Bay of Marennes-Oléron
Heavy metals
Sediments
Suspended Matter
Phytoplankton activity

Baie de Marennes-Oléron
Métaux lourds
Sédiments
MES
Activité phytoplanctonique

Distribution of Cd and Hg in the Bay of Marennes-Oléron

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ABSTRACT

The study of Cd and Hg distribution in the sediments, water and suspended matter of the Bay of Marennes-Oléron provided the opportunity to identify the factors governing the distribution of these two contaminants throughout the bay. On one hand, these elements are associated with the continental inputs from the Charente river which settle on arrival at the mouth of the estuary and in the eastern part of the bay. The Cd and Hg present in these deposits are associated with POC, as well as with Mn and Fe oxides and hydroxides. On the other hand, a portion of the dissolved inputs is recycled in the bay waters through phytoplankton activity. This mechanism contributes, particularly in the case of Cd, to increased particulate metal fluxes from the water column to the sediment.

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RÉSUMÉ

Répartition du Cd et du Hg dans la baie de Marennes-Oléron

L'étude de la répartition du Cd et du Hg dans les sédiments, les eaux et les matières en suspension de la baie de Marennes-Oléron a permis de mettre en évidence les facteurs qui gouvernent la distribution de ces deux contaminants dans la baie. D'une part, ces éléments sont associés aux apports continentaux de la Charente qui sédimentent au débouché de l'estuaire et dans la partie orientale de la baie. Dans ces dépôts, le Cd et le Hg sont liés au COP, aux oxydes et hydroxydes de Mn et Fe. D'autre part, une partie des apports dissous est recyclée dans les eaux de la baie par l'activité phytoplanctonique. Ce mécanisme contribue, notamment pour le Cd, à augmenter les flux métalliques particulaires de la colonne d'eau vers le sédiment.

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INTRODUCTION

Metal element contents in marine sediments are extremely variable. They are on one hand contingent upon the concentration, speciation and particle reactivity of a given metal in the water column, and on the other hand influenced by the size, geochemical characteristics and origin of the particles. Thorough knowledge of these different variables is required if sediments are to be used as indicators of the contamination levels in the environment and of their evolution.

This study focused on the distribution of Cd and Hg in the sediments and water column of the largest French oyster-producing site in the Bay of Marennes-Oléron (Fig. 1).

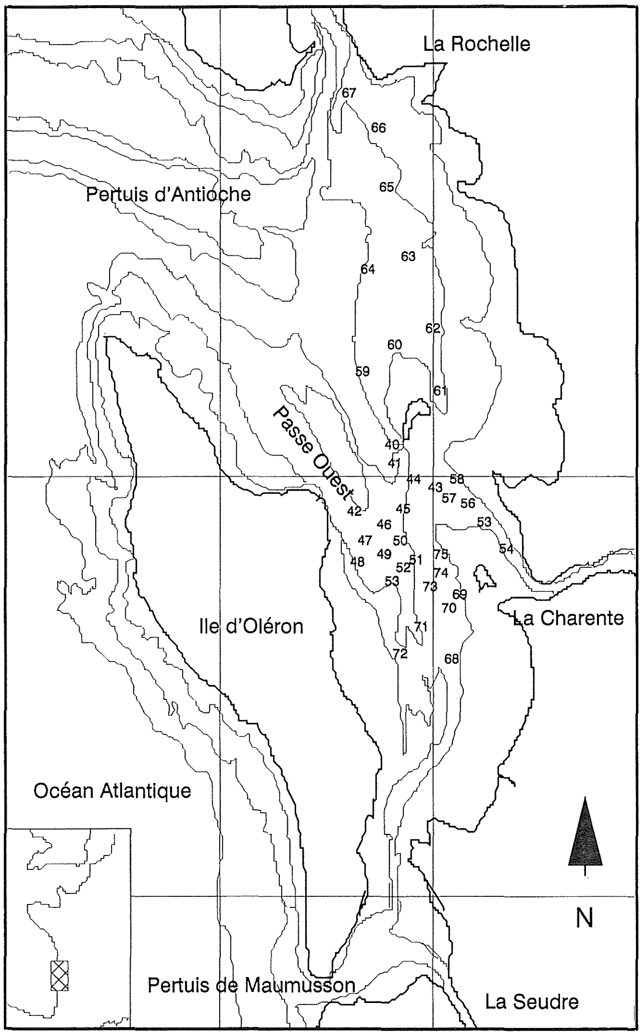

Figure 1

Location map of the studied area and sites for surficial sediment sampling.

Présentation de la zone étudiée et localisation des sédiments de surface prélevés.

Monitoring of water quality through measurement of metal pollutants in marine organisms had revealed a problem of oyster contamination by Cd and Hg in this area (Boutier, 1981). This observation prompted a number of studies on the origin of such contamination (Gonzalez, 1988 ; Boutier *et al.*, 1989 ; Gonzalez *et al.*, 1991). The objectives of this study are as follows :

- to determine the distribution of metals in sediments, their geochemical associations and their origin. To that purpose, and concurrently with trace metals, various geochemical tracers were measured in sediments;

- to establish which parameters, in the water column and suspended matter, govern Cd and Hg distributions and their evolution.

