Development of an Air-to-Leaf Vapor Phase Transfer Factor for Dioxins and Furans

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1. Introduction

Welsch-Pausch, et al[1] presented results of an experiment in which grass was grown in a greenhouse and outdoors, and in soils of different concentration levels of dioxins and furans. The purpose of the experiment was to understand the pathways by which dioxins and furans enter the grass. A principal finding of their research was that dry gaseous deposition of these compounds, rather than particle deposition or soil-to-plant transfers, explained the concentrations found. McLachlan used the outdoor air concentrations and the grass concentrations from a subset of the experimental data to validate a fugacity modeling approach of the dry gaseous deposition of dioxins to grass (the modeling work with this data was described in an unpublished manuscript sent in a personal communication from M. McLachlan to M. Lorber. Details on the fugacity model McLachlan used can be found in Tolls and McLachlan[2]).

The same subset of data used by McLachlan will be used in a modeling framework in this paper. Specifically, the subset includes ambient air concentrations from the summer sampling for 1991 (the experiments of Welsh-Pausch, et al[1] included a summer and a fall sampling period) and the outdoor grass concentrations during the same period. The air-to-plant modeling framework is a simple empirical framework described in detail in Lorber, et al[3]. Air-borne dioxin congeners are partitioned into a particle and a vapor phase. The particle phase dioxins settle onto plants and are weathered (washed off or blown off) from the plants using a simple first order weathering constant. Vapor phase dioxins "transfer" to plants using a simple air-to-leaf biotransfer factor. The data of Welsh-Pausch, et al[1] will be used to determine the air-to-leaf vapor phase biotransfer factor of this modeling framework.

2. Modeling Methodology and Results

The first version of the air-to-plant model used an empirical algorithm to estimate values for

B_{vpa}[4]. The algorithm was developed by Bacci and coworkers[5,6] who studied the vapor transfer of 14 organic chemicals, one of which was 1234-TCDD (not one of the 17 toxic congeners, but with similar fate properties to 2378-TCDD), to azalea leaves. These chamber experiments did not consider the effect of photodegradation on the transfer of the organic chemicals to the azalea leaves. Then, McCrady and Maggard[7] conducted chamber experiments on the transfer of 2378-TCDD vapors to grass leaves considering photodegradation. These experiments showed that the transfer of 2378-TCDD to grass leaves was about 40 times less than the transfer as calculated by the Bacci empirical algorithm. In addition to not considering photodegradation, McCrady and Maggard[7] considered the difference in plant species between azalea leaves and grass leaves to be important in explaining the lower rate of transfer in their experiments. McCrady and Maggard's results were used in the next version of the air-to-plant model and the assignment of values to B_{vpa}[3,8]. Specifically, the transfer factor for each dioxin congener was estimated using the Bacci algorithm, but this time all final results were divided by 40. Therefore, the B_{vpa} of the original model was reduced by a factor of 40 for all 17 dioxin and furan congeners for the second version of the air-to-leaf model.

Two key presumptions are inherent in using the Bacci algorithm divided by 40: 1) that the Bacci algorithm is generally appropriate for the dioxin congeners, despite the fact that the physical/chemical properties of the dioxin congeners are generally outside the range of the 14 organic chemicals used by Bacci, and 2) that the factor of 40 derived from one experiment on 2378-TCDD applies to all dioxin-like compounds.

The data of Welsh-Pausch, et al.[1] includes grass concentrations and air concentrations. Grass was grown in two flower boxes, with different agricultural soils in each box, beginning in May of 1991. The grass was cut back on July 17 in that year. On August 9, the grass was cut back again and the yield from the two boxes from the growth between July 17 and August 9 averaged 3900 g/m² fresh weight. This grass was analyzed for concentrations of dioxin congener groups, and these concentrations were provided on a fresh weight basis (i.e., pg/g fresh weight). On July 18, the first of two week long air samples were taken. These samples were taken very near the boxed grass. The samples were measured for the dioxin congener groups, not the individual congeners. Representative congener group air concentrations were then determined as the average of the concentrations from the two samples. The concentration of dioxins in air remained relatively constant during the experimental period.

