# SEDIMENT, PARAMETERS AND DISTRIBUTION OF METALS IN FINE SEDIMENTS OF THE LOIRE ESTUARY

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**Abstract.** The station to elevation of six metals (Cd, Cu, Fe, Mn, Pb and Zn) were studied in the fine sediments of five lateral mud flats of the Loire estuary. Sediment samples were taken at the lower and upper limits of the intertidal zone each season and at spring tide twice a month. The correlation between metal content and various sediment parameters was measured, such as water, carbonate and organic matter content, salinity and mineralogical composition. Metal content was always found to be highest at the top of the mud flat for all sites studied, as were water and organic matter content. However, salinity and carbonate content varied inversely with elevation. Metal content was always higher in summer than in winter. It eis essential to specify sampling location and season as well as the altimetric position at which each sample was taken.

## 1. Introduction

The levels of six metals (Cd, Cu, Fe, Mn, Pb, Zn) in the fine fraction <45 μm) of the sediments at five stations spaced out along the south bank of the Loire estuary were measured in order to study their spatial distribution. The estuary is wide open to the tide the influence of which can be felt to a point upstream of Nantes; salinity varied between 0‰* at Nantes to 33‰ at la Gravette (Map No. 1); the tidal range is 5.7 m at spring tides. At low tide, wide mud flats (70 to 400 m) are uncovered specially on the south side of the estuary. (Map from "Le Port Autonome Nantes – Saint-Nazaire, scale 1/25 000). previous work suggests that the characteristics of the mud at the top and bottom of these mud flats must be different considering the variation in emersion time (Barbaroux, 1982). The same may also be true for metal distribution in the mud flat. This led us to analyze the amounts of Cd, Cu, Fe, Mn, Pb, and Zn in the fine sediments of mud taken from the top and bottom of the mud flats along the south bank of the Loire estuary for each season. So, we studied, first of all the longitudinal variations of metal levels along the southern side of the estuary. Then the lateral distribution between the upper and lower limits of the uncovered mud flats and the seasonal distribution of the metals.

Finally we studied the sediment parameters: water content, salinity, mineralogical composition, carbonates and organic matter to determine the selective distribution of the metals as a function of location and time (Piron-Frenet, 1988).

* 1‰=0.1%

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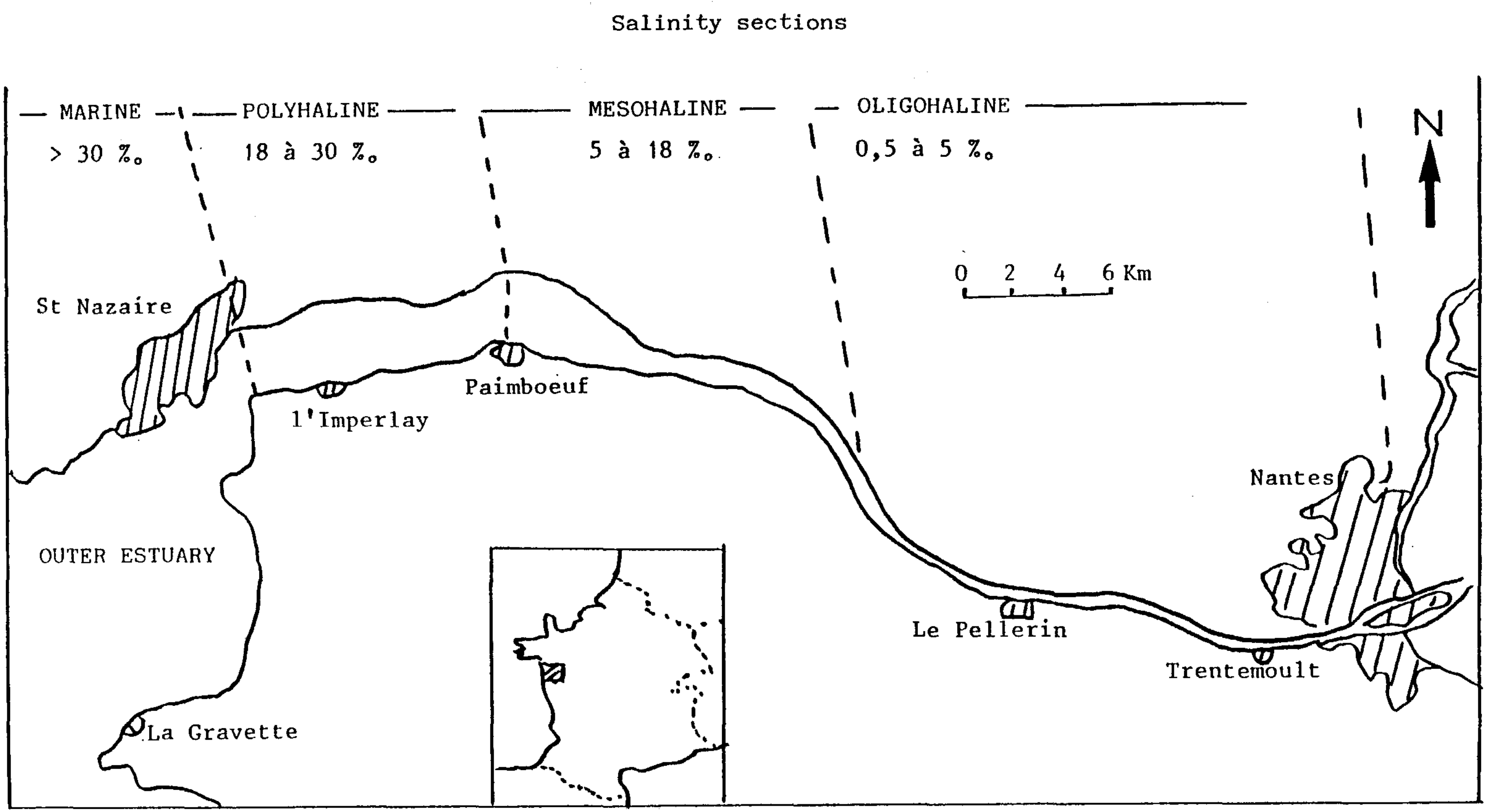


