Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Detecting long-term temporal trends in sediment-bound metals in the western Adriatic (Mediterranean Sea)

Marilia Lopes-Rocha[a,b,*], Leonardo Langone[c,**], Stefano Miserocchi[c], Patrizia Giordano[c], Roberta Guerra[b,d]

[a] Departamento de Química-Física, Facultad de Ciencias del Mar y Ambientales, Universidad de Cádiz, UNESCO/UNITWIN WiCoP, Campus de Excelencia International del Mar (CEIMAR), Polígono Río San Pedro s/n, Puerto Real 11510, Cádiz, Spain

[b] Centro Interdipartimentale di Ricerca per le Scienze Ambientali (C.I.R.S.A.), University of Bologna, Ravenna Campus, 48123 Ravenna, Italy

[c] National Research Council-Institute of Marine Sciences (CNR-ISMAR), 40129 Bologna, Italy

[d] Department of Physics and Astronomy, University of Bologna, 40127 Bologna, Italy

ARTICLE INFO

Keywords:
Trace metals
Background levels
Sediment records
Historical trends of contamination
Inventories of trace metals excess
Adriatic Sea

ABSTRACT

Major and trace metal concentrations were determined in western Adriatic sediment cores. Based on sediment chronology, the earliest anthropogenic influence appeared as a Zn and Pb increase in the Po River prodelta starting from ~1914. The increasing contamination signal of these trace metals propagated southward as far as 450 km with a growing delay, taking ~10 years to reach the south Adriatic Sea. Although greater inventories of excess trace metals in the northern sector pointed to the influence of the intense human activities in the Po River drainage basin and Venice lagoon system, we observed a reduction of excess trace metals from mid-1980s, related to the implementation of stricter environmental regulations on chemical wastewaters. In contrast, an increase in trace metal accumulation in surficial sediment from the 2000s in front of the cities of Ancona and Bari suggested a recent local input of trace metals, probably due to harbor activities.

1. Introduction

Human activities have accelerated the cycling of trace metals and increased metal deliveries to coastal zones in the last decades (Han et al., 2002). Because metals can be toxic to aquatic life, all changes in their loads or concentrations may have ecosystem-wide implications (Boyd, 2010). Therefore, it is important to understand how anthropogenic activities can change the concentrations of potentially toxic metals, which processes can affect such changes and which activities have the greatest effects (Richir and Gobert, 2016). In coastal and marine systems, most of the trace metals associated with the surfaces of particles are preferentially transported, deposited and eventually buried with fine grained sediments. Dated cores through sediment deposits can provide chronologies of metal concentration or input in areas of net sediment deposition (Hornberger et al., 1999; Miller et al., 2014). On the other hand, interpretation of human influences requires the determination of trace metal natural baselines (preindustrial levels) in the sedimentary archives.

The Adriatic Sea is a land-locked marginal sea where the intensity of the human pressure on its coastal areas enhances the natural concentrations of trace metals in sediments. In this basin, the main source of contaminants is the Po River, the largest Italian river along with the inputs of the Adige and Brenta rivers and the Venice Lagoon (Frignani et al., 1997; Cochran et al., 1998; Ianni et al., 2000; Bellucci et al., 2002). The Po River drainage basin is one of the major drainage basin in Europe and of great economic importance due to the presence of numerous large industries and small and medium-sized enterprises, as well as intensive agricultural and zootechnical activities. For these reasons, the effects of contamination and pollution are more pronounced in the northern Adriatic sector than in the central and southern ones (Guerzoni et al., 1984; Frascari et al., 1988; Faganeli et al., 1991; Covelli et al., 2016; Lopes-Rocha et al., 2017).

Although the Adriatic Sea is an important and interesting area for contamination studies encompassing heavily industrialized, urbanized and agriculturally productive areas (Cibic et al., 2008; Guerra et al., 2014; Migani et al., 2015; Mali et al., 2017), only few authors have assessed historical trace metal reconstructions based on sediment cores, which were mostly focused on restricted areas (Price et al., 1992; Romano et al., 2013; Ilijanić et al., 2014; Spagnoli et al., 2014).

