Input of particulate heavy metals from rivers and associated sedimentary deposits on the Gulf of Lion continental shelf

Olivier Radakovitch [a,*], Vincent Roussiez [b], Patrick Ollivier [c], Wolfgang Ludwig [b], Christian Grenz [c], Jean-Luc Probst [d]

[a] *CEREGE – Université Paul Cézanne Aix-Marseille III – CNRS BP 80, 13545 Aix-en-Provence, France*
[b] *CEFREM, CNRS-Université de Perpignan, 52, Avenue Paul Alduy, 66860 Perpignan, France*
[c] *COM, Station Marine d'Endoume, Rue de la Batterie des Lion, 13007 Marseille, France*
[d] *INP, ENSAT, Av Agrobiopole, BP 107, 31216 Castanet Tolosan, France*
* Corresponding author.
E-mail address: radakovitch@cerege.fr (O. Radakovitch).

Abstract

Fluxes of the heavy metals chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), lead (Pb), cadmium (Cd) and zinc (Zn) delivered by rivers to the Gulf of Lion (NW Mediterranean Sea) were estimated over a three year study of the River Rhone and its smaller tributaries. Most of the particulate metal fluxes (80–90%) delivered by these rivers occurred within a very short period of time (less than 12%), a typical trend for the Mediterranean environment, where highly contrasting hydrological regimes were observed over the year. Temporal and spatial variations in the fluxes of these particulate metals were driven by the fluxes in both water discharge and suspended particulate matter load. On the shelf, these particulate metal fluxes, largely arising from the Rhone watershed, were two to ten times more important than those resulting from atmospheric deposition. Co, Cr and Ni in the rivers and on the shelf surface sediments were mainly natural and associated with the finest particles. Cd and Phosphorus appeared to be associated with the silt fraction and to be enriched in the prodelta areas. Pb, Zn and Cu were more closely associated with the organic matter content and also showed enrichment in the organic rich prodeltaic sediments. Anthropogenic influences diminished offshore, except for Pb and Zn which could be supplied from the atmosphere by man-made aerosols. Although most of the metals tended to be enriched in the prodelta areas, these did not constitute a permanent sink due to resuspension processes affecting these shallow depths. A resuspension experiment conducted on sediment cores from the Rhone prodelta demonstrated that metal deposited on the surface layer, especially those associated with the organic matter, may be resuspended; this should be taken into account for a complete understanding of the biogeochemical cycle of these metals.

Keywords: heavy metals; sediment contamination; river inputs; Mediterranean Sea; prodelta; sediment resuspension

1. Introduction

The Gulf of Lion in the northwestern Mediterranean Sea (Fig. 1) is an important location for numerous environmental programs. Over the past 15 years, these programs have dealt with a wide range of important environmental factors such as: particulate matter transport and deposition, biology, currents, river plume dynamics, and contaminants. The Gulf of Lion is surrounded by European countries which have emitted numerous pollutants during the last decades from industry and gasoline consumption. It receives large inputs from the river Rhone which is the most important river of the western Mediterranean basin and it is, thus, one of the most productive regions of the Mediterranean Sea (Raimbault and Durrieu de Madron, 2003). It has a large continental shelf, which accumulates particulate matter especially on the mid-shelf mud bank and the deltaic areas of the river mouths (Durrieu de Madron et al., 2000). The low tidal range of the Mediterranean facilitates

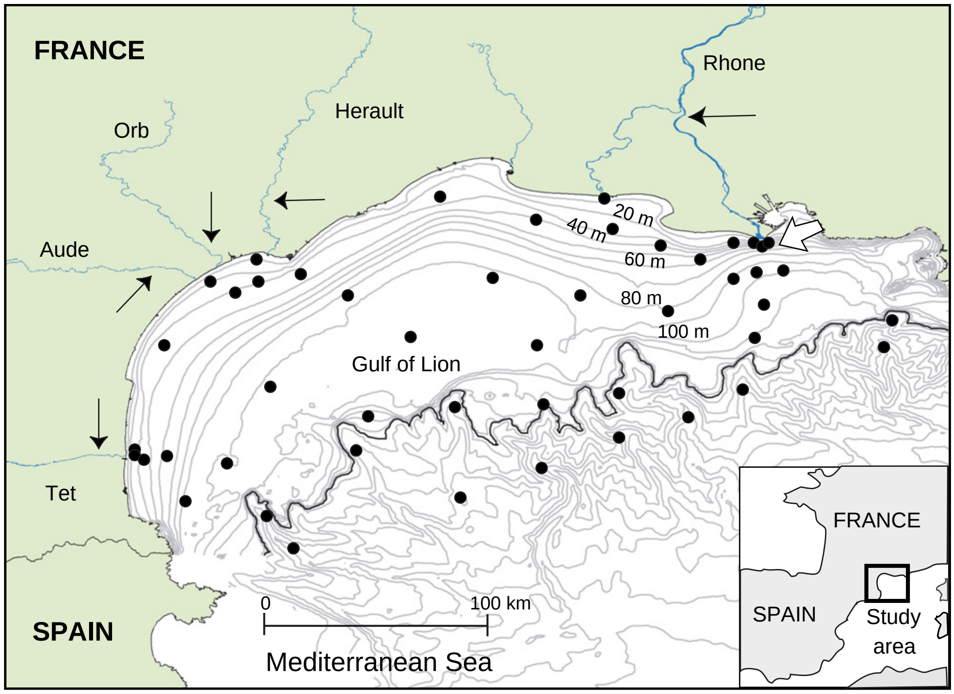

Fig. 1. Study area and location of sampling sites: sediment cores (●); rivers (→); sediments for resuspension experiment (⇐). Bathymetric lines at incremental intervals of 10 m from the coast to the continental margin (darker line) at 200 m depth.

this accumulation, and the Rhone prodelta is a sink for artificial radionuclides transported by the river. Indeed, like many metals, most of these radionuclides have an affinity for the particulate phase. Charmasson (2003) calculates, that the area of 500 km^2 around the mouth, traps all the particulate ^{137}Cs delivered by the Rhone as well as 20% of the total nuclear liquid discharge from the nuclear power and fuel reprocessing plants. However, such storage may be temporary due to sediment resuspension by storms and wind driven waves occurring at these shallow depths (Denis et al., 1996; Schaaff et al., 2002).

The studies on the shelf have enabled the construction of mass budgets for particulate matter, nutrients and the carbon cycle (e.g., Durrieu de Madron et al., 2000; Van der Broeck and Moutin, 2002; Durrieu de Madron et al., 2003 and references therein). In contrast, few works have been published on heavy metal contamination of the shelf sediments (Nolting and Helder, 1991; Ferrand et al., 1999). However, during recent years there have been studies on the biological importance of the shelf and the numerous potential pathways for contaminants to affect the heavy metal budget. In particular, there are estimates for dissolved and particulate heavy metal inputs from all the rivers draining the watershed of the Gulf of Lion, and the distribution of these metals on the surface sediment from the coast to the slope (Roussiez et al., 2006).

This paper summarizes the most important results from these studies, and presents also the first data from flume experiments on metal resuspension from sediments of the Rhone prodelta. It provides the general view necessary for the future construction of a box-model budget based on the budgets from the Land-Ocean Interactions in the Coastal Zone program-LOICZ (Gordon et al., 1996).

2. Study area

The Gulf of Lion continental shelf (Fig. 1) in the northwestern Mediterranean Sea has a surface area of 11,700 km^2 with a maximum width of 70 km. It comprises littoral sands interspersed by silty deposits (0−30 m) in front of the river mouths, a mud-bank (30−90 m) on the middle shelf, and a mixture of relict sands and modern muds (90−200 m) on the outer shelf (Durrieu de Madron et al., 2000).

