

VOV source and sink behaviour of porous building materials: Part I—model development and assessment

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ABSTRACT

Evaluating the VOC source and sink behaviour of porous materials is important for the determination of the VOC concentration levels in indoor air environment. The transfer mechanisms involved in the source and sink behaviour are the same, but the mass transfer is in the opposite direction (i.e. from material to air for source, and from air to material for sink). This paper presents a mass transfer model that can be used to predict both source and sink behaviour of porous materials. The model considers internal diffusion, sorption and VOC generation due to secondary emissions other than sorption within the solid, and the convective mass transfer over the solid with the third-kind boundary condition. The exact analytical solution was obtained using the integral transform method.

The performance of model prediction was assessed for primary source and sink behaviour. This involved comparison of the predictions made by the proposed model with those of the analytical model by Little *et al.* (1994) as well as the environmental chamber test data for emissions and sorption. The prediction of the proposed model agrees well with the test data. The proposed model and Little's model generally agree well after the early stage when the internal diffusion dominates. However, at the early stage, Little's model tends to overestimate the emission or sorption rates as compared with the proposed model, since Little's model does not consider the boundary layer resistance due to convection.

INDEX TERMS

VOC; Source; Sink; Mass transfer; Porous building materials

INTRODUCTION

Building materials and furnishings are major sources of VOC emission in non-industrial buildings. Many building materials and furnishings are porous materials and have large effective surface areas. As a result, these materials act as sinks and then become secondary sources as they re-emit absorbed VOCs, as well as emitting the originally contained VOCs as primary sources.

Analytical models are needed in order to predict and investigate the source and sink behaviour of building materials for long-term, up to the entire product service life. For dry building materials, only a few analytical models are currently available. The model proposed by Little *et al.* (1994, 1996) can be applied to predict both source and sink behaviour of dry building materials; however, it does not consider the boundary layer resistance due to convection, hence limiting its application to diffusion-controlled mass transfer in building materials. Lee *et al.* (2000) showed that for solid materials with high diffusion coefficient, i.e. porous materials, convection effect should not be ignored. Therefore, Little's model may overestimate the VOC emission/sorption rate from porous materials, especially at the early stage of emission when it is controlled by convection. The analytical model proposed by Yang *et al.* (1998) assumes zero VOC concentration at

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the solid surface, which can be applicable to VOC emission from aged materials when the emission rate is very small. The analytical model proposed by Huang and Haghighat (2002) considered the convection with the third-kind boundary condition with zero VOC concentration for the ambient air outside the boundary layer, which causes overestimation of VOC emission rate at the early stage of emission when the emission rate is high. Due to the zero VOC concentration assumption, the last two models cannot be applied for the VOC sink behaviour of dry building materials.

This paper presents an analytical model that can be used to predict both VOC source and sink behaviour of porous building materials. The proposed model considers the internal diffusion, adsorption/desorption and VOC generation due to secondary emissions within the material, as well as the convective mass transfer over the material. The performance of the proposed model was assessed by comparing its predictions with those made by the analytical model proposed by Little *et al.* (1994, 1996), and with experimental data.

ANALYTICAL MODELLING

The proposed model was developed for porous building materials using the multiple-phase approach (Murakami *et al.*, 1998; Blondeau *et al.*, 2000) to describe the internal diffusion process. In multiple-phase approach, VOCs exist both in the form of gas and adsorbed phases in the pores and these two phases are always in equilibrium assuming that adsorption/desorption is a much faster process compared with diffusion. Since the adsorbed-phase VOCs are less mobile, only gas-phase transfer is considered. Moreover, due to the relatively low VOC concentration levels in dry building materials, the adsorption processes in the building materials may not be significant for the adsorbed-phase flux to be noticeable. The multiple-phase approach also assumes that VOCs diffusion through the solid matrix is negligible compared with the one through pores.

