Estimating distribution and retention of mercury in three different soils contaminated by emissions from chlor-alkali plants: part I

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Abstract

Mercury emissions from chlor-alkali plants have been past and present sources of soil contamination with Hg. Here we calculate net mercury (Hg) deposition to soils in the vicinity (100–1000-m downwind) of three-chlor alkali plants. Calculations were based on spatial distribution patterns of Hg concentrations in soils, which were extrapolated by kriging. Moreover, we investigated to what extent Hg deposition depends on the elevation of receptors and canopy throughfall. Mercury concentrations in soil exceed background values up to a factor of 56 and show enrichment factors between 2 and 5.8 calculated from the median Hg concentration. Net deposition rates range between 2356 and 8952 \( \mu \text{g m}^{-2} \text{ year}^{-1} \), which is up to 224-fold the background values. Net deposition of Hg to soils at the three sites varies between 1.2 and 2.4% of total emitted Hg. Highest deposition rates were found at sites with extended elevated or forested areas. Here, Hg concentrations in soils increased by a factor of up to 7.3 in elevated (+180 m) forest areas compared to non-elevated grassland soils. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chlor alkali plants; Mercury; Soils; Hg deposition rates; Hg retention

1. Introduction

The amount of mercury (Hg) which mobilized and released into the biosphere has increased since the beginning of the industrial age. Estimates of Hg fluxes from natural and anthropogenic sources indicate that emissions from anthropogenic sources have exceeded those of natural sources (Mason et al., 1994). Most mercury in the atmosphere is elemental Hg, which circulates in the atmosphere and hence can be widely dispersed and transported over thousands of kilometers affecting soils and aquatic environments in remote areas (Fitzgerald et al., 1998). As it cycles between atmosphere, pedosphere and hydroosphere, mercury undergoes a series of complex chemical and physical transformations such as

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biotic and abiotic methylation or Hg(0) oxidation which may increase toxicity and bioavailability of the metal (Gavis and Ferguson, 1972; Andren and Nriagu, 1979; Lindqvist et al., 1991; Stein et al., 1996).

Due to the removal of Hg from many industrial processes and the reduction of Hg emission from power plants in the past decades, the amount of Hg released from anthropogenic sources steadily decreases (Pacyna and Keeler, 1995). Next to long distance transport and deposition of atmospheric-derived Hg in remote areas, there are still numerous point sources of Hg emissions which have caused elevated Hg levels in soil, water and sediments in their vicinity. Besides coal burning and waste incineration, one important source of Hg emissions are chlor-alkali plants (CAP) using metallic Hg for the electrolytical production of chlorine. The environmental impact of Hg emissions from CAPs has been demonstrated in several studies (e.g. Lodenius and Tulisalo, 1983; Baldi and Bargagli, 1984; Maserti and Ferrara, 1991; Gonzales, 1991). Several studies have shown that most Hg emitted from chlor-alkali plants is dispersed over long distances, and only small amounts are deposited in the vicinity of the sites (Jernelov and Wallin, 1973; Högström et al., 1979). Nevertheless, it has been reported that soils surrounding chlor-alkali plants show Hg concentrations up to 75 times the background (EPA, 1997).

In the present study, which consists of two parts, we investigated accumulation and binding of Hg in soils in the vicinity of three chlor-alkali plants. In this first part of the study, we analyzed total Hg concentrations in surface soils and interpolated the obtained Hg distribution to an area extending from 100 m to 1 km in the main downwind direction from the plants. Based on this Hg distribution and the vertical distribution of atmospheric-derived Hg in those soils we calculated how much of the Hg emitted from the plants has been retained in the soils and determined mean deposition rates. Moreover, we calculated differences in Hg deposition to grassland and to forest areas and to which extent Hg deposition is influenced by elevation of receptors.

2. Description of sites

The study was carried out at three different sites within Europe. Eurochlor pre-agreements require that exact locations of the sites have to be treated confidential. Locations of the sites were selected on the basis of differences in climatic and morphological conditions and in soil type. A more detailed description of the composition of the soils is given in Part II of this study (Biester et al., 2002, this issue).

