

# Pb, Zn, Cs, Sc and rare earth elements as tracers of the Loire and Gironde particles on the Biscay shelf (SW France)

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**Abstract** – The western Atlantic continental margin of the Bay of Biscay is characterised by a combined macro-tidal and a high energy environment. These conditions are responsible for the essentially sandy sedimentary cover along with well-defined fine deposit zones observed on the shelf. The main continental sources are the Loire, Gironde and Adour Rivers. It is estimated that 2.4 to 2.5 million tons of fine sediments are supplied annually to the ocean from these rivers of the French Atlantic coast. The Gironde and the Loire contribute with 84 % and the Gironde with 60 % of this amount.

Previous studies of the distribution of the clay mineral assemblages and of oligo-elements have distinguished two provinces (north and south Biscay areas) according to these riverine sources. The use of an inductively coupled plasma-mass spectrometry (ICP-MS) technique allowed us to analyse both heavy metals and rare earth elements (REE), thus permitting an effective characterisation of continental sources. On the basis of these results, it has been possible to better identify the respective contributions of the Loire and the Gironde Rivers to the fine-grained sedimentation on the inner shelf.

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**fine-grained sediment / origin / heavy metal / rare earth element / Bay of Biscay**

**Résumé** – Pb, Zn, Cs, Sc et terres rares, traceurs des apports sédimentaires de la Loire et de la Gironde sur le plateau continental du golfe de Gascogne. La marge continentale ouest-atlantique est un domaine macro-tidal à haut niveau d'énergie. Cette dynamique forte a mis en place sur la plate-forme du Golfe de Gascogne une couverture sédimentaire essentiellement sableuse et des zones de dépôts fins bien circonscrites. Les principales sources continentales sont la Loire, la Gironde et l'Adour. On estime que 2,4 à 2,5 millions de tonnes de sédiments fins sont issus chaque année de ces fleuves. La Gironde et la Loire contribuent pour 84 % à cet apport et la Gironde, à elle seule, pour 60 %.

Des études antérieures fondées sur la répartition des cortèges de minéraux argileux ou sur celle des éléments traces ont mis en évidence des domaines nord et sud-Gascogne. L'utilisation de techniques d'analyses multi-élémentaires telles que l'ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) dosant également les terres rares, a permis une meilleure caractérisation des sources continentales girondine et ligérienne. Ces résultats permettent de préciser les domaines d'influence respectifs de la Loire et de la Gironde dans la sédimentation fine actuelle sur la plate-forme interne. © Elsevier, Paris

**sédiment fin / source / métaux traces / terre rare / golfe de Gascogne**

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## 1. INTRODUCTION

The western Atlantic continental margin of the Bay of Biscay is characterised by a combined macro-tidal and a high energy environment where hydrodynamic forces are capable of transporting and reworking sediments to depths as great as 100 m. These conditions are responsible for the essentially sandy sedimentary cover along with well-defined fine deposit zones observed on the shelf [1].

Previous studies of the clay mineral distribution in the sedimentary cover of the continental shelf of Bay of Biscay [11, 12] revealed a great homogeneity: deposits of the coastal domain (above 50 m depth) are enriched in smectite and kaolinite, an outer domain with a predominance of illite, and the southern part (northward from the Spanish coast) was enriched in kaolinite. A geochemical study of superficial sediments from the very coastal zones and to the outer part of the shelf [15, 16], made it possible to separate the northern domain affected by inputs from a northern Hercynian geological province (Brittany), and a southern domain influenced by the Pyrenees mountains to the south. A more recent study [14], based on a statistical analysis of the mineralogical data from southern Biscay, confirms the importance of the Gironde estuary in the sedimentation of the west and south Gironde mud patches, as previously suggested by Latouche [13].

Castaing and Jouanneau [4], Jouanneau et al. [10] and Jouanneau and Latouche [9] stress that, at present day conditions, the Gironde and Loire Rivers are the main sources of fine sediments to the Bay of Biscay. A supply of  $2.5 \times 10^6$  t.y<sup>-1</sup> of continent-derived fine sediments is estimated, 84 % coming from the Gironde and Loire estuaries. Probably 65 % of this flux is stored on the shelf.

