Metals Levels in Rainwater from the Northern Galician Rias (NW Iberian Peninsula): preliminar results

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Introduction

Atmospheric inputs may be an important source of metals in oceanic and coastal areas (Duce et al. 1991), where metals in rainwater can be affected by anthropogenic sources (Eisenreich, 1980). In the Galician Rias the metal contributions from continental and oceanic sources has been considered (Prego and Cobelo-García, 2003) but the atmospheric reservoir was not take in account as a source of metals to the ria compartment. This lack of information about trace metals is tackled in this study over an annual period from rainwater samples collected between the Rias of Ortigueira and Barqueiro in the western zone of the Cantabrian Sea.

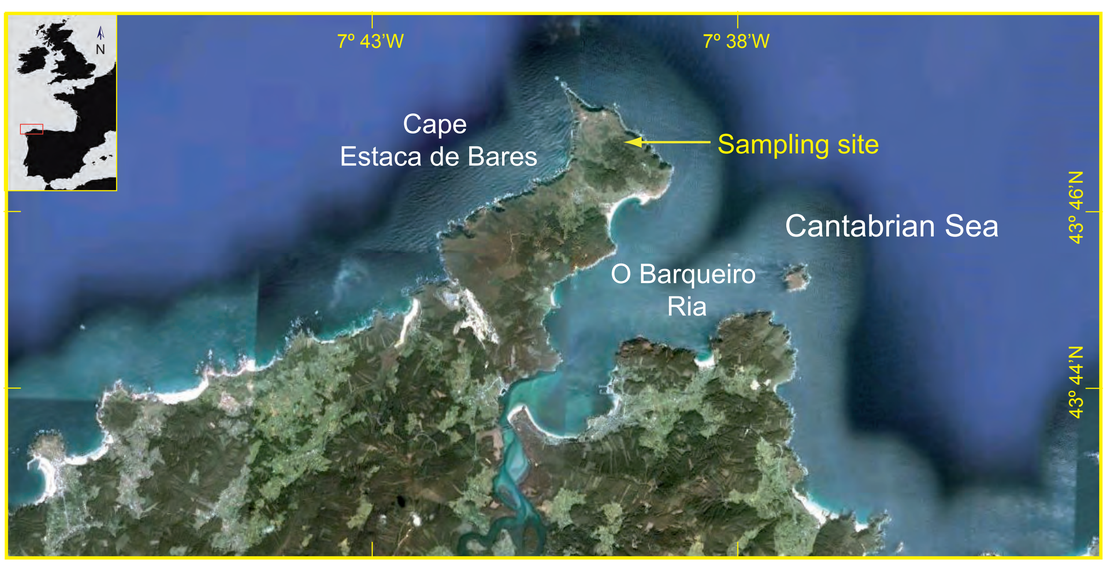


Figure 1. Map of the North of Galicia showing the sampling site.

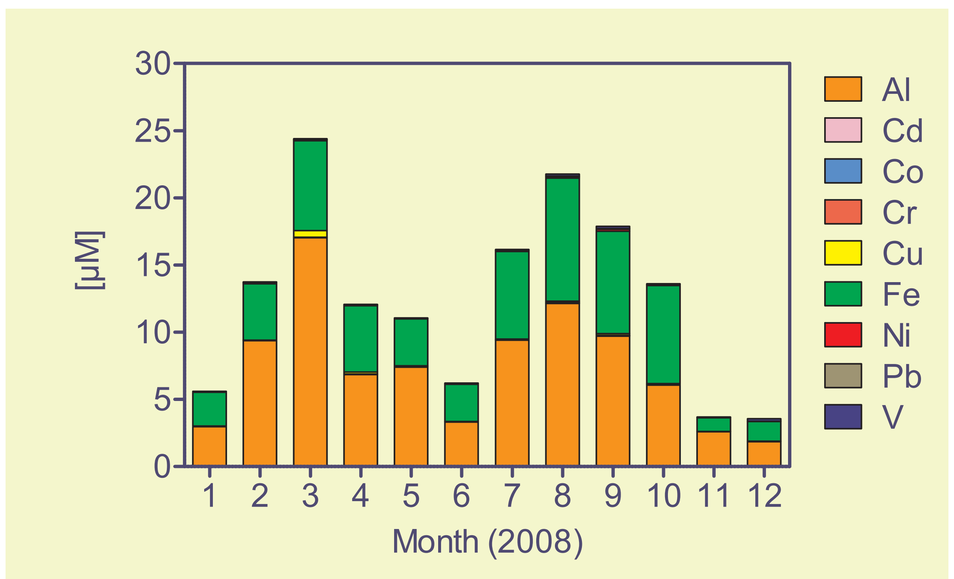
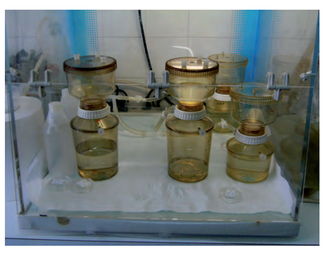