Site 1 (S1) is located at the seaside and surrounded by several other industrial facilities. The area is characterized by alternating forests and grassland. Differences in elevation do not exceed 50 m. The main winds are coming from southwest to west and annual mean precipitation rates are 600–950 mm. Most samples were taken northeast to east from the plant, which are the main downwind sectors. Soils are mostly sandy, organic rich in the forests and are more clayey in grassland areas. Approximately half of the area is estimated to be covered by buildings.

The second site (S2) is located within a valley running northeast to southwest. Mountains within the study area reach an altitude of approximately 450 m. To the west and the north, the plant is surrounded by other chemical sites. A narrow valley extends to the east and a mountain with steep slopes, densely covered by forest stands is situated southwards of the site in the main wind direction. The valley southwest from the site is covered by an urban area. Precipitation rates amount to approximately 900 mm year$^{-1}$, the main winds are coming from the north. All samples were taken from soils southwest to southeast from the plant, only two samples were taken directly on the site northeastwards from the plant.

The third site (S3) is located on a flat peninsula and is also surrounded by other chemical and petro-chemical plants. There is a large coal-fired plant approximately 2-km north of the site, emitting high amounts of smoke which produces a visible plume to the south extending all over the peninsula where the CAP was located. In the north and the west, the peninsula is marked by a
river to the east and the south by the sea. Vegetation in the area is very sparse and consists mostly of bushes and some small pine trees. High temperatures (mean = 17.8°C year⁻¹) and low precipitation rates (mean = 472 mm year⁻¹) are typical for the climate in this region. Most of the year the main winds come from south to south-west, but also from the landside (north) during winter. Most samples were taken northeast (main wind direction) from the plant alongside the main roads crossing the peninsula. The average distance of the sampling points from the road was approximately 25 m. Different from the other sites, soils around site S3 were not only sampled in the main wind direction (NE), but also in the opposite sector for two reasons. One is that winds during the winter months predominately come from the north and that emissions from a coal-fired plant located north of the site is assumed to be an additional source of Hg deposition to the soils. To determine the influence of the emissions of the coal-fired plant on the soils surrounding the CAP we have additionally analyzed Cd and As, which are typical elements released during coal burning.

3. Methods and materials

3.1. Sampling of soil surface samples

Surface soil samples were taken within a distance of 100 to 1000 m from each plant in the main wind direction. The minimum distance of 100 m from the plants was chosen to avoid sampling of soil contaminated by direct spillage of Hg. The number of samples ranged between 50 and 70 depending on the morphological conditions at the site and the size of the area where soil could be sampled. The areas around the sites are partly covered by other industrial plants or urban areas, the distribution of sampling points is therefore, more or less at random. Samples were cut from the soil surface by means of a stainless steel soil corer to a depth of 5 cm. Six sub-samples taken from a soil area of approximately 4 m² were combined to one sample. Background concentrations of Hg, including natural and anthropogenically elevated Hg in soils, were estimated from three samples taken several kilometers from the sampling area opposite to the main wind direction. This estimation of Hg background concentrations does not consider differences in composition of soils in the sampling area such as organic matter or clay content, which might cause variation of Hg background values. The used values are therefore, only a rough estimation of Hg background concentrations.

3.2. Sample preparation

All soil material was sampled and stored in polyethylene bags. Samples were not stored frozen as we assumed that volatile Hg compounds, such as free or adsorbed elemental Hg, which can exist under open field conditions (strong sun light, strong wind, precipitation etc.) would not become lost during sample transport at ambient temperatures. Twenty fresh samples taken nearest to the sites were analyzed by means of a solid phase Hg-thermal-desorption technique for any metallic Hg. The detection limit of this technique is 40–50 ng if all Hg in the sample is released within a single peak (Biester and Scholz, 1997). Due to this comparatively high detection limit this technique does not allow to determine traces of Hg in the soil gas, which is known to be ubiquitous in soils due to natural reduction processes of Hg(II) species. As metallic Hg could not be detected in any of the samples (Biester et al., 2002), the soils were freeze-dried and sieved to < 2 mm to remove most of the root material.

