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# **Fluvial Transports of Mercury Pollution in the Ill River Basin (Northeastern France): Partitioning into Aqueous Phases, Suspended Matter and Bottom Sediments**

J.L. PROBST, A. MESSAÏFFA, G. KREMPP, and P. BEHRA

## **1 Introduction**

The increase and dispersion in aquatic systems of mercury, which is not very abundant in the global environment, are mainly due to the industrial development and intensification of human activities (halogen chemicals, dental and pharmaceutical industries, agriculture, gold mining, etc.). In the Alsace region (northeastern France), the Ill river and one of its tributaries, the Thur, are the most polluted because of industrial wastewaters from the chlorine and soda industry which uses mercury as a cathode in electrolysis.

The Ill river, which is a tributary of the Rhine, drains the eastern side of the Vosges Massif and the Alsatian plain (Fig. 1). In this region, groundwater plays an important role in the economy and in hydrosystem equilibrium. In the upper part of the Ill drainage basin, the river greatly contributes to the groundwater supply (Esteves 1989; Roeck 1992), but the upper part of the Ill river presents strong positive anomalies in mercury concentrations which can be attributed to the industrial plants devoted to chlorine products in Vieux Thann (Dinh 1982).

Within the framework of French scientific programmes (i.e. GIP Hydro-systemes and Programme Environnement, Vie et Sociétés of CNRS), we have been studying the fate of mercury inputs into the Ill river from the pollution source in the upper part of the basin (Vieux Thann) to the downstream part of the basin, before the confluence with the Rhine, near Strasbourg (Probst 1996) since 1994.

The main objective of this study is to follow the fate of mercury in the river system, particularly in the different phases, i.e. aqueous phase, suspended matter and bottom sediments. It is also to determine the influence of physicochemical processes on the mercury fluvial transports in the different phases. This study is focused on the influence of the chloride concentration on mercury content in the solution, in a region where the chemical composition of the river water is highly influenced by saline industrial activity from potash mines, and also on the influence of sediment particle size on the distribution of mercury in river-suspended matter and in river bottom sediments.

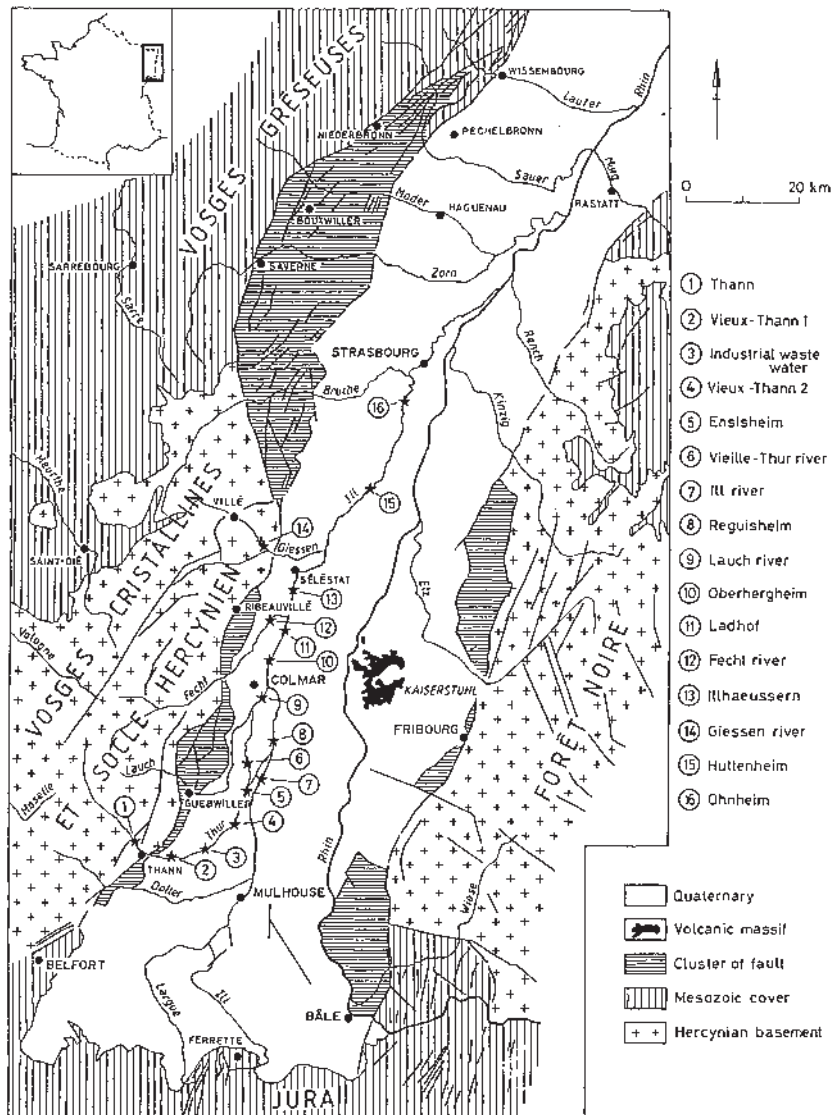


Fig. 1. Location map of the sampling stations in the Thur and Ill river basins

## 2 Material and Methods

Samples were collected during two low-water periods (October 1994 and July 1996) and two high-water periods (May 1995 and February 1996) at 16 sampling stations distributed along the Thur and the Ill rivers and at the outlet of the main

tributaries (Vieille Thur, Lauch, Fecht and Giessen; Fig. 1). For each water period, the samples were collected the same day for all stations; the hydrological conditions were thus the same for all the stations.

River water samples were immediately filtered in the field under nitrogen pressure using 0.45- $\mu\text{m}$  Millipore filters. For mercury analysis in the solute phase, the filtrate was put in a 500 ml Pyrex glass bottle with 20 ml of  $\text{HNO}_3$  (35%) and 20 ml of  $\text{H}_2\text{SO}_4$  (50%). To avoid mercury losses when the bottle is opened just before analyzing the filtrate, the bottle is closed with Parafilm and a cap. Some drops of  $\text{KMnO}_4$  (6%) are added to the filtrate just before analyzing to oxidize mercury. It is important to note that  $\text{KMnO}_4$  is added at the last moment rather than in the field after filtration because it could be observed that by adding  $\text{KMnO}_4$  in the field, a manganese precipitate is formed and traps mercury between the field and the laboratory.