Figure 2. Monthly-accumulated variation of mean concentrations of total metal (µM) in rainwater collected from the Cape "Estaca de Bares" during 2008



Materials and Methods

Concentrations of Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, and V were determined in rainfall from the Northern Galician Rias , based on a biweekly sampling between Jan 2008 to Feb 2009. Rainwater samples were collected in the meteorological station of AEMET (Spanish Meteorological Agency) located at the northernmost point of the Iberian Peninsula (Cape "Estaca de Bares", 7º41'N-43º47'W) between the Galician Rias of Ortigueira and Barqueiro. Sampling system consisted in a rain collector (30x60 cm) with four plastic funnels (10 cm diameter), covered with a plastic mesh to prevent entry of insects and plant debris into the sample, and adjusted to 500 mL LDPE bottles. Samples were separated into dissolved and particulate components by filtration through a polycarbonate filter (0.45 µm) in a laminar flow cabinet, before four hours after collection (Chapman, 1992). Particulate metals were determined by GFAAS in a Varian SpectrAA 220 apparatus equipped with Zeeman background correction at the laboratory of the Marine Biochemistry Group (CSIC, Vigo) and dissolved metals by ICP-MS in a Thermo-Elemental, X-Series, equipment at the laboratory of the Department of Aquatic Environment (IPIMAR, Lisbon) (APHA, 1995). Monthly variation in metals concentrations were checked by a one-way Kruskal-Wallis test, followed by a Dunn's post-hoc test.

Results and Discussion

Total fraction (dissolved+particulate) was mainly composed of Al (60%) and Fe (38%) (Fig. 2). Metal concentrations in the dissolved fraction showed a variation throughout the year for all studied metals (Kruskal-Wallis test, $p<0.05$). In the particulate fraction, with exception of aluminium, concentrations were also significantly different (Kruskal-Wallis test, $p<0.05$). If only the particulate fraction is considered, most of the metals were higher in spring, with exception of Fe and V, whose values were higher in summer. These maximum values of metal concentrations coincided with the maximum rainfall recorded during 2008. Total concentrations for Al and Fe were 7±4 µM and 5±3 µM respectively. The other elements analyzed represented only 2% of the total fraction, and their concentrations were 1.0±1.0 nM for Cd, 5.6±6.4 nM for Co, 35±20 nM for Cr, 88±134 nM for Cu, 51±39 nM for Ni, 14±17 nM for Pb and 84±53 nM for V.

The distribution of total metals concentrations in decreasing order was: Al>Fe>Cu>V>Ni>Cr>Pb>Cd (Fig. 3). According to previously reported by other authors (Rodrigo et al, 1999; Başak and Alagha, 2010), Cd was the less abundant metal in the rainwater. A correlation matrix between metals concentrations of the total fraction was also performed. Strong correlations ($p<0.05$) were observed between Al, Cu, Fe, and Ni. No relationship was found between Cr and the other metals analyzed, which may indicate a different source for this element, maybe associated with the presence of different geological complexes in the study area.

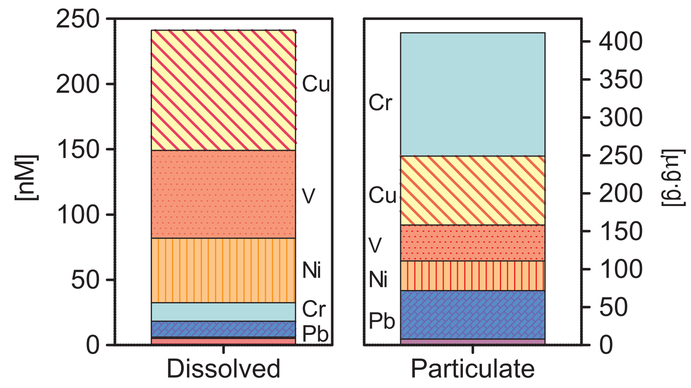


Figure 3. Annual accumulated concentration of dissolved (nM) and particulate (µg·g) metals in rain water collected from the Cape "Estaca de Bares" during 2008. The values of the major elements Al and Fe are not considered.

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