

An Investigation of the Deposition Pathways of Atmospheric PCDD/F to a Standardized Grass Culture

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Abstract

The accumulation of PCDD/F in *Lolium multiflorum* (welsh ray grass) was investigated using a system of experimental plots and chambers designed to identify the uptake pathways of organic contaminants in plants. The uptake of the Cl₄-Cl₆ homologue groups was found to occur primarily through dry gaseous deposition. Although the homologue pattern in the grass samples indicates that *Lolium multiflorum* is not representative of pasture grass, these results are first experimental evidence supporting the hypothesis that dry gaseous deposition plays a dominant role in the accumulation of PCDD/F in agricultural food chains.

Introduction

It has been shown that pasture grass is - indirectly through meat and dairy products - a major source of human exposure to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F)¹. The manner in which these compounds accumulate in the grass has remained unclear. There has been considerable research into the uptake of PCDD/F from soil. Recent studies have shown that soil does not contribute significantly to the levels in grass². Much less is known about plant uptake of PCDD/F from the atmosphere. A rough calculation based on limited deposition data indicated that the PCDD/F levels in pasture grass could be explained by any one of wet deposition, dry deposition of particles or dry gaseous deposition³. The purpose of the following experiment was to determine which of these deposition processes is responsible for the PCDD/F accumulation in a standardized grass culture - *Lolium multiflorum*.

Experimental

The experiment was designed to create different environments that exposed the grass to different possible uptake pathways. Seven environments were employed. Only the three most important will be described here:

1. *Reference Plot (Plot 1)* - The grass was grown in soil containing levels of PCDD/F typical for the Bayreuth area (ca. 1 ng I-TE/kg DW). The grass was placed on an

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open plot adjacent to the experimental chambers and exposed to all possible uptake pathways.

2. Reference Chamber (Chamber 1) - The grass was grown in the same soil as above but placed in a chamber (190 x 150 x 210 cm) that was supplied with 1000 m³/h of unfiltered air by a large fan. The chambers are described elsewhere⁴.

3. Particle Free Chamber (Chamber 2) - The grass was grown in the same soil as above and placed in an identical chamber. The only difference was that the air for this chamber was first passed through a glass fibre filter that removed the particles.

The seeding and care of the grass was conducted according to a method for standardized grass cultures⁵ with several modifications. The grass was grown in flower boxes. Water was provided through glass fibre wicks connecting the soil to a water reservoir. Following seeding the grass was allowed to grow outside for 4 weeks after which it was cut back to 4 cm. The grass boxes were then placed on the plot and in the chambers. The first exposure began on July 17, 1991. On August 9 the grass was once again cut back to 4 cm and the harvested grass was analysed (3 parallel samples for each exposure environment). A second exposure was conducted between August 9 and September 6. This grass was discarded. The third exposure ran from September 6 to October 18, and this harvest was also analysed (two parallel samples for each plot).

The exposure levels in each environment were quantified using air samples taken in both of the exposure chambers and adjacent to the reference plot. The samples were collected using a previously published method⁶ over a period of two weeks. Two samples were collected for each of the first and third exposures.

The grass samples were either freeze dried or dried in a special oven equipped with an XAD trap to capture any PCDD/F lost due to volatilization. The samples were minced in a blender and Soxhlet extracted for 48 hours in toluene. The filter samples were also Soxhlet extracted for 48 hours in toluene. The XAD traps from the gas phase sampling were eluted using n-hexane/acetone (1:1, v:v). All samples were cleaned up on LC columns of acid silica, basic silica and alox. The HRGC/HRMS analysis was conducted at a resolution of 10,000 on a VG Autospec Ultima.

Results

The concentrations of particle bound PCDD/F were similar in the reference chamber and outside for a particular sampling period, while the concentrations were 5 to 300 times lower in the particle free chamber. The concentrations of gaseous PCDD/F were also similar in the reference chamber and outside. The partitioning behaviour between particles and the gaseous phase reflected that previously observed at this location⁶. The concentrations of gaseous PCDD/F in the particle free chamber were comparable to those in the reference chamber during the third exposure period but up to 8 times higher during the first exposure. This can be attributed to blow-off of particle bound PCDD/F on the filter in the air supply. This effect was caused by the higher average temperatures during the first exposure (18.1°C) when compared with the preceding months during which the chamber had also operated. The temperature during the third exposure period was much lower (11.8°C) and the blow-off effect disappeared.

This blow-off effect was beneficial for the experiment, creating two distinct exposure scenarios for the two exposure periods. During the fall exposure period there is a large decrease in the concentration of particle bound PCDD/F between the two chamber while the concentrations in the gas phase are comparable. The first exposure period also has the decrease in the concentration of particle bound PCDD/F, but this is accompanied by a large increase in the gas phase concentration between chamber 1 and chamber 2.

The concentrations of $\Sigma\text{Cl}_4\text{DD}$ in the gas phase, on particles and in grass are plotted for the three exposure environments for the fall exposure period in Figure 1. The concentrations are all normalized with the concentration from the reference plot. The concentration in the particle phase fell by more than a factor of 6 between the reference plot and the particle free chamber. The concentration in the grass fell by only 20%, and this decrease was accompanied by a similar decrease in the concentration in the gas phase. This indicates that impaction of particles on the leaf surface was not an important deposition mechanism for Cl_4DD . A similar behaviour was observed for most of the other PCDD/F. Only Cl_8DD showed a large reaction to the decrease in exposure to particle bound substance.

