

AN ALTERNATIVE APPROACH FOR ESTIMATING PLANT UPTAKE OF DIOXIN VAPORS

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ABSTRACT

One of the key environmental pathways through which people may be exposed to dioxins involves the accumulation of dioxins in plant tissue, and subsequently in animal tissues. This paper addresses in particular the bioaccumulation pathway for dioxin which involves direct uptake of dioxin vapor into plant tissues. To evaluate the dioxin air-to-plant pathway, EPA currently recommends use of a bioaccumulation factor that relates the predicted concentration of dioxin in plant tissues to the long history of dioxin vapor concentration in the ambient air. EPA is updating its previous recommendations regarding the appropriate air dispersion and dry and wet deposition models to apply for these exposure calculations. This paper compares the EPA approach for calculating dioxin vapor concentrations in plants with an alternative approach that calculates a vapor deposition, or transfer, velocity.

Compared with the bioaccumulation factor approach, the alternative model offers several advantages. First it is mathematically compatible with the other deposition models currently used to calculate particle deposition and washout. As a boundary layer mass transport model, it establishes maximum upper limits to the physical rates of vapor transfer. Furthermore, it also is compatible with the fugacity models that have recently been progressing rapidly to enhance our understanding of the critical processes affecting transfer of dioxin-like compounds within the leaves of plants.

Results presented for an example case study illustrate the relative magnitude of risk predictions that would result from applying each approach to average background dioxin/furan (toxic equivalent) concentrations. Plant concentrations calculated using the alternative modeling approach were one to two orders of magnitude less than concentrations calculated by literal application of the EPA recommended bioconcentration factor approach. Comparative results, without correction factors that have recently been added to the EPA recommendations, are presented and discussed.

INTRODUCTION

A new regulatory effort by the U.S. EPA, the Combustion Strategy Initiative⁽¹⁾ commenced in 1993 and now is requiring hazardous waste incinerators and many boilers and industrial furnaces regulated under RCRA to conduct coordinated trial burns and multipathway risk assessments that include an evaluation of indirect exposure pathways. The risk assessment is to help ensure for the public that the facility is operating safely and not posing any significant health risks. Indirect exposure pathways are especially important for semi-volatile organic chemicals such as dioxins (i.e., all polychlorinated dibenzodioxin and dibenzofuran congeners), which have a high tendency to bioaccumulate. As the number of publicly available risk assessments for incinerator facilities has increased, it has become evident that intake of dioxin through ingestion of vegetables, meat, fish and dairy products is generally a major contributor to total facility risks.

This paper therefore briefly reviews the basis of the plant uptake of organic vapor (exposure) calculation methods recommended by the U.S. EPA in the latest related guidance documents

⁽²⁻⁴⁾, and then suggests an alternative modeling approach, developed by Smith and Heindl⁽⁵⁾ that is more consistent with generally accepted methods used for analogous mass transfer processes. The alternative method has several advantages. One of these is that, because it is developed from boundary layer resistance theory, it places finite limits on the possible total mass and maximum rates of transfer of vapors from ambient air onto plant leaves. As pointed out in previous papers by these authors and colleagues⁽⁶⁻⁷⁾, the bioconcentration factor method does not account for mass balance and predicts unrealistically high concentrations in plants.

The authors concur with EPA's draft *Addendum to the Methodology for Assessing Health Risks Associated with Indirect Exposure to Combustor Emissions*⁽²⁾ in its recommendation that both particulate matter containing semi-volatile dioxins and related vapor forms should be assessed. For the this paper, however, the discussion of alternative modeling methods, and the simple comparative assessment of risks from background levels of dioxins, will only consider the vapor-to-plant pathway, since that is the focus of the new modeling methods.

DIOXIN VAPOR-TO-PLANT MODELING

EPA Approach

In its 1993 and 1994 guidance documents⁽²⁻⁴⁾ the U.S. EPA recommends using the COMPDEP model to model airborne particle and vapor concentrations, as well as dry and wet deposition of particles. To estimate vapor-to-plant transfer, the undepleted airborne plume mass concentration was to be simply multiplied by the mass-based air-to-plant leaf biotransfer factor for the type of plant of interest, as illustrated below. In early 1995 the new draft version of the Industrial Source Code (ISCST2DFT) was published on the EPA computer bulletin board, and permitting groups are now shifting to that model as a recommendation for the atmospheric transport and deposition modeling aspect of risk assessments.

