

The dynamic partitioning of airborne phthalates in indoor environment: effects of ventilation

Subei Bu^{1,2}, Yanling Wang^{1,2}, Haiyan Wang^{1,2}, Fang Wang^{1*,2}, and Yufei Tan^{1,2}

¹School of Architecture, Harbin Institute of Technology, China.

²Key Laboratory of Cold Region Urban and Rural Human Settlement Environment Science and Technology, Ministry of Industry and Information Technology, Harbin Institute of Technology, China.

Abstract. Low energy consumption buildings with strong air tightness such as passive buildings are the development trend in the world. However, ventilation directly affects the emission and dynamic transport of indoor phthalates. A transient partition model considering the dynamic behavior of size-resolved particle was utilized to investigate the influence of ventilation on the airborne Di-2-ethylhexyl phthalate (DEHP). The air exchange rate (a) was set to 0.15 h⁻¹, 0.3 h⁻¹, 0.6 h⁻¹, 2h⁻¹ for the different conditions. The predicted gas-phase concentration of DEHP in the initial 70 days is unaffected for different a and constant h_{ms} , whereas it raises until the a increases to 2 h⁻¹. The equilibrium gas-phase concentration decreases from 0.257 to 0.203 µg/m³. Meanwhile, the higher a also reduced the particle-phase concentration of DEHP. Furthermore, the changes of airborne DEHP were analyzed by considering the impact of a on h_{ms} caused by ventilation. The results indicates that more ventilation leads to higher gas-phase concentration for the whole stage. The gas-phase concentration at equilibrium increases from 0.237 to 0.440 µg/m³. The total airborne (gas-phase + particle-phase) concentration decreases with the higher ventilation rate, which indicates that the ventilation has a positive effect on indoor airborne DEHP.

1 Introduction

Phthalates can persist indoors for years after being introduced, due to the low volatility and dynamic distribution characteristic. Phthalates tend to partition to the gas phase, airborne particles, settled dust, exposed surfaces etc. Exposure to phthalates may have adverse effects on reproduction and development[1]. It can also disturb the endocrine system and be associated with childhood asthma[2].

In the initial stage, the steady-state model was developed to obtain rapid assessments of non-dietary exposure of residents to semi-volatile organic compounds (SVOCs). Later, the instantaneous equilibrium model was used to investigate the influence of air exchange rate and particle concentration on DEHP concentration and emission rate. However, the assumption of instantaneous equilibrium can cause errors of two orders of magnitude in estimating the indoor gas-phase DEHP concentration[3]. In addition, the dynamic behavior of particulate matter has a significant effect on indoor airborne DEHP concentration[4]. The h_{ms} for DEHP source surface is influenced by the air velocity across flat surfaces[5]. Nevertheless, most studies have only focused on the influence of a , not considering the change in h_{ms} on account of a , when studying the effect of ventilation on indoor DEHP distribution.

In this paper, a transient partition model of phthalates was developed that considers the segmented emission

and dynamic behavior (penetration, deposition and resuspension) of size-resolved particle to assess the influence of ventilation on the distribution of airborne DEHP. We examined the sensitivity of the concentration of airborne DEHP to model parameter a . And the spatio-temporal changes of phthalates were further analyzed by considering the combinative impacts of a and h_{ms} caused by ventilation rate.

2 Model Description

The study was carried out in a room, with polyvinyl chloride (PVC) floor as the only DEHP emission source. The release of indoor particulate matter was set to take place once every two weeks by cooking, lasting for one hour at lunch time, to analyze the dynamic characteristics of particulate matter and phthalates.

The accumulation of size-resolved suspended particles (C_{mp}) in indoor environments obeys the following mass balance equation:

$$V \frac{dC_{mp}}{dt} = Q \cdot P_p \cdot C_{mp,out} - Q \cdot C_{mp} - v_{d,sp} \cdot (A_s + A_f) \cdot C_{mp} - v_{d,vert} \cdot (A_g + A_w) \cdot C_{mp} + R_p \cdot M_s \cdot A_s + R_p \cdot M_f \cdot A_f + S_p \quad (1)$$

Where C_{mp} is the mass concentration of indoor suspended particles, µg/m³; V is the room volume, m³; t is time, h; Q is the infiltration rate in the room, m³/h; P_p is the particle penetration factor; v_d is the deposition

