

Transfer of Airborne Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans into Dairy Milk[†]

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Polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) in dairy milk predominantly originate from contaminated fodder ingested by the cows. In the presented field study transfer rates were determined for 12 2,3,7,8-chlorosubstituted PCDD/F on their pathway from atmospheric deposition onto grass and into the milk of dairy cows. Samples of aerial deposition and fodder were collected simultaneously over periods of 35–100 days; milk samples were taken at the ends of these sampling periods. In the transfer from air onto fodder about 35% of the atmospheric PCDD/F fallout as determined by passive sampling using Bergerhoff vessels was retained on the grass. No congener specificity was observed in this transfer step. The levels in atmospheric fallout and in grass varied considerably among single samples, whereas the PCDD/F concentrations in milk were rather constant. However, the averaged transfer rates from grass to milk were in good accordance with data reported in the literature.

Keywords: PCDD; PCDF; atmospheric deposition; grass; cow's milk

INTRODUCTION

An important pathway of PCDD/F into the human body is the consumption of dairy products, which accounts for about 30% of the human exposure toward these substances (Beck et al., 1989; Fürst et al., 1990). Airborne PCDD/F are deposited on the fodder, which is ingested by the cows, and the PCDD/F are excreted mainly via the milk. The half-lives in the cow of most of the 2,3,7,8-chlorosubstituted congeners are between 30 and 65 days. The transfer from fodder into dairy milk has been investigated in several field studies as well as in feeding studies (Blüthgen et al., 1995; Firestone et al., 1979; Fürst et al., 1993; Jensen and Hummel 1982; Jones et al., 1987; Krause et al., 1993; Liem et al., 1991; McLachlan et al., 1990; Olling et al., 1991; Slob et al., 1995; Tuinstra et al., 1992). Some of these investigations provided quantitative congener-specific transfer calculations of PCDD/F from fodder into milk.

The contamination of the fodder is mainly due to atmospheric deposition of PCDD/F onto the grass, whereas the influence of the levels in soil on the contamination of the grass is minor (Fürst et al., 1993; Krause et al., 1993). In the transfer from air to vegetation the following processes have been considered (Matthies and Trapp, 1994; McLachlan et al., 1995; Müller et al., 1994; Trapp et al., 1994; Welsch-Pausch et al., 1995): direct uptake of volatile PCDD/F from the vapor phase (gaseous deposition); deposition of PCDD/F adsorbed to particles, e.g. dust (particulate deposition); and deposition of PCDD/F together with precipitation (wet deposition).

It is yet unclear which of these processes dominate under field conditions, and the deposition of PCDD/F

onto plants has not yet been satisfactorily quantified in field situations.

It was the aim of this study to quantify the transfer of single 2,3,7,8-chlorosubstituted PCDD/F from the atmospheric deposition to their occurrence in dairy milk. This is achieved by the simultaneous determination of the PCDD/F levels in atmospheric deposition, on grass, and in dairy milk over extended time periods. The study is based on the assumption that the vertical fallout of particulates from the atmosphere is the dominant contamination pathway for vegetation. The results of the present study should help to improve the risk assessment of environmental PCDD/F.

MATERIALS AND METHODS

Sampling. The investigation was conducted during the vegetation periods of the years 1994 and 1995 on a Swiss dairy farm situated at a distance of 1 km from a modern municipal solid waste incinerator. Averaged over 1 year, the 41 cows of the farm produced a total of 860 kg of milk day⁻¹, with an average fat content of 4.05%. The farm area used for the production of fodder covered 3.5 × 10⁵ m². Grass and maize (whole plants), both grown on the farmland, were the main components of the fodder besides lower amounts of grain and mineral salts. The cows were kept in a barn and were fed with freshly harvested grass from March to October and with hay from October to March. Maize was fed starting in July as freshly harvested material and as silage from November through March. Interrogation of the farmer and continuous inspection of the farm suggested no significant additional sources of PCDD/F. The sampling periods given in Table 1 were adapted to the growth of the grass; that is, the samples were taken at the dates of the regular harvesting by the farmer.

The same periods were selected for the sampling of the atmospheric deposition of PCDD/F, which was conducted at the same site. The deposition samples were collected using the Bergerhoff method (VDI, 1972). Thereby, glass vessels (volume = 1.5 L, opening surface = 56.7 cm²) are mounted in wire baskets about 2 m above ground in an open field. The Bergerhoff method predominantly samples vertical atmospheric fallout such as precipitation and particulate deposition. Its collecting efficiency for gaseous substances may be low. For one sample, the contents of 8–10 single vessels were pooled.