Various rivers drain from southeastern France into the Gulf of Lion. The river Rhone is the main source of terrigenous, solid material with a mean discharge of around 7.4 × 10^6 t y^{-1}, and an interannual variability ranging from 1.2 to 19.7 × 10^6 t y^{-1} (Pont et al., 2002). It accounts for more than 80% of total particulate inputs by rivers to the shelf and it is also the major source for the Mediterranean Sea since the construction of dams on the Nile and Ebro rivers. The annual mean water discharge of the Rhone is 1700 m^3 s^{-1}, ranging from 250 m^3 s^{-1} in summer to 10,600 m^3 s^{-1} at a major flood event (e.g. December 2003, see Ollivier et al., 2006). The watershed area is 99,000 km^2 including mountains, agricultural and urban catchments. Other small coastal rivers (Tet, Aude, Orb, Herault and smaller rivers in Fig. 1) drain inhabited and agricultural areas that can constitute important local sources of particles. Their discharge regime is highly variable and, typically for the Mediterranean, characterised by very low flow in summer and episodic floods in spring or autumn. Industrial activity is more important in the Rhone valley and the anthropogenic impact of the smaller rivers is related more to agricultural and tourism activities. In terms of geology, the Gulf of Lion's watershed is predominantly Jurassic and Cretaceaous sedimentary rocks (sandstones, conglomerates, limestones, dolomites, schists, calcareous and shales). Metamorphic and igneous rocks cover only 15% of the Rhone watershed (granite and gneiss in the Massif Central and Alpine mountains), but they constitute more than 50% of the Tet and Aude watershed (Pyrenees mountains).

On the shelf, the Rhone river plume forms a bulge generally deflected to the northeast along the coastline. However, this plume is separated from the coast and deflected to the southwest during the strong, frequent northwestern winds (Marsaleix et al., 1998). Fluvial particulate matter rapidly accumulates in the prodelta with a decrease in the rates of accumulation seaward, ranging from 300 to 500 mm y^{-1} at the mouth to 2–6 mm y^{-1} 20 km offshore (Miralles et al., 2005).

3. Methods

On the river Rhone, surface water samples were collected twice a month from November 2000 to December 2003 at Arles, 47 km upstream from the river mouth. More samples were taken during the floods in March 2001, September 2002, November 2002 and December 2003. Water was collected manually from the bank in a 5 l acid-cleaned polypropylene bottle and rapidly filtered in the laboratory through pre-weighed 0.2 μm cellulose acetate filters, used for the estimation of the suspended particulate matter (SPM) concentrations. The water discharge data was derived from one gauging station operated by the Compagnie Nationale du Rhone at Arles. For the smaller rivers, water discharges were taken from surveys by regional companies and SPM samples were collected during flood conditions using the above described procedure.

Suspended particulate matter was dissolved into Teflon beakers with a mixture of nitric, hydrofluoric and perchloric acid (HNO_3-HF-$HClO_4$). The major cations calcium (Ca), aluminium (Al), magnesium (Mg,) sodium (Na), potassium (K), manganese (Mn), iron (Fe) and titanium (Ti) were measured by Inductive Coupled Plasma-Atomic Emission Spectrophotometer (ICP-AES) at the CEREGE laboratory (Aix en Provence). The trace elements chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), antimony (Sb), caesium (Cs) and lead (Pb) were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS – Perkin Elmer, Elan 5000 and 6000 at the LMTG laboratory Toulouse) after addition of an indium internal standard solution. Riverine particles from reference material STSD-3 (National Research Council of Canada) were dissolved and analysed under the same conditions as the sampled particles for both the major cations and the trace elements. Differences between measured and certified values were between 2 and 5%. Also, analytical blanks always gave values less than 2% of the measured contents.

More than fifty sediment cores were collected by multi- or box corers on the continental shelf during 2002 and 2003 (Remora and Eurostrataform cruises). Sampling and analytical procedures are described in Roussiez et al. (2005b) and they are similar to those for the SPM (ICP-MS, Toulouse). Accuracy was controlled using GSMS3 standard (National Research Centre for Certified Reference materials). Differences between measured and certified values were generally below 5%, except for cadmium for which measured values were 25–40% higher than reference value. To reduce the effect of the sediment composition on the elemental abundances, results were examined using a two-tiered normalization procedure (Kersten and Smedes, 2002) based on restricting analysis to the clay plus silt fraction (<63 μm) of the sample and adding a geochemical correction using a clay mineral proxy (Cs content). In order to examine only the most recently deposited sediments, the analyses reported here were confined to the top five millimeters of the cores.

Resuspension experiments were conducted on sediment cores taken in the vicinity of the Rhone River mouth (Fig. 1). Twelve cores were collected with a Bowers and Connely multicorer (15 cm diameter) and kept refrigerated. One core was sampled for grain-size and metal analysis. It was sliced at intervals of 10 mm along its length except for the initial two layers sliced at 0–5 and 5–10 mm. The resuspension experiments were performed in the laboratory using a recirculating flume as described by Denis et al. (1996) and Redondo et al. (2001). The flume was a 3 m long channel filled with 300 l of seawater, corresponding to 100 mm of water depth from the bottom. The top 100 mm of 4 cores were carefully transferred to the test section following the technique described by Schaaff et al. (2002). The total sediment interface introduced in the flume represented a surface of 7070 mm^2. Flow velocities were measured with an Acoustic Doppler Velocimeter (ADV) operating at a sampling rate of 10 Hz and placed in the middle of the test section, 40 mm above the sediment. At the same time, evolution of SPM concentration was recorded with an Aanderaa turbidity sensor (T/T sensor 3712). During the erosion experiments, water samples were collected every 5 min with a peristaltic pump. SPM concentrations were determined by filtration through Whatman GF/F filters (0.7 μm pore size). These data were used to calibrate the turbidity sensor. Erosion experiments consisted of a continuous increase for 45 min in flow velocity up to 350 mm s^{-1}. This maximum velocity was maintained for 30 min. Then, 60 l of circulating water were collected and filtered immediately together with an initial blank, using only seawater. The experiment was repeated twice. Filters and particles were dissolved with a mixture of aqua regia (HNO_3-HCl) in a microwave oven and metals were analysed by ICP-AES.

4. Results and discussion

4.1. Rivers

The term *concentration* in the following text denotes a mass per unit volume (e.g. mg l^{-1}), whereas the term *content* always denotes a mass per unit mass (e.g. μg g^{-1} or ppm; Flemming and Delafontaine, 2000). Variability in heavy metal fluxes and contents variations in the Rhone river were discussed by Ollivier (2006) and Ollivier et al. (in preparation). The period 2001–2003 was characterized by four major floods, which were the fifth, fourth, second and first largest floods recorded in Arles since 1856. SPM concentrations ranged from 3 to 2911 mg l^{-1}, a high range of variation compared to that of the water discharge (247–10,600 $m^3 s^{-1}$), with lower SPM concentrations during low flow and higher values during the floods just before maximal water discharge.

SPM fluxes were calculated using linear interpolation and specific treatment during floods to take into account variations in SPM concentrations between increasing and decreasing water discharges (Ollivier et al., in preparation). The annual SPM fluxes were 5.1, 10.9 and 4.8 × 10^6 t for 2001, 2002 and 2003, respectively, giving an average of 6.9 × 10^6 t (Table 1). This high variability was directly due to flood events contributing, respectively, to 82%, 88% and 78% of the annual flux. The major part of the SPM was thus discharged within a very short time frame (83% of the total flux within 12% of the time). Presumably, the prevailing wind and sea conditions within this time frame would have had a major impact on the distribution of SPM on the shelf.

