

## DEPOSITION OF DIOXIN IN ATTICS FROM BACKYARD BURNING

Chan WR, Shields WJ

Exponent, Inc. 15375 SE 30<sup>th</sup> Place, Suite 250, Bellevue, WA 98007, USA.

### Abstract

We present a simple model to estimate the mass of PCDD/Fs deposited onto attic surfaces from backyard burning. The model considers the effects of attic ventilation, vapor phase sorption, and particle phase deposition on attic surfaces. Using the measured concentrations from published burn barrel experiments, we predicted a large fraction of the emitted PCDD/Fs would enter the attic of a nearby house. Roughly 10% of the mass that entered the attic would deposit on surfaces. Sorption of vapor phase PCDD/Fs onto indoor surfaces is expected to be rapid, thus contributing a significant fraction of the total mass accumulated. We also model congener-specific volatilization to show how the PCDD/F congener profile would change over time inside the attic. The less-chlorinated congeners are expected to volatilize at a faster rate, leaving the accumulation to be more enriched in -Hp and OCDD/F. This analysis demonstrates the mechanisms through which PCDD/F from a single backyard burn emission can deposit in an attic, and provides the basis for evaluating accumulation from repeated backyard burns. Future work will consider indoor processes more thoroughly, such as the relative accumulation on different attic surfaces.

### Introduction

Backyard burning of household waste in open burn barrels emits many products of incomplete combustion, including polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs).<sup>1</sup> Although many regional governments in the United States have banned backyard burning, the practice remains active in some rural areas. U.S. EPA estimated that backyard burning was the leading source of PCDD/Fs in 2000, contributing 35% of the total mass emission measured in g-TEQ.

The goal of this paper is to use a simple model to estimate the mass of PCDD/Fs deposited onto attic surfaces from burn barrel emissions. The mass deposited depends on attic ventilation, sorption of vapor phase PCDD/Fs, and deposition of particle phase on indoor surfaces.<sup>2,3</sup> We also modeled the change in congener profile by volatilization, which is important to consider when dust samples are used to identify potential PCDD/F sources.<sup>4</sup> In this paper, PCDD/Fs refers solely to the 17 2,3,7,8-substituted congeners.

### Materials and Methods

During a backyard burn, particles and gases containing PCDD/Fs can infiltrate into the attic through designed vents and other openings. A portion of the PCDD/Fs will be deposited onto attic surfaces, while the remainder leaves the attic through ventilation. Volatilization of PCDD/Fs occurs much slower than accumulation, and will be modeled separately. During the accumulation phase, the governing equations for the change in the particle-phase ( $C_p$ ) and vapor-phase ( $C_v$ ) PCDD/F concentration in the attic over time are:<sup>3,5</sup>

$$\frac{dC_p}{dt} = kC_{p,out} - kC_p - k_d C_p \quad \text{and} \quad \frac{dC_v}{dt} = kC_{v,out} - kC_v - k_a C_v \quad (1)$$

$C_{p,out}$  and  $C_{v,out}$  (pg/m<sup>3</sup>) are the PCDD/F concentrations, caused by backyard burning, in the outdoor air entering the attic,  $k$  (h<sup>-1</sup>) is the attic ventilation rate,  $k_d$  (h<sup>-1</sup>) is the particle deposition rate, and  $k_a$  (h<sup>-1</sup>) is the vapor sorption rate. Experiments that simulate open burning in burn barrels show that a typical burn lasts for a few hours.<sup>6</sup> In this simple model, the total mass of PCDD/F that would enter an attic of volume  $V$  (m<sup>3</sup>) during the backyard burn is simply  $kVT_r(C_{p,out} + C_{v,out})$ , assuming that  $C_{p,out}$ ,  $C_{v,out}$ ,  $k$ ,  $k_d$ , and  $k_a$  are all constants during the burn period  $T_r$  (h). The total mass of PCDD/F accumulated in attic,  $M$  (pg), is the time-integrated mass flux to surfaces from particle deposition and vapor sorption.

$$M = V \int_0^{T_r} (k_d C_p + k_a C_v) dt = kVT_r \left( \frac{k_d}{k + k_d} C_{p,out} + \frac{k_a}{k + k_a} C_{v,out} \right) \quad (2)$$

Equation (2) is obtained by first solving for  $C_p$  and  $C_v$ .  $C_p$  and  $C_v$  are solved by integrating Equation (1) from  $t = 0$  to  $T_r$  where the outdoor concentrations are constants, and from  $t = T_r$  to  $\infty$  where the outdoor concentrations are zero.

