

Comparative Study of the Fixation of Inorganic Mercury on the Principal Clay Minerals and the Sediments of the Loire Estuary

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Received 29 May 1976 and in revised form 10 January 1977

Keywords: mercury; clay; adsorption; desorption; salinity; turbidity; estuarine circulation; France coast

Samples of kaolinite, illite, and montmorillonites were agitated with solutions of mercuric chloride at different salinities, clay turbidities, and concentrations of mercuric ions. The rates of adsorption and maximum quantities adsorbed were obtained in terms of these factors. Clays with known quantities of adsorbed mercury were agitated with fresh and salt water to measure rates of desorption. The values obtained are compared with an analysis of the water and sediments of the Loire Estuary, based on a large number of samples taken over the period 1972-1975. Mercury pollution has considerably decreased over this period.

Introduction

The presence of mercury at rather high concentrations in the waters and sediments of the estuary of the river Loire during the years 1973 and 1974, lead us to study its fixation on clay minerals in the laboratory. An initial study has already been made with kaolinite alone (Robin & Ottmann, 1976). This consisted in trying to fix inorganic mercury artificially and systematically on suspensions of kaolinite with variable turbidities, pH and salinities, corresponding with those met in the estuary so as to compare these data with those of the study *in situ*.

Since then, we have extended our theoretical research to the other most common clay minerals in the suspended materials found in the river Loire from April 1974 to December 1975. This study *in situ* concerns 900 analyses of filtered water and 600 analyses of sediments in suspension taken from an area extending from Nantes to St. Nazaire^a (Figure 1) (Anders, Andren & Harriss, 1973). Consequently, this report deals with both the fixation of mercury on kaolinite, illite, montmorillonites and the rations found in the estuary.

^aSample taking was done by Miss Morisson, Mr Gallenne, Mr Fresnel, Mr le Douarec and Mr Fablet.

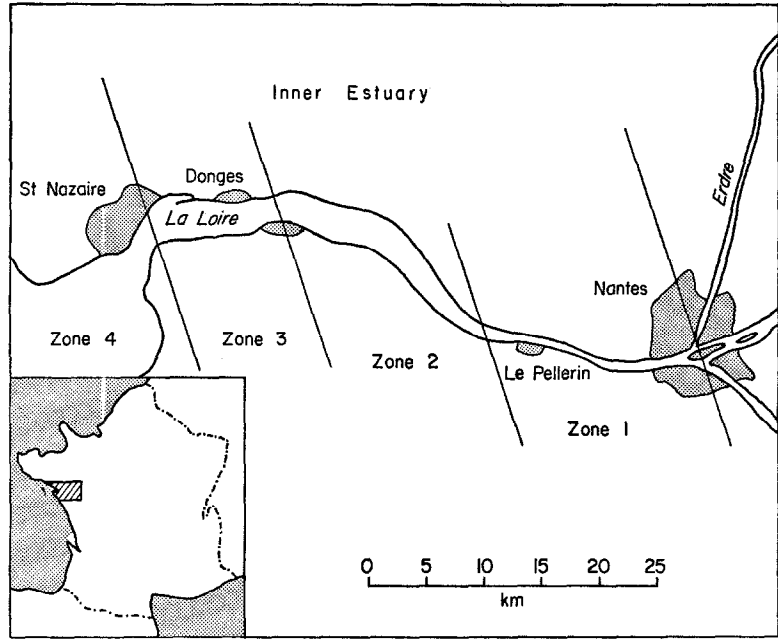


Figure 1. Map of the study area. Zone 1, dammed section; zone 2, intermediate section; zone 3, transitional zone; zone 4, outer estuary.

There is a problem arising about the kind of mercury that should be estimated. We have chosen 'total mercury' because according to Anders, *et al.* (1973) the ratio of organic mercury in solution is never more than 0.07% total mercury, and according to Jerneloew (1969) mercury is inorganic in sediments.

