Modeling of Alkane Emissions from a Wood Stain

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Abstract

Full-scale residential house tests were conducted to evaluate the effects of organic emissions from a wood finishing product – wood stain – on indoor air quality (IAQ). The test house concentrations of three alkane species, nonane, decane, and undecane, were measured as a function of time after the application of the wood stain. It was found that the test house concentrations can be simulated by an integrated IAQ model which takes into consideration source, sink and ventilation effects. The alkane emissions were controlled by an evaporation-like process. Data analysis indicated that there were significant sink effects in the test house. Different sink strengths were estimated by the model for the three alkane species. An inverse relationship between the test house sink strength and the alkane volatility was found.

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Introduction

The emission patterns of organic compounds from a wood stain have been characterized by Tichenor and Guo (1991) and Chang and Guo (1992a) based on chamber testing data. Normally, the majority (more than 95%) of the organics were emitted when the wood stain applied was still relatively wet. The organic emissions were controlled by an evaporation-like process which made the emission rate rather high. When the wood stain became relatively dry, the organics were emitted at an extremely low rate. For practical purposes, the dry-phase organic emissions can be neglected without significant effects on the total emissions.

To further evaluate the impact of wood stain emissions on the quality of indoor air, research has shown that sinks (i.e., surfaces that adsorb and re-emit indoor pollutants) play an important role in determining indoor pollutant concentrations (Berglund et al., 1988). To take into account the interactions between sources and sinks, an integrated IAQ model which includes emission rate, sink effect, and ventilation characteristics is required. This paper presents the development and application of an integrated IAQ model which was used to simulate the IAQ profiles (time/concentration curves) of three alkane species – nonane, decane, and undecane – emitted from a wood stain. The model results were validated by experimental data generated in a full-scale IAQ test house.

Test Facility

The IAQ test house (see Figure 1 for floor plan) is an unfurnished, single story, wood frame residential house with a central heating and air-conditioning (HAC) system. The HAC fan was operated continuously during the testing to ensure good mixing of indoor air and uniform distribution of alkane concentrations. Natural gas was the fuel used for central heating, hot water, and cooking. The volume of the house (V) was estimated to be 305 m³. The total

interior surface area (A_s) that could function as a sink was determined to be 402 m².

The wood stain, purchased from a local store, was applied to a wood (oak) floor near the kitchen (Figure 1). The floor was stained, using a clean brush on an area (A) of 6 m² (2.44 × 2.44 m). Only one coating was applied. The stain and the brush were weighed before and after the application. The amount of the stain applied to the floor was estimated to be 52.3 g/m² based on the weight differences. After application, the wood stain and the brush were removed from the house immediately.

Air samples were taken in the corner bedroom. The samples were collected on Tenax/charcoal sorbent tubes at the center of the corner bedroom, 160 cm above the floor, using a P4LC sampling pump. The pump was calibrated prior to the test, and the sampling flow was set at 1 l/min. The sampling tubes were then thermally desorbed and analyzed by a gas chromatograph equipped with a flame ionization detector.

The temperature inside the house was controlled at 22.2°C (72°F). The house air exchange rate was
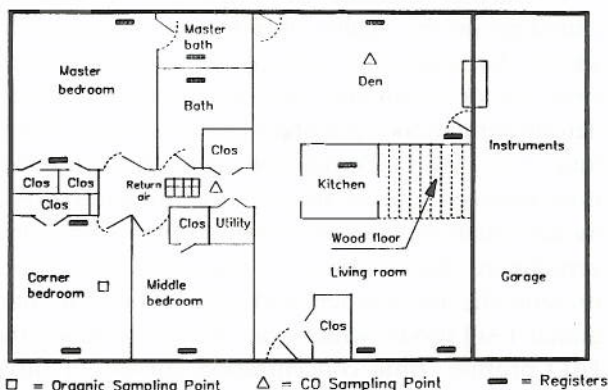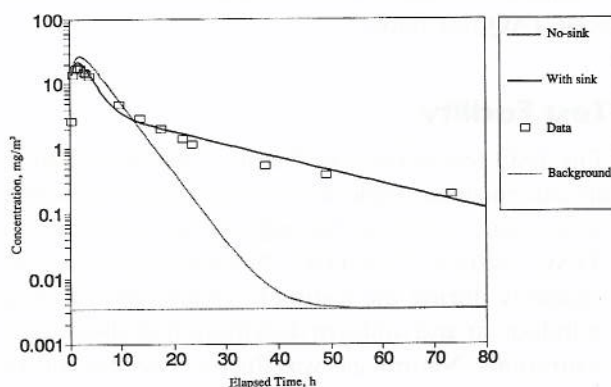

