

# Mercury speciation in soils of the industrialised Thur River catchment (Alsace, France)

Sandrine Remy<sup>a</sup>, Pascale Prudent<sup>a,\*</sup>, Jean-Luc Probst<sup>b,c</sup>

<sup>a</sup> *Laboratoire de Chimie et Environnement, Université de Provence, 3 place Victor Hugo, case 29, 13331 Marseille Cedex 03, France*

<sup>b</sup> *Laboratoire Agronomie Environnement Ecotoxicologie (LAEE), Ecole Nationale Supérieure Agronomique de Toulouse (ENSAT), Institut National Polytechnique (INP), Avenue de l'Agrobiopole, BP 32 607 Auzeville-Tolosane, 31326 Castanet-Tolosan Cedex, France*

<sup>c</sup> *Laboratoire des Mécanismes de Transfert en Géologie, UMR 5563 CNRS/IRD/Université Paul Sabatier, 14 Avenue Edouard Belin, 31400 Toulouse, France*

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## Abstract

Methylmercury (MeHg) and total Hg (THg) concentrations in soil profiles were monitored in the Thur River basin (Alsace, France), where a chlor-alkali plant has been located in the city of Vieux-Thann since the 1930s. Three soil types were studied according to their characteristics and location in the catchment: industrial soil, grassland soil and alluvial soil. Contamination of MeHg and THg in soil was important in the vicinity of the plant, especially in industrial and alluvial soil. Concentrations of MeHg reached 27 ng g<sup>-1</sup> and 29,000 ng g<sup>-1</sup> for THg, exceeding the predictable no effect concentration. Significant ecotoxicological risk exists in this area and remedial actions on several soil types are suggested. In each type of soil, MeHg concentrations were highest in topsoil, which decreased with depth. Concentrations of MeHg were negatively correlated with soil organic matter and total S, particularly when MeHg concentrations exceeded 8 ng g<sup>-1</sup>. Under these conditions, MeHg concentrations in soil seemed to be influenced by THg, soil organic matter and total S concentrations. It was found that high MeHg/THg ratios (near 2%) in soil were mainly related to the combined soil environmental conditions such as low THg concentrations, low organic C/N ratios (<11) and relatively low pH (5–5.5). Nevertheless, even when the MeHg/THg ratio was low (~0.04%), MeHg and THg concentrations were elevated, up to 13 ng g<sup>-1</sup> and to 29,000 ng g<sup>-1</sup>, respectively. Thus, both THg and MeHg concentrations should be taken into account to assess potential environmental risks of Hg.

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## 1. Introduction

Environmental Hg pollution remains a major concern in many regions of the world. The amount of Hg mobilized and released into the environment

has increased since the beginning of the industrialised age. Estimates of Hg flux indicate that emissions from anthropogenic sources have exceeded those of natural sources (Mason et al., 1994). Consequently, measures to control Hg releases to air, water and soil have been recently implemented in Europe and North America. In addition to long distance transport and deposition of Hg in remote areas, point sources of Hg are also problematic. Besides coal burning, waste incineration and

\* Corresponding author.

E-mail addresses: [sandrine.remy3@free.fr](mailto:sandrine.remy3@free.fr) (S. Remy), [pascale.prudent@up.univ-mrs.fr](mailto:pascale.prudent@up.univ-mrs.fr) (P. Prudent).

acetaldehyde production, chlor-alkali plants using metallic Hg for electrolytical production of Cl<sub>2</sub> represent significant sources of Hg emissions. In Europe, emissions from chlor-alkali plants constitute 14% of the total anthropogenic Hg emissions (Biester et al., 2002a; Heaven et al., 2000). In some instances, soil collected near chlor-alkali plants contains Hg concentrations up to 75 times background (Biester et al., 2002b). Concentrations of THg in soil in the vicinity (100–1000 m) of 3 chlor-alkali plants in Europe ranged from 200 to 4200 ng g<sup>-1</sup> dry weight (d.w.) (EPA, 1997; Biester et al., 2002a,b). These industrial installations have released a significant amount of Hg into the atmosphere and rivers, creating diffuse, locally concentrated and persistent contamination of the nearby ecosystem (Maserti and Ferrera, 1991; Lodenius, 1998; Biester et al., 2002a,b).

The authors studied Hg pollution in the Thur River catchment, where a chlor-alkali plant has been located in the city of Vieux-Thann since the 1930s. Recent studies carried out by the CGS-CNRS in Strasbourg and the LMTG-CNRS in Toulouse (Probst et al., 1999; Remy, 2002; Remy et al., 2002, 2003a,b; Hissler and Probst, 2006) showed the persistence of such Hg contamination. During these studies, the regional geochemical background concentration of THg was evaluated (Remy et al., 2003a). The mean background Hg concentration (not affected by human activities) estimated in river sediment and soil was 232 ng g<sup>-1</sup> d.w. (range: 27–406 ng g<sup>-1</sup> d.w.). Significant contamination by THg was found in both industrial soil and alluvial soil of the basin (Remy et al., 2003a). Moreover, two major pathways for Hg emissions have been demonstrated: atmospheric Hg emissions linked to the chlor-alkali plant (Remy, 2002; Hissler and Probst, 2006) and river-soil Hg transfer, especially during flooding (Remy et al., 2003a).

Deposition of Hg to soil is known to be subject to a wide array of chemical and biological transformation processes such as Hg<sup>0</sup> oxidation, and Hg(II) reduction or Hg methylation depending on physical and chemical conditions of the soil. The toxic MeHg compound is formed from inorganic Hg by SO<sub>4</sub>-reducing bacteria or by abiotic processes in soil. Concentrations of MeHg in soil are generally low, but owing to its lipophilic and S-binding properties, MeHg is readily accumulated and biomagnified in the food chain and is recognized as a major health hazard for humans and other organisms (Horvat, 1996).

