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Impact of oceanic floods on particulate metal inputs to coastal and deep-sea environments: A case study in the NW Mediterranean Sea

Vincent Roussiez [a,*], Serge Heussner [a], Wolfgang Ludwig [a], Olivier Radakovitch [b,c,d,e], Xavier Durrieu de Madron [a], Cécile Guieu [f], Jean-Luc Probst [g,h], André Monaco [a], Nicole Delsaut [a]

[a] CEFREM, CNRS—Université de Perpignan Via Domitia, 52 av. Paul Alduy, 66860 Perpignan Cedex, France
[b] Aix-Marseille Univ., CEREGE, UMR 6635, 13545 Aix en Provence cedex 4, France
[c] CNRS, CEREGE, UMR 6635, 13545 Aix en Provence cedex 4, France
[d] IRD, CEREGE, UMR 161, 13545 Aix en Provence cedex 4, France
[e] Collège de France, CEREGE, 13545 Aix en Provence cedex 4, France
[f] Laboratoire d'Océanographie de Villefranche-sur-Mer (LOV), Université Pierre et Marie Curie, CNRS, BP 8, 06238 Villefranche-sur-Mer, France
[g] Université de Toulouse; INPT, UPS; Laboratoire Ecologie Fonctionnelle et Environnement (EcoLab); ENSAT, 31326 Castanet Tolosan, France
[h] CNRS; EcoLab; ENSAT, 31326 Castanet Tolosan, France

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A B S T R A C T

An exceptional flood event, accompanying a marine storm, was investigated simultaneously at the entrance and the exit of the Gulf of Lion's hydrosystem (NW Mediterranean) in December 2003. Cs, Cr, Co, Ni, Cu, Zn, Cd and Pb signatures of both riverine and shelf-exported particles indicate that continental inputs and resuspended prodeltaic sediments were intensively mixed with resuspended sediments from middle/outer shelf areas during advective transport. As a result, particles leaving the Gulf of Lion inherited the mean signature of shelf bottom sediments, exporting anthropogenic Pb and Zn out into the open sea. When assessing the particulate metal budget in relation with the event, it appears that the output fluxes accounted for between 15% and 60% of the input fluxes, depending on the element and the period of reference. This trend is also observed for annual budgets, which were drawn up by compiling the data from this study and the literature. Results evidenced that, except some element fluxes during extreme output scenario, outputs never counterbalance the inputs. In its current functioning, the Gulf of Lion's shelf seems to act as a retention/sink zone for particulate metals. Regarding anthropogenic fluxes, the contribution of the oceanic flood of December 2003 to the mean annual scenario is considerable. Environmental impacts onto coastal and deep-sea ecosystems should therefore tightly depend on both the intensity and the frequency of event-dominated sediment transport.

1. Introduction

Coastal margins are active transition zones between continent and open sea, receiving and exporting energy, water and both dissolved and particulate materials. Stretching from shallow to deep waters, they form key-environments for biogeochemical cycles and primary production (Wollast, 1991), making them an important ecological and economic resource for humans. Concurrently, with ever-increasing number of people living in coastal watersheds, these areas have become one of the most exposed to the anthropogenic impact (Edgar et al., 2000). Preferentially associated with particles, contaminants are delivered to the littoral waters – mainly through the river pathway – where they can induce harmful effects onto local ecosystems, and presumably onto Man in the long term. Tracking the sediment transport in the coastal zone constitutes therefore a prerequisite to explore the fate of particulate contaminants, which cannot be fully illuminated on the basis of a geochemical approach alone. Hydro-sedimentary processes are controlled by a set of forcings such as river inputs, winds, general circulation of water masses, storm-induced seabed agitation, dense water cascading, internal waves and bottom-trawling (Nittrouer and Wright, 1994; Condie and Sherwood, 2006; Ferre et al., 2008). But to date, reports on these questions are sparse, and yet an important challenge is to examine in details the coastal sedimentary response to highly energetic physical disturbances and their implication for the biogeochemical behaviour of particulate contaminants.

Previous studies in the Gulf of Lion (NW Mediterranean Sea) suggested that event-dominated sediment transport across the continental shelf may account for a great part of the particulate matter budget (Lapouyade and Durrieu de Madron, 2001; Palanques et al., 2006; Ulses et al., 2008). This is an important consideration because in- and output solid fluxes to/from the shelf may dictate, at least

* Corresponding author. *Present address*: Service de Biogéochimie et Modélisation du Système Terre -Océanographie Chimique et Géochimie des Eaux, Département des Sciences de la Terre et de l'Environnement, Université Libre de Bruxelles, Campus Plaine - CP 208, B-1050 Brussels, Belgium.
E-mail address: vincent.roussiez@ulb.ac.be (V. Roussiez).

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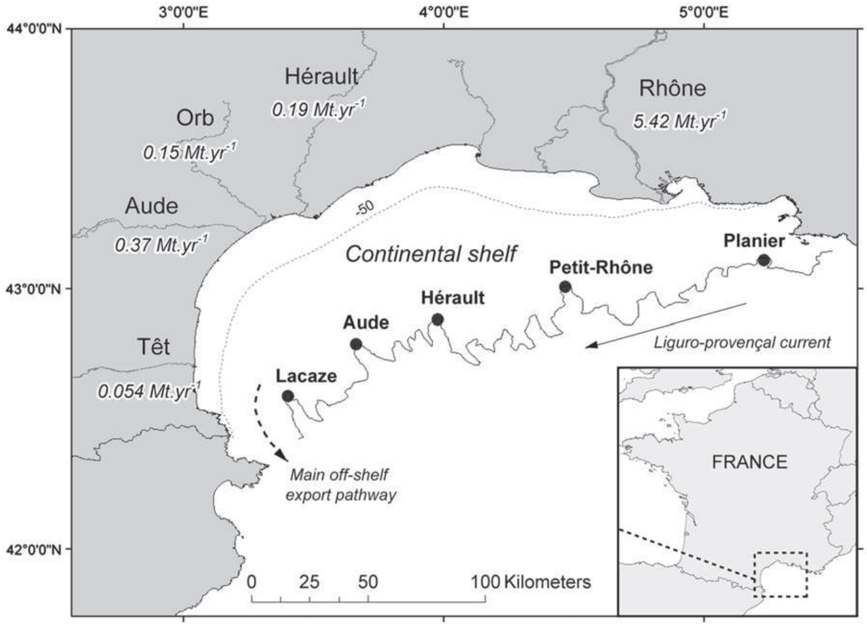

Fig. 1. Map of the study area. The main rivers and their mean annual sediment inputs to the Gulf of Lion are indicated. Black points show the deployment sites of the sediment traps and names refer to the visited canyon heads. The general circulation schema of water masses (driven by the Liguro-provençal current) from East to West makes that the main sediment off-shelf export takes place in the southwestern Gulf of Lion. The physiographic limit of the continental shelf (200 m isobath, solid line) and the 50 m isobath (dotted line) are shown.

partly, the associated in- and output particulate contaminant fluxes. By comparing these fluxes, one can gain insights into the functioning of the coastal zone in terms of sink or source of sediment-bound contaminants with respect to the open sea. Besides, sediment disturbance that results from hydro-meteorological events can affect the particulate/dissolved partitioning of pollutants, as well as their bioavailability (Eggleton and Thomas, 2004). Ideally, an integrated approach for this topic should combine both spatial and temporal sampling strategies along the downstream transport route of particles from their sources (mainly riverine), across the continental margin and out into the open sea. Although realistic along a fluvio-deltaic continuum (e.g. Roussiez et al., 2011), it is logistically more complicated and requires expensive operations at a shelf scale. However, an opportunity emerged from the EU/FP5 financed Eurostrataform program, which was devoted to elucidate the fate of riverborne particles in the marine system. In the Gulf of Lion, activities were principally based on the mooring of sediment traps in the heads of the main submarine canyons, which form deep incisions into the platform and slope. It is here that most of the shelf-exported particles transit by gravity flow before entering the open sea. Weekly time series of downward settling particulate matter were collected during long-term deployments and we could benefit from these operations to characterize a selection of materials leaving the shelf.

The research reported here aims to determine the significance of oceanic floods in the particulate metal inputs to coastal and deep-sea systems of the Gulf of Lion. To do so, two types of particulate metal budgets were built on the basis of in- and output solid fluxes. The former is focusing on the exceptional flood episode of early December 2003 – accompanying a severe marine storm – that affected the overall regional river discharges and resulted in a massive land-to-sea transfer of sediments. The latter refers to annual scenarios, derived from both observations and modelling experiments reported in the literature. Assessments of anthropogenic inputs to coastal and deep-sea environments are presented for both cases. Our strategy consisted in comparing metallic signatures between particulate materials entering the marine system (i.e. river suspended fine sediments) and those leaving the shelf (i.e. suspended sediments travelling through the main canyon heads). The elements we investigated are Cs, Cr, Co, Ni, Cu, Zn, Cd and Pb, both of natural and anthropogenic origin. To the best of our knowledge, this work constitutes the first integrated approach of its kind, taking into consideration both in- and output geochemical compositions of particles at a shelf scale.

