# PATHWAYS AND MECHANISMS OF PCDD/F-INPUT INTO AGRICULTURAL FOOD CHAINS

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## Introduction

The exposure of the general population to polychlorinated dibenzo-p-dioxins and *dibenzofurans (PCDD/F) occurs almost exclusively through the diet.* The most important source of human exposure is milk and milk products, which account for about one third of the daily intake of the average person in Germany and The Netherlands. Meat products, and in particular beef, account for a further third, while the remaining third of the PCDD/F in the general diet originates in fish (Fürst et al., 1990; Beck et al., 1989; Theelen et al., 1993). Hence, in order to develop effective strategies to reduce human exposure to PCDD/F, we must gain an understanding of the pathways by which these compounds enter and accumulate in agricultural food chains, most particularly in beef and dairy cattle.

In Bayreuth we focused our initial research on the behaviour of PCDD/F and other hydrophobic compounds in milk cows. The absorption of PCDD/F (McLachlan et al., 1990) and PCB (McLachlan, 1993) was measured in a lactating cow. This led to a mathematical model of the behaviour of hydrophobic organic contaminants in cattle (McLachlan, 1994). This work, which was summarised at the previous German Dioxin Information Meeting (McLachlan, 1991), has since been by and large substantiated by other authors (Olling et al., 1990; Heeschen et al., 1994).

An important result of this work was the observation that feed is the primary source of exposure of cattle to PCDD/F (McLachlan et al., 1990). Analyses of different feed components from farms in the Bayreuth area revealed that more than half of the PCDD/F uptake of cows comes from grass (McLachlan, 1992), making grass a crucial vector of PCDD/F to humans. We have therefore focused our more recent work on understanding the accumulation of PCDD/F in grass, working initially with Lolium multiflorum (ryegrass), an important feed grass.
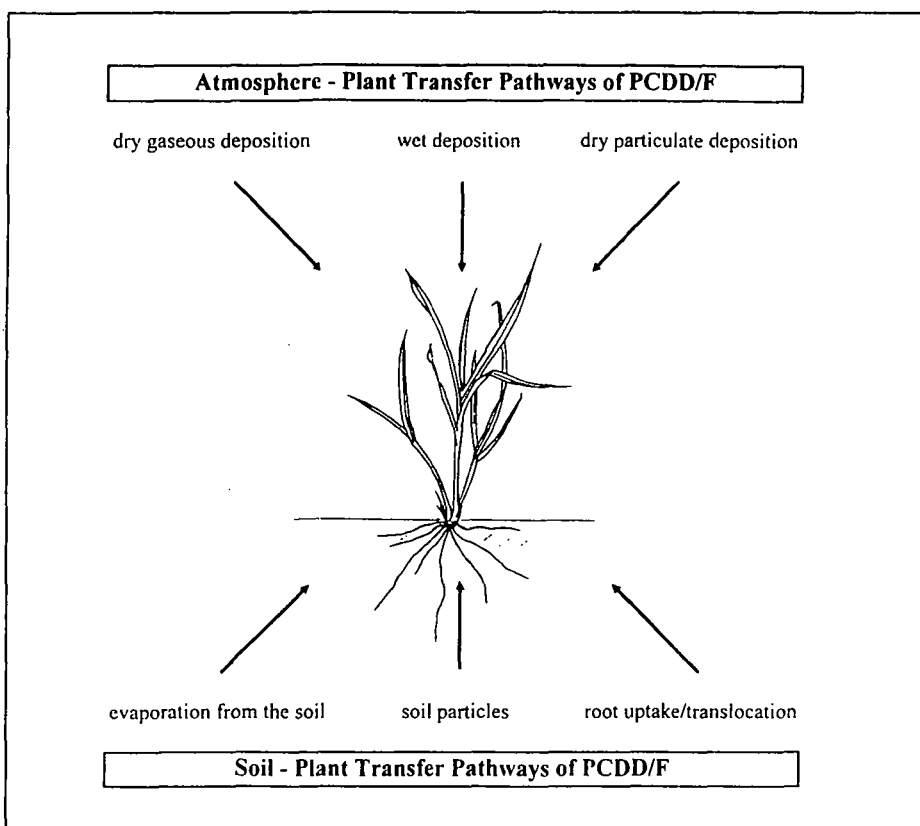
This paper begins with a description of possible pathways of PCDD/F into plants. An experiment is described which identified the primary pathway of PCDD/F to Lolium multiflorum. This is followed by a description of laboratory experiments to characterise the main mechanism of plant uptake. This work resulted in a

mathematical model of the accumulation of semivolatile organic compounds in the grass culture, which was tested using field data. The results and implications of this field validation are discussed. The paper closes with a short summary of what we know and a list of important open questions.

**Pathways of PCDD/F to Feed Crops**

There are two possible immediate sources of environmental contaminants to plants: air and soil. Each of these sources is associated with three possible pathways to the aerial plant parts (see Fig. 1).

Contaminants in soil can be taken up by the roots and translocated through the root tissue to the stem and leaves. Alternatively, contaminated soil particles can be transported directly to the leaf surface through wind or splash. A third possibility is the volatilisation of chemicals from soil and subsequent adsorption to aerial plant surfaces.



**Atmosphere - Plant Transfer Pathways of PCDD/F**

dry gaseous deposition      wet deposition      dry particulate deposition

evaporation from the soil      soil particles      root uptake/translocation

**Soil - Plant Transfer Pathways of PCDD/F**

**Figure 1:** Possible pathways of PCDD/F to aerial plant parts

Contaminants in the air can reach the plant through wet deposition in rain, snow or fog. If the contaminant is bound to atmospheric particles it can be deposited on leaves through dry particle deposition. The diffusion of gaseous chemical from the air to the leaf, referred to as dry gaseous deposition, is a third atmospheric deposition pathway.