Our study on the fixation of mercury on kaolinite (Robin & Ottmann, 1976) lead us to the following conclusions:

- fixation increases with time, and levels off after an agitation period of 4 h;
- fixation increases linearly with the initial concentration of mercury in the solution, in the range of weak concentrations between 20 and 100 $\mu\text{g l}^{-1}$;
- fixation increases when turbidity decreases for an initial constant concentration in mercury;
- fixation decreases from 5 to 15% when salinity goes up from 0 to 20 g l^{-1} sodium chloride;
- fixation decreases when the pH increases, but in weak proportions. If we consider that the average pH of the waters of the Loire varies between 7 and 8 pH units, the variations are of little significance.

Testing for the fixation of inorganic mercury on different clay minerals

Procedure

The choice of the parameters for the laboratory study and of their scope of variation were made according to the hydrological and sedimentological characteristics of the waters of the Loire.

We adopted the following values:

pH 7-7.5, the pH most often found in the estuary waters;

turbidities ranging between 0.4 g l⁻¹ for surface waters and up to 4 g l⁻¹ for the waters along the river bed;

sodium chloride titration ranging between 0 and 20 g l⁻¹;

mercury ratios 20, 50 and 100 µg l⁻¹.

This last relatively high value corresponds with the ratios found in some industrial wastes, though, in Japan, according to Folz (1973) the same went up to 1 mg l⁻¹.

For each of the clay minerals, kaolinite, illite and montmorillonite, we followed the same procedure that we had used in our study on kaolinite (Robin & Ottmann, 1976). This method consisted in stirring for a given time in large size test tubes (60 cm long by 3.5 cm in diameter) 250-cm³ suspension of one mineral, with a given turbidity, salinity ranging between 0 and 20 g l⁻¹, and a given concentration of mercuric ions; (mercuric chloride for reasons of compatibility with seawater). Each suspension is then centrifuged and the liquid analysed by flameless atomic absorption according to the method of Hatch & Ott (1968) with a Perkin-Elmer Coleman Mas 50 mercury analyser.

To 100 cm³ liquid which is to be titrated are added a few drops of a saturated solution with potassium permanganate, 5 cm³ nitric acid at 35% and, after 1 min contact, 5 cm³ sulphuric acid at 50%. The excess of potassium permanganate is destroyed by 5 cm³ of an hydroxylamine chlorhydrate solution at 1.5%.

Mercury is then liberated in atomic form by a stannous chloride solution at 10% prepared externally and transmitted into the analyser by a pump. All the reagents which are used belong to the type quality 'mercury-less'.

Validity of the method

The small mercury titrations used require us to take each measurement in six identical samplings and so the results, in Tables 1a, 1b, are the average of these six determinations. The errors in the titrations made on the standard solutions and on the centrifuged suspensions are of the same order.

In Table 1b we conducted a test on kaolinite suspensions to estimate the error from titration.

TABLE 1a. Estimation of errors in titration with standard solutions

Mercury quantity in µg in 100 cm ³ standard solution	0.1	0.2	1.0	2.0	5.0
Error on measurements, per cent	±23	±20	±7.9	±5.7	±2.7

TABLE 1b. Estimation of errors with kaolinite suspensions

Initial mercury concentration (µg l ⁻¹)	20	50	100
Mercury quantity in 100 cm ³ liquid to be analysed in µg l ⁻¹	0.56	1.36	2.78
Error on measurements, per cent	±15.8	±7.5	±4.9

Experimental results

Fixation of mercury in terms of time and initial mercury concentration

First we studied the time necessary for a maximum fixation, and the different fixation times for the different clays (Table 2, and Figure 1a, 1b).