2. Material and methods

2.1. Study area

The Gulf of Lion (Fig. 1) is one of the largest continental shelves of the Mediterranean Sea, receiving various sources of insoluble riverine and atmospheric particles. Moreover, this river-impacted shelf is a non-tidal environment, implying that estuaries and associated sediment decantation zones do not exist there. Marine water intrusion in riverine systems is limited and river-transported materials are directly injected into coastal waters. Particle/water exchanges of elements, due to physico-chemical changes, can therefore occur once entering the sea. The total solid discharge of the rivers draining the study area is somewhat difficult to estimate because it is largely controlled by the intensity and the frequency of flood events. Thus, a variability of a factor of 10 has been reported over the past 20 years (2.4 to 25 Mt yr^{-1}, after Ludwig et al., 2003). Furthermore, since 80% of this input arises from the Rhône River (Durrieu de Madron et al., 2000; Radakovitch et al., 2008), it is crucial to minimize the degree of uncertainty attached to the contribution of the latter point source. Several researchers have generated empirical relationships on the basis of large sampling datasets to extrapolate solid fluxes from the Rhône River (e.g. Sempéré et al., 2000; Pont et al., 2002). It appeared that reproducing as best the trends observed during flood episodes is of paramount importance.

In an attempt to provide a realistic estimate of the annual solid load from the Rhône River, we have averaged 3 estimates obtained by using 3 different empirical relationships applied to the daily water discharge dataset from the period 1970–2000. The first (1) is a 1-order regression relation constructed with the data from river samples taken at the town of Arles (50 km upstream the river mouth) between 2000 and 2003, defined by Ollivier et al. (2011), and giving 4.01 Mt yr^{-1}. The second (2) is a 1-order regression relation proposed by Rolland (2006), built with the data from river samples taken at Arles between 2002 and 2004, giving 5.81 Mt yr^{-1}. The third (3) is a 2-order regression model, established with the data of Pont (pers. com.) from samples collected at Arles during a one year survey (1994–1995, a period marked by a high solid discharge, ca. 14 Mt), giving 6.44 Mt yr^{-1}. Based on this approach, the mean annual solid discharge of the Rhône River can therefore be estimated at 5.42 (±1.26) Mt yr^{-1}.

$$\mathrm{Log}C_{spm} = 2.149\ \mathrm{Log}Q - 5.489 \quad (n = 85,\ r^2 = 0.85) \tag{1}$$

$$\mathrm{Log}C_{spm} = 2.17\ \mathrm{Log}Q - 5.4 \quad (n = 101,\ r^2 = 0.87) \tag{2}$$

$$\mathrm{Log}C_{spm} = 1.246\ \mathrm{Log}Q^2 - 6.3\ LogQ + 8.9 \quad (n = 365,\ r^2 = 0.72) \tag{3}$$

where C_{spm} and Q are the river suspended particulate matter (SPM) contents (mg l^{-1}) and the water discharge ($m^3\ s^{-1}$), respectively.

Based on daily discharge data from the same 3 decades, we also estimated the mean annual solid inputs from the other point sources, which are characterized by smaller watersheds and show a highly variable discharge regime governed by episodic flood events: Hérault, Orb, Aude and Têt Rivers (see Fig. 1). To do so, empirical relationships of Pethelet-Giraud et al. (2003) (4) for the Herault and Orb rivers, and Serrat et al. (2001) (5) for the Aude and Têt rivers, were used.

$$\mathrm{Log}C_{spm} = 1.196\ \mathrm{Log}Q - 0.9112 \quad (r^2 = 0.79) \tag{4}$$

$$\mathrm{Log}C_{spm} = 0.5057\ \mathrm{Log}Q^2 - 0.4537\ \mathrm{Log}Q + 1.087 \quad (r^2 = 0.67) \tag{5}$$

As a result, we obtained the following annual solid deliveries (in Mt yr^{-1}): 0.19 for the Hérault River, 0.15 for the Orb River, 0.37 for the Aude River and 0.054 for the Têt River (see also Fig. 1). The contribution of the smallest rivers (e.g. Agly and Tech Rivers, west of the Gulf, not shown on Fig. 1) amounts to 0.184 Mt yr^{-1} (Bourrin and Durrieu de Madron, 2006).

Finally, the mean total riverine input to the Gulf of Lion can be estimated at about 6.37 Mt yr^{-1}. It should be noted that the Var River (east of the Gulf), which is the second river in terms of mass flux for the French Mediterranean coast, is not taken into account here because these particles are supposed to be delivered directly to the open slope through the Var canyon.

Reconstructed *via* the recent mean Al deposition fluxes (Guieu et al., 2010) selected for the study area and the mean Al abundance in the aerosols (Ridame et al., 1999 and references therein), the particulate atmospheric input to the Gulf of Lion (13,000 km^2 including the shelf and the overall canyon heads) has been estimated to about 18 t km^{-2} yr^{-1}. This entails a total input of about 0.23 Mt yr^{-1} (slightly higher than a previous estimation in Roussiez et al., 2006). The local atmospheric input of particulate matter is thus about 28 times lower than the average riverine input, implying that the lithogenic particles in the Gulf of Lion mostly derive from rivers.

In terms of human impact, industrial activity in the Rhône valley is clearly more elevated than in the smaller river basins of the western part of the Gulf, where the socioeconomic activities are mainly related to agriculture and tourism. In terms of geology, the major part of the river catchments is composed of calcareous rocks, except for the Aude and especially Têt rivers, which drain metamorphic and igneous rocks from the Pyrenees mountains.

2.2. Particle transport in the Gulf of Lion: a brief overview

In situ observations of both currents and suspended loads in the coastal waters of the study area have highlighted the general mechanisms controlling the particle dispersal from river mouths to the shelf boundary (e.g. Aloisi et al., 1982; Durrieu de Madron and Panouse, 1996). The "stop-and-go" nature of sedimentation connects the shallow prodeltaic structures (i.e. developed in the direct vicinity of river mouths and fed by flocculation mechanisms of fine-grained particles) to the middle-shelf mudbelt and outer-shelf areas (Roussiez et al., 2005a). It was shown that the transport of particulate matter is mainly ensured by advective transfer within the benthic nepheloid layer – i.e. a permanent turbid bottom structure (Aloisi et al., 1979) where sedimentation/resuspension cycles take place – rather than vertical supplies from overlying waters (Naudin and Cauwet, 1997). This bottom layer is considered as one of the most dynamic environments of the entire ocean system (Chester, 1990).

The cross-margin particulate flux is constrained by the western general circulation, which is intensified during extreme meteorological forcings such as southeastern storms. Typical of the Mediterranean climate, these episodic 'wet' storms are responsible for both massive sediment input *via* river flash-floods and bottom sediment reworking by waves and currents (Guillén et al., 2006). Such hydro-dynamical conditions can thus explain why the suspended sediment load increases within a factor 3 to 10 towards the West (Monaco et al., 1999) and why southwestern submarine canyons represent the major pathways for particles leaving the shelf (Heussner et al., 2006).

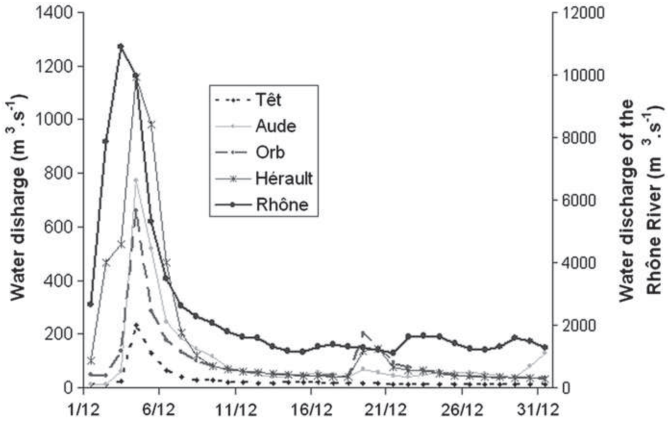

Fig. 2. Water discharges of the main rivers opening into the Gulf of Lion recorded in December 2003.

