

# Metal early diagenesis and pollution in the tidal flats of the Marennes Oleron Bay : application of metal sequential extraction

Metal associations  
Diagenesis  
Pollution  
Superficial sediments/cores  
Tidal-flats

Association des métaux  
Diagenèse  
Pollution  
Sédiments de surface/carottes  
Sédiments intertidaux

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## ABSTRACT

Metal partition patterns in the tidal flats of the Marennes Oleron Bay are studied in order to determine metal associations, metal availability for the biota, and the change of these associations after burial. It is a study leading to a better understanding of metal early diagenesis and differentiation between surface metal enrichment — caused by diagenetic migration, or by anthropogenic flux.

The metal partition patterns in the superficial sediments indicate that the major part of the mobile fraction of metals is in association with Fe-Mn oxides. The metal fractions associated with organic matter are relatively small. The decrease of metal reducible fraction with increasing depth is an evidence of oxide dissolution under reducing conditions. The increase of metal sulfide-organic fraction with an increasing depth of burial, supports the idea of metal sulfide formation. The calculation shows that the total sulfur in the sediments is in excess, with respect to iron extracted by the hydrogen peroxide treatment. This assumes the existence of Fe fraction as  $FeS_2$  or  $FeS$ . Mn enrichment in the surface sediments is the result of Mn dissolution and upward migration and precipitation. Nevertheless, Pb enrichment seems to be the result of high Pb anthropogenic flux.

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## RÉSUMÉ

Diagenèse précoce et pollution des sédiments de la baie de Marennes-Oléron : application de l'extraction séquentielle des métaux.

L'extraction séquentielle des métaux a été réalisée sur des sédiments de la baie de Marennes-Oléron dans le but de préciser les associations de ces métaux avec les différentes fractions lithologiques, leur disponibilité pour le biota, et les changements que subissent les associations au cours de l'enfouissement. L'étude conduit à une meilleure connaissance des effets de la diagenèse précoce sur les métaux et à une différenciation des enrichissements liés aux migrations diagénétiques, et de ceux qui sont dus aux apports anthropogéniques.

La répartition des métaux dans les sédiments superficiels montre que la fraction mobile est principalement liée aux oxydes de Fe et Mn. La fraction associée à la matière organique est relativement faible. La décroissance de la fraction réductible avec la profondeur montre que les conditions réductrices induisent une dissolution des oxydes. L'accroissement des teneurs en métaux liés à la fraction oxydable évoque une formation de sulfures métalliques croissante avec l'enfouissement. Le calcul montre que dans les sédiments le soufre total est en excès par rapport au fer extrait par le traitement à  $H_2O_2$ . Il paraît donc logique de penser que la majeure partie du fer extrait par cette attaque est sous forme de  $FeS_2$  ou  $FeS$ . L'enrichissement en Mn en surface est le résultat d'une dissolution de Mn en profondeur, de sa migration vers le haut et de sa précipitation à l'interface. Au contraire l'enrichissement en Pb semble dû à des apports d'origine anthropogénique.

*Oceanol. Acta*, 1982. Actes Symposium International sur les lagunes côtières, SCOR/IABO/UNESCO, Bordeaux, 8-14 septembre 1981, 119-128.

## INTRODUCTION

The trace metal partition patterns in the sediments in different environmental conditions have been recently studied by many authors who used different approaches and methods to study metal mobilization, associations, availability to biota pollution and diagenesis (e.g. Chester, Hughes, 1967; 1969; Chester, Messiha Hanna, 1970; Nissenbaum, 1972; Presley *et al.*, 1972; Gibbs, 1977; Brannon *et al.*, 1977; Loring, 1978; Filippek, Owen, 1978; Eaton, 1979; Skei, Paus, 1979; Bertrand, 1980; Kitano *et al.*, 1980). This study is concerned with Mn, Fe, Cu, Ni and Pb partition patterns determining metal associations with different components of sediments as well as factors controlling the metal associations in the surface sediments and after burial. The change of metal associations after burial gives us an idea about metal mobilization, early diagenesis and pollution. Three fractions are defined; they are reducible, oxidizable and residual.

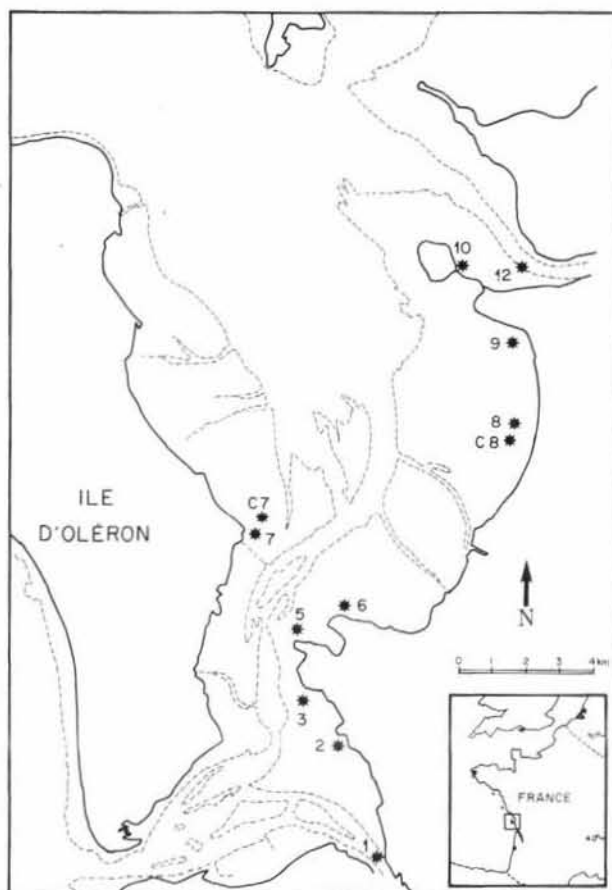


Figure 1  
Sample locations.  
Localisation des échantillons.

