

Total mercury concentrations in an industrialized catchment, the Thur River basin (north-eastern France): geochemical background level and contamination factors

S. Rémy^a, P. Prudent^{b,*}, C. Hissler^a, J.L. Probst^c, G. Krempf^a

^a Centre de Géochimie de la Surface, EOST, CNRS/Université Louis Pasteur, 1 rue Blessig, 67084 Strasbourg Cedex, France

^b Laboratoire de Chimie et Environnement, Université de Provence, 3 place Victor Hugo, 13331 Marseille Cedex, France

^c Laboratoire des Mécanismes de Transfert en Géologie, CNRS/Université Paul-Sabatier, 38 rue des 36 Ponts, 31400 Toulouse, France

Abstract

River bottom sediments and soils were collected from the industrialized Thur River basin (north-eastern France) to assess mercury contamination. The regional geochemical background level of total mercury was evaluated to calculate mercury contamination factors (Fc) in soils and river bottom sediments. Our estimate of the mean background mercury levels in river sediments and soils, not affected by human activities, was 232 ng g⁻¹ (range: 27–406 ng g⁻¹). Sediments contaminated by the effluent from a chlor-alkali plant yielded the highest contamination factors (Fc = 1784). Contamination factors of surficial soils within 1 km of the industrial site range from 6.3 to 43.6. This contamination is attributed to diffuse atmospheric deposition from this local plant. However, even upstream from this industrial area elevated contamination factors were recorded for river bottom sediments (Fc = 3.2 to 26.4) and for one alluvial soil profile (Fc = 10). This is possibly due to past pollution resulting from waste water discharges. Mercury contamination in the different horizons of alluvial soils is not correlated with soil organic carbon content, but may be the result of occasional accidental pollution arising from the introduction of contaminated suspended particulate matter by the Thur River during periods of flooding.

Keywords: Mercury; Soil; River sediment; Organic matter; CV-AFS

1. Introduction

Over the last 20 years, our understanding of mercury (Hg) biogeochemistry has improved significantly, particularly owing to the development of new analytical techniques available to environmental sciences. Mercury is transported over long distances from sites of natural sources and industrial and urban activities, and is deposited uniformly on environmental media by wet and

dry aeolian pathways (Dmytriw et al., 1995). The main anthropogenic Hg contamination sources are fuel combustion, waste incineration, waste water discharges and industrial processes such as chlor-alkali plants. Historically, and still in developing countries, the chlor-alkali industry is a significant source of atmospheric mercury emissions and direct releases in aquatic systems (Hintelmann and Wilken, 1995; Ebinghaus et al., 1999). Despite the fact that emissions have been drastically reduced in the last decade, the current atmospheric deposition rate still promotes an accumulation of mercury in the nearby environment (Lindqvist et al., 1991). Consequently, Hg contaminated sites persist and many studies have been performed to determine contamination levels, assessment of risks, behavior and fate of this

* Corresponding author. Tel.: +33-4-9110-6277; fax: +33-4-9110-6377.

E-mail address: prudent@up.univ-mrs.fr (P. Prudent).

element and its compounds in the different environmental compartments.

Generally speaking, the mercury deposited from the atmosphere onto terrestrial surfaces and into aquatic systems is quickly and strongly bound to the organic matter (e.g., humic substances) present in the upper layer of the soil or in the water (Andersson, 1979; Johansson and Iverfeldt, 1994). The topsoil layer may be regarded as a filter for mercury by precipitation infiltration as well as a repository for mercury absorbed in fallen leaves and needles (litterfall). Thus, the quantities currently found in the humic layer reflect accumulated mercury deposition, mainly from the last century. However, Hg in soil is susceptible to be leached by the surface water runoff and infiltration. In the river water column, Hg is also bound to organic matter, either to dissolved organic matter; consisting principally of humic and fulvic acids; or to suspended particulate matter. Riverine sedimentation of Hg bound to particulate matter is expected to be the dominant process for removal of this element from the river water column (US EPA, 1997). In the bottom sediment compartment, 50–75% of mercury is adsorbed to humic acids (Andersson et al., 1990). The remaining fraction is associated with inorganic components of the sediment, e.g. bound to sulphides, and to fine particles with a high specific surface area such as the clay fraction, or adsorbed to metal oxides such as manganese or iron (Stein et al., 1996).

The main objective of this study is to follow the distribution of mercury contamination in the riverine sediment and soil compartments of an industrialized catchment. Consequently, the geochemical background level of mercury was evaluated in order to calculate contamination factors in these different compartments. In this context, our research program is based on the influence of Hg anthropogenic sources, especially from an industrial site dedicated to chlorine and soda production.

2. Materials and methods

2.1. Site description

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 a chlorine and soda plant in Vieux-Thann (Probst et al., 1999). The Thur River drains a catchment area of 273 km² in the south-eastern part of the Vosges Mountains and the Alsatian plain (Fig. 1). In the industrialized Thur Valley, groundwater plays an important role in the economy and in the hydrosystem equilibrium, and the river greatly contributes to the groundwater supply (Roeck, 1992).