A detailed survey of different types of soil was conducted in this study to investigate the extent and nature of Hg contamination in the industrialised Thur River basin. The main objectives of this study were to determine THg concentrations in soil profiles, and for the first time, the MeHg concentrations in such an industrialised catchment in France. The study also aimed at identifying factors controlling Hg methylation (pH, organic matter, microbiological activity, etc.) and the behaviour of different Hg species in soil.

## 2. Materials and methods

### 2.1. Site description

The Thur River is located in the upper part of the Ill River basin (tributary of the Rhine), in the Alsace region (north-eastern France), 80 km SW of Strasbourg. The basin is historically polluted by Hg released by a chlorine and soda plant in Vieux-Thann (Probst et al., 1999; Remy et al., 2003a). The Thur River is 54 km long and drains a catchment area of 273 km<sup>2</sup> in the southeastern part of the Vosges Mountains and the Alsatian plain (Fig. 1). The elevation of the basin varies from 200 m in the alluvial plain to more than 1400 m in the Vosges Mountains. This elevation difference leads to contrasting climates spanning from mountainous oceanic climate in the high valley to continental climate in the plain. Generally, in the Alsatian region, the mountainous part of the basin receives more precipitation throughout the year than the plain (Hissler and Probst, 2006). The basin is subdivided into 3 main geomorphologic units: the Vosges Mountains (80% of the area), the Sub-Vosgian Hills (5%) and the alluvial plain (15%). The catchment is underlain by 5 main bedrocks: granitic series and schist–graywacke series in the mountainous area; volcanic (trachyandesites and labradorites) and sedimentary (sandstone and conglomerate) outcrops in the hilly part, and alluvial deposits in the plain. The main types of soil are brown soil, acid brown soil, alluvial soil and industrial soil (mainly banking material) (Remy, 2002; Remy et al., 2002).

### 2.2. Sampling and pre-treatment

Soil samples were collected in 3 different parts of the basin during 2000: industrial soil, grassland soil and alluvial soil. Concentrations of THg and MeHg were measured in the 14 collected soil profiles. Each

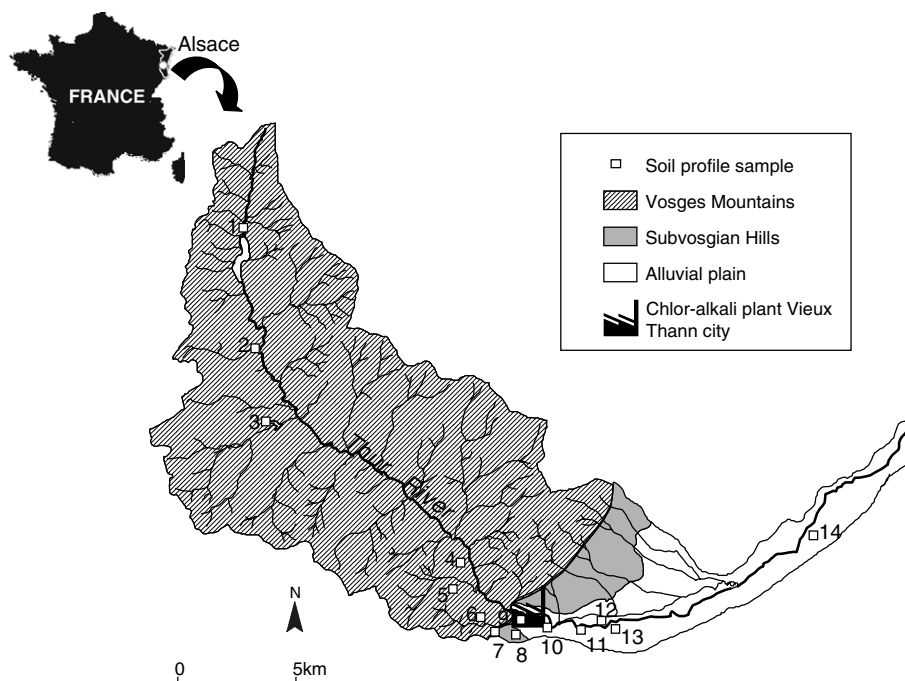


Fig. 1. Location of soil sample sites in the Thur River catchment.

soil profile was sectioned according to specific soil pedologic horizons (Fig. 1, Table 1). Thus, the collected soil samples had different thicknesses corresponding to each soil profile.

All samples were treated and stored in order to preserve THg and MeHg and to avoid Hg contamination. Soil horizons were sampled directly from an exposed soil profile or collected by drilling. Samples were transferred to polyethylene bags, frozen at  $-20^{\circ}\text{C}$  within 24 h of collection and later freeze-dried (lyophilized). No differences in MeHg concentrations were found between fresh and lyophilized solid samples (Muhaya et al., 1998; Leermakers et al., 2005). Samples were homogenized and sieved through a  $50\ \mu\text{m}$  nylon screen, which corresponded to the clay and coarse silt fractions. Concentrations of THg were determined on the fine soil fraction because it concentrates the highest THg.

Procedures were also followed to avoid contamination during sampling and storage: (1) Pyrex and Teflon dishes were soaked in acid baths at a temperature of  $80^{\circ}\text{C}$  for 6 days, rinsed using ultra-high purity water, dried in a drying oven at  $100^{\circ}\text{C}$  for 12 h and stored in polyethylene bags until use (Quemerais and Cossa, 1997); (2) gloved hands were used to manipulate all samples, and; (3) samples were stored in polyethylene bags at  $4^{\circ}\text{C}$  and in the dark. Blanks were tested to detect potential contamina-

tion during sampling, filtration, digestion and analysis.

### 2.3. Total mercury measurements

Concentrations of THg were measured in soil samples by automated cold vapour atomic fluorescence spectrometry (CVAFS) (PS Analytical, Merlin Plus) according to Quemerais and Cossa (1997) and Bloom and Fitzgerald (1988), with  $\text{SnCl}_2$  reduction following acid digestion (Remy et al., 2003a).

