MODELLING OF VOLATILE ORGANIC COMPOUNDS EMISSION FROM DRY BUILDING MATERIALS

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ABSTRACT

A numerical model was developed to predict volatile organic compound (VOC) emission rate from dry building materials. The model considers mass diffusion process within the material and mass convection & diffusion processes in the boundary layer. All the parameters, mass diffusion coefficient of the material, material/air partition coefficient, and mass transfer coefficient of the air can be either found in the literature or calculated using known principles.

The predictions of the model was validated at two levels: with experimental results from the specially designed test and with the prediction made by a CFD model. The results indicate that there is generally a good agreement between the model predictions, the experimental results, and the CFD results.

Keywords: dry building material, VOC emission, diffusion, and numerical model

INTRODUCTION

Volatile Organic Compounds emitted by building materials are recognized as major problems affecting human comfort, health and productivity. Therefore, accurate modeling of the material emission rate in buildings is important for predicting the contaminant concentration, occupant exposure and for the design of mechanical ventilation systems. Recently, there has been a growing interest in the development of mathematical models to predict the quality of indoor air.

Emission models include empirical models and physical models. The parameters of empirical models are determined by fitting experimental data to a predefined model. The main drawback of these models are that nonlinear regression curve fitting might lead to multiple solutions and the resulting empirical parameters may not be scaled up for use in actual buildings. Therefore, physical models based on the mass transfer processes are more attractive to most researchers for building material emission rate modeling.

Physical models are based on the fundamentals of mass transfer processes[1]; diffusion within the material as results of concentration, pressure, or temperature gradient, and surface emission between the material and the overlying air as a consequence of evaporation, convection and diffusion. Fick's second law describes the diffusion within the materials. For wet materials such as paints or wood stain, the diffusion coefficient within the material is very difficult to determine, and studies show that the surface emission usually dominates the emission processes. Therefore, most of the emission models for wet building materials are concentrated on the VOC transport in the air [2-4]. For dry building materials, the diffusion within the material cannot be ignored and the internal diffusion is more likely to be the dominating resistance. Recent review of existing emission models for dry material reveals some of their shortcomings. For example, the diffusion controlled emission models only consider the internal diffusion and ignore the surface convection process[5,6]. This simplification causes the model to underestimate VOC emission at the early stage when the surface concentration is relatively high. The conjugate mass transfer model assumes the VOC concentration at the material bottom is constant and ignores the sorption factor[7]. Those assumptions are not appropriate for real building material, since the concentration distribution inside the material is time dependent and the sorption factor cannot be ignored. Further, the model developed for the semi-infinite materials[8] are not suitable for thin building materials.

Therefore, some researchers turn to CFD to study emission from dry building materials and their concern is mainly on contaminant distributions in the air. Recently developed CFD models consider both the surface emission and the internal diffusion [9,10]. The critical problem of these models is the solution convergence, and the main inherent drawback of this technique is that the CFD simulation would be too expensive and time consuming to be used as a routine

procedure for long term VOC emission prediction.

Although there are a lot of achievements in the development of mathematical models for dry building materials, a model which could overcome the existing shortcomings is not yet available. This paper describes the development of a numerical model.

THE EMISSION MODEL

The physical system considered here is a dry building material (carpet, vinyl flooring, particleboard, etc.) and has its one surface exposed to the air. The VOC emission from this material is composed of three main processes as shown in Figure 1.

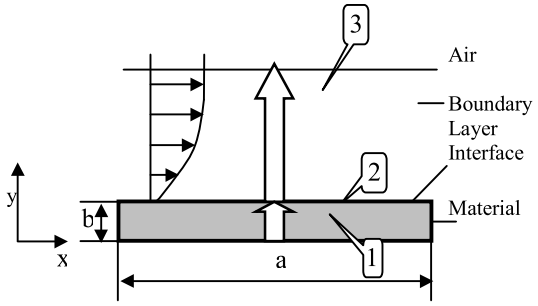

Figure 1: Physical configuration of VOC emission from the dry building material. 1: Internal diffusion; 2: Material /air interface; 3. External advection.

Mass transfer in the boundary layer

When air passes over the material surface, a mass boundary layer exists between the surface material and the main flow. The VOC mass transfer in this mass boundary layer is determined by diffusion and convection. The rate of VOC mass transfer in the boundary layer can be expressed as:

$$R = h(C_{as} - C_a) \tag{1}$$

Where h is the mean mass transfer coefficient (m/s), C_{as} is the VOC concentration in the air near material surface (ug/m^3) and C_a is the VOC concentration outside the mass boundary layer (ug/m^3).