Fig. 1. Map of the Loire estuary.

## 2. Material and Methods

### 2.1. Samples

Samples were collected each season at the upper and lower limits of five mud flats along the southern bank of the Loire estuary (Figure 1). Core samples of approximately 1 m in length were taken, using a staff type core drill (Ottman *et al.*, 1972). Sediment analyses and the metal content were conducted for each sample.

### 2.2. Analysis of sediment parameters

Water content was determined by the formula $\frac{\text{water weight}}{\text{dry sediment weight}} \times 100$. This ratio may be greater than 100. This water content includes: water trapped within the sediment's structural network, water absorbed by the surface of solid particles, water associated with mineral and organic colloids in the sediment. Mud samples were weighed in a stainless steel crucible of known weight and volume dried at 105 °C for 24 hr. It was then weighed after cooling to room temperature.

Carbonate levels were measured in the fine fraction of 2 g of fine dry sediment ($<$45 μm) with a Dietrich-Scheibler calcimeter (Osi-France). results are expressed as a percentage of dry weight.

The organic matter content was determined by heating 2 g of fine sediment to 450 °C for 2 hr; the loss of weight was used to determine the organic matter content, commonly named decomposable matter. There are slight differences between the percentage of weight lost by heating and the relation used by Trask and Patnode (1942): organic matter content = 1.8 × organic C.

Mineralogical composition analysis was made by X-ray diffractometry (Siemens) using the methods of Biscaye (1965), Robert (1975), and Srodon and Eberl (1980). Sediment in the Loire estuary is essentially composed of four main types of clays: illite, kaolinite, chlorite and smectite. There are also very small quantities of pyrophillite and palygorskite.

Circulating water was used for salinity measurement by the titrimetric method of Mohr-Knudsen (Ivanoff, 1972).

### 2.3. Analysis of metal content

Four g of fine sediment ($<$45 μm) were weighed in a silica crucible and placed in a muffle furnace at 420 °C for 24 hr. After cooling, the dry residue was added with a 5N solution of Suprapur Merck HCl and filtered through Whatman paper No. 42 into 10 mL single-use test tubes. The total volume was made up to 10 mL and the acid digest analyzed by air-acetylene flame atomic absorption using a Philips Pye Unicam SP9 spectrometer (Frenet, 1981; Frenet and Mougani, 1982).

## 3. Results

The results of analysis are summarized in Table I.