This data was used to determine a field-measured vapor phase transfer factor for congener groups in the following 3-step procedure:

Step 1: Partition the total concentrations measured into a vapor and a particle phase. McLachlan (unpublished manuscript) had used the glass fiber filter/XAD trap 2-stage high volume air samplers to estimate vapor and particle fractions from the total reservoir. This apparatus will yield "operationally defined" vapor and particle fractions. The vapor fraction estimated this way will be larger than the vapor fraction estimated using the Junge model as applied and described in an article by Bidleman[9]. The Bidleman model was used in the modeling in Lorber, et al[3] and in this paper as well. Whether the Bidleman model is more "correct" than the measurements of the 2-stage sampler is an ongoing technical issue. A full discussion of the issue can be found in EPA[8]. Table 1 shows the vapor/particle partitioning as developed using the Bidleman model and assumed for this paper compared against the measured vapor/particle partitioning from the air sampling apparatus. As an example of how the measured and the modeled vapor fractions are different, the air sampling apparatus measures 72% of the PCDD congener group to be in the vapor phase, whereas the Bidleman approach estimates that 26% of the PCDD dioxin-like congener is in the vapor phase.

The vapor and particle fractions for the congener groups are modeled assuming an air temperature of 20 °C, and a particle density in air corresponding to a condition which Bidleman described as "background plus local sources". The average air temperature between July 17 and August 9 of 1991 was 18 C (McLachlan, unpublished manuscript), and the "background plus local sources" designation also appears most appropriate for the university city of Bayreuth, described as a typical background situation for this area of Europe by Welsh-Pausch, et al[1). Two alternate options instead of background plus local sources appear less relevant for Bayreuth: an "urban" condition (higher particle densities) and a "background" condition (lower particle densities).

Step 2:   Model the deposition of particle-bound dioxins to the grass, and subtract out the resulting modeled grass concentration from the total concentration. Since an air-to-leaf vapor phase transfer factor is sought in this exercise, what is needed is the grass concentration due only to vapor transfers. The particle-bound impact to vegetations cannot be measured directly. Therefore, a model will be applied to estimate that part of total grass concentration of dioxin that was due to particle bound depositions. The model that will be applied is the one described in Lorber, et al[3).

Step 3:   What is now available after accomplishment of the above two steps is a concentration of vapor phase dioxins in air and a concentration of dioxins in grass due to vapor phase transfers. With appropriate conversions, the air-to-leaf transfer factor is now simply calculated as the vapor-impacted grass concentration divided by the vapor phase air concentration.

The particle deposition model is simply:

$$ GCp \; = \; \frac{F \; I \; (1 \; - \; e^{-kt})}{Y \; k} \tag{1} $$

where GCp is grass concentration due to particle deposition (ng/kg dry), F is the deposition of particle bound dioxins (ng/m^2-day), I is the interception fraction, k is the dissipation rate of dioxins which have deposited onto the plants (day^{-1}), t is the time during which deposition is occurring (day), and Y is the plant dry matter yield (kg/m^2). The deposition F can be estimated as the particle bound fraction times a deposition velocity. The velocity of deposition will be assumed to be 0.002 m/sec, which was the velocity of dry deposition of dioxins as measured by Koester and Hites[10). Wet deposition was not considered for this brief exercise; Welsh-Pausch, et al[1) indicates that only a small amount of rain fell during this time and that results implied that rain washed off the grass leaves. The interception fraction will be assumed to be 0.59, based on information provided in Baes, et al[11). As described in Lorber, et al[3), a first-order weathering rate of 0.0495 day^{-1}, corresponding to a 14-day half-life, is used in this model. The experiment occurred between July 17 and August 9, so a time t of 24 days is assumed. Assuming 15% dry matter in grass, the fresh weight yield of 3900 g/m^2 translates to a yield of 0.585 kg/m^2 dry. The final fresh weight concentrations due to particle depositions and vapor transfers are shown in Table 1.

Also shown in Table 1 in the last column is the percent of total plant concentration that is estimated to be due to vapor transfers. Except for the octa congeners, it would appear that the grass is mostly impacted by vapor transfers. This, of course, is contingent on the validity of the particle impact model.