#### 2.3.1. Procedure

The digestion procedure requires approximately 200 mg d.w. of sample accurately weighed in a closed 60 mL Teflon vial (Savilex). Each sample was stirred and digested at  $90^{\circ}\text{C}$  overnight with (8:2:2) concentrated  $\text{HNO}_3$ : concentrated  $\text{HCl}$ : 0.2 mM  $\text{BrCl}$  solution (potassium bromide-bromate in  $\text{HCl}$  medium), according to an analytical method modified from Muhaya et al. (1998). The digest was then diluted to 50 mL with ultra-pure water containing 1% of a 0.2 M  $\text{BrCl}$  solution and filtered through  $0.45\ \mu\text{m}$  PES syringe filters (Acrodisc Supor) before THg analysis. Blanks were included with each batch of digestion. Only analytical grade or ultra-pure quality reagents were used in this study. Mercuric chloride ( $\text{HgCl}_2$ ) standards were

Table 1  
Physico-chemical characteristics of soil profiles sampled in the Thur River catchment

Soil profile number (see Fig. 1)	Type of soil	Depth (cm)	Soil organic matter (%)	Total sulfur (%)	Organic C/N ratio	pH	Clay (%)	Silt (%)	Sand (%)
1	Alluvial	0–15	6.8	0.73	12.4	5.9	17.5	34.0	48.5
2	Alluvial	0–15	6.4	0.74	11.5	4.8	15.5	25.8	58.7
3	Peat bog	0–10	15.2	1.65	13.0	5.6	41.4	54.3	4.3
4	Alluvial	0–5	2.5	0.50	18.2	6.6	5.7	21.6	72.7
		5–90	2.8	0.29	26.5	6.5	5.9	24.8	63.9
		90–120	0.9	0.14	16.4	6.4	6.6	26.6	66.8
5	Grassland	0–15	4.0	0.53	10.3	5.2	22.4	62.3	15.3
		15–50	2.7	0.39	9.7	5.3	20.8	63.6	15.6
		50	0.9	0.22	10.2	5.5	18.1	64.8	17.1
6	Industrial	0–20	4.6	0.84	15.1	5.8	15.6	38.5	45.9
7	Industrial	0–20	3.0	0.42	12.5	5.6	22.3	53.0	24.7
8	Industrial	0–5	3.4	0.59	10.9	5.8	–	–	–
9	Industrial	0–10	6.8	0.90	15.8	6.9	18.0	39.4	42.6
		10–30	4.5	0.75	20.5	5.7	19.6	41.1	39.3
		30–85	1.2	0.33	12.1	6.3	23.8	36.7	39.5
10	Alluvial	0–10	1.7	0.26	17.1	6.8	6.2	16.8	77.0
11	Alluvial	0–30	2.2	0.35	18.9	6.9	6.4	20.7	72.9
		30–70	3.5	0.43	25.6	6.8	6.3	19.5	74.2
		70–80	5.4	0.62	21.7	6.9	11.6	30.3	58.1
12	Alluvial	0–10	8.0	1.12	14.5	6.4	20.5	43.5	36.0
		10–20	6.7	0.98	15.4	6.0	18.7	39.6	41.7
13	Grassland	0–15	3.4	0.43	11.2	5.3	20.2	36.1	43.7
		15–50	2.0	0.31	9.9	5.7	18.9	33.7	47.4
		50–80	0.9	0.16	8.5	6.0	14.4	31.1	54.5
14	Alluvial	0–15	3.7	0.49	15.6	6.5	8.5	21.2	70.3

prepared by serial dilution of a 1000  $\mu\text{g g}^{-1}$  certified stock solution with 0.5% (v/v) HCl.

### 2.3.2. Method performance

The detection limit, defined as 3 times the standard deviation of the procedural blanks, was 0.3  $\text{ng g}^{-1}$  d.w. for an aliquot of 200 mg, and the coefficient of variation determined using at least 3 replicate analyses was 8%. Recovery and accuracy of the THg method were tested by analyzing certified reference materials from BCR (sandy soil CRM 142R; river sediment CRM 320). The average concentrations obtained for CRM 142R ( $n = 7$  replicates) and for CRM 320 ( $n = 10$  replicates) were 99.3% and 94.2%, respectively, for the recovery and 7.6% and 3.9% for accuracy.

### 2.4. Methylmercury measurement

Determination of MeHg was performed by reversed-phase high performance liquid chromatography (HPLC) with on-line CVAFS detection after post-column oxidation (PCO) of organic com-

pounds by UV light irradiation and cold vapour generation by  $\text{SnCl}_2$  reduction (Falter and Ilgen, 1997). This method involved the extraction of MeHg from matrices using nitrogen-assisted water vapour distillation (Horvat et al., 1993a,b). The compounds in the distillate were then enriched as dithiocarbamate complexes and concentrated on a C18 pre-concentration column before separation and detection (Falter and Ilgen, 1997; Schwesig and Matzner, 2000).

#### 2.4.1. Procedure

In the distilled sample, MeHg was complexed with sodium pyrrolidinedithiocarbamate (NaPDC) and concentrated onto a pre-concentration column with bi-distilled water containing 0.5 mM ammonium acetate buffer (pH 6). After sample enrichment, the pre-concentration 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 mM ammonium acetate (pH 6). Methylmercury was desorbed and transported to the analytical column for separa-

tion. Subsequently, MeHg was oxidized by UV-irradiation. After reducing inorganic Hg in the gas–liquid separator by  $\text{SnCl}_2$ , the generated elemental Hg was transported by an Ar gas stream into the AFS detector for element specific detection, after removing water in the Hg-containing gas. This method allowed separation and quantification of MeHg within 13 min. A MeHgCl stock solution was prepared by dilution of a certified MeHgCl standard (Johnsson Matthey) in isopropanol/water (2/1, v/v). Working standards of MeHg were prepared by serial dilution of the stock solution in 0.1% (v/v) HCl and 5% (v/v) acetic acid, which were stored in the dark at 4 °C for a maximum of one month. It was necessary to UV irradiate working inorganic Hg standards for >0.5 h to ensure that no trace MeHg species were present.

