

Natural and anthropogenic contributions to mercury in soils and stream sediments of the upper Thur river basin (Alsace, France)

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Abstract. In an area where human activities (mainly chlorine and soda industry) have been releasing Hg in the environment, natural and anthropogenic contributions to mercury contents in soils and stream sediments could be assessed using mercury concentrations in the deepest soil horizons and in the stream bottom sediments located upstream from the industrial effluents. Hg concentrations have been measured by Cold Vapor Atomic Fluorescence Spectrometry. The regional natural background level could be estimated to $0,079 \pm 0,005 \mu\text{g}\cdot\text{g}^{-1}$ from the Hg contents in the deepest soil horizons (Hg deriving from rock weathering) which appear to be proportional to the organic matter percentage. Hg concentrations in stream sediments vary between $0,108 \pm 0,001$ and $8,42 \pm 0,44 \mu\text{g}\cdot\text{g}^{-1}$. The mercury enrichment factor (EF(Hg)) that could be calculated show that the anthropogenic contribution is not negligible, even in the upper part of the basin. The relationship between organic matter percentage and Hg content in the deepest soil horizons allows us to estimate by difference the anthropogenic contribution (18 to 86 % of the total Hg content) in the upper stream sediments. This contribution could probably be attributed to regional atmospheric deposition of Hg.

1. INTRODUCTION

The Thur is one of the most polluted rivers in the Alsatian region (North-Eastern France). The industrialization of this valley begun in the 18th century, has since increased and supplied many pollutants to the environment. Indeed, in 2000, a chlor-alkali plant still rejected the most important amount of mercury present in the environment (100 kg/year and 32 kg/year respectively into the atmosphere and into the river). In 1973, the Alsatian community realized the significance of this mercury pollution for people living there. Since then, the Regional Water Agency and the University of Strasbourg ([1]) have carried out studies on the river itself. But, no research has ever been made on the atmosphere within this area. Thus, the behavior of mercury in this atmospheric environment is still unknown.

The main objective of this study is to quantify the total mercury pollution in the river bottom sediments upstream and downstream from the chemical plant. It is also to determine the mercury background level in the soils of the watershed and the anthropogenic contribution of mercury into the stream sediments. We will not only demonstrate the importance of fluvial transport downstream from the industrial effluents, but also the significance of the atmospheric pathway in the mercury pollution upstream from the industrial site.

2. SITE DESCRIPTION

The study area is located in the East of France, 80 km South-West from Strasbourg and 10 km North-West from Mulhouse (figure 1). The Thur river is 25 km long and it drains a watershed of 275 km² before joining the Ill river which is a tributary of the Rhine river. The altitudes vary from 200 m in the Alsatian plain to more than 1400 m in the Vosges Mountains. This altitude difference lead to very contrasted climates going from mountain oceanic climate in the high valley to continental climate in the plain.

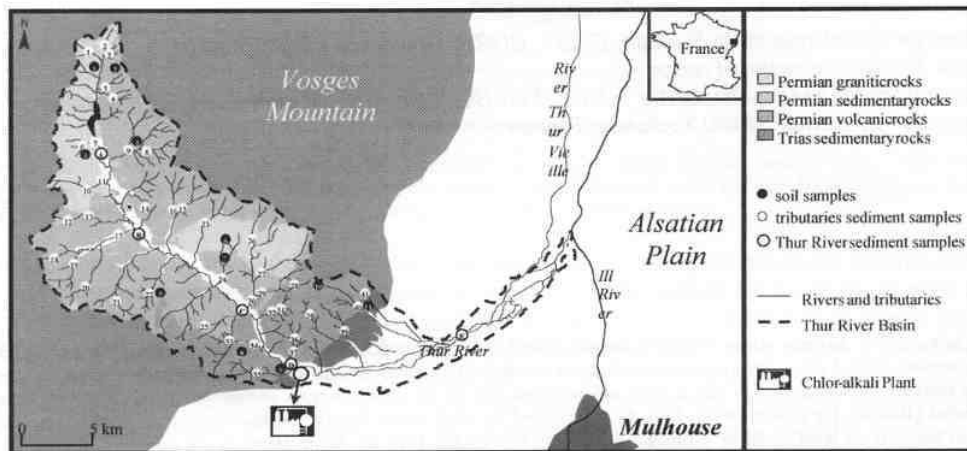


Fig.1 : General situation map of the Thur River Basin and localization of the soil and stream sediment sampling points.

The mountain area is made of Permian complexes of granitic, volcanic and sedimentary rocks (leucogranite, microgranite, trachyandesite, labradorite, graywackes, shales) and of Trias sedimentary rocks (sandstone, conglomerate). In these climatic and geological conditions, the soils evolve from brown to podzolic soils. They are more or less acid according to the bedrock, they develop sandy loam textures and they do not generally exceed 80 cm depth (most of them are ranker or podzolic ranker).

3. MATERIAL AND METHODS

To compare the natural signature of total mercury and its concentrations in the sediments, we work on the finest particles (< 63 µm) of the soil weathering horizons (C) and of the stream bottom sediments. As seen in figure 1, the sampling sites are well distributed all over the upper catchment and then give a good representativeness of the catchment. In June 2002, the deepest 11 soils we found were picked up with an earth auger. The bottom sediments have been collected in November 2000 for 41 small streams located upstream from all human activities and in November 2001 for 5 sites distributed along the Thur River. We followed careful procedures to avoid sampling, storage and analyze contaminations ([2]).

Total Hg was measured in soil and sediment samples 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 ng.g⁻¹ dry weight and the precision determined on three duplicate analysis is better than 10 %.

