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PREDICTING THE EMISSIONS OF INDIVIDUAL VOCs FROM PETROLEUM-BASED INDOOR COATINGS

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Abstract—The indoor use of petroleum-based coating materials may cause elevated volatile organic compound (VOC) concentrations. This paper presents a newly developed mass transfer model for estimating the emissions of individual VOCs from freshly coated surfaces. Results of a four-step validation show that the predicted individual VOC emissions are in good agreement with experimental data generated in small chambers and an indoor air quality test house. The values of the parameters introduced in this model are all easily obtained, and thus its utilization can provide indoor air quality professionals with emission rate estimates for individual VOCs without having to conduct costly dynamic chamber testing. © 1997 Elsevier Science Ltd.

Key word index: Indoor air, model, emissions, volatile organic compound, coating material.

INTRODUCTION

Emissions from petroleum-based indoor coating materials, such as wood stain, polyurethane wood finish, floor wax, conversion varnish and alkyd paint, often contain dozens of volatile organic compounds (VOCs). A fundamental mass transfer model has been developed for predicting the total VOC (TVOC) emissions from freshly applied petroleum-based indoor coatings (Tichenor *et al.*, 1993). This model, referred to here as the VB model, has been used to successfully predict the TVOC emissions from several petroleum-based indoor coating materials (Tichenor *et al.*, 1993; Sparks *et al.*, 1996).

Although the TVOC level is one of the commonly used parameters to measure the level of VOC contamination in indoor environments, exposure estimation and risk assessment often require knowledge about contamination levels of specific individual VOCs because the potential health effects of all VOCs are not equal. This paper presents a new mass transfer model that predicts the emissions of individual VOCs from solvents contained in petroleum-based indoor coatings. The model, although based on fundamental mass transfer theory, does contain several assumptions that make the model feasible in real world situations. These assumptions and their impacts are discussed in detail in the model development section of the paper.

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MODEL DEVELOPMENT

The development of the new model begins from the VB model, which assumes that the concentration difference between the coated surface and the indoor air is the driving force for the emissions (Tichenor *et al.*, 1993):

$$E(t) = -\mathrm{d}M/\mathrm{d}t = k_m(C_s - C) \quad (1)$$

where

$E(t)$ = the emission factor, mass length^{-2} time^{-1};

M = TVOC mass remaining in the source, mass length^{-2};

k_m = mass transfer coefficient ($= D/\delta$), length time^{-1};

D = molecular diffusivity, length^2 time^{-1};

δ = apparent boundary layer thickness above the source, length;

C_s = total vapor pressure at surface expressed as concentration, mass length^{-3};

C = concentration in room air, mass length^{-3}.

As the coated surface ages, C_s decreases gradually and is assumed to be proportional to the amount of TVOC remaining in the source:

$$C_s = C_v M/M_0 \quad (2)$$

where

C_v = initial total vapor pressure at surface expressed in concentration, mass length^{-3};

M_0 = TVOC amount applied to the source, mass length^{-2}.

In the VB model, the emission factor is therefore expressed as

$$E(t) = -\mathrm{d}M/\mathrm{d}t = k_m(C_v M/M_0 - C). \quad (3)$$

The validity of this assumption is demonstrated by Sparks *et al.* (1996).

The emission of an individual VOC from a coated film is a complex process, but the basic mass transfer process is the same as that for TVOC. Thus the mass transfer equation for an individual component is

$$E_i(t) = -\mathrm{d}M_i/\mathrm{d}t = k_{mi}(C_{pi} - C_i) \quad (4)$$

where subscript i represents component i and C_{pi} the partial pressure for i expressed in concentration units.

According to Raoult's law, the partial pressure for an individual component in a solvent mixture is determined by

$$C_{pi} = C_{vi}\, x_i \quad (5)$$

where C_{vi} is the vapor pressure for pure compound i expressed as concentration, in mass length^{-3}; and x_i is the dimensionless molar fraction of i in the solvent mixture. Substitute equation (5) into equation (4):

$$E_i(t) = -\mathrm{d}M_i/\mathrm{d}t = k_{mi}(C_{vi}\, x_i - C_i). \quad (6)$$

By definition,

$$x_i = \Pi_i/\Pi \quad (7)$$

where Π_i and Π are the molar amounts (moles length^{-2}) in the source for component i and TVOC, respectively, and

$$\Pi_i = M_i/\mathrm{mw}_i \quad (8)$$

$$\Pi = \sum \Pi_i \quad (9)$$

where M_i is the amount of i remaining (mass length^{-2}) and mw_i is the molecular weight of i. Note that, as the source emits, both Π_i and Π change. Substituting equation (7) into equation (6):

$$E_i(t) = -\mathrm{d}M_i/\mathrm{d}t = k_{mi}(C_{vi}\Pi_i/\Pi - C_i). \quad (10)$$