Particulate metal content decreased with increasing flow and SPM concentrations. As illustrated for Cu and Cr (Fig. 2), they attained low and, more or less, constant values giving an indication of the background value. However, this was probably not the actual pre-anthropogenic value, because anthropogenic metals introduced from atmospheric deposits were generally found down to depths of 100–200 mm in the soils, even from non-polluted areas (Baize and Sterckeman, 2001; Hernandez et al., 2003; Miralles et al., 2005). It was improbable that all the SPM transported during the flood peak originated from below this soil depth.

These low values were not constant during the flood cycle and both SPM and heavy metals showed clockwise hysteresis. Such a trend is illustrated in Fig. 3 by the variation in some of the particulate metal contents, during the rising and the falling phases of the November 2002 flood. For the same flow, higher SPM concentration and higher metal content occurred on the rising phase, inducing higher fluxes. This probably resulted from the weathering of more polluted particles from the soil's surface at the beginning of the flood, as well as the increase of the sand fraction during the flood. Other processes that might explain SPM hysteresis include resuspension of sediment deposited during the last flood, bank collapses; or exhaustion of sediment supply at the end of the storms (Walling, 1977; Eisma, 1993; Asselman, 1999). The hysteresis trend was not so evident for all metals or for all floods (Ollivier et al., in preparation).

Table 1 summarises the average contents and fluxes obtained for all the Gulf of Lion rivers. Except for the Rhone, annual water discharges and SPM fluxes were taken from estimates of Bourrin and Durrieu de Madron (2006). The mean metal contents used for the small rivers were the means of the rivers Tet, Orb, Aude and Herault. Annual metal fluxes for the Rhone were calculated and discussed in Ollivier (2006) and Ollivier et al. (in preparation), whereas the others were calculated from the mean metal content and annual SPM flux reported here.

Rhone metal contents were measured in the total sediments, whereas the others were measured on the clay plus silt fraction less than 63 μm. However, they were very similar since the sediments with the greatest fraction of sand (15%) were only observed from the rivers Tet and Orb. The river Herault did show higher content for Zn, Cd, Cs and Pb, but these results were based on two samples only. The main difference was found for Cu which clearly had lower values in the Rhone.

The Rhone constituted about 90% of the total SPM input to the shelf, and the same proportion was obtained for metal fluxes (varying from 87% for Cu to 94% for Ni). These values could be considered as maxima since the SPM flux from the Rhone took into account exceptional floods, but a mean decadal value would probably not be so different. For all the rivers, the range of variation in water discharge and SPM concentrations were more important than those for metal content. Indeed, water discharge ($m^3 s^{-1}$) ranged within a factor 10 for the Rhone and Tet over the study period, whereas SPM in the Rhone ranged within a factor 100 in terms of mg l^{-1} corresponding to a factor 2700 in terms of mg s^{-1}. At the same time, particulate heavy metal contents variations were within a factor of 2–3. Water discharge and SPM concentration were thus the two driving forces for the metal fluxes. A precise estimation of the SPM flux should lead to the correct estimation of metal fluxes, even if metal contents were analysed only few times a year, particularly, during episodes of flooding. Indeed, as for SPM, 70–90% of particulate metal fluxes in the river Rhone were delivered within 12% of the period from 2001 to 2003 (Ollivier et al., in preparation). Furthermore, the hysteresis trend implied that flood periods should be sampled both during the rising and the falling phases. Such a sampling plan was especially important for the Mediterranean area where floods were typical.

Ollivier et al. (2006, in preparation) showed that the above concept was valid for most of the dissolved metals in the Rhone. However, in the case of As, Sb and Ni, dissolved concentrations increased with increasing discharge, particularly, with floods on tributaries draining old mining tailings. In these specific cases, dissolved metal fluxes could not be approximated from a few analyses and required more intensive sampling during floods.

The degree of contamination of a metal compared to its natural background is generally defined by its enrichment factor EF expressed as:

$$\mathrm{EF} = \left([\mathrm{Metal}_{\mathrm{sample}}]/[X_{\mathrm{sample}}]\right)/\left([\mathrm{Metal}_{\mathrm{background}}]/[X_{\mathrm{background}}]\right)$$

Where *X* is a grain-size or geochemical proxy. In general, Al or Fe were used as a suitable element for *X* and shale as a suitable background (Taylor and McLennan, 1985). However, Roussiez et al. (2005b) demonstrated that Cs was a more suitable element for *X* in the Gulf of Lion as it had the highest correlation coefficients with both metals and the fine fraction of the sediments. They used Cs together with the sediments from the shelf to define the natural background ratios for the Gulf of Lion. Shale was not used as most of the input into the Gulf was from the calcareous watershed of the Rhone. The typical variability for EF was between 0.75 and 1.5 which was assumed to represent the natural background. The average

Table 1
Water discharges, annual SPM fluxes, river catchment areas, particulate metal contents and fluxes of the rivers opening into the Gulf of Lion. Mean contents correspond to arithmetic means and were not weighted for SPM flux or time. Mean contents errors are the standard deviation of the dataset. *n*: number of samples. (1) The fluxes correspond to the total fluxes of the Rhone including its two branches: Petit Rhone and Grand Rhone; see Ollivier (2006) for detail. (2) See text for details of the estimation: mean contents are the means from Tet, Orb, Herault and Aude rivers

River	Water discharge ($km^3\ y^{-1}$)	Annual SPM flux (10^3 t y^{-1})	River catchment (km^2)		Cr	Co	Ni	Cu	Zn	Cd	Cs	Pb
Rhone ($n = 55$)	56.3	6930 *(1)*	99,000	Mean content (ppm)	93 ± 21	14 ± 3	48 ± 13	48 ± 22	188 ± 64	0.61 ± 0.17	10 ± 3.6	47 ± 16
				Annual metal flux (t y^{-1}) *(1)*	707	104	388	330	1292	4.5	71	356
				Specific flux (kg km^{-2} y^{-1})*(1)*	7.1	1.1	3.9	3.3	13.1	0.05	0.7	3.6
Tet ($n = 7$)	0.3	70	1400	Mean content (ppm)	89 ± 9	17 ± 2	42 ± 3	91 ± 8	195 ± 21	0.40 ± 0.11	10 ± 1	49 ± 10
				Annual metal flux (t y^{-1})	5.3	1.0	2.5	5.4	11.6	0.024	0.6	2.9
				Specific flux (kg km^{-2} y^{-1})	3.8	0.7	1.8	3.9	8.3	0.014	0.4	2.1
Aude ($n = 1$)	1.5	180	4830	Mean content (ppm)	95	13	44	81	118	0.45	10	32
				Annual metal flux (t y^{-1})	16.2	2.2	7.4	13.9	20.2	0.077	1.7	5.5
				Specific flux kg km^{-2} y^{-1})	3.4	0.5	1.5	2.9	4.2	0.016	0.4	1.1
Orb ($n = 1$)	0.9	70	1400	Mean content (ppm)	89	17	48	52	187	0.65	13	89
				Annual metal flux (t. y^{-1})	5.3	1.0	2.9	3.1	11.1	0.039	0.7	5.3
				Specific flux (kg km^{-2} y^{-1})	3.8	0.7	2.0	2.2	7.9	0.028	0.5	3.8
Herault ($n = 2$)	1.5	120	2820	Mean content (ppm)	89	13	45	85	227	1.1	15	90
				Annual metal flux (t y^{-1})	10.7	1.5	5.4	10.2	27.2	0.13	1.8	10.8
				Specific flux (kg km^{-2} y^{-1})	3.8	0.5	1.9	3.6	9.6	0.05	0.6	3.8
Small rivers *(2)*	0.8	184		Mean content (ppm)	*90 ± 7*	*15 ± 3*	*44 ± 3*	*80 ± 17*	*184 ± 43*	*0.60 ± 0.31*	*12 ± 2*	*62 ± 27*
				Annual metal flux (t y^{-1})	16.6	2.8	8.1	14.7	33.9	0.11	2.2	11.4
Total	61.3	7554		Annual metal flux (t y^{-1})	761	112	414	377	1396	4.9	78	392
% from the Rhone	92	92			93	92	94	87	93	92	91	91