## MATERIAL AND METHOD

Ten surface sediment samples and two cores were collected from the tidal flats of the Marennes Oléron Bay (Fig. 1). Core 8 (100 cm length) is located at the eastern side of the bay and core 7 (30 cm length) at the western side. After the interstitial water extraction, the sediments are dried at a temperature of 60-70°C. Grain size analysis, clay mineralogy and mineral assemblages are performed. Organic carbon is determined by the wet oxidation of sediment samples (Strickland, Parsons, 1968). Total sulfur is determined in the sediments by the Leco method; CaCO<sub>3</sub> percentage by the volumetric CO<sub>2</sub> determination; Al % in the total sediment samples by atomic absorption. Mn, Fe, Cu, Ni and Pb in the three successive fractions and in the sediment completely dissolved by HF-HCl O<sub>3</sub> are also

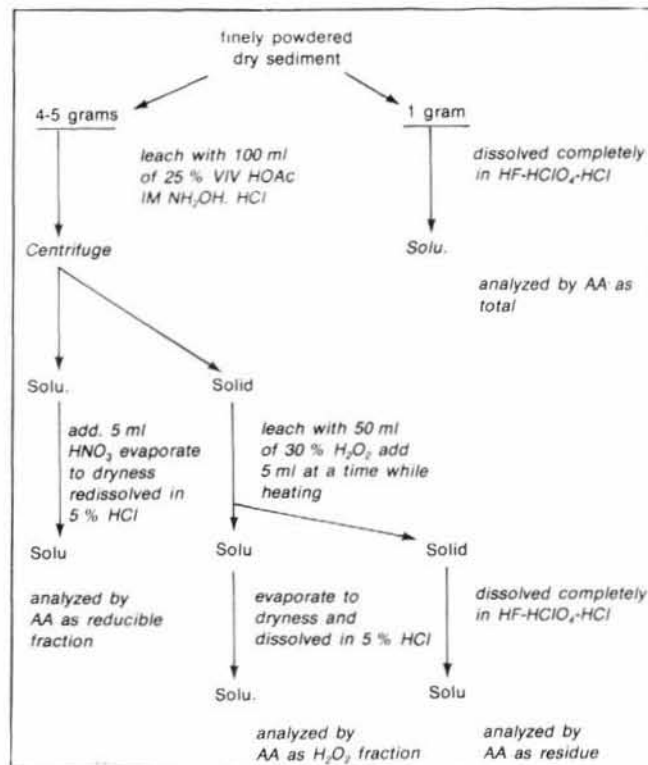


Figure 2  
Flow diagram for sediment analysis.  
Représentation schématique de l'analyse des sédiments.

analyzed by atomic absorption. This method is explained in Figure 2 (Chester, Hughes, 1967; Presley *et al.*, 1972). The total concentration of metals is in good agreement with the total sum of the fractions. They differ by less than 10% in most cases.

#### The hydroxylamine hydrochloride-acetic acid (reducible) fraction

This treatment removes that part of metal which is associated with the iron and manganese oxide phase. Carbonate and exchange metals are also included in this leachate, and acid soluble sulfides can contribute small amounts of heavy metals in the sulfide rich sediment. These contributions are nevertheless, minor compared to metals in oxides and carbonates in most circumstances (Presley *et al.*, 1972). Metals bound structurally in silicates are little affected by this treatment according to data by Chester and Hughes (1967).

#### The hydrogen peroxide (oxidizable) fraction

This extraction was intended to dissolve sulfides and organic matter and to have a minor effect on silicates. The remaining organic carbon resisting the extraction by H<sub>2</sub>O<sub>2</sub> was examined in some samples after the treatment; it represents 8-15% of the original organic carbon. Clay mineral assemblages for some samples before and after the two extractions were compared. It appears that clay mineral assemblages do not change after the two extractions.

#### The residual fraction

The residual fraction remaining after the hydroxylamine acetic acid and the peroxide leaches, would in most sediments, consist almost entirely of detrital silicate minerals.

## RESULTS AND DISCUSSION

#### Sediment characteristics

The surface sediments in the intertidal zone of the Marennes Oléron Bay (Fig. 1) represent a muddy sediment with a

variable proportion of clay, silt and sand. According to Pouliquen (1975) the distribution of the surface sediments in the bay is divided into three groups :

- clayey silt facies (35-65 % clay) situated in the east and the northeastern side of the Bay ;
- mixed facies, where clay represents an important fraction (10-40 %) situated in the western side of the Bay ;
- sand facies, where clay is less than 10 %, situated in the

axis of " Coureau Central " in the north and center of the Bay.

Table 1, represents grain size analysis, organic carbon percentage, CaCO<sub>3</sub> percentage, Al percentage, S percentage and clay minerals in the surface sediments and the two cores. The composition of the clay phase is illite, montmorillonite, kaolinite and chlorite with a predominance of illite and montmorillonite. The other minerals are quartz, calcite, dolomite and feldspars (alkaline and plagioclase).

Table 1

Grain size organic carbon, carbonate, S, Al and clay mineral distribution in the surface sediments ; core 8 and core 7 in the Marennes Oleron Bay. Granulométrie, carbone organique, carbonate, S, Al et distribution des minéraux argileux dans les sédiments de surface, les carottes 8 et 7 de la Baie de Marennes Oléron.

Sample	< 2 $\mu\text{m}$	2-16 $\mu\text{m}$	16-63 $\mu\text{m}$	> 63 $\mu\text{m}$	M.	I.	K.	Ch.	O.C. %	CaCO <sub>3</sub> %	S %	Al %
Superficial sediments												
1-S	50	39	9	2	29	45	16	10	1.32	11.5	0.200	9.18
2-S	35	30	4	31	31	43	15	11	0.63	15	0.160	7.27
3-S	40	36	20	4	22	48	16	14	1.15	15	0.160	6.58
5-S	34	41	18	7	26	47	14	13	0.99	15	0.152	7.53
6-S	35	40	10	25	24	47	16	13	1.01	25	0.176	6.66
7-S	25	27	34	14	27	46	15	12	0.86	16.5	0.136	6.80
8-S	45	36	2	17	24	47	15	14	1.10	16.5	0.149	8.09
9-S	33	31	3	33	12	56	17	15	0.74	16	0.142	7.67
10-S	19	20	8	53	18	55	14	13	0.63	23.5	0.168	4.09
12-S	32	38	19	11	21	48	17	14	1.02	19	0.189	7.45
Core 8												
(0-2) 8	17	40	6	37	17	58	12	13	1.51	18.5	0.140	7.59
(2-4) 8	25	16	1	48	21	50	14	15	2.00	11.5	0.133	8.38
(4-6) 8	19	20	1	60	18	53	14	15	1.63	16.5	0.125	8.01
(6-11) 8	37	37	2	24	22	50	13	15	1.55	15	0.190	8.38
(11-16) 8	39	36	5	20	27	45	15	13	1.53	16.5	0.347	7.94
(16-21) 8	36	45	7	12	30	44	13	13	1.51	15	0.310	8.92
(21-26) 8	32	35	5	28	28	46	13	13	1.32	15	0.310	9.29
(26-36) 8	31	38	8	23	26	48	13	13	1.36	11.5	0.335	9.36
(36-46) 8	26	30	30	14	26	46	14	14	1.53	18.5	0.490	8.91
(46-56) 8	37	41	13	9	27	45	14	14	1.13	15	0.480	8.48
(56-66) 8	34	35	10	21	26	50	12	12	1.43	8.3	0.675	9.23
(66-76) 8	35	34	19	12	23	48	14	15	1.53	8.3	0.770	9.36
(76-86) 8	36	43	13	8	25	47	14	14	2.02	10	1.390	9.29