Part of the filtrate is treated with  $\text{HNO}_3$  to analyze trace elements by ICP-AES (Samuel and Rouault 1983) or ICP-MS using a quick scanning method ( $\pm 10\%$  accuracy). The same techniques were used to analyze trace elements present in sediments. Major elements were determined for part of the filtrate without treatment in the field using the following classical techniques (Krempp 1988; Probst et al. 1992): atomic absorption for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  (accuracy 1  $\mu\text{mol/l}$ ), ionic chromatography for  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  (accuracy 1  $\mu\text{mol/l}$ ), Gran titration with  $\text{HCl}$  for alkalinity (accuracy 1  $\mu\text{mol/l}$ ) and colorimetric method for  $\text{H}_4\text{SiO}_4$  (accuracy 1  $\mu\text{mol/l}$ ).

The suspended matters and the bottom sediments were dried at room temperature to avoid mercury loss. As one can see in Fig. 2, when the drying temperature of the sediments increases, the mercury loss increases and the

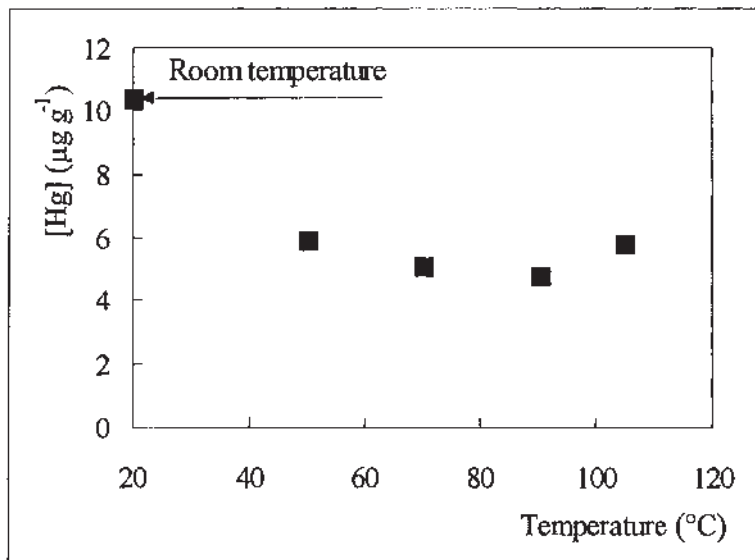


Fig. 2. Effect of the drying temperature of sediment on loss of mercury

mercury contents in the sediment decrease by about 50%, going from 20 to 80–100 °C drying temperature. For mercury analyses, the sediments are chemically digested with nitric and sulphuric acids in the presence of  $\text{KMnO}_4$ . Mercury is analyzed by cold vapour flameless atomic absorption spectrometry (CVFAAS) on a Perkin Elmer 430 with a preconcentration of gold powder if necessary (Krempp 1996). To avoid water vapour condensation on windows, the detection cell is heated at a temperature higher than the dewpoint. The absolute detection limit is 5 ng of mercury in the initial analyzed solution.

Mercury contents were analyzed in the different phases (aqueous phase, suspended matter and bottom sediments) and in the different granulometric fractions of the sediments. The bottom sediments were riddled to separate the different sand fractions (fine 50–200  $\mu\text{m}$  and coarse  $>200 \mu\text{m}$ ). The clay and silt fractions ( $<50 \mu\text{m}$ ) were separated by syphoning the sediments in suspension according to Stokes law [clays ( $<2 \mu\text{m}$ ), fine silts (2–20  $\mu\text{m}$ ) and coarse silts (20–50  $\mu\text{m}$ )]. This granulometric separation exercise was made only for the bottom sediments collected in February 1996.

### 3

#### **Spatial and Seasonal Variations in Mercury Content in the Ill River Basin**

Mercury concentrations measured at the different stations upstream to downstream are low in the solutions, as already shown for other rivers (Beim and Grosheva 1996; Grosheva and Hayashi 1996; Ikingura and Mutakyahwa 1996). These concentrations are sometimes even below the detection limit, even in industrial wastewater. All aqueous concentrations of mercury remain under the standard limit allowed for drinking water ( $1 \mu\text{g l}^{-1}$ , FAO/OMS 1972; EC 1980).

Nevertheless, the concentrations present a generally decreasing trend upstream to downstream in the basin, which can be attributed to river water dilution by the different tributary inputs and to sorption processes onto colloids (Fig. 3a).

It is interesting to note that the mercury concentrations in the aqueous phase are higher during the low-water period of July 1996 than during the high flows of February 1996. This difference between low and high-water periods must be related to the difference in solute mercury concentration in industrial wastewater ( $169 \text{ ng l}^{-1}$  in July and under the detection limit in February) and to the methylation processes of bottom sediment mercury. Contrary to the solutions, the suspended matter (Fig. 3b) and the bottom sediment (Fig. 3c) show high concentrations of mercury, as already shown for other rivers (Dauvalter et al. 1996; Dauvalter and Rognerud 1996; Ikingura and Mutakyahwa 1996). This is due to sorption processes onto sediments because of the high total dissolved solid concentrations in the river water (see next section) and of the high affinity of mercury for solid phase (Chapman et al. 1982; Dinh 1982; Behra 1987; Tiffreau et al. 1995; Tavares et al. 1996). However, as with the solutions, mercury

