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Influence of an upwelling filament on the distribution of labile fraction of dissolved Zn, Cd and Pb off Cape São Vicente, SW Iberia

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ABSTRACT

Under northerly winds upwelling is recurrent at the Cape São Vicente, SW Iberia, and plays a major role on the distribution of dissolved nutrients and metals. The aim of this work was to characterize the dissolved metals distribution of zinc (Zn), cadmium (Cd) and lead (Pb), associated with a filament of upwelled water that stretches seaward from the Cape. Additionally, the relationships between labile metals and other oceanographic parameters, such as current velocity and wind field patterns, temperature and salinity, nutrients, chlorophyll *a* and suspended solids were evaluated. The mass transport of the dissolved metals exported offshore was estimated, after a period of relatively strong and persistent upwelling. At the end of October 2004 a total of 42 CTD Rosette casts up to 400 dbar were sampled, distributed on an almost regular grid, together with along-track Acoustic Doppler Current Profile (ADCP) velocities. Seawater samples from two transects across the filament were analysed: one closest to the shore, where upwelling was intense and phytoplankton noticeably grew; and another further offshore where the filament was still well defined, but narrower and less marked despite with the maximum velocity currents. Labile dissolved metals were determined using anodic stripping voltammetry (ASV). The range of the metals recorded at the transect closest to the coast recorded was 0.26–3.8 nM (mean: 0.8 nM) for Zn, 2–11 pM (mean: 3 pM) for Cd and 8–60 pM (mean: 13 pM) while for the offshore transect was: 0.26–5.1 nM (mean: 1.2 nM) for Zn, 2–26 pM (mean 4 pM) for Cd and 8–74 pM (mean: 15 pM). Zinc recorded the highest concentrations, similar at both transects, and like Cd the lowest concentrations were found at near-surface depths. In opposition, the highest Pb concentrations were found at the near-surface depths at the northern stations in both transects. The filament exported more material in the offshore transect than in the transect closest to the coast, corresponding to a maximum export of ~135 kmol d^{-1} of Zn, 276 mol d^{-1} of Cd and ~1365 mol d^{-1} of Pb. The quantification of the cross-shelf fluxes imposed by the filament did show that metals fluxes are strong enough to play a key role in the oceanographic behaviour of the transition zone between the coastal and offshore waters in the region. Considering the periods of strong upwelling events and the extent of their duration along the year, the amounts of exported water mass which include nutrients, metals and particles must be hugely increased and responsible for the high productivity of the waters.

1. Introduction

Portuguese coastal upwelling results from northerly winds due to the northward displacement of the Azores high pressure cell and the weakening of the Iceland low pressure cell during the summer season. The seasonal pattern of the wind direction leads to changes in the Iberian oceanic surface circulation throughout the year (Cotté-Krief et al., 2000). As a consequence of this large scale climatological interplay, an equatorward surface current is established during the summer season as a geostrophic response to the upwelling that occurs along the western Iberian shelf. Continuity implies that subsurface water replaces the surface water, which is driven to the right in relation to the wind and taken offshore due to the Ekman mechanism. Upwelled subsurface water at the coast is cold, causing the decrease in sea surface temperature (SST) and its enrichment in nutrients from deeper levels increase the biological productivity (Cotté-Krief et al., 2000;

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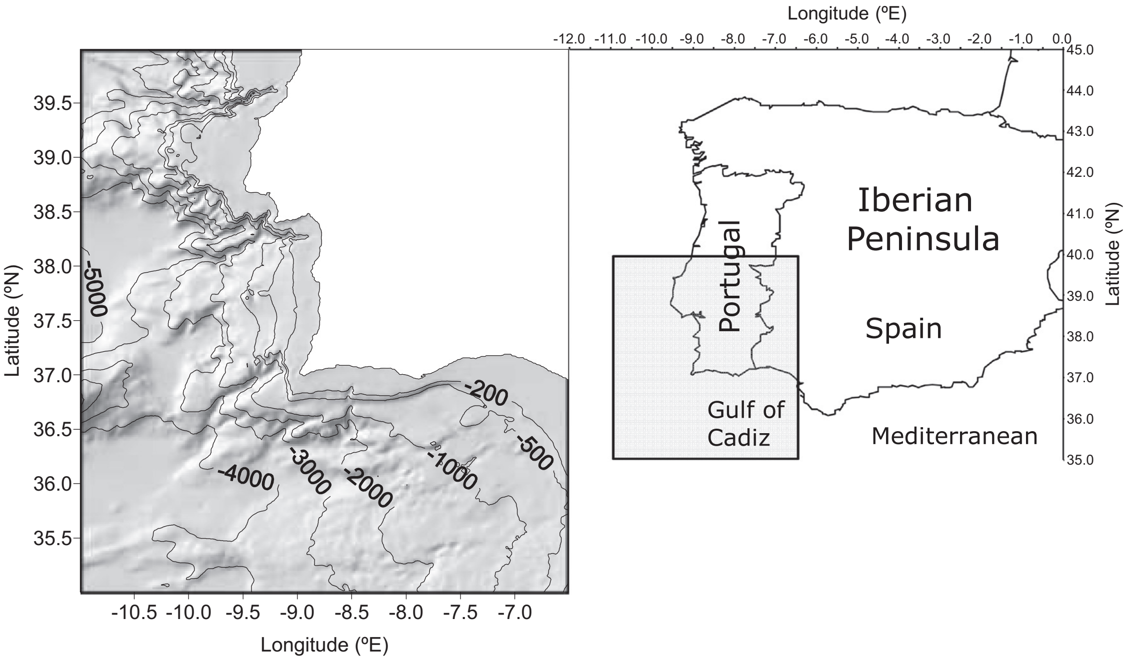

Fig. 1. Location of the study area. Bottom topography and some bathymetric contours are represented, in metres, for the shaded area.