TABLE I

Metal level and sediment parameter according to depth and location

| Location | Season | Sampling position on the bank | Metal level μg g⁻¹ (dry weight) | | | | | | Water content % | $CaCO_3$ % | Organic matter content % | Mineralogic composition % | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Cd | Cu | Fe×10 | Mn | Pb | Zn | | | | Kaolinite | Illite | Smectite | Chlorite |
| Trentemoult | Winter | Up | 1.2 | 1.3 | 5.12 | 146 | 22.5 | 84.0 | 193 | 11 | 8 | 27 | 27 | 21 | 25 |
| | | down | 1.1 | 1.3 | 3.06 | 334 | 24.5 | 36.0 | 185 | 12 | 8 | 26 | 32 | 20 | 22 |
| | Spring | Up | 0.5 | 0.5 | 2.50 | 361 | 21.0 | 29.0 | 201 | 11 | 10 | – | – | – | – |
| | | down | 0.5 | 0.5 | 1.60 | 226 | 15.0 | 17.5 | 167 | 14 | 10 | | | | |
| | Summer | Up | 1.7 | 5.6 | 13.44 | 460 | 32.5 | 78.0 | 189 | 14 | 9 | 26 | 32 | 19 | 23 |
| | | down | 1.4 | 7.5 | 14.25 | 575 | 39.0 | 102.0 | 180 | 16 | 10 | 26 | 34 | 17 | 23 |
| | Autumn | Up | 1.2 | 4.4 | 14.60 | 492 | 34.8 | 81.0 | – | – | – | – | – | – | – |
| | | down | 1.1 | 3.5 | 12.90 | 420 | 29.5 | 62.0 | 220 | 12 | 11 | 26 | 32 | 28 | 22 |
| Le Pellerin | Winter | Up | 1.0 | 1.1 | 2.87 | 225 | 12.0 | 16.0 | 178 | 9 | 8 | 25 | 35 | 17 | 23 |
| | | down | 0.9 | 0.7 | 1.62 | 251 | 17.5 | 17.5 | 180 | 12 | 9 | 27 | 33 | 19 | 21 |
| | Spring | Up | 1.1 | 1.4 | 2.09 | 296 | 14.4 | 25.9 | 222 | 11 | 10 | – | – | – | – |
| | | down | 0.9 | 1.0 | 1.50 | 223 | 5.6 | 15.6 | 187 | 13 | 7 | | | | |
| | Summer | Up | 1.6 | 13.0 | 17.50 | 865 | 35.0 | 147.0 | 193 | 12 | 10 | 25 | 30 | 20 | 25 |
| | | down | 1.5 | 6.4 | 21.00 | 732 | 34.3 | 109.0 | 114 | 14 | 7 | 25 | 32 | 21 | 22 |
| | Autumn | Up | 0.9 | 5.3 | 15.31 | 492 | 31.2 | 67.5 | 227 | 10 | 11 | 25 | 35 | 23 | 17 |
| | | down | 1.0 | 4.2 | 15.31 | 451 | 37.5 | 59.5 | 172 | 13 | 9 | 27 | 33 | 19 | 21 |
| Paimboeuf | Winter | Up | 1.2 | 4.5 | 2.18 | 123 | 27.5 | 36.8 | 151 | 10 | 9 | 25 | 35 | 16 | 24 |
| | | down | 0.8 | 3.0 | 0.85 | 204 | 10.0 | 7.5 | 170 | 12 | 10 | 25 | 37 | 17 | 21 |
| | Spring | Up | 1.4 | 3.8 | 1.90 | 196 | 16.0 | 18.0 | 234 | 10 | 10 | – | – | – | – |
| | | down | 1.2 | 2.7 | 1.28 | 215 | 15.0 | 12.5 | 92 | 11 | 8 | | | | |
| | Summer | Up | 1.6 | 13.0 | 25.78 | 334 | 45.5 | 98.0 | 160 | 10 | 10 | 28 | 31 | 22 | 19 |
| | | down | 1.2 | 9.2 | 11.56 | 546 | 37.5 | 66.0 | 88 | 12 | 9 | 21 | 28 | 27 | 24 |
| | Autumn | Up | 1.0 | 6.0 | 9.37 | 194 | 29.5 | 40.0 | 178 | 11 | 9 | 25 | 35 | 24 | 16 |
| | | down | 1.2 | 6.4 | 12.20 | 383 | 30.0 | 49.0 | 79 | 12 | 7 | 25 | 37 | 17 | 21 |

