

Comparison of Models used to Estimate Parameters of Organic Emissions from Materials Tested in Small Environmental Chambers

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Abstract

Two models, one physical and the other empirical, have been applied to the characterization of emission data of thin film products tested in small environmental chambers and have been compared in terms of emission results and ease of use. The physical model, being based on equations with coefficients bearing a physical meaning, is, in principle, more informative than the empirical one. However, it is uncertain whether it always gives accurate and unambiguous results. Moreover, in order to be exploited in a reasonable amount of time, it requires the use of non-linear regression routines, e.g. those from SAS Institute Inc., implemented on mainframes and, even then, it is often quite difficult to handle. The empirical model does not rely explicitly on physical effects. Although by definition it can only describe but not interpret the experimental data, it does estimate parameters describing the emission with an accuracy comparable to that of the physical model. It is easier to handle than the latter as it can employ non-linear regression routines such as those used on personal computers.

Introduction

Small environmental test chambers in which temperature, humidity, air exchange rate (i.e. the ratio between airflow rate and volume of the chamber) and product loading ratio (i.e. the ratio between sample area and volume of the chamber) can be controlled, are often employed to carry out investigations on volatile organic compounds (VOC) emitted from household products and building or furnishing materials under various test conditions.

The results of these experiments may serve for purposes such as establishing product/material ranking on the basis of emission characteristics and providing emission factors to estimate indoor population exposures through indoor air quality models.

Depending on the product/material source, emissions in the test chamber may be rather complex as far as their composition and variability over time are concerned. Individual compounds are often released in quite different amounts and with different time dependencies so that mathematical models commonly tuned to the emission profile of each individual compound (or of groupable compounds) are probably the most efficient tools for describing chamber emission data.

This paper compares, in terms of capability to describe the experimental data and of user friendliness, a relatively simple empirical model (Colombo et al., 1990) and a rather complex physical one (Dunn and Tichenor, 1988), both models being applied to well mixed chambers. The terms "simple" and "complex" refer to the increasing complexity of the algebraic equations defining the two models which, in turn, makes it increasingly difficult to obtain the equation coefficients through non-linear regression of chamber concentration on time data.

KEY WORDS:

Emission models, Emission rate, Environmental test chambers, Organic emissions, Volatile organic compounds.

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Description of Models

Empirical Model

This model has been successfully fitted to concentration/time data of a variety of emitting materials/products such as diffusion-limited thick sources (e.g. particle board, plywood, etc.) in which emission occurs over long periods of time (Colombo et al., 1990) and a thin film of products applied on inert supports (e.g. household products for surface cleaning or preservation) which usually exhaust within a few hours (Colombo et al., 1991). The above source distinction is relevant to the experimental procedure and to the emission characteristics but is immaterial to the model.

Basically, the time dependence of VOC concentrations in the chamber volume is described by the equation:

$$c = A[1 - \exp(-Bt)] - C[1 - \exp(-Dt)] \quad (1)$$

where, in consistent units, c (mg m^{-3}) and t (h) denote concentration and time, A , C (mg m^{-3}) are the linear coefficients and B , D (h^{-1}) are the rate coefficients of the equation.

Depending on the value of the coefficients, the model can fit to (a) data which, starting from zero, increase to a maximum and then decline towards zero or towards some intermediate steady state value and (b) data which simply increase with time and eventually reach a steady value. For the chamber concentration profiles met in practice A , B and D are positive. Case (a) occurs when $B > D$ and $1 < (AB/CD) < \infty$, case (b) when either $C \leq 0$ or $B \leq D$, the steady value being given in both cases by $A - C$.

For data that pass through a maximum and then approach zero, $A \approx C$, and the basic model may sometimes be simplified to:

$$c = A[\exp(-Dt) - \exp(-Bt)] \quad (2)$$

Analogously, for data that simply increase to a steady value, it may be found redundant and simplified to:

$$c = A[1 - \exp(-Bt)] \quad (3)$$

The principle of the extra-sum-of-squares (Draper and Smith, 1981; Kinniburgh, 1986), i.e. the statistical significance of the reduction of the residual sum of squares in passing from the simplified model to

the basic one, can in principle, at a given significance level (e.g. 5%), suggest which of them is preferable.