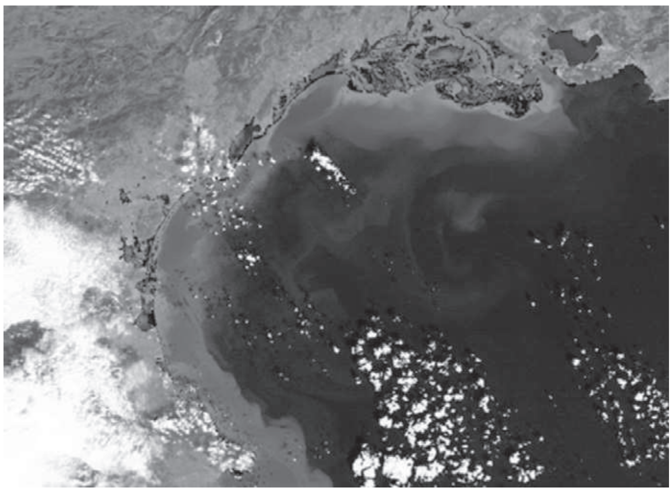

Fig. 3. Satellite view of the Gulf of Lion taken the 8th of December 2003 (consecutively to the river peak discharges related to the flood event).
Source: MERIS.

2.3. Hydro-sedimentary context in December 2003

The early December 2003 torrential precipitation over the coastal plain of the Gulf of Lion triggered a dramatic and simultaneous increase of the water discharges of the overall rivers draining this area (Fig. 2). Consequently, in a very short-time period (1–2 days around the flood-peak discharge dated December 3rd and 4th for the Rhône River and the other point sources, respectively), tremendous quantities of particulate material from different geographic origins were transported from the continent to the coastal zone. The latter was also impacted by a major marine storm, giving rise to an intense bottom sediment resuspension, preceding a 4-week relaxation period (Ulses et al., 2008). The importance of this phenomenon (one of the biggest floods for at least 150 yr, according to Antonelli et al., 2008) can be appraised, at least partly via satellite maps, when observing the large spatial extent of the flood-induced surface plume (Fig. 3), which is confined along the shoreline by strong southeastern winds. However, it is worth noting that the terrestrial particles introduced in the marine realm during this event mostly originate from the Rhône River, owing to its greater contribution in terms of water discharge (factor 14 to 40 when compared to the other continental sources, see Fig. 2).

The repercussion of both the flood and the marine storm events on the functioning of the hydrosystem and, more particularly, the export of particulate matter from the shelf is here assessed through the recording of downward settling particle fluxes in the main canyon heads. Sediment traps were deployed – as part of the EU/FP5 funded Eurostrataform program – in the upper sections of Lacaze-Duthiers, Aude, Hérault, Petit-Rhône and Planier canyons (in this order from West to East) at 30 m above the seabed. Weekly time series present a sharp flux increase in all deployment sites between the 1st and the 7th of December, a time interval embedding the peak of river water discharges (Fig. 4). Although no direct or even delayed relationship between river inputs and cross-slope fluxes have been observed in previous studies (e.g. Monaco et al., 1990), there is here an obvious link, hence underlining the very exceptional hydro-sedimentary conditions that prevailed in early December 2003. Indeed, at most, 4 days elapsed between the river flood-peak discharge of the Rhône River (the 3rd) and the flux increase in sediment traps (that could occur on December 7th at the latest). Also, in relation with the general circulation schema of water masses, it is worthy to note that the most important output fluxes are registered in the western part of the shelf boundary, especially in Lacaze-Duthiers and Herault canyon heads.

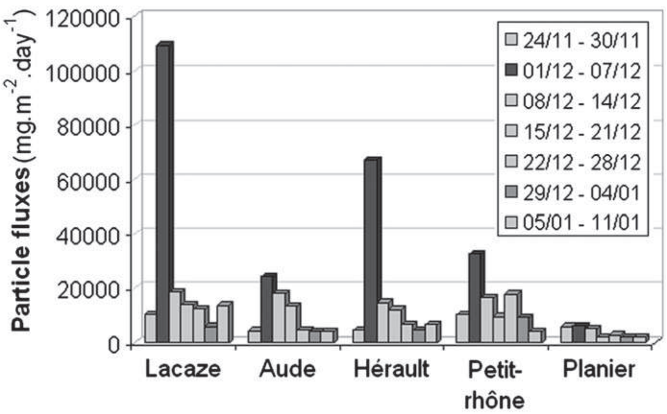

Fig. 4. Downward particulate fluxes in the main canyon heads of the Gulf of Lion, sorted from West to East on the increasing *x*-axis, in December 2003. The 2 weekly time series analysed in this work (i.e. 1st–7th December and 29th December–4th January) are shown in black and dark grey colours.

2.4. Sampling and analytical procedures

Water samples from the main rivers (Rhône, Orb, Aude and Têt) were punctually collected near their mouths, at subsurface depth (less than 1 m), upstream the salt front (freshwater zone), using a horizontal Niskin bottle launched from bridges, on the 4th of December 2003 (for the Rhône River, an additional sampling was performed the 2nd of December). At each site, 1 N HCl precleaned polypropylene bottles of 10 l were rapidly filled up by successive samples. Returned to the laboratory, waters were first filtered through precleaned 63 μm nylon mesh to eliminate the sand fraction and vegetal debris. The remaining solid phase (i.e. clay and silt fractions) in the samples was finally collected by filtration through preweighted, 0.1 N HCl precleaned cellulose acetate filters of 47 mm diameter, 0.22 μm pore size. Filters were dried at 40 °C during 24 h in clean oven and weighted. For each river, three aliquots (filters) per sample were used for analysis, except for the Rhône River (two aliquots).

Sediment trap samples have been selected on the basis of downward particle fluxes registered in December 2003 (Fig. 4). Two contrasting time series were chosen for comparative analyses: (i) the 1st–7th December sequence including the particle flux peak related to the oceanic flood (see Section 2.3), and (ii) the 29th December–4th January sequence taken at the end of the storm-relaxation period, which can be considered as representative of "normal" hydro-dynamical conditions. The techniques used for the settling particulate matter entrapment are described in details in Heussner et al. (1990). Succinctly, particles are collected in a plastic tube filled with a 5% formalin filtered sea water solution. After centrifugation, the supernatant phase (i.e. sea water + formol) was evaporated, which caused the crystallisation of formol–NaCl complexes at the sediment surface. These residues were easily removed in clean room and it was assumed that, at most, a negligible part of them was incorporated within the sediment. Besides, these residues were analysed for metals and results did not show any differences when compared to analytical blanks, indicating that these compounds did not alter the metal speciation in the sediments. For each sediment trap sample, two aliquots were obtained. Analyses concerned the bulk

Table 1
Trace metal contents (μg g^{-1}) of SPM collected in the main rivers opening into the Gulf of Lions, during the flood event of December 2003.

Rivers	Cs	Cr	Co	Ni	Cu	Zn	Cd	Pb
Rhône[a]	8.2	74.7	11.3	39	37.2	144	0.48	39.7
Orb[b]	12 ± 1	93 ± 8.3	16.8 ± 1.1	49 ± 2.7	54 ± 4.4	197 ± 24	0.67 ± 0.04	85 ± 5.4
Aude[b]	9.7 ± 0.4	95 ± 0.7	12.8 ± 0.03	44 ± 3.1	82 ± 1.7	118 ± 2.5	0.45 ± 0.01	31 ± 1.6
Têt[b]	9.8 ± 0.5	90 ± 4	18.2 ± 0.6	41 ± 1.7	75 ± 1.4	181 ± 9.5	0.41 ± 0.03	45 ± 1.8

[a] For the Rhône River, we benefited from 11 metal content references (9 taken from Ollivier et al., 2011, see Section 3.1.1. for explanation), stretching between the 1st and the 6th of December 2003. For each element, these 11 values were weighted by corresponding daily water discharges to give an average particulate metal content representative of the flood event.

[b] For Orb, Aude and Têt Rivers, 1 river sampling was performed the 4th of December 2003, i.e. during the particle flux peak. Each value is the arithmetic mean content of 3 aliquots (filters) and errors are the corresponding standard deviations.

fraction because gathered materials were very fine. Sandy particles and/or debris were not observed in the samples.

Both riverine and marine samples were totally digested to dryness in Teflon bombs, on a hot plate with a HF–HNO_3–$HClO_4$ mixture. To avoid mass bias, the procedure was applied to 0.1 g (d.w.) of particulate matter for both types of samples. The residues were solubilized by HNO_3 and diluted to volume. The solutions were analyzed for metals by inductively coupled plasma–mass spectrometer (ICP–MS) at the LMTG laboratory (Toulouse, France) and results on aliquots were averaged. Analytical 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, Cr and Ni, $<$ 5% for Co, Cu, Pb and Zn and $<$ 10% for Cd).

