

Determination of the Principal Pathways of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans to *Lolium multiflorum* (Welsh Ray Grass)

KERSTIN WELSCH-PAUSCH,
MICHAEL S. MCLACHLAN,* AND
GUNTHER UMLAUF

Ecological Chemistry and Geochemistry, University of Bayreuth, 95440 Bayreuth, Germany

This study presents experimental evidence that dry gaseous deposition is the dominant pathway of relatively involatile organic contaminants like polychlorinated dibenzo-*p*-dioxins and dibenzofurans to Welsh ray grass, an important species in agricultural food chains. The uptake pathways of these compounds to Welsh ray grass were studied under near natural conditions using a system of greenhouses and outdoor plots. Dry gaseous deposition was found to be the principal pathway of Cl₄–Cl₈DD/F to the grass leaves. The contribution of dry deposition of small particles (<2.9 µm) to the grass levels was negligible for all compounds studied. There was some evidence that the deposition of large particles was an important pathway for the uptake of Cl₇DD and Cl₈DD, particularly during the autumn period when the particle-bound concentrations of these compounds were higher. Soil-related pathways did not measurably influence the substance levels in the grass.

Introduction

Dairy products and beef are the source of about half of the exposure of the general population to polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) (1–3). Over 90% of the toxicity in the average diet that is associated with these compounds is attributable to the 2,3,7,8-substituted tetra- to hexachlorinated isomers. Tracing PCDD/F back through the agricultural food chain, it has been found that the dairy cow's uptake occurs primarily through the consumption of grass products such as hay and grass silage (4). The mechanism of accumulation of these substances in grass is thus a key process determining human exposure. A knowledge of this process would be desirable, both for risk analysis studies and in developing strategies to reduce human exposure.

Initially, research on plant uptake of PCDD/F focused on soil-related pathways. Although the early work was contradictory (5), recent studies by Hülster and co-workers have demonstrated that for a wide range of plants including a grass mixture the concentration of PCDD/F in soil has almost no influence on the concentration in aerial plant parts (6, 7). Although there are notable exceptions, such as plants of the genus *Cucurbita*, which are capable of taking up PCDD/F from the soil and efficiently translocating it to the leaves and fruits (8), it would appear that PCDD/F accumulate in plants largely through atmospheric deposition.

There are three general forms of atmospheric deposition: dry gaseous deposition; dry particle-bound deposition; and wet deposition of dissolved and/or particle-bound substance as rain, snow, or fog. Initially, it was thought that dry particle-bound deposition was the dominant atmospheric pathway to plants (9, 10). However, further study revealed that substantial fractions of airborne PCDD/F are present in the gas phase during the growing season (11, 12). A rough calculation of deposition using measured atmospheric concentrations showed that each of the three forms of deposition could plausibly explain the concentrations of 2,3,7,8-Cl₄DD measured in grass (13). The estimated deposition fluxes were very approximate due to the limited knowledge of the deposition and exchange processes occurring at and below the leaf surface. However, as none of the deposition processes can be readily neglected, a model of plant uptake of these compounds would be credible only if all of the major gaps in understanding for all three forms of deposition were to be eliminated.

Confronted with this imposing task, we decided to attempt to experimentally identify the major uptake pathway(s) under near natural conditions. If successful, research resources could then be more effectively focused on understanding just one form of deposition instead of three. A system of greenhouses and outdoor plots that creates environments where certain uptake pathways are amplified or excluded was constructed to address questions of this nature. This set up was initially employed in a study of the accumulation of polychlorinated biphenyls and a number of organochlorine pesticides in spruce needles. It was found that dry gaseous deposition was the dominant uptake pathway for these substances during the summer of 1990 (14, 15).

ambient air

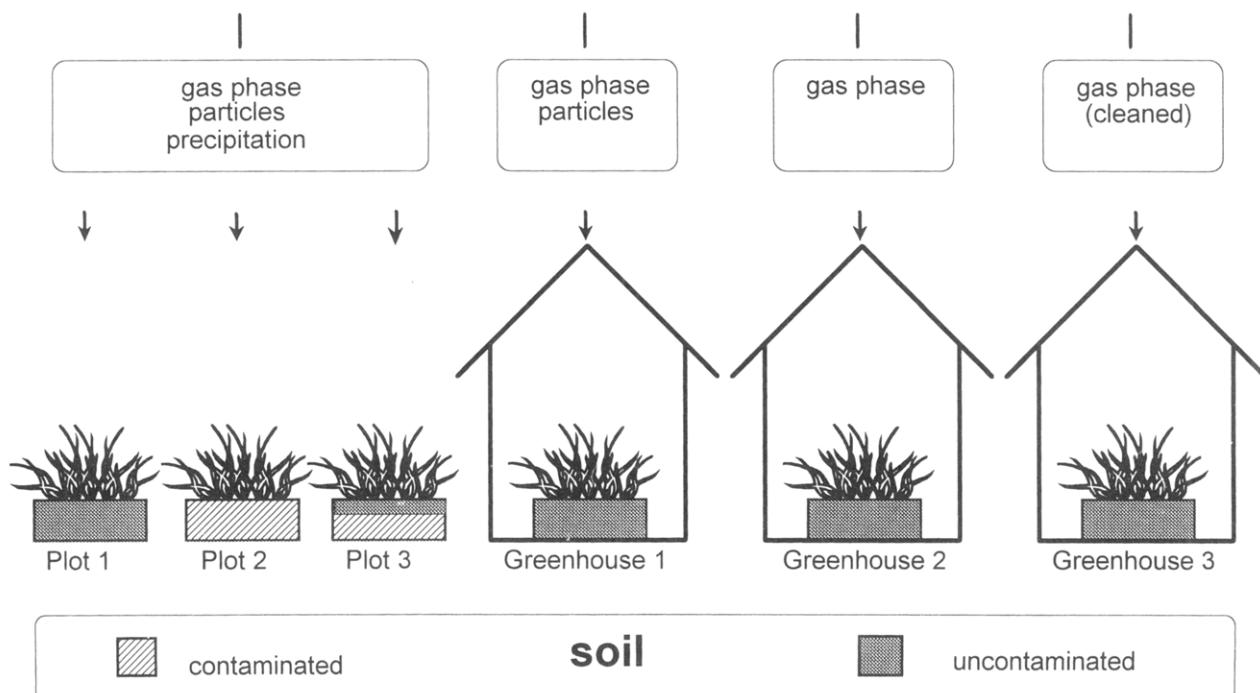


FIGURE 1. Illustration of the experimental concept with the intended exposure environments.