A rigorous chamber concentration model consists of two equations:

$$\mathrm{d}C_i/\mathrm{d}t = Lk_{mi}(C_{vi}\,\Pi_i/\Pi - C_i) - NC_i \quad (11)$$

$$\mathrm{d}\Pi_i/\mathrm{d}t = -k_{mi}(C_{vi}\,\Pi_i/\Pi - C_i)/\mathrm{mw}_i \quad (12)$$

where L is the source loading (length^{-1}) and N is the air exchange rate (time^{-1}).

Determining Π by summing the Π_i for all the individual components is a challenge in analytical chemistry and makes the model very complicated. For example, if a solvent contains 50 VOCs, 100 differential equations are needed to compute the TVOC mass. Obviously, some simplification must be made in order for the model to be useful. We propose that the total molar concentration in the source, Π, be calculated using a modified VB model, equations (13) and (14), below:

$$\mathrm{d}C/\mathrm{d}t = Lk_m(C_v\Pi/\Pi_0 - C) - NC \quad (13)$$

$$\mathrm{d}\Pi/\mathrm{d}t = -k_m(C_v\Pi/\Pi_0 - C)/\mathrm{mw}_{\mathrm{TVOC}} \quad (14)$$

where $\mathrm{mw}_{\mathrm{TVOC}}$ is the effective molecular weight of the TVOC mixture.

For convenience, we refer to equations (11)–(14) as the VBX model in which the letter X is from the symbol for molar fraction. Given a set of initial conditions, the above system of ordinary differential equations can be solved numerically. Typical initial conditions are: $t = 0$, $C_i = 0$, $\Pi_i = \Pi_{0i}$, $C = 0$, and $\Pi = \Pi_0$, where Π_{0i} and Π_0 are the amounts of compound i and TVOC, respectively, applied to a unit surface area. Note that the units for C_i and C remain mass volume^{-1}. They can be converted to mole volume^{-1} by eliminating mw_i and $\mathrm{mw}_{\mathrm{TVOC}}$ from the model.

One more issue must be resolved before using the VBX model: how do we determine the effective molecular weight of the TVOC? The TVOC mass can be determined, but an estimate of the TVOC molecular weight is required to convert this mass to moles. We propose to use the molecular weight of the most dominant component in the solvent mixture to approximate the average molecular weight of the TVOC mixture. This assumption is clearly an approximation because the composition of the mixture changes over time. For the class of indoor sources with emissions dominated by emissions from petroleum-based solvents, empirical studies in EPA's small chamber laboratory and indoor air quality (IAQ) test house show that the assumption is adequate. These studies are briefly discussed in the model validation section.

MODEL VALIDATION

Method and data

Preliminary validation of the VBX model included four steps: (1) testing of its compatibility with the original VB model, (2) validation with small chamber data for three petroleum-based indoor coating products, (3) validation with test house data for an artificial solvent mixture, and (4) validation with test house data for an indoor coating material. In all the petroleum-based indoor coating products used in the validation, C_{10} alkanes were the dominant component. Thus the molecular weight for decane (142) was used

as the average molecular weight of the TVOC in those products.

In addition to the parameters used in the VB model, there are three more parameters in the VBX model (k_{mi}, C_{vi}, and Π_{0i}), all of which are easy to come by. The mass transfer coefficient for an individual compound (k_{mi}) can be calculated based on the mass transfer coefficient for TVOC:

$$k_{mi} = k_m D_i / D \tag{15}$$

where D_i and D are diffusivity for the individual compound and the most dominant compound, respectively. Sparks *et al.* (1996) and Zhang *et al.* (1996) present methods for estimating k_m. Since the diffusivity values for different compounds in a petroleum-based solvent are very close to each other (Tichenor *et al.*, 1993), in many cases a single mass transfer coefficient can be used for both TVOC and the individual compounds.

