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

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ABSTRACT

A model for predicting concentrations of dioxin-like compounds in beef is developed and tested. The key premise of the model is that concentrations of these compounds in air are the source term, or starting point, for estimating beef concentrations. Vapor-phase concentrations transfer to vegetations cattle consume, and particle-bound concentrations deposit onto soils and these vegetations as well. Congener-specific bioconcentration parameters, coupled with assumptions on cattle diet, transform soil and vegetative concentrations into beef fat concentrations. The premise of the validation exercise is that a profile of typical air concentrations of dioxin-like compounds in a United States rural environment is an appropriate observed independent data set, and that a representative profile of United States beef concentrations of dioxin-like compounds

is an appropriate observed dependent result. These data were developed for the validation exercise. An observed concentration of dioxin toxic equivalents in whole beef of 0.48 ng/kg is compared with a predicted 0.36 ng/kg. Principal uncertainties in the approach are identified and discussed. A major finding of this exercise was that vapor phase transfers of dioxin-like compounds to vegetations that cattle consume dominate the estimation of final beef concentrations: over 80% of the modeled beef concentration was attributed to such transfers.

INTRODUCTION

Polychlorinated dibenzodioxins (CDDs) and polychlorinated dibenzofurans (CDFs; together abbreviated PCDD/Fs) are chemically classified as halogenated aromatic hydrocarbons. Seventeen of these compounds are commonly referred to as dioxin-like compounds; they have chlorine substituents in the 2,3,7,8 positions and are considered to have toxicity related to that of 2,3,7,8-tetrachloro-p-dioxin (commonly referred to as 2,3,7,8-TCDD or simply TCDD). This paper focuses on these 17 "dioxin-like" compounds. A toxic equivalent, or TEQ, concentration (in air, beef, or other media) is calculated by multiplying individual congener concentrations by congener-specific toxicity equivalency factors (TEFs; this paper uses the International scheme [1]) and then summing toxic equivalent individual congener concentrations to obtain a TEQ concentration. TEFs for the dioxin-like compounds are listed in Table 1, along with all other compound-specific parameters. A subset of polychlorinated biphenyls (PCBs) also *is* thought to have dioxin-like toxicity, but these compounds are not further considered in this paper.

In recent years, it has become clear that the principal route of exposure of humans to dioxin-like compounds in the environment is through the food chain, with the most concern directed at foods of high fat content including meats, dairy products and fish [2, 3, 4, 5, 6, 7]. The principal source of these compounds in the environment currently is thought to be industrial emissions from tall stacks, with secondary sources including effluent discharges into surface waters, land application of sludges containing these

compounds, and as by-products of industrial chemical production [2]. Other sources being studied include emissions from diesel vehicles [8], reservoir sources including soil resuspensions and water body sediments, forest fires [9] which may or may not be a reservoir source, and residential wood burning. These compounds are found in air throughout the world and notably in settings where no nearby source of release is identified.

Modelers have assumed that the "source" of dioxin-like compounds in cattle products including beef and milk is air concentrations [10, 11, 12, 13, 14]. These cited modeling efforts are all similar in that they route the air-borne contaminants to vegetations and soil, and subsequently to the beef or milk.

The modeling in this paper builds on these earlier efforts. A model structure, from air to beef, is described. A validation exercise is attempted by using this structure to predict average beef concentrations. The "observed" source, or independent, term in this modeling exercise are the ubiquitous air-borne reservoirs of dioxin-like compounds in rural environments. The "predicted", or dependent, results are the concentrations in whole beef. Both these quantities are developed from reported United States measurements. Best estimates of all model parameters are developed from information in the literature. The predicted concentrations in beef are compared with observed concentrations in beef.

While this exercise is called a validation exercise, it probably would not qualify as such in the traditional sense. Most environmental model validation exercises rely on data obtained from a single site. This exercise instead relies on the ubiquitous nature of dioxins in the environment and begins with a representative air concentration profile, not one from a specific site. Similarly, beef concentrations are generated from available data. Also, the uncertainties in both the "observed" data sets and in the assignment of parameter values, would indicate that refinements in the data are necessary before ascribing a significant amount of finality to the model structure, model parameter assignments, and the model results.

MODEL STRUCTURE

The model structure is shown in Figure 1. The total concentrations of these compounds in air shown on top of this figure and the beef concentrations on the bottom represent the measured quantities. In between these observations are the key model components, which include: 1) partitioning of total concentrations between a particle and a vapor phase, 2) particle bound depositions onto pasture grass, non-grass vegetations which cattle consume, and soil, 3) vapor-phase transfers onto these vegetations, 4) cattle dietary assumptions including the impact of feedlot fattening, and 5) derivation of congener-specific bioconcentration parameters which translate a weighted average concentration in the cattle diet to a beef fat concentration.

Sections below summarize the sources of information for the two key measured quantities. Below that are sections summarizing each model component and the final parameter values selected. All model parameters specific to congeners are given in Table 1, and all other parameters not specific to congeners are given in Table 2.

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. An evaluation of ambient air monitoring studies in the United States showed that nearly all of the data was from urban or suburban settings. Measurements which were attributed to a nearby identifiable source, such as an incinerator, were not considered for this effort. Data which were found according to these criteria include: a multiyear monitoring effort conducted at eight sampling locations in the Southern California area by the Research Division of the California Air Resources Board from December 1987 through March 1989 [15], additional studies in Los Angeles, CA [16], studies in cities and towns in New York [17, 18], studies in various towns in Connecticut [19,20], a study covering four sites in Ohio [21], and a long-term study of PCDD/Fs in the ambient air around Bloomington, Indiana [22].

From the above studies, 84 air samples were available. Generally, higher

substituted PCDD and PCDF congeners accounted for the majority of positive samples containing quantifiable CDD/CDF residues in these studies (i.e., HxCDD/F congeners and higher). To determine a profile of air concentrations, non-detects were evaluated as half the detection limit given in the reports. The mean TEQ level was computed as 0.095 pg/m^3. The mean total (not TEQ) concentration of dioxin-like congeners equaled 4.4 pg/m^3.

This TEQ concentration is consistent with reports from similar settings in Europe. Clayton, et al. [23] report median TEQ values for the cities of Cardiff and Manchester, England to be the same at 0.1 pg/m^3, with lower concentrations of 0.06 and 0.04 pg/m^3 in London and Stenvenage (an industrial town), although they caution that a large number of non-detects were found for tetra, penta-, and hexa-CDDs. Liebl, et al. [24] report a range of 0.04 pg TEQ/m^3 for a rural background situation to 0.15 pg/m^3 for an industrial area. Their data covered four sites and three annual samples in Germany.

There are a few references which do have congener-specific data which might be characterized as rural. One is outside of United States in Sweden [25]. Air samples were taken in four areas, ranging from the Stockholm urban area to the open coastal area of the Baltic Sea. Results indicate lower TEQs when going from the urbanized area to the remote areas. The Stockholm city center was 0.024 pg TEQ/m^3, a "suburb" was 0.013 pg TEQ/m^3, a "countryside remote" area was 0.0044 pg TEQ/m^3, and an "open coastal" area was 0.0026 pg TEQ/m^3. Twenty-five PCDD/F concentrations were listed at the fg/m^3 level (i.e., 0.001 pg/m^3).

The only reference found for the United States with congener specific data for an area described as rural was from Ohio [21]. Six sites were tested, one of which might be considered rural. The data contained many non-detects, with detection limits between 0.033 to 0.82 pg/m^3, although most non-detects had detection limits less than 0.3 pg/m^3. The following TEQ concentrations were derived only from the positive listings: two sites in Akron - 0.077 and 0.079 pg TEQ/m^3, two sites in Columbus - 0.092 and 0.179 pg TEQ/m^3, a site near a highway - 0.065 pg TEQ/m^3, and a rural site in a town called Waldo

- 0.045 pg TEQ/m^3. Like the data from Sweden, one can see a trend for lower concentrations in the Waldo site as compared to the sites in Columbus and Akron.

Other references did contain other pertinent data, such as total concentrations, TEQ concentrations, or congener group concentrations, in rural and urban settings. Eitzer and Hites [26] took data from Bloomington, Indiana and a remote area in Wisconsin known as Trout Lake. TEQ concentrations were not given, but total congener group concentrations were reported. The sum of congener group concentrations, or total concentrations of dioxins and furans, equaled 2.2 pg/m^3 for Bloomington, and 0.51 pg/m^3 for Trout Lake. This 0.51 pg/m^3 total concentration is similar to the total concentration found in the "countryside remote" area in Sweden discussed above, which is 0.41 pg/m^3 (TEQ concentration was 0.0044 pg/m^3, as noted above).

In an evaluation of air, soil, sediment, and fish in Elk River, Minnesota, a rural setting, again total congener concentrations in the air were reported [27]. Concentrations for three sites and for two sampling dates, one in the winter and one in the summer, were available. Two of the three sites were in rural settings and the third was near a refuse derived fuel incinerator. Total concentrations for the two rural sites were 2.29 and 2.91 pg/m^3 in winter, and 0.58 and 0.38 pg/m^3 in summer. For the third site near the incinerator, winter and summer concentrations were 15.2 and 0.35 pg/m^3, respectively. The average of the four data points for rural settings was 1.54 pg/m^3, while the average of the two data points near the incinerator was 7.78 pg/m^3.

Finally, Maisel and Hunt [16] list TEQ concentrations only for monitoring networks including: a Connecticut coastal location described as urban (measurements described as "wintertime"), a southern California urban setting ("annualized"), and a central Minnesota rural setting ("annualized"). While not identifying it as such, this central Minnesota setting could be the one described above in Elk River, Minnesota. The TEQ concentrations for the two urban and one rural setting were: 0.092, 0.091, and 0.021 pg TEQ/m^3.