Sample	< 2 $\mu\text{m}$	2-16 $\mu\text{m}$	16-63 $\mu\text{m}$	> 63 $\mu\text{m}$	M.	I.	K.	Ch.	O.C. %	CaCO <sub>3</sub> %	S %	Al %
Superficial sediments												
(86-96) 8	45	35	11	9	24	47	15	14	2.2	10	1.420	9.25
Core 7												
(0-2) 7	18	29	29	24	17	53	13	17	1.48	16.5	0.130	6.85
(2-4) 7	15	35	27	23	16	54	14	16	1.37	13.3	0.162	7.08
(4-6) 7	22	28	27	23	17	55	12	16	1.58	15	0.195	6.98
(6-11) 7	20	22	29	29	16	54	13	17	1.13	15	0.202	6.78
(11-16) 7	14	26	29	21	19	54	13	14	1.01	16.5	0.228	6.58
(16-21) 7	13	19	25	43	17	55	14	14	0.94	18.5	0.272	6.06
(21-26) 7	19	18	20	43	16	55	14	15	1.08	16.5	0.338	6.65
(26-30) 7	18	21	18	43	19	55	13	13	1.23	18.5	0.570	6.00

Legend : M. = Montmorillonite  
I. = Illite

K. = Kaolinite  
Ch. = Chlorite

O.C. = Organic carbon

## Chemical analysis

### Manganese

In the surface sediments a high percentage of Mn is soluble in the hydroxylamine fraction (66.6-79.8 %). Mn in the H<sub>2</sub>O<sub>2</sub> fraction represents only 3.5-6.5 % of the total. The residual Mn fraction represents 15.6-27.9 % of the total (Table 2). Gupta and Chen (1975) in nearshore sediments found that 17.25 % of the total Mn is non-residual ; they explained that this low value was due to the incomplete dissolution of Mn by the hydroxylamine acetic acid treatment. Chester and Hughes (1969) and Chester and Messiha-Hanna (1970) found that 68-88 % of the total Mn in deep-sea sediments was marine derived and 12-32 % was lithogenous.

In core 8, Mn percentage in the hydroxylamine fraction decreases at the bottom of the core. However, the maximum Mn in this fraction observed in the top 2 cm represents 77.5 % of the total ; the minimum Mn in this fraction observed at the bottom of the core represents 44.1 %. Mn soluble in the H<sub>2</sub>O<sub>2</sub> fraction varies slightly between 5-7 % of the total in the upper 66 cm of the core (Table 2). Nevertheless, a great variation is observed below 76 cm depth, where Mn in this fraction represents 21 % of the total (Fig. 3). Mn in the residual fraction varies between 17 and 49.5 %. The increase in the residual Mn percentage at the bottom of the core is the result of the decrease of the absolute leachable Mn. However, the absolute residual Mn does not change at the bottom of the core (Fig. 5).

In core 7, Mn in the reducible fraction varies between 68.7-59.2 % (of the total) where the highest values are observed at the top of the core (Table 2). Mn in the H<sub>2</sub>O<sub>2</sub> fraction represents 4.4-6.9 % of the total, the residual Mn varies between 26.1-36.4 % (of the total). Skei and Paus (1979) in a Norwegian fjord core, found that Mn leached by the acetic acid (non-detrital) decreased with depth from 96 % at the surface 0-2 cm to a constant 43 % below 10 cm.

Manganese leached by the hydroxylamine extraction in the surface sediment is mainly in the oxide (or hydroxide) form with a minor contribution of carbonate and exchangeable Mn. The decrease of the soluble Mn in this fraction with

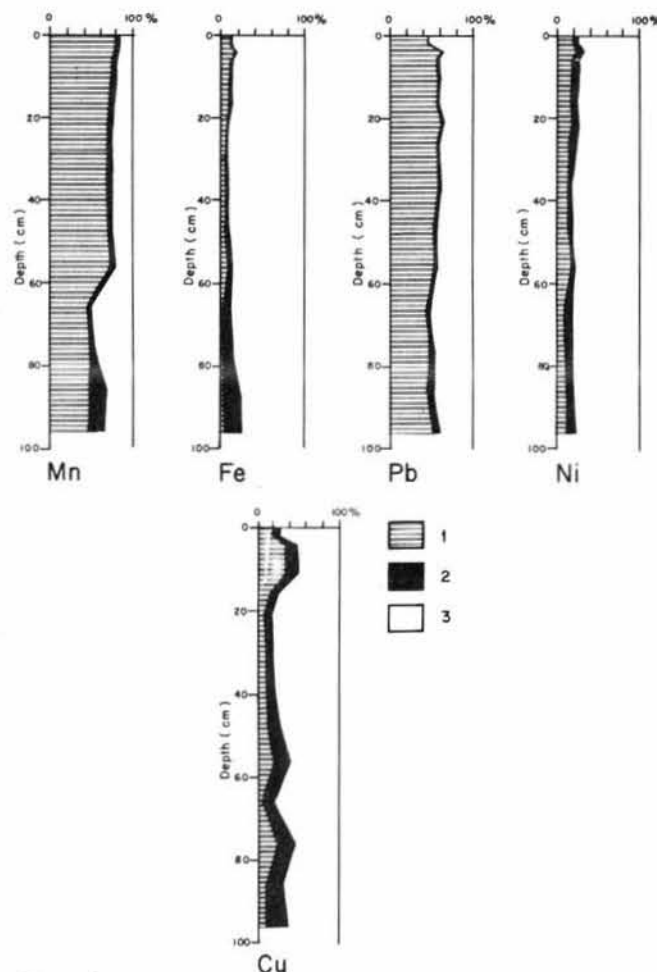


Figure 3

Mn, Fe, Pb, Ni and Cu percentage in the reducible (1) oxidizable (2) and residual (3) fractions in core 8.

Carotte 8 : pourcentages en Mn, Fe, Pb, Ni, et Cu dans les fractions réductibles (1), oxydables (2) et résiduelles (3).

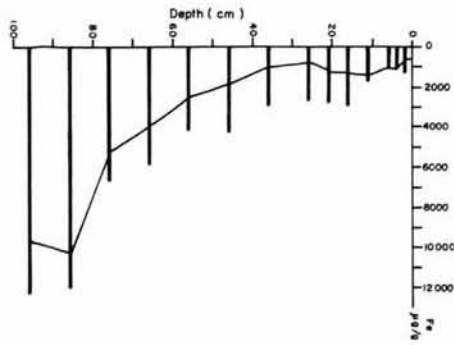


Figure 4

Fe leached by the  $H_2O_2$  treatment (the curve) and calculated Fe equivalent to the total sulfur (horizontal lines) in core 8.

