

Mercury contents and speciation in soils and river waters of an industrialised catchment, the Thur river basin (Alsace) Contribution of the atmospheric deposition

Teneurs en mercure et spéciation dans les sols et les eaux de rivière du bassin versant industrialisé de la Thur (Alsace) Contribution des apports atmosphériques

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NDLR : Article issu du Séminaire ADEME « Pollution atmosphérique et charges critiques : Bilan et perspectives des recherches menées en France », 15 mai 2001, Paris (MATE).

Abstract

River water, river sediment and soil samples were collected from the industrialised Thur river basin (north-eastern France) to assess the current extent of total mercury and methylmercury (MeHg) contamination. A high performance liquid chromatography (HPLC) method, coupled with an online Atomic Fluorescence Spectrometry after post column oxidation of the organomercury compounds by UV light irradiation and cold vapour generation (CV-AFS), was developed for mercury speciation. The regional geochemical background level of mercury has been first evaluated to calculate total mercury contamination factors (CF) in soils and river sediments. It was estimated to 232 ng.g⁻¹ for river sediments and soils not affected by anthropogenic activities. The highest contamination factors have been estimated for the riverine sediments (CF = 1 782) receiving the industrial waste effluent of a chlor-alkali plant. Contamination factors of surficial soils located 1 km around the industrial site range from 6.2 to 55.3. This contamination could be attributed to diffuse atmospheric deposition from the local industry. Mercury contamination in the different horizons of alluvial soils is not correlated with particulate organic carbon content but rather with historical accidental mercury pollution coming from the deposition of contaminated sediments settled from the Thur river during flood periods. First results on mercury speciation show that the proportion of MeHg in alluvial and industrial soils averages 0.03 to 0.15% of total Hg. Dissolved organic Hg represents the major component of total dissolved Hg in the river water and its proportion (70-100%) is seasonally variable.

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Résumé

Des eaux de rivière, des sédiments et des sols ont été échantillonnés dans le bassin versant industrialisé de la Thur (nord-est de la France) pour évaluer l'ampleur actuelle de la contamination en mercure total et en méthylmercure (MeHg). Une méthode de séparation par chromatographie liquide à haute performance (CLHP) couplée à une détection par spectrométrie de fluorescence atomique en ligne après oxydation des composés organomercuriels par irradiation UV et génération de vapeurs froides (CV-AFS) a été développée pour la spéciation de mercure et en particulier pour la détermination du méthylmercure. Le fond géochimique régional en mercure a tout d'abord été évalué pour calculer des facteurs de contamination (FC) en mercure total dans les sols et les sédiments de rivière. Il a été estimé à 232 ng.g^{-1} à partir de sédiments et de sols non perturbés par des activités anthropogéniques. Les facteurs de contamination les plus élevés sont situés dans les sédiments de la rivière (FC = 1 782) recevant les effluents d'une usine chlor-alkali. Les facteurs de contamination des horizons superficiels des sols localisés à 1 km autour du site industriel varient entre 6,2 à 55,3. Cette contamination est attribuée au dépôt atmosphérique diffus de l'industrie locale. La contamination mercurielle dans les différents horizons de sols alluviaux n'est pas corrélée avec leur teneur en carbone organique particulière mais plutôt avec une pollution historique de mercure provenant de sédiments contaminés déposés par la rivière Thur en période de crue. Les premiers résultats sur la spéciation du mercure ont montré que la proportion de MeHg par rapport au mercure total dans les sols alluviaux et industriels est en moyenne de 0,03 à 0,15 %. Le mercure organique dissous représente la composante principale du mercure total dissous dans l'eau de rivière (70-100%) et sa proportion varie de manière saisonnière.

Introduction

Most environmental studies dealing with toxic metals have only quantified the pollutants as their total inorganic and organic forms. However, it is well known that for some elements such as Hg, Sn, As, Pb or Se, toxicity problems are not related to the presence of their inorganic salts, but rather to their alkylated forms. Some of these compounds are now considered to be so toxic, even at the sub-ng.l⁻¹ range in the aquatic environment, that a need has been triggered for improved analytical techniques featuring both speciation and high sensitivity capabilities. The "speciation" term used in this study means the analytical approach enable to distinguish the chemical species of an element (individual organo-metallic or different oxidation state species) and to describe the distribution of these species in an environmental sample [1].

Mercury is transported over long distances from sites of natural sources and of industrial and urban activities, and is deposited uniformly on environmental media by wet and dry aeolian pathways [2]. The main anthropogenic Hg contamination sources are by-products of various industrial processes, including coal mining, fossil fuel combustion, waste incineration, waste water plant treatment and chlor-alkali production.

Historically and today in developing countries, chlor-alkali industry is a significant source of atmospheric mercury emission and direct releases in aquatic system [3]. Despite the fact that emissions have been drastically reduced in the last decades, the current atmospheric deposition rate still promotes an accumulation of mercury in the environment. Transformation and distribution of mercury in the environment can lead to appreciable concentrations of mercury in different media, such as water, soil and biota. One of the most interesting and important facets of the biogeochemistry of mercury is its propensity to be methylated in the environment, to mono- and dimethylmercury. Methylmercury (MeHg) comprises approximately

0.1-1.5% of the total mercury in sediments and about 2% of the total mercury in freshwater [4]. Owing to its lipophilic and protein-binding properties, MeHg is readily accumulated and biomagnified in the aquatic food chain and virtually all (80-90%) of the total mercury in fish comprises this form. This fact has long been recognised as a major environmental pollution issue and health hazard for humans. The important reactions or processes controlling the distribution of mercury compounds in environmental systems are methylation/demethylation, redox, precipitation/dissolution, and sorption/desorption [5].

Mercury contaminated sites are still remaining and many studies are developed to measure contamination levels, to assess risks, behaviour and fate of this element and its compounds in the different environmental compartments. Consequently, there is a need for accurate analytical methods that are able to determine the different chemical forms of mercury in the different sample compartments. The most widely used technique for speciation of mercury involves a chromatographic separation, followed by detection via an element specific detector. In this study, speciation of mercury analysis has been performed by high performance liquid chromatography (HPLC) coupled with on-line atomic fluorescence spectrometry (AFS) detection after post column oxidation of the organomercury compounds by UV light irradiation and cold vapour generation (CV-AFS) (Figure 1, p. 127). The main mercury species analysed using HPLC include methyl-, ethyl-, phenylHg and Hg²⁺.

The study was designed to assess the current extent of total mercury and methylmercury contamination in the riverine sediment and soil compartments and in river waters of an industrialised catchment. Consequently, the geochemical background level of total mercury has been first evaluated in order to calculate contamination factors in the soil and river sediment reservoirs. Besides, speciation studies – especially methylmercury measurements – were ini-

tiated in soils and river waters to take into account the toxicological aspect of the contamination. In this context, our research program is focused on the influence of Hg anthropogenic sources, especially from an industrial site devoted to chlorine and soda products.