The volumetric air-to-leaf transfer factor, referred to as B_{vol} in Lorber, et al[3], is defined as the volumetric concentration of dioxins in grass due to vapor phase transfers divided by the volumetric concentration of dioxins in air. Appropriate units expressing this ratio are: [pg dioxin/m^3 grass]/[pg dioxin/m^3 air]. The air concentrations are already in the appropriate units. The grass concentrations as given in Table 1 are in units of ng dioxins per kg plant fresh weight; these concentrations need to be converted into a volumetric basis. To do the conversion, the denominator in this grass concentration needs to be converted to a volumetric basis. McCrady and Maggard[7] use a volumetric factor of 0.77 kg fresh leaf/L volume. Two other conversions necessary are a conversion from L to m^3 and a conversion from ng to pg. The final volumetric plant concentration in appropriate units is given as:

$$GCv \ \frac{pg \ dioxin}{m^3 \ volume} \ = \ GCv \ \frac{ng \ dioxin}{kg \ plant \ fresh} \ \frac{0.77 \ kg/L}{0.001 \ m^3/L} \ \frac{1000 \ pg/ng}{} \qquad \textbf{(2)}$$

Table 2 now develops the final mass-based transfer factors, B_{vpa}. As described in Lorber, et al[3], the volumetric transfer factor needs to be converted to the mass-based transfer factor, B_{vpa}:

$$B_{vpa} \ = \ \frac{1.19 \ kg/m^3 \ B_{vol}}{0.15 \ 770 \ kg/m^3} \qquad \textbf{(3)}$$

The B_{vpa} calculated in this paper are compared against the B_{vpa} in Lorber, et al[3] in Table 2.

Key findings and observations from this exercise are as follows:

1. All B_{vpa} as calculated with the data of Welsh-Pausch, et al[1], are lower than the B_{vpa} as calculated in Lorber, et al[3]. For 7 of the 10 congener groups, the difference is less than an order of magnitude. The exceptions are the two octa congeners and the hepta dioxin congener, where the B_{vpa} calculated from the Welsh-Pausch, et al[1] data are two or more orders of magnitude lower for the octa congeners and 1.5 orders of magnitude lower for the hepta dioxin congener. In general, the trend of increasing B_{vpa} from the tetra through the octa congeners is consistent with both approaches. The general consistency in the two approaches lends some credibility to the approach in Lorber, et al[3], which developed B_{vpa} in the absence of any field data for dioxins and any data at all, laboratory or field data, for 16 of the 17 dioxin congeners.

2. It may be informative to speculate on why the transfer of vapor phase dioxins appears to be lower in the Welsh-Pausch, et al[1] data as compared to the McCrady data. There may be a relevant species difference, such as the lipid content for example, in the grass species used by McCrady and Maggard[3], Reed canarygrass (*Phalaris arundinacea L.*), and the grass in the Welsh-Pausch, et al[1] experiments, Welsh Ray Grass (*Lolium multiflorum*). The climate might have different in Bayreuth, leading to more photodegradative loss in the Welsh-Pausch data. Certainly the experimental designs were different. McCrady and Maggard[7] used a 2-stage chamber experimental design, including an uptake phase in which the grass was not exposed to sunlight, and a release phase where the grass was kept in sunlight. Uptake and release were occurring simultaneously and in sunlight in the Welsh-Pausch, et al[1] experiments. Certainly it seems possible that the net transfer rates might have been lower in the McCrady and Maggard[7] experiments had the uptake and release phases both occurred in sunlight.

3. The observations in Welsh-Pausch, et al[1], in Lorber, et al[3], and in the work in this paper continue to underscore the importance of vapor transfers of dioxins to vegetations. By extension, the assumptions on the fraction of the dioxins which exist in the vapor phase in the air are important. Air-to-leaf transfer factors can be recalculated using the measured vapor/particle fractions that are shown in parentheses in Table 1. Also, research to more fully understand the differences in the Bidleman model predictions and the measured vapor/particle partitioning is warranted.

3. References

1)   Welsch-Pausch, K.,M. McLachlan, and G. Umlauf. 1995. Determination of the principal pathways of polychlorinated dibenzo-p-dioxins and dibenzofurans to Lolium multiflorum (Welsh Ray Grass). Environmental Science and Technology 29:1090-1098.