MATERIAL AND METHODS

The results presented here are derived from two cruises (Fig. 2) :

- a campaign of sample collection of surface sediments in April 1989 ;

- a water sampling campaign throughout the entire bay in September 1990. Water samples were collected throughout the bay a few hours apart during the same tidal cycle, and with a virtually constant salinity (from 35.45 to 35.67). For a number of stations (11, 13, 14, 15, 16), samples were collected 1 m above the seabed, in addition to surface sampling.

Surface samples were collected with an "Fluscha"-type corer. The surface layer of the core (a few mm) was sampled by scraping with a teflon spatula.

Following oven-drying, a portion of the sample was used to determine water content, particle size, $CaCO_3$ content, particulate organic carbon (POC) content (Etcheber, 1981), and then to measure with X-ray fluorescence spectroscopy the various trace and major elements (SiO_2, Al_2O_3, MgO, Sr, Zr, Rb). Following freeze-drying and mineralization with the Toth and Ingle (1977) method for Hg and the Sturgeon *et al.* (1982) method for other metals, the remaining part of the sample was subsequently used to analyze trace metals. Particulate Hg content was measured by atomic fluorescence. Other metals (Cd, Cu, Pb, Zn, Fe) were analyzed by graphite furnace atomic absorption spectrophotometry. Mn was measured by flame atomic absorption spectrophotometry.

Surface water samples were hand collected from a rubber raft, a few hundred metres away from and windward of the boat. Bottom waters were sampled with a Teflon "Mercos"-type system.

Filtration was carried out on board under a clean bench. Samples intended for the determination of dissolved and particulate metals (except Hg) were filtered over 0.4 µm Nuclepore filters washed with acidified water. For purposes of Hg analysis, the water was filtered over glass fibre filters (Whatman GF/F) and stored in Teflon flasks. These filters had been previously heated at 400° C and washed with acidified water. Samples intended for the analysis of POC content (Strickland and Parsons, 1968), of chlorophyll *a* and phaeopigments (Neveux, 1976), of nutrients (Aminot, 1983) and of salinity were filtered over a Whatman GF/F filter with a pyrex glass system (Millipore).

Following mineralization (Eggiman and Betzer, 1976), particulate metal (Cd, Al) concentrations were measured by atomic absorption. Particulate Hg was analyzed by atomic fluorescence following mineralization with HCl and HNO_3.

After extraction (Danielsson *et al.*, 1982), dissolved Cd was measured by means of GFAAS. Dissolved reactive Hg was measured by atomic fluorescence following reduction with $SnCl_2$. For measurement of total Hg, the sample was previously oxidized with bromine (Gill and Fitzgerald, 1987).

Metal mineralization and analysis techniques were validated by using reference samples of sediments (MESS 1 and BCSS 1) and of marine and coastal waters (NASS 1 and CASS 1).

All the equipment used for sampling and storage of sediments or water intended for subsequent trace metal analysis was allowed to remain immersed in 50 % nitric acid for five days and in 10 % nitric acid for another five days before a final rinse with MilliQ water prior to utilization.

RESULTS AND DISCUSSION

Factors governing the distribution of heavy metals (Cd, Hg, Pb, Zn, Cu) in the sediments of the Bay of Marennes-Oléron

Particle nature and origin markers

Various markers were selected according to the indications they could supply on the nature and origin of particles, as well as on the solution/particle relationships (adsorption capacity, complexing, biological uptake...) :

- mean grain size is an indicator of dynamic conditions during settling and metal adsorption capacity of the particles which decreases as particle size increases;

- particulate organic carbon (POC) has a primarily continental origin (Vigneaux *et al.*, 1979). POC contents in sediments reflect the significance of continental inputs and the remoteness from the continent. Organic matter provides preferential sites for metal adsorption, which leads to a strong affinity of metal elements for POC;

- carbonates, strontium and magnesium: the presence of $CaCO_3$ in sediments may have two different origins: carbonates of continental origin resulting from the erosion of fossil formations, or remnants of testae and shells from existing marine organisms, composed of aragonite. The difference between both fractions may be determined on the basis of Sr content which decreases during fossilization when the transformation of aragonite into calcite releases strontium. Magnesium is present in magnesian carbonates and is a good marker of the carbonate phase of marine origin;

- aluminum and silica: Al is a tracer of aluminosilicates which are abundant in the clay fraction of sediments (< 2 µm). Due to their size, these particles present high adsorption capacities. Silica is associated with the quartz fraction of sediments which, due to its generally coarse particle size, presents low metal adsorption capacities;

- rubidium and zirconium: similarly to Al and Si, both of these elements are indicators of particle size. Furthermore, they provide information on the mineralogical nature of particles. Zr is predominant in siliceous rocks which, following erosion, will result in sediments in which the quartz phase is significant and particle size therefore large. On the other hand, Rb is associated with the clay phase;

- manganese is a good tracer of particulate continental inputs, in the form of oxides and hydroxides for which most metals show a considerable affinity.