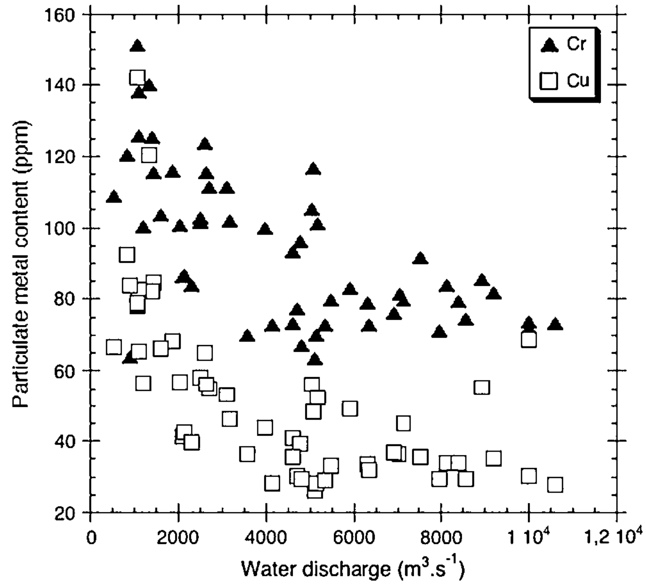

Fig. 2. Cr and Cu particulate concentration (ppm) relative to water discharge ($m^3\ s^{-1}$) in the Rhone river. The samples were taken at Arles (47 km upstream of the mouth) from 2001 to 2003 (modified from Ollivier, 2006).

EFs for the Gulf of Lion rivers were all below 3.5 (Fig. 4) and could be considered as moderate (from 2 to 5), according the classification proposed by Sutherland and Tolosa (2000). Cr, Co and Ni, with EFs around 1, clearly had a natural origin. Higher EFs for Pb, Zn, Cd and Cu indicated an anthropogenic origin for these metals. There was Cu enrichment in the rivers Tet, Aude and Herault (see Table 1), which may have had an anthropogenic origin from the use of copper sulphate ($CuSO_4$) on the extensive vineyards growing in the lower watershed (Besnard et al., 2001). However the diversity of metamorphic and igneous rocks in the watersheds for these rivers may also have been a source of natural Cu. Furthermore, despite the extensive industry in the watershed of the river Rhone, its EF for Cu and other metals was similar to that for the smaller rivers.

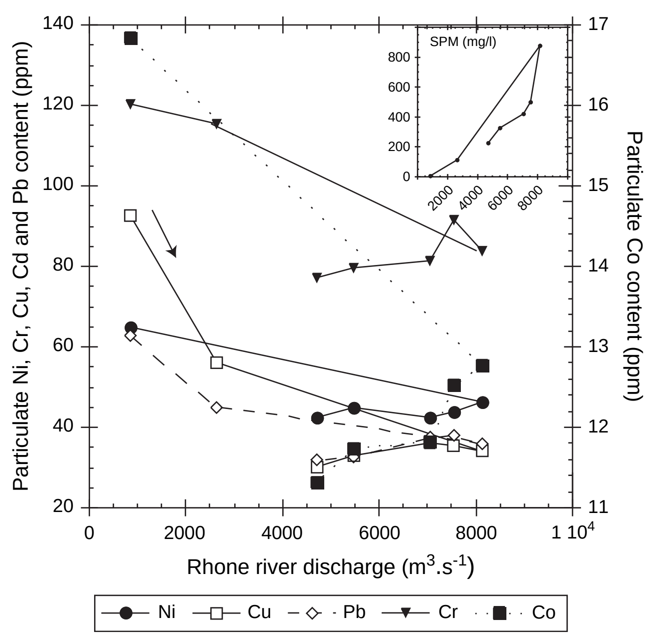

Fig. 3. Variation of particulate metal concentration (ppm) relative to the discharge of the Rhone river ($m^3\ s^{-1}$) during flood conditions, starting on the 27th September (at 850 $m^3\ s^{-1}$) and terminating on the 21st November 2002 (at 4700 $m^3\ s^{-1}$). The first three samples show the ‘‘rising phase’’ of the flood and the last four sample show the ‘‘falling phase’’. Inset: shows the SPM concentration ($mg\ l^{-1}$) relative to water discharge over the same period of flooding.

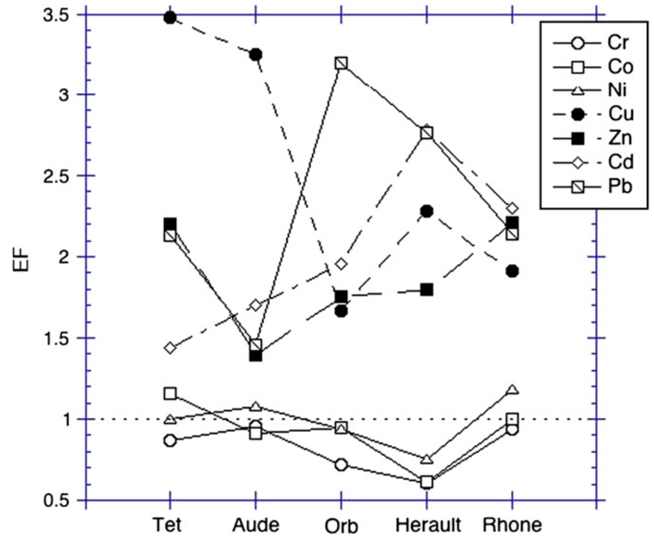

Fig. 4. Metal enrichment factors for river particles calculated from mean metal contents, mean Cs ratios and background metal:Cs ratios.

4.2. River and atmospheric fluxes

Rivers were the major sources of particulate metals to the shelf, as highlighted in Fig. 5. Assuming that all the river fluxes were deposited on the shelf, this total input could be compared to the atmospheric particulate deposits. Guieu et al. (1997) estimated dissolved and particulate metals fluxes from various sites around the northwestern Mediterranean Sea. They noted little variability between Cu, Ni and Pb fluxes at these sites. In contrast, other metals, especially Zn, showed a wide range of variability. The mean flux values for all these metals were used to compute Fig. 5.

Particulate atmospheric fluxes of metals constituted less than 5% of the total (rivers + atmosphere) inputs, with the exception of 17% for Zn and 35% for Cd. Guieu et al. (1997) suggested a localized contamination to explain the high variability for these two metals and that, in relation to the whole region, their particulate atmospheric fluxes were probably an overestimate. Thus, particulate atmospheric inputs were not important for most metals, even for Pb which was extensively dispersed in the atmosphere as submicron particles, mainly due to the use of leaded gasoline until the 1990’s (Grousset et al., 1995; Veron et al., 1999).

