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An Evaluation of Three Empirical Air-to-Leaf Models for Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans

Matthew Lorber*, Paul Pinsky**

*National Center for Environmental Assessment (8623D), US EPA, 401 M St, SW, Washington, DC, USA, 20460. email: lorber.matthew@epa.gov

** National Institute of Health, Executive Plaza North, Room 330, 6130 Executive Blvd, Rockville, MD, USA, 20892-7346 email: pinskyp@exchange.nih.gov

Abstract: Three empirical air-to-leaf models for estimating grass concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans (abbreviated dioxins and furans) from air concentrations of these compounds are described and tested against two field data sets. All are empirical in that they are founded on simplistic bioconcentration and related approaches which rely on field data for their parameterization. One of the models, identified as the EPA Model, partitions the total air concentration into vapor and particle phases, and separately models the impact of both. A second model addresses only the vapor phase; grass concentrations are modeled as a function of vapor deposition. For the third model, it is assumed that the grass plants “scavenge” a fixed volume of air of dioxins, and hence grass concentrations are modeled as a simple product of total air concentration and a constant scavenging coefficient. Field data from two sites, a rural and an industrial site in the United Kingdom, included concurrent measurements of dioxins in air and field grass, and dioxin and furan depositions, for one 6-week sampling period. Principal findings include: 1) the EPA Model underpredicted grass concentrations at the rural field site by a factor of 2, while the Scavenging Model underpredicted grass concentrations by a factor of 3.8, and the Vapor Deposition Model significantly underpredicted grass concentrations (by a factor greater than 10), 2) the presence of high soil concentrations for some of the dioxins and furans at the industrial site appears to have caused higher grass concentrations and confounded the air-to-plant modeling exercise, 3) the Scavenging Model could be calibrated to the data set; however, a key premise of this model - that vapor and particle phase dioxins equally impact the plants, is not supported by the field data, 4) measured depositions are highly correlated to but systematically lower than modeled depositions, which could be due to modeling assumptions or a systematic measurement bias.

Keywords: air-to-leaf vapor transfer, dioxins, furans, Scavenging model

Introduction

Numerous researchers have concluded that the exposure of man to dioxins is principally through consumption of terrestrial animal fats (and fish, although on average terrestrial animal consumption is much higher than fish consumption), and that terrestrial animals are exposed through an air-to-plant-to-animal pathway [1-3]. Subsequently, modeling efforts have focussed on the air-to-plant pathway as the first step in the terrestrial animal food chain model for dioxins. This paper evaluates three empirical models which have been used in modeling air-to-plant impacts for dioxin-like compounds. While more rigorous air-to-plant modeling frameworks are available, such as a fugacity model specifically evaluated for dioxins [4], these empirical approaches offer an ease of usage that has made them appealing for related contaminants such as PCBs [5]. This evaluation includes the description, parameterization, and application of the three models to data from two field sites. The field data includes concurrently measured air concentrations, depositions fluxes, and grass concentrations over a 45-day period.

The following sections include an overview of the field site data, model theory and parameterization for the field site, and results and discussions of the model tests.

Field Site Data

Jones and Duarte-Davidson [6] present key results of an extensive monitoring study of dioxin concentrations in air and grass, as well as deposition fluxes, from three sites over three time periods between 1992 and 1993 in the United Kingdom. The three sites include a rural background site, an urban site, and an industrial site. The regional background site was located about 6 km upwind of the industrial complex in Bolsover, the urban site was about 2 km in the town of Bolsover, and the industrial sampling location was located just outside the industrial complex, about 100 m away.

Jones and Duarte-Davidson [6] present two sets of data from this study which are appropriate for air-to-plant model evaluation purposes. Specifically, they presented concurrently measured concentrations of dioxin and furan congeners, and homologue groups, for air and grass sampled for two of the sites, the industrial and rural background site, for one of the sampling periods, Sep. 14 - Oct. 30, 1993. They also presented the results of their deposition collection for those two sites/sampling periods. Although other data sets of this kind were collected during the study, only these two sets were presented. For the study, air samples were taken using standard General Works high-volume samplers which took weekly samples of 300-500 m³ air for 4-6 week sampling periods. The glass fiber filters and the polyurethane foam plugs of these samplers (measuring, in theory, the vapor and particle phases, respectively) were collected weekly and composited for each full sampling period to allow for a single measurement of total air concentration of the dioxins, representing between 2000 and 3000 m³ of air volume. A bulk deposition sample for each

site/sampling period was also collected using “upturned frisbee” collectors. In each site, an area was fenced off to allow for the collection of grass samples without the possibility of the grass being grazed or otherwise disturbed. At the beginning of each sampling period, the grass was mowed. At the end of the sampling period, the grass was again mowed, so that the yield measured represented growth during the sampling period. The air, grass, and deposition data are provided in Table 1. The yields at the rural and industrial sites were 89 and 42 g/m² dry weight, respectively.

As will be described below, some of the data appear inconsistent (low grass concentration despite high air concentration, e.g.) and of poor quality, so some of the data were not used. Nonetheless, it is assumed that the data that were used from the Jones and Duarte-Davidson field sites were of sufficient quality for use in the current model testing. Further details on the sampling design, monitoring program, analytical methods, and other aspects of the study can be found in Jones and Duarte-Davidson [6] and more detailed reported cited therein.

Model Theory and Parameterization

The purpose of this section is to present the model equations, their derivation, and the parameters values used in this exercise, in sufficient detail such that others can independently code the models onto a spreadsheet and continue the model evaluation process. Readers are encouraged to obtain the original references [2,7,10,13,14] for more detail on the selected models and other references providing more of an examination of the real world processes of air-to-leaf transfer for dioxins and furans [4, 19, 25-27]. McLachlan [4], for example, argues that a steady state would not be reached for higher chlorinated dioxins and furans in as short a period of time as the 6 weeks of the UK field sites. Users should consider the results of the model tests presented here and elsewhere [5, 20], along with other theoretical and practical issues when deciding which model best suits their purposes.