Sedimentological and geochemical characteristics of sediments (Tab. 1)

The area under study was divided into five zones:

- the area located north of "Ile d'Aix" which is not included in the Bay of Marennes. It is open to ocean inputs and is not subjected to the influence of inputs from the Charente river. Conversely, its proximity to the city of La Rochelle may influence metal contents and metal distribution in the sediments.

As for the bay itself, a number of studies have shown that it may be divided into three parts (Tesson, 1973; Pouliquen, 1975). This division is based upon hydrological, sedimentological and geochemical criteria:

- a central channel and passes where sands are deposited. On both sides of the central channel, we distinguish:

· a western part where marine sediments are currently settling, transported by open-sea waters through the straits of Antioche and the west pass. These suspensions may be expected to originate from the Gironde Estuary, following successive recyclings in the marine environment, particularly in the "Vasière Ouest-Gironde". In addition, erosion materials from the coast of the island of Oléron settle as well in this are ;

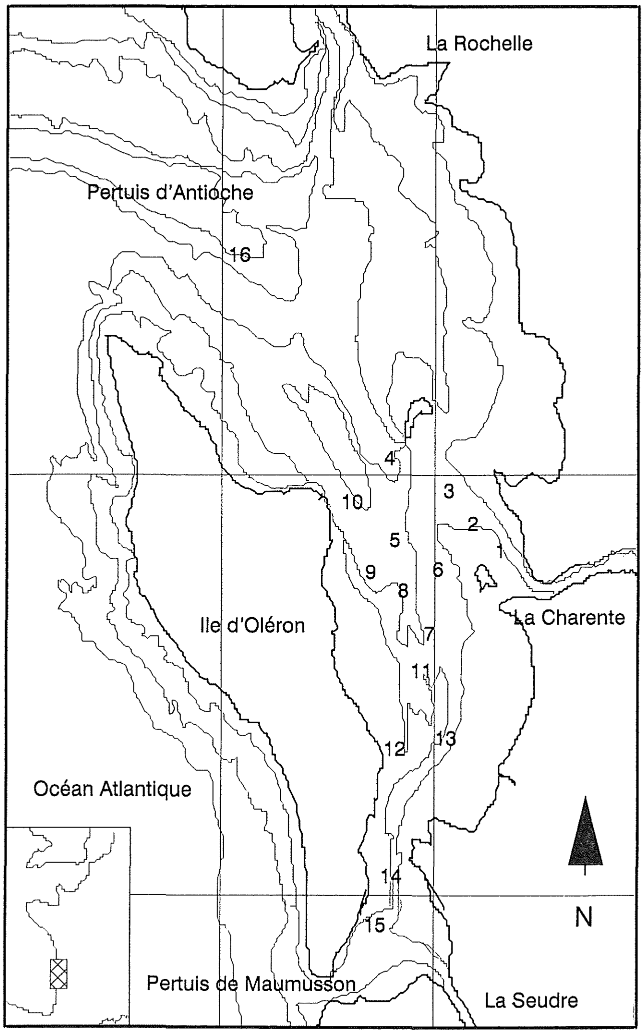

Figure 2

Location of the stations for water and SPM sampling.

Stations de prélèvement d'eau et de MES.

Table 1

Sedimentological and geochemical characteristics of the surficial sediments (N : station number; M : mean grain size in µm; Si02, Al203, CaC0$_3$, POC, MgO and Fe in percentages of dry weight ; trace elements in µg/g).

N	M	$Si0_2$	Al_20_3	$CaCO_3$	Sr	COP	Zr	Rb
59	10.2	41.78	13.98	16.5	362.2	1.35	74.4	171.9
60	11.7	37.89	13.04	16.5	359.2	1.20	94.8	165.2
61	9.9	42.44	14.14	18.3	374.0	1.21	84.2	170.4
62	9.7	41.04	15.06	16.5	385.7	1.27	78.1	177.6
63	9.9	41.89	13.15	16.5	400.4	1.20	85.9	181.4
64	13.1	40.89	11.94	16.5	432.8	1.29	108.9	171.2
65	14.3	43.13	12.68	20.0	430.1	1.10	92.2	168.0
66	9.2	44.77	14.46	18.3	392.9	1.18	94.1	172.2
67	10.5	40.60	11.73	23.0	424.5	1.27	89.8	146.7

North of the bay

N	M	$Si0_2$	Al_20_3	$CaCO_3$	Sr	COP	Zr	Rb
42	21.8	47.46	9.97	18.25	548.6	0.65	149.3	164.8
46	20.2	49.11	9.78	18.25	487.0	0.65	146.6	168.6
47	31.3	50.54	10.97	16.50	486.2	0.57	146.5	157.1