Despite the scientific effort made so far, important questions remain

* Correspondence to: M. Lopes-Rocha, Departamento de Química-Física, Facultad de Ciencias del Mar y Ambientales, Universidad de Cádiz, UNESCO/UNITWIN WiCoP, Campus de Excelencia International del Mar (CEIMAR), Polígono Río San Pedro s/n, Puerto Real 11510, Cádiz, Spain.
** Corresponding author.
E-mail addresses: marilia.lopes@alum.uca.es (M. Lopes-Rocha), leonardo.langone@ismar.cnr.it (L. Langone).

http://dx.doi.org/10.1016/j.marpolbul.2017.07.026
Received 4 June 2017; Received in revised form 10 July 2017; Accepted 11 July 2017

Please cite this article as: Lopes-Rocha, M., Marine Pollution Bulletin (2017), http://dx.doi.org/10.1016/j.marpolbul.2017.07.026

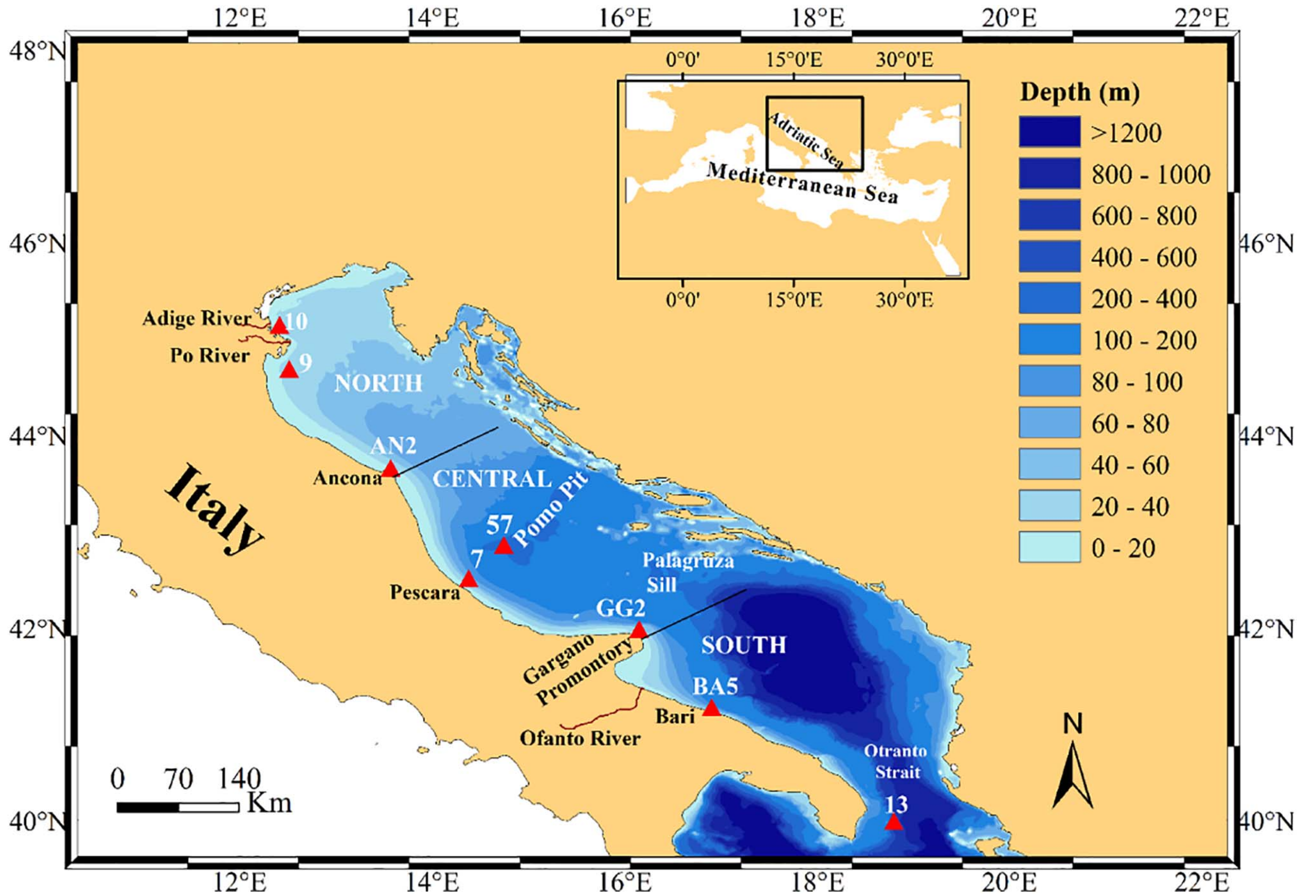

Fig. 1. Location map and bathymetry of the Adriatic Sea. Triangles represent sampling stations located in: the Adige River prodelta (core 10), the Po River prodelta (core 9), offshore Ancona (core AN2), offshore Pescara (core 7), Pomo Pit (core 57), offshore Gargano (core GG2), offshore Bari (core BA5) and Otranto Strait (core 13).

unresolved: a) what are the historical trends of trace metals that were released into the Adriatic Sea in the past and how much does it remain in the Adriatic sediments today? b) Does the application of Italian environmental regulations on chemical treatments have helped to reduce the discharge of anthropogenic trace metals into the Adriatic Sea? c) Being the Po River the main source of anthropogenic trace metals to the Adriatic Sea, how far is the anthropogenic signal detecting along the Po River dispersion system and how long does this signal take to move southward from the Po River prodelta?.

To answer these questions, we analyzed trace metal concentrations on ^{210}Pb-dated sediment cores collected at several locations along the western Adriatic Sea. We established trace metal background levels indicating preindustrial times, when the influence of human activities was still limited. Then, we reconstructed the historical trends of Zn and Pb concentrations and we dated the onset of their increase, and the beginning of their decreasing shift. This approach has been taken in an attempt to evaluate temporal patterns of the inventories of excess trace metals and to elucidate if the increasing and decreasing variations of trace metal concentrations are synchronous, progressive or scattered at basin scale.