Relvas and Barton, 2005; Relvas et al., 2007; Rossi et al., 2013).

During the upwelling process, a cold filament is recurrently formed off Cape São Vicente, the SW tip of the Iberian Peninsula (Fig. 1). It shows a jet structure stretching westward and exchanging almost one Sverdrup ($1\ \mathrm{Sv} = 10^{6}\ \mathrm{m}^{3}\ \mathrm{s}^{-1}$) of water between the coastal and open waters (Sánchez et al., 2008). This means that under upwelling events important offshore mass exchanges are not limited to nutrients but also comprise metals (Cotté-Krief et al., 2000; Biller and Bruland, 2013), among other materials. Consequentially, filaments represent very important structures controlling the ocean productivity (Alvarez-Salgado et al., 2001; García-Muñoz et al., 2004; Cravo et al., 2010; Rossi et al., 2013).

Some trace metals play a key role in biogeochemical processes in the water column, such as zinc (Ellwood and van den Berg, 2000; Franck et al., 2003; Wyatt et al., 2014) and cadmium (Abe, 2005; Cox et al., 2006; Baars et al., 2014), acting as micronutrients (Bruland and Lohan, 2003; Biller and Bruland, 2013; Wyatt et al., 2014), while others like Pb are not required biologically (Bruland and Lohan, 2003). Their vertical patterns of distribution and behaviour associated with upwelling events are not well described in literature (Biller and Bruland, 2013; Valdés et al., 2008).

In the ocean, trace metals generally occur at low concentrations, within the range 10 μM to 1 fM, and particularly for Zn: 0.05–9 nM; Cd: 1–1000 pM and Pb: 5–150 pM (Bruland and Lohan, 2003). The oceanic biogeochemistry of Zn, Cd and Pb, as well as their distribution, can be divided in two main groups: nutrient- and scavenged-type distributions, respectively (Bruland and Lohan, 2003). The first type shows a vertical distribution similar to the nutrients, usually depleted at surface layers contrasting with the increase of concentrations in depth. This distribution is mainly regulated by the plankton consumption in surface waters or euphotic zone (González-Dávila, 1995; Valdés et al., 2008; Pohl et al., 2011), or adsorption onto the particles surface, and followed by oxidation and remineralization from the sinking material in deeper waters, increasing their concentrations, also linked with the biogeochemical cycles of other elements such as the C, N, S and O (Bruland and Lohan, 2003). In addition, these metals can be accumulated at horizontal interfaces/boundaries such as the pycnocline because the velocity of the sinking particles is slow (Pohl et al., 2011). The last type presents an increase at surface layers with a significant decrease in depth due to a highly reactive behaviour, caused by strong interactions with particles (Bruland and Lohan, 2003). These reflect the high affinity to adsorb onto solid surfaces and be removed from solution in the surface layers (Muller, 1999; Brown Jr. and Parks, 2001; Cobelo-García et al., 2005; Santos-Echeandía et al., 2012). The residence time varies depending on the region (coastal or open ocean), distribution profile and is intimately related with the physical, chemical and biological processes in which the metals are involved. Residence times for Zn and Cd are estimated ∼50,000 years in the whole ocean (Croot et al., 2011; http://www.mbari.org/chemsensor/pteo.htm in Bruland and Lohan (2003)) and can be used as indirect proxies of past nutrient conditions (Bruland and Lohan, 2003; Croot et al., 2011). Residence time for Pb (∼100–1000 yr) induced by its reactive behaviour is lower than for Zn and Cd.

Metal concentrations can be affected by multiple factors rather than the physical forcing including also the inputs either natural or from anthropogenic origin (Saager et al., 1997; Kremling and Streu, 2001; Cotté-Krief et al., 2002; Valdés et al., 2008; Biller and Bruland, 2013). Their major sources are rivers, atmospheric dust, bottom sediments, and hydrothermal vents (Bruland and Lohan, 2003). Phytoplankton has an important role on the cycling and distribution of essential metals. Zinc is an ubiquitous metal and essential to biological activities (Morel and Price, 2003; Bruland and Lohan, 2003; Wyatt et al., 2014). Particularly in some species of diatoms it is involved in the carbonic anhydrase (CA) activity (Morel and Price, 2003) and in one coccolithophore species, it regulates the alkaline phosphatase activity (Shaked et al., 2006). Despite the controversial opinions about Cd behaviour (Morel et al., 1991; European Commission, 2002; Prego et al., 2013), some authors agree about Cd biological functions, which include competition with Zn bioavailability in CA activity under Zn-limited conditions (Morel et al., 1991; Morel and Price, 2003). Both metals have a nutrient-type distribution in the ocean (Bruland and Lohan, 2003; Wyatt et al., 2014), often strongly correlated with the phosphate, nitrate and silicic acid (Bruland and Lohan, 2003; Croot et al., 2011; Wyatt et al., 2014). Conversely, Pb is a non-essential