Sources and sinks of sediment-bound contaminants in the Gulf of Lions (NW Mediterranean Sea): A multi-tracer approach

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Abstract

Surficial sediments collected in 2002 throughout the Gulf of Lions continental shelf (NW Mediterranean) were analysed for trace metals (Cd, Co, Cr, Cs, Cu, Ni, Pb, Sr, Zn and Zr), major elements (Al, Ca, Fe, P and Ti) and the sewage marker coprostanol. In addition, particle size distribution, organic carbon (OC) and carbonates were also determined. Results showed that the metal contamination (Cd, P, Cu, Pb and Zn) is mainly introduced by the local rivers and accumulates—via a regulation by OC and silt fraction (2–63 µm)—in the direct vicinity of the mouths, in high shear stress environments. Here also the signal of sewage contamination is the best preserved, especially off the eastern point sources where local sedimentation rates save the faecal marker from biodegradation processes. It is demonstrated that the shallow prodeltas are the first repository areas for land-derived particles, exposing local ecosystems to both inorganic and organic contaminations. When going seaward, however, sediment dilution, particle sorting and biodegradation processes make that most riverborne contaminants rapidly reach natural levels. Only some metals (i.e. Pb and Zn)—closely associated with the clay fraction—still depict anthropogenic enrichment, which seems to be inherited from man-made aerosols.

Keywords: Heavy metals; Coprostanol; Contaminants; Riverborne and aerosol sources; Repository areas; Gulf of Lions

1. Introduction

The rapid development of human activities during the last decades within densely populated areas has continuously increased the risk of environmental deterioration, especially in coastal systems (Clark, 2001). Industry, agriculture, urban wastewaters, port activities and tourism release a wide variety of contaminants that mix with the natural constituents of the environment. Both natural and anthropogenic inputs reach finally the coastal zone mainly via river-transport but also by diffuse atmospheric deposition on the sea-atmosphere interface as dust and man-made aerosols. For these reasons, and according to the fact that sediments represent a preferential sink for contaminants, the survey of particulate discharges into sensitive littorals is of great importance.

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The Gulf of Lions (NW Mediterranean Sea) is an interesting site for studying the fate of land-derived contaminants in the marine environment because it is bordered by numerous industrialized/cultivated river catchments that discharge important quantities of particles into the coastal zone. Previous investigations on the sedimentary processes at the continent/sea interface highlighted the dynamic feature of the shallower shelf, alternatively acting as sink and source of particulate materials (Roussiez et al., 2005a and references therein). However, even if a large panel of studies have been conducted in this area (e.g. Durrieu de Madron et al., 2000), little is still known about the distribution pathways and entrapment of associated elements such as heavy metals and sewage-borne contaminants.

Improving our knowledge on this has two major interests: (i) on the one hand, the identification of the marine repository areas of terrestrial contaminants may help to combat their negative effects on the biological communities in the coastal areas. Heavy metals behave as conservative pollutants, entailing long-lasting toxic effects for living organisms and an increase of their concentrations in the trophic chain through biomagnification. Concurrently, organic compounds and pathogens deriving from human sewage pose additional environmental risks such as, for example, transmission of infection diseases (Lee and Glover, 1998) and bacterial resistance in aquatic organisms. (ii) On the other hand, anthropogenic compounds can be used for the tracking of particles, a necessary condition to determine the ultimate fate of the continental materials in the marine system.

Our purpose was therefore to identify the dispersion pathways and repository areas of natural and anthropogenic inputs through a large-scale mapping of the geochemical properties in surficial sediments of the Gulf of Lions. The elements we investigated are trace metals (i.e. Cd, Co, Cr, Cs, Cu, Ni, Pb, Sr, Zn and Zr), major oxides (i.e. Al, Ca, Fe, P and Ti) and coprostanol, a sterol associated with sewage solids (Kelly, 1995) widely used to trace the faecal contamination in aquatic environments (e.g. Readman et al., 2005). In addition, general sediment properties (i.e. clay, silt, organic carbon [OC] and carbonate contents) were also considered in order to improve our understanding of geochemical and sedimentological factors that likely control the elemental distributions. To the best of our knowledge, this paper constitutes the most complete survey to date of the extent of both inorganic and sewage contaminations over the continental shelf and gives important information on the particle dispersal throughout this key environment of the Mediterranean Sea.

2. Material and methods

2.1. Study area

The Gulf of Lions is one of the largest continental shelves of the Mediterranean Sea, receiving various sources of insoluble particles, both of riverine and atmospheric origins. The total river solid discharge to the study area can be estimated to about 6.5–10.5×10^6 t/yr (from Roussiez et al. (2005a) and references therein). More than 80% of this input arises from the Rhône River (Durrieu de Madron et al., 2000). The other rivers (e.g. Têt, Aude, Orb and Hérault—see Fig. 1) are characterized by smaller watersheds and show a highly variable discharge regime governed by episodic flood events. This makes that suspended sediments of the small coastal rivers are mainly delivered to the marine system in the form of intermittent pulses. The local atmospheric input of particulate matter derives mostly from crust-rich Saharan aerosols, although also anthropogenic-rich European aerosols are introduced into the study area (Löye-Pilot, pers. commun.). By extrapolating a recent estimation of annual aerosol flux in the western Mediterranean basin (Löye-Pilot, pers.com), the overall atmospheric particulate input to the study area can be calculated to about 0.17×10^6 t/yr. The atmospheric contribution is hence about 50 times lower than the riverine inputs, implying that the sediment particulate matter in the Gulf of Lions is mostly derived 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 Pyrenees mountains.

2.2. Sampling and geochemical analyses

In November 2002, 51 sediment cores were collected in the Gulf of Lions during the REMORA 3 oceanographic cruise. Sediment samples were
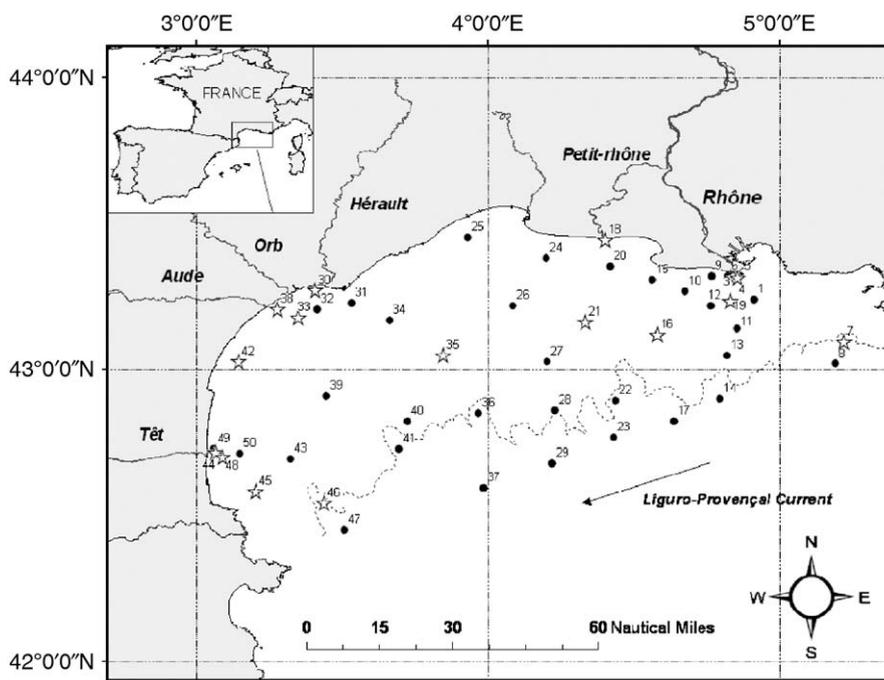
Fig. 1. Study area and sampling stations (black points and open stars). Stars refer to samples analysed for coprostanol contents. The boundary of the shelf has been represented by the 200 m isobath.

