

Characterization of Organic Emissions from a Wood Finishing Product – Wood Stain

John C. S. Chang¹ and Zhishi Guo²

Air and Energy Engineering Research Laboratory, North Carolina, USA

Abstract

The emission characteristics of four organic compounds (nonane, decane, undecane, and 1,2,4-trimethylbenzene) from wood stain have been measured in an environmental chamber. It was found that the emission patterns of the four organic compounds can be described by a two-phase model. Phase 1 represents the period when the wood stain is relatively wet. Phase 2 is when the wood stain becomes relatively dry. The changes of emission mechanisms between the two phases were reflected by the significantly different emission rate constants measured during the two periods and the relationship between the relative rate constant, the relative vapor pressure, and the relative diffusivity. A double-exponential model was established that can be used to predict the relative emission rates of the four organic compounds from the wood stain.

Introduction

The emission patterns of organic compounds from wet sources (e.g., stains, paints, waxes, caulks, and additives) are very different from those of dry sources (e.g., particle board, plywood, and moth crystal cakes). Studies have shown that the emission rates of organics from dry sources are usually near constant or slow decay and can be described by the evaporative diffusion processes (Tichenor et al., 1990; Meyer, 1986). However, the organic emission rates from wet sources are complicated by the drying processes (Tichenor, 1987).

The U.S. Environmental Protection Agency is conducting research to evaluate the processes affecting the emission rates of organic compounds from wet sources and their impacts on indoor air quality. This paper presents environmental chamber testing results on wood stain. The environmental chamber was made of electro-polished stainless steel to minimize the sink effects. The emission data of four organic compounds – nonane (C_9H_{20}), decane ($C_{10}H_{22}$), undecane ($C_{11}H_{24}$), and 1,2,4-trimethylbenzene (C_9H_{12}) – from wood stain brush-painted on hardwood board are reported. The data are interpreted with a two-phase emission model with the objectives of evaluating the relative emission rates, emission mechanisms, chamber concentrations, and total emissions of the four organic species. The model does not account for sink effects in the chamber, if any.

KEY WORDS:

Organics, Emissions, Patterns, Model, Mechanisms, Wood stain.

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¹ Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

² Acurex Corporation, P.O. Box 13109, Research Triangle Park, NC 27709

Test Facility

Environmental chambers (166 l each) were used to characterize the organic emissions (Tichenor and Guo, 1988). Prior to each run, the chambers were purged with clean air for several hours before placing samples in the chamber. Wood stain was brush-painted (as suggested by the manufacturer) on hardwood (poplar) boards that had their edges sealed with sodium silicate. The solvent in the wood

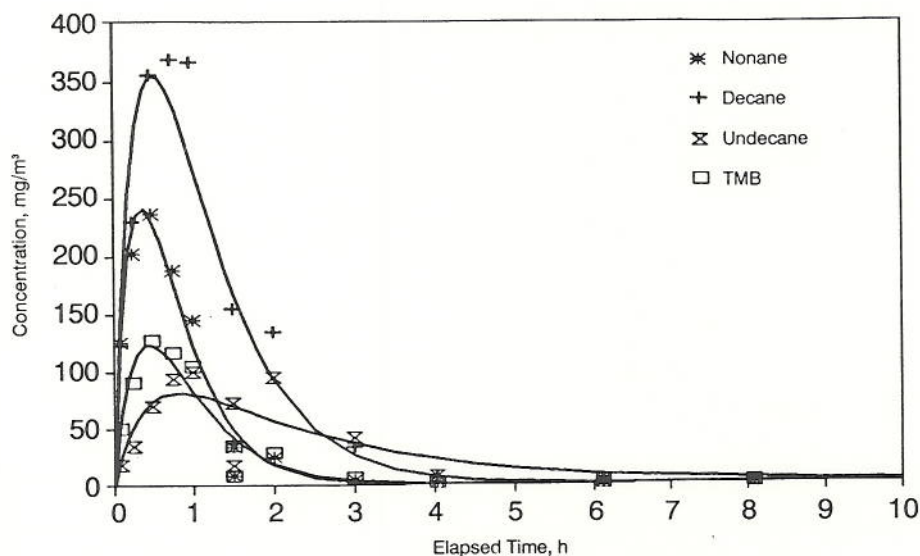


Fig. 1 Comparison of the first 10-h chamber data with model predictions for run WF-2.