Organic carbon (OC) and Sc concentrations were respectively determined using an infrared spectrometer (LECO[®] CS 125 analyzer) and an ICP-AE Spectrometer (Jobin Yvon[®] 124), following the procedures given by [3]. Maximum relative error on these measures is generally less than 10 %.

4. NATURAL MERCURY BACKGROUND LEVEL

The 11 different soils we studied contained total Hg concentrations varying from $0,016 \pm 0,000 \mu\text{g.g}^{-1}$ to $0,399 \pm 0,002 \mu\text{g.g}^{-1}$. The highest concentrations measured in samples 1, 9 and 11 can be attributed to the lowest depth of these soils (less than 20 cm depth). All the soils showed important variations in the amount of organic matter (0,1 – 10,2 %).

The mean Hg content of the 8 deepest soils ($0,079 \pm 0,005 \mu\text{g.g}^{-1}$) is close to the average Earth Crust values given by [4] for igneous and sedimentary rocks. Thus, we used this value as the mean natural Hg amount in the Thur River Basin.

Below 50 cm depth, OC and total Hg concentrations are proportional. There is a linear relationship between both variables: $[\text{Hg}] = 0,013 [\text{C}] + 0,025$ ($R^2=0,8753$, $n=8$). Organic Matter has a strong capacity to complex and fix Hg and other metals. Indeed, they create organic complexes with very high stability ([5] and [6]). This relation follows the weathered mercury variation in the soils of the Thur River valley.

5. ANTHROPOGENIC CONTRIBUTION OF MERCURY IN THE STREAM SEDIMENTS

In the bottom sediments of the Thur River (A, B, C, D, E), the concentrations of total Hg increase from $0,227 \pm 0,000$ to $8,42 \pm 0,44 \mu\text{g.g}^{-1}$ towards downstream. The concentrations of total mercury in the upper small stream sediments ($0,108 \pm 0,001$ – $0,639 \pm 0,005 \mu\text{g.g}^{-1}$) are generally higher than in the soils, with an average value of $0,251 \pm 0,003 \mu\text{g.g}^{-1}$.

To assess the extent of Hg enrichment in the sediments relative to the natural abundance in the soils, we use the enrichment factor introduced by [7]:

$$EF(\text{Hg}) = ([\text{Hg}]/[\text{Sc}]_{\text{sediment}}) / ([\text{Hg}]/[\text{Sc}]_{\text{soils}})$$

The amounts of Sc range from 10 to 19 $\mu\text{g.g}^{-1}$ in the soils and 6 to 20 $\mu\text{g.g}^{-1}$ in the stream sediments. The total Hg and Sc concentrations measured in the soils lead to a mean $[\text{Hg}]/[\text{Sc}]_{\text{soils}}$ of 0,0057. The mercury enrichment factor varies from 3,5 (sample A) to 105 (sample E) in the Thur river sediments and from 1 to 9 in the upper small stream sediments. These results show first that there is a mercury contamination even the upper part of the basin and second that the amount of mercury released in the river increases with the importance of human activities ([8] and [9]).

The organic carbon contents in the soils and in the stream sediments are very close and vary between 2,1 and 16,2 % of the finest particles. Using the relationship between total Hg concentration and organic carbon contents calculated for the deepest soil horizons, it was possible to estimate in the stream sediments the amount of Hg deriving from natural sources (soil erosion) and by difference the anthropogenic contribution deriving mainly from atmospheric deposition. The results of this calculation show that the anthropogenic contribution varies from 18 to 86% ($0,029$ – $0,463 \mu\text{g.g}^{-1}$) in this area. These values are in agreement with the percentages given by [10] who show that in industrial areas, 30 to 90% of the atmospheric Hg may have an anthropogenic origin.

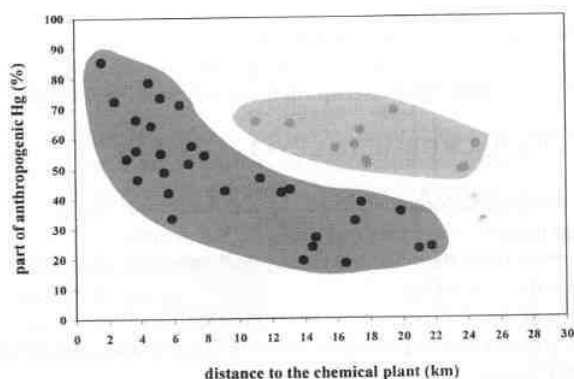


Figure 2. Relationship between the anthropogenic contribution of Hg (% of total mercury content) in the upper stream sediments and the distance of the sampling point from the chemical plant. The black points indicate the general trend and the grey points correspond to the upper sampling sites which receive more atmospheric deposits.

As seen in figure 2, the anthropogenic Hg contribution (in %) decreases when the distance to the chemical plant increases, showing the influence of atmospheric Hg released by the chemical plant and deposited in this region. In the first 10 kilometers, the wastes of the plant have a large impact on the atmospheric Hg deposits. Beyond this distance, the Hg anthropogenic content varies a lot. This is certainly due to the local conditions that disturb the bulk precipitations (wind direction, relief and vegetation). Indeed, the relief directly stops an important part of the local Hg deposition. Between 6 and 12 km, a rock bar (altitude: 1125 m) shields some tributaries from the industrial source. Their sediment samples contain less than $0,100 \mu\text{g}\cdot\text{g}^{-1}$ of anthropogenic Hg and this value increases with the distance to this relief. Nevertheless, in the upper part of the basin, important contaminations still remain (grey points in figure 2), due to the local atmospheric circulation.

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