Key points from this literature summary are:

1. Congener specific profiles for rural settings in the United States are generally not

available. Based on several studies encompassing 84 data points with specific congener concentrations which best represent urban/suburban settings, but are not near identified emission sources, a mean TEQ air concentration of 0.095 pg/m^3 is estimated.

2. Studies are available which do provide side by side data on urban and rural settings, although the literature references only list congener group concentrations or total TEQ concentrations (with the exception of the Edgarton, et al. [21] described above). What this summary shows is that rural air concentrations of dioxin-like compounds appear to be 4-6 times lower than in urban settings, and that a TEQ concentration for rural settings appear to range from 0.004 to 0.04 pg/m^3.

In order to develop a profile of air concentrations that will be considered representative of rural settings, what will be done, therefore, is to take the profile of congener-specific air concentrations for urban/suburban settings leading to a TEQ concentration of 0.095 pg/m^3, and divide each concentration by 5. The resulting TEQ concentration is 0.019 pg/m^3. The total concentration of CDD/Fs in this rural profile equals 1.09 pg/m^3. A simplistic division by five for all congeners essentially assumes that the profile of air concentrations proportionally remains the same from the urban sources to the rural settings. The specific concentrations used are shown in Table 3.

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. In one study beef samples were composited with veal and the results described as beef/veal. The three studies only encompassed 14 samples. These studies include one conducted by the California Air Resources Board [CARB; 28], the results of background analysis from a study conducted by the National Coalition for Air and Stream Improvement [NCASI; 29] and a survey of foods conducted in New York [30].

CARB collected foods in two urban areas of California. Food samples were collected from commercial food sources in Los Angeles and San Francisco with an

emphasis on food stuffs of California origin. A total of 8 composite samples of beef/veal were analyzed for 2,3,7,8-substituted PCDD/Fs. Each composite sample contained up to 31 individually collected food items. Beef/veal samples were analyzed on a lipid weight basis, but were subsequently converted to a wet weight basis by multiplying the lipid weight concentration of PCDD/Fs by the fraction of fat contained in the beef [28].

The NCASI study collected random food samples directly from the shelves of grocery stores located in the southern, midwestern and northwestern regions of the United States, without any further geographic delineation. The 3 beef samples were analyzed for 2,3,7,8-TCDD and 2,3,7,8-TCDF only [29].

Schecter et al. [30] conducted a complete congener analyses of 18 food samples collected directly from a supermarket in Binghamton, NY in early 1990. The samples included 5 fish, 3 types of beef, 1 chicken, 1 pork, 1 lamb, 1 ham, 1 bologna, 1 heavy cream and 4 types of cheese.

At least one congener was detected in 13 of the 14 composite beef/veal samples. One sample had no detectable congeners. The congeners most frequently detected in beef/veal were 1,2,3,4,6,7,8-HpCDD and OCDD, and only one congener was not detected in any of the samples. The total TEQ for beef and veal was calculated by using one-half the detection limits reported by the researchers to represent the concentration of nondetectable PCDD/F congeners in the samples. Using this methodology, the TEQ concentration was estimated to be 0.48 ng/kg (ppt) for beef and veal on a wet weight basis. If nondetectable concentrations are assumed to be zero, the estimated TEQ for beef and veal 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 beef concentrations, and they are shown in Table 3. All studies reported concentrations as lipid-based concentrations. Where lipid fractions were not supplied, 19% lipid content for beef was assumed to estimate whole beef concentrations.

Furst, et al. [3] analyzed 107 food samples collected in Germany. Three samples of beef showed a TEQ concentration in beef fat of 1.69 ng/kg. If beef fat is assumed to

be 19% of whole beef, this would imply a whole beef concentration of 0.32 ppt. This appears consistent with the 0.48 ppt TEQ concentration from the United States data.

Finally, it is important to note that the United States samples came from commercial food outlets (grocery stores, e.g.). This fact will be used to imply that the data represents beef cattle that went through a feedlot fattening process prior to slaughter. As will be discussed below, this has implications regarding final concentrations.

Model Development and Parameter Values

1. Partitioning total concentrations into a vapor and a particle phase

Several studies were retrieved which reported the partitioning of dioxins into a particle and a vapor phase [19, 22, 31, 32, 33, 34] . These ambient air monitoring studies used high-volume samplers consisting of a glass fiber particulate filter and polyurethane foam absorbent trap. The researchers estimated the fraction of the total measured concentration which was in the particulate phase from the particulate filter and which was in the vapor phases from the foam trap. The following averages are percentages of congener groups found in the vapor and particle phases (not reported and not detected are not included in the averages; 80/20 equals 80% vapor, 20% particle): TCDD - 87/13; PCDD - 69/31; HxCDD - 30/70; HpCDD - 10/90; OCDD - 4/96; TCDF - 83/17, PCDF - 65/35; HxCDF - 35/65; HpCDF - 11/89; OCDF - 2/98.

Because the sampler is not artificially heated or cooled, but is allowed to operate at existing ambient air temperatures during sampling sessions, the method can be used to imply the vapor phase and particle bound partitioning of PCDDs/Fs in ambient air. This is accomplished by separately extracting and analyzing the glass fiber filter and the polyurethane foam for the presence of CDD/CDF congeners. However, the V/P ratio interpreted from these results is operationally defined. This will only give an approximate indication of the V/P ratio since mass transfer between the particulate filter and the vapor trap cannot be ruled out. The particulate filter paper porosity is $\geq$ 0.1 microns, and

therefore it is possible that aerosol particles with diameters < 0.1 microns will pass through the filter and be trapped in the polyurethane foam plug. If this is the case, then the percent observed in vapor phase will be overestimated. The method involves ambient air sampling at a relatively high sample volume, e.g., 300-400 m^3 of air, over a 24-hour period. It is possible that PCDDs/Fs that are not sorbed to particulate matter captured in the filter may be volatilized by subtle changes in ambient temperature, and that CDD/CDF in the vapor phase may be carried with the sampling air flow to the PUF sorbent trap. This is a second possible reason why the percent of the CDD/CDFs partitioned to the vapor phase would be an overestimate. Unfortunately, no empirical data could be found demonstrating that any of these effects may actually occur.

Since these sampling results could overestimate the fraction in ambient air, a theoretical model for estimating the fraction of total concentration in the particulate and vapor phases will be used in this assessment. Bidleman [35] offers a theoretical construct for estimating the vapor phase/particle bound partitioning of CDDs/CDFs in ambient air. Bidleman presents the theory that a portion of the semivolatile compounds found in ambient air are freely exchangeable between the vapor and particle phases. Bidleman defines a second portion, the nonexchangeable fraction, as the quantity that is strongly and irreversibly adsorbed to particulate matter, and is not at equilibrium with a corresponding vapor phase. Bidleman cites an earlier model by Junge [36], a theoretical model based on adsorption theory, which mathematically described the exchangeable fraction of the 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. This is given by:

$$\phi = \frac{c\ S_T}{p + c\ S_T} \qquad (1)$$

where:

ϕ = adsorbed fraction, unitless

c = constant developed by Junge, atm-cm

S_T = total surface area of atmospheric aerosols in relation to total volume of air, cm^2/cm^3

p = solute saturation vapor pressure, atm^{-1}

Although Junge treated the term 'c' in Equation (1) as a constant, e.g., $c = 1.7 * 10^{-4}$ atm-cm, Bidleman notes that it actually is variable and dependent on the chemical's sorbate molecular weight, the surface concentration of the chemical on aerosol particles (assuming monolayer coverage), and the difference between the heat of desorption from the surface of a particle and the heat of vaporization of the liquid-phase sorbate.

Bidleman [35] poses the question as to whether it is the chemical's sub-cooled liquid vapor pressure (P_l) or the chemical's crystalline solid vapor pressure (P_s) that ultimately controls the rate of adsorption to aerosol particles. P_l and P_s are related, as given in Equation (2) below, taken from Bidleman [35]. The sub-cooled liquid vapor pressure is estimated by extrapolating below the melting point of the compound.

$$\ln\left(\frac{P_l}{P_s}\right) = \frac{\Delta S_f\,(T_m - T)}{R\,T} \qquad (2)$$

where:

P_s = crystalline solid vapor pressure, atm^{-1}

P_l = liquid sub-cooled vapor pressure, atm^{-1}

ΔS_f = entropy of fusion, atm-m^3/mole-deg ◦K

R = universal gas constant, atm-m^3/mole-deg ◦K

T_m = melting point, ◦K

T = ambient air temperature, ◦K

Bidleman notes that a satisfactory estimate of $\Delta S_f/R$ observed in other treatments of this

subject is 6.79. This can be substituted for $\Delta S_f/R$ in Equation (2), and used as a constant. Bidleman argues that the use of P_l in Junge's equation, the sub-cooled liquid vapor pressure, makes the most accurate estimation of the vapor phase/particle bound partitioning of semi-volatile organic compounds in ambient air, and this assumption is made here as well.

Bidleman [35] provides estimates of average total surface areas of aerosol particles relative to average total volume of air (cm^2/cm^3), the term S_T in Equation (1), citing a study by Whitby [37]. In addition, Whitby estimated the average total volume of aerosol particles per volume of air (V_t = cm^3 particles/cm^3 of air). Whitby's [37] calculations varied according to the density of aerosol particles in the ambient air in different air sheds. Bidleman [35] describes four air sheds from Whitby's work, in order of increasing particle density, as: clean continental background, average background, background plus local sources, and urban. The modeling exercise of this paper will assume that the category, background plus local sources, best fits settings where cattle are raised for beef. The local sources as used here do not refer to sources of contaminant release, but rather to sources which would increase the concentration of particles in the air. Dust generation from local agricultural practices and vehicular traffic justify the selection of background plus local sources over background. Urban settings are unlikely to be representative of cattle farms. The S_T and V_T for this setting are $3.5 * 10^{-6}$ cm^2/cm^3 and $4.3 * 10^{-11}$ cm^3/cm^3, respectively.