The basin is subdivided into three main geomorphologic landscapes: the Vosgian Mountains (80% of

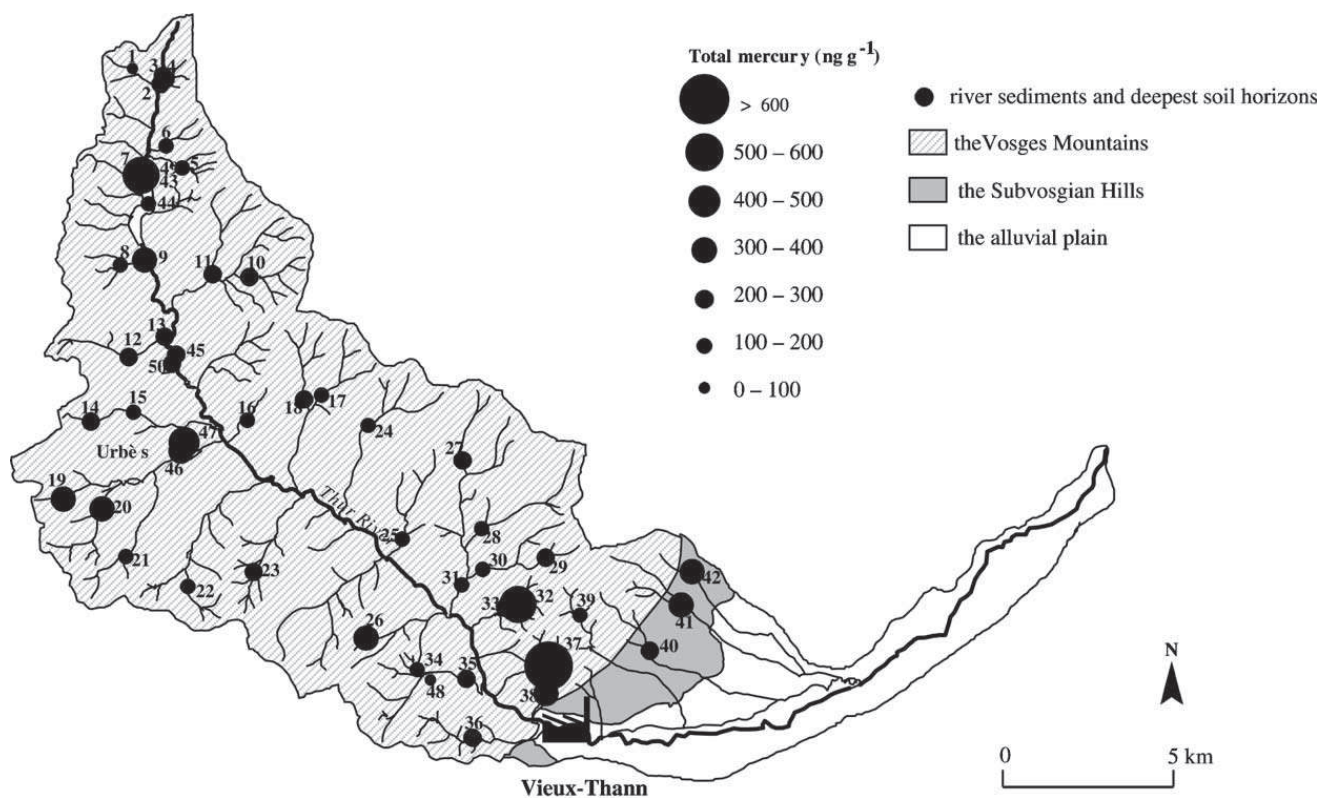


Fig. 1. Mercury geochemical background in the Thur catchment.

the area), the Subvosgian Hills (5%) and the alluvial plain (15%) (Fig. 1). The catchment is underlain by five main bedrocks: granitic series and schist-graywacke series cover the mountainous area, volcanic (trachytes) and sedimentary (sandstone and conglomerate) outcrops cover the hilly part, and alluvial deposits cover the plain. 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).

2.2. Sample collection

Soil and sediment samples for mercury analysis were collected in different parts of the basin during the period 1999–2000. The mercury geochemical background level was evaluated by measuring total mercury concentrations in the deep river bottom sediments and in the deepest soil horizon. These samples were located in the upper part of the basin, not influenced by any aquatic sources of anthropogenic activities and remote from urban or industrial areas. River sediments were collected in the main tributaries of the Thur River as well as in its upstream part.

To study mercury contamination in the catchment, several samples of river bottom sediments were collected along the Thur main channel, and soils were sampled according to their surficial characteristics: industrial soils from Vieux-Thann, agricultural soils, grassland soils and alluvial soils.

All samples were handled in such a way as to preserve their mercury content and avoid the risk of mercury contamination. All Teflon laboratory ware was acid washed, rinsed with ultrapure water (Millipore UHP) and dried at 110 °C in a class 100 oven (Quémerais and Cossa, 1997).

The river bottom sediments were collected with polyethylene flasks. The soil horizons were sampled directly from an exposed soil profile or collected by drilling.

River bottom sediment and soil samples were stored in ice, immediately frozen at –20 °C within 24 h of collection and then freeze-dried. They were homogenized, then sediment samples were sieved to <63 µm and soil samples to <50 µm, which correspond to the clay-silt fraction respectively.