Uptake from Soil

The groundbreaking work of Briggs et al. (1982) indicated that chemicals with a log octanol-water partition coefficient ($K_{OW}$) value larger than 4 are not translocated in plants due to their hydrophobic nature. Since the log $K_{OW}$ values for the PCDD/F are all larger than 5.5, these compounds would not be expected to be transported through the roots to the stem and leaves. While several early studies with 2,3,7,8-$Cl_4DD$ produced contradictory results (Kew et al., 1989), Hülster & Marschner (1993) and Müller et al. (1993) demonstrated convincingly that root uptake and translocation of PCDD/F is minimal for many plants. No influence of the soil concentration on the plant concentration was observed for grass and herbs growing outdoors where splash was inhibited by a layer of clay pebbles, even at soil concentrations 1000 times higher than those commonly found in German agricultural soils (Hülster & Marschner, 1993). This was also true for most other plants examined, and other authors have come to the same conclusion with studies of single PCDD/F congeners under laboratory conditions (Schroll & Scheunert, 1993; McCrady et al., 1990). One interesting exception to Briggs' rule has been reported. Members of the Cucurbita genus of the cucumber family were observed to translocate PCDD/F from the soil to the fruit and leaves (Hülster et al., 1994). However, since German cattle do not eat pumpkins or zucchinis, it can be concluded that root uptake and translocation plays a negligible role in the accumulation of PCDD/F in cattle.

The second soil related pathway, volatilisation of contaminant and subsequent adsorption to leaf surfaces, is unlikely to be important due to the very low vapour pressures of the PCDD/F which limit the rate at which the compounds can volatilise from the soil. As a result, Trapp & Matthies (1994) have suggested that even if there is a strong tendency for PCDD/F to evaporate from a soil, the slow rate of diffusion into the air will result in elevated plant concentrations only within a few centimetres of the ground. Estimates from McLachlan (1995) indicate that under summer conditions and typical background concentrations measured in Bayreuth the net diffusive flux of the PCDD/F will be from the air to the soil and not from the soil to the air. This suggests that volatilisation can only be a significant pathway of PCDD/F to plants in cases where the soil is very contaminated. However, in Maulach, where soil concentrations were about 1000 times higher than in typical German agricultural soils, the concentrations in hay averaged 2 ng TE/kg dw (Jilg et al., 1992), only

about 7 times higher than for hay grown in Bayreuth under typical background concentrations (McLachlan et al., 1994). This implies that if the hay from Maulach had been grown on typical German agricultural soils with concentrations 1000 times lower, all soil related pathways would have been of negligible importance. Krause et al. (1993) came to similar conclusions from the analysis of vegetation growing on soils contaminated with PCDD/F from "Kieselrot".

While soil makes a negligible contribution to PCDD/F levels in fodder under background conditions, the third soil related uptake pathway, direct transport of contaminated soil particles to aerial plant surfaces, can be important in some cases. All fodder plants are contaminated to a certain degree with soil particles, and this contamination is often enhanced during harvesting. Typical soil contamination of grass silage in The Netherlands has been reported to be about 2% on a dry weight basis (Berende, 1990), but values of 15% or more are possible. Important variables include the type of soil, weather conditions at the time of harvest, burrowing activity of moles in the field, the harvesting machinery used and the care employed by the operator. Where a high soil content in the feed and high soil concentrations coincide, soil can be expected to make a meaningful contribution to the PCDD/F uptake of the livestock. However, under typical German background conditions the levels of PCDD/F in soil and fodder are similar on a dry weight basis (McLachlan, 1995), so that even in cases of high soil levels in the feed the contribution of soil bound PCDD/F to the feed contamination will be small.

In summary, the uptake of PCDD/F from soil by feed plants is negligible under most conditions. The contribution of the root uptake/translocation and volatilisation/adsorption pathways is insignificant compared to contamination through soil contamination of the crop.

Uptake from the Air

Having established that the uptake of PCDD/F from soil is negligible, the contamination of feed crops must be mainly due to atmospheric deposition. It is, however, not clear which deposition mechanism is primarily responsible for the contamination of grass and other feed crops. Calculated estimates of the deposition of $2,3,7,8-Cl_4DD$ to grass (McLachlan, 1991) and of other organochlorine compounds to spruce needles (Umlauf & McLachlan, 1994) indicated that each of the three atmospheric deposition pathways outlined above could by itself plausibly account for the concentrations found in the vegetation.

In order to clarify this question, Welsch-Pausch et al. (1995) conducted an experiment in which a culture of ryegrass was exposed to different forms of deposition under near natural conditions. A system of three ventilated greenhouses was constructed: one