Using basic mathematics, the preferred equation can be integrated, differentiated or, e.g., C_{max} and t_{max} can be computed providing a number of emission parameters once its coefficients have been estimated.

Moreover, disregarding adsorption and desorption sites (i.e. sinks) in the chamber, one derives the following equation from the chamber mass balance over a small time increment dt for a given compound:

$$E = V(dc/dt) + Fc \quad (4)$$

which gives the emission rate E (mg h^{-1}) of the compound at any time, with V (m^3) the known volume of the chamber and F ($\text{m}^3 \text{h}^{-1}$) the known airflow rate through it.

Details, including considerations on the effect of disregarding sinks on emission rates, can be found in the paper previously referred to (Colombo et al., 1990).

Physical Model

This model applies only to thin film sources where "thin" means that emission is merely a surface phenomenon. As such it is not suitable for diffusion-limited thick materials. However, it may describe emissions from (a) materials applied as a thin film of mass decreasing with time (e.g. household products on inert supports) and (b) bulk materials which can mimic a thin film of mass constant for at least the duration of the experiment (e.g. a permeation device or a cake of moth crystal).

These two representations, referred to as *Decreasing Source* and *Constant Source* models, describe respectively chamber concentrations which increase from zero to a maximum and decline again to zero and those which simply increase to a steady value. Both are subdivided into four submodels of increasing complexity:

Dilution: the concentration of a compound in the chamber volume is the result of its emission at a rate proportional to its mass (decreasing or constant) in the source and of its release at the chamber outlet at a rate proportional (through the airflow) to its mass of vapour in the chamber.

Vapour pressure: as with the Dilution submodel, but with the additional assumption that the compound emission is contrasted by re-condensation of the compound itself at a rate proportional to its mass of vapour in the chamber.

Table 1 Supplementary information on chamber test conditions

Test No. and product type	Initial mass [g]	Delay ¹ [min]	Support material	Emitting surface area [cm ²]	Loading ratio [m ² m ⁻³]	Relative humidity [%]	Test duration [h]
1 liquid cleanser/disinfectant	1.1	2	ceramic paving tile	328	0.073	45 ± 1	24
2 liquid floor detergent ³	4.2	4	ceramic paving tile	1312	0.29	45 ± 1	24 ²
3 liquid floor detergent ³	2.1	2	ceramic paving tile	656	0.15	45 ± 1	9
4 spray cleanser for carpets	1.5	2	carpet	462	0.10	50 ± 1	9

¹ Time between application of the product on the support and its introduction into the chamber.

² 6.5 h for formaldehyde, detected by a different method; all measured compounds are reported in Table 2a.

³ Same product.

Sink: as with the Dilution submodel, but with the additional assumption that a reversible sink exists in the chamber which sorbs the compound at a rate proportional to its mass of vapour in the chamber and releases it at a rate proportional to the adsorbed mass.

Full: as with the Dilution submodel, but with the additional assumption that both Vapour pressure and Sink effects are present.

The mass balance of each submodel over a small time increment dt is seen as a set of ordinary differential equations, the solution of which provides a concentration vs. time analytical equation containing the rate coefficients it implies (from 2 to 5, respectively, including the known rate of release at the chamber outlet). Being dependent on the remaining mass of the compound in the source, the Decreasing Source submodels also contain its initial value as an additional equation coefficient. Unlike the empirical model, these coefficients have a physical meaning.

They are estimated by best-fitting the submodel analytical equations, from the simplest to the most complex, to the experimental data. These estimates can be used to calculate emission rates and other parameters of interest, the extra-sum-of-squares principle remaining as the basis for selecting the most suitable submodel. It is also worth mentioning that identical results can sometimes be given by different submodels.

For economy of space, the analytical equations have not been reported here but are given in the paper by Dunn and Tichenor (1988), to which the reader is referred.

