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# Impact of mercury atmospheric deposition on soils and streams in a mountainous catchment (Vosges, France) polluted by chlor-alkali industrial activity: The important trapping role of the organic matter

Christophe Hissler<sup>a,b</sup>, Jean-Luc Probst<sup>a,b,\*</sup>

<sup>a</sup>Laboratoire Agronomie Environnement Ecotoxicologie (AEE), 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>b</sup>Laboratoire des Mécanismes de Transfert en Géologie (LMTG), UMR no. 5563 CNRS/IRD/Université Paul Sabatier, 14 avenue Edouard Belin, 31400 Toulouse, France

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## Abstract

Total atmospheric Hg contamination in a French mountainous catchment upstream from a chlor-alkali industrial site was assessed using Hg concentrations in the deepest soil horizon, in the stream bottom sediments, in river waters and in bryophytes. The natural background level of Hg content deriving from rock weathering was estimated to 32 ng g<sup>-1</sup> in the deepest soil layers. The soils appear to be Hg contaminated in two stages: atmospheric deposition and leaching through the soil profiles of Hg-organic matter complexes. The Hg enrichment factor ( $EF_{Hg}^{Sc}$ ) which could be calculated by normalization to a conservative element like Sc, allows to estimate the major contribution (63% to 95%) of the atmospheric inputs, even in the upper part of the basin. This contribution may be attributed to diffuse regional atmospheric deposition of Hg and is mainly due to the geographic location of the chlor-alkali plant. This study shows for the first time that the mercury enrichment is proportional to the carbon content indicating that most of the atmospheric mercury deposition is trapped by the organic matter contained in the soils and in the stream sediments.

The Hg stock in the soils of the upper catchment and the soil erosion contribution to the riverine Hg fluxes are estimated for the first time and allow to assess the Hg residence time. It indicates that Hg is trapped in the soils of such a polluted catchment for probably several thousand years.

*Keywords:* Mercury; Chlor-alkali plant; Atmospheric deposition; Soils; Stream sediments; Bryophytes; Organic carbon; Background level; Enrichment factor; Mountainous catchment; Vosges France

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\* Corresponding author. Laboratoire Agronomie Environnement Ecotoxicologie (AEE), 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. Tel.: +33 5 62 19 39 49; fax: +33 5 62 19 39 01.

*E-mail addresses:* christophe-hissler@hotmail.fr (C. Hissler), jean-luc.probst@ensat.fr (J.-L. Probst).

## 1. Introduction

Mercury is a metal that exists naturally in the Earth's Crust. It can be released by rock weathering and transported by stream waters and may go through a series of chemical transformation according to the bio-physico-chemical conditions. Thus, in reaction with inorganic ligands or organic matter, different forms of mercury can bioaccumulate in the high organisms through the sediments and the food chain. A fraction of this trace element can be trapped into the soils by close relationship with organic matter, iron and aluminium oxides or sorbed onto the mineral particles. Some natural processes (water, soil and vegetation degassing, volcanic emissions) allow it to degas and to flow back into the atmosphere, creating an atmospheric dispersion and a diffuse deposition on the terrestrial ecosystems. But, under natural conditions and for non-contaminated sites, these amounts of mercury are not significant with a deposition rate lower than  $5 \mu\text{g m}^{-2} \text{y}^{-1}$ , except in the volcanic region (Tomiyasu et al., 2003) and in the "mercury belt" region where this deposition rate can approach  $30 \mu\text{g m}^{-2} \text{y}^{-1}$  (Ilyin et al., 2003).

However, it has become one of the most important environmental pollutants. Due to industrial, domestic and medical activities, the amount of total mercury in the environment and mainly in the atmosphere has been increasing since the 20th century. Approximately 5000 tons of mercury is introduced in the Earth's atmosphere every year (Mason et al., 1994). The overall anthropogenic emissions are close to 60–90% of the total mercury emitted in some industrialized regions (Lindqvist and Rhode, 1985; Nriagu, 1989) where the deposition rate grew up to  $50 \mu\text{g m}^{-2} \text{y}^{-1}$  (Iverfeldt, 1991; Jensen and Jensen, 1991; Steinnes and Anderson, 1991; Ilyin et al., 2003). Consequently, the flux of mercury deposited locally is 10 times more important than the fluvial flux (Mason et al., 1994), showing the essential role that the atmosphere is playing in the mercury cycle and in the diffuse mercury pollution of the terrestrial ecosystems localized near an industrial source.

The Thur is one of the most polluted rivers in the Alsace region (North-Eastern France). The industrialization of the Thur valley began in the 18th century and has since increased and introduced many pollutants into the environment. The principal source of

mercury pollution localized in this region is a chlor-alkali plant. It is actually recognized that these industrial installations have locally released a significant amount of mercury in the atmosphere and in the rivers, creating respectively diffuse and punctual persistent contaminations of the ecosystem nearby (Maserti and Ferrera, 1991; Ferrara et al., 1992; Calasans and Malm, 1997; Lodenius, 1998; Sensen and Richardson, 2002; Biester et al., 2002a,b). In 1973, the Alsatian community realized the significance of this mercury pollution for people living there and provoked a drastic decrease of these emissions. Thus, the waste of industrial activities decreased from  $700 \text{ kg y}^{-1}$  in 1976 to  $132 \text{ kg y}^{-1}$  in 2000. But recent studies carried out by the CGS-CNRS in Strasbourg and the LMTG-CNRS in Toulouse (Probst et al., 1999; Remy et al., 2002, 2003a,b; Hissler and Probst, 2002; Hissler et al., 2003) showed the persistence of such a contamination. No research has ever been made on the impact of an atmospheric contamination within this area. Thus, the behavior of atmospheric mercury in this area is still unknown although half the quantity of mercury emitted by the plant may be deposited near its source (Mason et al., 1994).

The main objective of this study is to quantify the real impact of the atmospheric mercury emissions upstream the chemical plant and to determine the mercury behavior in such an area. It is also to determine the mercury background level and to assess the relationship between organic matter and mercury in the soils and in the stream sediments of the upper catchment. The enrichment factor calculated from the background level will allow us to evaluate the contribution of atmospheric deposition to the total mercury content in soils and sediments. Then, the mercury dynamic will be assessed for the time in this mountainous catchment. This study is not only there to demonstrate the significance of the atmospheric pathway in the mercury pollution upstream the human activities, but also to show the major role of the organic matter in the persistent contamination of this mountainous catchment.

## 2. Site description

The Thur river basin is located in the East of France, at 80 km South–West from Strasbourg and

10 km North–West from Mulhouse (Fig. 1). This river is 54 km long and it drains a watershed of 270 km<sup>2</sup> before joining the Ill river which is the most important Alsatian tributary of the Rhine river.

The altitude of the basin varies from 200 m in the Alsatian plain to more than 1400 m in the Vosges Mountains. This important difference leads to very contrasted climates going 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 a higher amount of precipitation throughout the year than the plain (Table 1). Geomorphologic difference be-

tween these two parts more leads to very contrasted hydrological circulation. The annual hydrological balance revealed a low deficit for the runoff: the difference between the amount of precipitation ( $P$ ) and the evapotranspiration (ETP) represented 80% of the precipitation amount. In the mountainous area (W1 and W2 discharge gauging stations), the deficit is principally due to evapotranspiration processes and the infiltration in the local water tables may be negligible ( $\delta_R < 20\%$ — Table 1). On the contrary, the freshwater infiltration to the groundwater becomes more important in the alluvial fan sediments of the plain area (W3).