Materials and methods

Study area

In the Alsace region, (north-eastern France), the Thur river basin, in the upper part of the Ill river basin (tributary of the Rhine), is historically polluted by mercury principally released by the activity of a chlorine and soda industry in Vieux-Thann [6]. The Thur river drains a catchment area of 273 km² in the south-eastern part of the Vosges Mountains and the Alsatian Plain (Figure 2, p. 127). In the industrialised Thur Valley, groundwater plays an important role in the economy and in the hydrosystem equilibrium, and the river greatly contributes to the groundwater supply [7]. The main types of soils are brown soils, acid brown soils and alluvial soils, and most of the river sediment samples are coarse grained materials (quartz sand).

Sample collection and preparation

Soil and sediment samples have been collected during the period 1999-2000. Soils were sampled according to their surficial characteristics: industrial soils in Vieux-Thann, agricultural soils, grassland soils and alluvial soils. River water samples have been collected on ten sites located along the Thur main channel during two summer sampling periods, in July and September 2001.

All samples were correctly handled and stored in order to preserve total mercury and methylmercury and to avoid risks of Hg contamination. All Teflon labware was acid washed three days in 50% hot nitric acid, then three days in 10% hot nitric acid, triple rinsed with ultrapure water (Millipore UHP) and dried at 110 °C in a class 100 oven [8].

Sediment samples

The surficial sediments (0-3 cm) were collected with precleaned polyethylene flasks. The soil horizons were sampled directly on the soil profile or by a drill sampling.

River sediment and soil samples were stored in ice immediately, frozen at -20 °C within 24 h of collection and then freeze-dried. They were homogenised and sieved to <63 µm and to <50 µm, which correspond respectively for riverine sediments and soils to the limits between fine and coarse materials.

Water samples

Water samples were collected directly in the middle of the river by immersing an acid-cleaned 6 l Teflon bottle which is tightly closed after collection and put in two plastic bags.

Immediately after collection, once back to the laboratory, samples for dissolved Hg measurements were filtered with an acid-cleaned 0.45 µm pore size Teflon filter (Millipore LCR) with a Teflon filtration apparatus constructed in our laboratory. This system involved pressurised filtration with Hg-free nitrogen. Filtered water samples for total dissolved Hg were stored in 250 ml acid-cleaned Teflon bottles containing 0.5% 0.2N BrCl solution. Dissolved reactive analysis sample and dissolved methylmercury analysis samples were stored in Teflon bottles without any additive. Water samples for methylmercury analysis were stored in the dark and at -20 °C until analysis.

Analytical methods

Total mercury measurements

Total mercury concentration was analysed by an automated Cold Vapour Atomic Fluorescence Spectrometry (CV-AFS) detection technique according to Quémerais & Cossa [8] and Bloom & Fitzgerald [9]. This automated system consists of a continuous flow vapour generator coupled with an atomic fluorescence spectrometer (PS Analytical, Merlin Plus) and a amalgamation system for low Hg level liquid samples analysis.

Water samples

Total dissolved mercury was determined by tin chloride solution reduction following BrCl chemical oxidation of the sample [10]. Dissolved reactive mercury was determined by tin chloride reduction without any oxidation procedure. This fraction include inorganic complexed Hg species. Compounds containing C-Hg bonds will not be detected. The difference between a total dissolved and a dissolved reactive Hg determination is generally assumed to indicate very stable organo-Hg association [11].

Preconcentration of low level Hg from aqueous solution is performed by amalgamation of Hg⁰ (gaseous elementary mercury) onto an Au collection column and subsequent desorption by heating the trap at 600 °C [8, 12].

The detection limit (defined as three times the standard deviation of a purge blank) for the analysis of an aqueous sample is 100 pg.l⁻¹. The precision of 10 replicate measurements of a single sample was below 10% (RSD).

River sediment and soil samples

Total mercury measurement in river sediment and soil samples was performed by tin chloride solution reduction following oxidation by acid digestion. The digestion procedure required approximately 200 mg dry weight (dw) sample accurately weighted into a closed 60 ml Teflon vial (Savilex). The sample was stirred and digested at 90 °C over night with (8:2:2) concentrated nitric acid/concentrated hydrochloride acid/0.2M BrCl solution (potassium bromide-bromate in hydrochloride acid medium), according to the analytical method modified from Muhaya et al. [13]. The digest was then diluted to 50 ml with ultrapure

Table 1.
Recovery and accuracy of the measured certified reference materials.
Justesse et précision des matériaux de référence certifiés analysés.

CRM	Certified concentration		Measured concentration				
	Total Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	SD ($\mu\text{g}\cdot\text{g}^{-1}$)	Total Hg ($\mu\text{g}\cdot\text{g}^{-1}$)	SD ($\mu\text{g}\cdot\text{g}^{-1}$)	n	Recovery (%)	Accuracy (%)
Marine sediment IAEA 356	7.62 (6.74 - 7.98)	—	7.01	0.46	6	92.0	6.6
Sandy soil BCR 142 R	0.067	0.011	0.067	0.005	7	99.3	7.6
River sediment CRM 320	1.03	0.16	0.97	0.04	10	94.2	3.9
Estuarine sediment BCR 580	132.00	3.00	138.38	1.52	3	104.8	6.3

CRM: Certified Reference Material.
SD: Standard Deviations.

water containing 1% 0.2N BrCl solution and filtered with 0.45 μm PES syringe filters (Acrodisc Supor) before total Hg analysis. Blank were included with each batch of digestion.

The detection limit, three times the standard deviation of the procedural blanks, corresponds to 0.3 $\text{ng}\cdot\text{g}^{-1}$ (dw) for a typical 200 mg sample, and the relative standard deviation (<8%) was determined using at least three subsamples. The accuracy of the method was tested by analysing different certified reference materials obtained by Promochem (Molsheim, France) (Table 1).

Only analytical grade or ultrapure quality reagents were used in this study.

Methylmercury measurement

Determination of organic mercury species – especially methylmercury – is performed by a reversed-phase high performance liquid chromatography (HPLC) with on-line atomic fluorescence spectrometry (AFS) detection after post-column oxidation (PCO) of the organic compounds by UV light irradiation and cold vapour generation by SnCl_2 reduction [14] (Figure 1).

This method involves the pre-separation of the methylmercury compounds from the matrices sample using water vapour distillation [15, 16].

Procedure

In the distilled sample, Hg compounds are complexed with sodium pyrrolidinedithiocarmate (NaPDC) and preconcentrated onto a preconcentration column with a bidistilled water containing 0.5 $\text{mmol}\cdot\text{l}^{-1}$ ammonium acetate buffer (pH 6) before separation and detection. After sample enrichment, the preconcentration column was switched into the eluent flow with an automatic switching valve. The mobile phase consisted of a 70:30 acetonitrile/water eluent buffered with 0.5 $\text{mmol}\cdot\text{l}^{-1}$ ammonium acetate (pH 6). The compounds were desorbed and transported to the analytical column for separation. Subsequently the complexes were oxidised by UV-irradiation. After

reducing the inorganic mercury in the gas-liquid separator by stannous chloride, the generated elemental mercury was transported by the argon gas stream into the AFS detector for element specific detection after removing the water in the mercury-containing gas.

Methyl-, ethyl-, phenylHg and Hg^{2+} are well separated within 22 minutes.

Instrumentation

The experimental system for HPLC-UV-PCO-CVAFS experiments consisted of two HPLC pumps (Model 210, Varian®) with an attached standard injection valve (Rheodyne) equipped with a 100 μl loop. The preconcentration column (20 $\times$ 4.6 mm) and the separation column (250 $\times$ 4.6 mm) were both filled with an Hypersil ODS (RP C18, 5 μm) reversed-phase stationary material.