The vapor pressures for many common VOCs can be found in the literature. They can also be determined from inexpensive headspace analysis. The initial mass of an individual compound applied can be obtained from formulation analysis. In the absence of formulation information, they can be determined by integrating the concentration curves obtained from chamber testing for model evaluation purposes. In this validation, both methods were used.

Eight VOCs were evaluated in this validation: five alkanes and three aromatic compounds. They are octane, nonane, decane, undecane, dodecane, ethylbenzene (EB), ethyltoluene (ET), and trimethylbenzene (TMB). The properties of these compounds are summarized in Table 1.

The experimental data used in this validation were generated from small chambers and an IAQ test house. The test house is a wood-framed one-storey building with an interior volume of 300 m^3 and an effective sink area of about 700 m^2 (Sparks *et al.*, 1991). The data covered three commercial coating products and a synthetic solvent.

Unlike environmental chambers, the interior surfaces of a building can act as a strong sink for VOCs. A dynamic sink model (Tichenor *et al.*, 1991; Sparks *et al.*, 1991) was used in this validation:

$$\text{Adsorption rate} = k_a C \tag{16}$$

$$\text{Desorption rate} = k_d M \tag{17}$$

where

k_a = adsorption rate constant in m h^{-1};
k_d = adsorption rate constant in h^{-1}.

In the previous papers on test house simulation, $k_a = 0.15$ and $k_d = 0.2$ have been used for TVOC (Tichenor *et al.*, 1993; Sparks *et al.*, 1991). Although accurate parameters for individual VOCs are not available, it is known that for similar compounds, the less volatile the compound, the more severe the sink effect (Chang and Guo, 1995). Preliminary analysis showed that, when the carbon number of an alkane increases by 1, the ratio k_a/k_d roughly increases by a factor of 2. In the following validation with test house data, we used $k_a = 0.15$ for all the VOCs, and the k_d values were calculated based on their carbon numbers given $k_d = 0.2$ for C_{10} compounds.

Compatibility of the VBX model with the VB model

Before validating the model with experimental data, the compatibility between the VB and VBX models was checked to make sure they are internally consistent. If the VBX model is valid, the sum of the concentrations of all individual compounds must be close to the TVOC concentration predicted by the VB model. If the two models do not make similar predictions for TVOC, it is likely that the concept of the new model is questionable.

The evaluation was made by using a theoretical solvent mixture consisting of five consecutive alkanes: from *n*-octane to *n*-dodecane with molar fractions of 0.1, 0.2, 0.4, 0.2, and 0.1, respectively. The theoretical total vapor pressure for TVOC is 0.154 mol m^{-3} (Table 2). The average diffusivity for the five components is 0.0209 $m^2 h^{-1}$, which is very close to 0.0207 for decane. Calculations were made under the

Table 1. Physical properties of the eight VOCs evaluated

Compound	Chemical formula	Molecular weight	Vapor pressure[a] (10^{-3} mol m^{-3})	Diffusivity[b] ($m^2 h^{-1}$)
n-Octane	C_8H_{18}	114	668	0.0234
n-Nonane	C_9H_{20}	128	225	0.0219
n-Decane	$C_{10}H_{22}$	142	85	0.0207
n-Undecane	$C_{11}H_{24}$	156	34	0.0197
n-Dodecane	$C_{12}H_{26}$	170	14	0.0188
EB	C_8H_{10}	106	480	0.0262
ET	C_9H_{12}	120	150[c]	0.0243
TMB	C_9H_{12}	120	111[c]	0.0243

[a]At 23°C.
[b]Calculated by the FSG method.
[c]Average value for the three isomers.

Table 2. Calculation of total vapor pressure (expressed as concentration) for the solvent mixture containing five consecutive alkanes

Compound	Vapor pressure (10^{-3} mol m^{-3})	Molar fraction	Partial pressure (10^{-3} mol m^{-3})
n-Octane	668	0.1	66.8
n-Nonane	225	0.2	44.9
n-Decane	85.3	0.4	34.1
n-Undecane	33.4	0.2	6.67
n-Dodecane	13.7	0.1	1.37
Total vapor pressure for TVOC			154

following assumed environmental conditions:

Chamber volume	1 m^3
Source area	0.5 m^2
Apparent boundary layer thickness	0.02 m
Air exchange rate	0.5 h^{-1}
TVOC applied	0.2 mol m^{-2}

As shown in Fig. 1, the TVOC concentration predicted by the VBX model (i.e. the summed concentration of five individual compounds) is very close to that predicted by the VB model. The very slight difference between the two results is expected because of the approximations made in developing the VBX model.