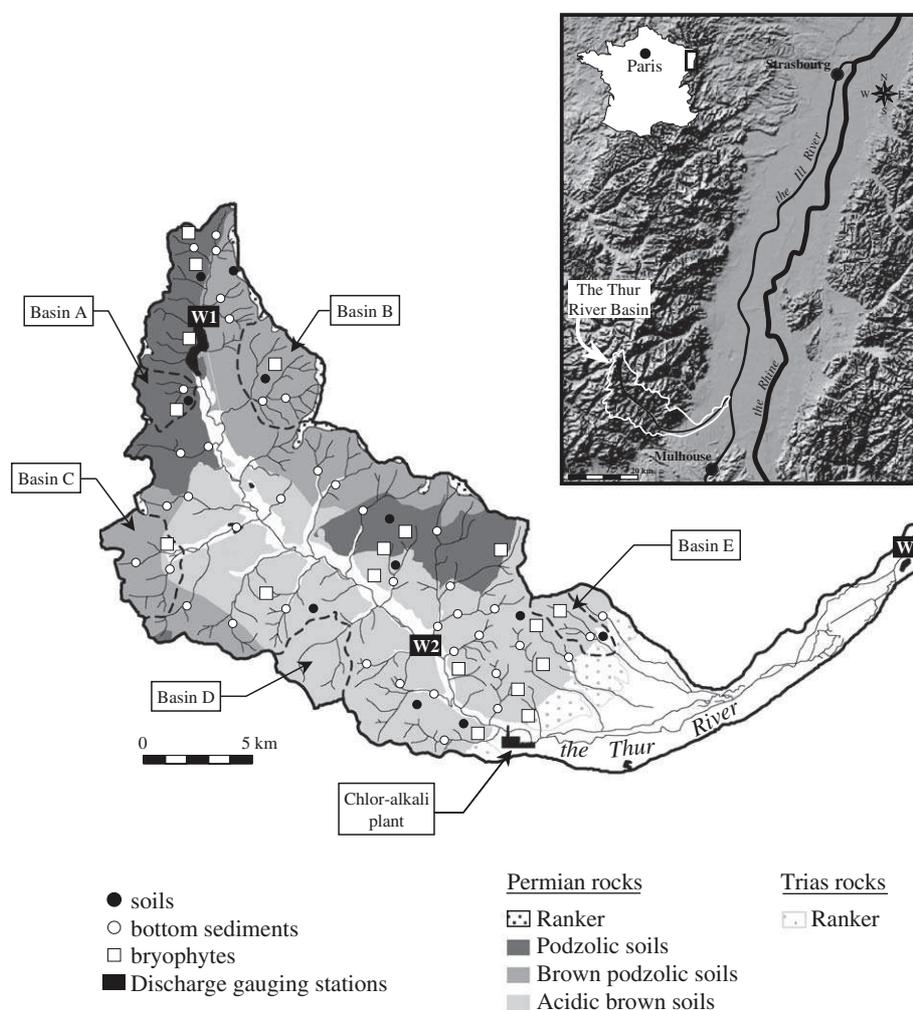


Fig. 1. General situation map of the Thur River Basin and localization of the soil, stream sediment and bryophyte sampling sites and of the discharge gauging stations.

Table 1

Water balance calculation of the Thur River Basin between July 2001 and June 2002 at three sites (W1, W2, W3) and deviation ( $\delta_R$ ) between calculated runoff ( $R_{cal}$ ) and measured runoff ( $R_{mes}$ )

Station	Area (km <sup>2</sup> )	$P_{cal}$ (mm)	ETP <sub>cal</sub> (mm)	$R_{cal}$ (mm)	$R_{mes}$ (mm)	$\delta_R$ (%)
W1	7.6	2306	444	1862	1776	4
W2	157.0	1790	481	1309	1096	18
W3	268.5	1558	501	1057	673	44

$P_{cal}$ : Precipitation (isohyet method).

ETP<sub>cal</sub>: Potential Evapotranspiration (COUTAGNE method).

$R_{cal} = P - ETP$ .

$R_{mes}$ : Runoff measured into the Thur River.

$\delta_R = 2 \times [R_{cal} - R_{mes}] / [R_{cal} + R_{mes}]$ .

The geological substratum is composed of Permian complexes of granitic (leucogranites and microgranites), volcanic (trachyandesites and labradorites) and sedimentary rocks (graywackes, shales) in the valley and of Trias sedimentary rocks (sandstone, conglomerate) in the piedmont area. Under such climatic and geological conditions, the soils evolve from brown to podzolic soils (Fig. 1). They are more or less acids according to the bedrock, they develop sandy loam texture and they do not generally exceed 80 cm depth.

The chlor-alkali plant is the only industrial activity that has been producing mercury waste in the Thur river basin. Since 1930, it uses mercury as cathode electrolysis and has been creating atmospheric and riverine pollution. Since 1973, effluent treatments have progressed a lot and the contamination of the chemical industry waste has been reducing. However, in 2000, this industrial activity still rejected the most important part of the mercury present in the environment of the basin: 100 kg y<sup>-1</sup>, 32 kg y<sup>-1</sup> and <1 kg y<sup>-1</sup> respectively into the atmosphere, the river, and the groundwater. Moreover, other waste producers worsen this mercury pollution. All domestic activities (hospitals, dentists and incinerators) are connected to a sanitation network or produced some mercury emissions after waste incineration. This waste is localized in the downstream part of the Thur river basin and totalized 7 kg y<sup>-1</sup> in the river water and <1 kg y<sup>-1</sup> in the atmosphere. The only current source of mercury in the agriculture is the waste sludge of the sanitation network, which liberates 3 kg y<sup>-1</sup> of mercury to the cultivated soils. The presence of heavy metal in the soil is a risk for the ecosystem. The risk increases with

the capacity the soils have to release mercury in the stream water, in the groundwater or in the atmosphere, provoking a large diffuse mercury contamination. The organic matter fixes most of the pollutant at the surface of the soil but the bio-physico-chemical reactions that occur in these systems can make part of this pollutant soluble or gaseous and cause its migration inside the soil profile or its volatilization into the atmosphere. The data we used did not allow us to calculate this real contribution to the water reservoirs.

### 3. Material and methods

#### 3.1. Sampling and pre-analysis procedures

The sampling sites are selected all over the upper basin (Fig. 1) to determine the background level of mercury in the soils of the Thur river basin and to evaluate the degree of contamination in the soils and in the stream bottom sediments. Then, these measurements will allow a first estimation of the different tributary contribution to the total annual mercury flux exported by the river and of the mercury quantity stored in the superficial soil layers.

In June 2002, the mineral layer (C) of 11 grassland soils was collected. For each soil, a composite sample was done from 4 samples taken over 4 m<sup>2</sup> area. Bottom sediments were collected in November 2000 for 40 small streams located upstream from all human activities. They were dried in Pyrex glass Petri dishes in a clean room during 2 weeks at 20 °C to avoid any external contamination and any loss of mercury (Probst et al., 1999). Then, we homogenized and sieved the samples through a 63 µm Nylon screen. We selected the clay and coarse silt fractions of the soil and of the stream bottom sediments because it concentrated the highest content of mercury and correspond to the size fraction of the total suspended sediment (TSS) in the rivers.

