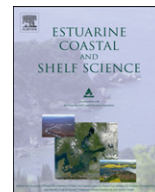




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## Fate of metals in coastal sediments of a Mediterranean flood-dominated system: An approach based on total and labile fractions

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### ABSTRACT

The dynamics of sediment-bound metals (Cs, Cu, Ni, Pb, Ti and Zn) were studied off the Têt River (western Gulf of Lion), a typical Mediterranean coastal river punctuated by short and violent flash-floods. Spatial and temporal sampling strategies were combined to elucidate the fate of these elements in response to both the riverine sediment input and the offshore transport of these sediments through hydrodynamics. Our results show the temporal entrapment of riverborne particles and associated metals, consecutively to a major flood event, in the nearshore sedimentary unit called prodelta. Here, deposition and resuspension mechanisms define a sedimentological cycle that could be followed completely in this study. In terms of speciation between reactive (labile) and residual fractions along the fluvio-deltaic continuum, our results show that Cu, Pb and Zn are the most labile (potentially mobile) metals in the river, in accordance with their contributions from anthropogenic sources. But in the marine surficial sediments, two main behaviours can be discriminated when compared to the riverine suspended particulate matter. While Pb and Zn depict rather a constant labile fraction, Cu is characterized by decreasing levels (up to 50% difference). In terms of environmental impact, these contrasting trends have direct repercussions for the contaminant dispersal in the coastal area. Whereas Pb and Zn conserve their enhanced levels because of their stronger affinity with fine sediments, Cu is marked by the entire loss of its anthropogenic component that is progressively transferred to the dissolved phase, likely mediated by organic ligands. We ascribe these behaviours to different post-depositional partition mechanisms with respect to oxidation of the particulate organic phase at the bottom sediment/water interface. Also, analysis of one sediment core from the prodelta indicates that these early diagenetic processes govern the chemical forms of land-derived contaminants sequestered in the nearshore sedimentary archives.

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### 1. Introduction

Coastal margins surrounded by densely populated watersheds are sensitive environments because they constitute repository areas for contaminated riverborne particles. About 90% of the latter can be deposited in the vicinity of river mouths, according to Martin and Windom (1991). Recently, it has been shown that riverine suspended sediment fluxes of some trace metals are similar to their anthropogenic fluxes to the atmosphere, soils and waters (Viers

et al., 2009). From both environmental and ecological viewpoints, studying the transfer of these contaminants to the marine realm is therefore of great concern and their distribution in many different coastal areas has been extensively studied so far (e.g. Chiffolleau et al., 1999; Angelidis and Aloupi, 2000; Cobelo-Garcia and Prego, 2004). Prevalent in the clay fraction, metals are predominantly delivered to the coastal waters in association with riverborne particles that act as transporting agents. Their behaviour and fate strongly depend on sedimentary dynamics (Zhang, 1999; Che et al., 2003), but also biological and physico-chemical interactions occurring in the mixing zone between fresh and salt waters can play an important role (Comans and Van Dijk, 1988; Regnier and Wollast, 1993; Eggleton and Thomas, 2004).

The Gulf of Lion (NW Mediterranean), a non tidal environment, is bordered by numerous industrialized/cultivated river catchments

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draining important quantities of materials into the coastal zone. Previous studies dealing with the fate of terrestrial particles and associated substances (e.g. metals, sewage tracer, organic matter) over the continental shelf contributed to new findings with respect to the particulate material budgets in the overall region (Durrieu de Madron et al., 2000), the degree of metallic pollution on the platform (Roussiez et al., 2006), and the river inputs of trace metals from the different drainage basins (Radakovitch et al., 2008). Also, more detailed approaches focusing on the sedimentary processes at the continent/sea interface demonstrated that part of the riverborne particles accumulate off the river mouths, in nearshore sedimentological units called prodeltas. This implies that sediment-bound contaminants tend to remain close to their point sources before eventually being transported further offshore (e.g. Roussiez et al., 2005a and references therein). However, to date, information regarding the sediment deposition/resuspension dynamics and its repercussion on the contaminant dispersal was clearly lacking. To improve this knowledge, strategies were developed to track riverborne particles in the direct vicinity of river mouths and thus explore the effects of short-term processes such as floods and storms on sediment delivery and erosion. Multi-scale sediment samplings and *in situ* monitoring have been carried out for the past five years within the fluvio-deltaic continuum of the Têt River, a typical Mediterranean flood-dominated system at the western border of the Gulf of Lion. Whereas previous approaches mainly focused on the overall sediment fluxes (e.g., Guillén et al., 2006), the research reported here is devoted to the geochemical tracing of these sediments.

Our main purpose is to examine the behaviour and fate of selected particulate trace metals (Cs, Cu, Ni, Pb, Ti and Zn) in the fluvio-deltaic continuum of the Têt River during variable hydrodynamic conditions in 2003 and 2004. Based on a combination of spatial and temporal sampling strategies, this study especially focuses on a typical hydro-sedimentary event (i.e. the flood episode of December 2003) and the geochemical changes induced by its development in the coastal area.

Total and labile fractions were analysed along the downstream transport pathway of sediments, through the main sedimentary compartments: river, prodelta and distal sedimentation area. Specific objectives were (i) to determine the metal dynamics in this highly energetic system with regard to riverine input and seabed erosion, (ii) to test whether temporal and spatial distributions of metals can indicate the movement of sediments in this area, and (iii) to assess the risks for ecosystems via linking the potential mobility of metals to their anthropogenic contributions.

