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Geochemical characterization of surface sediments from the northern Adriatic wetlands around the Po river delta. Part I: Bulk composition and relation to local background

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ABSTRACT

The impact of heavy metal pollution on coastal wetlands is a matter of concern worldwide. In the Po Delta (Italian North Adriatic coast) human presence around wetlands has increased considerably in recent years. This study assessed the geochemical composition of surface sediments of several wetlands within the historical Po deltaic system, and the influence of anthropogenic activities on the metal levels in the sediments. Eighty-nine samples were collected from 7 sites, and analysed for major and 16 trace elements using X-ray fluorescence and the results compared to background values obtained from bottom cores drilled near the wetlands. The Enrichment Factors (EFs) were calculated to evaluate metal contamination. In general, sediment composition were found to be consistent with a mixture of carbonate and clay, in agreement with the background composition. However there were some exceptions with some samples found to be enriched in organic matter (OM) and a few samples richer in carbonate than the background. The bulk composition is mainly characterized by the fine-grained fraction. The concentrations of Ba, Cr, Cu, Pb, Rb, Sr, Zn, and V exceeded background values in one or more sites. Copper and Zn enrichments were of anthropogenic origin, high concentrations of Ba, Rb, Sr, and V were the consequence of natural processes, while Cr peaks were likely to be a result of both natural and anthropogenic causes, depending on the site. Lead was generally high, reaching some unexpected high median EFs and a number of peaks. Lead in many sites, and Cu and Zn enrichments in the most polluted sites are preferably controlled by OM. One of the most polluted sites showed alarming peaks of Cr, and contamination of Cu and Zn involves the southern lagoons, due to industrial inputs from Ravenna and local settlements. Lead shot are widely dispersed in all wetlands and this may explain the highest levels found of Pb in the study area.

1. Introduction

Coastal wetlands represent a critically vulnerable environment since it is located at the boundary between continental and marine settings: i.e. between freshwater and seawater environments. This makes it particularly vulnerable to a large diversity of anthropogenic activities. Indeed, human presence around coastal wetlands has increased considerably in recent years, and the impact on these environments have become a matter of concern (e.g.: Yamamuro and Kanai, 2005). Moreover, coastal wetlands are transitional environments that can accumulate, temporarily or permanently, many contaminants carried by several pathways (Akoto et al., 2008). Such pollutants, and in particular metals, are not necessarily permanently linked to sediment, but once adsorbed, can be mobilized by chemical or biological agents within the sedimentary layer or may return in the water column (Salomons and Förstner, 1984). Due to their persistent and bioaccumulative nature in the aquatic ecosystem, trace metals are of major concern (Arnason and Fletcher, 2003). These elements are mostly derived from natural sources, influenced by bedrock geology of the drainage catchment and by weathering processes (Karbassi et al., 2008). However they are also introduced to the aquatic environment by a number of important anthropogenic processes (Akoto et al., 2008).

Sediments have been widely used as environmental indicators since they can easily be used to trace contamination sources and to monitor pollutants. They play an important role in the assessment of metal contamination in natural waters (Borovec, 1996, Duzzin et al., 1988, Gonçalves and Boaventura, 1991; Huang et al., 1994; Jha et al., 1990; Lietz and Galling, 1989; Pardo et al., 1990; Wardas et al., 1996). Indeed, sediments reveal a high propensity to accumulate, register and eventually integrate through time trace element presence in water. Therefore, they allow assessing environmental metal levels even if water concentrations are almost undetectable.

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The largest alluvial plain in Italy, namely "Pianura Padana" (Po River Plain) is composed by the alluvial deposits of the Po River, the largest river in Italy, and of its tributaries. The whole catchment, except for the mountain area, is characterized by heavy industrialization, extensive agricultural practices, diffuse animal husbandries and high human population densities. The coastlines north and south of the Po River mouth are also affected by considerable touristic pressure. The Po delta, although heavily modified by human intervention such as drainage, channelling, embankments and reinforcement of river channels, presents a considerable number of brackish wetlands distributed along a 130 km stretch of the northern Adriatic coast. The natural components of these environments have been affected at various degrees by management practices such as agriculture, fish farming, salt production, and various kinds of recreational activities (e.g. fishing, hunting, tourism), in many cases in combination. Only few of the wetlands within the Po delta area have been heavily affected by urban and industrial development with significant discharges of nutrients and pollutants (the Pialassa Baiona according to Covelli et al., 2011; Fabbri et al., 1998, 2000, 2003; Guerra, 2012; Trombini et al., 2003), and at present these inputs are less conspicuous.

The literature on the geological setting and palaeogeographic evolution of the area is extensive (Amorosi et al., 1999a, b, 2003, 2004, 2005, 2008; Stefani and Vincenzi, 2005), especially after the recent impulse given by the CARG (Geological CARtography) geological mapping project to scale 1:50,000 of the Geological Survey of Italy, promoted in the southern Po plain by the Geological Survey of Regione Emilia–Romagna. Importantly for this study, geochemical aspects were investigated and the data on sub-surface soils and deep cores give essential information on the local background levels for selected elements (e.g. Amorosi et al., 2002, 2007, 2008; Curzi et al., 2006; Dinelli et al., 2007, 2012). Conversely, the inorganic geochemistry of the Po delta coastal wetlands has received poor attention, except for the "Pialassa Baiona", a lagoon near the town of Ravenna, historically affected by mercury contamination (e.g.: Donnini et al., 2007; Fabbri et al., 1998; Guerra et al., 2009; Matteucci et al., 2005; Trombini et al., 2003). Consequently, more information on sediment composition is desirable. To improve that knowledge, the inorganic composition of sediments from seven Po delta coastal wetlands has been investigated. The main aims of this study were to gain insight into: 1) the geochemical composition of the surface sediments, including major and trace element concentrations, distributions, and sources; and 2) the influence of anthropogenic activities on the metal levels in the sediments. The latter can be achieved by comparing background values obtained from previous studies of element abundances in bottom sediments sampled around the investigated sites (Amorosi et al. 2002, 2007, 2008; Curzi et al. 2006; Dinelli et al., 2007, 2012; Dinelli, unpublished data) to values obtained from surface sediments, by using the Enrichment Factor (EF) (Zhang and Liu, 2002; Zhang et al., 2007).