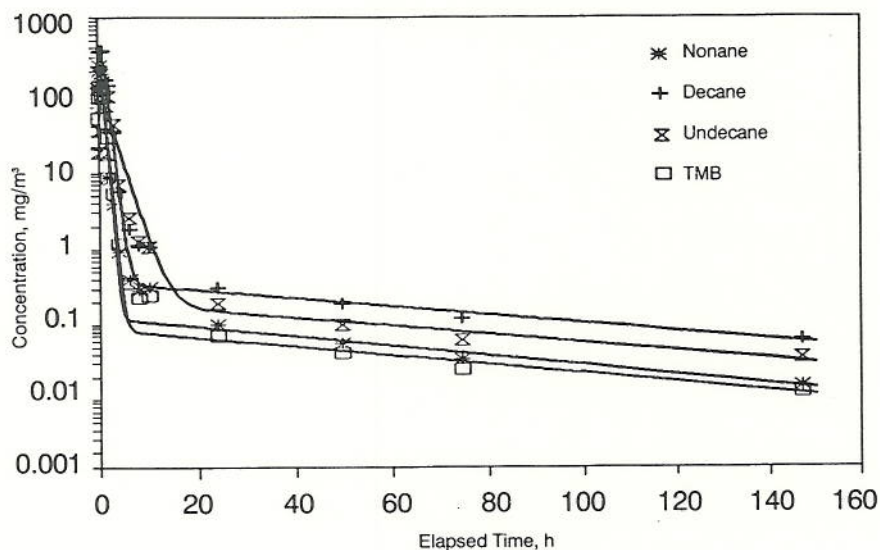


Fig. 2 Comparison of the entire run chamber data with model predictions for run WF-2.

stain was mineral spirits. The major organic species in the mineral spirits included nonane, decane, undecane, and trimethylbenzene. The painted samples were placed in the chamber shortly (less than 6 minutes) after the wood stain was applied. The test start ($t = 0$) was established when the door to the chamber was closed. The flow of clean air through the chamber (the air exchange rate) was maintained at a constant level for each run. A fan in each chamber ensured complete mixing. The organic concentrations in the air exiting from the chamber were collected by adsorption on Tenax tubes. The collected samples were thermally desorbed and analyzed by a gas chromatograph (GC) equipped with flame ionization detectors (FIDs). All testing was conducted at 23 °C and 50% relative humidity. Table 1 shows the

experimental conditions of each run. The symbols of the table are defined in the following.

Experimental Data

Typical results of a chamber testing (run WF-2) are illustrated in Figures 1 (for the first 10 h) and 2 (for the entire run). The concentrations of the four organic compounds – nonane, decane, undecane, and 1,2,4-trimethylbenzene (TMB) – were measured at an air exchange rate (N) of 2.5 h^{-1} and a painted area (A) equal to 0.116 m^2 . The figures show that the concentrations of all four compounds basically followed the same trend. The concentration of each species first increased rapidly, reached a peak within 2 h, and then declined by two to three orders of magni-

tude within 10 h. After the rapid decline, the rate of concentration decrease slowed down considerably and lasted for a long period of time. After 6 days of the test, the chamber concentration of each organic compound was still well above the background level. (The background level of the four organic compounds was less than 0.003 mg/m³ for run WF-2.)

Data Analysis

To mathematically analyze the data, the concentration curve of each organic species is divided into

two phases. Phase 1 is the rapid change period which includes the initial increase, the peak, and the fast decrease sections (the concentrations decreased by at least two orders of magnitude from the maximum in less than 10 h) of the curve. Phase 2 is the slow decline period which lasts for several days.

Phase 1

Models have been proposed to analyze the chamber data and to estimate emission rates (Tichenor and Guo, 1988; Dunn and Tichenor, 1988; Clausen et al., 1990; Colombo et al., 1991). For the phase 1 results a

Table 1. Experimental conditions and results.

