The Accumulation of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in the Food Chain

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Abstract

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) accumulate in biological tissues, leading to bioconcentration in the food chain. Uptake from soil and deposition from the atmosphere are the two possible pathways of PCDD/F accumulation in plants. In an effort to determine the accumulation mechanism, we analyzed air, soil, corn kernel, and corn leaf samples from a private farm in Felicity, Ohio. Corn is an important feed crop in the United States; both corn kernels and corn leaves (silage) are widely used. Thus, PCDD/F concentrations in corn may lead to bioaccumulation in beef and dairy products. Concentrations were below the detection limits (2 pg/g lipids) in the corn kernels. However, we found total PCDD/F concentrations of 1582 ± 235 fg/m^3, 3.9 ± 1.1 ng/g lipids, and 1982 ± 250 pg/g wet weight in air, corn leaves, and soil, respectively. Based on these data, we found that particle-phase deposition to corn contributes significantly to PCDD/F accumulation in the food chain.

Introduction

In order to fully evaluate human exposure to PCDD/F, a knowledge of their accumulation mechanisms in vegetation is crucial. There are two pathways for the accumulation of PCDD/F in plants: uptake from soil and direct deposition from the atmosphere. Accumulation from the soil may occur through several mechanisms: (a) uptake by the roots and further translocation to the shoots, (b) volatilization from the soil to the plant surfaces, or (c) contamination by suspended soil particles. Several studies have shown that transport of PCDD/F through the roots to the shoots is negligible,[1-3] except for zucchini and pumpkins.[3] Bacci *et al.*[4] performed controlled experiments in which azalea plants were grown in soil contaminated with 1,2,3,4-tetrachlorodibenzo-*p*-dioxin. Bacci *et al.* concluded that the lower chlorinated PCDD can volatilize from soil to leaf surfaces. Finally, soil particles contaminate plant surfaces close to the ground, although this route is considered negligible.[2]

The main route of PCDD/F accumulation in plants is deposition from the atmosphere to leafy surfaces. There are three types of atmospheric deposition: dry particle-phase deposition, dry gas-phase deposition, and wet deposition of both dissolved and particle-bound compounds. The deposition of dry gas-phase PCDD/F to vegetation has been studied almost exclusively in Germany using Welsh rye grass.[5-7] Researchers investigated the uptake pathways of PCDD/F using a series of greenhouses and outdoor plots and found that dry gas-phase deposition was the main pathway of Cl_4-Cl_6 dioxin and furan accumulation in the grass,[5,6] while dry particle-phase deposi-

tion may explain the uptake of Cl_7 and Cl_8 dioxins.[5] Welsch-Pausch and McLachlan[8] also studied a native German grassland culture in greenhouses in which the particle- and gas-phase fractions of air were controlled. In contrast to their earlier work with Welsh rye grass, dry particle-phase deposition was an important pathway of PCDD/F deposition. Wet deposition to plants has not been studied directly, but it may be estimated using concentrations in precipitation.

Clearly, more research into the mechanism of PCDD/F deposition to vegetation is needed. Plants other than Welsh rye grass must be evaluated. Differences in plant species may contribute to variations in PCDD/F accumulation. Atmospheric concentrations of PCDD/F are highly dependent on location, as are the corresponding concentrations in plants. Therefore, PCDD/F concentrations in various plant types from a variety of locations must be determined. Concentrations in plants are also dependent on weather conditions and length of exposure. Sampling strategies over an entire growing season, or even several seasons should be examined. Finally, the mechanism of Cl_7-Cl_8 dioxin and furan deposition remains to be fully explained.[9]

To address these issues, we collected air, soil, and entire corn plant samples from a private farm in Felicity, Ohio. We selected corn because of its importance as a feed crop in the United States; concentrations in corn kernels and leaves may contribute to the bioaccumulation of PCDD/F in beef and diary products.

Experimental

Whole corn plants (*Zea mays L.*) were collected on various dates in 1996 from a farm in Felicity, Ohio. Soil samples from various fields on this farm were collected in July, 1996. Air samples were collected once a month for 48 h using a high-volume air sampler located 1 km from the corn field. A glass fiber filter (GFF) was used to collect particulates, while a polyurethane foam plug (PUF) was used to collect gas phase constituents.

The areas and masses of corn leaves were determined. The corn leaves were then placed into 250 mL Erlenmeyer flasks, directly spiked with an internal standard solution consisting of $^{13}C_{12}$-1,2,3,4-Cl_4F, $^{13}C_{12}$-1,2,3,7,8-Cl_5F, $^{13}C_{12}$-1,2,3,6,7,8-Cl_6D, $^{13}C_{12}$-1,2,3,4,6,7,8-Cl_7D, and $^{13}C_{12}$-Cl_8D (Cambridge Isotope Laboratories, Inc., Andover, MA), and then the flasks were sealed with a glass stopper. Each sample was sonicated for 2 h in 200 mL of dichloromethane.

Husks were removed from the corn cobs, and the kernels were sliced off the cob with a knife. A Braun coffee grinder adapted for rigorous grinding was used to grind the kernels for 20 s. Approximately 50 g of ground kernels were then mixed with an equal amount of clean sodium sulfate, spiked with the above internal standard solution, and Soxhlet extracted for 24 h with 300 mL of toluene. Gel permeation chromatography (GPC) was used to remove lipids from the kernel extracts.

Soil samples (25-30 g) were mixed with enough sodium sulfate to make a loose, friable mixture. The samples were spiked with the above internal standard solution, transferred to a glass Soxhlet thimble, and extracted with 300 mL of isopropanol for 24 h, and then with 300 mL of dichloromethane for an additional 24 h. The two fractions were combined.