This paper describes the use of the same experimental system to determine the main pathway of PCDD/F to an agriculturally relevant grass culture. Grass leaves have very different surface properties than spruce needles, which could result in different deposition mechanisms dominating uptake. Furthermore, PCDD/F are considerably less volatile than the compounds studied in the first experiment and are thus more extensively bound to particles in the atmosphere, so that dry gaseous deposition would be expected to play a less dominant role. In this work, the focus was on dry particle-bound and dry gaseous deposition.

Experimental Section

Exposure Plots. The experiments were conducted in 1991 on the campus of the University of Bayreuth. The campus is situated to the south of the city, which has a population of 70 000 and lies in a rural area in northeastern Bavaria. The air concentrations of PCDD/F at this site are low, and we consider the site to represent a typical background situation for this area of Europe. The experiment was planned with six different exposure scenarios, three in greenhouses and three on outdoor plots. The experimental concept is illustrated in Figure 1. Experimental difficulties resulted in some deviations from this concept as is discussed in the Results section.

The greenhouses were made of normal window glass and measured 190 × 150 × 210 cm. Each greenhouse was ventilated with 1000 m³/h of air through a perforated ring tube placed along the walls on the floor of the greenhouse. Different exposure scenarios were created by introducing filters between the greenhouses and the radial fans that blew ambient air into the greenhouses. In the first greenhouse (G1), no filter was employed; in the second (G2), a glass fiber filter was used to remove the particle

phase from the air; and in the third (G3), an activated carbon filter and a glass fiber filter were installed in series with the purpose of generating a "contaminant free" atmosphere.

The outdoor plots were used to examine soil uptake pathways and to evaluate chamber effects. Although uptake from soil was expected to be of minor importance, we were aware of no studies of this question with Welsh ray grass and hence included the soil uptake pathways for the sake of completeness. The plots were adjacent to the greenhouses and were exposed to all forms of atmospheric deposition. A soil with a for this area typical background level of 1 ng of 2,3,7,8-Cl₄DD toxicity equivalents (TE, according to the NATO-CCMS system (16)) per kg dry weight (dw) was used for plot 1 (P1) and the greenhouses. Thus, P1 was the reference exposure scenario, being subject to soil and atmospheric conditions representative for the area. A mildly contaminated soil (17 ng of TE/kg dw) was used for P2. The same soil was used for P3, but it was covered by a 5 cm layer of the background soil to impair transfer of contaminated soil particles to the leaves or volatilization from the contaminated soil.

In Figure 1, the intended differences in the uptake pathways with respect to the reference plot (P1) are illustrated for each of the six exposure scenarios. In P2 and P3, the uptake from various soil-related pathways was increased, while in G1–G3, uptake from different atmospheric pathways was reduced or excluded. The greenhouse plots were subject to chamber effects, the relevance of which will be discussed later.

Grass Cultivation. *Lolium multiflorum* (Welsh ray grass) was selected as an important representative of the pasture grasses. On May 15, 75 g/m² seed (var. Ninak) was sown in flower boxes filled with the soil as described above. Both the contaminated and the uncontaminated soils were loamy

sands taken from farmers fields close to Bayreuth. The organic carbon contents were 1.5% and 1.3%, respectively. The flower boxes were initially watered from above until the seed had germinated. Thereafter water was supplied from a second flower box placed under the first. The ends of glass fiber wicks that had been placed in the soil of the upper box were immersed in the water reservoir in the lower box. A fertilizer solution was added to the water reservoir following each harvest (see below). Initially, all flower boxes were outside.

On July 17, the grass was cut back to a height of 4 cm, and the flower boxes were distributed among the different plots and greenhouses. The flower boxes on the outdoor plots were arranged adjacent to each other on the ground, and the surrounding grass was kept short. In the greenhouses, the boxes were placed on a grate that was installed above the ring tube that supplied the air. On August 9, the grass in the greenhouses and on the plots was cut back to 4 cm, packed in aluminum foil, and stored at -18 °C for future analysis. A second harvest on September 6 was discarded, while the third harvest on October 18 was also analyzed. The summer harvest (August 9) yielded sufficient material for three parallel grass samples per exposure variant, while the autumn harvest (October 18) sufficed for just two.

Monitoring of the Experimental Environments. The temperature and relative humidity were measured continuously in each of the greenhouses and outdoors.

The contaminant concentrations in the gas and particle phases were measured in the grass canopies in each of the three greenhouse atmospheres as well as outdoors. Two measurements, each lasting two weeks, were conducted in summer and two during the autumn exposure period. A glass fiber filter/XAD trap sampling system developed by our research group was employed. It has been shown that the values of the gas and particle phase concentrations of semivolatile organic compounds obtained with this sampler are comparable with those obtained using other methods of separately collecting gaseous and particle-bound substances (17). Furthermore, the PCDD/F collection efficiency and subsequent extractability of the XAD trap have been verified (12). The reproducibility of the method was demonstrated using a similar sampler (18). The samplers were operated at 10 m³/h for 14 days, yielding samples of about 3300 m³. The glass fiber filters (Schleicher & Schüll, no. 8) were dried in a desiccator for 24 h and weighed, both prior to and after sampling, in order to determine the concentration of particles in the sampled air. The filter, primary XAD (Amberlite XAD-2) cartridge, and backup XAD cartridge (used to detect breakthrough of the primary cartridge) were each analyzed separately.