The deposition modeling subroutine underlying this new model is derived from the ADOM model⁽⁸⁾, which has been adapted internationally for calculation of dry and wet chemical deposition processes, especially those related to "acid precipitation". The U.S. EPA has not yet attempted to integrate vapor deposition processes in a comparable manner, however. Instead, the currently recommended approach is to also restrict the use of ISCST2DFT to calculation of the geographical distribution of air concentrations (undepleted and particle-depleted plumes), as well as dry and wet particle deposition fluxes. The basis for calculating vapor-to-plant transfer for dioxin-like semi-volatile chemicals continues to be the several recent laboratory studies of uptake of 1,2,3,4 tetrachlorodibenzo-p-dioxin (TCDD) and several other semi-volatiles on azalea leaves by Bacci, et al.⁽⁹⁾ and of 2,3,7,8 TCDD on grasses by McCrady and Maggard⁽¹⁰⁾ and McCrady⁽¹¹⁾.

Accordingly, as an update to the method presented in its guidance documents^(2,4), in *Estimating Exposure to Dioxin-Like Compounds*⁽¹²⁾, U.S. EPA suggests:

$$C_{vpa} = B_{vpa} \times C_{va} / d_a \quad (\text{Eq. 1})$$

where:

$$C_{vpa} = \text{concentration due to vapor-phase absorption [mg chemical/kg plant dry weight (DW)]}$$

B_{vpa}	=	mass-based air-to-leaf biotransfer factor, unitless [(mg chemical/kg plant DW)/(mg chemical/kg air)]
C_{va}	=	vapor-phase concentration in air (mg/m ³)
d_a	=	density of air (1.19 kg/m ³)

The first two laboratory studies cited above^(8,10) provide the experimental information for values of B_{vpa} for the specific dioxin congeners studied. Bacchi's volume-based biotransfer factors lead to a mass-based B_{vpa} of 4.6×10^5 . There were several limitations in this study: it was conducted in azalea plants, which have a higher lipid content than grass and subsequently would be expected to accumulate more dioxin; it was conducted with 1,2,3,4-TCDD, which is considered a non-toxic dioxin congener; and it did not account for photodegradation.

McCrary and Maggard⁽¹⁰⁾ conducted uptake experiments with 2,3,7,8-TCDD using grass, instead of azaleas, and in sunlight to account for photodegradation effects. Based on these studies, they developed a B_{vpa} of 8.2×10^4 , which is 5.6 fold less than the value developed by Bacchi et al.⁽⁸⁾.

Both of these laboratory studies are limited in their ability to simulate the behavior of dioxin vapor under actual field conditions. As recently pointed out by Magee and Smith⁽⁹⁾, there are several general limitations to the EPA approach. The laboratory-based approach does not describe the situation in an actual field environment where the wind is blowing intermittently in different directions, and the concentration of dioxin vapor immediately available to the plant surface, and volatility of initially absorbed dioxin are likely to be limiting factors. The proposed EPA approach does not consider crop density, which would be expected to decrease the dioxin uptake into individual plants. Because it is difficult to perform an experiment with dioxin concentrations that are within the general range of concentrations expected from combustor facilities, laboratory experiments of both Bacchi et al.⁽⁸⁾ and McCrary and Maggard⁽¹⁰⁾ employ dioxin concentrations that are extremely high. Thus the behavior of dioxin vapor in experiments with very high concentrations may very well differ from its behavior at environmentally relevant concentrations.

Alternative Modeling Approach

An alternative vapor-to-plant transfer method that was developed by Smith and Heindl⁽⁷⁾ can be incorporated into an atmospheric dispersion model that accounts for mass balance. This model is conceptually analogous to the surface resistance model that is used to calculate transfer velocities to plant tissue for reactive gases such as sulfur dioxide studied in acid rain research. In this alternative method, dry deposition onto the surface is computed by the product of the air concentration near the ground and a deposition or transfer velocity (V_d). The transfer velocity is represented as the inverse of the sum of the resistance to transfer to the surface:

$$V_d = 1 / (R_a + R_b + R_c) \quad (\text{Eq. 2})$$

where:

R_a	=	atmospheric resistance (sec/cm), a function of vertical turbulent transport
R_b	=	surface boundary layer resistance (sec/cm), a function of molecular diffusivity
R_c	=	plant canopy/leaf resistance (sec/cm), a function of vegetative density, stomatal uptake, surface effects, humidity, etc. [The inverse of these resistance components, conductance is the quantity specified in developing fugacity models, such as that of Riederer ⁽¹³⁾]

AIR

As a typical but reasonably conservative example, Smith and Heinold⁽⁷⁾ compute the following resistance values pertaining to deposition of 2,3,7,8-TCDD to a flat open area with tall grass under neutral stability conditions: Ra = 0.4 sec/cm, Rb = 0.38 sec/cm, and Rc = 0.5 sec/cm, resulting in a transfer velocity of 0.78 cm/sec. (At night, Ra values can be as much as an order of magnitude higher, reducing the net transfer velocity).

