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Sediment quality assessment in a coastal lagoon (Ravenna, NE Italy) based on SEM-AVS and sequential extraction procedure

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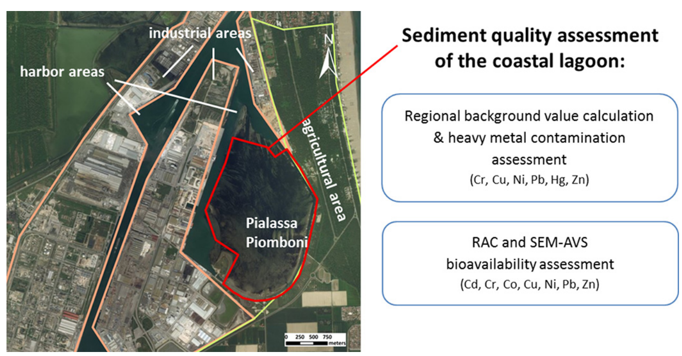
HIGHLIGHTS

- Sediment quality concerning trace metals in a coastal lagoon was assessed.
- An Enrichment Factor for Cr, Cu, Ni, Pb, Hg, Zn was determined.
- Trace metal bioavailability was estimated through RAC and SEM-AVS methods.
- Hg showed to be anthropogenically enriched in the entire study area.
- Zn was the most potentially bioavailable metal in the lagoon.

GRAPHICAL ABSTRACT



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ABSTRACT

Sediments from the Pialassa Piomboni coastal lagoon (NE Italy) were studied to assess the degree of contamination and ecological risk related to trace metals by combining a geochemical characterization of bulk sediments with the assessment of the bioavailable forms of trace metals. With this purpose, sediment contamination (Cd, Cu, Hg, Ni, Pb, and Zn) was assessed by Enrichment Factors (EFs), and potential bioavailability by the Simultaneously Extracted Metals and Acid Volatile Sulfides (SEM-AVS) approach (Cd, Cu, Ni, Pb, and Zn), and by Sequential Extraction Procedure (Co, Cr, Cu, Ni, Pb, and Zn). On average, Cr and Ni exhibited no contamination (EF ≤1.5), and a predominance in the residual fraction of the sediment, indicating natural origin for these metals. Cu, Pb and Zn displayed a local contamination, which resulted in a higher proportion of Cu bound to the reducible and oxidizable fractions (~30% and ~40% as median, respectively), and Pb mostly associated with the reducible phase (~60% as median). Hence, Cu and Pb could be mobilized when environmental conditions become reducing or oxidizing. Zn resulted mainly partitioned into the reducible and residual fractions (~50% as median, in both fractions). The Risk Assessment Code (RAC) indicated that approximately 30% of samples had >10% of total Zn weakly bound to the sediment, suggesting a medium risk of exposure for aquatic organisms. RAC results were consistent with the $\sum$SEM-AVS findings, pointing to possible adverse effects for aquatic biota in ~30% of samples, with Zn mostly accounting for the total metal bioavailability. Hg showed a moderate to very severe enrichment, indicating that a substantial amount of this metal derives from anthropogenic sources and may pose adverse effects on the aquatic biota of the Pialassa Piomboni lagoon.

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1. Introduction

Coastal lagoons are shallow water bodies located between land and sea, characterized by high fluctuations of physical, chemical and biological properties (Pérez-Ruzafa et al., 2013). The dynamics and fragility of these environments are often threatened by human activities (e.g. harbor and industrial activities, fishing, and tourism) mostly concentrated in coastal areas, which can affect both water and sediment quality. Sediments are the compartment of major concern, since they can be an important sink for potentially harmful inorganic and organic contaminants, acting as good scavengers and decreasing their bioavailability (Jonathan et al., 2011). They can also act as a secondary source of contamination when environmental conditions change (e.g. pH, redox potential), releasing contaminants in the water column. Trace metals are included in environmental monitoring programs given their bioaccumulation and toxic effects on aquatic organisms (Roussiez et al., 2011; Arfaeinia et al., 2016). Trace metals can occur in sediments in various forms, in association with different geochemical phases that determine their mobility, bioavailability and potential toxicity (Yu et al., 2001). Therefore, knowing their total content in the sediment alone is not exhaustive to assess their potential ecological risk for aquatic organisms (Baran and Tarnawski, 2015; Botwe et al., 2017). Analysis of Simultaneously Extracted Metals (SEM) coupled with the Acid-Volatile Sulfides (AVS) represent a useful approach to determine the potential bioavailability of trace metals. Sulfide minerals bind with trace metals under anoxic conditions, limiting their bioavailability in porewaters (Li et al., 2014). Based on the SEM-AVS model, the mobility of divalent metals (Cd, Cu, Ni, Pb and Zn) is expected to increase if total SEM exceeds AVS content (Zhang et al., 2014). A broader vision of the metal mobility is further given by the analysis of the metal fractionation through a Sequential Extraction Procedure (SEP). This methodology enables the determination of trace metals distribution within different sediment fractions, their mobility and consequent bioavailability.

