Geochimica Brasiliensis, 20(2)133-147, 2006

Geochimica
Brasiliensis

ANNUAL INORGANIC MERCURY SPECIATION IN RIVER WATER DISTURBED BY CHLOR-ALKALI EFFLUENTS: ROLE AND COMPETITION OF LIGANDS (CL^-, BR^-, DOC)

C. Hissler[1,*], J.L. Probst[1,2,**], J. Mortatti[3,***]

[1]Ecole Nationale Supérieure Agronomique de Toulouse,
Avenue de l'Agrobiopole, BP 107 Auzeville-Tolosane, 31326 Castanet-Tolosan, France.
[2]Laboratoire des Mécanismes de Transfert en Géologie,
UMR CNRS n° 5563, 38 rue des 36 Ponts, 31400 Toulouse, France.
[3]Centro de Energia Nuclear Na Agricultura, Universidade de São Paulo,
Caixa Postal 96, CEP 13416-970, Piracicaba, SP, Brasil.
e-mail: *christophe-hissler@hotmail.fr, **jean-luc.probst@ensat.fr e ***jmortatt@cena.usp.br

Recebido em abril de 2004, aprovado para publicação em dezembro de 2005

ABSTRACT

We used Cold Vapor Atomic Fluorescence Spectrometry to determine the annual evolution of the mercury speciation in a watershed disturbed by chlor-alkali effluents. Throughout the year, the river water is enriched in chloride, bromide and DOC due to punctual and diffuse industrial and domestic activities. Moreover, mercury concentrations are 50 to 100 times higher than the natural waters downstream to the chlor-alkali effluents. The hydrological regime and the water chemistry play an important role in the mercury speciation. During high water periods, the hydrological conditions (discharge, suspended sediment content and water temperature) may control the mercury partitioning in the river water, the pollutant being mainly adsorbed onto suspended particles. On the other hand, during the summers' low waters, higher concentrations in chloride, bromide and DOC may lead to form stable Hg-Cl, Hg-Br and Hg-DOC complexes in the aqueous phase, facilitating the mercury percolation towards the groundwater.

RESUMO

A técnica de espectrometria de emição de fluorescencia atômica com geração de vapor a frio (CV-AFS) foi utilizada no processo de especiação de mercúrio em uma bacia de drenagem sob impacto antrópico causado por uma indústria química de cloro. Durante o período de um ano as águas fluviais se mostraram enriquecidas em Cl^-, Br^- e COD oriundo de poluições industriais e domésticas. A jusante da empresa quimica, as concentrações de mercúrio foram de 50 até 100 vezes mais concentradas do que as das águas naturais. A hidrologia e a composição química da água regulam a especiação do mercúrio. Durante o período de cheia, a hidrologia (vazão, sedimento em suspensão, temperatura das aguas) controla a distribuição do mercúrio nas águas fluviais e o mercurio mostrou estar adsorvido principalmente nos sedimentos em suspensão. Durante o período de águas baixas do verão, o Hg tem como característica a formação de complexos estáveis solúveis com Cl^-, Br^- e COD podendo percolar para as águas subterrâneas.

INTRODUCTION

The massive intoxications of the Almadén minors in Spain, in the XVIth century (Menendez Navarro 1996) and, more recently, of the Minamata bay people in Japan in 1953 (Osame and Takizawa 2001) and of some people in Iraq in 1970 (Bakir *et al.* 1973), revealed the true lethal potential of mercury and especially its organic compounds (MeHg). Since these contaminations took place, the international scientific community has carried a great interest in studying the biogeochemical cycle of mercury and, especially its behavior which is very different from other heavy metals. Mercury exists in multiple forms in the aquatic environment, depending on the physical and chemical characteristics of the water, which condition its behavior: elemental dissolved mercury (Hg^0), divalent mercury (Hg^{2+}), particulate mercury, mercury organic compounds (MeHg). It also associates with the organic matter, as humic substances (Schuster 1991) or other inorganic compounds, as chloride (Andersson 1979, Michard 1989), bromide (Martell *et al.* 1998), iron (hydro)oxides (Probst *et al.* 1999, Roulet & Lucotte 1995, Cossa *et al.* 1996), iron sulfides (Morse 1994) and forms stable metallic complexes in the aqueous phase (Gavis & Ferguson, 1972). These complexes' stability determines the behavior of mercury in the water column, governing its sorption-desorption, complexation and methylation processes and leads the pollutant's capacity of bioavailability.

This pollutant volatilizes in the surface conditions of the earth ground and propagates easily into the various compartments of the environment by means of the atmospheric pathway. Consequently, the aquatic continental ecosystems play the double role of punctual or diffuse pollutions receptacle and of pollutant sink. Thus, they may contain worrisome total mercury amounts (Lawson & Mason 2001, Connaway *et al.* 2002; Bannermann *et al.* 2003, Remy *et al.* 2003). The Thur River basin (North-East of France) underwent an important historic contamination of mercury, which was associated to chlor-alkali effluents principally enriched in chloride. This mercury contamination presents a risk, not only for the river's ecosystem but also for the groundwater, especially in this region where the exchanges flow from the surface water to the groundwater. Indeed, the pollutant may easily be adsorbed on the aquifer particles and held in a saturated porous environment like the Alsatian water table. Furthermore, these adsorption processes are not irreversible and the mercury may be released at any time in the aqueous phase during changes of the groundwater physico-chemical conditions.

The resul_ts we present in this article do not only confirm the work done since 1994 on the Thur River mercury pollution (Probst *et al.* 1999, Remy et al. 2003), but also carry on trying to understand the dynamic of the mercury biogeochemical cycle within the heavy perturbed continental ecosystems. We also studied a part of the stream water total mercury balance:

$$Hg_T^{W} = Hg_T^{d} + Hg_T^{p} \qquad eq.\ 1$$

$$Hg_T^{d} = Hg^{0} + Hg_R^{d} + Hg_o^{d} + MeHg^{d} \qquad eq.\ 2$$

$$Hg_T^{p} = Hg^{p} + Hg_o^{p} + MeHg^{p} \qquad eq.\ 3$$

Where: Hg_T^W: total mercury present in the stream water; Hg_T^d: total dissolved mercury; Hg_T^p: total particulate mercury adsorbed on suspended sediments; Hg^0: dissolved elemental mercury; Hg_R^d: dissolved reactive mercury (labile mercury which could easily be reduced in Hg^0 during the reaction with $SnCl_2$ at pH=1 (Bloom 1994, Mason *et al.* 1994) and represents the inorganic and organic labile mercury complexes such as Hg^{2+}, $Hg(OH)_2$, $HgCl_2$); Hg_o^d: dissolved mercury strongly complexed with organic ligands (as thiols functional groups), $MeHg^d$: dissolved methylmercury; Hg^p: particulate inorganic mercury, Hg_o^p: particulate organic mercury, $MeHg^p$: particulate methylmercury.

The different dissolved and particulate mercury species analyzed allowed us to identify the mechanisms, which govern the pollutant's behavior in the water during an hydrological year. An additional study of the dissolved reactive mercury (Hg^{2+}) gave us some more information about the potential that water has to liberate divalent mercury in the solution throughout the year. The transformations of divalent mercury that occurred in aquatic environments by organic matter or photochemical reduction and methylation processes, greatly contribute to the evasion and the redistribution of mercury in the river water and thus to its bioavailability.