Run No.	N, h ⁻¹	Painted Area, m ²	Compound	R ₁ , mg/m ² /h	k ₁ , h ⁻¹	R ₂ , mg/m ² /h	k ₂ , h ⁻¹
WF-1	4.7	0.216	Nonane	6643	10.02	0.64	0.025
			TMB ^a	2816	6.22	0.47	0.024
			Decane	6673	4.16	1.79	0.022
			Undecane	1103	1.57	1.02	0.022
WF-2	2.5	0.116	Nonane	2499	2.83	0.44	0.016
			TMB	1063	1.91	0.31	0.015
			Decane	2659	1.39	1.31	0.014
			Undecane	425	0.47	0.72	0.014
WF-3	0.36	0.0166	Nonane	2016	2.52	1.10	0.019
			TMB	1320	1.73	0.97	0.016
			Decane	2489	1.34	2.63	0.015
			Undecane	594	0.71	1.27	0.014
WF-4	0.36	0.216	Nonane	220	0.59	1.41	0.020
			TMB	96	0.34	1.24	0.018
			Decane	242	0.22	5.34	0.018
			Undecane	N/A ^b	N/A	3.35	0.018
WF-5	4.7	0.116	Nonane	3412	4.77	1.17	0.026
			TMB	1835	3.89	1.00	0.026
			Decane	4803	2.87	4.40	0.025
			Undecane	813	1.09	3.30	0.033
WF-6	2.5	0.116	Nonane	1243	1.65	2.11	0.036
			TMB	579	0.99	0.76	0.028
			Decane	1520	0.65	6.03	0.029
			Undecane	319	0.24	6.65	0.035
WF-7	2.5	0.116	Nonane	N/A	N/A	N/A	N/A
			TMB	710	1.40	N/A	N/A
			Decane	2293	1.29	N/A	N/A
			Undecane	549	0.77	N/A	N/A
WF-8	0.36	0.219	Nonane	264	0.60	0.19	0.0073
			TMB	115	0.35	0.17	0.0063
			Decane	291	0.24	0.71	0.0054
			Undecane	51	0.10	0.52	0.0050
WF-9	4.7	0.216	Nonane	1534	3.36	N/A	N/A
			TMB	725	2.09	N/A	N/A
			Decane	1777	1.25	N/A	N/A
			Undecane	362	0.36	N/A	N/A

^a 1,2,4-trimethylbenzene

^b Not available due to insufficient data.

single-exponential, first-order decay model has been proven to be representative of the changes in the emission rate:

$$R(t) = R_i e^{-k_1 t} \quad (1)$$

Where,

- $R(t)$ = Phase I emission rate, $\text{mg}/\text{m}^2/\text{h}$
 R_i = Phase I initial emission rate, $\text{mg}/\text{m}^2/\text{h}$
 e = Natural log base
 k_1 = Phase I emission rate decay constant, h^{-1}
 t = Time, h

The mass balance for the chamber over a small time increment dt is:

$$dC/dt = (AR_i e^{-k_1 t}/V) - NC \quad (2)$$

Where,

- C = Chamber concentration, mg/m^3
 A = Painted area, m^2
 V = Chamber volume, m^3
 N = Air exchange rate, h^{-1}

With the initial condition of $C = 0$ at $t = 0$, the solution to Equation 2 is;

$$C = AR_i(e^{-k_1 t} - e^{-Nt})/[V(N - k_1)] \quad (3)$$

Table 2. Means and standard deviations^a of relative k_1 and k_2 .

Compound	Relative k_1	Relative k_2
Nonane	2.30 ± 0.39	1.20 ± 0.11
TMB ^b	1.42 ± 0.17	1.06 ± 0.06
Decane	1.00	1.00
Undecane	0.42 ± 0.10	1.05 ± 0.14

^a expressed as mean \pm standard deviation

^b 1,2,4-trimethylbenzene

Using a non-linear regression curve fit routine, implemented on a microcomputer, values of R_i and k_1 of each organic compound can be obtained by fitting Equation 3 to the first 10-h concentration vs. time data (as shown in Figure 1 for run WF-2). The non-linear regression values of R_i and k_1 for each organic compound tested are shown in Table 1.

The single-exponential model was developed based on the assumption that the emission rate from a unit area of the painted board is proportional to n , the amount of the organic compound on the surface in mg/m^2 (Guo et al., 1990). That is:

$$R(t) = -(dn/dt) = k_1 n \quad (4)$$

Equation 4 divides the emission driving force into two parts. One part, represented by n , is related to the quantity of the organic species on the surface.