Calculations of ϕ (the fraction that is bound to particulate) from Equation (1) were made on a congener-specific basis for the PCDD/Fs. The estimate of $1.7 * 10^{-4}$ atm-cm for the value c was assumed from the work of Junge [36]. The sub-cooled vapor pressures were converted from the crystalline solid vapor pressures of the specific congeners using Equation (2). The crystalline solid vapor pressures and melting points of the dioxin-like congeners *are* given in Table 1, along with the final calculated sorbed fraction, ϕ, as well as the vapor fraction ($1-\phi$) for each dioxin congener.

Note that the final calculated fractions sorbed to particles calculated by the

Bidleman approach exceed those as measured using high volume samplers. For example, the fraction sorbed as estimated by the Bidleman approach for 2,3,7,8-TCDD is 0.45 (see Table 1), whereas the measured fraction sorbed for TCDD congener group is 0.13 as discussed above. This is consistent with the concern described above for these high volume sample results - that they may have a tendency to underestimate the particle phase fraction. On the other hand, use of the Bidleman approach, as he defines it, implies that all dioxins are "exchangeable" with atmospheric particles in rural settings; that there is not an "unexchangeable" fraction. Nothing in the literature could be found to conclude that there is an unexchangeably bound fraction to consider in ambient air of rural environments. However, it is certainly possible that there may be an unexchangeable fraction, given the strong sorptive tendencies of these chemicals. If there is an "unexchangeable" fraction, then the sorbed fraction may be higher than the values shown in Table 1 which were used in this paper.

2. Particle Depositions to Soils and Vegetations

Several exposure efforts for 2,3,7,8-TCDD [11, 12, 13, 14], and a general exposure methodology for indirect impacts from incinerator emissions [38], have modeled the accumulation of residues in vegetative matter (grass, fodder, vegetables) resulting from deposition of contaminated particulates. The steady state solution for plant concentrations which they use, and which is used in this exercise, is:

$$C_{ppa} = \frac{F_d + R_w F_w}{k_w Y_j} \qquad (3)$$

where:

C_{ppa} = vegetative concentration due to settling of contaminated particulates onto plant matter, ng/kg or ppt

F_d = contaminant dry deposition rate onto plant surfaces, ng/m^2-yr

R_w = retention of wet deposition on plants, fraction

F_w = contaminant wet deposition rate onto plant surfaces, ng/m^2-yr

k_w = first-order weathering dissipation constant, 1/yr

Y_j = dry matter yield of crop j, kg/m^2

The contaminant dry deposition rate, F_d, is given as:

$$F_d = \frac{C_{pa} \; V_d \; I_j}{1000} \tag{4}$$

where:

F_d = unit contaminant dry deposition rate onto plant surfaces, ng/m^2-yr

C_{pa} = air-borne particulate phase contaminant concentration, pg/m^3

V_d = dry deposition velocity, m/yr

I_j = fraction of particulates intercepted by crop j during deposition, unitless

1000 = units conversion factor

The velocity of particle deposition will be assumed to be 0.2 cm/sec. This was the velocity assumed by Travis and Hattemer-Frey [13] in their air-to-beef modeling exercises. It is also consistent with the dry deposition velocities measured by Koester and Hites [39], who found dry deposition velocities of particle-bound total dioxins averaging 0.16 cm/sec in Bloomington and 0.23 cm/sec in Indianapolis, with an overall average in their data set of 0.19 cm/sec.

Koester and Hites [39] also measured wet deposition of total dioxins at these two sites, and generally found wet deposition to be comparable to dry deposition. Specifically, the estimated annual wet deposition of dioxins at Indianapolis was equal to 0.7 times dry deposition, while at Bloomington, wet deposition was 1.3 times dry deposition.

Therefore, it will be assumed in this modeling framework that wet deposition equals dry deposition, or $F_w = F_d$, using the parameter names of Equation (3).

It is assumed that dry depositions fully adhere to plant surfaces while the deposition is occurring; the weathering constant, k_w, models the loss of the vegetative reservoir of particle bound contaminants due to wind, rain, or other weathering process after deposition has occurred. However, it is not clear that wet deposition should also be assumed to fully adhere during a wet deposition event. Hence, the R_w parameter, or fraction of wet deposition adhering, was introduced. Prior modeling efforts of the impact of depositions of dioxin-like compounds to vegetations are unclear with regard to wet deposition. Several modeling efforts [11, 12, 13, 14], which included depositions of particle-bound 2,3,7,8-TCDD to vegetations and subsequent impacts to beef/milk, did not discuss the distinction in wet and dry deposition. They modeled "total deposition" impacts, describing total as wet and dry deposition, total deposition, or simply as deposition. On the other hand, McKone and Ryan [40] reduce the wet deposition portion of total deposition. They promote use of a "b", which they define as the fraction of material retained on vegetation from wet deposition. They recommend a value between 0.1 and 0.3.

The clearest indication of the fate of wet deposition of particles can be found in Hoffman, et al. [41]. In that field study, simulated rain containing soluble radionuclides and insoluble particles labeled with radionuclides was applied to pasture-type vegetation under conditions similar to those found during convective storms. The fraction of the labeled particles found to remain on the vegetation after the rainfall varied from 0.24 to 0.37. Nine values comprised this range, including particle sizes of 3, 9, and 25 μm, and cover described as clover, fescue, and mixed (a site with old field vegetations including fescue, grasses, weeds, and wild flowers). Based on this work, the R_w will be assumed to be 0.30 in the modeling of this paper.

Fries and Paustenbach [11] note that this approach may overestimate concentrations because crops can be harvested or pastures grazed before the plant

concentrations reach steady state, and that a kw based on a weathering half-life of 14 days may be too long given experimental results of Baes, et al. [42] which showed a range of 2-34 days, and a median value of 10 days. Stevens and Gerbec [12], and EPA [38], considered harvest intervals by including the exponential term, $(1-e^{-kt})$, and assigning values of t based on harvest intervals of different crops. Grazing or harvesting of cattle feeds are not considered in this modeling exercise; a kw of 18.01 yr^{-1} (half-life of 14 days) is used for all dioxin-like compounds.

Interception values and crop yields were determined in the *aforementioned* assessments based on geographic-specific crop yield data provided in Baes, et al. [42], and crop-specific relationships estimating interception fraction based on yield (Y), such as the following for hay/grasses presented in Baes, et al., [42]: $I = 1 - e^{-2.88Y}$. Fries and Paustenbach [11] presented estimates for high, medium, and low yields of silage, hay, and pasture grass, and used the interception equations given in Baes, et al. [42] to calculate interception fractions to go with their yields. Their assumptions on median yields and interceptions are used in this exercise.

As will be described below, this assessment will assume that, prior to feedlot fattening, the cattle diet consists of soil and two vegetative categories: pasture grass and non-pasture feeds such as hay, silage, or grain. Medium yields and interceptions for grass as given in Fries and Paustenbach [11] are 0.15 kg/m^2 and 0.35, respectively. The non-pasture grass feeds including hay, silages, and grains will be grouped together and abbreviated hay/silage/grain for the remainder of this paper. The yield and interception values are the average of the medium values for silage and hay estimated by Fries and Paustenbach [11]: 0.63 kg/m^3 yield and 0.62 interception.

This grass and hay/silage/grain distinction has been made for one principal reason, and this has to do with the transfer of vapor phase contaminants to the vegetations. Grasses are a leafy vegetation, and as will be explained, are the most impacted vegetation. Pasture grass is also a principal component of the cattle lifetime diet. Other vegetations are part leafy, such as hay and silage, and part bulky, such as silage and

grains. The transfer of vapors to these vegetations, as a group, will be lower than the transfer of vapors to grass. This will be further discussed below in the next section on vapor transfers.

The soil concentration depends on the rate that particle bound dioxins deposit onto a reservoir of soil, and the rate that they dissipate from soil:

$$C_s = \frac{F_d + F_w}{k_s M} \tag{5}$$

where:

C_s	=	soil concentration due to settling of contaminated particulates, ng/kg or ppt
F_d	=	contaminant dry deposition rate onto soils, ng/m^2-yr
F_w	=	contaminant wet deposition rate onto soils, ng/m^2-yr
k_s	=	first-order soil dissipation constant, 1/yr
M	=	mass of mixing soil per m^2 of area, kg/m^2

Note that there is no adherence consideration and no R_w term in Equation (5) as there is in Equation (3). Dry deposition, F_d, is calculated as in Equation (4), except that there is no crop interception. It is assumed that depositing particles reach the ground surface either immediately or over time (i.e., with the weathering processes removing particle bound reservoirs from the vegetative surfaces). The first-order dissipation constant, k_s, represents processes which dissipate surface residues of dioxin-like compounds, where the precise mechanisms of dissipation are not specified, but could include transport (volatilization, erosion) and degradation (principally photolysis for the dioxin-like compounds) mechanisms. The studies on 2,3,7,8-TCDD described in Young [43] imply a dissipation half-life of 10 years. Fries and Paustenbach [11] suggested the use of a half-life of at least 10 years, and used a 15 year half-life in their modeling of the

impact of air-borne deposition of 2,3,7,8-TCDD originating from incinerator emissions. A dissipation rate constant of 0.0693 yr^{-1}, corresponding to a half-life of 10 years, is used in this exercise. Finally, the mass of soil term, M, will assume a 1 cm depth of mixing, a mixing depth used by others for non-tilled situations such as in pastures [11, 38], and a soil bulk density of 1.5 g/cm^3. This leads to an M value of 10 kg/m^2.