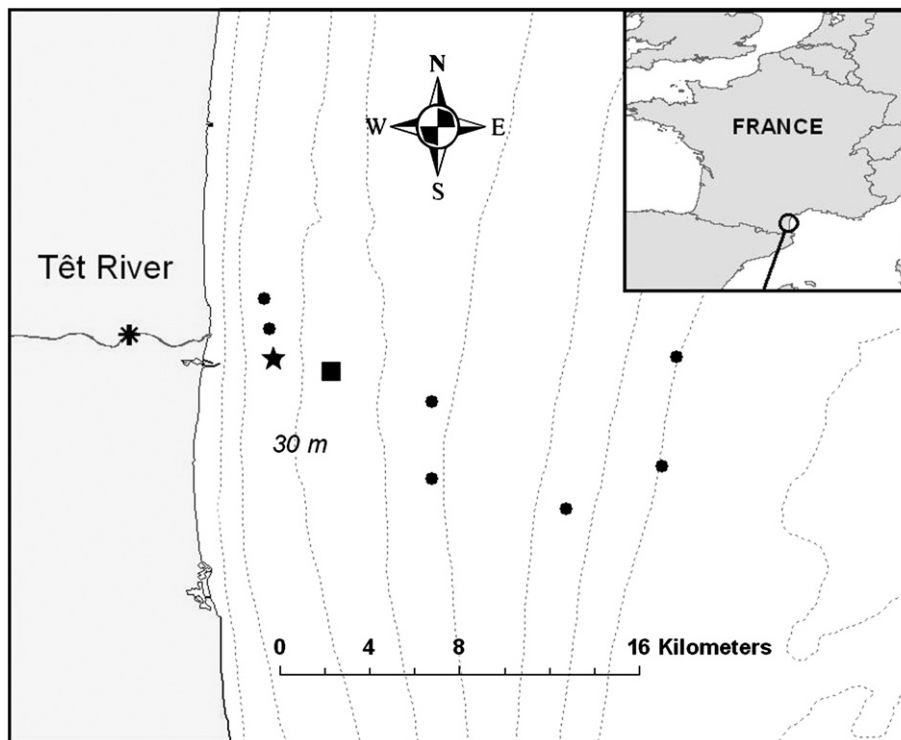
## 2. Material and methods

### 2.1. Site description

The Têt River is a short coastal river located in the western part of the Gulf of Lion in the Mediterranean Sea (Fig. 1). Its basin area is about 1400 km<sup>2</sup> and the river length is 120 km. The uppermost parts of the basin are located in elevated regions where population density is low. Most of the population is distributed near the river mouth, especially in the city of Perpignan (10 km from the coast), which supports 60% of the total basin population.

The river is characterized by a highly contrasted hydrological regime (Ludwig et al., 2004), typical for Mediterranean-type climates. The main part of the river suspended particulate matter (SPM) is delivered to the coastal waters during episodic flood events in autumn and winter (peak flows >300 m<sup>3</sup> s<sup>-1</sup> are frequently recorded at the outlet), contrasting with the usual low flow observed especially in summer (about 2–3 m<sup>3</sup> s<sup>-1</sup>). The average annual water discharge at the outlet is about 10 m<sup>3</sup> s<sup>-1</sup> and the mean annual solid flux is estimated to 0.7 × 10<sup>5</sup> t yr<sup>-1</sup> (Serrat et al., 2001; Garcia Esteves and Ludwig, 2003).

In terms of geology, the river drains metamorphic and igneous rocks from the eastern part of the French Pyrenean mountains. Further downstream, it enters its alluvial plain constituted of



**Fig. 1.** Study area showing the sampling locations. Asterisk and star correspond respectively to the river SPM and the surface prodeltaic sediment follows-up. Square symbolizes the location of the prodeltaic sediment core. Points represent the nine surficial sediments collected during the April 2004 transect (two of them are superimposed with star and square symbols, respectively). Dashed lines represent the 10 m isobath intervals.

erosion products from the upstream rocks. The natural part of SPM is thus a composite material of various origins, and the specific geochemical background values for the overall river basin are not known. However, average metal references for the marine sediments in the entire Gulf of Lion have been determined by Roussiez et al. (2005b). Due to the high spatial homogeneity of pre-anthropogenic levels over the platform, these values were found to be also representative for our coastal sediments and hence used as natural references in this work.

As shown through a recent characterization of both dissolved and particulate material fluxes in the Têt River (Garcia Esteves et al., 2007), agricultural activities (mostly fruit trees and vineyards) and urban wastewaters (mainly from the wastewater station of Perpignan) have a large impact on the water quality. The Têt River therefore represents a source of contamination for the nearby coastal waters, of importance as shallow submarine rock outcrops close to the river mouth constitute sensitive ecological niches for marine species.

The coastal zone off the Têt River can be divided into two main sedimentological units, based on the limit of the stormwave influence (i.e. 35 m isobath, Roussiez et al., 2005a): (i) the prodelta, i.e. the nearshore and wave-impacted area, where fine-grained sediments can accumulate through coagulation/flocculation processes, and (ii) the distal sedimentation area, not under the direct influence of riverine inputs and where less energetic hydrodynamical conditions favour longer residence times of particles on the seafloor.

## 2.2. Sampling strategy

### 2.2.1. River SPM

A total of 10 water samples from the Têt River were collected at subsurface depth during different river flow conditions via a horizontal Niskin bottle between mid October 2003 and late April 2004 (Fig. 2A). The two sampling stations were located in and downstream the city of Perpignan, respectively 10 and 1 km from the river mouth. For three dates, the samples were taken at both stations. Water samples were immediately stored in 1 N HCl pre-cleaned polypropylene bottles. Returned to the laboratory, samples assigned to trace metal analyses were pre-filtered through a pre-cleaned 63  $\mu\text{m}$  nylon mesh prior to filtration through preweighted and 0.1 N HCl pre-cleaned cellulose acetate filters with 47 mm in diameter and 0.22  $\mu\text{m}$  in pore size. Water samples used for granulometric analyses were directly filtered through polycarbonate filters (47 mm, 0.4  $\mu\text{m}$ ). Immediately after filtrations, filters were dried at 40 °C during 24 h in a clean oven and particle concentrations were calculated. All rinsing procedures (polypropylene bottles, cellulose acetate filters) were performed using Milli-Q deionised water.

### 2.2.2. Coastal sediments

The investigated marine sediments are a compilation of three sample series (see also Fig. 1): (i) one sediment core collected in the prodeltaic area in November 2002 using a multicorer during the “Remora 3” campaign (see Roussiez et al., 2005b); (ii) five surficial samples of sediment cores collected in monthly intervals by diving at one prodelta station between late November 2003 and late April 2004 (note that no core was taken in January); (iii) nine surficial samples of sediment cores stretching over the entire prodelta and the distal sedimentation area and collected in mid April 2004 using an Usnel-type box corer during the “Sed 2” campaign. The choice of the sampling stations was based on the discrimination between prodeltaic and distal sedimentation areas, respectively above and below the 35 m isobath. Surficial samples were taken as the first 0.5 cm of sub-sampled sediment cores using 1 N HCl pre-cleaned PVC tubes. Samples were stored in plastic bags and immediately deep-frozen and/or lyophilized.