The Thur River Basin

The Thur River drains an area of 270 km^2 in the Southern Vosges Mountains located one hundred of kilometers South of Strasbourg (Figure 1). The basin extends from the high crystalline Vosges Mountains (66 % of the surface of the area) as far as the Alsatian plain. The seasonal discharge regime registered there is thus strongly influenced by the amount of precipitations falling on the mountains, lowest in summer and highest in winter. Therefore, the Thur discharge undergoes strong variations during the year: a period of low waters from June until September (mean annual discharge of 2.9m^3 s^{-1} at T2 during the 30 last years) and a period of high waters from November until March with a maximum in December and in February (mean seasonal discharge of 7.3 m^3 s^{-1} at T2 during the

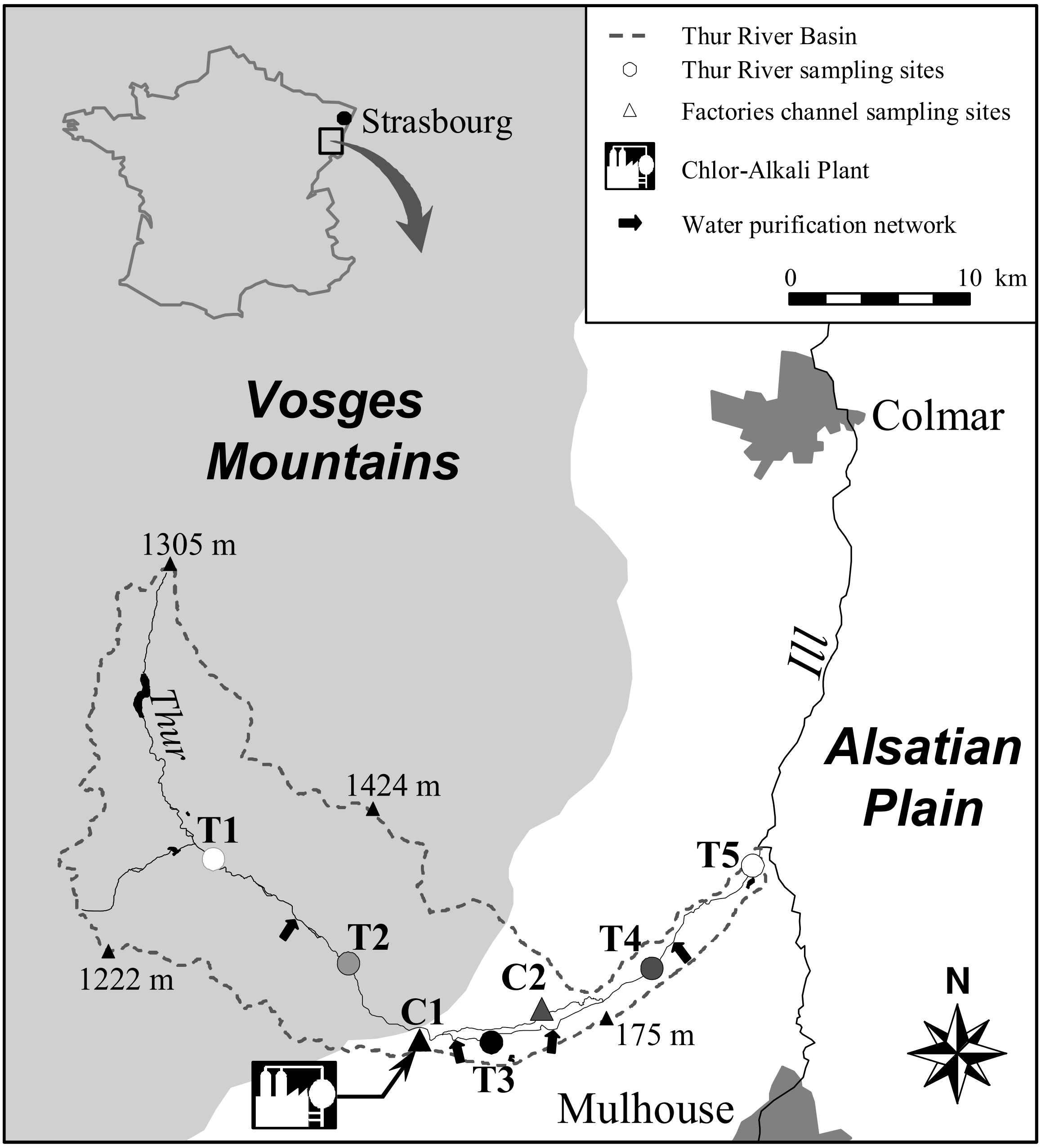

Figure 1: Localization of the Thur River basin and of the 7 sampling sites.

last 30 years). These variations describe a pluvio-nival-oceanic regime that one finds in all the region's streams.

The rocks, which constitute the basin group in four lithologic units: Visean sedimentary series (schist, graywackes), Visean volcanic series (trachyandesites, labradorites), Post-Visean granitic complexes and a Triassic-Oligocene detritic series (sandstones and conglomerates). In these climatic and geological conditions, the soils evolve from brown to podzolic soils. They are more or less acid according to the bedrock. The study of mineral layers silt and clays (granulometric fraction lower than 63 mm) allowed us to determine the mercury natural geochemical background of the soils that develop on the various lithologies (Table 1). The mean natural geochemical background we calculated for the whole basin is 0.032 ± 0.009 mg g^{-1} (Hissler *et al.* 2003).

The Thur river contamination by industrial activities goes back to the 18th century with the development of an important textile manufacturing pole. The crisis that appeared at the beginning of the 20th century caused the decline of the textile activity in the valley and the replacement of these factories by more attractive activities. Nowadays, the Thur River is considered to be one of the most polluted rivers of the Alsace region (North-East of France). The effluents released in the aquatic environment are preliminary collected in two derivations of the river course (C1 and C2, figure 1). C1 receives the effluents of the chlor-alkali (highly enriched in mercury and other mineral pollutants such as chloride, sodium, bromide) coupled with diffuse domestic effluents (enriched in organic matter, sulfates, phosphates) and C2 corresponds to the exclusive receptacle of other factories: the chemical industry (phytosanitary products, pharmaceutical industry), textile painting using organic coloring agents, the mechanical engineering industry and the plastic industry.

The historic and current sources of mercury in the Thur River basin are a chlor-alkali plant, the domestic activities (water purification networks, domestic garbage incinerator and ancient landfills) and agriculture. Since 1930, this area has been subject to an important industrial mercury pollution caused by an electrolysis unit that transforms potash salts into chlorine products. This production represents, with more than 99 % of the atmospheric emissions (100 kg yr^{-1}) and about 80 % of the effluents in the river (32 kg yr^{-1}), the main cause of mercury contamination in the basin. However, since 1982, the water purification networks' effluents connected to domestic activities (dentist's amalgams, hospitals, laboratories) may have taken an important part in the contamination, particularly upstream to C1. These treatment units reject 7 kg yr^{-1} in the river and are the first cause of contamination of the agricultural plain grounds (approximately 3 kg yr^{-1}).