Unlike in the outdoors where vapor-phase PCDD/Fs primarily partition with ambient particles, the above mathematical model accounts for the partitioning of vapor-phase PCDD/Fs with indoor surfaces. Even though vapor-phase PCDD/Fs can sorb to both ambient particles and indoor surfaces, the mass of PCDD/Fs sorbed on indoor airborne particles is expected to be less than the mass sorbed on indoor surfaces.<sup>2</sup> In this analysis, we will consider only the partitioning with indoor surfaces. Sorption occurs when gas molecules are transported to the surface and are bonded to the surface material. The sorption rate of many organic gases,  $k_a$ , has been experimentally shown to correlate well with the octanol-air partitioning coefficient ( $K_{oa}$ ) of the chemical.<sup>5</sup> PCDD/Fs have high log ( $K_{oa}$ ) values, in the range of 8 to 11.<sup>7</sup> Chemicals with high  $K_{oa}$  values have been shown to sorb to indoor surfaces at a rate that approaches the transport limit.<sup>5</sup> This means that the probability that a gas molecule will bond to the surface material after a collision does not constrain the rate at which sorption occurs.

Because  $k_a$  has not been measured for PCDD/Fs, we estimate it based on a chemical with similar  $K_{oa}$  value. Nicotine has the highest  $K_{oa}$  value (8.1) among the organic gases studied in a recent sorption experiment in a furnished room.<sup>5</sup> The best-fit  $k_a$  of nicotine is also the highest ( $8 \text{ h}^{-1}$ ). PCDD/Fs have  $K_{oa}$  values greater than or similar to nicotine, depending on the congener and ambient temperature. If nicotine is found to be sorbing to indoor surfaces at a transport-limited rate, the same is likely to be true for PCDD/Fs. Transport-limited rate is a function of near-surface airflow, and does not depend on the properties of a chemical. For this simple analysis, we assume the transport-limited rate measured in a room ( $k_a = 8 \text{ h}^{-1}$ ) also applies to sorption of PCDD/F congeners in an attic.

Deposition of particle-phase PCDD/Fs is a function of particle diameter as well as airflow conditions, surface-to-air temperature differences, and surface roughness. Particle deposition theory on smooth surfaces predicts deposition rate to reach a minimum at a particle diameter of  $0.1 \mu\text{m}$ .<sup>3</sup> Experimental studies that measured indoor particle deposition rate over a range of conditions agree with the theoretical prediction as a function of particle size.<sup>3</sup> We assume the attic is undisturbed, and ignore the effect of particle resuspension. We also assume that particles are not attenuated by the building envelope when entering into the attic. This is a reasonable assumption if most of the particles enter into the attic through a large opening, such as a vent.<sup>8</sup>

We divided particles into seven groups according to their diameter:  $<0.01 \mu\text{m}$ ,  $0.01\text{--}0.4 \mu\text{m}$ ,  $0.4\text{--}0.7 \mu\text{m}$ ,  $0.7\text{--}1.4 \mu\text{m}$ ,  $1.4\text{--}2.1 \mu\text{m}$ ,  $2.1\text{--}4.2 \mu\text{m}$ ,  $4.4\text{--}10 \mu\text{m}$ , and  $>10 \mu\text{m}$ . The respective deposition loss rate is 0.2, 0.1, 0.2, 0.7, 1.4, 4, and  $10 \text{ h}^{-1}$ .<sup>3</sup> For convenience, we chose to use the same particle size bins as the study that measures the concentration of PCDD/Fs as a function of particle mass distribution.<sup>9</sup> Oh et al. (2002) found that the less chlorinated congeners were mainly distributed among larger particles ( $>2.1 \mu\text{m}$ ) in ambient air, and the more chlorinated congeners were mainly found among finer particles ( $<2.1 \mu\text{m}$ ). We assume that their finding is also applicable to the near source.

Figure 1 shows the particle and vapor-phase PCDD/F (only the 17 congeners with 2,3,7,8-substitution) concentrations averaged from three garden waste burn experiments by Wevers et al. (2005) measured 6 m from the burning barrel.<sup>6</sup> Each burn experiment consumed 37 kg of waste in 4 hours. We assume that Figure 1 represents the outdoor concentrations to which a nearby house attic is exposed. Wevers et al. (2005) measured only the total particle phase concentration for each PCDD/F congener, but not as a function of particle size. We use data collected by Oh et al. (2002) to allocate the particle-phase concentrations into seven particle diameter bins as mentioned above.<sup>9</sup> As a result, we have an estimate of  $C_{p,out}$  as a function of particle diameter for each congener.