Material /air interface

At the material/air interface, the material is the adsorbent and the VOC gas is the adsorbate. The material exerts an attractive force normal to the surface plane. Consequently, the concentration of VOC at the material phase exceeds that in the gas phase. Langmuir and BET are the most common isotherm models which may be used to describe this process [11]. At atmospheric pressure, for low VOC concentration and isothermal conditions, equilibrium relation between the VOC concentration in the air phase and the VOC concentration in the material phase can be described by Henry's law [12]:

$$C_m(b,t) = kC_{as} \tag{2}$$

Where C_m (b,t) is VOC concentration at the material surface (ug/m^3) and C_{as} is the VOC concentration in the air near material surface (ug/m^3), k is the material/air partition coefficient, b is the thickness of the material (m), and t is the time (s).

Mass transfer in the material

For a dry material with homogeneous diffusivity, the transient VOC diffusion in the material can be described by the one-dimensional diffusion equation:

$$\frac{\partial C_m(y,t)}{\partial t} = D_m \frac{\partial^2 C_m(y,t)}{\partial y^2} \tag{3}$$

Where C_m is the VOC concentration in the material (ug/m^3), D_m is the VOC diffusion coefficient of the material (m^2/s) and y is the coordinate in which the VOC diffusion in the material takes place (m).

Mass balance in the room or chamber

Assuming that the VOC is totally mixed in the room air. The transient mass balance in the room or chamber can be expressed by:

$$\frac{\partial C_a(t)}{\partial t} = NC_{in} - NC_a - LD_m \left.\frac{\partial C_m(y,t)}{\partial y}\right|_{y=b} \tag{4}$$

Where C_a is the VOC concentration in the room air (ug/m^3), C_{in} is the VOC concentration in the supply air (ug/m^3), N is the air exchange rate (h^{-1}) and L is the material loading factor (m^2/m^3).

Boundary conditions and solutions

Some initial conditions and boundary conditions are needed to close the above equations.

a) Initial conditions:

A homogeneous new material with initial VOC concentration of

$$C_m(y,0) = C_0 \tag{5}$$

The initial VOC concentration in the room air (C_{a0}) is:

$$C_a(0) = C_{a0} \tag{6}$$

b) Boundary conditions:
At the material bottom, there is no VOC passing through this surface.

$$-D_m \frac{\partial C_m(y,t)}{\partial y}\bigg|_{y=0} = 0 \tag{7}$$

At the material surface and room air interface, the mass balance can be written as:

$$-D_m \frac{\partial C_m(y,t)}{\partial y}\bigg|_{y=b} = h(C_{as} - C_a) = h\left(\frac{C_m(b,t)}{k} - C_a\right) \tag{8}$$

There are four key parameters which need to be determined: the mass transfer coefficient in the air, h, the partition coefficient, k, the mass diffusion coefficient in the material, D_m, and the VOC initial concentration, C_0.

Mass transfer coefficient in the air, h
In the mass boundary layer, the following relationships exist [13]:

a) For laminar flow, (Re_l<500,000):

$$Sh = 0.664 Sc^{1/3} \mathrm{Re}_l^{1/2} \tag{9}$$

b) For turbulent flow, (Re_l>500,000):

$$Sh = 0.037 Sc^{1/3} \mathrm{Re}_l^{4/5} \tag{10}$$

c) Combined laminar /turbulent flow, (Re_l<10^7, Re_{tr}=500,000):

$$Sh = (0.037 \mathrm{Re}_l^{4/5} - 8700) Sc^{1/3} \tag{11}$$

Where, $Sh = \frac{hl}{D_a}, Sc = \frac{\nu}{D_a}, \mathrm{Re}_l = \frac{ul}{\nu}$, ν is the kinematic viscosity of the air (m^2/s), u is the mean air velocity over the material (m/s), l is the characteristic length of material (m) and D_a is the VOC diffusion coefficient in the air (m^2/s).

