



Multi-element Chemistry of Loire Estuary Sediments: Anthropogenic vs. Natural Sources

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The chemical composition of bed sediments in the Loire estuary, and their evolution between landward and seaward have been investigated. The concentrations of five major oxides (SiO_2 , K_2O , CaO , TiO_2 and Fe_2O_3) and nine trace elements (Rb, Sr, Zr, Zn, Pb, Sn, La, Ce and Ba) have been measured. Factors that govern element contents in bed sediments were examined by a combined descriptive (using indicator elements) and statistical (principal component analysis) approach.

Using descriptive tools, the results show that Fe_2O_3 , Zn, Pb and Sn are significantly enriched down estuary referred to a fluvialite normalization, whereas K_2O , Rb, Zr and Ba are depleted down estuary. SiO_2 , TiO_2 , CaO , Sr, La and Ce behave conservatively over the estuary profile.

Principal component analysis was performed for the 13 X/Fe ratios (X being Si, K, Ca, Ti, Rb, Sr, Zr, Zn, Pb, Sn, La, Ce and Ba). The variability of the data is explained by at least four components. Two components explain nine chemical elements; the first end-member is represented by the fluvialite particles, and the second one is represented by the particles produced *in situ* in the estuary area. Two other components are required to explain the variability of Zn and Sn on one hand, and Pb on the other hand. These components can be related to removal (adsorption, co-precipitation, flocculation) onto clay minerals, Fe oxyhydroxides and humic acid complexes.

Finally, a binary mixing model using rare earth elements (REE) and iron between the fluvialite particles and the particles produced *in situ* in the estuary area is developed. The results of the mixing model computation show that half of the particles exported by the Loire estuary system are of fluvialite origin.

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Introduction

Rock and soil erosion constitutes a major process at the Earth's surface (Garrels & McEnzie, 1971). Streams and rivers carry the results of these processes to the ocean in suspended form (Garrels & McEnzie, 1971; Berner-Kay & Berner, 1987; Drever, 1988). Estuaries represent a transfer box for the sediments between land and the open ocean (Meade, 1972; Burton, 1988) and are very reactive areas. The change in physico-chemical characteristics that occurs during mixing of river water and seawater leads to a variety of reactions of geochemical importance for sediments which modify the riverine fluxes of material to coastal seas. Sediments in estuaries react as traps for trace elements and, especially, for pollutant elements (Chester & Stones, 1975; Figueres *et al.*, 1985; Seyler & Martin, 1990; Turner *et al.*, 1994). In many river watersheds, several studies have shown that the sediment load (suspended particulate matter and bed sediments) can be significant in the transport of pollutant elements

(Presley *et al.*, 1980; Olsen *et al.*, 1989; Sinclair *et al.*, 1989). So, the need to understand anthropogenic inputs to the ocean through estuaries is a great challenge (Moore *et al.*, 1979; Koons *et al.*, 1980; Mayer, 1982; Chester *et al.*, 1985; Horowitz & Elrick, 1987).

Sediments in estuaries have multiple sources. The primary sources are rivers, offshore and littoral areas and shorelines of estuaries themselves (Meade, 1972; Burton, 1988). Riverine sources are the most common. Furthermore, flocculation which occurs at low-high salinity contact is an important phenomena with regard to elemental behaviour (Conley *et al.*, 1971; Sholkowitz, 1976; Martin *et al.*, 1976; Van der Weijden *et al.*, 1977; Moore *et al.*, 1979; Crerar *et al.*, 1981; Mayer, 1982; Hoyle *et al.*, 1984; Gordeev *et al.*, 1985; Goldstein & Jacobsen, 1988; Elderfield *et al.*, 1990; Olivarez & Owen, 1991; Sholkowitz, 1992; Tanizaki *et al.*, 1992), and represents the secondary source. The chemical composition of estuarine sediments can be explained largely by transport and mixing of the different source inputs.

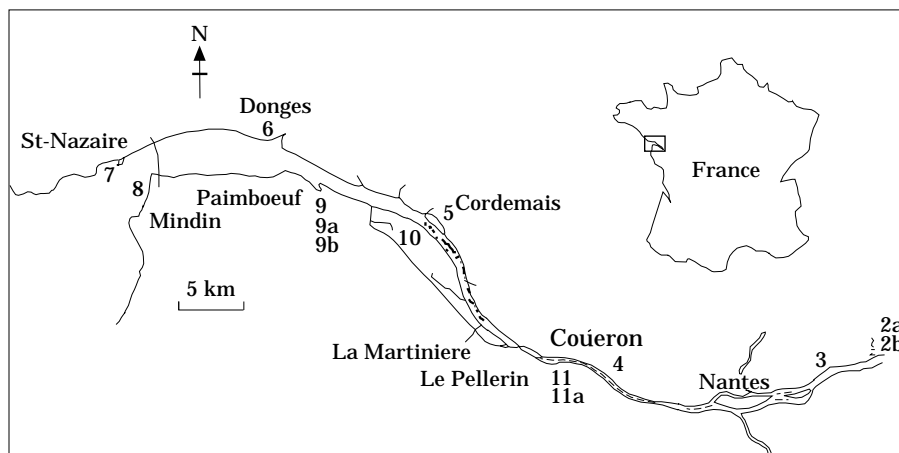


FIGURE 1. Location map of the Loire estuary and of Sampling Stations 2–11. The turbidity maximum (TM) is represented by a dark patch.

This study developed multi-element analysis on bulk sediments with the most simple methodology; analyses were performed on the $<165 \mu\text{m}$ wet sieved fraction with a non-destructive analyser. The aim of the present work was to study the spatial distribution of chemical species in bed sediments with regard to their chemical behaviour; soluble or insoluble elements, pollutant or 'reactive' elements. Another objective of this work was to identify the different particles, sources and determine the role of these materials in transporting pollutant elements. The occurrence of a turbidity maximum in meso- or macrotidal estuaries (like the Loire estuary) induce a more crucial importance in chemical processes, especially for anthropogenic fluxes (Turner & Millward, 1994). The chemical characteristics of bed sediments from the Loire estuary enabled determination of the origin, the quantification of particles and the role of the estuarine dynamic.

Study area

The Loire watershed is the greatest in France with a drainage area of around $120\,000 \text{ km}^2$. On a western European scale, the Loire river is one of the main riverine inputs to the Atlantic ocean. The water discharge of the Loire river is $26 \times 10^9 \text{ km}^3 \text{ year}^{-1}$ with a mean annual discharge of $850 \text{ m}^3 \text{ s}^{-1}$ (Figueres *et al.*, 1985; Tardy, 1986). Solid load output is $10^9 \text{ kg year}^{-1}$ and sediment volume represents $4 \times 10^6 \text{ m}^3 \text{ year}^{-1}$ (Figueres *et al.*, 1985).

The estuarine structure is a result of the interaction between hydrological conditions on one hand, and tidal amplitude plus morphology on the other hand. The Loire estuary is 80 km long with a partly mixed structure (Figueres *et al.*, 1985; Roger, 1988), and

is highly industrialized. The Loire system is shown in Figure 1. As a result of this structure, a zone of maximum suspended-sediment concentration bounded by lower concentrations both landward and seaward exists. This turbidity maximum (TM, represented by a dark patch in Figure 1) is accompanied by a zone of maximum sediment accumulation. The turbidity maximum extends near the landward limit of seasalts (Meade, 1972; Castaing, 1981; Burton, 1988; Uncles & Jordan, 1994). In the Loire estuary, TM occurred in September and was expelled into the open ocean during high winter river flows. In this study, 3.06 g l^{-1} of suspended particulate matter (SPM) were collected in the TM zone. The main reason for the extension and constancy of TM is the dredging of the river bed to approach dock basins between St Nazaire and Nantes. During the last century, the fairway depth has increased from 1 m in 1900 to more than 13 m. One consequence is the maximum tidal intrusion, up to 53 km inland, with a continual accretion of sediment deposits in the estuary.