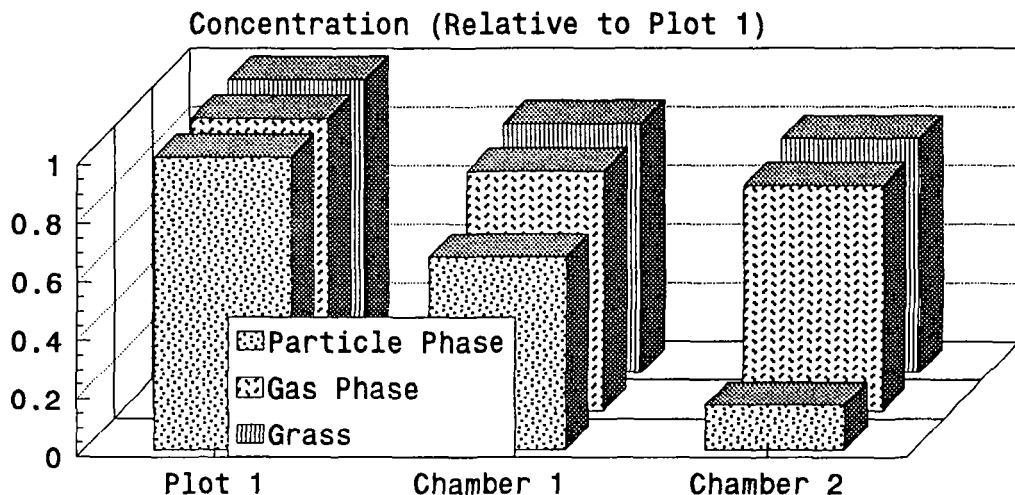


Figure 1: Plot of the Normalized Concentrations of $\Sigma\text{Cl}_4\text{DD}$ for the Fall Exposure

The results from the first exposure period are plotted for the same homologue group in Figure 2. Although the concentrations in the particle phase appear to have been only a factor of two lower in the particle free chamber than above the reference plot, the real difference was likely higher as the value in the particle free chamber represents the detection limit. Despite the decrease in the particle bound levels of Cl_4DD , the grass levels increased dramatically. This increase was accompanied by a nearly identical increase in the levels in the gas phase. This behaviour was observed for all $\text{Cl}_4\text{-Cl}_6\text{DD/F}$. A conclusive interpretation of the results for the $\text{Cl}_7\text{-}$ and $\text{Cl}_8\text{DD/F}$ was not possible due to the difficulty in obtaining artifact free samples of these compounds in the gas phase.

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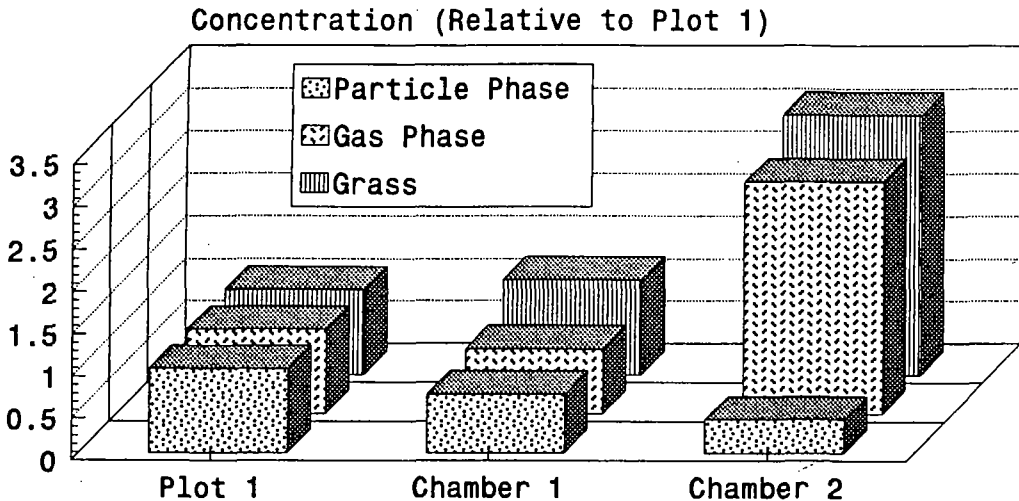


Figure 2: Plot of the Normalized Concentrations of $\Sigma\text{Cl}_4\text{DD}$ for the First Exposure

Discussion

The results show that dry gaseous deposition is the dominant uptake mechanism of $\text{Cl}_4\text{-Cl}_6\text{DD/F}$ in *Lolium multiflorum* grown under conditions typical for central Europe. Impaction of particle bound PCDD/F could be ruled out on the basis of the results from the third exposure period for almost all PCDD/F. Had other deposition mechanisms such as sedimentation of particles or wet deposition been important, one would have observed a significant decrease in the grass concentrations between the reference plot and the reference chamber where these processes were excluded. However, a small increase was generally observed for the $\text{Cl}_4\text{-Cl}_6\text{DD/F}$. This was attributed to a chamber effect which is the subject of continuing study.

References

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