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[†] Preliminary results of the study were presented by F.S. at "Dioxin '95" in Edmonton, Canada, 1995 (Schuler et al., 1995).

Table 1. Sampling Periods for Atmospheric Deposition, Grass, and Cow's Milk, with Average Midnight Temperatures and Growth Rates of Grass (Dry Weight Basis) Indicated

sampling period	duration (days)	temp (°C)	growth rate of grass (g m ⁻² day ⁻¹)	comment
July 1994				no milk samples taken
May 7–July 14	69	16.8	2.4	
Sept 1994				
July 15–Sept 7	55	19.7	2.3	
May 1995				
April 13–May 17	35	10.9	8.5	
June 1995				
May 18–June 22	36	13.6	7.4	
Oct 1995				grass sampling period:
June 26–Oct 3	100	17.1	2.9	Aug 10–Oct 3 (55 days)

Soil samples were taken at the beginning of the investigation from a field used for the production of fodder exclusively; the field had not been plowed for 20 years. Soil was cored to depths of 0–4, 4–10, and 0–10 cm, respectively. The soil samples were compared to an equally gained sample from a remote area in Switzerland (Schuler et al., 1997).

Sampling of grass was effected by mowing an area of 1 m² at a height of 2–3 cm. The sample taken in October 1995 had an exposure time of only 55 days as the grass was mown twice during the sampling period. A maize plant sample was taken in September 1994 from freshly harvested material.

Milk samples were taken from the daily pool of the last day of each investigation period. Due to the slow pharmacokinetics of PCDD/F in the cow, the levels in milk are determined by the past exposure of the cows. The farmland covers a relatively compact area and likely is exposed to a rather uniform atmospheric impact. We therefore compared the time integrated levels in deposition and on grass to the concentrations found in milk at the end of each exposure period.

Materials. All solvents used were of pesticide residue analysis quality (Burdick and Jackson, pesticide residue grade, distilled in glass, Fluka AG, Buchs, Switzerland). Cesium hydroxide (pract., ca. 95%), potassium hydroxide (puriss. p.a.), anhydrous sodium sulfate (puriss. p.a.), hydrochloric acid (puriss. p.a.), sulfuric acid (puriss. p.a.), and silica gel 60 (purum) were also bought from Fluka AG. Aluminum oxide Alumina B Super I was obtained from ICN Biomedicals (Eschwege, Germany). Reference PCDD/F were obtained from an interlaboratory comparison (second round on levels of PCDD/F in human milk and blood, organized by WHO, 1990), and the ¹³C₁₂-labeled internal standard PCDD/F were from Cambridge Isotope Laboratories (Woburn, MA).

Extraction and Sample Cleanup Procedures. *Deposition Samples.* Sediments in the Bergerhoff jars were carefully detached with a rubber spatula into the aqueous fraction. The precleaned jars were extracted twice with 150 mL of toluene in an ultrasonic bath for 3 min. The pooled aqueous fractions amounting to between 2 and 10 L were filtered, and aliquots of 1 L were extracted twice with a total of 200 mL of toluene. The filters containing the particulate fraction were leached by rinsing with ca. 20 mL of 1 M hydrochloric acid. After addition of the internal standard, the filters were extracted in the dark for 30 h in a Soxhlet apparatus using a fraction of the toluene used for the liquid extraction (Kirschmer et al., 1991).

Soil. Soil samples were dried by lyophilization and ground after separation of gravel. Internal standard was added to 30 g of dried soil, and the samples were extracted with toluene for 50 h in a Soxhlet apparatus.

Fodder. Grass and maize samples were frozen at –20 °C, cut in pieces of 2 cm length, and dried by lyophilization. After addition of the internal standard, 50 g of the dried material was extracted with toluene for 50 h in a Soxhlet apparatus. The solvent was evaporated, and the black, viscous residue was redissolved in 300 mL of *n*-hexane. Further purification of the crude extract included treatment with 200 mL of 50% sulfuric acid followed by two portions of 200 mL of concentrated sulfuric acid.

Milk. Fat extraction of the milk samples (sample size 300 g) was performed using a method described by Fürst et al.

(1989). After determination of the fat content, the internal standard was added.

