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Scientific Editors

Aquatic Ecology of the Mondego River Basin
Global Importance of Local Experience

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COORDENAÇÃO EDITORIAL
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ILUSTRAÇÃO DA CAPA
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ISBN
972-8704-04-6

DEPÓSITO LEGAL
175038/02

OBRA PUBLICADA COM O PATROCÍNIO DE:
IMAR – INSTITUTO DO MAR
IPIMAR – INSTITUTO DE INVESTIGAÇÃO DAS PESCAS E DO MAR

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ELEMENTAL COMPOSITION AND CONTAMINANTS IN SURFACE SEDIMENTS OF THE MONDEGO RIVER ESTUARY

Abstract

Major (Al, Si, Ca, Mg, Fe), minor (Mn) and trace elements (Zn, Pb, Cr, Cu, Ag, Cd), organochlorine (PCB congeners, pp'DDT and metabolites) and tri- and dibutyltin levels were determined in 47 surface sediments from the Mondego River estuary. Concentrations varied within different ranges in river, sand and sandy mud samples. Higher values of Si and Ca were found in sands from the lower estuary while levels of Fe, Mn, Zn, Cu, Cd, Cr, tPCB and tDDT were higher in sandy muds and fluvial sediments. Linear correlations between Fe, Mg, Mn, Zn, Cu, Cr, Cd and Al indicate that some variability in their concentrations may be explained by the Al fraction of the sediments. Poor correlations to Al were found for organic contaminants (tPCB, tDDT, TBT+DBT). The contrasting longitudinal distributions of tDDT Ag and Ca concentrations indicate the marine and river contribution, respectively. In spite of low contamination of sediments, levels of other contaminants seem to reflect the nature of the particles and the local anthropogenic sources.

Introduction

Chemical composition of bottom sediments has been determined in many estuaries and coastal lagoon in Europe and North America (Alderton 1985) and compared to the composition of the crust (Martin and Meybeck 1979). Geographical differences in elemental composition of sediments may be attributed to mixing of river and marine sediments (Muller and Forstner 1975) formation of new particles (Yeats et al. 1979) and post-depositional changes in the upper sediment layers (Sundby and Silverberg 1985, Gobeil et al. 1987). In estuaries surrounded by urban areas and industrial parks, enrichment of trace elements and synthetic organic pollutants in sediments are usually attributed to environmental contamination (Libes 1992). The deposition of contaminated particles are influenced by the sediment dynamics, which may be periodically ruled by the tides (Allen et al. 1980, Gelfenbaum 1983) and the

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episodic high river discharges (Castaing and Allen 1981, Vale et al. 1993). When contaminants are weakly mobilised in the sediments, depth variation of their concentrations elucidates the historical evolution of the contamination in the area (Bruland et al. 1974, Gobeil and Cossa 1993).

The Mondego River estuary consists of two channels separated by an island at about 7 km from the estuarine mouth. The north and south channels have different hydrographic characteristics (Marques et al. 1993). The south channel is almost silted up in the upstream areas and water circulation is mainly driven by the tide. The North Channel is deeper and ended in the Mondego River, which is the main freshwater input. The combination of the tidal rhythm and the regime of river water discharges determine how freshwater mixes with seawater, the salinity structure being profoundly modified during runoff periods in Winter. The Mondego River drains a hydrological basin with intensive agriculture and crosses the urbanised area of Coimbra. The North Channel has been dredged periodically in order to allow the navigation to the harbour facilities in Figueira da Foz. A large volume of sediments has been dredged in the early 90's followed by hydraulic engineering operations in the shorelines of the lower estuary. This paper reports the major, minor and trace element composition of surface sediments along the North Channel of the Mondego estuary and the concentrations of polychlorinated biphenyls (PCBs), DDTs and butyltin compounds after those modifications.