Consider a porous block of material of length L and thickness b has a constant diffusion coefficient D_s , sorption property K , porosity ε , and an initial concentration C_0 . VOCs can be generated by secondary emissions within the material and this is described by the generation function, $g(y, t)$. There is no mass transfer along the edges of the material. The boundary layer exists due to laminar or turbulent convection over the material and the VOC concentration in the ambient air (C_∞) can be a function of time. The convective mass transfer coefficient (h_D) can be obtained from Sherwood number correlations. The governing equation of one-dimensional diffusion within the porous material including sorption and generation of VOCs due to secondary emissions is given by

$$\varepsilon \frac{\partial C}{\partial t} + \frac{\partial C_{ad}}{\partial t} = D_s \cdot \frac{\partial^2 C}{\partial y^2} + g(y, t) \quad (1)$$

where C is the gas-phase VOC concentration (mg of gas-phase VOC/m³ of air), ε is the porosity of the solid material (m³ of air/m³ of material), t is the time (s), C_{ad} is the adsorbed-phase concentration (mg of adsorbed-phase VOC/m³ of material) and D_s is the effective diffusion coefficient of the solid (m²/s), y is the space coordinate (m) and $g(y, t)$ is VOC generation due to secondary emissions other than sorption (mg of VOC/m³ of material/s).

An adsorption isotherm relates the adsorbed-phase concentration (C_{ad}) with the gas-phase concentration (C). Since low VOC concentration levels are assumed in this model, Henry (linear) isotherm was used

$$C_{ad} = K \cdot C \quad (2)$$

Substituting this into Eqn (1) gives

$$\frac{\partial C}{\partial t} = \frac{D_s}{(\varepsilon + K)} \cdot \frac{\partial^2 C}{\partial y^2} + \frac{g(y, t)}{(\varepsilon + K)} \quad (3)$$

The third boundary condition was used to describe the convective mass transfer. This is imposed at the upper surface of the material as follows:

At $y = 0$

$$-D_s \frac{\partial C}{\partial y} = h_D (C_w - C_\infty(t)) \quad (4)$$

Since only one solid material is considered, there is no mass flux at the bottom surface of the material.

At $y = -b$

$$\frac{\partial C}{\partial y} = 0 \quad (5)$$

Initially (at $t = 0$), the porous material is assumed to have a uniform gas-phase VOC concentration (C_0).

At $t = 0$ and $-b \leq y \leq 0$

$$C = C_0 \quad (6)$$

The governing equation for $C(y, t)$, Eqn (3), together with the boundary conditions given in Eqns (4) and (5), and the initial condition given in Eqn (6) is the so-called diffusion type (parabolic in time and elliptic in space) equation and can be solved analytically using the integral transform method (Özisik, 1980). The VOC concentration, $C(y, t)$, in the material is given as

$$\begin{aligned} C(y, t) = & 2 \sum_{m=1}^{\infty} \left[\frac{\beta_m^2 + H^2}{b \cdot (\beta_m^2 + H^2) + H} \right] \cdot \cos\{\beta_m \cdot (y + b)\} \cdot e^{-D \cdot \beta_m^2 \cdot t} \\ & \times \left[\frac{C_o}{\beta_m} \cdot \sin(\beta_m \cdot b) + \frac{h_D}{(\varepsilon + K)} \cdot \cos(\beta_m \cdot b) \cdot \int_{t'=0}^t e^{D \cdot \beta_m^2 \cdot t'} \cdot C_\infty(t') dt' \right. \\ & \left. + \frac{1}{(\varepsilon + K)} \int_{t'=0}^t \int_{-b}^0 e^{D \cdot \beta_m^2 \cdot t'} \cdot \cos\{\beta_m \cdot (y + b)\} \cdot g(y, t') dy dt' \right] \end{aligned} \quad (7)$$

where $H = h_D / D_s$; $D = D_s / (\varepsilon + K)$; and β_m 's are the eigenvalues, which are the positive roots of the following equation:

$$\beta \tan(\beta \cdot b) = H \quad (8)$$

The emission rate at the upper surface of the material can be obtained by

$$R(y = 0, t) = h_D \cdot [C(y = 0, t) - C_\infty(t)] \quad (9)$$

Equations (7)–(9) give $C(y, t)$ and $R(0, t)$ once the material properties, convection property, and initial and boundary conditions are given.

MODEL ASSESSMENT FOR PRIMARY SOURCE BEHAVIOUR

The primary-source behaviour predicted by the proposed model was compared with the predictions by Little's model (1994) and carpet emission test data. The carpet emission test data were also used by Little *et al.* (1994) in the validation of their model. Little *et al.* (1994) reported 1-week-long VOC emission test results of carpets using a 20 m³ environmental chamber. The experimental conditions were air exchange rate of 0.98–1.00 h⁻¹, temperature of 22.8–23.5°C, relative humidity of 46.5–50.2%, air velocities of 0.065–0.09 m/s near the floor and a loading factor of 0.44 m²/m³. Little *et al.* (1994) used the material-phase approach to develop their model and the reported material properties are in that format, therefore the material properties were converted to gas-phase assuming that material-phase VOCs are a combination of the gas-phase and the adsorbed-phase. Whilst Little's model requires only the material properties as input, the proposed model requires the convective mass transfer coefficient h_D , which was estimated from the Sherwood number relations for laminar forced convection flow over a flat plate by using the averaged air velocity, i.e. 0.0775 m/s