The extracts of soil, fodder, and deposition samples were further purified using a slightly modified method described by Hagenmaier et al. (1986). The method includes several chromatographic steps with alumina, silica gel, and silica gel impregnated with sulfuric acid. The first column (10 mm i.d.) contained (all sequences from bottom to top) 20 g of Alumina B Super I and 3 g of anhydrous sodium sulfate. The column was prerinced with 120 mL of *n*-hexane/dichloromethane (1:1, v/v) and with 120 mL of benzene. After application in toluene or *n*-hexane, the samples were rinsed with 170 mL of benzene and 170 mL of *n*-hexane/dichloromethane (50:1, v/v) and eluted with 120 mL of *n*-hexane/dichloromethane (1:1, v/v). The second column (8 mm i.d.) contained 1.5 g of activated silica gel (190 °C, 24 h), 2.5 g of sulfuric acid coated silica gel (44% concentrated sulfuric acid, w/w), 1.5 g of cesium silicate, 1 g of activated silica gel, and 2 g of anhydrous sodium sulfate. The column was prerinced, and the samples were eluted with 30 mL of *n*-hexane. After evaporation of the major part of the solvent in a rotary evaporator, the samples were applied to the third column (7 mm i.d.) containing 2.5 g of alumina and 2.0 g of anhydrous sodium sulfate. After application of the sample, the column was rinsed with 40 mL of *n*-hexane/dichloromethane (50:1) followed by elution of the compounds of interest with 25 mL of *n*-hexane/dichloromethane (1:1).

The milk fat samples were processed using a standard procedure (Smith et al., 1984) that is based on saponification with potassium silicate and retention on silica gel followed by adsorption of the PCDD/F on active carbon and selective elution with toluene. The loading and elution of the active carbon column was automated using a column switching unit. The extract was passed through a disposable Pasteur pipet filled with 0.5 g of sulfuric acid coated silica gel, 0.4 g of cesium silicate, and 0.25 g of anhydrous sodium sulfate and further onto an alumina column containing 2.5 g of alumina and 2.0 g of anhydrous sodium sulfate. The column was rinsed with 40 mL of *n*-hexane/dichloromethane (50:1) and eluted with 25 mL of *n*-hexane/dichloromethane (1:1). The solvents were evaporated and the samples dissolved in 10 µL of isoctane.

Analytical Procedure. A gas chromatograph Fisons HRGC Mega 2 series was used. Separation was performed on a glass capillary column (length 20 m, i.d. = 0.27 mm) coated with a 0.15 µm film of polysiloxane PS 086 (Hüls America, Inc.) for the milk samples and of OV-225-OH (Ohio Valley, Specialty Chemicals, Marietta, OH) for the other samples (Schmid, 1989; Schmid and Schlatter, 1990). The carrier gas was hydrogen at a head pressure of 50 kPa. Samples of 1 µL were injected "on column" at 100 °C oven temperature. After 1 min, the temperature was raised at 20 °C min⁻¹ to 240 °C and then at 3 °C min⁻¹ to a final temperature of 280 °C. The mass spectrometer (Finnigan MAT 95) was run in electron impact ionization mode at 70 eV electron energy and at a mass resolution of 10 000. The two most abundant ions within the molecular ion clusters of the native and ¹³C-labeled PCDD/F congeners were recorded using single ion monitoring (SIM). Quantification was based on signal areas in the mass chromatograms.

All congeners reported under the result section were accompanied by their ¹³C₁₂ surrogates as internal standards. As

Table 2. Atmospheric Deposition of PCDD/F Determined by Passive Sampling Using Bergerhoff Vessels ($\mu\text{g m}^{-2} \text{day}^{-1}$)

congener	July 1994	Sept 1994	May 1995	June 1995	Oct 1995
2378-TCDD	0.38	0.60	1.1	0.79	0.64
12378-PeCDD	1.3	1.4	2.5	8.6	1.5
123478-HxCDD	0.82	1.2	nd ^a	19	nd
123678-HxCDD	2.1	2.0	5.8	22	3.5
1234678-HpCDD	nd	nd	39	nd	47
OCDD	41	96	106	5106	168
2378-TCDF	0.93	3.0	9.1	2.7	3.1
12378-PeCDF	1.6	1.8	6.3	2.2	1.4
23478-PeCDF	nd	nd	6.8	nd	4.6
123478-HxCDF	1.7	2.6	9.5	6.6	2.7
1234678-HpCDF	7.0	11	34	14	11
OCDF	5.3	8.1	18	7.9	15

^a nd, not determined.

internal standard mixtures with different congener composition were used in the course of the study, the data of several congeners are incomplete (see Tables 2–5). A signal to noise ratio of 3:1 was applied as detection limit.

