



## Origin and accumulation of trace elements in sediments of the northwestern Mediterranean margin



D. Cossa<sup>a,\*</sup>, R. Buscail<sup>b</sup>, P. Puig<sup>c</sup>, J.-F. Chiffolleau<sup>d</sup>, O. Radakovitch<sup>e</sup>, G. Jeanty<sup>b</sup>, S. Heussner<sup>b</sup>

<sup>a</sup> IFREMER, Centre de Méditerranée, BP 330, F-83507 La Seyne-sur-Mer, France

<sup>b</sup> CNRS, Centre de Formation et de Recherche sur les Environnements Méditerranéens, UMR 5110, F-66860 Perpignan, France

<sup>c</sup> Marine Sciences Institute, CSIC, E-08003 Barcelona, Spain

<sup>d</sup> IFREMER, Centre Atlantique, BP 21105, F-44311 Nantes Cedex 03, France

<sup>e</sup> CEREGE, Université Aix-Marseille, CNRS UMR 7330, F-13545 Aix-en-Provence Cedex 4, France

### ARTICLE INFO

#### Article history:

Received 1 October 2013

Received in revised form 13 April 2014

Accepted 19 April 2014

Available online 8 May 2014

Editor: David R. Hilton

#### Keywords:

Trace-element

Sediment

Canyon

Continental margin

Mediterranean

### ABSTRACT

Continental margins receive natural and anthropogenic trace elements (TEs) from direct atmospheric deposition of aerosols onto the sea surface and from advection of riverine suspended particles and/or resuspended sediments from the continental shelf/slope. When the margin is incised by submarine canyons, as for example in the Northwestern Mediterranean Sea, most of these particles are preferentially transferred via these topographic features towards their final repositories in the abyssal plain. The Gulf of Lions (GoL) shelf receives the largest particulate riverine input to the Western Mediterranean, with its associated chemical contaminants originating from the industrialized and urbanized Rhone Valley. Sediment samples (grabs, cores and moored traps) collected in the Cap de Creus (CdC) Canyon and its adjacent areas at the Southwestern exit of the GoL were analyzed to explore the origin, dispersion, transfer and accumulation of a suite of TEs (Ag, Cd, Co, Cr, Cu, Ni, Pb, Zn and V) from the GoL shelf to the adjacent continental rise. Distributions of Cu, Cr, Ni, Pb, Zn and V in the surface sediments of the shelf confirm their terrigenous origin in association with clay minerals, whereas Ag and Cd are more associated with organic matter (OM). All these TEs are anthropogenically enriched in the Rhone prodelta sediments. Anthropogenic influence remains clearly discernible in the GoL shelf surface sediments for Ag, Pb and Zn. Hydrodynamical resuspension and sorting of shelf sediments occur at the head of the CdC Canyon during dense shelf-water cascading events. During these events, the material collected in moored sediment traps contains a higher coarse carbonate fraction slightly impoverished in TEs compared to the clays of the nepheloid layer and the organically-rich particles deposited before and at the end of the cascading period. Upper and middle canyon sediments are characterized by high sedimentation rates ( $\sim 0.2 \text{ cm yr}^{-1}$ ) of fine clay material. Conversely, sediments from the lower continental slope and rise exhibit low sedimentation rates ( $\sim 0.06 \text{ cm yr}^{-1}$ ) and receive carbonaceous planktonic detritus from the water column. At the lower continental slope, coarse material includes foraminifers and pteropods, whereas at the continental rise finer planktonic-derived material is more abundant. Both in the CdC Canyon and in its adjacent lower continental slope/rise sediments, Co, Cu, Cr, Ni and V are associated with clay, whereas Ag, Cu and Pb are preferentially associated with OM. Cadmium, Cr, and Zn are also associated with OM in canyon sediments. Carbonaceous plankton appears to be especially efficient for scavenging Ag, whereas, Cr, V, Zn and Pb are diluted by biogenic carbonates. An authigenic Mn fraction is enriched with Co and Ni. Lead and Zn concentration levels and vertical profile patterns, along with Pb stable isotopic ratios, indicate that significant parts of Pb and Zn are of anthropogenic origin. A sediment chronology based on  $^{210}\text{Pb}$  dating reveals that Pb anthropization, mainly from gasoline additives, culminated between 1960 and 1980, being the current concentrations  $>40\%$  lower than 30 years ago. A similar distribution is observed for Zn, which originates mainly from combustion processes; but the reduction of Zn contamination amounts to only 20% during the same period. The largest anthropogenic Pb accumulation occurs in the middle part of CdC Canyon, with an inventory of  $200 \mu\text{g cm}^{-2}$ . At the most distal part of the continental rise anthropogenic Pb accumulation within the first  $\sim 10 \text{ cm}$  below the surface sediment is estimated around  $10 \mu\text{g cm}^{-2}$ , which is similar to the direct atmospheric deposition estimate.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Open ocean deep ecosystems are generally considered as being less impacted by human activities than coastal areas. Indeed, they mainly

\* Corresponding author at. ISTERRE, Université J. Fourier, BP 53, F-38041 Grenoble, France. Tel.: +33 476 63 5928.