In June 2002, we collected the filtered water and the TSS of five sub-basins (basin A to basin E in Fig. 1), which are located upstream the anthropogenic pollutions. They characterize the different lithologies and soils present in the valley. The filtration was performed directly after sampling with a Teflon® system using mercury clean nitrogen pressure and hydrophilic PTFE Teflon® filter, rinsed with HCl

(25%) during three days before their utilization. The suspended sediments were frozen and stored at  $-20^{\circ}\text{C}$  until digestion. The water samples were oxidized using  $\text{BrCl}$  (0.2 N) prior to analyze dissolved Hg in order to destroy organic Hg complexes.

We collected the bryophyte samples in June 2002. On each sampling site 5 to 10 sub-samples were taken within a  $20 \times 20$  m grassland area and mixed in the same bag (Steinnes and Anderson, 1991). *Hypnum cupressiforme* were chosen because of its presence in most of the sampling sites. The samples were frozen, lyophilized and cleaned at the laboratory. We conserved the last yearly growth that corresponds to the mercury absorbed by the organisms during the past year.

We followed careful procedures to avoid sampling and storage contamination: wash up the Pyrex and Teflon dishes in acid bath at a temperature of  $80^{\circ}\text{C}$  during 6 days, rinsed using UHP water, dried in a drying stove at  $100^{\circ}\text{C}$  during 12 h and stored in polyethylene bags until we used them (Quesmerais and Cossa, 1997): gloved hands to manipulate all samples; storage in polyethylene bags or flasks (bryophytes, soils, sediments) or Teflon bottles (filtered water) at  $4^{\circ}\text{C}$ ; blanks to detect potential contamination during sampling, filtration, digestion and analysis: they were generally measured below the detection limit.

The mercury determinations in soils, stream sediments (bottom and suspended) and bryophytes were performed using digested samples in a 60 ml Teflon bomb with 12 ml of  $\text{HNO}_3:\text{HCl}:\text{BrCl}$  (4:1:1) melting at  $90^{\circ}\text{C}$  during 14 h.

### 3.2. Analytical methods

We measured total mercury in soils, sediments and bryophyte with Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS). This system consists of an atomic fluorescence spectrometer (PS Analytical, Merlin Plus) coupled with a continuous vapor flow generator. The detection limit for solid materials is  $0.3 \text{ ng g}^{-1}$  for an aliquot of 200 mg sample and the coefficient of variation determined on three replicate analyses was 10% maximum. During digestion and measurement, the reference material was analyzed every 13 samples and blanks every 6 samples. Recovery and accuracy were tested using certified reference

materials for river bottom sediments (Promochem CRM 320) and bryophytes (Promochem RM 60). The average values obtained for CRM 320 ( $n=10$  replicates) and RM 60 ( $n=5$  replicates) are respectively 94.2% and 111.8% for the recovery and 4.1% and 7.9% for the accuracy.

Total dissolved Mercury was measured with Cold Vapor Atomic Fluorescence Spectrometry (CV-AFS) after gold amalgamation trapping. The method achieved a detection limit of  $0.12 \text{ ng l}^{-1}$  and the coefficient of variation was 10% maximum as determined by three replicate analyses of all water samples.

Organic carbon (OC) and Sc concentrations were respectively determined using an infrared spectrometer (LECO<sup>®</sup> CS 125 analyzer) and an ICP-AE Spectrometer (Jobin Yvon<sup>®</sup> 124), following the procedures given by Samuel and Rouault (1985). Maximum relative error on these measures was generally less than 10%.

### 3.3. Data analysis

To assess the elemental excess against the natural abundance in the sediment and soil samples, we normalized the element concentrations in samples using Sc, because of his conservative behavior, even if the use of such conservative element is still under discussion (Reimann and de Caritat, 2005). Sc, like Al and Zr (Faure, 1991; Remy et al., 2003a,b), U (Kurtz et al., 2001) or Cs (Roussiez et al., in press) is widely used in geochemical studies to evaluate the relative enrichments or depletions of other more reactive trace elements. This trace element forms oxides of extremely low solubility that are highly resistant to chemical weathering and has a conservative behavior during the rock alteration (Shotyk, 1996). Nevertheless, it is the first time we use Sc to normalize Hg concentration.

The elemental (X) enrichment factor (Eq. (1)) can be defined by considering the ratio between abundance in the sample ( $(X/\text{Sc})_{\text{sample}}$ ) and in the geochemical background ( $(X/\text{Sc})_{\text{back}}$ ) as follows:

$$\text{EF}_X^{\text{Sc}} = (X/\text{Sc})_{\text{sample}} / (X/\text{Sc})_{\text{back}} \quad (1)$$

Using the approach of Shotyk et al. (2000) for quantifying the anthropogenic contribution of heavy metal, we distinguished the lithogenic ( $\text{Hg}_{\text{Lit}}$ ) and

atmospheric ( $\text{Hg}_{\text{Atm}}$ ) contributions of mercury as follows:

$$[\text{Hg}_{\text{Lit}}] = [\text{Sc}]_{\text{sample}} \times ([\text{Hg}] / [\text{Sc}])_{\text{back}} \quad (2)$$

$$[\text{Hg}_{\text{Atm}}] = [[\text{Hg}_T]_{\text{sample}} - [\text{Hg}_{\text{Lit}}] \quad (3)$$

For the calculation of the total mercury stock, the area investigated was divided into five soil types: ranker soils (2% of the total basin area on sedimentary Permian substratum and 4% of the area on sedimentary Triassic substratum), brown acidic soils (46% of the area), brown podzolic soils (27% of the area) and podzolic soils (21% of the area). The volume of the soil layers and their bulk density were determined using the RENECOFOR and the CEE-Network soil database for the South Vosges Mountains (Br thes and Ulrich, 1997).

We calculated the mean annual runoff by difference between the mean annual precipitation (isohyet method) and the potential evapotranspiration (Coutagne's method, Dubant, 1970). These results were obtained using the monthly temperature and pluviometry of the Meteo France database measured at 11 sites localized into or near the Thur river basin.

The spatial distribution calculations within the valley (runoff, atmospheric contamination, total mercury fluxes, mercury stock in soils) were obtained with Geographic Information System analysis treatment (clarklabs IDRISI ).

## 4. Results and discussion

### 4.1. Mercury concentrations

The soils samples contain total Hg concentrations varying from  $16 \text{ ng g}^{-1}$  to  $399 \text{ ng g}^{-1}$  and organic carbon (OC) concentrations varying from 0.1% to 10.2%. We found similar variations than Roulet et al. (1998) in some Amazonian Hg-enriched soils by ancient atmospheric depositions: from  $170$  to  $360 \text{ ng g}^{-1}$  and into contaminated soils of mine areas (Bailey and Gray, 1995; Higuera et al., 2003). These values, however, are lower than those reported for the Thur river plain area:  $580$ – $13\,800 \text{ ng g}^{-1}$  (Remy et al., 2003a,b), or for other European regions contaminated by chlor-alkali activity:  $24$ – $49\,000 \text{ ng g}^{-1}$  (Inacio et

al., 1998). Unlike total Hg and OC, the Sc concentrations we found in these 11 samples are function of the bedrock. The soils which developed on granites show the most important variations with an average value of  $14.9 \pm 6.1 \text{ } \mu\text{g g}^{-1}$ . All samples taken in volcanic and sedimentary substratum give some constant amount of Sc with respective mean values of  $11.4 \pm 1.9 \text{ } \mu\text{g g}^{-1}$  and  $16.4 \pm 1.8 \text{ } \mu\text{g g}^{-1}$ . These results show that Sc is, for this area, a lithogenic reference element which conserves the bedrock signature during the weathering processes.