The EPA Model: The first model was developed for the United States Environmental Protection Agency’s Reassessment for Dioxin and Related Compounds [7]. First, total dioxin concentrations are partitioned into a vapor and a particle phase. A relationship first proposed by Junge [8], and later reviewed and critically evaluated by Pankow [9], is the most widely used model for estimating the adsorption of semivolatile compounds to aerosols:

$$\phi = \frac{c \Theta}{p_L^\circ + c \Theta} \quad (1)$$

where ϕ is the fraction of the compound adsorbed to aerosol particles, p_L° is the saturation liquid phase vapor pressure of the pure compound at ambient temperature (Pa), Θ is the particle surface area per unit volume of air (cm² aerosol/cm³air), and c is a constant which is related to the difference between the heat of

Table 1. Observed data for the air-to-plant model validation exercise.*

Compounds	Rural Background Site			Industrial Site		
	Air	Deposition	Grass	Air	Deposition	Grass
2378-TCDD	0.01	<0.46	0.72	0.017	1.6	2.8
12378-PCDD	0.03	2.3	1.3	0.04	3.8	<0.08
123478-HxCDD	0.04	2.3	0.93	0.04	3.2	0.73
123678-HxCDD	0.08	4.8	2.3	0.09	10.8	6
123789-HxCDD	0.1	3.8	1.8	0.13	8.9	4.2
1234678-HpCDD	0.82	41	22	0.84	51	13
OCDD	2.5	166	94	2.5	153	43
2378-TCDF	0.33	12	14	0.57	18	16
12378-PCDF	0.06	2.5	1.8	0.1	2.2	<0.09
23478-PCDF	0.1	4.1	2.2	0.19	6	1.2
123478-HxCDF	0.3	11	5.6	0.45	12	4.6
123678-HxCDF	0.1	4.5	2.2	0.16	5.7	1.8
123789-HxCDF	0.02	1.8	0.61	0.07	1.9	0.54
234678-HxCDF	0.14	4.8	2.6	0.19	6	2.4
1234678-HpCDF	0.53	19	12	0.71	25	11
1234789-HpCDF	0.11	2.9	1.1	0.14	3.2	0.89
OCDF	0.42	28	13	0.48	35	8
TCDD	0.72	73	66	3.1	509	750
PCDD	0.56	54	33	1.2	477	410
HxCDD	0.65	38	26	0.78	73	38
HpCDD	0.71	41	22	0.73	48	11
TCDF	1.6	24	93	3.3	131	290
PCDF	0.84	27	31	2.3	64	21
HxCDF	0.45	18	13	1.4	26	19
HpCDF	0.22	<1.8	<0.22	0.43	<1.6	<0.31

* Units: air - pg/m^3 ; deposition - $\text{pg}/\text{m}^2\text{-day}$; grass - pg/g dry weight of dioxin in the grass. Grass yield for rural = 89 g/m^2 dry weight, for industrial = 42 g/m^2 dry weight.

desorption from the particle surface, Q_d , and the heat of vaporization of the compound, Q_v . The value of c is often estimated at 17.2 Pa-cm, the value used by Bidleman [22] for 2,3,7,8-TCDD and the value used here. Pankow [9] argued that different values of $Q_d - Q_v$ (and therefore c) may be appropriate for different

classes of compounds. The values of p_L° were determined from field data of Eitzer and Hites [23,24], who used a capillary GC method to determine liquid-phase vapor pressures for 63 PCDD/F congeners. Values they developed at 25 °C were corrected to 20 °C in EPA [7].

EPA [7] describes the development of the ϕ values for dioxin-like compounds for four airsheds characterized by different particle densities in air (as defined by Θ) and at an ambient air temperature of 20 °C. These four airsheds are described qualitatively as: clean continental, background, background plus local sources, and urban. Jones and Duarte-Davidson [6] did not provide the average air temperature for their experimental period of Sep 14 to Oct 30, 1993, but the average air temperatures for the months of September and October for the nearby city of Sheffield, UK, are 13.4 and 9.9 °C (www.worldclimate.com), respectively, so an air temperature of 10 °C will be assumed for the assignment of ϕ . A “background” setting will be assumed for the rural site in the Jones and Duarte-Davidson [6] data set, and ϕ values for an “urban” setting will be assumed for the industrial site. Given particle fractions, ϕ , vapor fractions are easily calculated as, $1 - \phi$. Table 2 lists the ϕ for the four possible airsheds at 20 °C and for the background and urban settings at 10 °C for all the dioxin-like compounds of this exercise. As seen on Table 2, cooler temperatures result in more of the compounds modeled to be sorbed to aerosol particles rather than in the vapor phase.

As a final note on vapor/particle partitioning, it is important to understand that application of the EPA Model requires use of modeled rather than measured ϕ . EPA [7] described how measured vapor/particle partitioning differs systematically from modeled partitioning - the measured vapor fractions are much larger than then the modeled fractions. Lorber [10] calibrated the vapor transfer algorithm (to be described shortly) and the critical air-to-leaf transfer factor, B_v , using modeled vapor fractions. Therefore, the calibrated B_v must always be used in conjunction with modeled vapor fractions. Using B_v in conjunction with measured vapor reservoirs will incorrectly overestimate vapor impacts of dioxins to plants.