Field measurements of attic ventilation rates show that  $k$  is primarily driven by wind pressure acting on the attic envelope.<sup>10</sup> Attic features such as soffits and roof vents can greatly increase ventilation rates from  $2 \text{ h}^{-1}$  to  $10 \text{ h}^{-1}$  under the direct, unsheltered influence of wind. At 4 m/s wind, a tight attic can have 3 times the ventilation rate

than when the wind is calmer, at 1 m/s. The ventilation rate of attics with soffits and roof vents is even more affected by wind speed. In this analysis, we model  $k = 2, 5,$  and  $10 \text{ h}^{-1}$  to illustrate the sensitivity of predictions with respect to this parameter. We use  $V = 180 \text{ m}^3$  as the attic volume of an average size home having  $2,000 \text{ ft}^2$  in floor area (e.g., 15 m house length  $\times$  12 m house width  $\times$   $\frac{1}{2}$  [2 m attic height]).

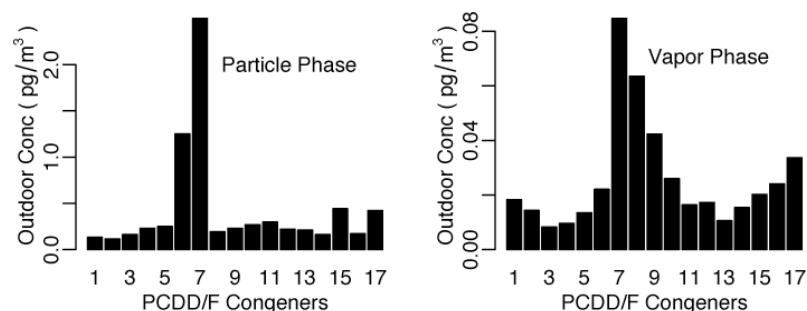


Figure 1. Average in-plume PCDD/F concentrations measured at 6 m from household waste backyard burn.<sup>6</sup> Congeners 1 to 7 are PCDDs (e.g., congener 7 is OCDD), and 8 to 17 are PCDFs (e.g., congener 17 is OCDF). The same congener notation is used in Figures 2 and 3.

### Results and Discussion

We estimate the mass of PCDD/Fs that will deposit onto attic surfaces from one burn event (Table 1) using Equation (2). At  $k = 5 \text{ h}^{-1}$ , 28 ng of PCDD/F is predicted to enter into the attic. Out of the total mass that enters the attic, roughly 10% is retained on surfaces. The remaining 90% is removed from the attic by ventilation. At a higher ventilation rate, more PCDD/Fs are brought indoors by ventilation, but the fraction that would accumulate on attic surfaces is lower because there is less time for deposition and sorption to occur. Overall, the mass deposited is only moderately sensitive to the ventilation rate. Increasing  $k$  by a factor of 5 from  $2 \text{ h}^{-1}$  to  $10 \text{ h}^{-1}$  only caused the mass of PCDD/Fs deposited to increase by 80%.

Figure 2 shows the predicted congener profile of PCDD/F accumulation on attic surfaces. The resulting profile is a superposition of the particle and vapor phase outdoor concentration profile shown in Figure 1. Even though 94% of the PCDD/Fs by mass were in the particle-phase, the vapor-phase outdoor concentrations still influenced the result because sorption is estimated to occur at a faster rate than particle deposition, except for the very large particles with diameter  $>10 \mu\text{m}$ . In this particular case, roughly 1/3 of the total mass accumulated on attic surfaces originated from vapor-phase outdoor PCDD/Fs. Even though we consider all attic surfaces as a whole, vapor and particle phase PCDD/Fs might have a different affinity to the various types of surfaces present. For example, particle phase PCDD/Fs are likely to preferentially accumulate on the attic floor and tops of beams because of gravitational settling. This means that dust samples collected from the attic floor could have more of the less volatile congeners than the profile presented in Figure 2.

	Mass (ng) PCDD/F		
	Entered Attic	Accumulated on Attic Surfaces	Fraction Accumulated
$k = 2 \text{ h}^{-1}$	11	2.0	0.18
$k = 5 \text{ h}^{-1}$	28	2.9	0.10
$k = 10 \text{ h}^{-1}$	56	3.6	0.07

Table 1. Summary of predicted PCDD/F accumulated on attic surfaces by particle deposition and vapor sorption.

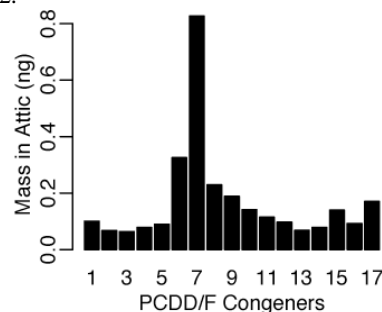


Figure 2. Predicted PCDD/F accumulated on attic surfaces for case  $k = 5 \text{ h}^{-1}$ .