Precision and detection limit

Methylmercury detection limit is 20 pg as Hg, e.g. 0.08 $\text{ng}\cdot\text{l}^{-1}$ as Hg in water samples (preconcentration of 250 ml sample) and 0.2 $\text{ng}\cdot\text{g}^{-1}$ in solid samples (100 mg).

The precision of the method was determined by 10 successive injections of methylmercury (100 pg). The relative standard deviation (RSD) of the fluorescence measurement (peak height) was 6%. Certified reference materials (BCR 580, IAEA 356) were checked for analytical performance and to ensure that the speciation protocol used is accurate and without systematic bias.

Other analytical parameters

Particulate Organic Carbon (POC) was analysed by infra-red spectrometry (LECO® CS 125 analyser).

The different granulometric fractions of sediments and soils were conducted by manual dry sieving. We used three nylon sieves placed in series for the determination of a fine (silty/clayey) fraction (< 50 μm or < 63 μm), a sand fraction (50/63 – 2000 μm) and a coarse fraction (> 2000 μm). In avoiding possible

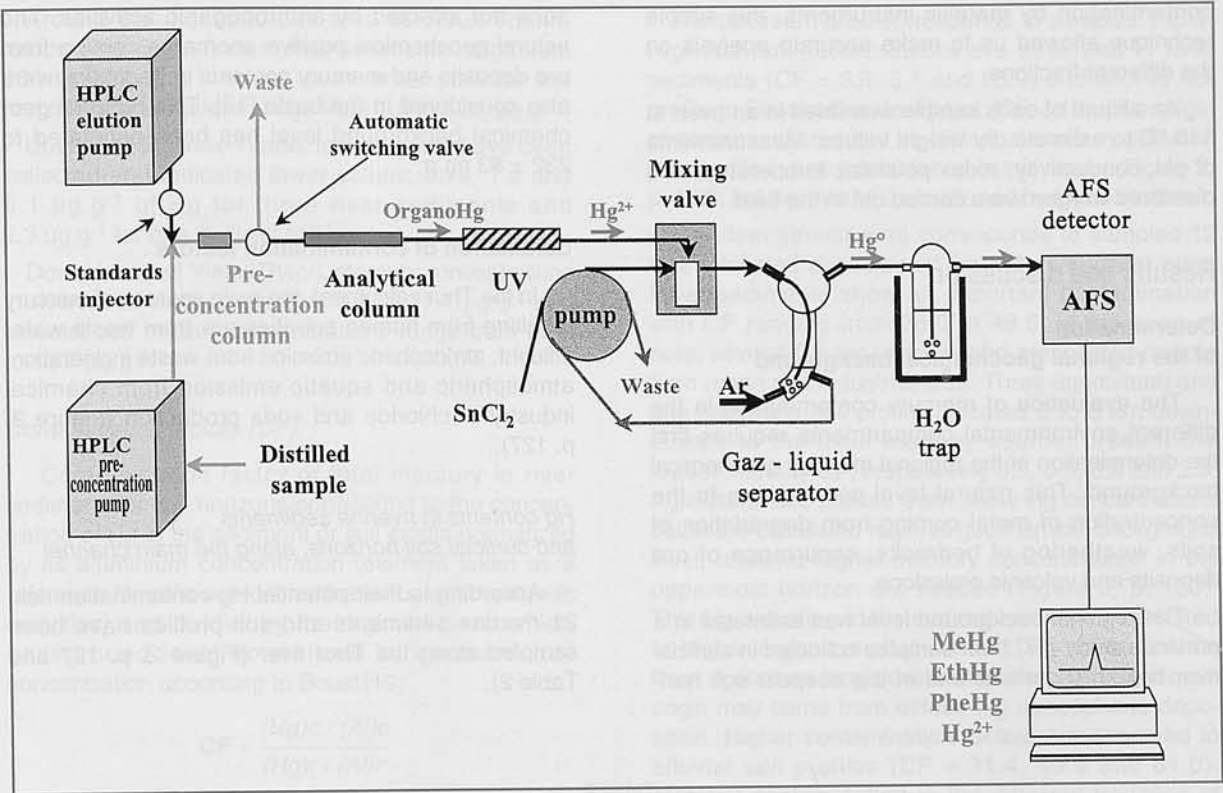


Figure 1.
The HPLC-UV-PCO-CVAFS system with on-line preconcentration unit.
Le système HPLC-UV-PCO-CVAFS avec son unité de préconcentration en série.

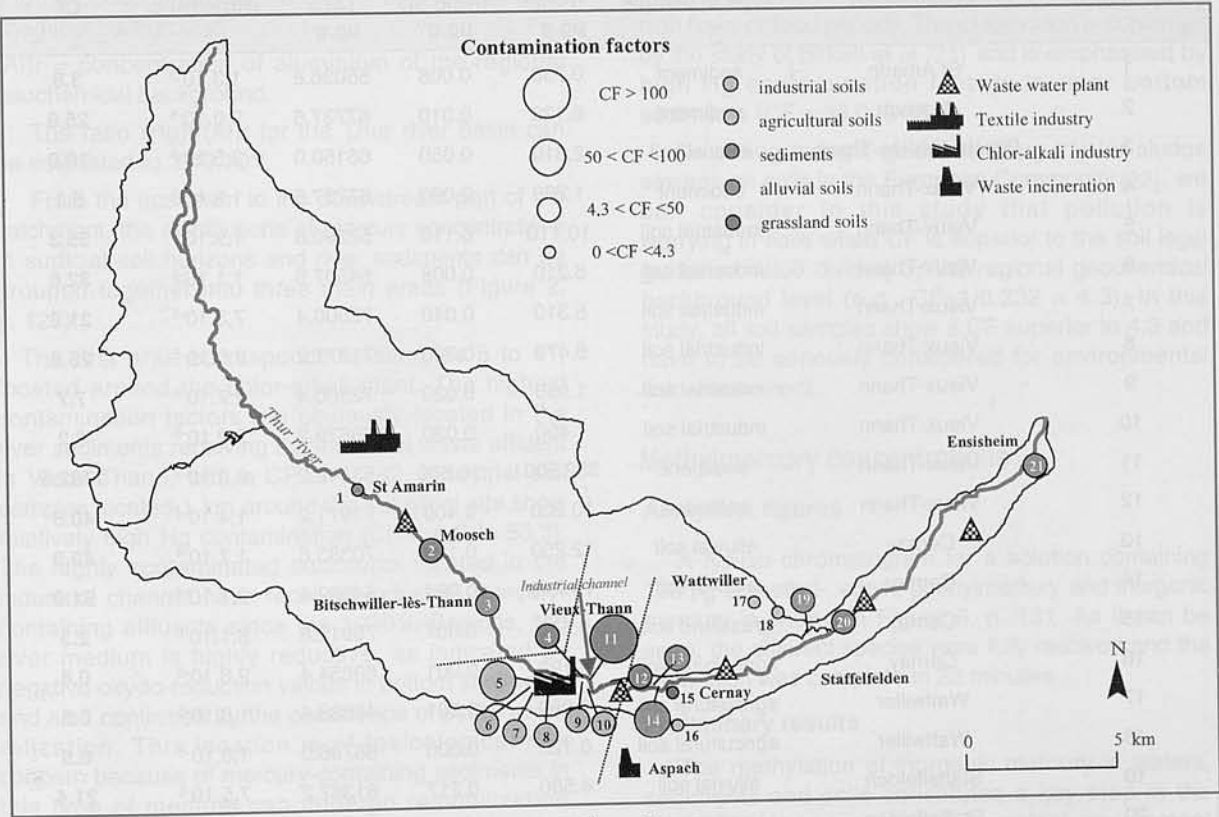


Figure 2.
Mercury contamination factors in the Thur catchment.
Facteurs de contamination en mercure dans le bassin versant de la Thur.

contamination by metallic instruments, this simple technique allowed us to make accurate analysis on the different fractions.