Total plant concentrations are the sum of vapor phase and particle phase impacts. The particle-phase model is the steady state solution for a simple reservoir model:

$$C_{gp} = \frac{F_p I_g (1 - e^{-k_w t})}{k_w Y_g} \quad (2)$$

where C_{gp} is the grass concentration due to settling of dioxin-laden particles onto plant matter (pg/g dry weight), F_p is the dioxin wet plus dry deposition rate onto plant surfaces (pg/m²-d), I_g is the grass interception, k_w is the first-order weathering dissipation constant (d⁻¹), t is the growing period (d), and Y_g is the dry matter yield of grass (g/m² dry weight). Jones and Duarte-Davidson [6] do not provide the rainfall data for the sampling period necessary to estimate wet deposition. Therefore, total deposition will be modeled simply as the particle bound air concentration times a deposition velocity. The deposition velocity

Table 2. Fate and transport parameters for the dioxin-like congeners for the EPA Model.

Congeners	Particle fractions, ϕ^* , at 20 °C				ϕ^* , at 10 °C		Bv*
	C.C	B	B+LS	U	B	U	
2378-TCDD	0.1	0.29	0.49	0.75	0.58	0.91	6.55*10 ⁴
12378-PCDD	0.44	0.74	0.87	0.95	0.91	0.99	2.39*10 ⁵
123478-HxCDD	0.78	0.93	0.97	0.99	0.98	0.997	5.20*10 ⁵
123678-HxCDD	0.78	0.93	0.97	0.99	0.98	0.997	5.20*10 ⁵
123789-HxCDD	0.78	0.93	0.97	0.99	0.98	0.997	5.20*10 ⁵
1234678-HpCDD	0.93	0.98	0.99	0.997	0.99	0.999	9.10*10 ⁵
OCDD	0.98	0.995	0.998	0.999	1	1	2.36*10 ⁶
2378-TCDF	0.09	0.27	0.47	0.73	0.56	0.9	4.57*10 ⁴
12378-PCDF	0.27	0.57	0.75	0.91	0.89	0.98	9.75*10 ⁴
23478-PCDF	0.38	0.69	0.84	0.94	0.82	0.97	9.75*10 ⁴
123478-HxCDF	0.63	0.86	0.93	0.98	0.96	0.99	1.62*10 ⁵
123678-HxCDF	0.63	0.86	0.93	0.98	0.96	0.99	1.62*10 ⁵
123789-HxCDF	0.74	0.91	0.96	0.99	0.98	0.997	1.62*10 ⁵
234678-HxCDF	0.74	0.91	0.96	0.99	0.98	0.997	1.62*10 ⁵
1234678-HpCDF	0.86	0.96	0.98	0.99	0.99	0.999	8.30*10 ⁵
1234789-HpCDF	0.92	0.98	0.99	0.997	0.99	0.999	8.30*10 ⁵
OCDF	0.98	0.995	0.998	0.999	1	1	2.28*10 ⁶

* C.C: Clean continental; B = Background; B+LS: Background plus local sources; U = urban
 B_v: Air-to-leaf biotransfer factor, (pg PCDD/g leaf dry)/(pg PCDD/g air)

employed will be 0.2 cm/sec, based on measurements of dry deposition of 2,3,7,8-TCDD in Indianapolis, Indiana, USA, and Bloomington, Indiana, USA [11]. Total deposition is reduced to an effective amount of deposition onto the grass by multiplication with a plant interception fraction, I_g . Baes [12] provided the following relationship between yield, Y, of hay/grasses and plant interception: $I_g = 1 - e^{-2.88Y_g}$, where Y_g is yield in kg/m² dry weight. Given the rural and industrial site yields of 0.089 and 0.042 kg/m² dry weight from this data set, I_g is solved as 0.23 and 0.11, respectively. The effective deposition weathers off the plant, which is modeled by the first-order dissipation rate constant, k_w , of Equation (2). The first-order weathering constant will be assigned a value of 0.0495 day⁻¹, corresponding to a half-life of 14 days. This half-life was originally developed from field data of particle deposition onto plants, which showed a range of half-lives of 2 to 34 days, and a median value of 10 days [12].

Vapor phase impacts to leafy vegetation are modeled quite simply using a bioconcentration

approach:

$$C_{gv} = \frac{B_v C_v}{d_a} \quad (3)$$

where C_{gv} is the vapor component of grass concentration (pg/g dry weight), B_v is the mass-based air-to-leaf biotransfer factor, unitless [(pg dioxin/g plant dry)/(pg dioxin/g air)], C_v is the vapor-phase concentration of dioxin in air (pg/m³), and d_a is the density of air (1190 g/m³). This B_v has been calibrated for dioxins [10]. That modeling exercise was similar to the exercise described in this paper: air and grass concentrations were known and the model was parameterized to test against the field data. The importance difference was that the B_v was *calibrated* so that the grass predictions exactly matched the field data [10]. Recent revisions have been made to this calibration exercise to account for updates to the vapor/particle partitioning model. Table 2 displays the revised set of B_v used in this exercise.

The Vapor Deposition Model: The second model to be evaluated addresses only vapor phase impacts to plants. It will be referred to as the Vapor Deposition Model. It is, in fact, analogous to the EPA Model for particle phase impacts to plants; it is based on a transfer velocity (or conductance) term, a plant dissipation term, and a plant yield term. This approach has been described and parameterized for vapor phase 2,3,7,8-TCDD impacts to grassy plants in two articles, Trapp and Matthies [13] and Smith et al. [14]. Vapor impacts of dioxins to grass are simply modeled with the steady state reservoir model which is also used to model particle-phase impacts in the EPA Model:

$$C_{gv} = \frac{F_v}{k_v Y_g} \quad (4)$$

where C_{gv} is the grass concentration due to vapor-phase dioxins (pg/g dry weight), F_v is the deposition of vapor-phase congener onto grass (pg/m²-d), k_v is a first-order dissipation constant (d⁻¹), and Y_g is the grass yield (g/m² dry weight). As in the EPA particle deposition model, this steady state solution has the additional term in the numerator, $1-e^{-(k_v t)}$, where t is the growing period. However, given that the k_v was assigned a relatively large value by both researchers for 2,3,7,8-TCDD vapors depositing onto plants (a large k_v corresponds to a short half-life), and the growing period for grasses is 45+ days in the field data set applied, this additional term approaches 1.0, and it can therefore be neglected for this application. F_v is calculated as the product of a velocity term (in units of distance/time, typically m/s) and the vapor phase air-borne concentration.