The transfer rate (flux) of dioxin vapor, F_v , is then computed by multiplying the transfer velocity, V_{iv} , by the local air concentration, C_{va} . After computing the deposition rate, the dioxin vapor concentration in plants, C_{vpd} , may be calculated using the following equation¹:

$$C_{vpd} = (F_v \times f_o) / (K_{wt} \times Y_j) = [(C_{va} \times V_{iv}) \times f_o] / (K_{wt} \times Y_j) \quad (\text{Eq. 3})$$

where:

C_{vpd}	=	plant concentration contribution due to vapor-phase deposition (ug chemical/kg plant dry weight-day)
F_v	=	deposition flux (mg/m ² -day)
f_o	=	chemical equilibrium factor [$1 - e^{-(K_{wt} \times t)}$] (unitless)
K_{wt}	=	degradation constant (day ⁻¹)
f_w	=	weathering, including photodegradation, half-life (day)
t	=	time until harvest (days)
Y_j	=	crop j yield, dry weight (kg/m ²)
C_{va}	=	concentration of vapor in air at plant receptor (ug/m ³)
V_{iv}	=	Effective transfer velocity of vapor to plant (m/day)

For the case example presented below, the following values were used for the parameters listed in Eq. 3. The deposition rate was calculated by multiplying the transfer velocity (Eq. 2) with the average North American background air concentration of dioxin-TE reported in 1994 by the U.S.EPA⁽¹⁴⁾. A crop interception factor of unity is assumed, since the vapor transfer process is assumed to be completely described by the transfer velocity, V_{iv} . The weathering and photodegradation constant of 0.495 day⁻¹ was calculated assuming that the photodegradation half-life of 1.4 days reported by McCrady and Maggard⁽¹⁰⁾ would dominate the typical 14 day weathering half life which would otherwise be used⁽¹²⁾. The time until harvest for leafy crops used here is 122 days⁽¹⁵⁾. The crop density used here is 2 kg/m²⁹.

CALCULATION OF PLANT CONCENTRATIONS

Using these two different approaches, plant concentrations were calculated assuming a dioxin vapor concentration equal to ambient concentrations of 2,3,7,8-TCDD toxic equivalents (TCDD-TE) measured in the United States⁽¹⁴⁾. The average TCDD-TE concentration among 84 ambient air samples from rural, pristine and urban locations not expected to be impacted by industrial sources is 9.5×10^{-11} mg/m³. This value is for total TCDD-TE in both particulate and vapor form.

There is very little reliable measurement data published on the vapor/particle partitioning of dioxin. EPA⁽¹⁴⁾ reports one study by Eitzer and Hites⁽¹⁶⁾ on ambient air measurements conducted in Bloomington, Indiana. In their study, the vapor fraction of dioxin was found to be 30% of the total, as will be assumed for the present example: TCDD-TE vapor form = 2.85×10^{-11} mg/m³.

As shown in Table 1, plant concentrations of dioxin were calculated using the bioconcentration factor developed by Bacci et al.⁽⁹⁾ for 1,2,3,4-TCDD, the bioconcentration factor developed by McCrady and Maggard⁽¹⁰⁾ for 2,3,7,8-TCDD, and the deposition model developed by Smith and Heinold⁽⁷⁾. For the bioconcentration factor approach, it was necessary to convert from dry weight to wet weight of plant. A dry weight-to-wet weight conversion factor of 0.22 was used⁽¹⁵⁾. As shown in Table 1, the plant concentration predicted using the more realistic Smith and Heinold⁽⁷⁾ model is between one to two orders of magnitude less than plant concentrations predicted using the bioconcentration factor approach.