Carotte 8 : Fe extrait par le traitement à  $H_2O_2$  (courbe) et Fe calculé d'après la teneur en S total (traits horizontaux).

depth of burial paralleled the decrease of total Mn content. This decrease is the result of Mn solubilisation and upward migration and precipitation of Mn in the surface layer (Lynn, Bonatti, 1965 ; Skei, Paus, 1979). Froelich *et al.* (1979) in equatorial cores, found that the dissolved Fe and Mn profiles suggest reduction of the solid oxide phases, upward fluxes of dissolved metals and subsequent entrapment in the sediment column. El Ghobary (1982) stated the same phenomenon of recycling of Mn from the interstitial water profiles in near shore sediments. In fact, the soluble

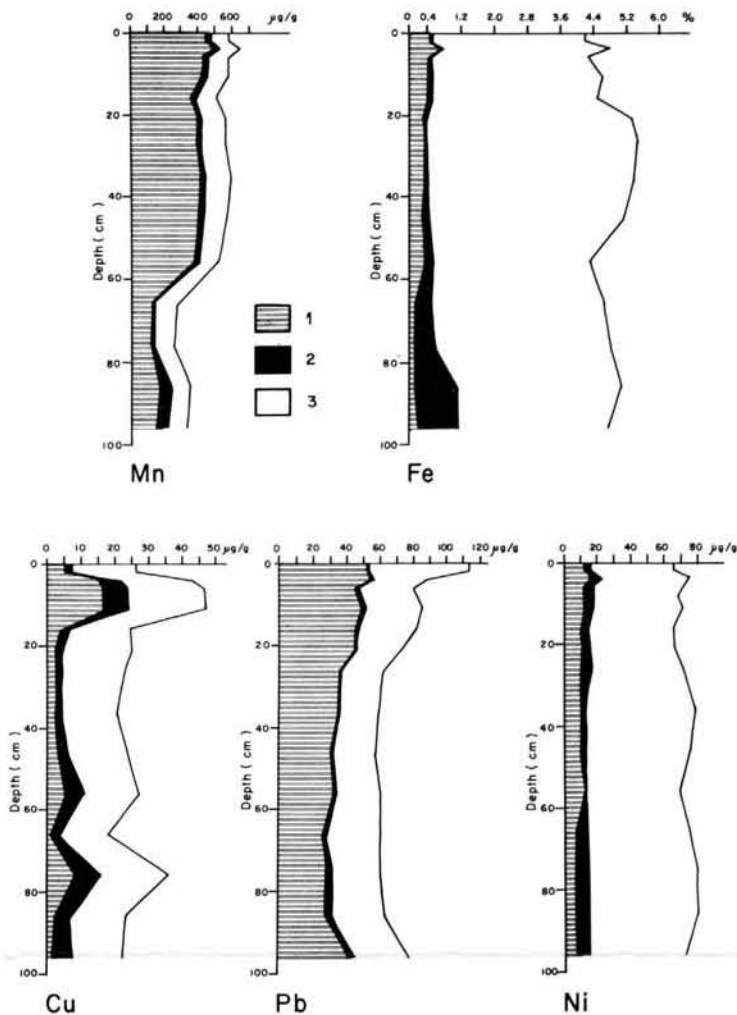


Figure 5

Mn, Fe, Cu, Pb and Ni content in the reducible (1), oxidizable (2) and residual (3) fractions (Mn, Cu, Ni and Pb in  $\mu\text{g/g}$ , Fe in %) in core 8.

Mn under reducing conditions could be precipitated as  $MnCO_3$  in the presence of high bicarbonate concentration (Li *et al.*, 1969 ; El Ghobary, 1982). The solid solution formation of  $MnCO_3$  by the sorption of Mn into the surfaces of  $CaCO_3$  phases (Hager, 1980) could also take place. However, carbonate is leached in the first fraction. It is possible that at the bottom of core 8, Mn in the first fraction is mainly in the form of  $MnCO_3$ . The high percentage of Mn in the  $H_2O_2$  fraction (21 %) at the bottom of core 8 shows that an important fraction of Mn is controlled by the formation of sulfide minerals. It is evident that Mn distribution and associations throughout the entire length of core 8 depend on the physico-chemical and biochemical state of the sediments and that diagenetic reactions are the main factors affecting Mn vertical distribution and associations ultimately leading to the Mn enrichment in the surface sediments.

### Iron

In the surface sediments, Fe extracted by the first treatment represents 7.4-11.5 %. However, Fe in the  $H_2O_2$  fraction represents only 0.3-1 % of the total Fe (Table 2). The major fraction of Fe in the surface sediments is residual (87.5-92.3 %). Gupta and Chen (1975) stated that 74-82 % of the total Fe is of lithogenous origin. Chester and Hughes (1969) and Chester and Messiha-Hanna (1970) maintain that 82-96 % of the total Fe was of lithogenous origin in deep-sea sediments.

In core 8, Fe leached by the hydroxylamine treatment shows its highest percentage at the top of the core (14.8 %) and it decreases with depth to 2.4 % at the bottom of the core (Fig. 3 and 5). Fe in the  $H_2O_2$  fraction represents a gradient increasing with depth especially at the bottom of the core (1.5-20.3 %), where Fe in this fraction represents 20 % of the total Fe. Residual Fe fraction represents 92.1-75.4 % of the total Fe. The residual Fe percentage increases slowly with depth and decreases at the bottom of the core. The increase of residual Fe % may be the result of recrystallization of Fe-oxide (Nissenbaum, 1972). However, with the increasing depth of burial and reduction conditions, Fe is extracted from residual fraction (crystalline) and Fe-sulfides are formed ; this is evident at the bottom of the core.

In core 7, Fe in the reducible fraction varies between 9.8-4.2 % (Table 2) and follows the same pattern as Fe in the same fraction in core 8. Fe leached by the  $H_2O_2$  increases at the bottom of the core (0.7-2.7 %) and the residual Fe varies between 89.3-93.1 %.

Iron extracted by the first leach represents the most highly mobile Fe, available for sulfide formation. According to Berner (1970 ; 1981) the reactive Fe available for pyrite formation in the marine sediments is the strong HCl soluble Fe. However, this treatment affects the silicate structure especially the fine grain size particles (e.g. chlorite, Berner, 1970) and therefore, it extracts a high percentage of the total Fe in marine mud. In contrast, Fe extracted by the hydroxylamine treatment represents only the poor crystalline Fe oxyhydroxides in the sediments. It is a treatment which extracts the most reactive Fe (towards  $H_2S$ ) ; the decrease of Fe in this fraction with increasing depth of burial e.g. in core 8 supports this idea. Nonetheless, it represents only a small fraction of Fe available for the pyrite formation defined by Berner.

In core 8, the increase of Fe leached by  $H_2O_2$  is parallel to an increase of the total sulfur in the sediments and a decrease in the Fe extracted by the reducible fraction. Even a decrease of the residual Fe is observed. The calculation of Fe equivalent to total sulfur in the sediment forming  $FeS_2$  (Fig. 4) or  $FeS$ , indicates that along the entire length of the two cores, there exists excess sulfur which forms  $FeS_2$  or  $FeS$  with Fe extracted by the  $H_2O_2$  treatment. The major sources of Fe in the peroxide fraction are organic matter and sulfides. Organic matter represents an important fraction of Fe at the surface sediments and at the top of the cores.