The two modeling efforts diverge at this point. Trapp and Matthies [13] calculate the velocity term as the product of a “conductance” term and the leaf area index to arrive at a velocity term of 0.005 m/s. Smith et al. [14] estimate a “transfer velocity” as a function of resistances to plant surfaces including an atmospheric resistance term, a surface boundary layer resistance term, and a plant canopy/leaf resistance. Despite a different approach to estimating the velocity, they arrive at a value of 0.0076 m/s, similar to the

0.005 m/s determined by Trapp and Matthies [13].

Both researchers used the same experimental work of McCrady and Maggard [15] to develop values for k_v . Trapp and Matthies [13] assumed that the overall k term was a function of losses by photodegradation, volatilization, and dilution from plant growth. They used the photodegradation k term of 0.3744 day^{-1} taken from McCrady and Maggard [15], but then multiplied it by 0.30 assuming that the plant was in full sunlight only 30% of the time. They calculated a volatilization rate term of 0.012 day^{-1} , and assumed a dilution term of 0.035 day^{-1} , leading to an overall k_v term of 0.159 day^{-1} . Smith, et al. [14] took the full photodegradation plus volatilization rates determined by McCrady and Maggard [15], without any correction for time in sunlight, to arrive at a k of 0.495 day^{-1} . They did not consider dilution by plant growth.

In the model test for this vapor transfer model, the air concentration will first be partitioned into a vapor and particle fraction using the model described above. Then, the vapor phase dioxins will be used to model the vapor portion of plant concentration. Since the two authors parameterized the model only for 2,3,7,8-TCDD, only this congener will be evaluated.

The Scavenging Model: McLachlan [2] developed a simple “scavenging” approach to predict grass concentrations of dioxins from air concentrations of dioxins. He suggests that grass scavenges the equivalent of 9 m^3 of air per gram of grass, and that corn scavenges 4.5 m^3 of air. The important assumption in this approach is that plants can scavenge vapors and particles equivalently; therefore, vapor/particle partitioning is unnecessary, and grass concentrations are very simply modeled as:

$$C_g = SC C_a \quad (7)$$

where C_g is the total grass concentration of any dioxin compound (pg/g dry weight), SC is the scavenging coefficient (m^3/g), and C_a is the total (vapor + particle phase) air concentration of the dioxin compound (pg/m^3). In the application of this model to the Jones and Duarte-Davidson [6] data set, total air concentrations are simply multiplied by 9.0 to predict grass concentrations.

Evaluation Procedures

There were 25 modeled/measured concentration pairs in the data sets of both the rural and industrial sites, including the 17 individual congeners and the 8 homologue groups. In order to obtain independent data points for model testing, the measured air and grass concentrations of the individual congeners were subtracted from the homologue group concentrations; individual congener concentrations are, by definition, contained within the homologue group concentrations. Doing this subtraction should have resulted in 25 independent measured/modeled pairs for model testing. However, after this subtraction and in further data examination, anomalous data were found in both the rural and industrial sites.

For the rural site, it was found that subtraction of the congener air concentrations from the homologue group air concentrations of HpCDD, HxCDF, and HpCDF resulted in negative concentrations; i.e., the congener concentrations were greater than the homologue group concentrations. There was obviously some measurement error in this data set. The air, grass, and deposition data for these three homologue groups in the rural data set were, therefore, not considered for further model testing. Without these three readings, the air and grass data at the rural site were quite correlated; the correlation coefficient of the remaining 22 data pairs was 0.92.

Similar measurement error resulted in the deletion of 4 sets of data in the industrial data set. The air concentrations of the homologue groups HpCDD and HpCDF also were lower than the sum of the individual congener concentrations. The grass concentrations of 1,2,3,7,8-PCDD and 1,2,3,7,8-PCDF were given as non-detected, but the air concentrations of these congeners in the urban settings were similar to the air concentrations in the rural settings, and significant grass concentrations were noted in the rural setting. For this reason, data for these two congeners were not used as well.

Even with these four pairs deleted, the industrial site data was not as correlated as the rural data. The correlation coefficient for the remaining 21 data pairs was 0.66. An examination of the data highlights some of the differences between the two data sets. In some instances, air concentrations that were similar in the rural and industrial sites led to grass concentrations that were *higher* in the industrial site. For example, the air concentration of 2,3,7,8-TCDD in the rural setting was 0.01 pg/m³, while it was 70% higher than that in the industrial setting at 0.017 pg/m³. However, the grass concentration in the industrial site was about 4 times as high as in the rural setting, 2.8 pg/g in the industrial site versus 0.72 pg/g in the rural site. Similar observations can be made for 4 other compounds: TCDD, PCDD, TCDF, and 1,2,3,6,7,8-HxCDD. On the other hand, there were several instances where similar rural and industrial air concentrations resulted in *lower* grass concentrations in the industrial as compared to the rural setting. Similar OCDD concentrations of 2.5 pg/m³ in the two settings resulted in a grass concentration of 94 pg/g in the rural setting but only 43 pg/g in the industrial site setting. This trend can be found in 13 other instances.

In summary, then, 22 sets of data (air, grass, and deposition data) for the rural data set and 21 sets of data for the industrial site were retained for model testing.