was supplied with unfiltered ambient air; the second was supplied with particle free ambient air; and the third was supplied with particle free ambient air which was also passed through an activated carbon filter to reduce the gas phase concentrations (see Figure 2). Hence three theoretical exposure scenarios were created: The grass in Greenhouse 1 (G1) was to be exposed to dry particle bound and gaseous deposition, in Greenhouse 2 (G2) to just gaseous deposition, and in Greenhouse 3 to just gaseous deposition, but at a reduced level. A reference culture (P1) placed outdoors adjacent to the greenhouses was exposed to gaseous deposition, dry particle bound deposition and wet deposition. Since no data were available on root uptake and translocation of PCDD/F for this species, two further exposure plots were included. Plot 2 (P2) was the same as P1 with the exception that a mildly contaminated agricultural soil (17 ng TE/kg dw) was used instead of the soil with PCDD/F concentrations typical for the Bayreuth area (1 ng TE/kg dw) used in P1 and G1-G3. In Plot 3 (P3) the more contaminated soil was also used, but in this case it was covered with a 5 cm layer of the less contaminated soil. Hence the grass on P2 was subject to increased uptake from all soil related pathways, while on P3 only the exposure to root uptake/translocation was elevated in comparison to P1. Two grass harvests were analysed, the first exposure lasting from July 17 to August 9 and the second from September 6 to October 18, 1991. The gaseous and particle bound concentrations in ambient air and in the greenhouses were also measured. A more detailed description of the experiment is found in Welsch-Pausch et al. (1995).
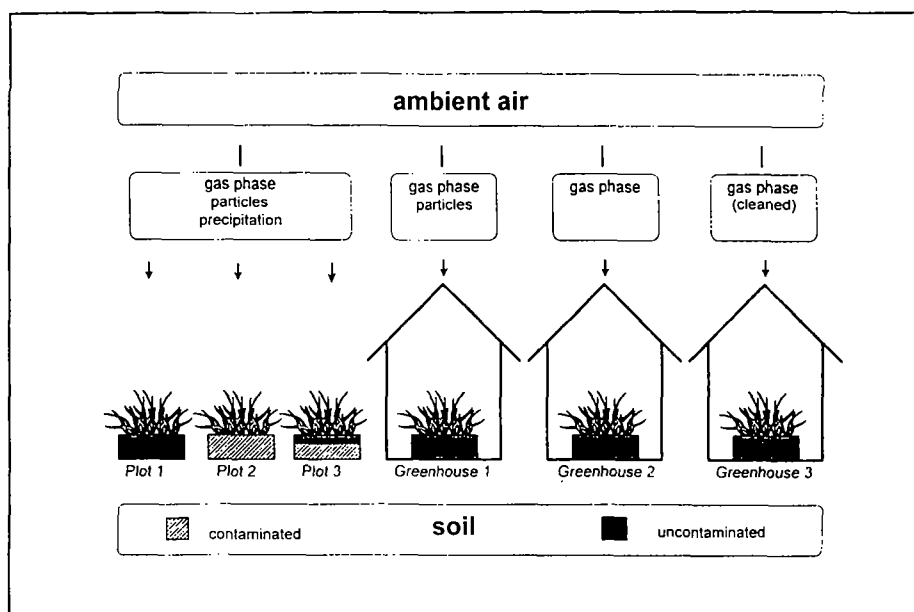


**Figure 2:** The experimental design for identifying the primary uptake pathway

The results of the different soil exposure scenarios are summarised in Figure 3 for the summer harvest. The quotients of the grass concentrations from P2 and P3 with respect to P1 are plotted for the 10 $Cl_4$-$Cl_8DD/F$ homologues. If the soil uptake pathways were important, this should have been reflected in Grass (P2)/Grass (P1) quotients considerably larger than 1. However, the measured quotients were generally less than 1 and, given the variability in the data, not significantly different than 1. These results support the conclusion reached above that soil is not an important source of PCDD/F to grass under typical background conditions in Germany.
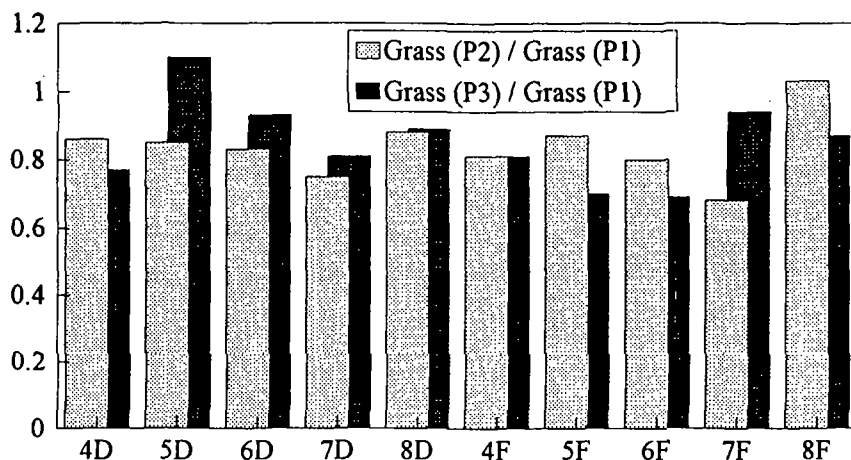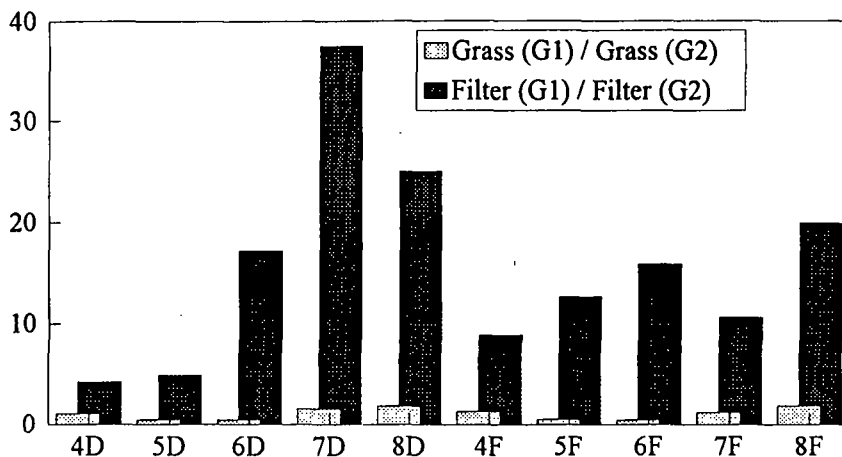


**Figure 3:** Plot of the PCDD/F levels in ryegrass grown on contaminated soil (P2, P3) normalized to the levels in grass grown on uncontaminated (P1) soil

The influence of dry particle bound deposition on the grass concentrations is illustrated in Figure 4. Here the quotients of the grass concentrations in G1 and G2 and the quotients of the particle bound concentrations of PCDD/F in G1 and G2 for the autumn harvest are plotted. The influence of dry particle deposition on the grass accumulation would be expected to be higher in autumn than in summer due to the higher particle bound fractions of the PCDD/F at this time of the year. The particle bound concentrations were up to 38 times higher in G1 than in G2 while all other conditions were approximately the same in the two greenhouses. This gradient in the particle bound concentrations was however not reflected in a similar gradient in the grass concentrations, which were similar in the two greenhouses. Thus dry particle bound deposition was not the dominant pathway of PCDD/F to the grass culture under these conditions. This conclusion must be restricted to the deposition of small particles ($<2.9$ $\mu$m) however, since larger particles were lost in the ventilation system supplying G1.