3.3. Analysis of Hg, Cd and As in soils

Analyses of total Hg were carried out by means of a cold vapor atomic absorption (CV-AAS) Hg analyzer (TSP-mercury Monitor 3200) after digestion of a 3-g sample in concentrated nitric acid for 3 h at 160°C. Arsenic in the S3 soil samples was determined by means of a Perkin-Elmer FIAS 200 Hydride-Generation system coupled to a Perkin-Elmer 4100 AAS. Cadmium was analyzed from the same digests by means of graphite furnace atomic absorption spectroscopy. Accuracy of analysis was checked using standard reference soil materials (NIST 2710, 2711, RTC-CRM008-
050). Relative standard deviation of replicate measurements \((n = 4)\) did not exceed 4\% for Hg, 7\% for As and 0.8\% for Cd in the reference samples and 8\% for Hg, 9\% for As and 3\% for Cd in the soil samples.

3.4. Calculation of total Hg in soils

Spatial distribution of Hg concentrations based on kriging was calculated using SURFER 6.04 (Golden Software). Kriging was based on a linear variogram model. Based on the surface plots of Hg concentrations (Figs. 1–3) we calculated the amount of Hg stored in the soils around the sites and compared the data to the amount of Hg emitted from the plants. For all sites we set an angle of spread of 90\(^\circ\) for Hg dispersion from the site in the main wind direction. The calculated area was framed by this angle and the stretch between 100 and 1000 m distance from the plant. The amount of Hg in the soils was obtained by summing up the amount of Hg calculated for each Hg concentration area separately. The amount of Hg in each single Hg concentration area was calculated using the surface of the area between two isolines, the mean concentration of

![Fig. 1. Mean proportional decrease of Hg and organic carbon (C\(_{org}\)) concentrations calculated from data of two soil profiles (Biester et al., 2002) from the sites S1, S2 and S3, respectively. S1 profiles were taken 240 m NNE and 300 m E of the plant. S2 profiles were sampled 420 m SSW and 930 SE from the plant. S3 profiles were collected 250 m S and 600 m NNW from the plant.](image)
Hg between two isolines, the thickness of the soil layer and the mean soil density. Soil density was calculated from the median amount of organic matter ($\delta = 1.4$ g cm$^{-3}$) and mineral matter ($\delta = 2.65$ g cm$^{-3}$) of 20 samples from each site, respectively. This calculation was carried out for each soil layer (5 cm) down to a soil depth of 20 cm. The Hg content and the soil density in sub-surface soil layers were calculated for each Hg concentration area based on the proportional decrease of Hg and organic carbon concentrations in the soil column (Fig. 1) which was calculated from the data given in Biester et al. (2002). Background Hg concentrations were set to be constant in the upper 20 cm of the soils. The total amount of atmospheric-derived Hg retained in the soils was obtained by adding up the amount of Hg calculated for each soil layer and substracting the amount of background Hg.

Fig. 2. Distribution of mercury in surface soils within 1-km distance from plant S1 in the main wind direction.

4. Results and discussion

4.1. Distribution of mercury

Soils of all sites show highly elevated Hg concentrations if compared to local background values. Maximum enrichment factors were 56-fold for S1, 20-fold for S2, and 40-fold for site S3. Site S3 shows the most widespread soil contamination expressed by a median Hg concentration of 571 µg kg$^{-1}$ ($n = 70$) which is 5.8-fold the background compared to a median of only 157 µg kg$^{-1}$ for S1 ($n = 56$) which corresponds to an enrichment factor of approximately 2 and a median of 541 µg kg$^{-1}$ for S2 ($n = 51$) which is 3.6-fold the background of this site. Samples showing isolated high Hg concentrations, which were not attributed to atmospheric Hg emission
of Hg from the plant, but e.g. to direct spillage to the soils, were not considered.

Soil Hg concentrations at S1 range from 24.2 μg kg⁻¹ to 4188 μg kg⁻¹ and show a mean of 442 μg kg⁻¹. The low median Hg concentrations of 157 μg kg⁻¹ indicate that only a comparatively small number of samples show a high enrichment in Hg. The local background concentration of Hg in soils was estimated to be 75 μg kg⁻¹ ± 25. The distribution of Hg concentrations at this site (Fig. 2) shows that the highest Hg concentrations were found downwind (main wind direction) from the plant in a distance of approximately 250 m from the plant. All these samples were taken from soils of a pine forest located on a small hill.

