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Decline of trace metal pollution in the bottom sediments of the Barcelona City continental shelf (NW Mediterranean)

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HIGHLIGHTS

- Trace metals evolution in the sediment record of polluted areas from industrial times.
- Identify effects of environmental management on the Barcelona City Continental Shelf.
- Trace metal decrease of up to an order of magnitude after taking corrective measures.
- Extremely high mercury levels drastically reduced by environmental regulations.
- Still high pollution because of the difficulty of pollutant management during floods.

GRAPHICAL ABSTRACT

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ABSTRACT

The evolution of trace metal pollution on the Barcelona city continental shelf during the last few decades was studied by analyzing the historical records of trace metals in sediment cores and surface sediment samples taken at the same locations in 1987 and in 2008. Polluted surface samples taken in 1987 reached enrichment factors of up to 490 for Hg, about 40 for Pb and Cd, and about 17 for Zn, Cr and Cu. The data show a decline of up to one order of magnitude in the trace metal content of surface sediments during the last few decades, with maximum enrichment factors of between 20 and 30 for Hg and Cd and between 5 and 12 for Zn, Cr, Pb and Cu. Although present-day pollution is still significant, it is evident that environmental regulations that are in place, including the operation since 1979 of wastewater treatment plants built in the Besòs River watershed, have drastically reduced the pollution levels in this highly populated and industrialized Mediterranean area. However, water discharge during heavy rain events exceeds the treatment capacity of the existing facilities, leading to the maintenance of still high levels of metals in sediments of the Barcelona city shelf.

1. Introduction

Trace metals are common pollutants resulting from domestic and industrial activities that are delivered into the sea through rivers, waste effluents and atmospheric emissions (Lee and Cundy, 2001; Bellucci et

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al., 2002 Munksgaard et al., 2003; Spencer et al., 2003; Maanan, 2008; Clark, 2001). The levels of contaminants transported by rivers into the sea depend on the type of waste dumped into the river watershed and the amount of water and sediment discharge. The same contamination input will generate higher concentrations of toxic elements in small rather than in large rivers due to their lower capacity for diluting the contaminated load. Once discharged into the sea, trace metals are scavenged when flocculation occurs along the freshwater-saltwater interface (Beck et al., 1974), where they may be subsequently affected by dilution, desorption, absorption, aggregation and precipitation, and are often associated with fine sediment particles (Salomon and Förstner, 1984; Fernex et al., 1986; Garnier et al., 1991; Turner and Millward, 2002). In addition, offshore dispersion of pollutants associated with fine sediments is controlled by dynamic marine processes (mainly currents and waves) that govern their transport, accumulation and/or resuspension and determine their final fate (Krom et al., 1983; Milliman and Syviski, 1992; Nittrouer and Wright, 1994).

In many zones of the oceans, energetic processes transport and dilute the marine pollution load in the transit to the deep sea. However, in the tideless and semi-enclosed Mediterranean Sea, the transport capacity of the dynamic processes is lower than in large oceans, so a large part of the particulate pollutant load can settle quickly along with fine sediment particles on the seabed near the coast, favoring the formation and persistence of anomalous concentrations in shallow sediments (e.g. Frignani et al., 1997; Palanques et al., 1998; Bay et al., 2003; Garcia-Orellana et al., 2011).

Trace metal contamination recorded in marine sediments has been studied at many sites all over the world (e.g. Bryan and Langston, 1992; Cearreta et al., 2000; Santschi et al., 2001). In several countries, the distribution of trace metals in the marine environment is being studied systematically and extensively in order to estimate their impact and their economic and social effects, and to take preventive and corrective measures. Also, many studies have traced and dated the impact of anthropogenic activity on sediments, which record the historical inputs and trends of these pollutants (Ravichandran et al., 1995; Borg and Jonsson, 1996; Hornberger et al., 1999; Ip et al., 2004; Mason et al., 2004; Schintu and Degetto, 1999; Di Leonardo et al., 2008; Kostaschuk et al., 2008; Xu et al., 2009; Hosono et al., 2010a; Liu et al., 2011; Dong et al., 2012; Morelli et al., 2012). These studies generally show continuous anthropogenic enrichment of trace metals in coastal areas during the last century due to the increase in industry, urban development, population, agriculture and mining (Nriagu, 1996; Natesan and Seshan, 2010; Pan and Wang, 2011).