Material and Methods

Surface sediments (0-2 cm) have been collected along the North Channel of the Mondego River estuary in 1994, after a large dredging operation upstream the commercial harbour of Figueira da Foz, and near the mouth of estuary in 1998. Sediments were collected in the middle of the channel and near the shoreline where fine material was deposited. The number of sampling sites was: 2 in the river, 27 in upper and middle estuary, and 18 in the lower estuary (fig 1). Metal concentrations (Al, Si, Ca, Mg, Fe, Mn, Zn, Pb, Cr, Cu, Ag and Cd) in sediments were determined after a total acid digestion of the samples following the procedure of Rantala and Loring (1977) and analysed by flame and furnace atomic absorption spectrophotometry. For tri- and dibutyltin compounds (TBT and DBT) the sediments were acidified and extracted with hexane following procedures originally described by M&T Chemicals, and modified by Bryan et al. (1986) and Langston et al. (1987). Tri- and dibutyltin, were measured, as tin, by atomic absorption in a Perkin-Elmer atomic absorption spectrophotometer with an electrodeless discharge tin lamp at a wavelength of 286.3 nm. For the determination of organochlorine compounds (PCB congeners and pp'DDT and its metabolites) the dry sediments were soxhlet extracted in n-hexane for 16 hours and cleaned up with a Florisil column and sulfuric acid. They were analysed in a Hewlett Packard gas chromatograph with an electron capture detector and capillary column (DB5, J&W, 60m). In this study tDDT means the sum of pp'DDE, pp'DDD and pp'DDT and tPCB the sum of the congeners CB18, CB26, CB31, CB44,

CB49, CB52, CB101, CB105, CB118, CB128, CB138, CB149, CB151, CB153, CB170, CB180, CB183, CB187 and CB194 (IUPAC n°s). International certified standards (AGV-1, GSP-1, G-2, MESS-2 and BCSS-2) and standard solutions were used to control the accuracy of our procedures. For all metals and compounds investigated, obtained and certified values were not statistically different ($p<0.01$).

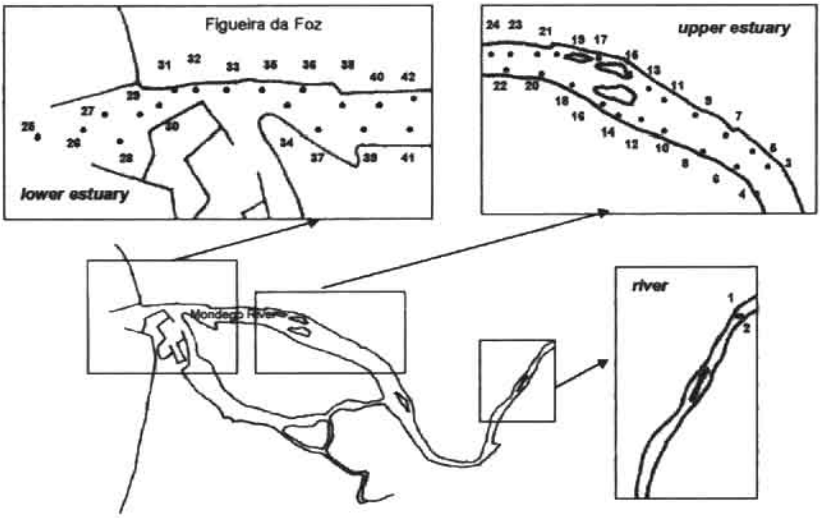

Figure 1. Map of Mondego river estuary with sampling sites.

Results and Discussion

Concentrations of metals, organochlorines and butyltin in surface sediments

Elemental composition and concentrations of organochlorines (pp'DDT and its metabolites and PCB congeners) and TBT+DBT in surface sediments of the Mondego River estuary ranged within broad intervals of values (Table 1). The ranges in fluvial sediments differed from those found in sands and sandy muds. The sands are naturally enriched in Si and presented higher concentrations of Ca and lower levels of Fe, Mn, Zn, Cu, Cd, Cr, tPCB and tDDT than sandy muds and fluvial sediments. The pp'DDT and its most stable metabolite (pp'DDE) are the major contributors to the values of tDDT. Among the analysed PCB congeners the tri- and tetrachlorinated compounds accounted to more than 65% of tPCB concentrations. The more toxic congeners with six to eight atoms of chlorine had a smaller contribution. The concentrations of TBT in lower estuary sediments were relatively uniform, and DBT were presented only in four samples nearby the shipyard factory, showing concentrations comparable to TBT. Levels of trace elements, organochlorines and butyltin compounds were low when compared to values registered in sediments from other estuarine areas of Portugal (Caetano 1998, Castro and Vale 1995, Cortesão and Vale 1995, Cortez et al. 1993, Vale 1990).

Table 1. Concentrations of major, minor and trace elements (% and $\mu g.g^{-1}$) and of tDDT, tPCB and TBT+DBT ($ng.g^{-1}$) in fluvial sediments, coarse sands and sandy mud deposited in the estuarine zone.

