Atmospheric Environment Vol. 26A, No. 13, pp. 2365–2370, 1992.
Printed in Great Britain.

0004-6981/92 $5.00 + 0.00
Pergamon Press Ltd

MODELING OF THE FAST ORGANIC EMISSIONS FROM A WOOD-FINISHING PRODUCT—FLOOR WAX

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(*First received* 7 *October* 1991 *and in final form* 26 *January* 1992)

Abstract—Environmental chamber and full-scale residential house tests were conducted to evaluate the fast organic emissions from a wood-finishing product—floor wax. For the environmental chamber tests, a very small amount ($< 5\ g\ m^{-2}$) of the wax was applied to an aluminum plate. It was found that the chamber exit organic concentrations can be estimated by a model with an initial condition of instant organic emissions. The model was applied to the house data to interpret the octane and nonane emissions. Significant sink effects were found in the house that prolonged the elevated octane and nonane concentrations for more than 2 days.

Key word index: Volatile organic compounds, indoor air quality, floor wax emissions, sinks, sources, modeling.

INTRODUCTION

Methods for characterizing the emission rates and patterns of a variety of indoor sources using small environmental chambers have been developed (Tichenor, 1987). Environmental chambers can provide a well-mixed space with controlled temperature, humidity and air exchange. The chamber outlet concentrations resulting from the emissions of the source inside the chamber are measured over time. Emission models can be established from the analysis of the time history concentration curves.

After the emission rates have been characterized, scale-up experiments can be conducted in a facility such as a full-scale indoor air quality (IAQ) test house. The results are used to evaluate the effects of emissions from various sources on IAQ (Tichenor *et al.*, 1990a). Test house results usually exhibit characteristics different from those of environmental chambers due to sink effects (Tichenor *et al.*, 1990b). The sink effects involve sorption and desorption of the compounds emitted from the sources by common indoor surfaces such as gypsum wallboard and carpet (Tichenor *et al.*, 1991). Analysis of test house data has led to the development of IAQ models which take into account both sources and sinks (Sparks, 1988). The IAQ model can be used to evaluate indoor air pollution sources and sinks and to perform exposure assessments.

The U.S. Environmental Protection Agency is conducting research to determine the interactions between various sources and sinks and their impacts on IAQ. The program involves the characterization of emission rates, the development of IAQ models and the validation of the models by IAQ test house experiments. This paper describes how this program was applied to evaluate the impacts of fast organic emissions on IAQ and presents the results obtained from a wood-finishing product—an acrylic floor wax.

TEST FACILITIES

Environmental chambers

Environmental chambers were used to obtain the time history data of organic concentrations resulting from the floor wax emissions. The volume of each chamber (V) was 166 ℓ. For each run, the chamber was purged with clean air for several hours before placing samples in the chamber. The liquid wax, purchased from a local store, was applied to a clean and tared aluminum plate. A common shoe polisher with a sponge top was used as the wax applicator. The applicator was weighed before and after the waxing. By weight differences, it was found that the amount of the wax applied was less than $5\ g\ m^{-2}$ for all the tests. The chamber door was closed immediately after the wax application (usually within 2 min) to start the test.

Clean air with virtually no organics was pumped through the chamber at a constant rate for each test. Air samples were collected on Tenax/charcoal traps from glass sampling manifolds at the exit port of the chamber. The collected samples were thermally desorbed from the trap to the concentrator column of a purge and trap concentrator and then desorbed to the analytical column (megabore DB-1 fused silica capillary column) from which the organic concentrations in the air exiting the chamber were analysed by a gas chromatograph

(GC) equipped with a flame ionization detector (FID). The concentrations of 11 organic species were measured:

(1) isononane
(2) trimethylcyclohexane (TMC)
(3) methylethylcyclohexane (MEC)
(4) 1-methylethylcyclohexane (1-MEC)
(5) 2-methyloctane (2-MO)
(6) 2,6-dimethyloctane (2,6-DMO)
(7) trimethylbenzene (TMB)
(8) *p*-ethyltoluene (p-ET)
(9) *n*-nonane (Nonane)
(10) *n*-decane (Decane)
(11) *n*-undecane (Undecane).

The concentrations were measured by calibrating against the standard of each compound. Table 1 lists the experimental conditions such as waxed area (A), air flow rate (Q), temperature and relative humidity of each run.