3. Vapor Phase Transfers to Vegetations

The algorithm estimating plant concentrations as a function of vapor-phase air concentrations is:

$$C_{vpa} = \frac{B_{vpa} \quad C_{va} \quad VG_{ag}}{1000 \ d_a} \tag{6}$$

where:

C_{vpa} = concentration due to vapor-phase transfer of airborne contaminants, ng/kg or ppt

B_{vpa} = mass-based air-to-leaf biotransfer factor, unitless [(µg contaminant/kg plant dry)/(µg contaminant/kg air)]

C_{va} = vapor-phase concentration of contaminant in air, pg/m^3

VG_{ag} = empirical correction factor which reduces vegetative concentrations considering that B_{vpa} was developed for transfer of air-borne contaminants into leaves rather than into bulky above ground vegetation

d_a = density of air, 1.19 kg/m^3,

1000 = units conversion factor

Bacci, et al. [44, 45, 46] conducted laboratory experiments on the air-to-leaf transfer of vapor-phase concentrations of 14 organic contaminants to azalea leaves. With

their results, they developed an empirical relationship for a vapor-phase bioconcentration factor from air to azalea leaves, termed in this paper the B_{vpa}, but which was termed BCF by Bacci and coworkers. They related the B_{vpa} to the chemical octanol-water and air-water partition coefficients, Kow and Kaw. The air-water partition coefficient, Kaw, is a dimensionless form of Henry's Law constant, H, derived by dividing H by the product of the ideal gas constant, R, and the temperature, T. The most general form of the air-to-leaf transfer factor is on a unitless volumetric basis: [ng contaminant/L or leaf]/[ng contaminant/L of air], and is given as:

$$\log B_{vol} = 1.065 \log Kow - \log \left(\frac{H}{R\ T} \right) - 1.654 \qquad (7)$$

where:

B_{vol}	=	Bacci volumetric air-to-leaf biotransfer factor, unitless [(µg contaminant/L of wet leaf)/(µg contaminant/L air)]
Kow	=	contaminant octanol water partition coefficient, unitless
H	=	contaminant Henry's Constant, atm-m^3/mol
R	=	ideal gas constant, 8.205 x 10^{-5} atm-m^3/mol- ◦K
T	=	temperature, 298.1 ◦K
-1.654	=	empirical constant

Bacci, et al. [45] showed that the volumetric transfer factor can be transformed to a mass-based transfer factor by assuming that 70% of the wet leaf is water, the leaf density is 890 g/L, and the air density is 1.19 g/L:

$$B_{vpa} = \frac{1.19\ g/L\ \ B_{vol}}{0.3\ \ 890\ g/L} \qquad (8)$$

where:

B_{vpa} = mass-based air-to-leaf biotransfer factor, unitless [(µg contaminant/kg plant dry)/(µg contaminant/kg air)]

B_{vol} = Bacci volumetric air-to-leaf biotransfer factor, unitless [(µg contaminant/L of wet leaf)/(µg contaminant/L air)]

Bacci's experiments were conducted under conditions which would not account for photodegradation of his test chemicals from the leaf surfaces. A recent study by McCrady and Maggard [47] which investigated the uptake and photodegradation of 2,3,7,8-TCDD sorbed to grass foliage suggests a significant difference in experimental B_{vol} for grass plants. The authors note that the log B_{vol} for 2,3,7,8-TCDD and azalea plants, using Bacci's empirical relationship, was estimated as 8.5. The experimental log B_{vol} for 2,3,7,8-TCDD and grass plants reported by McCrady was 6.9 when photodegradation was accounted for, and 7.5 in the absence of photodegradation. Since the photodegradation experiments by McCrady best represent outdoor conditions, their work suggests that the air-to-leaf transfer factor estimated by Bacci's algorithm may be 40 times too high for vapor-phase transfer of 2,3,7,8-TCDD onto grass leaves.

While McCrady's experiments included consideration of photodegradation of 2,3,7,8-TCDD, it is uncertain how their results can be generalized to other dioxin-like compounds and vegetations other than grass. There is very little information in the literature on the photodegradation of dioxins and furans on plant surfaces. McCrady and Maggard [47] cite Crosby and Wong [48] as the only other work measuring photodegradation of 2,3,7,8-TCDD from leaf surfaces. In that work, 2,3,7,8-TCDD was applied as a 15 ppm concentration in Agent Orange, and McCrady speculated that the rapid photodegradation measured in those experiments occurred because the herbicide formulation contained carriers and organic solvents that may have promoted photodegradation. Some experiments conducted in organic solvents [49, 50] and in water [51] noted reductive dechlorination resulting in dioxin compounds of lower chlorination.

Other experiments did not find such reductive dechlorination [52, Friessen, et al. [51], who found reductive dechlorination in one experiment, but not in another]. An important issue to consider, at least, for the process of photodegradation of dioxins and furans on leaf surfaces is the possible formation of lower chlorinated congeners of non-zero toxic equivalency.

Another issue discussed by McCrady is that the theoretical time for the grass tissue to reach a steady state in his experiments is much shorter than that indicated in the Bacci experiments. Using Bacci's results, McCrady noted that the azalea leaves theoretically take greater than 400 days to reach equilibrium, in comparison to less than 20 days to reach equilibrium for the grass plants in his experiments. This difference is not entirely due to photodegradation. McCrady (personal communication, J. McCrady, Corvallis Environmental Research Laboratory, EPA) suggests that the 50-day exposure time used in Bacci's experiments may allow for considerable diffusion into the newly formed plant surface wax. The sorbed TCDD residues may be trapped and unable to volatilize. Thus, for estimating contaminant concentrations in animal feeds such as relatively short-lived grass plants, the equilibrium B_{vol} from the Bacci azalea model may overestimate the contaminant concentration in grass. On the other hand, McCrady's experiments may have been conducted in too short a time frame, with the sum of uptake and elimination phases being less than 10 days in the various experimental designs. The volatilization and photodegradation rates reported by McCrady may be higher than what might occur for the longer exposure times expected in real world situations, where growth and residue trapping may occur.

These arguments are being presented to demonstrate the uncertainty in choosing either of the two reported B_{vol} values for estimating plant contaminant concentrations. McCrady's results pertaining to 2,3,7,8-TCDD cannot be generalized to other dioxin-like compounds or other contaminants in terms of commonly available contaminant parameters such as H or Kow. Therefore, a McCrady framework similar to Bacci's for estimating congener-specific B_{vpa} cannot be offered at this time. On the other hand, their work

strongly suggests that the Bacci model may be inappropriate for terrestrial vegetations of the beef food chain, and Bacci's experiments, because of their length of time, the use of an azalea leaf of high wax content, and lack of an artificial light source simulating photodegradation, are likely to have overestimated the air to leaf transfers.

What will be done for this assessment is to first estimate a congener-specific B_{vol} using the Bacci algorithm of Equation (7) above. Then, it will be transformed into a mass-based B_{vpa} as in Equation (8), except that the assumptions McCrady and Maggard [47] used for fraction of grass plant that is wet weight, 85%, and the grass leaf density, 770 g/L, will instead be used as more representative of beef food chain vegetations. Most importantly, the B_{vpa} calculated this way will be empirically reduced by a factor of 40 for all dioxin-like congeners as suggested by the difference in McCrady's experiments as compared to Bacci's.

A second empirical adjustment also is warranted, as given by the VG term of Equation (4) above. Several research efforts have shown that contamination of above ground vegetations by dioxin-like compounds does not occur through translocation from the soil, but rather from air transfers, and that the contamination resides principally on the surface of the vegetation with little within-plant translocation [53, 54, 55, 56, 57, 58, 59]. One notable exception to this trend was a recent experiment by Huelster and Marschner [60], who demonstrated experimentally that zucchinis and pumpkins grown in soil containing dioxins and furans become contaminated as a result of root uptake and translocation. The principal evidence of this was the uniform and extensive concentrations in these plants, coupled with careful experimental controls. Also, other vegetations including tomato plants and a third vegetation of the cucumber family included in Huelster's field testing, cucumber, did not have this trend. The zucchini and pumpkin results indicate that some plant species are exceptions to the conventional wisdom that dioxin contamination of above ground vegetations is a outer plant surface phenomena with little within-plant translocation, and no root to shoot translocation.

Assuming grasses and non-grass cattle feeds are not like zucchini or pumpkins, an

issue of comparability arises when extrapolating results from an azalea or grass leaf experiment to above ground bulky vegetations. An air to whole plant concentration transfer factor (whether on a volume or mass basis) for a thin vegetation such as an azalea leaf or a grass leaf would only be appropriate for outer few millimeters of vegetative material for a bulky vegetation such as an ear of corn. Obviously, this is not an issue for pasture grass, and the VG of Equation (7) for pasture grass is 1.00. However, it is an issue for the other general category of cattle vegetations used in this paper, "hay/silage/grain". In this case, there are some thin leafy (hay) as well as bulky (corn silage and other grains) vegetations to consider. A ratio of outer surface area volume to whole plant volume could be used to assign a value to VG, if specific assumptions concerning proportions of each type of vegetative cattle intake were made. EPA [2] showed that such a ratio would be around 0.01 for a bulky vegetation such as an apple or carrot. An appropriate assumption for a fully protected vegetation such as grain would be zero. Silage can be considered part protected and part leafy. Since specific assumptions concerning the amounts of hay/silage/grain intake are not being made for this paper, a simple assumption that VG equals 0.50 for hay/silage/grain is instead made, without rigorous justification.