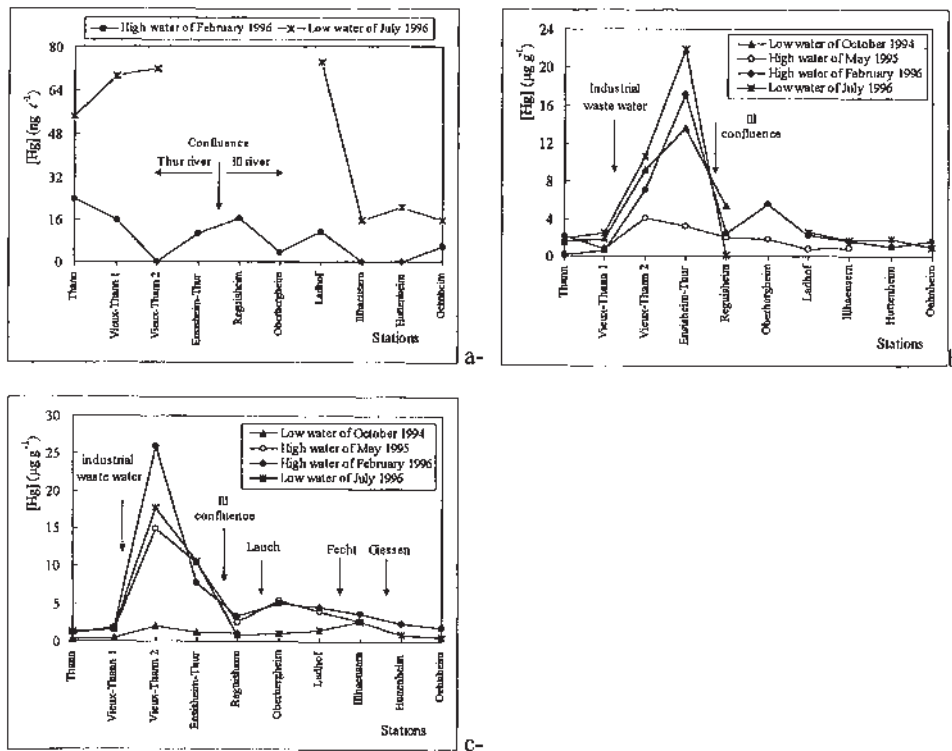


Fig. 3. Longitudinal profiles of mercury contents in the Ill river basin going from the Thur river (upstream) to the Ill river (downstream). a- In solution b- In suspended matters c- In bottom sediments

concentrations decrease upstream to downstream in the Ill river basin. The suspended sediments supplied by industrial wastewater to the Ill river in Vieux Thann station (between Vieux Thann 1 and 2) contain 13 to 438  $\mu\text{g g}^{-1}$  mercury depending on the sampling period. Then, these mercury-polluted sediments are progressively diluted in the river water by the input of unpolluted suspended matter coming from the physical erosion of the drainage basin.

In the river bottom sediments, concentrations of mercury are always greater than the regional geochemical background, which could be determined in this study by using previous measurements in river bottom sediments of several Ill tributaries which are not a priori polluted by mercury. As we can see in Fig. 4, the regional geochemical background value could be estimated at 0.3  $\mu\text{g g}^{-1}$  mercury in the bottom sediments by taking the average of values between 0.05 and 0.5  $\mu\text{g g}^{-1}$  mercury, which correspond to the world natural background limits (Chesterikoff et al. 1973; AFEE 1975; Martin and Scolari 1977; Lindqvist et al. 1984; Lindqvist 1986) and which are the most frequent values in the unpolluted areas of the Ill river basin. Nevertheless, it can also be seen in Fig. 4 that some bottom sediments present a relatively high mercury concentration, even in a

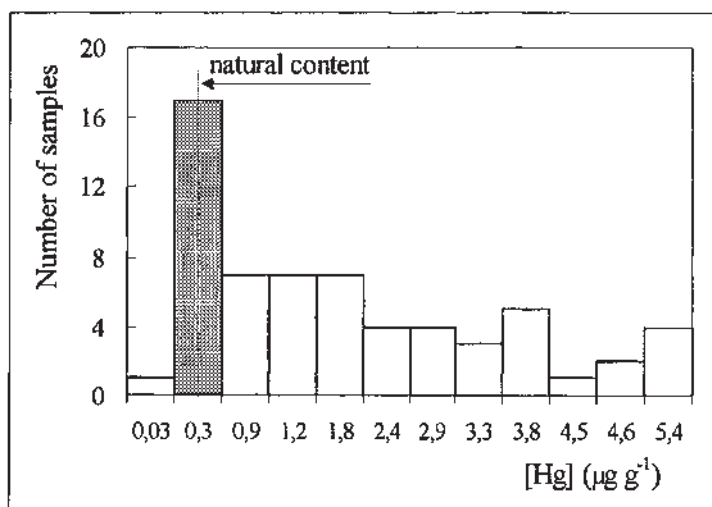


Fig. 4. Regional natural background of mercury content in river bottom sediments in the Ill basin (Data from Collin and Gendrin 1976 and Carbiener 1978)

priori unpolluted areas; but we are not totally sure that these areas have never been contaminated by mercury pollution in the past.

The differences that can be observed in Fig. 3 between longitudinal mercury concentration profiles corresponding to different sampling periods could be attributed to two main factors:

1. The amount of mercury discharged into the Thur river by industrial point pollution.
2. The climatic and hydrologic conditions of the sampling period, including the total river suspended sediment concentrations (TSS).

During the high-water period of May 1995, mercury concentrations in the suspended matter were generally lower than during the high-water periods of February 1996, in May 1995 the mercury concentration ( $110 \mu\text{g g}^{-1}$ ) in the suspended sediments of the industrial wastewater being four times lower than in February 1996 ( $438 \mu\text{g g}^{-1}$ ). In the Thur river part (until the Ill confluence), this difference could not be attributed to a dilution effect of the polluted suspended sediments by suspended matters coming from slope erosion because the total suspended sediment concentration is more or less the same during the two periods (Fig. 5) whereas in the Ill river part of the system, the dilution effect contributes to the decrease in mercury content in the sediment because the TSS concentrations are higher during February 1996 than during May 1995 (Fig. 5).

If one compares mercury concentrations in bottom sediments and in suspended matter, it is important to note that during the high-water periods of May 1995 and February 1996 the concentrations are higher in the bottom sediments than in the suspended matter, whereas during the low-water period of October 1994, on the contrary, the suspended matter is more concentrated. One

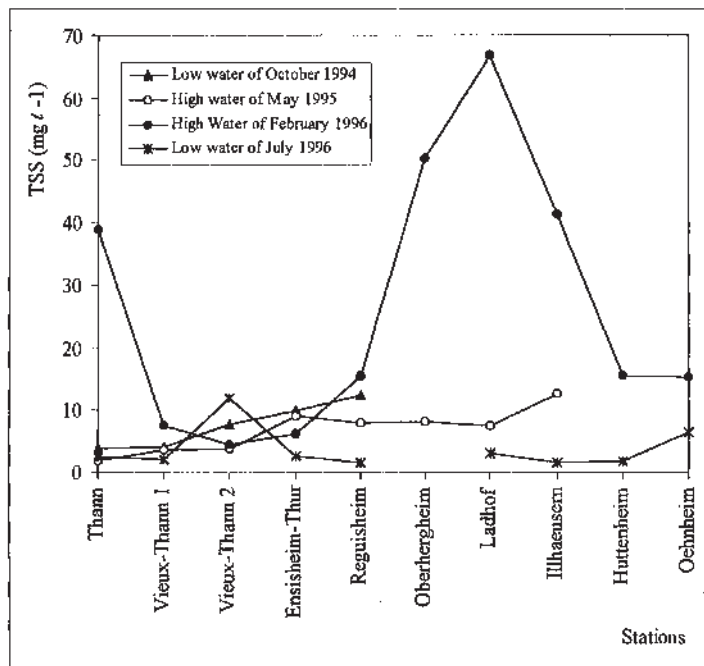


Fig. 5. Longitudinal profiles of total suspended sediment concentration (TSS) in the Thur and Ill rivers during the different sampling periods. a- High flows of February 1996 b- Low flows of July 1996

