Accumulation of PCDD/F in an Agricultural Food Chain

Michael S. McLachlan

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

Abstract

The accumulation of PCDD/F in a the air-soil/feed-cattle-beef/milk agricultural food chain is described. A simple model describing the food chain accumulation is presented. The model is employed to predict the concentrations of PCDD/F in milk in southern Bavaria and found to be in very good agreement with measured milk concentrations from a monitoring study.

Introduction

Cattle represent through beef and dairy products the most important source of human exposure to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in the general population, accounting for around 50% of dietary uptake[1,2]. Developing an understanding for the processes that determine the accumulation of PCDD/F in cattle is hence a particularly important aspect of the environmental chemistry of these compounds. This paper summarizes the work that has been conducted in this area at the University of Bayreuth over the last years, moving step by step backwards through the food chain. At the end a simple model for predicting the concentrations of PCDD/F in milk is presented.

Uptake in Cattle

It has been demonstrated that feed is the primary vector of PCDD/F to cattle. Water and inhalation make negligible contributions to the total PCDD/F exposure[3].

Given that exposure occurs primarily through ingestion, it is then important to establish what fraction of the ingested compound is absorbed. This question was addressed in a mass balance study of a lactating cow eating unmodified feed with low "natural" levels of PCDD/F[3,4]. The absorption rates from this study are listed in Table 1 (Note that these values differ somewhat from those in ref. 3 due to an error in the earlier paper). These results were found to be consistent with the limited information in the literature about absorption from feeding studies.

Table 1: Absorption of 2,3,7,8-substituted PCDD/F congeners in a cow (from ref 4)

PCDDs		PCDFs	
2,3,7,8-Cl_4DD	0.36	2,3,7,8-Cl_4DF	0.07
1,2,3,7,8-Cl_5DD	0.32	1,2,3,7,8-Cl_5DF	0.05
		2,3,4,7,8-Cl_5DF	0.33
1,2,3,4,7,8-Cl_6DD	0.16	1,2,3,4,7,8-Cl_6DF	0.15
1,2,3,6,7,8-Cl_6DD	0.15	1,2,3,6,7,8-Cl_6DF	0.15
1,2,3,7,8,9-Cl_6DD	0.15	2,3,4,6,7,8-Cl_6DF	0.14
1,2,3,4,6,7,8-Cl_7DD	0.03	1,2,3,4,6,7,8-Cl_7DF	0.03
		1,2,3,4,7,8,9-Cl_7DF	0.08
Cl_8DD	0.04	Cl_8DF	0.02

Using these and further results for other compounds[5], a model of hydrophobic organic contaminant absorption in cows was assembled[6]. It was found that the absorption remained relatively constant around 80% until the log K_{ow} of the compound exceeded 6.5. Increasing K_{ow} was then accompanied by a rapidly decreasing absorption, an effect which was attributed to the restricted transport of very hydrophobic compounds through an aqueous film in the diffusive absorption process at the intestinal wall. While this model offers a predictive capability, it is felt that the large uncertainties associated with the K_{ow} values of the PCDD/F makes the use of the values in Table 1 preferable at this time.

Once absorbed in the cow, the next process of potential importance is metabolism. In the mass balance study it was established that many of the 2,3,7,8 substituted PCDD/F congeners are for practical purposes virtually fully persistent in the cow. However, several 2,3,7,8 substituted congeners, most notably 2,3,7,8-Cl_4DF and 1,2,3,7,8-Cl_5DF, were found in very low levels in milk, an observation that was attributed to metabolism of these compounds[3].

For those molecules which are absorbed in cattle but not metabolized, there are two main alternatives: either storage in the tissues of the animal or excretion in milk. PCDD/F are stored primarily in fat within cattle. Due to the very high rate of fat excretion in the milk dairy cattle are generally very close to a steady state in which the PCDD/F uptake is equal to the PCDD/F excretion through milk and feces, the amount stored in tissue not changing very much with time. Beef cattle on the other hand store the PCDD/F that they absorb, as they are not able to excrete PCDD/F through milk fat. However, the growth rate of beef cattle is so large that there is extensive growth dilution of PCDD/F stored in the animal. As a result, the PCDD/F concentrations measured in commercial beef fat are generally not much higher than the concentrations measured in milk fat[6].

