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Fundamental Mass Transfer Model for Indoor Air Emissions from Surface Coatings

Bruce A. Tichenor[1], Zhishi Guo[2] and Leslie E. Sparks[1]

Abstract

Emissions from freshly applied paints and other coatings can cause elevated indoor concentrations of vapor-phase organics. Methods are needed to determine the emission rates over time for these products. Some success has been achieved using simple first-order decay models to evaluate data from small dynamic test chambers. While such empirical approaches may be useful for assessing the emission potential of indoor sources, a more fundamental approach is needed to fully elucidate the relevant mass transfer processes. As a first step, a simple model based on boundary layer theory has been developed. In this model, the mass transfer rate is assumed to be controlled by the boundary layer mass transfer coefficient, the saturation vapor pressure of the material being emitted, and the mass of volatile material remaining in the source at any point in time. Static and dynamic chamber tests and test house experiments were conducted to obtain model validation data. Preliminary validation results indicated that the model can be applied to different products with similar solvents. The model provides a better fit to chamber-derived emissions data than the empirical first-order decay model, especially over the decaying portion of the concentration vs. time curve.

KEY WORDS:
Volatile organic compounds, Emission model, Mass transfer processes, Boundary layer coefficient

Introduction

Indoor concentrations of total VOCs (volatile organic compounds) of several hundred to several thousand milligrams per cubic meter can occur after petroleum-based interior coatings are used (Schriever and Marutzky, 1990; Tichenor et al., 1990; Sparks et al., 1991). Small environmental test chambers have been used to develop emission rate data for such products (Tichenor, 1990; American Society for Testing and Materials, 1990). These tests involve placing samples of coated substrates in the chambers and measuring total VOC (or individual compound) concentrations at various times as the coatings dry. The concentration vs. time data are then used to determine the parameters of empirical emission rate models. The first-order decay model is probably the most common (Tichenor and Guo, 1991):

$$R = R_0 e^{-kt} \qquad (1)$$

where R = VOC emission rate (mg/m^2-h) at time t, R_0 = VOC emission rate (mg/m^2-h) at time zero, k = first-order emission rate decay constant (h^{-1}), and t = time (h). In order to fit a wider variety of chamber concentration vs. time curves, a double exponential decay model has also been developed (Colombo et al., 1990). While empirical models often do a reasonable job of describing emission rates, they do not provide a physical description of the emission process, nor do they separate the parameters describing the source from those describing the environment. In addition, first-order emission rate decay models are often deficient in characterizing the "tail" of the emission curve for rapidly decaying sources. For these reasons, models based on fundamental mass transfer processes need to be developed and validated for indoor sources.

The emissions of solvents from indoor coatings are controlled by physical processes, including

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[1] U.S. Environmental Protection Agency, Air and Energy Engineering Research Laboratory, Indoor Air Branch (MD-54), Research Triangle Park, NC 27711 (Fax (919) 541-2157)
[2] Acurex Environmental Corporation, P.O. Box 13109, Research Triangle Park, NC 27709

evaporation and internal diffusion (Sullivan, 1975). Evaporative mass transfer rates are limited by resistance in the gas phase, and internal diffusion rates are limited by resistance in the coating film. In general, evaporation is the predominant mechanism early in the drying process. For latex paints, Hansen (1974) found that internal diffusion was not a controlling factor in water-based paints and that evaporation controlled the loss of volatiles "even at very long times". Clausen et al. (1991) assumed that both mechanisms were important and developed empirical models that included consideration of the paint film thickness. While these studies properly accounted for the relevant mass transfer processes, they did not propose emission models that include evaporative mass transfer coefficients based on both the source (e.g., paint) and the mass transfer zone (e.g., boundary layer). Axley (1991) presented models for sorption to and from indoor surfaces based on equilibrium adsorption and boundary layer diffusion-controlled adsorption. The model described herein is similar to classical chemical engineering models for gas-phase boundary layer diffusion-controlled mass transfer (Bennet and Myers, 1962).