The curves obtained show a levelling off at the end of 4 h, and accordingly we have carried out our studies with an agitation period of 4 h which seems at first approximation the maximum time during which the particles remain in the same mass of water during a tide. We have varied the initial concentration in mercury from $20 \mu\text{g l}^{-1}$ to $5000 \mu\text{g l}^{-1}$ for a turbidity of 0.4 g l^{-1} and for the four clay minerals (Figure 3). We ascertain that for the

TABLE 2. Fixed mercury level on clay minerals ($\mu\text{g g}^{-1}$) in terms of time at 1 g l^{-1} turbidity and $50 \mu\text{g l}^{-1}$ initial mercury concentration

Salinity(‰)	Sediments	Time (h)				
		1	2	4	6	8
0	Kaolinite	31.7	36.8	37.8	37.9	38.0
	Calcic Bentonite	28.5	37.8	42.2	43.0	42.8
	Sodic Bentonite	31.2	41.2	45.9	45.2	45.6
	Illite	30.7	37.5	40.7	40.9	40.5
20	Kaolinite	23.3	28.6	30.5	31.2	31.0
	Calcic Bentonite	39.3	45.5	48.1	48.6	48.4
	Sodic Bentonite	25.5	35.9	41.3	41.7	41.9
	Illite	23.2	31.4	35.1	36.0	35.9

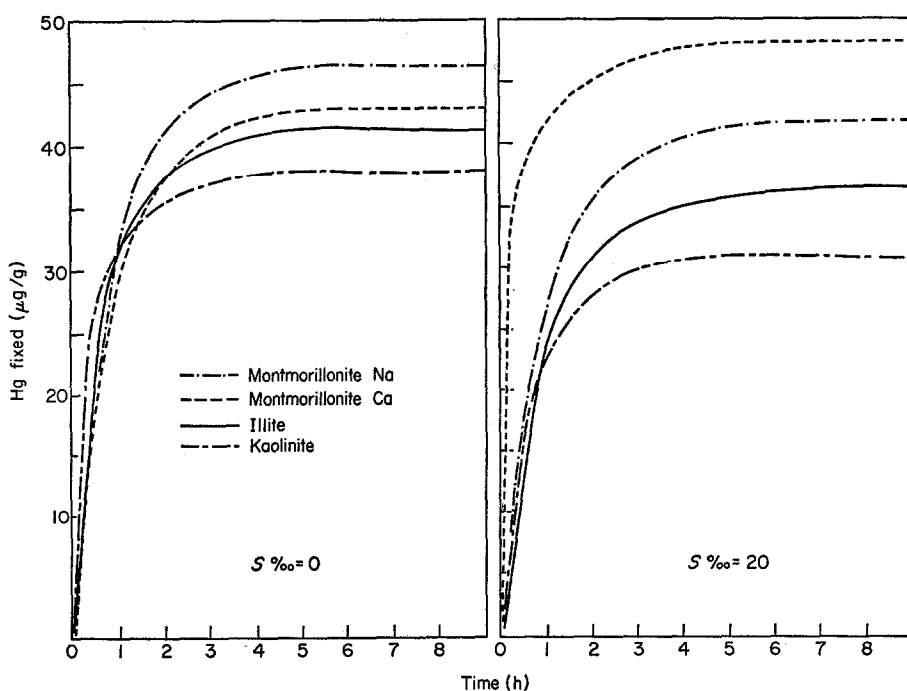
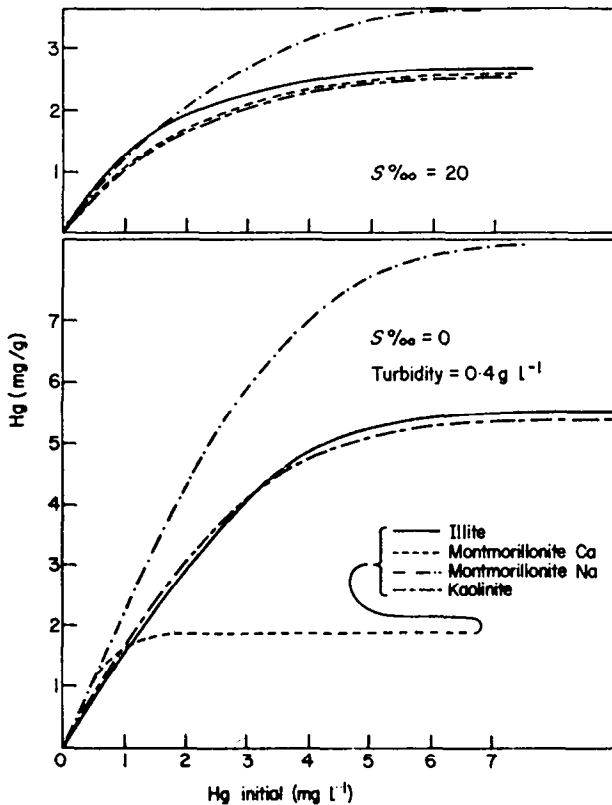


