A METHOD FOR ESTIMATING DIET TO MILK TRANSFER COEFFICIENTS OF POLYCHLORINATED BIPHENYL CONGENERS

George F. Fries[1] and Donna J. Vorhees[2]

1 2205 Bucknell Terrace, Silver Spring, MD 20902, USA
2 Menzie-Cura &Associates, Inc., 1 Courthouse Lane, Suite 2, Chelmsford, MA 01824, USA

Introduction

Risk assessments of agricultural sites with polychlorinated biphenyl (PCB)-contaminated soil often require an estimate of the transfer of dioxin-like congeners from diet to milk of cows. Three studies include adequate data on feed consumption and milk fat production to permit calculation of transfer coefficients of individual PCB congeners. However, these data sets do not contain measurements for many of the dioxin-like PCB congeners.[1-3] A method to estimate transfer of PCB congeners from diet to milk is described in this paper.

Data Sets and Methods

Several coefficients are used to characterize transfer of a compound from diet to milk. The bioconcentration factor (BCF), which is the concentration of a compound in the milk fat divided by the concentration in the diet, is used here. The approach used for BCF would be applicable to other diet to milk transfer coefficients, which are interchangeable in practice.[4]

Two studies of the transfer of PCB congeners from diet to milk measured background concentrations that normally occur in feed.[2,3] The third study involved dosing cows with Aroclor 1260 for 60 days.[1] The BCFs derived in the dosing study were lower than the BCFs measured in the other two studies even though 60 days is usually sufficient to provide a stable concentration of many persistent organics in milk.[5,6] Of the two studies involving background concentrations, one is deficient because the quantities excreted in milk exceeded intake significantly, and because data were aggregated by homolog groups.[2] The other study also exhibited a few congeners with excess excretion but the excesses were not as great.[3]

Equations have been derived to predict biotransfer factors for diet-to-milk and diet-to-beef based on log K_{ow}.[7] However, these equations are not applicable to compounds with log K_{ow} values > 6.[2] Another deficiency in using K_{ow} to predict concentrations in milk is that K_{ow} is not predictive for metabolism. For example, two congeners in a PCB homolog group may have similar K_{ow}s but metabolism rates could differ because of the arrangement of chlorines.[3,4]

Our model for estimating BCFs of dioxin-like PCB congeners utilized published data on absorption of congeners from the gastrointestinal tract and observations of the effect on chlorine substitution patterns on metabolism. The model for fate of lipophilic compounds in cows proposed by McLachlan suggests that the fraction of an ingested compound absorbed from the gastrointestinal tract is a constant for a given matrix.[8] If animals are in physiological equilibrium,

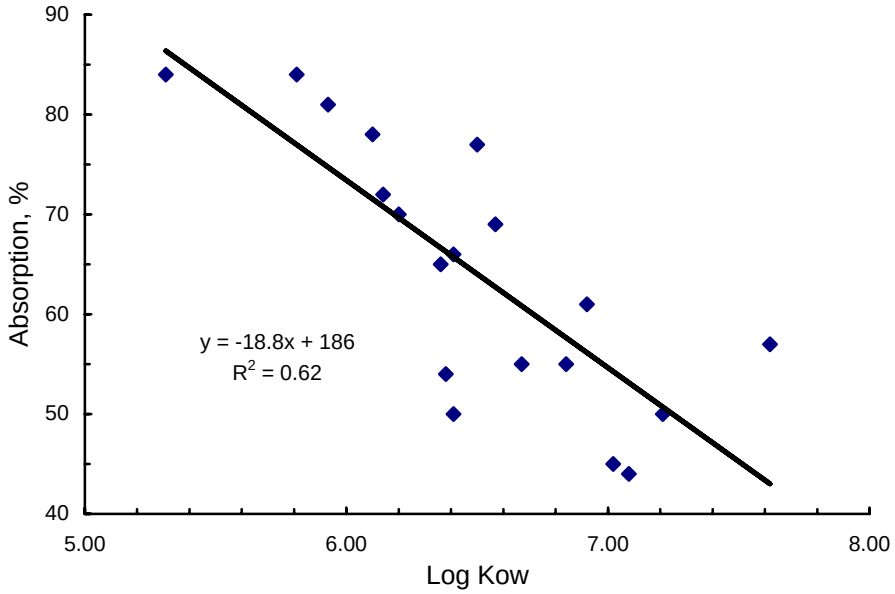

Figure 1. The absorption of PCB congeners as a function of log K_{ow}. Absorption values are from Thomas et al. and log K_{ow}s are from Brodsky and Ballschmiter.[3,9]