$$Sh_L = 0.664 \cdot Re_L^{0.5} \cdot Sc^{1/3} \quad (10)$$

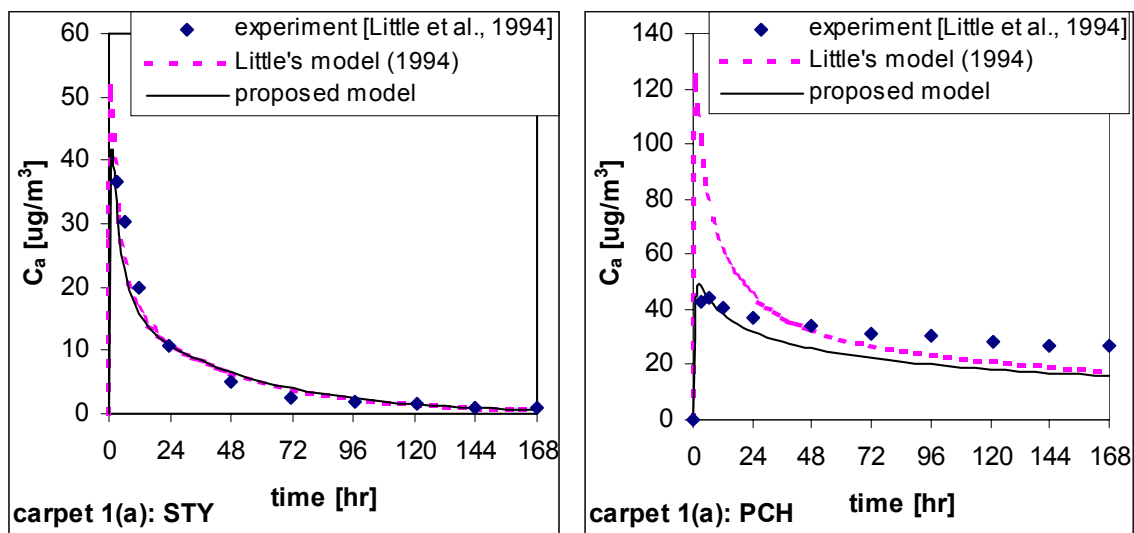


Figure 1 Model assessment for carpet emission.

Figure 1 shows the comparison between the proposed model and Little's model for styrene (STY) and phenylcyclohexene (PCH) emissions. Considering the fact that one or more material properties, e.g. diffusion coefficient, were obtained from the best-fit values for the predictions of Little's model, the simulation results of the proposed model agree well with the experimental data. Little's model tends to overestimate the chamber air VOC concentration at the early stage of emission compared with the proposed model since it does not consider the boundary layer resistance due to convection. At the early stage when the emissive power of a material is strong, both convection and diffusion control the emission rates but as time goes by the mass transfer becomes dominated by diffusion. Also, the difference between the proposed model predictions and those of Little's model was observed to be larger when $(\varepsilon + K)$ is larger, i.e. $(\varepsilon + K)$ is 4200 for STY and 81 000 for PCH.

MODEL ASSESSMENT FOR SINK BEHAVIOUR

For sink behaviour, the prediction of the proposed model was assessed by comparing its results with the dynamic sorption tests data of acetone on wood chipboard, conducted by Tiffonnet (2001) in the Indoor Air Quality Laboratory at Concordia University. Chipboards of various thicknesses (i.e. 0.5, 1.0, 1.5, 2.0 cm) were tested in a small-scale environmental chamber with 0.0522 m^3 in volume. Typical sorption tests were carried out for 8 h at two levels of supplied air VOC concentrations and air exchange rate of 75.25 mg/m^3 , 1.16 h^{-1} , and 15.05 mg/m^3 , 1.0 h^{-1} , respectively. The experimental conditions were temperature of 25°C , a relative humidity of 0% and a loading factor of $0.24 \text{ m}^2/\text{m}^3$.