#### 2.4.2. Instrumentation

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

#### 2.4.3. Quality controls

The detection limit for MeHg was calculated to be 24 pg (absolute amount), i.e., 0.2  $\text{ng g}^{-1}$  in solid samples, and the linearity of the system ranged from 24 to 200 pg. The precision of the method (6%) was determined by 10 successive injections of 100 pg of MeHg.

Recovery studies are an essential component of the validation of extraction-based techniques. A recent overview of the certification of MeHg in estuarine sediment recommended the use of MeHg spike additions as the best means to establish the efficiency of the method (Leermakers et al., 2005). Recoveries of the distillation procedure were assured by spiking 5 ng MeHgCl into a solid certified reference material (CRM 580, BCR) and in natural soil and sediment samples. The natural samples used in these recovery tests were other samples than those used in this study. The certified reference material (CRM 580, coastal marine sediment) was the only available and accurate material for both MeHg and THg analysis in mineral material, at the time of the experiment. The average values obtained for CRM 580 and natural samples

( $n = 15$  replicates) were 80% for the recovery and 5.8% for accuracy. A 20% recovery compensation factor was applied in order to achieve a better approximation of the true concentration in the samples.

The production of artificial MeHg during the analytical procedure has been reported, and may result in a significant bias in measurements, especially when the distillation method is applied to soil or sediment (Bloom et al., 1997; Hintelmann, 1999; Bowles and Apte, 2000; Leermakers et al., 2005). A proportion of inorganic Hg present in the sample can be methylated to form MeHg (Bloom et al., 1997). The magnitude of artifact formation increases linearly with THg concentration and is highest in the presence of carboxylic acids, humic materials and particles with high surface areas (Falter et al., 1999). The nitrogen-assisted water vapour distillation used to extract MeHg from samples caused MeHg artifact formation, but this extraction method was well adapted to HPLC-UV-PCO-CVAFS coupled analytical technique (Falter and Ilgen, 1997; Schwesig and Matzner, 2000).

The MeHg artifact measurement was achieved by spiking the material under investigation with different concentrations of inorganic Hg (added as  $\text{HgCl}_2$  10  $\text{mg L}^{-1}$ ) prior to distillation. Spike addition varied according to the THg concentration: when THg concentrations were >1000  $\text{ng g}^{-1}$ , 1  $\mu\text{g Hg(II)}$  was added; when THg was <1000  $\text{ng g}^{-1}$ , 0.1  $\mu\text{g Hg(II)}$  was added. The spike was added to dried samples prior to addition of reagents and the sample was allowed to equilibrate with the added spike (Falter et al., 1999; Leermakers et al., 2005). These evaluations using spikes imply that the reactivity of Hg(II) added is the same as the Hg(II) naturally present in the sample.

The certified reference material CRM 580 ( $75.5 \pm 3.7$   $\text{ng g}^{-1}$  MeHg certified concentration and  $13,200 \pm 300$   $\text{ng g}^{-1}$  THg certified concentration) was also spiked to check artifact formation. The methylation yield resulting from distillation was calculated to be 0.02% and the corrected MeHg concentration obtained was  $64.9 \pm 3.9$   $\text{ng g}^{-1}$  (corresponding to the estimated 80% recovery).

The “corrected” concentration of MeHg in soil was calculated using the linear back extrapolation correction method proposed by Bloom et al. (1997): MeHg concentration (corrected) = MeHg concentration (measured) – (methylation yield  $\times$  THg concentration).

## 2.5. Other analytical parameters

For soil pH measurements, 50 mL of distilled water was mixed with 10 g of sample. Soil pH was determined using a glass electrode after equilibrating for 1 h (Espiau and Peyronel, 1976). Total N and soil organic matter (SOM) concentrations were determined by dry combustion (1030 °C) and detection by thermal conductivity (Carlo Erba NA 1500, NF ISO 10694). The SOM corresponds to the percentage of soil organic C. Total S concentration was quantified by dry combustion (INRA method, France).

The different grain size fractions of soil samples were separated by dry sieving. Three nylon sieves were used and placed in series for the determination of a fine (silt-clay) fraction (<50 µm), a sand fraction (50–2000 µm) and a coarse fraction (>2000 µm). By avoiding possible contamination by metallic instruments, this simple technique allowed the performance of accurate analyses of the different fractions. An aliquot of each sample was dried in an oven at 110 °C to estimate % dry weight.

## 3. Results and discussion

### 3.1. Soil compositions

Grassland soil was fine silty soil showing a slight decrease of clay proportion with depth (Table 1). SOM and total S were low (<4% and <0.53%, respectively) and decreased with depth. These soils exhibited a relatively low pH (5.0–5.5) and a low C/N ratio (<11), which are often related to humification (Gobat et al., 1998).

Industrial soil consisted of bank material located in the vicinity of the chlor-alkali plant (within a distance of less than 100 m) and were characterized as silty soil (Table 1). These soil samples contained low organic matter (SOM <6.5%) and intermediate total S concentrations (0.33–0.90%) that decreased with depth. The soils had near neutral pH (5.7–6.9) and a C/N ratio between 12 and 20.

Alluvial soil was located in floodplain areas of the Thur River and were sandy-silty soil (Table 1). Organic matter distribution in these soil profiles was different from the other types of soil because the SOM content varied randomly along the profiles according to their formation (random deposition of river alluvial materials). Total S concentrations in these alluvial soils vary considerably from 0.14%

to 1.12%. The C/N ratio was high compared to the other soils (19–26), and the pH was close to 7.

### 3.2. Distribution of total mercury and methylmercury in soil profiles

Three soil categories (grassland soil, industrial soil and alluvial soil) were investigated to assess the distribution of THg and MeHg concentrations in soil profiles from the upstream to the downstream part of the basin. Mercury species were studied in the different pedologic horizons.