Analytical Methodology. All analyses were conducted using HRGC/HRMS with quantification by isotope dilution. A mixture of 12 ¹³C₁₂-labeled 2,3,7,8-substituted PCDD/F congeners representing all 10 Cl₄-Cl₈ homolog groups was added to the extraction solvent prior to extraction.

The grass samples were dried, pulverized in a blender, and Soxhlet extracted in toluene for 48 h. A minimum of 50 g dry weight (dw) was extracted. Two different drying procedures were employed. One sample from each exposure variant and harvest was dried at 100 °C for 20 h in a glass column. The moisture was removed from the column by a gentle stream of purified nitrogen. After leaving the column, the nitrogen was passed through an XAD trap at room temperature to collect any PCDD/F that might

have been carried out of the column. The XAD was extracted together with the pulverized grass. The remaining grass samples were freeze dried.

The filter samples were Soxhlet extracted for 48 h in toluene. The XAD samples were extracted by immersing the XAD in *n*-hexane/acetone (1:1; v:v) for 30 min and then draining off the solvent. The XAD was then immersed a second and a third time in fresh solvent, which was drained off immediately and added to the first extract. The efficiency of this extraction procedure was confirmed in preliminary experiments by post extracting the XAD for 48 h in toluene.

The extracts were first cleaned up on a combined Na₂SO₄, H₂SO₄/silica gel, silica gel, and NaOH/silica gel column that was eluted with *n*-hexane (19). The dimensions of the column and the volume of *n*-hexane varied with the sample matrix and sample size. The purified extract was then fractionated on a basic alumina column (19). The PCDD/F fraction was reduced almost to dryness, a labeled recovery standard was added; the sample was again reduced almost to dryness and then taken up in a small amount of toluene. The recovery of the recovery standard using this method is virtually quantitative.

The samples were analyzed using an HP-5890 II gas chromatograph coupled to a VG-Autospec Ultima mass spectrometer operating in EI mode at 34 eV with a resolution of 10 000. An HP Ultra 2 capillary column (0.25 mm × 0.10 μm) was employed. Two masses in the M⁺ isotope cluster were monitored for each analyte and each internal standard. When interferences were encountered, more masses were monitored.

Results and Discussion

Analytical Quality Control and Variability of the Measured Values. The recovery of the internal standards was in all cases satisfactory. It was somewhat lower for the grass samples (70–80% for 2,3,7,8-Cl₄DD) than for filter and XAD samples (85–95%), likely due to the larger sample volume and more extensive handling of the grass samples.

The analytical blanks, which were run regularly, were relatively stable. When the quantity in the sample did not exceed the maximum blank by a factor of 3, the value was not included in the data set.

A comparison of the plant samples that had been freeze dried (two of three parallel samples from the summer, one of two parallel samples from the autumn harvest) with those that had been oven dried showed no significant differences for most of the substances studied. However, the concentrations of Cl₇DD and Cl₈DD were significantly higher (paired *t*-test, 95% confidence level) in the oven-dried samples. A comparison of the results for these two substances in samples from different plots that showed similar concentrations for all other compounds (e.g., P1, P2, and P3 in summer, see below) revealed a much higher variability in the oven-dried samples. It was concluded that oven drying did not produce reliable results for Cl₇DD and Cl₈DD, and these data were not included in the final dataset.

As the limited amount of sample material restricted the number of parallel grass samples, it was important to have a reproducible analytical method. Three parallel samples from P1/summer were analyzed following freeze drying. The agreement between the parallels was very good, with the maximum coefficient of variance (CV) being 18% (mean 12%).

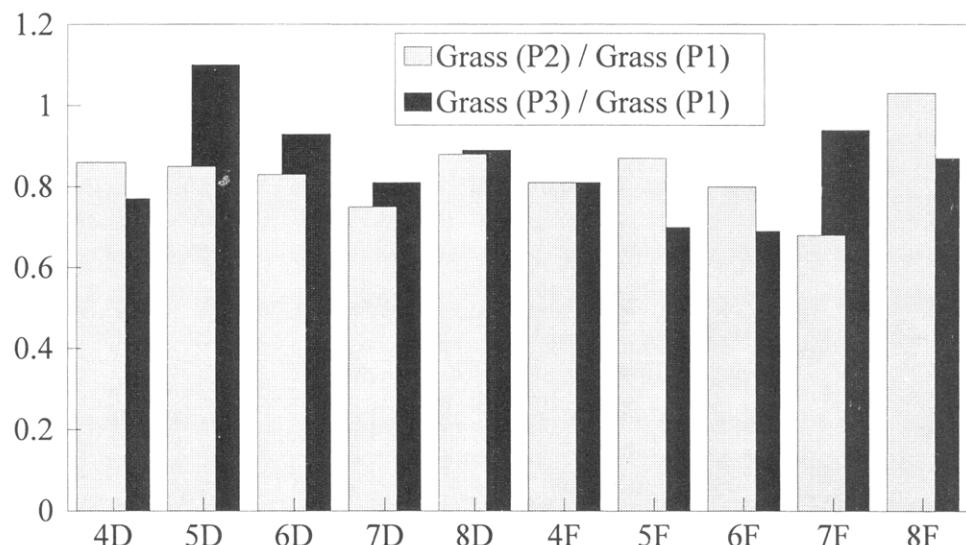


FIGURE 2. Plot of the quotients of the PCDD/F homolog concentrations in grass between P2 and P1 and between P3 and P1 for the summer harvest.