Mineralogical studies of SPM and bed sediments in the Loire estuary by Roger (1988) show that clay minerals comprise smectites (30%), illites (33%), kaolinites (27%) and chlorites (10%). Feldspars, calcite, biotites, zircons and accessory minerals issued from the weathering processes of intrusive rocks in the upper Loire watershed can also be seen in the fine sand fraction.

Sampling and analytical methodology

Recent bed sediment samples were collected along the 100 km profile (Stations 2–11) shown in Figure 1. Station 2 represents the most fluvial point of the estuary, while Stations 7 and 8 represent the most

TABLE 1. Means, standard deviations and % standard deviations per major oxide (wt%) and trace element (ppm) contents in the two in-house standards, LOT 11 and LOT 23

Element	Mean	Standard deviation	Standard deviation (%)	Detection limit
SiO ₂ (%)	60.39/69.75	1.32/1.24	2.2/1.8	0.6
K ₂ O	3.32/2.65	0.09/0.11	2.7/4.2	0.02
CaO	1.85/2.16	0.04/0.07	2.3/3.5	0.01
TiO ₂	0.87/0.71	0.03/0.03	3.6/4.3	0
Fe ₂ O ₃	7.95/5.39	0.1/0.1	1.3/1.9	0
Zn (ppm)	3896/123	49/7.9	1.3/6.4	15–23
Pb	290/35	12/2.7	4.1/10.6	15–20
Rb	159/120	3.2/2.4	2/2	3–6
Sr	310/146	5.7/2.8	1.8/1.9	2–5
Zr	158/187	2.3/3.5	1.5/1.9	2–4
Sn	41/4	2.4/1.5	5.8/39	2
Ba	<4100/675	0/9.9	0/1.5	2
La	25.5/18	12.7/2	50/11	2
Ce	69/46	3.3/1.8	4.8/4	2

During this study, 19 (LOT 11) and 21 (LOT 23) replicate analyses were made, respectively. Detection limits for all the elements measured with the SYRANO are also indicated.

marine points. To avoid contamination during sampling, sediments were collected with plastic spatulas and stored in polypropylene boxes. Sediments were oven-dried at 70 °C and powdered prior to analysis. In order to obtain representative aliquots for analyses, samples were homogenized, quartered and dry-sieved through a 165 µm nylon mesh, without dispersion agent, to avoid contamination and modification of the samples.

Fluviatile sediments were collected more than 300 km upstream from the estuary every month for 1 year. Samples were treated following the same procedure as for estuarine sediments.

Surface water samples and SPM were collected together with bed sediments at each location. Suspended particulate matter was isolated by filtration through 0.45 µm acetate cellulose membranes. Total SPM masses were determined by weighing air-dried filters before and after sample filtration. Surface water master variables [temperature (°C), pH, redox potential (Eh in mV) and electrical conductivity (C in µS cm⁻¹ at 25 °C)] were all measured on site.

All bulk sediment samples were analysed for major and trace elements by X-ray fluorescence energy dispersive spectrometry (XRF) using a SYRANO 2/501 (SYstem for Research and ANalysis of Ores) developed by BRGM. Contents of five major oxides (SiO₂, K₂O, CaO, TiO₂ and Fe₂O₃) and nine trace elements (Rb, Sr, Zr, Zn, Pb, Sn, La, Ce and Ba) were determined using 9 g of pressed powder. Twenty reference standards for major oxides and trace elements were used to calibrate the analytical pro-

gramme. In addition, two certified reference materials (stream sediments GBW 07311; GBW 07306) were run to verify the calibration. Accuracy and reproducibility of SYRANO were determined by mean values and 1 standard deviation of two selected in-house standards (stream sediments of Lot River, France). Table 1 summarizes the results of LOT 11 and LOT 23 in-house standard (mean values, standard deviation and % standard deviation are indicated). Results demonstrate that the SYRANO X-ray instrument is both extremely precise and accurate for the 14 analysed elements. On the basis of replicate analyses ($n=19$ for LOT 11 and $n=21$ for LOT 23 during this study), precisions are better than $\pm 2\%$ for Fe₂O₃, Sr, Zr and Ba, better than $\pm 5\%$ for SiO₂, K₂O, CaO, TiO₂ and Rb, and better than $\pm 10\%$ for Zn, Pb, Sn, La and Ce. For La in LOT 11, the worst standard deviation is due to the high content of Ba (<4100 ppm); for Sn in LOT 23, the worst standard deviation is due to the low content (4 ppm) with regard to the detection limit of 2 ppm.

Results and discussion

Estuarine master variables

Data are summarized in Table 2. The water temperature during the survey ranged between 8.6 and 15.5 °C. The pH ranged between 7.11 and 7.80. Neither the marine value (pH=8) nor the fluviatile values (8 < pH < 9, unpubl. data) were observed. However, departures from equilibrium with atmospheric

TABLE 2. Estuarine master variables: temperature, pH, Eh (corrected from the electrode potential), electrical conductivity and suspended particulate matter (SPM)

Points	Location	Distance to ocean (km)	T (°C)	pH	Eh (mV)	C ($\mu\text{S cm}^{-1}$)	SPM (mg l^{-1})
1	St Florent	109	10.2	7.48	377	341	132
2	Champtoceaux	86	11.5	7.35	364	298	29
3	Thouaré	68	14.5	7.47	356	325	70
4	Indre	45	13.2	7.37	379	317	13
5	Cordemais	24	15.1	7.88	603	317	26
6	Donges	10	11.2	7.19	607	4510	105
7	St Nazaire	0	9.4	7.52	733	16 100	159
8	Mindin	2	10.1	7.82	693	13 550	—
9	Paimboeuf	16	12.5	7.22	471	1544	3026
10	Pt Carnet	23	11.7	7.11	424	353	625
11	Le Pellerin	38	11.5	7.41	397	319	34

partial pressure of CO_2 occur frequently in estuarine waters (Burton, 1988) and could explain the discrepancy. Electrical conductivity (C in $\mu\text{S cm}^{-1}$ at 25°C) was close to the $300 \mu\text{S cm}^{-1}$ between 110 and 20 km from the estuary mouth [Figure 2(a)], whereas between 20 km and the mouth (Point 0), C

increased up to $16\,000 \mu\text{S cm}^{-1}$. Redox potential (corrected from electrode potential) fluctuated correlatively with C [Figure 2(b)]. Eh values were close to $+350 \text{ mV}$ between 110 and 20 km from the estuary mouth. Between 20 km and Point 0, Eh increased up to $+730 \text{ mV}$. Eh values observed in the Loire estuary