*Table I (continued).*

| Location | Season | Sampling position on the bank | Metal level µg $g^{-1}$ (dry weight) | | | | | | Water content % | $CaCO_3$ % | Organic matter content % | Mineralogic composition % | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Cd | Cu | Fe×10 | Mn | Pb | Zn | | | | Kaolinite | Illite | Smectite | Chlorite |
| L'Imperlay | Winter | Up | 0.9 | 0.4 | 4.37 | 16 | 18.7 | 25.0 | 161 | 8 | 8 | 30 | 36 | 19 | 15 |
| | | down | 0.5 | 1.1 | 12.81 | 160 | 16.2 | 20.9 | 126 | 11 | 10 | 25 | 32 | 20 | 23 |
| | Spring | Up | 1.0 | 1.2 | 5.90 | 145 | 35.0 | 54.0 | 109 | 10 | 9 | | | | |
| | | down | 0.9 | 1.7 | 3.12 | 168 | 22.5 | 35.6 | 118 | 10 | 9 | – | – | – | – |
| | Summer | Up | 1.5 | 8.0 | 1.90 | 285 | 32.0 | 100.0 | 100 | 10 | 9 | 27 | 38 | 16 | 20 |
| | | down | 1.4 | 7.0 | 1.50 | 402 | 24.5 | 71.5 | 120 | 13 | 9 | 26 | 39 | 14 | 21 |
| | Autumn | Up | 0.6 | 1.1 | 3.20 | 112 | 16.2 | 23.7 | 122 | 10 | 8 | 30 | 36 | 15 | 19 |
| | | down | 1.1 | 0.7 | 3.74 | 203 | 18.5 | 24.0 | 101 | 12 | 6 | 25 | 32 | 20 | 23 |
| La Gravette | Winter | Up | 1.2 | 1.7 | 3.12 | 159 | 20.0 | 25.5 | 206 | 11 | 9 | 23 | 33 | 21 | 23 |
| | | down | 0.7 | 2.1 | 2.65 | 148 | 24.0 | 39.0 | 164 | 10 | 11 | 29 | 31 | 21 | 19 |
| | Spring | Up | 0.9 | 1.9 | 4.80 | 239 | 38.4 | 49.0 | – | – | – | | | | |
| | | down | 0.7 | 2.6 | 2.34 | 109 | 21.7 | 33.1 | 98 | 10 | 11 | – | – | – | – |
| | Summer | Up | 1.5 | 8.7 | 3.50 | 285 | 41.0 | 112.0 | – | – | – | | | | |
| | | down | 1.1 | 8.0 | 2.43 | 346 | 43.1 | 120.0 | 285 | 11 | 11 | – | – | – | – |
| | Autumn | Up | 1.0 | 3.5 | 4.06 | 130 | 17.4 | 31.2 | 167 | 11 | 8 | 26 | 37 | 15 | 22 |
| | | down | 0.9 | 2.5 | 4.37 | 156 | 22.4 | 31.2 | 161 | 12 | 7 | 29 | 31 | 21 | 19 |

### 3.1. Sediment parameters

The water content (Figure 2) decreased in the estuary from Trentemoult (Near Nantes) to Paimboeuf-l'Imperlay, then increased considerably at La Gravette in the outer estuary (Table I). It was always greater at the upper part of the mud flat regardless of the sampling area. Seasonal variations indicated that water content was greaster in winter than in summer.