Model goodness-of-fit tests were applied to evaluate how well model predictions matched observations. The absolute and signed difference between the natural logs of the measured and modeled grass concentrations provided the goodness-of-fit measure. The signed error, or bias, measures the systematic tendency of the model to under or overpredict; a bias near 0 suggests that the model underpredicts and overpredicts by about the same amount. The absolute error calculation describes model variation; how close the model predictions come to the observations, regardless of whether the model over or underpredicted. A value close to 0 suggests a very good match between predictions and observations. Log concentrations were used because there were a wide range in grass concentrations, from sub-ppt

concentrations for the lower chlorinated dioxins to concentrations near 100 ppt for the homologue groups.

Generation of dioxin toxic equivalent (TEQ) concentrations were developed using the International Toxicity Equivalency Factors [16].

Results of Model Testing

Comparison of modeled and measured grass concentrations

Figures 1 and 2 compare the measured grass concentrations with the EPA and the Scavenging Model for the rural and urban site, respectively. The natural log of the observed concentrations are shown on the x-axis and the predicted concentrations on the y-axis. The dashed line shows where predicted equals observed; points above the line show overpredictions by the models while points below the line show model underpredictions. As seen in Figure 1, model predictions of rural grass concentrations using the EPA Model matched the observed concentrations better than the Scavenging model, but both models underpredicted concentrations. The predicted total toxic equivalent (TEQ) concentration of the EPA model was 3.7 pg/g, compared to the observed TEQ concentration of 6.0 pg/g. The bias was -0.66, giving a bias factor of $\exp[-0.66] = 0.51$ and suggesting that the EPA model underpredicted by about a factor of 2.0. The absolute error was close to the bias at 0.68, again indicating that the EPA model mostly underpredicted plant concentrations; of 22 observation:prediction pairs, the EPA model underpredicted concentrations 21 times.

Figure 1 shows that the Scavenging Model underpredicted grass concentration at the rural site more than the EPA model. The modeled TEQ concentration was 1.85 pg/g, less than one-third the measured TEQ concentration of 6.0 pg/g. The absolute error was 1.325, and the bias was its negative counterpart, -1.325. This means that the model underpredicted concentrations in all instances, and that this underprediction was by an average factor of 3.8 ($e^{1.325}$).

Figure 2 shows the EPA and the Scavenging Model predicting essentially the same concentration for nearly every data point, and both underpredicted grass concentrations significantly. The TEQ concentrations predicted by the EPA and the Scavenging Models were 3.26 and 2.94 pg/g, respectively, while the observed TEQ concentration was 7.35 pg/g. The bias and absolute differences for both models on this data set also mirrored each other. For the EPA Model, the bias and absolute differences were -1.01 and 1.09, and for the Scavenging Model, the bias and absolute difference were nearly the same at -1.07 and 1.15. These results indicate that both models underpredicted by about the same factor of 3.

One reason for this similarity in performance is that the EPA model reduced to principally a particle-phase deposition model; nearly all the dioxin was in the particle phase as seen in Table 2 for the “urban” setting at 10 °C. Like the Scavenging Model, therefore, plant concentrations were mostly a linear function of total air concentrations for the application of the EPA Model at the industrial site. Specifically,

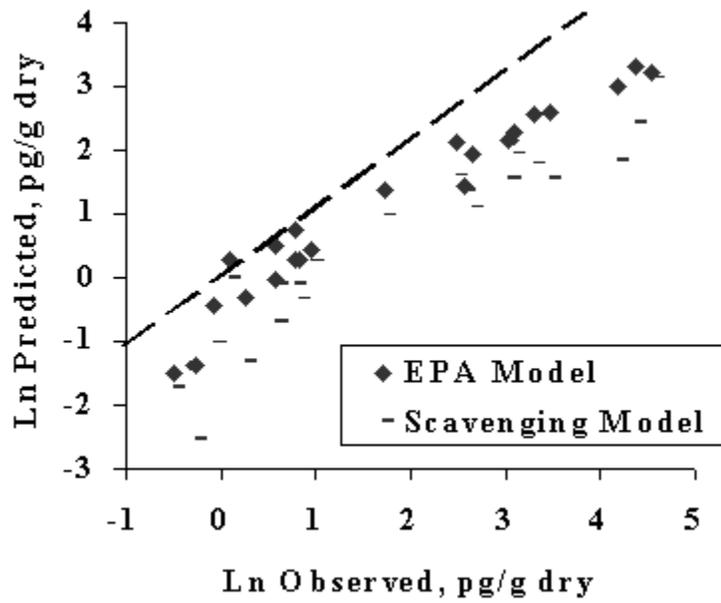


Figure 1. Comparison of observed and predicted grass concentrations of dioxin and furan congeners for the EPA and the Scavenging Models at the rural site. The perfect match of observed and predicted is shown in the dashed observed = predicted line.

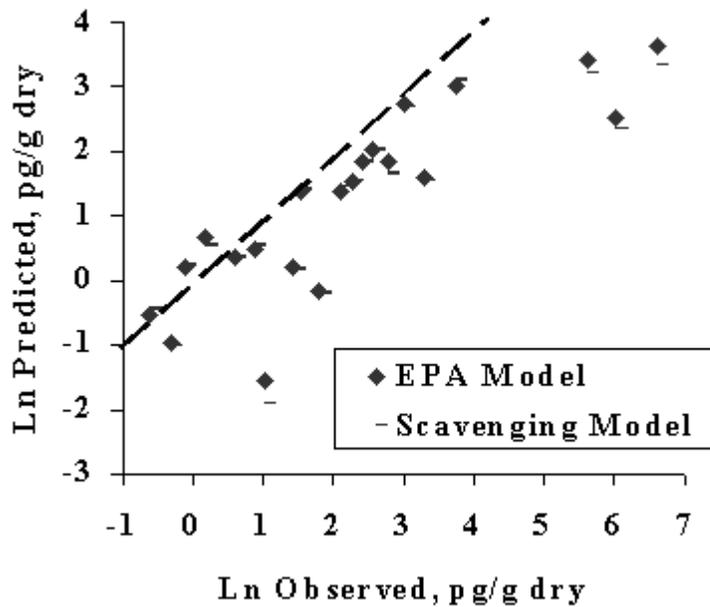


Figure 2. Comparison of observed and predicted grass concentrations of dioxin and furan congeners for the EPA and the Scavenging Models at the industrial site. The perfect match of observed and predicted is shown in the dashed observed = predicted line.

all the parameters in Equation (2) reduce to roughly $8.1 * C_p$, where C_p is the particle-bound concentration of dioxins in the air. Therefore, when most of the airborne dioxin is modeled to partition into the particle phase, then plant concentrations are modeled as the product of (nearly) total air concentration and 8.1, which will mirror the Scavenging Model's approach of total air concentration times 9.0.