The coefficient of variance could also be determined for the summer grass harvest for each of the other exposure plots, it being noted that in these cases both of the grass drying methods were employed. The mean CV was in this case 16%; the maximum was 43%. For the Cl₄-Cl₆DD/F from P1, G1, and G2 that are of primary importance in the following discussion, there were only two values above 20% (23% and 30%). Although no CV could be determined for the autumn harvest as only two grass samples could be analyzed, there was no evidence that the error was larger than during the summer, the average percent deviation from the mean being 12%.

No parallel air samples were collected. However, in a previous study using a very similar method the mean CV for the PCDD/F homologs in a set of three parallel air samples was 5%; the maximum was 9% (18).

In the following, the results are discussed using quotients of grass concentrations and quotients of air concentrations. Using conservative CV values of 23% for grass and 9% for air, the 95% confidence intervals for the estimated quotients are $\pm 38\%$ and $\pm 15\%$ of the respective values. Hence, only changes in the quotients larger than a factor of about 2 for grass and 1.4 for air can be considered to be significant.

Uptake Pathways Related to Soil. The influence of PCDD/F uptake from soil on the grass concentration can be seen by comparing P1, P2, and P3. If any soil uptake pathway (e.g. root uptake and translocation; soil particle advection to leaves; or volatilization from soil and adsorption on leaves) made a significant contribution, then the substance levels from P2 should be higher than from the reference P1. If root uptake and translocation was an important pathway, then the concentration from P3 should also be higher.

The quotients of the concentrations of the PCDD/F homologs in grass from P2 and P1 and from P3 and P1 (summer) are shown in Figure 2. In light of the variability in the data as discussed above, there is no evidence that the concentrations in grass from P2 or P3 were significantly higher than those in grass from P1 for any homolog, even though the soil levels in P2 and P3 were more than an order of magnitude higher. The results for the autumn harvest were similar. This is further evidence that soil is not a

direct source of the majority of PCDD/F in grass grown under conditions typical for central Europe.

Atmospheric Exposure Conditions. The average temperature in the greenhouses was 5 °C higher than outdoors; the average relative humidity was 10% lower.

The PCDD/F concentrations measured in ambient air varied between 750 and 2500 fg¹ m⁻³ ΣPCDD/F and lay in the same range as the levels measured at a nearby site 2 years previously (12, 20). The concentrations in the two summer samples were similar, whereas the levels increased during autumn. This is in agreement with the results of the earlier study. The average concentrations of the two summer samples were used in the interpretation of the summer data, while the average concentrations of the autumn samples were used for the autumn data set. No PCDD/F were detected in the backup cartridges above the level of the laboratory blanks.

In G1 (unfiltered), the concentration of particle mass in the air was 40–50% lower than outdoors, reflecting the loss of large particles in the air ducts. Parallel impactor measurements of the particle size distribution in G1 and outside showed that while the concentrations of particles with aerodynamic diameters <2.9 μm were similar in both environments, the greenhouse air contained less than 20% of the particles with aerodynamic diameters >2.9 μm that were present in the outdoor air. As a result the dry deposition of particles will be subdivided into the deposition of “small” particles and “large” particles in the remainder of the paper.

The particle-bound concentrations of PCDD/F were reduced to a lesser extent (5–40%) than the concentration of particle mass. This is in agreement with other work, which has shown that most particle-bound PCDD/F at this site is associated with smaller particles (21).

Interestingly, the losses between ambient air and G1 decreased with increasing degree of chlorination. Since the PCDD/F homolog pattern has been found to be very similar in all particle size classes (21), particle losses in the duct cannot explain this effect. It may be that the shift in the gas/particle partitioning equilibrium caused by the higher temperatures in G1 resulted in losses of the more volatile compounds from the particles on the filter (sampling blow-off). This effect was not discernible in the gas-phase

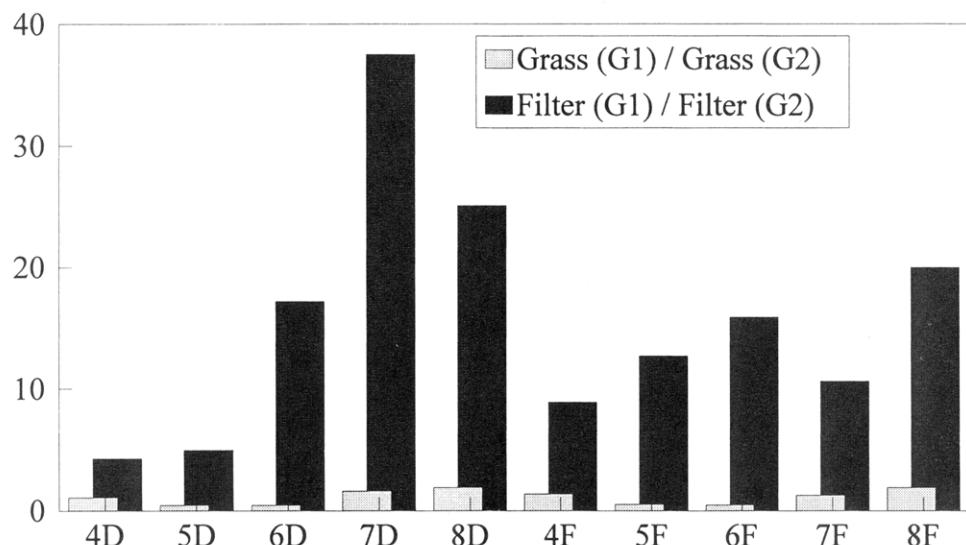


FIGURE 3. Plot of the quotients of the PCDD/F homolog concentrations between G1 and G2 for the grass and filter samples from the autumn harvest. The filter (G2) values represent blank levels.

concentrations, which were similar in G1 and outside. However, the gas-phase concentrations of the lower chlorinated homologs were higher than the particle-phase levels, making it difficult to observe such an effect.