Chemical parameters	River sediments (n=2)	Estuarine sands (n= 33)	Estuarine sandy muds (n=13)
Al (%)	6.5 - 9.5	2.8 - 4.6	4.9 - 7.5
Si (%)	19 - 20	12 - 44	14 - 33
Ca (%)	0.60 - 1.1	0.010 - 1.8	0.060 - 2.3
Mg (%)	1.0 - 1.9	0.18 - 0.49	0.26 - 3.7
Fe (%)	2.3 - 3.5	0.30 - 1.1	0.94 - 3.2
Mn ($\mu g\,g^{-1}$)	499 - 893	26 - 433	98 - 1093
Zn ($\mu g\,g^{-1}$)	73 - 105	7 - 74	33 - 159
Pb ($\mu g\,g^{-1}$)	41 - 55	14 - 35	16 - 52
Cr ($\mu g\,g^{-1}$)	46 - 65	2.8 - 28	19 - 62
Cu ($\mu g\,g^{-1}$)	23 - 36	1.0 - 9.5	3.0 - 43
Ag ($\mu g\,g^{-1}$)	1.3 - 1.7	0.010 - 0.060	0.050 - 1.4
Cd ($\mu g\,g^{-1}$)	0.23 - 0.27	<0.010 - 0.070	0.040 - 0.32
tPCB ($ng\,g^{-1}$)	1.1 - 1.9	0.19 - 3.6	0.32 - 5.2
tDDT ($ng\,g^{-1}$)	0.40 - 1.2	0.010 - 0.12	0.030 - 1.7
TBT+ DBT ($ng\,g^{-1}$)	-	8.0 - 11*	8.0 - 21

* n = 5

Relationships to Al

Some samples were mainly constituted by sand and others had a larger fraction of fine particles. In order to assess weather the nature of the particle influences the metal distribution, relationships between element concentrations and Al content were examined. Concentrations of most metals were linearly correlated to Al content (Table 2). The higher correlation was obtained for Fe-Al (r^2 = 0.93), suggesting that iron in surface sediments is closely associated with aluminosilicates which are mainly present in fine sediments. Iron oxides that usually precipitated near the sediment surface (Sundby and Silvergerg 1985) appear to be a minor contributor to the total iron concentrations in Mondego sediments. High correlation coefficients were also found for Cr, Cu, Cd, Zn, Mn and Mg, indicating that some variability in their concentrations may be explained by the Al fraction in the sediments. These elements are either incorporated in the aluminosilicates or associated with the fine fraction of the sediments that is expressed by the Al content. The sand and calcium carbonates can thus be considered dilutors of iron and trace metals. The Pb-Al and Ag-Al relationships showed poorer correlations, meaning broader distributions of these elements among the particles. The levels of Ca, tDDT, tPCB and TBT+DBT were not related to Al suggesting that association of these substances to sediment particles is not related with grain size distribution. An illustration of the different situations is depicted in figure 2.

Table 2. Correlation coefficients and levels of significance between Al and major-, minor- and trace-elements, tDDT, tPCB (n= 46) and TBT+DBT (n= 18) in sediments of Mondego river estuary.

	Fe	Ca	Mg	Mn	Zn	Pb	Cr	Cu	Ag	Cd	tPCB	tDDT	TBT+DBT
r (p)	0.93 (p<0.001)	<0.10 (p>0.1)	0.75 (p<0.001)	0.79 (p<0.001)	0.82 (p<0.001)	0.41 (p<0.005)	0.83 (p<0.001)	0.83 (p<0.001)	0.22 (p>0.1)	0.81 (p<0.001)	<0.10 (p>0.1)	<0.10 (p>0.1)	<0.10 (p>0.1)