**Figure 4:** Plot of the levels of PCDD/F in ryegrass grown in air containing particles (G1) normalized to the levels in ryegrass grown in a particle free atmosphere (G2)

Figure 5 shows the influence of dry gaseous deposition on PCDD/F accumulation in Lolium multiflorum. Whereas a defect in the ventilation system rendered the results from G3 unusable, a blowoff artifact from the particle filter in G2 during the summer exposure proved very beneficial. It resulted in considerably higher gas phase concentrations in G2 compared to G1 while at the same time the particle bound concentrations were much lower. The results of this gradient in the gas phase concentrations are seen in Figure 5. The higher gas phase concentrations in G2 are accompanied by equally high or higher grass concentrations compared to G1, despite the lower particle bound concentrations. This provides convincing evidence that dry gaseous deposition was the dominant uptake pathway for the $Cl_4$-$Cl_6DD/F$ in the ryegrass culture. The same conclusion was reached in earlier studies of the accumulation of PCB in corn leaves (McLachlan, 1991) and a variety of chlorinated compounds in spruce needles (Umlauf et al., 1994).

Whereas dry gaseous deposition was identified as the dominant pathway of the lower chlorinated PCDD/F to the ryegrass, no firm conclusions could be drawn regarding the $Cl_7$-$Cl_8DD/F$ due to the difficulty in reliably measuring gradients in the gaseous concentrations of these compounds. When the concentrations in G1 were compared with the grass exposed outdoors, some evidence was found indicating input of these compounds from wet deposition and/or dry deposition of large particles for the autumn harvest. However, for the toxicologically important lower chlorinated congeners, dry gaseous deposition is the uptake process of primary interest.
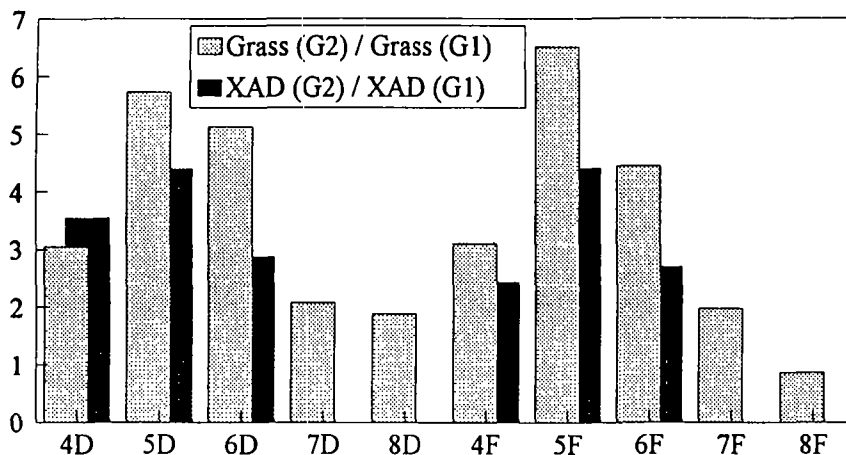
**Figure 5:** Plot of the PCDD/F levels in ryegrass grown in an atmosphere containing elevated levels of gaseous PCDD/F normalized to the PCDD/F levels in grass grown in an atmosphere with ambient levels of gaseous PCDD/F

Interestingly, no evidence of photodegradation of PCDD/F on the leaf surfaces was found. McCrady & Maggard (1993) reported that $2,3,7,8\text{-Cl}_4\text{DD}$ is subject to rapid photodegradation on reed canarygrass following dry gaseous deposition. If this had occurred in the experiment described here, differences in the isomer patterns found in the grass grown in the greenhouses and outdoors should have been apparent as the outdoor cultures were exposed to UV radiation in the 295-330 nm range whereas the greenhouse cultures were not. The different energy distribution in the different PCDD/F isomers would result in different photolytic reaction rates for the different isomers and hence in changes in the isomer patterns. However, no such changes were observed.

**Laboratory Studies of Dry Gaseous Deposition**

Having established that dry gaseous deposition is the dominant pathway of $Cl_4$-$Cl_6DD/F$ to an important feed grass, the next task is to understand the mechanism and variables underlying this process. Dry gaseous deposition is a diffusive process between the atmosphere and the leaf. Like all diffusive processes, dry gaseous deposition is driven by a gradient in chemical potential. A net deposition to the leaf only occurs if the chemical potential in the atmosphere is higher than the potential in the leaf. The rate of deposition is determined by the magnitude of this gradient and the diffusion resistance. The overall diffusion resistance consists of an atmospheric resistance and a plant resistance which are aligned in series between the atmospheric and plant contaminant reservoirs (see Figure 6). In the simplest case where the plant behaves as a well-mixed homogenous contaminant reservoir, the deposition flux $N_{dep}$ can be defined by the equation

$$N_{dep} = A/R_T (c_A - c_P/K_{PA}) \tag{1}$$

where A is the surface area through which diffusion is occurring ($m^2$), $c_A$ and $c_P$ are the air and plant concentrations respectively ($g^1 m^{-3}$), $K_{PA}$ is the dimensionless plant/air partition coefficient on a volume/volume basis, and $R_T$ is the overall diffusion resistance ($h^1 m^{-1}$) defined by