RESULTS AND DISCUSSION

In the present study, measurement of the deposition was based on passive collection of the precipitation using the Bergerhoff sampling method (Kirschmer et al., 1991; VDI, 1972). Thereby, the vertical fallout from the atmosphere is trapped in glass pots. To obtain sufficient sensitivity, sampling periods in the order of several weeks are required. In consequence, this sampling method provides long-term averages rather than momentary values. This is appropriate for the present study as the deposition measurements will be compared to the levels in grass that are built up by accumulation during the growth periods between harvests.

In Table 2 the deposition of PCDD/F during five periods is given. Despite the proximity of a municipal solid waste incinerator and the suburban characteristics of the area, the deposition levels were in the range of such typically observed in remote areas in central Europe (Kurz et al., 1993; Liebl et al., 1993; Sievers et al., 1993; Wallenhorst et al., 1995), whereas levels reported for urban areas in Great Britain were significantly higher (Duarte-Davidson et al., 1994). The relatively low deposition levels of the present investigation indicate that the impact of the neighboring waste incinerator is minimal.

The congener pattern of the PCDD/F varied considerably between the five observation periods: in June 1995 the relative levels of the highly chlorinated PCDD were strongly elevated, whereas the PCDF levels remained low. Such a sudden change in the congener pattern may be explained by a temporal point source. Similar congener patterns were observed in soil after accidental pentachlorophenol burning (Draper et al., 1988). The deposition sample of May 1995 exhibited slightly elevated levels of the lower chlorinated PCDD/F. This could be related to an enhanced adsorption of the more volatile congeners to particles in May 1995 due to the lower ambient temperature.

The soil levels of PCDD/F at the investigation site together with the levels in a reference soil from a remote area (Schuler et al., 1997) are given in Table 3. Comparison of the two soils shows that the PCDD/F levels at the location under investigation were clearly higher than in soil without specific exposure. Samples taken at different depths show that the PCDD/F are homogeneously distributed from the surface to a depth

Table 3. Levels of PCDD/F at Different Sampling Depths in Soil of the Investigated Site and in Reference Soil ($\mu\text{g g}^{-1}$, Dry Weight Basis)

congener	soil at investigation site			ref soil
	0–4 cm	4–10 cm	0–10 cm	0–10 cm
2378-TCDD	0.36	0.37	0.37	0.13
12378-PeCDD	2.4	2.7	2.5	0.32
123478-HxCDD	3.9	4.0	4.0	0.39
123678-HxCDD	6.5	6.6	7.1	1.1
OCDD	266	234	235	33
2378-TCDF	1.8	1.9	1.8	0.91
12378-PeCDF	2.3	2.6	2.3	1.1
123478-HxCDF	6.2	7.4	7.4	1.8
1234678-HpCDF	38	40	42	5.7
OCDF	22	19	19	6.5

Table 4. PCDD/F Concentrations in One Maize Sample and the Grass Samples ($\mu\text{g g}^{-1}$, Dry Weight Basis)

congener	maize	grass				
	Sept 1994	July 1994	Sept 1994	May 1995	June 1995	Oct 1995 ^a
2378-TCDD	0.01	0.01	0.08	0.17	0.04	0.06
12378-PeCDD	0.03	0.05	0.16	0.12	0.26	0.16
123478-HxCDD	0.03	0.06	0.20	nd ^b	0.63	nd
123678-HxCDD	0.04	0.11	0.39	0.14	0.97	0.36
1234678-HpCDD	nd	nd	nd	1.1	nd	3.2
OCDD	1.1	5.8	16	5.5	132	11
2378-TCDF	0.08	0.18	0.58	0.27	0.15	0.42
12378-PeCDF	0.10	0.09	0.29	0.20	0.13	0.25
23478-PeCDF	nd	nd	nd	0.09	nd	0.19
123478-HxCDF	0.05	0.12	0.45	0.18	0.28	0.35
1234678-HpCDF	0.28	0.52	2.3	0.92	0.70	1.7
OCDF	0.94	0.48	1.5	0.59	0.64	0.98

^a Exposure period only 55 days (corresponding deposition sample 100 days). ^b nd, not determined.

of 10 cm. As the present atmospheric input of PCDD/F is low (see Table 2), the elevated soil contamination suggests a higher atmospheric input rate in the past when the adjacent incinerator was run with a less efficient flue gas scrubber system.