E-mail address: [dcossa@ifremer.fr](mailto:dcossa@ifremer.fr) (D. Cossa).

receive contaminants from atmospheric deposition, whereas continental margins additionally receive riverine inputs often loaded with chemicals (e.g., Hickey et al., 1986; Monaco et al., 1999; Puig et al., 2003, 2014; Canals et al., 2006; Heussner et al., 2006; de Stigter et al., 2007; Ogston et al., 2008). Chemical contaminants have been found in sediments within various submarine canyons around the world ocean (e.g., Maurer et al., 1996; Puig et al., 1999; Palanques et al., 2008; Richter et al., 2009; Heimbürger et al., 2012; Salvado et al., 2012a,b), suggesting that these morphological features act as natural sediment traps. Nevertheless, the main processes controlling the transfer of these chemicals within submarine canyons and towards deep sediments are still poorly known.

Sediment dynamics of the Gulf of Lions (GoL) and its canyons, in the Northwestern Mediterranean (NWM), are well documented (see for example the *Continental Shelf Research*, 28, 2008 special issue). The main inputs of sedimentary material to the GoL shelf are provided by Rhone River floods (discharges  $>3000 \text{ m}^3 \text{ s}^{-1}$ ), which are identifiable in the deposits of its proximal delta (Cathalot et al., 2010; Pastor et al., 2011; Révillon et al., 2011; Fanget et al., 2013). Other riverine sources in the same area are poorly preserved due to wave-induced sediment resuspension especially during storms (Guillen et al., 2006; Bourrin et al., 2007; Kim et al., 2009) and dense shelf-water cascading events (Durrieu de Madron et al., 2008; Roussiez et al., 2012). These two wind-driven processes limit the long-term sediment deposition on the shelf, and the general westward water mass circulation directs most of the export of suspended sediment towards the southwestern exit of the GoL, (Durrieu de Madron et al., 2008), especially the Cap de Creus (CdC) Canyon (Palanques et al., 2006; DeGeest et al., 2008). Tesi et al. (2010) estimated that 98% of the entire terrigenous organic matter (OM) export in the CdC Canyon occurred during dense shelf-water cascading events. Part of the sediments entering the GoL canyons forms temporary deposits in their upper/middle reaches, which act as a trap for particulate OM and associated trace elements (TEs) (Buscaill et al., 1997). However, these sediments are periodically resuspended and flushed to deeper canyon reaches, and further down to the abyssal plain (DeGeest et al., 2008; Puig et al., 2008; Palanques et al., 2012; Stabholz et al., 2013). Being the main outlet of sediment temporarily trapped on the GoL shelf, the CdC Canyon represents thus an interesting site for assessing the contamination transfer from the industrialized Rhone Valley to the NWM deep ecosystems.

In order to assess the offshore dispersal of natural and anthropogenic TEs in the NWM margin, we have determined the elemental composition of settling particles and deposited sediments from the Rhone prodelta to the Catalan continental rise following the GoL shelf and the CdC Canyon dispersal pathway. The following specific questions were also addressed in this article: (i) is the canyon a trap or just a channel for the oceanic transfer of particulate TEs? (ii) what is the role of the cascading events in this transfer? (iii) what is the part of the direct atmospheric deposition at open sea in sedimentary TE of the continental rise? (iv) what are the magnitude of anthropogenic fractions of TEs, their sources and the chronology of their inputs, both in the canyon and on the continental slope and rise?

## 2. Material and methods

### 2.1. Sampling

Four sediment cores were collected along the CdC Canyon with the R/V *Universitatis* in October 2005 at stations G, H, I and L (Fig. 1) using a multicore sampler (Multiple corer type) allowing the sampling of the undisturbed benthic interface (Barnett et al., 1984). Cores G (960 m depth, 28 cm long) and H (1473 m depth, 34 cm long) were located within the upper and middle part of the canyon (Lastras et al., 2007), whereas cores I (1874 m depth, 20 cm long) and L (2335 m depth, 8 cm long) were located at the lower continental slope and on the continental rise, respectively. The cores were sliced on board every

half centimeter until 2 cm, then every centimeter until 20 cm, and finally every two centimeters. Undisturbed surface sediments (0–1 cm) were also collected on the GoL shelf, from the Rhone prodelta to the head of the CdC Canyon using a box corer during the R/V *Endeavor* cruise in April 2004 (Fig. 1). Sediments were quickly frozen ( $-18 \text{ }^\circ\text{C}$ ) on board after sub-sampling, then freeze-dried and stored in the dark in the laboratory until analysis. Coordinates of the sampling stations are given in Table S1.