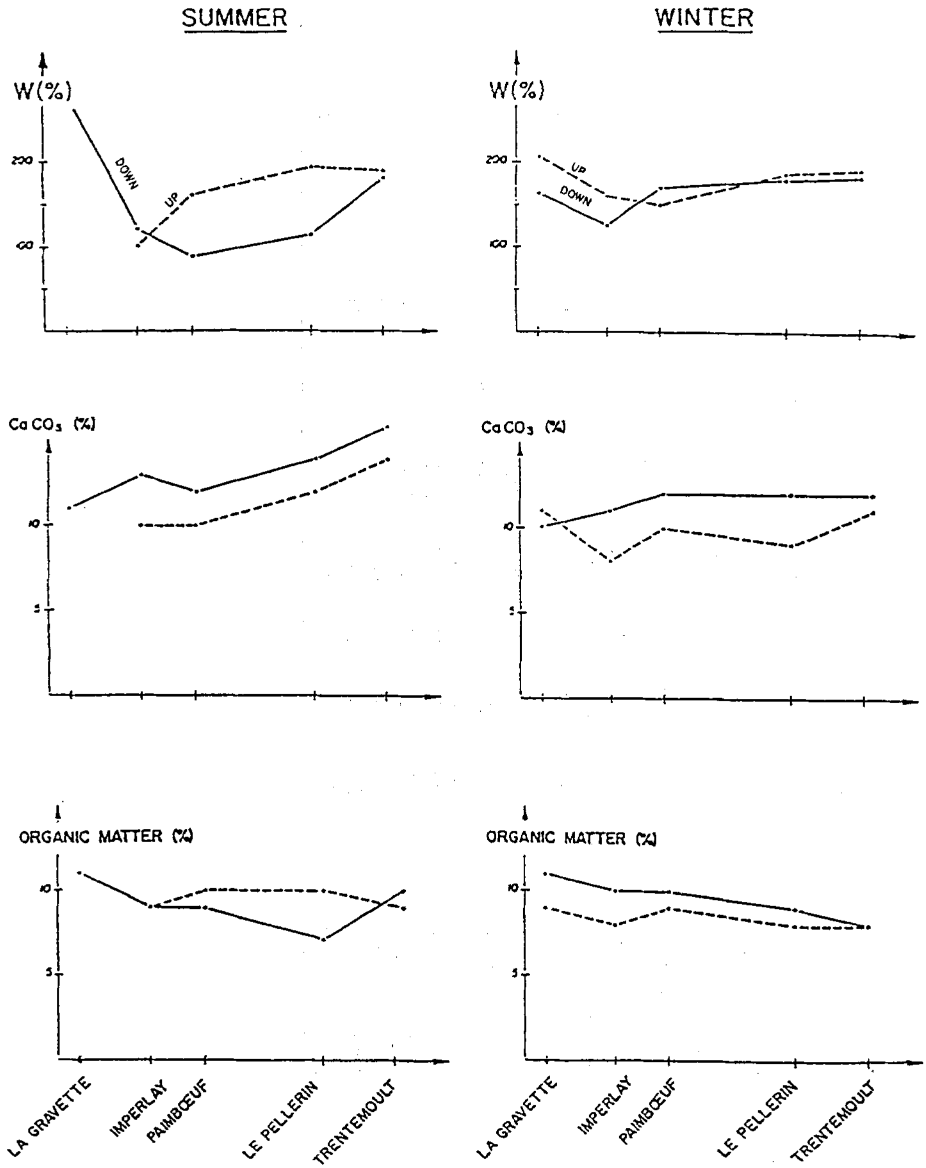


Fig. 2. Longitudinal profiles of the sediment parameters according to time and sampling location (--- top of the mud flat; —— bottom of the mud flat).

TABLE II

Seasonal and spatial distribution of salinity (S ‰) in the fairway of the Loire estuary

| Season | Location | | | | |
|---|---|---|---|---|---|
| | Trentemoult | Le Pellerin | Paimboeuf | L'Imperlay | La Gravette |
| Winter | 0 | 0 | 0.5 | 14 | 22 |
| Spring | 0 | 0 | 1.0 | 10 | 22 |
| Summer | 0 | 0 | 2.0 | 18 | 33 |
| Autumn | 0 | 0 | 5.0 | 22 | 28 |

The carbonate content (Figure 2) varied from 6 to 16%. It decreased from Trentemoult to La Gravette, and was higher at the bottom of the mud flat and during summer throughout the estuary.

The percentage of organic matter decreased from upstream to downstream, and was higher at the top of the mud flat than at the bottom. Seasonal variations were of little importance (Figure 2).

The spatial and seasonal variations for kaolinite and chlorite (Table I) were relatively minor. Their mean contents are, respectively, 25 and 21%. The behavior of illite and smectite was opposite but their lateral and seasonal variations were minor.