The particle-phase concentrations in G2 were low as expected. No PCDD/F was detected above the level of the blanks. The gas-phase concentrations in G2 should have been the same as in G1. This was the case for the autumn samples, but in the summer the concentrations in G2 were up to four times higher. This effect, which had not been observed during preliminary tests of the greenhouses, was attributed to blow-off of PCDD/F from the particles that had collected on the glass fiber filter in the air supply system. The high temperatures during the summer growth period likely induced a shift in the gas/particle equilibrium of the particles collected during the cooler preceding weeks.

In G3, both the gas-phase and the particle-phase concentrations should have been considerably lower than in G1. This was not the case. Both the gas phase and, more markedly, the particle phase had high concentrations of PCDD/F that in some cases exceeded those in G1. Particularly surprising were the high levels of lower chlorinated PCDD/F found in the particle phase. This had not been observed during preliminary tests or during previous experiments. Prior to this study, the air supply system in G3 had been modified to increase the efficiency of the activated carbon filter. In the process, a second particle filter located upstream of the activated carbon filter was removed, leaving only the downstream particle filter. It was concluded that the artifact was due to atmospheric particles eroding activated carbon that had adsorbed PCDD/F out of the gas phase (i.e., predominantly the lower chlorinated compounds). The eroded activated carbon must have been fine enough to pass through the particle filter in the air duct but was then collected on the filter in the air sampler. As a new activated carbon filter was installed prior to this study, nothing unusual was observed during the preliminary testing. When a second particle filter was placed upstream of the activated carbon filter the year following this experiment, the artifact disappeared, and both the particle-phase and gas-phase concentrations in the greenhouse were well below the levels in ambient air.

In summary, the experimental setup did not perform as intended, but it nevertheless provided a useful basis for the interpretation of the PCDD/F concentrations in grass. While the results from G3 had to be discarded as the atmospheric environment in this greenhouse was dominated by an unnatural artifact, this was to some degree compensated by the—in hindsight fortuitous—blow-off artifact in the air supply of G2 during the summer. The two harvests provided two different exposure scenarios for G1 and G2:

(a) During the autumn, the gas-phase levels in the two greenhouses were similar while the particle-bound levels were much lower in G2. This allowed an evaluation of the importance of the dry particle-bound deposition pathway during that part of the growing season when particle-bound concentrations in the air are highest.

(b) During the summer, there was a similar gradient in the particle-bound concentrations between G1 and G2, but this was accompanied by gas-phase levels in G2 that were up to 4 times higher than in G1. This situation yielded information on the importance of dry gaseous deposition.

Dry Deposition of Small Particles. The results for the autumn harvest are shown for the 10 PCDD/F homologs in Figure 3. The quotients of the grass concentrations in G1 and G2 are plotted, as are the quotients of the particle-bound concentrations. Note that the latter represent minimum values since the quotients were calculated using the method blanks for the particle filters in G2. The particle-bound concentrations were up to a factor of 35 higher in G1 than the blank levels measured in G2. However, the concentrations in grass were at most a factor of 1.9 higher and in some cases lower in G1 than in G2. In view of the data variability, these differences are not significant. Since all other environmental parameters such as temperature, humidity, air turbulence, gas-phase concentrations, etc. were similar or virtually identical in the two greenhouses, it can be concluded that the deposition of small particles did not measurably influence the concentrations of the PCDD/F in the grass.

Dry Gaseous Deposition. Figure 4 summarizes the results for PCDD/F from the summer harvest. In this case, the quotients of the gas-phase concentrations in G2 and G1 are plotted as well as the quotients of the grass concentrations. The blow-off effect is manifested in up to

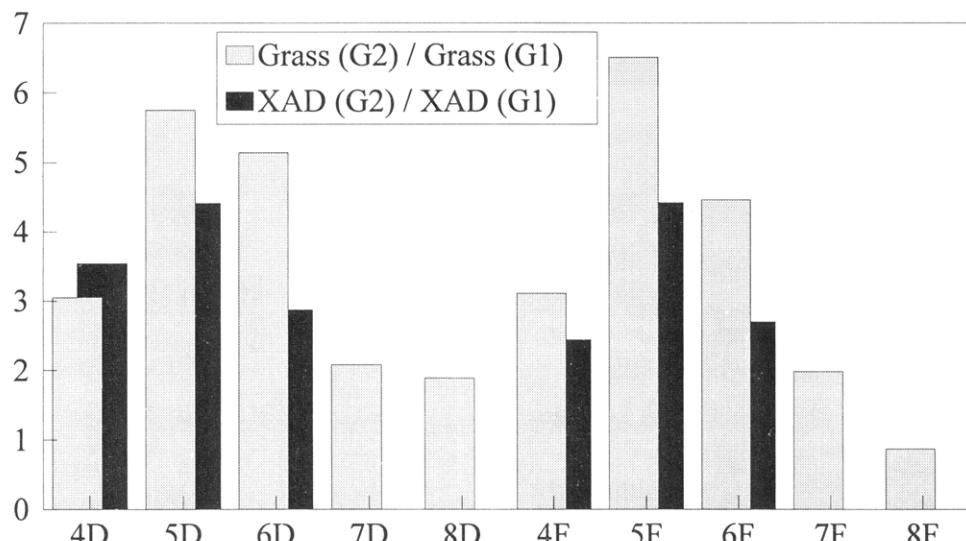


FIGURE 4. Plot of the quotients of the PCDD/F homolog concentrations between G2 and G1 for the grass and XAD samples from the summer harvest. The XAD quotients are not included for Cl₇–Cl₈DD/F due to the sampling artifacts suspected to be associated with the measured values.

4.5 times higher levels of gaseous Cl₄–Cl₆DD/F in G2 compared to G1. These differences are highly significant (see the discussion of data variability above). The presence of a blow-off effect for the Cl₇–Cl₈DD/F could not be verified due to their very low concentrations in the gas phase and the likelihood of sampling artifacts for compounds with such low vapor pressures.

