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Metal distributions and their fluxes at the coastal boundary of a semi-enclosed ria

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Abstract

Water column samples have been collected in the outer channel of the Ferrol Ria (NW Spain) during four occasions over a tidal cycle. The objective was to study the exchange of dissolved and particulate Cd, Cu, Pb and Zn and particulate Al, Fe and Si between the ria and the adjacent coastal waters. This study provides the first extensive dataset on dissolved and particulate metal concentrations in the water column of a Galician ria. Typical concentrations of dissolved Cd (96 ± 31 pM), Cu (8 ± 4 nM), Pb (270 ± 170 pM) and Zn (21 ± 10 nM) were similar than in other European Atlantic shelf and coastal waters. The fraction of metals in the particulate phase followed the trend: Pb > Cu ~ Zn > Cd. The outgoing water from the ria was enriched in dissolved and particulate Cu, Pb and Zn compared with incoming waters, whereas Cd concentrations were similar for both waters. The suspended particulate matter was composed of a mixture of marine and continental material. The latter end-member was found to arise from the metal-rich ria bed sediments, which is diluted by the dominant metal-poor marine end-member. The net output flux of Cu from the channel is balanced by the freshwater inputs to the ria, and the net Zn flux gave a positive output to coastal waters. For Pb, the net flux to the coastal waters is less than that input from the rivers, as a result of its particle reactivity and deposition in sediments. On the contrary, a net input flux of dissolved Cd from coastal waters was observed, highlighting the oceanic source of this metal in the Galician rias. Results from the budget calculations are in agreement with the differential geochemical behavior of these elements in coastal waters.

Keywords: Metals; Rias; Biogeochemical cycle; Fluxes; NE Atlantic; Galicia, 43°27′–43°30′ N, 8°9′–8°21′ W

1. Introduction

The ocean margin is a critical land–ocean interface as at its boundaries the ocean receives most of the land-based contaminant inputs (Martin and Windom, 1991). Accordingly, biogeochemical processes in coastal systems are of considerable interest

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because of their consequences for the net fluxes of dissolved and particulate matter from land to ocean. Whereas most of the studies on metal behavior have been focused on 'typical' estuaries (e.g., Zwolsman et al., 1997; Chiffoleau et al., 1999; Robert et al., 2004), there is a lack of information on processes affecting metals in rias. The term 'ria' is used to define incised valleys on the coasts of Spain, Portugal, Brittany, SW England, SW Ireland, Argentina, SE China and SE Australia. The 18 Galician rias, located in the NW of the Iberian Peninsula (Fig. 1), are significant examples of this type of coastal system. Due to the low freshwater discharge at their head, only their innermost part can be considered as an estuary from both hydrographic and sedimentological considerations (Evans and Prego, 2003), the greater part of the rias being dominated by marine processes. The Galician rias are of increasing socioeconomic importance particularly because of aquaculture, producing over 200,000 tons year^{-1} of mussels (*Mytilus galloprovincialis*) and 40% of European Union seafood production, in addition to industrial, port, fishing and tourist activities. However, processes controlling the behavior and distribution of metals in the Galician rias are still poorly understood (Prego and Cobelo-Garcia, 2003).

1.1. Study site

The Ferrol Ria (Fig. 1) is a semi-enclosed embayment with a total length of 15 km and a surface area of 21 km^2, containing an average water volume of 250 Hm^3. The freshwater discharges to the ria are low, the main rivers being the *Xubia* (mean annual flow of 5.5 m^3 s^{-1}) and *Belelle* (mean annual flow of 0.8 m^3 s^{-1}) discharging at the ria head, and an overall mean annual freshwater contribution to the ria of approximately 10 m^3 s^{-1}. Due to the low river inflow, the main factor controlling the water exchange between the ria and the shelf is tidal forcing, inducing a near-periodic circulation, with a tidal range of 3–4 m on spring tides and 1–2 on neaps (deCastro et al., 2003). During spring tides, 17% of the total water volume of the ria is removed during every ebb phase. The Ferrol Ria constitutes one of the most important industrial centres on the coast of Galicia. The anthropogenic influence in the ria began in the second part of the 18th century and continued to the present day (Cobelo-Garcia and Prego, 2003b, 2004). Presently, the ria supports a population of 143,000 inhabitants and industrial activities such as shipbuilding, commercial port operations and metallurgy. Thus, it is unlike many of the Galician rias, where aquaculture is a

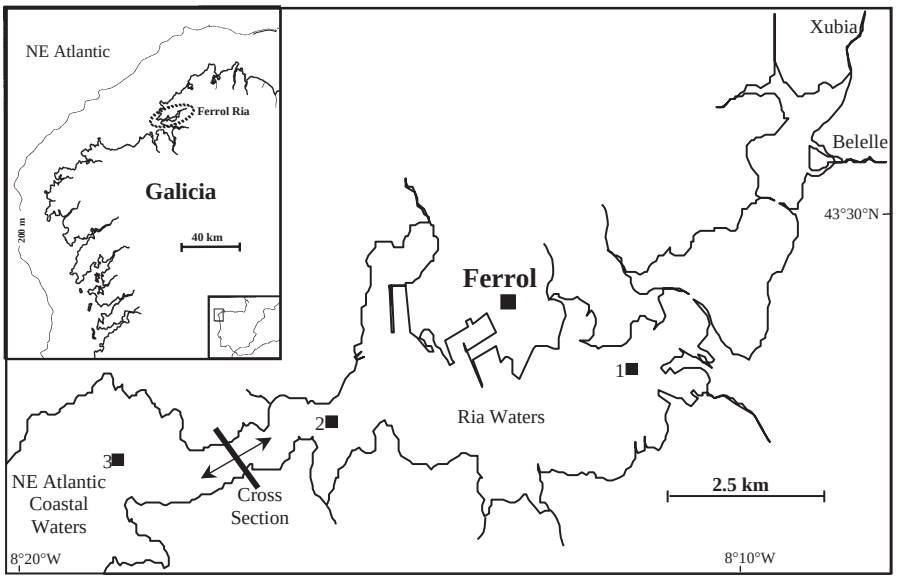

Fig. 1. Map of the Ferrol Ria showing the cross-sections where the water column samples were taken, together with the location of the sediment traps (black squares).