The salinity (Table II) of free-circulating water decreased from upstream to downstream (outer estuary). Salinity was highest in summer at all points of the estuary and at the bottom of mud flats. Channel water in the Loire estuary was stratified whereas marginal waters were fresher (Gallenne, 1974). At Paimboeuf, for example, salinity was 10 g $L^{-1}$ in the middle of the fairway and 1 g $L^{-1}$ at the top of the mud flat (Boutelier *et al.*, 1982).

### 3.2. Metal analysis results

Cadmium (Figure 3) was present in small amounts which varied little. However the content at the top of the mud flat was always slightly higher. Copper content was higher at the top of the mud flat than at bottom. It may be 10 and even 19 times higher in summer than in winter (Table I – Figure 3). Iron content variations with respect to location and season were the same as for Cu, and were always highest at the top of the mud flat and in summer. The largest variations were noted between Le Pellerin and Paimboeuf (Figure 3). Manganese content was highest in samples taken at the bottom of the mud flat in summer (Figure 4). Lead content did not vary substantially. There was very little difference in winter between the top and bottom of the mud flat. In summer, the Pb content of samples taken from the top of the mud flat were highest. However, Pb content was higher in the summer (Figure 4). Zinc content decreased from Nantes to l'Imperlay and then increased appreciably at La Gravette. It was higher in summer and at the top of the mud flat for all sites studied (Figure 4).