An aliquot of each sample was dried in an oven at 110 °C to estimate dry weight values. Measurements of pH, conductivity, redox potential, temperature and dissolved oxygen were carried out in the field.

Results and discussion

Determination of the regional geochemical background

The evaluation of mercury contamination in the different environmental compartments requires first the determination of the regional mercury geochemical background. This natural level corresponds to the concentration of metal coming from degradation of soils, weathering of bedrocks, occurrence of ore deposits and volcanic emissions.

The regional background level was estimated in a previous study [17] from samples collected in surficial river bottom sediments and in the deepest soil hori-

zons not affected by anthropogenic activities. The natural geochemical positive anomalies coming from ore deposits and mercury contents in bedrocks, were also considered in the basin [18]. This regional geochemical background level has been estimated to $232 \pm 83 \text{ ng.g}^{-1}$.

Calculation of contamination factors

In the Thur catchment, the main sources of mercury resulting from human activities are from waste water effluent, atmospheric emission from waste incineration, atmospheric and aquatic emission from chemical industry of chloride and soda production (Figure 2, p. 127).

Hg contents in riverine sediments and surficial soil horizons, along the main channel

According to their potential Hg contamination risk, 21 riverine sediments and soil profiles have been sampled along the Thur river (Figure 2, p. 127 and Table 2).

Table 2.
Total mercury and aluminium contents, standard deviations (SD), Hg/Al ratio and contamination factors (CF) in contaminated soil and sediment samples.

Concentrations en mercure total, en aluminium, déviations standard (SD), rapport Hg/Al et facteurs de contamination (FC) dans les échantillons de sol et de sédiment contaminés.

Map number	Localisation	Type of sample	(Hg)c $\mu\text{g.g}^{-1}$	(Hg)c SD $\mu\text{g.g}^{-1}$	(Al)c $\mu\text{g.g}^{-1}$	(Hg)c/(Al)c	CF
1	St Amarin	sediment	0.738	0.008	55036.8	$1,3 \cdot 10^{-5}$	3.8
2	Moosch	sediment	6.120	0.010	67737.6	$9,0 \cdot 10^{-5}$	25.9
3	Bitschwiller-lès-Thann	alluvial soil	2.310	0.050	66150.0	$3,5 \cdot 10^{-5}$	10.0
4	Vieux-Thann	sediment	1.200	0.060	67737.6	$1,8 \cdot 10^{-5}$	5.1
5	Vieux-Thann	industrial soil	10.110	0.110	52390.8	$1,9 \cdot 10^{-4}$	55.3
6	Vieux-Thann	industrial soil	6.210	0.008	54507.6	$1,1 \cdot 10^{-4}$	32.6
7	Vieux-Thann	industrial soil	5.310	0.040	72500.4	$7,3 \cdot 10^{-5}$	21.0
8	Vieux-Thann	industrial soil	6.470	0.020	71971.2	$9,0 \cdot 10^{-5}$	25.8
9	Vieux-Thann	industrial soil	1.950	0.020	72500.4	$2,7 \cdot 10^{-5}$	7.7
10	Vieux-Thann	industrial soil	1.450	0.030	66679.2	$2,2 \cdot 10^{-5}$	6.2
11	Vieux-Thann	sediment	332.500	16.600	53449.2	$6,2 \cdot 10^{-3}$	1782.5
12	Vieux-Thann	sediment	10.200	0.400	71971.2	$1,4 \cdot 10^{-4}$	40.6
13	Cernay	alluvial soil	12.250	0.180	70383.6	$1,7 \cdot 10^{-4}$	49.9
14	Cernay	alluvial soil	13.748	0.094	64562.4	$2,1 \cdot 10^{-4}$	61.0
15	Cernay	grassland soil	0.577	0.007	70912.8	$8,1 \cdot 10^{-6}$	2.3
16	Cernay	agricultural soil	0.193	0.001	69854.4	$2,8 \cdot 10^{-6}$	0.8
17	Wattwiller	agricultural soil	0.090	0.001	48686.4	$1,8 \cdot 10^{-6}$	0.5
18	Wattwiller	agricultural soil	0.123	0.000	68796.0	$1,8 \cdot 10^{-6}$	0.5
19	Staffelfelden	alluvial soil	4.580	0.217	61387.2	$7,5 \cdot 10^{-5}$	21.4
20	Staffelfelden	sediment	11.700	0.450	67737.6	$1,7 \cdot 10^{-4}$	49.5
21	Ensisheim	sediment	8.900	0.340	70912.8	$1,3 \cdot 10^{-4}$	36.0

- Around the industrial site area in Vieux-Thann, mercury concentrations in river sediments range from 300 to 600 $\mu\text{g.g}^{-1}$. In the same area, surficial soil horizon concentrations range from 1.5 to 10.1 $\mu\text{g.g}^{-1}$.
- Upstream of Vieux-Thann, four samples have been collected and indicated lower values: 0.74, 1.2 and 6.1 $\mu\text{g.g}^{-1}$ of Hg for three river sediments and 2.3 $\mu\text{g.g}^{-1}$ for one surficial soil horizon.
- Downstream of Vieux-Thann, mercury concentrations in river sediments range from 8.9 to 11.7 $\mu\text{g.g}^{-1}$ and surficial soil horizon concentrations range from 0.09 to 13.7 $\mu\text{g.g}^{-1}$.

Contamination factors (CF)

Contamination factor of total mercury in river sediments or soil horizons correspond to the concentration of Hg in the sediment or soil media normalized by its aluminium concentration (element taken as a reference for soils non contaminated by anthropogenic activities) and divided by the regional geochemical background level normalized by its aluminium concentration according to Boust[19].

$$CF = \frac{(Hg)c / (Al)c}{(Hg)r / (Al)r}$$

(Hg)c = concentration of mercury in the contaminated samples;

(Al)c = concentration of aluminium in the contaminated samples;

(Hg)r = concentration of mercury of the regional geochemical background;

(Al)r = concentration of aluminium of the regional geochemical background.

The ratio (Hg)r/(Al)r for the Thur river basin can be estimated to $3.49 \cdot 10^{-6}$.