This work was part of PERSEUS (Policy-oriented marine Environmental research in the Southern European Seas) project which aims to identify the most relevant pressures exerted on the ecosystems of the Southern European Seas (SES), linking them to the Marine Strategy Framework Directive (2008/56/EC, European Commission, 2008) (MSFD) descriptors, criteria and indicators. Based on the descriptor 8, this work aims to ensure that the levels of trace metal contaminants in the marine environment do not to give rise to pollution effects at regional and subregional scale.

2. Material and methods

2.1. Study area

The Adriatic Sea is a shallow semi-enclosed basin connected to the Mediterranean Sea through the Otranto Strait (Manca et al., 2002). It is commonly divided into three sub-basins (North, Central and South), which are characterized by different sedimentary settings, organic matter inputs and metal concentrations. The northern Adriatic has a wide and shallow continental shelf (down to 100 m deep); the Central Adriatic extends from Ancona to the Gargano Promontory, including the Pomo Pit (270 m depth); whereas the southern Adriatic basin extends from the Palagruza Sill (Split-Gargano transect) to the Otranto Strait, including the deepest areas of the whole Adriatic basin (down to 1200 m) (Fig. 1).

The Po River, located in the northern Italy, is one of the dominant drainage basins in Europe and the primary fluvial dispersal system entering the Adriatic Sea, along with additional inputs from several smaller Alpine rivers in the North, and Apennine rivers in the Central and South sectors (Dinelli and Lucchini, 1999; Frignani et al., 2005a). The geology of the Po River watershed presents mineral deposits and ultramafic rocks that are naturally enriched in metals (e.g. chromium and nickel) relative to the main composition of the continental crust (Amorosi, 2012).

The Adriatic basin is characterized by a microtidal regime and the hydrodynamics is dominated by a cyclonic circulation driven by thermohaline density differences, which in turn, are modulated seasonally (Nittrouer et al., 2004). This cyclonic circulation, known as the Western Adriatic Current (WAC), restricts the freshwater discharges by the Po River and Apennine rivers to a narrow band along the western side of