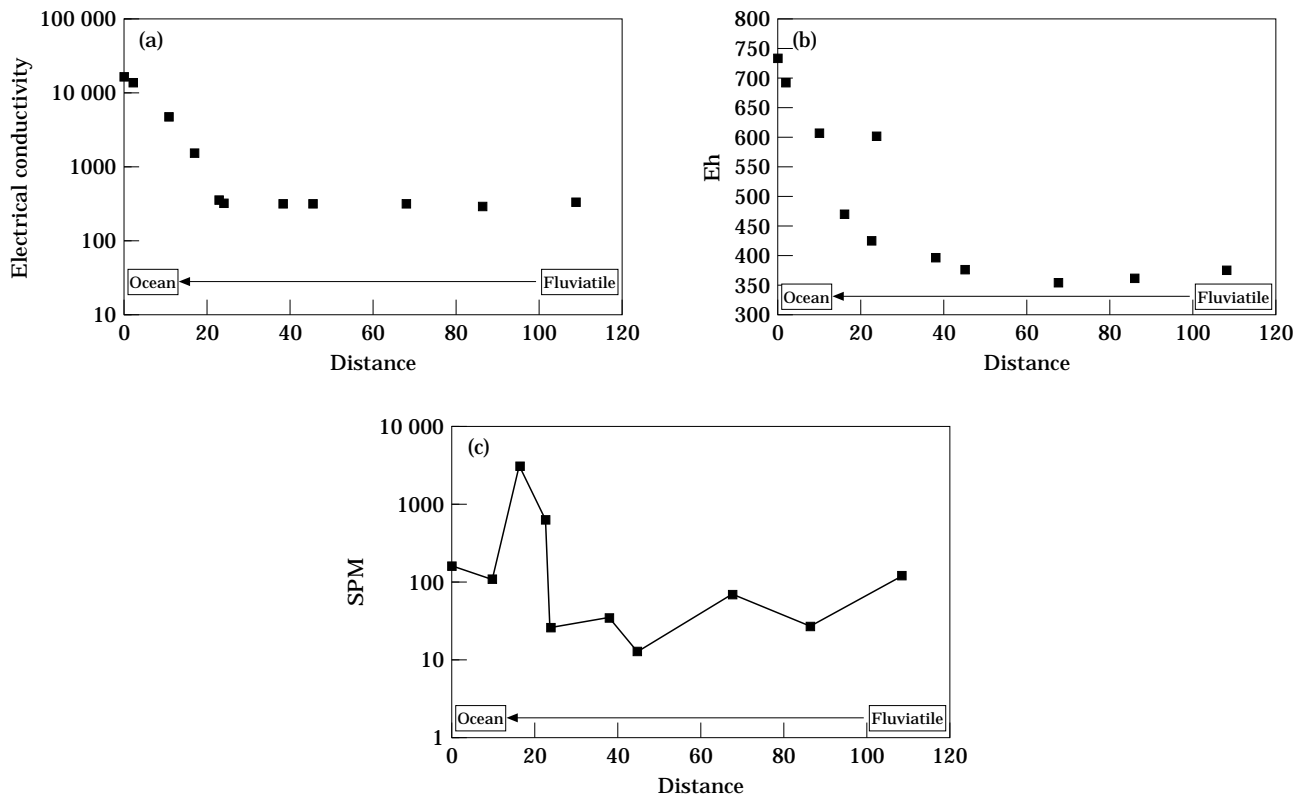


FIGURE 2. Estuarine master variables. (a) Electrical conductivity; (b) Eh; (c) suspended particulate matter vs. the distance from the most oceanic point.

are similar to those obtained by Crerar *et al.* (1981) in the Mullica river estuary.

The SPM concentrations ranged between 13 and 3026 mg l⁻¹ [Figure 2(c)]. Highest SPM values occurred in the low salinity waters of the Loire estuary, and represented the TM phenomenon common to several estuaries (Castaing, 1981; Burton, 1988; Uncles & Jordan, 1994).

Estuarine sediments

Major element compositions in weight percentage (wt%) together with trace element abundances in part per million (ppm) are listed in Table 3.

Major element compositions. As shown in Table 3, SiO₂ is the most abundant major oxide in the 14 samples (57.45 ± 5.23 wt%); CaO and Fe₂O₃ are also present in high concentrations (5.51 ± 0.58 and 6.34 ± 0.93 wt%, respectively), while K₂O and TiO₂ are present in low concentrations in all of the samples (2.04 ± 0.22 and 0.89 ± 0.06 wt%, respectively). The lowest fluctuations, expressed in percentage of the standard deviation, are observed for SiO₂ and TiO₂ (7 and 9%, respectively), while the largest is observed for Fe₂O₃ (15%). K₂O and CaO have intermediate fluctuations (11%).

Trace elements. Some of the trace element abundances in these sediments (Table 3) are highly variable: Pb, Zr, Sn, and Ba range by more than 20%; the highest fluctuation is observed for Sn (25 ± 8 ppm; standard deviation: 31%). Zn, La and Ce have closer fluctuations (13–14%); the lowest fluctuations are observed for Rb and Sr (8–10%).

Measured contents of SiO₂, CaO, Fe₂O₃, Zn and Pb can be compared with previous values reported by Roger (1988), data from this work in italics. Compatible values are found for mean SiO₂ (268 100 ± 24 400 ppm; 241 000 ± 26 700 ppm); CaO (39 360 ± 4140 ppm; 40 000 ppm); Zn (195 ± 26 ppm; 158 ± 40 ppm) and Pb (81 ± 19 ppm; 61 ± 21 ppm). Higher Fe₂O₃ values were found by Roger (1988) with 37 100 ± 7080 ppm against 22 190 ± 3300 ppm in the present study. Ba, Rb, La and Ce contents measured in this work (also in italics) can be compared with previous values reported by Thomas and Martin (1982). Identical values are found for Rb (164 ± 13 ppm; 185 ppm); La (41 ± 5 ppm; 51 ppm) and Ce (92 ± 13 ppm; 95 ppm), while higher Ba contents were found in the present study than have been reported previously (512 ± 115 ppm; 336 ppm).

Likewise, the TM sample (9) can be compared with the bed sediments collected at the same location (9a,

9b). For major elements, the concentrations of SiO₂, K₂O, CaO and TiO₂ are higher in SPM collected in the TM zone than in associated bed sediments. The excess ranges between 10 (TiO₂) and 20% (CaO). For Fe₂O₃ and some trace elements (Sr, Zr, La and Ce), the concentrations are higher in bed sediments than in the SPM, whereas Sn, Pb, Zn, Rb and Ba contents are always found to be higher in bed sediments than in the SPM. The opposite observations for La, Ce, Rb and Zn were reported previously by Sarmani (1989) for SPM and sediments in the Langat river, Malaysia. The present data demonstrate that significant differences exist between the SPM and the sediment samples. Concentrations in SPM can be shown to be statistically different from bed sediments collected at the same location. The differences for insoluble elements (Zr, La, Ce) can be explained by the presence of mineral phases like zirconium and monazite, and by the hydrodynamics of the estuarine system. However, the highest metal contents observed in bed sediments when compared to SPM do not reflect the location of the major input sources of metals. More generally, variations in the bulk chemical composition between SPM in the TM zone and associated bed sediments result from the mixing between permanently suspended particles and re-suspended sediments (Morris *et al.*, 1987).

Fluviatile sediments

Four bed sediments were collected in the Loire river at Orleans, 300 km from the estuary. The data are summarized in Table 4.

Major element compositions. As for estuarine sediments, SiO₂ is the most abundant oxide but also the least variable (60.37 ± 2.63 wt%, % standard deviation 4%). The second most abundant oxide is CaO (10.6 ± 4.52 wt%), but for this element, the % standard deviation is the largest observed (43%). The ranges for K₂O, TiO₂ and Fe₂O₃ are 20, 11 and 15% standard deviation, respectively.

Trace elements. All of the measured trace elements exhibited % standard deviation ranging between 10 and 20%. The lowest variations observed were for Rb and Sr (11%), while the highest were for Zn, La and Ce (20%).