Mass Transfer Model Development

The mass transfer model presented here is based on fundamental boundary layer theory. The model assumes that all mass transfer is by molecular diffusion across a laminar boundary layer at the source/air interface. According to Fick's First Law, the rate of mass transfer between the source surface and the indoor air is approximately given as:

$$R = -(D_f/\delta)(C - C_s) \qquad (2)$$

where D_f = molecular diffusivity (m^2/h), δ = boundary layer thickness (m), C = VOC concentration (mg/m^3) in the bulk air, and C_s = vapor pressure (expressed as concentration) of the surface (mg/m^3). The ratio D_f/δ represents the mass transfer coefficient, k_m.

The model can be applied to individual compounds or mixed solvents. For mixtures, the model parameters are represented by the characteristic properties of the mixture, as discussed below.

(1) For a given wet product, all freshly applied surfaces have the same VOC equilibrium vapor pressure, C_v (mg/m^3), which is characteristic of that product. In other words, C_v is independent of the amount of coating applied. This assumption was examined using dynamic chamber experiments. Three different products (woodstain, polyurethane, and liquid wood floor wax) were tested at three different application levels (mg/m^2). Each of the three products contained mixed solvents (mineral spirits). Each data set was fit with the first-order decay model, and values of R_0 and k were calculated. Figure 1 shows values of R_0 vs. the mass applied. These data were analyzed using linear regression techniques (Li, 1957) and the following statistics were obtained: $r^2 = 0.28$, estimated regression coefficient (b) = 0.026, and F value = 2.77. Using the F distribution at the 5% level of significance, F = 5.59 for 1 and 7 degrees of freedom. Thus, the hypothesis that the true regression coefficient (β) = 0 is accepted, and no statistically significant relationship exists between R_0 and the mass applied. At time t = 0, $C_v = C_s$, $R = R_0$, and C = 0; thus, equating Equation 1 to Equation 2, R_0 is directly proportional to C_v. Accordingly, the assumption that C_v is independent of the amount of coating applied is confirmed.

(2) As the coated surface ages, the vapor pressures of the remaining VOC decrease gradually. If the fresh surface has a VOC vapor pressure of C_v and if M_0 (mg/m^2) is the initial mass per unit area of VOC applied, the vapor pressure C_s during the aging period is assumed to be proportional to the mass of VOC left, M (mg/m^2):

$$C_s = C_v(M/M_0) \qquad (3)$$

Figure 2 shows a linear relationship ($r^2 = 0.95$) between 1/k and the mass of material applied for the experiments discussed above. Thus, the testing showed that the greater the amount of material applied, the slower the decay, which is consistent with

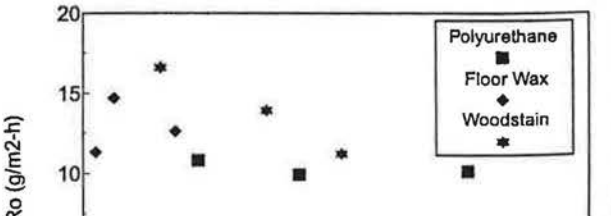

Fig. 1 Initial emission rate (R_0) vs. mass applied (small chamber tests).

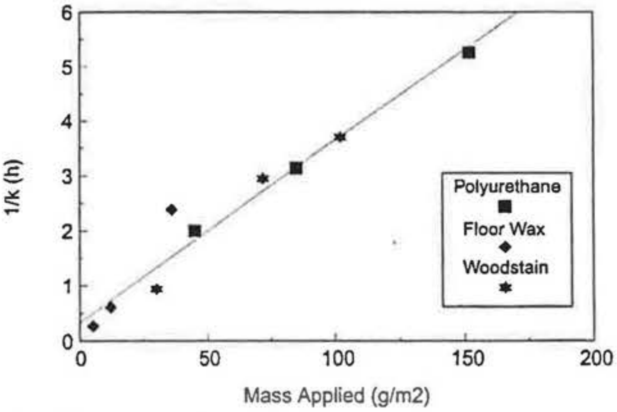

Fig. 2 Correlation ($r^2 = 0.95$) of 1/k with mass applied (small chamber tests).