IAQ test house

The IAQ test house (see Fig. 1 for floor plan) is an unfurnished, single-storey, wood-framed house with a central heating and air conditioning (HAC) system. Natural gas is used for central heating, hot water and cooking. The volume of the house (V_h) is estimated to be 300 ± 3 m^3. The total interior surface area (A_s) that could function as a sink is determined to be 400 ± 4 m^2. The floor wax was applied to a 6 m^2 (2.44 × 2.44 m) oak wood floor using a sponge. After the application, the wax bottle and the sponge were immediately removed from the house.

Air samples were taken in the corner bedroom. The samples were collected on Tenax/charcoal sorbent tubes in the center of the corner bedroom, 160 cm above the floor using P4LC sampling pumps. The pumps were calibrated prior to each test and the sampling flow was set at 1 ℓ min^{-1}. The sampling tubes were then thermally desorbed and analysed by GC-FID.

The house air exchange rate was measured by 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 Fig. 1). The average effective air exchange rate (N) was estimated to be 0.37 air change per hour (ach).

During the test house experiments, all the inside doors were open, all the outside doors and windows were closed, the fireplace damper was closed, the hot water heater was on, the pilot flames of the cooking stove were off, all the HAC registers were open and the indoor temperature was set at 22°C.

Table 1. Chamber test conditions and results

Run no.	Waxed area (A) (m^2)	Temperature (°C)	Relative humidity (%)	N* (h^{-1})
FW-1	0.02	21	50	1.404 ± 0.041
FW-2	0.02	22	50	0.333 ± 0.002
FW-3	0.01	20	50	0.409 ± 0.005
FW-4	0.02	22	50	0.811 ± 0.060
FW-5	0.02	20	50	0.172 ± 0.005
FW-6	0.04	22	50	1.651 ± 0.098
FW-7	0.02	20	50	0.461 ± 0.003
FW-8	0.02	35	20	0.445 ± 0.024
FW-9	0.02	35	50	0.421 ± 0.002

*Obtained from the 11 individual organic compounds. Expressed as mean ± standard deviation.

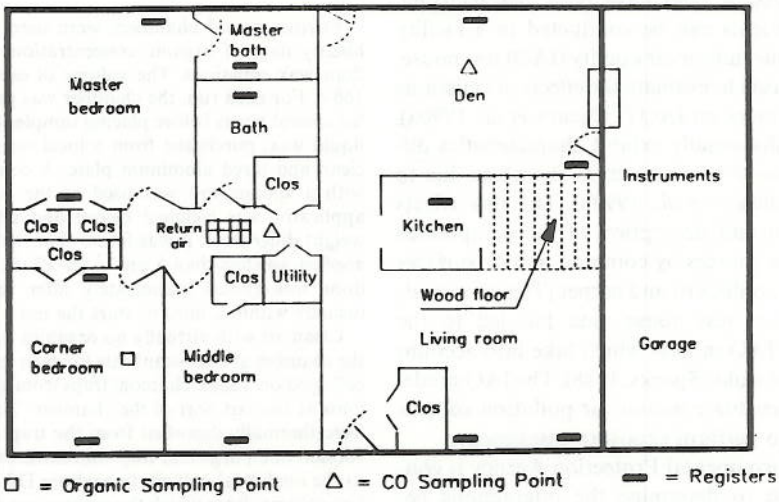

Fig. 1. IAQ test house.

RESULTS AND DISCUSSION

Chamber data

The chamber exit organic concentrations all exhibited the same pattern as represented by the results of run FW-3 shown in Figs 2 and 3. The first sample of each run, taken about 15 min after the start of the experiment, always had the highest concentrations. The organic concentrations decreased monotonically as the experiment proceeded. When the chamber exit concentrations were plotted against time on a semi-logarithmic scale, the data for each organic species fell on a straight line. In addition, the straight lines seemed to be parallel to each other.

Chamber model

It was found that the chamber exit concentration data can be simulated by a mass balance model:

$$dC/dt = -NC, \quad (1)$$

with initial condition of $C = C_o$ at $t = 0$, and where C is chamber exit concentration ($\mu g\,m^{-3}$), t is time (h), N is average effective air exchange rate (ach) and C_o is initial chamber exit concentration ($\mu g\,m^{-3}$).

The solution of Equation (1) is:

$$C = C_o e^{-Nt}, \quad (2)$$

where e is natural log base.

