

## Comparison of Bulk Deposition of PCDD/Fs in a Forest and an Adjacent Clearing

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### Abstract

Atmospheric (bulk) deposition of PCDD/F was measured in a spruce forest and in an adjacent clearing. The deposition rate at the two sites was comparable during the winter months. In summer the deposition in the forest was approximately eight times higher than in the clearing. The difference between the two sites could not be explained by the deposition of needles. Further studies are underway to identify the mechanisms responsible for the higher deposition of PCDD/F in forest ecosystems.

### Introduction

Hagenmaier and Krauss [1] recently demonstrated that forest soils are more contaminated with PCDD/F than agricultural soils. In a survey of soils from the German province of Baden-Württemberg they found that the soil under 1 m<sup>2</sup> of forest contains on average approximately three times more PCDD/F than an equivalent patch of agricultural soil. Forests are known to filter atmospheric pollutants out of the air, and it has been shown that semivolatile compounds like PCDD/F accumulate on needle surfaces [2]. It is conceivable that falling needles and leaves carry a considerable flux of PCDD/F to the forest floor, resulting in higher concentrations in forest soils than in non-forest soils. In this study we report on an experiment designed to explore the role of this mechanism in the accumulation of PCDD/F in forest soils.

### Experimental and Analytical Methods

Beginning in December 1993 bulk deposition was collected in a mature spruce forest and in a nearby clearing. The sampling sites are about 200 m from each other and are located 2 km south of the University of Bayreuth campus. The samples were collected using the German VDI 2119 (Bergerhoff) standard method. Three sets of 10 glass bottles with an opening of 9 cm were exposed at a height of 2 m at each of the sites. In addition, the needle fall was collected in metal sieves (Ø 20 cm), two of which were mounted on each post supporting a glass bottle. Both the bulk deposition and the sieve samples were collected in one month intervals. The contents of the 10 bottles comprising one bulk deposition sample were filtered on-site through glass wool into a single glass bottle for transport to the laboratory. The sampling bottles were subsequently rinsed with 50 ml. of acetone, 50

mL of toluene and again with 50 mL of acetone. After the toluene rinse the glass surface of the sample bottle was wiped out with a glass fibre filter. The rinsing solvents were filtered through the same glass wool as the water sample into a second glass bottle for transport. The material in the 20 sieves corresponding to a particular deposition sample were packed in aluminum foil and stored at  $-16^{\circ}\text{C}$ .

In the laboratory the water sub-samples were enriched on octadecyl silane ( $\text{C}_{18}$ ) bonded to a silica substrate (VARIAN MEGA BOND ELUT; 10g sorbent). The sorbent was cleaned and conditioned with 20 mL of n-hexane, 20 mL of dichloromethane, 20 mL of methanol and 300 mL of aqua bidest under low vacuum. The water was drawn through the  $\text{C}_{18}$ -sorbent at a maximum flow rate of 50 mL/min by applying a mild vacuum. The empty glass bottles were rinsed with 100 mL toluene. After the enrichment the remaining water on the sorbent was removed by sucking air through for 5 minutes and drying the cartridge for 2 days at room temperature. The PCDD/F were eluted from the sorbent with 50 mL of toluene. All rinsing solvents for this sample were evaporated almost to dryness and added to the toluene extract along with an internal standard mixture containing twelve isotope labelled PCDD/F. This was in turn added to the toluene used for the 24 h soxhlet extraction of the filter and the glass wool. The contents of the sieves were also soxhlet extracted in toluene for 24 hours.

The extracts were cleaned up using the procedure described in [3]. The HRGC/HRMS analyses were performed on a VG AUTOSPEC ULTIMA at a resolution of 10,000 in the selected ion mode.

## Results

Figure 1 gives the bulk deposition (average of 3 samples) in TEQ per  $\text{m}^2$  and month for both the forest and the clearing. Note that the forest deposition included the needle fall.