Equations 1 and 3. Further experiments are planned to verify this assumption.

(3) The average gas phase diffusivity (D_f) of solvent molecules can be represented by the diffusivity of the most abundant component in the solvent mixture. The diffusivity of a given compound can be obtained through theoretical calculations; for example, the method of Fuller, Schettler, and Giddings (FSG) and the method of Wilke and Lee (Layman et al., 1982). The diffusivity values of consecutive alkanes, the major components of mineral spirits, are fairly close; with a molecular weight increase from C_8H_{18} (octane) to $C_{12}H_{24}$ (dodecane), the diffusivity decreases by only 20%. The average diffusivity for the five alkanes from C_8H_{18} to $C_{12}H_{24}$ is 0.0209 m^2/h, which is very close to the decane diffusivity of 0.0207 m^2/h.

Substitution of Equation 2 into Equation 3 gives:

$$R = -(D_f/\delta)\,[C - C_v(M/M_0)] \tag{4}$$

If dynamic chamber tests are conducted to validate the model, the mass balance equation for VOC in chamber air is:

$$V(dC/dt) = -QC - S(D_f/\delta)\,[C - C_v(M/M_0)] \tag{5}$$

where V = chamber volume (m^3), Q = chamber airflow rate (m^3/h), and S = source area (m^2). The mass balance for the VOCs in the source is:

$$S(dM/dt) = S(D_f/\delta)\,[C - C_v(M/M_0)] \tag{6}$$

For the initial conditions at $t = 0$, $C = 0$ (an empty chamber), and $M = M_0$. The solutions of Equations 5 and 6 give the following expressions for chamber concentration (Equation 7) and emission rate (Equation 8):

$$C = \{LC_vD_f/[\delta(r_1 - r_2)]\}[\exp(r_1t) - \exp(r_2t)] \tag{7}$$

where L = product loading = S/V (m^2/m^3) and $r_{1,2}$ is described by Equation 9.

$$\begin{aligned} R = -dM/dt = {} & \{C_vD_f/[\delta(r_1 - r_2)]\} \\ & [(r_1 + N)\exp(r_1t) - (r_2 + N)\exp(r_2t)] \end{aligned} \tag{8}$$

where N = Q/V = air exchange rate (h^{-1}), and:

$$\begin{aligned} r_{1,2} = {} & \{-[N + LD_f/\delta + D_fC_v/(\delta M_0)] \\ & \pm [(N + LD_f/\delta + D_fC_v/(\delta M_0))^2 \\ & - 4D_fNC_v/(\delta M_0)]^{1/2}\}/2 \end{aligned} \tag{9}$$

Model Validation

There are seven parameters in the mass transfer model: M_0, C_v, D_f, S, V, N, and δ. The first four are properties of the source, and the rest are properties of the environment. The mass transfer coefficient, k_m, is a function of the source (via D_f) and the environment (via δ). All of the model parameters can be determined or calculated independently.

The initial mass transfer model validation step involved small chamber testing of emissions of VOC from wood finishing products (Guo and Tichenor, 1992). First, emissions of woodstain were measured. All the parameters, except δ, were measured or known before the tests. Five sets of concentration vs. time data were obtained. The parameters used were: initial vapor pressure, $C_v = 22.8$ g/m^3 (based on static headspace measurement at 23°C); average diffusivity (based on the most abundant compound, decane), $D_f = 0.0207$ m^2/h; sample size, $S = 0.021$ m^2; chamber volume, $V = 0.053$ m^3; and air exchange rate, $N = 0.5$ hr^{-1}. The value of M_0 varied from test to test. The value of the mass transfer coefficient, obtained through non-linear regression, was $k_m = 0.85 \pm 0.13$ m/h. This value was used with $D_f = 0.0207$ m^2/h to calculate the boundary layer thickness, $\delta = 0.024 \pm 0.004$ m.