3. Results and discussion

3.1. Case study of the December 2003 flood event

3.1.1. Metal contents in riverine/marine SPM and contamination levels

The assessment of particulate metal fluxes in relation with the oceanic flood of December 2003 requires the determination of the metal contents in the SPM transported during the event. They have been established for particles collected at both the entrance (river outlets) and the exit (canyon heads) of the hydrosystem, during the particle flux peak (see Section 2.4), and are illustrated in Tables 1 and 2, respectively. Although water discharge and SPM loads vary much more than metal contents in fluvial systems (Audry et al., 2004), we improved the accuracy of the SPM signature for the Rhône River (which accounts by far for the major particle yield to the coastal area) by integrating some results published in Ollivier et al. (2011). These authors have followed-up metal contents in SPM of this river between late 2000 and late 2003, a period including the flood event studied here. As a result, our dataset for the Rhône River is based on 11 samplings (9 from Ollivier et al., 2011), stretching between the 1st and the 6th of December 2003, instead of 1 for the other minor point sources (see Section 2.4). It is worthy to note that the metal concentrations in the Rhône River SPM depict rather low variability during the event, i.e. relative standard deviation $<$ 10% for most elements and $<$ 18% for Pb and Cu. For a given metal, the 11 values were weighted by corresponding daily water discharges to obtain an "average" particulate content representative of the flood.

Table 2
Mean trace metal contents ($\mu g\, g^{-1}$) in the sediment trap samples collected between the 1st and the 7th of December 2003, a time period including the particle flux peak related to the oceanic flood. Each value is the arithmetic mean content of 2 duplicates.

Canyons	Cs	Cr	Co	Ni	Cu	Zn	Cd	Pb
Lacaze	8.1	74	11.2	37	30	128	0.17	38
Aude	7.5	76	10.6	39	28	120	0.17	33
Hérault	5.8	61	9.0	31	19	84	0.14	27
Petit-Rhône	8.3	87	11.4	42	24	121	0.18	40
Planier	6.6	80	9.7	40	34	114	0.19	46

Table 3
Mean enrichment factors in both the river SPM and the sediment trap samples corresponding to the December 2003 flood event. The mean EF signature of superficial shelf sediments from middle- and outershelf areas has been added as a reference. Each value is the arithmetic mean EF of 2 duplicates.

Sites	Cr	Co	Ni	Cu	Zn	Cd	Pb
Rivers							
Rhône	0.9	1.0	1.2	1.8	2.2	2.2	2.2
Orb	0.8	1.0	1.0	1.8	2.1	3.0	3.2
Aude	1.0	0.9	1.1	3.4	1.6	2.1	1.5
Têt	0.9	1.3	1.0	3.1	2.4	1.9	2.1
Canyons							
Lacaze	0.9	1.0	1.1	1.44	2.0	0.8	2.1
Aude	1.0	1.0	1.3	1.47	2.0	0.8	2.0
Hérault	1.1	1.1	1.3	1.3	1.9	0.6	2.2
Petit-Rhône	1.1	1.0	1.3	1.2	1.9	0.8	2.2
Planier	1.2	1.1	1.5	2.1	2.2	0.9	3.2
Shelf sediments							
Middle/outershelf ref.	1.0	1.0	1.1	1.0	1.7	1.3	2.2

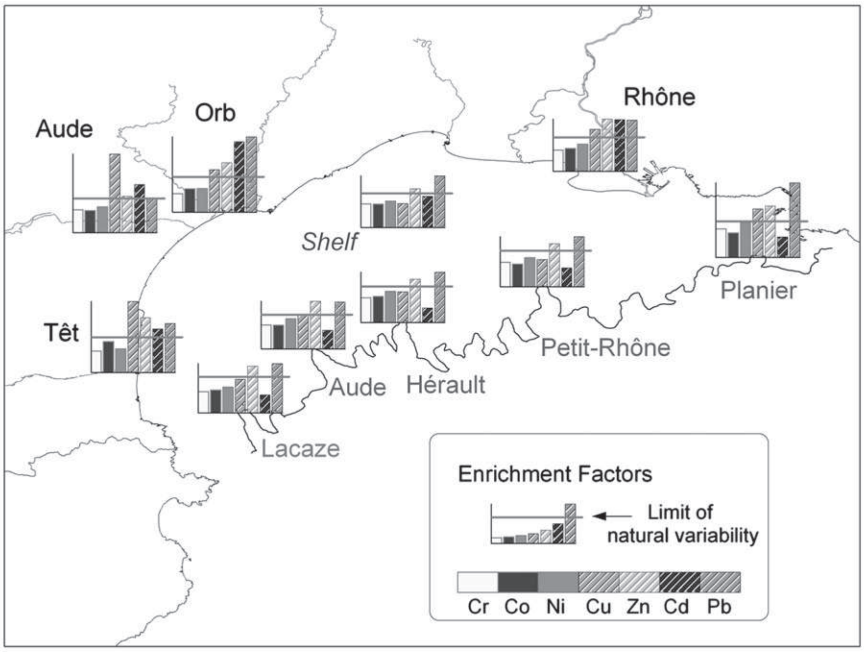

Fig. 5. Qualitative description of metal enrichment factors in river SPM collected on 4th December 2003 (between the 1st and the 6th of December for the Rhône River) and sediment trap samples collected between the 1st and the 7th of December 2003, during the flood-dominated sediment transfer. As a guideline, mean enrichment factors of marine bottom sediments (from middle- and outershelf areas) are shown. The natural variability threshold (horizontal line as indicated in the legend) corresponds to enrichment factor equal to 1.5.

At first inspection, contents in river SPM are somewhat more elevated than for shelf-exported particles, especially regarding the elements that are frequently enriched by anthropogenic emissions (i.e. Cu, Zn, Cd and Pb). One can also observe that the latter elements show the greatest variability between sampling sites, notably from one river basin to another. This is not surprising according to the highly contrasted human imprints registered in the catchments. Conversely, the variability of the contents is generally less marked between samples from canyon heads.

Based on the metal contents alone, it is difficult to conclude on the main contamination trends, because of probable different grain-size compositions between samples. To discriminate natural from anthropogenic sources for a given metal, enrichment factors (EFs) are commonly used. These indices are defined as the observed metal/normalizer ratios in the samples divided by the corresponding ratios of a reference material (Sutherland, 2000). The method for calculating metal EFs as accurate as possible in the Gulf of Lion is fully described in Roussiez et al. (2006). Briefly, they were determined taking ^{133}Cs as normalizer element (depicting the best ability to correct for the grain-size effect in the study area) and regional natural levels as background references (see Roussiez et al., 2005b). For Cd, due to a probable association with the silt fraction, EFs were calculated by dividing the contents by the lowest value registered in the Gulf of Lion (i.e. 0.22 $\mu g\, g^{-1}$). A mapping of these indexes is illustrated in Fig. 5, which allows to identify the main geochemical signatures with regard to the natural variability threshold. Since EFs + standard deviations of regional natural sediments are always < 1.5 (Roussiez et al., 2006), we considered that EFs standing above this value might be indicative for significant contamination. Besides, this limit of the natural variability has already been used in studies dealing with trace metal enrichment in riverine/coastal sediments (e.g. Zhang and Liu, 2002). Results are also detailed in Table 3.

Concerning the inputs, our results confirm an anthropogenic influence for Cu, Zn, Cd and Pb in the overall rivers. But riverine particles are characterized by different contamination types, in relation with the dominant human activities in the corresponding watersheds. The contamination by Cu in the western river basins (especially Têt and Aude) might derive from the agricultural use of $CuSO_4$ in the vineyards soils, which is in line with the results presented by Garcia-Esteves et al. (2007) for the Têt river basin. Also, contaminations by Cd and Pb in the Orb river basin are likely the consequence of the past mining activities that still release ore residues in the local environment (Casio et al., 2007), while those by Cd, Pb and Zn in the Rhône river basin are rather indicative of both diffuse and point sources related to industries and cities. Nevertheless, the Rhône River is by far the major source of particles to the Gulf of Lion. The nature of the SPM in the shelf waters should therefore derive from this industry-oriented signature.

Concerning the outputs, particles travelling through the canyon heads globally depict homogeneous EFs, hence contrasting with those calculated for the inputs, and differences between the two end-members mainly concern the group of Cu, Zn, Cd and Pb. In details, both Cd and Cu drop below the anthropogenic threshold, while conversely, Pb and Zn preserve their anthropogenic contributions with values slightly lower than those measured in Rhône River SPM. One can note, however, that Cu almost exceeds the natural variability threshold in the western Lacaze and Aude canyons, showing an EF about 25% higher than for the Petit-Rhône site. It could be due to the influence of the nearby Têt and Aude rivers, for which the contamination levels for this element are high compared to the other point sources. One exception is the eastern canyon (Planier), which displays a specific signature. Here, Cu and Pb present significant contamination levels, even exceeding those registered in the nearby Rhône River. This site is known to receive off-shore industrial inputs derived from bauxite exploitation, which generates a local contamination (Roussiez et al., 2006). Because of the low particulate matter fluxes recorded here (Fig. 4), the dilution effect of the contaminated particles by detrital ones is small, as suggested by the red tint of our sediment samples collected in this area.