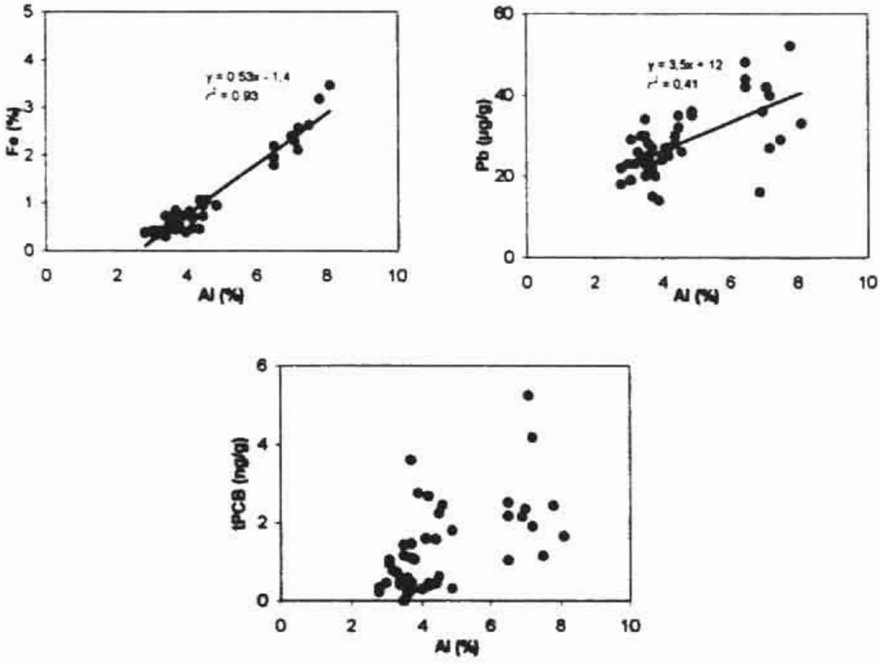

Figure 2. Relationships between Fe, Pb and tPCB with Al in sediments of Mondego River estuary

Longitudinal distribution pattern of marine and fluvial tracers

The longitudinal distribution of Ca exhibits a considerable concentration increase in sands and fine particles of the lower estuary (fig. 3). A similar distribution pattern of Ca was registered in the Tagus and Sado estuaries (Vale 1986). The increase of Ca concentrations in sediments and suspended particulate matter of the lower part of estuaries has been interpreted as the presence of material from marine origin enriched in biogenic calcium carbonates. The drastic differences on Ca content may be useful to distinguish and delimit the marine influence on the sediment sources. It appears that marine-derived sediments are mainly deposited in the lower Mondego estuary and upstream the commercial harbour the sediments are transported by the river, presumably during the periods of runoff. An opposite distribution was found for tDDT and Ag (fig. 3). Levels in the river sediments and in fine material from the upper estuary were ten times the concentrations found in the material deposited in the estuary. High levels of Ag reflect probably the urban source

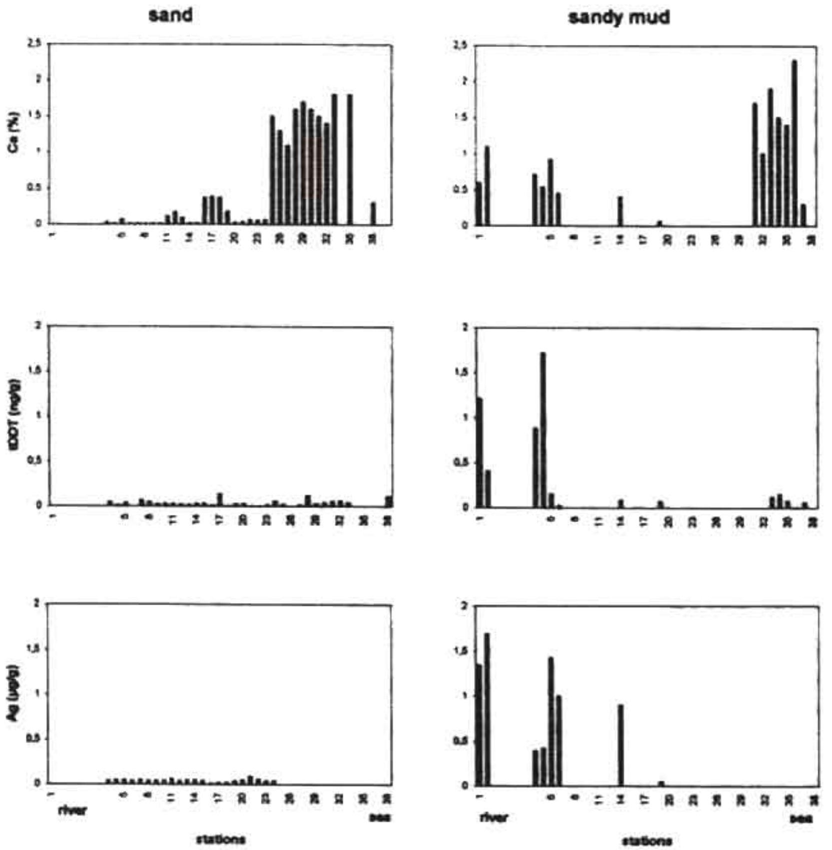

Figure 3. Longitudinal distribution of Ca (%), tDDT ($ng.g^{-1}$) and Ag ($\mu g.g^{-1}$) in sands and fine particles of Mondego River estuary.