The aim of this study was to evaluate the sediment quality of the Pialassa Piomboni, a coastal lagoon located in the south-eastern part of the Po delta area (northern Italy) in close connection with the Ravenna harbor, one of the largest commercial harbors in Italy. To this end, the geochemical composition of surficial sediments have been determined to quantify the level of contamination, and SEM-AVS and the SEP analyses have been accomplished to quantify and explain the spatial distribution, bioavailability and potential ecological risk of trace metals (Cd, Cr, Cu, Ni, Pb, Zn).

2. Materials and methods

2.1. Study area

The Pialassa Piomboni lagoon is part of a wetland system formed over the last 250 years together with the northern lagoon area, the Pialassa Baiona, as a result of the dynamic evolution of the Po delta system. It is located 8 km North-East of the city of Ravenna (Fig. 1). The Pialassa Piomboni has a significant relevance from an ecological point of view. It was designated as a Site of Community Importance (SCI) and Special Protection Area (SPA), according to Habitats Directive 92/43/CEE, and it belongs to the Natura 2000 network. However, its western and northern sectors are in connection with the Ravenna harbor area, also known as the Candiano Channel directly flowing in the Adriatic Sea, and are affected by intense and diversified human activities.

The current morphology of the Pialassa Piomboni is the result of both natural and human actions aimed at maintaining the hydrological characteristics of the area (Airoldi et al., 2016). The water depth is shallow in the eastern, central and southern areas (maximum 1.50 m), whereas in the western part and in connection with the main harbor channel, water depth is >10 m. Water circulation is dominated by the tidal flows, which guarantee a natural water exchange, and also by freshwater inputs coming from a number of artificial channels. The most important freshwater input is the San Vitale draining pump, situated in the southern part of the Pialassa Piomboni, which collects municipal wastewaters and agricultural effluents (Farina et al., 1994; Soprani and Giaquinta, 1992). Water quality in this area is poor because of the high amounts of organic compounds and chemical and biological contaminants released by human and harbor activities that occur along the perimeter of the study area (Bandini, 1996; Soprani and Giaquinta, 1992; Migani et al., 2015).

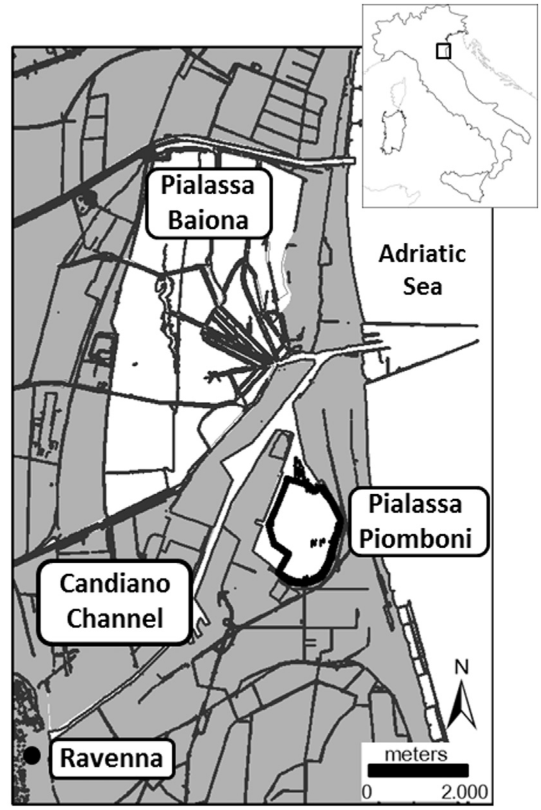

Fig. 1. Map of the study area.

2.2. Sample collection and chemical analysis

Fifty sediment samples were collected over an area of about 3 km^2 using a 0.1 × 0.1 km regular grid. The top 5-cm of sediment was collected by manual coring; sediment samples were then placed in pre-cleaned glass containers, transported to the laboratory and stored at +4 °C for sample treatment and further analysis.

The sampled sediments were treated with deionized water to remove sea salts; they were then centrifuged, dried in the oven at 60 °C and ground in an agate mortar.

The X-ray fluorescence spectrometer Philips PW1480 with Rh tube was used for the detection of major and trace elements (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pb, Th, S, Br, Mo, Sn) on pressed powder pellets, following the matrix correction methods of Franzini et al. (1972, 1975), Leoni and Saitta (1976), and Leoni et al. (1986). Precision and accuracy have been tested including certified reference material SCo-1 (Silty Marine Shale, United States Geological Survey, USGS) in the analytical routine; trace elements determination was better than 5%, except for those elements at 10 ppm or lower (10–15%).

The total Hg content was determined using a Direct Mercury Analyzer (DMA-80, Milestone®) on approximately 30 mg of material according to US-EPA Method 7473. Quality control was tested using Certified Reference Material PACS-2 (Harbour Sediment, NCR-CNRC,