Castaing [3] suggests the mixing processes in the Bay of Biscay would preclude any geochemical identification of the individual input sources. Here, we propose to address this question as well as to determine whether a geochemical fingerprinting of the estuarine sources makes it possible to trace the corresponding signatures in the fine-grained sediments of the shelf and, thus improve our understanding of the processes that actually control the terrigenous supply to the Bay of Biscay.

Toward this goal, we have considered, on the one hand, some elements likely to be tracers of regional lithogenic origins such as rare earth elements (REE), Cs and Sc, the last usually being used for normalisation, and, on the

other hand, two heavy metals, Zn and Pb, which display high enrichment factors because they are largely involved in human activities and therefore able to yield information on present day sedimentary processes.

## 2. SAMPLES AND METHODS

Two different sets of samples were analysed. The first set consisted of estuarine suspended particulate matter (SPM) and sediments representing the three potential sources (Loire, Gironde, Adour). The second comprised approximately 30 undisturbed surface sediment samples collected by a box corer from the shelf in the main fine-grained deposits of the Bay of Biscay (*figure 1*) collected during recent cruises. The first centimetre was sliced with a plastic cutter and stored in clean plastic bags. Only this first centimetre has been studied, primarily because it better represents the most recent deposits and because it has been deposited within the same oxidised environment as the one occurring in the water column from which the particles are settling down.

After sieving the < 63 µm fraction (sediments of the shelf), subsamples weighing about 10 mg were dissolved for 12 h in pressurised PTFE beakers at a temperature of about 125 °C in a ≈ 6N equimolar mixture of [HF + HClO<sub>4</sub> + HNO<sub>3</sub>]. Element concentrations were determined using an ICP-MS Elan 5000 P.E.-Sciex. MESS 2. BCSS 1 standards from NRCC have been systematically analysed, and ensure that precision was better than 10 % for all elements. Accuracy was found to be 5 % at 10 µl.L<sup>-1</sup>. The instrument was operated under standard settings in nearly clean room conditions (US class 10 000).

To establish a broad comparison with the open sea, we compared our results with those obtained (on the same ICP-MS) for sediment trap samples collected [19] across the slope, along the Cap Ferret canyon axis.

## 3. RESULTS

Concerning potential estuarine sources, we present, on the one hand, results obtained on bulk samples and, on the other hand, on the fine-grained fraction (< 63 µm) of the same samples in order to be comparable with those of the shelf, for which only results obtained on this fine-grained fraction have been considered (*table I*).