Validation with small chamber data for three petroleum-based coating products

Three petroleum-based coating materials, wood stain (WS), polyurethane wood finish (PU), and floor wax (WX1), were tested in small environmental chambers (Tichenor and Guo, 1991; Tichenor *et al.*, 1993). The experimental conditions are summarized in Table 3. All the parameters for TVOC were previously determined; thus, the predictions were generated without any data fitting or parameter adjustment for individual VOCs. As shown in Figs 2–5, the VBX model made accurate predictions for the concentrations of the four VOCs evaluated.

The fact that the agreement between model predictions and data is good supports the assumptions that the information about TVOC emissions required by the VBX model can be obtained using the VB model in place of the summation of all individual species, and that the molecular weight of the dominant species can be used to approximate the TVOC molecular weight.

Validation with test house experiments for a synthetic solvent mixture

The next validation experiment was conducted in an IAQ test house. The purpose of validating the VBX model with test house data was to demonstrate that the model is scalable from one environment to another and that the accuracy of the predictions is adequate for use in indoor exposure estimation and risk assessment.

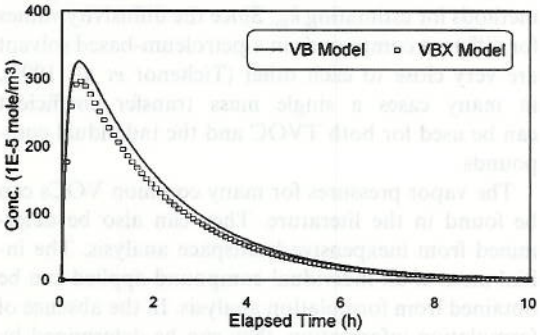

Fig. 1. Predicted TVOC emissions from a synthetic solvent by two source models.

In order to provide a solvent with known composition, a synthetic solvent mixture (SS) was made up according to the formulation described in Table 2. The solvent was applied to a new oak floor with an area of 6 m^2. The average air exchange rate was 0.43 air change per hour (ACH), and the mass transfer coefficient for TVOC was 1.3 m h^{-1} (Tichenor *et al.*, 1993). Air samples were taken from two locations with an auto-sampler and analyzed by an on-site gas chromatograph (GC). The mean of the two concentrations was used as the average concentration in the house. The total vapor pressure for TVOC, based on the formulation, is 0.154 mol m^{-3}, which was confirmed by headspace analysis (8% error). The amounts of VOCs applied to the board (M_{i0}) were obtained from the solvent formulation and the weight of solvent applied to the board (192 g). They are 2.25×10^{-3}, 4.51×10^{-3}, 9.02×10^{-3}, 4.51×10^{-3}, and 2.25×10^{-3} mol m^{-2}, respectively. As shown in Figs 6 and 7, the predicted results are generally in good agreement with the experimental data. It is unclear, however, why the prediction error for dodecane is significantly greater than those for the other four compounds (see Table 4).

Validation with test house experiments for a floor wax

The VBX model was further evaluated by comparing its predicted concentrations for three minor components in a floor wax (WX2): ethylbenzene,

Table 3. List of model parameters for small chamber experiments

Parameter	PU	WX1	WS
Chamber volume (m^3)	0.053	0.053	0.166
Air exchange rate (h^{-1})	0.528	0.515	2.5
Source area (m^2)	0.0211	0.0211	0.116
Mass transfer coeff. of TVOC ($m\ h^{-1}$)	0.85[a]	0.85[a]	2.5[b]
TVOC vapor pressure (10^{-3} mol m^{-3})	153[c]	129[c]	94.5[d]
Initial amount of TVOC (10^{-3} mol m^{-2})	138	214	83.1
Initial amount of nonane (10^{-3} mol m^{-2})	3.77	8.35	4.35
Initial amount of decane (10^{-3} mol m^{-2})	15.2	2.36	17.8
Initial amount of undecane (10^{-3} mol m^{-2})	6.56	1.59	4.88
Initial amount of TMB (10^{-3} mol m^{-2})	[e]	[e]	3.47

[a]No circulation fan in the chamber, previously determined value (Tichenor *et al.*, 1993).
[b]There was an electric stirrer in the chamber, estimated from the VB model.
[c]Determined from headspace analysis (Tichenor *et al.*, 1993).
[d]No headspace analysis available; estimated from the VB model.
[e] Not quantified.

