DEVELOPMENT AND VALIDATION OF AN AIR-TO-BEEF FOOD CHAIN MODEL FOR DIOXIN-LIKE COMPOUNDS

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This paper presents a model for predicting concentrations of dioxin-like compounds in beef. Components of the air-to-beef model are diagrammed in Figure 1. Model parameters for the dioxin-like compounds are shown in Table 1. Observed air and beef concentrations, along with predicted beef concentrations, are shown in Table 2. Further detail on this modeling study can be found in Lorber, et al[1].

1. MODEL DEVELOPMENT AND OBSERVED DATA

1. Partitioning Total Concentrations Into a Vapor (V) and a Particle (P) Phase. A theoretical model for estimating the V/P partitioning of semi-volatile organic compounds in the atmosphere is given in Bidleman[2]. Bidleman cites an earlier theoretical model by Junge[3] based on adsorption theory which described the exchangeable fraction of a semivolatile organic compound adsorbed to aerosol particles as a function of solute saturation vapor pressure and total surface area of atmospheric aerosol particles available for adsorption. Citing Whitby[4], Bidleman describes four air sheds, in order of increasing particle density, as: clean continental background, average background, background plus local sources, and urban. The modeling exercise of this paper assumes that the category, background plus local sources, best fits settings where cattle are raised for beef.

2. Particle Depositions to Vegetations and Soils. The steady state solution for plant concentrations due to particle phase depositions considers dry and wet deposition amounts, adherence to plants during wet deposition, weathering rate from the plants, and plant yields. Dry deposition is estimated as the particle-phase concentration times a deposition velocity of 0.2 cm/sec. This velocity was measured by Koester and Hites[5] for dioxin-like compounds under ambient conditions. Wet deposition is assumed to be equal to dry deposition, also based on observations from Koester and Hites[5]. It is assumed that 30% of wet deposition adheres to plants, which was observed by Hoffman, et al.[6] in experiments involving simulated rainfall of insoluble particles labeled with radionuclides onto different types of vegetation. Particle-bound dioxins are modeled to dissipate from vegetations via weathering with a 14-day half-life, based on experiments of Baes, et al.[7]

A steady state model is also used to estimate soil concentrations due to particle phase depositions: a total (dry + wet) deposition to the soil mixes in a reservoir and dissipates with a ten-year half-life. This half-life is based on the observations of Young[8] on an experimental field sprayed with 2,4,5-T. Depositions are assumed to mix in a surface soil depth of 1 cm.

remaining 0.96 to be split equally, 0.48 each, to pasture grass and hay/silage/grain.

Approximately 80% of all the beef consumed in the United States comes from cattle which have gone through a feedlot fattening process. A representative feedlot finishing process would span 120 days and include a diet consisting of 20% corn silage and 80% grain. Cattle increase their body weight up to 60% during this time. The grains are likely to be dioxin-free, since grains are protected from atmospheric dioxins. Corn silage is largely protected as well. Although no before and after feedlot monitoring for dioxins is available, two modeling studies[12,14] estimate that feedlot fattening reduces body concentrations of 2,3,7,8-TCDD by about 50%. Therefore, a final reduction of 50% of estimated body fat concentrations of the dioxin-like compounds is assumed.

5. Observed Air Concentrations. Very little data are available worldwide on air concentrations of individual dioxin-like congeners in a rural setting. This is the kind of air concentration data that would be needed for this exercise. Eighty-four data points with reported concentrations of the 17 congeners were found in the United States. Measurements which were attributed to a nearby identifiable source, such as an incinerator, were not considered for this effort. The average TEQ air concentration was 0.095 pg/m^3. Since the data was from urban/suburban settings and not rural settings, information was then sought on the difference between urban and rural air concentrations. Four studies were found which listed rural air concentrations of dioxin-like compounds side-by-side with urban air concentration[15,16,17,18]. Generally, urban air concentrations were found to be 4-6 times higher than rural air concentrations. For this paper, a rural air profile of dioxin-like compounds was derived by taking the urban air profile and dividing each congener concentration by 5. The TEQ concentration for the rural setting equals 0.019 pg/m^3.

6. Observed Beef Concentrations. A review of data on concentrations of dioxin-like compounds in beef showed that very limited data was available worldwide, much less for the United States. Only three studies contained congener-specific data of dioxins and furans in beef in the United States[19,20,21]. In one study, beef samples were composited with veal and the results described as beef/veal. The three studies only encompassed 14 samples. All studies collected samples from grocery store shelves. This is important because of the assumption that the beef likely went through feedlot finishing processes, which would reduce their body concentrations of dioxin-like compounds (as discussed above). Beef fat concentrations were reported. To estimate whole beef concentrations, the fat content of the whole sample as listed by the researchers was used, or else 19% fat was assumed. The average TEQ concentration, calculated by using one-half the detection limits reported by the researchers, was estimated to be 0.48 ng/kg (ppt) for beef on a whole weight basis. If nondetectable concentrations are assumed to be zero, the estimated TEQ for whole beef is 0.29 ppt. The average whole beef congener-specific concentrations, calculated assuming non-detects were one-half the detection limit, are to be used to represent observed beef concentrations in this study.