could explain these patterns by higher suspended sediment concentrations and higher water column depth, which, respectively, dilute the mercury concentration in the suspended matters and probably decreases the methylation processes of mercury in the bottom sediments. It is also important to note that the methylation processes which increase the losses of mercury in the bottom sediments are also limited by low temperature during the winter high-water periods. For example, it is interesting to note that the mercury content in the bottom sediment collected in the industrial channel is five times higher during the high-water period of February 1996 (winter time) than during the low flows of July 1996 (summer). Such methylation processes have already been observed on river basin or lake catchment scales, and the mercury fluxes which have been measured indicate relatively high specific values: 0.08–0.17 g methylmercury (MeHg)/km<sup>2</sup>/a for the Gardsjön catchment in Sweden (Lee et al. 1995), 0.07–0.30 g MeHg/km<sup>2</sup>/a for tributaries of Onondaga Lake in New York state, USA (Henry et al. 1995), 0.8–5.9 g MeHg/km<sup>2</sup>/a for Swedish catchments receiving mercury atmospheric deposition (Johanson et al. 1991), 0.3–2.3 g MeHg/km<sup>2</sup>/a for an unperturbed drainage basin in a Canadian boreal forest (St. Louis et al. 1994). If one considers that 2% (Mason and Morel 1993) to 89% (Gill and Bruland 1990) of total dissolved mercury originates from methylation processes, it is possible to estimate the methylation fluxes in the Ill river water (0.2–0.6 to 7–26 g MeHg/



km<sup>2</sup> per year). Even if these values are only rough estimations, they are in the same order of magnitude as the literature values quoted above.

The longitudinal profiles of July 1996 are rather exceptional because the high mercury concentrations which can be observed both in the suspended matter and in the bottom sediments must be attributed to the highest solute mercury concentrations (169 ng l<sup>-1</sup>) measured in the industrial wastewater in Vieux Thann and to accidental pollution of the Thur from the wastewater treatment station in Cernay.

The mercury concentrations measured in the different tributaries of the Ill river after the confluence with the Thur river, i.e. the Lauch upstream Colmar, the Fecht between Colmar and Selestat and the Giessen downstream from Selestat are very low in the different phases and within the ranges of natural values.

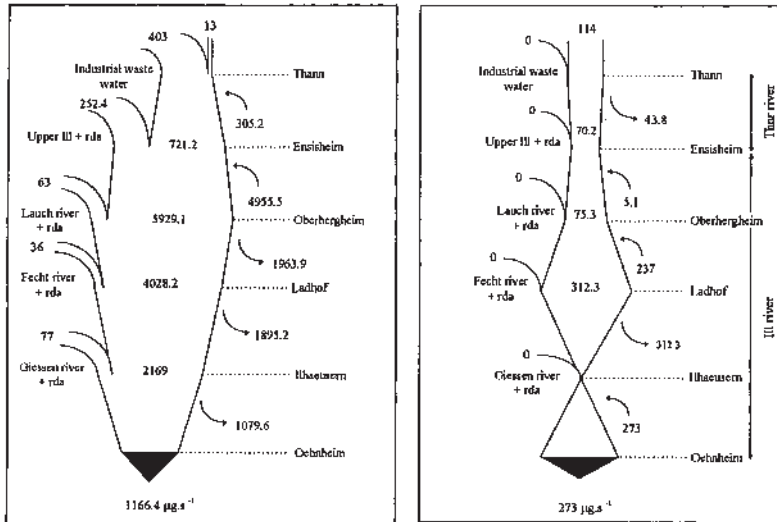
#### 4

#### Mercury River Fluxes in Particulate and Dissolved Phases

Using mercury content in the dissolved and particulate phases and river discharge measurements at different gauging stations, it has been possible to calculate the amount of mercury transported in solution and in suspension by the Ill river and its tributaries. For each sampling period, one can follow the spatial evolution of mercury fluxes going from the upstream part of the basin to downstream (Fig. 6a, b). Globally for the whole basin, the particulate river fluxes of mercury appear to be higher during the high-water period of February 1996 than during the low flows of July 1996 (Fig. 6a). This is mainly due to higher industrial mercury fluxes, higher river-suspended sediment transports and important remobilization of river bottom sediments. In contrast to particulate phases, the solute mercury river fluxes are higher during low flows than during high-water periods (Fig. 6b). This can be attributed to a higher solute mercury content in the industrial wastewater and to methylation processes of bottom sediment mercury which increase the mercury concentration in the solution. It is interesting to note in Fig. 6b that solute mercury fluxes are rather important downstream from Oberhergheim station, even if at this station the river discharge decreases to zero because of river water infiltration to groundwater. This means that downstream from this station, mercury in dissolved phases mainly originates from methylation processes of mercury previously adsorbed on bottom sediments.