3.1.2. *Anthropogenic metals as tracers of particle dynamics*

The explanation for the spatial contamination pattern that pairs with the development of the December 2003 oceanic flood (Fig. 5) could be a combined effect of two main processes. On the one hand, the high energetic conditions attributed to both flood and marine storm likely favoured a mixing of riverborne particles with less contaminated marine sediments. On the other hand, the intense sediment disturbance could be responsible of metal release into the dissolved phase, as reviewed by Eggleton and Thomas (2004). Unfortunately, it is difficult here to appraise the respective contributions of these two mechanisms for the decrease (i.e. Pb, Zn) and the loss (i.e. Cd, Cu) of the anthropogenic metal components, especially regarding desorption reactions because they are both sediment- and element-specific. However, some insights are gained in the following.

The behaviour of selected metals along the Têt fluvio-deltaic continuum (western Gulf of Lion) has been examined by Roussiez et al. (2011) during the development of the oceanic flood studied here at a greater spatial scale. These authors demonstrated that, once in the coastal system, land-derived anthropogenic Cu was slowly released from the particulate phase and natural levels in the post-flood deposits were only recovered after a few months. In the meantime, Pb and Zn depicted persistent anthropogenic components rather similar to their corresponding levels in the river SPM. These findings indicate that metals behave almost conservatively in the coastal environment, at least within the time period of flood development. This is in line with the results of previous works dealing with the behaviour of dissolved metals in the Rhône river plume (Chou and Wollast, 1990; Elbaz-Poulichet et al., 1996) and, to a larger extent, with the conclusions of many studies in estuarine environments (in Chester, 1990). Assuming that these local trends can be extrapolated to the overall riverine point sources in the Gulf of Lion, it is unlikely that desorption reactions play a dominant role in the fate of most man-made metals during the December 2003 oceanic flood. One exception here is probably Cd, for which the solubility in seawater is known to be extremely high (e.g. Comans and Van Dijk, 1988; Guieu et al., 1998) and may have contributed to a significant release of its anthropogenic component in the dissolved phase during fresh and salt water mixing.

The influence of particle mixing along the downstream transport pathway can be addressed by comparing the in- and output EF signatures with the mean EFs of shelf sediments (see Fig. 5 and Table 3). The latter are calculated on the basis of a dataset from 20 surficial sediment samples stretching along middle and outer shelf areas (thus excluding river mouths environments), collected in November 2002 during the "Remora 3" cruise (see Roussiez et al., 2006). The most relevant finding is the high similitude of the signatures between shelf samples and sediment trap samples (apart from Planier), in opposition to river SPM samples. We interpret this as being indicative of an intense mixing between riverborne/resuspended prodeltaic sediment and resuspended shelf sediment stocks during advective transport. This can be explained by the considerable quantity of marine sediments resuspended by waves and high bottom current velocities induced by the marine storm. According to Ulses et al. (2008), the event of early December 2003 caused the net resuspension of around 8 Mt of surficial shelf sediments, while in the meantime the total riverine input of suspended solids amounted to 5.8 Mt (see below). In these highly energetic conditions, the riverine signals are thus diluted in the coastal zone and shelf-exported particles partly inherit the characteristics of surficial shelf sediments (we will see further below that comparable signatures are obtained during "normal" hydro-dynamical conditions). This assumption is strengthened by the conclusions of recent modelling studies in the Gulf of Lion (Ferre et al., 2008). Nevertheless, the impact of this mixing phenomenon seems somewhat less important for Cu in the western canyon heads, probably in relation with the Cu-enriched inputs of the nearby Têt and Aude rivers (see Section 3.1.1). Also, the case of Cd is interesting since lower EFs are found in the sediment trap samples in comparison with the shelf sediments. Because of the original association of this element with the silt fraction (see above), a preferential resuspension of clay particles by bottom currents may have caused a depletion of this element in the traps.

3.1.3. Particulate metal budget related to the oceanic flood of December 2003

In the context of severe hydro-dynamical conditions, resulting from the combination of river flooding and marine storm, it is somewhat difficult to choose the most convenient periods that fully describe the event. We therefore arbitrarily considered the SPM fluxes as a criterion for distinguishing the key-phases of the hydro-meteorological event. On this basis, two periods have been investigated: (i) a 1-wk period, 1st–7th December, during which the particle flux peaks are recorded in both rivers and canyon heads, (ii) a 1-m period, 1st–31st December, including the 4-wk relaxation period at the end of which particles initially resuspended by the marine storm have settled to the sea floor or left the shelf (see Section 2.4).

3.1.3.1. In- and output solid fluxes. Daily suspended sediment discharges were inferred from daily water discharges at the river mouths, on the basis of river-specific empirical relationships. For the Rhône river, our estimations were driven by an empirical power law (6), constructed with the data of Ollivier et al. (2011) (period 2000–2003), that has the definite advantage of reproducing well the trends observed during flood episodes. This is an important consideration regarding the hydro-dynamic context in December 2003:

$$\mathrm{Log}C_{spm} = 0.0089\ \mathrm{Log}Q^{4.27} \quad (n = 85,\ r^2 = 0.81) \tag{6}$$

where C_{spm} and Q are the river SPM contents (mg l^{-1}) and the water discharge (m^3 s^{-1}), respectively.

For Hérault, Orb, Aude and Têt rivers, we applied the equations presented in Section 2.1. Moreover, the contributions of Tech and Agly rivers were also estimated for the flood event, using Eq. (5) for the former (this simplification was made because of both the close vicinity and similar geology of the watersheds), and the empirical relationship of Serrat (1999) (7) for the latter:

$$Q_s = 13.27\ Q_w^{1.434} \tag{7}$$

where Q_s and Q_w correspond to mean daily suspended sediment discharge (t d^{-1}) and mean daily water discharge (m^3 s^{-1}), respectively.

According to our results, it appears that 5.41 Mt of sediments were injected by the Rhône River into the coastal zone between the 1st and the 7th of December 2003, and 5.47 Mt during the entire month. These values are greater than the estimation of 3.7 Mt given by Ulses et al. (2008), who mentioned, however, a probable underestimation, but in perfect agreement with the estimation of 5.4 Mt calculated by Antonelli et al. (2008) on the basis of high frequency sampling during the flood. When taking into account the contributions of the other point sources, we estimated at 5.74 and 5.82 Mt the total riverine inputs of suspended solids during the 1-wk and the 1-m periods, respectively. One can therefore observe that 99% of the total land-to-sea transfer of sediments in December 2003 is clustered during the first week, notably between the 2nd and the 4th.

Estimations of the amount of sediments exported from the shelf derive from 3D-sediment transport modelling validated against data collected in the field. Ulses et al. (2008) concluded that about 3.73 Mt (the December marine storm contributed to about 41% of the total export estimated at 9.1 Mt over 6 months) were transferred to the deep-sea during the December 2003 marine storm (1-m period). However, the extrapolation to the 1-wk period cannot be simply computed from the latter estimation since weekly fluxes for a given canyon were not constant over December (Fig. 4). We followed therefore the idea that our weekly records from the traps were accurate enough to estimate the contribution of each canyon to the particle shelf-export during the 1-wk period with respect to the 1-m period. By weighting these contributions by the fluxes registered in the corresponding traps during the 1-wk period, it appears that 72% of the off-shelf export in December 2003 took place during the first week. As a result, about 2.67 Mt of suspended solids would have left the shelf between the 1st and the 7th of December 2003. This implies that the net increase of particulate material in the coastal area amounted to 3.07 Mt during the first week of December 2003, and 2.09 Mt at the end of the one-month period. The significance of this is that almost 1 Mt left the shelf during the storm-relaxation phase.

3.1.3.2. In- and output particulate metal fluxes. In relation with the in- and output suspended solid fluxes recorded during the two periods under consideration (see above), particulate metal budgets have been constructed using the mean metal concentrations determined in river and marine SPM. Also, a distinction between

Table 4
River input fluxes of particulate metals (total and anthropogenic) to the Gulf of Lion between the 1st and the 7th of December 2003, a time period characterized by an exceptional flood episode.

