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Spatial patterns of metals, PCDDs/Fs, PCBs, PBDEs and chemical status of sediments from a coastal lagoon (Pialassa Baiona, NW Adriatic, Italy)

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ABSTRACT

The European Water Framework Directive (WFD) establishes a framework for the protection and improvement of all water bodies including transitional waters; its final objective is to achieve at least 'good status' by 2015. In the present work, a hierarchical sampling design was applied to analyze the influence of anthropogenic inputs on the spatial distribution of metals, polychlorinated dibenzo-p-dioxins (PCDDs) dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in sediment at four areas in Pialassa Baiona coastal lagoon. In order to assess the chemical status, levels of priority substances and other pollutants were compared with the recently developed national Environmental Quality Standards (EQS) and site specific background levels for metals. Levels of mercury and PCBs were particularly high and exceeded their national EQS values at all sampled areas, thus not contributing to the achievement of a good chemical status of this transitional water body according to the WFD classification.

In Europe, water protection from chemical pollution in continental, marine and transitional water bodies is based on regular monitoring of a selected list of dangerous substances in different matrices (e.g., water, sediment and biota). In this respect, one of the objectives of the Water Framework Directive (WFD, 2000/60/EC; European Commission, 2000) is to achieve a good chemical status for all European waters by 2015. The WFD assessment of the chemical status of a water body is based, together with the background levels used as reference conditions, on compliance with Environmental Quality Standards (EQS) which, if met, allow the chemical status of the water body to be described as 'good'. To supplement the WFD, a new amending directive has been approved (Directive 2013/39/EU; European Commission, 2013) to establish EQS limits for 33 priority substances and 8 other pollutants for water and biota, only, but the Member States (MS) should monitor these substances in the sediment and establish their national EQS. According to these Directives, Italy established its own sediment EQS for priority and non-priority substances for the classification of the 'chemical status' of the sediment in marine and transitional water bodies by "the Ministerial Decree November 8, 2010, No. 260 (D.M. 260/2010)".

In this study, a spatial survey was conducted on metal and organic contaminant levels including mercury, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), and polybrominated diphenyl ethers (PBDEs) in sediments at multiple areas within a transitional water body, the Pialassa Baiona coastal lagoon. Chemical data were analyzed with respect to the existing national EQS, when available,

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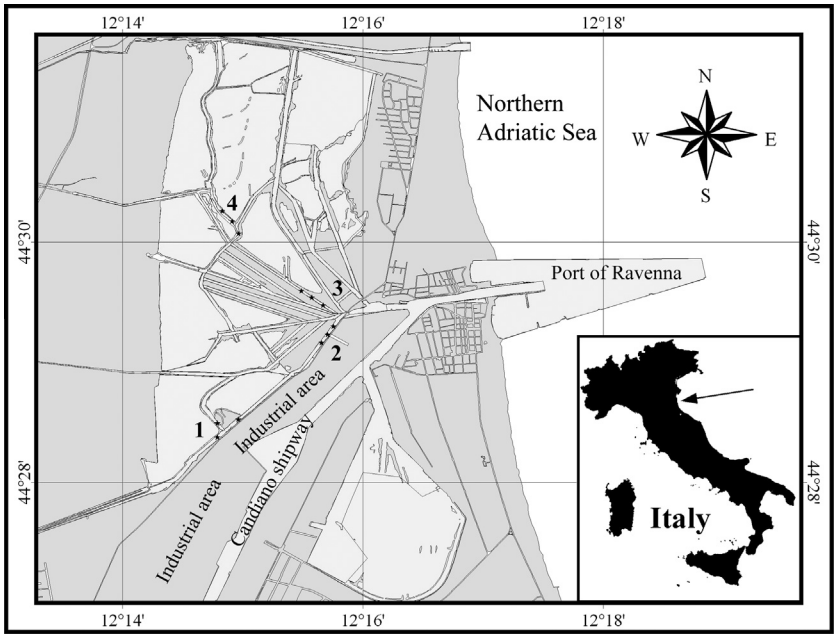

Fig. 1. Map of Pialassa Baiona lagoon, showing sampling sites (stars) within areas labeled by numbers (Geographic coordinates, European Datum 1950).

and to the natural background levels used as reference conditions for metals. Overall, there is still very little understanding of the spatial patterns of Persistent Organic Pollutants (POPs) and new emergent POPs contamination in Pialassa Baiona ecosystem and a need to understand the extent of the potential problem, to identify potential sources and areas of concern for monitoring purposes. Thus, in the light of above, and due to the intense anthropic forcing in this area, this study may help to link studied pollutants occurrence and levels with their potential sources, with implications for the monitoring of sediment contamination in this transitional water body, in accordance with the WFD.