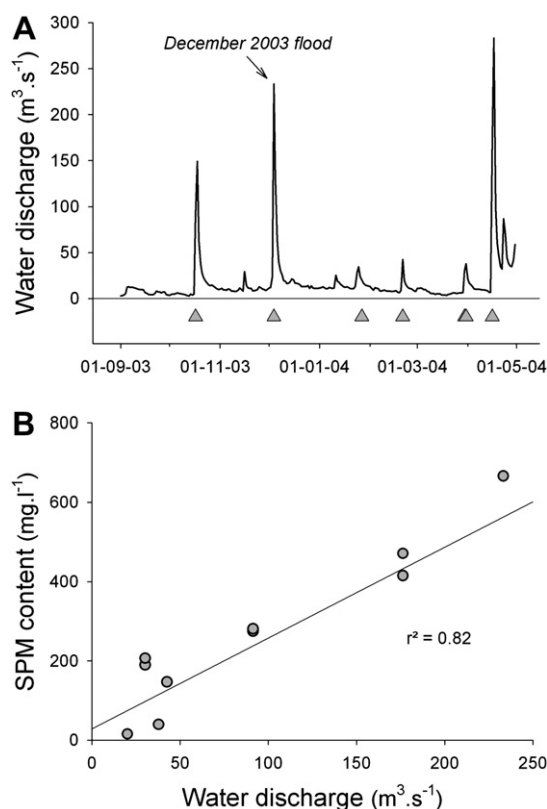


Fig. 2. (A) Water discharge of the Têt River between September 2003 and April 2004. River water samplings are indicated by triangles. (B) Relationship between the water discharge and the suspended particulate matter content in the Têt River, based on the 10 water samplings from this study.

## 2.3. Hydro-sedimentary context over the study period

The coastal system off the Têt River, and especially its prodelta, is a highly energetic environment, frequently perturbed by both “wet” and “dry” storms (Guillén et al., 2006). The former type induces torrential floods whereas the latter is only responsible of seabed agitation and sediment reworking. Hence the above described sampling strategy was designed to track the development of floods along the fluvio-deltaic continuum of the Têt River.

Two floods occurred during the prodelta follow-up, one in early December 2003 and one in mid April 2004 (Fig. 2A). But only the first event left new deposits at our sampling site. The depocenter related to the flood episode of April 2004 was confined closer to the shoreline due to strong North-South currents (Guillén et al., 2006) and hence out of reach of our monitoring site. It is also worth noting that very low water discharge (implying low sediment transport) of the Têt River was recorded between these two floods (Fig. 2A). This means that, during the study period, almost all of the riverine material that settled in the prodeltaic area corresponds to the December 2003 flood deposits. As a consequence, the seaward transect in mid April 2004 is representative for both sedimentary and geochemical conditions that prevail in the surficial sediments at this date after a relative long period without any significant fresh riverborne particle delivery.

## 2.4. Geochemical analyses and particle-size distribution

Total and non-residual trace metal concentrations were determined in both river SPM and coastal sediments. Geochemical

analyses were restricted to the less than 63  $\mu\text{m}$  sediment fraction. Filters were treated in the same way than sediments. The analytical procedures and accuracies related to total metal measurements were described in details in Roussiez et al. (2005b). Briefly, it consists in a total digestion using a HF–HNO<sub>3</sub>–HClO<sub>4</sub> mixture. Accuracy was controlled by the use of certified standards (i.e. MESS-2 and GSMS-3) and provided suitable recoveries ( $\pm 0.5\%$  for Cs and Ni, and  $\leq 5\%$  for Cu, Pb and Zn). For the sediment core samples, the activity of <sup>210</sup>Pb, a natural radionuclide used as a tracer of sediment mixing and accumulation (e.g. Krishnaswami et al., 1980) was determined by total alpha measurements after total sediment digestion following the procedure described by Radakovitch et al. (1999). Granulometry was determined by laser granulometer LISST-100 on bulk river SPM and sediment core samples. Each result is a mean of two measurement runs, during which 100 values are collected. Finally, the surficial sediment samples collected at the prodelta site during the follow-up were also analysed for organic carbon (OC) contents (% dry weight sediment) by combustion in a LECO CN 2000 analyser after acidification with HCl 2 N to remove carbonates.

### 2.5. Single-step leaching procedure

The use of total metal concentrations in sediments, albeit suitable for determining contamination levels, limits the understanding of element dynamics since all forms of a given metal do not exhibit a similar behaviour (Sims and Sklin, 1991; Hsu and Lo, 2001). In this respect, substantial information can be gained from rapid and low cost procedures such as single-step acid leaches that target the non-residual (non-detrital) metallic fraction in sediments (e.g. Chester and Voutsinou, 1981; Fiszman et al., 1984). This fraction is composed of reactive (labile) metal phases, which are acid extractable, reducible and oxidizable (Rauret et al., 1999). Metals included in these phases are at different degrees potentially mobile, as they may equilibrate with the aqueous phase and thus become easily bioavailable and toxic (Pardo et al., 1990). To measure the labile fraction, certain authors recommend a 1 N HCl leach (Szefer et al., 1995; Santos et al., 2005) based on high correlations that can be found between metals in benthic organisms and 1 N HCl extracted metals in surface sediments (Bryan and Langston, 1992). However, when compared to sequential extraction procedures, the 0.5 N HCl single leach technique appears to be the most effective approach to extract labile metal phases (Sutherland, 2002). We therefore used this method and assumed that leached metals correspond to the total of non-residual metals in the samples.

Single leaches were conducted on a subset of samples: four flood-type SPM samples collected during the river follow-up and nine surficial marine sediments collected during the mid April 2004 transect (four and five for prodeltaic and offshore areas, respectively). It was done by using 10 ml of 0.5 N HCl with (i) 0.5 g (d.w.) of sieved sediment ( $< 63 \mu\text{m}$ ), or (ii) the available SPM collected on filters. The samples were passed into a sonification bath during 10 s to eliminate aggregates, prior to agitation at room temperature during 60 min. Then, they were centrifuged at 2500 rpm during 10 min and 9 ml of the supernatant phase was collected for evaporation to dryness on a hot plate (45 °C). The residues were solubilized by HNO<sub>3</sub> and diluted to volume, prior to analysis by ICP-MS. Dilution factors allowed calculation of the contents in 100% of the supernatant phase. The possible alteration of the crystal lattice was checked with Cs, a residual phase proxy. A release of less than 0.2% on average was registered for this element, confirming the negligible impact of the single leach procedure on aluminosilicates. Blanks did not reveal any contamination.