As described earlier in the Model Evaluation Procedures section, the data at the industrial site was not nearly as well correlated as the data at the rural site - the correlation between air and grass data at the industrial site was 0.66 compared to 0.92 at the rural site. One factor likely to have influenced this is the fact that the soil at the industrial site was much higher for some of the dioxins as compared to the rural site. While the soil concentrations were not reported by Jones and Duarte-Davidson [6], Sandalls [21] reported exceedingly high concentrations of TCDD (up to 9400 ppt, and several hundred ppt even 4-5 km from the major air source identified in the Bolsover area), and elevations in 2,3,7,8-TCDD, PCDD and TCDF in soils near the industrial site. Not ironically, these same four compounds, along with 1,2,3,6,7,8-HxCDD, were identified earlier as the compounds which had high grass concentrations at the industrial site despite air concentrations that were comparable to air concentrations of the same compounds at the rural site. If these five air:grass pairs are subtracted from the industrial site data set, the correlation between air and grass data now is much improved: it is at 0.80, up from 0.66. Also, the absolute error for both the Scavenging and the EPA Model for this smaller observed:predicted test improve to 0.61, indicating that modeled grass concentrations are now within $\exp [0.61] = 1.85$ of measurements concentrations, rather than within a factor of 3.0. Obviously, the grass concentrations of these five compounds appear to have been influenced by high soil concentrations, and the ability of the models to reproduce these concentrations is limited because they are air-to-grass models and not air/soil-to-grass models. While it has been demonstrated that there is essentially no translocation from soil to above-ground plants (although pumpkins, cucumbers, squash, and other members of the cucumber family have been shown to translocate dioxins for an unknown reason [17]), there may have been some rainsplash impact or soil-to-air-to-plant impacts such as from wind erosion or soil volatilization for these compounds at the industrial site.

On the other hand, it was also true that air concentrations reasonably similar at the industrial and rural site led to lower grass concentrations at the industrial site for all the other dioxin and furan compounds. This is a trend that can possibly be explained and modeled by the EPA Model of this evaluation. For an urban setting, more of the dioxins are modeled to partition into the particle phase, as seen in Table 2. As will be described below in the next section on the calibration of the Scavenging Model, vapor phase dioxins have been shown to have a greater impact to plants compared to particle phase dioxins. Therefore, equivalent total air concentrations in a rural and an urban setting would lead to higher vegetation concentrations in the rural setting, because dioxins partition more into the vapor phase in such a

setting, both in reality and as modeled by the EPA Model.

Table 3 shows the comparison of the measured grass concentration of 2,3,7,8-TCDD with the modeled vapor transfer concentration using the EPA vapor transfer model and the two Vapor Deposition Models. It is clear from this table that the vapor deposition algorithm, as parameterized by Smith et al. [14] and Trapp and Mattheis [13], predicts concentrations that are 2 to 4 times lower than predictions made by the vapor transfer algorithms of the EPA Model, and even lower still than observed grass concentrations. As will be described below, vapor phase deposition velocity and the decay rate of the dioxins on the plant are two parameters likely to have been assigned inappropriate values for this exercise, and also likely to be difficult to assign in any application of the vapor deposition approach.

Table 3. Model results comparing the EPA vapor transfer model and the Vapor Deposition Model with the field data for 2,3,7,8-TCDD (concentrations in pg/g dry weight).

Description	2,3,7,8-TCDD grass concentrations, pg/g dry	
	Rural	Industrial
Observed data	0.72	2.8
EPA vapor transfer model	0.25	0.21
Smith et al. (1995) model	0.06	0.05
Trapp & Mattheis (1995) model	0.13	0.1

Calibration of the Scavenging Model

Whereas the scavenging ratio of 9.0 may have been appropriate for the field data used by McLachlan [2] in the development of this approach, it is by far too low for this particular data set. A calibration exercise was performed on the 22 rural air/grass data points. In this exercise, the least squares fit of the difference between predicted and measured log grass concentrations was sought. The best fit was found at the constant scavenging coefficient of 36.4. With this value, the goodness-of-fit measures improve substantially: the bias goes to 0 (by definition of the least squares fit) from -1.325, and an absolute error goes to 0.417 (predictions are within a factor of 1.5, sometimes higher, sometimes lower) from 1.325 (predictions are always lower by about a factor of 4.0).

A critical assumption of the scavenging approach is that vapor and particle-phase dioxins are scavenged equivalently from the air. Therefore, a constant scavenging coefficient can be applied to total air concentration to predict total grass concentration. The error terms for the best-fit scavenging ratio suggest this might be reasonable. However, this assumption is not supported by the data in this field site.