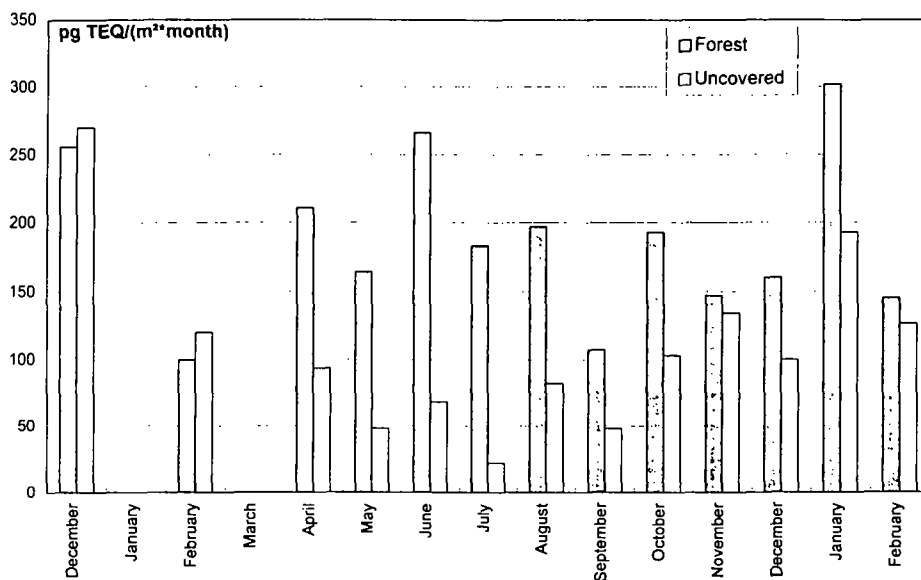


Fig. 1: Bulk deposition of PCDD/F in a mature spruce forest and in an adjacent clearing

The bulk deposition of PCDD/F in the clearing decreased from winter to summer by a factor of 10, which is in agreement with the strong decrease in ambient air concentrations from winter to summer measured in Germany [4]. In contrast the bulk deposition measured in the spruce forest soil remained relatively constant throughout the year, varying by a factor of about 3. A comparison of the deposition in winter months (November - February) shows comparable fluxes at both sites with differences below factor 2. In summer (July) the deposition measured in the forest was eight times higher than in the clearing. The PCDD/F associated with needle fall could not explain the difference. The needles and other material present in the sieves accounted for a deposition of 36 pg TEQ/m<sup>2</sup> in July, which is only 22% of the excess bulk deposition at the forest site during the same period. Possible mechanisms related to wet deposition can also be excluded as an explanation because only two short rain events amounting to less than 10 mm occurred during the July sampling period. The average rainfall amounts to 50-70 mm per month in Bayreuth. Other processes must be responsible for the higher deposition rate in the forest.

The differences in the deposition fluxes at the two sites during the summer was larger for the lower chlorinated and smaller for the higher chlorinated PCDD/F. In Figures 2 and 3 the deposition of  $\Sigma\text{Cl}_4\text{DF}$  and  $\text{Cl}_4\text{DD}$  are plotted.