MATERIAL & METHODS

Sampling and pre-analysis procedures

The monthly sampling took place from July 07 2001 until June 11 2002. The 7 sampling sites define the annual chemistry network of stream water. We chose their location according to the results obtained during previous studies and to the anthropogenic effluents. T1 to T5 are localized in the Thur River, when both C1 and C2, characterize waste channels for industrial and domestic activities (Figure 1).

We collected stream water at 20 cm's depth in teflon PFA bottles, previously rinsed in the river channel. We stored the samples at 4°C

Table 1: Natural amount of total mercury in the saprolites of the Thur River basin and the area occupied by the different lithologies (Hissler et al. 2003).

lithology	*Hg (ng g^{-1})*	*Area (km^2)*
trachy-andesites	0.016 ± 0.000	54
schists and graywackes	0.045 ± 0.002	132
granites	0.022 ± 0.001	51
sandstones and conglomerates	0.017 ± 0.000	33

until they got filtered (5 hours approximately). The water filtration was performed in the laboratory using a teflon system with mercury clean nitrogen pressure and hydrophilic PTFE teflon filter (Æ<0,45 mm, Millipore^{Ó}), rinsed with HCl (25%) during three days before their utilization.

We preserved the Total Suspended Sediments (TSS), and the associated total particulate mercury, collected on the filters at -20°C until their digestion with HNO_3: HCl: BrCl (4:1:1) (Remy *et al.* 2003). The samples intended for the total dissolved mercury (Hg_T^d) were oxidized using 0.5% BrCl (0.2N) prior to being analyzed in order to destroy organic mercury complexes. Then, they were stored in teflon PFA flasks at 4°C and were analyzed within 2 days after the filtration. The samples intended for the dissolved reactive mercury (Hg_R^d) were directly analyzed after filtration and without addition of any reagent.

The analysis of the Dissolved Organic Carbon (DOC) was directly made after the filtration. We used pyrex dishes washed using HCl 10%, rinsed with ultrapure water (Millipore UHP) and burned at 600°C in a clean oven in order to destroy all traces of organic matter. The samples used for determination of the dissolved cations and anions were stored in polyethylene flasks at 4 °C and were analyzed during the two weeks, which follow the filtration.

Mercury measurements

We measured mercury concentrations with Cold Vapor Atomic Fluorescence Spectrometry (AFS-Merlin, PS Analytical Ltd) using reduction by $SnCl_2$. The mercury contained in the particulate phase and contaminated waters (concentration > 5 ng l^{-1}) was directly measured at the release of the vapor generator, while the mercury contained in natural and less contaminated waters (concentration < 5 ng l^{-1}) was measured using gold amalgamation trapping, after an addition of NH_2OHHCl. Table 2 summarizes the sensibility and the precision of the analyses made with both methods.

We followed careful procedures to avoid sampling, storage and analysis of mercury contamination (Quesmerais & Cossa 1997). Only analytical grade or ultrapure reagents were used in this study (HCl suprapur Merck…). Blanks to detect potential contamination during sampling, filtration, digestion and analysis were generally measured below the detection limit (table 2).

Measures of other analytical parameters

The conductivity and the pH were measured at the time of the sampling. We analyzed the dissolved cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) with an Atomic Absorption Spectrophometer (HITACHI® Z-8200) adding lantanium for divalent cations detection, the dissolved anions (Cl^-, HCO_3^-, SO_4^{2-}) by Ionic Chromatography (DIONEX®), the dissolved organic carbon (DOC) with an Infrared Spectrophotometer (SHIMATZU® TOC 5000) and the bromide by colorimetry (TECHNICON®).

RESULTS AND DISCUSSION

The Thur River water chemistry

The sampling site localization allowed us to define the water chemistry evolution between the river spring and the basin outlet. Due to a dilution effect, chemical elements in Thur River waters were globally higher during low flows for all sampling sites located in the river. For example, downstream to C1, chloride concentrations were observed from 13 to 50 mg l^{-1} between October

Table 2: Analytical sensibility for both methods of mercury determination.

Analytical Methodology	***Detection Limit***	***Analysis Precision***^{a}
direct analysis	water : 1.02 ng l^{-1}	12 % (concentrations <5 ng l^{-1})
	solids : 0.3 ng g^{-1}	3.2 % (concentrations > 25 ng l^{-1})
gold-trap amalgamation	0.12 ng l^{-1}	10 %

^{a} Determined on three duplicate analyses

2001 and March 2002 and from 40 to 180 mg l^{-1} between July to September 2001 and April to June 2002, while DOC concentrations respectively evolved from 1.5 to 2.0 mg l^{-1} and from 1.9 to 3.3 mg l^{-1}.

But, the hydrological conditions didn't interfere on the water charge balance (Sanions=Scations calculated in meq l^{-1}), which is invariant throughout the year for each sampling site. Consequently, the annual concentrations' average of the various parameters followed in this study allows us to present the evolution of the anthropogenic input in the aquatic environment (Table 3).

The Thur River water is strongly disturbed by the anthropogenic activities situated downstream to T1. The increase of conductivity and pH from upstream to downstream illustrates that contamination. The chemical composition of waters evolves between two characteristic poles: less contaminated waters (T1), which directly flow out of the Vosges Mountains and the water collected in the channel C1. The first ones present a chemical composition close to the natural waters found in the streams of the Thur river basin (Hissler & Probst 2002). They are neutral (7.1<pH<7.4) and alkaline with dominant Ca^{2+} and HCO_3^- respectively in cationic and anionic total loads. The Saline waters taken in C1 are extremely rich in monovalent cations and in chlorides which result from the treatment of potash salts and in sulfates which come from domestic activities (Meybeck 1983). The water collected at C1 and C2 waste channels indicate a more important disturbance with higher concentrations in micro pollutants such as bromide and DOC.

Evolution of the mercury contents in the Thur River water

Figure 2 illustrates the importance of the chlor-alkali activity in the mercury pollution of this valley. Upstream from C1, the total dissolved mercury concentrations (Hg_T^d) are comparable for both sampling sites (0.1 to 2.2 ng l^{-1}) and are close to the natural water concentrations found in other fluvial systems (Coquery *et al.* 1995). TSS collected at T1 and T2 show higher concentrations in total particulate mercury (0.1 to 5 mg g^{-1}) than the natural geochemical background estimated for the soils of the Thur river basin (Table 1). First, diffuse atmospheric pollution due to chlor-alkali emissions contaminates the grounds of the mountainous region (Hissler *et al.* 2003). This explains the high mercury concentrations in suspended sediments, which arise from the erosion of the soils and flow out from the river tributaries to the main channel. On the other hand, diffuse contamination due to domestic activities (former landfills) and punctual contamination due to the water purification networks situated upstream to T2 may occasionally increase this enrichment, as in December at T1 (1.9 mg g^{-1}) and in August at T2 (4.9 mg g^{-1}).