2.3. Analytical methods

2.3.1. Total mercury measurements

Total mercury measurement was performed by reduction with stannous chloride solution following oxidation by acid digestion. The digestion procedure required approximately a 200 mg dry weight (dw) sample. The sample placed inside a closed 60 ml Teflon vial (Savilex), was stirred and digested at 90 °C overnight with concentrated nitric acid/concentrated hydrochloride acid/0.2 M BrCl solution (potassium bromide–bromate in hydrochloric acid medium) (8:2:2, v/v), using a modification of the method of Muhaya et al. (1998). The digest was then diluted to 50 ml with ultrapure water containing 1% 0.2 M BrCl solution and filtered with 0.45 µm PES seringe filters (Acrodisc Supor) before total analysis. Blanks were included with each digestion batch. Total mercury concentration in each digest was measured by an automated Cold Vapour Atomic Fluorescence Spectrometry (CV-AFS) detection technique according to Quémerais and Cossa (1997) and Bloom and Fitzgerald (1988). This automated system consists of a continuous flow vapor generator coupled with an atomic fluorescence spectrometer (PS Analytical, Merlin Plus).

The detection limit, three times the standard deviation of the procedural blanks, corresponds to 0.3 ng g⁻¹ (dw) for a typical 200 mg sample, and the coefficient of variation (<8%) was determined using at least three subsamples. Recovery and accuracy of the method were tested by analyzing different certified reference materials obtained by Promochem (Molsheim, France). Results tests range from 92% to 104.8% for recovery and from 3.9% to 7.6% for accuracy (Table 1). Only analytical grade or ultrapure quality reagents were used in this study.

2.3.2. Other analytical parameters

Sediment particulate organic carbon and soil organic matter (SOM) were determined by infra-red spectrometry (LECO® CS 125 analyzer).

The different grain size fractions of sediments and soils were separated by manual dry sieving. Three nylon sieves were used and placed in series for the

Table 1
Recovery and accuracy of total mercury in certified reference material

Certified reference material	Hg reference value (µg g ⁻¹)	Standard deviation (µg g ⁻¹)	Measured Hg (µg g ⁻¹)	Standard deviation (µg g ⁻¹)	<i>n</i>	Recovery (%)	Accuracy (%)
Marine sediment IAEA 356	7.620	(6.740–7.980)	7.010	0.460	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	1.030	0.160	0.970	0.040	10	94.2	3.9
Estuarine sediment BCR 580	132.000	3.000	138.380	1.520	3	104.8	6.3

determination of a fine (silt-clay) fraction (<50 µm or <63 µm), a sand fraction (50–2000 µm) and a coarse fraction (>2000 µm). By avoiding possible contamination by metallic instruments, this simple technique allowed us to perform accurate analyses of the different fractions.

An aliquot of each sample was dried in an oven at 110 °C to estimate dry weight values. Mercury analysis have been done on the fine fraction.

3. Results and discussion

3.1. Determination of the regional geochemical background

The evaluation of mercury contamination in the different environmental compartments requires 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.

In this study, the regional background level was established from river bottom sediments and soils not perturbed by anthropogenic activities. Furthermore, we took into consideration the possible occurrence of anomalously high levels of background mercury in the

basin owing to the presence of ore deposits in the bedrock (Baize, 1997). Sulphide ore deposits are the principal cause of mercury positive anomalies (Ebinghaus et al., 1999). Thus, different geochemical ore deposits were identified in the Thur catchment. They mainly consist of lead, zinc, silver and copper mineralizations (Bonney, 1980). The occurrence and outcrops of the different kinds of bedrock were established using a geological map of the catchment basin (BRGM, 1976). The average natural mercury concentrations in these rocks are listed in Table 3.

3.1.1. Hg concentrations in river sediment and soil profiles in the upper part of the basin

Fifty samples were collected from river bottom sediments and soils to evaluate the geochemical background level (Fig. 1). The mercury concentrations in these sediments range from 108 to 639 ng g⁻¹, with an average value of 255 ng g⁻¹. Soil concentrations range from 27 to 406 ng g⁻¹, with an average value 154 ng g⁻¹.

3.1.2. Background level calculation

Mercury concentrations obtained in soils and river bottom sediments were classified into seven classes ranging from 0 to more than 600 ng g⁻¹, with an increment of 100 ng g⁻¹ for each class. The frequency of samples in each class of mercury concentration is presented in Fig. 2. The background level calculation was

Table 2

Total mercury and aluminium concentrations, standard deviations (SD), Hg/Al ratio and contamination factors (Fc) in contaminated soil and sediment samples