Concentrations of MeHg were corrected by taking into account the potential positive MeHg accidental artifact (Table 2). In the study, the methylation yield estimated as a result of artifact formation ranged from 0.001% to 0.154% and the percentage of artifact formation ranged from 3.6% to 50% (Table 2). In the literature, the yield of artificially-produced MeHg formed during nitrogen-assisted distillation in sediments typically ranges from 0.005% to 0.1% (Bloom et al., 1997; Hintelmann, 1999), and the percentage of artifact formation typically ranges from 10% to 40% (Bloom et al., 1997). In the 14 profiles, MeHg corrected concentrations ranged from 0.34 to 27 ng g<sup>-1</sup> d.w. and THg concentrations ranged from 16 ng g<sup>-1</sup> to 29,000 ng g<sup>-1</sup> d.w. (Table 3). Grassland soil contained low MeHg concentrations (<3 ng g<sup>-1</sup> d.w.) and low THg concentrations (<600 ng g<sup>-1</sup> d.w.). However, the MeHg/THg ratio were relatively high (0.14–2.19%). Industrial soil exhibited higher MeHg (0.59–21 ng g<sup>-1</sup> d.w.) and THg concentrations (1100–29,000 ng g<sup>-1</sup> d.w.), but lower MeHg/THg ratios (0.04–0.35%). In the case of alluvial soil, MeHg concentrations were also high, ranging from 0.41 to 27 ng g<sup>-1</sup> d.w. THg concentrations ranged from 210 to 22,000 ng g<sup>-1</sup> d.w. MeHg/THg ratios ranged from 0.03% to 0.57% and were intermediate compared to those recorded in the two previous categories of soil.

#### 3.2.1. Total mercury concentrations

The regional geochemical background concentration of THg (232 ng g<sup>-1</sup> d.w., range: 27–406 ng g<sup>-1</sup> d.w.) was determined previously (Remy et al., 2003a). Significant contamination by THg was found in both industrial (enrichment factors between 6 and 55) and alluvial soils (enrichment factors between 10 and 61) of the basin. The THg enrichment factor corresponded with the concentration of Hg in the soil normalized to its Al concentration

Table 2  
Estimated MeHg artifact resulting from distillation of natural soils (based on methylation yield of a Hg(II) spike)

Soil profile number (see Fig. 1)	Type of soil	Depth (cm)	THg (ng g <sup>-1</sup> )	Methylation yield <sup>a</sup> (%)	MeHg measured <sup>b</sup> (ng g <sup>-1</sup> )	Artifact <sup>c</sup> (ng g <sup>-1</sup> )	Artifact (%) <sup>d</sup>
1	Alluvial	0–15	208	0.120	2.12	0.25	11.8
2	Alluvial	0–15	228	0.032	0.48	0.07	14.6
3	Peat bog	0–10	296	0.151	1.62	0.45	27.7
4	Alluvial	0–5	4015	0.063	25.60	2.53	9.9
		5–90	15,470	0.001	4.32	0.15	3.5
		90–120	2190	0.002	0.61	0.04	6.5
5	Grassland	0–15	48	0.154	1.12	0.07	6.2
		15–50	38	0.125	0.79	0.05	6.3
		50–	16	0.104	0.36	0.02	5.5
6	Industrial	0–20	6210	0.053	24.72	3.29	13.3
7	Industrial	0–20	5310	0.041	8.26	2.17	26.3
8	Industrial	0–5	7700	0.042	7.85	3.23	41.1
9	Industrial	0–10	29,030	0.040	24.51	11.61	47.4
		10–30	8650	0.040	9.00	3.46	38.4
		30–85	1070	0.051	1.13	0.54	47.8
10	Alluvial	0–10	2620	0.003	2.24	0.08	3.6
11	Alluvial	0–30	12,850	0.038	31.53	4.88	15.5
		30–70	7800	0.026	23.03	2.03	8.8
		70–80	13,010	0.021	20.09	2.73	13.6
12	Alluvial	0–10	17,750	0.038	13.94	6.74	48.3
		10–20	21,500	0.041	19.34	8.81	45.5
13	Grassland	0–15	580	0.060	3.08	0.35	11.4
		15–50	320	0.026	0.53	0.08	15.1
		50–80	100	0.063	0.77	0.06	7.8
14	Alluvial	0–15	4580	0.040	3.59	1.83	50.9

<sup>a</sup> Percentage of Hg(II) spike methylated during distillation.

<sup>b</sup> MeHg measured concentration with no addition of Hg(II).

<sup>c</sup> Artifact = methylation yield × THg concentration.

<sup>d</sup> Artifact % = 100 × (Artifact)/(MeHg measured).

(element taken as a reference for soil uncontaminated by anthropogenic activity) and divided by the regional geochemical background concentration normalized by its Al concentration. Concentrations of THg observed in the different soil samples within 100 m from the industrial site in Vieux-Thann were 5-fold higher than the concentrations reported in other European chlor-alkali sites (Biestler et al., 2002a,b). Higher THg concentrations were generally observed in the topsoil layer and may be correlated to atmospheric inputs (Remy et al., 2002; Hissler and Probst, 2006). These results were observed in soil profiles sectioned according to their specific soil pedologic horizons. However, future studies on soil Hg atmospheric deposition should focus on the first 5 cm of the soil section.

Total Hg in grassland soil reflects background concentrations. However, higher THg concentra-

tions were found in the topsoil layer. Grassland soil located downstream of the industrial area showed significantly higher THg concentrations than those located in the upstream part (Table 3).