4. Bioconcentration Model

The algorithm to estimate the concentration of dioxin-like compounds in beef was based on the model developed by Fries and Paustenbach [11]. Their BCF translated a weighted average concentration of 2,3,7,8-TCDD in the diet of beef cattle to a beef fat concentration. They examined various data sets to arrive at a BCF for 2,3,7,8-TCDD of 5.0. They discussed bioavailability, which, as they define it, is the fraction of ingested contaminant which is absorbed into the body. It depends on the vehicle of ingestion - dioxin in corn oil has a bioavailability in the range of 0.7 to 0.8, in rodent feed it has an estimate of 0.5, while in soil it has a range of 0.3 to 0.4. They also discuss the importance of the diets of beef and dairy cows as a principal factor in determining the

concentrations in cattle food products. The concentration in beef fat is given as:

$$C_{fat} = (BCF\ DF_s\ B_s\ C_s) + (BCF\ DF_g\ C_g) + (BCF\ DF_{h/s}\ C_{h/s}) \quad (9)$$

where:

C_{fat}	=	concentration in beef fat or milk fat, ng/kg
BCF	=	bioconcentration ratio of contaminant, equalling the concentration in beef/milk fat divided by the dry weight intake concentration, unitless
DF_s	=	fraction of cattle diet that is soil, unitless
B_s	=	bioavailability of contaminant on the soil vehicle relative to the vegetative vehicle, unitless
C_s	=	average contaminant soil concentration, ng/kg
DF_g	=	fraction of cattle diet that is pasture grass, unitless
C_g	=	average concentration of contaminant on pasture grass, ng/kg
$DF_{h/s}$	=	fraction of cattle diet that is hay/silage/grain, unitless
$C_{h/s}$	=	average concentration of contaminant in hay/silage/grain, ng/kg

Whole beef concentrations equal the concentration in fat times the fraction of whole beef that is fat. Since the observed whole beef concentrations were derived assuming 19% fat, the same assumption is made here.

Fries and Paustenbach [11] reviewed literature studies of cattle consuming feed contaminated with dioxin-like compounds. They calculated a BCF of between 4 and 6, and assumed a value of 5.0 for 2,3,7,8-TCDD. They also observed that bioconcentration ratios for PCDD/Fs decreased significantly as chlorination increased, although their literature seems to imply that this effect is most pronounced for hepta- and octa-PCDD/Fs. They could not locate data in the literature for penta-PCDD/Fs.

McLachlan, et al. [61] was the only study found where BCFs for cow milk could be generated for 16 of the 17 dioxin-like compounds. They conducted a mass balance of

dioxin and furan congeners in a lactating cow. They carefully accounted for all dioxin-like congeners in the intake of a lactating cow in food, air, and water, and measured amounts in feces, urine, and milk, while attributing the rest of the intake to a compartment they termed, storage/degradation/experimental error. They obtained data well into steady state, and provided information necessary to estimate milk BCFs including: average daily wet weight food ingestion intake by the cattle (dry weight assumed to be 15% of wet weight for cattle feed); ng/day congeners in feed, water, and air; L/day milk production (density assumed to be 0.9 g/cm^3); and percent fat in milk (5% as listed in their study).

The McLachlan congener-specific BCFs are listed in Table 1 and are used in this assessment for bioconcentration in beef fat. Although there is likely to be some difference in bioaccumulation tendencies in beef and milk fat, no literature could be found which clearly delineates this difference for the simple bioconcentration model of this paper. The Fries and Paustenbach [11] literature interpretation of the experiments of Firestone, et al. [62] did indicate a slightly higher BCF for beef fat as compared to milk fat for a hexa- and hepta-CDD. However, their overall literature summary including beef and milk bioconcentration factors did support a BCF of 5.0 for 2,3,7,8-TCDD, which they used in modeling of beef and milk fat concentrations. Note that the BCF for 2,3,7,8-TCDD estimated using McLachlan's data is 4.32.

A final note for the BCFs is that they are identified, along with other parameters, as a key and uncertain parameter in this model. The McLachlan data is the only complete set found, but it includes one cow and one lactating period. In addition to the issue of whether a milk fat BCF differs from a beef fat BCF, a simpler issue is the assignment of BCFs themselves. The data of Firestone, et al. [62], as interpreted by Fries and Paustenbach [11], shows a BCF for milk fat of 5.7 for 1,2,3,6,7,8-HxCDD, compared to the milk fat BCF of 1.74 developed for this congener from McLachlan data.

Fries and Paustenbach [11] also discuss the importance of bioavailability in the bioconcentration model. The 2,3,7,8-TCDD BCF of 5.0 developed by Fries and Paustenbach [11] from literature studies were from data of cattle ingesting contaminated

feed. Therefore, this BCF value of 5.0 already considers the bioavailability of the experimental contaminated feed. The McLachlan experiments were conducted in the wintertime, where the cows were kept in a stall with straw-covered cement floors. Their mass balance was based on intake from the cattle feed rations, which included fodder beets, corn silage, grass silage, hay, and grain feed. It will be assumed that the bioavailability of the cattle hay/silage/grain and pasture grass, the two categories of cattle vegetative diet in this paper, equals that of the feeds in McLachlan's experiments. Therefore, the BCFs from his experiment can go directly into Equation (9) when applied to concentrations in grass and hay/silage/grain.

However, these value should not be applied to soil. It has been shown that 2,3,7,8-TCDD on soil is less bioavailable than 2,3,7,8-TCDD on other vehicles. Fries and Paustenbach [11] reviewed several studies on the oral bioavailability of 2,3,7,8-TCDD in soil in the diet of rats, and concluded that soil is a less efficient vehicle of transfer as compared to rat feed. If the same is true for cattle - that soil is less efficient than their feed - then the BCF value must be reduced when applied to soil ingestion. Most studies reviewed by Fries and Paustenbach [11] used corn oil as the positive control, since there is a high absorption of 2,3,7,8-TCDD in rats when corn oil is used as the vehicle, with 70-83% of the administered dose absorbed. Their literature review on rat data showed that the bioavailability of 2,3,7,8-TCDD in soil was between 0.4 and 0.5 that in corn oil, or 0.3 to 0.4 overall. The literature implied a range of 0.5 to 0.6 of 2,3,7,8-TCDD in standard rat feed is absorbed, and although few studies were available, a similar 50% absorption rate of 2,3,7,8-TCDD in cattle feed was noted. They concluded, therefore, that the rat data was a reasonable surrogate for cattle. The B_s can be thought of as the ratio of BCF values between soil and feed, or, $(BCF_{soil})/(BCF_{feed})$. The key assumption is that the difference in BCF_{soil} and BCF_{feed} is explained solely by bioavailability differences. As described above for rat data, the overall bioavailability of soil was 0.3-0.4, and the overall bioavailability of feed was 0.5-0.6. The ratio of overall bioavailabilities is, therefore, (0.3-0.4)/(0.5-0.6). This leads to a B_s of 0.5 to 0.8. These assumptions and

implications are made for this exercise, and the soil bioavailability term, B_s in Equation (9) above, used for all dioxin-like compounds, will be equal to 0.65.

5. Dietary Exposure of Cattle to Dioxins

The final key area in this model concerns cattle exposure to dioxin-like compounds through their diet. Included in this is the impact of feedlot fattening on final beef concentrations.

With varying climates and feeding regimes across the county, an assignment of fractions of beef cattle diet in pasture grass, non-pasture vegetations, and soil, is not obvious. Certainly the task is simplified by not further describing a "typical" beef cattle diet in terms of the types of non-pasture feeds. Fries and Paustenbach [11] demonstrate the impact of assuming a range of exposure conditions, from the "worst case" lifetime of grazing ("worst case" in their judgement because of soil exposure and because they assumed grains were residue free) to the "best case" of lifetime confinement of paved areas with equal parts hay and silage.

This exercise will assume that the cattle diet prior to feedlot fattening (which is discussed below) is comprised of equal parts of pasture grass and non-pasture vegetations. Fries and Paustenbach [11] discuss a range of a soil intake fraction of 0.0 (lush pasture) to 0.08 (sparse pasture), with a worst case assumption possibly as high as 15%. This exercise will assume 4% soil intake, leaving the remaining 96% dietary intakes to be split equally, 48% each, to pasture grass and hay/silage/grain.

Fries and Paustenbach [11] summarize pertinent literature to conclude that cattle raised for beef are not slaughtered without an intervening period of high-level grain feeding. Agricultural statistics [63] show that 32.9 million cattle were slaughtered in 1991. Of this number, 6.1 million were cows and bulls that likely did not go through a feedlot prior to slaughter. Quarterly statistics from 1991 show that at any time, cattle and calves on feed for slaughter range from 10 to 12 million. Fries (personal communication, G. Fries, USDA Agricultural Research Service, Beltsville, Maryland,

20705) uses these statistics to conclude that 75 to 80% of the total beef supply is from animals that went through a feedlot finishing process, and that the portion of beef that did not go through a feedlot process are (generally speaking) those 6.1 million cows and bulls. He suggests that a representative feedlot finishing process would include a length of 120 days and diet consisting of 20% corn silage and 80% grain. The grains can be assumed to be residue-free, since grains are protected and, as discussed above, little within-plant translocation of outer contamination can be assumed. Also, the ears of the corn silage are in the same category, leaving only the stalks and leaves of the corn silage impacted by atmospheric transfers of dioxin-like compounds.

A feedlot finishing process is important to consider. Given that the samples in the three studies from which "observed" beef concentrations were derived were from grocery stores, it seems reasonable to assume that the cattle went through a feedlot finishing process prior to slaughter and distribution. Fries and Paustenbach [11] and Stevens and Gerbec [12] modeled the impact of a residue-free grain-only diet for four months prior to slaughter. Based on within-cow dilution and depuration considerations, both efforts estimated that the feedlot process would reduce beef concentrations by about one-half. This is the same assumption that will be made in this assessment. Beef concentrations estimated using all the modeling described above will be halved as a final step in the modeling process.