Fig. 1 IAQ test house.

☐ = Organic Sampling Point   △ = CO Sampling Point   ▬ = Registers

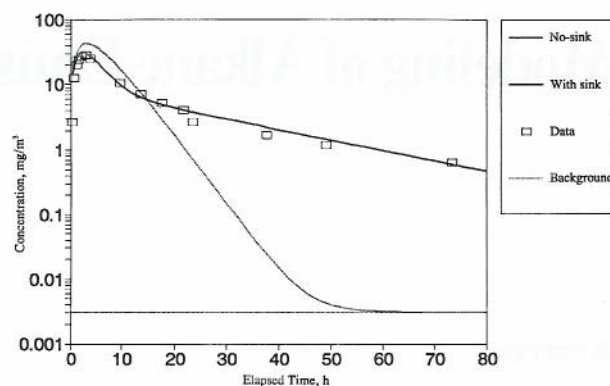**Fig. 2** Comparison of test house nonane data with predicitons of IAQ models.

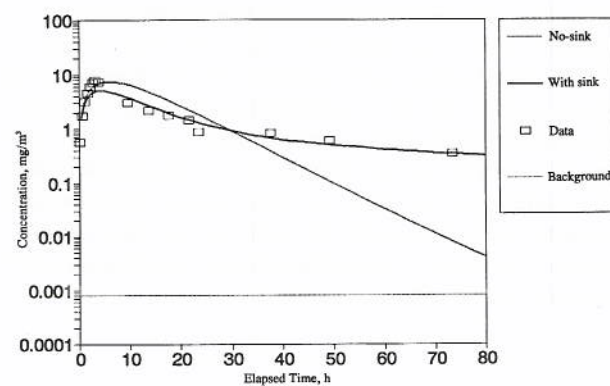**Fig. 3** Comparison of test house decane data with predictions of IAQ models.

Fig. 4 Comparison of test house undecane data with predictions of IAQ models.

measured, using carbon monoxide (CO) as a tracer gas. CO was released into the house near the return air vent and monitored by a continuous CO monitor (Thermo Electron Model 48) in two locations (see Figure 1). The average air exchange rate (N) during the wood stain experiment was estimated to be 0.25 air change per hour (ach).

Experimental Data

The results of the test house experiments are presented in Figures 2, 3, and 4 for nonane, decane, and undecane, respectively. The test house organic concentrations are plotted against time on a semi-logarithmic scale. Figures 2 to 4 show that the concentrations of the three compounds basically followed the same trend. The concentration of each species first increased rapidly, reached a peak within a few hours, and then declined at a moderate rate for the rest of the test. After 70 h of the test, the concentration of each organic compound was still well above the background level. (The background

levels of nonane, decane, and undecane in the test house were estimated to be 0.0034, 0.0031, and 0.0008 mg/m^3, respectively.)

Integrated IAQ Model

Source Model

The emission model developed based on the chamber testing of the wood stain (Tichenor and Guo, 1991) was adopted as the source model:

$$R = R_o e^{-kt} \qquad (1)$$

Where, R = Total emission rate, mg/m^2/h
R$_o$ = Initial emission rate, mg/m^2/h
e = Natural log base
k = Emission rate decay constant, h^{-1}
t = Time, h

The source model represented by Equation 1 implies that only the wet-phase organic emissions were significant during the test period, and the dry-phase emissions were negligible.

