Comparing sediment heavy metal concentrations in Italian harbors with the Environmental Quality Standards

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Introduction: The Environmental Quality Standards (EQSs) are the tools to define the status of surface water bodies, according to the Water Framework Directive. While the EQSs for assessing the chemical status of waters were established at a European level, member states defined those of specific substances in sediments. In Italy, the EQSs for marine coastal and transitional environment sediments were determined based on a chemical-physical and ecotoxicological approach. Up to now, these threshold values have been considered not applicable in areas of high environmental criticality, such as harbors.

This study aimed to verify the applicability of the EQSs of heavy metals for defining the chemical status in Italian harbors and identifying the main pollutants of sediments in these areas.

Methods: A dataset was arranged with the concentrations of the same heavy metals (As, Cd, Cr, Hg, Ni, and Pb) recorded in 34 Italian harbors having a corresponding EQS in the national legislation for a total of 3187 stations and 7036 samples. The harbors have different shapes, sizes, sediment textures, sediment geochemistry, and degree of contamination. Different institutions and authorities acquired data between 2001 and 2013 during several environmental characterizations. The total data distribution of each chemical parameter was studied by applying Johnson's method [1] using the R 3.6.2 software, SuppDists package. The output of these analyses was a control chart for each metal with a normalized curve of concentration data, reporting the Overall Median (OM), the Upper Bound (UB) of the whole distribution, and the median concentrations of each harbor. Moreover, the position of the EQS (defined by the percentile) was highlighted on the curve (Fig. 1).

Results: The positioning of the EQS on Johnson's curve (EQS percentile) with respect to the Overall Median (OM) and the Upper Bound (UB) of data distribution served to recognize the capability of this value to discriminate different chemical statuses (Fig. 1, Tab. 1). The EQSs resulted for all metals coinciding or very close to the OM, in the range between 46 and 62 percentiles (Tab. 1).

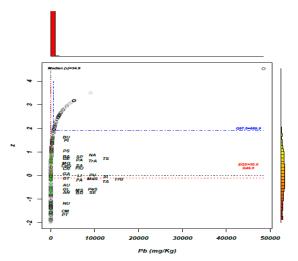


Fig. 1: Johnson's control chart of Pb (Black line: OM; blue line: UB; red line: EQS). The medians of harbors (abbreviated names) are also reported.

The rate UB/EQS, which quantified to what extent concentrations exceeded the EQSs, was very high for Cd, Hg, and Pb (Tab. 1).

Tab. 1: Positioning the EQSs in the whole data distribution.

	As	Cd	Cr	Hg	Ni	Pb
EQS (mg kg ⁻¹)	12.0	0.3	50.0	0.3	30.0	30.0
EQS percentile	50.0	62.0	54.4	51.0	46.1	46.0
OM (mg kg ⁻¹)	12.0	0.2	46.5	0.29	32.6	34.9
UB (mg kg ⁻¹)	54.2	7.4	212.5	6.8	95.3	670.0
UB/EQS	4.5	24.6	4.3	22.7	3.2	22.3

Discussion: The positioning of the EQSs in the comprehensive data distribution pointed to the suitability of the EQSs to be successfully applied on harbor sediments to define the chemical status. It also showed that, in many observations, all metals largely exceeded the EQSs, pointing to the widespread contamination of metals. Among these, Cd, Hg, and Pb were identified as the heavy metals mostly contributing to the contamination of the Italian harbors.

References: [1] Johnson (1949) *Biometrika* **36**: 149-176.