Results and discussion

A final comparison of predicted versus observed whole beef concentrations is shown in Table 4. Total TEQ concentrations compare favorably, with observed total TEQ at 0.48 ppt and predicted TEQ at 0.36 ppt. The congeners of most toxicity also had the best match of predicted and observed concentrations: 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.

As a way of further examining these results, limited examinations are now presented on the two key components of this food chain model - the air to vegetation algorithm, and the air to soil algorithms.

One data set in the literature allows some limited comparisons between model predictions and observations of vegetation concentrations. This data was from a rural setting in Elk River, Minnesota [27]. This site was mentioned in the section above describing the derivation of the rural air concentration profile. The reference listed air concentrations by congener grouping for a rural setting (2 air sampling sites) and near an incinerator (1 site). It was noted that the average annual air concentration near the incinerator was about 5 times higher than the average annual air concentration at the two rural sampling stations. The total PCDD/F air concentration in the rural setting was estimated at 1.54 pg/m^3. The corresponding TEQ concentration cannot be estimated without knowing the concentration of the congeners with non-zero toxicity. Therefore, a comparison to the crafted 0.019 pg TEQ/m^3 concentration for the rural setting in this paper cannot be made. However, a data set earlier described from Sweden [25], listed a total concentration of 0.42 pg/m^3 and a corresponding TEQ concentration of 0.004 pg/m^3 for a rural Swedish countryside. This ratio of 100 between total and TEQ concentrations indicates that the Elk River total concentration of 1.54 pg/m^3 may translate to a TEQ concentration around 0.015 pg/m^3, which would be consistent with the 0.019 pg TEQ/m^3 developed in this paper.

This study also took samples of vegetations in this rural setting, including two hay and two corn samples. The limits of detection for these vegetation samples varied between 0.31 and 6.5 ppt on a congener-specific and site-specific basis. With this range of detection limits and the model predicting vegetation concentrations in this range, the data cannot be rigorously informative. The congener found with the highest concentration is OCDD, found at 72 (site 1) and 170 (site 2) ppt in two corn samples, and 270 (site 1)

and 300 (site 2) ppt in two hay samples. In addition to this higher finding in the hay samples, generally more positives were detected in hay rather in corn. This is consistent with discussions in this paper indicating that vegetation concentrations of dioxin-like compounds is a surface phenomena with little within plant translocation. Hay, in this observation, is considered a leafy vegetation, whereas corn is considered a bulky vegetation.

Table 5 lists the average congener specific hay concentrations observed in Elk River (the average of two hay samples, with non-detects counted as 0.0 when one of the two samples had a positive, and just listed as ND when both hay samples showed non-detects) compared against the model's predicted concentrations in grass. This is felt to be a valid comparison. It assumes that hay alone is reasonably similar to grass in that both are "leafy" vegetations and would be modeled similarly in the framework of this paper.

What is now available to interpret and analyze are the predicted and observed beef concentrations, the predicted and observed leafy vegetation concentrations, and further model trends. Several observations are now summarized based on these anaylses:

1) Given the range of the detection limit, 0.31-6.5 ppt for the hay sampling, the model's predictions of grass concentrations are generally consistent with observations, with the exception of the OCDD and OCDF concentrations. It is noted that the second highest congener observation of 30 ppt of 1,2,3,4,6,7,8-HpCDD is matched by the model's prediction of 21.0 ppt for 1,2,3,4,6,7,8-HpCDD.

2) The analysis of the OCDD and OCDF results for hay is very telling. First, it is noted that the crafted rural air concentrations of these two congeners matches very well with the observed air concentrations at this Elk River site: OCDD observed at 0.5 pg/m^3 and crafted at 0.57 pg/m^3; and OCDF observed at 0.09 pg/m^3 and crafted at 0.034 pg/m^3 (note: the observed concentrations for OCDD/F congeners is the average of four listed concentrations of OCDD/F congeners in [27] - rural sites 1 and 2 and winter and summer listings). Since the crafted air concentrations match well with the observed air

concentrations, one would hope that the vegetative concentrations also match. An analysis of why they did not indicates the importance of vapor phase contributions to vegetative concentrations.

According to the application of the Bidleman [35] approach for estimating the bound fraction, ϕ, in the air, both these congeners were assigned a ϕ of 1.00. In fact, using the OCDD/F vapor pressures and melting points, these ϕ values were both 0.998. If one allows for the possibility that ϕ for OCDD/F could be less than one, and calibrates ϕ for OCDD/F for this exercise, one can show that small reductions in ϕ result in better predictions of both grass and beef concentrations. Recall that the observed "grass" concentrations are, in fact, the hay concentrations found at Elk River, Minnesota, and that the observed beef concentrations are those which were generated using available data from around the country. Table 6 shows the results of a calibration, where ϕ is first 1.00 as initially assumed, and then calibrated so that grass/hay and subsequently beef are more in line. As seen, the calibrated ϕ are 0.9998 for OCDD and 0.998 for OCDF, and the grass and beef concentrations predicted are now much closer to observations.

The main reason for these very large differences in model predictions of hay concentrations with seemingly small differences in the amount assumed to be in the particle phase is that the air-to-leaf transfer factor, the B_{vpa}, is 2 to 4 orders of magnitude higher for OCDD and OCDF as compared to all other transfer factors. For OCDD, it is also noteworthy that the total air concentration is 1 to 2 orders of magnitude higher than the concentrations for all other congeners.

3) The one congener whose air concentration is within an order of magnitude of OCDD is that of 1,2,3,4,6,7,8-HpCDD, at 0.116 pg/m^3. Also, the calculated B_{vpa} for this congener is second in magnitude behind the OCDD/F congeners. Since 2% of this air concentration is, in fact, predicted to be in vapor phase according to the Bidleman model, vapor transfers are considered and the model predicted 21.0 ppt grass concentration, which compared favorably with the observed 30 ppt concentration.

4) Calibrations for some of the other congeners for which a discrepancy exists

between hay/grass predictions and beef predictions were not attempted. However, one can see with the following how the trend between predicted grass to beef concentrations followed the observed grass to beef trend. That is, when the model underpredicted grass, it also underpredicted beef, and likewise for overpredicting:

	grass/hay, ng/kg (ppt)		whole beef, ng/kg (ppt)	
	Pred.	Obs.	Pred.	Obs.
1,2,3,6,7,8-HxCDD	0.2	1.2	0.029	0.84
2,3,7,8-TCDF	7.1	ND*	0.46	0.06
1,2,3,4,6,7,8-HpCDF	1.4	5.4	0.04	0.40

* the detection limits for hay sampling ranged from 0.30 to 6.5 ppt.

5) A simple analysis of model performance indicates that vegetation concentrations explain beef concentrations. Looking only at 2,3,7,8-TCDD, it is seen that cattle soil ingestion, 4% of total diet, explains only 8.5% of final beef concentration, with grass explaining 60.6% and hay/silage/grain 30.9%. The main difference in grass and hay/silage/grain, as discussed above, is that vapor transfers are halved for hay/silage/grain with the use of the empirical VG parameter. Further, 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. Since grass and hay/silage/grain explain over 90% of beef concentration, 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. Allowing for the calibration described above, now the OCDD/F beef concentrations are dominated by vapor transfers.

The importance of vapor transfers of dioxin-like compounds to vegetations and subsequently in the food chain is a relatively recent finding. The model of Fries and

Paustenbach [11], who developed the BCF model used in this model, did not consider vapor transfers. Webster and Connett [64] reviewed five other 2,3,7,8-TCDD bioconcentration in milk modeling efforts [65, 14, 66, 12, 40], and none of them considered vapor transfers. Webster and Connett [64] further go on to note that the deposition of particle bound 2,3,7,8-TCDD, as considered by four of the five models (the fifth considered soil to plant only, and greatly underpredicted vegetation concentrations), still underpredicts vegetation concentration, and they suggest that lack of consideration of vapor transfers could explain this underprediction.

In an update to their 1987 modeling efforts [66], Travis and Hattemer-Frey [13] did include vapor transfers of 2,3,7,8-TCDD to cattle "forage". They assumed a 20% vapor/ 80% particle split, and modeled vapor transfers using the Bacci model. They estimated that vapor transfers explained 56% of forage concentrations and also discussed the importance of vapor transfers. However, this result does not show as much dominance of vapor transfers as the results in this paper. A simple examination of their input data shows why. The air-to-leaf transfer factor estimated by Travis and Hattemer-Frey [13] for 2,3,7,8-TCDD is an order of magnitude lower at 9883 than the transfer factor developed in this paper at 100,000.

The importance of vapor transfers to leafy vegetations was discussed in two separate papers in the 13th International Symposium on Chlorinated Dioxins and Related Compounds, held in Vienna in September, 1993. Welsh-Paush, et al [67] compared grass grown outside of chambers with grass grown in two outdoor chambers: one which circulated air replete with particles (reference chamber), and one which circulated air but first filtered out particles (particle-free chamber). By measuring the concentrations of dioxins and dust particles in air, and grass concentrations over time, they were able to show that the grass grown in particle-free air was substantially similar in concentration to the grass in the reference chamber as well as the grass grown outside of chambers. They concluded that vapor transfers dominate the grass concentrations based on these results, and because of the role of grass in the bioconcentration food chain, they also concluded

that vapor transfers play an important role in the food chain.