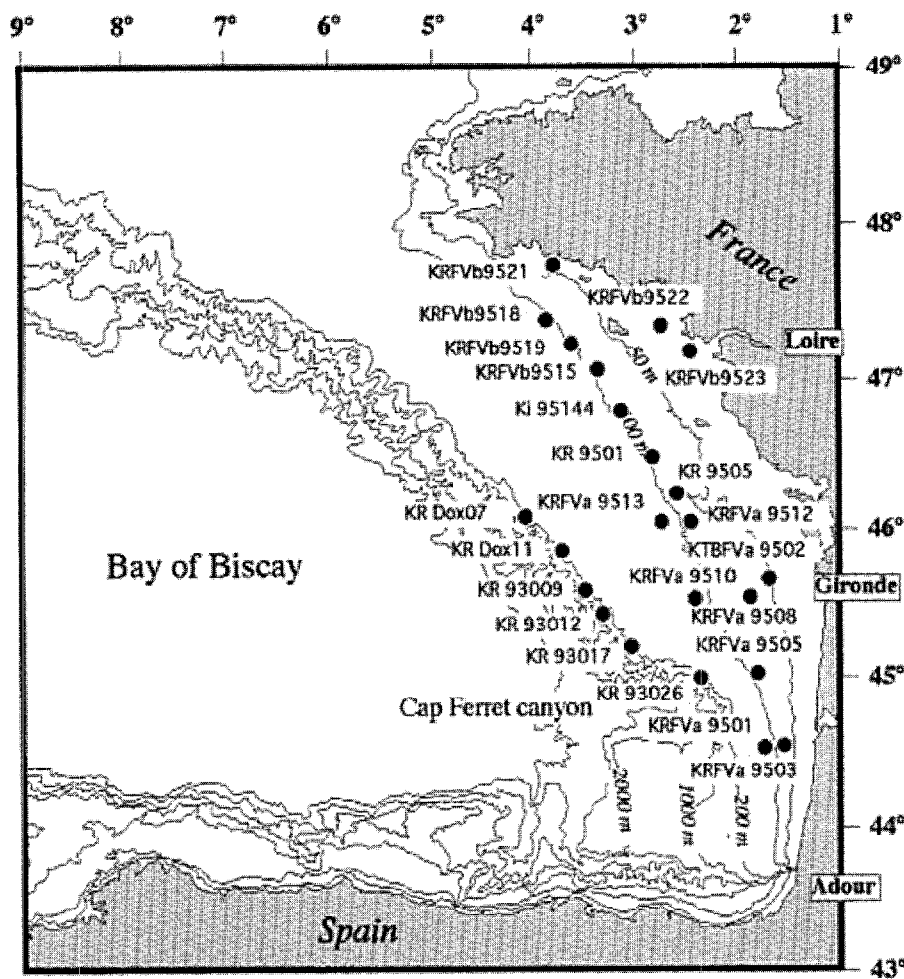


Figure 1. Sampling locations.

Figure 1. Localisation de l'échantillonnage.

### 3.1. Rare earth elements

The REE patterns, normalised to the shales (after Taylor and McLennan [18]), do not display any significant differences between the three sources (*figure 2a*) either on bulk sediment or on fine fraction ( $< 63 \mu\text{m}$ ). Samples from the Loire River, however, are characterised by a small positive europium anomaly. In the fine fraction ( $< 63 \mu\text{m}$ ) of these same samples, this anomaly disappears. The difference between REE patterns of bulk sediment and fine fraction could be linked to mineralogical differences that will have to be documented.

In the fine-grained fraction of the shelf itself (*figure 2b*), we do not observe any major REE trend and the minor

differences observed in some samples could be attributed to slight mineralogical changes.

### 3.2. Trace metals

Cesium (Cs) is a poorly particle-reactive element, strongly associated to clay minerals (principally illite) and to mica, which is the dominant phyllosilicate in the fine-grained fraction of the Bay of Biscay. Zn and Pb are mostly derived from the industrial activity, so they are reliable markers of anthropogenic inputs and hence, of present day supplies. In other respects, zinc is particularly abundant in the Gironde SPM [8] and lead in the Loire SPM [17].

**Table I.** Inductively coupled plasma-mass spectrometry (ICP-MS) results, rare earth elements (normalised to European shales), trace metals (normalised to Sc).