The total Hg sediment concentrations range from  $108$  to  $639 \text{ ng g}^{-1}$ . They correspond to the values found in stream sediment samples collected in regions of gold or cinnabar mine activity (Ferrara et al., 1991; Domagalski, 2001). The OC content in the stream bottom sediments range from 2.1% to 16.2% with an average value of 6.8%, which is close to the concentrations measured in the soils. However, we found higher OC contents (15.2% and 16.2%) for samples collected in an area, which presented some post-glaciation peat bogs. The Sc content in the stream sediments varies between  $8.8$  and  $20.1 \text{ } \mu\text{g g}^{-1}$ , with an average of  $13.8 \pm 2.4 \text{ } \mu\text{g g}^{-1}$ , very close to those found in the soils and corroborate the conservative behavior of this element during the rock weathering and the fluvial transport.

Total dissolved Hg concentrations are under or near the detection limit ( $0.12 \text{ ng l}^{-1}$ ). These values are generally lower than those reported for different river systems in the world:  $0.08$  to  $34 \text{ ng l}^{-1}$  in the North American rivers (Gill and Bruland, 1990; Stordal et al., 1996; Quesmerais et al., 1998; Lawson and Mason, 2001; Connaway et al., 2002),  $0.4$  to  $70 \text{ ng l}^{-1}$  in the European rivers (Ferrara et al., 1991; Probst et al., 1999),  $0.5$  to  $1.1 \text{ ng l}^{-1}$  in the Asian rivers (Coquery et al., 1995). On the other hand, the total particulate mercury concentrations range from  $111 \text{ ng g}^{-1}$  to  $241 \text{ ng g}^{-1}$ . They are in the same order of magnitude than the Hg content in the bottom sediments. The environmental conditions present during the sampling lead TSS to be the principal phase which transports Hg into the Thur river catchment. The main Hg amount transported in these streams result from the physical erosion of the soils. Nevertheless, the average TSS is very low:  $1.4 \pm 0.5 \text{ mg l}^{-1}$  in valley catchments (A to D) and  $7.2 \text{ mg l}^{-1}$  in catchment E.

The total Hg analyzed in the bryophytes range from  $29 \text{ ng g}^{-1}$  to  $840 \text{ ng g}^{-1}$  near to the chlor-alkali activity. These values rejoin the concentrations measured by [Fernandez et al. in 2000](#) ( $70\text{--}1250 \text{ ng g}^{-1}$ ) for the same bryophyte specie collected in the area of another chlor-alkali plant. Like bottom sediments, we found *H. cupressiform* Hg content 30 times higher near the plant and particularly at a distance below 5 km around it ([Fig. 2](#)) than in the rest of the basin. But, some sampling sites localized in the upper part of the basin indicate concentrations 2 to 3 times higher than the minimum observed value ( $29 \text{ ng g}^{-1}$ ), which characterize a non-negligible atmospheric contamination.

#### 4.2. Relationship between soil organic carbon content and total mercury

During weathering processes, Hg can be released from the minerals into the soil solution and subsequently transported by the freshwater or groundwater. But, in presence of organic matter and Fe-Al oxides, the metal may accumulate in the soil profile, particularly in the organic horizons and/or may be physically eroded and exported to the streamwater. But, it is also continually introduced into the atmosphere by volcanoes and other degassing processes (soils degassing, water degassing), which thereby produce an important diffuse source for land areas. Similarly, in some of these regions, there are many punctual sources (efflu-

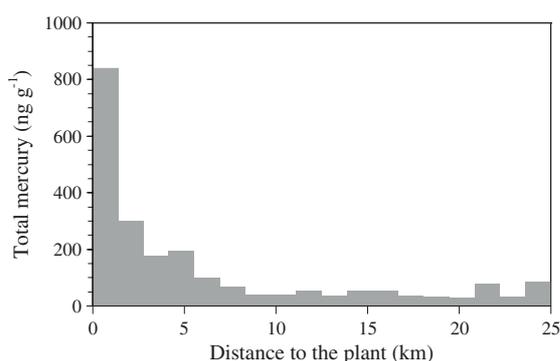


Fig. 2. Concentrations of total mercury analyzed in the bryophytes as a function of the distance from chlor-alkali plant. Each bar represents the total mercury concentrations measured on one composite bryophyte sample obtained from 5 to 10 sub-samples collected for each sampling site in an area of  $400 \text{ m}^2$  according to the method proposed by [Steinnes and Anderson \(1991\)](#).

ent pollution) and diffuse sources (atmospheric pollution) of anthropogenic Hg that disturb the natural signal. The origin of the recent Hg accumulation in ecosystems is still uncertain but the quantification of local Hg natural amount allows us to estimate the anthropogenic emissions impact on a regional scale.

As seen in the paragraph “Site description” and in [Fig. 1](#), the soils of this catchment belong to the sequenced brown soils to podzolic soils. The pedogenetic evolution of these kinds of soils is greatly controlled by lixiviation processes through the soil profile. These processes mainly concern the organic matter complexes, Fe and Al oxides and trace elements like Hg which are associated to these complexes. Consequently, in such soils, the Hg lixiviation is greatly enhanced.

Among the eleven sampled soils, eight soils are thicker than 30 cm with a mineral layer (C horizon) showing Hg concentrations lower than  $150 \text{ ng g}^{-1}$  and three ranker soils are thinner than 30 cm with Hg concentrations higher than  $230 \text{ ng g}^{-1}$ .

The organic carbon (OC) content in the mineral soil layers is not always related to the sampling depth but depends also on the soil evolution processes. The importance of lixiviation and bioturbation processes in the temperate soils may create organic matter enrichment inside the profile up to the soil mineral layers. These organic particles have a strong capacity to complex and to fix Hg. There is a good relationship between OC (%) and total Hg ( $\text{ng g}^{-1}$ ) for the 8 soil samples of the deepest horizons ([Fig. 3](#)); the equation is the following:

$$\text{Hg} = 13.3 \times \text{OC} + 24.7 \quad \text{with } r = 0.9356 \quad (4)$$

They create organic complexes with very high stability ([Lindqvist, 1991](#); [Schuster, 1991](#); [Biester et al., 2002a](#); [Tomiyasu et al., 2003](#)). [Bourg and Schindler \(1985\)](#) and [Semu et al. \(1987\)](#) showed that the amount and the quality of organic matter and the mechanisms regulating the partition of organic matter between aqueous and solid phases might play a major role in the control of Hg concentrations and in the Hg transport through the soils. This explains the accumulation of Hg in organic rich upper-soil layers and the predominance of organic-Hg binding in the mineral layers. Consequently, the OC enrichment through the soil profile will allow us to explain the variation of Hg content.