$$R_T = R_A + R_P/K_{PA} \tag{2}$$

In order to describe the dry deposition process, one needs to know the plant/air partition coefficient $K_{PA}$ and the overall diffusion resistance $R_T$.
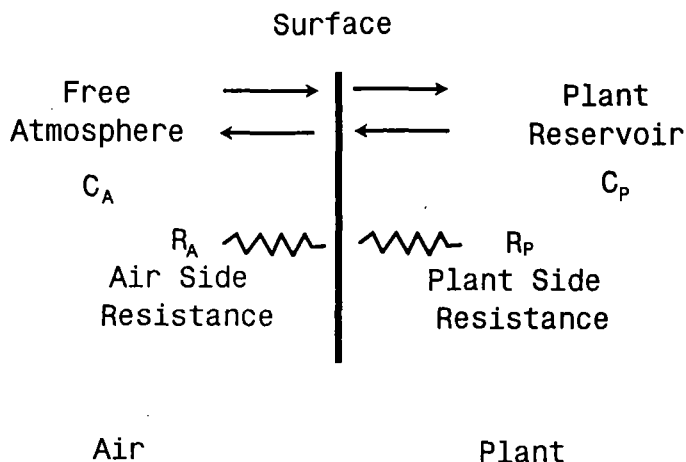


**Figure 6:** Schematic of the process of dry gaseous deposition

The pioneering work in measuring plant/air partition coefficients and diffusion resistances of semivolatile organic compounds (SOC) was conducted by Bacci and co-workers. They exposed azalea plants to high levels of gaseous organic contaminants and measured the increase in chemical concentration in the plant with time. After several weeks they then transferred the azalea plants to a chamber with much lower contaminant concentrations and monitored the subsequent decrease in chemical concentration in the azalea leaves. The results of this classical uptake/clearance experiment were interpreted using a simple one compartment linear first order model of diffusive exchange as described in equation 1 above. This experiment was repeated for a wide range of organic compounds, including $1,2,3,4-Cl_4DD$ (Bacci et al., 1992) and a predictive relationship describing the dependence of $K_{PA}$ on the physical-chemical properties of the chemical was developed (Bacci et al., 1990)

$$K_{PA} = 0.022 \, K_{OA} \tag{3}$$

where $K_{OA}$ is the octanol-air partition coefficient, calculated as

$$K_{OA} = K_{OW}/H \tag{4}$$

where H is the dimensionless Henry's Law constant or air-water partition coefficient. Equation 3 implies that the air-plant equilibrium state can be described as a partitioning of contaminant between air and an octanol-like phase within the plant.

The linear relationship between $K_{PA}$ and $K_{OA}$ is in agreement with theoretical expectations based on organic chemical partitioning behaviour in soil-water systems. Further evidence in support of a partitioning phenomenon to an octanol-like phase in the leaf is found in the work of Schönherr and co-workers (e.g. Kerler & Schönherr, 1988a; Sabljic et al., 1990) and Chaumat et al. (1992) with isolated plant cuticles and Gobas et al. (1991) with whole plants in aqueous systems, where they observed a linear relationship between the plant-water partition coefficient $K_{PW}$ and octanol-water partition coefficient. However, in a recent study using the air chamber method employed by Bacci, Hauk et al. (1994) concluded that the uptake of DDE in spruce needles and in azalea leaves cannot be appropriately described using a one compartment model of the leaf. Furthermore, they showed that the $K_{PA}$ values determined using this method are unreliable when the plants do not approach equilibrium during either the uptake or clearance experiment. Equilibrium was not approached for many of the less volatile compounds studied in Azalea. Hence, there is some doubt as to the validity of equation 3 for less volatile chemicals such as the PCDD/F.

Another factor of potential importance is the variability in $K_{PA}$ and $R_T$ between plant species. There is virtually no information available from studies of air/plant systems.

However, the Schönherr group has established a considerable data base for cuticle/water (e.g. Kerler & Schönherr, 1988b; Bauer & Schönherr, 1992) and needle/water systems (Schreiber & Schönherr, 1992). Whereas cuticle/water partition coefficients are relatively constant between different species, the plant resistance to diffusion uptake $R_P$ as measured with isolated cuticles in aqueous systems has been found to vary by orders of magnitude between species (Schafer & Schönherr, 1985). It remains to be seen if these findings are also applicable to air-plant systems.

Returning to the question of PCDD/F accumulation in grass, no estimates of $K_{PA}$ and $R_T$ can be readily obtained from the literature. The estimates of $K_{PA}$ provided by equation 3 are of questionable validity for less volatile compounds such as the PCDD/F, and their extrapolation from azalea to grass is at best uncertain. No studies employing grass were found in either plant-air or plant-water systems with the exception of the paper by McCrady and Maggard (1993). These authors contaminated reed canarygrass with $2,3,7,8\text{-}Cl_4DD$ in a contamination chamber and then conducted the clearance phase outdoors. However, since the uptake and clearance phases were short (4 days) and the plants did not approach equilibrium, the calculated $K_{PA}$ values cannot be viewed as reliable (see above).

Hence we decided to investigate the partitioning of organic compounds between the gas phase and the same ryegrass culture used in the greenhouse experiments described in the last section. A number of PCB congeners, organochlorine pesticides, PAHs and chlorinated PAHs were employed. A solid phase fugacity meter, a new method developed in our group to investigate diffusive transport between solids and gases, was utilised. The principle of the fugacity meter is simple. A column is packed with the solid material, and an air stream is passed through the column in such a way that an equilibrium is achieved between the surface of the solid and the air. The air is collected on a trap at the outlet of the column, which is subsequently extracted and analysed to determine the air concentration (see Figure 7). The concentration in the solid phase is also measured. If there is an internal equilibrium between the surface and the interior of the solid phase then the partition coefficient can be calculated from the quotient of the concentrations in the solid phase and the air (Horstmann & McLachlan, 1992).