In contrast to the autumn experiment, the grass concentrations in this case responded to the differences in the exposure situation. The grass levels in G2 were significantly higher than the levels in G1. The levels increased with increasing gaseous levels, and the relative increases for the homologs in grass and in the gas phase generally ran parallel to each other. Apart from the significantly different gaseous concentrations, the only other difference in the greenhouse environments was the much lower levels of particle-bound PCDD/F in G2, which would have resulted in lower not higher grass concentrations. Hence, it is concluded that the accumulation of Cl₄–Cl₆DD/F in the greenhouses was largely determined by the gas-phase concentration of these compounds. While most of the Cl₇–Cl₈DD/F also show higher levels in G2, no firm conclusions can be drawn since it was not possible to accurately monitor the gas-phase concentrations for these compounds.

Interestingly, the relative increase in the grass concentrations was higher than the relative increase in the gaseous concentrations. While this could be interpreted as evidence of nonlinearity in the grass/gas-phase uptake behavior, we think it was due to the different dynamics in the gaseous concentrations. The elevated concentrations in G2 were caused by filter blow-off, which is much stronger at elevated temperatures. At night when it was cool, there was likely little blow-off, resulting in similar levels of gaseous PCDD/F in G1 and G2. Under hot midday conditions, blow-off would be much more significant, resulting in concentration differences between G2 and G1 far in excess of the average behavior that was measured. These peaks in the gaseous concentration would lead to an accumulation in excess of that expected from the average levels.

Comparison of the Greenhouses and the Outdoor Reference Plot. The results from the greenhouse with untreated air (G1) and the outdoor reference plot (P1) are

compared in Figures 5 (summer harvest) and 6 (autumn harvest). The quotients of the grass concentrations are plotted as well as the quotients of the gas-phase concentrations. Most of the quotients are close to 1, indicating that both the gas phase and the grass concentrations were similar in the two environments. Two notable exceptions are the high values for Cl₄DD and Cl₈DD in the grass from the fall exposure, which reflect the much higher concentrations of these compounds found in the grass of all three outdoor plots. The grass quotients are also generally less than the gas-phase quotients for the more volatile homologs. Since the results above indicated that the gas-phase concentration is the major factor determining the grass level for the Cl₄–Cl₆DD/F, the systematic differences in the quotients indicate that the grass outside did not accumulate gaseous Cl₄–Cl₆DD/F as fast as would be expected from the greenhouse results. However, before the greenhouse results are extrapolated to the outdoor situation, the following chamber effects should be considered:

(1) *Differences in Plant Properties.* The different climate in the greenhouses may have influenced the development of the plants and resulted in grass indoors that had different contaminant uptake properties than the grass grown outside. This was not explicitly investigated, but no differences in plant texture, plant color or biomass production were observed.

(2) *Differences in Temperature.* The gas/solid partitioning of organic compounds can be expected to vary with temperature, with higher temperatures resulting in a shift in partitioning away from the solid phase (grass) toward the gas phase. Since dry gaseous deposition was the major pathway for the uptake of Cl₄–Cl₆DD/F, one might expect the concentrations in grass from the greenhouses to be lower. However, this temperature effect is only to be expected at or close to an air/plant equilibrium condition. When the plant levels are far below the equilibrium state, the contaminant concentration is determined by the uptake kinetics for which no strong temperature dependency is expected. As a subsequent paper will show (22), it is unlikely that the PCDD/F in the grass and in the gas phase were close to a state of equilibrium. Furthermore, there was no evidence of this chamber effect in the experimental results,

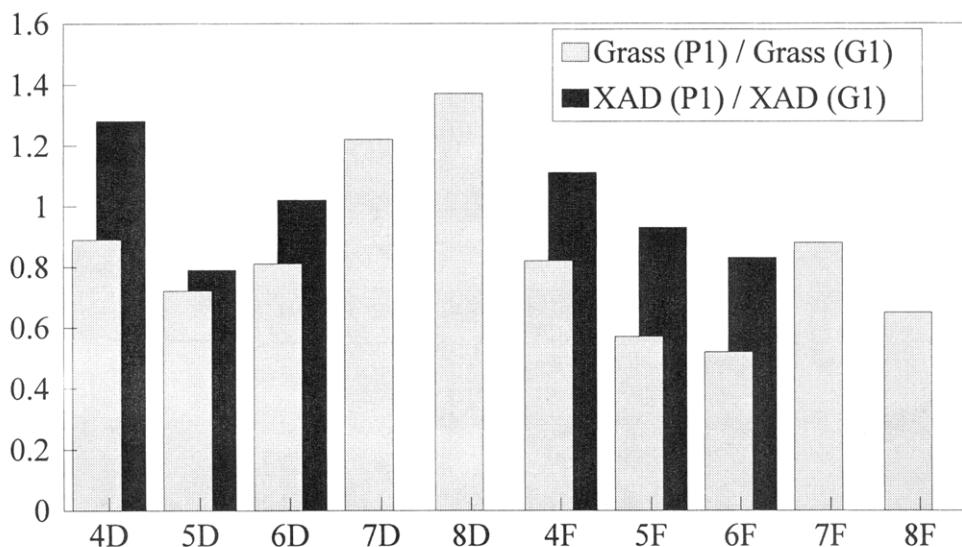


FIGURE 5. Plot of the quotients of the PCDD/F homolog concentrations between P1 and G1 for the grass and XAD samples from the summer harvest. The XAD quotients are not included for $\text{Cl}_7\text{-Cl}_8\text{DD/F}$ due to the sampling artifacts suspected to be associated with the measured values.