We conclude that mercury enrichment in the forest soils is attributed to two main processes which is filtering from the atmosphere and uptake by foliage followed by Hg deposition through canopy throughfall and litterfall (Rea et al., 2000). The high variability of Hg concentrations within the small area downwind from the plant is assumed to be attributed to changes of elevation of sampling locations or alternating forested and non-forested areas. There is no evidence that Hg in soils at this part of the site is attributed to non-atmospheric anthropogenic sources. Fig. 2 also shows that the strong Hg enrichment is restricted to the forest located downwind from the plant in the main wind direction (NE). Soils in the east to south-east part of the area seem to be generally only weakly affected by Hg emissions from the plant, which we attributed to the absence of elevated sampling points or forests (Fig. 2).

Mercury concentrations in the soil of site S2 range from 122 to 3005 μg kg⁻¹, but despite this,
maximum values are lower than those found for samples from site S1; the high mean (674 μg kg⁻¹) and median (541 μg kg⁻¹) Hg concentrations indicate that soil contamination attributed to Hg emissions from the plant is more widespread at this site. The local background Hg concentration are estimated to be 150 ± 50 μg kg⁻¹. Fig. 3 shows that the highest Hg concentrations in soils were found within a distance of less than 500 m southward from the plant. As found in soils of S1 all samples with Hg concentrations above 1000 μg kg⁻¹ were collected in forest areas. Highest Hg concentrations were found in soils of two small forest stands within the urban area at a distance of approximately 300 and 500 m from the plant, respectively. In samples taken from grassland soils, Hg concentrations were only slightly elevated compared to background values. Moreover, Hg concentrations in soils sampled in the valley at a distance of more than 500 m from the plant rapidly decrease to values near the background, whereas Hg concentrations in forest soils on the mountain exceed 1000 μg kg⁻¹ even at a distance of 1 km. All samples higher than S2-40 were taken in the forests on the western slope and on the top of the mountain located south to southeastwards from the plant. As clearly indicated by the high Hg concentrations in these forest soils, the Hg emitted from the plant has been mostly transported by northern winds to the south against the mountain. The steep slopes and the high trees act as a barrier so that Hg is effectively removed from the atmosphere and reaches the soil through canopy throughfall or direct foliage uptake and litterfall.

Soils in the area of S3 show Hg concentrations between 94 and 2296 μg kg⁻¹. Some samples from this site show isolated Hg concentrations between 4000 and 6000 μg kg⁻¹ and were assumed to be not attributed to atmospheric deposition. These samples were excluded from all calculations of atmosphere to soil fluxes. Soils of S3 show highest mean (696 μg kg⁻¹), and median (571 μg kg⁻¹) Hg concentrations of all sites. Background Hg concentrations determined from comparable soils sampled approximately 4-km southeast from the plant on the mainland were 58 ± 35 μg kg⁻¹. Accordingly, Hg concentrations in soils of this site indicate that all samples show highly elevated Hg levels. Different from the other sites, the distribution of Hg concentrations in soils of this site do not indicate Hg dispersion in a preferential direction, but seems to be at random (Fig. 4). Despite the fact there are only a few sampling points in the western part of the area it seems that Hg concentrations tend to be higher on the west side of the peninsula.

However, if the samples 2–39 (upwind sector, SW) and 40–70 (downwind sector, NE) are regarded separately, the median Hg concentration will be 460 μg kg⁻¹ for the upwind sector and 771 μg kg⁻¹ for the downwind sector. Compared to S1 and S2, Hg concentrations in soils at S3 are unexpectedly high taking into account that the area is flat and that there are only a few small trees which might filter Hg from the atmosphere. Moreover, the amount of organic matter and clay minerals in these sandy soils is very low (Biester et al., 2002) suggesting that retention of Hg is generally low. As emission of Hg attributed to the combustion of coal is well known, we consider that emissions from the coal-fired plant situated north from the CAP contributes to the Hg load in these soils. Regarding the higher Hg concentration in soils of the downwind sector it must be considered that during the winter month winds are coming predominately from the north instead of S/SW, which is the main wind direction in summer. This means that in winter the N/NE part of the peninsula where the CAP is located is the downwind sector of the coal-fired plant. Therefore, the higher Hg levels in soils of the NE sector could be explained by emissions from the CAP as well as by those from the coal-fired plant.