the amount of a congener excreted in milk cannot exceed the amount that was absorbed from the gastrointestinal tract. The fraction absorbed provides a basis for estimating the upper limit of the BCF if no net retention or metabolism at equilibrium is assumed. The upper limit can be calculated with the equation

$$BCF_{Max} = A*I_{feed}/F_{milk}$$

where A is the fraction of a compound absorbed, I_{feed} is the amount of dry matter consumed, and F_{milk} is the amount of milk fat produced. Average dry matter intake was 19.3 kg/day and milk fat production was 1.08 kg/day in the study of Thomas et al.[3] Thus, the maximum BCF for cows in that study would be

$$BCF_{Max} = A*19.3/1.08 = A* 17.9$$

Absorption of PCB congeners from the gastrointestinal tract tends to be inversely related to log K_{ow}.[2,3] This relationship can be observed in Figure 1, which includes the absorption data from Thomas et al. and log K_{ow}s are from Brodsky and Ballschmiter.[3,9] The log K_{ow}s were limited to a single source in order to avoid the large differences among values determined by different methods or laboratories.

The second factor that affects the magnitude of BCFs is metabolism. McLachlan viewed chlorine substitution in the 4,4' (para) positions as an important factor that contributed to the persistence of congeners in cows.[2] Because all dioxin-like PCBs have chlorines in the 4,4' positions, little

Table 1. The predicted BCFs of the dioxin-like PCBs.

PCB	Structure	Log Kow	Metab. Score	Predicted Absorp.	BCF Predicted	BCF Thomas[3]	BCF McL.[2]
77	3,3',4,4'	6.11	2	71	6.4	--	--
81	3, 4,4',5	--	2	*71*	6.4	--	--
105	2,3,3',4,4'	6.41	2	66	5.9	0.0	--
114	2,3, 4,4',5	6.65	2	61	5.5	--	--
118	2,3',4,4',5	6.57	1	63	11.2	18.3	18.3
123	2',3,4,4',5	6.64	1	61	10.9	--	18.3
126	3,3',4,4',5	--	0	*64*	11.5	--	--
156	2,3,3',4,4',5	7.13	1	52	9.3	12.8	18.0
157	2,3,3',4,4',5'	--	1	*49*	8.9	--	18.0
167	2,3',4,4',5,5'	7.29	0	49	8.8	15.3	--
169	3,3',4,4',5,5'	7.42	0	47	8.4	--	--
189	2,3,3',4,4',5,5'	7.72	0	41	7.4	--	--

Notes: Log K_{ow}s are from Brodsky and Ballschmiter.[9] Metabolism scores calculated according to Thomas et al.[3] Absorption was calculated using the equation in Figure 1. For the three congeners with no log K_{ow}s, average values for congeners with the same degree of chlorination were used.

metabolism is expected. Thomas et al. refined this observation and proposed a classification system based on chlorine substitution pattern for scoring the propensity for PCB congeners to be metabolized.[3] A score of 1 was assigned for each ortho-meta pair of hydrogen atoms and a score of 3 was assigned for each meta-para pair. Scores were then summed for each congener. Those with totals < 2 had metabolism rates of < 10%, those with totals of 2 had varying levels of metabolism from 10-90%, and those with > 2 were completely metabolized.