From the upstream to the downstream part of the catchment, the distributions of mercury concentrations in surficial soil horizons and river sediments can be grouped together into three main areas (Figure 2, p. 127):

- The first area corresponds to samples 5 to 11, located around the chlor-alkali plant. The highest contamination factors are obviously located in the river sediments receiving the industrial waste effluent in Vieux-Thann, with a CF of 1 782. Industrial soil samples located 1 km around the industrial site show relatively high Hg contamination (CF = 6.2 to 55.3). The highly contaminated sediments located in the industrial channel have received industrial mercury-containing effluents since the 1930's. Besides, the river medium is highly reductive, as indicated by negative oxydo-reduction values in bottom sediments and also confirmed by the occurrence of pyrite mineralization. This location is of toxicological risk concern because of mercury-containing sediments in this type of medium can undergo remobilization processes in water column, reduction of dissolved Hg released to the atmosphere or methylation processes [20].

- The upstream area corresponds to samples 1 to 4. High contamination factors are observed in river sediments (CF = 3.8, 5.1 and 25.9) and alluvial soil profile in Bitschwiller-lès-Thann (CF = 10). The origin of contamination might be historical mercury pollution from textile industry established in this region (Figure 2, p. 127); but this has to be confirmed by future studies.
- The downstream area corresponds to samples 12 to 21, located downstream from the industrial area. River sediments show an important contamination with CF ranging from 36.0 to 49.5. In the case of soils, several CF are very low and are located remote from urban and industrial area. Three agricultural and one grassland soil profiles, located 5 to 8 km downstream to the main mercury source, present the lowest mercury CF, respectively 0.5, 0.5, 0.8 and 2.3. Agricultural soil profiles even show Hg concentrations below the calculated regional geochemical background level, however higher mercury concentrations in the uppermost horizon are noticed (Figure 3, p. 130). This Hg elevation in the surficial soil horizon is linked to higher organic matter content. Hg contamination from agriculture fungicides is excluded. Thus, the main origin may come from diffuse Hg atmospheric deposition. Higher contamination factors are observed in alluvial soil profiles (CF = 21.4, 49.9 and 61.0). Mercury contamination in the different horizons of alluvial soils is not correlated with particulate organic carbon (POC) content (Figures 4, p. 130 and 5, p. 131) but is rather linked with historical accidental mercury pollution coming from the deposition of contaminated sediments settled from the Thur river during high flows or flood periods. This observation is confirmed by the study of Birkett et al. [21] and is emphasised by high Hg contamination factors in river bottom sediments (CF = 36.0 to 49.5).

According to legal guidance (1 $\mu\text{g.g}^{-1}$) for sludge sewage on soils in the European Community [22], we can consider in this study that pollution is worrying in soils when CF is superior to the soil legal guidance value divided by the regional geochemical background level (e.g., $CF > 1/0.232 = 4.3$). In this study, all soil samples show a CF superior to 4.3 and have to be seriously considered for environmental risk assessment.

Methylmercury concentrations

Analytical figures

A typical chromatogram for a solution containing 100 pg of methyl-, ethyl-, phenylmercury and inorganic mercury is shown in Figure 6, p. 131. As it can be seen, the different species were fully resolved and the separation was complete in 22 minutes.

Preliminary results

The methylation of inorganic mercury in waters, sediments and soils constitutes a key step in the cycling of Hg in aquatic and terrestrial environment and takes place in both polluted and non-polluted environments [23].

Methylmercury contents in soils

Methylmercury measurements have been carried out in alluvial and industrial soils (Table 3, p. 132) previously analysed for total mercury. The first speciation results showed that methylmercury

contents in alluvial soils were around 1.76 to 10.53 ng.g⁻¹ and accounted for 0.03 to 0.05% of total mercury. As for industrial soils, methylmercury accounted for 0.15% of total mercury.

Besides, we could observe that methylmercury concentrations were related to total mercury content

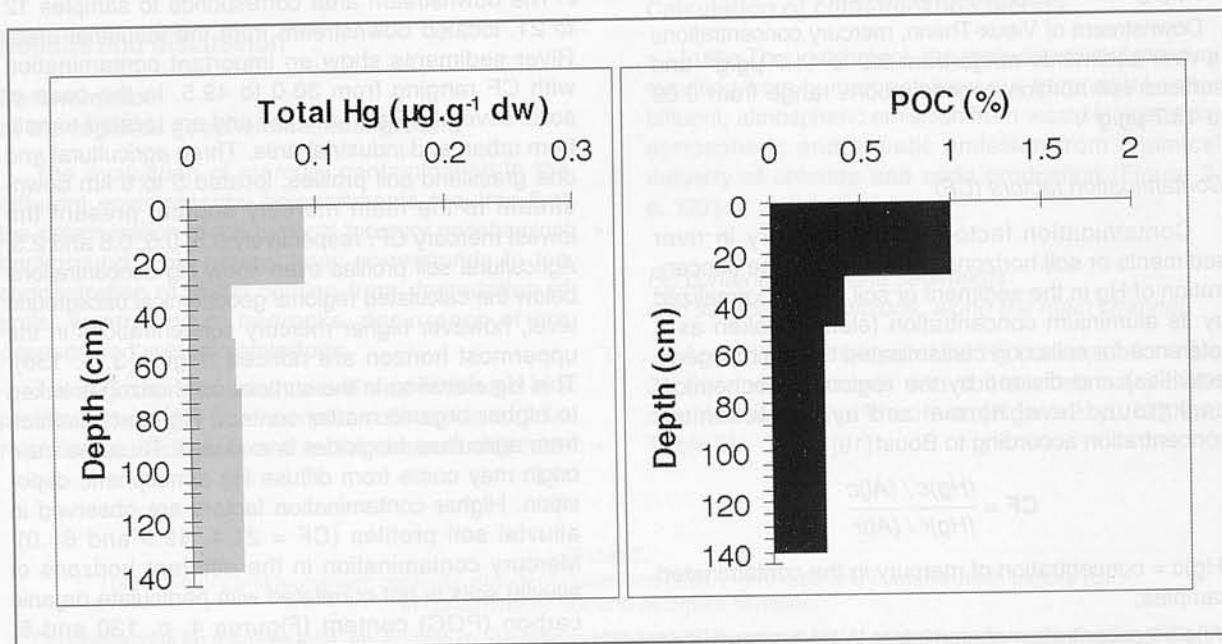


Figure 3.

Distribution of total Hg and particulate organic carbon (POC) contents in the different horizons of an agricultural soil profile (Wattwiller, site 17, see Figure 2, p. 127).

Distribution des concentrations en Hg total et en carbone organique particulaire (COP) dans les différents horizons d'un profil de sol agricole (Wattwiller, site n° 17, voir Figure 2, p. 127).