#### 4.3. Natural mercury background level

The background abundance of organic carbon is estimated in the mineral layers of 4 soils which are the most depleted in organic carbon and it is normalized to Sc average concentration in these horizons ( $(OC/Sc)_{back}$ ). This  $OC(\%)/Sc(\mu g\ g^{-1})$  ratio varies from 0.01 for the soil developed on Trias sandstones, 0.03 for soil on granitic bedrock to 0.08 for soil on both Permian volcanic and sedimentary bedrocks. An average ratio of 0.05 could be calculated for the upper catchment taking into account of the area occupied by each soil type. An OC enrichment factor ( $EF_{OC}^{Sc}$ ) can be calculated for all the soil horizons by using Eq. (1) (normalization to Sc).

Soils 6, 7 and 8 indicate  $EF_{OC}^{Sc}$  lower than 2, which characterize non-enriched soils in organic matter (Spósito, 1989) and consequently Hg content level close to natural background value (Fig. 3). Their total Hg content is even lower than the average Earth Crust values given by Faure in 1998 ( $98\ ng\ g^{-1}$ ) for igneous and sedimentary rocks. Considering the different bedrock area distribution, one can evaluate a mean lithogenic Hg concentration of  $32 \pm 9\ ng\ g^{-1}$  and a mean lithogenic  $Hg(ng\ g^{-1})/Sc(\mu g\ g^{-1})$  ratio ( $(Hg/Sc)_{back}$ ) of 1.8 for the soil mineral layers of the Thur river basin. This background value is in accordance with Hg content of some Canadian soils studied by Gracey and Stewart (1974):  $23 \pm 5\ ng\ g^{-1}$ , Dudas and Pawluk

(1976):  $44 \pm 5\ ng\ g^{-1}$ , McKeague and Kloosterman (1974):  $33 \pm 7\ ng\ g^{-1}$  and the total mercury concentrations measured in some other non-contaminated soils of the Vosges Mountain (Février et al., 1999).

#### 4.4. Mercury enrichment in the soils

Most of the soil profiles are Hg contaminated mainly because of atmospheric deposition and Hg leaching processes through the soil profiles thanks to Hg complexing by soil organic matter. As seen in Fig. 3, the OC enrichment factor ranges from 3.1 to 13.8 indicating a non-negligible organic matter enrichment through these soil profiles.

The 5 deepest soil horizon samples, with Hg enrichment factors ranging from 2 to 6, represent the Hg-organic matter-leaching phase through these soil profiles. They illustrate the organic matter trapping of Hg in the soils of the valley and show that the organic matter eluviation causes Hg enrichment up to the deepest soil layers. Indeed, the migration of Hg to deeper soil layers is more effective if the pollutant is bound to organic complexes (Aastrup et al., 1991; Biester et al., 2002b). The importance of such a contamination is generally related to the local geomorphological, physical (structure and texture of soil) and biological conditions, which control the trace element circulation through the soil profiles and create the largest variations of OC and associated total Hg

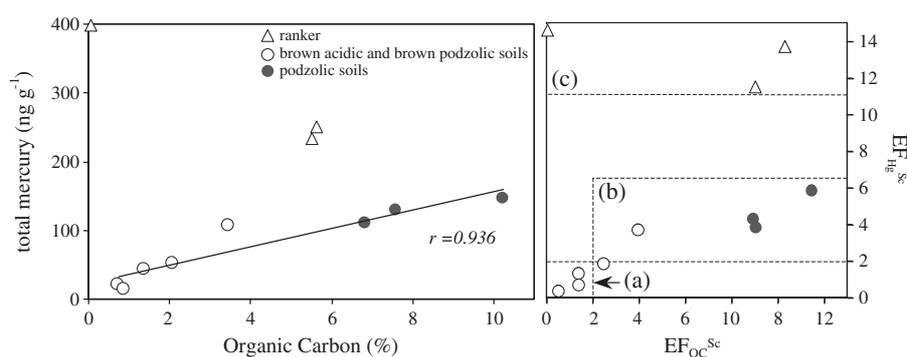


Fig. 3. Relationships between total mercury concentration and organic carbon content (left side) and between the organic carbon enrichment factor (normalized to Sc) and the mercury enrichment factor (normalized to Sc) in the finest particles ( $\varnothing < 63\ \mu m$ ) of the soil C horizons of the upper Thur catchment. On the right side, the different areas represent the different mercury enrichment processes: (a) the natural background level area corresponds to the uncontaminated sites, (b) corresponds to the soils where the mercury is enriched in the profile by lixiviation processes (mercury complexed by organic compounds) and (c) corresponds to the soils highly contaminated by mercury atmospheric deposition.

contents. In a mountainous region with steep slopes, soil leaching increases, resulting of an oblique water drainage (Roulet et al., 1998). Furthermore, Hg vertical migration was found to be reduced in soils with higher clay contents (Biester et al., 2002b). The vegetation may also play an important role: Hg concentration increased by a factor of 2 (Lacerda et al., 2004) to 7.3 (Biester et al., 2002a) in forested area compared to grassland soils. Moreover, Higuera et al. (2003) showed that in the Almaden mine area (Spain), local plants indicate a Hg incorporation into roots that may participate to the soil Hg distribution.

The 3 most superficial horizons (Fig. 3) show Hg enrichment factors higher than 10 and characterize the atmospheric Hg deposition phase that occurs at the soil surface where the organic carbon content is higher. This contamination process was already observed within the Thur river agricultural soils of the floodplain area where the Hg enrichment factor ranges from 2 to 55 (Remy et al., 2003a,b). Biester et al. (2002a) studied soils of three different Hg-contaminated sites by chlor-alkali within Europe. They found Hg concentrations in superficial layers that exceed background values up to a factor of 56. In 1998, Inacio et al. (1998) showed such a contamination created maximum Hg enrichment ( $117\text{--}49,000\text{ ng g}^{-1}$ ) in the first 5 cm of Portuguese sandy soils. Investigations of South African sandy soils contaminated by industrial effluents (Macnab et al., 1997) showed that Hg is trapped in the upper topsoil (mean of  $980\text{ ng g}^{-1}$  at 0–10 cm), the subsoil indicating lower concentrations (mean of  $299\text{ ng g}^{-1}$  at 90–100 cm). Tomiyasu et al. (2003) made the same observation on the accumulation of volcanic Hg in Japanese soils: the values of the upper 5 cm ranged from 1400 to 2600  $\text{ng g}^{-1}$  when the subsoils conserved lithogenic concentrations.

#### 4.5. Total mercury atmospheric contamination

Stream sediments indicate the same excess of Hg than the ranker mineral layers but with larger variations. The Hg enrichment factors ( $EF_{\text{Hg}}^{\text{Sc}}$ ) range from 2.7 to 21.3, also indicating a significant contamination of all the streams due to atmospheric deposition.