Figure 2. Fixed mercury level in the sediments in terms of (a) time in freshwater expressed in $\mu\text{g/g}$ of sediment (b) time in salt water (20‰) expressed in $\mu\text{g/g}$ of sediment.

TABLE 3. Mercury fixture in the sediments ($\mu\text{g g}^{-1}$) in terms of initial mercury concentration (mg l^{-1})

Salinity (‰)	Sediments Turbidity = 0.4 g l^{-1}	Initial mercury concentration (mg l^{-1})					
		0.02	0.05	0.1	0.5	1.0	5.0
0	Kaolinite	36.0	88.0	181.0	880	1 720	5 120
	Calcic bentonite	48.7	97.7	208.5	1 068	1 685	1 900
	Sodic bentonite	49.7	116.0	239.0	1 135	2 251	7 725
	Illite	32.2	90.7	188.0	815	1 595	5 275
20	Kaolinite	29.5	69.6	149.0	520	970	2 470
	Calcic bentonite	49.5	116.0	241.0	550	1 030	2 500
	Sodic bentonite	49.0	109.0	227.0	450	1 210	3 450
	Illite	27.2	71.5	133.0	675	1 275	2 625

Figure 3. Mercury level in the sediments in terms of initial mercury concentration at 0.4 g l^{-1} turbidity.

weak initial strengths in mercury, the rate of mercury fixed is a linear function of the initial rate (Table 3). Kudo & Hart (1974) also note that sediments accumulate mercury at different ratios depending upon the initial mercury concentration of the waters.

In freshwater, with the exception of illite, the variation of mercury fixed in terms of the initial concentration in mercury is linear up to $500 \mu\text{g l}^{-1}$, whereas in salt water (20 g l^{-1}) linearity is only verified up to $100 \mu\text{g l}^{-1}$. Figure 3 shows the mercury fixed ratio on the four

clay minerals in terms of the initial ratio in mercury at the two extreme values of the salinity (0 and 20 g l⁻¹). The curves that we get tend asymptotically towards what we shall call the 'limit of attraction' for the mercuric ion, valid for given turbidity and mineral.

The study of Table 3 and of the curves shows that montmorillonite is the clay mineral which fixes the most mercury in freshwater as well as in salt water. The 'limit of attraction' in soft water with high initial concentrations is nearly double the one we get in salt water with kaolinite, sodic montmorillonite, and illite. Calcic Montmorillonite can fix a greatest quantity of mercury in salt water. That is of importance for the freshwater-salt water transition in estuaries. If we compare these results to the interchanging capacities of cations of these clays (Table 4), we find variations in the same direction.