**Tableau I.** Résultats ICP-MS, Terres Rares (normalisées aux shales européennes), métaux traces (normalisés au Sc).

	<i>Rare Earth Elements (normalized to Shales)</i>														<i>Heavy metal (normalized to Sc)</i>			
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc	Cs/Sc	Pb/Sc	Zn/Sc
KRFVb9523	1.92	1.92	1.83	1.76	1.76	0.93	1.81	1.29	1.15	0.74	0.65	0.48	0.52	0.44	9.91	1.08	3.46	10.88
KRFVb9522	0.63	0.65	0.59	0.58	0.62	0.67	0.68	0.55	0.57	0.42	0.40	0.34	0.37	0.32	10.60	1.14	4.16	10.48
KRFVb9521	0.60	0.59	0.55	0.54	0.57	0.57	0.60	0.48	0.50	0.36	0.34	0.29	0.32	0.27	9.57	1.10	3.58	9.82
KTBFVa9502	0.92	0.95	0.87	0.85	0.89	0.79	0.91	0.69	0.67	0.47	0.44	0.38	0.42	0.36	8.34	0.78	3.82	9.66
KRFVa9508	0.71	0.74	0.67	0.65	0.69	0.71	0.71	0.56	0.57	0.42	0.40	0.36	0.39	0.33	12.00	0.86	3.75	10.63
KRFVa9503	2.56	2.56	2.47	2.38	2.38	1.04	2.44	1.68	1.40	0.85	0.72	0.50	0.53	0.42	7.76	0.57	4.10	10.52
KRFVa9505	n.d.	n.d.	13.75	13.68	13.94	3.57	13.89	9.04	6.92	3.75	2.97	1.54	1.56	1.20	9.27	0.66	4.08	9.87
KRFVa9512	0.92	0.93	0.86	0.83	0.85	0.60	0.89	0.64	0.61	0.42	0.38	0.31	0.34	0.29	7.60	0.75	4.42	10.45
KR 9505	0.75	0.78	0.69	0.67	0.70	0.63	0.75	0.57	0.57	0.41	0.39	0.33	0.37	0.31	10.40	0.85	3.39	10.13
KR 9501	0.71	0.72	0.66	0.65	0.69	0.60	0.73	0.55	0.56	0.41	n.d.	0.32	0.36	0.31	10.00	0.87	3.11	9.44
KRFVb9518	0.60	0.60	0.55	0.53	0.57	0.58	0.61	0.48	0.51	0.37	0.35	0.31	0.33	0.28	11.50	1.00	2.58	8.70
KR 95144	0.65	0.66	0.60	0.59	0.63	0.62	0.65	0.50	0.52	0.38	0.37	0.32	0.36	0.31	10.60	0.95	2.87	9.51
KRFVb9515	0.71	0.72	0.66	0.64	0.65	0.60	0.69	0.53	0.53	0.38	0.37	0.32	0.35	0.30	9.58	0.90	2.82	8.69
KRFVb9519	0.72	0.73	0.67	0.65	0.69	0.61	0.71	0.54	0.54	0.38	0.36	0.31	0.34	0.28	9.36	0.93	2.57	8.86
KRFVa9501	1.14	1.17	1.09	1.05	1.06	0.75	1.12	0.81	0.79	0.54	0.51	0.42	0.47	0.41	8.93	0.65	3.40	9.56
KRFVa9510	0.95	0.96	0.89	0.86	0.88	0.56	0.89	0.64	0.57	0.38	0.34	0.26	0.28	0.23	6.39	0.72	3.67	9.74
KRFVa9513	0.66	0.67	0.62	0.60	0.63	0.52	0.66	0.50	0.50	0.35	0.33	0.27	0.30	0.25	8.80	0.82	3.67	9.67
KR 93017	0.86	0.88	0.81	0.80	0.83	0.66	0.90	0.67	0.66	0.48	0.46	0.39	0.44	0.38	7.28	0.69	3.53	7.57
KR 93009	0.74	0.76	0.70	0.69	0.72	0.72	0.77	0.60	0.62	0.46	0.43	0.37	0.42	0.35	9.65	0.90	2.60	7.24
KR 93012	0.79	0.80	0.74	0.73	0.74	0.63	0.79	0.59	0.60	0.43	0.42	0.36	0.41	0.35	7.71	0.72	2.69	6.74
KR Dox07	0.80	0.82	0.77	0.77	0.80	0.66	0.87	0.66	0.66	0.46	0.45	0.39	0.43	0.37	7.80	0.75	6.11	7.40
KR 93026	0.75	0.77	0.71	0.69	0.72	0.76	0.76	0.58	0.60	0.44	0.42	0.38	0.42	0.35	11.10	0.79	2.20	7.06
LOIRE*	0.60	0.67	0.82	0.76	0.90	1.29	1.21	1.06	1.58	1.33	1.65	2.01	3.28	3.56	11.60	0.35	7.86	18.12
GIRONDE*	0.76	0.80	0.99	0.92	1.17	1.42	1.59	1.40	2.15	1.84	2.43	2.88	5.18	5.55	10.90	0.14	7.07	18.14
ADOUR*	0.64	0.66	0.80	0.75	0.93	1.15	1.23	1.10	1.63	1.37	1.77	2.14	3.50	3.86	10.60	0.04	5.66	20.56
LOIRE#	0.90	n.d.	0.85	0.83	0.89	0.94	0.95	0.76	0.81	0.59	0.55	0.47	0.52	0.42	11.58	1.44	7.65	13.63
GIRONDE#	0.74	n.d.	0.68	0.68	0.74	0.79	0.80	0.66	0.73	0.54	0.52	0.45	0.49	0.41	12.53	0.89	4.83	18.91
ADOUR#	0.54	0.55	0.51	0.51	0.57	0.64	0.63	0.53	0.57	0.42	0.40	0.34	0.37	0.31	9.49	0.55	5.39	19.03

\* Bulk sediment

# < 63 µm

Results were normalised to scandium (Sc), an element of 100 % natural origin, almost entirely associated with the lithic fraction [2]. Thus, normalising the concentrations to scandium allows us to minimise possible dilution effects introduced by variable matrices.