from the city of Coimbra. Longitudinal distribution of tDDT, which is a typical contaminant from agriculture areas (Vale et al. 1993), point to the presence of eroded soil particles in river and upper estuarine sediments. Although these values were low in comparison to other estuarine areas (Ferreira and Vale 1995) the longitudinal distributions of their concentrations are indicative of the fluvial influence on the sediments of the Mondego River estuary.

Distribution pattern of contaminants

When element concentration is correlated to Al content its geographic distribution in coastal sediments and suspended particles matter is frequently expressed as element/Al ratio in order to minimise differences related to the nature and grain size of the particles (Windom et al. 1989). The element/Al ratios in sands and sandy muds of Mondego River estuary are shown separately in figure 4. Clearly, Fe, Mn,

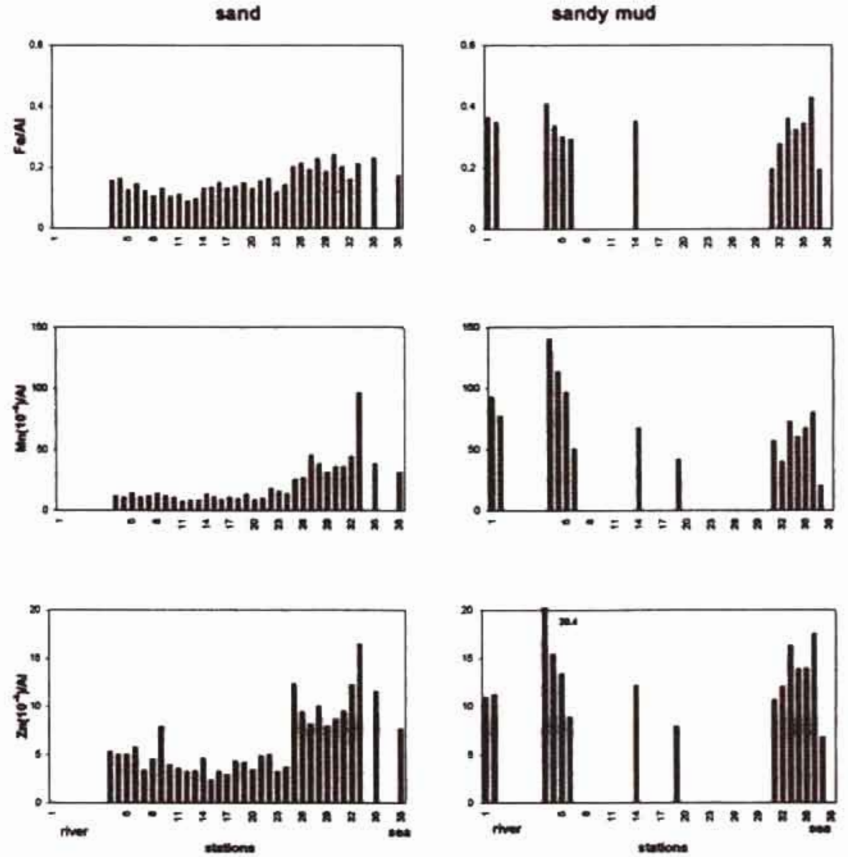

Figure 4. Metal/Al ratios in sands and sandy muds of Mondego river estuary.