As a final step, lifetime cancer risk levels from human consumption of leafy crops were estimated. The same standard exposure assumptions were used for each case, with the plant concentration as the only parameter that was varied. The following equation was used:

$$\text{ELCR} = C_{\text{vpa}} \times \text{CR} \times \text{LCF} \times \text{UCF} \times \text{ED} \times \text{CSF} / (\text{LT} \times \text{BW}) \quad (\text{Eq. 4})$$

where:

ELCR	=	excess lifetime cancer risk (unitless)
$C_{\text{vpa,vpd}}$	=	concentration due to vapor phase absorption (mg/kg)
CR	=	crop consumption rate (g/day)
LCF	=	local consumption factor (unitless)
UCF	=	unit conversion factor (10^{-3} kg/g)
ED	=	exposure duration (years)
CSF	=	cancer slope factor for dioxin [1.5×10^5 / (mg/kg-day)]
LT	=	lifetime (years)
BW	=	body weight (kg)

Two different values for C_{vpa} , and one for C_{vpd} , were calculated for the three approaches. A crop consumption rate of 52.3 g/day was used for leafy crops¹². A local consumption factor of 0.4 was used¹³. The values for exposure duration (30 years), lifetime (70 years) and body weight (70 kg) are all standard factors based on EPA guidance¹⁴.

Table 1 shows the estimated cancer risk levels from consuming crops exposed to background dioxin concentrations in ambient air. When the Bacci bioconcentration factor⁽⁹⁾ was used for calculating plant concentrations, the predicted risk level (4.6×10^{-5}) actually exceeded the cancer risk level of 10^{-5} , which is EPA's risk criterion for incinerator and similar combustor facilities¹⁵. The McCrady bioconcentration factor⁽¹⁰⁾ also yielded a cancer risk result (8.4×10^{-6}) that closely approached the 10^{-5} cancer risk level. The Smith and Heinold⁽⁷⁾ vapor-to-plant modeling approach yielded a cancer risk result (3.7×10^{-7}) that was significantly below the 10^{-5} cancer risk level. These results suggest the importance of having realistic models available for risk assessment use when regulatory policy is potentially affected.

CONCLUSIONS

For hazardous compounds which have high bioaccumulation potential, such as dioxin, exposure through indirect pathways tend to contribute most to overall risk. After an evaluation of the technical basis and example results for the method currently recommended by the U.S. EPA for indirect exposure pathway risks associated with vapors of dioxins and similar compounds, it appears that further scientific analysis of modeling alternatives and their inherent uncertainties--

including those of the model proposed by Smith and Heinold and compared in this paper--should be considered before adopting conclusions drawn from application of the U.S. EPA approach. This paper also indicates advantages to using an overall deposition and uptake modeling framework that is mathematically compatible with the modeling methods utilized for calculating the impact of particulate-attached forms of similar chemicals.

For the plant dioxin vapor accumulation pathway, EPA suggests multiplying concentrations of dioxin vapor in air with a bioconcentration factor. In this paper, we evaluated two experimentally-derived bioconcentration factors^(9,10). An alternative approach was developed by Smith and Heinold⁽⁷⁾ to predict dioxin plant concentrations that is a logical extension of deposition modeling methods. The alternative results suggest that, under field conditions, accumulation of dioxin vapor in plants is much less than concentrations predicted by directly using bioconcentration factors developed from laboratory tests.

Comparative results given here indicate that when these laboratory-derived models include adequate "correction" factors, similar to those newly recommended by the U.S. EPA's own practice, the predicted concentrations of 2,3,7,8 TCDD may be relatively close to one another. This does not, however, adequately address the issue of accurate predictions for higher molecular weight congeners, which are principally present in particulate form, and which are expected to have much slower rates of diffusion through plant surface boundary layers.

To enhance our opportunities to continually improve the accuracy and the potential for model validation testing, it is suggested that it will be more fruitful to utilize the alternative form of mass transfer model suggested here, since it is also compatible with the latest research efforts on fugacity measurements and models being developed to better describe the vapor-to-plant uptake and re-emission processes.

TABLE I
Estimated Plant Concentrations of Dioxin and Risk Levels
Using Different Models

<u>Model</u>	<u>Value</u>	<u>Plant Concentration^(a) (mg/kg)</u>	<u>Estimated Lifetime Cancer Risk Level^(d)</u>
Bacci bioconcentration factor for 1,2,3,4-TCDD	4.6x10 ⁵	2.4x10 ⁻⁶ ^(b)	2.2x10 ⁻⁵
McCrary bioconcentration factor for 2,3,7,8-TCDD	8.2x10 ⁴	4.4x10 ⁻⁷ ^(b)	8.4x10 ⁻⁶
Smith and Heinold transfer velocity	0.78 cm/sec	1.9x10 ⁻⁸ ^(c)	3.7x10 ⁻⁷

- (a) Plant concentrations calculated assuming an ambient background vapor concentration of 2.85x10⁻¹¹ mg/m³
 (b) This value was calculated using Eq. 1 and multiplied by a dry weight-to-wet weight conversion factor of 0.22.
 (c) This value was calculated using Eqs. 3, 4, and 5.
 (d) These values were calculated using Eq. 6.

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