### 3.3. Cs/Sc

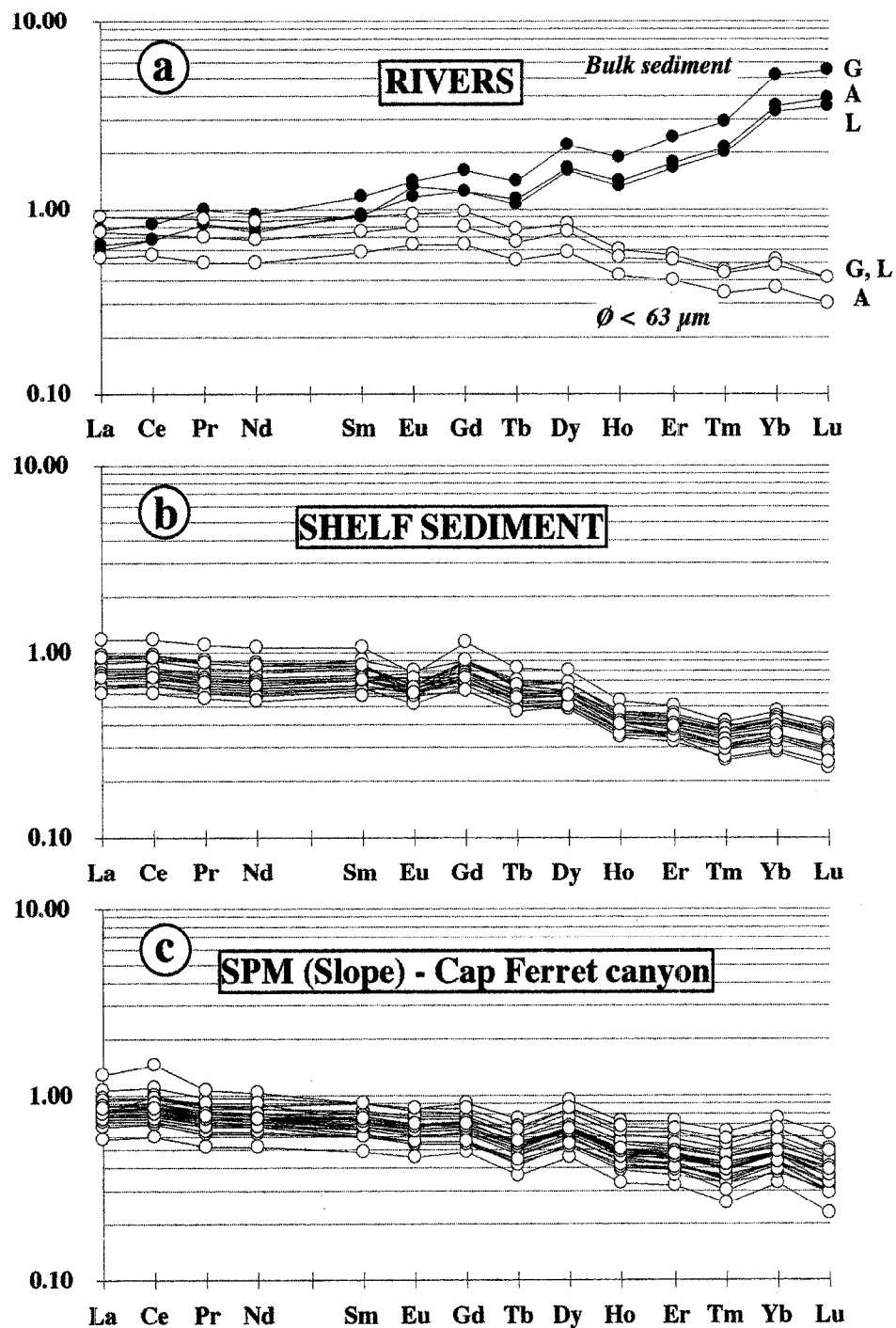
The cesium distribution is presented in figure 3a. It clearly appears that the main source for Cs is the Loire estuary. Despite the minor influence of the Gironde, weak

enrichments are observed in the west and south Gironde mud patches as well. The main feature is a latitudinal gradient decreasing from north to south, and reflecting dilution processes. In the southern part of the Bay of Biscay, the impact of the Adour River cannot be recognised.