Map number ^a	Localisation	Type of sample	(Hg)c ng g ⁻¹	(Hg)c SD ng g ⁻¹	(Al)c mg g ⁻¹	(Hg)c/(Al)c × 10 ⁻⁶	Fc
1	St Amarin	Sediment	740	10	55.0	13.5	3.8
2	Moosch	Sediment	6100	10	67.7	90.4	25.9
3	Bitschwiller-lès-Thann	Alluvial soil	2300	50	66.2	34.9	10.0
4	Vieux-Thann	Sediment	1200	60	67.7	17.7	5.1
5	Vieux-Thann	Industrial soil	10 100	100	52.4	192.9	55.3
6	Vieux-Thann	Industrial soil	6200	10	54.5	113.9	32.6
7	Vieux-Thann	Industrial soil	5300	40	72.5	73.2	21.0
8	Vieux-Thann	Industrial soil	6500	20	72.0	89.9	25.8
9	Vieux-Thann	Industrial soil	2000	20	72.5	26.9	7.7
10	Vieux-Thann	Industrial soil	1500	30	66.7	21.7	6.2
11	Vieux-Thann	Sediment	332 500	20	53.4	6226.6	1784.0
12	Vieux-Thann	Sediment	10 200	400	72.0	141.7	40.6
13	Cernay	Alluvial soil	12 300	200	70.4	174.0	49.9
14	Cernay	Alluvial soil	13 800	90	64.6	212.8	61.0
15	Cernay	Grassland soil	580	10	70.9	8.2	2.3
16	Cernay	Agricultural soil	190	1	69.9	2.7	0.8
17	Wattwiller	Agricultural soil	90	1	48.7	1.8	0.5
18	Wattwiller	Agricultural soil	120	1	68.8	1.7	0.5
19	Staffelfelden	Alluvial soil	4600	200	61.4	74.6	21.4
20	Staffelfelden	Sediment	11 700	500	67.7	172.8	49.5
21	Ensisheim	Sediment	8900	400	70.9	125.5	36.0

^a See Fig. 3.

Table 3
Occurrence, outcropping area and average natural Hg concentration interval of the different bedrocks of the Thur catchment

Bedrocks	Outcropping area (%)	Average natural Hg concentration interval (ng g ⁻¹) ^a
Granitic series	19	7–200
Schist-graywacke series	49	10–1000
Volcanic series	20	2–200
Sedimentary series	12	10–300

^a Calculated after the data of Vernet and Thomas (1972).

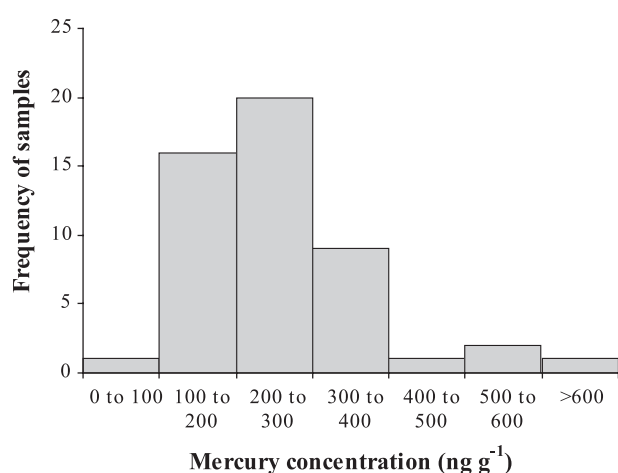


Fig. 2. Classes of mercury concentration for the calculation of the regional geochemical background.

based on the average value of the first five classes (from 0 to 500 ng g⁻¹) selected for the calculation:

- The first one (0 to 100 ng g⁻¹) was selected because of a low mercury concentration (27 ng g⁻¹) that could be considered as a natural value.
- The three following classes (100–400 ng g⁻¹) were chosen because they represent the great majority (90%) of mercury concentration in the samples.
- The last selected one (400 to 500 ng g⁻¹) contains only one sample. It is a peat sample containing 406 ng g⁻¹ of mercury. Another sediment sample (380 ng g⁻¹) collected in the same area confirms the selection of this class for the background calculation. The peat sample shows the highest mercury concentration among all the selected samples; this can easily be explained by its high concentration of organic matter (9.3%) and the well-known affinity of mercury for organic matter. Several authors have reported that sediments of wetlands show higher accumulation of mercury than non-wetland sediments (Zilioux et al., 1993; Carpi et al., 1994). Moreover, all Hg con-

tents in samples chosen for the background level calculation are in accordance with the average natural values for the regional bedrock (Table 3).

The last two class values remained unselected. They contain only three samples (sediments) in which Hg concentrations are above 530 ng g⁻¹. These samples are not influenced by geochemical positive anomalies. However, two of them were taken from areas 3 and 6 km north of Vieux-Thann industrial site and may have received Hg atmospheric deposits. The last sample was taken from an upstream Thur tributary river bottom sediment. This high concentration corresponded to an analytical error during preparation, as the reanalyzed sample concentration was 371 ± 1 ng g⁻¹.

Taking all these observations into consideration, it can be estimated that the mean regional geochemical background level is 232 ± 83 ng g⁻¹ (range: 27–406 ng g⁻¹, Table 4).

3.2. Calculation of contamination factors and discussion

In the Thur catchment, the main sources of mercury resulting from human activities are from wastewater water effluent, atmospheric emission from waste incineration, and atmospheric emission and aquatic discharge resulting from chloride and soda production (Fig. 3).

3.2.1. Hg concentrations in river bottom sediments and surficial soil horizons, along the river stream

Twenty one river bottom sediment and soil profile samples were collected along the Thur River (Fig. 3 and Table 2). The locations for collecting these samples were chosen taking into account the risk of them being potentially contaminated by Hg.