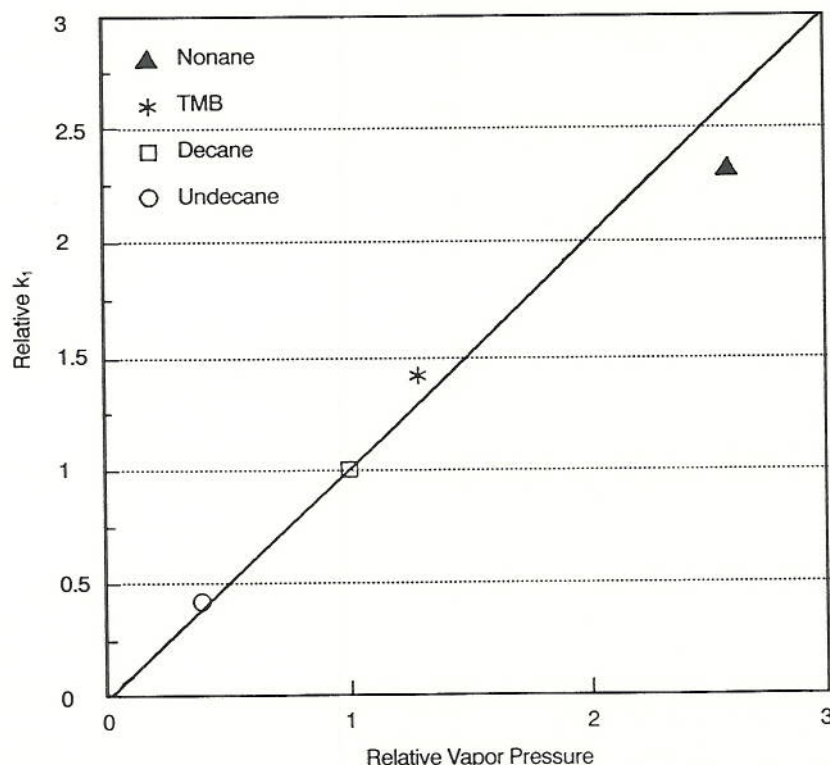


Fig. 3 Comparison of relative k_1 with relative vapor pressure.

Table 3. Values of coefficients (Weast, 1973) used by Equation 5.

Compound	A	B
Nonane	10456.9	8.332532
TMB ^a	10710.2	8.209013
Decane	10912.0	8.248089
Undecane	11481.7	8.260477

^a 1,2,4-trimethylbenzene

The other part, k_1 , should be a function of the physical/chemical conditions and the mass transfer mechanisms. Although the exact values of k_1 under different conditions are difficult to predict, the relative values of k_1 of the four organic compounds should reveal some clues which can lead to the identification of the controlling emission mechanisms.

Therefore, the data listed in Table 1 are further reduced by taking the relative values of k_1 . The relative k_1 is defined as the ratios of k_1 between the organic compounds by using the corresponding values of decane from the same run as the common denominator. For example, the relative k_1 of nonane and undecane was calculated as $k_{1,\text{nonane}}/k_{1,\text{decane}}$ and $k_{1,\text{undecane}}/k_{1,\text{decane}}$, respectively. The means and the standard deviations of the relative k_1 of the nine runs are listed in the first column of Table 2.

It is seen that the relative k_1 of each organic compound was fairly consistent among the nine runs, which is reflected by the relatively small standard deviations. Table 2 shows that the relative k_1 of nonane is considerably greater than that of decane and undecane. Figure 3 shows the comparison of the relative k_1 with the relative vapor pressure of the four organic compounds. The vapor pressure of

pure nonane, decane, undecane, and TMB at 23 °C was estimated according to the following equation (Weast, 1973):

$$\text{Log}_{10}P = (-0.2185A/T) + B \quad (5)$$

Where,

Log_{10} = Logarithm to the base 10

P = Pressure, Torrs

A = Molar heat of vaporization, cal/g-mole

T = Temperature, °K

B = Coefficient

The values of A and B for the four organic compounds are listed in Table 3.

Using the same definition as relative k_1 , the relative vapor pressure of nonane, decane, undecane, and TMB estimated by Equation 5 is 2.6, 1.0, 0.39, and 1.29, respectively. The almost one-to-one relationship between the relative k_1 and relative vapor pressure shown in Figure 3 indicates that the emission rate of the four organic compounds in phase I was a strong function of volatility. It also implies that the emission was probably controlled by mechanisms related to evaporation processes.