West pass

N	M	$Si0_2$	Al_20_3	$CaCO_3$	Sr	COP	Zr	Rb
48	13.6	40.03	11.06	20.0	495.9	0.99	116.8	161.5
49	13.2	44.14	11.76	16.5	413.2	1.01	91.7	167.7
50	10.4	46.86	12.68	16.5	370.8	1.06	108.3	180.5
51	15.1	47.16	12.65	16.5	408.2	0.98	116.8	175.8
52	10.8	43.78	12.73	16.5	390.9	1.30	87.4	190.8
53	11.2	43.32	12.94	16.5	397.3	1.16	84.6	175.6
72	41.5	42.66	9.73	20.0	460.0	0.57	112.3	133.9
73	12.7	47.14	13.09	16.5	353.9	1.13	92.9	163.5

West part of the bay

N	M	$Si0_2$	Al_20_3	$CaCO_3$	Sr	COP	Zr	Rb
40	10.7	40.05	13.67	15.00	393.7	1.41	96.4	190.1
41	11.4	39.73	12.17	15.00	403.7	1.34	94.6	187.4
43	14.9	44.59	11.20	16.50	393.0	1.14	124.7	181.7
44	9.4	40.72	13.26	15.00	421.7	1.41	96.4	199.6
45	9.6	41.76	12.71	16.50	405.6	1.38	90.9	201.7
68	8.4	40.98	14.45	14.75	334.8	1.36	69.4	173.0
69	11.4	41.96	14.64	16.50	341.7	1.31	94.5	157.8
70	10.6	43.07	14.46	14.75	326.8	1.38	69.7	170.5
71	10.8	43.41	13.91	16.50	360.3	1.40	79.9	169.6
74	12.0	43.70	13.34	16.50	347.9	1.19	93.2	159.0
75	10.7	43.49	13.33	16.50	346.7	1.30	78.5	156.0

East part of the bay

N	M	$Si0_2$	Al_20_3	$CaCO_3$	Sr	COP	Zr	Rb
54	8.0	40.41	13.63	16.50	367.6	1.44	71.0	192.6
55	10.9	43.03	12.98	18.25	392.3	1.17	101.7	181.0
56	10.1	43.15	13.45	18.25	392.6	1.18	105.8	183.6
57	10.1	42.19	13.34	16.50	389.4	1.36	94.8	190.3
58	9.7	41.97	13.38	16.50	412.3	1.28	100.3	193.6

Charente outlet

- an eastern part of the bay where the currents force continental waters against the shoreline, thereby conferring to sediments a more terrigenous character.

These inputs may originate from the Charente river; however its influence is currently very low and linked essentially to flooding periods (Gonzalez *et al.*, 1991). Furthermore, the presence of marshes bordering the eastern tidal flats may be responsible for non-negligible inputs due to runoff waters.

In addition, another area was defined at the mouth of the Charente river which receives deposits of materials originating primarily from the estuary.

Table 1 *(continuation)*

Caractéristiques sédimentologiques et géochimiques des sédiments de surface (N : numéro de station ; M : médiane en µm ; les oxydes, le COP et Fe sont exprimés en pourcentages ; métaux traces en µg/g).

MgO	Fe	Mn	Cu	Pb	Zn	Cd	Hg
2.54	2.68	558	15.5	40.8	162.5	0.41	0.101
2.76	2.47	573	12.2	37.1	145.7	0.35	0.084
2.66	2.62	652	12.7	37.8	155.6	0.32	0.087
2.65	2.69	731	12.9	41.2	163.9	0.28	0.091
2.56	2.78	716	12.5	39.5	157.0	0.27	0.087
2.89	2.17	630	11.2	33.0	125.2	0.28	0.072
3.35	2.54	414	12.6	31.0	153.3	0.31	0.072
3.16	1.71	413	8.1	25.4	96.1	0.21	0.052
3.08	2.63	543	13.5	38.7	152.7	0.27	0.069

NORTH OF THE BAY

MgO	Fe	Mn	Cu	Pb	Zn	Cd	Hg
3.93	1.82	479	9.8	21.0	97.3	0.20	0.045
3.01	1.94	458	14.2	31.8	110.3	0.21	0.054
4.39	1.43	391	10.3	23.1	77.0	0.23	0.044

WEST PASS

MgO	Fe	Mn	Cu	Pb	Zn	Cd	Hg
3.44	2.38	541	12.1	35.5	134.1	0.19	0.048
2.63	2.10	493	14.1	33.1	121.3	0.29	0.056
2.44	2.47	410	14.7	41.1	163.4	0.37	0.093
2.51	2.40	475	13.3	39.4	156.9	0.38	0.086
2.28	2.76	579	15.7	45.3	171.5	0.28	0.083
2.74	2.49	521	13.4	37.8	148.9	0.27	0.060
3.23	1.51	393	7.3	16.0	91.3	0.20	0.049
2.43	2.52	684	12.5	33.4	158.0	0.26	0.086