taken by using multicorer or box corer and stretch over the entire shelf, from the river mouths to the canyon heads (Fig. 1). The investigated sediments correspond to the first half centimetre of the sediment cores, representing hence the modern particle deposits in the study area. As described in Roussiez et al. (2005a), sediment samples were stored in plastic bags and immediately deep-frozen on board. On return to the laboratory, they were lyophilized. Granulometric analyses were performed on bulk sediment aliquots ($n = 49$) using a laser granulometer LISST-100. Each result is a mean of two measurement runs during which 100 values are collected. To be representative with the geochemical analyses, we focused on the grain-size distribution in the $<63\,\mu m$ fraction.

Preparation of samples prior to analytical procedures consisted in breaking up aggregates in a mortar and in separating the fine sediment fraction ($<63\,\mu m$) by dry sieving with an acid pre-cleaned nylon mesh. Using Teflon bombs, fine fractions were completely digested to dryness on a hot plate with an acid mixture of $HF-HNO_3-HClO_4$. The residues were solubilized by HNO_3 and diluted to volume. The solutions were analysed for major and trace metals by ICP–AES ($n = 47$) and ICP–MS

($n = 49$), respectively. Accuracy was controlled by the use of numerous certified standards (e.g. MESS-2, GSMS-3) and provided excellent recoveries, excepted for Cd, for which measurement uncertainties reach 20% on average, due to contents close to the detection limit value. Total carbon (TC) and OC contents (% dry weight sediment, $n = 49$) were obtained by combustion in a LECO CN 2000 analyser after acidification with HCl 2N to remove carbonates in the case of OC analysis. Calcium carbonate content ($CaCO_3$) was calculated from mineral carbon ($TC-OC$) using the molecular ratio 100:12 (i.e. $CaCO_3$:C). A pre-selected number of representative samples ($n = 15$, see Fig. 1) was devoted to molecular lipid analysis at the Laboratoire de Biogéochimie et Chimie Marines (Paris VI, France) after solvent extraction of total lipids and separation of lipid classes by column chromatography. The analysis of the sewage marker coprostanol, included in the fatty acid and sterol fraction, was performed by gas chromatography (GC).

2.3. Normalization approach

It is well established that grain-size distribution and the contents of carbonate, heavy mineral and

sediment organic matter strongly influence background and/or pollutant concentrations (Loring, 1990 and references therein, Salomons and Forstner, 1984). In this work, we used a two-tiered correction approach that consists in the isolation of the fine sediment fraction (i.e. $< 63 \mu m$) by sieving, followed by an additional geochemical normalization, as recommended by Kersten and Smedes (2002). This procedure has the advantage to attenuate significantly the effect of the inherent variability of the sediment composition. For trace metals, Roussiez et al. (2005b) have demonstrated the use of stable Cs as a successful alternative of Al to trace the clay content in the sediments of the Gulf of Lions. Their results have shown that Cs is a tracer not only for clays but also for the less than $20 \mu m$ fraction, considered as a relevant metal-bearing phase (Ackermann, 1980). In the case of major elements, however, Cs is considered too sensitive and hence Al is used for normalization. For coprostanol, much less experience is available as compared to metals. It is known that coprostanol concentrations in sediments can be influenced by particle size and/or the OC content in sediments (Writer et al., 1995). Nevertheless, at the scale of the continental margin, terrestrial organic matter is diluted by in situ marine production and hence normalization by OC can be misleading. Thus, we assume that the normalization procedure adopted for heavy metals is also suitable for the interpretation of our coprostanol data.

3. Results and discussion

3.1. General sediment composition

3.1.1. Grain-size

The investigated sediments are very fine in general and the less than $63 \mu m$ fraction represents in average 90% of the bulk sediment. The distribution patterns of the relevant fractions (i.e. < 2, < 20 and $2-63 \mu m$) that compose the sieved sediments are illustrated in Fig. 2. Both the clay and the $< 20 \mu m$ contour maps follow the sedimentological setting described first by Aloisi et al. (1973). Briefly, the different geological facies are distributed according to the prevailing sedimentary dynamics. One can observe going seaward: (i) littoral sands, characterized by the lowest fine-grained contents, (ii) a middle-shelf mudbank, below the storm wave influence, where the highest fine-grained sediment
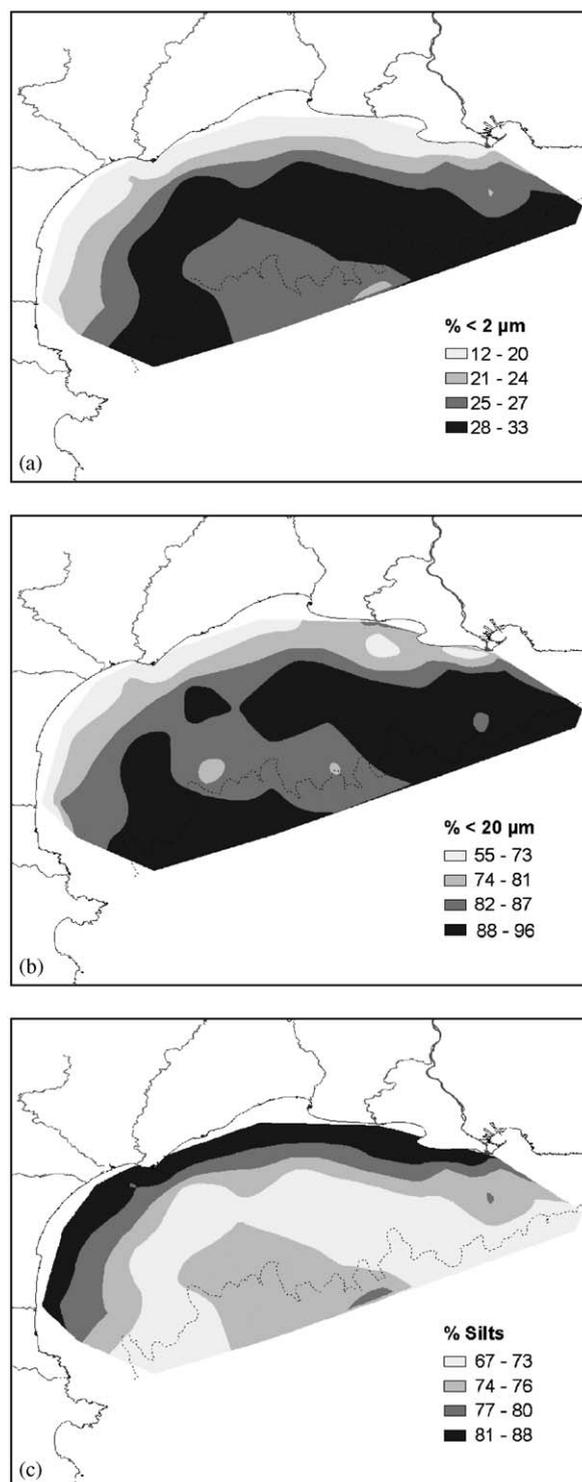

Fig. 2. Spatial contour maps of the abundances of relevant sediment fractions in the less than $63 \mu m$ fraction of surficial sediments in the Gulf of Lions.

contents are recorded, and (iii) outcrops of relict sand and modern mud in the outer-shelf.