Although the distribution of As or Cd concentrations do not match those for Hg (Figs. 4 and 5a,b), both elements show partly elevated concentrations in these soils. Arsenic concentrations range between 0.33 and 96 mg kg⁻¹ with a median of 24 mg kg⁻¹ (mean = 24.7 mg kg⁻¹), which is in the range of the local background (22 mg kg⁻¹). Cadmium levels range between 30 and 1609 μg kg⁻¹, with a median of 230 μg kg⁻¹ which is approximately five times the local background (46 μg kg⁻¹). From these results we con-
clude that soils in the vicinity of the CAP are also affected by deposition of metals emitted from the coal-fired plant. It is, however, unknown to what extent the Hg load in these soils is attributed to the emissions from the coal-fired plant.

4.2. Retention of Hg in soils and Hg deposition rates

The amount of Hg stored in the soils around the sites was calculated as described above and compared to the amount of Hg which was emitted from the plants during time of operation. With this calculation we intend to estimate how much of the emitted Hg was retained in the soils and how much attributed to long range transport. Moreover, we compared Hg deposition in forested and unforested and elevated and non-elevated areas, respectively, and compared our results to
data from the literature, where Hg deposition around a model CAP site was calculated by means of the atmospheric deposition model ISC3 (EPA, 1997).

Data on the mercury budget are given in Table 1. The calculated average values of surface soil densities were 2.11 g cm$^{-3}$ for soils of S1, 2.41 g cm$^{-3}$ for S2 and 2.62 g cm$^{-3}$ for S3, respectively. The amount of Hg in the soil, which is of natural origin was calculated based on the background concentrations given above. Annual Hg emission rates, which were derived from measurements at the ventilation shafts, were obtained from the companies operating the plants.

Re-emission of Hg from soil could be caused by directed re-emission of deposited Hg(0) or emission of Hg(0) formed by biotic or abiotic reduction of Hg(II) (Alberts et al., 1974; Rogers and McFarlane, 1979; Allard and Arsenie, 1991). Data on Hg emission rates from soils were not ana-

<table>
<thead>
<tr>
<th>Site</th>
<th>$H_{\text{em}}$ (kg)</th>
<th>$H_{\text{soil}}$ (kg)</th>
<th>$H_{\text{dep}}$ (kg)</th>
<th>$H_{\text{atm}}$ (kg)</th>
<th>$H_{\text{reem}}$ (kg)</th>
<th>Net $H_{\text{em}}$ rate ($\mu$g m$^{-2}$ year$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>29.9</td>
<td>2271</td>
<td>83.8</td>
<td>53.9 (2.37)</td>
<td>5.7–19 (28)</td>
<td>2475</td>
</tr>
<tr>
<td>S2</td>
<td>57.6</td>
<td>19 232</td>
<td>287.4</td>
<td>229.8 (1.19)</td>
<td>6.1–20.4 (30)</td>
<td>8952</td>
</tr>
<tr>
<td>S3</td>
<td>26</td>
<td>4157</td>
<td>71.8</td>
<td>48.8 (1.17)</td>
<td>5–17 (25)</td>
<td>2356</td>
</tr>
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</table>

Estimated amount of re-emitted Hg from the soils based on re-emission rates of 30–100 ng m$^{-2}$ h$^{-1}$ ($H_{\text{reem}}$) and the mean net deposition rates calculated from the amount of atmospheric-derived Hg in the soils ($H_{\text{dep}}$).
lyzed in this study. Mercury emissions from soil reported in the literature range e.g. between 30 and 160 ng m$^{-2}$ h$^{-1}$ and can reach up to 2000 ng m$^{-2}$ h$^{-1}$ over Hg contaminated mine tailings (Lindberg et al., 1991; Sexauer-Gustin et al., 1991). Background Hg emissions from soil used for calculations of global Hg mass-balances are 1.5 ng m$^{-2}$ h$^{-1}$. Estimating re-emission rates of Hg of 30–100 ng m$^{-2}$ h$^{-1}$ for soils of all sites would sum up to a total of re-emitted Hg of 5–20.4 kg during time of operation. Therefore, the amount of Hg deposited to the soils might be initially between 10.6 and 35.3% (S1), 2.7–8.9% (S2) and 10.2–34.8% (S3) higher than calculated from the actual Hg content in soils. This data supports the assumption of Högström et al. (1979) who assumed that up to 25% of Hg deposited to soils around CAPs is reemitted within a short time.