In the outdoor environment, there can be some degradation by photolysis and/or volatilization after PCDD/Fs are deposited on soil.<sup>11</sup> Volatilization of PCDD/Fs can also occur indoors, especially in the summer when the attic is hot. For example, 0.57% and 0.51% of 2,3,7,8-TCDD and 2,3,7,8-TCDF was lost from the attic dust sample after it was heated at 60°C for 4 weeks.<sup>12</sup> The fraction of volatilization decreases for the more chlorinated congeners. Roughly 0.2%, 0.05%, and 0.02% of the -Pe, -Hx, and -Hp congeners were lost over the same time period. The change in OCDD/F was <0.02%. If we were to assume that the loss of PCDD/Fs by volatilization follows first-order exponential decay, we can predict the change in mass as  $M(t) = M(t_0)\exp(-k_v t)$ , where  $k_v$  is the volatilization constant. This equation is used to determine the value of  $k_v$  using the heated attic dust experiment.<sup>12</sup> For example, the volatilization constant of TCDD at 60°C is  $-\ln(1 - 0.0057)/28 \text{ days} = 9.3 \text{ year}^{-1}$ . Under more realistic attic conditions, we would expect the volatilization rate of PCDD/Fs to be even slower.

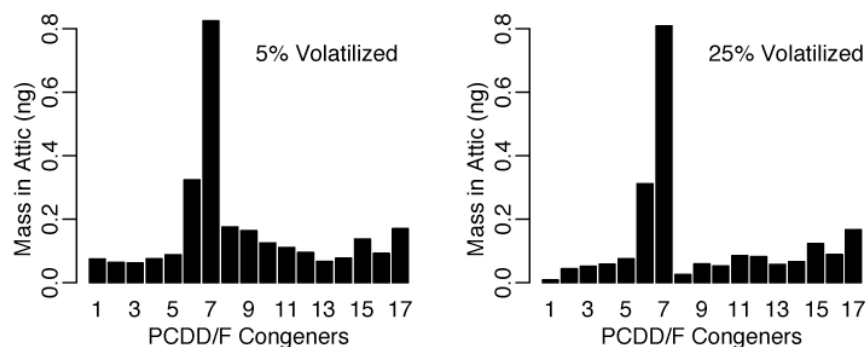


Figure 3. Predicted PCDD/F congener profile retained on attic surfaces at a time when 5% and 25% of the mass is volatilized. The initial profile following an open burn emission is shown in Figure 2. The attic ventilation rate is  $5 \text{ h}^{-1}$ .

Figure 3 shows the 2,3,7,8-congener profile of PCDD/Fs retained on attic surfaces at a time when 5% and 25% of the mass originally deposited has volatilized. The model predicted significant depletion of the less chlorinated congeners. The decrease in terms of ng-TEQ would therefore occur at a faster rate than in terms of mass ng. The congener profiles shown in Figure 3 would occur roughly 4 years (5% volatilized) and 33 years (25% volatilized) from the open burn emission. Under more realistic attic temperatures, the value of  $k_v$  is likely to be lower because the rate of volatilization is a function of temperature. Therefore, we would expect change in congener profiles similar to what is shown in Figure 3 to occur after a longer time lag from the time of emission.

#### Acknowledgements

We would like to thank Mai Wevers and her colleagues for sharing their raw measurement data with us.

#### References

1. US EPA. *An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds* 2006.
2. Wechsler CJ. *Atmospheric Environment* 2003; 37:5455.
3. Riley WJ, McKone TE, Lai ACK, Nazaroff WW. *Environmental Science & Technology* 2002; 36:200.
4. Shields WJ, Tondeur Y, Benton L, Edwards MR. Dioxins and Furans. In: *Environmental Forensics: Contaminant Specific Guide*. Academic Press, San Diego, 2006; 293.
5. Singer BC, Revamp KL, Hotchi T, Hodgson AT, Brown NJ. *Atmospheric Environment* 2004; 38:2483.
6. Wevers M, Fre RD, Desmids M. *Chemosphere* 2004; 54:1351. Also through personal communication 2005.
7. Harmer T, Green NJL, Jones KC. *Environmental Science & Technology* 2000; 34:3109.
8. Liu DL, Nazaroff WW. *Aerosol Science and Technology* 2003; 37:565.
9. Oh JE, Chang YS, Kim EJ, Lee DW. *Atmospheric Environment* 2002; 36:5109.
10. Walker IS, Forest TW. *Building and Environment* 1995; 30:333.
11. US EPA. *Dioxin Reassessment (NAS Review Draft)* 2003; 2(2).
12. Hansen D. *Otto- Graf- Journal* 1997; 7:53.