TABLE 4. Comparison of interchange capacity and maximum rate of mercury fixation

	Interchanging capacities of cations in milli-equivalent for 100 g	Maximum rate of mercury fixed mg g ⁻¹	
		Freshwater	Salt water(20‰)
Montmorillonite	100 to 130	7.7	3.6
Kaolinite	20	5.4	2.5
Illite	20 to 30	5.5	2.7

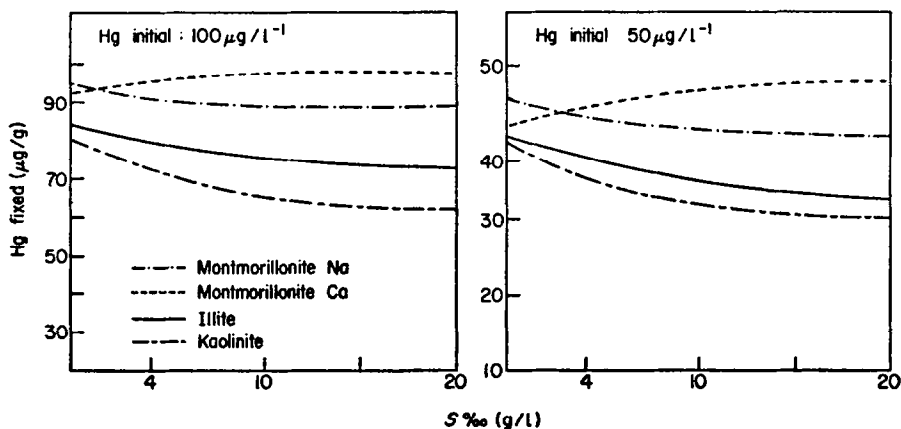


Figure 4. Fixed mercury level in the sediments in terms of salinity at 1 g l⁻¹ turbidity.

Fixation of mercury in relation to salinity

We have worked at the four following values: 0, 4, 10 and 20 g anhydrous sodium chloride per litre. The fixation of mercury decreases when the salinity increases for kaolinite, illite and sodic montmorillonite. Reimers & Krenkel (1974) arrive at the same conclusions for illite and montmorillonite. Hahne & Kroonje (1973a, b) explain that mercury does not fix much on clay minerals in the presence of a high chloric ion concentration (superior to 10⁻¹ M, that is to say 5.6 g l⁻¹ sodium chloride), because of the formation of a very resistant complex Hg Cl₄⁻ with a near 8 pH.

Figure 4 shows, as an example, the quantity of mercury fixed in µg g⁻¹ of dry sediment for a turbidity of 1 g l⁻¹ and for two different initial concentrations in mercury (50 and 100 µg l⁻¹), in terms of salinity and for each clay which is studied.

Fixation of mercury in relation to turbidity

We chose to use the finest granulometric fractions to make our suspensions (80% of the particles have a diameter between 3.5 and 0.2 μ). In effect, Renzoni, Bacci & Falciai (1973) have shown that mercury is fixed only on the smallest particles and that the quantity of mercury fixed on the sediments in suspension is inversely proportional to D , the diameter of the particle. Figure 5 shows, for an initial concentration in mercury equal to 100 $\mu\text{g l}^{-1}$, in fresh water, the rate of mercury fixed in terms of turbidity and for the four given clays.

We then studied fixation of mercury in terms of turbidity at three different values of the initial concentration in mercury (20, 50, 100 $\mu\text{g l}^{-1}$) and at four values of salinity (0, 4, 10, 20 g l^{-1}). This study allows us to conclude that the quantity of mercury fixed is in inverse ratio to turbidity, all the other parameters remaining unchanged (Table 5). The relation is most marked for sodic montmorillonite which is the most receptive clay mineral for mercury.