If one compares the shape of the spatial evolution of particulate mercury fluxes during the two sampling periods (February and July 1996), it becomes evident that for the high-water period the fluxes increase until Oberhergheim and decrease in the lower part of the basin, whereas for the low flows it is the contrary. In the upper part of the river, the increase during high flows is due to remobilization of mercury-enriched bottom sediments while the decrease during low flows can be attributed to sedimentation processes. In the downstream part, after Oberhergheim station, the slope of the main channel decreases and the sedimentation processes become active even during high-water periods, as could

a- High flows of February 1996



b- Low flows of July 1996

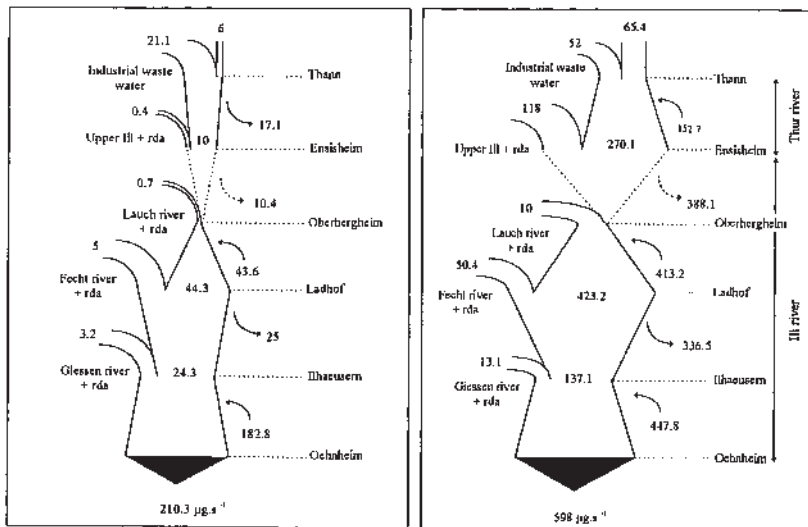


Fig. 6. Spatial evolution of mercury fluxes (in  $\mu\text{g}\cdot\text{s}^{-1}$ ) in particulate (left side) and dissolved (right side) phases in the upper Ill river basin during high (a) and low (b) water periods. rda; Residual drainage area

be observed in the spatial behaviour of total suspended sediment transports (Messaitfa 1997). On the contrary, during the low flows, the particulate fluxes of mercury increase in the downstream part, from Oberhergheim to Oehnheim,

mainly because of methylation processes and biological autochthonous production, which increase the total suspended matter concentrations and the mercury content in suspended matter.

As one can see in Fig. 6a, b, it was possible, using input-output budgets between two sampling stations, to calculate the flux of particulate mercury which was lost by sedimentation processes or supplied by remobilization of bottom sediments. These mercury losses or gains during the river-suspended sediment transport could be compared in Fig. 7 with mercury content behaviour in bottom sediments for each river channel section. As seen in Fig. 7, there is a good relationship for each sample between the mercury concentration calculated for the remobilized or deposited part of the suspended sediment fluxes and the mercury content in the downstream bottom sediments.

## 5 Influence of Particle Size on Mercury Content in the Sediments

To determine the influence of particle size on mercury content, we decided to work on bottom sediments because the suspended matters are always fine fractions (clays and silts), particularly during the low-water flows. As can be seen in Fig. 8, the granulometry of the bottom sediments has a great influence on the distribution of mercury content. Fine particles (clays and silts,  $<50 \mu\text{m}$ ) are more concentrated in mercury (in  $\mu\text{g g}^{-1}$ ) than the coarse fractions (sand  $>50 \mu\text{m}$ ).

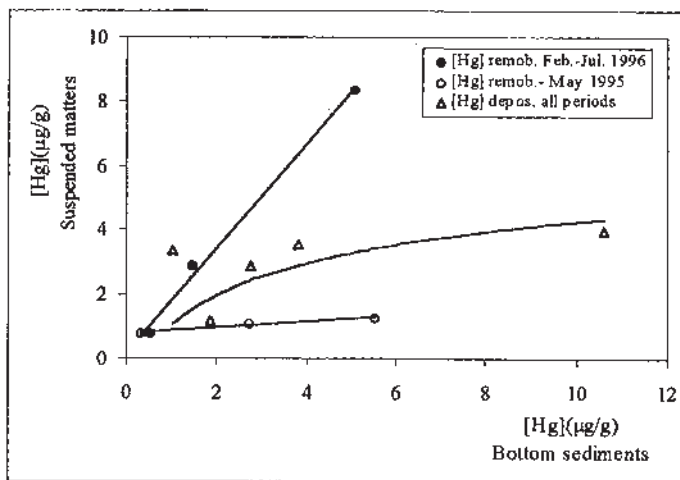


Fig. 7. Seasonal relationships between mercury content in suspended matter deposited (triangle) in the river bed or remobilized (black and white circles) from bottom sediments between two stations and mercury concentration in bottom sediments at the downstream station

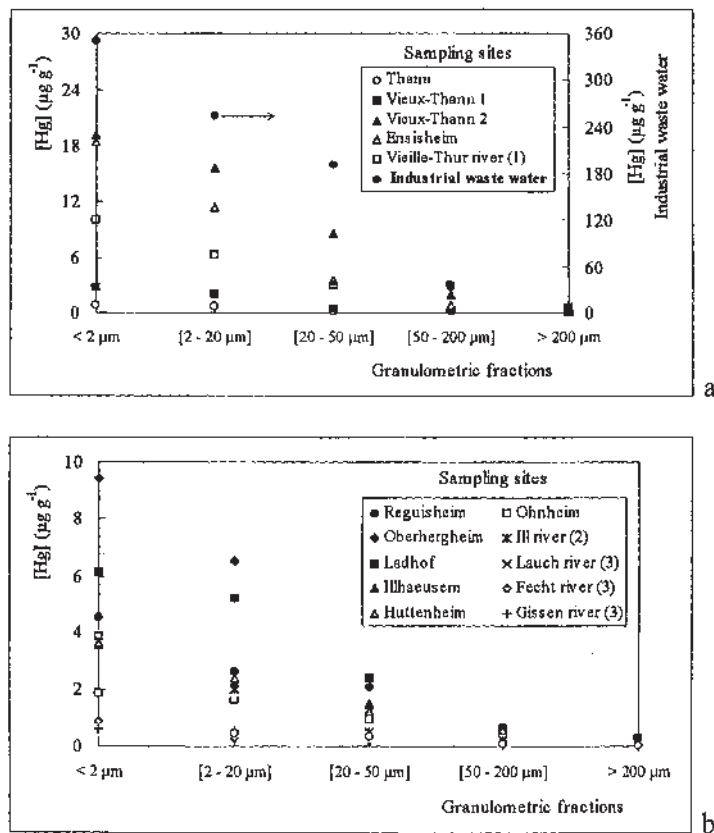


Fig. 8a,b. Mercury content in the different granulometric fractions of the bottom sediments collected during the sampling mission of February 1996 at the different stations of the Thur river (a) and of the Ill river basin (b)