Using the approach of Shoty et al. (2000) and Hernandez et al. (2003) for quantifying the anthro-

pogenic contribution of heavy metal, we distinguished the lithogenic ( $Hg_{\text{Lit}}$ ) and atmospheric ( $Hg_{\text{Atm}}$ ) contributions of Hg in the stream bottom sediments (Eqs. (2) and (3)). The mean lithogenic Hg content estimated with this method ( $28 \pm 5\text{ ng g}^{-1}$ ) is close to the natural background level found previously for the soils. This accordance makes the calculation valid for the study area and will give a very representative atmospheric contribution for each stream sediment sample. The atmospheric component represents from 63% to 95% of the total mercury content in the stream sediments and it is comparable to the percentage which can be calculated for the 3 ranker soils. This Hg enrichment can be also observed in the bryophytes and in the TSS, even in the upper part of the watershed. The finest particles of the sediments result from rock and soil physical erosion. Some sediment particles should be only Hg-enriched before their transport into the streams, as indicated by the highest amount of pollutant present in the soils. But the contamination that occurs during the river transportation through bulk (dry and wet) atmospheric and/or throughfall deposits (Iverfeldt, 1991; Lodenius, 1998; Biester et al., 2002b) could also be an important process in the Hg contamination of stream sediments.

A distribution map of  $EF_{\text{Hg}}^{\text{Sc}}$  could be drawn for the upper Thur river catchment and it corresponds to the distribution of the atmospheric contamination within this valley (Fig. 4). It probably reflects also the Hg content in the upper soil horizons. Anomalies in Hg enrichment are scattered in all the basin area, but the most important ones are situated North and West from the industrial plant with respectively average Hg concentration of  $493\text{ ng g}^{-1}$  and  $212\text{ ng g}^{-1}$ . This figure shows that the contamination area reaches at least 25 km from the industrial site contrary to what have been shown by different authors. Indeed, most of the other works indicate that Hg atmospheric fallouts from a chlor-alkali plant are not dropped beyond 5 km (Maserti and Ferrera, 1991; Sensen and Richardson, 2002). In these contaminated areas, Lindqvist and Rhode (1985) show that 30% to 90% of the atmospheric Hg originates from anthropogenic sources. Moreover, Biester et al. (2002a) showed that the amount of Hg deposited within an area of 1 km around a chlor-alkali plant corresponded to less than 2.5% of the total Hg emissions, which indicates that most of the Hg emitted from such an industry is

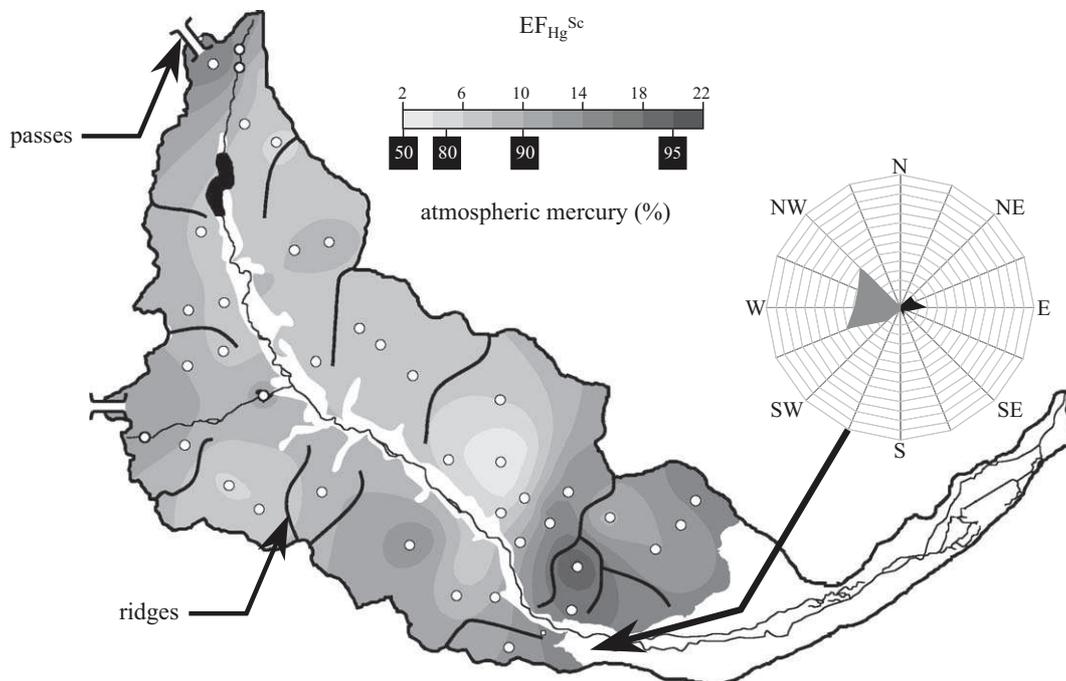


Fig. 4. Spatial distribution of mercury enrichment factor ( $EF_{Hg}^{Sc}$ ) and of the atmospheric mercury contribution in the finest particles ( $\varnothing < 63 \mu m$ ) of the bottom sediments in the upper Thur River Basin. The white circles represent the sampling sites. The compass card on the right shows the main annual wind directions during the year 2000. The spatial interpolation has been made using Surfer<sup>®</sup> software and a linear kriging. The double scale  $EF_{Hg}^{Sc}$ —Atmospheric mercury (%) could be established from the nice relationship we have between these two variables (% atmospheric mercury =  $13.5 \ln EF_{Hg}^{Sc} + 56.5$  with  $r = 0.951$  for  $n = 40$  samples).

subject to atmospheric dispersion and to a long-range atmospheric transportation.

Considering an atmospheric pollution, the area of influence does not extend evenly in all directions, but is influenced by wind directions and local topography. In our case study, the plant localization at the valley outlet and the Vosges Mountains play together an important role for the diffusion of the atmospheric pollution. We can observe, for example, that inside the watershed, some ridges can stop a non-negligible quantity of Hg and can create less-contaminated areas behind this relief. That is the case near the industrial plant in the Northwestern direction where the atmospheric Hg contribution is the lowest (70% to 75%). Furthermore, high levels of contamination are related to the geomorphology in the most upper part of the basin, up to a distance of 25 km from the plant. The relief defines the preferential directions of air circulation and can control the local degree of contamination. Breezes blowing from the valley toward the moun-

tains can be observed all along the year and may represent up to 20% of the annual winds (Fig. 4). They appear during anticyclonic events, between 5 and 23 h, and are characterized by low wind velocities on the ridges ( $3.6 \text{ ms}^{-1}$ ) and inside the valley ( $2.9 \text{ ms}^{-1}$ ) (Kastendeuch, 1996). These breeze incidents supply higher atmospheric deposition of Hg, particularly near the passes where atmospheric circulation increases (Baumann et al., 2001; Prevôt et al., 2000).

#### 4.6. Bioaccumulation of mercury in the bryophytes

The bryophytes are currently recognized as bio-indicator of Hg atmospheric deposition. Since the 70s, they have been easily used in Europe and mainly in the Scandinavian countries to quantify the spatial and temporal variations of the atmospheric contamination (Rühling and Tyler, 1970; Berg et al., 1994; Sucharova and Suchara, 1998; Fernandez et al., 2000; Loppi and Bonini, 2000).