Table 2

Mn, Fe, Cu, Ni and Pb partitioning in the reducible (AR), oxidizable ( $H_2O_2$ ) and residual (R) fractions (in  $\mu\text{g/g}$  dry sediment and in percentage of the total sum) in the surficial sediments, core 8 and core 7.  
Répartition de Mn, Fe, Cu, Ni et Pb dans les fractions réductibles (AR) oxydables  $H_2O_2$  et résiduelles (R) de l'ensemble des échantillons (résultats en  $\mu\text{g/g}$  du sédiment sec et en % de la somme totale).

Sediment sample	Mn AR	Mn $H_2O_2$	Mn R	Mn TS	Fe AR	Fe $H_2O_2$	Fe R	Fe TS	Cu AR	Cu $H_2O_2$	Cu R	Cu TS	Ni AR	Ni $H_2O_2$	Ni R	Ni TS	Pb AR	Pb $H_2O_2$	Pb R	Pb TS
1-S	559 77.6 %	33 4.6 %	128 17.8 %	720	4960 11.5 %	425 1.0 %	37850 87.5 %	43235	3.5 14.3 %	2.6 10.6 %	18.4 75.1 %	24.5	11.00 15.6 %	2.6 3.7 %	57 80.7 %	70.6	42 57.2 %	1.4 1.9 %	30 40.9 %	73.4
2-S	341 69.0 %	32 6.5 %	121 24.5 %	494	3074 9.9 %	94 0.3 %	27901 89.8 %	31069	1.8 9.1 %	0.9 4.5 %	17.1 86.4 %	19.8	9.8 19.2 %	2.3 4.5 %	39 76.3 %	51.1	29 52.7 %	1.0 1.8 %	25 45.5 %	55
3-S	383 71.5 %	32 6.0 %	121 22.5 %	536	4326 11.2 %	386 1.0 %	34051 87.8 %	38763	2.4 11.9 %	2.4 11.9 %	15.3 76.2 %	20.1	11.2 17.9 %	2.5 4 %	49 78.1 %	62.7	40 56.4 %	1.9 2.7 %	29 40.9 %	70.9
5-S	301 66.6 %	25 5.5 %	126 27.9 %	452	3340 9.1 %	328 0.9 %	33055 90.0 %	36723	3.7 15.1 %	2.8 11.5 %	17.9 73.4 %	24.4	9.2 13.8 %	3.3 5 %	54 81.2 %	66.5	39 56.1 %	2.5 3.6 %	28 40.3 %	69.5
6-S	429 74.2 %	27 4.7 %	122 21.1 %	578	4047 11.1 %	138 0.4 %	32203 88.5 %	36388	3.1 15.7 %	1.4 7.1 %	15.2 77.2 %	19.7	15 22.8 %	2.7 4.1 %	48 73.1 %	65.7	42 61.8 %	1.0 1.50 %	25 36.7 %	68
7	373 72.7 %	19 3.7 %	121 23.6 %	513	3197 9.8 %	80 0.3 %	29360 89.9 %	32637	2.1 11.9 %	1.2 6.8 %	14.3 81.3 %	17.6	9.8 17.6 %	2.7 4.9 %	43 77.5 %	55.5	32 56.1 %	1.0 1.8 %	24 42.1 %	57
8-S	638 79.8 %	37 4.6 %	125 15.6 %	800	5700 11.2 %	380 0.8 %	44590 88 %	50670	3.4 14.4 %	2.5 10.6 %	17.7 75 %	23.6	12.0 17.3 %	3.4 4.9 %	54 77.8 %	69.4	50 54.3 %	3.1 3.4 %	39 42.3 %	92.1
9-S	521 77.6 %	34 5.1 %	116 17.3 %	671	4365 9.2 %	375 0.8 %	42599 90 %	47339	2.9 13.5 %	2.3 10.7 %	16.3 75.8 %	21.5	10.9 16.0 %	4.4 6.4 %	53 77.6 %	68.3	41 52 %	2.8 3.6 %	35 44.4 %	78.8
10-S	387 79.3 %	17 3.5 %	84 17.2 %	488	2685 7.4 %	92 0.3 %	33412 92.3 %	36189	2.7 18.1 %	1.1 7.4 %	11.10 74.5 %	14.9	13.4 27 %	3.3 6.6 %	33 66.4 %	49.7	36 53.2 %	1.7 2.5 %	30 44.3 %	67.7
12-S	506 75.9 %	27 4.0 %	134 20.1 %	667	3540 8.2 %	279 0.6 %	39504 91.2 %	43323	3.8 14.8 %	3.0 11.7 %	18.9 73.5 %	25.7	13.2 18.5 %	3.1 4.4 %	55 77.1 %	71.3	49 56.7 %	1.4 1.6 %	36 41.7 %	86.4
Core 8																				
(0-2) 8	450 77.5 %	32 5.5 %	99 17 %	581	4767 11.4 %	616 1.5 %	36530 87.1 %	41913	5.0 19.4 %	2.5 9.7 %	18.3 70.9 %	25.8	12.6 19.2 %	3.9 6.0 %	49 74.8 %	65.5	52 45.6 %	2.0 1.8 %	60 52.6 %	114
(2-4) 8	496 76.4 %	39 6.0 %	114 17.6 %	649	7143 14.8 %	1101 2.3 %	39878 82.9 %	48122	15.0 34.9 %	6.7 15.6 %	21.3 49.5 %	43	16.7 22.1 %	6.9 9.1 %	52 68.8 %	75.6	54 61.5 %	2.8 3.2 %	31 35.3 %	87.8
(4-6) 8	431 73.7 %	39 6.7 %	115 19.6 %	585	4559 10.7 %	1063 2.5 %	37095 86.8 %	42717	15.9 34.3 %	8.1 17.4 %	22.4 48.3 %	46.4	11.5 16.7 %	7.2 10.5 %	50 72.8 %	68.7	45 56 %	3.3 4.1 %	32 39.9 %	80.3
(6-11) 8	421 73.2 %	38 6.6 %	116 20.2 %	575	4260 9.2 %	1439 3.1 %	40651 87.7 %	46350	16.3 34.7 %	8.1 17.2 %	22.6 48.1 %	47	11.7 16.5 %	7.4 10.4 %	52 73.1 %	71.1	49 57.3 %	3.5 4.1 %	33 38.6 %	85.5
(11-16) 8	358 70.3 %	35 6.9 %	116 22.8 %	509	4335 9.6 %	1240 2.8 %	39361 87.6 %	44936	3.9 15.9 %	3.1 12.6 %	17.6 71.5 %	24.6	10.1 15.4 %	5.6 8.5 %	50 76.1 %	65.7	46 56.5 %	2.4 3.0 %	33 40.5 %	81.4