- Around the area of the industrial site in Vieux-Thann, mercury concentrations in sediments are extremely high (332 500 ng g⁻¹). In the same area, surficial soil horizon concentrations range from 1500 to 10 100 ng g⁻¹.
- Four samples were collected upstream of Vieux-Thann: three river sediments (740; 1200 and 6100 ng g⁻¹ of Hg) and one soil (surficial horizon: 2300 ng g⁻¹).
- Downstream of Vieux-Thann, mercury concentrations in river sediments range from 8900 to 11 700 ng g⁻¹ and surficial soil horizon concentrations range from 90 to 13 800 ng g⁻¹.

3.2.2. Contamination factors (F_c) and discussion

The total mercury contamination factor in river bottom sediments or soil horizons corresponds to

Table 4

Mercury and aluminium concentrations, standard deviation (SD), respective mean concentration of the samples used for the calculation of the regional geochemical background level, respective and mean Hg/Al ratio used for the calculation of contamination factors

Map number (see Fig. 1)	Type of sample	(Hg)r (ng g ⁻¹)	(Hg)r SD (ng g ⁻¹)	(Al)r (mg g ⁻¹)	(Hg)r/(Al)r ($\times 10^{-6}$)
1	Sediment	319	1	72.8	4.4
2	Sediment	260	3	63.0	4.1
3	Sediment	243	2	76.2	3.2
4	Sediment	231	6	63.0	3.7
5	Sediment	159	4	65.6	2.4
6	Sediment	192	2	65.1	2.9
7	Sediment	533	1	72.0	7.4
8	Sediment	155	2	83.6	1.9
9	Sediment	314	1	84.7	3.7
10	Sediment	244	1	65.6	3.7
11	Sediment	231	2	69.3	3.3
12	Sediment	220	2	71.4	3.1
13	Sediment	249	5	73.6	3.4
14	Sediment	229	1	58.2	3.9
15	Sediment	175	2	66.7	2.6
16	Sediment	153	1	67.2	2.3
17	Sediment	178	2	67.2	2.6
18	Sediment	220	2	76.4	2.9
19	Sediment	353	7	64.0	5.5
20	Sediment	318	3	64.0	5.0
21	Sediment	169	1	67.2	2.5
22	Sediment	168	6	68.8	2.4
23	Sediment	299	4	79.4	3.8
24	Sediment	185	6	60.9	3.0
25	Sediment	142	2	69.9	2.0
26	Sediment	397	2	62.4	6.4
27	Sediment	207	2	62.4	3.3
28	Sediment	108	1	75.7	1.4
29	Sediment	241	5	59.3	4.1
30	Sediment	129	2	72.5	1.8
31	Sediment	127	3	78.3	1.6
33	Sediment	255	1	65.1	3.9
34	Sediment	175	1	77.3	2.3
35	Sediment	220	6	67.7	3.2
36	Sediment	247	1	55.0	4.5
38	Sediment	398	2	61.4	6.5
39	Sediment	198	1	64.6	3.1
40	Sediment	260	4	53.4	4.9
41	Sediment	364	2	66.7	5.5
42	Sediment	341	6	66.2	5.2
43	Sediment	212	1	66.7	3.2
44	Sediment	134	1	72.0	1.9
45	Sediment	236	2	65.1	3.6
46	Sediment	373	50	65.6	5.7
47	Soil	406	1	60.9	6.7
48	Soil	27	1	60.3	0.4
49	Soil	208	1	72.0	2.9
50	Soil	228	1	65.1	3.5
	Mean	232	83	67.6	3.5×10^{-6}

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 (1981).