In Table 4 the PCDD/F levels in maize and in grass collected at the end of each investigation period are given. The fodder of the cows consisted of approximately 80% grass and 20% maize (dry weight basis) and low amounts of grain and mineral salts. The PCDD/F could not be determined in a grain sample as even a more rigorous cleanup procedure was insufficient. The mineral salts were not analyzed for PCDD/F. However, both matrices are very unlikely to contribute significantly to the PCDD/F exposure of the cows as they are fed in small amounts and their PCDD/F content most likely is low (Beck et al., 1989; Furst et al., 1990). In the sampling period September 1994 (see Table 1) the PCDD/F levels in grass were 5–10 times higher than in the maize sample. Taking into account that the portion of maize in the fodder amounts to only about 20%, the contribution to the total PCDD/F exposure of the cows is <5%. Therefore, the analysis of maize was discontinued in the followup of the study.

The PCDD/F concentrations in grass depend on the amount of PCDD/F in the atmospheric fallout, on the efficiency of the vegetation to retain the deposited PCDD/F (the transfer rate from atmosphere to vegetation), on the exposure time, and on the growth rate of the grass. A high growth rate will lead to a dilution of the deposited substances. Delschen et al. (1992) also found that the PCDD/F levels in grass depend on the duration of the growth periods and the growth rates of the grass. A slight contamination of the grass with soil particles, e.g. due to rain splashes, cannot be entirely

Table 5. Deposition Rates of PCDD/F on Grass ($\mu\text{g m}^{-2} \text{day}^{-1}$)

congener	July 1994	Sept 1994	May 1995	June 1995	Oct 1995
2378-TCDD	0.03	0.19	1.4	0.28	0.16
12378-PeCDD	0.11	0.36	0.99	1.9	0.47
123478-HxCDD	0.14	0.45	nd ^a	4.9	nd
123678-HxCDD	0.26	0.89	1.2	7.1	1.1
1234678-HpCDD	nd	nd	9.6	nd	9.5
OCDD	14	37	47	992	33
2378-TCDF	0.42	1.3	2.3	1.1	1.2
12378-PeCDF	0.21	0.66	1.7	0.97	0.72
23478-PeCDF	nd	nd	0.73	nd	0.55
123478-HxCDF	0.27	1.0	1.5	1.9	1.0
1234678-HpCDF	1.2	5.2	7.9	5.1	5.1
OCDF	1.1	3.5	5.1	4.8	2.9

^a nd, not determined.

Table 6. Transfer Rates (Dimensionless) of PCDD/F from Atmosphere to Grass as the Ratio of Deposition Rates on Grass (Table 5) and in Bergerhoff Vessels (Table 2)

congener	July 1994	Sept 1994	May 1995	June 1995	av
2378-TCDD	0.1	0.3	1.3	0.4	0.5
12378-PeCDD	0.1	0.3	0.4	0.2	0.2
123478-HxCDD	0.2	0.4	nd ^a	0.3	0.3
123678-HxCDD	0.1	0.5	0.2	0.3	0.3
1234678-HpCDD	nd	nd	0.2	nd	0.2
OCDD	0.3	0.4	0.4	0.2	0.3
2378-TCDF	0.5	0.4	0.3	0.4	0.4
12378-PeCDF	0.1	0.4	0.3	0.4	0.3
23478-PeCDF	nd	nd	0.1	nd	0.1
123478-HxCDF	0.2	0.4	0.3	0.3	0.3
1234678-HpCDF	0.2	0.5	0.2	0.4	0.3
OCDF	0.2	0.4	0.3	0.6	0.4

^a nd, not determined.

ruled out. This could affect mainly the levels of the higher chlorinated congeners in grass as these congeners are by far the most abundant in soil. However, there is strong evidence in the literature that the PCDD/F levels in grass are not influenced by the levels in soil, even at very high soil contamination (Fürst et al., 1993; Krause et al., 1993). We therefore omitted in the transfer calculations an impact of the moderately contaminated soil on the PCDD/F levels in grass.