Rivers	Inputs (t)							
	Cs	Cr	Co	Ni	Cu	Zn	Cd	Pb
Rhône								
Total	44	404	61	211	201	779	2.61	215
Anthropogenic	/	/	/	/	34	258	0.82	69
Têt								
Total	0.1	0.8	0.2	0.3	0.6	1.5	0.003	0.4
Anthropogenic	/	/	/	/	0.3	0.6	0.001	0.1
Aude								
Total	0.6	5.8	0.8	2.7	5.0	7.2	0.028	1.9
Anthropogenic	/	/	/	/	2.8	0.2	0.008	0.0
Orb								
Total	0.3	2.0	0.4	1.0	1.1	4.1	0.014	1.8
Anthropogenic	/	/	/	/	0.2	1.2	0.007	1.0
Hérault[a]								
Total	1.9	11.0	1.6	5.6	10.5	28.1	0.136	11.1
Anthropogenic	/	/	/	/	3.5	6.3	0.095	5.0
Other small rivers[a]								
Total	2.2	16.6	2.8	8.1	14.7	33.9	0.110	11.4
Anthropogenic	/	/	/	/	6.4	8.0	0.072	4.1
Total	**49**	**440**	**67**	**229**	**233**	**854**	**2.9**	**241**
% from the Rhône	90	92	91	92	86	91	90	89
Anthropogenic	/	/	/	/	**49**	**275**	**1.0**	**79**
% from the Rhône	/	/	/	/	72	94	82	87
Anth./Tot. (%)	/	/	/	/	20	32	35	33

Fluxes calculated on the basis of the metal contents in river SPM collected on 4th December 2003 (see Table 1) except for Hérault River (flood event of 10 October 2002). For small rivers: contents are the means from Têt, Aude, Orb and Hérault rivers.

[a] Calculated/taken from Radakovitch et al. (2008).

natural (at maximum level) and anthropogenic fluxes could be readily done, deriving from the calculation of enrichment factors. The respective contributions were determined as follows:

$$\text{Total flux}(M) = [M] \times \text{Particulate flux}$$

$$\text{Natural flux}_{max}(M) = 1.5 \times [N] \times \text{Particulate flux} \times \left(\frac{[M]}{[N]}\right)_{\text{Background}}$$

$$\text{Anthropogenic flux}(M) = \text{Total flux}(M) - \text{Natural flux}_{max}(M)$$

where $[M]$ and $[N]$ correspond to the particulate contents of the metal of concern and the suitable normalizer, respectively. Background references, normalizer (i.e. ^{133}Cs) and the natural variability threshold (i.e. 1.5) are those previously described for EF calculations (see Section 3.1.1.).

On the one hand, river SPM contents measured during the flood event in the main rivers (Section 3.1.1) and available data for the smallest rivers (from Radakovitch et al., 2008) were used to determine the inputs of particulate metals during the 1-wk period. This exercise needs data to be representative of the flood episode and we assume that this requirement is met for the most important source of particles to the study area, i.e. the Rhône River, owing to 11 metal content references at our disposal (Section 3.1.1). Regarding the other point sources, one can expect that the single river sampling during the particle flux peak is representative of the entire episode, notably because of the low variability of metal contents observed in SPM of the Rhône River at that occasion and, much generally, in small-scale fluvio-deltaic continuums (e.g. Roussiez et al., 2011). Note that these values are also suitable to be applied for the 1-m period since 99% of the flux transported during this month correspond to the flood event. Thus, the mean total input of a given particulate metal was calculated as the sum of the inputs from the overall rivers opening into the Gulf of Lion. Results are presented in Table 4 for the 1-wk period only (no significant changes when compared to the 1-m period, not shown). Unsurprisingly, inputs are by far dominated by the Rhône River, which accounts for between 86% and 92% of the total riverine supply when considering the total metal fractions. This predominance concerns also the anthropogenic parts, with the same range of variation, except, however, for Cu. About 72% of this element is delivered by the Rhône River to the coastal zone *via* its man-made form, as against 86% for its total fraction. This is explained by the lower Cu enrichments in SPM of the Rhône River in comparison with small rivers. The latter can therefore be reasonably considered as a significant source of metallic contaminants despite relatively low solid input contributions.

On the other hand, marine SPM contents used for the assessment of output metal fluxes are those determined in the material gathered between the 1st and the 7th of December 2003. Here also we estimated that these values are adequate for both the 1-week and the 1-month periods. This simplification was made for two reasons: (i) the comparative analysis between these samples and those obtained at the end of the storm-relaxation period (see Section 2.4) did not show any significant difference (Table 5), and (ii) 72% of the export of particles in December 2003 occurred during the first week (see above). A mean signature of the particles leaving the shelf was then obtained by weighting the SPM metal contents recorded in the visited canyon heads by the fluxes estimated in the corresponding traps between the 1st and the 7th of December 2003. This is a necessary procedure to take into account the variability of sediment export between canyons. The resulting output fluxes are shown in Table 6 and difference between the two periods only derives from difference between output particulate fluxes. Consequently, output metal fluxes increased by a factor of 1.4 between the 7th and the 31st of December. Only Zn and Pb depict anthropogenic output fluxes (Section 3.1.1), which account, respectively, for 23% and 30% of the fluxes of their total fractions.

In terms of budget, outputs of particulate metals are lower compared to the inputs (Table 6). In agreement with the spatial pattern of EFs (Fig. 5), the output/input total flux ratios of Pb and Zn are close to those measured for lithogenic elements (i.e. Cs, Cr, Co and Ni). This reflects the affinity of these contaminants for the particulate phase irrespective of physico-chemical changes and sediment disturbance along their transport route. In contrast, the lower percentages obtained for Cu and Cd rather indicate the loss of their anthropogenic loads in shelf-exported particles (as also reported for surficial marine sediments), which raises important questions regarding their fate and ecological impact in the coastal zone. The metal outputs represent between 15% and 44% of the inputs at the end of the 1-wk period, and between 21% and 60% after the 1-m period owing to the export of suspended matter during the relaxation phase. As a conclusion, these results point in the direction of a retention of particulate metals in the shelf area during the event of December 2003, which is mainly explained by the net mass balance of solid materials during this period (Section 3.1.3.1). This general trend appears strengthened for Cu and Cd, but it likely obscures desorption mechanisms that have taken place earlier in marine particles, making that part of these metals entered a different distribution pathway.

Table 5
Mean enrichment factors in the sediment trap samples corresponding to the 29th December–4th January sequence, representative of "usual" hydro-sedimentary conditions. Each value is the mean EF of 2 duplicates.

Canyons	Cr	Co	Ni	Cu	Zn	Cd	Pb
Lacaze	1.0	1.0	1.2	1.8	2.4	0.7	2.0
Aude	1.0	1.1	1.3	1.3	2.0	0.8	2.1
Hérault	1.0	1.1	1.3	1.3	1.9	0.8	2.1
Petit-Rhône	1.0	1.0	1.2	1.3	1.9	0.9	2.2
Planier	1.2	1.3	1.5	2.7	2.8	0.8	3.3

Table 6
Output fluxes of particulate metals (total and anthropogenic) from the continental shelf of the Gulf of Lion, during the two reference periods for the oceanic flood of December 2003.

	Off-shelf export (t)							
Periods	Cs	Cr	Co	Ni	Cu	Zn	Cd	Pb
1st–7th December 2003								
Total	20	193	28	97	69	303	0.43	93
Anthropogenic	/	/	/	/	/	71	/	28
% from river inputs	40	44	42	42	30	36	15	39
1st–31st December 2003								
Total	28	270	39	135	96	424	0.61	130
Anthropogenic	/	/	/	/	/	99	/	39
% from river inputs	55	60	58	58	41	49	21	53

3.2. Annual particulate metal budget in the Gulf of Lion

3.2.1. Compilation of the data and suspended solid flux scenarios

Studies comparing the annual metal inputs and outputs in the Mediterranean Sea environment are sparse, mainly concern the dissolved fraction (Elbaz-Poulichet et al., 2001; Gomez, 2003) and cover important surfaces, entailing some uncertainties on the fluxes. By compiling the data from the present study and those from the literature, it is possible to draw up a realistic annual budget of particulate metals for the Gulf of Lion. Inputs are composed by riverine and atmospheric annual fluxes, while outputs correspond to shelf-exported annual fluxes. The latter are estimated according to different hydro-meteorological scenarios (see below).

Following the same approach than for the event-targeted budgets, mean annual input fluxes of particulate metals have been calculated on the basis of the mean metal contents in the

Table 7
Mean annual input fluxes of particulate metals (total and anthropogenic) to the Gulf of Lion, both of riverine and atmospheric origins.