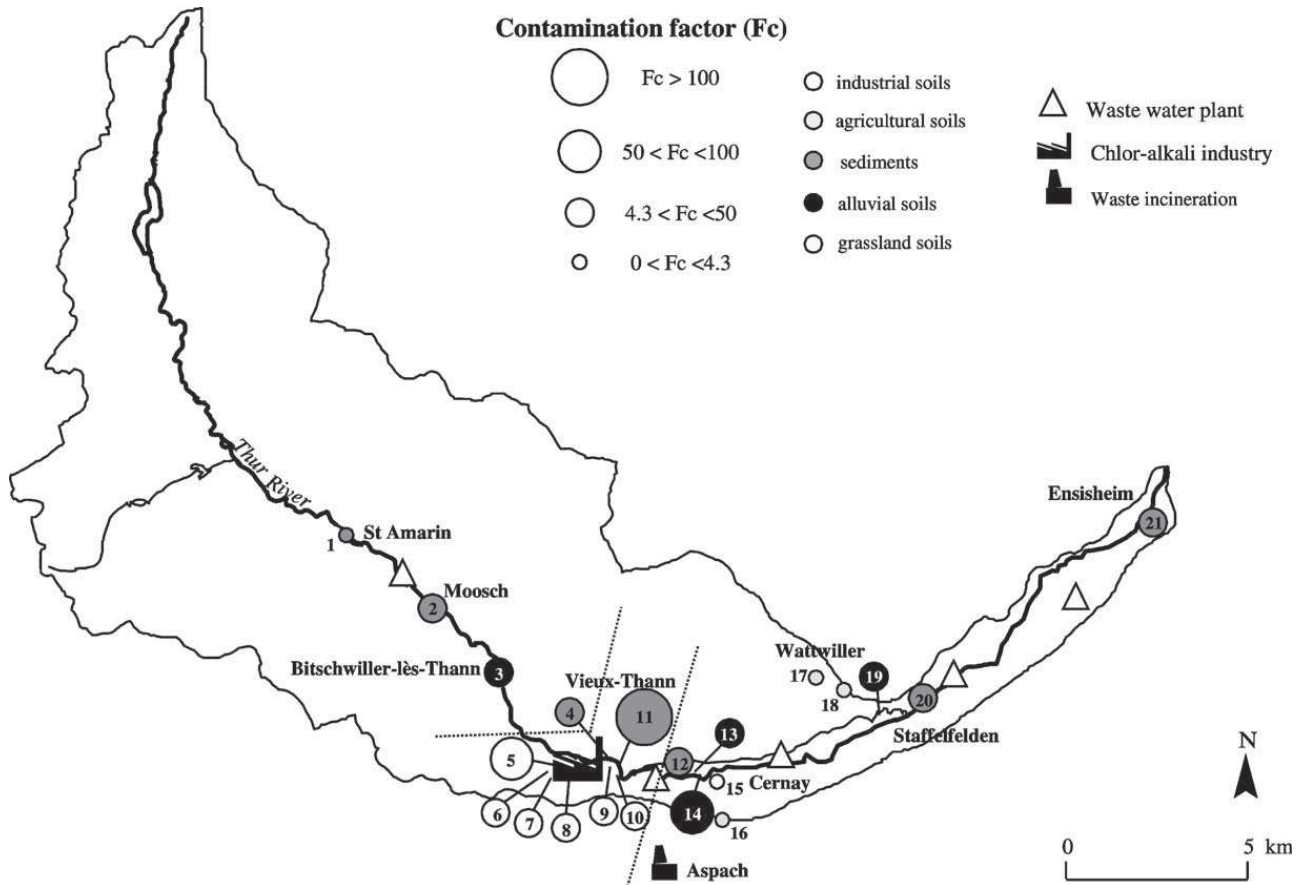


Fig. 3. Mercury contamination factors in the Thur catchment.

$$F_c = \frac{(Hg)_c / (Al)_c}{(Hg)_r / (Al)_r}$$

(Hg)_c = concentration of mercury in the contaminated samples, (Al)_c = concentration of aluminium in the contaminated sample, (Hg)_r = concentration of mercury of the regional geochemical background, (Al)_r = concentration of aluminium of the regional geochemical background.

The mean ratio (Hg)_r/(Al)_r for the Thur river basin can be estimated at 3.5×10^{-6} (Table 4). From the upstream to the downstream part of the catchment, the distribution of mercury concentrations in surficial soil horizons and river bottom sediments can be grouped together into three main areas (Fig. 3):

- The first area corresponds to samples 5–11 located around the chlor-alkali plant. The highest contamination factors are obviously located in the river bottom sediments receiving the industrial waste effluent in Vieux-Thann (in the industrial channel), with a Fc of 1784. Industrial soil samples collected from an area 1 km around the industrial site, show relatively high Hg contamination (Fc = 6.2 to 55.3). The highly

contaminated sediments located in the industrial channel have been receiving industrial effluents containing mercury since the 1930s. Furthermore, the river medium in the industrial channel, where the water is practically stagnant, is highly reducing as shown by negative oxidation–reduction values in bottom sediments and also confirmed by the occurrence of pyrite mineralization. Surveys to prevent an ecotoxicological risk have to be undertaken in this location, as mercury-containing sediments in this type of medium can undergo remobilization processes in the water column and methylation processes. In addition this risk may increase in anoxic medium, although Hg immobilization processes by sulfide are limiting factors (Stein et al., 1996).

- The upstream area corresponds to samples 1–4. High contamination factors are observed in river sediments (Fc = 5.1, site 2 see Fig. 3 and 25.9, site 4 see Fig. 3) and in an alluvial soil profile coming from Bitschwiller-lès-Thann (Fc = 10, site 3 see Fig. 3). The origin of the contamination may be due to past mercury pollution from waste water effluents. Several waste water plants are established in different locations along the Thur River and especially one in the town of

Moosch, located upstream from the contaminated samples (site 2–4).

- The downstream area corresponds to samples 12–21, located downstream from the industrial area. River bottom sediments show significant contamination with Fc ranging from 36.0 to 49.5. In the case of the soils, several Fc are very low and are located remote from urban and industrial areas. Three agricultural and one grassland soil profiles, collected 5–8 km downstream from the main mercury source, present the lowest mercury Fc, 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 were recorded. This high level of Hg in the surficial soil horizon, is linked to higher soil organic matter content (Fig. 4). Hg contamination from agriculture fungicides is excluded. Thus, the contamination may principally be due principally to diffuse Hg atmospheric deposition. Higher contamination factors were observed in alluvial soil profiles (Fc = 21.4, 49.9 and 61.0). Mercury contamination in the different horizons of alluvial soils is not correlated with soil organic matter (SOM) concentrations (Figs. 5 and 6) but is linked

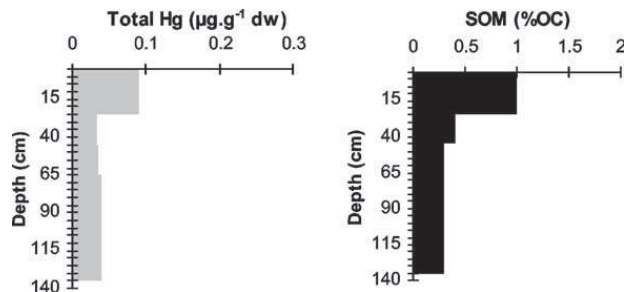


Fig. 4. Distribution of total Hg and soil organic matter (SOM) contents in the different horizons of an agricultural soil profile (Wattwiller, site 17, see Fig. 3).