3.1.2. Organic carbon

Fig. 3A displays the spatial distribution pattern of OC contents. Values range between 0.61% and 1.85% (d.w.), with maximum contents observed off the Rhône and Petit-rhône river mouths. Two main decreasing gradients can be discriminated from the latter point sources. One is stretching along the canyon heads, whereas the other is confined along the shoreline. The origin of the organic matter in the study area has been discussed by Kerherve et al. (2005). It was concluded that the continental signature is predominant in the vicinity of the river mouths. But while the terrestrial signal is rapidly diluted by the marine production off the small coastal rivers in the western part, it is better preserved off the eastern point sources, which are considered as important suppliers of organic matter to the Gulf of Lions. However, because of the well-known affinity of OC with the finest particles, it is also interesting to look at the enrichment of OC for a given amount of clay when normalizing it to a grain-size proxy (Fig. 3B). As a result, the contour map of Cs-normalized OC contents shows that all the river mouth exhibit an enrichment of OC decreasing seaward, which permits demonstrating that also the small coastal rivers supply OC to the marine environment.
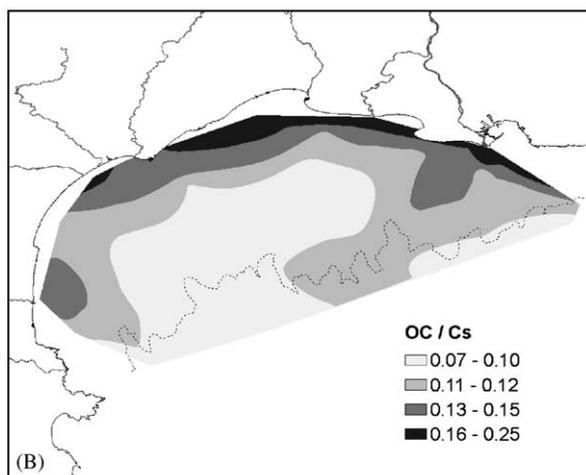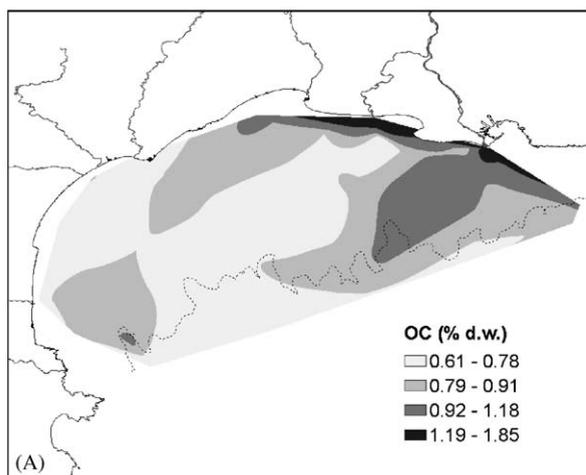
3.1.3. Carbonates

Carbonate contents vary between 15% and 38% (d.w.) with highest values recorded in the eastern and central parts of the study area. Their origin (i.e. lithogenic and/or biogenic) is difficult to determine. But, when looking at Fig. 4, it is evident that the Rhône and Petit-Rhône Rivers have a strong impact on the carbonate distribution. A striking feature is the relatively constant contents that prevail in the major part of the Gulf of Lions, except in front of the Têt River mouth where the concentrations decrease strongly, revealing a siliclastic province. This is in agreement with the strong dominance of siliclastic rocks in the river basins that drain the Pyrenean Mountains.
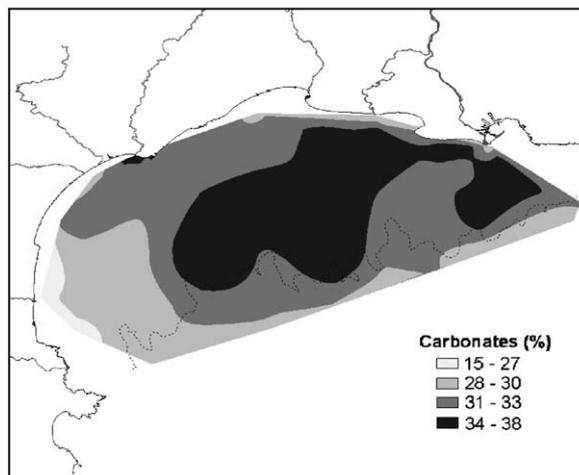

Fig. 3. Spatial distribution of organic carbon in surficial sediments of the Gulf of Lions ($<63\,\mu m$): (A) organic carbon contents (%); (B) Cs-normalized OC contents.

Fig. 4. Spatial distribution of carbonate contents (%) in surficial sediments of the Gulf of Lions ($<63\,\mu m$).

Table 1
Range of surficial concentrations of the investigated metals

Components	This work			PAAS
	Min	Max	Mean	
Majors (%)				
Al_2O_3	7.4	12.7	10.0	18.9
CaO	9.6	20.5	17.2	/
CaO[a]	0	3.3	0.9	1.3[a]
Fe_2O_3	3.0	4.8	3.8	7.2
P_2O_5	0.09	0.25	0.13	0.16
TiO_2	0.48	1.05	0.59	1.00
Traces (ppm)				
Cd	0.22	0.82	0.36	0.2[b]
Co	6.8	15.4	10.2	23
Cr	53.4	117.3	73.3	110
Cs	4.5	9.0	7.2	15
Cu	9.0	45.8	22.7	50
Ni	18.2	61.9	31.8	55
Pb	20.6	69.7	39.2	20
Sr	215	600	418	200
Zn	65.6	144.9	102.2	85
Zr	51	250	77	210

For comparison, world average references are added.
[a]CaO content in the silicate fraction only.
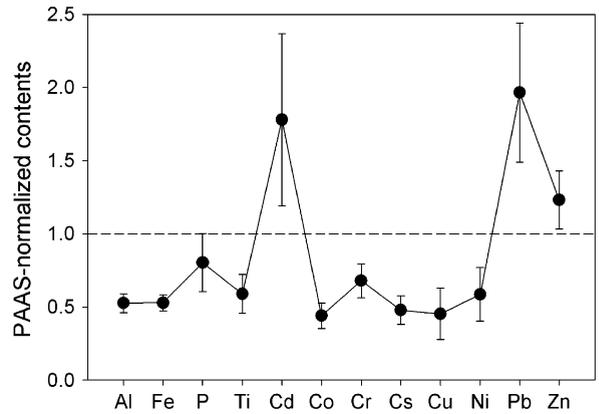[b]Crustal average (Taylor, 1964).