Results and Discussion

The predicted BCFs of the dioxin-like PCBs together with the measured BCFs, log K_{ow}s, metabolism scores, and predicted absorptions are listed in Table 1. The BCFs were calculated using the equation

$$BCF_{Pred} = A_{Pred} * (I_{Feed}/F_{Milk}) * M$$

where BCF_{Pred} is the predicted BCF, A_{Pred} is the predicted fraction of the congener absorbed, I_{Feed} is the amount of feed dry matter consumed, F_{Milk} is the milk fat production, and M is the metabolism factor. The regression equation in Figure 1 was used to estimate absorption. The feed intake and milk fat production values were derived from data in Thomas et al.[3] Following the Thomas et al. methodology, a metabolism factor of 1.0 was assigned to congeners with scores of 0 or 1, and a median factor of 0.5 was assigned to the four congeners with scores of 2 because congener specific metabolism information is not available. Values for log K_{OW} were taken from Brodsky and Ballschmitter, but their study does not provide log K_{ow}s for three congeners.[2] To avoid using K_{ow}s determined in different laboratories, or different methods, the three congeners were assigned the average value for congeners with the same number of chlorines because log K_{ow} tends to be correlated with the degree of chlorination.

Table 2. Comparison of predicted BCFs and measured BCFs from the literature.

PCB	Structure	Metab. Score	Predicted	Tuinstra[1]	Thomas[3]	McLachlan[2]
128	2,2',3,3',4,4'	2	5.7	6.2	10.9	18.0
138	2,2',3,,4,4',5'	1	10.9	4.5	12.5	18.0
153	2,2',4,4',5,5'	0	10.3	4.9	14.0	18.0
170	2,2',3,3',4,4',5	1	9.5	4.2	10.9	12.6
180	2,2',3,,4,4',5,5'	0	9.1	4.1	11.3	12.6
187	2,2',3,4',5,5',6	0	10.0	1.5	1.5	10.3
194	2,2',3,3',4,4',5,5'	0	7.7	4.2	0.0	9.6

The predicted BCFs are point estimates that are intended to be reasonable upper bound values. The four congeners with metabolism scores of 2 may be exceptions to this generality. The fractional metabolism of these congeners could range from 0.1 to 0.9.[3] Thus, use of the 0.5 metabolism factor introduces error in the estimates for congeners with metabolism scores of 2, potentially underestimating accumulation of congeners with metabolism factors less than 0.5.

A comparison of the predicted BCFs with those determined experimentally is presented in Table 2. Data on seven congeners common to the three studies are included. None were congeners with dioxin-like activity, and the limited BCF data available for these congeners are provided in Table 1. These measured BCF data illustrate the differences among the studies that were described previously. Generally, the values predicted by our method are within the range of the published values, but there is no consistent pattern in the relative magnitude of the predicted BCFs and the results of any individual study. These discrepancies probably reflect the analytical uncertainties associated with concentrations near the detection limits.

The BCFs for dioxin-like PCB congeners estimated by our method may be used until experimental values are obtained. Although the BCFs in this paper were derived for milk fat, the values may also be used for diet-to-beef BCFs because empirical observations indicate that BCFs of persistent organics for milk and beef fats are approximately equal.[4]

References

1. Tuinstra L.G.M.T., Vreman K., Roos A.H. and Keukans H.J. (1981) Neth. Milk Dairy J. 35:147-157
2. McLachlan M.S. (1993) J. Agric. Food Chem. 41:474-480
3. Thomas G.O., Sweetman A.J. and Jones K.C. (1999) Environ. Sci Technol. 33:104-112
4. Fries, G.F. (2002) in: Human and Ecological Risk Assessment (Paustenbach, D.J., Ed.), John Wiley and Sons, Inc. ISBN 0-471-14747-8
5. Willett L.B., Liu T.Y. and Fries G.F. (1990) J. Dairy Sci. 73:2136-2142
6. Fries G.F., Paustenbach D.B., Mather D.B. and Luksemburg W.J. (1999) Environ. Sci Technol. 33:1165-1170
7. Travis C.C. and Arms A.D. (1988) Environ. Sci Technol. 22:271-274
8. McLachlan M.S. (1994) Environ. Sci Technol. 28:2407-2414
9. Brodsky J. and Ballschmiter K. (1988) Fren. Z. Anal. Chem. 331:295-301