	Input fluxes (t yr^{-1})							
	Cs	Cr	Co	Ni	Cu	Zn	Cd	Pb
Rivers (solid flux: 6.37 Mt yr^{-1})								
Rhône[a]								
Total	54	504	76	260	260	1019	3.31	255
Anthropogenic	/	/	/	/	56	382	1.52	76
Têt[b]								
Total	0.5	4.7	0.9	2.3	4.6	10.4	0.022	2.6
Anthropogenic	/	/	/	/	2.6	4.0	0.004	0.9
Aude[a]								
Total	3.7	35.2	4.8	16.3	30.0	43.7	0.167	11.8
Anthropogenic	/	/	/	/	16.0	0.1	0.044	0.0
Orb[a]								
Total	2.0	13.4	2.6	7.2	7.8	28.1	0.098	13.4
Anthropogenic	/	/	/	/	0.5	5.1	0.048	6.9
Hérault[a]								
Total	2.9	16.9	2.5	8.6	16.2	43.1	0.209	17.1
Anthropogenic	/	/	/	/	5.4	9.6	0.146	7.7
Other small rivers[a]								
Total	2.2	16.6	2.8	8.1	14.7	33.9	0.110	11.4
Anthropogenic	/	/	/	/	6.4	8.0	0.049	4.1
Total from rivers								
Total	65	591	89	303	333	1178	3.9	311
Anthropogenic	/	/	/	/	87	408	1.8	95
Anth./Tot. (%)	/	/	/	/	26	35	46	31
Atmosphere (solid flux: 0.23 Mt yr^{-1})								
Total	/	32.5[c]	2.6[c]	14.3[d]	23.2[d]	113[e]	0.5[e]	12.5[e]
Anthropogenic	/	13.6	0.1	8.8	15.4	80.6	0.4	11.9
Anth./Tot. (%)	/	42	2	62	67	71	90	95
Total input (riv. + atm.)	**65**	**623**	**92**	**317**	**357**	**1291**	**4.4**	**324**
Anth./Tot. (riv. + atm.) (%)	/	2.2	0.06	2.8	29	38	51	33

[a] Calculated/taken from Radakovitch et al. (2008).
[b] Calculated from Roussiez et al. (2011).
[c] Calculated from Guieu et al. (1997), by averaging the mean annual deposition fluxes from Tour du Valat (northern Gulf of Lion) and Cap Ferrat (northeastern Gulf of Lion).
[d] Calculated from Ridame et al. (1999), by averaging the mean annual deposition fluxes from Tour du Valat (northern Gulf of Lion), Cap Ferrat (northeastern Gulf of Lion) and Pirio (western Corsica Island).
[e] Calculated from Guieu et al. (2010), by averaging the mean annual deposition fluxes from Cap Bear (western Gulf of Lion) and Ostriconi (northern Corsica Island).

river SPM (here taken from Radakovitch et al., 2008 and Roussiez et al., 2011) and the corresponding annual solid fluxes, for which the total contribution amounts to 6.37 Mt yr^{-1} on average (see Section 2.1). Shelf-exported metal fluxes are estimated *via* the contents measured in materials trapped in December 2003. It is worth noting that these values are similar to those obtained for samples gathered during other 6-month trap deployments from a long-term time series in the same area (Heussner et al., 2006; unpublished data not shown here). It seems that, irrespective of hydro-dynamical conditions, shelf-exported particles display a very constant signature with respect to metal enrichment. This provides evidence for the permanence and importance of mixing processes between riverborne/resuspended prodeltaic particles and resuspended shelf sediments. The mean contents in marine SPM were weighted by the fluxes recorded in the corresponding sampling sites, as for Section 3.1.3.2. The resulting references have been applied to 3 different scenarios in terms of annual off-shelf export: (i) minimum: 1.9 Mt yr^{-1}, (ii) maximum: 10 Mt yr^{-1} and (iii) mean: 6 Mt yr^{-1}. The first scenario corresponds to the annual sediment export during "normal" hydro-dynamical conditions (i.e. no flood event registered), which has been estimated from the results of Durrieu De Madron et al. (2000). The second is an estimation of the maximum annual export based on the results of Ulses et al. (2008). These authors estimated at 9.1 Mt the off-shelf export between November 2003 and May 2004, a 6-month period marked by an unusual occurrence of flood and marine storm events. To cover a complete year, we added a minimal export for the 6 other months, representative of the usual hydro-dynamical conditions in spring and summer. The third is the arithmetic mean of the two above-described

Table 8
Mean annual output fluxes of particulate metals (total and anthropogenic) from the continental shelf of the Gulf of Lion, according to 3 scenarios of particle off-shelf export.

	Output fluxes (t yr^{-1})							
	Cs	Cr	Co	Ni	Cu	Zn	Cd	Pb
Scenario max. 10 Mt yr^{-1}								
Total	74	723	105	363	258	1136	1.62	349
Anthropogenic	/	/	/	/	/	266	/	105
% from total inputs	113	116	114	114	72	88	37	108
Scenario mean 6 Mt yr^{-1}								
Total	44	434	63	218	155	682	0.97	210
Anthropogenic	/	/	/	/	/	160	/	63
% from total inputs	68	70	69	69	43	53	22	65
Scenario min. 1.9 Mt yr^{-1}								
Total	14	137	20	69	49	216	0.31	66
Anthropogenic	/	/	/	/	/	51	/	20
% from total inputs	21	22	22	22	14	17	7	21

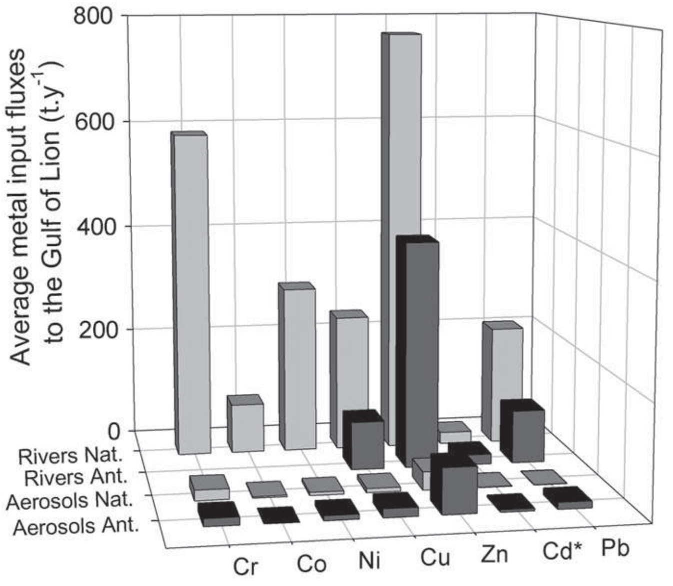

Fig. 6. Mean annual input fluxes of particulate metals to the Gulf of Lion, both of riverine and atmospheric origins. Natural (Nat.) and anthropogenic (Ant.) fractions are discriminated. *Cd fluxes are multiplied by 10.

scenarios. Anthropogenic fluxes have been estimated for both in- and output fluxes of metals, as previously described.

Considering the mean in- and output sediment fluxes, and keeping in mind that their interannual variability can strongly distort the budget, it appears that they are roughly in balance in the Gulf of Lion. In other coastal areas, budget construction can lead to different trends, in relation with the size of the shelf, river and atmospheric inputs, latitude and associated climate/meteorology, as well as tide influence. For instance, one can report shelf trapping efficiency ranging from about 25% (Poverty continental shelf, New Zealand, after Miller and Kuehl, 2010) to about 90% (Mackenzie continental shelf, Canada, after Macdonald et al., 1998) of the annual sediment inputs.

Atmospheric fluxes of particulate metals are extrapolated from long-term monitoring datasets of deposition fluxes: Cr and Co from Guieu et al. (1997), Cu and Ni from Ridame et al. (1999) and Cd, Pb and Zn from Guieu et al. (2010). By selecting the suitable data (details are given in the related table), we have estimated the metal input fluxes to the Gulf of Lion originating from the atmosphere. In addition, the anthropogenic contribution could be also estimated on the basis of the non-crustal fractions measured in both Saharan and European aerosols (from Guieu et al., 1997) that accounts respectively for about 95% and 5% of the mass of the total atmospheric input in the study area (Löye-Pilot, pers. com.). For each metal of interest, the man-made component has been established by weighting the non-crustal fractions measured in the two aerosol types by their respective contributions for the total deposition.

Results are summarized in Tables 7 and 8 for in- and output fluxes, respectively, and are discussed further below.

3.2.2. In- and output particulate metal fluxes

In general terms, the inputs of particulate metals are by far dominated by the riverine contribution (Table 7), which accounts for more than 90% of the total supply for a given element. The anthropogenic fluxes coming from the watersheds, which concern only Cd, Cu, Pb and Zn, vary between 26% and 46% of the riverine inputs. The contribution of the Rhône River to these contaminated inputs is predominant, although less important for Cu, following here the same trend than for the December 2003 oceanic flood. This similitude has to be related to the few differences existing between flood-related SPM contents and those determined from long-term monitoring. Nevertheless, the anthropogenic part of the fluxes is greater when originating from the atmosphere (Fig. 6 and Table 7). This is due to the highly elevated contamination levels that characterize the aerosols deposited in the study area (Guerzoni et al., 1989). For Cr, Co and Ni, contamination fluxes – although of minor importance compared to the total inputs – are only derived from the atmosphere. For the other anthropogenic elements, the atmospheric fallout accounts for between 11% and 18% of the total anthropogenic inputs (i.e. rivers plus aerosols), but represents about half of the contribution of the overall small rivers (calculated from Table 7) in the case of Cu and Pb, and even exceed them for Cd and Zn by a factor of 1.4 and 3, respectively.

