Comparing spatial and temporal changes in metal enrichment (Cr, Ni, Pb and Zn) on the Portuguese shelf since the 1970s

Mário Mil-Homens[1], Rodney Stevens[2], Ingemar Cato[3], Fátima Abrantes[4]

[1]Instituto Português do Mar e da Atmosfera, I.P., Divisão de Oceanografia Ambiental e Bioprospeção, Avenida de Brasília, 1449-006 Lisboa, Portugal

[2]University of Gothenburg, Department of Earth Sciences, P.O. Box 460, SE-405 30 Gothenburg, Sweden

[3]Geological Survey of Sweden, Division of Geophysics and Marine Geology, P.O. Box 670, SE-75 128 Uppsala, Sweden

[4]Instituto Português do Mar e da Atmosfera, I.P., Divisão de Geologia Marinha e Georrecursos, Avenida de Brasília, 1449-006 Lisboa, Portugal

Phone: +351-(21)- 3027039

E-mail: mario.milhomens@ipma.pt

Introduction: Comparison between an archive dataset (1977ArchDS), collected during the 1970s, and samples taken during the PALEO1 cruise (2002) enabled evaluation of large-scale and long-term spatiotemporal changes in Al and metals (Cr, Ni, Pb, Zn) in surface sediments (<2 mm fraction) in 3 areas of the Portuguese shelf (PS), using the so-called Gradient Method (GM). The GM [1] is a graphic approach that attempts to compensate for natural variability in sediment grain size and organic matter by considering the gradient (slope) between a given metal and contents of organic matter, or a reference element (e.g. Al) used as a proxy for fine-grained particles. To date, the GM has been tested mainly with fine-grained coastal marine and estuarine sediments. In the present work, we apply GM to the mainly sandy sediments of the PS. Our main aim is to assess contamination in 3 areas of the PS by characterizing and interpreting spatial and temporal changes of Cr, Ni, Pb and Zn.

Methods: From the 1977ArchDS (155 samples collected during several oceanographic cruises between 1974 and 1977 using Van Veen and Shipeck grab samplers), 3 western shelf areas (Ave-Douro (A-D) n=43, the Lis (L) n=34 and the Mira (M) n=43) were selected that overlapped with the PALEO1 cruise. A 4th area covered by the 1977 dataset was selected along the southern shelf, offshore the Algarve (Alg77) region (n=35). The second set of samples was taken during the PALEO1 cruise, when 29 box-cores were collected in the three western areas (A-D n=9, L n=9 and the M n=11). Elemental levels (Al, Cr, Ni, Pb & Zn) for the two separate sampling periods were determined by ICP-OES after total decomposition with HCl, HNO_3, $HClO_4$ and HF of 0.2 g homogenized sediment. Quality control was assessed by analysis of blanks, duplicates and standard reference materials.

Results: Population differences in metal contents between study areas and periods of sample collection were tested using one-way ANOVA and Kruskal–Wallis test for normally and non-normally distributed metals, respectively. Significant differences in metal contents ($p<0.05$) among the 4 study areas was determined using the Dunnett's T3 post-hoc tests. Metal contents in the Alg77 study area are significantly different from the other 3 areas located on the western shelf. For the 2002 dataset, the results indicate that A-D is significantly different than M for all metals, while L is significantly different than A-D for Pb and Zn. Studied metals in the L area are not significantly different than M. Regarding the 2 distinct sampling periods; Cr, Ni and Zn levels are significantly different between datasets in the western areas, while Pb is not significantly different in the A-D and L.

Discussion: The Alg and M areas had higher metal loads relative to Al, plausibly explained by these lying offshore of metal-rich geological formations of the Iberian Pyrite Belt. These enrichments reflect a natural source, amplified by the intense mining activity that has occurred in the past. The metal to Al gradients for Cr, Ni and Zn increased in the L and A-D shelf areas during the 25-year sampling interval. This may reflect enhanced anthropogenic input, despite improved treatment of industrial and domestic effluents in these highly industrialized and urbanized more northern coastal regions. In 2002, the A-D samples had even steeper Cr, Ni and Zn gradients than those recorded in the L samples, probably reflecting an important contribution from the Douro River. Nevertheless, 2002 gradients of Pb to Al contents had become less pronounced in both the L and A-D shelf areas, which may reflect a decrease in the use of leaded fuel in motor vehicles, which became totally forbidden at the end of the 1990s. For quality evaluation of marine sediments, especially when using total metal contents, this study shows the importance of considering all the sources of metal loading and the natural grain-size and composition variability since these features are crucially influential on the metal contents and allow a more holistic perspective.

References: [1] Cato (1989) *ICES* **2**:88–108.