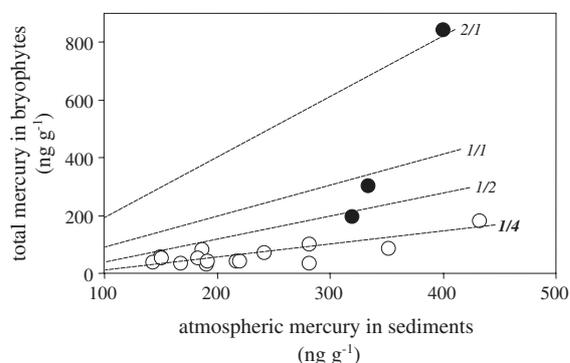


Fig. 5. Relationship between total mercury concentration in the bryophytes (*H. cupressiform*) and atmospheric mercury contribution calculated in the finest particles ( $\varnothing < 63 \mu\text{m}$ ) of the upper Thur River Basin bottom sediments. White and black circles correspond to the sampling sites which are respectively far and close to the industry. The dotted lines indicate the different Hg concentration ratios between the bryophytes and the atmospheric part of the riverine sediments.

For each bryophyte sampling site, the atmospheric Hg content in the corresponding bottom sediments was estimated using the data of Fig. 4. As seen in Fig. 5, there is a good relationship between the mercury content in the bryophyte and the atmospheric mercury concentration in the stream sediments, showing that mercury transported by the streams mainly originates from the atmospheric deposition. For most of the samples, the concentration ratio between the

bryophyte and the sediment is around 1/4, except 3 samples which are close to the plant and for which the ratio can reach 2/1, indicating that *H. cupressiform* may have a better absorption capacity related to more important atmospheric bulk-deposition.

#### 4.7. Control of mercury contamination by organic carbon contents

As seen in Fig. 6, mercury content in soils and stream sediments is related to the organic matter concentration, even in the deepest soil horizons. That means that the soil profiles and the riverine sediments can be naturally Hg enriched by organic matter complexation. Consequently if we want to determine if a Hg enrichment due to atmospheric Hg deposition – that we could observe by normalizing to Sc – is only proportional to the Hg complexation by organic compounds or if there is a surplus of Hg which could be linked to different mineral phases, we have also to normalize to the organic carbon content.

For the deepest soil horizons, the mean  $\text{Hg}(\text{ng g}^{-1})/\text{OC}(\%)$  ratio is calculated to 27 and could be considered as the background ratio  $(\text{Hg}/\text{OC})_{\text{back}}$ . Then for the other soil horizons, for the stream bottom sediments and for the peats, one can normalize the Hg concentration to the organic carbon content using this ratio and a Hg enrichment factor,  $\text{EF}_{\text{Hg}}^{\text{OC}}$  (Eq. (5)), with

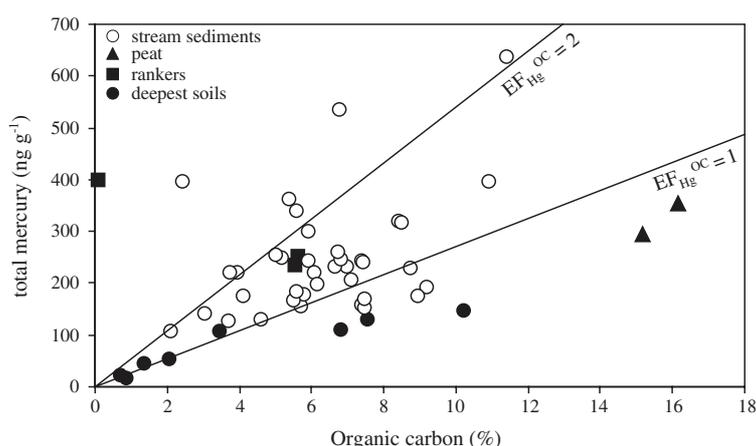


Fig. 6. Relationship between the total mercury concentrations and the organic carbon contents for soils, peats and stream bottom sediments in the upper Thur River basin. The two lines corresponds respectively to mercury enrichment factor ( $\text{EF}_{\text{Hg}}^{\text{OC}}$ , normalized to the organic carbon content) of 1 and 2, showing that there is no significant mercury enrichment when EF is normalized to OC.

regard to the organic carbon can be calculated following the same procedure than for Sc normalization (see Eq. (1)):

$$EF_{Hg}^{OC} = (Hg/OC)_{sample} / (Hg/OC)_{back} \quad (5)$$

As seen in Fig. 6,  $EF_{Hg}^{OC}$  does not exceed 2 for most of the stream bottom sediments, ranker soils and peats, showing that there is generally no Hg enrichment with regard to the organic carbon content, except one ranker soil which is depleted in organic matter and one stream sediment which is located near the plant (1.6 km). The results obtained in Fig. 7 confirm that the Hg enrichment, which could be calculated by normalizing to Sc, is mainly proportional to the organic carbon content. Consequently, the organic matter contained in the soils and in the stream sediments traps most of the atmospheric Hg deposition.

#### 4.8. Residence time of mercury in the upper catchment

##### 4.8.1. Soil mercury stocks

The Hg stocks in the soils (mainly in the finest particles —  $\varnothing < 63 \mu m$ ) of the study area have been estimated by considering two main soil layers: the upper soil horizons (0–30 cm) and the deepest soil horizons (30–60 cm).

In the superficial layer, one has seen in Fig. 4 that the enrichment factor (calculated by normalizing to Sc) is related to the percentage of atmospheric Hg. A mean  $EF_{Hg}^{Sc}$  has been calculated for each soil type

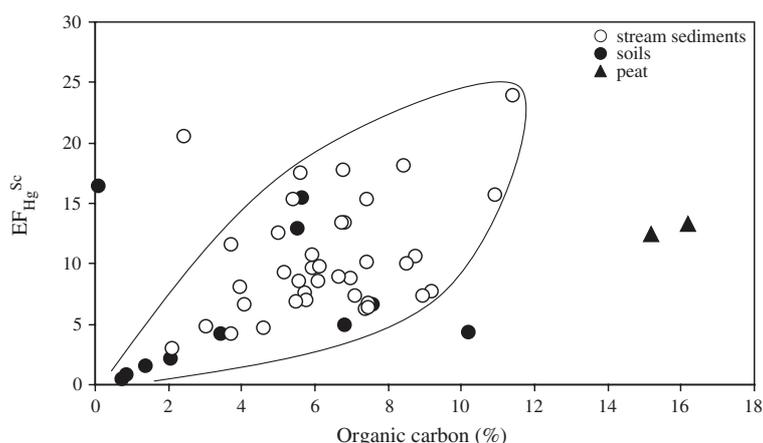


Fig. 7. Relationship between the mercury enrichment factor normalized to Sc and the organic carbon content in soils, peats and stream bottom sediments of the Thur river basin. The line is drawn to show the general positive trend of this relationship.

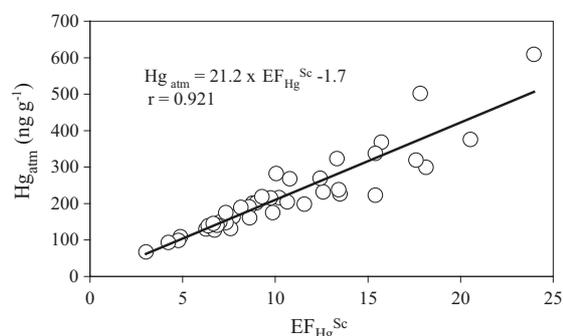


Fig. 8. Relationship between Hg enrichment factor ( $EF_{Hg}^{Sc}$ ) and the concentration of atmospheric Hg ( $Hg_{atm}$ ) in the bottom sediments of the upper Thur river catchment (see Fig. 4).