Rippen and Wesp [68] measured the concentrations of dioxins and furans in soils and green kale at 10 sites in Germany. They studied the differences in the concentration profiles from soil and the green kale by deriving "soil/plant ratios" for individual congeners. If the ratios were the same for all congeners, one might assume that soil provided the source of contaminants to the plant, via soil suspensions followed by depositions, for example. They made the observation, however, that soil/plant ratios were not consistent among the congeners - that the lower chlorinated PCDD/Fs, the tetra and penta congeners, had lower soil/plant ratios as compared to the higher congeners; i.e., that the tetra and penta congener concentrations in plants were relatively higher than other congeners. They also note that the lower chlorinated congeners are dominated by the vapor phase in the air (citing literature). This paper as well concludes that the tetra and penta dioxin congeners, whose vapor phase fractions range from 0.26 to 0.70, are significantly more in the vapor phase as compared to other congeners, whose vapor fractions range from 0.00 to 0.11. Given the lower soil/plant ratios for the tetras and pentas, Rippen and Wesp [68] conclude that the relatively higher concentrations of tetras and pentas in the kale are unlikely to be explained by soil suspensions and depositions, but rather by vapor transfers.

An air to soil examination begins with a comparison of predicted soil concentrations of the dioxin-like compounds and an observed concentration in soils, which is shown in Table 7. The observed data originated from four studies in North America where soils were characterized as "rural" or "background" [27, 69, 70, 71]. As seen in Table 7, there is clearly an underprediction trend for air to soil impacts. For the nine congeners where the literature allowed for a non-zero average soil concentration, the model appears to underpredict soil concentrations by a range of about 2 to 10 times (i.e., observed concentrations are twice as high to about ten times higher than predicted concentrations). While this is a non-trivial result, in fact the model would not predict a substantially different beef concentration if soil concentrations were more in line with observations. If

the soil concentrations were artificially increased by a factor of 10, than whole beef concentrations of total dioxins increase from 2.13 ppt to 3.62 ppt, and TEQ concentrations increase from 0.36 ppt to 0.45 ppt. The reason for this trend is that soil is only 4% of the beef cattle diet prior to feedlot fattening.

The observation made is that the current formulation and/or parameter assignments for an air to soil impact will underpredict soil concentrations of dioxins by about 2-10 times. If this observation is, in fact, a statement of truth, then the following is offered as the most likely causes for model underprediction:

1. The soil dissipation rate: The dissipation rate of 0.0693 yr^{-1}, corresponding to a half-life of 10 years, was developed from field data of 2,3,7,8-TCDD applied to soils in the herbicide 2,4,5-T [44]. This may be an appropriate rate of dissipation from a bounded area of high soil contamination. However, mechanisms for dissipation from this bounded area, such as dust suspension and volatilization, may not directly apply for background settings where such losses in one background area may be redeposited downwind in another background area. From Equation (5) above, one can see that the estimated soil concentration is an inverse function of the dissipation rate. If the dissipation rate is reduced to 0.00693 yr^{-1}, corresponding to a half-life of 100 years, than the soil concentrations are increased by an order of magnitude.

2. Depositions of vapors: Koester and Hites [39] developed the argument that their collection apparatus for dry deposition of dioxins would not scavenge vapor phase dioxins from the air; that they would only be measuring dry deposition of particle bound dioxins. Since the dry deposition velocities used in this paper originate from their work, and if their arguments are valid, then the algorithms of this paper do not consider the dry deposition of vapors. Their methods for measurement of wet deposition did not preclude the scavenging of vapors, although they do argue that rainfall is more effective at scavenging particle-bound dioxins compared to vapor-phase dioxins. Therefore, the assumption made that total annual wet deposition equals dry deposition made in this paper, based on the results of Koester and Hites, means that wet deposition of vapor

phase dioxins are considered. In any case, algorithms to estimate the additional dry deposition loadings of vapor-phase dioxins to soil could not be found, so the impact of including them cannot be estimated.

3. Detritus recycling: This is another loading not considered, and also a loading tied directly to vapor-phase dioxins. As discussed above, vegetation concentrations are dominated by vapor transfers. Barbour, et al. [72] list a detritus production rate for a setting described as "tallgrass prairie" as 520 g/m^2-yr. Given the concentrations predicted to occur in grass, one can estimate the loadings of dioxin corresponding to a detritus production of this magnitude. This was done and compared against the estimated total deposition rates from the air to soil of individual congeners. It was found that detritus loadings varied by congener, and was equal to a range of 2% of atmospheric deposition to 100% (equal to) of deposition. Summing the depositions and the detritus loadings of all congeners, it was found that detritus loadings are equal to about 20% of atmospheric deposition loadings of dioxins.

Conclusions

An air-to-beef model was developed and tested. A profile of air concentrations was crafted to be typical of rural environments where cattle are raised for production of beef. This profile was routed through the model to predict concentrations of dioxin-like compounds in beef. These predictions were compared with a profile of measured concentrations. An "observed" TEQ concentration of 0.48 ng/kg in whole beef was compared with a "predicted" 0.36 ng/kg. An observed total concentration PCDD/Fs of 8.15 ppt in beef was compared against the predicted 2.13 ppt. Further evaluations of the air to vegetation algorithm indicate the model appears to predict vegetation concentrations consistent with one set of literature observations, with the exception of the octa congeners, OCDD and OCDF. However, when assuming only a minute amount of the airborne reservoirs of these congeners are in the vapor phase, model predictions of both vegetations and subsequently beef concentrations fall in line. A final evaluation of the air

to soil model indicates that the model and/or the parameter assignments tend to underpredict soil concentration by as much as an order of magnitude. Refinements to the model which would bring soil concentrations more in line with observations were offered. It was observed that while the model appears to be underpredicting soil concentrations, a more appropriate prediction would not change beef predictions significantly since soil is only a small part of the cattle diet. A major conclusion of this work is the overwhelming dominance of the vapor phase transfers to vegetations which cattle consume, which in turn implies that the appearance of these chemicals in beef and milk is due to vapor transfers.

Another and more broad conclusion offered is that the validation exercise in general demonstrates the validity of the air-to-beef model framework and parameter assignments. This is a cautious conclusion, obviously, given the uncertainty in the many parameter assignments and real world observations. The introduction to this paper noted that this exercise would need refinement in several areas before ascribing any finality to the model structure and results. Further research is recommended for the following areas:

1. A characteristic rural air environment: A profile of air concentrations of dioxin-like congeners in a rural environment in the United States could not be found for this exercise, and instead one was crafted given a representative profile for urban/suburban areas and a simple proportional reduction.

2. A characteristic profile of dioxin-like congeners in beef: Only 14 samples from three literature references, one of which only reported on 2,3,7,8-TCDD and 2,3,7,8-TCDF, were found for this exercise.

3. Vapor/particle partitioning: While several air monitoring studies were available which gave vapor/particle partitioning measurements for congener groups, these were speculated as generally tending to overpredict the vapor phase. Instead, a theoretical approach was used, which did lead to greater proportions in the adsorbed phase. A carefully designed monitoring experiment could shed some light on vapor/particle partitioning for dioxin-like compounds. This is obviously critical given the major

conclusion of the dominance of vapor phase concentrations in explaining beef concentrations.

4. Vapor transfers to vegetations: Like the partitioning issue, the quantification of transfers onto vegetations is critical. The generalized model of Bacci [44, 45, 46] was used with an empirical refinement suggested by McCrady and Maggard [47]. Specifically, the Bacci algorithm was used first to determine a congener-specific air-to-leaf transfer factor. This factor was then divided by 40, which was the difference of the McCrady transfer factor measured for 2,3,7,8-TCDD transfer to grass leaves, as compared to the factor estimated using the Bacci empirical relationship. To highlight the importance of this empirical reduction, consider what would happen to model predictions had this reduction not been made: vegetation and hence beef concentrations would be increased by about this factor of 40 (even with the reduction, vapor transfers were shown to dominate vegetation and beef concentrations). Said another way, the model would have predicted a whole beef concentration greater than 10 ppt, instead of 0.36 ppt. Also, a second empirical refinement reduced the transfer into bulky vegetations. While the need for both refinements is argued to be justified for dioxin-like compounds, the precise numerical adjustments used in the exercises above cannot be rigorously defended without further data.

5. Particle depositions onto vegetations: The impact of wet deposition needs to be further investigated. A literature article suggesting that about 30% of particles depositing in rain are retained on the canopy after the rainfall justified the assignment of 0.30 to the parameter, R_w (fraction retained on vegetation from wet deposition). The weathering half-life of 14 days, while often used for dioxins, is also identified as uncertain. Finally, the dry deposition velocity of 0.2 cm/sec should be considered further.

6. Air-to-soil impacts: The trend here is that the model appears to underpredict soil concentrations by an order of magnitude or more. Three aspects of the model were offered above as possible candidates for refinement and further research. These included: vapor impacts to soils, dissipation rate in soils, and detritus loadings to soils.

7. The bioconcentration factor: Only one study was found from which congener-specific bioconcentration factors for the suite of congeners could be developed, and this was for one cow, for one lactating period, and was for milk and not beef. The differences in bioconcentration between beef and milk need to be further investigated and quantified.

8. Cattle diet and the impact of feedlot fattening: A cattle diet was simplistically assumed to consist of 4% soil and equal parts of grass and non-grass feeds. Perhaps a more representative diet could be crafted, which would lead to a different exposure pattern by the beef cow prior to feedlot fattening. Equally if not more important is the impact of this feedlot fattening. It is clear that commercial beef cattle in the United States undergo a period of feedlot fattening. However, before and after monitoring quantifying the impact of this practice could not be found. Two modeling studies, which assumed that dilution and depuration were occurring during feedlot fattening, estimated that concentrations were halved due to this process. This was the assumption also made in this paper, and it needs to be further evaluated.

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Table 1. Fate parameters for individual dioxin and furan congeners with non-zero TEFs[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
H: Henry's Constant, atm-m^3-mole
log Kow: Log octanol water part. coefficient
T_m: Melting point temperature, ◦ K
P_s: Crystalline solid vapor pressure, atm^{-1}
Vapor: Vapor fraction in ambient air
BCF: beef biotransfer factor, unitless
B_{vpa}: air-to-leaf transfer factor, unitless
Particle: Particle fraction in ambient air

* McLachlin, et al. [61] did not provide data on 123789-HxCDF; the value for 123678-HxCDF was used instead.