Chamber tests were then conducted for polyurethane and liquid wood floor wax using the same sample substrate (oak boards). These two products contain mixed solvents (mineral spirits) similar to those used in the woodstain; $C_v = 21.7$ g/m^3 for polyurethane and $C_v = 18.3$ g/m^3 for floor wax (based on static headspace analyses). The mass

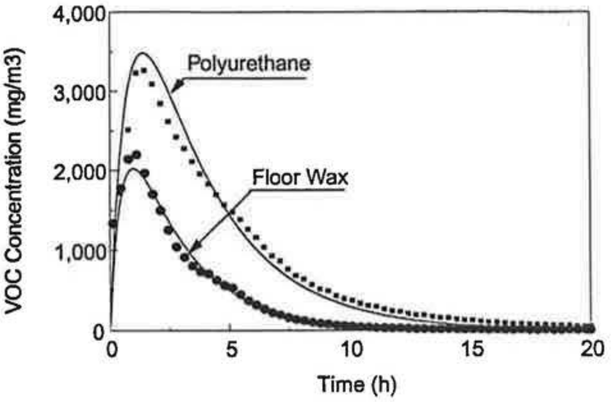

Fig. 3 Mass transfer model predictions for polyurethane and floor wax (small chamber tests).

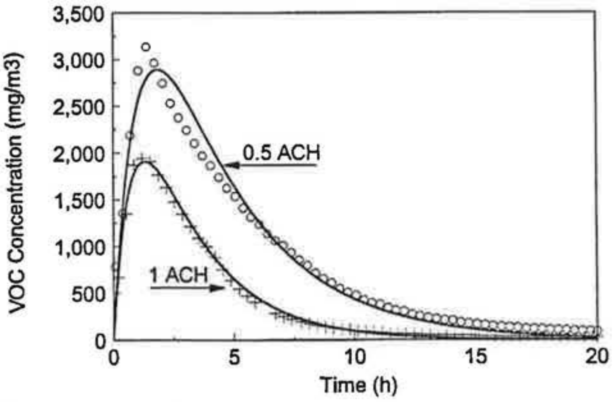

Fig. 4 Mass transfer model predictions for woodstain at two air exchange rates (small chamber tests).

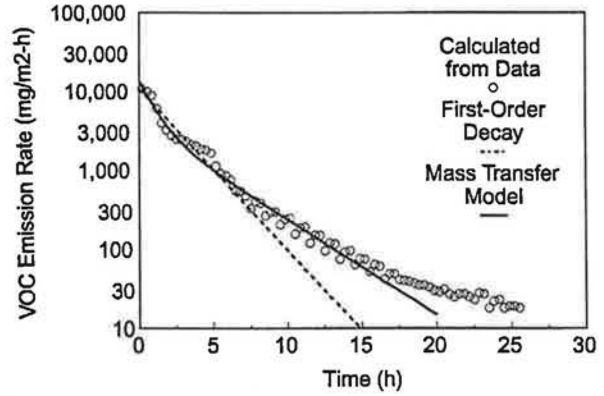

Fig. 5 Polyurethane emission rates predicted by mass transfer and first-order decay models (small chamber tests).

transfer model was used, with the k_m value obtained in the woodstain test, to predict the chamber concentration vs. time. Comparisons between model predictions (solid line) and chamber data are shown in Figure 3.

When the parameters change, the model adjusts itself automatically to give proper predictions. Figure 4 shows model predictions for two sets of woodstain data at different air exchange rates.