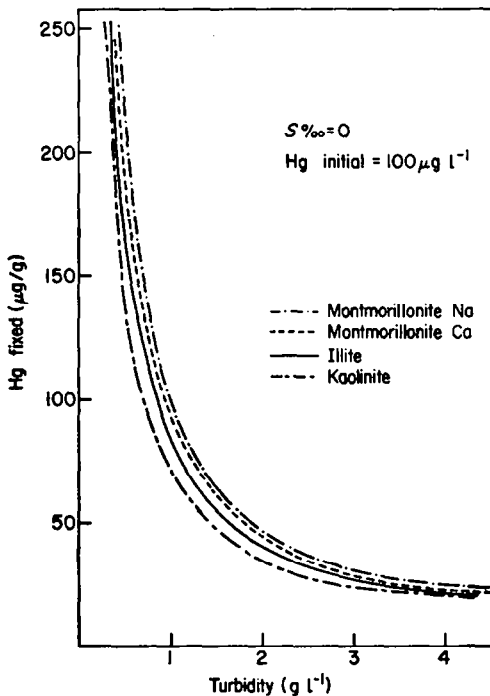


Figure 5. Fixed mercury level in the sediments in terms of turbidity.

Experimental results

Fixation of mercury in terms of time and initial mercury concentration

The study of Table 3 and of the curves shows that montmorillonite is the clay mineral which fixes the most mercury in fresh water as well as in salt water. The 'limit of attraction' in soft water with high initial concentrations is nearly double the one we get in salt water with kaolinite, sodic montmorillonite and illite. Calcic montmorillonite can fix a greatest quantity of mercury in salt water. That is of importance for the freshwater-salt water transition in estuaries.

TABLE 5. Quantity of mercury in relation to salinity, turbidity and initial concentration

Initial mercury concentration ($\mu\text{g l}^{-1}$)	Salinity (‰)	Turbidity (g l^{-1})	Fixed Mercury ($\mu\text{g l}^{-1}$)
20	0	0.4	49.7
		1	19.8
		4	5.0
	20	0.4	49.0
		1	19.5
		4	4.9
50	0	0.4	116.0
		1	45.9
		4	11.4
	20	0.4	109.5
		1	41.3
		4	10.1
100	0	0.4	239.5
		1	94.9
		4	23.5
		8	12.0
	20	0.4	227.0
		1	89.4
1000	0	4	22.2
		8	10.9
		1	828
		4	211
	20	10	86
		16	53.7
20	1	404	
	4	100	
	10	39.7	

Desorption of mercury fixed artificially on clay minerals

We have seen that the increasing of salinity causes a decreasing in mercury fixation on clay minerals. Thus it was necessary to know whether complete desorption is produced when going from freshwater to salt water.

Starting with sediments with given quantities of absorbed mercury, we stirred them for 1, 2, and 4 h in freshwater and salt water (20‰). Then we analysed the obtained liquids. Table 6 shows the percentage of mercury desorbed after a 4 h time of agitation.

Table 6 also shows that Montmorillonites fix mercury more permanently than do illite and kaolinite. This last is the one which can desorb the greatest quantity of mercury in salt water. This is of importance in an estuary because kaolinite is one of the most plentiful clay minerals in the nature. According to Gallenne (1974), in the Loire estuary, we can find 30% kaolinite, 30 to 35% montmorillonite and 25 to 40% illite.

Results of the studies *in situ* in the Loire estuary

Introduction

The aim of our laboratory study was to compare the ratios of inorganic mercury fixed on clay minerals with those found on the sediments in suspension. The samples of water were

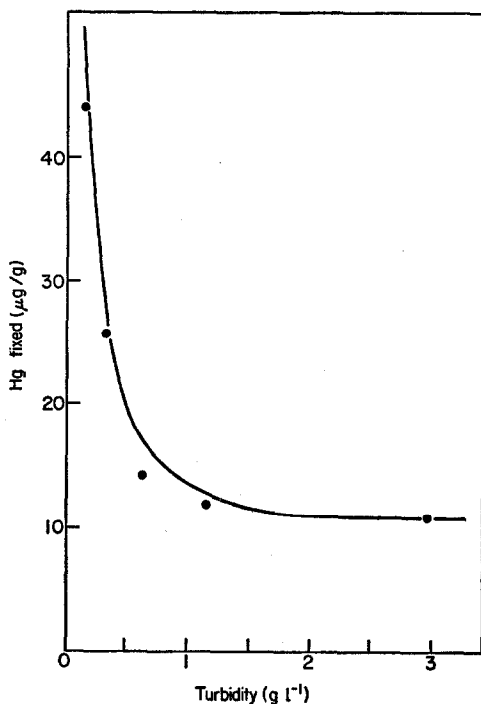


Figure 6. Fixed mercury level in the sediments in terms of turbidity. Statistical results of *in situ* studies.