Settling particles were collected from October 2004 to May 2005, a period of major cascading and storm events in the GoL (Puig et al., 2008; Tesi et al., 2010), using a sediment trap (PPS3, Technicap) placed at 30 m above the bottom on a mooring deployed at 500 m water depth at the CdC Canyon head ( $42^\circ22.27'\text{N}$ ;  $3^\circ21.69'\text{E}$ , ST, Fig. 1). Sediment trap cups were filled with buffered formaldehyde; the collected material was stored at  $+4 \text{ }^\circ\text{C}$  after sieving through a 1 mm nylon mesh to retain the large swimming organisms that occasionally enter the traps during sampling. It was then precisely divided into sub-samples for subsequent analyses using a WSD-10 McLane wet sample divider. A sub-sample from each trap was inspected under a microscope to remove the remaining small swimmers with tweezers and was freeze-dried and stored in the dark until analysis.

### 2.2. Dating and mixing

Activities of  $^{210}\text{Pb}$  in sediments were measured according to the method described by Radakovitch and Heussner (1999). Briefly, after complete acid digestion of the sample, its granddaughter  $^{210}\text{Po}$  was spontaneously deposited on a silver disc. The disc was then placed between ZnS(Ag) phosphors and counted on a total alpha counter. As  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are in secular equilibrium within sediments, only one deposition and counting was performed on the sediment samples. Supported  $^{210}\text{Pb}$  was calculated from the mean of constant activities measured at the bottom of each core, and excess  $^{210}\text{Pb}$  equals total  $^{210}\text{Pb}$  minus supported. Sedimentation rates have been calculated using both constant flux-constant sedimentation (CFCS) and constant initial concentration (CIC) models, based on  $^{210}\text{Pb}$  in excess ( $^{210}\text{Pb}_{\text{ex}}$ ) distributions (Appleby and Oldfield, 1978).

$$\left[^{210}\text{Pb}_{\text{xs}}\right]_z = \left[^{210}\text{Pb}_{\text{xs}}\right]_0 e^{-\lambda(z/\tau)}$$

where  $\left[^{210}\text{Pb}_{\text{xs}}\right]_{0,z}$  are the activities of excess  $^{210}\text{Pb}$  at surface, or the base of the mixed layer, and depth  $z$ ,  $\lambda$  the decay constant of  $^{210}\text{Pb}$  ( $0.03114 \text{ yr}^{-1}$ ), and  $\tau$  the sedimentation rate.

### 2.3. Analytical techniques

Total carbon (Ct), organic carbon ( $\text{C}_{\text{org}}$ ) and total nitrogen (Nt) contents were analyzed by combustion in an automatic CN-analyzer (Leco 2000), after acidification of the samples with 2 M HCl (overnight at  $50 \text{ }^\circ\text{C}$ ) to remove inorganic carbon prior to the analyses of  $\text{C}_{\text{org}}$  (Cauwet et al., 1990). Calcium carbonate content was calculated from mineral carbon ( $\text{Ct} - \text{C}_{\text{org}}$ ) using the molecular mass ratio ( $\text{CaCO}_3:\text{C} = 100:12$ ). Extensive testing at Cefrem laboratory showed long-term precisions for  $\text{C}_{\text{org}}$  and Nt of about 2% and for Ct of 0.3%.

Elemental composition (Ca, Al, Fe, Li, V, Cr, Mn, Ni, Cu, Zn, Ag, Cd, Co and Pb with its stable isotopes) was performed after total dissolution of sediment with a mixture of HCl,  $\text{HNO}_3$ , and HF in hermetically sealed Teflon bombs according to the protocol described by Loring and Rantala (1990) and modified by Chiffoleau et al. (2004). All reagents used were SupraPur®, obtained from Merck. The concentrations were determined using an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Electron Corporation, Element X Series®). Iron and Al concentrations were determined by atomic absorption spectrophotometry (AAS, Varian, SpectraAA 600®). The determinations were validated using certified reference materials

Download English Version:

<https://daneshyari.com/en/article/4698730>

Download Persian Version:

<https://daneshyari.com/article/4698730>

[Daneshyari.com](https://daneshyari.com)