The impact of the chemical industry remains the most worrying for the mercury pollution in this area. The mercury concentrations measured downstream to C1 are up to 500 times higher than those found at T1 and T2, indicating that the mercury pollution from the chlor-alkali effluents has still been important in spite of the drastic decrease of mercury losses into the aquatic environment since 1970. However, the total mercury concentrations in the river water

Table 3: Average annual evolution of the Thur River water chemistry from T1 to the basin outlet (T5), between July 2001 and July 2002 (TSS : Total Suspended Sediments ; C : conductivity ; DOC : Dissolved Organic Carbon).

Site	*pH*	*C*	*Na^+*	*K^+*	*Mg^{2+}*	*Ca^{2+}*	*HCO_3^-*	*Cl^-*	*SO_4^{2-}*	*Br^-*	*DOC*
		$\mu S.cm^{-1}$	*mg l^{-1}*								
T1	7.28	62.5	4.7	0.54	1.2	6.0	17.9	6.7	4.0	<0.08	1.4
T2	7.56	112	12.8	1.5	1.7	8.2	35.2	9.0	10.4	<0.08	1.8
C1	7.43	1390	115	253	2.1	11.8	46.4	292	129.6	26.3	7.1
T3	7.63	384	34.4	28.4	2.9	23.4	43.4	65.5	42.9	1.8	2.3
C2	7.71	405	56.2	26.2	2.1	11.1	57.5	53.2	62.5	2.0	4.9
T4	7.70	316	30.9	22.8	2.5	17.3	44.5	49.0	34.5	4.0	2.2
T5	8.10	349	33.0	26.9	2.9	18.9	47.6	57.5	36.5	1.6	2.1

(dissolved + particulate) remain under the standard limit allowed for drinking water (1000 ng l^{-1}, EC 1980).

Downstream to C1, the concentrations abruptly decrease due to the dilution with less-mercury-polluted waters from the river. Moreover, some changes appear in the variations between total particulate and total dissolved mercury concentrations. Their evolution are quite similar from C1 to T4 and show many opposite trends at T4 (December)

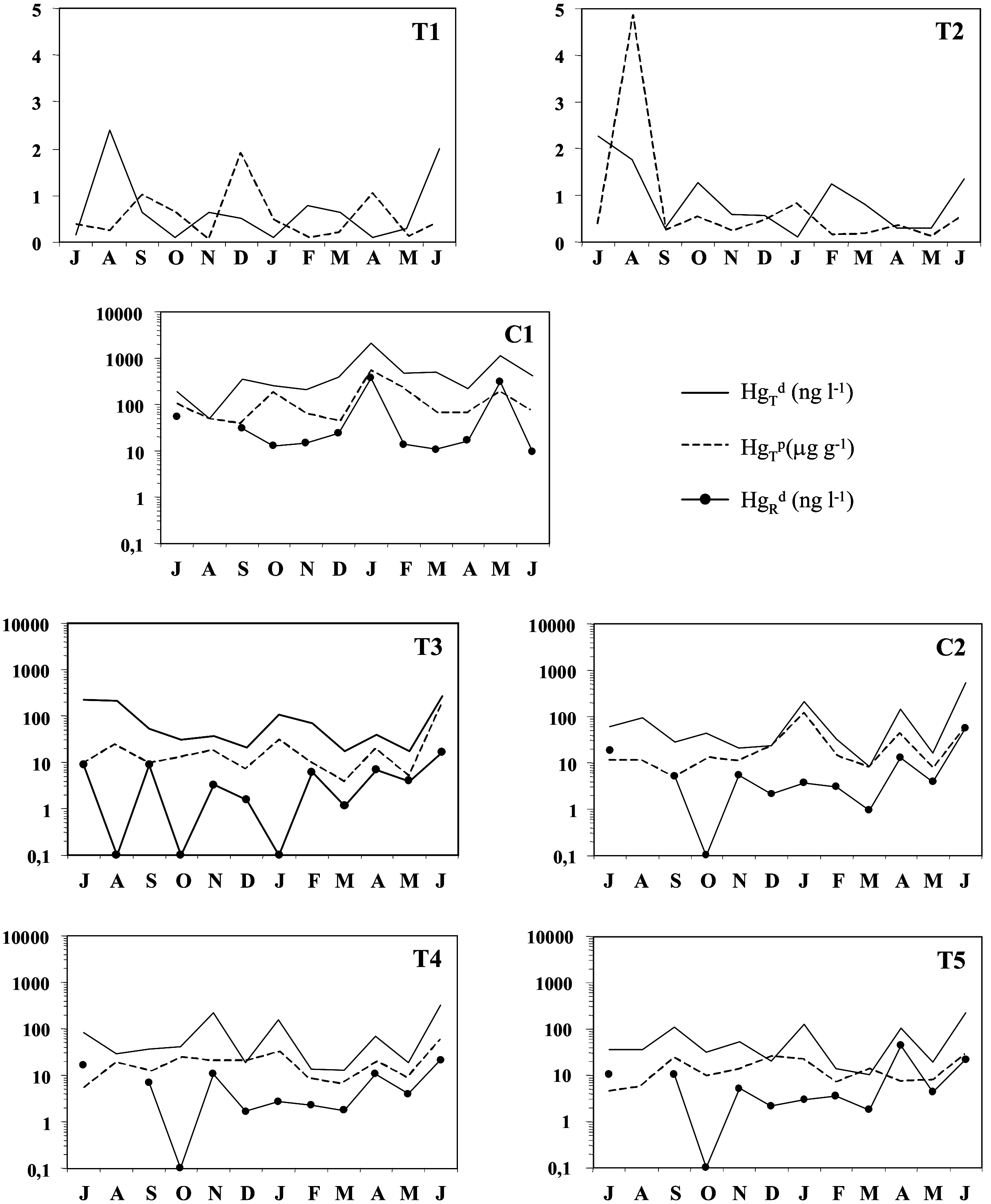

Figure 2: Seasonal variations of the total dissolved mercury (Hg_T^d), the dissolved reactive mercury (Hg_R^d) and the total particulate mercury (Hg_T^p) concentrations at the 7 sampling sites, between July 2001 and July 2002.

and T5 (December and March), illustrating that an increase of mercury reactivity in waters may proceed before the outlet of the basin. Thus, the quantity and the distribution of mercury in the river may principally be controlled by the chlor-alkali input downstream to C1. And, function of the physico-chemical conditions, some sorption, methylation and complexation processes may disturb the distribution of mercury between particulate and aqueous phases.

We only measured dissolved reactive mercury (Hg_R^d) at the most polluted sites (C1, C2, T3, T4, T5). These concentrations showed more important monthly variations than those of total dissolved mercury and the Hg_R^d annual average ranged from 5.1 ng l^{-1} at T3 to 78.2 ng l^{-1} at C1. Globally (except for January) the monthly variations of reactive dissolved mercury follow the evolution of total dissolved mercury for each sampling site.