For evaporation-related processes, the gas evaporated has to pass the gas-phase boundary layer which makes the gas-phase mass transfer part of the emission mechanisms. In an environmental chamber, the gas-phase mass transfer is usually a function of air exchange rate. When the air exchange rate increases, the emission rate should also increase as a result of the more turbulent air flow over the painted surface. In other words, the value of k_1 should

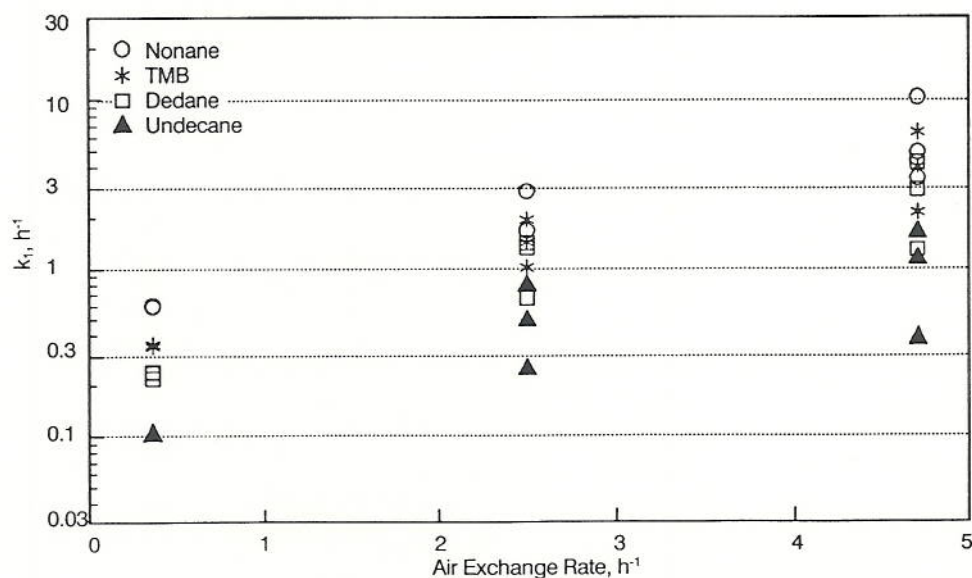


Fig. 4 Effects of air exchange rate on k_1 .

increase with the increase of air exchange rate. Figure 4 shows that, when k_1 is plotted against the air exchange rate, the data from the majority of the runs (except run WF-3) follow the trend.

Phase 2

It was found that the phase 2 chamber concentration data can also be described by an exponentially decreasing emission rate identical to that used for phase 1:

$$R(2) = R_2 e^{-k_2 t} = k_2 n \quad (6)$$

Where,

$R(2)$ = Phase 2 emission rate, $\text{mg}/\text{m}^2/\text{h}$

R_2 = Phase 2 initial emission rate, $\text{mg}/\text{m}^2/\text{h}$

k_2 = Phase 2 emission rate decay constant, h^{-1}

The chamber mass balance equation is identical to Equation 2 except that R_1 and k_1 are replaced by R_2 and k_2 . The initial condition of phase 2 has to be defined to solve the mass balance equation. However, this is rather difficult due to the uncertainty of the exact initiation time of phase 2. For estimation purposes, the initial condition, $C = 0$ when $t = 0$, was used to solve the mass balance equation of phase 2 which yields a concentration equation similar to Equation 3. The concentration equation derived from the mass balance was used to calculate the values of R_2 and k_2 . Because of the long-term nature of the phase 2 emissions, values of k_2 should not be affected by this initial condition substitution. Actually, values of $-k_2$ were found to be equal to the

slopes of the straight line sections of the phase 2 concentration curves shown in Figure 2.

The values of R_2 and k_2 , estimated by using data sampled after 20 hours, are listed in Table 1. The means and standard deviations of the relative k_2 are shown in the second column of Table 2. In contrast to relative k_1 (column 1 of Table 2), the values of relative k_2 of all four organic compounds (column 2 of Table 2) are not significantly different from each other. If Equations 4 and 6 can represent the emission rates of phases 1 and 2, respectively, comparisons of the two columns in Table 2 indicate that the organic emissions in the two phases were controlled by different emission mechanisms.