The VOC diffusion coefficient (D_a) can be directly obtained from literature[14] or can be estimated through other methods. Two main methods have been used to estimate the VOC diffusion coefficient in the air[15]: Fuller, Schettler and Giddings (FSG) method and Wilke and Lee (WL) method. FSG method is the most accurate for non-polar gasses at low to moderate temperatures. In this study, the FGS method was used to estimate VOC diffusion coefficient in the air. This method is based on the following correlation:

$$D_a = \frac{10^{-7} T^{1.75} \sqrt{M_r}}{P\left(V_a^{1/3} + V_{VOC}^{1/3}\right)^2} \tag{12}$$

Where $M_r = \frac{(M_a + M_{VOC})}{M_a M_{VOC}}$, T is the absolute temperature (K), P is the pressure (atm), V_a is the air molar volume (cm^3/mol), V_{VOC} is the VOC molar volume (cm^3/mol), M_a is the air molecular weight (g/mol) and M_{VOC} is the VOC molecular weight (g/mol).

Therefore, the mass transfer coefficient can be estimated using Equations 9-12. Those correlations are only valid when the concentration at the bottom of mass boundary layer is constant. Since the VOC concentration at the material surface is very low and the VOC diffusion through the material is very slow: the VOC concentration near the material surface will be relatively stable. Thus, we may assume that the concentration near the material surface is constant in a given time step.

Material/air partition coefficient, k
The material/air partition coefficient describes the relationship between the concentration in the gas phase and the concentration in the material phase. It is a material property and is obtained experimentally [5,16].

Mass diffusion coefficient in the material, D_m
The diffusion coefficient in the material is usually a function of many factors, such as the pore structure, the material type, compound properties and temperature, as well as VOC concentration. The dependence of the diffusion coefficient on the VOC concentration can be ignored considering that the VOC concentration in the material is usually very low. The diffusion coefficient is usually determined experimentally [5,16].

Initial concentration, C_0
Initial concentration in the material can be obtained through solvent extraction, high temperature thermal desorption or direct analysis[17]. Recently a cryogenic grinding/ fluidized bed desorption method was

developed to measure the initial concentration[6]. The VOC concentration in the material, VOC emission rate and the VOC concentration in the room are a function of the initial concentration, thus a small error in initial concentration estimation may cause a significant error in prediction results.

SOLUTION TECHNIQUES

A numerical finite difference method was used to simultaneously solve equations 1-4 using the initial conditions, Equations 5 and 6, and boundary conditions, Equations 7 and 8. The outcomes are:

a) The VOC concentration at the material surface $C_m(b,t)$:

$$\left(\frac{D_m}{\Delta y}+\frac{\Delta y}{\Delta t}+\frac{h}{k}-\frac{Lh^2\Delta t}{k\left(N\Delta t+Lh\Delta t+1\right)}\right)C_m(b,t)$$
$$=\frac{D_m}{\Delta y}C_m(b-\Delta y,t)+\frac{\Delta y}{\Delta t}C_m(b,t-\Delta t)$$
$$+\frac{h}{\left(N\Delta t+Lh\Delta t+1\right)}C_a(t-\Delta t) \qquad (13)$$

b) The VOC concentration in the room air, $C_a(t)$:

$$C_a(t)=\frac{Lh\Delta t}{k\left(N\Delta t+Lh\Delta t+1\right)}C_m(b,t)$$
$$+\frac{1}{\left(N\Delta t+Lh\Delta t+1\right)}C_a(t-\Delta t) \qquad (14)$$

c) The VOC emission rate, R(t):

$$R(t)=h\left(\frac{C_m(b.t)}{k}-C_a(t)\right) \qquad (15)$$

d) The normalized emitted mass, M/M_0:

$$\frac{M}{M_0}=\frac{\sum_{j=1}^{m}R(t)\Delta t}{bC_0} \qquad (16)$$

Where Δy is the space grid distance (m), Δt is the calculation time step (s).

THE MODEL VALIDATION

The model's prediction was compared with the experimental results of two particleboard tests as well as the predictions made by a CFD model [9].

The model predictions were compared with experimental data obtained at Massachusetts Institute of Technology [9]. The experiments were carried out in a small-scale chamber of 0.5×0.4×0.25 m^3 at a temperature of 23±0.5 ^{0}C, relative humidity 50±0.5%, and air exchange rate 1.0±0.05h^{-1}. Two different specimens of particleboard were tested. Major compounds identified for the tested particleboards were the same: hexanal, α-pinene, camphene, and limonene. The particleboard properties (D_m, k, and C_0) were estimated by using the chamber emission data (concentration vs. time) to fit the CFD model [9]. The physical properties of the particleboard were supplied by the experimenter and they are given in Table 1. The airflow inside the chamber is treated as laminar flow over a flat plate.

