

The influence of lithology and human pressure on sediment elemental composition: the case of nine estuaries in Portugal

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Introduction: Estuaries are natural repository of suspended sediments derived from rivers, tributaries and human activities. The sediment nature in estuaries reflects mainly the velocity field, which is highly influenced by the morphology associated with the dissipation of fluvial and tidal energies. The lithology of the river drainage basin and the present discharge of urban and industrial effluents, as well as other human activities, influence the elemental composition of surface sediments.

This work reports minor- and trace-element concentrations of surface sediments in nine Portuguese estuaries and examines the dichotomy lithology *versus* human pressure influence.

Methods: Ninety-one surface sediments were collected in the water bodies (according to the WFD) of Minho, Lima, Douro, Vouga, Mondego, Tagus, Sado, Mira and Guadiana estuaries. Sediments were digested according to the methodology described by [1]. Aluminum, Cr, Co, Ni, As, Cu, Zn, Cd, Pb were determined by ICP-MS and Hg by AAS. Organic matter (Corg) was estimated by loss on ignition. Quality control solutions, procedural blanks and certified reference materials were used to ensure accuracy of the obtained data.

Results: Figure 1 shows the median (max., min., and 25th and 75th percentiles) of Ni/Al and Cd/Al ratios in sediments of the nine estuaries. The ratios to Al of Ni, as well as Co and As, were higher in sediments from the southern estuaries. The Cd/Al ratio showed higher variability within estuaries (e.g. Tagus) and among the estuarine systems. The Cr/Al ratios presented similar median values for all the studied estuaries and Pb/Al lower values in Mira and Guadiana. The Zn/Al and Cu/Al ratios were characterized by elevated variability. The highest median Hg/Corg ratios were registered in Tagus and Sado estuaries.

In general, elements (excluding Hg) determined in the sediments from all estuaries were positively correlated with Al (exceptions for As in Guadiana, Ni and Co in Mira and Cu in Sado).

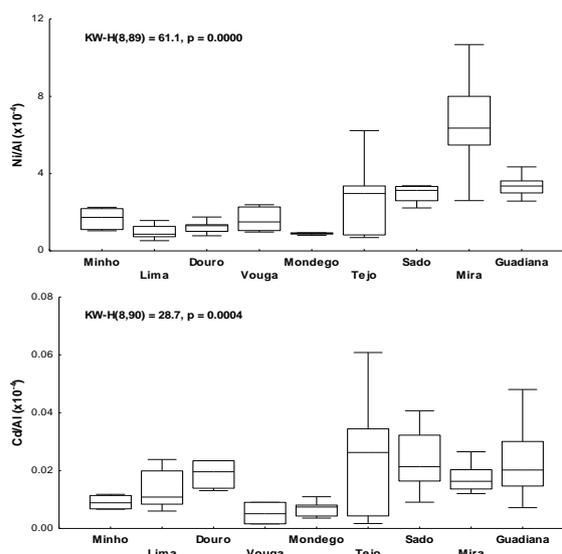


Figure 1. Median, 25th and 75th percentiles, min. and max. of Ni/Al and Cd/Al ratios in sediments from the Minho, Lima, Douro, Vouga, Mondego, Tagus, Sado, Mira and Guadiana estuaries.

Discussion: Elevated Ni, Co and As Al-normalized values in the southern estuaries reflect the influence of the river drainage basin lithologies, mostly crossing the Iberian Pyrite Belt. The distribution of the Cd, Zn, Cu and Hg ratios shows the combination human pressure effect (agriculture, industries, cities) with the natural variability in the estuarine systems. The two effects are mirrored by elevated variability in the Tagus and enhanced median ratios in Douro, two estuaries characterized by highly populated and industrialized areas. The lowest median Pb/Al ratios obtained in the Mira and Guadiana estuaries suggests that their fine-grained fractions may have lower Pb concentrations, reflecting the importance of the lithogenic origin and the low influence of anthropogenic sources.

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References: [1] Caetano et al. (2009) *Mar Chem* 116:36-46;