2. RESULTS

As seen in Table 3, observed and predicted TEQ concentrations in beef compare favorably, with observed at 0.48 ppt and predicted at 0.36 ppt. The congeners of most toxicity also had the best comparison: 2,3,7,8-TCDD - 0.03 ppt observed and 0.03 ppt predicted; 1,2,3,7,8-PCDD - 0.22 observed and 0.27 ppt predicted; 2,3,4,7,8-PCDF - 0.21 ppt observed and 0.17 ppt predicted. The largest discrepancies, an order of magnitude and more, were for two of the HxCDDs and for all HpCDD/Fs and OCDD/Fs. The total concentrations did not compare as well as the TEQ concentrations, with observed total whole beef concentration of 8.15 ppt and predicted at 2.13 ppt.

Limited examinations are presented on the two key components of this food chain model, the air to vegetation algorithm and the air to soil algorithms, in Lorber, et al.[1]. It was found that the air to soil algorithm appears to underpredict the soil concentrations by up to an order an order of magnitude. Explanations offered for this finding were: 1) the soil dissipation half-life of 10 years was too low, 2) vapor phase impacts to soils were not considered, and 3) detritus additions to the soil reservoir were not considered. Another finding was that the octa congeners, OCDD and OCDF, were significantly underpredicted in both the vegetation and the beef. The V/P modeling estimated that all of these congeners existed in the particle phase. In fact, the fraction in the particle phase was estimated at just below 1.00 (around 0.998) using the OCDD and OCDF parameters listed in Table 1. One can calibrate the V/P partitioning so as to match predicted and observed concentrations of the octa congeners. When doing so for OCDD (calibrated at 0.9998) and OCDF (0.998), both grass/hay and beef concentration predictions matched observations.

A key finding of this model validation exercise is that beef concentrations are dominated by the vapor transfer of dioxins to vegetations that cattle consume. It was found that grass and hay/silage/grain concentrations are overwhelmingly dominated by vapor transfers for 2,3,7,8-TCDD, explaining 93% (grass) and 94% (hay/silage/grain) of final plant concentration. Further, grass and hay/silage/grain explain over 90% of beef concentration (soil accounting for the remaining concentration). Therefore, vapor transfers onto vegetations cattle consume are predicted to explain about 85% of final 2,3,7,8-TCDD beef concentrations. Very similar predictions occur for all congeners, with the exception of OCDD/F where 100% was initially assumed to be in the particle phase. However, the calibration described above for the OCDD and OCDF implies that beef concentrations are also dominated by vapor transfers for these congeners.

3. REFERENCES

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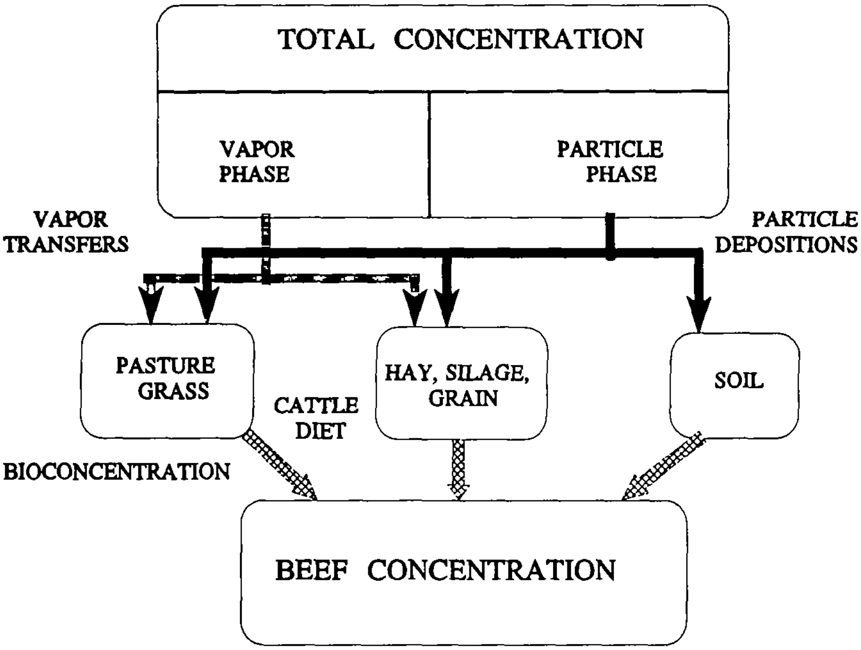

Figure 1. Overview of model to predict beef concentrations from air concentrations.

Table 1. Fate parameters for individual dioxin and furan congeners[1].