The Decreasing Source-Dilution submodel can be shown to be equivalent to a model for the analysis of data from thin sources emitting approximately by a first order decay, suggested elsewhere (Tichenor, 1989).

Experimental Methods

Chamber Tests

The test equipment, including devices for controlling temperature, humidity and airflow rate of the chamber, as well as the validation of its performance and that of the gas chromatography-mass spectrometer analytical system have already been described in a previous paper (Colombo et al., 1990). The emitted compounds (in the volatility range C6 to C18) are sampled (at first as soon as possible and then every 5-15 min during the first hour and at increasing intervals later) on solid sorbent cartridges (Tenax or Carbotrap), desorbed thermally and injected in the gas chromatography capillary column after cryofocussing.

Chamber tests were carried out on products suitable for comparing the models. Therefore diffusion-limited thick sources were not considered for use.

Tests of products applied as a thin film on support materials representing a decreasing mass source were carried out at 23 ± 0.5 °C, air exchange rate (N) of 0.507 h⁻¹ (corresponding to a flow rate of 3.8 l min⁻¹ for the 450 l chamber) and relative humidity (RH) of 45 or $50 \pm 1\%$. Characteristics of products and supports, exact RH 's adopted and other information on test conditions, including product initial mass, loading ratio and test duration, can be found in Table 1.

Two experiments, later on referred to as tests No. 5 and No. 6, were carried out on permeation devices representing pseudo constant mass thin film sources. They consisted of glass vials almost completely filled with toluene, tetrachloroethene and 1,3-xylene, the opening of which was closed by a porous septum in order to achieve an appropriate emission rate. These two tests were performed for 96 and 120 h, respectively, at a chamber temperature of 23 ± 0.5 °C, RH of $40 \pm 1\%$ and N values of 1 and 0.525 h⁻¹, re-

Table 2a Comparison of models for emissions from decreasing mass sources (see footnote 1 at the end of Table 2b for an explanation of the reported values)