The ryegrass cultures were first contaminated in a chamber containing elevated gaseous levels of the study compounds. Seven exposure periods of 2, 5, 12, 24, 48, 120 and 240 hours were employed during which the gaseous concentrations were maintained approximately constant. The rate of uptake of the compounds in the grass was measured and used to estimate the diffusion resistance $R_P$. Following exposure the grass was cut and placed in the fugacity meter. The measurements of the air concentration in the fugacity meter commenced immediately and were repeated over a

period of several days.  The experiments and results are described in detail in Tolls &
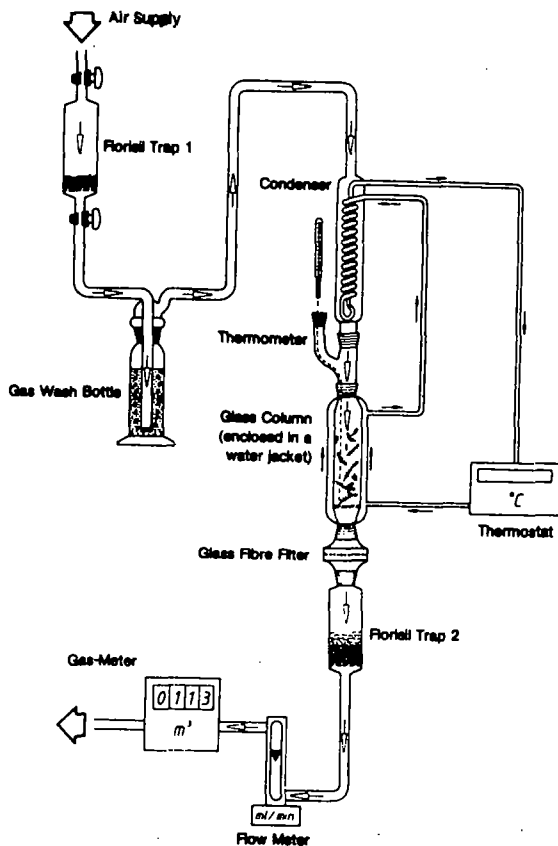McLachlan (1994).



**Figure 7:** Sketch of the solid phase fugacity meter

The kinetic information gathered from the experiment indicated that $R_P$ was
considerably lower in ryegrass, with half lives in the order of several days as opposed
to several months in azalea.  Thus, if $R_P$ is the limiting resistance it is reasonable to
assume that levels of a given chemical in ryegrass will approach equilibrium with the
atmosphere during the 30 to 90 day growth period typical for pasture grasses.
Furthermore, the results indicated that for periods longer than several hours the
contaminant kinetics in ryegrass can be successfully modelled using a one
compartment model, in contrast to spruce needles and azalea.  Thus equations 1 and 2
give a valid approximation of dry gaseous deposition to this species.

The values of $R_P$ ranged over a factor of eight between the study compounds, some of
this variation being attributable to the imprecision of the experimental method.  Since

the molecular sizes of the study compounds were similar and compounds of similar molecular size have been reported to have similar permeances in cuticles over a wide range of $K_{OW}$ (Bauer & Schönherr, 1992), an average $R_P$ value was calculated from the data for all study compounds. Since the size of the PCDD/F is comparable to that of the compounds used in the experiment, this value of $3.6 \times 10^7$ $h^1 m^{-1}$ should give a good first estimate of $R_P$ for the PCDD/F as well.

The measured values of $K_{PA}$ obtained from each of the seven different exposure periods were in good agreement with each other. The average values are plotted in Figure 8 against $K_{OA}$ on a log-log scale. A strong correlation was obtained, and the simple equation

$$K_{PA} = 0.01\ K_{OA} \tag{5}$$

gives a good fit to the data ($r^2 = 0.89$), it being noted that the $K_{PA}$ values were measured at 18°C while the $K_{OA}$ values were calculated from physical-chemical properties measured at 25°C. Simply stated, for the purposes of dry deposition of SOC ryegrass can be regarded as 1% octanol.
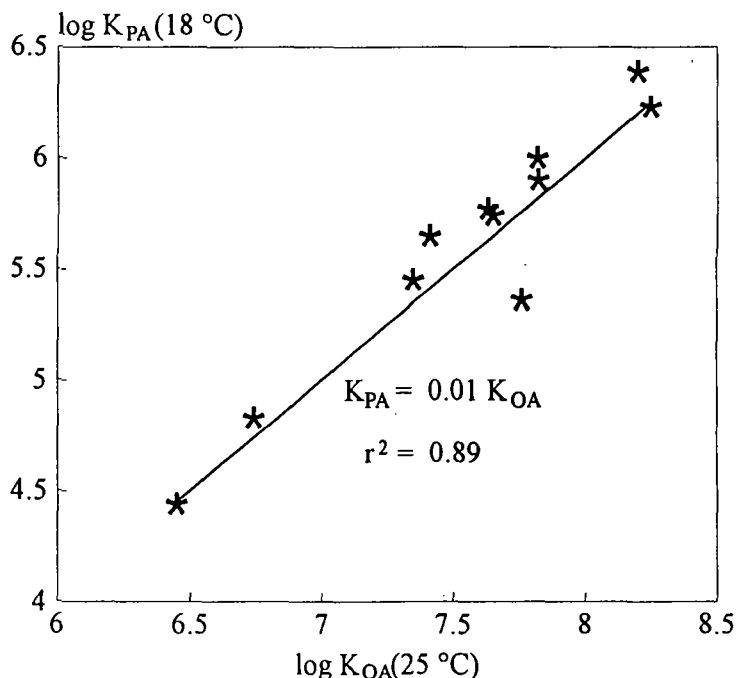


Figure 8: Plot of log $K_{PA}$ vs log $K_{OA}$ for various SOC as measured using the fugacity meter

Having obtained estimates for $R_P$ and $K_{PA}$, two of the three unknowns in equations 1 and 2 have been quantified. The remaining coefficient, $R_A$, is more difficult to estimate. This parameter describes the air resistance to diffusion of a compound from the free atmosphere to the plant surface. It is highly variable and a complex function of plant species, canopy density, wind speed, atmospheric stability, irradiation, air temperature, soil temperature and other factors. There has been considerable research about contaminant deposition to plant canopies, but this research has focused primarily on inorganic contaminants which are taken up through the stomata. The PCDD/F on the other hand are deposited on the cuticle which covers the whole surface of the plant. This completely different target surface will be associated with a different atmospheric resistance than the stomata. At the moment this parameter can at best be estimated. One approach to obtaining more reliable values will be discussed in the next section.