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10)   Koester, C.J. and R.A. Hites. 1992. Wet and dry deposition of chlorinated dioxins and furans. Environmental Science and Technology 26:1375-1382.

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Table 1. Data and parameters used to determine the part of the plant concentrations which was due to the deposition of particle bound dioxins (see below table for definition of columns).

#1	#2	#3	#4	#5	#6	#7	#8
Cl_4DD	0.55/0.45 (0.90/0.10)	0.029	0.013	0.007	0.13	0.123	94
Cl_5DD	0.26/0.74 (0.72/0.28)	0.029	0.021	0.011	0.13	0.119	92
Cl_6DD	0.04/0.96 (0.55/0.45)	0.053	0.051	0.026	0.14	0.114	81
Cl_7DD	0.02/0.98 (0.23/0.77)	0.088	0.086	0.043	0.13	0.087	67
OCDD	0.0002/0.9998 (0.07/0.93)	0.163	0.1629	0.082	0.19	0.108	57
Cl_4DF	0.29/0.71 (0.91/0.09)	0.190	0.135	0.068	0.63	0.562	89
Cl_5DF	0.36/0.64 (0.78/0.22)	0.104	0.067	0.034	0.25	0.216	86
Cl_6DF	0.07/0.93 (0.52/0.48)	0.082	0.076	0.038	0.15	0.112	74
Cl_7DF	0.04/0.96 (0.23/0.77)	0.057	0.055	0.028	0.14	0.112	80
OCDF	0.0002/0.9998 (0.11/0.89)	0.026	0.0259	0.013	0.029	0.016	55

Column Definition:
#1 - Congener Group
#2 - Vapor/Particle Fractions. Ratios in parenthesis were the fractions measured in the 2-stage air sampling equipment. See text for more detail.
#3 - Total air concentration, pg/m^3
#4 - Particle bound air concentration, pg/m^3
#5 - Plant concentration calculated to be due to particle deposition, ng/kg fresh
#6 - Total plant concentration, ng/kg fresh
#7 - Plant concentration calculated to be due to vapor transfer, estimated as Column 6 - Column 5, ng/kg fresh
#8 - Percent of plant concentration due to vapor transfers.

Table 2. Development of the B_{vpa} using data of Welsch-Pausch, et al[1] compared against the B_{vpa} as developed in Lorber, et al[3] (see below table for column definitions).

# 1	# 2	# 3	# 4	# 5	# 6
Cl_4DD	94710	0.016	$5.92*10^6$	$6.1*10^4$	$1.0*10^5$
Cl_5DD	91630	0.008	$1.15*10^7$	$1.2*10^5$	$6.3*10^5$
Cl_6DD	87780	0.002	$4.39*10^7$	$4.5*10^5$	$6.9*10^5$ - $2.3*10^6$
Cl_7DD	66990	0.002	$3.35*10^7$	$3.5*10^5$	$1.0*10^7$
OCDD	83160	0.0001	$8.32*10^8$	$8.6*10^6$	$2.4*10^9$
Cl_4DF	432740	0.055	$7.87*10^6$	$8.1*10^4$	$1.5*10^5$
Cl_5DF	166320	0.037	$4.50*10^6$	$4.6*10^4$	$3.8*10^5$ - $5.3*10^5$
Cl_6DF	86240	0.006	$1.44*10^7$	$1.5*10^5$	$5.9*10^5$ - $1.4*10^6$
Cl_7DF	86240	0.002	$4.31*10^7$	$4.4*10^5$	$6.8*10^5$
OCDF	12320	0.0001	$1.23*10^8$	$1.3*10^6$	$1.7*10^8$

Column Definitions:
#1 - Congener
#2 - Vapor phase volumetric grass concentration, pg/m^3
#3 - Vapor phase volumetric air concentration, pg/m^3
#4 - B_{vol} calculated from the data of Welsh-Pausch, et al[1]
#5 - B_{vpa} calculated from the data of Welsh-Pausch, et al[1]
#6 - B_{vpa} as developed in Lorber, et al[3]. These B_{vpa} were calculated for the individual dioxin-like congeners. Where a range is presented, such as for Cl_6DF, this was the range for the dioxin-like congeners in the congener group.