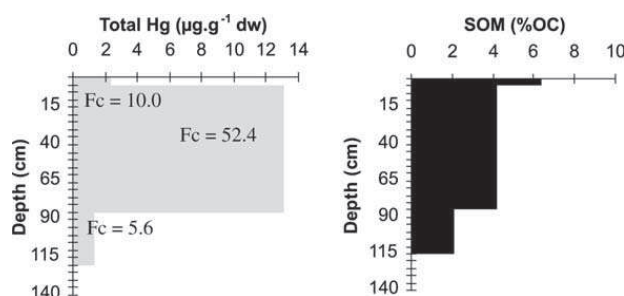


Fig. 5. Distribution of total Hg, SOM contents and Fc in the different horizons of an alluvial soil profile located upstream of the industrial site of Vieux-Thann (Bitchwiller-lès-Thann, site 3, see Fig. 3).

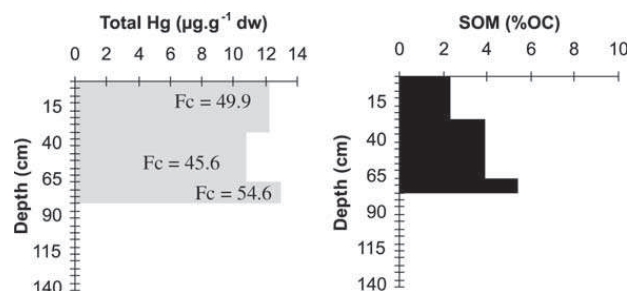


Fig. 6. Distribution of total Hg, SOM contents and Fc in the different horizons of an alluvial soil profile located downstream of the industrial site of Vieux-Thann (Cernay, site 13, see Fig. 3).

with past accidental mercury pollution coming from suspended particulate matter transported from the Thur River and deposited on the alluvial soils during high flows or flood periods. This observation is confirmed by the study of Birkett et al. (2002) and is emphasized by high Hg contamination factors (Fc = 36.0 to 49.5) in the same place.

According to the legal upper limit ($1 \mu\text{g g}^{-1}$) established by the European Community (1998) (Journal Officiel de la République Française, 1998) for mercury in sewage sludge applied to soils, we can consider the results presented here to be of concern when Fc is greater than 4.3. This value results from the upper legal limit divided by the regional geochemical background level (i.e., $Fc > 1/0.232 = 4.3$). In this study, all soil samples show Fc values greater than 4.3, indicating serious risks of harmful environmental effects.

4. Conclusions

The results of this study show that agricultural and grassland soils are generally less contaminated than industrial or alluvial soils. Industrial and grassland soils are usually farther from the river than alluvial soils, highlighting that the main origin of Hg contamination in industrial and grassland soils is diffuse atmospheric deposition from local activities; and that alluvial soil contamination comes from the alluvial deposits of contaminated river suspended particulate matter, constituting this type of soil. Unfortunately, there has so far been a lack of information on mercury in the atmosphere of the Thur catchment.

Soil constitutes a large reservoir for anthropogenic mercury emission. However, atmospheric input of Hg to soil greatly exceeds the amount leached from soil; e.g., Hg has a long residence time in the soil system (Stein et al., 1996). A substantial amount of Hg is retained in soils and river sediments every year, which are regarded as the main accumulations of mercury.

Highly contaminated soils might become an import future source of mobile and transformable Hg compounds. Mercury species are undergoing transformation processes in the different media of the environment, notably soluble/particulate Hg exchanges in rivers, Hg immobilization in particulate matter and methylation processes.

In the Thur catchment, these processes are apt to occur in soil, sediment, and water. More research is needed (and is in progress) to determine methylmercury in the different environmental compartments of the basin. Future studies should focus, in particular, on the peatland occurring in the upper part of the Thur catchment (the Urbès peatland). Anoxic conditions and the high concentration of organic matter common to wetlands facilitate the transformation of mercury into methylmercury (Montgomery et al., 2000). In addition, sediments situated in the industrial channel receiving the water effluent have to be monitored closely, as the upper sediment zone corresponds to areas of great importance for the spawning and feeding of many invertebrates and fish (Andersson et al., 1990).

Acknowledgements

The authors wish to thank the ADEME (Agence de l'Environnement et de la Maîtrise de l'Energie), Atofina, Albemarle PPC and the CNRS Programme Environnement, Vie et Sociétés (MOTIVE MODélisation, Transfert d'Informations, Valorisation pour l'Environnement) for funding this work.