To deduce transfer rates from atmosphere to vegetation, the PCDD/F levels in the two matrices have to be expressed in the same unit. The levels in grass (given on a weight basis) can be transformed to the units of the deposition measurements by multiplication with the average growth rates of the grass during each investigation period (Table 1). These transformed "area and time based" PCDD/F levels in grass (Table 5) express the amount of PCDD/F added to a given area of grassland in a certain time span (e.g. $\mu\text{g m}^{-2} \text{day}^{-1}$). Comparison of the values in Table 5 to those in Table 4 reveals the strong influence of the growth rate on the PCDD/F concentration in grass; for example, the low concentrations in the grass of May 1995 turn into rather high levels, which is now in line with the elevated levels in the synchronously collected deposition sample.

Division of the levels in Table 5 by the corresponding deposition measurements (Table 2) yields the transfer rates of atmospheric PCDD/F to the grass (Table 6). As the sampling periods of the grass and of the deposition did not correspond in October 1995, no data were calculated for this period. The rates given in Table 6 indicate that between 10% and 60% of the fallout is retained on the grass. Despite the considerably varying physicochemical properties of different homologues, no

Table 7. PCDD/F in Cow's Milk ($\mu\text{g g}^{-1}$, Fat Basis)

congener	Sept 1994	May 1995	June 1995	Oct 1995	av
2378-TCDD	0.20	0.18	0.50	0.39	0.32
12378-PeCDD	0.23	0.49	1.4	0.57	0.67
123678-HxCDD	0.73	0.64	1.4	0.38	0.79
1234678-HpCDD	0.59	0.71	2.0	0.77	1.0
OCDD	1.4	1.7	2.6	2.0	1.9
2378-TCDF	0.08	0.11	0.13	0.18	0.13
12378-PeCDF	0.09	0.17	0.09	0.21	0.14
23478-PeCDF	0.96	1.19	0.76	0.79	0.92
123478-HxCDF	0.43	0.47	0.32	0.28	0.37
1234678-HpCDF	0.19	0.24	0.24	0.34	0.25
OCDF	0.42	0.10	0.22	0.27	0.25

clear congener specificity could be observed. This is surprising as dry gaseous deposition is reported as the major pathway for low chlorinated PCDD/F onto pasture grass in a greenhouse experiment (Welsch-Pausch et al., 1995). The Bergerhoff method is commonly applied for the determination of wet and dry particulate deposition. It is yet unclear whether the Bergerhoff method possesses an unexpectedly high sampling efficiency for gaseous PCDD/F or whether the results of the greenhouse experiments do not apply to our field situation. In July 1994 a generally lower fraction of the deposited PCDD/F was retained on the grass. This may be due to the different meteorological conditions (e.g. higher precipitation) during this exposure period.

Obviously, the chosen approach for the determination of the air-to-grass transfer of single PCDD/F is an approximation of the real processes. It is likely that the retention efficiency of the grass for PCDD/F increases during the growth period when the canopy becomes more dense. Also, varying climatic conditions can influence the transfer within one growth period. It is therefore reasonable to monitor the total portion of PCDD/F entering the food chain by choosing sampling periods adjusted to the growth periods.

The relatively constant transfer rates throughout the five homologous groups of PCDD and PCDF demonstrate that the Bergerhoff method records the major pathways of the atmospheric PCDD/F leading to the contamination of the fodder. From the data given in Table 6 it can be concluded that an average of 35% of the PCDD/F fallout as determined by the Bergerhoff method is retained on the grass during the vegetation period.

The PCDD/F concentrations in cow's milk are given in Table 7; they are similar to the average levels detected in an investigation on Swiss cow's milk from various locations (Schmid and Schlatter, 1992). To compensate for interindividual variations between single cows, pooled milk of the farm was investigated. The PCDD/F levels observed in milk are a consequence of the respective levels in fodder (Fürst et al., 1993; McLachlan, 1992). A comparison of the influence of PCDD/F in soil and on grass on the resulting levels in milk revealed that the transfer of PCDD/F from soil is negligible even at very high PCDD/F levels (Fürst et al., 1993; Krause et al., 1993).