Blondeau *et al.* (2000) measured D_s and ε of chipboard using the Mercury Intrusion Porosimetry (MIP) tests. The reported ε (i.e. $\varepsilon = 0.2579 [\text{m}^3 \text{ air}/\text{m}^3 \text{ material}]$) was used as input to the model. D_s for acetone was not reported; however, in measurement of D_s using the MIP test, it was assumed that D_s is proportional to the diffusion coefficient of acetone in the air D_a and the D_a/D_s ratio is given as 7.78. K was calculated from the measured sorption test data. Since the equilibrium will reach faster for thinner material, sorption test data for the cases of thickness 0.005 m were analysed to calculate K , the partition coefficient. The total mass sorbed to the chipboard was calculated by applying the mass balance. The adsorbed concentration is then calculated dividing the total sorbed mass by the volume of material specimen. With the known gas-phase concentration K can be obtained using Eqn (2). The convective mass transfer coefficient h_D was calculated using Eqn (10) for air velocity of 0.1 m/s, which is the median air velocity inside the same chamber when the air exchange rate is 1.01 h^{-1} (Popa, 2002).

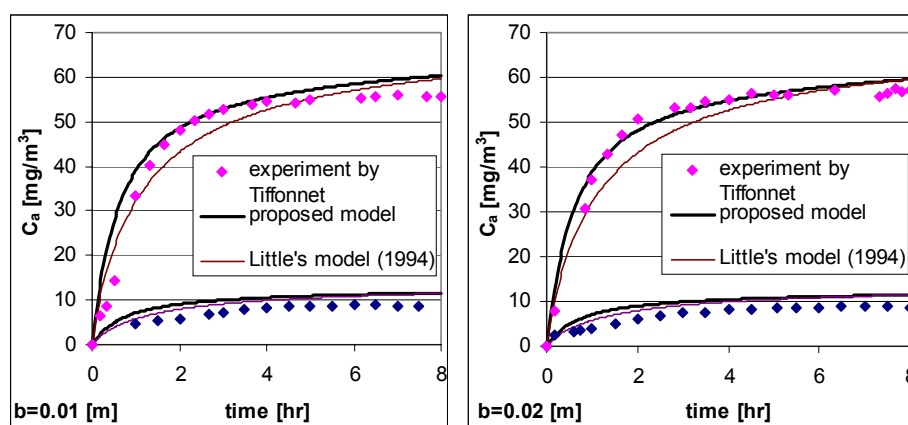


Figure 2 Model assessment for sink behaviour of chipboard.

The predictions made by the proposed model after plugging the above mentioned parameters as inputs were compared with the experimental data as well as the predictions by the Little's model. Figure 2 presents comparisons for chipboard thicknesses of 0.01 and 0.02 m. Generally, the prediction by the proposed model agrees well with experimental data. The prediction made by both models tends to overestimate the VOC concentration in the chamber air. Since the edges of the specimen were not sealed but were directly exposed to the chamber air in the experiments, sorption occurs not only from the specimen face but also from the edges. However, the proposed model considers the sorption only from the exposed face of the specimen to the air, which assumes the specimen to be sealed at its edges. Hence, the measured sorption rate may be greater in the early stage and may get smaller in the later stages. Also, the experimental system has reached the equilibrium state faster than it would have reached if the specimen was sealed. Unlike the predictions, the experimental data exhibit the equilibrium states in the end stages of sorption tests. For the given air velocity level, C_a predicted by the proposed model is higher than that by

Little's model and the difference become smaller as time increases. As mentioned in the model validation for the primary emissions, Little's model only considers the internal diffusion while the convective resistance is neglected. This explains the fact that, in the early stage, the sorption rates estimated using Little's model are greater than the experimental data as well as those obtained by the proposed model.

CONCLUSION

An analytical model based on the fundamentals of mass transfer was developed for the prediction of VOC source and sink behaviour of porous building materials. The proposed model considers convective mass transfer over the material as well as internal diffusion, sorption and VOC generation due to secondary emission. The proposed model was assessed for the primary source and sink behaviour and it agrees well with the VOC emission test data of carpets and sorption test data of chipboard. The proposed model was compared with an existing analytical model (Little *et al.*, 1994). For given test conditions, both models generally agree well after the early stage of emission/sorption, when the internal diffusion dominates. In the early stage, Little's model tends to overestimate the emission/sorption rates as compared with the proposed model: Little's model does not consider the boundary layer resistance due to convection. The difference tends to be larger when the sorption partition coefficient is larger.

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