The calculations show that at most, only 2.4% of the Hg emitted from the plants is retained in the soils in the area within 1-km downwind from the plants (Table 1). Taking into account that to a lower extent, Hg was dispersed in other directions, we conclude that the amount of Hg deposited in the total area will be below 10% in case of S1 and below 5% of total emitted mercury in case of S2 and S3. It is generally known that such kind of calculations potentially include large errors due to the extrapolation of the spatial Hg distribution, varying background concentrations, and varying composition of soils at a single site etc. However, the results clearly show that most of the emitted Hg contributes rather to long range transport than to local retention in soils.

Net deposition rates of Hg range between 2356 and 8952 µg m$^{-2}$ year$^{-1}$ (Table 1), which are, in case of S1 and S3, similar to that found by Bull et al. (1977) for deposition on moss bags (2300 µg m$^{-2}$ year$^{-1}$) at a distance <500 m from a CAP. Highest deposition rates were found at S2 which exceeds that of the other sites by a factor of approximately 3.7. However, due to the 4.5-times higher Hg emission rates of this plant the proportion of Hg retained in the soil is almost similar to that found at the other sites. Background deposition rates determined in throughfall and litterfall are estimated to 0.9–40 µg m$^{-2}$ year$^{-1}$ (Iverfeld, 1991; Driscoll et al., 1994; Lindberg et al., 1995), hence deposition rates at S2 increased at least by a factor of 224.

Our results also suggest that differences in precipitation rates have no obvious effect on Hg deposition at the investigated sites. The main reason for this is, that dry deposition of Hg was found to be the predominant process of Hg deposition around chlor-alkali plants (Högström et al., 1979; Lodeniус, 1998). EPA model calculations estimated that 22.7% of total Hg emission from CAPs were deposited within 50 km on a humid site (17.2 by dry and 5.5% by wet deposition) compared to 17.7 on an arid site (16.7% by dry and 1% by wet deposition) suggesting that higher precipitation rates will increase total Hg deposition by only 5%. The predominant process calculated here was dry deposition of Hg(II) accounting for 13.6% at the humid site and 13.1% at the arid site (EPA, 1997).

Our data provides no clear evidence for which parameters favor the deposition of Hg to soil. Highest proportional retention of Hg was found at S1 despite that the amount of emitted Hg is the lowest of all sites and only a comparatively small area was affected. Moreover, we expected to find higher amounts of Hg retained in soils of S2 due to the large amounts of emitted Hg and the occurrence of large forested and elevated areas at this site, which have been found to be areas of increased Hg deposition. In contrast, the area around S3 is totally flat and only sparsely forested, but shows almost the same relative amount of retained Hg. However, the percentage of emitted Hg retained in these soils might be overestimated, as Hg deposition here is assumed to be partly attributed to emissions from the coal-fired plant nearby.

It seems that morphological characteristics of an area or the filtering-effect of trees determine differences in deposition rates within an area, but are negligible comparing proportions of Hg deposited to soils at different sites. We assume that the generally low proportion of Hg deposited to the soils is the reason. Accordingly, the fate of Hg emitted from CAPs is determined by fast dispersion in the atmosphere and long range transport.

The proportions of Hg which has been deposited to soils in this investigation are similar to
those found in other studies. Högström et al. (1979) reported deposition of less than 5% of total emitted Hg within 3 km from a CAP. Studies based on Hg deposition to mosses and lichens also indicated that approximately 6% of Hg emitted from a CAP in Finland has been deposited within 5 km (Lodenius and Tulisalo, 1983; Lodenius, 1998). Similar results were found for Hg deposition on snow around several plants in Sweden (Jernelöv and Wallin, 1973; Wallin, 1976). Some of these studies indicate that airborne Hg deposition of Hg emitted from CAPs extend to more than 100 km from the plants.