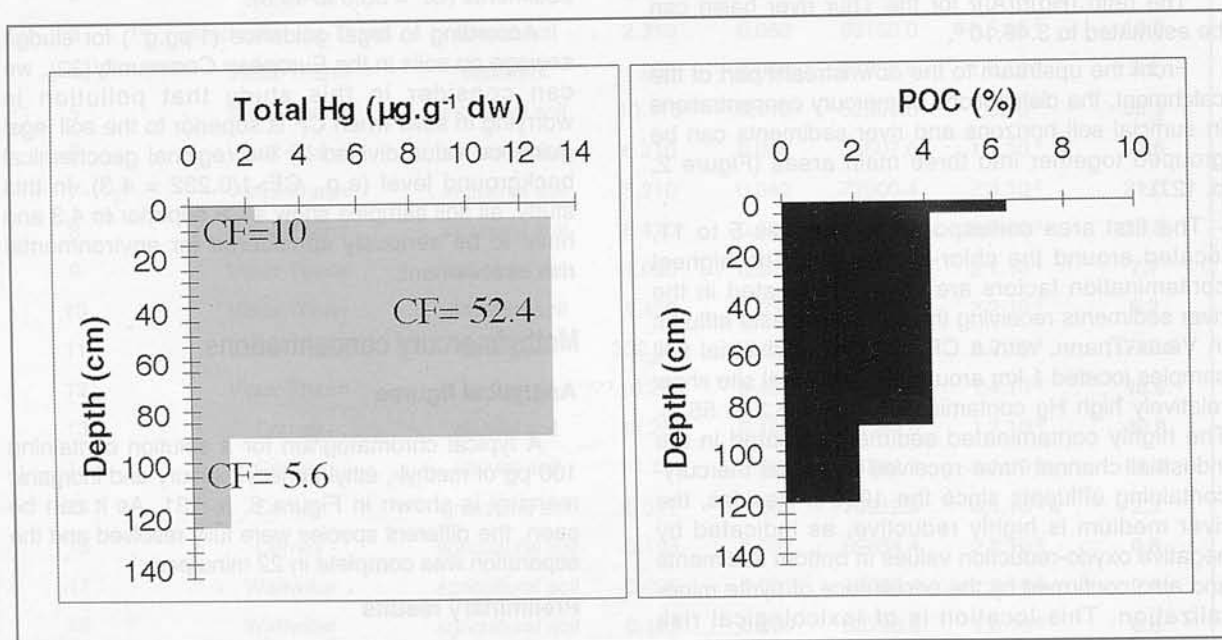


Figure 4.

Distribution of total Hg, POC contents and FC in the different horizons of an alluvial soil profile located upstream of the industrial site of Vieux-Thann (Bitchwiller-lès-Thann, site 3, see Figure 2, p. 127).

Distribution des concentrations en Hg total, COP et FC dans les différents horizons d'un profil de sol alluvial localisé en amont du site industriel de Vieux-Thann (Bitchwiller-lès-Thann, site n° 3, voir Figure 2, p. 127).

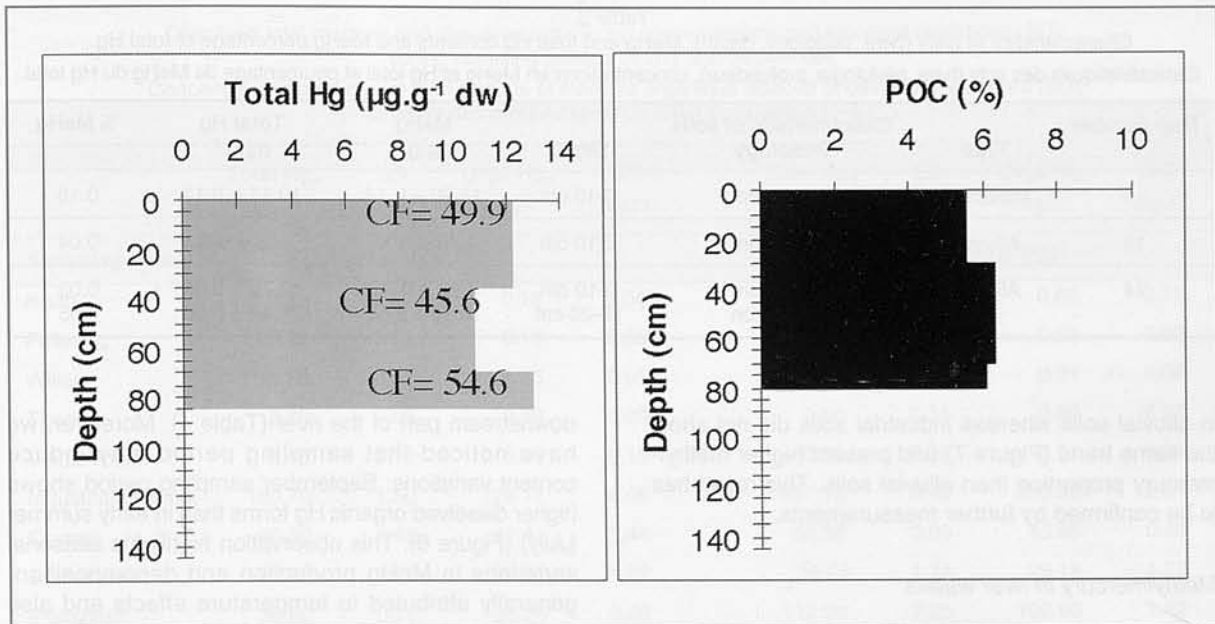


Figure 5.

Distribution of total Hg, POC contents and FC in the different horizons of an alluvial soil profile located downstream of the industrial site of Vieux-Thann (Cernay, site 13, see Figure 2, p. 127).

Distribution des concentrations en Hg total, COP et FC dans les différents horizons d'un profil de sol alluvial localisé en aval du site industriel de Vieux-Thann (Cernay, site n° 13, voir Figure 2, p. 127).