Binary correlations

The first step to characterizing the behaviour of chemical elements is to use binary correlations. Table 5 summarizes correlation coefficients between the

TABLE 3. Location of sampling points, distance to the ocean, major oxide (wt%) and trace element (ppm) contents in the Loire estuary sediments

Points	Location	Distance to ocean	SiO ₂ (wt%)	K ₂ O (wt%)	CaO (wt%)	TiO ₂ (wt%)	Fe ₂ O ₃ (wt%)	Zn (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	Zr (ppm)	Sn (ppm)	Ba (ppm)	La (ppm)	Ce (ppm)
2a	Champtoceaux	86	64.17	2.29	5.49	0.86	4.7	139	61	162	233	293	12	758	40	98
2b	Champtoceaux	86	63.24	2.14	6.38	0.97	5.68	177	50	152	218	367	15	688	49	113
3	Thouaré	68	64.31	2.08	6.13	0.96	5.53	169	58	154	211	322	16	704	48	107
4	Indre	45	49.38	1.6	4.28	0.79	6.1	210	79	152	164	253	44	442	36	82
5	Cordernais	24	51.86	1.98	5.34	0.91	6.42	205	87	164	191	225	31	527	37	85
6	Donges	10	57.67	2.09	5.56	0.89	7.32	229	106	176	211	215	27	464	41	96
7	St Nazaire	0	59.71	2.22	5.44	0.92	7.05	212	103	173	222	277	25	448	48	104
8	Mindin	2	54.38	2.28	5.54	0.83	6.5	192	97	174	210	192	28	434	36	76
9	Paimboeuf	16	61.98	2.2	5.91	0.96	6.95	197	81	169	200	272	23	423	37	76
9a	Paimboeuf	16	52.48	1.96	4.66	0.86	7.55	226	97	182	191	186	27	421	32	73
9b	Paimboeuf	16	58.71	2.15	5.03	0.91	7.53	225	92	180	193	198	25	455	40	88
10	Pt Carnet	23	59.61	2.16	5.46	0.93	6.95	210	94	175	231	288	24	457	47	103
11a	Le Pellerin	38	57.56	1.76	6.25	0.83	5.3	167	68	146	191	327	24	483	44	99
11	Le Pellerin	38	49.21	1.65	5.6	0.81	5.19	178	57	141	183	309	23	465	43	91
Mean			57.45	2.04	5.51	0.89	6.34	195	81	164	204	266	25	512	41	92
SD			5.23	0.22	0.58	0.06	0.93	26	19	13	19	56	8	115	5	13
SD (%)			9	11	11	7	15	14	23	8	10	21	31	22	13	14

TABLE 4. Mean major oxides (wt%) and trace elements (ppm) contents, standard deviations and percentage standard deviations in the fluvial Loire sediments at Orleans

Elements	SD	% SD
SiO ₂ (wt%)	60.37 ± 2.63	4
K ₂ O	2.1 ± 0.41	20
CaO	10.6 ± 4.52	43
TiO ₂	0.88 ± 0.1	11
Fe ₂ O ₃	4.8 ± 0.71	15
Zn (ppm)	138 ± 34	24
Pb	52 ± 6	12
Rb	152 ± 17	11
Sr	280 ± 31	11
Zr	326 ± 59	18
Sn	19 ± 3	15
Ba	719 ± 98	14
La	53 ± 13	25
Ce	120 ± 27	23

14 analysed elements and the distance to estuary mouth D (in km). *Italic coefficients in Table 5* are statistically representative ($R > 0.52$, $n = 15$).

The coefficient correlations obtained between D and element contents can be divided into three categories. Zr, Ba and Ce decrease down estuary while Fe₂O₃, Zn, Pb, Rb and Sr increase down estuary. The other elements exhibit R less than 0.52 and are not correlated with D. Compared to previous work on the Loire estuary (Roger, 1988), the opposite evolution of metals is observed. In the study by Roger (1988), six elements (Pb, Zn, Cu, Cr, Ni and Cd) decreased down estuary and this decrease is explained by dilution of estuarine sediments by marine particles with low metal load (Etcheber, 1983; Robbe *et al.*, 1985), by organic matter mineralization (De Groot *et al.*, 1976), or by particles recycling (Boust, 1981; Frenet, 1981; Jouanneau, 1982). Pb and Zn are the two common elements between the work by Roger (1988) and the present study. For these elements, Roger (1988) concluded that the Loire estuary was unpolluted. The high levels of Pb, Zn and some other elements in the present study implies a meaningful enrichment of sediments with regards to trace metals, and therefore an important susceptibility of the Loire estuary to pollution. These results suggest a source of metals in industrialized zones bordering the estuary, and are consistent with the previous studies on the same area of As (Seyler & Martin, 1990) and Hg (Figueres *et al.*, 1985).

The coefficient correlations obtained between element contents are sometimes statistically significant and are noted in italics; however, a large number of R

coefficients are not significant, reflecting the lack of elemental relationships. For example, CaO and Sr are not correlated; likewise Fe₂O₃ and SiO₂, CaO, TiO₂ and K₂O.

Multi-element profiles in the Loire estuary

The second way to explore element variability is to look at the spatial variations using indicator elements. The normalization of the contents of chemical species to a background indicator element is often used in geochemistry (Rahn, 1975; Nesbitt, 1979; Chester *et al.*, 1985; Goldstein & Jacobsen, 1988; McLennan, 1989; Mogollon & Bifano, 1994). However, normalization to just one element (e.g. Al, Ti . . .) can be of limited use in estuarine studies because the chosen reference element can be 'unreactive' while the pollutant elements of interest are 'reactive'.

Thus, in the present study, each element Z measured in estuarine sediments is normalized to the same element Z measured in fluvial sediments, as measured previously by Cullers *et al.* (1987). Fluvial sediments (Table 4) can be polluted too but the aim of this normalization is to focus on the sediment evolution along the estuary profile. Enrichment or depletion factors (F) are located above and below a given unity line. Figure 3 summarizes the patterns for the 15 samples of estuarine sediments for the 14 measured elements. According to the precisions of the analyses, F values ranging from 0.98 to 1.02 represent any departure from unity for Fe₂O₃, Sr, Zr and Ba. Likewise, F values ranging from 0.95 to 1.05 represent any departure from unity for SiO₂, K₂O, CaO, TiO₂ and Rb, and F values ranging from 0.90 to 1.10 represent any departure from unity for Zn, Pb, Sn, La and Ce.

Fe₂O₃, Pb, Zn and Sn are significantly enriched in sediments of the estuary, except for Samples 2a and 10 for Fe₂O₃, and Samples 3 and 11 for Pb where the enrichment factor is not significantly different from unity. Zn, Pb and Sn are clearly identified as pollutant elements (Chester *et al.*, 1985; Sakai *et al.*, 1986; Mogollon & Bifano, 1994), and iron is often associated with these elements in estuarine processes (Martin *et al.*, 1976; Sholkowitz, 1976, 1992; Boyle *et al.*, 1977; Crerar *et al.*, 1981; Hoyle *et al.*, 1984; Yuan-Hui *et al.*, 1984; Goldstein & Jacobsen, 1988; Olivarez & Owen, 1991; Tanizaki *et al.*, 1992). CaO and Sr are clearly depleted for all the samples and the departure is always significant. SiO₂, K₂O, Ba, Zr, La and Ce have $F \leq 1$ but the departure from unity was not significant in six samples for SiO₂ (Samples 2a, 7, 9, 9b, 10, 11a); in five samples for K₂O (Samples 3, 6, 9, 9b, 10); in Sample 3 for Ba; in two samples for Zr

TABLE 5. Correlation coefficient R between the 14 analysed elements and the distance to the ocean

	D	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Zn	Pb	Rb	Sr	Zr	Sn	Ba	La	Ce
D	1														
SiO ₂	0.41	1													
K ₂ O	-0.09	0.71	1												
CaO	0.34	0.62	0.29	1											
TiO ₂	0.11	0.73	0.62	0.5	1										
Fe ₂ O ₃	-0.78	-0.14	0.28	-0.43	0.26	1									
Zn	-0.76	-0.4	-0.03	-0.57	0.06	0.93	1								
Pb	-0.88	-0.25	0.28	-0.5	-0.04	0.86	0.82	1							
Rb	-0.63	0.11	0.63	-0.38	0.27	0.85	0.67	0.84	1						
Sr	0.17	0.76	0.83	0.47	0.55	-0.04	-0.28	0.04	0.32	1					
Zr	0.71	0.46	-0.14	0.69	0.27	0.71	-0.69	-0.8	-0.75	0.26	1				
Sn	-0.53	-0.78	-0.54	-0.72	-0.52	0.4	0.63	0.51	0.11	-0.71	-0.54	1			
Ba	0.89	0.61	0.27	0.46	0.33	-0.68	-0.74	-0.7	-0.38	0.47	0.58	-0.7	1		
La	0.35	0.56	0.15	0.65	0.48	-0.32	-0.32	-0.38	-0.35	0.52	0.77	-0.53	0.43	1	
Ce	0.53	0.6	0.16	0.59	0.44	-0.4	-0.39	-0.42	-0.35	0.56	0.76	-0.57	0.61	0.95	1

Italic coefficients are statistically representative.