WEST PART OF THE BAY

MgO	Fe	Mn	Cu	Pb	Zn	Cd	Hg
2.82	2.64	647	14.6	33.4	152.3	0.38	0.074
2.53	2.90	711	16.1	38.2	170.7	0.37	0.096
2.60	2.38	482	10.8	31.0	159.8	0.39	0.104
2.61	2.70	670	15.6	32.1	158.3	0.39	0.089
2.38	2.78	624	10.5	46.6	163.4	0.35	0.098
2.70	2.83	738	14.1	43.5	164.8	0.34	0.093
2.93	3.02	580	14.3	33.8	165.5	0.38	0.103
2.40	2.95	766	15.7	35.3	174.3	0.32	0.100
2.58	2.57	667	13.1	28.2	154.1	0.27	0.070
2.50	2.76	596	14.0	30.0	169.9	0.27	0.049
2.61	2.65	688	13.7	30.4	174.0	0.29	0.097

EAST PART OF THE BAY

MgO	Fe	Mn	Cu	Pb	Zn	Cd	Hg
2.33	2.90	763	15.8	46.5	178.6	0.34	0.111
2.65	2.57	704	14.6	39.3	162.4	0.38	0.105
2.98	2.38	630	12.8	37.6	153.5	0.27	0.092
2.47	2.67	604	14.5	41.2	159.9	0.36	0.085
2.68	2.73	615	14.8	32.2	159.6	0.31	0.090

CHARENTE OUTLET

An examination of the mean values of parameters measured on a site-by-site basis (Tab. 2) reveals that each predetermined zone presents individualized sedimentological and geochemical characteristics.

The west pass is characterized by the coarsest sediments (median, SiO_2, Zr), matched by the lowest contents in Al_2O_3, Rb and trace metals. High, Sr and MgO values, along with low concentrations in POC and Mn, underline the marine origin of these deposits.

Conversely, the finest materials (median, Rb) settle at the mouth of the Charente river. Their continental origin is reflected in high POC and Mn contents. The highest

Table 2

Means of the different variables for each area.

Valeurs moyennes des différentes variables mesurées dans les sédiments de surface.

Zone	Median	SiO_2	Al_2O_3	$CaCO_3$	Sr	COP	Zr	Rb
North of the bay	10.9	41.60	13.35	18.00	395.7	1.23	89.1	169.4
West pass	24.4	49.03	10.24	17.67	507.3	0.62	147.5	163.5
West of bay	16.1	44.39	12.08	17.40	411.3	1.02	101.3	168.7
East of bay	10.9	42.13	13.38	15.77	370.5	1.33	89.8	176.9
Charente	9.8	42.15	13.36	17.20	390.8	1.29	94.7	188.2

Zone	MgO	Fe	Mn	Cu	Pb	Zn	Cd	Hg
North of bay	2.85	2.50	581	12.3	36.0	145.8	0.30	0.079
West pass	3.78	1.73	443	11.4	25.3	94.9	0.21	0.048
West of bay	2.71	2.33	512	12.9	35.2	143.2	0.28	0.070
East of bay	2.60	2.74	652	13.9	34.8	164.3	0.34	0.093
Charente	2.62	2.65	663	14.5	39.4	162.8	0.33	0.097

concentrations in Cu, Pb, and Hg were found in these sediments.

Materials found in the east part of the bay and in the Charente river present very similar characteristics. The continental origin of these deposits is indicated by their high concentrations in POC and Mn as well as by their low concentrations in $CaCO_3$, Sr and MgO. Nevertheless, the east area shows lower carbonate contents than the estuary mouth. This difference may be explained by the fact that the Charente river drains a calcareous catchment basin which results in inputs into the bay containing a greater amount of carbonate phases. On the other hand, materials carried to the east of the bay by the Charente plume are diluted by non-carbonate inputs from the marshes bordering the eastern tidal flat. As for trace metals, the contents encountered in this site are among the highest, especially for Cd.

North of "Ile d'Aix", the nature of deposits is very similar to materials from the east part of the bay. The values of all parameters linked to particle size (median, SiO, Al_2O_3, Zr, Rb) are comparable. However in this area, the environment is open to marine inputs as shown by higher $CaCO_3$, Sr and MgO contents. These inputs dilute materials from continental origin, thereby decreasing POC and Mn concentrations and metal contents. This exception may be traced to the influence of inputs from the city of La Rochelle which may constitute an additional source of Pb.

The characteristics of sediments found in the west part of the bay show that these deposits are relatively coarse and present a more marine nature in comparison with sediments from the east area (higher $CaCO_3$, Sr and MgO contents, lower POC and Mn contents). Inputs of marine origin are more substantial in this area and are reflected in a decrease of concentration for trace metals (Cu, Zn, Cd, Hg).

Correlation coefficients between the different variables (Tab. 3) reveal that the particle size of sediments (as represented by their median) can explain relatively well the variations in the other parameters. A distinction may be made between a finer fraction with high POC and Al_2O_3 contents, and a coarser fraction characterized by the presence of Zr, MgO and Sr. The concentrations of metals are influenced by continental inputs represented by fine particles with the highest POC content.