## 3. Results and discussion

### 3.1. Sediment and associated metal delivery to the coastal system

Before considering the fate of particulate trace metals off the Têt River, it is fundamental to analyse the main factors that control their input to the coastal sea. Especially the variability of both the fluxes and textural composition of river SPM may have a dominant role in this respect. As is typical of flood-dominated river system, most of the total sediment delivery occurs in the form of intermittent pulses with different intensities. Previous studies showed that the concentrations of SPM in the Têt are closely linked to water discharge (Serrat et al., 2001; Garcia Esteves et al., 2007). The few data collected in our study also confirm this close relationship (Fig. 2B), indicating that river SPM fluxes can be easily estimated from water discharge. Regarding granulometry, which has a strong influence on elemental abundances in the particulate phase, our data indicate that grain-size distribution in bulk river SPM samples is rather invariant irrespective of the sediment load (around 99% of SPM is  $< 63 \mu\text{m}$ ). It is therefore not surprising that the investigated metal contents generally display a very limited variability (Table 1), especially for Cs, a suitable proxy for clays in this region (Roussiez et al., 2005b). While suspended sediment concentrations ( $\text{mg l}^{-1}$ ) can vary by a factor of 40, metal concentrations in the solid fraction ( $\mu\text{g g}^{-1}$ ) only vary by 1.5 for Cs and Ni and by 2 for Cu, Pb and Zn. The latter are the elements for which there is evidence of significant anthropogenic perturbation (see below). All these metals exhibit strong positive correlations with Cs (not shown), except for Cu ( $r^2 = 0.33$ ). The outlier behaviour of Cu is presumably due to a different introduction pathway. Anthropogenic Cu in watersheds such as the Têt basin may be derived from fungicides (Garcia Esteves et al., 2007), which are sporadically released from the periodicity of agricultural activities. Furthermore, the retention of this element by organic amendments in vineyards soils (Besnard et al., 2001) should contribute to a highly variable remobilisation with time. Conversely, anthropogenic Pb and Zn are rather diffused through atmospheric fallout (Roussiez et al., 2006) that leads to a more uniform spread on soils.

According to the very low variability of metal contents in SPM, we conclude that the particulate metal discharge to the coastal area largely depends on SPM fluxes. Consequently, it is assumed here that our results on river SPM can be taken as representative for riverine signatures in the Têt River in general.

### 3.2. Trace metal distribution in response to particle deposit and resuspension

#### 3.2.1. Monthly follow-up of the prodeltaic area

The monthly sediment sampling of the Têt prodelta was carried out at a representative station (Fig. 1) where riverborne particles frequently settle to the seabed. During the period covered by this study, almost all of the riverine material that sedimented in the

**Table 1**

Total metal contents (ppm) of the Têt river SPM collected during the period from mid October 2003 to late April 2004. The corresponding annual fluxes have been calculated on the basis of available data in Garcia Esteves and Ludwig (2003) and Serrat et al. (2001), e.g. annual solid flux ( $0.7 \times 10^5 \text{ t yr}^{-1}$ ) and river catchment area ( $1400 \text{ km}^2$ ).

	Cs	Cu	Ni	Pb	Zn	Ti
Mean contents (ppm)	10	85	43	48	192	4320
SD	$\pm 1$	$\pm 25$	$\pm 6$	$\pm 10$	$\pm 31$	$\pm 219$
Annual flux (t/yr)	0.6	5.1	2.6	2.9	11.5	257
Specific annual flux ( $\text{kg/km}^2/\text{yr}$ )	0.4	3.6	1.8	2.0	8.2	184



prodelta area corresponds to the December 2003 post-flood deposit (see Section 2.3). The residence time of these materials is highly variable, depending on the intensity and frequency of both deposition and resuspension processes.

The temporal evolution of metal contents in surficial sediments of the prodelta-type station is illustrated in Fig. 3 and reveals two main trends. A sharp increase of the metal (including the clay proxy Cs) contents is registered on 12 December 2003. Only Ti, a typical heavy mineral indicator associated with particle sorting processes (Dellwig et al., 2000) and prevalent in silty fractions (Taboada et al., 2006), shows an opposite trend. This change in the geochemical composition implicitly traduces the new settling of fine-grained and metal-rich sediments on the nearshore seabed. The riverine origin of this deposit is confirmed by its elemental contents close to the river SPM references (Table 1) and may be related to the major flood event that occurred on 4 December. Subsequently, one can observe the progressive decrease of the clay-bound metal contents (concomitantly the increase of silt-bound Ti contents) that continues to mid April 2004, when pre-flood geochemical signatures are recovered. This second trend highlights the decrease of clay abundance in the surficial sediments, which is in line with the evolution of Cs contents. It likely means that, once deposited to the seabed, fine and metal-rich riverborne sediments are exposed to hydrodynamics and progressively remobilized and flushed further offshore.

It is clear here that the temporal evolution of clay-bound metal and particularly clay tracer Cs contents can indicate the movement of sediments at the continent/sea interface. Without any other significant particle settling at our station after the December flood, the deposition/resuspension cycle could be completely followed in time. According to the period between the sharp increase of metal contents and the recovery of pre-flood levels on Fig. 3, it is suggested that it lasted about 3–4 months.

### 3.2.2. Spatial variability off the Têt River mouth

To trace the fate of sediment-bound metals outside the physiographic limits of the prodelta, a metal transect was conducted off the Têt River mouth on mid April 2004 (Fig. 1), i.e. consecutively to the total erosion of the December 2003 post-flood deposit (see also Section 2.3). As seen in Fig. 4, the most striking result is the seaward increasing gradient of elemental contents (here Pb and Zn, taken as examples). All clay-bound metals display this trend (not shown), which agrees with their close relationship with the Cs distribution ( $r = 0.88, 0.98, 0.99$  and  $0.8$  for Cu, Ni, Pb and Zn, respectively). As particulate metal concentrations in coastal regions can be affected by fine sediment transportation and deposition conditions (Carman

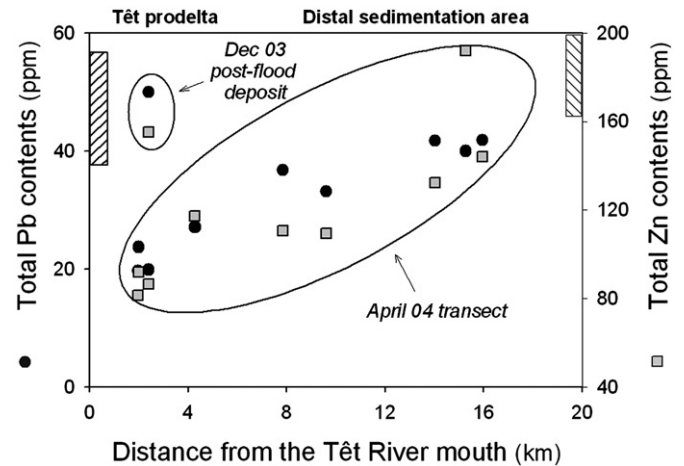


Fig. 4. Spatial evolution of Pb and Zn total contents in surface sediments collected in mid April 2004 off the Têt River mouth ( $n = 9$ ). For comparison, contents in the flood deposit of December 2003 recorded in the prodelta ( $n = 1$ ) are added. Also, river SPM references are illustrated by hatched bars along the Y axes, and are expressed as the standard deviation intervals around the means ( $n = 10$ ). Units are ppm.

et al., 2007), this spatial pattern likely obscures an important granulometric control that can be explained by the hydrodynamic context. Indeed, the lowest metal contents are registered in the prodelta where the fine-grained sediments have been eroded at the time of the sampling (i.e. April 2004). The highest values correspond to the distal zone and match well with the signatures of both the river SPM and the post-flood deposit of December 2003, for which the respective values have been added to Fig. 4 for comparison. Therefore, the seaward gradients of the contents suggest that clayey particles exported from the river and/or the previously nourished prodelta are advectively transported and progressively deposited in deeper environments. This remote settling is favoured by low energetic conditions, below the storm-wave base, making the distal area a stable and probably long lasting repository for particles compared to the proximal area. Because of the low direct inputs of the Têt River between December 2003 and April 2004, one can suppose that the prodelta was the major supplier of fine metal-rich sediments to the distal area during this period. This was possible according to the important stock of mud on the prodelta surface in early December 2003 that was identified using downcore granulometric profiles (Bourrin et al., 2007).