In general, the application of environmental regulations, new water treatment plants and other protection measures have helped to reduce the discharge of trace metals in coastal areas. However, the effects of these reductions in terms of trace metal concentrations in the marine systems have rarely been studied (e.g. Pirrie et al., 1995; Cearreta et al., 2000). In many cases, they are difficult to identify because it may take several years until the effects are clearly recorded in metal concentrations of coastal sediments, and also because of disturbing effects caused by dredging, changes of river mouths, extreme storms and river avenues, harbor constructions, and changes in the pollution sources.

The continental shelf off Barcelona (Fig. 1) is an example of a coastal environment that is highly affected by urban and industrial activity. The Barcelona Metropolitan Area is the sixth most populous urban area in the European Union (4.4 million inhabitants) and the second most populous on the Mediterranean Coast (Eurostat, 2012). This region received large amounts of pollutants during most of the XXth century (Palanques et al., 1998). However, new environmental regulations, and protection measures have been applied and developed in the areas since the eighties.

The objective of this study was to analyze the records of trace metal pollution, including Hg, in sediments of the Besòs prodelta, in order to evaluate trends during the last few decades in comparison with previous industrial times and to identify the effects on the seabed of corrective measures applied in this area.

2. Study area

The sea along the Barcelona coast has a microtidal regime (<20 cm). Waves have a mean significant height (H_s) of 0.70 m and an averaged mean period of 4.29 s.[1] The Hs maxima during the 1984–2004 period was 4.61 m. The most persistent current direction is along-shelf toward the SW, following the general circulation pattern of the mean current of the north-western Mediterranean (the northern current), and with an average velocity of between 5 and 10 cm s^{-1} (Grifoll et al., 2013). On the inner part of the shelf, the frictional forces tend to prevail, leading to a dominant along-shelf flow in comparison with the across-shelf flow (Grifoll et al., 2012, 2013).

The study area receives discharges mainly from the Besòs River, with a mean water discharge of 5 $m^3 s^{-1}$, although its hydrographic regime is extremely variable (maximum values of >2000 $m^3 s^{-1}$ during strong flood events). The watershed size is 1000 km^2 and it traverses urban, industrial and rural settings. The mean Besòs River annual sediment discharge has been estimated as15000 t/year (Liquete et al., 2007).

The sediments discharged by the Besòs River form a muddy prodelta that extends southwestward from the river mouth between about 20 and 60 m depth along the inner and mid-continental shelf. The seabed consists of sand and gravels near the coast, mud between about 20 and 60 m depth and biogenic relict sands from 60 m depth to the continental slope. Sediment distribution is controlled by hydrodynamic processes (Palanques and Díaz, 1994). Wave-induced bottom shear stress is the main stirring factor for sediment resuspension and is mainly effective in the inner-shelf region (López, 2013, Grifoll et al., 2014).

This river is highly polluted by trace metals from industrial and urban activities. During the 1980s the sediments of the proximal parts of the Besòs prodelta were highly polluted by Cr, Pb and Zn (Hg was not analyzed) and enhanced concentrations of these metals have been detected even in bottom sediments of the Foix submarine canyon sediment down to 800 m depth (Palanques et al., 1998; Puig et al., 1999; Palanques et al., 2008).

In 1979, the first wastewater treatment plant constructed near the Besòs River mouth, was only able to partially treat the Besòs River supplies. This plant discharged very polluted sewage sludge through a 4-km-long pipeline at 56 m depth, forming a sewage sludge mound covering several km^2 and several meters high on the mid-shelf (Palanques et al., 1991). This discharge lasted until the early 1990s, when this pipeline was closed and removed and a new pipeline for treated water discharge was built. Several other sewers also discharged along this part of the Barcelona coast. The Besòs River, the ancient Besòs wastewater treatment plant and the sewers have been generating high trace metal contents in the bottom sediment of the Besòs prodelta for decades (Palanques et al., 1991; Palanques et al., 1998).

3. Materials and methods

3.1. Sampling

A total of 22 surface sediment samples and 7 sediment cores were taken in the study area in 2008 during the SEDMET I cruise with a HAPS corer (Fig. 1; Table S1 of Supplementary data). The surface sediment samples were taken at the same locations where they were collected in 1987 (see Palanques and Díaz, 1994; Palanques et al., 1998). Furthermore, one of the 7 sediment cores (Be08) was taken at the same location as a previously dated sediment core taken in 1987 (Palanques et al., 1998). Sediment cores were sliced in 1-cm-thick intervals aboard the vessel and all the surface and core sediment samples were stored at 4 °C for further laboratory analysis.