Taking the grass as the major source for the PCDD/F contamination of the milk, the levels in the fodder should be reflected in the PCDD/F contamination of the milk. Due to the pharmacokinetics of PCDD/F in the cow (Olling et al., 1991; Tuinstra et al., 1992), short-term fluctuations of the levels in fodder are equalized and are therefore hardly noticeable in the milk. Comparison of the milk data to the respective deposition and grass data (Tables 2 and 5) indeed shows that the

Table 8. Transfer Rates (Dimensionless) for PCDD/F from Grass into Milk as the Ratio of the Concentrations in Grass (Table 4) and the Concentrations in Milk (Table 7) for Four Periods and Averaged over the Four Periods

congener	Sept 1994	May 1995	June 1995	Oct 1995	av
2378-TCDD	0.1	0.06	0.7	0.4	0.3
12378-PeCDD	0.08	0.2	0.3	0.2	0.2
123478-HxCDD	0.05	0.06	0.07	0.1	0.08
1234678-HpCDD	nd ^a	0.03	nd	0.01	0.02
OCDD	0.004	0.02	0.001	0.009	0.008
2378-TCDF	0.01	0.02	0.04	0.02	0.02
12378-PeCDF	0.02	0.04	0.04	0.05	0.04
23478-PeCDF	nd	0.7	nd	0.2	0.5
123478-HxCDF	0.05	0.1	0.1	0.04	0.07
1234678-HpCDF	0.004	0.01	0.02	0.01	0.01
OCDF	0.01	0.009	0.02	0.01	0.01

^a nd, not determined.

variations between single exposure periods are much smaller in the milk samples than in the deposition and grass samples; for example, the relatively high deposition rates observed in June 1995 (Tables 2 and 5) are hardly recognizable in the milk levels.

The transfer of PCDD/F from grass into cow's milk is quantitatively described by the ratio of the excreted amounts to the ingested amounts:

$$TR_{\text{grass/milk}}^i = (c_{\text{milk}}^i / c_{\text{grass}}^i) PR_{\text{milk/grass}} \quad (1)$$

$TR_{\text{grass/milk}}^i$ is the transfer rate of PCDD/F congener i from grass into milk (dimensionless), c_{milk}^i is the concentration of PCDD/F congener i in milk (pg g^{-1} , fat basis), c_{grass}^i is the concentration of PCDD/F congener i in grass (pg g^{-1} , dry weight basis), and $PR_{\text{milk/grass}}$ is the production rate of milk (g, fat basis) from grass (g, dry weight basis) under the specific feeding conditions [$PR = 0.05$ (B. Schuler, personal communication, 1995)].

The transfer rates given in Table 8 are calculated from the grass and milk data in Tables 4 and 7. Due to relatively constant levels in the milk, the fluctuations in the PCDD/F levels in grass between the different periods propagate into the transfer rates. Therefore, these fluctuations are due to the slow adaption of the milk levels to the fodder levels rather than to real fluctuations in the transfer rates. This difficulty can be overcome by calculation of averaged transfer rates. The resulting values (Table 8) showing the strong congener specificity for the transfer of PCDD/F from fodder to milk are in line with findings already reported in the literature (McLachlan, 1992; Olling et al., 1991).

CONCLUSION

It has been shown that the transfer of the PCDD/F congeners from the atmosphere to grass is proportional to the atmospheric deposition of PCDD/F as determined by the Bergerhoff method. About 35% of the deposited PCDD/F are retained on the grass; no congener-specific behavior could be observed. These results substantiate the suitability of the Bergerhoff method as a monitoring tool for PCDD/F entering the terrestrial food chain from the atmosphere. Comparison of the deposition data of several growth periods revealed significant fluctuations. The reasons for these fluctuations could not be elucidated. The variabilities of the PCDD/F levels in the fodder are equalized in the cow by the pharmacokinetics involved in the transfer into milk. Therefore, if exposure assessments are based on single measurements of aerial deposition or fodder, the variability of the atmo-

spheric deposition has to be taken into consideration; that is, the variability could lead to unreliable estimates of the resulting exposure.

The findings of the present study demonstrate the correlation between the PCDD/F levels in dairy milk and the local atmospheric deposition of PCDD/F in the case of exclusive feeding of locally grown fodder. The combination of the transfer rates of PCDD/F from grass into milk and the rates of the transfer from atmosphere to the grass enables the prediction of the congener-specific entrance of single PCDD/F into the food chain based on measurement of the local atmospheric deposition.

ABBREVIATIONS USED

PCDD, polychlorinated dibenzo-*p*-dioxins; PCDF, polychlorinated dibenzofurans; PCDD/F, polychlorinated dibenzo-*p*-dioxins and dibenzofurans; SIM, single ion monitoring.

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