As already found from observations on temporal evolutions of metal contents (see Section 3.2.1), also their spatial distributions

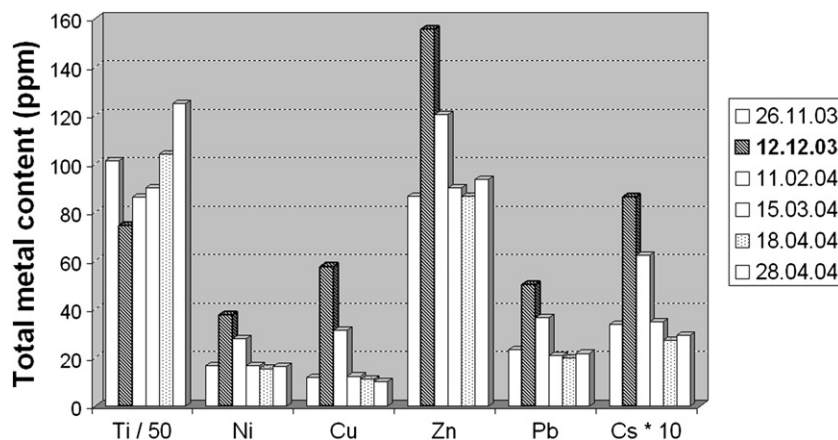


Fig. 3. Temporal variation of Ti, Ni, Cu, Zn, Pb and Cs total contents (ppm) in surficial sediments at the prodelta-type station (see Fig. 1). To be meaningful, Ti values are divided by 50 while those of Cs are multiplied by 10. Samplings of 12 December 2003 and 18 April 2004 are consecutive to flood episodes but only the first event left new fine deposits on the investigated site.

reflect the transport of particles by hydrodynamics. A similar conclusion has been advanced by Che et al. (2003) when studying the sediment transfer from Changjiang Estuary to Hangzhou Bay, China.

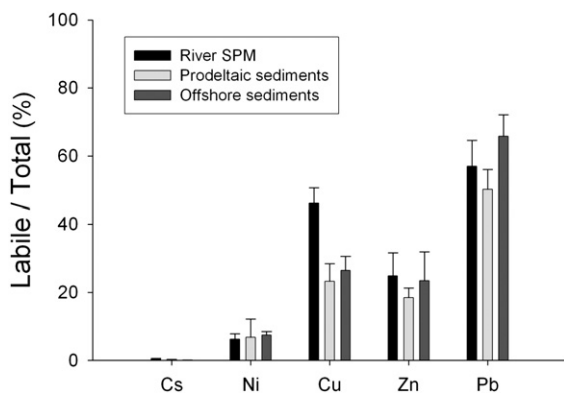
### 3.3. Behaviour patterns of riverborne metals in the coastal system

#### 3.3.1. Residual/labile speciation along the continuum in April 2004

In the particulate phase, trace metals exist in different chemical forms, which govern their behaviour in terms of chemical interaction, mobility, biological availability and potential toxicity (Norvell, 1984). Following the partitioning of these elements along the downstream transport pathway could therefore explain their dynamics under changing environmental conditions as well as the potential risks for biota. A selection of particulate samples were therefore analysed for element speciation between residual and reactive (labile) phases.

The land-to-sea evolution of labile/total fraction ratios in the investigated samples (see Section 2.5) reveals two populations of elements (Fig. 5). On the one hand are those for which the labile contribution is weak to non-existent (Ni and Cs, respectively). This indicates a detrital origin derived from rock weathering and attributes mainly natural sources to these elements. From an ecological viewpoint, they can be regarded as inert because of their sequestration in the crystal lattice; only long-term weathering processes could mobilize them (Calmano et al., 1993). On the other hand are those elements for which an important labile fraction is present (i.e. Cu, Pb and Zn). They are known to be frequently enriched by contamination and their important labile contributions reflect the incorporation of anthropogenic metals in the sediment *via* instable and easily reactive forms (Salomons and Forstner, 1984; Singh et al., 2005). These elements might therefore be the most problematic metals for exposed aquatic habitats, according to their higher mobility potential.

It is of note that the lability of both Pb and Zn is rather constant in the investigated physiographic areas. However, this is lower for Cu (about 50% difference) in surficial marine sediments compared to the average lability in river SPM. A similar spatial pattern was observed by Carman et al. (2007) in surficial sediments of the estuarine/coastal continuum off the Pearl River, South China. In particular, the seaward percentage decrease of Cu bound to the non-residual fraction was attributed to sorption–desorption mechanisms occurring at the mixing zone between fresh and salt waters (see also Baeyens et al., 1998). More detailed studies suggest the role of strong Cu-complexing ligands such as organic colloids (Waeles et al., 2008) and dissolved organic matter (Gerringa, 1990; Shank et al., 2004; Sakellari et al., 2010) in the removal of particulate



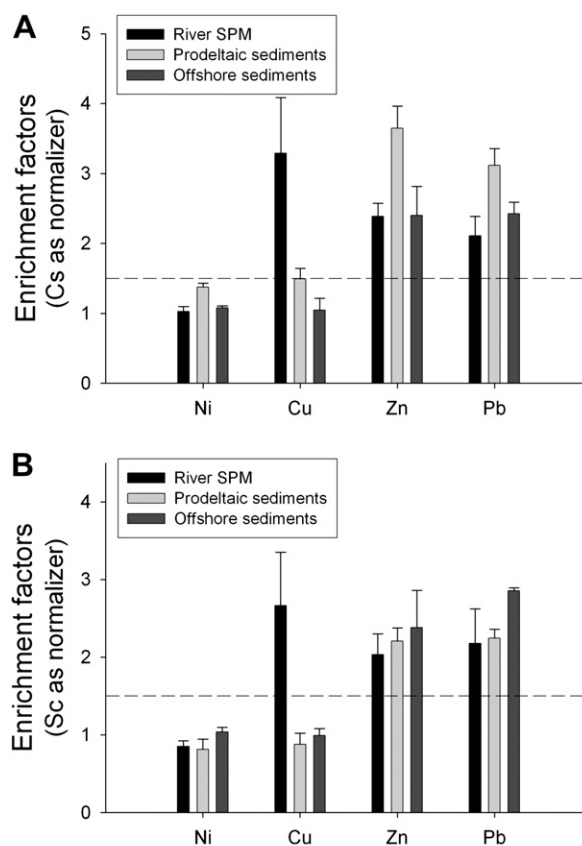
**Fig. 5.** Non-residual/total content ratios of particulate metals in the different sampling areas ( $n = 4$ , 4 and 5 for river SPM, prodeltaic and offshore samples, respectively). River SPM are selected samples collected during the river follow-up. Marine samples are the surficial sediments collected during the April 2004 transect.