In alluvial soil, THg concentrations showed a random distribution along the soil profiles. This heterogeneity was linked to random deposition of contaminated suspended particulate matter during high flow or flooding of the Thur River (Remy et al., 2003a). Alluvial soil located upstream from the industrial area contained low THg concentrations ranging from 210 to 230 ng g<sup>-1</sup> d.w., except for one soil (site 4, Fig. 1). The origin of this alluvial soil contamination may be from past Hg pollution from wastewater effluents. Several wastewater plants are located along the Thur River and especially one in the town of Moosch, located upstream from the contaminated area (Remy et al., 2003a). Downstream of

Table 3

Methylmercury (MeHg, with artifact correction), total mercury (THg) concentrations (and their respective standard deviation SD) and MeHg/THg ratios in the soil profiles sampled in the Thur River catchment

Soil profile number (see Fig. 1)	Type of soil	Depth (cm)	MeHg <sup>a</sup> (ng g <sup>-1</sup> )	SD (ng g <sup>-1</sup> )	THg (ng g <sup>-1</sup> )	SD (ng g <sup>-1</sup> )	MeHg/THg (%)
1	Alluvial	0–15	1.87	0.08	208	1	0.90
2	Alluvial	0–15	0.41	0.01	228	1	0.18
3	Peat bog	0–10	1.17	0.14	296	3	0.39
4	Alluvial	0–5	23.07	3.01	4015	100	0.57
		5–90	4.17	0.04	15,470	200	0.03
		90–120	0.57	0.06	2190	20	0.03
5	Grassland	0–15	1.05	0.01	48	1	2.19
		15–50	0.74	0.02	38	1	1.94
		50–	0.34	0.01	16	1	2.13
6	Industrial	0–20	21.43	2.06	6210	10	0.35
7	Industrial	0–20	6.09	0.45	5310	40	0.11
8	Industrial	0–5	4.62	0.72	7700	20	0.06
9	Industrial	0–10	12.90	0.70	29,030	660	0.04
		10–30	5.54	0.06	8650	160	0.06
		30–85	0.59	0.09	1070	20	0.06
10	Alluvial	0–10	2.16	0.53	2620	30	0.08
11	Alluvial	0–30	26.65	2.32	12,850	760	0.21
		30–70	21.00	1.39	7800	100	0.27
		70–80	17.36	1.31	13,010	120	0.13
12	Alluvial	0–10	7.20	1.01	17,750	100	0.04
		10–20	10.53	2.55	21,500	70	0.05
13	Grassland	0–15	2.73	0.07	580	10	0.47
		15–50	0.45	0.15	320	20	0.14
		50–80	0.71	0.23	100	1	0.71
14	Alluvial	0–15	1.76	0.05	4580	220	0.04

<sup>a</sup> MeHg concentration (corrected) = MeHg concentration (measured) – (methylation yield × THg concentration).

the industrial area, alluvial soil showed significant THg contamination ranging from 2600 to 22,000 ng g<sup>-1</sup> d.w.

This significant soil Hg contamination raises the problem of related environmental and human health effects. In order to take into account these risks, a predictable no effect concentration (PNEC) has been proposed for THg in soils by Euro Chlor (1999) and the French National Institute of Industrial Environment and Risks (INERIS) (Pichard et al., 2000). The PNEC THg concentrations range from 27 to 300 ng g<sup>-1</sup> d.w. and represent background. Thus, Hg concentrations reported for soils during this study indicate important harmful effects.

### 3.2.2. Methylmercury concentrations

Concentrations of MeHg measured in this study probably resulted from both methylation and demethylation processes in this environment. Soil MeHg concentrations reported by Schwesig and

Matzner (2000) and Tremblay et al. (1998) ranged from 0.1 ng g<sup>-1</sup> (forest soil) to 5 ng g<sup>-1</sup> (peat bogs) in remote areas. In this study, MeHg concentrations ranged from 0.34 to 2.7 ng g<sup>-1</sup> d.w. in grassland soil and were significantly higher in alluvial soil (0.41–27 ng g<sup>-1</sup> d.w.) and in industrial soil (0.59–21 ng g<sup>-1</sup> d.w.), especially in top soil (Table 3). The distribution of MeHg along soil profiles showed higher concentrations in the surficial horizon, which decreased with depth, except in an alluvial soil located at site 12 (Fig. 1, Table 3). The PNEC proposed for MeHg in soil is 23 ng g<sup>-1</sup> d.w. (Euro Chlor, 1999; Pichard et al., 2000) and two alluvial topsoil samples collected in this study equal or exceed this concentration (Table 3).

The distribution of MeHg/THg ratios calculated in soil profiles enabled an estimate of MeHg relative abundance. The MeHg/THg ratios were low in industrial and alluvial soil samples, however, MeHg and THg concentrations were relatively high. In

contrast, in soil collected from areas uncontaminated by Hg, the relative abundance of MeHg was high (up to 2.19%, Table 3). Even when the MeHg/THg ratio was low (0.04%) in areas highly contaminated with Hg, MeHg and THg concentrations were elevated (up to  $13 \text{ ng g}^{-1}$  d.w. and to  $29,000 \text{ ng g}^{-1}$  d.w., respectively). Thus, both THg and MeHg concentrations should be taken into account to assess potential Hg environmental risks.

### 3.3. Methylmercury occurrence

This MeHg contamination brings up the question about the origin of MeHg in the Thur catchment soils. Is MeHg released directly from the chlor-alkali plant or produced by in situ methylation of inorganic Hg? What are the environmental conditions and parameters influencing the presence of MeHg? Mercury deposited to soil is known to be affected by a wide array of chemical and biological transformation processes such as  $\text{Hg}^0$  oxidation, and  $\text{Hg(II)}$  reduction or methylation depending on several various soil parameters (pH, temperature, soil humic substances content, etc.; Weber, 1993). Consequently, relationships were investigated between soil characteristics (Table 1) and Hg species concentrations and MeHg/THg ratios (Table 3).

Studies have shown that Hg species are bound to soil organic matter, especially to humic substances via S-containing functional groups (Wallschläger et al., 1998; Schuster, 1991; Yin et al., 1997). Although Hg species have a great affinity for soil organic matter, the distribution of MeHg was not obviously related to SOM concentrations (Fig. 2a) or to soil total S concentrations (Fig. 2b). Nevertheless, it was observed that in MeHg contaminated soil ( $\text{MeHg} > 8 \text{ ng g}^{-1}$  d.w.), MeHg concentrations

decreased with increasing SOM or total S concentrations, whereas there was no significant relationship between these parameters in less MeHg contaminated soil ( $\text{MeHg} < 8 \text{ ng g}^{-1}$  d.w.) (Fig. 2a and b). Furthermore, THg concentrations were negatively correlated to MeHg concentrations when MeHg concentrations also exceeded  $8 \text{ ng g}^{-1}$  (Fig. 3). Under these conditions, MeHg concentrations in soil seemed to be influenced by THg, SOM and total S concentrations.