* Corresponding author: hit_wfang71@hit.edu.cn

velocity of indoor particulate matter to interior surfaces, m/h; A is the area of surface, m^2 ; R_p is the resuspension rate of indoor particulate matter, h^{-1} ; M_s and M_{ns} are the mass loadings of settled dust on source and non-source surfaces, respectively, g/m^2 ; S_p is the emission rate of indoor particles, $\mu g/h$. The subscript *out* represents outdoor; *up* and *vert* represent the horizontal and vertical surface, respectively; the subscript *s*, *f*, *g*, *w* and *c* represent source, furniture, glass, wall and ceiling surface, respectively.

The mass loading of settled dust on source or non-source surfaces is controlled by particle deposition to and resuspension from the surfaces[6]. The airborne concentration of phthalates in indoor environments obeys the following equation:

$$V \cdot \frac{dC_g}{dt} + V \cdot \frac{dC_{sp}}{dt} = Q \cdot (C_{g,out} + C_{sp,out}) - Q \cdot (C_g - C_{sp}) + h_{ms} \cdot A_s \cdot (y_0 - C_g) - (A_f + A_w + A_c) \cdot K_{ns} \cdot \frac{dC_g}{dt} + A_g \cdot K_g \cdot \frac{dC_g^{1.5}}{dt} - v_{d,up} \cdot (A_s + A_f) \cdot C_{sp} - v_{d,vert} \cdot (A_g + A_w) \cdot C_{sp} + R_p \cdot M_s \cdot A_s \cdot C_{dust,s} + R_p \cdot M_{ns,f} \cdot A_f \cdot C_{dust,f} \quad (2)$$

Where C_g and C_{sp} are the gas phase and particle phase concentration of phthalates, respectively, ($\mu g/m^3$); h_{ms} is the mass transfer coefficients for source surface, (m/h); y_0 is the gas phase concentration of phthalates in the boundary layer immediately adjacent to the source surface, $\mu g/m^3$; K_{ns} is the partition coefficient of the non-source surfaces, m. $C_{dust,s}$ and $C_{dust,ns}$ are the dust phase concentration of phthalate on source surface and non-source surface, respectively, $\mu g/g$.

A nonlinear instantaneously reversible equilibrium relationship was assumed to describe the adsorption behavior between non-source surfaces and air[7]. The instantaneous equilibrium was assumed between $C_{dust,s}$ and y_0 , based on the gas-dust partition coefficient.

The model room (Table 1) is the same as the experiments carried out by Thatcher and Layton[8]. We used the measurement of outdoor gas-phase ($0.22 \mu g/m^3$) and particle-phase ($0.21 \mu g/m^3$) concentrations of DEHP in Hangzhou[9]. The h_{ms} was estimated using correlation equations by Axley[5], with the value of 4×10^{-4} m/s. The y_0 were obtained based on the Xu and Little[7], with the value of $1.1 \mu g/m^3$. The K_{ns} and K_g was determined according to equilibrium coefficient derived from the CTEPP study (US.EPA, 2005)[10]. The relevant parameters of size-resolved particle (Table 2) were determined based on the study by Liang et al.[6].

Table 1 Conditions for the model room.

Parameter	V	Q	A_s	A_g	A_f	A_w	A_c
Value	192	57.6	80	7	144	86.4	80
Unit	m^3	m^3/h	m^2	m^2	m^2	m^2	m^2

Table 2 The relevant parameters of size-resolved particle.

Parameter	PM _{2.5}	PM _{2.5-10}	PM ₁₀₋₁₅₀	Unit
$v_{d,up}$	0.19	4.24	42.6	m/h
$v_{d,vert}$	3.34×10^{-4}	1.1×10^{-4}	5.51×10^{-5}	m/h
R_p	1.22×10^{-5}	7.17×10^{-5}	3.8×10^{-4}	h^{-1}
P_p	0.82	0.65	0.10	--
S_p	1.42×10^5	9×10^3	--	$\mu g/h$
$C_{mp,out}$	65.70	25.37	29.87	$\mu g/m^3$

The above dynamic partition model was validated with experimental measurements by Benning et al.[11]. The model predicted results are in good agreement with the experimental results (Figure 1). Thus, the dynamic partition model is verified to be reasonable and reliable to predict indoor multi-phase concentrations of phthalates.

