Assessment of Heavy Metal Contamination in Three Areas of the Portuguese Shelf

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Abstract

Twenty-nine surface samples collected during the PALEO1 cruise (2002) from three areas of the western Portuguese shelf (Ave-Douro, Lis & Mira areas) were analysed for organic carbon, nitrogen, stable N and C isotopes, carbonate, grain size, heavy metals, major and trace elements. These three areas have different oceanographic and onshore source-area characteristics (lithology, climate, industrial activities and human occupation). Comparison of the total metal contents does not allow a correct evaluation of the presence or absence of contamination. The variability of sediment geochemistry is complicated by the interdependencies between elements and sediment grain size, mineralogy and organic carbon contents. A sequential approach for the assessment of heavy metals contamination based on five commonly used evaluation procedures is proposed. The combined application of the different methods helps compensate for parameter interdependencies, facilitates the comparison of geographically distant areas and strengthens the results individually obtained.

Comparison with the Sediment Quality Guidelines indicates good environmental quality for Cr, Cu, Ni, Pb and Zn. A large archive dataset from the 1970's allows, through the application of the Gradient Method (GM) and the definition of Regional Geochemical Baselines (RGB), a comparison with the 2002 samples regarding different environmental settings and changes over time. High metal loadings relatively to Al (a proxy for the fine fraction) are found in areas draining metal-enriched formations, such as the Algarve coast and the Mira area. GM results indicate increased metal loading in the 2002 samples collected in the Ave-Douro and Lis areas, probably reflecting increased anthropogenic influence in the source areas. A few surface samples from 2002 are slightly enriched relative Al, and plot above the 95% predicted confidence limit of the RGBs obtained for the western shelf. Pb has decreased since the 1970's, coinciding with use of unleaded fuel.

Influences upon sediment accumulation have been interpreted from the temporal distribution of Al, Ca, Fe, Mg, Mn, S, Li, Sc, Sr, Cr, Cu, Ni, Pb, Zn, Hg and the fine fraction contents at selected sites. The chronology of box cores was defined using the excess ^{210}Pb and ^{226}Ra activities. These parameters are associated with detrital, biogenic, diagenetic and anthropogenic factors, using factor analysis. Historical trends in the Ave-Douro area reveal a change from predominately detrital to biogenic influences since the 1940's. Bioturbation and hydrodynamic processes occurring at water-depths shallower than 100 m are also responsible for dispersion and dilution of contaminated marine sediments, reducing the anthropogenic signal. The anthropogenic factor dominates in the Lis area since the 1960's, represented by the contents of Hg, Pb and Zn that have varied in connection with the combustion of leaded gasoline and industrial activity in general. Despite the relatively low total Hg content, Hg presents the highest level of enrichment relative to Al ($2 < EF_{Hg} < 3$), followed by Pb. The relative low discharge of the Lis River suggests that atmospheric supply may have importance as a source for Hg and Pb in shelf sediments. In the Mira area vertical trends are largely explained by diagenetic modifications, especially of Mn, Fe and S, rather than by the detrital and biogenic factors.

Despite the high-energy conditions and the generally sandy character of the Portuguese shelf environment, it is possible to identify slight anthropogenic enrichments in mud accumulation areas of the Ave-Douro and Lis areas.

Keywords: Portuguese shelf, marine sediments, geochemistry, heavy metals, geochemical normalisation, regional background, Gradient Method, sediment quality guidelines, enrichment factors, ^{210}Pb isotopes