2. Materials and methods

2.1. Study area and sampling sites

The seven investigated wetlands are: "Valli di Rosolina" (ROS), "Valle Bertuzzi" (BER), "Valli di Comacchio" (COM), "Vene di Bellocchio" (BEL), "Valle Mandriole" (MAN), "Pialassa della Baiona" (BAI), and "Pialassa dei Piomboni" (PIO) (Fig. 1). All the sites are part of the historical Po deltaic system along the stretch of the northern Adriatic coastline between the towns of Ravenna and Chioggia (Bondesan et al., 1995a). At present, they are all included in the Emilia Romagna Po Delta Regional Park, except ROS that is included in the Veneto Po Delta Regional Park. The main characteristics of the sampling sites and the number of samples collected are summarized in Table. 1.

The evolution of the Po Delta was determined by the combination and the overlap of a set of complex geological, sedimentological and meteorological processes, both terrestrial and coastal marine, with human intervention an additional contributing factor over the years. The most recent geomorphological evolution was mainly controlled by three concomitant factors: the progressive eastward shift of the coastline, eustatic variations in sea level and subsidence (Bondesan et al., 1995a; Ciabatti, 1967; Nelson, 1970; Simeoni and Corbau, 2009; Simeoni et al., 2000). Recent investigations associated with an extensive drilling campaign promoted by the Geological Survey of Regione Emilia–Romagna as part of the geological mapping project of Italy, have provided more data for a better characterization of the late Quaternary deposits in the area.

The recent sediments have a structure closely related to the climatic events that occurred since the last glacial period, known as Würm glaciation (started approximately 75,000 years ago). Above the Last Glacial Maximum (LGM) alluvial deposits, the Ravenna and Comacchio coastal plains, as well as the subsurface of the modern Po Delta, display a common stratigraphic framework: a transgressive–regressive depositional cycle of Holocene age (approximately 30 m thick) made up of retrogradational back-barrier, transgressive shoreline and offshore-transition deposits, overlain by a shallowing-upward succession of prodelta, delta front, delta plain and alluvial plain sediments. This stratigraphic architecture reflects the landward migration of barrier–lagoon–estuary systems, followed by extensive deltaic and coastal plain eastward progradation (e.g. Amorosi et al., 1999a, 1999b, 2007, 2008; Curzi et al., 2006; Stefani and Vincenzi, 2005). The presence of a series of beach ridges of various ages is evidence of the latter process, as shown in Fig. 2. However, the delta progradation has stopped in the 1950s and was caused by the progressive reduction of sedimentary inputs related to heavy anthropogenic alteration of rivers as well as gravel and sand extraction from their bed. This process led to the gradual and still ongoing retreat of the coastline (Dal Cin, 1983; Dal Cin and Simeoni, 1984; Simeoni and Bondesan, 1997; Simeoni et al., 2000). As the coast gradually was moving eastwards, the rise of subsidence led to the formation of extensive marshes and lagoons (Bondesan and Simeoni, 1983; Bondesan et al., 1995b; Caputo et al., 1970; CENAS, 1997). Simultaneously, the need to allocate new land for agricultural activities led to the onset of reclamation activities since ancient times, particularly intense from the second half of 1800s until the end of the 1960s, causing the deposition of a fine-grained surface layer where drainage was difficult (Stefani and Vincenzi, 2005).

Among the studied sites, BER, COM and MAN represent the residual parts of the submerged lands after these reclaiming actions. A different origin is attributed to the remaining sampling sites (ROS, BEL, BAI and PIO), created by the closure of a sea portion between the original coastline and the peninsulas developed at the river mouth as a result of deposition of fluvial sediments (e.g. Reno river for BEL). The latter four lagoons are characterized by a direct connection to the Adriatic Sea and the influence of the tidal oscillations (Table 1). "Valli di Comacchio" are also connected to the sea by three artificial channels, whereas MAN and BER are completely isolated from the Adriatic Sea and in this case the water salinity is due only to the saltwater intrusion, a phenomenon that, in recent years, heavily affects the aquifers of the entire deltaic area (COSTA21, 2004; Regione Emilia-Romagna, 2004; Antonellini et al., 2006; ARPA, 2006). All of the seven sites receive freshwater from a regulated system of rivers and channels which drain the surrounding agricultural lands. "Pialassa Baiona" and PIO also receive the effluents from industrial and municipal treatment plants. In the 1960s and 1970s high quantities of chemical compounds were discharged in BAI through the southernmost channel, carrying waste waters from the chemical settlement near the city of Ravenna (e.g.: Anconelli et al., 1980; Angelini and Strumia, 1994; Fabbri et al., 1998, 2000; Miserocchi et al., 1990).

With the exception of BEL and MAN, all the sampling sites are used for human activities, such as fishing or regulated hunting, or both (Table. 1). "Piomboni" is a particular case of an important industrial settlement (harbour) that includes a Special Protected Area (SPA). Just after sampling, the construction of an embankment started in order to