Comparison between atmospheric and river inputs was restricted to the sampling period in this study, particularly, as both atmospheric and riverine fluxes had changed during recent decades in response to various forcings: reduction of

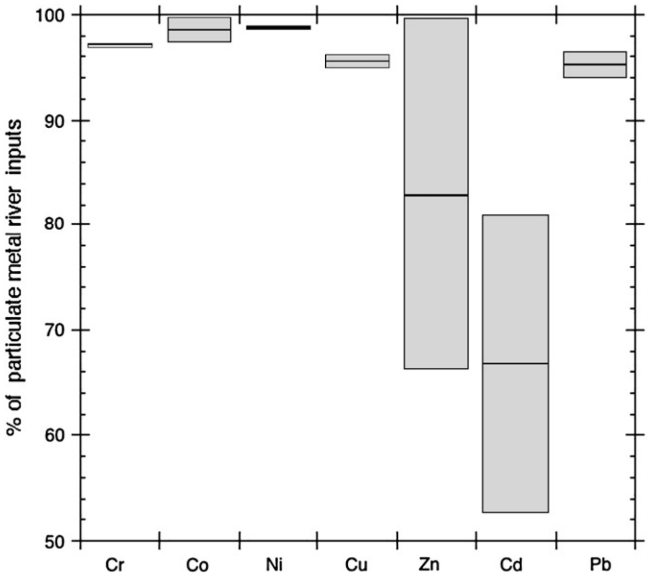

Fig. 5. Percent of river particulate metal inputs into the Gulf of Lion with respect to the total inputs (atmospheric + rivers). The minimum and maximum values of the box plots are fixed by the range of atmospheric estimates given by Guieu et al. (1997).

leaded gasoline; variations in particulate river fluxes due to dam construction; increasing pollution of the soil surfaces; and successive implementation of environmental laws by manufacturers (Miralles et al., 2006). Although, fluxes should be calculated for a twenty year period to obtain significant values, such an extensive data base did not exist for the Gulf of Lion. An interpretation of the more limited data base provided here must also account for:

(1) flood events: the estimate of fluxes for the Rhone included three years of floods, whilst in 2004 the mean river inputs were much lower because there were no floods;
(2) delimiting how much of the river flux was trapped on the shelf and how much was exported to the basin: Cr, Co or Ni from rivers (Fig. 5) could be used as indicators of such depositional areas, but they were essentially natural (Fig. 4) and clear information about anthropogenic input could not be inferred from their distribution;
(3) geographical scale for the estimates of fluxes: Martin et al. (1989) calculated that particulate atmospheric inputs of Pb, Cd and Cu over the entire western Mediterranean basin were two to three times higher than those from the rivers, but these factors were a little bit lower for the northwestern basin scale only. For the latter northwestern basin, Guieu et al. (1997) and Guerzoni et al. (1999) estimated that atmospheric particulate inputs of Cd and Zn were four times higher than rivers fluxes, whereas atmospheric particulate Pb was higher by factor of 2, only. Atmospheric particle fluxes for other metals were lower than those for the rivers, especially for Ni and Co. In contrast to these trends for particulate metals, more than 50% of the fluxes for dissolved metal were introduced from the atmosphere both in the northwestern basin (Guieu et al., 1997) and in the Adriatic Sea (Guerzoni et al., 1999).

4.3. Deposition on the shelf

The contents of major and trace elements in the fine (<63 μm) surface sediments of the continental shelf were discussed by Roussiez et al. (2005a,b,2006). The spatial distribution patterns of the trace metal concentrations exhibited two main trends:

(1) Most of the elements including Co, Cr, Cu, Ni, Pb and Zn increased in content in a gradient away from the river mouths (e.g. Cr, Fig. 6). This gradient appeared to be related to the depositional pattern of the finest sedimentary particles (<2 μm and <20 μm). This relationship suggested a common origin for the metals and the finest particles that were supported by the positive and significant correlations between these metals and the clay mineral proxies (Cs, Al and Fe in Roussiez et al., 2006). Superimposed on this trend in the coastal zone was the higher contents of Cu, Zn and Pb, adjacent to river mouths, that could be explained by the greater affinity of these metals for locally high concentrations of organic carbon (OC) compared to the finest sediment fraction (Roussiez et al., 2006).

(2) In the case of Cd (and P), the opposite trend was apparent with a decrease in content away from the river mouth (Fig. 7). These elements apparently had an affinity for the silt fraction of the sediment (2−63 μm), which was not transported as far from the river mouths during high energy periods associated with river run off and wave action (Roussiez et al., 2006). Indeed, particle sorting processes in coastal systems (Dellwig et al., 2000) showed that often a greater abundance of coarse grains was associated with a higher concentration of the heavy metals zircon and titanium; these metals were also positively and significantly correlated with both Cd and P in the Gulf of Lion (Roussiez et al., 2006).

As expected from the river data, the EFs for Co, Cr and Ni did not show any spatial trend, with contents close to background levels over the entire shelf (Roussiez et al., 2006).

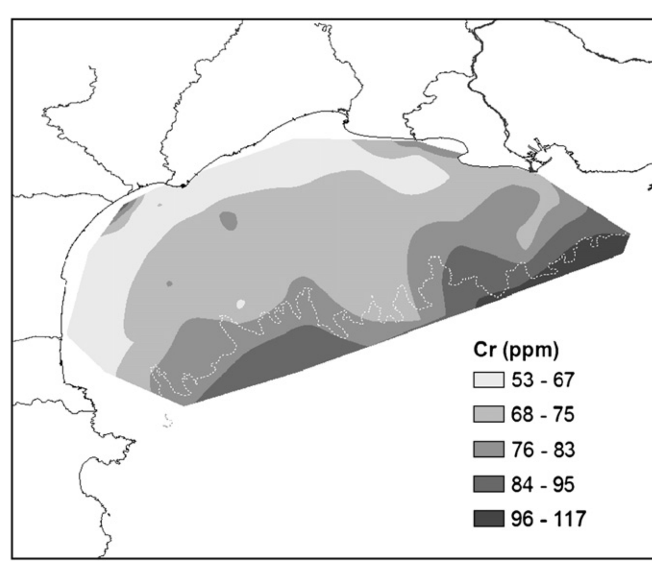

Fig. 6. Spatial contour map of the Gulf of Lion showing Cr content in the particulate fraction of surface sediments under 63 μm.

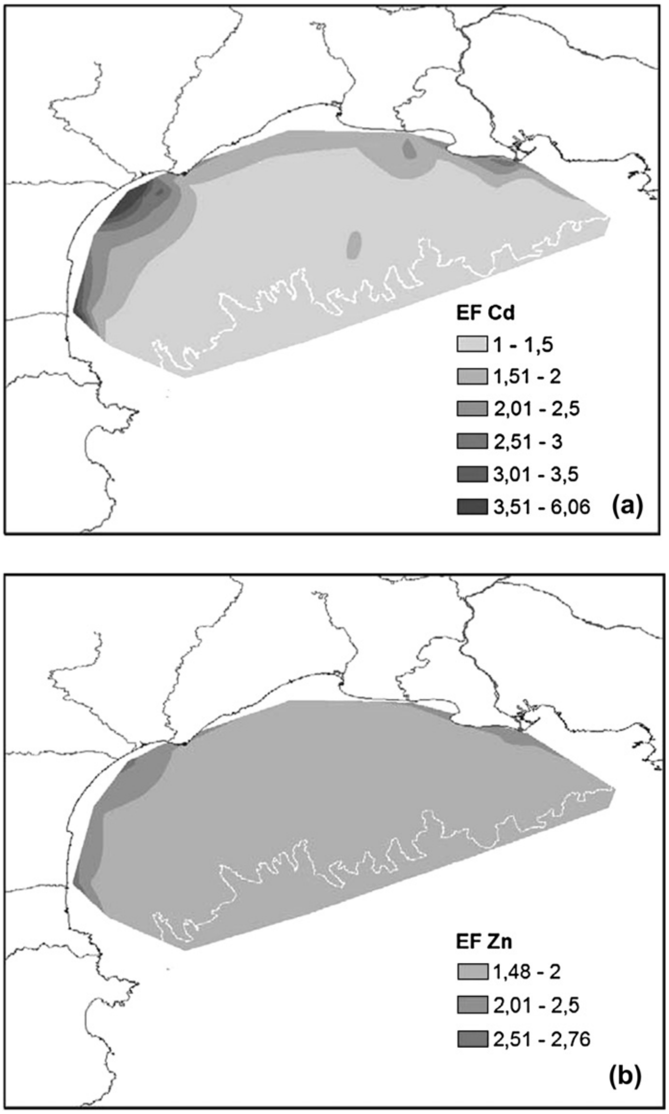

Fig. 7. Spatial contour maps of the Gulf of Lion showing enrichment factors in the particulate fraction of surface sediments under 63 μm for: (a) Cd; and (b) Zn.