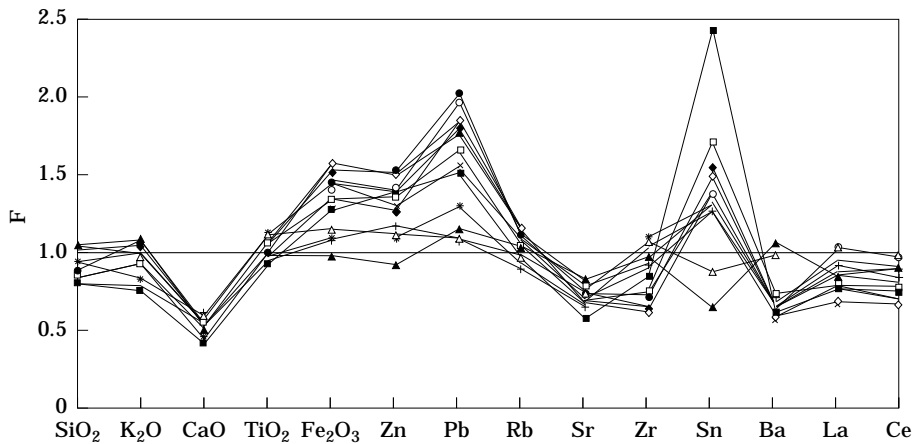


FIGURE 3. Graphs of elements *vs.* enrichment or depletion factor (F) in the 15 Loire estuary sediment samples.

(Samples 2a, 10); in four samples for La (Samples 3, 10, 11, 11a); and in five samples for Ce (Samples 2a, 3, 6, 7, 11a).

When the departure from unity is significant, the depletion of these elements can be explained either by sorption-desorption processes or dissolution of mineral phases, in which case the river-dissolved load would become enriched (Gordeev *et al.*, 1985; Goldstein & Jacobsen, 1988); or by intra-estuarine processes such as sedimentation of mineral phases and/or mixing between marine and fluvial phases (Jouanneau, 1982). Rb and TiO₂ have F close to unity, and the departure from this line is not significant for Samples 2a, 3 and 4 for Rb and for six samples for TiO₂ (Samples 2a, 6, 8, 9, 11 and 11a).

Figure 4 represents the pattern of the most fluvial and oceanic sediments collected in the Loire estuary. F for SiO₂, K₂O, TiO₂, CaO, Sr, Zr, Rb and Ce does not fluctuate between these two furthest samples. SiO₂, K₂O, TiO₂, Rb and Zr have F close to unity between landward and seaward. Likewise, Ca, Sr

show F less than 1 but close between fluvial and oceanic samples. For Ca and Sr, the mean F values are, respectively, close to 0.53 ± 0.05 and 0.73 ± 0.07 .

F for Fe₂O₃, Zn, Pb and Sn increases between these two furthest samples and this increase is significant. The highest increase is for Sn (57%), then Pb (40%), Fe and Zn (33%). A weak increase between the fluvial and the most oceanic sample is also observed for La but this increase is not significant. Finally, Ba is depleted between the fluvial and the most oceanic sample. The depletion is around 50% and can be related to sorption-desorption processes with an increase of Ba in the dissolved phase (Gordeev *et al.*, 1985; Goldstein & Jacobsen, 1988).

This pattern allows determination of two populations of chemical species according to their behaviour over the estuary. For each element, F fluctuations along the estuary profile are summarized in Figure 5.

The first group comprises the conservative elements, i.e. no general trend between F and the distance over the estuary exists although weak F fluctuations are observed during the estuary profile. Figure 5(a-f) represents the F fluctuations between the most fluvial and oceanic points for SiO₂, TiO₂, CaO, Sr, La and Ce. However, F for Ca is less than 1 but exhibits a constancy over the estuary profile. The constancy of F for Ca allows rejection of the input of marine particles which may increase the Ca content in sediments (Turner *et al.*, 1992). Sedimentation of mineral phases before the most fluvial point of the estuary can explain this value less than unity for Ca, Sr and the constancy through the estuary. For La and Ce, Gordeev *et al.* (1985) have shown similar behaviour in an Amazon estuary profile.

The second group [Figure 5(g-n)] comprises non-conservative elements over the estuary profile. For

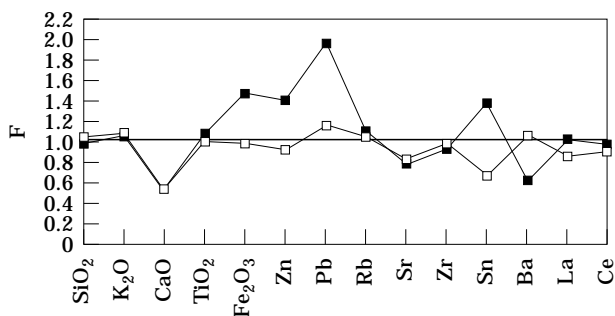


FIGURE 4. Graphs of elements *vs.* enrichment or depletion factor (F) in the most fluvial (□) and oceanic (■) samples collected in the Loire estuary.