MeHg concentrations and MeHg/THg ratios observed in the study may be the result of Hg methylation and/or MeHg demethylation processes. It is possible that low MeHg/THg ratios can be due to low Hg methylation or to high MeHg demethylation rates. Studies have demonstrated that high or low concentrations of inorganic Hg may depress MeHg production or may favor demethylation (Ullrich et al., 2001).

Demethylation reactions can be stimulated when inorganic Hg concentrations increase (Gilmour and Henry, 1991), especially with respect to the induction of the *mer* operon genes (present in many Hg-resistant bacteria; Spangler et al., 1973; Robinson and Tuovinen, 1984; Summers, 1986; Baldi, 1997; Hobman and Brown, 1997), that lead to reductive demethylation of MeHg. There is also an oxidative demethylation process by  $\text{SO}_4$  reducing bacteria and methanogens, which can be very active in sites that are low in THg (Oremland et al., 1995; Hines et al., 2000).

Methylation of Hg can be inhibited when bio-availability of  $\text{Hg}^{2+}$  is low. The availability of Hg for methylation may be decreased by complexation with sulfide ligands (in reducing conditions) or with organic ligands (Winfrey and Rudd, 1990; Gilmour and Henry, 1991; Leermakers et al., 1993). The role

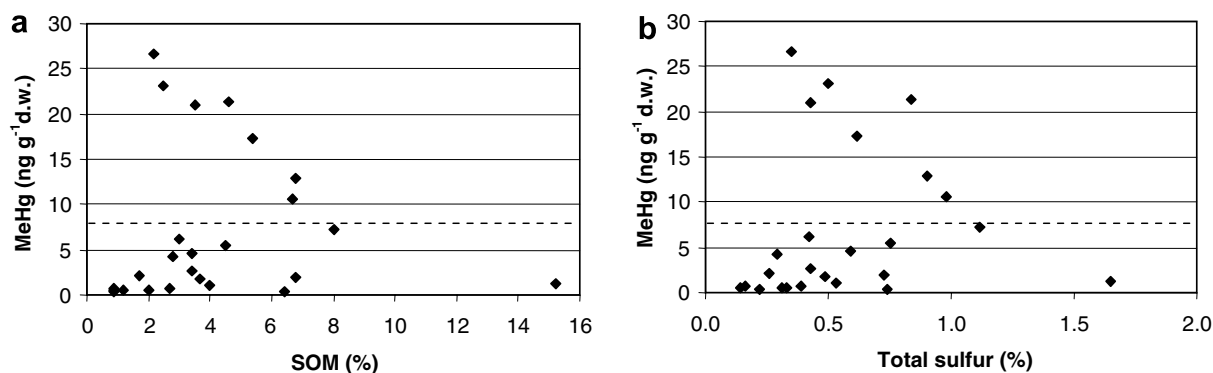


Fig. 2. MeHg concentrations vs. soil organic matter (SOM) (a) and total S concentrations (b) in different soil horizons (fine fraction  $< 50 \mu\text{m}$ ). Dotted line equals  $8 \text{ ng g}^{-1}$ .

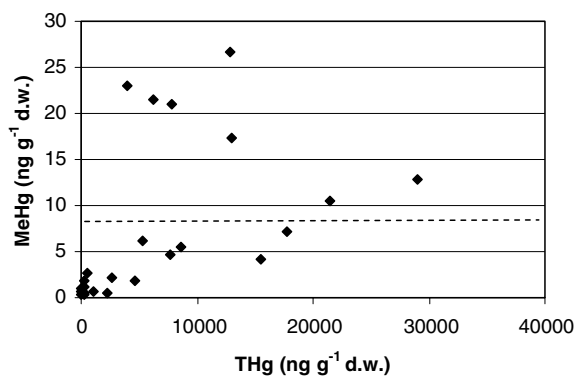


Fig. 3. MeHg vs. THg concentrations in different soil horizons (fine fraction  $<50 \mu\text{m}$ ). Dotted line equals  $8 \text{ ng g}^{-1}$ .

of organic matter in Hg methylation remains unclear. On the one hand, it seems that organic C can enhance Hg methylation by stimulating micro-organism activity or through direct abiotic methylation by humic and fulvic substances (Weber et al., 1985; Weber, 1993). Conversely, Hg methylation may be inhibited at high organic matter concentrations due to increased complexation of Hg with

organic ligands, reducing Hg bioavailability to bacteria particularly at near neutral pH.

Soil organic matter concentrations did not seem to influence MeHg/THg ratios (Fig. 4a). However, high MeHg proportions were linked to low organic C/N ratios ( $<11$ , Fig. 4b), which is characteristic of a high humification state of organic matter and of significant bacterial activity (Semu et al., 1987; Gobat et al., 1998). Thus, the nature of organic matter rather than its quantity may have a significant influence on Hg complexation and formation of MeHg. It was also observed that high MeHg/THg ratios (1.9–2.2%) seemed to be more important at relative low soil pH (5–5.5) (Fig. 4c). Simultaneous environmental conditions contributing to a higher MeHg proportion in soil appeared to be low Hg concentrations, low C/N ratios and relatively low pH. In this study, these conditions were combined in grassland soil, where microbiological activities and organic matter evolution were enhanced, and in which low Hg contamination could not induce reductive Hg demethylation. However, oxidative demethylation may occur, but it is not known at present which of the two degradation pathways