Pialassa Baiona is a eutrophic micro-tidal coastal lagoon in Italy, which forms part of the Natura 2000 European network for nature conservation (Fig. 1). The area is a Ramsar wetland of international importance, and it is included in the Special Bird Protection Areas (European Directive 79/409/EEC) and in the Special Areas of Conservation (European Directive 92/43/EEC). Natural and man-made changes over time have led to the existing physiographical features comprised of shallow bodies of saline, brackish or fresh water wetlands, isolated or semi-isolated by levees and crossed by a network of artificial channels dug in 1850. The inner channels converge into a main channel connected to the sea through the shipway channel. Salinity in the lagoon (25–35 psu) is mainly controlled by water exchange with the Adriatic Sea through this channel. The average depth varies from 0.5 m in the shallowest areas to 3 m in the channels with a tidal range variable from 0.3 to 1 m, excluding extreme events. On average, the water covers an area of 10 km^2, and the total water volume is approximately 10^7 m^3 with an estimated turnover of 3 days. The lagoon receives limited freshwater inputs from five channels (Fig. 1) draining a watershed of 264 km^2, including urban, industrial and agricultural areas (Ponti et al., 2005). The lagoon also receives discharges from urban and industrial sewage treatment plants, and from two thermal power plants conveyed into the southern channel. The main freshwater and nutrient inputs are due to runoff from the watershed and to the sewage inputs with similar mean flows of about 10^3 m^3 d^{-1}, and to cooling waters coming from two thermal power plants accounting for about 10^6 m^3 d^{-1} (Ponti et al., 2005). Phytoplankton blooms and intense growth of seaweeds (*Ulva* sp., *Enteromorpha* sp., *Gracilaria* sp.) were frequently observed during the summer, especially in the southern part (Guerra et al., 2013; Sfriso et al., 2012), and dystrophic crises were often recorded in the summer (Ponti and Abbiati, 2004).

Main industries bordering the southern edge of the lagoon include plastic polymer-producing factories (e.g. polyvinyl acetate), styrene polymers, and polyvinyl chloride (PVC)), a steel metallurgy plant (chemical pickling, cold rolling, annealing, galvanizing, and pre-painting of steel coils), carbon black manufacturing, an oil seed processing plant, and storage systems for petroleum products, fertilizers, and grains. Environmental contamination and human health concerns in Pialassa Baiona lagoon have been pressing in recent decades with the discovery of higher than expected concentrations of mercury in sediments and mussels (Cattani et al., 1999; Fabbri et al., 2001a). Sediment contamination in Pialassa Baiona has also been an issue in recent years with the need to widen and deepen natural channels to increase tidal circulation, water quality and biological diversity, and hence dredge and appropriately dispose of sediments that may potentially be contaminated (Guerra et al., 2007, 2009).

In the Pialassa Baiona lagoon, spatial distribution of contaminants is affected by the location of anthropogenic inputs (Fabbri et al., 2003; Guerra, 2012), the hydrodynamic of the system and the heterogeneity of the physical and chemical variables (Trombini et al., 2003), which could vary at a wide range of spatial scales. Hence, a hierarchical sampling design was applied to analyze the spatial distribution of metals, PCDD/Fs, PCBs and PBDEs. Four channel areas (labeled 1–4) were selected. Areas 1 and 2 were located in the southern edge of the lagoon, in the channel that receives industrial/municipal wastewater discharges, with area 1 being the closest to the point of inputs. Areas 3 and 4 were located northward, far from the industrial discharges. On the other hand, areas 2 and 3 were near the seaward channels confluence and more directly connected to the sea through the shipway channel, in comparison to areas 1 and 3. Three sites, spaced 100–300 m apart, were randomly selected for each area and three sediment replicate samples (top 5 cm) were collected at each site by means of a Wildco® box corer. Samples were removed from the top of each core using a stainless steel spoon to avoid contamination and then distributed into separate pre-labeled, acid-washed and solvent-rinsed glass jars with Teflon-lined caps for chemical anal-