Trace elements and application of the environmental quality standards (WFD) in the Marano-Grado Lagoon (North Adriatic Sea, Italy)

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Introduction: The European water framework directive (WFD 2000/60/EC) introduces the concept of ecological quality status based upon biological, hydromorphological and physico-chemical elements. Sediments are considered to be very important in assessment of anthropogenic impacts to coastal and estuarine environment [1]. Under the WFD the investigation of priority substances has the purposes to monitor the progressive reduction in the contamination and to demonstrate conditions of no deterioration in sediment quality [2].

The Marano-Grado Lagoon is an important natural site located in the North Adriatic Sea (Italy). It undergoes the Habitat Directive and has been identified among the sites of Community importance (SCIs - IT3320037). The presence of several economic and industrial activities poses a risk for the environmental quality of this area.

Trace elements are recognized to be an important class of compounds which may have both a pristine or anthropogenic origin. Several factors such as redox conditions, OM contents and association onto the surface of minerals, like clay minerals, Fe and Mn oxi-hydroxides influence their behaviour and, finally, the possible ecotoxicological effects.

In the Marano-Grado Lagoon system there is a lack of comprehensive study for the whole basin. In fact, only the distribution of Hg and trace elements in a limited area have been previously investigated [3,4].

The aim of this work was to (1) characterize the distribution and concentration of selected trace metals (Al, As, Cr, Cu, Fe, Hg, Ni, Pb, V and Zn), (2) apply the EQSs set by the WFD and (3) to hypothesize their possible source.

Methods: The sampling program undertaken in autumn 2009 in 24 sites. Surface sediment samples were collected using an automatic KC haps bottom corer. The topmost part of sediment (0-5 cm) was selected for the analyses. A granulometer laser (Malvern Mastersizer 2000) was used for grain-size determination, whereas TOC and TN were determined by Elemental Analyzer.

Heavy metals determination was performed after decomposition with HNO_3 -HClO₄ (5:1) by means of AAS spectrometry.

Results: The whole lagoon basin is strongly contaminated by the presence of Hg $(4.0\pm2.2 \text{ mg Kg}^{-1})$ due to historical input [4,5] with a positive gradient moving eastward. The other elements are characterized by an homogenous spatial distribution; however, Cr and Zn showed enrichments in sites where scarce water circulation and higher freshwater inputs occur. All the elements, except Hg, are significantly correlated with best proxies elements (Al and Fe), thus testifying their probably natural origin.

Application of the EQSs confirms that Hg is the main concern for lagoon quality status. Nevertheless, also Ni always exceeds recommended values and some hot spots for Cr were also found.

Discussion: Trace elements of Marano-Grado Lagoon are found to be high correlated with proxies elements and show a similar pattern suggesting a common sources and/or similar enrichment mechanisms.

The application of EQSs clearly indicates that Hg represents a potential hazard for the whole ecosystem. On the other hand, no evidence of poor biological quality has been pointed out during the monitoring program. Further investigation (i.e., speciation, bioaccumulation) will be necessary for a better understanding of the Hg behaviour. Ni values are probably linked to natural origin as suggested by the significant correlation with Fe (r=0.8331,p<0.01) where chemical species with FeS-FeS₂ should prevail.

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