Table 1 shows that, in general, the values of k_2 are about two orders of magnitude smaller than that of k_1 . One likely scenario is that, in phase 2, the gas molecules had to diffuse from the rather dense paints embedded in the substrate through the small pores of the wood grain structure before they were released to the air, which made the phase 2 emission diffusion-controlled. From the kinetic theory of gases, the diffusivity of gases in porous solids (Knudsen diffusivity, D) can be expressed as (Bennett and Myers, 1982):

$$D = a/(M)^{0.5} \quad (7)$$

Where,

D = diffusivity, cm^2/s

a = parameter related to pore diameter and temperature, $(\text{cm}^2/\text{s})(\text{mole}/\text{g})^{0.5}$

M = molecular weight of the gas species, g/mole

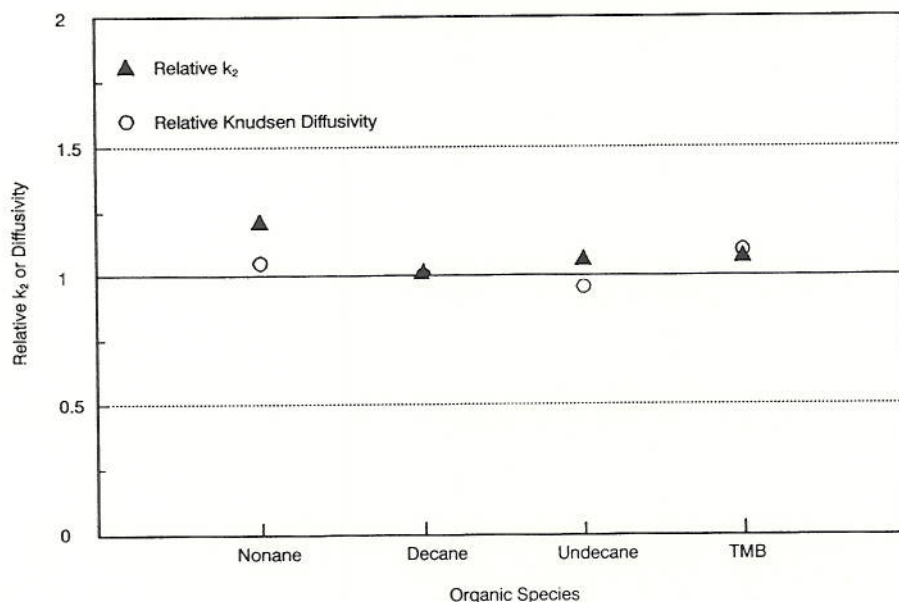


Fig. 5 Comparison of relative k_2 with relative Knudsen diffusivity.

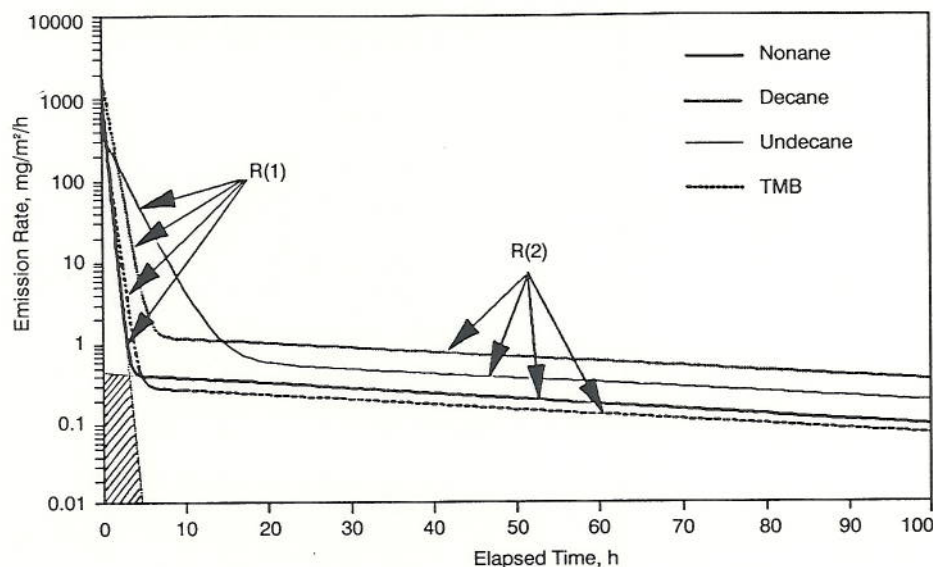


Fig. 6 Emission rates predicted by the double-exponential model for run WF-2.