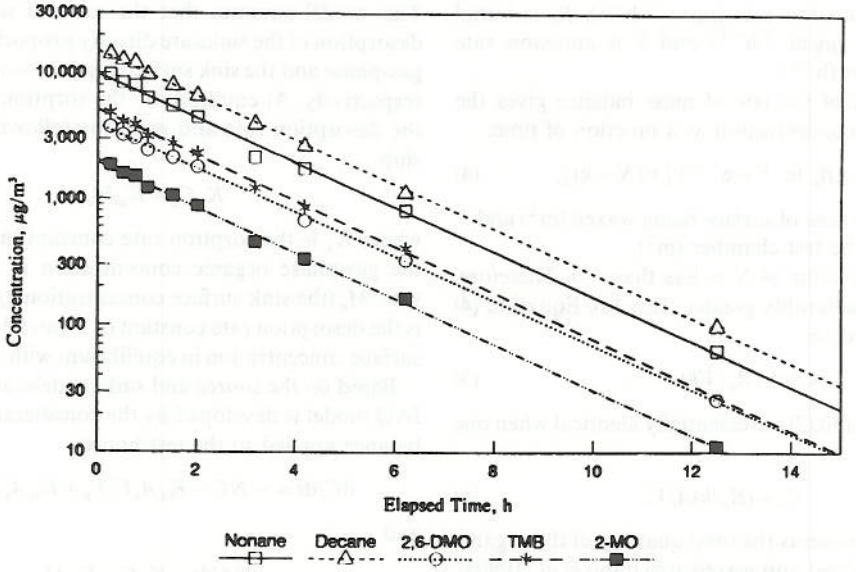

Fig. 2. Environmental chamber time-history data of five organic species.

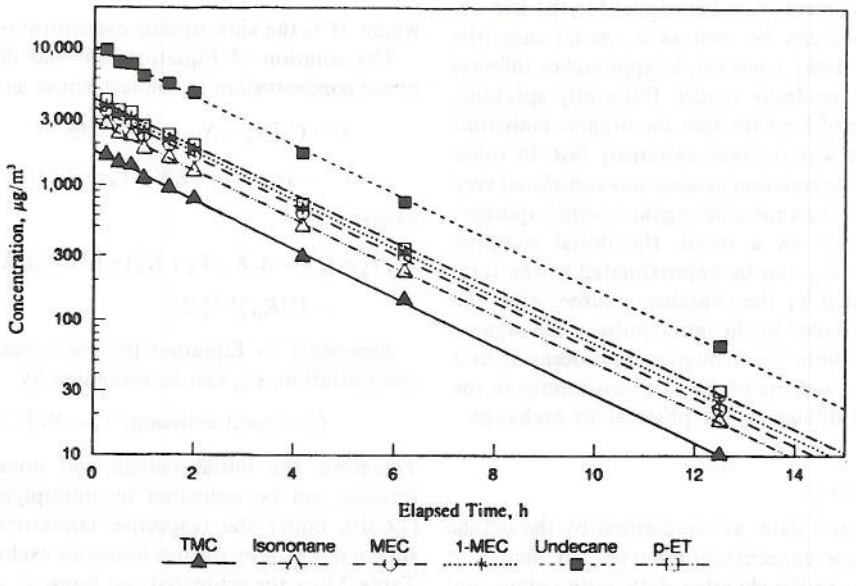

Fig. 3. Environmental chamber time-history data of six organic species.

The means and standard deviations of N obtained by linear regression of the data are listed in Table 1. Table 1 shows that the standard deviations are mostly less than 5% of the corresponding means which indicates that the slopes of the concentration lines of the 11 organic species shown in Figs 2 and 3 all have about the same value.

Model comparison

Previous data have shown that the organic emission rates from wood-finishing products could be represented by a first-order decay model (Tichenor and Guo, 1988; Clausen *et al.*, 1990; Colombo *et al.*, 1991):

$$R = R_o e^{-kt}, \tag{3}$$

where R is emission rate ($\mu g\,m^{-2}\,h^{-1}$), R_o is initial emission rate ($\mu g\,m^{-2}\,h^{-1}$) and k is emission rate decay constant (h^{-1}).

Application of the law of mass balance gives the chamber exit concentration as a function of time:

$$C = AR_o\,(e^{-kt} - e^{-Nt})/[V(N-k)], \tag{4}$$

where A is the area of surface being waxed (m^2) and V is volume of the test chamber (m^3).

