides and wind episodes induce the mixing of surface sediments with the overlying water promoting changes in the sorption equilibrium (Simon, 1989).

Most researches have addressed separately inputs from rivers or fluxes across the sediment–water interface. However, the relevance of each process that introduces trace elements in the coastal ecosystems has not been studied. Thus, the main goal of this work was to compare the magnitude of trace-element input from freshwaters, molecular diffusion fluxes and tide-induced transport. This study reports the concentration of arsenic, cobalt, chromium, manganese and nickel in (i) river water, (ii) surface sediments and (iii) flooding and pore water during the first 50 min of tidal inundation. River inputs, diffuse fluxes and

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tide-induced transport of trace elements were estimated in order to evaluate their importance to the total budget in the ria ecosystem.

2. Material and methods

2.1. Study area

Rias are coastal inlets formed during the Flandrian Transgression by the drowning of a former river valley characterized by irregular coastlines and exposed rock platform (Goudie, 2004). Several ria-type systems are located at the Galician coast of Spain (NW Iberian Peninsula). The Ria of Ortigueira represents one of the largest intertidal systems of the Northern Galician rias (Torre-Enciso, 1958). The ria covers an area of 38 km², considering the 30-m depth isoline as the ria–shelf boundary, of which 48% corresponds to the intertidal area. It is a mesotidal systems dominated by marine processes, and contrasting geological features characterize its surrounding area. Located at the west of the ria, the Cape Ortegal complex is rich in mafic and ultramafic rocks and eastward, the Olla-de-Sapo domain, is composed of metamorphic (mostly gneisses) and granite-type rocks (Aparicio et al., 1987; IGME, 1977) (Fig. 1). The main fluvial sources are the Mera (basin area: 127 km²) and Lourido River (10 km²), which present a hydrological and hydrochemical behavior similar to that of other basins in the area (Bernárdez et al., 2013).

2.2. River water sampling

All plastic labware employed for sampling, storage and sample treatment was previously acid-washed for 48 h in 50% HNO₃ and rinsed with Milli-Q water (18.2 MΩ cm), then transferred into a container filled

with 10% HCl for at least a week. Labware was rinsed several times with Milli-Q water and dried into a laminar flow cabin (ISO Class 5) before use. One liter LDPE bottles were filled with Milli-Q water at pH 2 until use. Sampling was performed following clean techniques for trace element analysis (GEOTRACES, 2010; US-EPA, 1996). Monthly water samples were collected in the Lourido and Mera rivers (mean flow 2008: 0.5 and 6.0 m³·s⁻¹) from January to December 2008.

Salinity and temperature were measured in situ using a WTW MultiLine P4 Set (error range ± 0.1). Dissolved oxygen concentration and their saturation percentages were determined within 24 h after collection. Samples for dissolved organic carbon (DOC) were taken into 50 mL polyethylene bottles previously cleaned and washed with HCl, and then frozen at –20 °C until analysis. Samples for trace elements were collected in 1-L LDPE bottles previously acid-washed and rinsed with Milli-Q water.

At a clean portable-laboratory and within 4 h after collection (Chapman, 1992), samples were separated into dissolved and particulate fractions in a laminar flow cabinet (ISO Class 5) by filtration through Pall-Gelman polycarbonate membranes (0.45 μm), previously acid washed (Suprapur HCl 1%) and weighed. Samples for dissolved trace elements analysis were acidified with Suprapur HNO₃ (pH < 2). Afterward membranes were dried, weighed again and suspended particulate matter (SPM) calculated. Filters were placed into plastic petri dishes and stored at –20 °C until digestion for particulate metal analysis.

2.3. Surface sediment sampling

Six samples of surface sediment (sites A to F, Fig. 1) were collected in the Ria of Ortigueira on July 2007, on board the R/V Lura and small boats,

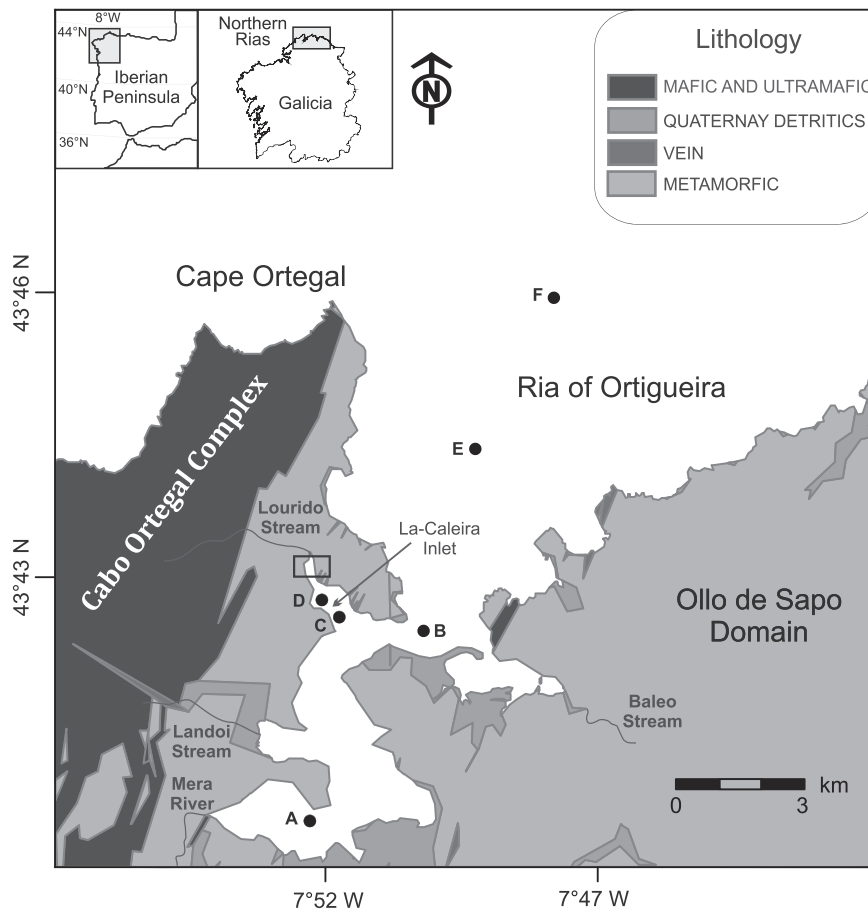


Fig. 1. Lithological map of the Ria of Ortigueira. The rectangular area at La Caleira Inlet shows the location of the water–sediment sampling station and black circles indicate the position of the surface sediment samples.

Lithology map was obtained from the Spatial Data Infrastructure of Galicia <http://sitga.xunta.es/sitganet/index.aspx?lang=gl>.

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