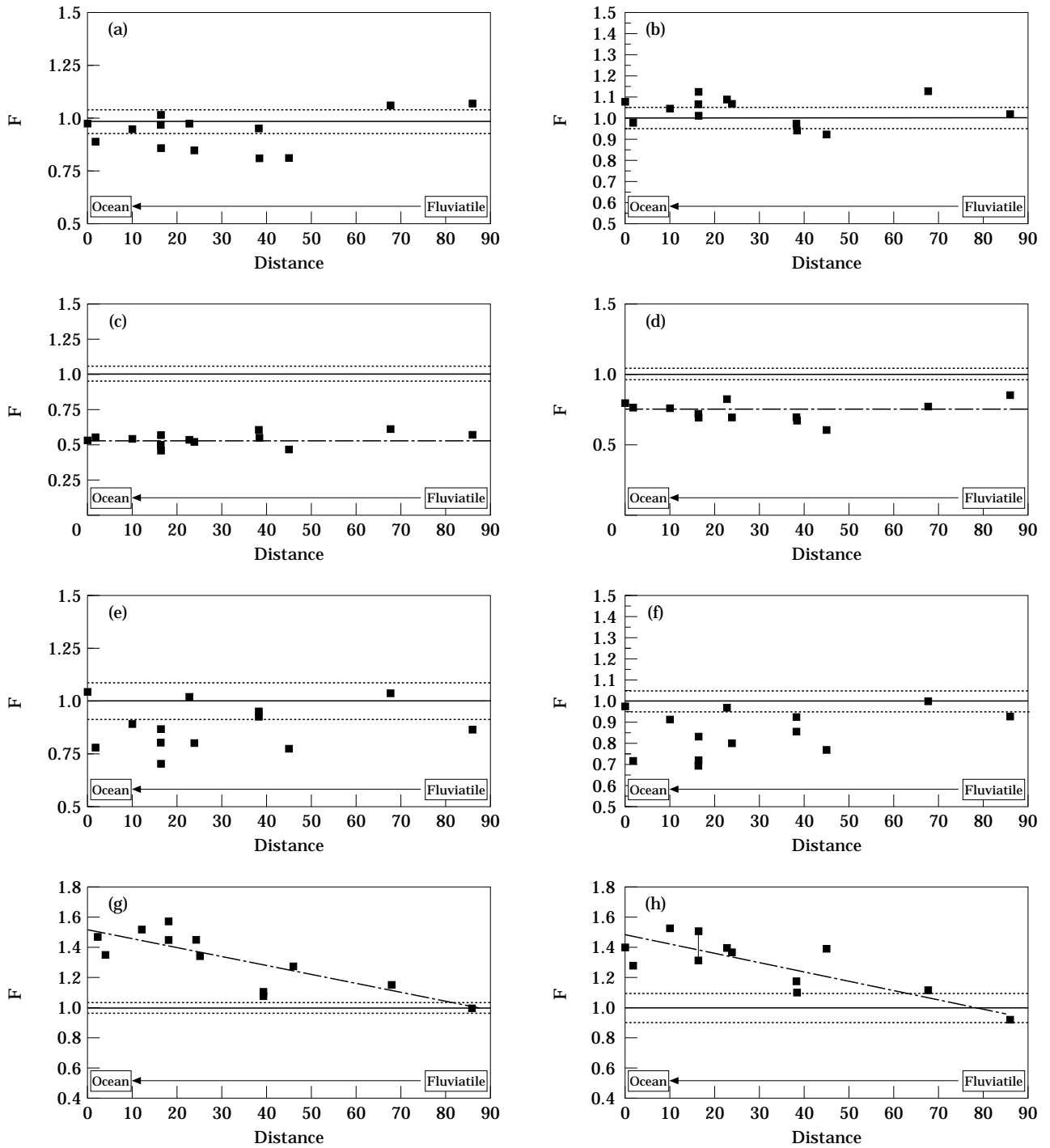


FIGURE 5. Plot of F factor vs. the distance from the ocean for each measured element. —, unity (neither enrichment nor depletion); ---, general trend, if it existed; · · ·, area where the departure from unity is not significant. (a) SiO_2 , (b) TiO_2 , (c) CaO , (d) Sr , (e) La , (f) Ce , (g) Fe_2O_3 , (h) Zn , (i) Pb , (j) Sn , (k) K_2O , (l) Rb , (m) Ba , (n) Zr .

these elements, although weak F fluctuations are observed between the most fluviatile and oceanic points, a general trend can be viewed. This group can be divided into two sub-populations. For the first

population, Fe [Figure 5(g)], Zn [Figure 5(h)], Pb [Figure 5(i)] and Sn [Figure 5(j)] exhibit F close to unity in the fluviatile part of the estuary, and F increases down estuary. All of the elements in the

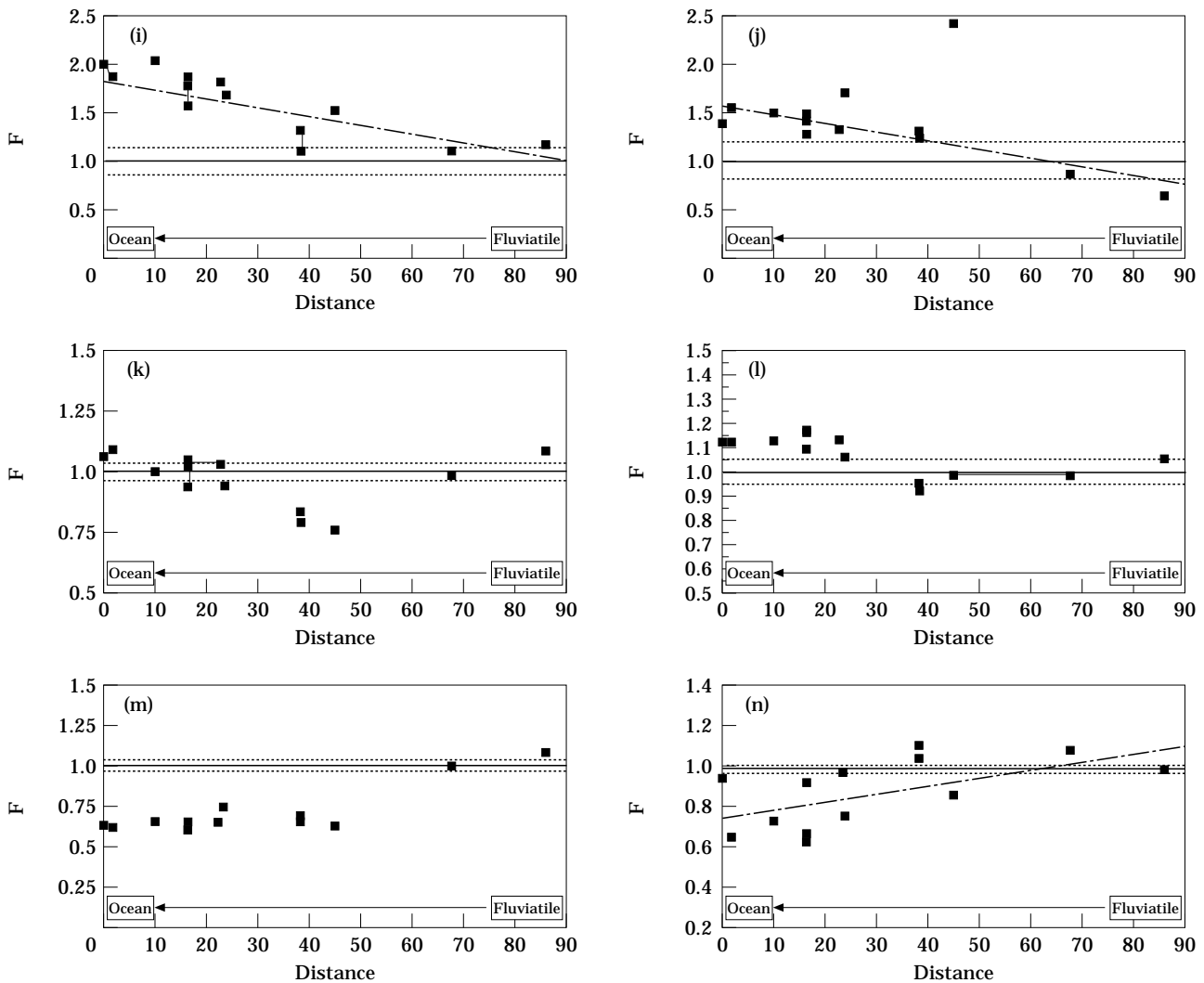


FIGURE 5. Plot of F factor *vs.* the distance from the ocean for each measured element. —, unity (neither enrichment nor depletion); ---, general trend, if it existed; ···, area where the departure from unity is not significant. (a) SiO₂, (b) TiO₂, (c) CaO, (d) Sr, (e) La, (f) Ce, (g) Fe₂O₃, (h) Zn, (i) Pb, (j) Sn, (k) K₂O, (l) Rb, (m) Ba, (n) Zr.

second population [K₂O, Figure 5(k); Rb, Figure 5(l); Ba, Figure 5(m); Zr, Figure 5(n)] are depleted down estuary.

The increase of the F parameter in sediments for Sn, Pb and Zn may probably be explained by physico-chemical interactions involving metals. These interactions occur in the freshwater/seawater mixing zone. It could be suggested that Sn, Pb and Zn are being removed from the overlying waters. Processes of removal could be adsorption and/or co-precipitation involving clay minerals and iron oxides (Moore *et al.*, 1979; Koons *et al.*, 1980; Mayer, 1982; Chester *et al.*, 1985). Koons *et al.* (1980) have shown that FeOx (which included Fe oxides, hydroxydes and oxyhydroxides) control the concentrations of many elements, especially transition metals, in estuaries.

Removal of colloidal iron material in estuaries through flocculation has been largely documented (Boyle *et al.*, 1977; Sholkowitz, 1978; Moore *et al.*, 1979; Mayer, 1982; Fox & Wofsy, 1983; Turner *et al.*, 1991), likewise for the removal of dissolved constituents in an estuarine turbidity maximum (Ackroyd *et al.*, 1986; Cossa *et al.*, 1988; Turner & Millward, 1994). This removal process may occur over long time periods in any given estuary as bed sediments undergo repeated episodes of re-suspension during tidal transport up and down estuary.