Table 2. Model parameters used for all dioxin-like congeners.

Parameter	Description	Value
I. For Vapor/Particle Partitioning		
C	constant to estimate sorbed fraction in Equation (1), atm-cm	$1.7*10^{-4}$
T	ambient air temperature, ◦K	298.1
$\Delta S_f/R$	entropy of fusion/universal gas constant, unitless	6.79
S_T	average total surface area of aerosol particles relative to average total volume of air, cm^2/cm^3	$3.5*10^{-6}$
V_T	average total volume of aerosol particles per volume of air, cm^3/cm^3	$3*10^{-11}$
II. Particle Depositions		
k_w	first-order plant weathering constant, yr^{-1}	18.01
k_s	first-order soil dissipation constant, yr^{-1}	0.0693
Y_g	yield of grass, kg/m^2	0.15
I_g	interception fraction of grass	0.35
$Y_{h/s}$	yield of hay/silage/grain	0.63
$I_{h/s}$	interception fraction of hay/silage/grain	0.62
V_d	velocity of particle deposition, m/sec	0.002
M	mass of mixing soil, kg/m^2	10
R_w	retention of wet deposition on vegetations, fraction	0.30
III. Vapor Transfers		
VG_{gr}	empirical correction factor for grass, unitless	1.00
$VG_{h/s}$	empirical correction factor for hay/silage/grain, unitless	0.50

(continued on next page)

Table 2. (cont'd).

Parameter	Description	Value
IV. Bioconcentration		
B_s	bioavailability of contaminant on the soil vehicle relative to the vegetative vehicle, unitless	0.65
DF_s	cattle soil diet fraction	0.04
DF_g	cattle grass diet fraction	0.48
$DF_{h/s}$	cattle hay/silage/grain diet fraction	0.48
V. Other		
	fat content of beef	0.19
	concentration reduction due to feedlot fattening	0.50
	assumption: wet deposition equals dry deposition	

Table 3. Summary of air and whole beef concentrations of dioxin-like compounds used as "independent" observed data and "dependent" predicted concentrations.

Compound	Total air concentration, pg/m^3	Whole beef concentration, ng/kg
2378-TCDD	0.002	0.03
12378-PCDD	0.006	0.22
123478-HxCDD	0.005	0.26
123678-HxCDD	0.007	0.84
123789-HxCDD	0.010	0.21
1234678-HpCDD	0.116	1.92
OCDD	0.586	2.91
2378-TCDF	0.023	0.06
12378-PCDF	0.010	0.04
23478-PCDF	0.006	0.21
123478-HxCDF	0.012	0.51
123678-HxCDF	0.012	0.06
123789-HxCDF	0.003	0.06
234678-HxCDF	0.009	0.07
1234678-HpCDF	0.042	0.40
1234789-HpCDF	0.006	0.13
OCDF	0.034	0.22
TOTALS	0.872	8.15

Table 4. Results of validation exercise showing observed and predicted concentrations of dioxin-like compounds in whole beef.

Compound	Observed whole beef concentrations, ng/kg	Predicted whole beef concentrations, ng/kg
2378-TCDD	0.03	0.03
12378-PCDD	0.22	0.27
123478-HxCDD	0.26	0.10
123678-HxCDD	0.84	0.03
123789-HxCDD	0.21	0.04
1234678-HpCDD	1.92	0.29
OCDD	2.91	0.29
2378-TCDF	0.06	0.46
12378-PCDF	0.04	0.07
23478-PCDF	0.21	0.17
123478-HxCDF	0.51	0.08
123678-HxCDF	0.06	0.13
123789-HxCDF	0.06	0.04
234678-HxCDF	0.07	0.07
1234678-HpCDF	0.4	0.04
1234789-HpCDF	0.13	0.01
OCDF	0.22	0.01
TOTAL CONCENTRATION	8.15	2.13
TEQ CONCENTRATION	0.48	0.36

Table 5. Comparison of concentrations of dioxin-like compounds found in hay in a rural setting with model predictions of grass concentrations.

Compound	Observed hay concentration, ng/kg[1]	Predicted grass concentrations, ng/kg
2378-TCDD	ND	0.1
12378-PCDD	ND	0.9
123478-HxCDD	ND	0.7
123678-HxCDD	1.2	0.2
123789-HxCDD	ND	0.2
1234678-HpCDD	30	21.0
OCDD	285	6.0
2378-TCDF	ND	7.2
12378-PCDF	ND	1.4
23478-PCDF	ND	0.8
123478-HxCDF	ND	0.5
123678-HxCDF	ND	0.9
123789-HxCDF	ND	0.3
234678-HxCDF	ND	0.5
1234678-HpCDF	5.4	1.4
1234789-HpCDF	ND	0.1
OCDF	7.5	0.4

[1] Observed data from Reed, et al. [27]. Concentrations listed are the mean of two observations for hay grown in rural settings. ND assumed to be zero for calculation of means. Limits of detection described in Reed, et al. [27] as ranging between 0.31 and 6.5 ppt, on a congener-specific and site-specific basis.

Table 6. Calibration exercise showing improvements in grass and beef concentrations when the fraction sorbed parameter, ϕ, drops minutely below 1.00 for OCDD and OCDF.

I. Uncalibrated: ϕ = 1.00 for OCDD and OCDF

	grass/hay, ng/kg (ppt)		whole beef, ng/kg (ppt)	
	Pred.	Obs.	Pred.	Obs.
OCDD	6.0	285	0.29	2.91
OCDF	0.4	7.5	0.01	0.22

II. Calibrated: ϕ = 0.9998 for OCDD and 0.998 for OCDF

	grass/hay, ng/kg (ppt)		whole beef, ng/kg (ppt)	
	Pred.	Obs.	Pred.	Obs.
OCDD	237	285	8.51	2.91
OCDF	10.2	7.5	0.14	0.22

Table 7. Comparison of concentrations of dioxin-like compounds found in soils described as "rural" or "background" with model predictions of soil concentrations.

Compound	Observed soil concentration, ng/kg[1]	Predicted soil concentrations, ng/kg
2378-TCDD	0.88	0.12
12378-PCDD	ND	0.57
123478-HxCDD	ND	0.56
123678-HxCDD	4.0	0.87
123789-HxCDD	9.0	1.17
1234678-HpCDD	194	13.9
OCDD	237[2]	69.3
2378-TCDF	1.59	0.8
12378-PCDF	ND	0.7
23478-PCDF	ND	0.5
123478-HxCDF	ND	1.4
123678-HxCDF	ND	1.3
123789-HxCDF	ND	0.3
234678-HxCDF	2.0	1.0
1234678-HpCDF	47	4.9
1234789-HpCDF	ND	0.7
OCDF	30.2	4.1

[1] Concentrations listed are the arithmetic mean of all observations available, counting non-detects as 1/2 detection limit. Only one study of the four used had measurements for the eight congeners above with Non-Detects. This study, Reed, et al. [27] listed soil detection limits as varying between 0.79 and 2.9 ppt, depending on site and congener.
[2] Geometric means were also determined for this data set. A wide range of concentrations of OCDD, ND to 10,600 ppt, led to a geometric mean of 60 ppt for this congener. For all other congeners, geometric means were within a factor of 2 of arithmetic means.

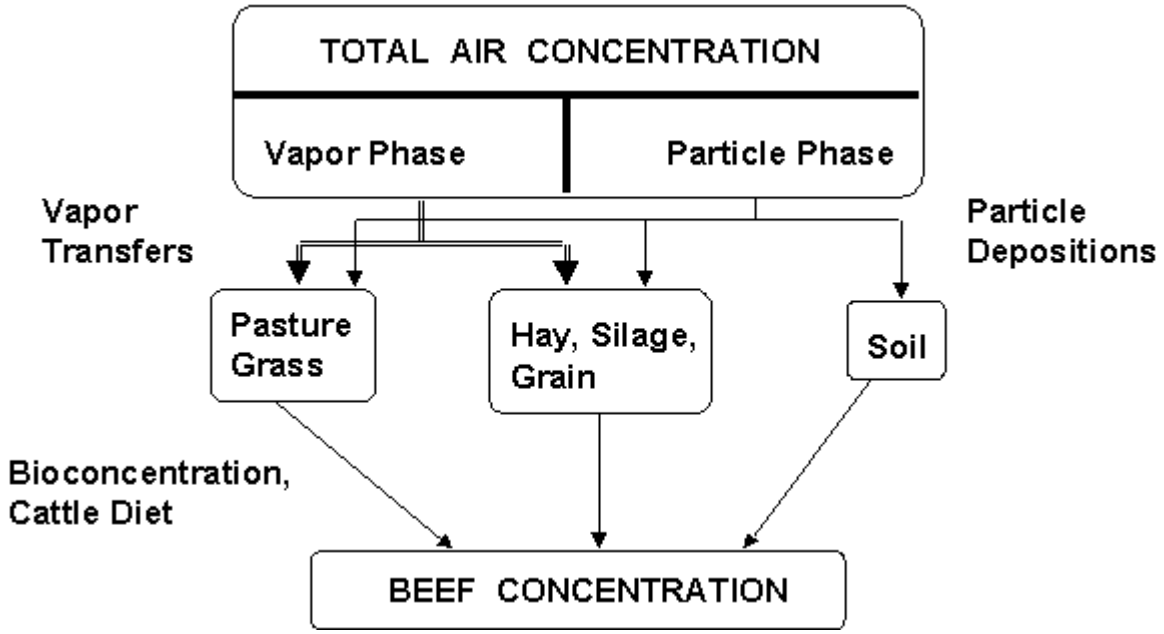

Figure 1. Overview of model to predict beef concentrations from air concentrations.