These patterns are in agreement with previous results obtained by different authors (De Groot et al. 1971; Oliver 1973; Smith et al. 1973; Jaffe and Walters 1977; Robbe 1984). Thus, it is evident that mercury sorption is more important onto the finest particles (Reimers and Krenkel 1974; Reimers et al. 1974) which have the highest specific surface area, particularly onto the so-called clay fractions as is also the case for other metals (Kudo 1977; Boust 1981; Boust et al. 1981). Nevertheless, the abundance of mercury in the different fractions (Fig. 9) depends also on the relative abundance of these fractions. Indeed, even if the mercury concentrations are lower in the coarse fractions, the total mercury contained in these fractions is not negligible, if these fractions are abundant. This mercury sorption onto sandy sediments must be taken into consideration in such a study. This is the case, for example, for the stations of Thann and Vieux Thann 2 on the Thur river and Illhauserm on the Ill river and for two other stations on the Vieille-Thur and Fecht rivers (Fig. 9). Of course, the sorption of

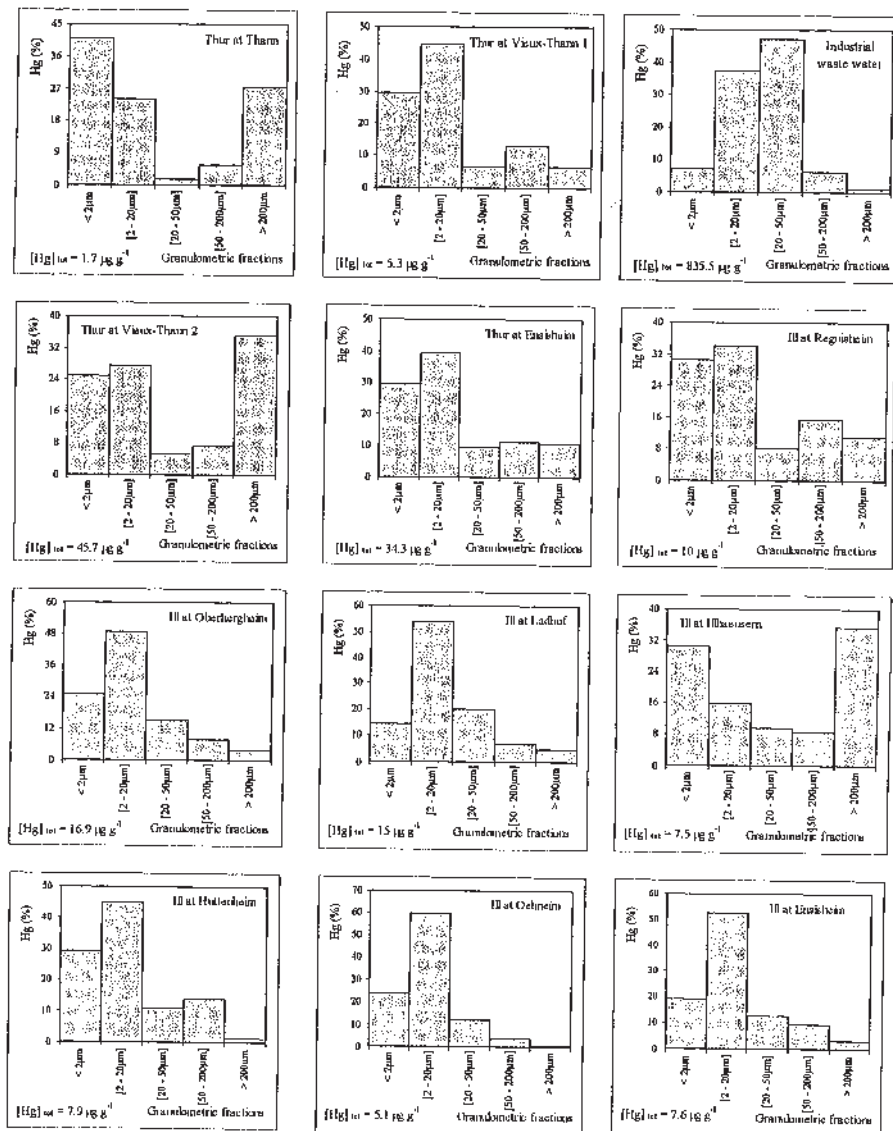


Fig. 9. Distribution of total mercury in different granulometric fractions of the river bottom sediments collected during the sampling mission of February 1996 at the different stations. The mercury content in each fraction is expressed as a percentage of total mercury content in the whole sediment

mercury onto sediments depends not only on the particle size distribution but also on the physicochemical, mineralogical and surface composition of these particles. ICP-AES and ICP-MS analyses show that mercury pollution in the sediments is associated with high concentrations of Al, Fe, Mn and Ti (Messaitfa 1997).

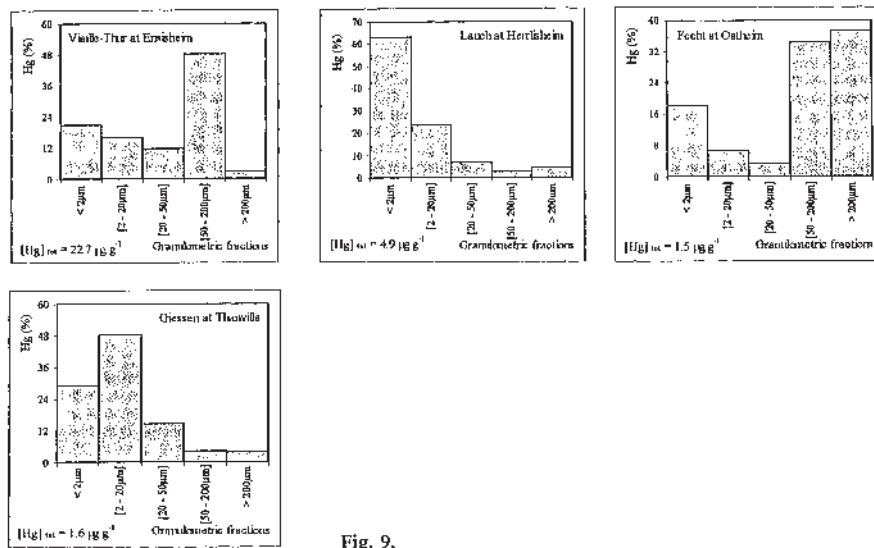


Fig. 9.