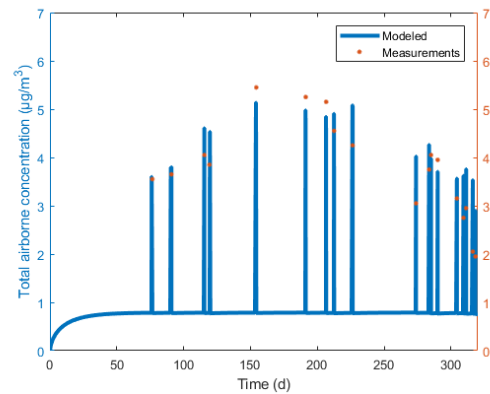


Figure 1. The comparison between modeled and measured airborne concentrations of DEHP

3 Results and Discussion

In this model, the air exchange rate (a) was set to $0.15 h^{-1}$, $0.3 h^{-1}$, $0.6 h^{-1}$, $2 h^{-1}$ for the passive house, conventional residence with windows closed, windows half open and windows fully open, respectively. Usually the effect of ventilation on DEHP emission is ignored in previous literature, which means the mass transfer coefficients (h_{ms}) for source surface is set to constant. As shown in Figure 2, the cooking results in the fluctuation up and down of gas-phase and particle-phase concentrations of DEHP, while the amplitude of particle-phase concentration is larger. The predicted gas-phase concentration of DEHP in the initial 70 days is unaffected by increasing the air exchange rate from 0.15 to $0.6 h^{-1}$, whereas it raises when the air exchange rate is increased to $2 h^{-1}$. The gas-phase concentration of DEHP at equilibrium decreases from 0.257 to $0.203 \mu g/m^3$, due to different ventilation removal effect. The predicted steady-state gas phase concentration of DEHP is generally consistent with previous measurements within residences by Luongo et al.[12]. Meanwhile, the higher air exchange rate also reduced the particle and particle-phase DEHP concentrations. The maximum particle-phase concentration of DEHP at equilibrium decreases from 11.92 to $1.36 \mu g/m^3$, the amplitude decreases from 10.85 to $1.04 \mu g/m^3$.

However, the h_{ms} for DEHP source surface is influenced by the air velocity across flat surfaces. The mass transfer coefficients at other air exchange rate a were approximated using the correlation developed by Axley[5] as equation 3. Where the h_{ms0} and a_0 are the reference value in the literature. The h_{ms} increases with the a , which suggests that more DEHP emission from source surfaces.

$$\frac{h_{ms}}{h_{ms0}} = \left(\frac{a}{a_0}\right)^{0.5} \quad (3)$$

As shown in Figure 3, more ventilation leads to higher gas-phase concentration for the whole stage, and less time to reach equilibrium. The gas-phase concentration at equilibrium increases from 0.237 to 0.440 $\mu\text{g}/\text{m}^3$, the time to reach equilibrium reduces from 250 to 150 days. Because the effect of DEHP source emission due to the h_{ms} change is greater than that of ventilation removal, which means the more emission of DEHP across source surfaces due to the increased h_{ms} masked the dilution of DEHP by ventilation. Nevertheless, the particle-phase concentration of DEHP decreases with the higher air exchange rate, which has the similar characteristics as constant h_{ms} . Altogether the total airborne (gas-phase + particle-phase) concentration decreases with the higher air exchange rate, which indicates that the increased ventilation rate has a positive effect on indoor airborne DEHP. The changes of air exchange rate (a) and mass transfer coefficient (h_{ms}) should be taken into account at the same time, in order to investigate the influence of ventilation on dynamic partition of phthalates, and better reflect the actual situation.