TABLE 6. Proportion of mercury desorbed from different clays after 4 h agitation. Highest concentrations of mercury found for each salinity in the study area

Clay minerals	Freshwater (0)	Salt water (20 ‰)
Calcic montmorillonite	6.8%	5.4%
Sodic montmorillonite	3.5%	4.2%
Illite	10.6%	14.6%
Kaolinite	4.1%	19.6%

collected in polyethylene bottles of 250 cm³, containing nitric acid. They were analysed between 24 and 48 h after obtaining them to avoid losses of mercury due to fixation on the polyethylene. The sediments in suspension were collected on millipore filters, mineralized at 50°C in stoppered test tubes placed in a hot water-bath by a sulphonic mixture in the presence of potassium permanganate.

The values of turbidity, salinity, pH corresponding to these samplings have been furnished to us by the laboratoire de Géologie Marine de Nantes.

Results

The highest rates of mercury in estuarine waters are seen for salinities between 5 and 20‰ inclusive, as is shown by Table 7 in which appears the average of the results (in µg l⁻¹) we obtained between 1975-75.

The decreasing of the mercury ratio, as regard for salinities above 20‰, can be explained through the extreme dilution of river waters by the sea in the outer estuary off St. Nazaire. Table 8 shows the average values of the mercury ratios found in the filtered water samples with respect to tide and geographic area. The geographic classification of the results was carried out according to the same divisions of the Loire as those used by Gallenne (1974) (Figure 1):

TABLE 7. Concentrations of mercury found in the Loire at different salinities

Salinity (‰)	0-5 g l ⁻¹	6-10 g l ⁻¹	11-15 g l ⁻¹	16-20 g l ⁻¹	21-25 g l ⁻¹	26-30 g l ⁻¹
Average ratio of mercury in µg l ⁻¹	1.1	2.7	2.2	2.9	2.3	0.7

TABLE 8. Mercury concentrations at three states of tide in the four zones of the river and estuary designated in Figure 1

Zone:	1	2	3	4
Flood tide	1.1	1.3	2.5	1.1
Slack tide	1.1	0.7	1.0	0.6
Ebb tide	0.7	0.8	1.5	1.0

zone no. 1: dammed section (Nantes-le Pellerin)

zone no. 2: intermediate section (Le Pellerin-Paimboeuf)

zone no. 3: transitional zone (Paimboeuf-Donges)

zone no. 4: outer estuary (beyond St. Nazaire)

We can see that the rates of mercury in the water are higher during the flood tide whatever the zone is. This is due to the increasing salinity as tide rises towards Nantes.

The filtered surface waters are richer in mercury than those from along the river bed. This is explained by the fact that with a stratified estuary the surface waters contain few sediments and the removal by fixation is weak. On the other hand the waters along the river bed which are very rich in sediments, grow poorer in mercury by absorption on these sediments.

Sediments in suspension

The ratio of mercury fixed on the sediments in terms of turbidity is found to be the form of an exponential curve (Figure 6), the same type as those obtained for the four clay minerals (Figure 5) in the laboratory. If we express the mercury ratio in µg g⁻¹ of dry sediments, we can see that mercury fixes most on sediments in suspension in surface waters. This is because they are made of thin particles. Gallenne (1974) has shown that the upper part of the mud layer in the turbidity maximum contained the thinnest particles and so the more clayey and the richest in montmorillonite.

Smith, Nicholson & Moore (1973) have equally found in the Thames estuary higher concentrations of mercury fixed on the sediments which have a high proportion of thin particles.