The off-shelf export of particulate metals is detailed in Table 8 for the 3 above-described scenarios of output solid fluxes. The most striking result is that output fluxes never exceed the input fluxes from the rivers and the atmosphere, except slightly for Cs, Cr, Co, Ni and Pb during the scenario of maximum output. A realistic budget can be roughly estimated for the sediment-bound metals studied in this work. On the basis of in- and output mean solid fluxes, the amount of metals leaving the shelf in association with particles represents about 65–70% of the inputs, except for Zn (53%), Cu (43%) and Cd (22%). Moreover, considering the invariant "platform-like" signature of shelf-exported particles, anthropogenic output fluxes of Zn and Pb (respectively 23% and 30% of the fluxes from their total fractions, see Section 3.1.3.2) can be directly extrapolated from sediment output fluxes.

Although these estimations deserves caution according to the variability of both the intensity and frequency of hydro-meteorological events in the area, it can be advanced that, in its current functioning, the Gulf of Lion's shelf rather acts as a sink for riverine particulate metals. This is in agreement with the generally accepted idea of sediment accumulation in estuarine and shelf areas (Martin and Windom, 1991).

3.2.3. Anthropogenic budget: significance of hydro-meteorological events

The surplus of particulate metals deriving from anthropogenic activities and introduced into the Gulf of Lion represents a

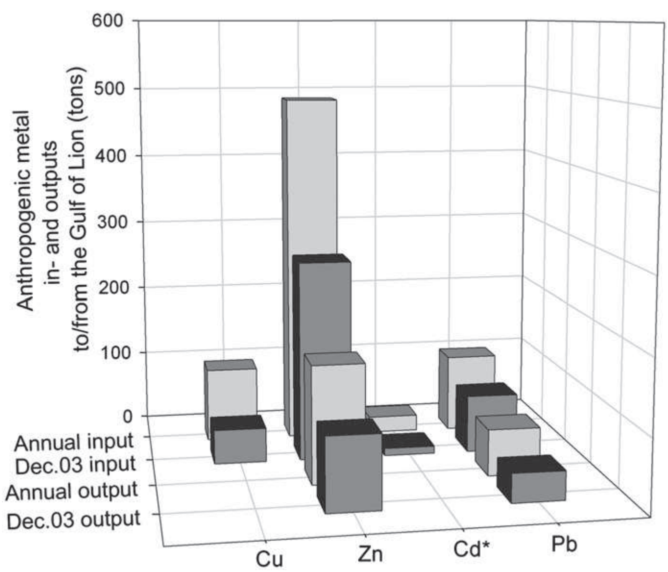

Fig. 7. In- and outputs of anthropogenic particulate metals to/from the Gulf of Lion, according to the mean annual sedimentary budget on the one hand, and the oceanic flood that occurred in early December 2003 on the other hand. *Cd fluxes are multiplied by 10.

potential threat for living species and, by extension, to humans that exploit these resources. Estimating the budget of metallic contaminants in this area can provide a guideline for specialists involved in eco-toxicological studies on coastal biota. Besides, when considering the important variability of hydro-dynamical conditions in the study area, it is important to understand the degree in which extreme hydro-meteorological events could account for annual budgets. In- and output fluxes of particulate anthropogenic metals were thus compared according to two distinct cases: the above-described mean annual scenario and the oceanic flood event of December 2003. Results are displayed in Fig. 7. The contribution of the oceanic flood episode to the mean annual budget is shown to be considerable. This is especially the case for anthropogenic Pb, for which 74% of the mean annual input (i.e. 107 t) is concentrated in the event of December 2003. This is also notable for Zn (56% of 489 t), Cd (45% of 2.2 t) and Cu (46% of 102 t). Although this event is exceptionally intense in comparison with recurrent flash-floods in the study area, these estimations suggest that a large part of the metallic contaminants is delivered within very short time periods, in opposition with the idea of a diffuse release into the coastal environment. Another point is the fact that, since most of the particles are deposited on the prodelta areas under very high accumulation rates (e.g. Miralles et al., 2005), these metals are rapidly accumulated under reductive conditions and could undergo some diagenetic processes. This results in vertical migrations and reprecipitations in oxic top layers, hence exposing local benthic species to enhanced threat. At the conclusion of the 4-wk relaxation period, about 62% of the mean annual output of anthropogenic Zn and Pb were exported to deep-sea (as against 44% after the 1-week period, not shown). In relation with the frequency of marine storms (and hence the output solid fluxes) in the study area, most of the export of metallic contaminants rather occurs through sporadic and intense processes, as for the inputs.

From an ecological viewpoint, the fast incursion of massive quantities of metal-enriched particles into the Gulf of Lion, their rapid deposition in prodeltaic areas and the redistribution of part of them towards the open sea (after dilution by resuspended shelf sediments) might exert an acute anthropogenic pressure onto marine organisms. In this context, it is of great concern to understand where and how far this contamination goes. Results gained from metal analyses of a deep sediment core from the Balearic basin (western Mediterranean) by Angelidis et al. (2011), attributed Pb, Zn and Cd contaminations to the atmospheric deposition. Although this area is known to receive little lateral inputs from continental slopes, it is possible that Pb- and Zn-enriched particles exported from the nearby Gulf of Lion, partly account for the particulate contaminant inventories in Mediterranean deep-sea environments, and entail therefore harmful effects on remote ecosystems.

4. Conclusions

The exceptional oceanic flood that developed in early December 2003 in the Gulf of Lion has been tracked by particulate metals through a simultaneous investigation at both the entrance and the exit of the continental shelf. While the riverine particles entering the coastal waters are marked by watershed-specific signatures, those leaving the shelf *via* the canyon heads exhibit rather homogeneous values. The continental signals for which an anthropogenic fraction is found here for Cd, Cu, Pb and Zn, are diluted in the coastal zone during the oceanic flood, and only particulate Pb and Zn depict an anthropogenic influence at the exit of the hydrosystem.

The tight similarity between the output signatures and those from the shelf sediments, notably regarding the natural occurrence of both Cu and Cd, suggest an intense mixing of riverborne particles (and resuspended prodeltaic sediments) with less contaminated marine materials during advective cross-shelf transport. Although element-specific desorptions can explain in general the loss of the anthropogenic fractions of Cu and Cd in marine sediments, they should not significantly take place at the scale of the event. Under these circumstances, the output signatures seem to testify that tremendous quantities of surficial shelf sediments have been resuspended in the water column by the marine storm, contributing massively to the particle export, which corroborates the results from models.

Two types of particulate metal budgets for the Gulf of Lion (NW Mediterranean) were assessed. Regarding the event of December 2003: inputs of particulate metals are by far dominated by the Rhône River, which accounts for about 90% of both total and anthropogenic fractions of particulate metals (less marked for Cu). In agreement with the mass balance, output fluxes of particulate metals are less important than the inputs. They account for between 15% and 60% of the latter, depending on the element and the period of reference. Regarding annual scenarios: inputs of particulate metals derive mainly from the riverine contribution (especially from the Rhône). Considering the mean scenario – likely representative of current sedimentary budgets – about 65–70% of most of particulate metals introduced into the Gulf of Lion leave the platform in association with particles. The fraction is lower for Zn (53%), and especially Cu (43%) and Cd (22%), which is explained for the two latter elements by their mobility in the marine system.

The contribution of the December 2003 oceanic flood to the mean annual anthropogenic budget is shown to be considerable. Our estimations indicate that hydro-meteorological events can account for a large part in the transfer of land-derived contamination to the coastal waters but also in the redistribution of contaminated particles towards deep-sea. Moreover, considering the invariant metal enrichment levels of shelf-exported particles, the ecological impact on remote marine ecosystems may depend directly on the off-shelf sediment fluxes, which rely on both the intensity and frequency of flood and marine storm events.

In its current functioning, the Gulf of Lion's shelf seems to act as a retention/sink zone for riverborne particulate metals. Nevertheless, from the perspective of global warming that may increase the frequency of intense hydro-meteorological events in the Mediterranean region (Ottlé et al., 2001), this trend could be reversed. In these conditions, the shelf could become a dominant source of metals to the open sea in comparison with both rivers and atmosphere, implying increasing pressure on biota.

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