Fig. 5. Multi-elemental normalization diagram. Elemental contents are normalized to PAAS values (From Taylor and Mc Lennan, 1985), excepted Cd which is normalized to the crustal average of Taylor (1964). Results are expressed as the dataset means and include error bars.

3.2. Geochemistry of major and trace elements

3.2.1. Average concentrations

The results of the total metal concentrations in the $< 63\,\mu m$ sediment fraction are summarized in Table 1, including world average values commonly considered as natural background references (i.e. Post-Archean Australian Shale (PAAS) from Taylor and Mc Lennan (1985) and crustal average from Taylor, 1964). At first sight, most of the mean elemental contents in our sediments are about 2-fold lower than the corresponding literature values, except for CaO, Cd, Pb, Zn and Sr that display enhanced mean concentrations. This main result is clearly illustrated through a multi-elemental diagram, when normalizing contents to the PAAS values (Fig. 5). According to the well-known dependence of elemental concentrations with grain-size, the notable depletion of clay proxies such as Al, Fe and Cs—suggesting moderate aluminous clay mineral abundance—could explain, at least partly, the depletion of other elements. On the contrary, adsorption phenomena may result in the enrichment of metals like Pb, Zn, and Cd, whose enhanced concentrations are most likely the result

of anthropogenic inputs. In the cases of CaO and Sr, however, enrichments may be related to the high carbonate contents, as it is generally observed on continental margins (e.g. Carranza-Edwards et al., 2005). This is confirmed when determining the CaO contents in the silicate fraction only (Table 1), which are now close to the reference values.

3.2.2. Spatial distribution patterns

In this paper, contour maps were constructed using ArcGIS^{TM} spatial interpolation routines based on a natural neighbour method. The resulting patterns allow to divide the investigated metals within two major groups.

On one hand are the elements (e.g. Fe, Co, Cu, Ni, Pb, Zn) that are characterized by a seaward increase of the concentrations (Fig. 6, taking Cu and Ni as examples). They globally follow the depositional feature of the finest sediment fractions (see Fig. 2). A major common origin is therefore highly probable, as this is supported by the high degree of correlation between these elements (not presented). Superimposed to this trend are the highest contents of Cu, Zn and Pb registered off the river mouths, notably off the eastern point sources. According to the well-known affinity of these three metals with OC, it is possible that the presence of organic-rich sediments in the inner-shelf (see Fig. 3B) results in the accumulation of additional Cu, Zn and Pb, overwhelming locally the influence of the granulometry. For the other elements (e.g. Fe, Co and Ni) the near-shore enrichment, albeit noticeable, is less
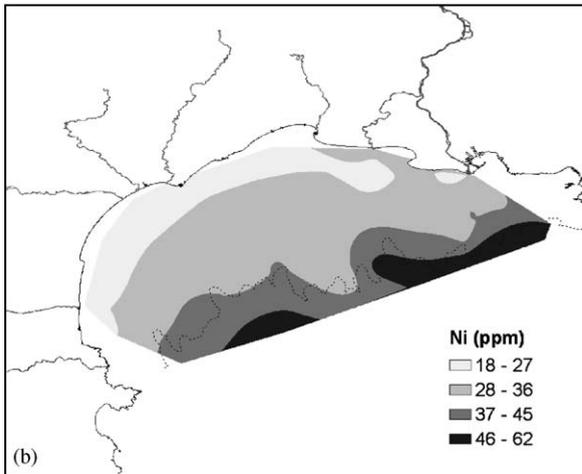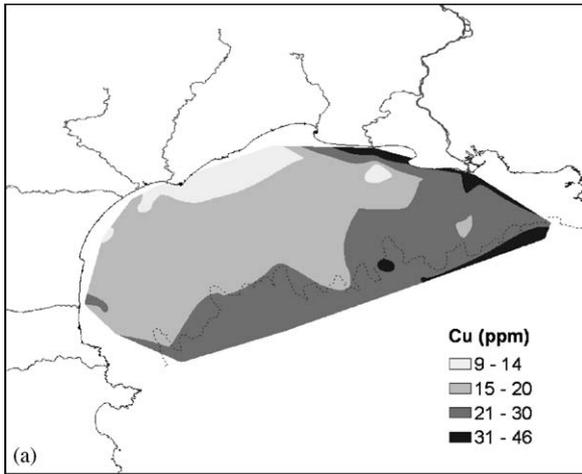
Fig. 6. Spatial distribution of Cu and Ni contents in the less than 63 μm surficial sediment fraction. Notice that the higher enrichment of Cu off the river mouths is likely influenced by its affinity with organic carbon.

Fig. 7. Spatial distribution of Cd contents in the less than 63 μm surficial sediment fraction.

pronounced and appears to be more influenced by the moderate abundance of fine particles (i.e. < 20 μm).

On the other hand are the elements Cd, P, Ti and Zr, which exhibit an opposite trend, globally characterized by a seaward decrease of the concentrations from the river mouths (Fig. 7, taking Cd as an example). Surprisingly, these metals are enriched in areas of high shear stress, where the finest sediment fractions and associated elements are frequently resuspended. This could signify that these metals are not necessarily associated with the fine-grained alumino-silicates, but rather with the coarser silt fraction. This is in good agreement, at least for Cd, with the conclusions of Marin (1998)
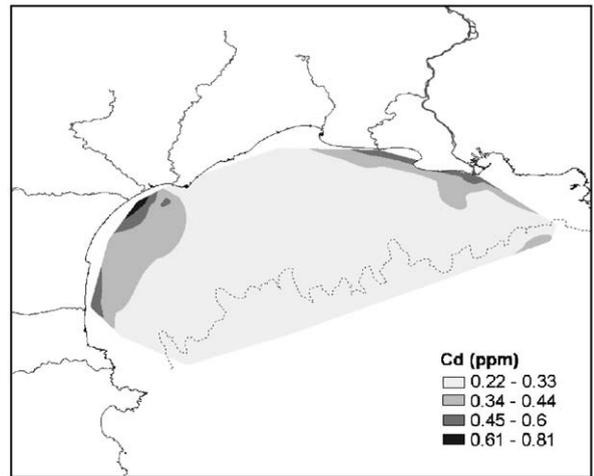
who denoted a dilution of this metal by alumino-silicates in the study area.