		Parameters for B_{vpa}			Parameters for Vapor/Particle Partitioning				
Compound	TEF	H	log Kow	B_{vpa}	T_m, K	VP_s, atm	Vapor	Particle	BCF
2378-TCDD	1.0	$1.6*10^{-5}$	6.64	$1.0*10^{5}$	578	$9.7*10^{-13}$	0.55	0.45	4.32
12378-PeCDD	0.5	$2.6*10^{-6}$	6.64	$6.3*10^{5}$	513	$1.3*10^{-12}$	0.26	0.74	4.16
123478-HxCDD	0.1	$1.2*10^{-5}$	7.79	$2.3*10^{6}$	547	$1.3*10^{-13}$	0.07	0.93	2.02
123789-HxCDD	0.1	$1.2*10^{-5}$	7.79	$6.9*10^{5}$	516	$6.5*10^{-14}$	0.02	0.98	2.24
123678-HxCDD	0.1	$1.2*10^{-5}$	7.30	$6.9*10^{5}$	558	$4.7*10^{-14}$	0.04	0.96	1.74
1234678-HpCDD	0.01	$7.5*10^{-6}$	8.20	$1.0*10^{7}$	538	$4.2*10^{-14}$	0.02	0.98	0.36
OctaCDD	0.001	$7.0*10^{-9}$	7.59	$2.4*10^{9}$	598	$1.1*10^{-15}$	0.00	1.00	0.52
2378-TCDF	0.1	$8.6*10^{-6}$	6.53	$1.5*10^{5}$	500	$1.2*10^{-11}$	0.71	0.29	0.94
23478-PeCDF	0.5	$6.2*10^{-6}$	6.92	$5.3*10^{5}$	469	$4.3*10^{-12}$	0.30	0.70	3.10
12378-PeCDF	0.05	$6.2*10^{-6}$	6.79	$3.8*10^{5}$	499	$3.6*10^{-12}$	0.42	0.58	0.73
123478-HxCDF	0.1	$1.4*10^{-5}$	7.30	$5.9*10^{5}$	499	$3.2*10^{-13}$	0.06	0.94	2.34
123678-HxCDF	0.1	$6.1*10^{-6}$	7.30	$1.4*10^{6}$	506	$2.9*10^{-13}$	0.06	0.94	2.00
123789-HxCDF	0.1	$1.0*10^{-5}$	7.30	$8.3*10^{5}$	520	$3.7*10^{-13}$	0.11	0.89	2.00*
234678-HxCDF	0.1	$1.0*10^{-5}$	7.30	$8.3*10^{5}$	512	$2.6*10^{-13}$	0.07	0.93	1.78
1234678-HpCDF	0.01	$5.3*10^{-5}$	7.90	$6.8*10^{5}$	509	$1.8*10^{-13}$	0.04	0.96	0.41
1234789-HpCDF	0.01	$5.3*10^{-5}$	7.90	$6.8*10^{5}$	495	$1.4*10^{-13}$	0.03	0.98	0.99
OctaCDF	0.001	$1.9*10^{-6}$	8.80	$1.7*10^{8}$	532	$4.9*10^{-15}$	0.00	1.00	0.20

[1] Column headings are:

TEF: Toxic Equivalency Factor
log Kow: Log octanol water partition coefficient
T_m: Melting point temperature, o K
Vapor: Vapor fraction in ambient air
BCF: Beef biotransfer factor, unitless

H: Henry's Constant, atm-m^3-mole
B_{vpa}: air-to-leaf transfer factor, unitless
VP_s: Crystalline solid vapor pressure, atm^{-1}
Particle: Particle fraction in ambient air

* McLachlan, et al.[13] did not provide data on 123789-HxCDF; the value for this congener was assumed to be identical to 123678-HxCDF.

Table 2. Summary of air and whole beef concentrations of dioxin-like compounds used as observed data, and predicted whole beef concentrations.

Compound	Air, pg/m^3	Observed beef, ng/kg	Predicted beef, ng/kg
2378-TCDD	0.002	0.03	0.03
12378-PCDD	0.006	0.22	0.27
123478-HxCDD	0.005	0.26	0.10
123678-HxCDD	0.007	0.84	0.03
123789-HxCDD	0.010	0.21	0.04
1234678-HpCDD	0.116	1.92	0.29
OCDD	0.586	2.91	0.29
2378-TCDF	0.023	0.06	0.46
12378-PCDF	0.010	0.04	0.07
23478-PCDF	0.006	0.21	0.17
123478-HxCDF	0.012	0.51	0.08
123678-HxCDF	0.012	0.06	0.13
123789-HxCDF	0.003	0.06	0.04
234678-HxCDF	0.009	0.07	0.07
1234678-HpCDF	0.042	0.40	0.04
1234789-HpCDF	0.006	0.13	0.01
OCDF	0.034	0.22	0.01
TOTAL CONCENTRATION	0.872	8.15	2.13
TEQ CONCENTRATION	0.019	0.48	0.36