labile Cu. Although chemical structures of these substances remain unresolved, researchers have elucidated many of their sources. They can originate from the continent *via* riverine inputs (Xue and Sigg, 1999; Shank et al., 2004) or directly come from the benthic estuarine sediments (Skrabal et al., 1997). In the present work, desorption from particles and ligand entrapment could therefore explain the non conservative behaviour of particulate Cu, in comparison with Pb and Zn. Nevertheless, according to the sedimentary context in April 2004, it is unclear whether the desorption mechanism occurs rapidly during the mixing of fresh and salt waters or also continues once particles are deposited to the prodelta (see Section 3.3.3).

In terms of ecological impact, the behaviour patterns of Cu, Pb and Zn suggest two kinds of threat. On the one hand, it is likely that, once in the form of water-soluble complex, Cu becomes available and toxic for both benthic and pelagic marine animals and plants. Unfortunately, there is no general consensus defining the degree of copper toxicity in this context. Conflicting results have been reported about the reducing (e.g. Meador, 1991) or increasing (e.g. Florence et al., 1992) influence of complexing ligands on Cu toxicity. On the other hand, labile Pb and Zn keep maintained in the particulate phase and should represent a risk only by sediment ingestion. The significance of this, in terms of contaminant dispersal, is further discussed below.

#### 3.3.2. Metal contamination along the continuum in April 2004

The distinction between natural and anthropogenic contributions of particulate metals can be estimated using enrichment



**Fig. 6.** Enrichment factors (EFs) of particulate metals in the different sampling areas ( $n = 10$ , 4 and 5 for river SPM, prodeltaic and offshore samples, respectively). Dashed line symbolizes the limit of natural variability (i.e.  $EF = 1.5$ ). River SPM samples were collected during the river follow-up. Marine samples were collected during the April 2004 transect. Figures A and B correspond to EFs calculated by taking Cs and Sc as normalizers, respectively.

factors (EFs). These indices are defined as the observed metal/normalizer ratios in the samples divided by the corresponding ratios of a reference material (Sutherland, 2000). They were calculated in this work using the regional background levels of Roussiez et al. (2005b). Following the same geospatial approach than in 3.3.1, the results are illustrated in Fig. 6A, using Cs as normalizer element. Based on a threshold value of  $EF = 1.5$  (see Roussiez et al., 2006), it is shown that Ni is mostly of natural origins, whilst Cu, Pb and Zn are characterized by significant anthropogenic contributions. EF indices are thus consistent with the hypothesis that anthropogenically enriched metals display greater labile fractions (Fig. 5).

In the cases of Pb and Zn, there is a notable increase in the enrichment in the prodeltaic area when compared to the riverine and distal levels. In addition, this phenomenon also concerns Ni, which discredits an anthropogenic origin. A plausible explanation for this could be a change in the mineralogical composition (Goldsmith et al., 2001) in response to erosion processes. In mid April 2004, as suggested by both Cs and Ti contents (Fig. 3), surficial prodeltaic sediments are predominantly composed of silt-size particles. As a consequence, metal/Cs ratios of our prodeltaic samples are more influenced by the silt fraction, likely generating slightly overestimated EFs. The use of Sc seems to be more convenient for the calculation of EFs in these clay-depleted sediments. Taking this element, no significant enrichment is observed in the prodelta with respect to the other compartments (Fig. 6B). Note that the resulting spatial pattern is now in very good agreement with the one observed for metal lability (Fig. 5), which reinforces the assumption that single-step leaching procedures represent an effective approach to determine trends in metallic contaminations (Chester et al., 1985). These observations suggest that, in mid April 2004, despite erosive conditions in the close inner-shelf, contamination by Pb and Zn is homogeneously distributed in the fluvio-deltaic continuum. In terms of sedimentological functioning, this result implies the persistence of contaminated clays within coarse silts in the prodelta.

In contrast to Pb and Zn, Cu is marked by the total loss of its anthropogenic contribution in the surficial coastal sediments, and the EFs clearly drop below the 1.5 threshold. This phenomenon matches with the results illustrated in Fig. 5 and is the result of the above described removal of labile Cu. These two different element dynamics may entail two different distribution pathways. Whereas

anthropogenic Pb and Zn remain restricted to the fine particles where they settle, remobilized anthropogenic Cu may be spread to a wider zone through the hydrodynamic transport of water masses. This is possible because of the effect of strong complexing ligands that inhibit Cu re-adsorption onto particles and hence favour its long-range dispersal in the marine system (Van den Berg et al., 1987).

### 3.3.3. Organic matter control of metals in the prodelta

The importance of the prodeltaic sedimentary unit as a transitional platform for particle and associated metal transfers between the continent and the sea requires further investigation, notably regarding the persistence of the contaminants with time. Hence, the temporal evolutions of metallic enrichments at the prodelta site were studied and show various trends (Fig. 7). Regarding Cu, the contamination peak occurs consecutively to the December 2003 flood event and hence corresponds to freshly deposited materials. This enhanced level is similar to the average Cu enrichment recorded in river SPM (Fig. 6B). From this EF peak, one can then observe a progressive and strong decrease until natural level is reached. This means that desorption of Cu is not instantaneous when entering the coastal waters and predominantly takes place over the prodelta surface at the sediment-water interface. A comparable trend is shown for Pb and Ni, but it is much less marked and only concerns a minor fraction of these elements. Unlike Cu, Pb preserves most of its anthropogenic component in the sediments and enrichment levels of Zn even remain non-varying. This notable behaviour of Cu may explain why it depicts a natural occurrence in the surficial sediments when going seaward. Furthermore, as burial of the December 2003 flood deposit by younger sediments was impossible because of both hydrodynamical and sedimentary conditions (see Section 2.3), it is likely that the behaviour and fate of Cu are dictated by the physico-chemical conditions encountered at the sediment/water interface.