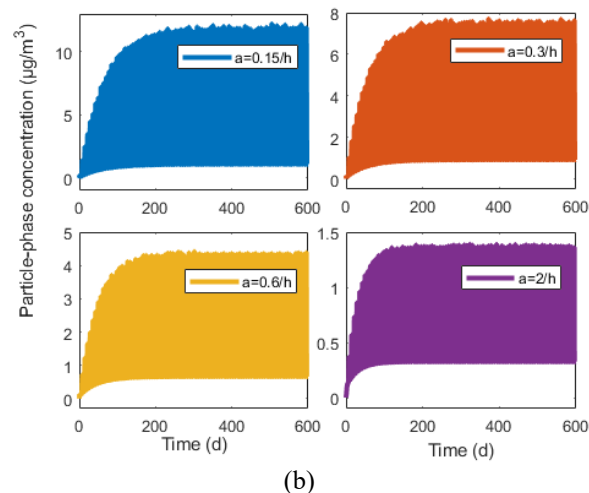
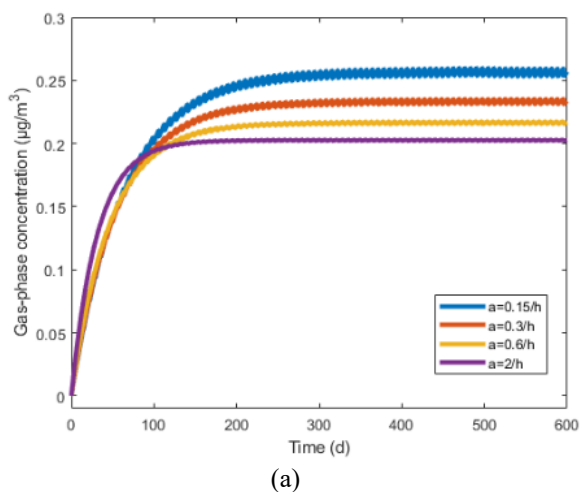


Figure 2. DEHP concentration for different a and constant h_{ms} (a) gas-phase (b) particle-phase.

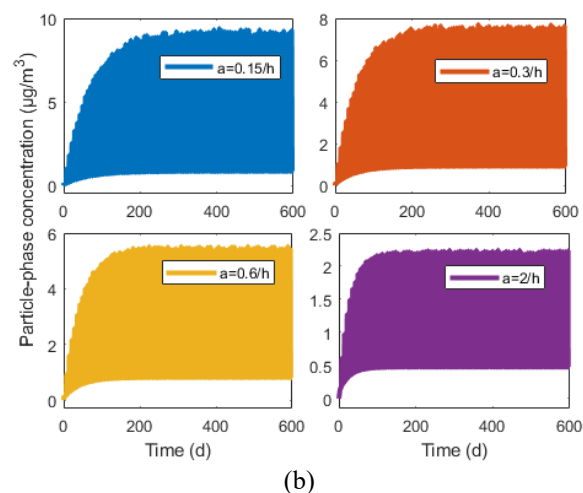
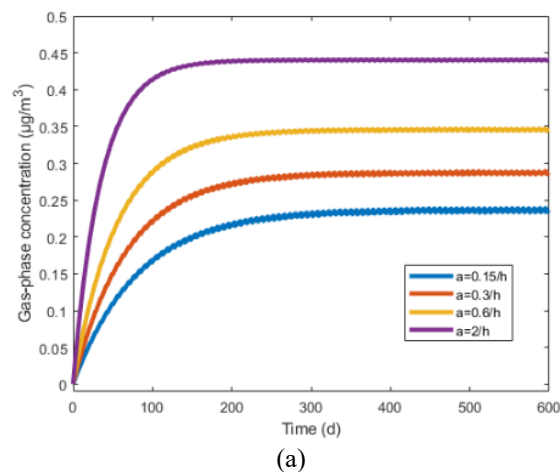


Figure 3. DEHP concentration for different a and considering the impact of a on h_{ms} (a) gas-phase (b) particle-phase.

4 Conclusion

The transient partition model considering the dynamic behavior of size-resolved particulate matter is necessary to investigate the influence of ventilation on the multi-media distribution of DEHP, due to the long experiment period and complex partition. The predicted gas-phase

concentration of DEHP in the initial 70 days is unaffected by increasing a from 0.15 to 0.6 h⁻¹, whereas it raises when the air exchange rate is increased to 2 h⁻¹. The equilibrium gas-phase concentration decreases by only considering the increase in a . While the more ventilation increase the gas-phase concentration for the whole stage by considering the impact of a on h_{ms} . The total airborne concentration decreases with the more ventilation, which indicates that it has a positive effect on the removal of indoor airborne DEHP.

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