(16-21) 8	389 69.6 %	30 5.4 %	140 25 %	559	3359 6.3 %	1219 2.3 %	48531 91.4 %	53109	2.5 10 %	2.5 10 %	20.0 80 %	25	10.6 16 %	5.7 8.6 %	50 75.4 %	66.3	45 61.7 %	1.9 2.6 %	26 35.7 %	72.9
(21-26) 8	393 69.7 %	28 5 %	143 25.3 %	564	3488 6.4 %	827 1.5 %	50301 92.1 %	54616	2.7 11.7 %	2.0 8.7 %	18.3 79.6 %	23	10.1 14.2 %	6.7 9.5 %	54 76.3 %	70.8	36 57.3 %	1.8 2.9 %	25 39.8 %	62.8
(26-36) 8	417 70.1 %	31 5.2 %	147 24.7 %	595	3475 6.4 %	1023 1.9 %	49575 91.7 %	54073	2.5 11.5 %	2.1 9.7 %	17.1 78.8 %	21.7	9.7 12.4 %	3.8 4.8 %	65 82.8 %	78.5	35 58.6 %	1.7 2.9 %	23 38.5 %	59.7
(36-46) 8	402 70.4 %	32 5.6 %	137 24 %	571	3024 5.9 %	1836 3.6 %	46341 90.5 %	51201	2.9 12.3 %	3.5 14.8 %	17.2 72.9 %	23.6	9.6 12.7 %	3.9 5.2 %	62 82.1 %	75.5	31 53.2 %	2.3 3.9 %	25 42.9 %	58.3
(46-56) 8	378 73 %	29 5.6 %	111 21.4 %	518	3498 8.0 %	2480 5.7 %	37502 86.3 %	43480	5.2 19.3 %	5.7 21.1 %	16.1 59.6 %	27	42.1 17.3 %	2.0 2.8 %	56 79.9 %	70.1	33 53.8 %	2.4 3.9 %	26 42.3 %	61.4
(56-66) 8	124 44.1 %	18 6.4 %	139 49.5 %	281	1483 3.2 %	4004 8.5 %	41387 88.3 %	46874	0.8 4.5 %	2.9 16.3 %	14.1 79.2 %	17.8	7.3 9.8 %	6.2 8.3 %	61 81.9 %	74.5	27 43.8 %	2.7 4.4 %	32 51.8 %	61.7
(66-76) 8	123 47.8 %	20 7.8 %	114 44.4 %	257	1141 2.4 %	5319 11 %	41934 86.6 %	48394	7.7 21.5 %	8.0 22.3 %	20.1 56.2 %	35.8	6.8 8.5 %	7.7 9.7 %	65 81.8 %	79.5	29 47 %	3.7 6 %	29 47 %	61.7
(76-86) 8	164 47.4 %	71 20.5 %	111 32.1 %	346	1298 2.5 %	10353 20.3 %	39368 77.2 %	51019	1.8 7.9 %	5.3 23.1 %	15.8 69.0 %	22.9	7.1 8.9 %	7.8 9.8 %	65 81.3 %	79.9	29 44.5 %	4.2 6.4 %	32 49.1 %	65.2
(86-96) 8	150 45.2 %	70 21.1 %	112 33.7 %	332	2077 4.4 %	9674 20.2 %	36057 75.4 %	47808	1.9 8.6 %	5.9 26.7 %	14.3 64.7 %	22.1	7.6 10.4 %	8.2 11.3 %	57 78.3 %	72.8	42 53.5 %	4.5 5.7 %	32 40.8 %	78.5
Core 7																				
(0-2) 7	250 68.7 %	19 5.2 %	95 26.1 %	364	3557 9 %	527 1.3 %	35478 89.7 %	39562	3.7 17.9 %	2.0 9.7 %	15.0 72.4 %	20.7	10.9 19.2 %	2.0 3.5 %	44 77.3 %	56.9	42 50.3 %	1.5 1.8 %	40 47.9 %	83.5
(2-4) 7	231 65.6 %	17 4.8 %	104 29.6 %	352	3442 8.5 %	465 1.2 %	36551 90.3 %	40458	3.2 17.7 %	1.3 7.2 %	13.6 75.1 %	18.1	11.5 18.7 %	2.0 3.3 %	48 78 %	61.5	60 62.9 %	1.4 1.5 %	34 35.6 %	95.4
(4-6) 7	217 64.6 %	18 5.3 %	101 30.1 %	336	3904 9.8 %	342 0.9 %	35622 89.3 %	39868	3.2 17.7 %	1.2 6.6 %	13.7 75.7 %	18.1	11.9 19.2 %	2.0 3.2 %	48 77.6 %	61.9	39 50.4 %	1.4 1.8 %	37 47.8 %	77.4
(6-11) 7	213 59.2 %	16 4.4 %	131 36.4 %	360	3228 7.4 %	302 0.7 %	40210 91.9 %	43740	2.8 14.8 %	1.1 5.8 %	15.0 79.4 %	18.9	9.9 16.8 %	2.0 3.4 %	47 79.8 %	58.9	34 48.1 %	1.7 2.4 %	35 49.5 %	70.7
(11-16) 7	208 65.4 %	16 5.0 %	94 29.6 %	318	3114 8.2 %	468 1.2 %	34303 90.6 %	37885	2.6 16.6 %	1.2 7.6 %	11.9 75.8 %	15.7	9.6 16.7 %	2.0 3.5 %	46 79.8 %	57.6	33 46.3 %	1.2 1.7 %	37 52 %	71.2
(16-21) 7	200 61.0 %	15 4.6 %	113 34.4 %	328	2681 7.6 %	406 1.1 %	32284 91.3 %	35371	2.6 18.3 %	1.1 7.8 %	10.5 73.9 %	14.2	10.7 18.5 %	2.0 3.5 %	45 78 %	57.7	30 46 %	1.2 1.8 %	34 52.2 %	65.2
(21-26) 7	201 59.8 %	19 5.7 %	116 34.5 %	336	2169 5.5 %	1046 2.7 %	35856 91.8 %	39071	2.3 14.5 %	1.9 11.9 %	11.7 73.6 %	15.9 3	10.3 18.0 %	2.0 3.5 %	45 78.5 %	57.3	33 46.9 %	1.4 2 %	36 51.1 %	70.4
(26-30) 7	228 63 %	25 6.9 %	109 30.1 %	362	1680 4.2 %	1069 2.7 %	36953 93.1 %	39702	2.2 13.4 %	2.2 13.4 %	12.0 73.2 %	16.4	12.2 19.6 %	2.0 3.2 %	48 77.2 %	62.2	40 52.2 %	1.6 2.1 %	35 45.7 %	76.6

TS = Total Sum-

However, with establishing reducing conditions, Fe solubilization under an atmosphere of  $H_2S$  is expected and Fe is precipitated as  $FeS_2$  and  $FeS$ .