References

- Andersson, A., 1979. Mercury in soils. In: Nriagu, J. (Ed.), *The Biochemistry of Mercury in the Environment*. Elsevier, North-Holland, Biomedical press, Amsterdam, pp. 79–112.
- Andersson, I., Parkman, H., Jernelov, A., 1990. The role of sediments as sink or source for environmental contaminants: A case study of mercury and chlorinated organic compounds. *Limnologica* 20, 347–354.
- Baize, D., 1997. *Teneurs Totales en éléments traces Métalliques dans les sols (France)*. INRA, Paris.
- Birkett, J.W., Noreng, J.M.K., Lester, J.N., 2002. Spatial distribution in the sediments and riparian environment of the River Yare, Norfolk, UK. *Environ. Pollut.* 116, 65–74.
- Bloom, N.S., Fitzgerald, W.F., 1988. Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold vapour atomic fluorescence detection. *Anal. Chim. Acta* 208, 151–161.
- Bonnefoy, D., 1980. *Essai d'utilisation des résultats de l'inventaire géochimique pour l'étude des fonds naturels en éléments traces des bassins versants de la Thur et de la Doller*. Rapport BRGM ALS/2232, Région Alsace, Établissement Public Régional Alsace.
- Boust, D., 1981. *Les métaux traces dans l'estuaire de la Seine*. Thèse de 3^{ème} cycle, Univ. de Caen, 207p.
- BRGM Geological map, 1976. Carte géologique de la France au 1/50000. Feuille de Munster no. 377. Feuille de Mulhouse no. 413.
- Carpi, A., Weinstein, L.H., Ditz, D.W., 1994. Bioaccumulation of mercury by sphagnum moss near a municipal solid waste incinerator. *Air Waste* 44, 669–678.
- Dmytriw, R., Mucci, A., Lucotte, M., Pichet, P., 1995. The partition of mercury in the solid components of dry and flooded forest soils and sediments from a hydroelectric reservoir, Quebec (Canada). *Water Air Soil Pollut.* 80, 1099–1103.
- Ebinghaus, R., Tripathi, R.M., Wallschäer, D., Lindberg, S.E., 1999. Natural and anthropogenic mercury sources and their impact on the air–surface exchange of mercury on regional and global scale. In: Ebinghaus, R., Turner, R.R., De Lacerda, L.D., Vasiliev, O., Salomons, W. (Eds.), *Mercury Contaminated Sites*. Springer-Verlag, Berlin Heidelberg, Germany, pp. 3–50.
- Hintelmann, H., Wilken, R.D., 1995. Levels of total mercury and methylmercury compounds in sediments of the polluted Elbe River; influence of seasonally and spatially varying environmental factors. *Sci. Total Environ.* 166, 1–10.
- Journal Officiel de la République Française, 1998. Arrêté du 8 janvier 1998 fixant les prescriptions techniques applicables aux épandages des boues sur les sols agricoles, pris en application du décret no. 97-1133 du 8 décembre 1997 relatif à l'épandage des boues issues du traitement des eaux usées. 31 janvier 1998, 1563–1571.
- Johansson, K., Iverfeldt, Å., 1994. The relation between mercury content in soil and the transport of mercury from small catchments in Sweden. In: *Mercury Pollution: Integration and Synthesis*. Lewis Publishers, pp. 323–328. (Chapter III).
- Lindqvist, O., Johansson, K., Aasrup, M., Andersson, A., Bringmark, L., Hovsenius, G., Iverfeldt, Å., 1991. Mercury in the Swedish environment. Recent research on causes, consequences and corrective methods. *Water Air Soil Pollut.* 55, 261.
- Montgomery, S., Lucotte, M., Rheault, I., 2000. Temporal and spatial influences of flooding on dissolved mercury in boreal reservoirs. *Sci. Total Environ.* 260, 147–157.
- Muhaya, B., Leermakers, M., Baeyens, W., 1998. Influence of sediment preservation on total mercury and methylmercury analyses. *Water Air Soil Pollut.* 107, 277–288.
- 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: Ebinghaus, R. (Ed.), *Mercury Contaminated Sites: Characterization, Risk Assessment and Remediation*. In: *Environmental Science Series*. Springer-Verlag, pp. 501–520.
- Quémerais, B., Cossa, D., 1997. Procedures for sampling and analysis of mercury in natural waters. *Environment Canada–Quebec Region*. In: *Environmental Conservation, St. Lawrence Centre. Scientific and Technical Report ST-31E*.
- Roeck, U., 1992. *Le transfert du mercure (Hg) utilisé comme descripteur du fonctionnement hydrologique (échange cours d'eau-nappe) dans la plaine du Rhin supérieur en Alsace*. Ph.D. dissertation, Université Louis Pasteur, Strasbourg I. p. 195.

- Stein, E.D., Cohen, Y., Winer, A.M., 1996. Environmental distribution and transformation of mercury compounds. *Crit. Rev. Environ. Sci. Technol.* 26, 1–43.
- US EPA, 1997. Mercury study report to congress. Volume III: Fate and transport of mercury in the environment. EPA-452/R-97-005, Air, December 1997.
- Vernet, J.P., Thomas, R.L., 1972. Le mercure dans l'environnement et le rôle de la géologie sédimentaire. *Bulletin du BRGM (serie 2), section III (3)*, pp. 43–61.
- Zilioux, E.J., Porcella, D.B., Benoit, J.M., 1993. Mercury cycling and effects in freshwater wetland ecosystem. *Environ. Toxicol. Chem.* 12, 2245–2257.