The second population comprises K₂O [Figure 5(k)], Rb [Figure 5(l)], Ba [Figure 5(m)] and Zr [Figure 5(n)]; F is close to unity in the fluviatile part of the estuary and decreases down estuary. For Zr and Ba, F falls significantly below 1 between 60 and

50 km from the estuary mouth, and then a decrease of the F parameter is observed until the ocean. For Zr, sedimentation of minerals such as zircon in the estuary can be considered. For Ba, as mentioned previously, the depletion can be related to sorption-desorption processes with an increase of Ba in the dissolved phase (Gordeev *et al.*, 1985; Goldstein & Jacobsen, 1988). For K₂O and Rb, a significant decrease of the F parameter can be observed until 40 km from the estuary mouth, and then F increases between 40 km and the mouth. Hydrodynamic processes are thought to be responsible for the fluctuations of F for K and Rb. These two elements are generally associated in mineral phases like biotites and feldspars (Faure, 1986), which are present in sand and silt fractions. Huang *et al.* (1985) have shown that these fractions in sediments from the Yellow river estuary were higher in the surface layers of cores, while clay fractions were higher in the lower layers of the same cores. This partition reflects the different transportation and re-suspension characteristics of minerals in estuaries. In the Loire estuary, re-suspension of particles in the TM due to tidal currents can explain the observed fluctuations of F for K and Rb.

Sources of particles in the Loire estuary

Pollutant metals increase over the estuary profile whereas other elements decrease or remain constant. It has been shown above that Fe, Pb, Zn and Sn exhibit identical patterns, and one can conclude that metals like Pb, Zn and Sn are highly linked with Fe behaviour. Several studies on estuarine processes (Conley *et al.*, 1971; Sholkowitz, 1976; Moore *et al.*, 1979; Crerar *et al.*, 1981; Mayer, 1982; Tanizaki *et al.*, 1992) have demonstrated the occurrence of Fe oxide, hydroxide flocculation and organic matter-metal complexation at the river-oceanic interface. One of the most important trace element concentrators in sediments is Fe oxide and hydroxide phases (Moore *et al.*, 1979; Koons *et al.*, 1980; Mayer, 1982; Chester *et al.*, 1985; Horowitz & Elrick, 1987). In order to investigate the evolution of chemical species

TABLE 6. Principal component analysis (PCA) results for the 13 X/Fe ratios (X being Si, Ca, K, Ti, Pb, Zn, Sn, Zr, Rb, Sr, Ba, La, Ce) for the Loire estuary sediments

	First direction	Second direction	Third direction
% variance	71	15	8
Si/Fe	<i>0.98</i>	-0.1	0.1
Ca/Fe	<i>0.94</i>	0.12	0
K/Fe	<i>0.89</i>	-0.36	0.21
Ti/Fe	<i>0.98</i>	0.1	-0.1
Rb/Fe	<i>0.87</i>	-0.14	0.4
Sr/Fe	<i>0.96</i>	-0.15	0.21
Zr/Fe	<i>0.92</i>	0.31	0.12
Ba/Fe	<i>0.95</i>	0	0.1
La/Fe	<i>0.92</i>	0.24	-0.1
Ce/Fe	<i>0.95</i>	0.20	0
Pb/Fe	-0.5	-0.24	<i>0.77</i>
Zn/Fe	0.03	<i>0.96</i>	0.12
Sn/Fe	-0.4	<i>0.76</i>	0.4

Italic coefficients are statistically representative.

relative to Fe behaviour in Loire estuary sediments, X/Fe ratios (X=Si, Ca, K, Ti, Pb, Zn, Sn, Zr, Rb, Sr, Ba, La, Ce) are used. Previously, it has been shown that one component of the sediment particles is of fluvial origin and that most elements are not linked together (see Table 5). The spatial variability of X/Fe ratios can be examined through principal component analysis (PCA). A PCA was performed for the 13 X/Fe ratios among the 15 estuarine samples, and results are presented in Table 6. Results are described in terms of percentage of the total variance of the data, and indicate that 94% of the variability is explained by three principal directions. Seventy-one percent of the total variance is explained by the first principal component, 15% by the second one and 8% by the third one. Considering different origins for particles in sediments, it is necessary to take four components into account to explain such data dispersion.

Table 7 gives the correlation coefficients between each element ratio data series and the project along the different directions. The first principal direction

TABLE 7. Relationship between La/Fe and Ce/Fe ratios with the four individualized groups, the corresponding samples and the percentages of the fluvial end-member (FPEM)

Group	La/Fe	Ce/Fe	Samples	FPEM (%)
1	0.0024/0.0025	0.005/0.006	2a, 2b, 3, 11, 11a,	85-90
2	0.0019	0.0042	7, 10	68
3	0.0015	0.003	4, 5, 6, 8, 9, 9b	50-60
4	0.0012	0.0028	9a	44

results from a simultaneous effect of Si, Ca, K, Ti, Rb, Sr, Zr, Ba, La and Ce *vs.* Fe ratios ($0.87 < R < 0.98$). The second principal direction results from an effect of Zn and Sn *vs.* Fe ratios (R close to 0.96 and 0.76, respectively). The third principal direction is linked with a Pb/Fe effect ($R = 0.77$). The main conclusion of PCA is that four components are required to explain the variability of the 13 X/Fe ratios. Two components explain nine of the chemical species' fluctuations and their variability is included in a plane. This is surprising considering to the mineralogical composition of sediments with four clay types plus primary minerals like potassic feldspars, biotites, zircons, heavy minerals etc. In spite of the mineralogical heterogeneity, two components are enough to explain the observed variations.

Two other components are required to explain both Zn and Sn on one hand and Pb on the other hand. It has been shown previously that Pb, Sn and Zn could be linked with adsorption and/or co-precipitation involving clay minerals and iron oxides (Moore *et al.*, 1979; Koons *et al.*, 1980; Mayer, 1982; Chester *et al.*, 1985). Likewise, Chester and Stones (1975) have shown a similar partition between Pb and Zn and an opposite one for Sn in sediments from the Bristol Channel. Moreover, they showed that leachable Zn and Pb have probably been removed from the overlying waters while this process cannot explain the excess concentration of Sn. In the present study, opposing observations are made and different processes must be considered. For example, the observed Zn and Sn distributions could result from the flocculation of humic acids-metal complexes (Yuan-Hui *et al.*, 1984) and Pb by adsorption onto iron oxides (Horowitz & Elrick, 1987; Evans & Davies, 1994). For further investigations, leaching experiments and selective extractions will need to be carried out to increase our knowledge of metal behaviour in the Loire estuary, and to determine the primitive origin of Zn, Pb and Sn before their control by these processes.

Mixing of particles in the Loire estuary

The next step of this study is to formalize a mixing model between the two main components which explains the fluctuations of nine chemical species. For this, constraints on the source reservoirs that correspond to the end-members must be added.

To investigate binary mixtures in sediments, the relationship between rare earth elements (REE) and iron will be used. The REE are generally considered to be resistant to weathering and so are mainly associated with residual mineral phases (Nesbitt, 1979; Faure, 1986; Cullers *et al.*, 1987; Middelburg *et al.*, 1988).

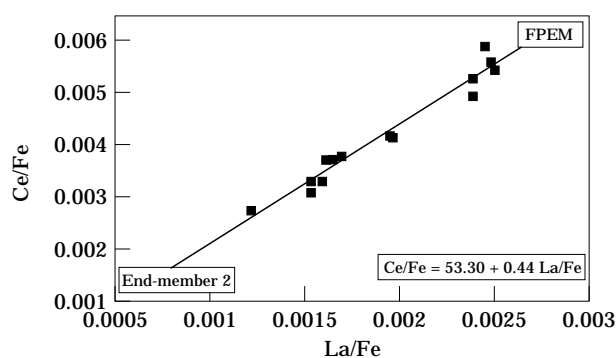


FIGURE 6. Relationship between La/Fe and Ce/Fe ratios in the Loire estuary sediment samples. Fluvial particles end-member (FPEM) and *in situ* end-members are indicated.