Mercury speciation downstream the chlor-alkali effluent

To understand the inorganic mercury distribution in the river water according to the hydrological and physico-chemical conditions, we dissociated it in its three most important forms (Figure 3): dissolved reactive mercury (Hg_R^d), dissolved mercury strongly complexed to the organic matter (Hg_o^d) and total particulate mercury (Hg_T^p). We obtained the Hg_o^d concentration (equation 2) by difference between the dissolved total mercury concentration and the dissolved reactive mercury concentration. This fraction characterizes all the mercury-organic matter complexes that can't be dissociated without a strong oxidation of the sample (Bloom 1994). These chemical forms are strongly associated to the organic ligands, as covalent binding at thiol-type functional groups (Ravichandran 2004). It could represent 90% of the dissolved mercury in freshwaters (Meili *et al.*, 1997).

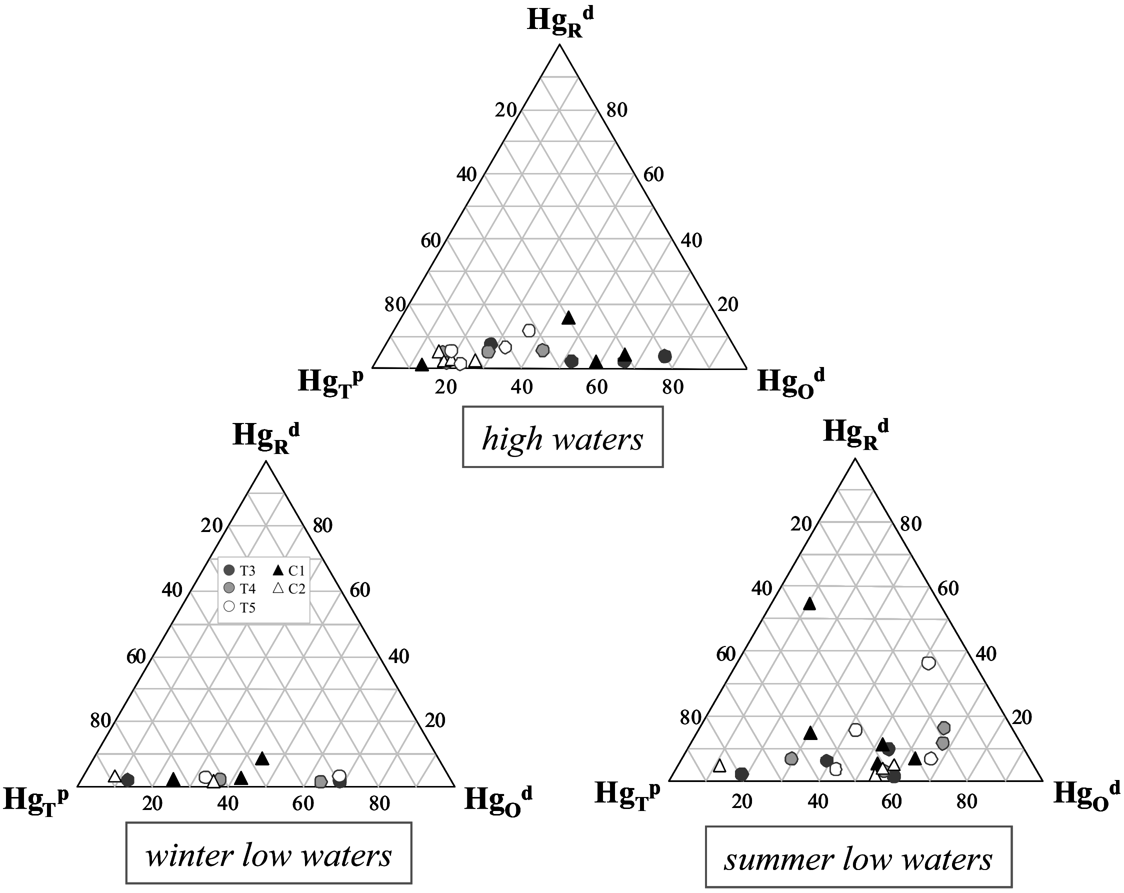

Figure 3: Seasonal evolution of the mercury speciation in the Thur River water, downstream the chlor-alkali effluents. Hg_T^p: total particulate mercury; Hg_R^d: dissolved reactive mercury Hg_o^d: dissolved mercury strongly associated with organic ligands.

Dissolved elemental mercury (Hg^0, equation 2) shows a low solubility in aerobic conditions (Schroeder *et al.* 1991). It may rapidly be oxidized in divalent mercury, particularly if chloride is present (Yamamoto 1996), or may escape into the atmosphere. We have not taken Hg^0 into account because of its low residence time and low contribution in such oxygenated and dynamic stream waters enriched in chloride and organic matter.

Mercury speciation during high flows (from October to March)

Most of the year, mercury is distributed between the dissolved organic complexes (Hg_o^d) and the particulate phase (Hg_T^p) from C1 to T5 (Figure 3). The dissolved reactive mercury normally contributes only between 0 and 10 % to the total mercury load in the waters from October to March, and very rarely up to 15% at C1. This distribution is strongly controlled by the hydrological and climatic conditions as Probst *et al.* (1999) had already demonstrated when they studied the rivers of this region.

During high water periods, the Thur River water is more enriched in total particulate mercury (more than 50 % of the total mercury measured in water), except for some cases at C1 and T3. The chlor-alkali effluents essentially contain dissolved mercury, which may explain this specific distribution of the pollutant in the aquatic environment from C1 to the closest sampling site (T3). Moreover, the factory channel (C2) contains more fine sediments than C1 and the Thur River itself (Remy et al. 2003). The specific surface area of these particles trap a more important amount of mercury and the pollutant may be released in bigger quantities from the C2 channel into the Thur River towards the last sampling sites. Both these observations can explain the ascendancy of the total particulate mercury contribution at T3, C2, T4 and T5.

During the low water periods in winter, mercury is principally transported by the particulate phase. But, in extreme hydroclimatic conditions, Hg_O^d may become the main specie (60-70 %) in the Thur river water between T3 and T5. Indeed, in January 2002, the water temperatures (2-3°C) and the unusual lower discharge together with associated lower TSS concentrations respectively neutralized the chemical activity and decreased the potential of mercury sorption onto the particulate phase.

Mercury speciation during low flows (from April to September)

During the low water periods in summer, the dissolved reactive mercury can even contribute to more than 10 % or up to more than 50 % (at C1) of the total mercury measured in waters. The climatic and hydrologic conditions of the summer period (higher water temperature, higher ligands concentrations) favor the mercury reduction (Hg(II) to Hg^0), methylation and complexation in the solution. Mercury speciation in the aquatic environment is affected by inorganic and organic ligands present in the water. The relative importance of each ligand for the mercury complexation depends on the concentrations of both the metal and the ligand and the binding strength of the metal-ligand complex (Martell *et al.* 1998).

The chloride's concentrations may have a considerable importance on the behavior of mercury during this period of the year, the concentrations in dissolved reactive mercury increasing with the chlorides' amount downstream to C1 (Figure 4).