Table 1 Physical properties of particleboard emissions

Compound	TVOC	Hexanal	α-Pinene
	Particleboard 1		
$D_m(m^2/s)$	7.65×10^{-11}	7.65×10^{-11}	1.2×10^{-10}
$C_0(ug/m^3)$	5.28×10^{7}	1.15×10^{7}	3.45×10^{6}
k	3289	3289	5602
	Particleboard 2		
$D_m(m^3/s)$	7.65×10^{-11}	7.65×10^{-11}	1.2×10^{-10}
$C_0(ug/m^3)$	9.86×10^{7}	2.96×10^{7}	7.89×10^{6}
k	3289	3289	5602

Figures 2 to 7 show the comparison of the predicted TVOC, hexanal and α-pinene concentrations with the experimental results for particleboard 1. The experiment was carried out for 96 hours. There is good agreement between predicted concentrations and experimental measurements. There are some discrepancies between predicted results (both with the proposed numerical model and the CFD model) and experimental results during the initial hours. This might be due to instability and partial mixing in the chamber at the beginning of the tests.

Figures 5 to 7 compare the model predicted TVOC, hexanal and α-pinene concentrations with the experimental ones for particleboard 2. The experiment was carried out for 840h in the chamber. As shown in the figures the predictions of the TVOC, hexanal and α-pinene made by the proposed model fit the experimental data very well. The predicted results and

experimental results closely follow the same trend, especially for the long term; see Figures 5b, 6b and 7b.

The model predictions were also compared with the prediction of a CFD model [9]. Figures 2 to 7 also compare the model predicted TVOC, hexanal and α-pinene concentrations with the results predicted by a CFD model. In general, there is excellent agreement between predicted numerical results, measurement data and CFD predictions. As shown in Figures 2 and 3, for short term, the predictions made by CFD for sample 1 (PB1) fit the experimental data better than the proposed numerical model. While, for long term, Figures 5, 6 and 7 show that the prediction made by the proposed model fit the experimental data better than the prediction made by CFD. However, over all, the predicted curves of the two models follow the experimental results closely.

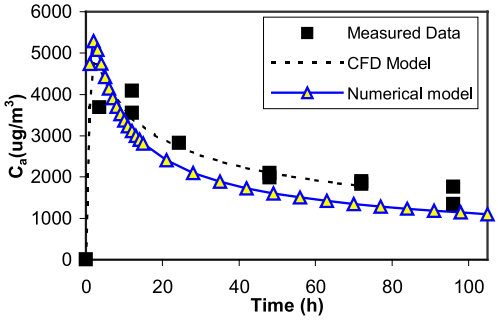

Figure 2 Comparison of TVOC concentrations (PB1)

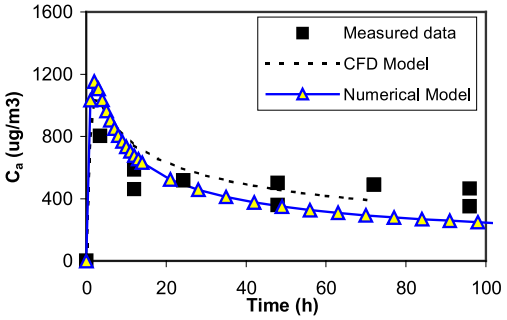

Figure 3 Comparison of hexanal concentrations (PB1)

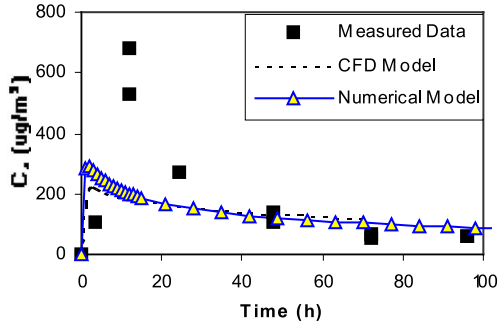

Figure 4 Comparison of α-pinene concentrations (PB1)