3.2.3. Enrichment factors

The above-described distribution patterns are the result of the dispersal of both natural and anthropogenic particulate discharges that finally mix into the sediments. To discriminate these sources, and hence to determine with confidence the degree of enrichment/contamination of a given metal M, a common practice is to calculate grain-size-corrected enrichment factors (EFs), which can be defined as the ratio between the sample and the natural background normalized concentrations:

$$EF_M^{(C)} = \frac{(M/C)sample}{(M/C)background}, \tag{1}$$

where C is a conservative element that is strongly associated with the finest sediment fraction (clays), correcting hence the values between samples with variable grain-size distributions.

Five degrees of contamination are commonly defined (Sutherland, 2000):

EF < 2	deficiency to low enrichment
EF = 2–5	moderate enrichment
EF = 5–20	significant enrichment
EF = 20–40	very high enrichment
EF > 40	extremely high enrichment

The choice of the natural background reference is an important step because it influences strongly the conclusions about how the system is disturbed or

not by human activities. In general, authors refer to world average shales and/or crust composition but these data are not representative of the local lithology and can mislead the interpretations. To overcome this difficulty, we used in this work the available local references for Co, Cr, Cu, Ni, Pb and Zn determined by Roussiez et al. (2005b), with Cs as normalizer element. For major elements, we assumed that the lowest element/Al ratios in our dataset are a good alternative to literature references and suitable for being used as natural background levels. However, both Cd and P show behaviours that do not support their strong association with clays (see above), making that normalization with clay mineral indicators can be misleading. The best compromise to calculate their enrichment could therefore consist in dividing the measured concentrations by the lowest ones registered seaward (about 0.22 ppm and 0.09% for Cd and P oxide, respectively), which might be, in this context, a good approximation of the natural background concentrations.

The above-mentioned methods were consequently used to calculate the corresponding EFs for each of the investigated elements. We considered that EF values >1.5 might be indicative for significant enrichment, since the use of natural background concentrations we determined should considerably reduce the effect of the inherent natural variability of the sediment. This can also be confirmed when looking at the variability of the EFs in the available local pre-industrial sediments data ($n = 5$) of Marin (1998). Standard deviations (SD) are very low and the average EFs + SD are always <1.5. The resulting EFs are presented in Fig. 8 in the form of box and whisker plots, showing also each outlier. Three main groups of elements can be distinguished on the basis of our data and different literature sources:

 (i) The crustal elements Fe, Co, Cr, and Ni plot close to the local background level. No suspect values are detected among the entire dataset (i.e. all EFs <1.5), except for 1 sample that present a slight enhancement in Cr and 2 samples in Ni, pointing out an exceptional enrichment in these metals.
 (ii) Cd, P, Cu, Pb and Zn display enrichments that likely come from human activities. Especially Pb and Zn present ranges that confirm a widespread enrichment in the study area. In the case of Cd, P and Cu, the range of EFs
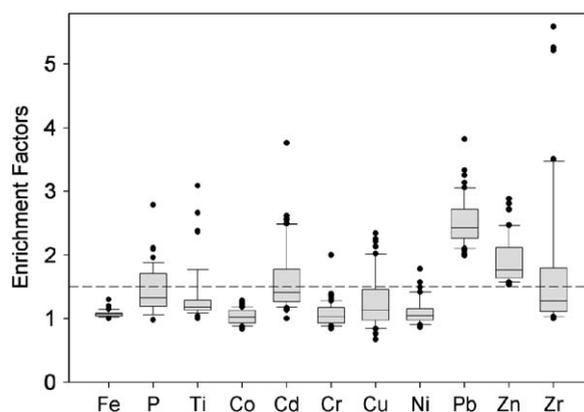

Fig. 8. Enrichment factors of investigated elements in the less than 63 μm surficial sediment fraction. Major and trace elements were normalized using the local backgrounds as natural references (see text). The dashed line represents the natural variability threshold (EF = 1.5).

rather indicates restricted contamination in the vicinity of point sources since a significant number of samples seem to be unpolluted while the rest depict anthropogenic contributions. Enrichments of Cd and P may derive from the same sources since high contents of P can be linked to enhanced nutrient inputs (Radach et al., 1990) and Cd is well-known to be present in phosphate-rich fertilizers (Otero et al., 2005).
 (iii) Enhanced EF values for Ti and Zr might translate elevated heavy mineral contents (e.g. ilmenite, rutile, zircon).

Of special interest is also the extent to which the metal EFs spread over our study area. Fig. 9 shows the spatial contour maps of some relevant EFs, which allow us to distinguish human-impacted areas from uncontaminated ones. The contamination is well identified in the inner-shelf and can globally be considered as "moderate", especially close to the river mouth environments, where enhancement is the greatest. This pattern contrasts sharply with the natural feature of Ni, taken as example. Indeed, this element displays no enrichment off the river mouths, reflecting the conservative behaviour of the lithological input, as it can be observed with all detrital elements (not shown). In the case of Cd, P and Cu, the anthropogenic signature decreases seaward and the natural background is progressively reached, whereas an enriched base level is found for Pb and Zn outside the river mouths, highlighting a widespread contamination over the
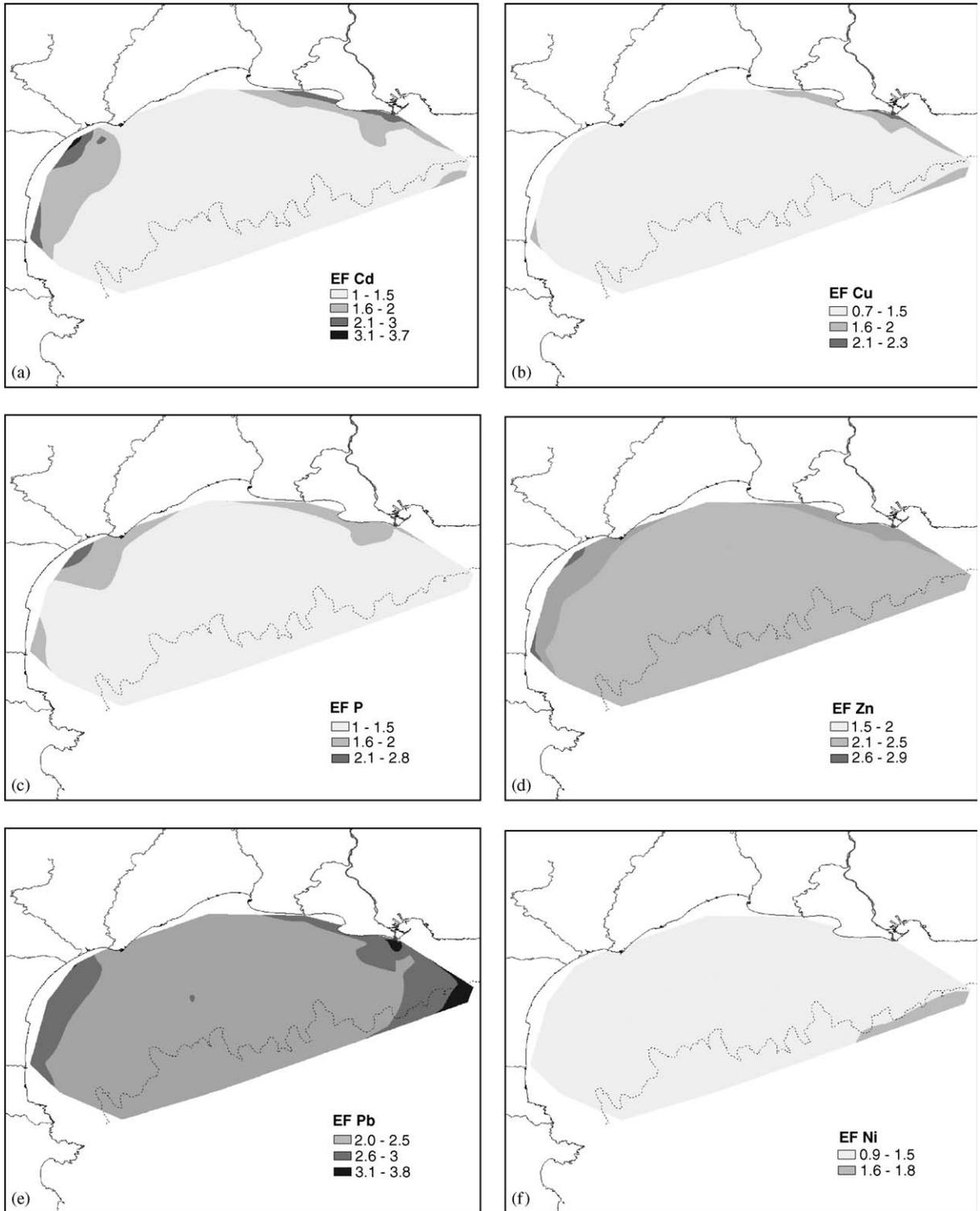
Fig. 9. Spatial contour maps of the most relevant heavy metal enrichment factors.