The role of soil ingestion as a source of PCDD/F contamination in beef and dairy products is the subject of some controversy. Three parameters determine the relative influence of soil on the PCDD/F exposure of cattle: the concentration in the soil relative to the concentration in feed; the amount of soil ingested compared to the amount of feed; and the absorption of PCDD/F from soil compared to the absorption from feed. When the concentrations in soil are much higher than in feed then soil ingestion can be expected to be an important parameter. However, in background areas in Germany the concentrations of the toxicologically important Cl_4-Cl_6DD/F tend to be only 2 to 5 times higher in soil than in feed on a dry weight basis[7]. Cattle ingest 8 to 20 kg of dry feed per day, whereas the soil ingestion is estimated to be in the order of several hundred grams, almost two orders of magnitude less[8]. However, under certain conditions soil ingestion can exceed 1 kg per day. While a reduced absorption of PCDD/F from some soils has been reported for laboratory animals[9,10], it is as yet unclear as to whether the absorption from soil is different from the absorption from feed in cattle. Assuming that the absorption from soil is as effective as that from feed, soil ingestion will still play a secondary role at levels of background contamination (the typical case), even if the soil ingestion is quite high, since the higher rate of feed ingestion compared to soil more than compensates the somewhat higher PCDD/F levels in soil. However, in those special cases where the PCDD/F levels in the soil are elevated, soil ingestion may be an important factor. In this regard it is also important to note that feed is also often contaminated with soil and that this vector may also be important.

Accumulation in Feed

Of the different feed components, grass has been shown to contribute the majority of the PCDD/F uptake in cattle. For this reason we initially focused our work on a typical pasture grass - Lolium multiflorum or Welsh ray grass.

The first experiment was designed to establish the dominant pathway of PCDD/F to this species. The grass was exposed under near natural conditions in modified greenhouses that were supplied with either unfiltered air, particle free air or particle free air with a reduced gas phase concentration. Soil related pathways were also investigated by employing soil of different concentrations. It was found that dry gaseous deposition was the dominant pathway of the Cl_4-Cl_6DD/F to the grass culture. No firm conclusions could be drawn for the Cl_7-Cl_8DD/F[11].

Laboratory experiments were then conducted to examine the dry gaseous deposition phenomenon. A solid phase fugacity meter developed in our group was used to measure the grass/air partitioning coefficients, and information on the uptake kinetics was obtained from contaminant chamber experiments. Using PCBs as model compounds, a linear relationship between the grass/air partition coefficient and the octanol/air partition coefficient was obtained. This information was used to assemble a model of the dry gaseous deposition process[12)].

This model was then validated using the air and grass data from the greenhouse experiment. The model indicated that the PCDD/F in the grass had not achieved equilibrium with the gas phase[13)]. The grass/air partition coefficients for the PCDD/F are so large (10^7 - 10^{10} on a volume/volume basis) that during its growth the grass simply did not "see" the amount of air needed for it to reach equilibrium (i.e. 10^7 - 10^{10} m^3 of air per m^3 of grass). The consequence of this behavior is that the transfer of PCDD/F to Welsh ray grass is independent of the physical-chemical properties of the PCDD/F. The transfer can be described using a single deposition velocity for all congeners. Or, expressed in an oversimplified but useful way, each gram of grass scavenges the PCDD/F out of the gas phase of a certain volume of air.

A Simple Food Chain Model

Using this knowledge, it was then possible to reevaluate some earlier data that had been collected in the Bayreuth area. The average air concentrations determined from 12 hi-vol samples collected continuously between July 12 and October 4, 1989 were compared with the PCDD/F concentrations measured in several hay and corn silage samples harvested in the same year. It was found that for these crops (in contrast to the Welsh ray grass culture) the dry gaseous and particle bound deposition velocities of the PCDD/F were approximately equal. Hence, the meadow grass/corn did not just scavenge the gas phase of a certain volume of air, but also the particle phase of an equal volume.

The data indicated that the meadow grass scavenged the equivalent of 9 m^3 of air per g dry grass while corn plants scavenged the equivalent of 4.5 m^3/g dw. A typical feed ration for a lactating cow in Bavaria is 9 kg dw of grass and 4 kg dw of corn silage (there are other feed components, but there contribution to the PCDD/F uptake is minor). Multiplying the feed uptake by the air scavenging ratios and adding:

$$9\ m^3/g\ dw \times 9000\ g\ dw/d + 4{,}5\ m^3/g\ dw \times 4000\ g\ dw/d$$
$$= 99{,}000\ m^3/d$$

This says that each day a cow ingests the amount of PCDD/F present in approximately 100,000 m^3 of air. We can then write a very simple equation to describe the PCDD/F accumulation in this agricultural food chain:

$$C(\text{milk fat}) = \frac{C(\text{air}) \times 100{,}000 \times \text{Absorption}}{\text{Lactation (g milk fat/d)}}$$

where C(air) is the air concentration during the growing season.