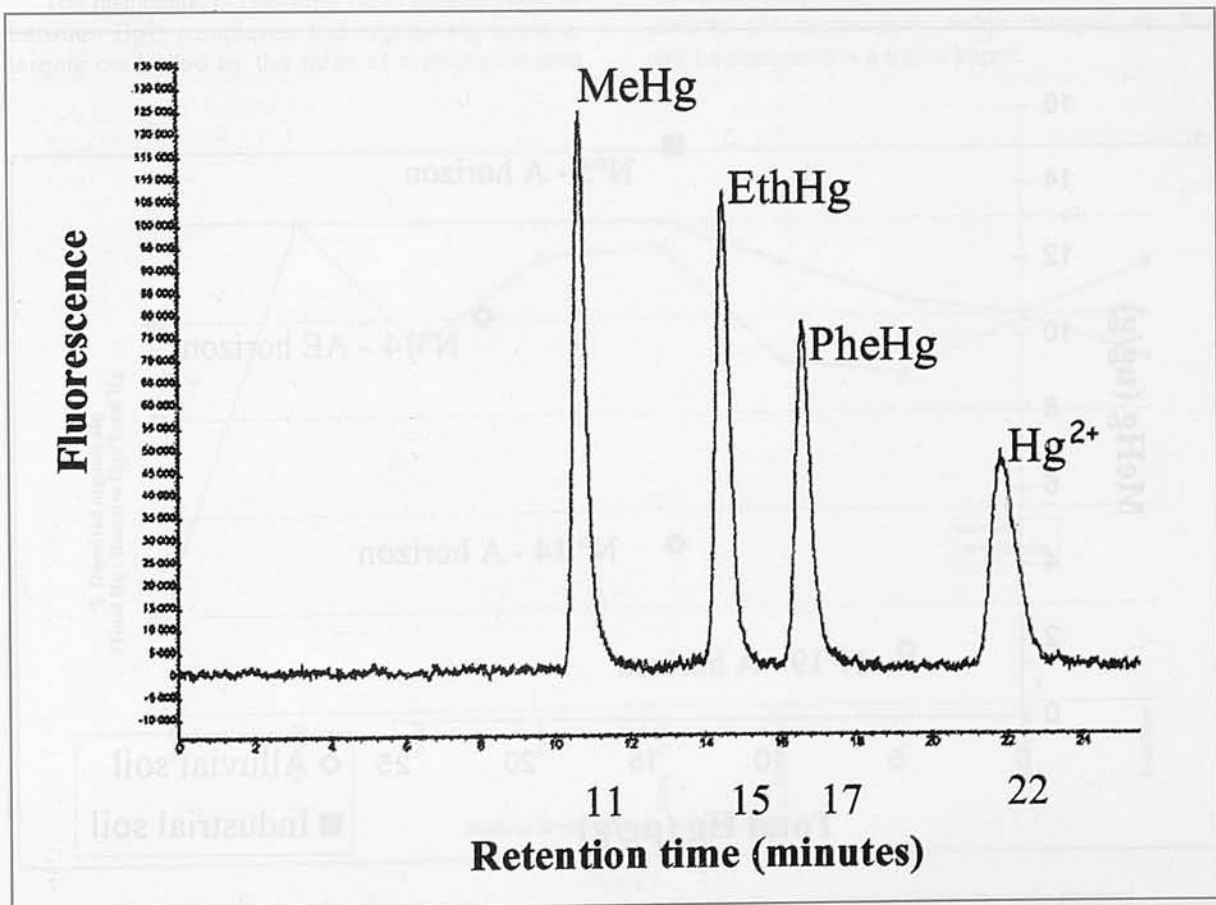


Figure 6.

Chromatogram of 100 pg methylmercury, ethylmercury, phenylmercury and inorganic Hg^{2+} .

Chromatogramme correspondant à l'injection de 100 pg de méthylmercure, éthylmercure, phénylmercure et Hg^{2+} inorganique.

Table 3.

Characteristics of soils (type, pedology, depth), MeHg and total Hg contents and MeHg percentage of total Hg.
 Caractéristiques des sols (type, pédologie, profondeur), concentrations en MeHg et Hg total et pourcentage de MeHg du Hg total.

Map number	Type	Characteristic of soils Pedology	Depth	MeHg ng.g ⁻¹	Total Hg µg.g ⁻¹	% MeHg
5	Industrial	A horizon	0-10 cm	14.96 ± 0.14	10.11 ± 0.11	0.15
19	Alluvial	A horizon	0-10 cm	1.76 ± 0.13	4.58 ± 0.22	0.04
14	Alluvial	A horizon	0-10 cm	4.56 ± 0.21	13.75 ± 0.09	0.03
		AE horizon	10-20 cm	10.53 ± 2.55	21.44 ± 0.06	0.05

in alluvial soils whereas industrial soils did not show the same trend (Figure 7) and present higher methylmercury proportion than alluvial soils. This result has to be confirmed by further measurements.

Methylmercury in river waters

Dissolved organic Hg component can comprise a majority of total dissolved Hg in the river water. Dissolved organic Hg concentrations observed in this survey ranged from 0.12 to 5.19 ng.l⁻¹ in the upstream part of the Thur river before the industrial effluent in Vieux-Thann and from 26.2 to 326.9 ng.l⁻¹ in the

downstream part of the river (Table 4). Moreover, we have noticed that sampling period may induce content variations. September sampling period shows higher dissolved organic Hg forms than in early summer (July) (Figure 8). This observation highlights seasonal variations in MeHg production and decomposition, generally attributed to temperature effects and also to changes in productivity/nutrient supply and redox conditions. Several authors have found that demethylation is favoured by low temperatures, whereas higher temperature favours methylation, leading to a large increase in net MeHg production in summer [24, 25].

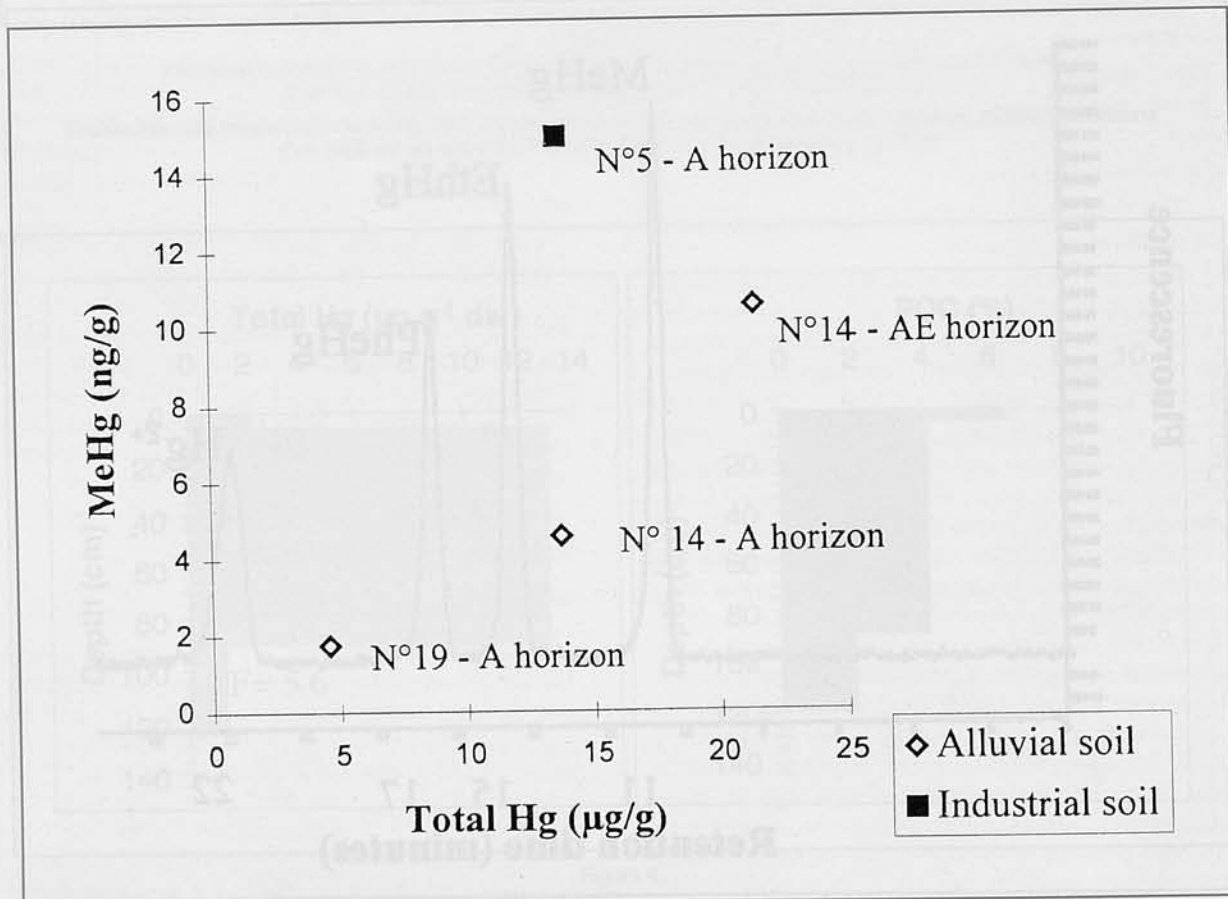


Figure 7.