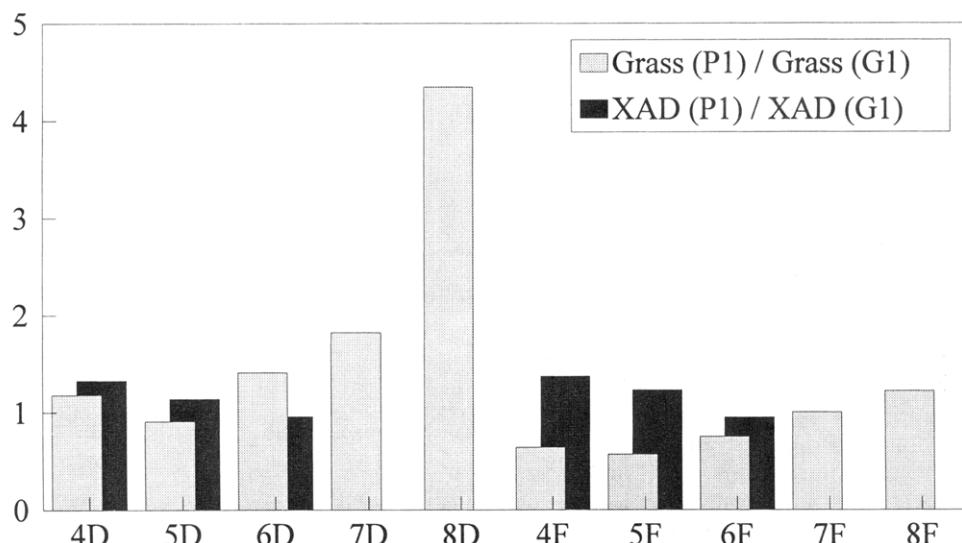


FIGURE 6. Plot of the quotients of the PCDD/F homolog concentrations between P1 and G1 for the grass and XAD samples from the autumn harvest. The XAD quotients are not included for $\text{Cl}_7\text{-Cl}_8\text{DD/F}$ due to the sampling artifacts suspected to be associated with the measured values.

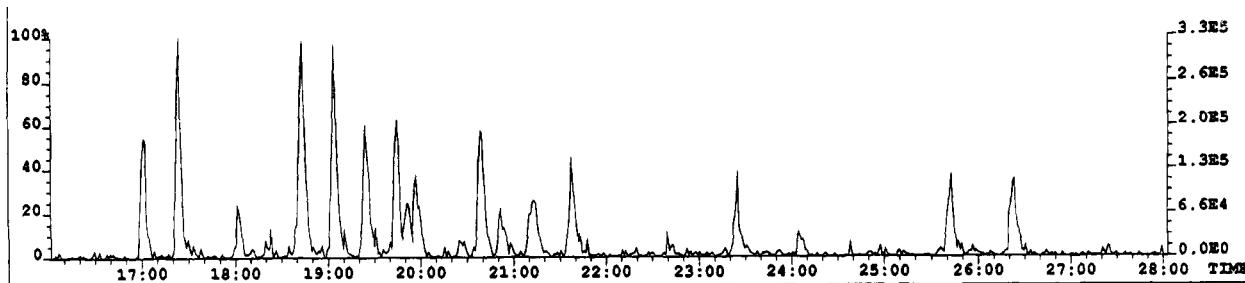
as the concentrations of $\text{Cl}_4\text{-Cl}_6\text{DD/F}$ in grass from the greenhouses tended to be higher, not lower, than the concentrations in grass from the outdoor plots. Hence, it is felt that this chamber effect was not significant.

(3) *Differences in Turbulence.* The turbulence in the plant canopy influences the deposition velocity of particles and gases to the plant surfaces. Higher turbulence results in a thinner laminar boundary layer at the leaf surface and hence higher deposition velocities. The turbulence in the greenhouses caused by the high ventilation rate was greater than the average turbulence on the outdoor plots. Thus, one would expect that small particles which are deposited by impaction or diffusion would accumulate more rapidly on grass in the greenhouses. Since this pathway did not make a measurable contribution to the grass levels in the greenhouses, it was likely even less important outdoors. A similar effect, namely, higher concentrations in the grass from the greenhouses, could be expected for contaminants for which the gas-phase resistance is the dominant resistance for dry gaseous deposition and where the concentra-

tions in the grass were determined by the deposition velocity, i.e., the grass was well below equilibrium with the air. Both of these conditions were likely met in the experiments (22). Hence, the greater turbulence in the greenhouses is a plausible explanation for the lower quotients of the grass concentrations compared to the gas-phase concentrations that were noted for $\text{Cl}_4\text{-Cl}_6\text{DD/F}$ in Figures 5 and 6.

(4) *Differences in Particle Size Spectrum.* As was previously mentioned, large particles were lost in the air supply system of G1, creating a further difference between the greenhouse and outdoor environments. If the deposition of these particles were a significant source of the PCDD/F in the grass, then the homolog pattern in the grass should show evidence of the homolog pattern in the particles. The particle pattern was dominated by Cl_7DD and Cl_8DD , with only small quantities of the lower chlorinated congeners. In the summer the homolog pattern in the grass from the outdoor plots was dominated by Cl_4DF , with relatively low quantities of the Cl_7DD and Cl_8DD homologs. This indicates

P 1:



G 1:

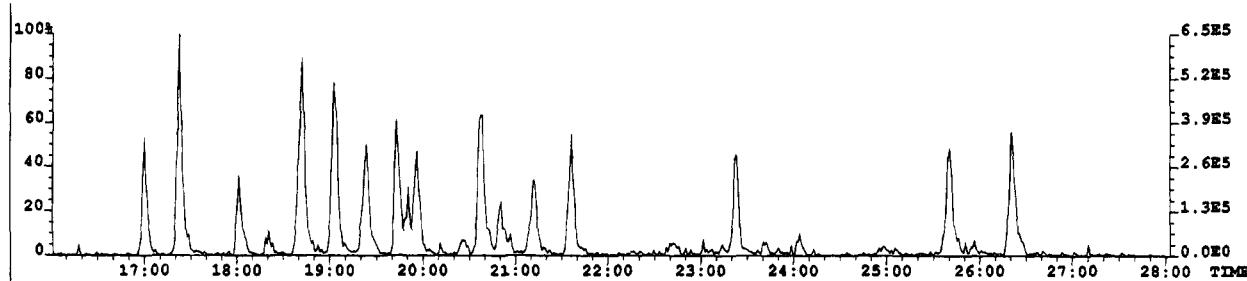


FIGURE 7. Typical chromatograms of Cl₅DF in grass from the summer harvest of P1 and G1.

