Sediment monitoring of PAHs for the European Water Framework Directive: the case of the Marano and Grado Lagoon (Italy)

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Introduction: Aiming to monitor the quality of the water, the EU introduced the Water Framework Directive (WFD) with the final goal to achieve a "good ecological and chemical status" by the year 2015 [1]. Under the WFD the investigation of priority substances has the purposes to monitor the reduction in the contamination and to demonstrate conditions of no deterioration in sediment quality [2]. Due to their shallow depth, poor circulation and water renewal, lagoons represent systems with a high degree of vulnerability. Within these environment sediments act as the main depot and secondary source for the hazardous compounds.

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.

Polycyclic aromatic hydrocarbons (PAH) are ubiquitously distributed contaminants. Previous work relate to origin and distribution of PAH in the nearby Gulf of Trieste showed values exceeding EQSs set by WFD [3, 4], whereas the lagoon system have never been investigated.

The present study focuses on the contents, distribution, origin and application of the EQSs, suggested in the WFD, in the Marano-Grado Lagoon.

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 as reported by [5]. Determination of selected PAH was performed with HPLC coupled with fluorescence detection (FLD).

Results: 16 PAHs indicated as priority pollutants by US EPA were considered.

Total PAH concentration varies from not detected to 1736 ng g⁻¹ (dry weight basis). Due to this the majority of samples can be classified as negligible or

fairly contaminated (total PAH<500 ng g⁻¹), whereas relatively highly contaminated samples were found in two sites located in the central sector of the lagoon and in the Isonzo River mouth.

Among the individual PAH compounds the dominant are Fluo, Phe, Chr and Py. The exception was showed for the highly polluted sites, where B[a]Py and B[b]Fluo were present in the same concentration range as the previously mentioned dominant PAH.

No significant correlation with both TOC and grain size (clay and silt) was found.

PAH-groups profile, according to their number of aromatic rings (2-3, 4, 5 and 6), showed a higher proportion of 4-ring PAH (45%) followed by 5-ring PAH (34%).

Specific ratios were applied in order to determine the possible source (pyrogenic vs petrogenic). Phe/Ant ratio demonstrates the classical value of a pyrogenic source (<<10). This hypothesis is supported also by Fluo/Pyr and Fluo/(Fluo+Pyr) ratios.

EQS proposed as Σ PAH is 800 ng g⁻¹. This value is only exceeded in two sites. However, some hot spots, especially related to Fluo contents, have been highlighted especially where the scarce water circulation occurs.

Discussion: Levels of total PAH were found to be almost very low, thus suggesting a good quality state, and prevalently of pyrolitic origin. For 8 PAH compounds for which sediment quality guidelines exist, only 3 sites exceed the recommended values. This suggest that data related to both water column and biota should be carefully considered in order to fully define the environmental status of these water bodies.

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