However, the EFs of Cd, P, Cu, Pb and Zn decreased seaward, with an EF of 3.5 in the vicinity of all local river mouths, similar to the anthropogenic levels measured in the rivers (Fig. 7). This highlighted again the predominant role of riverine inputs to the shelf, even those of the small rivers. This near-shore contamination results from depositional conditions that favored the temporary storage of fine river particles, and associated metals, leading to formation of prodeltas (Aloisi and Monaco, 1975; Eisma, 1993). Accumulation of metals in prodeltas were observed in other deltaic zones (Puig et al., 1999; Chen et al., 2004) and was also typical of estuaries (e.g., Feng et al., 1998; Cave et al., 2005). In terms of content, such accumulation was not directly dependent on the quantity of sediment delivered, as can be seen from the similarities in the pattern anthropogenic Zn (Fig. 8) and Pb (Roussiez et al., 2005a), at the mouths of the rivers Tet and Rhone. The riverine particles were retained by rapid settlement, induced by organo-mineral complexation and flocculation mechanisms (Kranck, 1973; Aloisi and Monaco, 1975; Thill et al., 2001), but as these deposits were localized at sites affected by storm-waves, the freshly settled particles could be regularly flushed. The combination of both resuspension events and advection contributed to the nourishment of the off-shore sediments via the benthic nepheloid layer. Consequently, these near-shore dynamic units act both as a sink and a source of contaminant-bearing particles and, hence, probably contributed to the seaward export of pollutants.

Zn and Pb were the only metals showing an anthropogenic contamination (EF > 1.5) over the entire shelf area. Away from the river mouths, the other metals occurred at background levels (e.g. Cd in Fig. 7). The widespread distribution of Zn and Pb was partly linked to the high EFs of atmospheric deposits (Guerzoni et al., 1999) and diffuse atmospheric deposition.

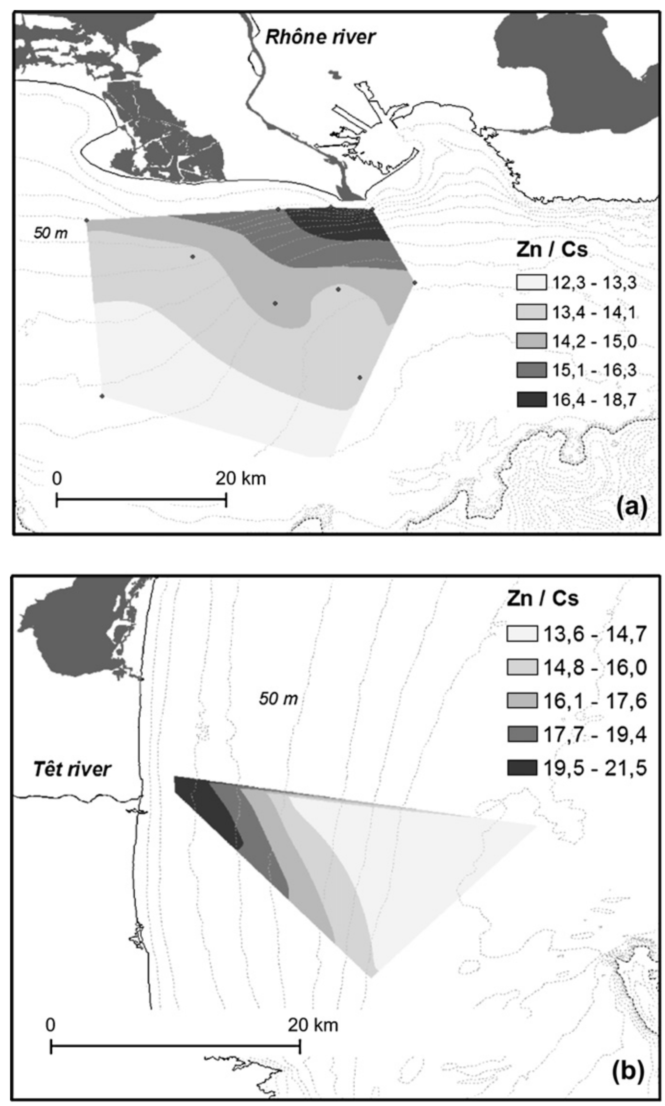

Fig. 8. Spatial contour maps of the Gulf of Lion showing Zn:Cs ratios in the particulate fraction of surface sediments under 63 μm at the prodeltas for: (a) the Rhone river; and (b) the Tet river.

In conclusion, with the exception of Zn and Pb, the anthropogenic signature of the metals on the continental shelf was progressively diluted by uncontaminated sediments and/or was confined to the vicinity of the river mouths due to the dynamics of the geochemical carriers. Organic carbon and silt fractions had a major role in this accumulation, masking those of the clay fraction in the inner-shelf.

4.4. Metal resuspension in the Rhone prodelta

An important part of the anthropogenic metals was probably trapped in the prodeltas, but these areas did not constitute definitive sinks because of the occurrence of sediment resuspension. Sediment erosion occurred when a critical value of shear stress exerted by moving fluids was exceeded. Sediment resuspension depended on local hydrodynamic conditions at the bottom boundary layer and was dominated in shallow waters by wave, tide and wind induced currents or locally by anthropogenic activities such as dredging and trawling. Critical shear stress and erosion rates were thus important parameters for understanding sediment transport and biogeochemical processes over the shelf. In addition, changes in sediment chemistry induced by the seabed disturbance and in the water surrounding the particles could result in contaminant remobilization via desorption or transformation (Eggleton and Thomas, 2004).

