

BASELINE CONTENTS OF Cr, Ni, Pb AND Zn IN THE PORTUGUESE SHELF SEDIMENTS

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Considering the differences in the oceanographic and sedimentologic settings between the western shelf segment and the southern Algarve coast of Portugal, the trace metal (Cr, Ni, Pb and Zn) contents from the DGM-INETI archive dataset (composed by 267 surface sediment samples collected during the seventies and eighties) were used to assess regional geochemical variations through the establishment of regional geochemical baselines (RGB). Thirty-two surface samples recovered during the PALEO1 cruise (2002) from four distinct areas of the Portuguese shelf near river mouths, with potential contaminant risks, are superimposed with RGB models to identify and compare possible metal enrichments relative to the natural background population. The relative quantification of these metal enrichments is assessed through the determination of metal Enrichment Factors (EFs) relative to Al.

RGB are defined for both shelf segments using the aluminium as a reference element. Changes in sediment grain-size, mineralogical composition and organic carbon content influence the total trace metal concentrations in sediments. High metal concentrations may be due to abundant clay minerals or derived from weathering of natural, metal enriched rock formations. Therefore, high total metal content does not necessarily indicate contamination. The assessment of the anthropogenic contribution to sediments must be accompanied by the estimation of metal contribution by natural processes. In order to compensate for the natural variability of sediments and to detect and quantify anthropogenic enrichments, several normalisation procedures have been developed. Mathematical normalisation of metal concentrations is often done in relation to a reference element, such as Al and Li. These normaliser elements are tracers of the natural, metal-binding phases and are ideally not influenced by anthropogenic inputs. Furthermore, their application as a normalising factor implies a strong correlation to the fine-grained sediment fraction and naturally occurring metals. If these relationships are established, anthropogenic metal enrichments can be identified by deviations from the trend defined between the metal contents and the normalising elements. Scatter plots of metals against the reference element for uncontaminated samples within a geographically coherent area allow the definition of regression lines representing the regional geochemical baseline (RGB). The natural population can be defined by the 95% confidence interval of the plotted population, while the sampling points that fall above the upper 95% confidence limit are considered to belong to a metal-enriched population.

The obtained results demonstrate the importance of defining the background variation of the natural metal concentrations in specific areas. Considered against the RGB for the Algarve coast, 2002 samples generally have trace metal contents consistent with or lower than the background sediments. However, this RGB is influenced by the source-area lithology (metal enriched Iberian Pyrite Belt formations), and the baseline population is relatively metal enriched. In comparison, the western shelf dataset has lower, natural concentrations (Fig. 1).

Metal enrichments associated with anthropogenic enrichments are identified in the 3 samples collected nearby the Tejo River. Enrichment Factors (EF) obtained from the RGB indicates values close to one for the majority of the elements, which suggests mainly a natural origin. The highest metal EF relative to Al is observed in the Tejo pro-delta samples (e.g. $2 < EF_{Pb} < 3$; $3 < EF_{Zn} < 4$). But the Mira area also shows EF values for Cr and Zn between 2 and 3 in other words, a slight enrichment. This additional enrichment may be explained by either anthropogenic sources of pollution or by the natural supply of metal-bearing minerals, from the source area.

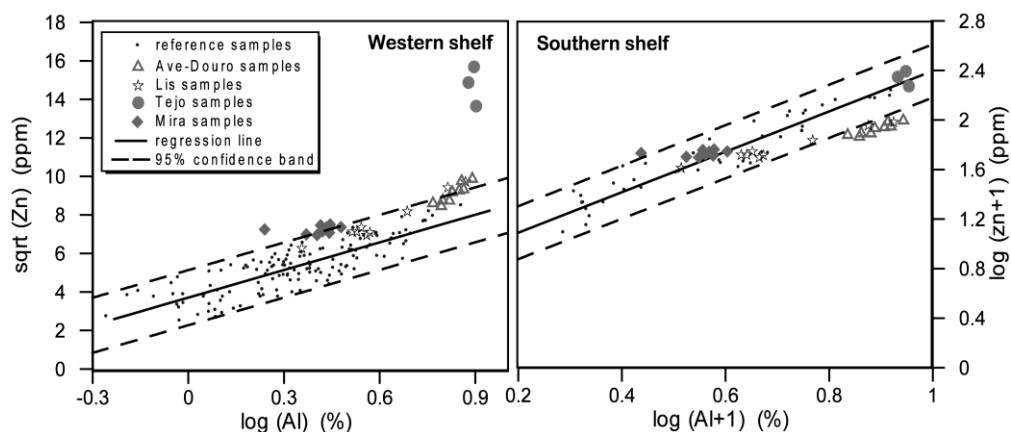


Fig. 1 - Scatter plots showing the relationships among Zn concentrations (ppm) and Al (%) in surface sediments from the western Portuguese shelf and from the southern shelf. PALEO1 samples (large symbols) are plotted against the archive data included in the definition of the RGB. Sample sites that fall above the upper 95% confidence limit are considered enriched.

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