It is recognized that particulate organic carbon (OC) binds a variety of trace elements, notably in estuarine environments (Krupadam et al., 2003). This is especially true in our prodeltaic sediments for Cu, Pb and Zn, as previously reported (Roussiez et al., 2006). Organic matter on particles is prevalent in the clay fraction (Rubio et al., 2000), and hence its distribution is also strongly influenced by particle sorting processes. To clarify the role of particulate OC in the control of metallic contamination within the prodeltaic area, we propose to correct OC data for the grain-size

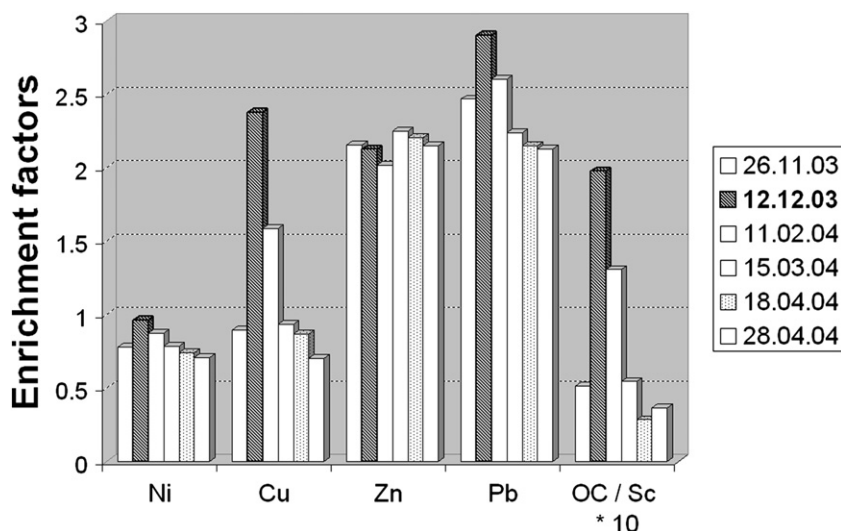


Fig. 7. Temporal variation of metal EFs (normalized to Sc) and Sc-normalized OC contents (multiplied by 10) in surficial sediments collected at the prodelta-type station. Samplings of 12 December 2003 and 18 April 2004 are consecutive to flood episodes but only the first event left new fine deposits on the investigated site.

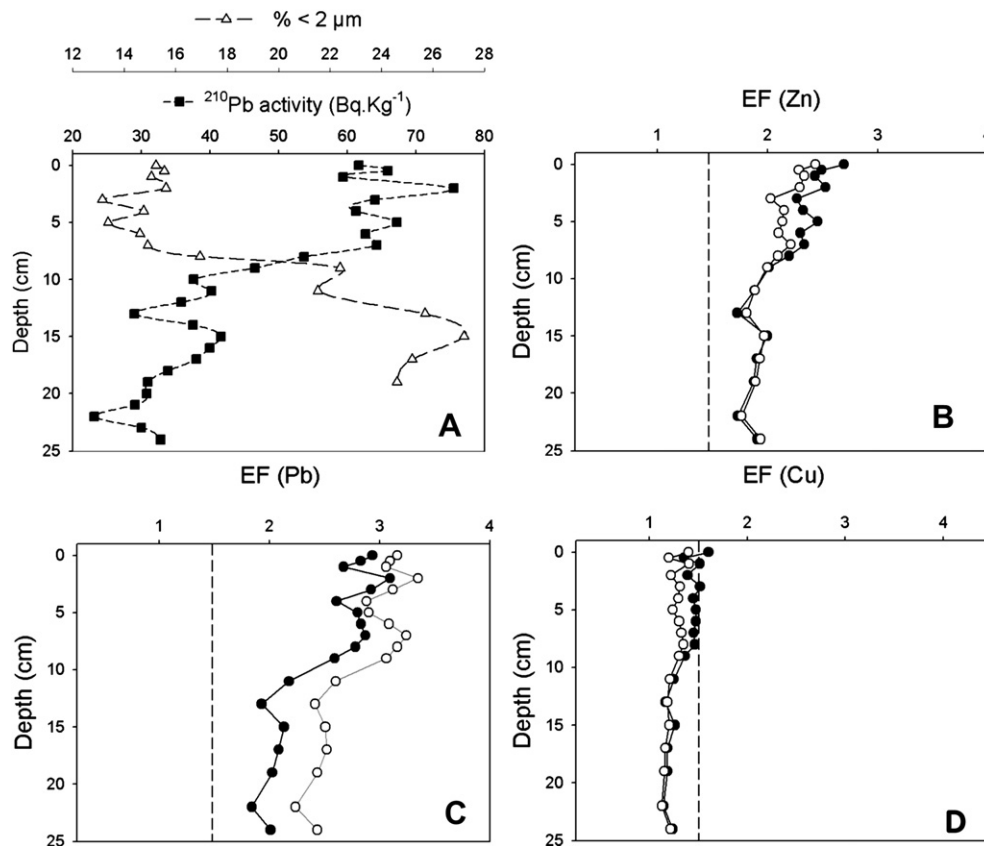
effect, thus making it comparable with metal EF indices. Consequently, OC “enrichment” (i.e. OC abundance per unit of clay) in the prodeltaic sediment is expressed as Sc-normalized OC contents, and its evolution with time is added in Fig. 7. The different patterns indicate that the enrichment of Cu – and to a limited extent Pb and Ni – in the surficial sediments is directly linked to the enrichment of OC. This is particularly visible in December 2003, consecutively to the rapid settling of organic-rich riverborne materials, and supported by the high correlations between OC/Sc ratios and metal EFs ( $r = 0.99, 0.98$  and  $0.95$  for Cu, Ni and Pb respectively), except Zn, for which the value is not significant.

The decline in OC enrichment, observed after December 2003 in the surficial sediments, is probably the result of early diagenetic processes, rather than a preferential erosion of particulate organic matter. The oxic conditions that prevail at the sediment/water interface in the study area (Buscaill et al., 1995) support this hypothesis. In this respect, the loss of OC by oxidation could be estimated at about 70% between December 2003 and March 2004. This result has to be put in context with the 61% decrease of the Cu EF calculated during the same period (the corresponding percentages for Pb and Zn are 23 and 0, respectively). These differences may traduce specific element dynamics in response to the degradation of organic matter. Indeed, the subsequent fate of Cu, Pb and Zn fractions initially bound to the organic phase will depend on electro-chemical affinities with available carriers in the other labile phases (e.g. carbonates, Fe/Mn oxides, degradation products of pre-existing organic materials). Thus, our results suggest two post-depositional mechanisms following the rapid oxidation of particulate OC: (i) a release of Cu in the dissolved phase – likely favoured by the presence of organic ligands as suggested in

Section 3.3.1 – and (ii) a migration of Pb and Zn towards mineral binding sites within clays. These physico-chemical processes could explain why the two latter elements still exhibit significant anthropogenic levels in coastal sediments in contrast with Cu (Figs. 6 and 7). Although sequential extraction analyses would be necessary to estimate the fractions of Cu, Pb and Zn associated with particulate organic matter over the study period, such partition mechanisms derived from organic phase oxidation have already been described in other studies. For example, laboratory experiments presented by Gerringa (1990) reveal an important release of Cu to solution, whereas Pb (and to a lesser extent Zn) remains in the particulate phase, probably precipitated as a salt or oxide. Similar trends were observed for Cu and Pb in benthic flux-chamber by Westerlund et al. (1986). Also, in a study at St. Helena Bay (South Africa), Monteiro and Roychoudhury (2005) argue that, in the long term, metals deposited in association with senescent phytoplankton are partitioned between remaining particulate organic matter, terrigenous clays and sulphide complexes attributable to early diagenetic processes.