### 3.4. Pb/Sc

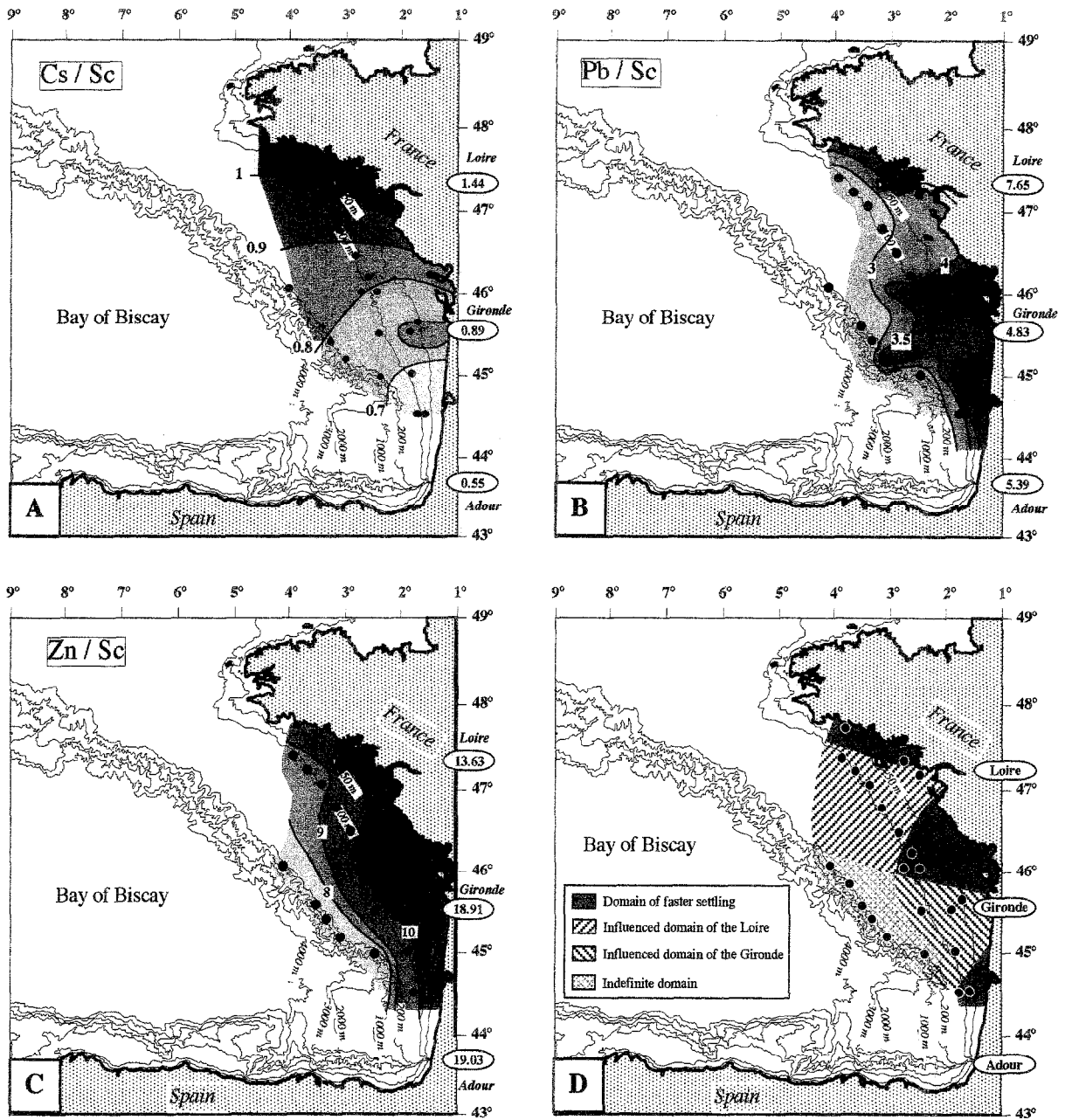
The lead distribution (figure 3b) presents a different picture. The highest values are observed next to the mouth of the Loire River. Nevertheless, the impact of the Gironde

conc. sample / conc. shales



**Figure 2.** Rare earth elements (REE) patterns (normalised to European shales; Taylor and McLennan [18]): a: estuarine sources; b: shelf samples; c: sediment trap samples (suspended matter) from the Cap Ferret canyon (Thomas et al. [19]).