The total Fe content in the two cores does not demonstrate any depth dependency (Fig. 5). This indicates a detrital origin for the Fe. However, dissolution and diagenetic transformation of Fe-associations to the sulfide form is evident. This phenomenon does not change the total Fe vertical distribution in the sediments, but it affects the partition pattern of Fe with the different phases of the sediments.

#### Copper

In the surface sediments, Cu in the  $H_2O_2$  fraction (4.5-11.9%) is lower in order of magnitude than Cu in the reducible fraction (9.1-18.1%). In spite of that it represents the highest percentage relative to the other metals, extracted by the  $H_2O_2$  treatment. Residual Cu fraction varies between 73.4-86.4% (Table 2). Gupta and Chen (1975) found out that 12-32% of the total Cu is non-residual and 90% of the non-residual Cu is associated with nodular and non-nodular hydrogenous fraction.

In core 8, Cu in the reducible fraction decreases with depth (34.9-4.5%) except for the two intervals (46-56; 66-76 cm). It is possible that in these two intervals, a fraction of the acid soluble sulfides was dissolved in this leach. Cu in the oxidizable fraction increases generally with depth (8.7-26.7%). The residual Cu fraction varies between 48.1-80%. The residual Cu % decreases in the intervals between 2-11 cm and decreases variably at the bottom of the core. The decrease between 2-11 cm is the result of the high absolute value of the leachable Cu in these levels and not the result of the decrease of the absolute residual Cu value. These data can be an evidence of migration of Cu to the surface sediments. However, the great difference between the Cu content below and above an 11 cm level, makes one assume that a source of Cu pollution is also possible; the relative decrease of residual Cu at the bottom of the core parallel to the increase of Cu in the  $H_2O_2$  fraction, indicates the mobilization of the residual Cu to the sulfide form.

In core 7, Cu in the reducible fraction shows a trend decreasing with depth (18.3-13.4%). Cu in the  $H_2O_2$  fraction decreases with depth followed by an increase of Cu at the bottom of the core (5.8-13.4%). The residual Cu varies between 72.4-79.4% (Table 2).

#### Nickel

In the surface sediments, Ni extracted by the reducible fraction represents 13.8-27% of the total Ni while Ni leached by the  $H_2O_2$  fraction represents only 3.7-6.6%. A high percentage of the Ni is associated with the residual (crystalline) fraction (66.4-81.2%) (Table 2). Gupta and Chen (1975) showed that in nearshore sediments 37% of the total Ni is non-residual and most of the non-residual Ni is extracted by the hydroxylamine leach. This result is similar to that obtained in this study and confirms that a large fraction of Ni is removed by the scavenging action of Fe and Mn oxides (hydroxides).

In core 8, the highest percentage of Ni in the reducible fraction is reported at the top of the core (22.1-8.5%). The data indicate the change of Ni association with oxides, with increasing depth. Ni extracted by  $H_2O_2$  (2.8-11.3%) is generally lower than Ni leached by the hydroxylamine treatment except for the intervals between 66-96 cm which could be the reason for Ni transformation to the sulfide form. Residual Ni varies between 68.8-82.8% of the total. It increases slightly with depth indicating the transformation of fraction of Ni to more resistant form. Nissenbaum (1972) reported on one core in Okhotsk Sea, where Ni leached with acetic acid reduced in the lower zone of the core and a corresponding increase appears in the residual fraction.

In core 7, Ni in the reducible fraction varies between 19.6-16.7% of the total Ni. In the hydrogen peroxide fraction it

does not show any variation (3.2-3.5%). The residual Ni represents 77.2-79.8% of the total. The total Ni content along the entire length of the two cores does not show a tendency of gradient. It is evident that the vertical distribution of Ni mainly depends on its detrital contributions in the sediments and the changes of Ni associations with depth does not demonstrate any vertical migration.

#### Lead

In the surface sediments, Pb in the reducible fraction represents an important fraction of the total Pb (52-61.8%). Inversely, Pb leached by the  $H_2O_2$  treatment represents only small fraction of the total Pb (1.5-3.6%). The residual Pb varies between 36.7-45.5% (Table 2). Gupta and Chen (1975) stated that in near-shore sediments 52-65% of the total Pb is a non-residual Pb. Chester and Stoner (1975) found that an average 68% of the total Pb is leached with the hydroxylamine hydrochloride acetic acid from the lower Severn Estuary and Bristol Channel. It appears from all these results that the scavenging of trace metals especially Pb, by hydrous oxides of Fe and Mn appears to be important in their retention by near-shore sediments (Grieve, Fletcher, 1976).

In core 8, Pb percentage in the reducible fraction (43.8-61.5%) does not represent a trend with depth. However, the absolute Pb in  $\mu g/gm$  in this fraction shows a gradient decrease with depth. Pb in the  $H_2O_2$  fraction is much lower (1.8-6.4%) in comparison with Pb in the reducible fraction along the entire length of the core and reaches its highest value at the bottom of the core. Residual Pb % does not show a trend with depth (35.3-52.6%).

In core 7, Pb in the reducible fraction (62.9-46%) shows the same pattern as Pb in the same fraction of core 8. In the  $H_2O_2$  fraction Pb represents a small fraction of the total (1.5-2.4%) and the residual Pb varies between 35.6-52.2% (Table 2).

It appears from the data of the three fractions along the cores, that the enrichment of Pb at the top of the cores cannot be explained by the dissolution and upward migration of Pb as in the case of Mn. Indeed, the enrichment of Pb at the top of the cores do not follow the same pattern as that of Mn. It is more likely that the enrichment of Pb is the result of high Pb flux. Skei and Paus (1979) in a Norwegian fjord stated that the enrichment of Pb at the surface layer is assumed to be mainly the result of mining, while Mn is apparently enriched in the surface due to migration of dissolved Mn and precipitation in the oxide surface layer. Chow *et al.* (1973), Thomson *et al.* (1975) stated that the enrichment of Pb in near-shore and coastal sediments is the result of pollution. Thus according to previous studies and Pb partition patterns in the two cores, it is clear that Pb enrichment in the surface sediments is the result of high anthropogenic Pb flux during the last decades. Unfortunately we have no data on sediment accumulation rates to estimate quantitatively the anthropogenic Pb flux.

#### Trace metal behaviour in the various particulate fractions

After having discussed the partitioning of each trace metal, we shall now consider the metal relationship in the three different fractions; some of them may show a different metal behaviour before and after burial. Linear correlation coefficients ( $r$ ) were calculated for 10 surface samples and 14 core 8 samples at 5% significant level.

