Distribution of major and trace elements in coastal sediments and identification of their continental, marine and anthropogenic sources

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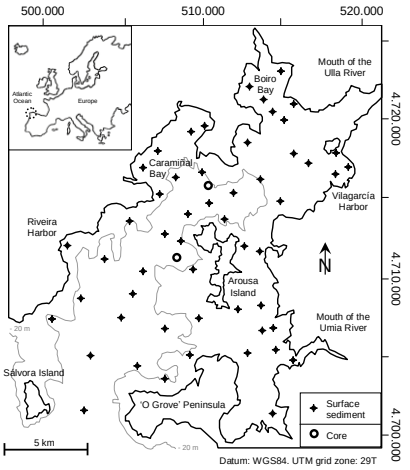
Introduction: The northwestern margin of the Iberian Peninsula is a coastal ria system made up of eighteen Galician rias, which has been defined as incised valleys where the estuarine zone can move according to environmental changes. The input of major and trace elements to ria sediments may occur by natural processes through fluvial loads or by plankton fall, mainly. Moreover, the rias are exposed to environmental impacts due to urban and industrial discharges and harbor activities. For these reasons, the quantification of elements in the sedimentary reservoir and the identification of their continental, marine and anthropogenic sources is a key question that was not studied together as a whole in the Galician Rias [1]. So, this matter is surveyed in this communication from the simultaneous determination of Ti, V, Mn, Fe, Cu, Zn, As, Rb, Sr and Pb in the sediments of the Ria of Arousa (NW Spain) by Total Reflection X-Ray fluorescence (TXRF).

Methods: The sediments under study were sampled from the R/V Mytilus and its auxiliary boat Zoea in the shallow water zones of the Ria of Arousa



(Figure); 53 surface sediments (top centimeter) were collected using Shipeck grabs and 2 core sediments using a Gravity-Corer. Samples were gently dried in oven at 45±5° C and fine fraction selected through 0.063 sieves. The analytical TXRF procedure was adapted from [2] and validate with marine sediment CRMs (SRM 2702 and PACS-2). A Bruker S2 PICOFOXTM analyzer with a Molybdenum cathode was used.

Results: Elemental contents in fine surface sediments were as follows: 10-32 mgAs·kg^{-1}, 7-105 mgCu·kg^{-1}, 12-40 gFe·kg^{-1}, 97-474 mgMn·kg^{-1}, 15-217 mgPb·kg^{-1}, 86 -192 mgRb·kg^{-1}, 88-880 mgSr·kg^{-1}, 1.5-3.8 gTi·kg^{-1}, 30-94 mgV·kg^{-1} and 59-170 mgZn·kg^{-1}. The highest sediment contents of Fe, Mn, Rb, Ti and V were near the estuarine mouths of Ulla and Umia rivers and the northward littoral of the ria; As, Cu and Zn decreased seaward while Sr did landward; Pb was located in two small ria zones, *i.e.*, the vicinity of the Vilagarcía Harbor and the sallow fishing boats port of Cambados. Based on metal-iron pre-industrial relationships from the Arousa cores, the enrichment factors of ten elements in the surface sediments were calculated. Cu and As showed a moderate localized contamination but Pb reach severe contamination. A statistical PCA analysis allowed the identification of the main sources of theses elements to the Ria sediments from a two-component function: Component 1 displayed high positive scores for Ti and Rb and negative for Sr. Component 2 loaded positively for As, Zn, Pb and Cu and negatively for Sr. Results provided a grouping for Mn, Rb and Ti and another for As, Zn and Cu.

Discussion: Iron and Zn contents in sediments were partially considered in the Ria of Arousa [1] and distributions of Cu and Pb tackled [3,4]; they were of the same order of magnitude as those aforementioned in Results. Titanium, V and Rb, were only previously studied in the sediments of the Ria of Vigo [5]. Now the distribution patterns of these ten elements were described and their prevailing origins distinguished: autochthonous (Sr) from biogenic ria processes, and allochtonous from continental (V, Mn, Rb and Ti), associated to the geochemical composition of river basins, and anthropogenic (Pb, Cu, Zn, As) sources.

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References: [1] Prego & Cobelo-García (2003) *Mar Pollut Bull* **46**:1253-1262. [2] De la Calle et al. (2012). *Spectrochim Acta* B **67**:43-49. [3] García et al. (2013) *Sci Mar* **77S1**:91-99. [4] Barciela-Alonso et al. (2004) *Anal Chim Acta* **524**:115-120. [5] Rubio et al. (2000) *Mar Pollut Bull* **40**:968-980.