**Figure 2.** Spectres des Terres Rares (normalisées aux schistes européens, Taylor et McLennan 1985), a : sources estuariennes, b : échantillons de pièges (matières en suspension) du canyon du Cap Ferret (Thomas et al. [19]).



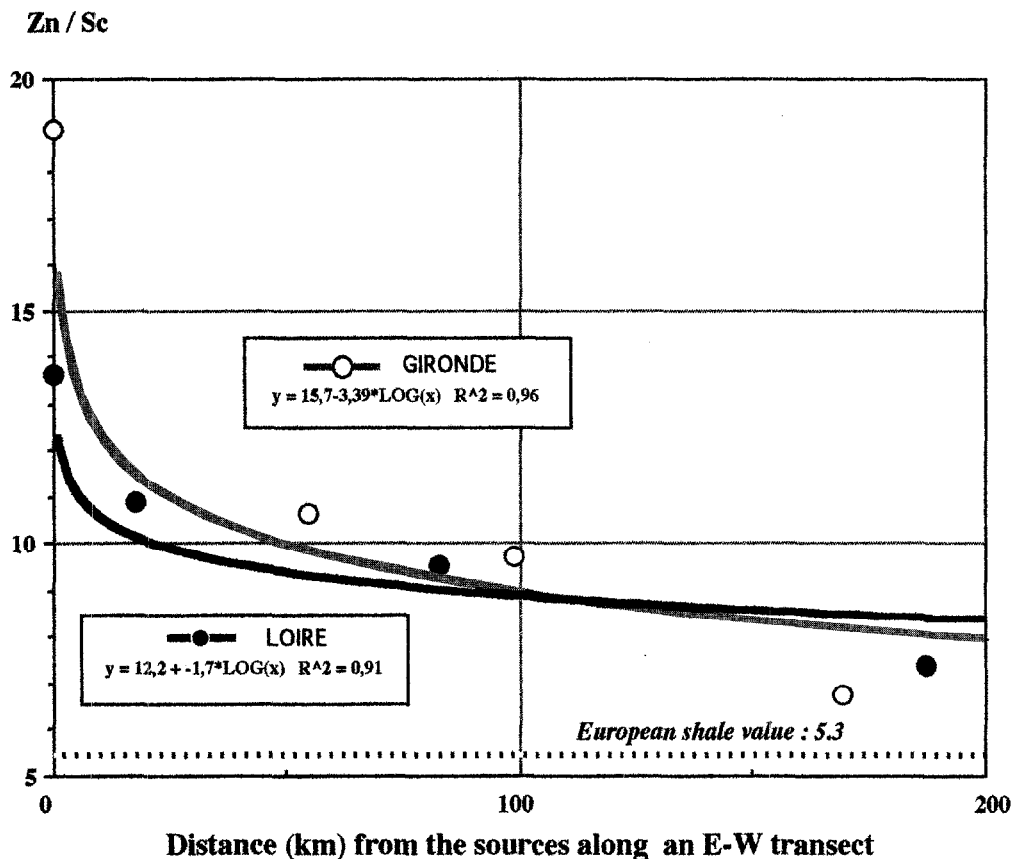
**Figure 3.** Cesium (Cs) distribution in the <math>< 63 \mu\text{m}</math> fraction of the samples (A); lead distribution in the <math>< 63 \mu\text{m}</math> fraction of the samples (B); zinc distribution in the <math>< 63 \mu\text{m}</math> fraction of the samples (C); respective influence domains of the Loire and Gironde estuaries in the Bay of Biscay (D).