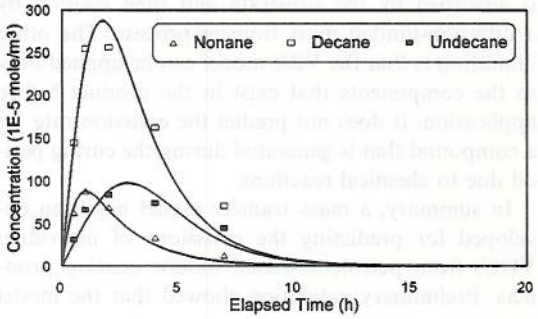

Fig. 2. Modeling the VOC emissions from a polyurethane wood finish in a 53-ℓ chamber (solid lines are model predictions).

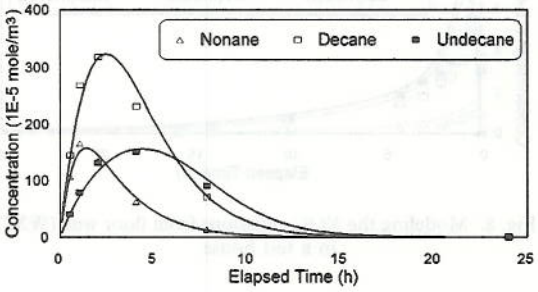

Fig. 3. Modeling the VOC emissions from a floor wax (WX1) in a 53-ℓ chamber (solid lines are model predictions).

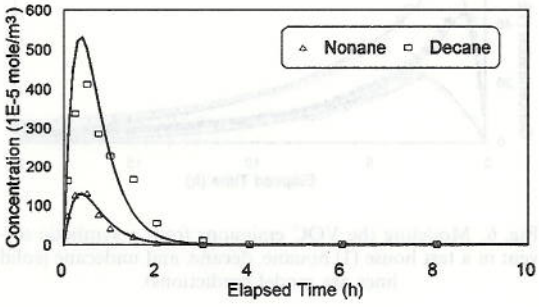

Fig. 4. Modeling the VOC emissions from a wood stain in a 166-ℓ chamber (1) nonane and decane (solid lines are model predictions).

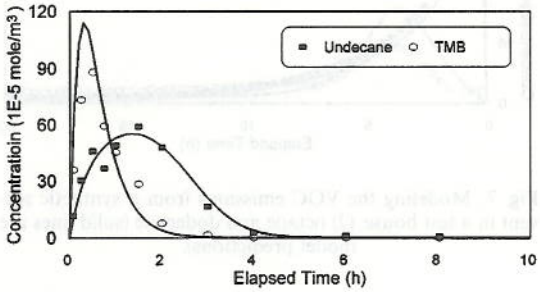

Fig. 5. Modeling the VOC emissions from a wood stain in a 166-ℓ chamber (2) undecane and TMB (solid lines are model predictions).

ethyltoluene and trimethylbenzene. The emission data were generated in the test house mentioned above. A 6 m^2 oak floor was coated with 73.4 g of the product. Air samples were collected on Tenax sorbent tubes from the living room and one bedroom. The samples were then thermally desorbed and analyzed for VOCs by GC with flame ioniation detection (FID). The average air exchange rate from tracer gas measurements was 0.37 ACH. The mass transfer coefficient (k_m = 1.34 $m\ h^{-1}$) and total vapor pressure (0.129 mol m^{-3}) for TVOC were previously determined (Tichenor *et al.*, 1993). The amount of TVOC applied was calculated by multiplying the amount applied by the TVOC contents as determined by ASTM Method D2369-87 (Brezinski, 1989). Because no formulation analysis was available for

this product, the amount of each VOC applied was obtained by integrating the concentration curve: the results were 1.02×10^{-3}, 5.08×10^{-3}, and 6.21×10^{-3} mol m^{-2} for EB, ET, and TMB, respectively. As shown in Fig. 8, the three VOC concentrations predicted by the IAQ model follow the experimental results well.