MgO and Sr correlations with metals indicate that inputs of marine origin, represented by both of these elements, have low metal contents and dilute the continental inputs. The lack of any correlation between $CaCO_3$ and all other variables, and particularly with the carbonate phase of marine origin (Sr, MgO), may be explained by the geological context of this area. The region under study is lined with calcareous formations from the secondary era, reflected by fossil carbonate inputs of continental origin which do not have the same geochemical characteristics as the carbonate inputs formed in the marine environment.

Hg is well correlated to Fe, Zn and Cd. Its correlation, positive with POC and negative with Sr and MgO, suggests a continental origin for this element in the bay.

Cd shows only a clear correlation with Hg. The worst correlation of Cd with the other variables may be explained by the fact that Cd distribution in sediments may be partially governed by factors other than those measured in this study. This element is one of the trace metals most rapidly desorbed during its estuarine transit (Van de Weidjen *et al.*, 1977; Tada and Suzuki, 1982), particularly in macrotidal estuaries with long residence time of particles (Elbaz-Poulichet *et al.*, 1987). This behaviour was identified in the Charente river (unpublished results). Furthermore, results from a previous study (Gonzalez *et al.*, 1991) have shown that the particulate Cd inputs from this estuary cannot alone explain the Cd fluxes from the water column to the sediment which were recorded in the bay. It would thus appear that Cd inputs occur primarily in dissolved state, while the transition into particulate form results from the uptake of this element by phytoplankton. This hypothesis would explain how a portion of the Cd found in sediments could be linked to an organic fraction not taken into account by any of the measured variables.

Table 3

Correlation matrix of the different variables in the sediment (36 samples). The correlation coefficients > 10.51 are shown.

Matrice de corrélation des variables mesurées dans les sédiments de surface (36 échantillons). Seuls les coefficients dont la valeur absolue est supérieure à 0.5 sont représentés.

	Med	**SiO_2**	**Al_2O_3**	**Zr**	**Rb**	**$CaCO_3$**	**Sr**	**MgO**	**COP**	**Mn**	**Fe**	**Cu**	**Pb**	**Zn**	**Cd**
Hg	- 0,60	—	0,64	- 0,54	—	—	- 0,74	- 0,73	0,71	0,64	0,80	0,57	0,63	0,87	0,77
Cd	—	—	—	—	0,52	—	- 0,54	- 0,57	0,60	—	0,62	0,56	0,53	0,66	
Zn	- 0,74	—	0,65	- 0,68	—	—	- 0,74	- 0,80	0,81	0,67	0,95	0,72	0,72		
Pb	- 0,71	—	—	- 0,52	0,59	—	—	- 0,65	0,63	0,50	0,71	0,60			
Cu	- 0,60	—	—	—	—	—	—	- 0,57	0,57	0,52	0,74				
Fe	- 0,77	- 0,57	0,68	- 0,71	—	—	- 0,68	- 0,72	0,85	0,73					
Mn	- 0,59	- 0,53	0,61	- 0,64	—	—	- 0,54	- 0,57	0,72						
COP	- 0,85	- 0,68	0,78	- 0,81	0,54	—	0,73	- 0,71							
MgO	0,63	—	- 0,54	0,66	- 0,50	—	- 0,74								
Sr	0,60	—	- 0,81	0,80	—	—									
$CaCO_3$	—	—	—	—	- 0,53										
Rb	- 0,58	—	—	—											
Zr	0,63	0,61	- 0,79												
Al_2O_3	- 0,72	—													
SiO_2	—														

Cadmium and mercury in the water column

In the bay waters (Fig. 2 and Tab. 4), Cd contents in suspended particulate matter (SPM) range from 0.32 to 2.1 µg/g ; in the case of Hg, they vary between 0.25 and 2.6 µg/g. Their distribution is similar with the highest concentrations observed at the stations most remote from the continental inputs in sectors where SPM content is low, while in the more turbid areas close to the Charente river mouth and along the eastern coastline, particulate Cd and Hg contents are lower.

A comparison of contents for both metals respectively between suspended particles (Tab. 4) and sediments in the bay (Tab. 1) shows that concentrations are always higher in suspensions. Inside the bay, Cd contents in SPM are approximately double or equal to those found in sediments. In the case of Hg, contents are markedly different, with concentrations in SPM up to ten times higher. These differences may be explained by the fact that the size of suspended particles is finer and that POC percentages are higher, which leads to greater metal adsorption capacities. Furthermore in the top most layers of sediment, a portion of the Cd and Hg associated with the particles, is solubilized at the water/sediment interface during the aerobic degradation of organic matter (unpublished findings). The Hg enrichment factor in suspended matter as compared with Cd reflects a greater affinity of this element for particles, whereas in a coastal environment, Cd is more stable in dissolved state in the form of chlorocomplexes (Long and Angino, 1977).

As for the dissolved state of both elements (Tab. 4), concentrations range from 13 to 23 ng/l for Cd, from 0.34 to 0.81 ng/l for reactive Hg and from 0.53 to 0.86 ng/l for total Hg.