#### Hydroxylamine hydrochloride fraction

There exists a good relationship between soluble Fe and Mn in this fraction in the surface and core sediments. In the surface sediments Fe and Mn correlate only with pb and in the core sediments Fe and Mn correlate with most metal fractions in this treatment and most of the metal fractions correlate among them.

Fe in this fraction correlates with fraction  $< 2 \mu m$  and Al percentage in the superficial sediments. These relationships



imply that Fe exists in the form of oxide coating the fine particles and especially in clay minerals (Carroll, 1958). Nevertheless, the opposite relationship between Fe, in this fraction with Al % and the absence of relationship between Fe in this fraction with fraction  $< 2 \mu\text{m}$  in the core sediments confirm the idea of oxide dissolutions under reducing conditions. It appears that Mn-Fe oxyhydroxides are the main source of metals in this fraction in the superficial sediments with a carbonate minor contribution. Trace metals are scavenged or reacting with Fe-Mn oxyhydroxides (Goldberg, 1954; Jenne, 1968 and Hem, 1977). According to previous studies (Gupta, Chen, 1975; Brannon *et al.*, 1977; Gibbs, 1977; Bertrand, 1980; Tessier *et al.*, 1980) metals — especially those concerned in the present work — in the exchangeable sites are negligible in comparison with the other metal fractions.

The negative correlation exists between Fe extracted by this fraction and Fe in the peroxide fraction in the core sediments. Inversely, the positive correlation between both Fe fractions in the superficial sediments suggests the dissolution of Fe oxyhydroxides with increasing depth (under reduced conditions) and the formation of Fe-sulfides. Fe, Mn, Ni and Pb in this fraction have opposite relationships with the total sulfur in the core sediments. These relationships show clearly that the increase of the total sulfur (sulfides) with increasing depth of burial (due to the reduced conditions) is the direct reason for decreasing metal associations with the oxide phase.

#### Hydrogen peroxide fraction

In the superficial sediments Cu and Fe correlate with organic carbon and no relationship exists between these metals (in this fraction) and the total sulfur. This indicates that the metal oxidizable fractions are mainly associated with the organic matter due to the relative oxidation state of the superficial sediments. However, in the core sediments, Mn, Fe and Pb, in this fraction, are correlated with both organic carbon and sulfur. This indicates the importance of organic matter and sulfides as controlling factors for the three metal fractions. Indeed, we believe that organic matter is the main controlling factor in this fraction at the top of the core and in the surface sediments. The physical processes especially the tide cycles and to a lesser extent the biological processes (bioturbation causing irrigation and ventilation) change continually the redox conditions in the superficial sediments. Therefore, they reduce the effect of the anaerobic bacterial decomposition of organic matter by the oxidation of sulfides and can reduce the rate of anaerobic bacterial activity where oxygen becomes available. In fact, Fe oxyhydroxides and Fe organic-sulfide form data, together with the low total sulfur content at the top of the cores suggest the importance of the physical and biological processes mentioned above. However, the formation of metal sulfides is more evident at the bottom of the core (there is even a net increase of organic carbon at the bottom). Ni correlates only with organic carbon in the core sediments. However, the increase of the Ni in this fraction at the bottom of the core seems to be due to sulfide formations. Cu in this fraction does not demonstrate any relationship with both organic carbon and sulfur, in the core sediments.

Fe and Mn have a relationship with both Al % and fraction  $< 2 \mu\text{m}$  in the superficial sediments. This relationship shows the existence of the metal peroxide fraction in association with the fine particles in the superficial sediments, caused by the presence of organic matter in the fine fraction of the sediments (organic carbon correlates with fraction  $< 2 \mu\text{m}$ ). In the superficial sediments most of the metal oxidizable fractions are in relationship with Fe fraction in the same treatment. However, in the core sediments all the metal  $\text{H}_2\text{O}_2$  fractions correlate with Pb in the same fraction.

#### Residual fraction

In the surface sediments, the residual Mn, Cu and Ni

correlate with each other and with both the fraction  $< 2 \mu\text{m}$  and Al %. These relationships demonstrate the association of the three metals in the lattice of silicate minerals especially with clay minerals. The residual Fe correlate with both residual Ni and residual Pb. In the core sediments the residual Mn and Fe correlate together. The residual Mn, Fe and Ni correlate positively with Al %. This indicates the associations of the three metals in the lattice of the silicate minerals. Nevertheless, Al % correlates negatively with the reducible fractions of the three metals mentioned above. These relationships demonstrate the different modes of metal associations in the sediments on the one hand and that the hydroxylamine does not affect the silicate structure (Chester, Hughes, 1967) on the other hand.

## GENERAL STATEMENTS AND CONCLUSIONS

The study is concerned with metal partition patterns in the surface sediments and the change of these partition patterns after burial as a result of early diagenesis and pollution in the tidal flats of the Marennes Oleron Bay.

#### In the surface sediments

The metal fraction extracted by the hydroxylamine treatment represents the main mobile fraction at the surface sediments. The mobility of metals in this fraction decreased in the order of  $\text{Mn} > \text{Pb} > \text{Ni} > \text{Cu} > \text{Fe}$ . It appears from the result of this fraction, in the superficial sediments, that Fe and Mn oxides are the main factors governing the available fraction of trace metals. Fe and Mn oxides can be a surface coating the particles during the terrigenous transportation and they can also be *in situ*, precipitated hydroxides of both metals.

The sulfide organic metal fraction is relatively small and the metal fraction in the treatment is mainly associated with organic matter. The mobility of metal in it decreased in the order of  $\text{Cu} > \text{Ni} > \text{Mn} > \text{Pb} > \text{Fe}$ . More than 50 % of Fe, Cu and Ni exists in the residual fraction. Inversely, Mn and Pb represent less than 50 % in this fraction.

#### After burial

The metal partition patterns are changed. It appears that these changes are in relation with oxidation-reduction state of the tidal flat sediments and with time. The tide cycles play also an important role for the alternative oxidation and reduction of the superficial layer of the sediments. The metal reducible fraction decreased with increasing depth of burial. The dissolution of oxides (or hydroxides) under reducing conditions leads to this decrease. However, when establishing the reduced conditions, metal-sulfides are formed in the bottom of the core and represent an increase in the  $\text{H}_2\text{O}_2$  fractions for all the metals studied.

Mobile Mn in the bottom of core 8 appears to be controlled by carbonates and sulfides. Nonetheless, Mn enrichment at the surface sediments is the result of Mn solubilization and upward migration. On the contrary, Pb surface enrichment is apparently due to high Pb anthropogenic flux during the last decades. Cu may make apparent both phenomena at the top of core 8.

The decrease of Fe and Cu residual fractions at the bottom of core 8 is considered as a diagenetic reaction. Fe and Ni contents are mainly governed by detrital contribution: diagenetic reactions change only their partitions and not their total content in the sediments.

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