Measurement of critical shear stress and erosion fluxes were difficult to perform in situ and could be approached by flume experiments in laboratory. Such values were quantified from sediment cores collected in the vicinity of the Rhone river mouth at 8 m water depth. Local conditions (strong winds) influenced resuspension which occurred 15–30% of the time in this area (Lansard et al., 2006). The top layer (0–10 mm) of the core used for the flume experiment consisted of 95% sand, decreasing further along to 70–75%. This core was thus not really representative of the silty, prodelta deposits, and the sand content was perhaps due to previous resuspension of the finest particles. Fig. 9 reports the total concentrations of metals in the resuspended particles compared to those of the first twenty millimetres of sediment. Except for Cr and N, metal concentrations in the resuspended particles were higher than those for the 0.5 mm layer and even those of the underlying layers. The ratio of the metal concentrations, between resuspended particles and top layer, was generally between 1 and 2, except for Zn and Pb, and Cu where it was 3–4 and 20, respectively. Interestingly, these three metals were more closely associated with the organic matter than clay particles on the shelf sediments. Schaaf et al. (2002) reported that POM represented 9–12% of the eroded particles from a nearby site, and argued that low density particulate organic matter in the upper, oxygenated layer of the sediment was preferentially eroded. Both organic matter degradation and resuspension processes could be of major importance for the biogeochemical cycles of these three metals. However the flux of these two processes could not be evaluated because of the lack of data on resuspension events and on the temporal evolution of eroded particles within a single

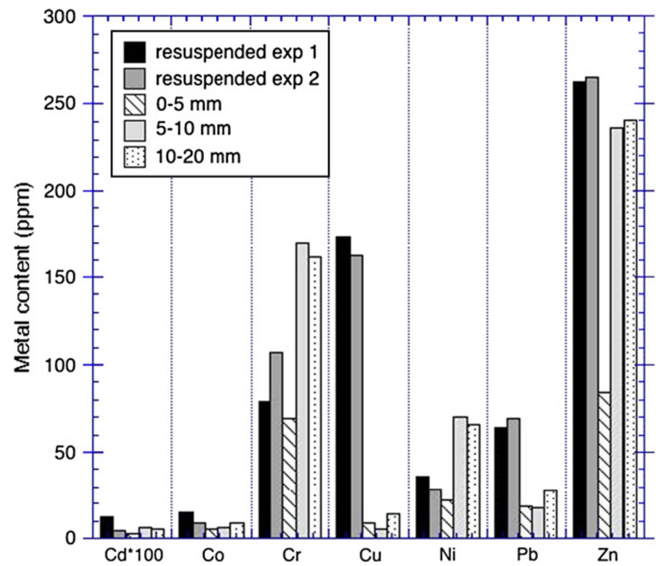

Fig. 9. Metals contents of resuspended particles from the flume experiment and from the top layers of the corresponding sediment core (0–2 cm depth). Total fraction was analyzed in each case. The two "resuspended" samples 1 and 2 correspond to the two experiments conducted with cores from the same site (see text for details).

site. Nonetheless, these processes could be a regular mechanism for supplying metals to the water column: both in the particulate phase and, possibly, in the dissolved phase from pore water which was usually enriched with dissolved metals in coastal sediments (e.g. Emerson et al., 1984; Cheevaporn et al., 1995). This mechanism differed from the more sporadic inputs observed by Puig et al. (1999) on a similar shelf that were associated with periodic flooding of rivers where particles contaminated by metals were transported directly into the coastal zone without mixing with particles from uncontaminated sediments. The fate of metal contaminants during sediment erosion clearly requires further investigation (Eggleton and Thomas, 2004).

5. Conclusions

- The major part of the particulate metal fluxes delivered by rivers to the Gulf of Lion occurred over a short time period. This was typical of the Mediterranean environment where highly contrasting hydrological regimes were observed over the year.
- Particulate metal content generally exhibited a hysteresis trend during flood periods.
- Variations of particulate metal fluxes in the rivers were driven by those of the water discharge and SPM concentration. Thus, a precise estimation of these two parameters combined with some metal analyses could provide good approximation of particulate metal fluxes. However, sampling must be done during both the rising and the falling phases of the floods.
- The budget on the shelf of metal particulate fluxes from rivers was more important than atmospheric deposition.

This was due to the importance of the input from the Rhone river.

- Co, Cr and Ni in the shelf surface sediments were mainly natural and associated with the finest particles. Cd and phosphorus appeared more related to the silt fraction and were enriched in the prodelta areas. Zn, Pb and Cu were more closely associated with the organic matter content and were also enriched in the prodelta areas, although the influence of anthropogenic Zn and Pb was observed over the entire shelf.
- Although most of the metals tended to be enriched in the prodelta, this was not a permanent sink because disturbances to these shallow areas may have resuspended some of the deposited sediments. In common with the organic matter, Zn, Pb and Cu were enriched in resuspended particles compared to the sediment, These observations need to be confirmed and taken into account to fully understand the biogeochemical cycle in coastal sediments.

Acknowledgements

This work was supported by two national programs (ORME and PNEC-Chantier Nord Méditerannée-Golfe du Lion) and by the European EUROSTRATAFORM program (EVK3-CT-2002-00079). P. Ollivier and V. Roussiez benefited from PhD grants of the French Ministry of Research. We thank the crews of the French vessels for their help with the collection of sediment cores, and R. Freydier in Toulouse for his assistance on ICP-MS analyses. Metal analyses of the resuspension experiment were done by M. Clavier. We thank the three anonymous reviewers and the special editor for their helpful comments.

References

Aloisi, J.C., Monaco, A., 1975. La sédimentation infra-littorale. Les prodeltas nord-méditerranéens. Comptes Rendus Académie Science Paris 280, 2833−2836.

Asselman, N.E.M., 1999. Suspended sediment dynamics in a large drainage basin: the river Rhine. Hydrological Process 13, 1437−1450.

Baize, D., Sterckeman, T., 2001. Of the necessity of knowledge of the natural pedo-geochemical background content in the evaluation of the contamination of soils by trace elements. Science of the Total Environment 264. 127−13.

Besnard, E., Chenu, C., Robert, M., 2001. Influence of organic amendments on copper distribution among particle-size and density fractions in Champagne vineyard soils. Environmental Pollution 112, 329−337.

Bourrin, F., Durrieu de Madron, X., 2006. Contribution to the study of coastal rivers and associated prodeltas to sediment supply in Gulf of Lions (NW Mediterranean Sea). Life and Environment 56, 1−8.

Cave, R.R., Andrews, J.E., Jickells, T., Coombes, E.G., 2005. A review of sediment contamination by trace metals in the Humber Catchment and estuary, and the implications for future estuary water quality. Estuarine, Coastal and Shelf Science 62, 547−557.

Charmasson, S., 2003. ^{137}Cs inventory in sediment near the Rhone mouth: role played by different sources. Oceanologica Acta 26, 435−441.

Cheevaporn, V., Jacinto, G.S., San diego-McGlone, M.L., 1995. Heavy metal fluxes in Bang Pakong river estuary, Thailand: sedimentary vs diffusive fluxes. Marine Pollution Bulletin 31, 4−12.

Chen, Z., Saito, Y., Kanai, Y., Wei, T., Li, L., Yao, H., Wang, Z., 2004. Low concentrations of heavy metals in the Yangtze estuarine sediments, China: a diluting setting. Estuarine, Coastal and Shelf Science 60, 91−100.

Dellwig, O., Hinrichs, J., Hild, A., Brumsack, H.J., 2000. Changing sedimentation in tidal flat sediments of the southern North Sea from the Holocene to the present: a geochemical approach. Journal of Sea Research 44, 195−208.

Denis, L., Grenz, C., Plante-Cuny, M.R., 1996. Experimental study of microphytobenthos resuspension. Comptes Rendus Académie Science Paris Life Science 319, 529−535.

Durrieu de Madron, X., Abderrazzak, A., Heussner, S., Monaco, A., Aloisi, J.C., Radakovitch, O., Giresse, P., Buscail, R., Kerherve, P., 2000. Particulate matter and organic carbon budgets for the Gulf of Lion (NW Mediterranean). Oceanologica Acta 23, 717−730.

Durrieu de Madron, X., Denis, L., Diaz, F., Garcia, N., Guieu, C., Grenz, C., Loye-Pilot, M., Ludwig, W., Moutin, T., Raimbault, P., Ridame, C., 2003. Nutrients and carbon budgets for the Gulf of Lion during the Moogli cruises. Oceanologica Acta 26, 421−434.

Eggleton, J., Thomas, K.V., 2004. A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events. Environment International 30, 973−980.

Eisma, D., 1993. Suspended Matter in the Aquatic Environment. Springer-Verlag, Berlin, Germany, 442 pp.