$Hg(OH)_2$ and $HgCl_2$ are the two dominant mercury species in the natural waters (Dyrssen & Wedborg 1991). Nevertheless, depending on pH and chloride concentrations, other mercury compounds may appear: Hg^{2+}, $HgCl^+$, HgOHCl, $HgCl_3^-$, $HgCl_4^{2-}$ (Benes & Havlik 1979, Michard 1989). Upstream to downstream, the Thur waters get closer to the stability domain of the chloride richest species (Table 3 and Figure 5). When the chloride concentration increases without organic ligands, hydroxyle complexes, which dominate in low chloride content, are replaced by chlorocomplexes (Morel 1983). These complexes are less adsorbed on particles than OH-Hg. The transition from the $Hg(OH)_2$ stability domain into the ones of Hg(OH)Cl and $HgCl_2$ is one of the factors that decrease the mercury adsorption in the aquatic particulate

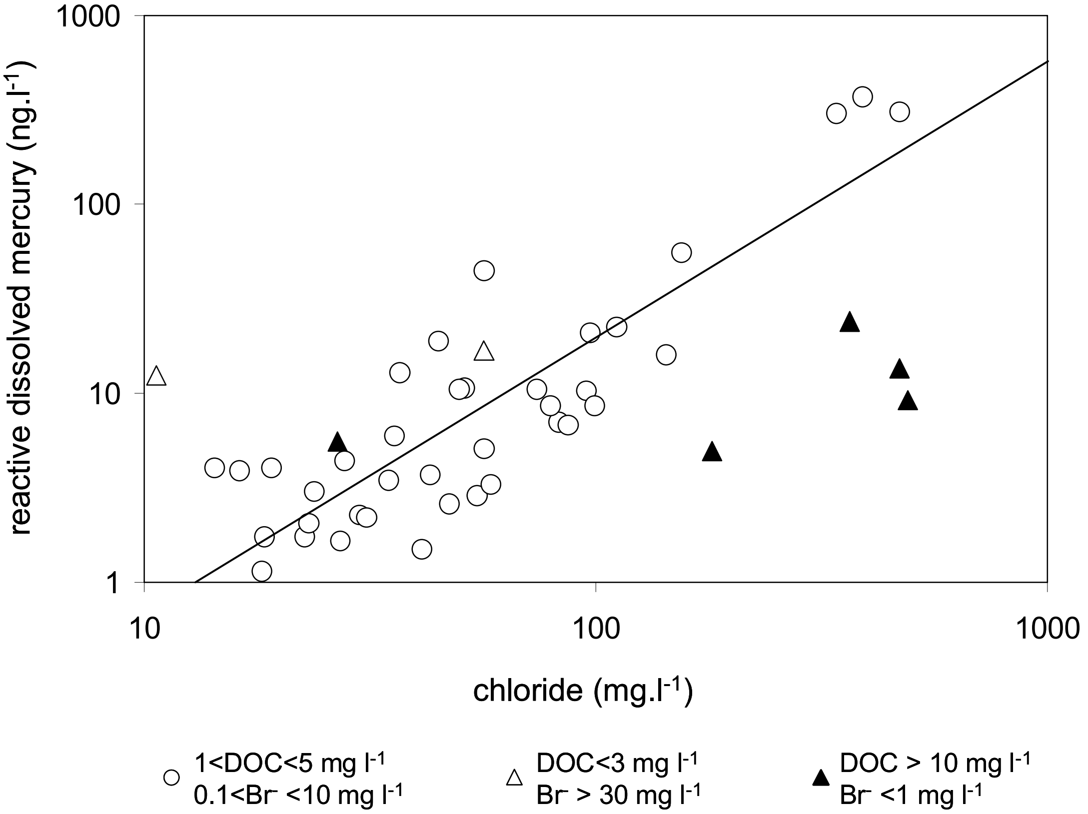

Figure 4: Relationship between chloride and dissolved reactive mercury in the Thur River downstream the chlor-alkali plant. The line defines the trend of this relation. The triangles illustrate the influence of bromide and DOC concentrations on the reactive dissolved mercury concentration.

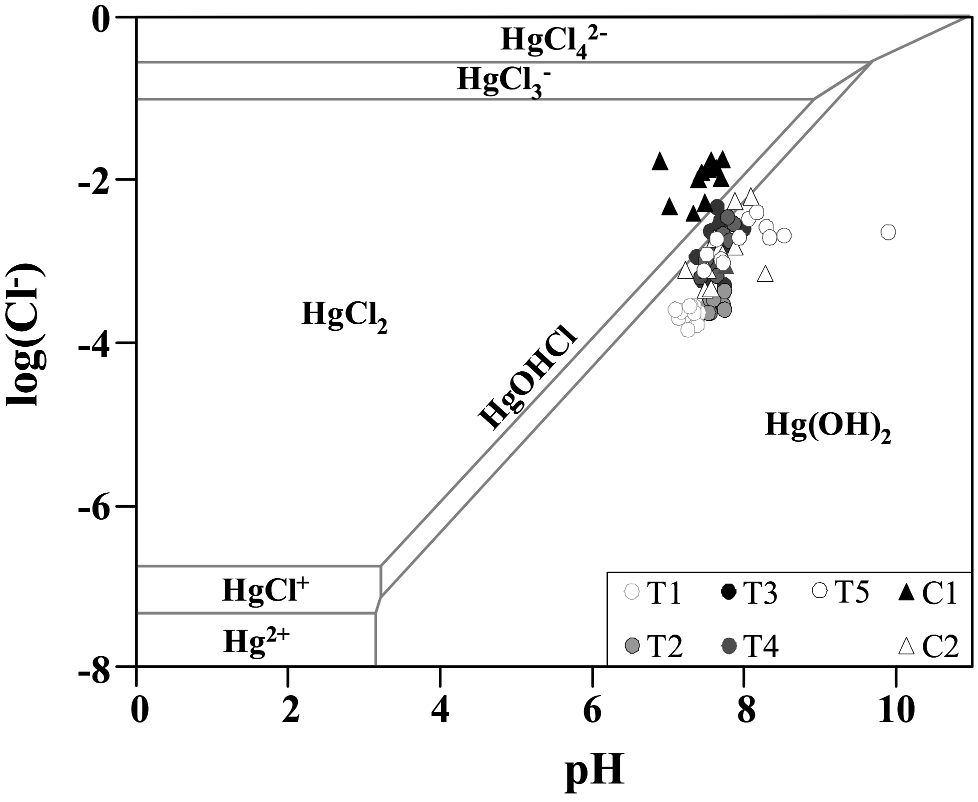

Figure 5: Thermodynamic diagram (T=25°C, I=0, P=1 atm) for the chlorocomplexes of mercury that may have appeared in the Thur River water, between July 2001 and July 2002, from Benes & Havlik (1979).

2

phases (Forbes *et al.* 1974, Kinniburgh & Jackson 1978, Randle & Hartmann 1987). The water chemistry evolution downstream to C1, especially the chloride concentrations, allows the formation of mercury species, which show a higher affinity with the aqueous phase (Hissler & Probst 2002).