Cd and Hg concentrations in particulate and dissolved states were used to calculate the partition coefficient (Kd) of both elements (Tab. 4). It is the ratio of concentration in the particulate phase in µg/g to concentration in the solution in ng/l (concentration of total dissolved Hg in the case of Hg). This parameter permits an evaluation of relative enrichment or impoverishment of an element in its particulate phase as compared to its dissolved phase. Due to the relatively narrow range of dissolved metal concentrations, the coefficients of correlation of Kd with the other variables are very closed to the coefficients of correlation of the metals in the particulate phase with the same variables. A comparison of Kd for both elements (Tab. 4) reveals a greater affinity of Hg for the particulate phase. The negative correlation of Kd with the quantity of SPM (Tab. 5) may be explained by the link existing between SPM and POC contents (r = - 0.80) and between SPM and Al contents (r = 0.40). These relations show that an increase in SPM concentrations is accompanied by a decrease in POC contents and therefore of metal contents as well which are closely associated to particulate organic matter (Tab. 5). This decrease in POC percentages is due partly to a dilution of detrital particles represented by higher Al contents in suspended matter. On the other hand, in the sediments Al is abundant in the clay phase and this is the fraction for which POC and metals present the strongest affinity (Tab. 3). The waters with the highest SPM contents have a continental origin as shown by the strong positive correlations between SPM and dissolved nutrients (Tab. 5).

Kd correlations for Cd and Hg with the other variables (Tab. 5) invite a number of comments. In the particulate state, both metals are associated with organic matter. Cd contents rise in particles whenever chlorophyll concentration increases. The relation of Cd with chlorophyll, representing the living phytoplankton portion in suspensions, showns a behavior of Cd similar to that of nutrient elements. This association with nutrient cycles has been illustrated in the oceanic water column (Boyle *et al.*, 1976 ; Bruland *et al.*, 1978) and is not characteristic of shelf waters.

Table 4

Results of analyses of water and SPM (N : station number; SPM in mg/l; chlorophyll a *in mg/g and pheopigments in g/g; POC and Al in percentages; particulate Cd and Hg(p) in µg/g; nutrients in µM/l; dissolved Cd and Hg (d) in ng/l; Kd is the ratio of concentration in the particulate phase expressed in µg/g to concentration in the solution expressed in ng/l).*

Caractéristiques des échantillons d'eau et de MES (N : numéro de station ; MES en mg/l ; chlorophylle *a* en mg/g et phaéopigments en g/g ; COP et Al en pourcentages ; éléments nutritifs en µM/l ; Cd et Hg sous forme particulaire en µg/g ; Cd et Hg sous forme dissoute en ng/l ; Kd est le rapport de la concentration sous forme particulaire en µg/g sur la concentration sous forme dissoute en ng/l).

N	Depth	SPM	POC	Chloro	Pheo	Cdp	Hgp	Alp
1	Surface	13.9	1.61	0.20	52.59	0.32	0.48	8.06
2	Surface	16.4	2.16	0.12	16.46	0.38	0.25	9.45
3	Surface	8.2	3.30	0.24	18.36	0.34	0.40	8.48
4	Surface	—	4.04	—	—	0.89	—	6.52
5	Surface	3.0	3.79	1.39	3.30	0.57	0.45	8.40
6	Surface	3.5	4.00	1.08	2.87	0.48	0.49	6.35
7	Surface	2.9	5.78	0.59	3.50	0.50	0.65	8.70
8	Surface	2.3	—	1.68	4.31	0.49	0.51	5.59
9	Surface	2.2	4.18	1.24	36.20	0.71	0.91	6.78
10	Surface	0.7	—	—	—	2.09	1.27	7.42
11	Surface	1.5	5.39	1.56	164.47	0.74	0.64	5.83
11	8-5 m	2.3	—	1.21	97.35	0.64	1.54	3.75
12	Surface	1.6	5.40	3.19	6.17	0.89	0.62	6.85
13	Surface	—	4.62	—	—	0.58	—	10.40
13	8 m	—	—	—	—	—	—	—
14	Surface	5.1	2.17	0.23	54.47	0.37	0.51	7.88
14	7 m	—	3.22	—	—	0.46	—	9.58
15	Surface	2.9	—	0.36	124.14	0.46	0.51	6.73
15	6.5 m	3.9	—	0.31	134.72	0.46	0.80	8.33
16	Surface	0.8	—	1.18	457.83	1.15	2.65	10.31
16	27.5 m	1.8	—	0.51	361.11	0.50	0.88	4.75