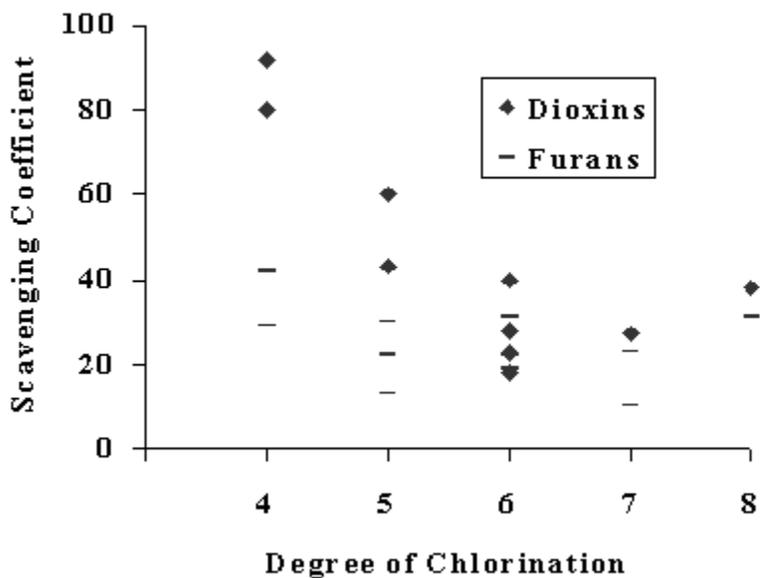


Figure 3. The observed scavenging coefficient (grass concentration over air concentration) calculated from the rural site data.

Figure 3 shows the scavenging ratios calculated for the 22 air:grass data points of the rural field site graphed as a function of the degree of chlorination. For example, there are four data points plotted for 4 on the x-axis: 2,3,7,8-TCDD, 2,3,7,8-TCDF, the TCDD homologue group, and the TCDF homologue group. The scavenging ratios are simply calculated as the grass concentration (in pg/g dry weight) divided by the air concentration (in pg/m³) at the rural field site (with subtractions of congener concentrations from homologue group concentrations). As seen in the figure, there is a clear trend in that the scavenging ratio appears to generally decrease from the tetra to the hepta degrees of chlorination, with perhaps an increase at the octa degree of chlorination. It also suggests more of a trend for the dioxins as compared to the furans: there may be a higher scavenging ratio, in general, for the dioxins.

The experiments on Welsh Ray Grass [19] used to calibrate the EPA's air-to-leaf transfer factor [10] provided a reason for this trend: when blocking out the particle deposition impacts to potted grass, the authors found that the grass concentrations of the tetra through hexa chlorinated dioxins and furans were similar to concentrations in potted grass where particle depositions were not blocked out. The authors concluded that the plant concentrations for these dioxin/furan homologue groups were dominated by vapor-phase dioxins, even though the total air concentration itself was not necessarily dominated by the vapor phase [19]. These same authors [27] continued their experiments confirming that the importance of vapor phase dioxins for lower chlorinated dioxins and the predominance of particle-phase depositions for hexa congeners and beyond. Therefore, given these experimental results, it follows that the lower

chlorinated congeners would have a larger overall scavenging coefficient. The field data certainly shows that trend; Figure 3 shows larger scavenging coefficients for the lower chlorinated dioxins and furans.

Comparison of modeled and measured deposition

The particle-phase portion of the EPA air-to-plant model includes these components: a rate of dioxin deposition on particles, a plant dry matter mixing reservoir, and a rate of washoff of dioxin-laden particles. The first part of this model, the rate of dioxin particle-phase deposition, is a simple multiplication of the particle-phase air-borne concentration times a velocity of deposition. This velocity was assigned a value of 0.2 cm/s in this modeling application. This section compares dioxin deposition modeled this way with deposition measured by upturned frisbees.

Figure 4 compares these two quantities for the rural and industrial site combined. It is clear that the modeled rates of deposition were consistently higher than the measured rates. There was a high degree of correlation between measured and modeled rates, however, with a correlation coefficient of 0.99. The absolute error and bias were 1.16 and 1.11, respectively, suggesting that the model predictions were about 3.2 times higher than observed. This would indicate a systematic bias, either that the model tended to overpredict depositions or that the measurements tended to under-represent depositions.

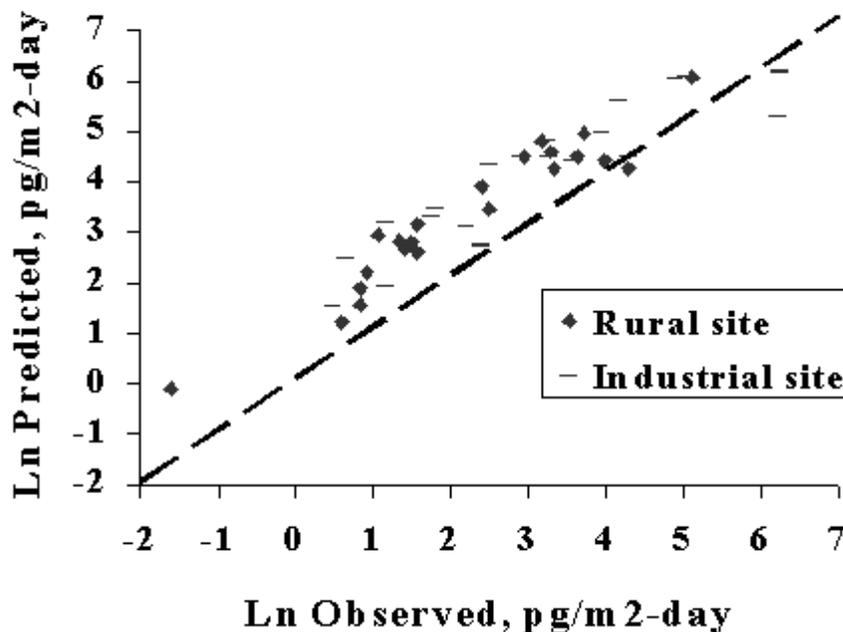


Figure 4. Comparison of observed and predicted deposition at the rural and industrial sites. The perfect match of observed and predicted is shown in the dashed observed = predicted line.