4.3. Effects of elevation and forests on Hg deposition

Pronounced differences in morphological elevation were only found at S2. Here, the largest difference in elevation within 1 km from the site was 250 m. To evaluate the effect of elevation on Hg deposition rates we compared samples pairs taken at the same distance from the plant but at different elevation. Samples were taken from grassland soils in the valley (S2-19, S2-21) and from forest soils on the mountains (S2-41, S2-48), respectively. The plant is also located in the valley at the same altitude as the grassland samples, which means that the difference in elevation between the two samples is the same as that between the elevated sample and the emission source. Samples of each pair were chosen as close as possible so that differences in exposure to the main winds coming from the plant were small. The sample pair S2-19/S2-41 show a difference in altitude of 100 m and a difference in Hg concentration of 822 μg kg⁻¹ (200/1022 μg kg⁻¹). The distance of both samples from the plant is approximately 600 m. The second pair of samples (S2-21, S2-48) shows a difference in altitude of 180 m and a difference in Hg concentration of 1189 μg kg⁻¹ (186.5/1375 μg kg⁻¹). The distance from the plant was approximately 700 m. Accordingly, at a difference in elevation of 100 m compared to the emission source Hg concentration in soils are a factor of 5 higher, and at a difference of 180 m by a factor of 7.3. In the EPA model study, a maximum factor of 2.79 was calculated for increasing Hg deposition to a receptor located 100 m higher than the emission source but at a distance of 2.5 km (EPA, 1997). This modeled factor decrease to 1.72 at 10 km and 1.36 km at 25 km due to increasing dispersion of the plume with distance (these data were calculated based on a municipal waste combustor emitting 60% Hg(0), 30 Hg(II) and 10% Hg(II) in particulates (EPA, 1997). A higher amount of Hg(0) and the absence of Hg in particulates as estimated for CAPs, would probably increase the dispersion effect of the plume. The fivefold increase of Hg deposition found for an increase in elevation of 100 m at S2 (S2-19/S2-41) fits well with the modeled values to a negative, exponential correlation ($r^2 = 0.9927$) of Hg deposition factors and distance from the plant.

To evaluate the effect of canopy throughfall alone, we compared pairs of samples taken in forested areas and from grassland, respectively. All four samples were taken in the valley within the main wind direction (S). Forest soil samples were collected in two small oak forests located in the urban area. At a distance of approximately 300 m from the plant the samples S2-3 (with trees) and S2-5 (without trees) e.g. show a difference in soil Hg concentration of 539 μg kg⁻¹ (1265/736 μg kg⁻¹) which is a factor of 1.74. S2-14 (with trees) and S2-13 (without trees) sampled approximately 600 m from the plant shows a difference of 578 μg kg⁻¹ (826/248 μg kg⁻¹) which is a factor of 3.33. The higher factor at a greater distance from the plant probably indicates that Hg deposition to grassland decreases more strongly than to forested areas with increasing dispersion of the plume. These data show that canopy throughfall also has a strong effect on Hg deposition to soils. However, from our data it could hardly be determined if elevation or canopy throughfall has the stronger effect on Hg deposition. All elevated sample points were located in forested areas and thus show both effects.

5. Conclusions

All three sites show an enrichment of Hg concentration in soils within 1 km from the plant in the main wind direction. Enrichment factors of
median Hg concentrations in the soils were 2, 3.6 and 5.8. The amount of Hg deposited within the investigated area was in all cases, below 2.5% of total emitted Hg, indicating that most Hg emitted from CAPs is subject to atmospheric dispersion and long distance transport. Elevation of receptors and canopy throughfall have been found to increase Hg deposition drastically if compared to non-elevated grassland areas. However, this effect was found to be negligible comparing the total amount of Hg retained in soils of sites differing in trees or morphological characteristics. This study has shown that Hg retention in soils and rates of Hg deposition in the vicinity of chlor-alkali plants could be calculated in approximation based on extrapolated spatial distribution of atmospherically-derived Hg in soils.

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