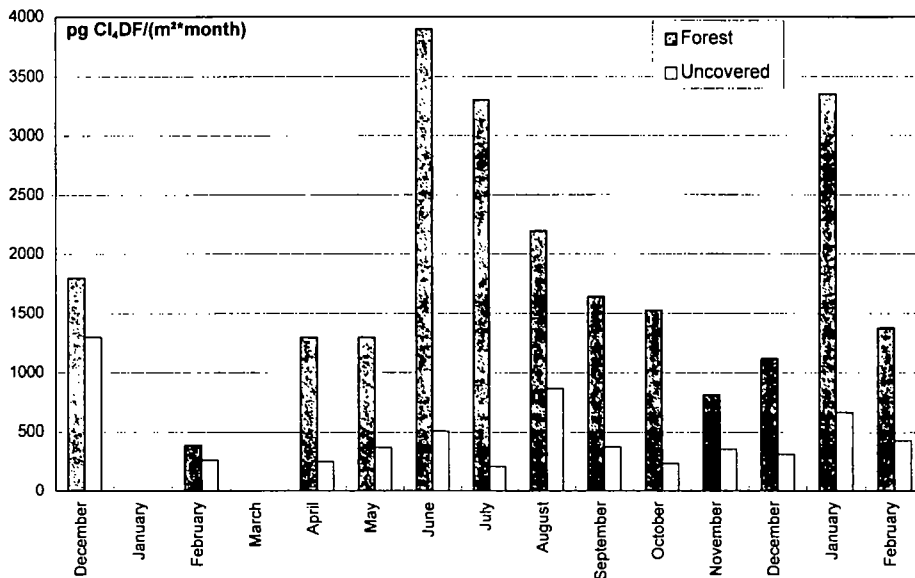


Fig. 2: Bulk deposition of  $\Sigma\text{Cl}_4\text{DF}$  in a mature spruce forest and in an adjacent clearing

The bulk deposition of  $\Sigma\text{Cl}_4\text{DF}$  was higher in the forest than in the clearing throughout the year and up to fifteen times higher in summer. On the other hand, bulk deposition of  $\text{Cl}_4\text{DD}$  was at most 3 times higher in the forest than in the clearing and during the winter months it was considerably lower. Since  $\text{Cl}_4\text{DD}$  is associated with airborne particulate matter, while  $\text{Cl}_4\text{DF}$  is in comparison much more strongly associated with the gas phase [5], the results suggest that the higher deposition fluxes observed in the forest in summer is related to dry gaseous deposition. The mechanism is however unclear.

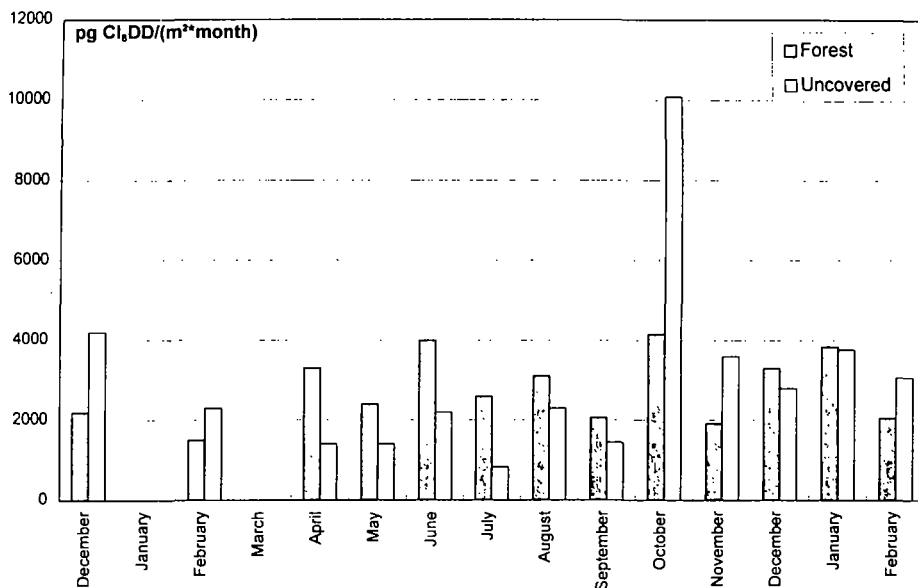


Fig. 3: Bulk deposition of Cl<sub>8</sub>DD in a mature spruce forest and in an adjacent clearing

The higher bulk deposition observed in the forest provides an explanation for the higher contamination of forest soils compared to unforested soils reported by Hagenmaier and Krauss [1]. Further investigations are underway with the aim of identifying the mechanism responsible for the higher deposition in this forest.

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