**Comparison of Model Predictions and Field Measurements of Dry Gaseous Deposition of PCDD/F to Ryegrass**

While the last section described moderately extensive laboratory research of dry gaseous deposition of SOC to plants, there have to our knowledge been virtually no field validations of this work. In one paper Hauk et al. (1994) compared their laboratory model for DDE uptake in spruce needles with field measurements and obtained poor agreement, leading them to emphasise the importance of field validation in studying the uptake of SOC in plants. In order to address this deficit, we conducted a field validation of the model presented above.

The simple model described in equations 1 and 2 was incorporated into a computer program giving a dynamic simulation of chemical concentration in ryegrass as a function of air concentration, temperature and time. The magnitude of $R_T$ was assumed to be independent of temperature, while the temperature dependence of $K_{PA}$ was assumed to be equal to the temperature dependence of the vapour pressure of the chemical. This is logical, since $K_{PA}$ is proportional to $K_{OA}$, and the temperature dependence of $K_{OA}$ is primarily determined by the temperature dependence of the vapour pressure. The value of $R_A$ was fitted. A detailed description of the model and of the results of the validation can be found in McLachlan et al. (1995).

The field data used were the air concentrations and grass concentrations measured on the outdoor plots during the summer exposure in the uptake pathway experiment described above. The average gas phase concentrations of hexachlorobenzene (HCB), several PCB congeners and the PCDD/F homologues were fed into the model along with the temperature as recorded in 2 hour intervals during the experiment. A linear growth function was assumed for the grass. Values for the physical-chemical properties of the compounds required for the model ($K_{OW}$, H and the enthalpy of vaporisation) were selected from the literature.

The concentrations in the ryegrass at the end of the exposure as predicted by the model were then compared with the measured concentrations. The results are plotted in Figure 9, with the log of the quotient of the grass and air concentrations on the y-axis and the log $K_{OA}$ of the compound on the x-axis. The agreement between the measured and predicted grass concentrations was excellent, with the difference not exceeding 30% for almost all compounds studied. Only for the $Cl_7$-$Cl_8$DD/F were larger deviations observed, with the measured concentrations lying considerably higher than the predicted values. As was mentioned above, dry particle bound deposition and/or wet deposition, which were not accounted for in the model, were possibly important pathways of these compounds to the ryegrass.
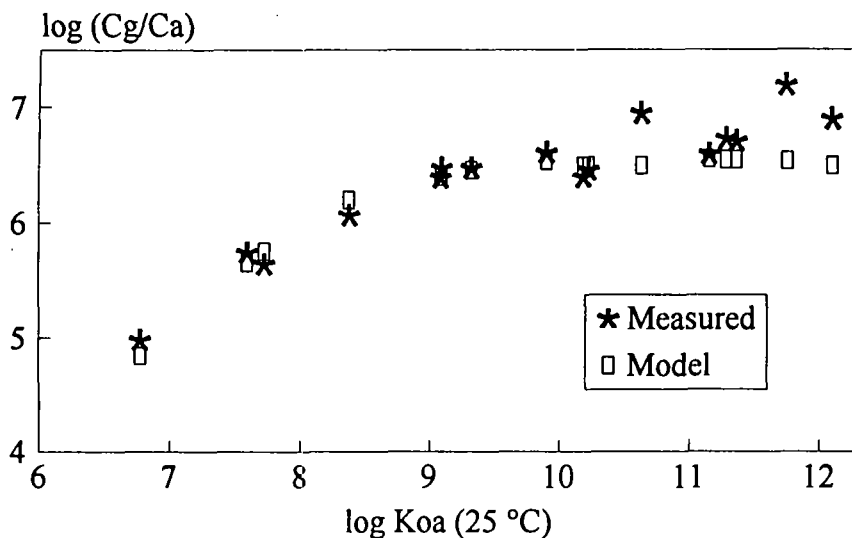
**Figure 9:** Log-log plot of the quotient of the grass and gas phase concentrations vs $K_{OA}$ for PCB and PCDD/F in ryegrass as modelled and measured in the field.

Equation 5 states that the quotient of the grass and air concentrations is linearly proportional to $K_{OA}$ if the grass and air are in equilibrium. In Figure 9 a linear relationship is seen for the first 4 compounds, but then the curve flattens off, and for all compounds with log $K_{OA}$ > 9, which includes all of the PCDD/F, the quotient of the plant and air concentrations is constant and independent of the $K_{OA}$ value. This indicates that the PCDD/F in the grass did not approach equilibrium with the PCDD/F in the air. The reason: The air side resistance $R_A$ limits the uptake of these compounds in the grass. Expressed simply, the storage capacity of the grass for the PCDD/F is so large that the grass simply did not "see" the amount of air during the 4 week growth period that it would need to "clean" in order to reach equilibrium.

This observation has important consequences. Since the air side resistance $R_A$ is virtually independent of the physical-chemical properties of the diffusing substance for compounds of similar size, the grass/gas phase concentration ratio for a certain crop will be a single constant for all PCDD/F. Furthermore, the concentrations in the grass will increase with the length of exposure, since grass which grows longer will "see" more air than grass which grows rapidly, assuming that the biomass density is similar at the time of harvest. This result is in agreement with the observations of Delschen et al. (1992), who reported higher concentrations in grass from the third hay harvest compared to the first and second hay harvests and attributed this to the longer exposure of the third harvest.