Some samples have higher dissolved reactive mercury concentrations than the ones they should have for the same chloride concentrations. Depending on the chlor-alkali effluents composition, bromides may be much more concentrated in waters (higher than 30 mg l^{-1}) with less than 20 mg.l^{-1} chloride (Figure 4). Viewing the stability constant (K) for Hg-Br complexes in the aquatic environment (table 4), bromide (K=10^9 to 10^{17}) may compete with chloride (K=10^7 to 10^{14}) in the mercury complexation processes when they are present at comparable concentrations. Consequently, during the summer period, when the input of DOC by human activities is less important, bromide content in the Thur river water may increase the concentration of dissolved reactive mercury and may then control the mercury evasion, transformation and bioavailability in the aquatic environment, such as chloride.

Some other samples show lower dissolved reactive mercury concentrations, for chloride concentrations higher than 100 mg.l^{-1} (Figure 4). We can associate these findings with unusual DOC increases due to punctual anthropogenic pollutions (DOC concentrations higher than 10 mg l^{-1}). It is generally agreed that chloride is unlikely to compete with organic matter for mercury binding in most freshwaters (Table 4). Indeed, the stability constants for Hg-DOC complexes reported in the literature are about 10^{20}-10^{28} in the aquatic environment (Benoit *et al.* 2001, Haitzer *et al.* 2002, Lamborg *et al.* 2003) and higher than 10^{30} in waste water treatment plants (Hsu & Sedlack 2003). These values are much larger than the ones reported for Hg-Cl complexes (10^7 to 10^{14}) or Hg-OH complexes (10^{10} to 10^{22}). Depending on the anthropogenic input into the Thur water that occurs from April to September, the DOC (in concentrations>10 mg l^{-1}) would thus constitute the main ligand for mercury complexation (Iverfeldt 1991, Driscoll *et al.* 1995). The high stability of most Hg-DOC complexes decreases the amount of reactive mercury in the aqueous phase and principally in the pH conditions of the investigation period. Indeed, the effect of DOC on mercury bioavailability may be affected by the pH of the solution. At a pH higher than 7, DOC is more negatively charged and therefore more likely to complex mercury (Barkay et al. 1997). In the Thur River environment, DOC has the potential to reduce the amount of reactive mercury available for methylation through DOC-complexation or reduction of Hg(II) to Hg^0 (Alberts *et al.* 1974) and then to inhibit mercury bioavailability.

CONCLUSION

In spite of the net decrease of the mercury input in the aquatic environment since 1973, the chlor-alkali plant has remained the main source of mercury pollution within the environment of the Thur River. The chemistry of the anthropogenic effluents released into the aquatic environment controls the strong concentrations

Table 4: Stability constants (K) of mercury and dominant ligands complexes in natural and saline stream water of the Thur River.

Ligand (L)	log K	T	I	HgL_n	
		°C	*$mol\ l^{-1}$*		
rganic Matter (DOC)**	18.4 to 34.5	25	0.1	Hg – organic acids	
ydroxyde (OH^-)*	10.6 to 21.8	25	0	$Hg(OH)_2$	$HgOHCl$, $HgCl_2Br^-$, $HgCl_3Br^{2-}$
hloride (Cl^-)*	7.3 to 14	25	0	$HgCl_2$	
romide (Br^-)*	9.1 to 17.3	25	0.5	---	

Martell *et al.* (1998)

*Mantoura and Riley (1975), Benoit et al; (2001), Haitzer et al; (2002), Drexel et al; (2002), Hsu edlack (2003), Lamborg et al. (2003).

of mercury that we observed in the various sampling sites located downstream. It also intervenes strongly in the behavior of the mercury within the river waters.

The study on the inorganic mercury speciation in water indicates that the metal can go through both particulate and dissolved phases throughout the year. The ascendancy of a mercury specie with regard to others is controlled by the hydrological conditions and the content of inorganic (Cl^-, Br^-) and organic (DOC) ligands. During high flow periods with no extreme conditions (the lowest discharge and temperatures in winter), mercury is mainly adsorbed in the particulate phase. The pollution is then transferred into the river bed to the floodplain areas situated downstream the Thur River basin. The summer season is favorable to the presence of dissolved mercury in more important quantities, increasing the risk for the pollution to migrate towards the groundwater. Dissolved reactive mercury may appear in more important quantities caused by a net increase in chloride and bromide concentrations. Both anthropogenic inorganic ligands may then play an important role in the speciation of mercury and its potential for methylation. Nevertheless, it seems that, in unusual conditions (concentrations > 10 mg l^{-1}), DOC may control the evolution of anthropogenic mercury released in the Thur River and especially decrease its bioavailability.

REFERENCES

ALBERTS, J.J.; SCHINDLER, J.E.; MILLER, R.W.; NUTTER, D.E. (1974) Elemental mercury evolution mediated by humic acid. Science, 184: 895-897.

ANDERSSON, A. (1979) Mercury in soils. in: J. O. NRIAGU (Ed.) The Biochemistry of Mercury in the Environment. Elsevier Science, Amsterdam, p: 79-112.

BAKIR, F.; DAMLUJI, S.F.; AMIN-ZAKI, L.; MURTHADA, M.; KHALIDI, A.; AL-RAWI, N.Y.; TIKRITI, S.; DHAHIR, H.I.; CLARKSON, T.W.; SMITH, J.C.; DOHERTY, R.A. (1973) Methylmercury poisoning in Iraq. Science, 181: 230-241.

BANNERMAN, W.; POTIN-GAUTIER, M.; AMOUROUX, D.; TELLIER, S.; RAMBAUD, A.; BABUT, M.; ADIMADO, A.; BEINHOFF, C. (2003) Mercury and arsenic in the gold mining region of the Ankobra River basin in Ghana. *In*: XIIth International Conference on the Heavy Metals in the Environment, Grenoble. Journal of Physic IV.

BARKAY, T.; GILLMANN, M.; TURNER, R.R. (1997) Effects of dissolved organic carbon and salinity on bioavailability of mercury. Applied Environmental Microbiology, 63: 4267-4271.

BENES, P. & HAVLIK, B. (1979) Speciation of mercury in naturel water. in: J. O. NRIAGU (Ed.) The biochemistry of mercury in the Environment. Elsevier Science, Amsterdam, p: 175-202.

BENOIT, J.M.; MASON, R.P.; GILMOUR, C.C.; AIKEN, G.R.. (2001) Constants for mercury binding by dissolved organic matter isolated from the Florida Everglades. Geochimica et Cosmochimica Acta, 65: 4445-4451.

BLOOM, N.S. (1994) Influence of analytical conditions on the observed reactive mercury concentration in natural freshwaters. *In*: Mercury as a global pollutant, Lewis Publishers, Boca Raton, p: 541-552.

CONNAWAY, C.H.; SQUIRE, S.; MASON, R.P.; FLEGAL, A.R. (2002) Mercury speciation in the San Francisco Bay estuary. Marine Chemistry, 77: 1-27.

COQUERY, M.; COSSA, D.; MARTIN, J.M. (1995) The distribution of dissolved and particulate mercury on three Siberian estuaries. Water, Air & Soil Pollution, 80: 653-664.

COSSA, D.; MASON, R.P.; FITZGERALD, W.F. (1996) Chemical speciation of mercury in a meromictic lake. in: W. BAEYENS (Ed.) Global and regional mercury cycles: sources, fluxes and mass balances. Kluwer Academic, Dordrecht, p: 57-67.