Geographical distribution

Table 9 shows an important pollution of the waters as well as of the sediments corresponding with zone 3. It is by definition the zone of occurrence of the obturating mud layer with salinities averaging 20‰.

Change of pollution in time

Tables 10 and 11 show that pollution by mercury has appreciably decreased from 1972 to 1975. Following our first studies in 1972, we informed the responsible authorities of the existence of serious mercurial wastes upstream of the estuary. Administrative inquiries were carried out amongst the local industrial managers. It is probable that, once informed and conscious of the problem, the industrial managers reduced the volume of wastes.

TABLE 9. Quantity of mercury in waters and sediments

Subdivisions of the River Loire	Mercury in waters ($\mu\text{g l}^{-1}$)	Mercury in sediments ($\mu\text{g g}^{-1}$)	Salinities
Zone 1	1.1	46.8	Freshwater (‰)
Zone 2	1.2	22.9	Brackish (1–10‰)
Zone 3	2.5	28.0	Brackish (10–20‰)
Zone 4	0.7	13.2	Seawater (20–30‰)

TABLE 10. Averages of the different mercury analyses carried out in the Loire according to each zone—water

Subdivisions of the River Loire:	Zone 1	Zone 2	Zone 3	Zone 4	Entire Estuary	
Salinity:	0–1	1–10	10–20	20–30		
Year	1972	9.2	7.0	11.6	—	9.2
	1973	15.1	—	—	—	15.1
	1974	1.0	1.6	3.6	—	3.2
	1975	1.0	1.0	1.4	—	1.1

TABLE 11. Averages of the different mercury analyses carried out in the Loire according to each zone—suspended sediments

Subdivisions of the River Loire:	Zone 1	Zone 2	Zone 3	Zone 4	Entire Estuary	
Salinity:	0–1	1–10	10–20	20–30		
Year	1972	10.9	16.5	25.0	—	10.9
	1973	21.6	—	—	—	21.6
	1974		16.9	25.5	—	23.7
	1975	50.0	27.0	34.4	13.2	34.3

We ascertain with satisfaction that pollution by mercury has practically disappeared in 1975 in the waters. However one must keep in mind the concentration of mercury in the sediments in suspension which often arise from the river bed being put back into suspension. This conforms with the observations of Vernet & Thomas (1972) on the Rhône.

If we consider an average turbidity of 0.4 g l^{-1} for the estuary waters, we get an accumulation factor of 20 between Nantes and Le Pellerin. It reaches about 10 in zone 2 and falls to 5 in the outer estuary.

Conclusion

These experimental studies on clay minerals emphasize the process of fixation-desorption of mercury on sediments, especially in an estuary.

Fixation is rapid (4 h for the clays studied). This is important for the suspended materials which are in transit before arriving in the zone of the industrial wastes. Four to 6 h corresponds to the period necessary to transport sediments through the polluted areas. Fixation increases in a linear fashion for initial concentrations of mercury between 0 and $100 \mu\text{g l}^{-1}$ inclusive. For higher concentrations, fixation increases, tending asymptotically towards a levelling off depending on the turbidity and salinity of the sample.

The greatest proportion of mercury is fixed on the clay part of the sediments in suspension with in ascending order: kaolinite, calcic montmorillonite, sodic montmorillonite.

Desorption of mercury fixed artificially on clays is negligible for Montmorillonites and slightly less negligible for Kaolinite, which is a plentiful mineral in the estuary. Desorption is more effective in salt water than in freshwater, which explains the desorption of mercury fixed on sediments at high tide, or transported towards the open sea.

These studies show the prime role of the fixation of mercury on sediments in suspension. The obturating mud layer behaves as a 'purifying filter' in the waters of the estuary. Mercury in solution in the water is at an average ratio of $1 \mu\text{g l}^{-1}$; by contrast, in the sediments in suspension given an average turbidity of 0.4 g l^{-1} , there is 10 to 20 times more mercury.

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