N	Nitrate	Phosphate	Silicon	Cdd	HgRd	HgTd	KdCd	KdHg
1	3.1	0.85	14.0	16	0.70	0.78	0.02	0.62
2	1.1	0.52	6.5	14	0.58	0.84	0.03	0.30
3	1.1	0.60	9.4	15	0.60	0.73	0.02	0.55
4	0.2	0.29	5.8	—	0.61	0.63		
5	0.1	0.27	4.3	16	0.70	0.72	0.04	0.63
6	0.6	0.31	5.5	18	0.54	0.57	0.03	0.86
7	0.1	0.22	4.4	18	0.66	0.86	0.03	0.76
8	0.1	0.38	3.5	15	0.56	0.58	0.03	0.88
9	0.2	0.20	3.8	17	0.54	0.55	0.04	1.65
10	0.2	0.20	3.6	19	0.54	0.67	0.11	1.90
11	0.3	0.24	4.4	15	0.51	0.62	0.05	1.03
11	3.1	0.24	4.2	13	0.64	0.70	0.05	2.20
12	0.6	0.28	3.0	15	0.50	0.53	0.06	1.17
13	1.1	0.45	8.4	18	0.67	0.84	0.03	
13	1.2	0.47	6.3	21	0.63	0.63		
14	1.1	0.51	7.5	23	0.81	0.81	0.02	0.63
14	1.6	0.61	8.4	23	0.77	0.86	0.02	
15	0.5	0.38	6.0	18	0.65	0.76	0.03	0.67
15	0.6	0.43	6.1	20	0.75	0.77	0.02	1.04
16	1.0	0.25	3.4	15	0.34	0.63	0.08	4.21
16	1.3	0.27	3.3	16	0.61	0.77	0.03	1.14

In the case of Hg, there is no such relation with phytoplankton, which indicates that the Hg-POC association in particles would seem to occur in the form of complexes or through adsorption phenomena, unlike for Cd where, in addition to this type of link, there occurs also a mechanism of assimilation by the phytoplankton (Price and Morel, 1990). This may explain the poorer correlation coefficient of Hg with POC. Kd correlation with phaeopigments indicates that these two elements could present an affinity, stronger in the case of Hg, for the byproducts from phytoplankton cell degradation. The relations with nutrients (phosphates and silicates) derive from the fact that these elements are markers of continental waters in which, as mentioned earlier, suspended matter presents the lowest metal contents. Furthermore in the case of Cd, its link with phytoplankton activity causes its Kd to decrease whenever nutrients concentrations increase, *i.e.* when primary production is low.

This set of data provides an explanation for the difference existing between the spatial distribution of Cd and Hg contents in suspended matter and in sediments. As discussed previously, metal concentrations in sediments are higher close to the mouth of the Charente river and in the east ern part of the bay, while the opposite is true in the case of SPM for which Cd and Hg contents increase from the estuary to the open sea. This reversal may be attributed to the fact that, for the totality of particulate matter originating from the continent, the sedimenting fraction contains higher metal concentrations as compared with deposits from marine origin localized in the west part of the bay. Conversely in the Charente river plume, suspensions with high metal contents are diluted by detrital particles with impoverished metal contents and represented partly by aluminum. In areas removed from continental sources, water turbidity decreases by dilution and the organic fraction of suspensions increases; this is the fraction for which Cd and Hg present the strongest affinity.

CONCLUSIONS

This study has demonstrated that metal distribution in sediments is governed by the origin of these deposits and by their geochemical nature, as well as by the hydrodynamics controlling the distribution of sediments within the bay. Metals are associated with sediments of continental origin presenting high adsorption and complexing capacities (particle size, POC contents, Mn and Fe oxides and hydroxides).

In suspended matter, Cd and Hg contents are higher, particularly in less turbid areas remote from continental inputs, where primary productivity as well as organic carbon contents reach their maximum values. In the case of Hg, adsorption or complexing phenomena explain these high contents in the suspensions, as indicated by its extremely high Kd. As for Cd, in addition to the above phenomena, this element is assimilated by phytoplankton as a nutrient.

This recycling carried out by the phytoplankton may be responsible for the metal fluxes towards sediments recor-

Table 5

Correlation matrix of the different variables measured in the water column and in the SPM.

Matrice de corrélation des variables mesurées dans l'eau et les MES.

	SPM	Al	COP	Chlo	Pheo	Nit	Phos	Si	Kd Cd
Kd Hg	- 0,48	0.08	0,56	0,27	0,71	0,11	- 0,45	- 0,42	0,68
Kd Cd	- 0,48	- 0,08	0,70	0,68	0,50	- 0,21	- 0,58	- 0,53	
Si	0,76	0,40	- 0,71	- 0,59	- 0,26	0,56	0,93		
Phos	0,82	0,40	- 0,80	- 0,53	- 0,25	0,56			
Nit	0,45	- 0,08	- 0,71	- 0,28	0,14				
Pheo	- 0,33	0,03	0,09	- 0,09					
Chlo	- 0,54	- 0,31	0,68						
COP	- 0,80	- 0,30							
Al	0,40								

ded in the bay which cannot be explained merely by the particulate flows from the Charente river alone, particularly in the case of Cd (Gonzalez *et al.* 1991). Thus, cadmium inputs from the Charente river would seem to occur essentially in dissolved state. Within the bay, a portion of the dissolved Cd is assimilated by phytoplankton which in turn increases cadmium inputs into the sediment through its residues and the fecal pellets of phytoplankton-consuming organisms.

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