DREXEL, R.T.; HAITZER, M.; RYAN, J.M.; AIKEN, G.R.; NAGY, K.L. (2002) Mercury(II) sorption to two Florida Everglades peats: evidence for strong and weak binding and competition by dissolved organic matter released from the peat. Environmental Science & Technology, 36: 4058-4064.

DRISCOLL, C.T.; BLETTE, V.; YAN, C.; SCHOFIELD, C.L.; MUNSOR, R.; HOLSAPPLE, J. (1995) The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote Adirondack. Water, Air & Soil Pollution, 80: 499-508.

DYRSSEN, D. & WEDBORG, M. (1991) The sulfur-mercury (II) system in natural waters. Water, Air & Soil Pollution, 56: 507-519.

EC (European Communities) (1980) Directive du conseil du 15 juillet 1980 relative à la qualité des eaux destinées à la consummation humaine (80/778/CEE). Journal Official d'Communauté Europeene, L229: 11-29.

FORBES, E.; POSNER, A.M.; QUIRK, J.P. (1974) The specific adsorption of inorganic Hg(II) species and Co(III) complex ions on goethite. Journal of Colloides Interface Science, 49: 403-409.

GAVIS, J. & FERGUSSON, J.F. (1972) The cycling of mercury through the environment. Water Research, 6: 989-1008.

GILMOUR (1971) Inorganic complexes of divalent mercury in natural water systems. Environmental Letters, 2: 143-152.

HAITZER, M.; AIKEN, G.R.; RYAN, J.N. (2002) Binding of mercury(II) to dissolved organic matter: the role of the mercury-to-DOM concentration ratio. Environmental Science & Technology, 36: 3564-3570.

HISSLER, C.; REMY, S.; PROBST, J.L. (2003) Natural and anthropogenic contributions to mercury in soils and stream sediments of the upper Thur river basin (Alsace, France). Journal of Physic IV, 107: 621-624

HISSLER, C. & PROBST, J.L. (2002) Mercury Pollution in the Thur River Basin (North-East of France): Dissolved Organic Carbon and Chloride concentration control on mercury partitioning between dissolved and particulate phases. in: Goldschmidt Conference, Davos. Geochimica Cosmochimica Acta. A332: *(in press)*

HSU, H. & SEDLACK, D.L. (2003) Strong Hg(II) complexation in municipal wastewater effluent and surface waters. Environmental Science & Technology, 37: 2743-2749.

IVERFELDT, A. (1991) Mercury in forest canopy throughfall water and its relation to atmospheric deposition. Water, Air & Soil Pollution, 56: 553-564.

KINNIBURGH, D.G. & JACKSON, M.L. (1978) Adsorption of Mercury (II) by iron hydrous oxide gel. Soil Science of Society American Journal, 42: 45-47.

LAMBORG, C.H.; TSENG, C.M.; FITZGERALD, W.F.; BALCOM, P.H.; HAMMERSCHMIDT, C.R. (2003) Determination of the mercury complexation characteristics of dissolved organic matter in natural waters with "reducible mercury" titrations. Environmental Science & Technology, 37: 3316-3322.

LAWSON, N.M. & MASON, R.P. (2001) Concentration of mercury, methylmercury, cadmium, lead, arsenic and selenium in the rain and stream water of two contrasting watersheds in western Maryland. Water Research, 35: 4039-4052.

MANTOURA, R.F. & RILEY, J.P. (1975) The use of gel filtration in the study of metal binding by humic acids and related compounds. Analytical Chimica Acta, 78: 193-200.

MASON, R.P.; FITZGERALD, W.F.; MOREL, F.M.M. (1994) The biochemical cycling of elementary mercury: anthropogenic influences. Geochimica et Cosmochimica Acta, 58: 3191-3198.

MEILI, M. (1997) Mercury in lakes and Rivers. *In*: A. SIEGEL and H. SIGEL (Ed.) Metal ions in biological systems. Mercury and its effects on environment and biology. Ed. Marcel Dekker Inc, San Diego, p: 21-51.

MENENDEZ NAVARRO, A. (1996) Un mundo sin sol. La salud de los trabajadores de las minas de Almaden 1750-1900. Report. Universidad de Castilla - La Mancha, Granada: 100 p.

MEYBECK, M. (2003) Global occurrence of major elements in Rivers. *In*: H.D. Holland and K.K. Turekian (Ed.) Treatise in Geochemistry, Elsevier Science Amsterdam, vol. 2: 1-17.

MICHARD, G. (1989) Equilibre chimique dans les eaux naturelles. Publisud, 357 p.

MOREL, F.M.M. (1983) Principles of aquatic chemistry. John Willey & Sons Inc., New York.

MORSE, J.W. (1994) Interaction of trace metals with authigenic sulfide minerals: implications for their bioavailability. Marine Chemistry, 46: 1-6.

OSAME, M. & TAKIZAWA, Y. (2001) Methylmercury poisoning in Minamata and Niigata, Japan. Report. Japan Public Health Association, Tokyo, 154 p.

PROBST, J.L.; MESSAITFA, A.; BEHRA, P. (1999) Fluvial transports of mercury pollution in the Ill river basin (North-eastern France): partitioning into aqueous phases, suspended matters and bottom sediments. *In*: Ebinhaus, R.; Salomons, W.; Turner, R.R.; Lacerda, L.D.; Vasiliev, O. (Eds.) Mercury contaminated sites: characterization, risk assessment and remediation. Springer-Verlag, Berlin, p: 501-520.

QUESMERAIS, B. & COSSA, D. (1997) Procedures for sampling and analysis of mercury in natural waters. Report. Centre St Laurent, Canada, 36 p.

RANDLE, K. & HARTMANN, E.H. (1987) Application of the Continuous Flow Stirred Cell (CSFC) technique to adsorption of zinc, cadmium and mercury on humic acids. Geoderma, 40 (3-4): 281-296.

RAVICHANDRAN, M. (2004) Interactions between mercury and dissolved organic matter - a review. Chemosphere, 55: 319-331.

REMY, S.; PRUDENT, P.; HISSLER, C.; PROBST, J.L.; KREMPP, G. (2003) Total mercury concentration in an industrialized catchment, the Thur river basin (North-eastern france): geochemical background level and contamination factor. Chemosphere, 52: 635-644.

ROULET, M. & LUCOTTE, M. (1995) Geochemistry of mercury in pristine and flooded ferralitic soils of a tropical rainforest in French Guyana, South America. Water, Air & Soil Pollution, 80: 1079-1088.

SCHROEDER, W.H.; YARWOOD, Y.; NIKI, H. (1991) Transformation processes involving mercury species in the atmosphere: results from a literature survey. Water, Air & Soil Pollution, 56: 667-680.

SCHUSTER, E. (1991) The behaviour of mercury in the soil with special emphasis on complexation and adsorption processes, a review of the literature. Water, Air & Soil Pollution, 56: 667-680.

YAMAMOTO, M. (1996) Stimulation of elemental mercury oxydation in the presence of chloride ion in aquatic environments. Chemosphere, 32: 1217-1230.

(Footnotes)

To whom the correspondence should be sent: christophe-hissler@hotmail.fr