PCDD/F were isolated from the above leaf, kernel, air, and soil sample extracts by silica gel column chromatography, followed by alumina microcolumn chromatography.

Sample Analysis. Two μL of each sample was analyzed on a Hewlett Packard 5989A gas chromatographic mass spectrometer equipped with a 30 m x 250 μm i.d. DB-5MS capillary column with a 0.25 μm film thickness (J & W Scientific, Folsom, CA). The GC temperature program was held at 40 °C for 2 min, ramped at 30 °C/min to a temperature of 210 °C, ramped at 2 °C/min to a final temperature of 285 °C, and held for 10 min. The mass spectrometer was operated in the electron capture, negative ionization mode with the ion source temperature at 175 °C. The pressure of the reagent gas, methane, in the ion source was maintained at 0.43 torr. Selected ion monitoring and relative response factors were used to quantitate all congeners.

Results and Discussion

All concentrations are listed in Table 1. Air concentrations in both gas- and particle-phases are similar to those found in remote locations such as Gothenberg, Sweden,[10] and Trout Lake, Wisconsin,[11] as expected. The low soil concentrations are comparable to those found in remote areas.[12] The exception is the high concentration of Cl_8D in soil (relative to the low concentrations of the other dioxin homologues). Concentrations were below the detection limits (2 pg/ g lipids) in the corn kernels. This indicates that PCDD/F are neither translocated through the stalk to the corn kernels nor accumulated from the atmosphere (due to the layers of husks surrounding the kernels). We did find PCDD/F in corn leaves (see the last column in Table 1). Whole corn plants are used in making silage, which is an important source of fiber for beef and dairy cattle. PCDD/F are probably not degraded in the silage fermentation process; thus, silage could be an important source of PCDD/F in the food chain.

Table 1. Average PCDD/F concentrations with standard errors. n is the number of samples.

Homologue	Air (Gas) (fg/m^3) n = 10	Air (Particle) (fg/m^3) n = 10	Soil (pg/ g wet) n = 4	Corn Leaves (pg/ g lipids) n = 8
Cl_4F	32 ± 6	4.7 ± 1.9	2.4 ± 0.8	209 ± 105
Cl_5F	56 ± 8	20 ± 3	2.5 ± 0.7	160 ± 68
Cl_6F	73 ± 11	58 ± 10	3.0 ± 0.4	190 ± 69
Cl_7F	14 ± 3	33 ± 6	1.3 ± 0.3	106 ± 40
Cl_8F	7.5 ± 2.5	40 ± 10	6.6 ± 0.6	250 ± 71
Cl_4D	< 1	< 1	< 0.1	< 20
Cl_5D	12 ± 6	8.7 ± 2.8	0.15 ± 0.15	140 ± 60
Cl_6D	120 ± 29	86 ± 11	14 ± 2	290 ± 110
Cl_7D	110 ± 23	240 ± 53	52 ± 5	370 ± 120
Cl_8D	87 ± 45	580 ± 220	1900 ± 250	2200 ± 1100
TOTAL	512 ± 61	1070 ± 227	1982 ± 250	3915 ± 1126

Homologue profiles of PCDD/F in Ohio air (gas- and particle-phases), corn leaves, and soil, cattle fat,[13, 14] cow's milk,[15, 16] and humans[17-27] are shown in Figure 1. Because of the variation in concentrations and burdens, profiles have been normalized to the total concentration. Inspection of these profiles indicates that the atmospheric particle-phase, corn leaf, cattle, and human PCDD/F

profiles are similar. Therefore, particle-phase deposition significantly contributes to food chain contamination.

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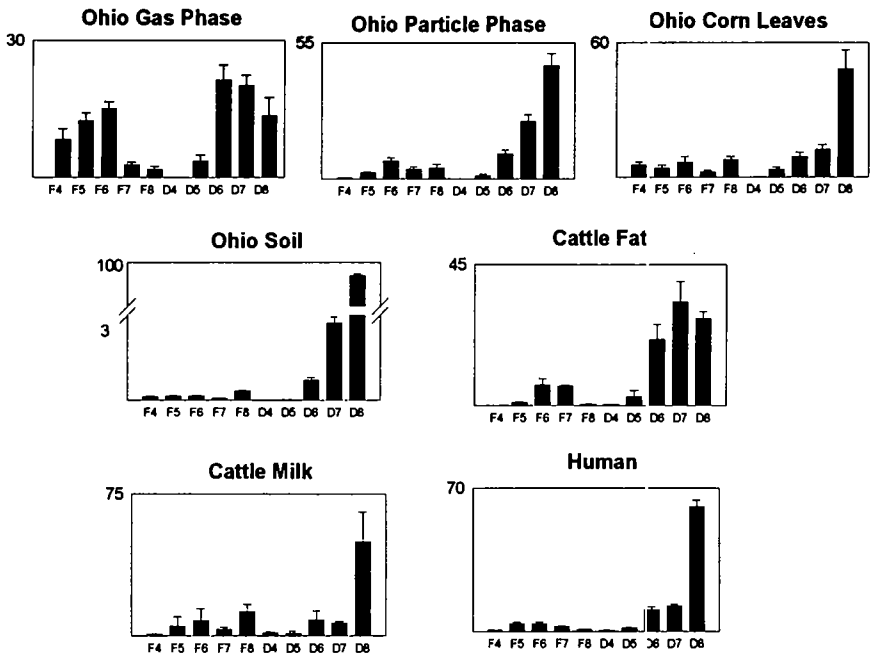

Figure 1. Homologue profiles (normalized to the total) of PCDD/F in a variety of environmental matrices. See text for details. The letter F refers to furans, and the letter D refers to dioxins. The number indicates the level of chlorination. Error bars indicate the standard error.

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