Usually the value of N is less than 1.0. Therefore, when k is considerably greater than 1.0, Equation (4) can be reduced to:

$$C = (AR_o/Vk)e^{-Nt}. \tag{5}$$

Equations (5) and (2) are essentially identical when one lets:

$$C_o = (R_o/k)A/V. \tag{6}$$

Since R_o/k represents the total quantity of the organic species emitted per unit waxed area (Guo *et al.*, 1990a), Equation (6) indicates that C_o is equivalent to the total available emissions of the organic species divided by the chamber volume.

Therefore, current chamber model for the fast organic emissions can be seen as a special case (the emission rate decay constant, k, approaches infinity) of the first-order decay model. Physically speaking, the high value of k means that the organic emissions from the floor wax decayed extremely fast. In other words, the whole emission process was completed very quickly and all the emittable organics were vaporized almost instantly. As a result, the initial chamber concentration, C_o, can be approximated as the total emission divided by the chamber volume. After the chamber was loaded by the initial pulse of the organic emissions, the floor wax emission rate decayed to a negligible level and the organic concentrations in the chamber were diluted by the physical air exchange.

Test house data

The test house data, as represented by the octane and the nonane concentration curves, are shown in Fig. 4. Similar to the chamber data, both octane and nonane curves exhibit a maximum concentration with the first sample which was taken about 12 min after the start of the floor wax application. The octane and nonane concentrations decreased monotonically as the experiment proceeded. But, unlike the chamber data, the concentration decreases did not follow a straight line on a semi-logarithmic scale.

IAQ model

The organic emissions from the applied floor wax were the major source of octane and nonane in the test house. The instant emission model based on the chamber results is adopted as the source model. The sink effects which reflect the sorption and desorption phenomena of the interior surfaces are simulated by a first-order reversible sink model (Guo *et al.*, 1990b). This model assumes that the rates of sorption and desorption of the sinks are directly proportional to the gas-phase and the sink surface organic concentrations, respectively. At equilibrium, the sorption rate equals the desorption rate and gives the following relationship:

$$K_a C_e = K_d M_e, \tag{7}$$

where K_a is the sorption rate constant ($m\,h^{-1}$), C_e is the gas-phase organic concentration in equilibrium with M_e (the sink surface concentration) ($\mu g\,m^{-3}$), K_d is the desorption rate constant (h^{-1}) and M_e is the sink surface concentration in equilibrium with C_e ($\mu g\,m^{-2}$).

Based on the source and sink models, an integrated IAQ model is developed by the consideration of mass balance applied to the test house:

$$dC/dt = -NC - K_a A_s C/V_h + K_d A_s M/V_h \tag{8}$$

and

$$dM/dt = K_a C - K_d M \tag{9}$$

with initial conditions:

$$\text{at} \quad t=0, \quad C=C_o \quad \text{and} \quad M=0,$$

where M is the sink surface concentration ($\mu g\,m^{-2}$).

The solution of Equations (8) and (9) gives gas-phase concentration in the test house as:

$$C = C_o[(r_1 - N - A_s K_a/V_h)e^{-r_2 t} - (r_2 - N - A_s K_a/V_h)e^{-r_1 t}]/(r_1 - r_2), \tag{10}$$

where

$$r_1, r_2 = \{(N + A_s K_a/V_h + K_d) \pm [(N + A_s K_a/V_h + K_d)^2 - 4NK_d]^{1/2}\}/2. \tag{11}$$

According to Equation (6), the initial test house concentration, C_o, can be estimated by:

$$C_o = (\text{total emission})/V_h = N(\int C\,dt). \tag{12}$$

Therefore, the initial octane and nonane concentrations can be estimated by multiplying the area, $(\int C\,dt)$, under the respective concentration curves shown in Fig. 4 by the test house air exchange rate, N. Table 2 lists the estimated test house C_os for nonane and octane.