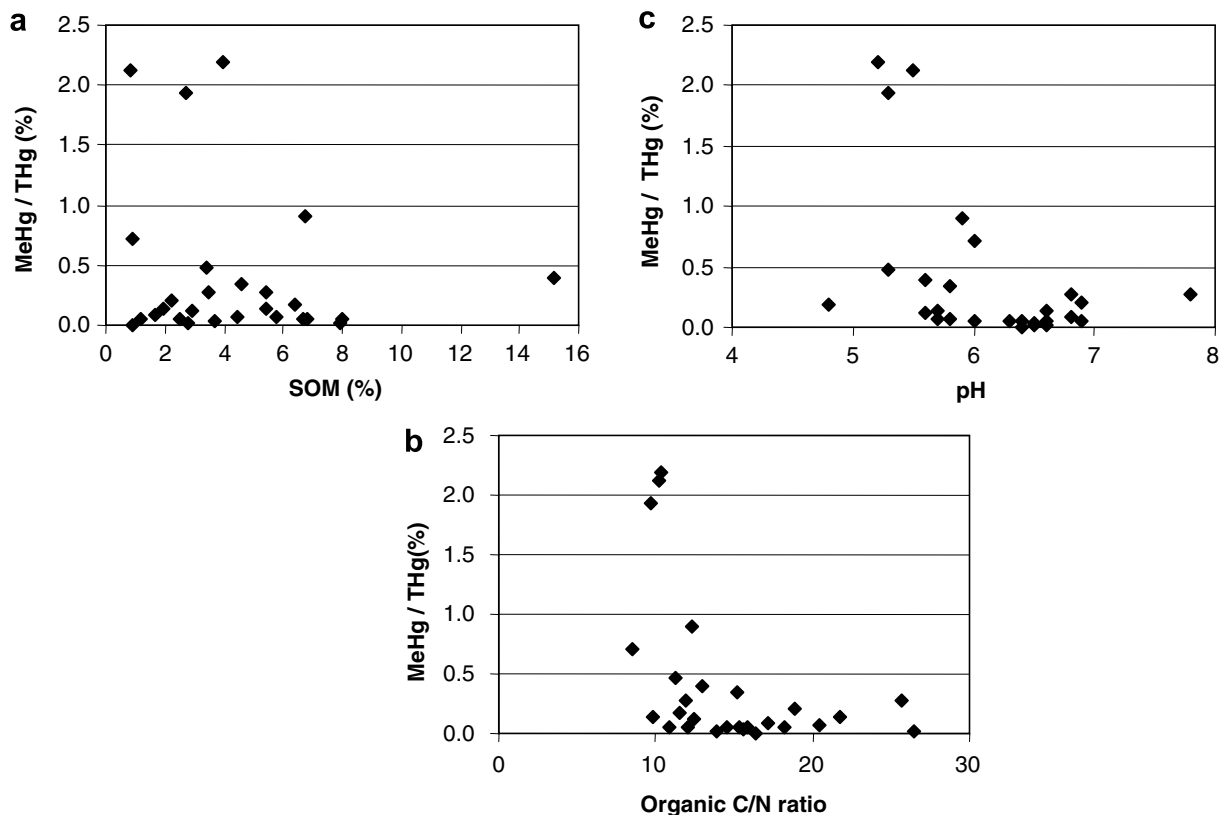


Fig. 4. MeHg/THg ratios vs. soil organic matter (a), organic C/N ratio (b) and pH (c) (fine fraction  $<50 \mu\text{m}$ ).

dominate under specific environmental conditions (Ullrich et al., 2001).

In industrial soil, MeHg and THg concentrations were high, but MeHg/THg ratios were low (0.04–0.06%). This result could be due to higher inorganic Hg concentrations that may depress MeHg production or may favour demethylation. The nature of the soil (banking material, neutral pH, and non-stabilized organic matter, aerobic conditions) may also be unfavourable to methylation.

In the case of wetlands, such as alluvial soil, high MeHg concentrations were reported in the soil profile (up to 27 ng g<sup>-1</sup> d.w.) and were probably linked to soil anaerobic micro-zones that are active sites of methylation (Van Der Lee et al., 1999). Studies have also shown that newly flooded reservoirs can be significant sources of MeHg, probably due to a stimulating effect on microbial activity of the decomposition of organic matter in the newly flooded soil (Jackson, 1991; Kelly et al., 1995). Additional flooding of contaminated areas of the Thur River should be minimized in order to limit mobilization and transformation of inorganic Hg into more toxic and mobile organic forms. Finally, as alluvial soil is permeable sandy soil with low SOM contents, presuming a low Hg species retention capacity, they represent a potential risk of transfers of Hg in the soil–water system via groundwater.

#### 4. Conclusions

Results of this study showed that soil THg and MeHg contamination was significant in the vicinity of the chlor-alkali plant, especially in industrial and alluvial soil. In the Thur River catchment, many samples contained THg concentrations up to 5-fold greater than those observed in other European chlor-alkali plant sites (Biester et al., 2002a,b). In some soil samples, both THg and MeHg concentrations exceeded the PNEC (27–300 ng g<sup>-1</sup> for THg and 23 ng g<sup>-1</sup> for MeHg). Some soil also exceeded the Dutch intervention value (generally employed in Europe) defined for soil concentrations above 10 µg g<sup>-1</sup> THg (Heaven et al., 2000). Thus, there is a need for remedial action in some soil of the Thur River catchment.

In this study, MeHg concentrations did not seem to be linked to soil organic matter nor to total S concentrations. However, the nature of organic matter rather than its quantity may have a significant influence on MeHg occurrence. The relative

abundance of MeHg in contaminated industrial and alluvial soil was low compared to grassland soil. Grassland soil had higher MeHg/THg ratios, but THg concentrations near the background concentration. It was found that MeHg/THg ratios in soil were probably related primarily to the combined soil environmental conditions such as SOM nature, microbiologic activity, pH and THg concentration that affect demethylation.

The rates of MeHg originating from soil methylation/demethylation processes or from direct plant emissions are still undetermined. Such information could enable an estimation of the precise conditions of MeHg formation and evolution in soil. Future investigations should also focus, in particular, on the distribution of MeHg adsorption sites in soil, quantification of MeHg in soil solutions in order to assess MeHg potential mobilization processes, and qualification and quantification of atmospheric Hg species. To complete the study of this catchment, a survey has been carried out in the different aquatic compartments (Remy et al., in preparation).

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