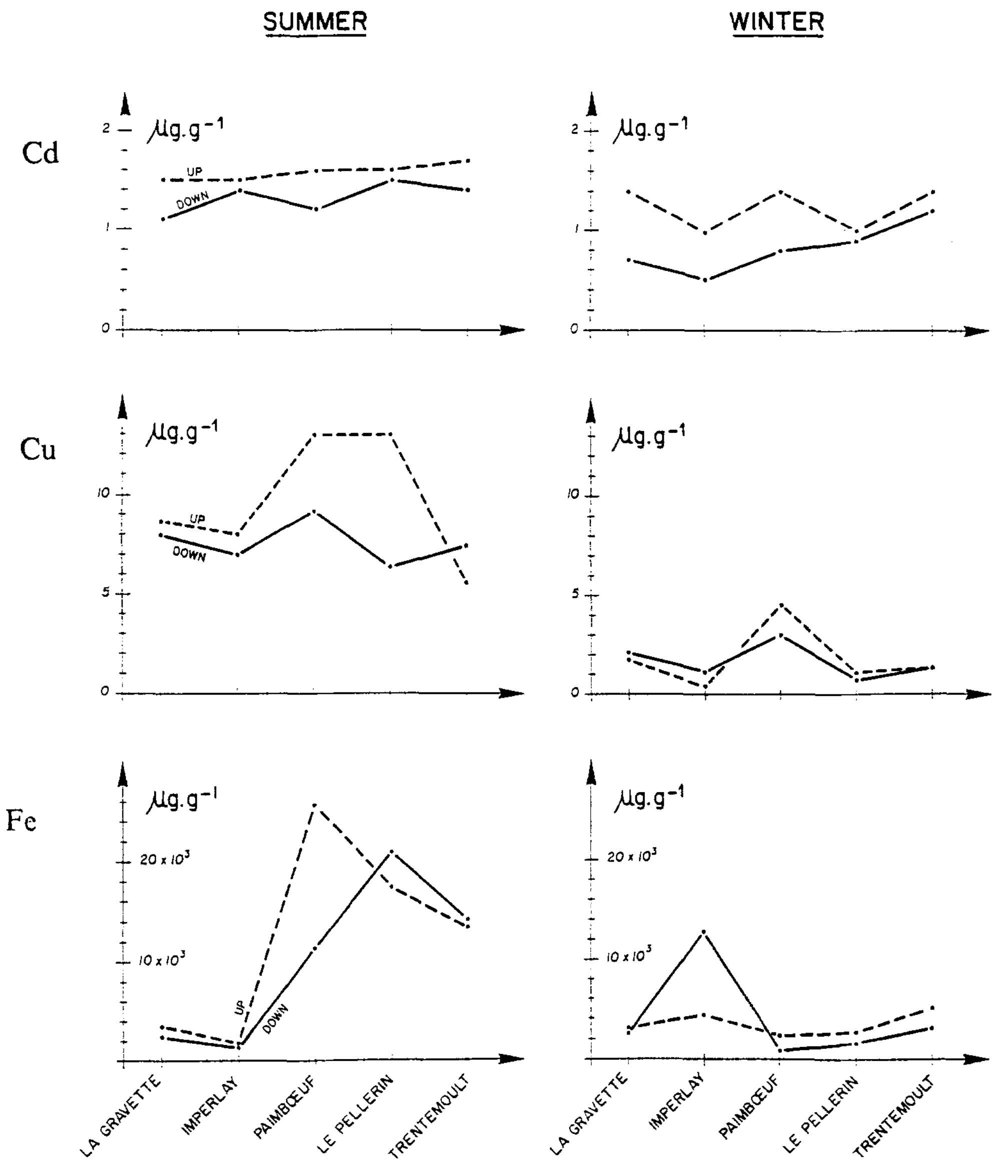


Fig. 3. Longitudinal profiles of metal content according to time and sampling location (. . . top of the mud flat; —— bottom of the mud flat).

## 4. Discussion

Parameters such as water, organic matter content and metal content (with the exception of Mn) varied similary from upstream to downstream and laterally. Their respective amounts decreased in the inner estuary from Nantes up to a point opposite Paimboeuf-l'Imperlay, then increased in the outer estuary. Quantities were always

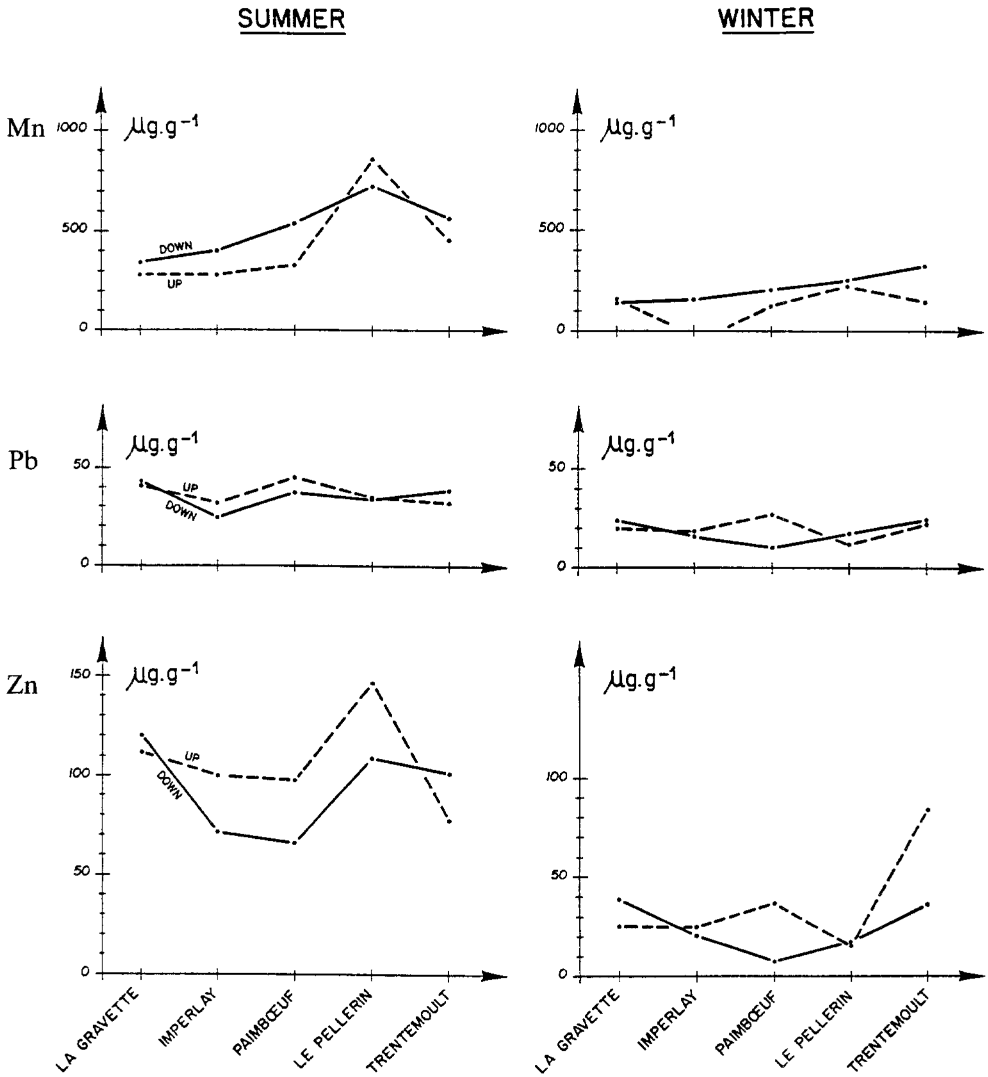


Fig. 4. Longitudinal profiles of metal content according to time and sampling location (. . . top of the mud flat; —— bottom of the mud flat).

higher at the top of the mud flat.