that sedimentation of large particles was not the dominant pathway of the PCDD/F to the grass. While in autumn the same homolog pattern was seen in the grass from the two greenhouses, the grass from the outdoor plots showed a stronger contribution from Cl₇DD and, in particular, Cl₈-DD. This suggests that the deposition of large particles may contribute to the uptake of these two compounds in grass during the cooler parts of the growing season (spring and autumn), perhaps because of the temperature-driven shift in atmospheric partitioning toward the particle phase, or perhaps because of the presence of more contaminated large particles due to higher local emissions as a result of home heating. In summary, this chamber effect provides a plausible explanation for the high quotients of the grass concentration observed for Cl₇DD and Cl₈DD in Figure 6.

(5) *Absence of Precipitation.* Precipitation could both transport contaminants to as well as remove them from plant surfaces. A total of 31 mm of rain fell during the summer, and 76 mm fell during the autumn exposure. While rain samples were not collected throughout this experiment, measurements in this and later years indicate that the wet deposition of PCDD/F lay in the same order of magnitude as the amount taken up by the grass. The homolog pattern in rain at this site is also dominated by Cl₇DD and Cl₈DD (23). The absence (summer) or weak expression (autumn) of this pattern in the grass would indicate that a large fraction of the PCDD/F in rain did not remain on the grass leaves. However, the high quotients of the grass concentration observed for Cl₇DD and Cl₈DD in Figure 6 might well be attributable to precipitation and not the dry deposition of large particles as suggested above. This experiment does not allow firm conclusions regarding the influence of rain or other forms of wet deposition like fog.

(6) *Differences in the UV Light Spectrum.* It has been reported that 2,3,7,8-Cl₄DD is photolytically degraded on

the surfaces of reed canarygrass leaves (24). This indicates that photodegradation could have a significant influence on the accumulation of PCDD/F in grass. High-energy UV radiation in the 295–340-nm range is necessary for photolytic reactions of PCDD/F. The greenhouses were made out of normal window glass with a UV cutoff at 350 nm. Hence, the UV radiation present in the greenhouse was much lower than that present outdoors. The possible consequences of this chamber effect can only be indirectly estimated. If the PCDD/F reacted photochemically, it is unlikely that they all reacted with the same time constants. The chlorine substitution pattern would be expected to influence the lability of the molecule. If the reaction was important, the relative concentrations of the isomers should have been different when the grass was exposed to much higher levels of UV light. However, the isomer patterns in the grass from G1 and P1 were very similar, as illustrated for Cl₅DF in Figure 7. This indicates that photodegradation was not an important factor in the accumulation of the PCDD/F in the grass. However, this interpretation needs to be verified.

To summarize, there are a number of possible chamber effects that could speak against an extrapolation of the chamber results to outdoor conditions. In two cases, namely, the differences in the turbulence levels and the differences in the particle size spectra, the effects are plausible and can be observed in the experimental results. For the remaining chamber effects that were identified, no evidence was found indicating that these effects would significantly impair the comparison of the greenhouse and outdoor results. Furthermore, the good agreement between the grass concentrations measured in G1 and P1 means that if one of these chamber effects was indeed strong, it must have been almost exactly compensated by another chamber effect, which is unlikely. Hence, while the role of

photodegradation and wet deposition should be further investigated, it would appear reasonable to extrapolate the principal results of the greenhouse experiments to the outdoor plots, namely, the dominance of dry gaseous deposition for the uptake of Cl₄-Cl₆DD/F and the absence of a significant input from the deposition of small particles.

Discussion of the Results

These results are valid for this species and for these conditions. The gas/particle partitioning of the compounds, which is one important factor influencing the relative importance of the different atmospheric pathways, is likely similar in many agricultural environments. A second set of factors, the particle concentration and size spectrum, can vary considerably. Dry particulate deposition and/or wet deposition could play a more important role, particularly for the higher chlorinated compounds, when larger quantities of large particles are present. Extrapolation to other plant species remains uncertain. The variability in root translocation behavior has been demonstrated elsewhere (6-8). There is an enormous diversity in the chemistry and structure of leaf surfaces that could influence the relative contributions of the different atmospheric deposition pathways. More study is needed in this area.

Nevertheless, these results represent first experimental evidence that dry gaseous deposition is the key process governing the accumulation of relatively involatile compounds like PCDD/F in agricultural food chains. As such, the plant concentrations can be expected to be governed by time in the case of uptake limited by kinetics or by temperature in the case of equilibrium partitioning. Which of these two situations prevails will be the subject of a subsequent paper (22). The gas-phase concentrations will in either case determine the plant concentrations. This could lead to the ironic situation that a reduction in atmospheric particle loads leads to an increase in the contamination of the food chain by shifting the gas/particle equilibrium of PCDD/F in the atmosphere toward the gas phase. Furthermore, the dominance of dry gaseous deposition means that deposition measurements using dust collectors, which collect predominantly particulate matter, will not be reliable indicators of plant or food chain contamination. Finally, dry gaseous deposition is at least partly reversible. Hence, plants will act as buffers for these compounds in the atmosphere. Although this buffering effect is not currently observed for PCDD/F due to the predominance of continuing emissions in determining the air concentrations, it could play an important role in the long-term fate of these compounds.

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Supplementary Material Available

The original XAD, filter, and grass data obtained in this study (6 pages) will appear following these pages in the microfilm

edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for \$16.50 for photocopy (\$18.50 foreign) or \$12.00 for microfiche (\$13.00 foreign), are required. Canadian residents should add 7% GST.

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