The emission rates predicted by the mass transfer model and the first-order decay model were compared with those directly calculated from chamber data for polyurethane. Figure 5 shows that the mass transfer model follows the experimental results more closely than the first-order decay model, even though the data depart from the predictions in the tail.

The next model validation experiment was conducted in an indoor air quality (IAQ) test house (Sparks et al., 1991). In order to provide a known source composition, a synthetic solvent was used. The solvent consisted of the following five alkanes with the mole fraction shown in parentheses: octane (0.1), nonane (0.2), decane (0.4), undecane (0.2), and dodecane (0.1). The solvent was applied to a new oak floor with an area of 6 m^2. VOC samples were collected on sorbents at two locations in the house. Air exchange rates were measured with carbon monoxide (CO) and SF_6 tracers. The experiments were conducted to determine the value of the mass transfer coefficient under various environmental conditions. In one test, a high air exchange rate was achieved by opening doors and windows. In another test, a ceiling fan at high speed was used to create elevated velocities at the floor level. Four tests were conducted with the test floor in the dining room (see Table 1).

Table 1 IAQ test house experiments with synthetic solvent

Test No.	Solvent coverage (g/m^2)	Air exchange rate (hr^{-1})	Ceiling fan (on/off)	Air velocity[a] (m/s)
1	32.2	0.40	off	0.08
2	33.6	0.41	off	0.08
3	36.4	3.0[b]	off	0.08
4	28.6	0.42	on	0.6

[a] Velocity measured 1.5 cm above the floor.

[b] Living room windows and back door open.

Table 2 Mass transfer coefficients determined from test house experiments

Test No.	Boundary layer thickness, δ (m)	Mass transfer coefficient, k_m (m/h)
1	0.016	1.3
2	0.015	1.4
3	0.014	1.5
4	0.003	6.9

The values of δ and k_m for each test were calculated (see Table 2) by fitting the test house data with an IAQ model (Sparks et al., 1991), including the effects of indoor sinks, using Equation 4 as the source model and using the following parameters: $D_f = 0.0207$ m²/h (the diffusivity of decane), $C_v = 18.6$ g/m³ (calculated for the mixture based on Raoult's Law and experimentally confirmed), and M_0 = solvent coverage (see Table 1). Note the elevated mass transfer coefficient for test 4 when a higher surface velocity occurred. Figure 6 shows the data and model fit for tests 1 and 4. The test house sinks included carpet floors and painted gypsumboard walls (Sparks et al., 1991). Langmuir sink behavior was assumed (Tichenor, et al., 1991).

The mass transfer model was further validated using concentrations of VOC from wood finishing products previously evaluated in the test house (Tichenor, et al., 1990). Emissions from woodstain, polyurethane, and floor wax were evaluated under conditions similar to tests 1 and 2, above. Since decane is the most prominent VOC for each of these sources, $D_f = 0.0207$ m²/h. Thus, for $\delta = 0.0155$ m (average of tests 1 and 2), $k_m = 1.34$ m/h. Values for M_0 were obtained by multiplying the amount applied (g/m²) by the VOC content as determined by ASTM Method D 2369-87 (Brezinski, 1989). C_v values (see above) were determined experimentally using static headspace analyses. Air exchange rates were determined by tracer gas measurements. Figure 7 shows IAQ model predictions, including the effects of indoor sinks, based on the mass transfer model for woodstain and floor wax; Figure 8 is for polyurethane. No curve fitting or parameter adjustments were made to achieve the predictions. Note that the experiments were conducted at different times.