However, carbonate, Mn content, and salinity were always higher at the bottom of the mud flat. There are various possible explanations for these differing modes of variation.

In terms of estuary shape, the river bed is banked by two major narrow areas: one at Donges – Paimboeuf and another at Saint-Nazaire – Mindin (Gilbert, 1885). These two points define a zone characterized by the following: a percentage of coarse sediment ($>45$ µm) which may reach 30% resulting in more compact sediment, (Mabiala-Mabélé, 1989). Secondly, strong currents causing considerable agitation hindering clay sedimentation. This situation is accentuated by the fact that salinity here is high which further hinders metal fixation to clays (Waldhaver *et al.*, 1978; Frenet, 1981). This may explain the decreased metal content in water which then increases towards the ocean downstream and in the fresher water upstream.

Organic matter content was higher (Figure 2) at the top of the mud flat than at the bottom. It is known that organic matter fixed 2 to 3 times more metal than clays (Frenet, 1979, 1981).

Water content increases linearly with the amount of organic matter (Barbaroux, 1980) and is always higher at the top of the mud flat. During emersion, a certain amount of water is trapped within the sediments and adds its metal pollution as it evaporates when the mud is processed.

In the Loire River, tide salinity is felt up to Le Pellerin (Figure 1), and sometimes as far as Nantes during low water periods. Salinity increases from upstream to downstream and is always lower at the top of the mud flat, which favors metal fixation (Frenet, 1978). Metals and metalloids compete with each other to occupy exchangeable clay areas (ion exchange capacity), and Na and Ca exchanges are favored in high salinity waters, hence low metal fixation in salty water except for Mn which, according to Morris *et al.* (1981), tends to precipitate in salty water and remain in solution in fresh water.

Carbonates vary inversely compared to metals. Mook and Koene (1975) showed that pH and salinity vary as a 'carbonate system' in an estuary. Salinity is always lower along the banks of the Loire, and carbonate content is lower at the top of the mud flat.

Variations between winter and summer differ depending on the parameter studied. Metal concentrations, carbonate content and salinity are always higher in summer, which seems to contradict the previous observations since we showed that for different locations high levels of salinity in reduced metal fixation to sediments. This apparent contradiction may be explained by the high water flow rate in winter which, reduces potential fixation by diluting metal pollution, and reduces settling, as expelling the obturating mud layer from the estuary reduces sedimentation on the mud flat and causes currents that disperse the recently deposited sediments. Water content is higher in winter since evaporation is substantially less (Gouleau, 1975).

The organic matter content of the mud is basically the same in summer as in winter, which also seems contradictory. Indeed, the increases in water and air temperature favor the development of organic matter, but the higher bacterial activity in summer favors consumption and mineralization of organic matter. Lastly, smectite content is higher in summer. Smectite has the highest ion exchange capacity of the clay minerals (kaolinite: 5 to 15, chlorite: approx 10, smectite: 95 to 125, for 100 g, Fripiat, 1976).

## 5. Conclusion

This study shows the relationships between metal content and various physico-chemical characteristics of estuarine sediments. In terms of location, some parameters, such as water content, organic matter and metals war related to salinity and to the specific hydrological environment of the estuaries.

Furthermore, salinity also affects carbonate and Mn inversely with respect to the above parameters.

One very important and new point is the difference between the top and bottom of the mud flat where, in most cases, metal contents may vary by a factor of two or even more. In addition differential selection in the sedimentation related to emersion which itself is responsible for many physico-chemical and biological phenomena. Lastly, we should keep in mind that this altimetric factor varies considerably with the seasons, especially in summer when metal contents may be 10 times greater than in winter. When measuring the metal content of muds, it is therefore essential to specify at what exact altimetric level the sample was taken and during what season.

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