Another consequence of their low solubilities is the weak dissolved REE fraction in natural waters (Keasler & Loveland, 1982; Brookins, 1989). The affinity of REE for Fe oxyhydroxides in supergene environments has already been established (Fleet, 1984). Likewise, in estuarine environments, REE and iron behave similarly in the dissolved load. Martin *et al.* (1976), Hoyle *et al.* (1984), Gordeev *et al.* (1985), Goldstein and Jacobsen (1988), Elderfield *et al.* (1990), Olivarez and Owen (1991) and Sholkowitz (1992) have shown that removal of colloidal Fe material through coagulation and Fe oxide and hydroxide flocculation both result in REE co-precipitation. Goldstein and Jacobsen (1988) and Elderfield *et al.* (1990) have shown that more than 70% of dissolved REE was removed with Fe colloidal material during estuarine mixing as soon as salinity values reached 5.

Figure 6 demonstrates the close relationship between La/Fe and Ce/Fe ratios. The linear relationship for all of the sediment samples agrees with two end-member mixing, and the linear regression analysis for REE/Fe (REE=La, Ce) ratios shows a correlation coefficient R of 0.98. Thus, it is assumed that this linear relationship is the result of mixtures of a fluvial particles end-member (FPEM) originating from the Loire river and particles produced *in situ* in the estuary. In Figure 6, four groups of points can be specified. The range of La/Fe and Ce/Fe ratios and the associate samples are indicated in Table 7.

Assuming two end-member mixing, the following mixing equation can be applied (Faure, 1986):

$$X_m/Y_m = aX_a/Y_a + (1 - a)X_b/Y_b \quad (1)$$

where X/Y is the La/Fe or Ce/Fe ratio, m is mixing, a and b are the two components involved in the mixing, a is the proportion of a in $a+b$, and $1 - a$ is the proportion of b in $a+b$.

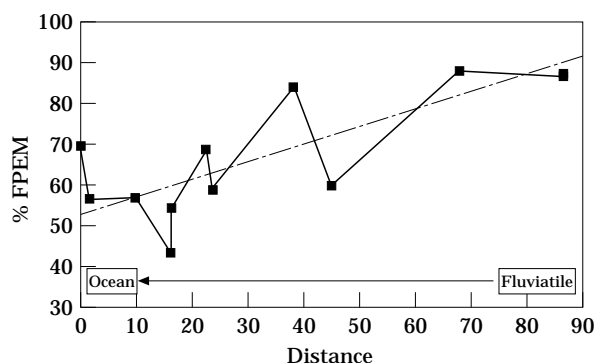


FIGURE 7. Relationship between fluvial particles end-member (FPEM) and the distance from the ocean; ---, linear regression analysis ($R=0.80$); the intercept at $D=0$ is 53%.

The next step is to characterize the end-members before computing the calculation of a and $1 - a$. Data for fluvial sediments suggest that this type of material (FPEM) constitutes one of the end-members. Therefore, FPEM La/Fe and Ce/Fe ratios are close to 0.003 and 0.006, respectively. The second end-member corresponds to the particles issued from estuarine processes. Gordeev *et al.* (1985) have shown that in the Amazon estuary, these types of particles have La/Fe ratios ranging between 0.0006 and 0.0008, and Ce/Fe ratios ranging between 0.001 and 0.0015.

Assuming a two component mixing between fluvial particles and particles produced *in situ*, it would appear that FPEM contributes ~ 85 – 90% of the sediment in the fluvial zone of the estuary and $\sim 44\%$ in the lower estuary near the mouth (Table 7). Conversely, the particles produced *in situ* contribute ~ 10 – 15% in the most landward area of the estuary and $\sim 56\%$ in the most seaward zone. In the TM, measured SPM is close to 3.06 g l^{-1} ; the result of the mixing model shows that FPEM contributes 52% of this load. This result implies that 1.58 g l^{-1} of SPM originates in the riverine Loire.

The results over the estuary profile are exemplified for the fluvial source (Figure 7). Although the general trend in Figure 7 suggests a substantial decrease of FPEM down estuary (50% over a profile of 100 km), reflecting sedimentation processes of terrigenous particles, a decrease of FPEM in the TM area (FPEM close to 44–54%) and an increase of FPEM over the last 20 km of the estuary can also be seen. Fluvial particles end-member proportions vary from 44 to 54% at Station 9 (Paimboeuf), 20 km from the mouth, to 70% at the most oceanic point of the present survey.

The fluctuations of FPEM which occur in the moist seaward part of the Loire estuary can be explained by

transportation and deposition processes of sediments. The high permanently suspended matter load in the TM zone could induce sedimentation of terrigenous particles with high density (Morris *et al.*, 1987). The FPEM increase between the TM and the estuary mouth of up to 70% can be explained by re-suspension of detrital particles in the vicinity of the region of maximal tidal stress (Morris *et al.*, 1987). However, an input of terrigenous particles via the marine intrusion could also be possible. These particles could have originated in coastal erosion or in continental erosion processes located in watersheds other than the Loire river.

The general trend in Figure 7 can be used to constrain the percentage FPEM export by the Loire estuary. The linear regression analysis for FPEM *vs.* the distance of the ocean shows that the intercept at $D=0$ is close to 53% and the correlation coefficient R is 0.80. If the SPM near the estuary mouth (160 mg l^{-1} in this study) is constant over the year, according to the mean annual water discharge of $850 \text{ m}^3 \text{ s}^{-1}$, the annual exportation load by the Loire river is $4.3 \times 10^9 \text{ kg year}^{-1}$. The present estimate is greater (factor 4) than the value ($10^9 \text{ kg year}^{-1}$) given by Figueres *et al.* (1985). According to the mixing model, a flux of around $2.3 \times 10^9 \text{ kg year}^{-1}$ was obtained for terrigenous particles and a flux of around $2 \times 10^9 \text{ kg year}^{-1}$ was obtained for particles produced *in situ* in the estuary.

This first approximate flux of suspended materials from the Loire estuary and their genetic origin give an idea of the input to coastal zone, which is otherwise extremely difficult to evaluate (Turner *et al.*, 1991).

Conclusions

The chemical composition of bed sediments in the Loire estuary and their evolution between landward and seaward have been investigated. The concentrations of five major oxides (SiO_2 , K_2O , CaO , TiO_2 and Fe_2O_3) and nine trace elements (Rb, Sr, Zr, Zn, Pb, Sn, La, Ce and Ba) have been measured.

Enrichment or depletion factors when normalized to fluvial concentrations show that Fe_2O_3 , Zn, Pb and Sn are significantly enriched down estuary, whereas K_2O , Rb, Zr and Ba are depleted down estuary. SiO_2 , TiO_2 , CaO , Sr, La and Ce behave conservatively over the estuary profile.

Principal component analysis performed for X/Fe ratios shows that the variability of the data is explained by at least four components. Two components explain nine chemical elements; the first end-member is represented by the fluvial particles, the second one is represented by particles produced *in situ* in the estuary

area. Two other components are required to explain the variability of Zn and Sn on one hand and Pb on the other hand. These components can be related to adsorption and/or co-precipitation and/or flocculation onto clay minerals, Fe oxyhydroxides and/or humic acids complexes.

The relationship between REE (La and Ce) *vs.* Fe ratios can be used as a tool for quantifying the amount of the two particle sources in the estuarine area. In addition, these results illustrate the important contribution that sediments of a fluvial origin make to the bed sediments within the Loire estuary system. Approximately 50% of the sediments transported seaward is of terrestrial origin.

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