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The work of McCrady (1994) should also be seen in this context. He measured uptake rate constants for gaseous 2,3,7,8-$Cl_4DD$ in various crops and fruits, obtaining a relatively constant rate constant when the results were normalised for leaf/fruit surface area. Since the uptake was likely limited by an air side resistance, neither this finding nor the fact that he could find no influence of cuticular wax or lipid content on the uptake rate are surprising. Instead, the uptake was determined by the turbulence generated in his contamination chamber.

The validation effort demonstrated that of the three coefficients in eqs 1 & 2, $R_A$ alone determines the concentrations of the toxicologically important $Cl_4$-$Cl_6DD/F$ in ryegrass. $R_P$ is smaller than $R_A$, and the partition coefficient $K_{PA}$ has no influence since equilibrium is not approached, meaning that the grass functions like an infinite sink for the chemicals. As was mentioned above, the prediction of a value for $R_A$ is extremely difficult. In Fig. 9 it was fitted, accounting for the good agreement between the modelled and the measured concentrations for those compounds with log $K_{OA} > 9$. However, neither the value of $R_A$ nor the grass/gas phase concentration ratio obtained here can be extrapolated to real feed crops, since the micrometeorological conditions (which determine $R_A$) are certainly very different in a meadow than in the flower box cultures used in the field validation.

Rather than attempting to predict $R_A$ through micrometeorological simulations, it is suggested that a more pragmatic approach be taken, namely directly measuring the grass/gas phase concentration ratios. Sampling of feed crops accompanied by ambient air monitoring of PCDD/F or other contaminants with similar $K_{OA}$ values during the growing season should be conducted to generate a database of crop/gas phase concentration ratios, which could then be used to back out $R_A$ values. This approach has one prerequisite: It must be demonstrated that the chemical accumulation in these crops is also due primarily to dry gaseous deposition. Crop concentrations could then be predicted with a high degree of accuracy using the data base and measured or hypothetical ambient air concentrations.

**Summary and Open Questions**

To summarise, of the different pathways of soilborne PCDD/F to feed, contamination of feed crops with soil particles is by far the most important. The degree of contamination can easily be calculated from the soil concentration and the soil content of the feed. However, this is generally a minor source compared to atmospheric deposition of PCDD/F to plants. Dry gaseous deposition was shown to be the primary pathway of $Cl_4$-$Cl_6$DD/F to a ryegrass culture. In contrast to more volatile compounds, it was found that the accumulation of PCDD/F in ryegrass is limited by the atmospheric resistance, i.e. the speed at which the PCDD/F can be transported from the free atmosphere to the plant surface. Hence, the ryegrass/gas phase concentration ratio is a constant for all PCDD/F for a given grass culture. Although oversimplified, the concentration of the $Cl_4$-$Cl_6$DD/F in ryegrass can be thought of as the product of the gas phase concentration and the amount of air flowing over the grass in its lifetime. The contamination of ryegrass (and of the agricultural food chain and humans if ryegrass is representative for fodder) can be reduced by either reducing the gaseous concentration in ambient air or reducing the amount of air "seen" by a unit of grass during its lifetime.

This paper demonstrates that the last years have brought important progress in our understanding of the sources of PCDD/F in agricultural food chains. It has been established that the atmosphere is the general source, and for one plant species the specific pathway has been identified and the mechanism characterised. However, there are many questions that have not yet been fully resolved and others that remain to be addressed:

- Is dry gaseous deposition the main pathway of the toxicologically relevant PCDD/F to other feed plants besides ryegrass? There are indications that other forms of deposition may play a more important role in other plants. The homologue pattern measured in mixed pasture grass and corn from the Bayreuth area is different than that measured in the ryegrass, the former having comparatively high levels of the higher chlorinated homologues. This is inconsistent with the hypothesis that dry gaseous deposition is the dominant pathway of all PCDD/F to the corn and pasture grass. If this were the case then the homologue pattern in all plants grown in a particular period would be the same, since the deposition velocity - while different from plant to plant - is the same for all PCDD/F for a given plant. The higher levels of the higher chlorinated homologues in corn and pasture grass compared to ryegrass suggests that wet and/or particle bound deposition are contributing more significantly to the uptake of these homologues.

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- Is the dominant pathway of the PCDD/F to feed crops different in other environments? For instance, dry particle bound deposition will be higher in environments with higher atmospheric particle loads and/or particle size spectrums displaying a stronger contribution from larger particles. This may be the case in built up areas or close to point sources, and is to be expected in industrialised areas lacking in modern pollution abatement equipment. On the other hand, more wet deposition can be expected in maritime climates than in Bayreuth. The stronger contribution of these other forms of atmospheric deposition might possibly increase the plant contamination to such an extent that dry gaseous deposition is no longer the dominant pathway. This would require taking a closer look at the mechanisms governing these other forms of deposition.

- What are typical values of plant/gas phase concentration ratios for PCDD/F in feed crops? As was mentioned above, there are currently no validated estimates for this parameter, and it was suggested that they be measured directly. Since the concentration ratios depend on $R_A$, the parameters that influence $R_A$ such as plant species, canopy density and weather will also influence the concentration ratios. While it is likely that the short term variations in $R_A$ will be smoothed out during the (in comparison) long growth period of the plant, the variations in the concentration ratio with crop type, location, climate, and from year to year need to be investigated.

- What role does photodegradation of PCDD/F on leaf surfaces play in the accumulation of these compounds in feed crops? As was mentioned in the paper, there are contradictory reports in the literature. It needs to be clarified if photodegradation is an important process for typical feed crops under natural conditions. Furthermore, if there is photodegradation, does it result in a reduction in PCDD/F uptake or in an increase in the concentrations of the lower chlorinated more toxic congeners through photolytic dechlorination of the higher chlorinated congeners.

- What is the major pathway of $Cl_7$-$Cl_8DD/F$ to ryegrass and to other feed crops? While some evidence was found suggesting wet and/or dry particle deposition, no firm conclusions can yet be drawn.

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