**Figure 3.** Distribution du césium dans la fraction  $\varnothing < 63 \mu\text{m}$  des échantillons (A) ; Distribution du plomb dans la fraction  $< 63 \mu\text{m}$  des échantillons (B) ; Distribution du zinc dans la fraction  $\varnothing < 63 \mu\text{m}$  des échantillons (C) ; Domaines d'influences respectifs de la Loire et de la Gironde dans le Golfe de Gascogne (D).

is the strongest, and can be identified in the whole southern Biscay area. In this region, however, a contribution of the Adour River cannot be excluded, but its identification would require a more extensive sampling.

### 3.5. Zn/Sc

The zinc distribution (figure 3c) is a good illustration of the signature of the estuarine supplies. The Zn/Sc ratio



**Figure 4.** Decrease of the zinc contents along an east–west axis off the Gironde (lighter line) and the Loire (darker line) estuaries; dotted line: European shale reference (Taylor and McLennan [18]).

**Figure 4.** Décroissance des teneurs en zinc selon un axe Est-Ouest en face des estuaires de la Gironde (ligne ombrée) et de la Loire (ligne noire), ligne pointillée : valeur de référence des shales européennes (Taylor et McLennan [18]).

distribution displays a well marked east–west decreasing gradient, isolines being distributed parallel to the isobaths. The importance of the Gironde is clearly evident.

#### 4. DISCUSSION

REE patterns do not allow us to discriminate between sources. This could be due to the fact that present day supply of matter from estuaries to the shelf is dominated by transport of suspended matter, i.e. with the same grain-size distribution inherited from mineralogically homogeneous drainage basins. Moreover, it is important to observe that the REE patterns of the continental sources (rivers) are quite similar to those observed by Thomas et al. [19] in sediment trap samples from the Cap

Ferret canyon (*figure 2c*). This observation is compatible with the idea that the margin is currently fed by materials originating from the Atlantic coastal zone (estuaries and shelf undifferentiated). We cannot rule out, however, any possible contribution from the south by northern Spanish rivers, but considering the small size of their drainage basins, these fluxes could be neglected. Moreover, the Spanish sector of the Biscay shelf is very narrow, and estuarine fluxes must be mostly channelised down to the abyssal plain by the several canyons transecting this part of the shelf.

The latitudinal distribution of Cs reflects a dominant southward dilution of the Loire outputs. We may therefore consider that Cs is a good tracer of the lithogenic fraction.

Both the Pb and Zn distributions are the consequence of more complex processes. In addition to physical dilution (mixing), the decreasing gradient of the specific metal contents can be attributed to a progressive removal of the metallic mobilisable fraction which corresponds essentially to the anthropogenic contribution of the total content. Previous works [5, 6, 7] have demonstrated that a partial solubilisation of the particular metallic content may occur in the estuarine environment, and even in the shelf environment. This very general behaviour has already been recognised in the Gironde estuary [8] for Zn and Pb.

The distribution of Zn/Sc in surficial sediments on the shelf displays a progressive logarithmic decrease as a function of the distance from the source, along an east-west axis observed in front of both the Loire and the Gironde mouths (*figure 4*). This corresponds to the ongoing effects of solubilisation processes which affect the mobilisable fraction. Given an allowance of about 10 % on both sides of this curve, it is possible to determine the respective areas of influence of the two main estuaries (*figure 3d*). Beyond these domains, one can define: an outer undifferentiated area (below the detection limits of the method), an intermediate area where none of the main source imprints can be clearly defined, and some small areas of preferential settling where unexplained anomalous values are observed. These could correspond to areas where the transport of matter that originates from the estuaries is faster than everywhere else, thus reflecting a

weaker removal of the metal fraction absorbed on the settled material.

## 5. CONCLUSIONS

It has been shown that REE patterns of the estuarine sources were not different enough to be used as a discriminating factor. No enrichment (compared to natural European shales) was noted in samples collected both in estuaries and the fine-grained shelf deposits. On the other hand, despite chemical removal affecting the metal mobilisable fraction of the suspended matter, some heavy metals that can be used as anthropogenic tracers allow the recognition of the respective influences of the Loire (Cs and Pb) and the Gironde (Zn and Pb) Rivers. Moreover, it appears that the present day contamination is still visible on (at least) the inner shelf, despite the physical mixing induced by hydrological processes as first proposed by Castaing [3].

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