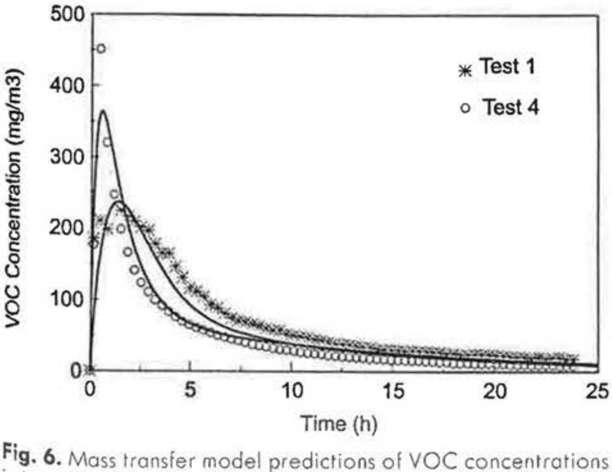

Fig. 6. Mass transfer model predictions of VOC concentrations in IAQ test house – synthetic stain.

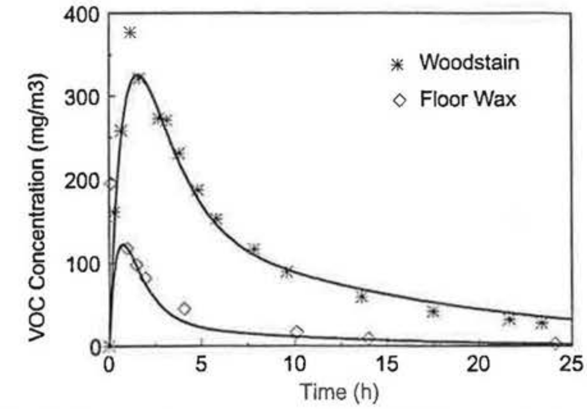

Fig. 7 Mass transfer model predictions of VOC concentrations in IAQ test house – woodstain and floor wax.

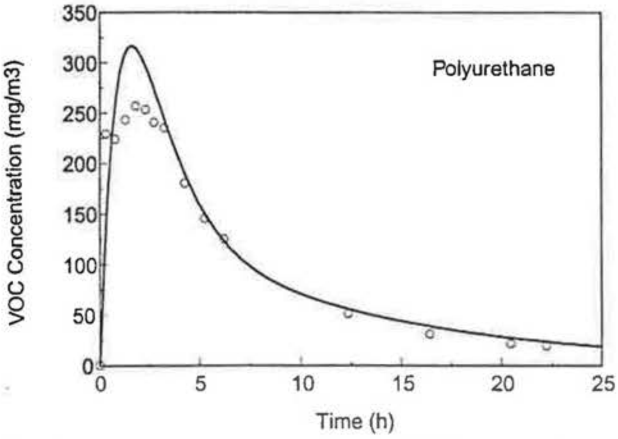

Fig. 8 Mass transfer model predictions of VOC concentrations in IAQ test house – polyurethane.

Discussion

A mass transfer model has been developed to predict VOC emission rates from indoor coatings. Validation results indicate that the mass transfer model can be applied to different products with similar solvents. The model provides a better fit to chamber-derived emissions data than an empirical first-order decay model. Test house validation results are also encouraging.

One of the major features of the mass transfer model is that all the parameters have clear physical definitions and can be either experimentally determined or calculated. The other desirable feature is that each parameter represents a property of either the source or the environment, but not both.

In addition, the development of fundamental mass transfer models may result in simpler, less expensive source tests methods. At present, empirical emission rate decay models require data from dynamic chamber experiments. Five to ten samples are needed to ensure a valid curve fit for such experiments. Source data (i.e., C_v and M_0) can be obtained from static chamber tests, and values for D_f are available in the literature or can be calculated. Estimates of δ for various indoor environments can be determined experimentally. Thus, emission rates based on mass transfer models can be obtained without resorting to more expensive and difficult dynamic chamber testing. Further validation of this approach is needed for a variety of indoor sources.

It is recognized that the mass transfer coefficient in test chambers can be different from those in full-scale indoor environments. Such differences may cause scaleup problems in the use of chamber-derived emission rates in IAQ models. Correlations of the Nusselt number with the Reynolds number are being developed to properly scale the mass transfer coefficient.