#### 3.4. Downcore profiles of metal EFs in the prodeltaic sediments

Considering the instability of nearshore deposits and their ecological importance, it is instructive to observe the manner in which the riverborne metallic contamination can be preserved in prodeltaic sediments. To do so, we examined a sediment core (see Fig. 1) that was sampled in early fall 2002, i.e. before the usual flood season and probably with no fresh post-flood deposit available on its top. Both granulometric and geochemical analyses were conducted comparatively.



**Fig. 8.** Downcore trends for the prodelta sediment core collected in November 2002, before the flood season. (A) Clay abundance ( $< 63 \mu\text{m}$  fraction) and  $^{210}\text{Pb}$  activity (bulk fraction). (B, C and D) EFs of Zn, Pb and Cu, respectively. Open and black circles correspond to EFs calculated using Sc and Cs as normalizers, respectively. Dashed line symbolizes the limit of natural variability (i.e. EF = 1.5).



Particle sorting processes have a strong influence on vertical element distributions. To interrogate this phenomenon, a preliminary approach consisted in plotting the clay abundance with data of  $^{210}\text{Pb}$  activity (Fig. 8A). The latter element generally exhibits a downcore decrease in unperturbed environments that permits estimation of sedimentation rates. Here, the profile reveals the influence of reworking processes on the shallow seabed with a clay-depleted and well homogenized sediment layer (0–7 cm), where radionuclide activities are constant. This is indicative of strong sediment reshaping due to high bottom current velocities and storm-induced wave action (and perhaps bioturbation). Further downcore, clay abundance increases, while, concomitantly,  $^{210}\text{Pb}$  activity declines. A transitional layer (7–10 cm) is identified and corresponds to the mixing of sediments from the upper layer with some older deposits from the bottom layer. A maximum sedimentation rate based on the CIC model could be calculated here (i.e.  $0.28 \text{ cm}\cdot\text{yr}^{-1}$ ) but no other tracers could be used to evaluate the influence of mixing on such values.

EFs were determined for the sediment core levels. Both Cs and Sc were taken as normalizers and results did not reveal a significant difference (Fig. 8B, C and D). It can be seen that Pb and Zn display anthropogenic profiles along the core (EFs > 1.5), while Cu depicts a general natural occurrence. In detail, enrichments of the remaining contaminants Pb and Zn reveal two distinct homogeneous levels, within the reshaped and unperturbed parts of the core respectively. The top layer is characterized by the highest EF values, presumably reflecting the modern contamination, whereas the deeper one is testament of past inputs. Also for Cu, upcore levels stand closer to the natural variability threshold and even one sample depicts a slight anthropogenic contribution. These results are in very good agreement with the contamination trends observed in surficial prodeltaic sediments after relatively long lasting repository of riverborne particles. From these findings, one can therefore suggest that the chemical forms and nature of the riverborne contaminants sequestered in the prodeltaic sediments are fixed by chemical interactions occurring in oxic surface sediments (see above) before burial. However, broader studies based on high frequency sediment core sampling are needed to confirm this assumption.

#### 4. Conclusions

Based on a recombination of different sample series, this work improved our knowledge on the delivery and subsequent fate of particulate metals – especially contaminants – in the Têt fluvio-deltaic system, a small Mediterranean point source driven by episodic floods.

In terms of land-to-sea fluxes, both temporal and spatial distributions of total metal contents reflect the dominant transfer pathways of particles from the river to the coastal system. An important sedimentological control occurs in the direct vicinity of the river mouth, where deposition and resuspension processes involve the entrapment of metal-rich particles. The persistence of these fine-grained sediments in the shallow sedimentary unit (called prodelta) tightly depends on the intensity and frequency of both flood episodes and storm-induced seabed agitation. This work shows that the deposits related to the flood event of December 2003 remained around 3–4 months in the prodelta area before their complete erosion by hydrodynamics. During this period, the prodelta was the major source of particulate metals to the distal and stable sedimentation area, underlining the important role of Mediterranean prodeltas for controlling land-to-sea transfer of particulate matter and associated chemicals.

In terms of speciation between residual and labile (reactive) fractions, spatial investigations show that Cu, Pb and Zn are potentially the most mobile metals in the river particles, which

agrees with their contributions from anthropogenic sources. When entering the marine realm, however, two behaviours can be distinguished. While Pb and Zn exhibit rather a constant lability in the particulate phase along the continuum, Cu is marked by lower fractions (up to 50% difference) in the marine sediments, which can be attributed to desorption processes over time. These trends have direct repercussions for the fate of the contaminants, as shown clearly when correcting for the grain-size effect *via* enrichment factors: Pb and Zn homogeneously contaminate the coastal sediments, whereas Cu is characterized by the total loss of its anthropogenic component. Temporal investigations at the prodelta site revealed that desorption of Cu from riverborne particles is not instantaneous when entering the coastal system and predominantly occurs after the settling of flood materials.

These contrasting metal dynamics may derive from different post-depositional behaviours with respect to the oxidation of the organic phase, an important metal carrier in the prodeltaic sediments. Together with the decline in organic carbon enrichment, Pb and Zn appear to migrate to mineral binding sites within clays, while Cu is released to the dissolved phase probably under the influence of organic ligands. This leads to two main distribution pathways, which determine the fate and hence the ecological impact of these contaminants. Whereas riverborne anthropogenic Pb and Zn remain in association with fine particles and may rather affect benthic organisms at the sites of deposition, one can suppose that mobilized anthropogenic Cu impacts a wider zone because of its dispersal in the dissolved phase.

Finally, the question of the riverborne contaminant persistence in the sedimentary archives of the prodelta was addressed using enrichment factors in downcore profiles. Downcore contamination trends follow those shown in the surficial sediments, since only Pb and Zn present significant anthropogenic perturbations along the investigated core. It seems that the chemical forms and nature of land-derived metals in the Têt prodelta is likely controlled by the partition mechanisms at the oxic sediment/water interface before burial.

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