## 6

### Influence of Chloride Concentration on the Mercury Content in the Different Phases

#### 6.1

##### Field Measurements

The upstream part of the Ill river basin is also polluted by saline industrial activity of potash mines which supply mainly sodium chloride indirectly into the river. Consequently, chloride concentrations are very high in the Thur and Ill rivers. Contrary to what has already been reported by different authors (Beijer et al. quoted by Fagerström and Jernelöv 1972; Robin and Ottmann 1976; Frenet 1979; Behra 1987; Melamed and Villas Bôas 1996), mercury content in suspended matter and in bottom sediments of the Thur-Ill river system increases with chloride concentration (Fig. 10b, c). At the same time, mercury concentration in the solution decreases (Fig. 10a). Thus it is possible that increasing chloride concentration in the solution could play a role in mercury sorption onto metal (hydr)oxides present in the sediments.

#### 6.2

##### Laboratory Experiments

In order to test the influence of chloride concentration on mercury sorption, we carried out two laboratory experiments during the same time: the first with bottom sediments of the Thur river collected at Ensisheim and the second with a

mercury solution prepared in our laboratory. In the first experiment, we wanted to test the reactivity of a mercury-polluted sediment containing  $10.4 \mu\text{g/g}$  of mercury to increasing NaCl concentration solutions by measuring the mercury concentration in the sediment and in the solution at each step of the experiment. The second experiment is not directly related to the field observations. Nevertheless, it is important to test the competition between mercury ( $\text{HgCl}_4^{2-}$ ) and  $\text{HPO}_4^{2-}$  (which is well known to have a great affinity for particulate surfaces; Sposito 1989) present in the solution in order to be sure that mercury is really trapped by manganese precipitate when the NaCl concentration of the solution increases. This hypothesis could be verified by measuring the evolution of mercury concentration when the NaCl concentration increases in the presence or absence of  $\text{Na}_2\text{HPO}_4$ .

The results obtained during the first experiment (Fig. 11a, b) show that the mercury desorbed from the sediment into the saline solution decreases when the salinity increases. Nevertheless, it can be observed that for the silt fractions ( $2\text{--}50 \mu\text{m}$ ), the total mercury desorbed increases during the first three steps of salinity increase, until  $3.4 \text{ mmol/l}$  of NaCl, and after decrease, as for the clay fractions ( $<2 \mu\text{m}$ ). It is surprising to note that when the NaCl concentration increases, the mercury contents decrease, not only in the solution but also in the sediments, and could not even be detected in the two phases when NaCl concentration reaches  $0.1 \text{ mol/l}$ . This behaviour could be explained by the sorption of mercury onto metal (hydr)oxides when salinity increases; but mercury trapped in this complex could not be detected. Indeed, the classical chemical digestion with nitric and sulphuric acids did not allow the release of mercury to be analyzed because at pH1 and high chloride concentration, the

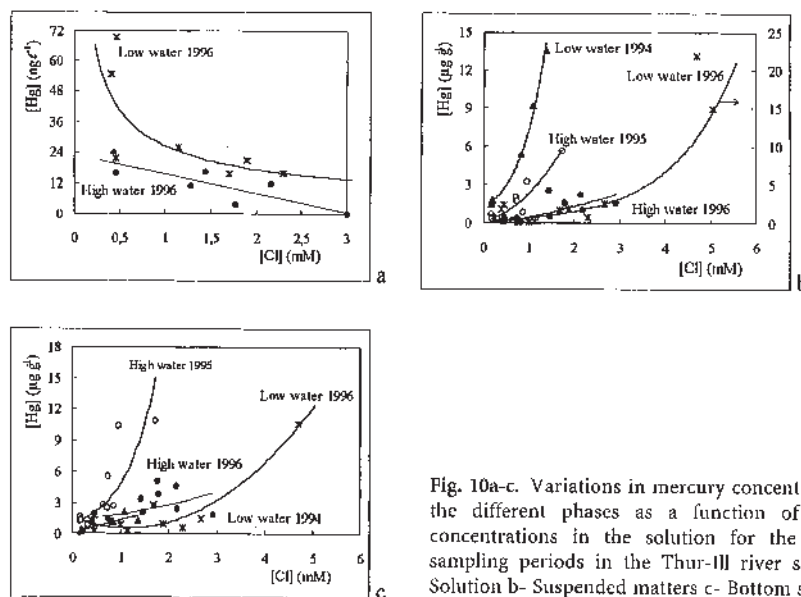


Fig. 10a-c. Variations in mercury concentrations in the different phases as a function of chloride concentrations in the solution for the different sampling periods in the Thur-III river system. a- Solution b- Suspended matters c- Bottom sediments

**Table 1.** Experimental conditions of the second experiment. Competition between mercury and  $\text{HPO}_4^{2-}$ 

	Step 1	Step 2	Step 3
Experimental conditions	- $\text{KMnO}_4$ = 5 drops - $\text{HNO}_3$ (35%) = 4 ml - $\text{H}_2\text{SO}_4$ (50%) = 4 ml - $[\text{NaCl}] = 0.001 - 0.4 \text{ M}$	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (4.2 g $\text{l}^{-1}$ )	$[\text{Hg}] = 5 \mu\text{g l}^{-1}$
Reaction times (h)	24	24	24
Observations	Manganese precipitate	Addition of phosphate	Addition of mercury

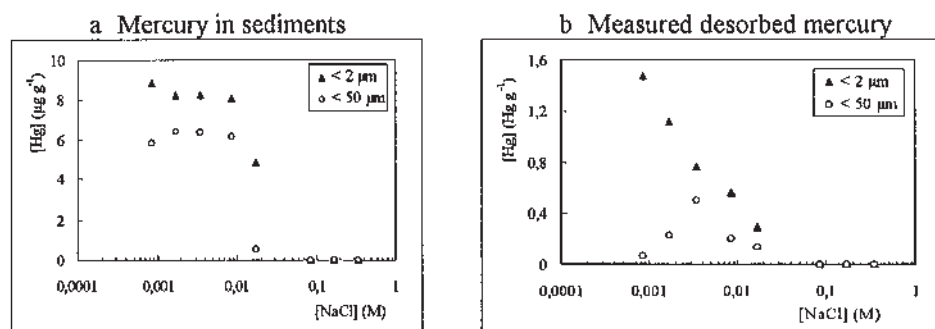
stable mercury species ( $\text{HgCl}_4^{2-}$ ) (Michard 1989) is strongly adsorbed onto metal oxides due to the oxide protonation surface ( $\equiv\text{S-OH}^+$ ).