Summary

A fundamentally based mass transfer model has been developed to predict organic emission rates from oil-based indoor architectural coatings. Preliminary validation results indicated that the model can be applied to different products with similar solvents. The model provides a better fit to chamber-derived emissions data than the empirical first-order decay model, especially over the decaying portion of the concentration vs. time curve. Another benefit of developing mass transfer models is the potential to simplify methods for determining emission rates. The approach has been validated using data from test house experiments. Further validation studies are required for other common indoor coatings (e.g., latex paints).

References

American Society for Testing and Materials (1990) *Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions From Indoor Materials/Products*, Philadelphia, PA (ASTM Standard D-5116-90).

Axley, J.W. (1991) "Adsorption modelling for building contaminant dispersal analysis", *Indoor Air*, **2**, 147–171.

Bennet, C.O. and Myers, J.E. (1962) *Momentum, Heat, and Mass Transfer*, New York, McGraw-Hill.

Brezinski, J.J. (ed.) (1989) *Manual on Determination of Volatile Organic Compounds in Paints, Inks, and Related Coating Products*, Philadelphia, PA, American Society for Testing and Materials (ASTM Manual Series: MNL 4).

Clausen, P.A., Wolkoff, P., Holst, E. and Nielsen, P.A. (1991) "Long-term emission of volatile organic compounds from waterborne paints – methods of comparison", *Indoor Air*, **1**, 562–576.

Colombo, A., DeBortoli, M., Pecchio, E., Schauenburg, H., Schlitt, H. and Visser, H. (1990) "Chamber testing of organic emission from building and furnishing materials", *Science of the Total Environment*, **91**, 237–249.

Guo, Z. and Tichenor, B. A. (1992) *Fundamental Mass Transfer Models applied to Evaluating the Emissions of Vapor-Phase Organics from Interior Architectural Coatings*. Paper presented at the 1992 EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants, Durham, NC.

Hansen, C.M. (1974) "The air drying of latex coatings", *Industrial and Engineering Chemistry, Product Research and Development*, **13**, 150–152.

Layman, W.J., Reehl, W.F. and Rosenblatt, D.H. (1982) *Handbook of Chemical Property Estimation Methods*, New York, McGraw-Hill, pp. 9–17.

Li, J.C.R. (1957) *Introduction to Statistical Inference*, Ann Arbor, MI, Edwards Brothers Inc., pp. 244–268.

Schriever, R. and Marutzky, R. (1990) "VOC emissions of coated parqueted floors". In: Walkinshaw, D.S. (ed.) *Proceedings of Indoor Air '90*, Ottawa, Canada, Canadian Mortgage and Housing Corporation, Vol. 5, pp. 551–555.

Sparks, L.E., Tichenor, B.A., White, J.B. and Jackson, M.D. (1991) "Comparison of data from an IAQ test house with predictions of an IAQ computer model", *Indoor Air*, **1**, 577–592.

Sullivan, D.A. (1975) "Water and solvent evaporation from latex and latex paint films", *Journal of Paint Technology*, **47**, 60–67.

Tichenor, B.A., Sparks, L.E., Jackson, M.D., Guo, Z. and Rasor, S.A. (1990) "The effect of wood finishing products on indoor air quality". In: *Proceedings of the 1990 U.S. EPA/A&WMA International Symposium on Measurement of Toxic and Related Air Pollutants*, Raleigh, NC, pp. 968-973, (EPA 600/9-90-026 (NTIS PB91-120279)).

Tichenor, B.A. (1990) *Indoor Air Sources: Using Small Environmental Test Chambers to Characterize Organic Emissions from Indoor Materials and Products*, Research Triangle Park, NC, U.S. EPA, Air and Energy Engineering Research Laboratory (EPA/600/8-89-074 (NTIS PB90-110131)).

Tichenor, B.A. and Guo, Z. (1991) "The effect of ventilation on emission rates of wood finishing materials", *Environment International*, **17**, 317–323.

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**, 23–35.