platform at low to moderate levels. One can suppose that the dilution of the contamination by uncontamined/less contamined off-shore sediments can partly explain this seaward decline. Unrelated to the river inputs, there exists another noticeable repository area for contaminated particles in the south-eastern part of the study site, corresponding to deep sedimentary environments in the eastern canyon head (stations 7 and 8). There, EF values of Pb, Cu, Cd and Ni exhibit anthropogenic levels, which likely traduce the impact of well-known off-shore discharges of red mud derived from bauxite exploitation for the past two decades.

3.2.4. Statistical approach

Our findings, notably the detected influence of the sediment properties on the elemental contents, are corroborated by the results of a principal component analysis (PCA) applied to our data. In the absence of sequential extraction analyses, such statistical procedures can provide meaningful information for the identification of the most important geochemical carriers (Santos et al., 2005). Two principal components (PC) have been identified, explaining 73% of the total variance. The related plot shows a distribution of the investigated variables in four groups (Fig. 10) that may be indicative for different origins of the minor and major elements. PC1 represents the grain-size component, whereas PC2 is rather characterized
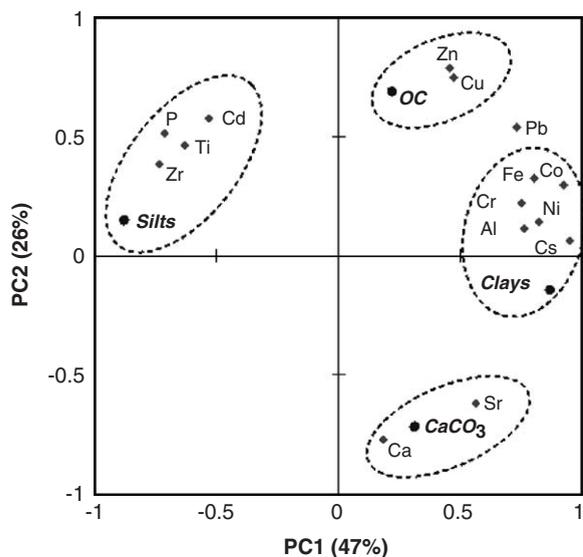
Fig. 10. Principal component analysis performed on the entire heavy metal dataset, including sediment properties (i.e. clay, silt, OC and carbonate contents, $n = 47$).

by a positive contribution of the organic matter in opposition with the contribution from carbonates. The first group reflects the clay mineral input in the area, including the most common clay mineral proxies (i.e. Al, Fe, and Cs) and some trace elements (i.e. Co, Cr, and Ni). Showing an opposite trend, the second lithological input is represented by the silt fraction, assembling Cd and P with the heavy mineral indicators Ti and Zr, often associated with particle sorting due to wave action (Dellwig et al., 2000). A third group points out the well-known affinity of OC for Cu and Zn. The last group is composed of Sr and Ca, which are associated with carbonates. Pb cannot be clearly included neither in the OC group nor in the clay group and presents an intermediate position between the two association phases.

With the exception of lead, what is striking is that potential contaminants are preferentially correlated with either OC or the silt fraction, whereas natural compounds separate clearly from the contaminants, being strongly correlated with the clay fraction. These results suggest that, on the basis of the total contents alone, OC and silts should play a deciding role in the distribution of the land-derived contaminants in the marine environment. Nevertheless, if the origin of the relationship between silts and both Cd and P is obviously authentic, this is not implicitly the case for the one between OC and other metals, which could derive from the well-known affinity of OC for clays (Balls et al., 1997).

3.2.5. Carrier phases of anthropogenic metals

The interpretation of PCA results (Fig. 10) is complicated by the fact that the entire dataset corresponds to areas of different sedimentological and geochemical characteristics. When looking at the distribution of the metallic contamination in the Gulf of Lions (Fig. 9), it is evident that two populations of samples can be distinguished: (i) the most contaminated and organic-rich sediments in the vicinity of the river mouths and (ii) the uncontaminated/less contaminated sediments that characterize both the middle and outer-shelf areas. In order to unravel the respective roles of the major carrier phases, i.e. clay minerals or OC, for the entrapment of the outstanding metals Cu, Pb and Zn, we therefore looked at the relationships between the variables within each of the two populations.

The choice of the nearshore samples was mainly based on our knowledge of the characteristics of the Mediterranean prodeltas, which are localized in the

shallower shelf, above the storm wave base (i.e. up to 30 m water depth—see Roussiez et al., 2005a). Unfortunately, we did not dispose enough samples to study each river mouth environment and formed a subset of prodeltaic samples that cover all river mouths ($n = 14$ of which one half belongs to the Rhône and Petit-Rhône prodeltas and the other half to the Aude/Orb/Hérault and Têt prodeltas). As expected, Cu, Pb and Zn contents in the prodeltaic sediments are positively correlated with the organic matter content, which suggests that the near-shore samples could be enriched in these metals by organic matter complexation. However, although no correlation is found at the scale of the continental shelf, OC and clays are here strongly correlated (Fig. 11). In these conditions, we have to examine if the enrichment of a given metal against natural abundance is only proportional to the element complexation with the organic phase or if there is an excess of the metals that is brought by the finest mineral phases. To do so, an effective procedure consists of normalization to OC, as demonstrated by Hissler and Probst (2005). Based on the same method as for Cs normalization (Eq. (1)), EFs with respect to the OC content can be formulated as follows:

$$EF_M^{(OC)} = \frac{(M/OC)\text{sample}}{(M/OC)\text{background}}. \tag{2}$$

The background ratios were estimated by averaging the ratios calculated from the local pre-industrial sediments ($n = 5$) of Marin (1998). Taking Pb as an example (Fig. 12), one can see
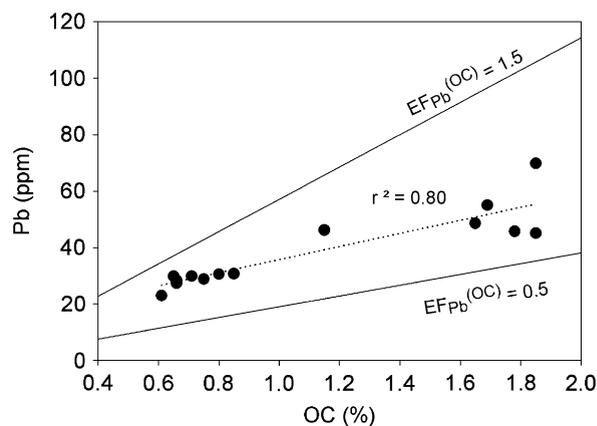
Fig. 12. Relationship between OC contents and total Pb contents in the surficial prodeltaic sediments ($n = 14$). The two lines correspond to metal enrichment factor of 1.5 and 0.5, respectively, showing that no significant enrichment is found when EF is normalized to OC. Similar results are found with Cu and Zn.

that the metal enrichment with regard to the organic phase ($EF^{(OC)}$) plots in the range of the natural variability (i.e. all EFs < 1.5), underscoring that no surplus is found on the basis of the OC content in the samples. This confirms that the enrichment of Cu, Pb and Zn covaries in proportion with the organic matter content in the prodeltaic sediments. Here, OC is the major carrier of the latter metals and is responsible of their accumulation, as it has also been observed in other estuaries and coastal embayments (e.g. Cobelo-Garcia and Prego, 2004).

When going seaward, Pb and Zn remain the only heavy metals that still depict anthropogenic contributions (Fig. 9). Excluding the samples under the direct influence of point sources (i.e. riverine and industrial off-shore inputs), we selected 20 representative sediments of the middle and outer-shelf areas. Although the samples stretch over a wide spatial range, it is found that both the distributions of both Pb and Zn on the platform is most likely controlled by the clay fraction (Fig. 13). No significant correlations were found between OC and, respectively, Pb ($r = 0.136$) and Zn ($r = 0.214$), proving that the abundance of the organic matter cannot explain the heavy metal contents outside the river mouth sediments.

The reason for the strong contrast in the contamination levels between the near-shore and off-shore areas remains somewhat unclear and has probably other explanations than the dilution effect only. One may argue that this is related to the biodegradation of the organic phase in the shallow
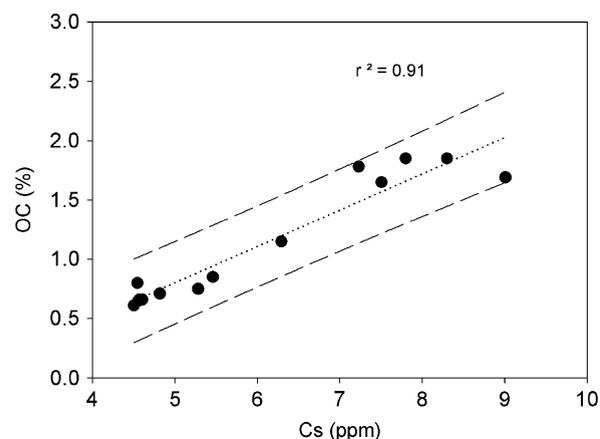

Fig. 11. Relationship between the clay mineral indicator Cs and the organic carbon content in the prodeltaic surface sediments ($n = 14$). The dashed lines represent prediction interval at the 95% confidence level.
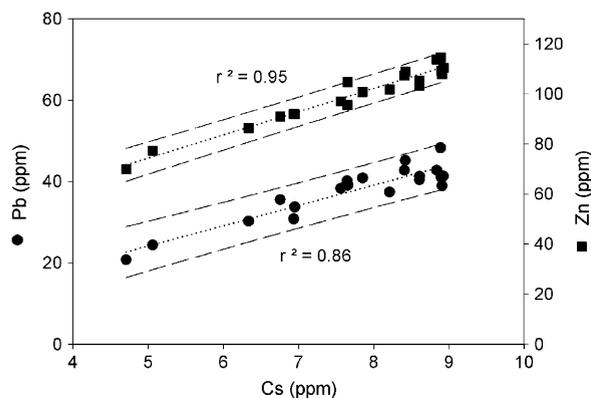
Fig. 13. Relationships between the clay mineral indicator Cs and total Pb and Zn contents in middle and outer-shelf sediments ($n = 20$). The dashed lines represent prediction intervals at the 95% confidence level.

and agitated sites, releasing a major part of the associated contaminants that are further dissolved (Cu) and/or migrate towards the finest mineral carrier (Pb and Zn). As reviewed by Eggleton and Thomas (2004), changes induced by the seabed disturbance in sediment chemistry and in the water surrounding the particles can result in contaminant remobilization via desorption or transformation. In the cases of Pb and Zn, however, the seaward persistence of enriched concentrations together with the homogeneity of contamination levels could also be explained by the diffusion of man-made aerosols over the entire platform. Indeed, these atmospheric deposits are characterized by high anthropogenic levels of Pb and Zn (Guerzoni et al., 1989), and hence could be an important source for these metals in the sediments (Nolting and Helder, 1991). The two main introduction pathways for these aerosols—i.e. direct deposit on the sea/atmosphere interface and river-transport—lead to their uniform spread over the bottom sediments favoured by hydrodynamics and sediment resuspension from enriched prodeltas, as has been suggested by Roussiez et al. (2005b).

3.3. Sewage contamination

The results of our analyses of coprostanol, which stands here as a tracer for sewage solids and associated organic contaminants that are released by waste water stations, are shown in Fig. 14 and summarized in Table 2. Despite some very low values, coprostanol was detected in all samples, with concentrations ranging from 9 to 4240 ng g^{-1}, in
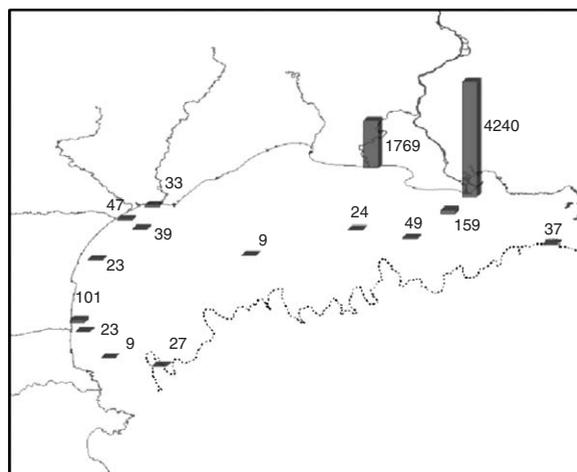

Fig. 14. Coprostanol contents in the fine ($<63\,\mu m$) surficial sediments ($n = 15$). Values are expressed in ng g^{-1} (d.w.). Symbols are proportional to the contents.