(Fig. 1) from the spatial distribution given in Fig. 4. Using the relationships between  $EF_{Hg}^{Sc}$  and the concentration of atmospheric Hg in the sediments (Fig. 8), one can calculate for each soil type the amount of atmospheric Hg. The amount of lithogenic Hg has been calculated for each soil type in the same way using the spatial distribution of lithogenic Hg which is estimated for each sampling site using Eq. (2). The total mercury concentration is calculated for each soil type by summing the two components (atmospheric and lithogenic).

In the deeper layer (30–60 cm), the total Hg (lithogenic plus atmospheric) concentration has been calculated using the relationship between Hg concentration and organic carbon content (Eq. (4) and Fig. 4) and the

average organic carbon percentage one has estimated for each soil type (Table 2).

For each soil layer, the Hg stocks have been estimated using the total Hg concentration and the average soil density (see Table 2).

The 0–30 cm layer contains 43.6 to 120 mg m<sup>-2</sup> of Hg. The amount of Hg trapped in deeper layers (30–60 cm) ranges between 23.3 and 35.4 mg m<sup>-2</sup>, i.e. 3 times more than the Hg stock of lithogenic origin. But, this calculation may underestimate the real stock for each soil type. Because our samples have been collected mainly in grassland areas and the forest soils should normally contain higher Hg concentration because of higher deposition rates. Indeed, canopy throughfall which is more concentrated in atmospheric pollutants has a strong effect on Hg deposition to the soils (Iverfeldt, 1991; Biester et al., 2002a; Lacerda et al., 2004). For the whole upper catchment, the stock of Hg in the total soil profile (0–60 cm) can be estimated to 19 tons and its corresponds to 70 years of local anthropogenic atmospheric deposition, that means an average Hg deposition rate of 270 kg y<sup>-1</sup>, i.e. 1.3 mg m<sup>-2</sup> y<sup>-1</sup>. This deposition rate is probably underestimated because we did not take into account of the amount of Hg released by soil erosion and exported by the river. Nevertheless, as seen below, the erosion rate of Hg is probably very low compared to this deposition rate.

#### 4.8.2. Riverine mercury fluxes

Concerning the stream sediments, Hg adsorbed onto the suspended matter is in the same order of magnitude than the Hg content in the bottom sediments, particularly if we compare with the atmospheric part of Hg in the bottom sediments (Fig. 9). The contamination is

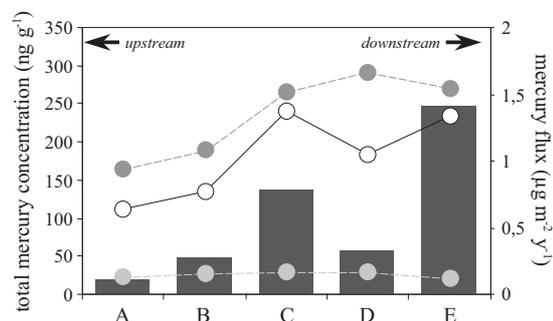


Fig. 9. Comparison of mercury concentrations measured in the total suspended sediment (TSS, white circles) of the five Thur river sub-basins (A, B, C, D and E, see also Fig. 1), mean atmospheric (upper grey circles and dotted line) and lithogenic (lower grey circles and dotted line) mercury concentrations calculated in the stream bottom sediments and particulate mercury fluxes (dark bars) estimated for each sub-basin.

mainly significant from sub-catchment B to E. The pollution level depends on the distance from the industrial plant and on the main wind direction, as we previously showed for stream bottom sediments and bryophytes. The total flux of Hg transported by the small streams in the upper part of the Thur river basin can be estimated by using the particulate Hg concentrations and the annual runoff. The specific Hg fluxes vary from 0.11 to 0.78 µg m<sup>-2</sup> y<sup>-1</sup> in the upper part of the catchment and reach 1.42 µg m<sup>-2</sup> y<sup>-1</sup> in the Piedmont area (sub-catchment E) (Fig. 9). Specific Hg fluxes and Hg concentrations increase together from upstream to downstream following the mercury enrichment factor. For the whole upper catchment, a first annual Hg specific flux can be estimated to 0.53 µg m<sup>-2</sup> y<sup>-1</sup>, i.e. 110 g y<sup>-1</sup>. This value is certainly underestimated because TSS collected in June are not repre-

Table 2  
Total mercury stocks calculated for the each soil type and each soil layer of the Thur River basin

Soil types	Area (km <sup>2</sup> )	EF <sub>Hg</sub> <sup>Sc</sup>	Layer (cm)	OC (%)	Bulk density (g cm <sup>-3</sup> )	Lithogenic Hg stock		Total Hg Stock	
						(mg m <sup>-2</sup> )	(kg)	(mg m <sup>-2</sup> )	(kg)
Ranker P	3.5	8	0–30	14.3	0.89	–	–	63.4	222
Ranker T	9.3	14	0–30	1.5	1.13	–	–	120	1116
Brown acidic	97.4	10	0–30	14.3	0.89	–	–	70.6	6876
			30–60	5.8	1.16	9.74	949	35.4	3448
Brown podzolic	57.3	8	0–30	15.6	0.67	–	–	43.6	2498
			30–60	4.1	0.98	8.23	472	23.3	1335
Podzolic	43.2	9	0–30	11.3	0.80	–	–	57.7	2493
			30–60	5.0	1.10	9.24	399	30.1	1300

sentative of the yearly hydrological conditions and particularly of the high water periods when the TSS can be very high. Moreover, the snowmelt periods may also present higher total dissolved Hg concentrations. Indeed, important quantities of atmospheric Hg should be trapped in the snow during winter and liberate in the stream waters during the spring (Dommergue et al., 2003). But, this first estimation allows us to show that total Hg released by weathering from the upper basin is negligible compare to the amount of Hg rejected by the anthropogenic effluents into the Thur river ( $40 \text{ kg y}^{-1}$ ).

These results allow us to estimate a mean residence time of Hg in this basin by dividing the soil Hg stock (19 tons) by the riverine Hg fluxes ( $110 \text{ g y}^{-1}$ ), knowing that we have not considered the flux of Hg from the soils to the atmosphere. Nevertheless the calculation indicate that the residence time of anthropogenic Hg in the upper Thur catchment must be very long, probably several thousands years.

## 5. Conclusion

Hg atmospheric emission from the chlor-alkali plant appears to be mainly responsible for the Hg contamination of soils and streambed sediments in the upper part of the Thur river basin. This contamination covers a large area (up to 25 km) and is due to the unusual localization of the industrial site at the entrance of this valley which is submitted to breeze events throughout the year. The breezes are the main pathway of Hg contamination for the upper part of this catchment. Consequently in this area, the superficial soil horizons and the stream sediments are highly impacted by the Hg atmospheric deposition that represents from 63% up to 95% of the total Hg concentration in these terrestrial reservoirs.

An important part of the atmospheric Hg deposited on this area is fixed by the organic matter and migrates through the soil profiles where it causes high Hg enrichment. But this enrichment appears to be only proportional to organic carbon content. Consequently, the organic matter fraction plays an important role in the long residence time of Hg in this soil system. They both create complexes with high stability, indicating that the soils make up the first large reservoir for local anthropogenic Hg trapping.

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