Sink Model

A first order reversible model (Tichenor et al., 1990 and 1991) was adopted as the sink model for the test house. This model assumes that the sorption and desorption rates by the sinks are directly proportional to the gas-phase and the sink surface organic concentrations, respectively.

$$\text{Sorption rate} = K_a C \qquad (2)$$

$$\text{Desorption rate} = K_d M \qquad (3)$$

Where, K$_a$ = Sorption rate constant, m/h
C = Gas-phase organic concentration, mg/m^3
K$_d$ = Desorption rate constant, h^{-1}
M = Sink surface organic concentration, mg/m^2

At equilibrium, the sorption rate equals the desorption rate to give the relationship:

$$K_a C_e = K_d M_e \qquad (4)$$

Where, C$_e$ = Gas-phase organic concentration in equilibrium with M$_e$, mg/m^3
M$_e$ = Sink surface organic concentration in equilibrium with C$_e$, mg/m^2

IAQ Model

Assuming the indoor air was well mixed and the alkane concentrations were uniformly distributed, an integrated IAQ model is developed by test house mass balance based on the source and the sink models:

$$V dC/dt = -NVC + AR_o e^{-kt} - A_s K_a C + A_s K_d M \quad (5)$$

$$dM/dt = = K_a C - K_d M \qquad (6)$$

with initial conditions:

at t = 0, C = 0, and M = 0

Data Analysis

The values of the four parameters, R$_o$, k, K$_a$, and K$_d$, in Equations 5 and 6 can be estimated for each of the three organic compounds tested by using the IAQ model to analyze the test house concentration data shown in Figures 2 to 4.

According to the source model, A(R$_o$/k) represents the total quantities of the organic species emitted (Guo et al., 1990). Therefore,

$$A(R_o/k) = (\text{Total emission}) = NV(\int C dt) \qquad (7)$$

The concentration/time integration, ($\int C dt$), is the area under the test house concentration curves, as shown in Figures 2 to 4, being linearly extrapolated to background levels. The total emissions of nonane, decane, and undecane estimated by integration and Equation 7 are listed in Table 1.

With the initial condition of C = 0 and M = 0 at t = 0, Equation 5 can be reduced to:

$$dC/dt \mid_{t=0} = AR_o/V \qquad (8)$$

Therefore, the values of R$_o$ can be estimated by taking the slope of the concentration curves at t =

Table 1 Values of IAQ model parameters estimated by analysis of the test house data

	Nonane	Decane	Undecane
Total emission, mg	2222	4814	1616
R$_o$, mg/m^2/h	1973	1887	181
k, h^{-1}	0.89	0.39	0.11
Relative k	2.28	1.0	0.28
K$_a$, m/h	0.15	0.19	0.15
K$_d$, h^{-1}	0.09	0.081	0.024
K$_e$, m	1.67	2.35	6.25

0, $(dC/dt|_{t=0})$. When the values of R_o are known, the corresponding values of k can be calculated by Equation 7. The estimated values of R_o and k for nonane, decane, and undecane are listed in Table 1.

Substituting the values of R_o and k into Equation 5, the values of K_a and K_d can be estimated by using a non-linear regression curve fit routine, implemented on a microcomputer, to fit the concentration curves shown in Figures 2 to 4 to the IAQ model represented by Equations 5 and 6. The non-linear regression values of K_a and K_d for the three organic compounds tested are listed in Table 1.

Sink Effects

A comparison between the predictions of the integrated IAQ model (solid curves) and the test house data (open squares) is shown in Figures 2 to 4. Also shown (dotted curves) are the predictions by the IAQ model without consideration of the sink effects (i.e., $K_a = K_d = 0$).

It is seen that, if there were no sink effects, the test house alkane concentrations should have declined rapidly after the peak. The nonane and decane concentrations should have decreased to the background levels within 50 and 60 h, respectively. The undecane concentration should have decreased to less than 0.01 mg/m^3 within 70 h. However, considerably higher concentrations were measured in the test house. The data shown in Figures 2 and 3 indicate that the test house nonane and decane concentrations at hour 80 were both well above (more than one order of magnitude) the background levels. Figure 4 also shows that the undecane concentration at hour 80 was still greater than 0.1 mg/m^3.

