Marine Environmental Research 79 (2012) 86–99

Contents lists available at SciVerse ScienceDirect

Marine Environmental Research

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

The relevance of defining trace metal baselines in coastal waters at a regional scale: The case of the Portuguese coast (SW Europe)

Juan Santos-Echeandía[a,b,*], Miguel Caetano[a], Pedro Brito[a], Joao Canario[a], Carlos Vale[a]

[a] IPMA, Instituto Portugues do Mar e Atmosfera, Avenida Brasília, 1446-006 Lisboa, Portugal
[b] Marine Biogeochemistry, Marine Research Institute (CSIC), Eduardo Cabello, 6. 36208. Vigo, Spain

ARTICLE INFO

Article history:
Received 14 March 2012
Received in revised form
28 May 2012
Accepted 30 May 2012

Keywords:
Dissolved
Particulate
Metals
Coastal waters
SW Europe
Upwelling
Poleward current
Pyritic belt

ABSTRACT

The Water Framework Directives aims a reduction in concentration of hazardous substances in the marine environment. Consequently, there is a need to distinguish between anthropogenically influenced metal concentrations from natural background levels. To better achieve this goal in the Portuguese coast, dissolved and particulate trace metal (TM) concentrations along the Portuguese coast were determined in 46 sites distance 1–3 km from the shoreline. Dissolved values ranged within the following intervals: 0.01–0.89 nM for Cd, 0.01–3.37 nM for Co, 0.90–45.4 nM for Cu, 3.30–140 pM for Hg, 1.88–15.1 nM for Ni, 0.01–0.15 nM for Pb and 1.40–62.0 nM for Zn. Whereas Cd, Co, Cu, Ni and Zn were enhanced in the southern coast, while Pb values were higher in the central part of the western coast. Mercury concentrations showed punctual increases all along the coast. Values of trace metals in suspended particulate matter varied in a broad range: 36–2902 μmol g^{-1} for Al, 0.10–15.1 nmol g^{-1} for Cd, 1.50–165 nmol g^{-1} for Co, 50.0–990 nmol g^{-1} for Cu, 2.80–76.4 nmol g^{-1} for Hg, 22–1471 nmol g^{-1} for Ni, 10.0–347 nmol g^{-1} for Pb and 416–10,981 nmol g^{-1} for Zn. Higher values for Al, Ni and Co were found in the central part of the western coast. However, Cd, Cu, Pb and Zn increased their levels from the north coast towards the central and south areas. The variability of both dissolved and particulate metals appears to be mainly associated with oceanographic conditions and continental inputs at North and central areas of the coast, and in the south coast to geological features rather than to anthropogenic pressures. On the basis of these results, regional baseline concentrations are proposed for the three typologies in Portuguese coastal waters defined under the Water Framework Directive.

\

1. Introduction

The ocean margin is the critical land–ocean interface. At its inner boundary, coastal waters are characterized by steep physical and chemical gradients although being highly dynamic over short time-scales (Braungardt et al., 1998). Several studies have shown that coastal waters contain higher trace element concentrations than open ocean waters (e.g., Bruland and Franks, 1983; Kremling, 1985; Kremling and Hydes, 1988; Kremling and Pohl, 1989; Landing et al., 1995; Le Gal et al., 1999). Natural weathering processes at basins of major world wide rivers have been pointed as major supplier of dissolved and particulate material to the ocean (Martin and Meybeck, 1979). The enrichment of coastal waters in trace metals has been ascribed to river discharges (Martin and Whitfield, 1983), atmospheric transport (Martin et al., 1989), and anthropogenic sources (Cotté-Krief et al., 2000). Major internal sources are diagenetic exchanges of trace elements across the water–sediment interface (Klinkhammer et al., 1982; Cotté-Krief et al., 2000) and upwelling of bottom waters (Bruland et al., 1978; van Geen et al., 1990). Multiple factors influence the chemical speciation and water-particle partitioning of trace elements in coastal waters, namely complexation by dissolved organic matter, formation of colloids, precipitation, sorption to particulate phases and biological uptake (Muller, 1996; Morris et al., 1986; Olsen et al., 1982). In addition, accidental episodes of contamination may lead to punctual enhancement of trace-element concentrations. Examples are Aznalcollar mining spill (Grimalt et al., 1999; Achterberg et al., 1999; Elbaz-Poulichet et al., 2001), Erika and Prestige oil spills (Baars, 2002; Amiard et al., 2004; Chiffoleau et al., 2004; Prego and Cobelo-García, 2003; Santos-Echeandía et al., 2005, 2008). The intensity and extension of these contaminating events could not be determined if baseline concentrations are not previously established.

Trace-element concentrations in dissolved and suspended particulate matter (SPM) along the Portuguese coast are reported in

* Corresponding author. Marine Biogeochemistry, Marine Research Institute (CSIC), Eduardo Cabello, 6. 36208. Vigo, Spain.
E-mail address: jusae@iim.csic.es (J. Santos-Echeandía).

0141-1136/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.marenvres.2012.05.010

a few works, covering the south and southwest sectors (van Geen et al., 1997; Cotté-Krief et al., 2000) and nearby estuarine mouths (Caetano and Vale, 2003). These works show a high variability in trace metal concentrations with several hypotheses to explain it. However, results with a high spatial resolution of the entire coast are still lacking.

The current work reports the Cd, Co, Cu, Hg, Ni, Pb and Zn concentrations at 46 sites sampled in March 2010. Water was sampled within the first 3 km of the entire Portuguese coast, which correspond to the coastal waters defined within the Water Framework Directive. On the basis of these results, the anthropogenic influence and the regional differences are examined, and baseline concentrations of these elements for the three typologies of Portuguese coastal waters are proposed.