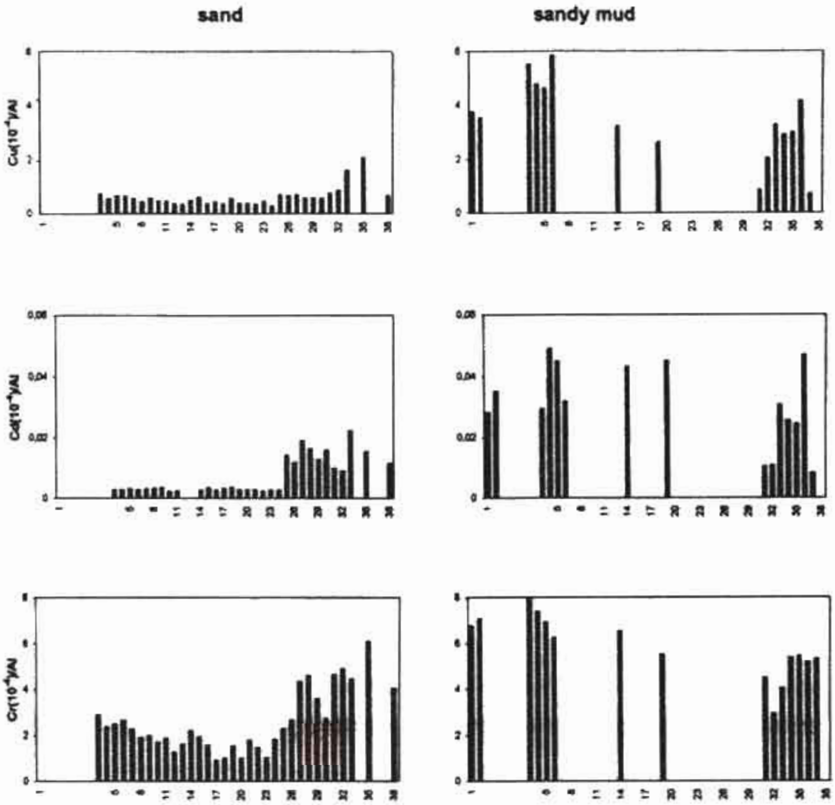

Figure 4. (cont.)

Zn, Cu and Cd ratios to Al were higher in fine particles than in sand. The ratios recorded in river material are comparable to those found in fine particles trapped in North Channel of the Mondego estuary. The Zn/Al, Cd/Al, Cr/Al and Cu/Al ratios were higher in sand from the lower estuary than in coarse material collected upstream. A similar distribution was found for tPCB concentrations (fig. 5). The increments of these metal/Al ratios and tPCB may reflect the incorporation from local anthropogenic sources. The levels of Pb were relatively uniform along the estuary and lower in sands than in fine particles (fig. 5).

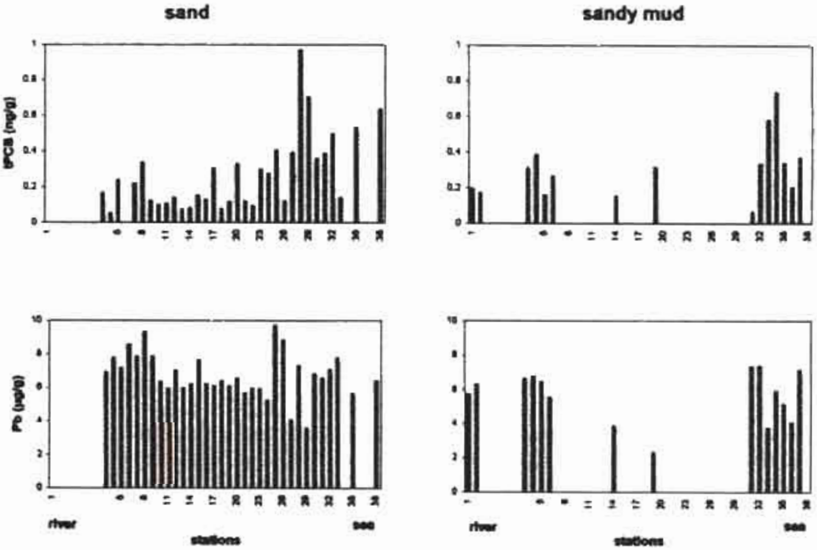

Figure 5. Concentrations of tPCB (ng.g⁻¹) and Pb (µg.g⁻¹) in sands and sandy muds of Mondego river estuary.

Conclusions

In spite of the low contamination of sediments along the Mondego River estuary, its chemical composition indicates that lower estuary sediments are mainly derived from the sea (Ca content) and slightly contaminated by metals, tPCB and butyl tin compounds from anthropogenic sources located around Figueira da Foz. River-derived material exhibited higher concentrations of tDDT and Ag. Geographic distribution of these chemicals and the periodical record will contribute to a better understanding of the sediment dynamics in the Mondego estuary.

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