DISCUSSION AND CONCLUSION

The VBX model was developed from and is closely related to the VB model. Once the parameters for TVOC are determined, the effort needed to predict the emission of an individual VOC is minimal. The three parameters required to describe a VOC are its vapor pressure (C_{vi}), diffusivity (D_i), and amount applied (Π_{0i}), all of which can be easily obtained.

As a measure of the magnitude of the prediction errors, the normalized mean square error (NMSE) was computed for each case by following the ASTM Standard Guide for Statistical Evaluation of Indoor Air Quality Models (ASTM, 1995). As shown in Table 4, the VBX model made more accurate predictions for data from small chambers than for data from the test house. This is partly because there are more error sources associated with the latter environment. Overall, the accuracy of the predictions are adequate for exposure estimation and risk assessment purposes.

It should be pointed out that the VBX and the VB models are for gas-phase-limited mass transfer. They do not predict internal-diffusion-controlled emissions such as can exist when a small amount of the solvent is adsorbed by the substrate and then emitted by a diffusion-limited mass transfer process. The other limitation is that the VBX model can be applied only to the components that exist in the product before application. It does not predict the emission rate for a compound that is generated during the curing period due to chemical reactions.

In summary, a mass transfer model has been developed for predicting the emissions of individual VOCs from petroleum-based indoor coating products. Preliminary validation showed that the model

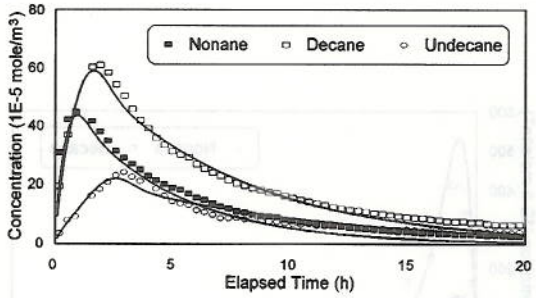

Fig. 6. Modeling the VOC emissions from a synthetic solvent in a test house (1) nonane, decane, and undecane (solid lines are model predictions).

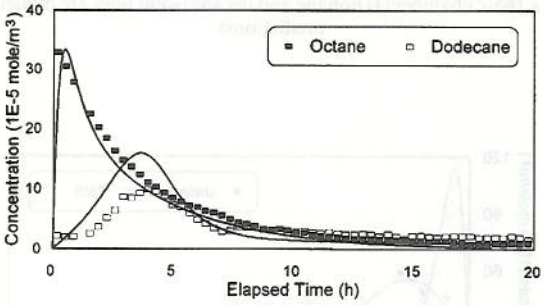

Fig. 7. Modeling the VOC emissions from a synthetic solvent in a test house: (2) octane and dodecane (solid lines are model predictions).

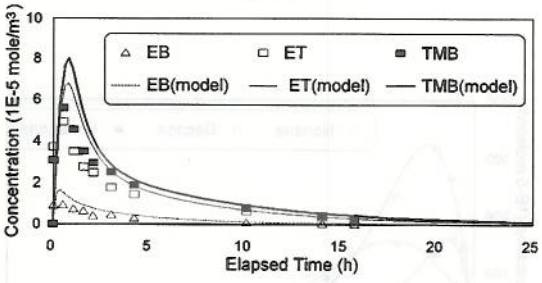

Fig. 8. Modeling the VOC emissions from floor wax (WX2) in a test house.

Table 4. Normalized mean square error (NMSE) as a measure of prediction error

Product	PU	WX1	WS	SS	WX2
Test facility	53-ℓ chamber	53-ℓ chamber	166-ℓ chamber	Test house	Test house
Octane	–	–	–	0.092	–
Nonane	0.017	0.010	0.044	0.076	–
Decane	0.020	0.013	0.183	0.015	–
Undecane	0.044	0.010	0.032	0.035	–
Dodecane	–	–	–	0.473	–
EB	–	–	–	–	0.411
ET	–	–	0.197	–	0.457
TMB	–	–	–	–	0.290

predictions are in good agreement with experimental data generated from both small chambers and the test house. Since all the parameters are easy to come by, the VBX model has the potential to provide emission rate information for individual VOCs without having to rely on costly chamber testing.

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