Trace element regressions in coastal sediments from the Tuscany Region (Italy)

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Introduction: Traditional techniques applied to sediment characterizations are based on the concentration limit approach, a comparison of pollutants levels measured in sediments with the legislative limits. In Italy results obtained from characterizations are compared to the general reference levels of pollution defined by the Central Institute of Marine Applied Research [1]. The application of this approach is affected by severe limitations. Due to these problems, in order to evaluate trace element enrichments in marine ecosystems, different normalizations methods based on chemical approaches by representative elements [2] have been proposed by the literature [2][3]. The use of normalizing elements allowed to notably reduce environmental variables of interest excluding grain-size and total organic carbon data. The rationale on the basis of which these techniques are developed is represented by the fact that some elements, such as Al and Fe, evidence a geological origin linked to feldspars and a fixed local-based correlation to other trace elements. In fact, these elements represent aluminosilicates, the main group of minerals generally found in finer sediment fractions, are considered to normalize both for grain size and mineralogical variability [4-5] and are supposed to have negligible origin from human inputs. The aim of this work was to characterize in not polluted areas, relationships among normalized and normalizing elements (Al, Fe) proposed by the literature as tracers for the natural levels of alluminosilicates. This study defines natural trends in studied areas and could represents an useful tool for environmental monitoring in polluted sites.

Methods: Superficial sediments samples (0-10 cm) were collected using an HDPE corer from three areas of the Tuscany coast (Carbonifera, Punta Ala, and Follonica). Ecotoxicological tests on *Vibrio fisheri*, *Dunaliella tertiolecta*, (elutriates), and *Corophium orientale* (whole sediment) were performed according to Microtox® procedures and national guidelines to determine sediment toxicity on marine species. Sediments that do not evidenced toxicity (n = 60) were selected for this study. Trace element levels (Al, Fe, Ba, As, Cd, Cr, Cu, Pb, Zn, Hg, Ni, V), expressed as mg kg^{-1} dry weight were measured according to US-EPA methods. Statistical univariate and multivariate analyses were performed using the GraphPad Prism version 5.00 for Windows (GraphPad Software, San Diego California USA) and the Primer-E v6.0 (Plymouth Marine Laboratory, UK) software packages according to bibliography [6].

Results and discussion: Coastal marine sediments evidence wide fluctuations of considered trace elements. Comparing measured levels to values defined by the Italian guidelines [1] for marine sediments, As levels exceeded minimum level indicating sediment pollution for this element (32 $mgkg^{-1}$ d.w.). On the contrary Cr (50 $mgkg^{-1}$ d.w.), Cu (15 $mgkg^{-1}$ d.w.), Pb (25 $mgkg^{-1}$ d.w.), Zn (50 $mgkg^{-1}$ d.w.), Hg (0.2 $mgkg^{-1}$ d.w.) and Ni (32 $mgkg^{-1}$ d.w.) exceeded maximum value referred to presumed natural concentrations in Italian sediments. Traditional techniques based on the concentration limit approach evidenced some severe limitations in the definition of critical areas. Concerning As, the application of the concentration limit approach could determine an excess of observed critical areas. This occurrence is evidenced by the fact that sampling sites located far from coastal pollution sources and characterized by no ecotoxicological effects on tested species such as those selected in this study, exceeded maximum allowed levels.

Multi-element normalizations developed using local regressions could represent an useful tool which could allow to avoid possible misleading due to the application of traditional techniques in marine areas affected by geological anomalies, such Tuscany is.

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