It is apparent from comparisons between model predictions and test house data that the high alkane concentrations toward the end of the test were caused by the sink effects. As shown in Figures 2 to 4, during the first few hours of the experiment, the alkanes emitted from the wood stain were sorbed by the sinks which made the test house concentrations slightly lower than the no-sink model predictions (dotted curves). However, when the test house concentrations decreased, the sorbed alkanes slowly re-emitted from the sinks and caused the test house nonane, decane, and undecane concentrations to be higher than the no-sink model predictions.

The sink strength of the test house interior surfaces can be characterized by a factor K_e defined as:

$$K_e = K_a/K_d = M_e/C_e \qquad (9)$$

K_e can be seen as the equilibrium capacity of the sink surfaces toward the organic compound. In other words, K_e indicates the quantity (mg/m^2) of the chemical compound sorbed by the test house interior surfaces in equilibrium with each unit (1 mg/m^3) of gas-phase concentration.

The values of test house K_e toward nonane, decane, and undecane, calculated based on the wood stain data, are listed at the bottom of Table 1. Figure 5 shows a comparison of estimated K_e with vapor pressure (Chang and Guo, 1992a; Weast, 1973) of the corresponding alkane species. Figure 5 indicates that there is an inverse relationship between the sink strength and the volatility. The more volatile the organic compound, the weaker the sink strength. This trend is also supported by the two literature
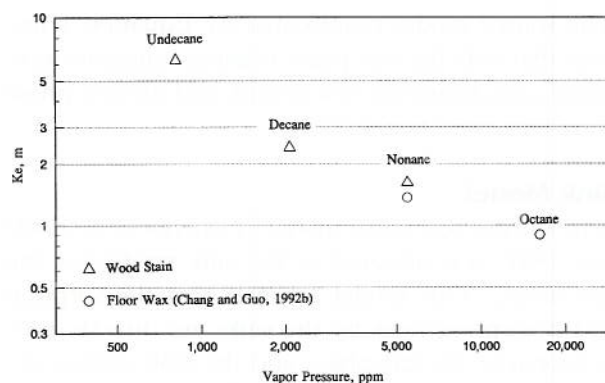
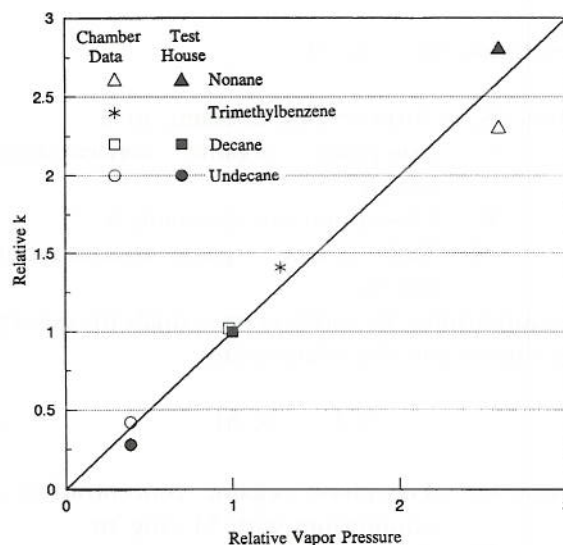**Fig. 5** Comparison of K_e with vapor pressure at 22.2°C (72°F).

Fig. 6 Comparison of chamber (Chang and Guo, 1992a) and test house relative k with relative vapor pressure at 22.2°C (72°F).

data points (represented by circles) generated from a previous test with floor wax (Chang and Guo, 1992b).