Relationship between total mercury and methylmercury contents in alluvial and industrial soils.
 Relation entre les teneurs en mercure total et en méthylmercure dans les sols alluviaux et industriels.

Table 4.
Dissolved total mercury and dissolved organic Hg concentrations and standard deviations (SD)
during sampling periods of July and September.
Concentrations en mercure total dissous et mercure organique dissous et déviations standard (SD)
au cours des prélèvements de juillet et de septembre.

	Total Hg _d ng.l ⁻¹	SD ng.l ⁻¹	Orga Hg _d ng.l ⁻¹	SD ng.l ⁻¹	Total Hg _d ng.l ⁻¹	SD ng.l ⁻¹	Orga Hg _d ng.l ⁻¹	SD ng.l ⁻¹
Sampling point	July 2001				September 2001			
Kruth	0.43	0.07	0.12	0.04	0.69	0.17	0.69	0.17
Fellering	0.16	0.05	0.16	0.05	0.65	1.14	0.65	0.03
Willer	2.23	0.11	1.65	0.05	0.31	0.04	0.31	0.04
Thann	2.79	0.03	2.59	0.00	0.60	0.31	0.60	0.21
Vieux-Thann	5.48	0.10	5.19	0.10	0.91	0.29	0.91	0.29
Industrial channel	180.70	1.50	128.11	4.06	357.75	3.40	326.93	2.01
Cernay	60.50	1.46	41.41	1.44	52.58	0.63	43.98	0.48
Staffelfelden	82.90	0.70	66.01	1.22	36.23	1.74	29.18	1.27
Ensisheim	36.80	0.70	26.26	0.08	112.90	2.25	102.60	1.62

While the specific identity of the organic Hg forms has not yet been established, we believe that methylmercury species are the major contributors.

The distribution of dissolved Hg in aquatic systems between Hg²⁺ complexes and organic Hg forms is largely controlled by the rates of methylation and

demethylation [11]. These rates are controlled by a number of environmental parameters such as biological activity, availability of nutrients and complexing agents, organic matter, sulfide content, salinity, pH, temperature, redox changes, etc. that will be discussed in a future paper.

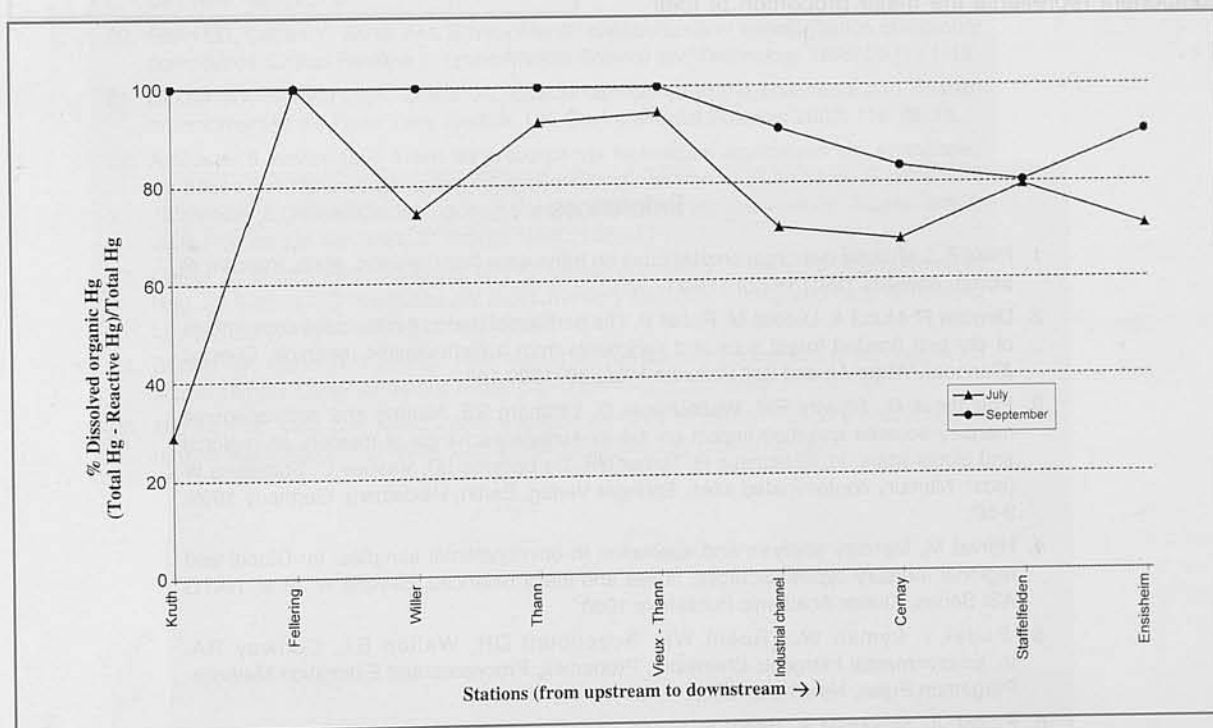


Figure 8.
Evolution of the percentage of dissolved organic Hg along the sampling stations located in the main channel of the Thur river during July and September sampling periods.

Évolution du pourcentage de Hg organique dissous au niveau des stations de prélèvement situées le long du cours principal de la Thur pendant les périodes d'échantillonnage de juillet à septembre.

Conclusion

The first results obtained in this study show that agricultural and grassland soils are generally less contaminated than industrial or alluvial soils. Industrial and grassland soils are generally farther from the river than alluvial soils, highlighting that the main source of Hg contamination of these soils is diffuse atmospheric deposition from local activities and that alluvial soil contamination comes from the alluvial deposits of contaminated sediments constituting this type of soil.

Soil and river sediments are acting as a large reservoir for anthropogenic mercury emission. A substantial amount of Hg accumulates in soils and river sediments every year, which are considered as the main sinks for mercury [20]. Unfortunately, there is until now a lack of information on mercury data in the atmosphere of the Thur catchment in order to assess atmospheric mercury transport and deposition.

Highly contaminated soils might become an important future source of mobile and transformable Hg compounds. Mercury species are undergoing transformation processes in the different media of the environment: mainly Hg reduction and methylation processes. MeHg species have been found in alluvial and industrial soils of the Thur basin and their proportions represent 0.03 to 0.15% of the total Hg content.

The first dissolved Hg speciation results presented in this work emphasize that dissolved organic Hg component represents the major proportion of total

dissolved Hg in the Thur river water. Further research is needed and new measurements are in progress to identify methylmercury compounds in the Thur river basin.

Acknowledgements

The authors wish to thank the ADEME (Agence de l'environnement et de la maîtrise de l'énergie), Atofina, Albemarle PPC, and the CNRS Programme Environnement, Vie et Sociétés (MOTIVE – Modélisation, transfert d'informations, valorisation pour l'environnement) for funding this work.

Keywords

Mercury. Methylmercury. Soil. River sediments. River waters. Organic matter. Cold Vapour-Atomic Fluorescence Spectrometry, CV-AFS. High Performance Liquid Chromatography, HPLC.

Mots clés

Mercurie. Méthylmercure. Sols. Sédiments de rivière. Eaux de rivière. Matière organique. Spectrométrie de fluorescence atomique après génération de vapeurs froides, CV-AFS. Chromatographie liquide à haute performance, CLHP.

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