This simple model was used to estimate typical concentrations of PCDD/F in milk fat for Bavaria. The air data from the summer of 1989 mentioned above were substituted into the equation along with a typical average fat lactation of 600 g/d. The absorption rates in Table 1 were used with the exception of Cl_8DD/F, where the values were reduced to 0.005 on the basis of unpublished results from a recent study. In Figure 1 the results are compared with the average concentrations obtained from a survey of over 100 milk samples collected in Bavaria during 1989 and 1990[14)]. The results are very good, indicating that this simple model provides a good approximation of the accumulation of PCDD/F in the air-plant-cow agricultural food chain. However, more study is required to further validate the model.

HEX

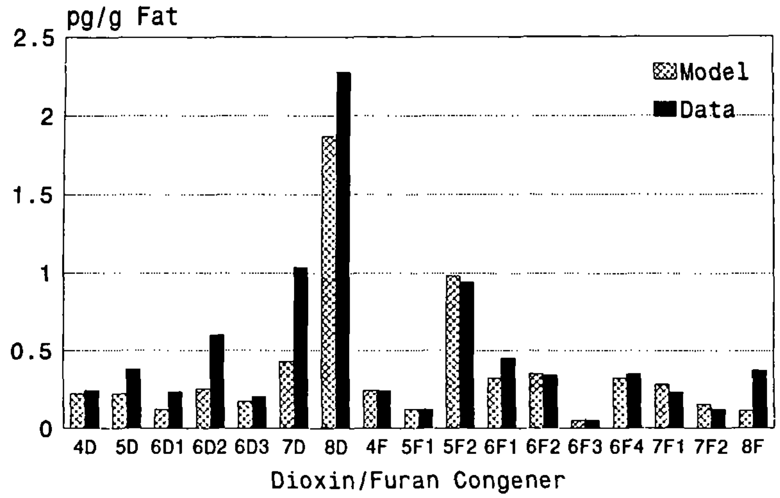

Figure 1: Comparison of the predicted and measured concentrations of PCDD/F in milk

References

1) Fürst P., C. Fürst, W. Groebel (1990): Levels of PCDDs and PCDFs in Food-Stuffs from the Federal Republic of Germany. *Chemosphere* **20**, 787-792.
2) Theelen R.M.C., A.K.D. Liem, W. Slob, and J.H. van Wijnen (1993): Intake of 2,3,7,8-Chlorine Substituted Dioxins, Furans, and Polar PCBs from Food in the Netherlands: Median and Distribution. *Chemosphere* **27**, 1625-1635.
3) McLachlan M.S., H. Thoma, M. Reissinger, and O. Hutzinger (1990): PCDD/F in an Agricultural Food Chain. Part 1: PCDD/F Mass Balance of a Lactating Cow. *Chemosphere* **20**, 1013-1020.
4) McLachlan M.S. (1992): Das Verhalten hydrophober chlororganischer Verbindungen in laktierenden Rindern. Doctoral Dissertation, University of Bayreuth.
5) McLachlan M.S. (1993): Mass Balance of Polychlorinated Biphenyls and Other Organochlorine Compounds in a Lactating Cow. *J. Agric. Food Chem.* **41**, 474-480.
6) McLachlan M.S. (1994): Model of the Fate of Hydrophobic Contaminants in Cows. *Environ. Sci. Technol.* **28**, 2407-2414.
7) McLachlan M.S. (1995): Bioaccumulation of Hydrophobic Chemicals in Agricultural Food Chains. *Environ. Sci. Technol.* submitted.
8) Fries G.F. (1987): Assessment of Potential Residues in Foods Derived from Animals Exposed to TCDD-Contaminated Soil. *Chemosphere* **16**, 2123-2128.
9) Van den Berg M., K. Olie, and O. Hutzinger (1983): Uptake and Selective Retention in Rats of Orally Administered Chlorinated Dioxins and Dibenzofurans from Fly-Ash. *Chemosphere* **12**, 537-544.
10) Umbreit T.H., E.J. Hesse, and M.A. Gallo (1986): Bioavailability of Dioxin in Soil from a 2,4,5-T Manufacturing Site. *Science* **232**, 497-499.
11) Welsch-Pausch K., M.S. McLachlan, and G. Umlauf (1995): Determination of the Principal Pathways of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans to Lolium multiflorum (Welsh Ray Grass). *Environ. Sci. Technol.* **29**, 1090-1098.
12) Tolls J., and M.S. McLachlan (1994): Partitioning of Semivolatile Organic Compounds between Air and Lolium multiflorum (Welsh Ray Grass). *Environ. Sci. Technol.* **28**, 159-166.
13) McLachlan M.S., K. Welsch-Pausch, and J. Tolls (1995): A Field Validation of a Model of the Uptake of Gaseous SOC in Lolium multiflorum (Welsh Ray Grass). *Environ. Sci. Technol.* **29**, in Press.