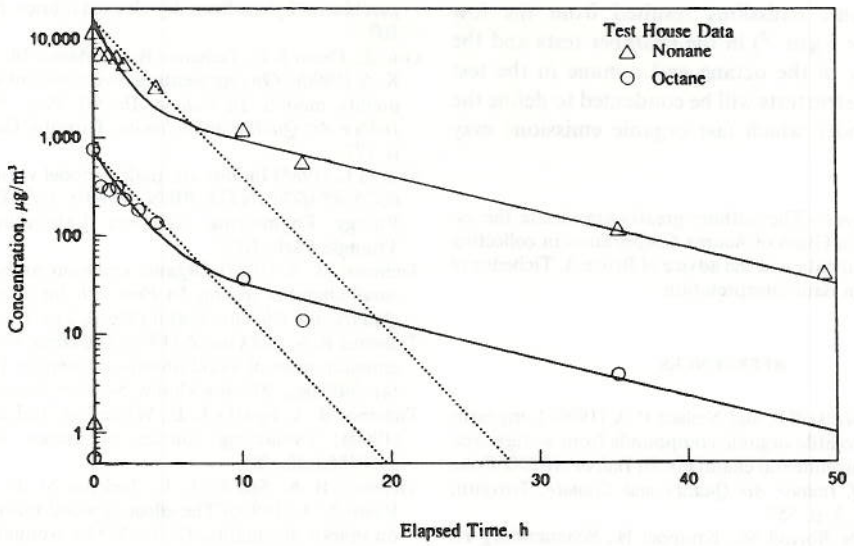

Fig. 4. Comparison of test house octane and nonane data with the predictions of the IAQ models with sinks (solid curves) and without sinks (dotted lines).

Table 2. Estimated values of parameters used by IAQ models for predictions of test house nonane and octane concentrations

	Nonane	Octane
C_o ($\mu g/m^3$)	15,900	730
N (h^{-1})	0.37	0.37
A_s (m^2)	400	400
V_h (m^3)	300	300
K_a ($m\,h^{-1}$)	0.252	0.121
K_d (h^{-1})	0.185	0.135
r_1 (h^{-1})	0.806	0.580
r_2 (h^{-1})	0.085	0.086

Sink effects

Using the values of the parameters (N, A_s and V_h) listed in Table 2, the values of K_a and K_d were estimated by the best fit of the test house nonane and octane data shown in Fig. 4 by the IAQ model represented by Equations (11) and (12). The results of the best-fit analysis for K_a and K_d are shown in Table 2. Figure 4 shows the comparison of the IAQ model predictions (solid curves) with the test house nonane (triangles) and octane (circles) data.

Also shown are the predictions (dotted lines) of the model without the consideration of sink effects ($K_a = K_d = 0$). It is seen that, if there were no sink effects, the test house octane and nonane concentrations should have decreased rapidly and reached the background levels (octane 0.6 $\mu g\,m^{-3}$ and nonane 1.2 $\mu g\,m^{-3}$) within 20 and 25 h, respectively. However, Fig. 4 shows that the test house octane and nonane concentrations were still at least one order of magnitude higher than the background levels, even at 30 h.

Therefore, data analysis by the IAQ models indicates that the prolonged decay of the test house octane and nonane concentrations is due to the sink effects. For the first few hours of the experiment, the octane and nonane emitted from the wax were sorbed by the sinks which caused the test house concentrations to be slightly less than the no-sink model predictions (Fig. 4, dotted lines). However, when the test house concentrations decreased, the sorbed octane and nonane re-emitted from the sinks very slowly. The sink re-emission effects caused the test house octane and nonane concentrations to stay above the background levels for more than 50 h as shown in Fig. 4.

SUMMARY

The fast organic emissions from an acrylic floor wax have been characterized by environmental chamber data. The chamber exit organic concentrations can be described by a model which assumes that all the organics were emitted immediately after the application of the wax. An IAQ model was developed based on the instant emission source model and the first-order sink model. Analysis of the IAQ test house data indicates that there were significant sink effects. The sink effects caused elevated concentrations of octane and nonane in the test house to persist longer than the wax emission alone could have. As a result, the sink effects increased the risk of long-term exposure to organics, even from instant emission sources.

Model comparison indicates that the fast emission pattern can be seen as a special case of the emission pattern described by the first-order decay model reported previously (Tichenor and Guo, 1988; Clausen *et al.*, 1990; Colombo *et al.*, 1991). It is suspected that

the fast organic emissions resulted from the low application ($<5\ g\ m^{-2}$) in the chamber tests and the high volatility of the octane and nonane in the test house. Parametric tests will be conducted to define the conditions under which fast organic emissions may prevail.

Acknowledgements—The authors greatly appreciate the assistance of Kevin Gunn of Acurex Corporation in collecting the experimental data and the advice of Bruce A. Tichenor of the U.S. EPA in data interpretation.

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