Figure 5 shows the comparison of the relative k_2 with the relative Knudsen diffusivity of the four organic compounds. It is seen that, due to the narrow range of the molecular weight of the four organic compounds, all the relative Knudsen diffusivities are about 1.0, which is very similar to the values of relative k_2 . The similarity between the relative k_2 and the relative Knudsen diffusivity implies that the emissions of the four organic compounds in phase 2 were probably diffusion-controlled.

When diffusion through the solids is the controlling mechanism, the air exchange rate should have little effect on the phase 2 emission rate. In other words, the value of k_2 should be independent of the air exchange rate in the chamber. This trend is confirmed by the majority of the data (except run WF-8) shown in Table 1.

Double-exponential Model

Figure 6 shows the emission rates, $R(1)$ and $R(2)$, predicted by Equations 1 and 6, respectively, for run WF-2. The predictions were made by using the values of k_1 , k_2 , R_1 , and R_2 listed in Table 1. It is seen that, during most of phase 1, $R(1)$ is considerably larger than $R(2)$. However, $R(1)$ decays so fast that, in phase 2, $R(2)$ becomes dominant. This is because the values of R_1 and k_1 are significantly higher than those of R_2 and k_2 .

Since $R(1)$ and $R(2)$ dominate in phases 1 and 2, respectively, it was found that the two-phase time-concentration curves shown in Figures 1 and 2 can be simulated by a concentration equation which is the algebraic sum of those of phases 1 and 2 which implies a double-exponential model:

$$R = R(1) + R(2) = R_1 e^{-k_1 t} + R_2 e^{-k_2 t} \quad (8)$$

Comparisons of the chamber nonane, decane, undecane, and TMB concentrations with the predictions of the double-exponential model for run WF-2 are shown in Figures 1 and 2.

Physically speaking, phase 1 probably corresponds to the period when the wood stain applied was still relatively wet. The evaporation-like process makes the initial emission rates rather fast. But the fast emissions also cause the depletion of the organic compounds which resulted in the rapid decline of the emission rates as shown in Figure 6. Phase 2 corresponds to the period when the wood stain applied is relatively dry. The organic species has to diffuse through the substrate, making the emission rates low, but the emission lasted for a long time (see Figure 6). This is evidenced by the experience that one could still smell the characteristic odor of wood stain, although very light, even a few days after its application.

The over-estimation caused by using Equation 8 as an approximation technique for total emission, mainly due to the overlap of $R(1)$ and $R(2)$, is expected to be insignificant. For example, the error caused by Equation 8 for nonane emission in run WF-2 is represented by the shaded area of the tetrahedron in the left-bottom corner of Figure 6. It is seen that most errors occur in phase 1. Compared with the total emission, which is represented by the total area under the solid curve, the error is almost negligible (notice the logarithmic scale).

Summary

The emissions of nonane, decane, undecane, and TMB from wood stain were measured in an environmental chamber. The chamber concentrations were characterized by a two-phase emission pattern. A double-exponential mathematical model was adopted based on the two-phase emission analysis to simulate the time-concentration curves obtained from the environmental chamber. When the organic emission rates of the two phases are sufficiently different, the double-exponential model can be used as an approximation of the entire two-phase emissions.

The model calculations indicate that evaporation-like mechanisms were controlling the emissions of the four organic compounds during phase 1, which covers the first few hours after applying the wood stain. This mechanism was evidenced by the strong influence of vapor pressure and gas-phase mass transfer on the estimated emission rates.

The phase 2 emission rates measured are considerably lower than those in phase 1. The emission rates also decayed very slowly, which made phase 2 last for several hundred hours. It was suspected that the phase 2 emission was controlled by the diffusion of the organic species through the relatively dry paint, which made the emission rates of all four organic compounds decay in a similar fashion. The diffusion control mechanism is also supported by the evidence that little effect of gas-phase mass transfer on the phase 2 emission rates was found.

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