Emerson, S., Jahnke, R., Heggie, D., 1984. Sediment water exchange in shallow water estuarine sediments. Journal of Marine Research 4, 709−730.

Feng, H., Cochran, J.K., Lwiza, H., Brownawell, B.J., Hirschberg, D.J., 1998. Distribution of heavy metal and PCB contaminants in the sediments of an urban estuary: the Hudson river. Marine Environmental Research 45, 69−88.

Ferrand, J.L., Hamelin, B., Monaco, A., 1999. Isotopic tracing of anthropogenic Pb inventories and sedimentary fluxes in the Gulf of Lion (NW Mediterranean Sea). Continental Shelf Research 19, 23−47.

Flemming, B.W., Delafontaine, M.T., 2000. Mass physical properties of muddy intertidal sediments: some applications, misapplications and non-applications. Continental Shelf Research 20, 1179−1197.

Gordon Jr., D.C., Boudreau, P.R., Mann, K.H., Ong, J.E., Silvert, W.L., Smith, S.V., Wattayakorn, G., Wulff, F., Yanagi, T., 1996. LOICZ Biogeochemical Modeling Guidelines. LOICZ reports & studies, 5. LOICZ Texcel, The Netherlands, 96 pp.

Guerzoni, S., Chester, R., Dulac, F., Herut, B., Loye-Pilot, M.D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Rossini, P., Saydam, C., Soudine, A., Ziveri, P., 1999. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. Progress in Oceanography 44, 147−190.

Guieu, C., Chester, R., Nimmo, M., Martin, J.M., Guerzoni, S., Nicolas, E., Mateu, J., Keyse, S., 1997. Atmospheric input of dissolved and particulate metals to the northwestern Mediterranean. Deep-Sea Research II 44, 655−674.

Grousset, F.E., Quetel, C.R., Thomas, B., Donard, O.F.X., Lambert, C.E., Guillard, F., Monaco, A., 1995. Anthropogenic vs lithogenic origins of trace elements (As, Cd, Pb, Rb, Sc, Sn, Zn) in water column particles: northwestern Mediterranean Sea. Marine Chemistry 48, 291−310.

Hernandez, L., Probst, A., Probst, J.L., Ulrich, E., 2003. Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. Science of Total Environment 312, 195−219.

Kersten, M., Smedes, F., 2002. Normalization procedures for sediment contaminants in spatial and temporal trend monitoring. Journal of Environmental Monitoring 4, 109−115.

Kranck, K., 1973. Sediment deposition from flocculated suspensions. Nature 246, 348−350.

Lansard, B., Grenz, C., Charmasson, S., Schaaff, E., Pinazo, C., 2006. Potential plutonium remobilisation linked to marine sediment resuspension. First estimates based on a flume experiment. Journal of Sea Research 55, 74−85.

Marsaleix, P., Estournel, C., Kondrachoff, V., Vehil, R., 1998. A numerical study of the formation of the Rhone river plume. Journal of Marine Systems 14, 99−115.

Martin, J.M., Elbaz-Poulichet, F., Guieu, C., Loye-Pilot, M.D., Han, G., 1989. River versus atmospheric input of material to the Mediterranean Sea; an overview. Marine Chemistry 28, 159−182.

Miralles, J., Radakovitch, O., Aloisi, J.C., 2005. ^{210}Pb sedimentation rates from the northwestern Mediterranean margin. Marine Geology 216, 155−167.

Miralles, J., Veron, A., Radakovitch, O., Hamelin, B., Deschamps, P., 2006. Atmospheric lead fallout over the last century recorded in Gulf of Lions sediments (Mediterranean Sea). Marine Pollution Bulletin 52, 1364−1371.

Nolting, R.F., Helder, W., 1991. Lead and zinc as indicators for atmospheric and riverine particle transport to sediments in the Gulf of Lion. Oceanologica Acta 14, 357−367.

Ollivier, P., 2006. Interface continent-ocean. Geochimie du Rhone et transferts d'eaux souterraines en Camargue. PhD thesis, University Paul Cezanne Aix Marseille III.

Ollivier, P., Radakovitch, O., Hamelin, B., 2006. Unusual variations of dissolved As, Sb and Ni in the Rhone River during flood events. Journal of Geochemical Exploration 88, 394−398.

Ollivier, P., Radakovitch, O., Hamelin, B. Major and trace elements partition and fluxes in the Rhone river. Chemical Geology, in preparation.

Pont, D., Simonnet, J.P., Walter, A.V., 2002. Medium-term changes in suspended sediment delivery to the ocean: consequences of catchment heterogeneity and river management (Rhone river, France). Estuarine, Coastal and Shelf Science 54, 1−18.

Puig, P., Palanques, A., Sanchez-Cabeza, J., Masque, P., 1999. Heavy metals in particulate matter and sediments in the southern Barcelona sedimentation system (North Western Mediterranean). Marine Chemistry 63, 311−329.

Raimbault, P., Durrieu de Madron, X., 2003. Research activities in the Gulf of Lion (NW Mediterranean) within the 1997−2001 PNEC project. Oceanologica Acta 26, 291−299.

Redondo, J.M., Durrieu de Madron, X., Medina, P., Sanchez, M.A., Schaaff, E., 2001. Comparison of sediment resuspension measurements in sheared and zero-mean turbulent flows. Continental Shelf Research 21, 2095−2103.

Roussiez, V., Aloisi, J.C., Monaco, A., Ludwig, W., 2005a. Early muddy deposits along the Gulf of Lion shoreline: a key for a better understanding of land-to-sea transfer of sediments and associated pollutant fluxes. Marine Geology 222−223, 345−358.

Roussiez, V., Ludwig, W., Probst, J.L., Monaco, A., 2005b. Background levels of heavy metals in surficial sediments of the Gulf of Lion (NW Mediterranean): an approach based on 133Cs normalization and lead isotope measurements. Environmental Pollution 138, 167−177.

Roussiez, V., Ludwig, W., Probst, J.L., Monaco, A., Bouloubassi, I., Buscail, R., Saragoni, G., 2006. Sources and sinks of sediment-bound contaminant in the Gulf of Lions (NW Mediterranean Sea): a multi-tracer approach. Continental Shelf Research 26, 1843−1857.

Schaaff, E., Grenz, C., Pinazo, C., 2002. Erosion of particulate inorganic and organic matter in the Gulf of Lion. Comptes Rendus Geosciences 334, 1071−1077.

Sutherland, R.A., Tolosa, C.A., 2000. Multi-element analysis of road-deposited sediment in an urban drainage basin, Honolulu. Hawaii. Environmental Pollution 110, 483−495.

Taylor, S.R., McLennan, S.M., 1985. The Continental Crust: Its Composition and Evolution. Blackwell, Oxford, 312 pp.

Thill, A., Moustier, S., Garnier, J.M., Estournel, C., Naudin, J.J., Bottero, J.Y., 2001. Evolution of particle size and concentration in the Rhone river mixing zone: influence of salt flocculation. Continental Shelf Research 21, 2127−2140.

Van der Broeck, N., Moutin, T., 2002. Phosphate in the sediments of the Gulf of Lion (NW Mediterranean Sea), relationship with input by the river Rhone. Hydrobiologia 472, 85−94.

Veron, A., Flament, P., Bertho, M.L., Alleman, L., Flegal, R., Hamelin, B., 1999. Isotopic evidence of lead pollutant sources in Northwestern France. Atmospheric Environment 33, 3377−3388.

Walling, D.E., 1977. Assessing the accuracy of suspended sediment rating curves for a small basin. Water Resource Research 13, 531−538.