Source Characteristics – Comparison with Chamber Results

The source model represented by Equation 1 was adopted based on the assumption that the dry-phase organic emissions were negligible and the dominant emissions were from the wood stain while it was still relatively wet. Chang and Guo (1992a) analyzed chamber test results and concluded that, under such conditions, the organic emissions were controlled by an evaporation-like process. In addition, there should be an almost one-to-one relationship between the relative value of k and the relative vapor pressure as illustrated by Figure 6. In Figure 6, the relative k was defined as the ratios of k between the alkane species by using the corresponding values of decane as the common denominator (Chang and Guo, 1992a). For example, the relative k of nonane and undecane was calculated as k_{nonane}/k_{decane} and $k_{undecane}/k_{decane}$, respectively. The relative vapor pressure was defined similarly. The values of relative k obtained from the test house data are listed in Table 1 for nonane, decane, and undecane.

Figure 6 shows a comparison of the relative k obtained from test house and previous chamber tests (Chang and Guo, 1992a) with the relative vapor pressure (Weast, 1973) of the three alkane species tested. There is good agreement between the test house and chamber relative k. Both test house and chamber relative k's exhibit an almost one-to-one relationship with respect to relative vapor pressure. The good agreement between the test house and chamber data confirms that the evaporation-like mechanisms were controlling the wood stain organic emissions during the test house experiment.

Conclusions

The indoor air concentrations of nonane, decane, and undecane, emitted from a wood stain, were measured in an IAQ test house. The time/concentration curves of the three alkane species in the test house can be simulated by an integrated IAQ model which takes into account the interactions between source emissions and sink effects.

Comparison with previous chamber data confirmed that the wood stain alkane emissions during the test house experiment were controlled by an evaporation-like process. A one-to-one relationship existed between the vapor pressure and the emission rate constant which made the alkane emission rate increase proportionally with the increase of vapor pressure.

Significant sink effects were found in the test house for the three alkane species. The IAQ model indicated that, without sinks, the test house alkane concentrations should have decreased rapidly within 5 h after the wood stain was applied. However, the sinks in the test house caused prolonged high alkane concentrations in the indoor air. Especially in the period between 30 and 80 h after the wood stain application, the indoor air alkane concentrations were several orders of magnitude higher than those without sinks.

Data analysis also indicated that there seemed to be an inverse relationship between the sink strength of the test house and the vapor pressure of alkane species. The highest sink strength was found with undecane which has the lowest vapor pressure among the alkane species tested.

References

Berglund, B., Johansson, I. and Lindvall, T. (1988) "Adsorption and desorption of organic compounds in indoor materials." In: *Proceedings of Healthy Buildings '88*, Stockholm, Swedish Council for Building Research, Vol. 3, p. 299.

Chang, J.C.S. and Guo, Z. (1992a) "Characterization of organic emissions from a wood finishing product – wood stain," *Indoor Air*, **2**, 146.

Chang, J.C.S. and Guo, Z. (1992b) "Modeling of the fast organic emissions from a wood-finishing product – floor wax," *Atmospheric Environment*, **26A**(13), 2365.

Guo, Z., Tichenor, B.A., Mason, M.A. and Plunket, C.M. (1990) "The temperature dependence of the emission of perchloroethylene from dry cleaned fabrics," *Environmental Research*, **52**, 107.

Tichenor, B.A., Guo, Z., Mason, M A. and Dunn, J.E. (1990) "Evaluation of indoor air pollutant sinks for vapor phase organic compounds," In: Walkinshaw, D.S. (ed.), *Proceedings of Indoor Air '90*, Ottawa, Canada Mortgage and Housing Association, Vol. 3, p. 263.

Tichenor, B.A. and Guo, Z. (1991) "The effect of ventilation on emission rates of wood finishing materials," *Environment International*, **17**(4), 317.

Tichenor, B.A., Guo, Z., Dunn, J.E., Sparks, L.E. and Mason, M. A. (1991) "The interaction of vapor phase organic compounds with indoor sinks," *Indoor Air*, **1**(1), 23.

Weast, R.C. (1973) *Handbook of Chemistry and Physics*, Chemical Rubber Co., 53rd ed., D-151.