Trace elements enrichment of coastal sediments near geological complexes: the relevance of defining proxies to element normalization

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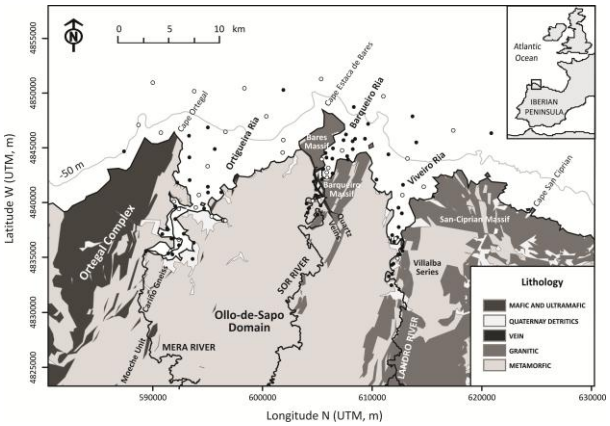
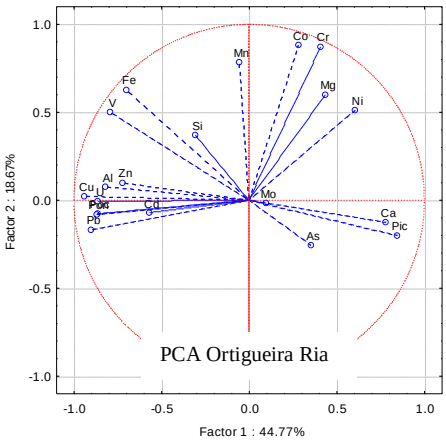
Introduction: Sediment contamination by trace elements (TEs) is estimated by comparison to natural levels at unpolluted reference sites or to Earth' Crust composition [1]. Enrichment factors are calculated by dividing concentrations normalized to Al, Fe, Li or Sc to preindustrial values [2]. However, coastal sediments could be naturally enriched by TEs from nearby geochemical domains inshore [3]. Identification of proxies to select the best normalization element is crucial to distinguish between natural enrichment from anthropogenic derived contamination. This work examine this problematic in coastal sediments nearby the geological complex of Cape Ortegal (Western Cantabrian Sea).

Methods: 103 grab sediments were collected in the Rias of Ortigueira, Barqueiro and Viveiro and their adjacent shelf onboard the R/V *Mytilus* (June 2008), R/V *Lura* and small boats (July 2007).



The top centimeter of each sediment sample was removed and oven dried at 45±5°C; sandy and muddy fractions were separated through a 2 mm sieve, homogenized grounding with an agate mortar; 100 mg of each sample were completely digested with HF and Aqua Regia in closed Teflon bombs at 100° C for 1 h. Major and minor elements were analyzed by flame atomic absorption spectrometry on a Perkin Elmer AA100 with a nitrous oxide-acetylene flame (Al, Si Ca and Mg) and air-acetylene flame (Fe and Mn). Trace elements (V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Pb and U) were determined using a quadrupole ICP-MS (Thermo Elemental, X-Series). The precision and accuracy of the analytical procedures was controlled through CRM analysis (MAG-1 and PACS-2; NRCC). The obtained concentrations were not different from certified values (t-student; α=0.05).

Results and Discussion: Sands are the major components of coastal sediments and fine particles were more abundant in sediments of the innermost parts of the rias. The highest values of Si (29%), Fe (6%) and Mg (13%) were registered in sediments nearby the Cape Ortegal; while Ca increased seaward (up to 33%), and Al landward in the rias (max. 6%). TEs showed concentrations similar to the other rias [4] except near the Ortegal Cape. Enrichment was found in Cr (up to 1700 mg·kg^{-1}), Ni (1400 mg·kg^{-1}), Mn (1200 mg·kg^{-1}) and Co 70 mg·kg^{-1}). Minerals from the Ortegal geological complex appear to influence the sediment composition [3]. A PCA analysis grouped these four elements to Mg. This



association points to Mg as a proxy of the geological complex in coastal sediments. Normalization to Mg is proposed to interpret the natural enrichment of these elements. The remaining TEs were mainly associated with Al. Ratios to Al indicate a moderate contamination of Cu, Pb and Zn in fishing harbour of Viveiro Ria.

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References: [1] Rudnick (2007) *Treatise on Geochemistry*, chap 3.01; [2] Prego et al. (2008) *Mar Pollut Bull* 56:1022-1042; [3] Bernárdez et al. (2012) *Mar Geol* 291-294:63-72; [4] Caetano et al. (2009) [4] Prego and Cobelo-García (2003) *Environ Pollut* 121:425-452.