2. Material and methods

2.1. Brief description of the Portuguese coast

The Portuguese coast is 943 km long. In the northern west coast, several funnel-shaped rivers discharge to coastal waters, like the Minho, Lima, Douro and Mondego rivers (annual average is 388 ± 444 m^3 s^{-1}, 74 ± 64 m^3 s^{-1}, 650 ± 300 m^3 s^{-1}, 2 ± 3 m^3 s^{-1} respectively, http://www.inag.pt) (Fig. 1a). Higher freshwater discharges in winter induce stratification of the coastal waters (Moita, 2001). Conversely, the major rivers in the southwest coast, Tagus and Sado rivers (annual average is 324 ± 436 m^3 s^{-1}, 11 ± 15 m^3 s^{-1} respectively, http://www.inag.pt) end into large estuaries. Their morphology favors the trapping of river-borne material inside the estuaries under moderate to low flow conditions (Fig. 1a). The Mira and Guadiana rivers (SW and S coast) have lower discharges (3 ± 3 m^3 s^{-1} and 37 ± 59 m^3 s^{-1}, respectively, http://www.inag.pt) and estuaries consist of single channels. SPM concentration and Al concentration presented by Caetano and Vale (2003) evidenced the contrasting north-south influence of river inputs to the Portuguese coastal waters. Episodically, some of these estuaries receive abrupt quantities of freshwater and land-derived contaminants (Vale, 1990; Martins et al., 2005; Caetano and Vale, 2003; Quental et al., 2003). The geology of the north Portugal river basins is dominated by granitic complexes while the south is greatly influenced by the Iberian Pyritic belt (Munha et al., 1986) (Fig. 1b), which is admittedly the largest sulphide mineralization in the world (Leistel et al., 1998). Weathering and mining activities have led to extremely high metal concentrations and acidity (pH < 3) in the rivers crossing this belt (Delgado et al., 2009). The most densely populated areas in the Portuguese coast are Porto, Aveiro, Lisbon and Faro (Fig. 1b) while the industrialized regions are located in the north part (Aveiro-Porto) and close to the Lisbon area.

Surface waters of the Iberian coast change circulation according to the season (Wooster et al., 1976; Frouin et al., 1990; Barton, 1998), being, in autumn-winter, northwards to the Bay of Biscay in France, and in spring-summer, it becomes weaker and reverses due to the North trade wind regime (Fiuza, 1983). This southward current promotes cooling and wind-induced upwelling along the shelf break (Fiuza, 1983; Abrantes and Moita, 1999). The Portuguese continental shelf is crossed by several canyons influencing the water circulation (Fiuza, 1983). The Nazaré canyon cuts-cross the NW continental shelf and has its head located close to the present-day shoreline. Northern from this canyon, coastal waters are characterized by a homogeneous upwelling of ENACW (Eastern North Atlantic Central Water) along the shore (Fiuza, 1983). From Lisbon to Cape Sines, the upwelling is affected by several canyon-systems like the Cascais, Lisbon and Setúbal canyons. South of the Cape Sines until Cape S. Vicente, the upwelling structure becomes more regular but is affected by warmer and saltier offshore surface waters (Moita et al., 2003). Finally, the southern Portuguese coast is controlled by a cyclonic gyre circulation in winter that turns anti-cyclonic in summer (Batteen et al., 2000; Mauritzen et al., 2001;

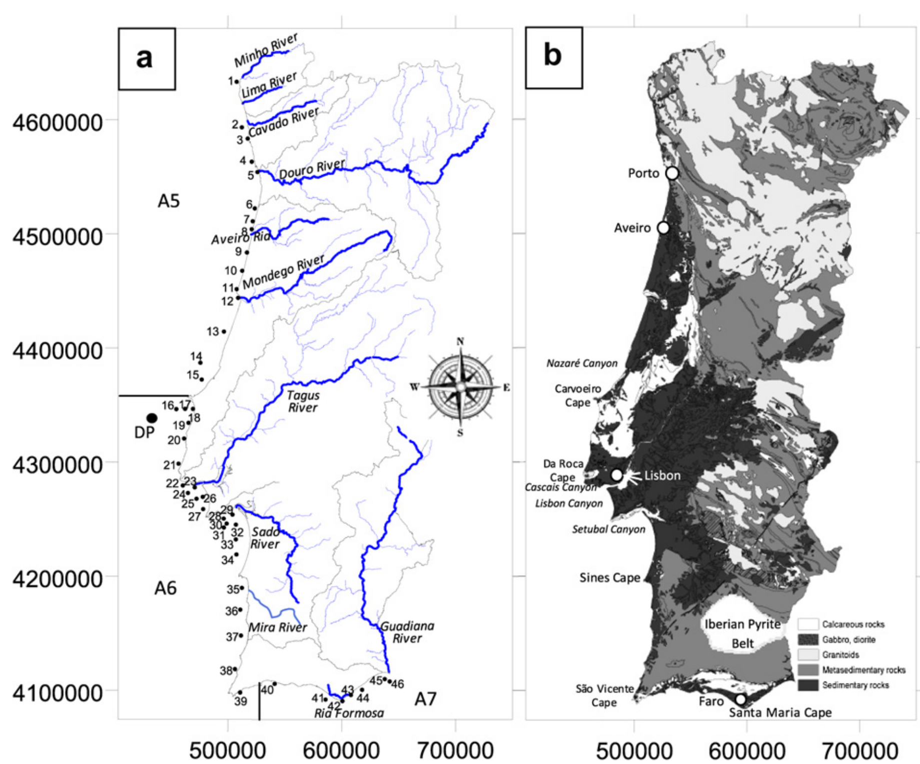

Fig. 1. Study area map with the a) surface water sampling stations and main river inputs and b) main capes and lithological facies.