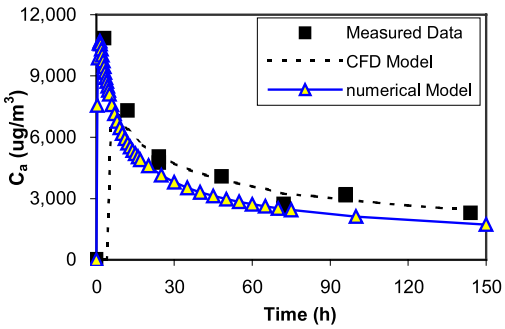

Figure 5 (a) Comparison of TVOC concentrations (PB2)

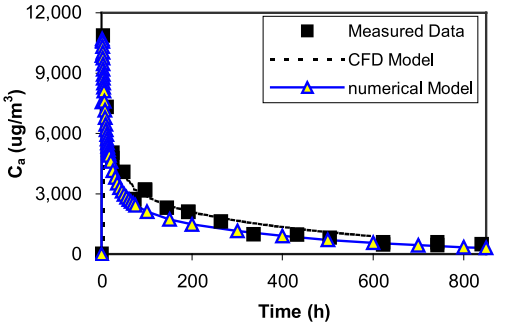

Figure 5 (b) Comparison of TVOC concentrations (PB2)

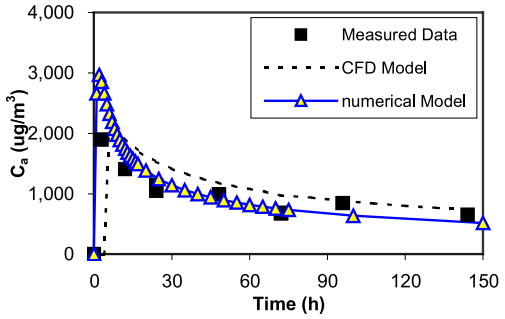

Figure 6 (a) Comparison of hexanal concentrations (PB2)

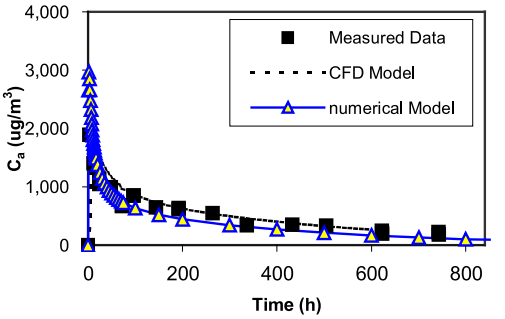

Figure 6 (b) Comparison of hexanal concentrations (PB2)

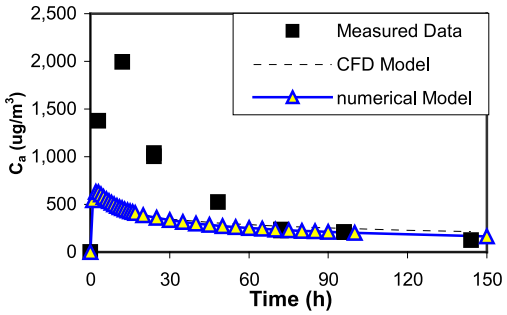

Figure 7(a) Comparison of α-pinene concentrations (PB2)

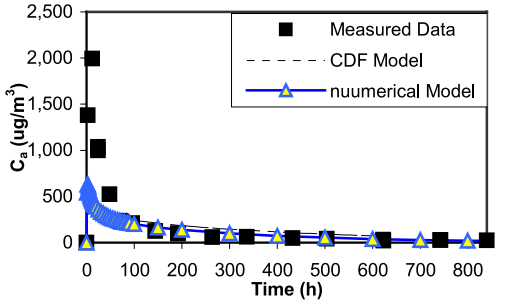

Figure 7(b) Comparison of α-pinene concentrations (PB2)

CONCLUSIONS

A numerical model was developed to predict the VOC concentration within the material, the VOC emission rate and the VOC concentration in the room air. This model uses four parameters, the diffusion coefficient in the material (D_m), material / air partition coefficient (k), the initial concentration in the material (C_0) and the mass transfer coefficient in the air (h). The first three parameters are properties of the material and can be determined by experiment, and the last one, h, can be estimated using fundamentals of fluid dynamics.

The predictions of the model were validated at two levels: with experimental results from the specially designed test and with the predictions made by a CFD model. The results indicate that there is generally good agreement between the model predictions, the experimental results and the CFD results.

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