The second laboratory experiment exemplified the effect of manganese precipitation which could be observed during the first sampling because  $\text{KMnO}_4$  was added to the solution in the field (see Material and Methods). The experimental conditions are described in Table 1; pH values remain acidic during the experiment.

As during the first experiment, the mercury concentration in the solution decreases to zero when the sodium chloride concentration reaches 0.1 mol/l in the absence of  $\text{Na}_2\text{HPO}_4$  (Fig. 12a).

It is important to note that below 0.1 M NaCl, the solution remains coloured purple by the  $\text{KMnO}_4$ . Whereas when the NaCl concentration exceeds 0.1 M, a manganese precipitate appears at the bottom of the bottle and the solution becomes colourless. Coprecipitation with or sorption of mercury onto manganese precipitate could explain why the concentration decreased to zero in the solution.

In the presence of  $\text{Na}_2\text{HPO}_4$ , mercury and  $\text{HPO}_4^{2-}$  appear to compete to be adsorbed onto the manganese precipitate; but mercury presents a greater affinity on manganese precipitate than  $\text{HPO}_4^{2-}$ . Consequently, when the NaCl concen-



**Fig. 11a,b.** Results of laboratory experiments with the fine fractions (<50  $\mu\text{m}$ ) of the Thur river bottom sediments collected at Ensisheim. a Evolution of mercury content in the sediments (clay and silt fractions) when NaCl concentration in the solution increases. b Evolution of desorbed mercury concentration in the solution when the NaCl concentration of the solution increases.



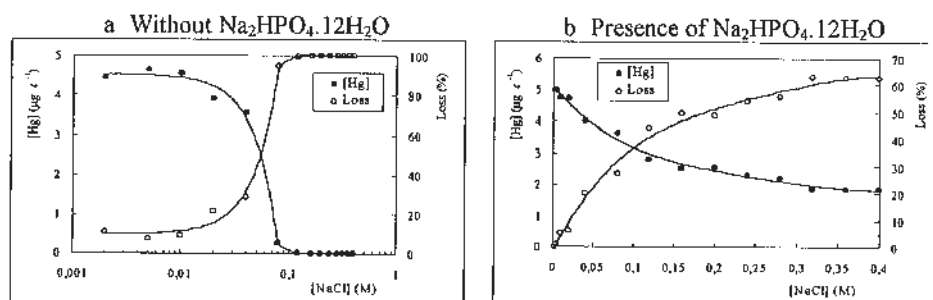


Fig. 12. Evolution of mercury concentration in the solution when chloride concentration increases. a- Without  $\text{Na}_2\text{HPO}_4$ , b- With  $\text{Na}_2\text{HPO}_4$  (see experimental conditions in table 1). The losses of mercury are expressed in % of the initial mercury content in the solution ( $5 \mu\text{g l}^{-1}$ ).

tration increases (Fig. 12b), the mercury content in the solution decreases also, but less than in the absence of  $\text{Na}_2\text{HPO}_4$ . For NaCl concentration greater than 0.1 M, the losses of mercury in the solution are only 30–60% of the initial mercury content ( $5 \mu\text{g l}^{-1}$ ), instead of 100% in the absence of  $\text{Na}_2\text{HPO}_4$ . As quoted by Tiffreau (1996), Mn oxides are very good sorbents for mercury even at very low pH, due to their low point of zero charge.

## 7

### Conclusion

The Ill river and one of its tributaries, the Thur river, show evidence of mercury contamination which could be attributed to industrial wastewater input in the upstream part of the Thur river. The study of mercury pollution behaviour in the Thur-Ill river system during four sampling periods shows that mercury is highly concentrated in suspended matter and in bottom sediments, whereas in solution, the mercury content is very low and often below the detection limit. Mercury concentrations in sediments are largely superior to the regional natural background of mercury content in the river bottom sediments, which could be determined in this study as  $0.3 \mu\text{g/g}$  in the unpolluted areas of the different Ill tributaries. The longitudinal profiles of mercury content established from 16 measurement stations present more or less the same pattern in the different fractions (solution, suspended matter, bottom sediments): the mercury concentrations progressively decrease from the pollution source to the downstream part of the Ill basin by natural dilution processes due to water and suspended sediment inputs by the different tributaries. The differences observed between the sampling periods could be due to the initial mercury concentration in the pollution source and to hydrological and climatological conditions. High mercury concentrations in the industrial wastewater induce high mercury content in the river system. Low-water periods corresponding generally to high

air temperature, low-water column depth and low-river suspended sediment concentration could be favourable to methylation processes in the river itself, decreasing the mercury content, particularly in the river bottom sediments. The mercury methylation fluxes which could be roughly estimated for the Ill river are in good agreement with the values literature. On the contrary, during high flows, these processes are relatively limited and mercury contents in the river system could be higher even if the dilution effect is more important.

Input-output budgets of mercury river fluxes from upstream to downstream in the basin showed the different processes which control the particulate and solute river transports of mercury pollution, such as mercury methylation in bottom sediments particularly during low-water periods, deposition or remobilization of suspended matter according to the hydrological season and the channel section.

A granulometric study of the bottom sediments shows that mercury concentrations are higher in the finest particles (clays and silts  $<50 \mu\text{m}$ ) for all the stations, but the abundance of the different granulometric fractions must be taken into account in the global mercury budget of the sediment. That means that if coarse fractions (sand  $>50 \mu\text{m}$ ) are abundant, the contribution of these fractions to total mercury content in the sediment must be considered.

It could be shown also that river water salinity could play an important role in the mercury sorption onto river sediments, particularly in the Ill river basin, where industrial saline activity supplies high sodium chloride wastewater to the Thur and Ill rivers. Our field measurements show that when the chloride concentrations increase in the river water, the decrease in mercury content in the solution is associated with an increase in mercury concentration in the suspended matter and in river bottom sediments. Laboratory experiments showed that when the salinity increases, mercury can be trapped, for example, by manganese precipitates. This example illustrates the possibility of solute mercury being adsorbed onto colloidal phases when salinity increases, as could be observed in the field.

New laboratory experiments and other field sampling missions are planned to confirm the different assumptions. It is also very important now to study mercury speciation in the different phases and to determine the impact of this mercury contamination on the groundwater and on the Ill river ecosystem by studying, for example, mercury content in mosses and in fishes.

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