Table 2
Range of coprostanol contents in the study area

	Coprostanol (ng g^{-1})
Min. value	9
Max. value	4240
Mean value	439
SD	1142
Venice Lagoon, Italy[a]	40–4410
Tokyo Bay, Japan[b]	20–243

Some references are added, for comparison.
[a]Fattore et al. (1997).
[b]Chalaux et al. (1995).

accordance with what has been found elsewhere. As a guideline, coprostanol contents greater than 500 ng g^{-1} are considered to be indicative of "significant" sewage contamination (Nichols et al., 1996). Such a level is largely exceeded in the case of the Rhône and Petit-Rhône river mouth samples. On the other hand, the Têt River mouth presents an intermediate value (101 ng g^{-1}), whereas Aude/Orb/ Hérault river mouths exhibit rather low concentrations, ranging from 33 to 47 ng g^{-1}. The lowest value (i.e. 9 ng g^{-1}) was recorded in the middle-shelf. Also, one can notice the enhanced concentration recorded in the Southwestern canyon head (station 46), which can be the result of the contribution of the nearby rivers (e.g. Têt). The same trend was observed for OC surficial contents and has been explained by resuspension processes from the nearby prodeltas (Buscail and Germain, 1997).

Regarding these results, it can be assumed that the general distribution pattern of sedimentary coprostanol contents shows an important seaward decline from the point sources, hence following the trend for normalized anthropogenic metals (Fig. 9). This observation confirms that the accumulation of land-derived contaminants, both inorganic and organic, is a common feature for Mediterranean prodeltas.

An interesting point is nevertheless the strong difference existing between western and eastern river mouth sample contaminations. The population density is quite similar in both areas and the difference of both the granulometry and the OC contents cannot explain this large contrast. However, it is known that coprostanol can be subjected to biodegradation under oxic conditions (Bartlett, 1987). The degree of alteration of this biomarker may consequently depend on the time exposure to oxic conditions in both the water column and the surficial sediments. The difference in size and in the hydrological regimes of the local rivers makes that sedimentation rates are clearly more elevated in front of the eastern point sources. Values up to $60\,\mathrm{cm\,yr^{-1}}$ off the Rhône River mouth can be encountered (Miralles et al., 2005) whereas they reach only $0.4\,\mathrm{cm\,yr^{-1}}$ off the Têt river mouth (Roussiez, unpublished data). In these conditions, in situ preservation of sedimentary coprostanol strongly depends on sediment burial rates. High sedimentation rates, like those observed in the eastern Gulf of Lions, reflect the continuous process of particle settling that strongly reduce time exposure of freshly deposited sediments to oxic conditions. This particular feature is also confirmed by the good relationship between available modern
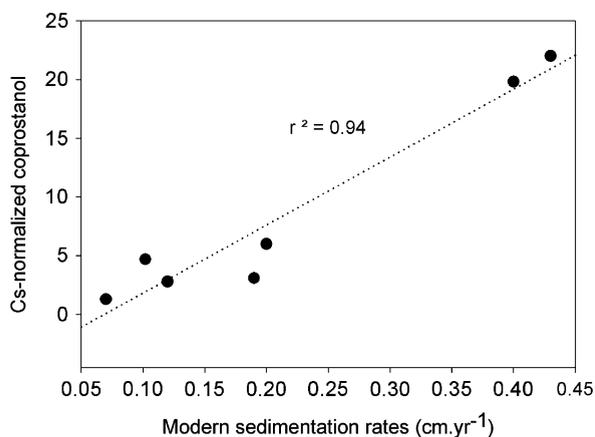
accumulation rate data (from Radakovitch, 1995 and references therein) close enough to some of our samplings (stations 7, 16, 19, 21, 45, 46 and 49) and Cs-normalized coprostanol concentrations in the corresponding dry sediments (Fig. 15, excluding the extreme value of the Rhône prodelta that tends to increase R^2 to 1). Coprostanol appears therefore as an indirect but meaningful tracer of the sedimentological conditions in the close inner-shelf and highlights the difference in the functioning between western and eastern prodeltas of the Gulf of Lions due to different preservation conditions.

4. Conclusions

Based on a suitable normalization that account for the regional background of contents, this work allowed us to distinguish metal-impacted areas from uncontaminated ones in the Gulf of Lions. Contamination was found mostly in the direct vicinity of the river mouths, especially in the near-shore sedimentary units (called prodeltas), where the depositional conditions favour the storage of riverborne particles and associated anthropogenic metals (i.e. Cd, P, Cu, Pb and Zn). When going seaward, however, only Pb and Zn depict anthropogenic contributions, likely widespread by a diffuse deposition of contaminated aerosols.

Principal component analysis offered valuable insights into the geochemical carriers of investigated metals. Whereas it was found that the clay fraction controls the distribution of most of the natural elements, a particular role of the silt fraction was revealed, likely regulating the accumulation of anthropogenic Cd and P. In the case of anthropogenic Cu, Zn and Pb, however, the major carrier phase could only be identified when adopting a more detailed approach. It could be shown that, in the prodeltaic sediments, OC plays a deciding role in the accumulation and the distribution of anthropogenic Cu, Pb and Zn. On the contrary, clay minerals obviously govern the distribution of remaining contaminants (i.e. Pb and Zn) on the rest of the platform.

Sewage contamination follows the trend of anthropogenic heavy metals, with higher contents of coprostanol off the river mouths. Critical contamination was found in the Rhône and Petit-rhône prodeltas and was explained by the sedimentological conditions that locally preserve this biomarker via sediment burial. Subjected to biodegradation, coprostanol is actually very sensitive to

Fig. 15. Relationship between Cs-normalized coprostanol contents and available modern accumulation rates ($n = 7$).

the time exposure to oxic conditions, making that the persistence of the sewage contamination signal in the sediments strongly depends on sedimentation rates. In this respect, coprostanol could provide very pertinent information about sedimentary processes in coastal systems, which it has been probably overlooked in other studies. Further investigations in different environments should be carried out to confirm this.

As a general conclusion, it has to be pointed out that the anthropogenic enrichment of certain contaminants can be used as a tool for the tracking of terrestrial particles on the shelf sediments of the Gulf of Lions. Both for organic and inorganic contaminant enrichments, one observes decreasing gradients seaward that seem to be the results of a combination of several phenomena such as dilution, particle sorting and biodegradation processes. But while it can be supposed that a part of the land-derived contaminants will finally leave the shelf, it is still unclear how long they are maintained within the shallow prodeltas. This is an important question because these key-areas coincide in space with species-rich marine ecosystems. Further investigations involving high-frequency sampling are therefore required to better understand the sedimentation/resuspension cycles at the continent/sea interface.

Acknowledgements

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