If the model tended to overpredict deposition, this may have been due to inappropriate parameter assignment: too rapid a velocity of deposition, or too much dioxins assumed to be in particle phase. Measured deposition velocities can be calculated from the data of Jones and Duarte-Davidson [6] in Table

l simply as the deposition flux divided by the air concentration (with proper conversions). Average velocities calculated this way were 0.06 cm/s for the rural site and 0.08 cm/s for the industrial site and only one calculated deposition velocity was greater than the 0.20 cm/s velocity assigned for this modeling exercise. As described earlier, the particle phase fraction, represented by ϕ , was higher at the assumption of 10 °C than at 20 °C. The predicted depositions would be lower still if measured particle phase fractions were used instead of modeled fractions since, as discussed earlier, measured particle-particle fractions of dioxins tend to be lower than modeled using the Junge model for vapor/particle partitioning. For this particular field site, measured vapor/particle fractions were not available to evaluate this possibility.

On the other hand, it could be the case that the deposition collectors are underestimating depositions. Jones and Duarte-Davidson [6] suggest two possible causes for the upturned frisbees to be underestimating deposition: 1) they are smooth and therefore less efficient at capturing particles as compared to leafy vegetations or ground surfaces, and 2) dioxins in wet deposition can be adsorbed onto the sampler surface and presumably, not be available to be measured.

In any case, it can be concluded that the deposition model, which was the simple product of the particle-phase reservoir times a deposition velocity of 0.20 cm/s, resulted in the deposition amounts that about 3 times higher than were measured in the rural and industrial sites of this data set.

Model uncertainty and issues for general model usage

All three models underestimated grass concentrations. Assignment of model parameters has to be considered part of the problem. Model “validity” must also be considered - i.e., even given the simplicity and steady state nature of the selected models, one must question whether the algorithms chosen to represent dioxin transfers from air to vegetation are appropriately identified and modeled.

For the Vapor Deposition Model, critical parameters include the deposition velocity and the rate of degradation on the plant. The deposition velocities assigned by Smith et al. [14] and Trapp and Mattheis [13] were less than 1.0 cm/s. It seems unlikely that their assigned velocities, or conductance terms, were significantly low, if low at all. In the absence of data, Sehmel [18] recommends use of a 1 cm/s deposition velocity for both organic and inorganic vapor phase contaminants. The degradation term is more likely inappropriately assigned by these researchers, at least for this field data set. That rate was based on a controlled chamber study, which included an uptake and a degradation phase. The degradation phase was conducted in outdoor bright sunlight (personal communication, J. McCrady, US EPA, 1995). Degradation rates derived under these sunlight conditions may not be appropriate for most conditions. A longer half-life would improve model predictions; just a doubling to quadrupling the half-lives brings the Trapp and Mattheis [13] and Smith et al [14] predictions in line with the EPA Model predictions. Besides McCrady and Maggard [15], there are not other good studies which can help in assigning photodegradative half-lives for vapor-phase dioxins depositing on vegetations. In an experiment where various dioxin congeners

were dissolved in cuticular wax from laurel cherry leaves and exposed to sunlight and mercury lamps, degradation half-lives were all less than 1 day [25], but this was a poor measure of photodegradation under field conditions. Welsch-Pausch and McLachlan [26] did an experiment comparing grass grown in a greenhouse not exposed to UV-light (UV cutoff at 320 nm) with the same culture of grass grown in a second greenhouse with UV-light transmission of >50% in the 280-320 nm range, which the authors claim to be relevant to photolytic reactions of PCDD/Fs. They found insignificant differences in dioxin concentrations for the two cultures, prompting them to conclude that photolytic degradation was a relatively insignificant factor in the accumulation of PCDD/Fs in the pasture grass they studied.

Jones and Duarte-Davidson [6] state that their field data support the contention that vapor and particle phase dioxins transfer equivalently, the key premise of the scavenging approach. As shown in Figure 3, this contention does not appear to hold with the field site data presented in their article. Also, they derive scavenging coefficients of: 33 for their summer samplings, 11 for the sampling prior to the September/October sampling used in this paper, and 45 for the industrial site fall sampling. Together with McLachlan's derived value of 9 for grass and the 36 value derived in this paper for the rural field site of the fall sampling, this results in 5 possible selections for a scavenging coefficient ranging from 9 to 45. It may be possible at some time to develop assignment rules for general use of the Scavenging Model - i.e., assignments based on degree of chlorination and characteristics of the field site (background vs. rural vs. urban setting, for example), but at this point the Scavenging Model, like the Vapor Deposition Model, does not appear to hold promise as a valid and practical tool for general predictive purposes for modeling air-to-grass transfers of the dioxin-like compounds.

It can be said that the EPA model performed the best of the three tested on this field site: it came the closest to the grass concentrations of 2,3,7,8-TCDD of the three at both sites (Table 3), and it modeled consistently to within an average factor of 2 at the rural field site (Figure 1). The high soil concentrations at the industrial site was shown to be a confounder for 5 congeners from that field data; however, evaluation of the other 16 compounds suggests that the both the Scavenging and EPA Models were underestimating air-to-plant transfers to within about the same factor of 2. The EPA Model does separately consider vapor and particle phases, including the difference in vapor:particle partitioning as a function of air temperature and airshed particle density, and the difference in air-to-plant transfer trends between vapor and particle phases, and that appears to be an important consideration for dioxins and furans. It does appear, however, that while the calibration of the EPA Model at a field site in Germany [10] forced the model to reproduce that field data, the results of that calibration may not be immediately transferable to other field site conditions.

As the study of dioxin and related compounds in the terrestrial food chain continue, the interplay between vapor and particle-phases, the processes which transfer dioxins to plants, the attainment of steady state or the lack thereof, the role of elevated soil concentrations, and other issues, will need to continue to

be studied. Until then, it is the responsibility of modelers to consider and identify model uncertainties, and to continue efforts to field test the models.

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