Test No. and compound	Model						
	Dilution	Vapour pressure	Sink	Full	Empirical (simplified)	Empirical (basic)	Trapezoid rule ²
No. 1							
Total VOC	34.1*	36.1	34.5	34.9	35.5*	34.9	
	0.145*	0.153	0.148 (100.0)	0.174 (97.6)	0.153*	0.180	0.181
	3.47*	3.68	3.55	4.29	3.68*	4.33	4.33
Bornyl acetate	29.9*	29.9	28.2	29.0	29.3*	28.7	
	0.113*	0.113	0.117 (100.0)	0.128 (97.7)	0.113*	0.133	0.132
	2.72*	2.72	2.81	3.15	2.71*	3.19	3.17
α -terpineol	0.362	0.582*	0.673		0.577*	0.578	
	0.00517	0.00888*	0.00873 (99.7)		0.00888*	0.00869	0.00961
	0.124	0.213*	0.210		0.213*	0.209	0.231
Camphene	0.130*	0.130	0.118		0.115*	0.117	
	0.00198*	0.00198	0.00282 (77.0)		0.00165*	0.00300	0.00296
	0.0476*	0.0476	0.0881		0.0397*	0.0720	0.0709
Camphor	1.14*	1.27	1.33		1.20*	1.19	
	0.00253*	0.00263	0.00265 (100.0)		0.00262*	0.00270	0.00284
	0.0608*	0.0631	0.0637		0.0629*	0.0649	0.0681
No. 2							
Total VOC	2.42*	2.42	2.07		2.34*	2.20	
	0.0128*	0.0128	0.0151 (99.6)		0.0124*	0.0203	0.0203
	0.307*	0.307	0.363		0.298*	0.487	0.487
Dicyclopentadiene alcohol	0.415*	0.444	0.380	0.411	0.442	0.420*	
	0.00343*	0.00381	0.00421 (99.9)	0.00520 (92.0)	0.00381	0.00557*	0.00527
	0.0824*	0.0916	0.101	0.136	0.0915	0.134*	0.126
Benzylalcohol	0.219	0.219	0.184*	0.187	0.183*	0.190	
	0.00217	0.00217	0.00187*(43.8)	0.00289 (51.8)	0.00157*	0.00209	0.00258
	0.0521	0.0521	0.103*	0.134	0.0376*	0.0501	0.0620
Menthol	³	³	1.31*	1.37	1.42	1.32*	
	0.00198	0.00198	0.00203*(95.1)	0.00221 (72.2)	0.00164	0.00226*	0.00220
	0.0475	0.0475	0.0513*	0.0736	0.0393	0.0543*	0.0528
Formaldehyde	2.96*	3.12	3.13		2.89*	2.89	
	0.0438*	0.0469	0.0469 (99.5)		0.0466*	0.0464	0.0482
	0.285*	0.305	0.307		0.303*	0.302	0.313
No. 3							
Total VOC	³	³	4.79*		5.06*	4.79	
	0.0281	0.0281	0.0237*(67.8)		0.0189*	0.0243	0.0247
	0.253	0.253	0.315*		0.170*	0.219	0.222
Dicyclopentadiene alcohol	1.60	1.60	0.823*	0.854	0.919	0.843*	
	0.00530	0.00530	0.00524*(78.1)	0.00527 (60.9)	0.00384	0.00531*	0.00533
	0.0477	0.0477	0.0604*	0.0779	0.0346	0.0478*	0.0479
Benzylalcohol	0.644	0.644	0.399*		0.398*	0.393	
	0.00341	0.00341	0.00240*(51.1)		0.00215*	0.00244	0.00262
	0.0307	0.0307	0.0424*		0.0193*	0.0220	0.0235
Menthol	³	³	6.20*		³	³ *	
	0.00519	0.00519	0.00432*(69.7)		0.00351	0.00435*	0.00422
	0.0467	0.0467	0.557		0.0316	0.0392*	0.0380
No. 4							
1-methoxy-2-propanol	58.6*	58.6	50.2		51.8*	50.4	
	1.23*	1.23	1.12 (69.0)		1.01*	1.11	1.16
	11.1*	11.1	14.6		9.12*	10.0	10.4
2-methoxy-1-propanol	1.31*	1.31	1.14		1.18*	1.14	
	0.0193*	0.0193	0.0188 (83.4)		0.0167*	0.0183	0.0191
	0.174*	0.174	0.203		0.150*	0.165	0.171

Table 2b Comparison of models for emissions from pseudo constant mass sources

Test No. and compound	Model							
	Dilution	Vapour pressure	Sink	Full	Empirical (simplified)	Empirical (basic)	Trapezoid rule ²	Compound weight loss ⁴
No. 5								
Toluene	0.594	0.594	0.635*	0.635	0.632*	0.643		
	0.594	0.594	0.632*(99.6)	0.632 (99.6)	0.630*	0.638	0.641	
	57.0	57.0	61.0*	60.9	60.5*	61.2	61.5	62.1
Tetrachloroethene	0.846	0.846	0.923*	0.922	0.916*	0.962		
	0.846	0.846	0.918*(99.5)	0.917 (99.5)	0.911*	0.944	0.942	
	81.2	81.2	88.6*	88.5	87.5*	90.6	90.4	90.4
1, 3-xylene	0.245	0.245	0.259*	0.259	0.259*	0.250		
	0.245	0.245	0.258*(99.7)	0.258 (99.7)	0.258*	0.250	0.250	
	23.5	23.5	24.9*	24.9	24.8*	24.0	24.0	23.8
No. 6								
Toluene	0.520	0.509*	0.571		0.511*	0.495		
	0.520	0.509*	0.509 (89.2)		0.512*	0.506	0.506	
	62.4	61.1*	68.5		61.4*	60.8	60.8	85.2
Tetrachloroethene	0.810	0.785*	0.922		0.790*	0.760		
	0.810	0.787*	0.786 (85.3)		0.792*	0.782	0.781	
	97.2	94.4*	110.6		95.1*	93.8	93.8	126.8
1, 3-xylene	0.229	0.225*	0.244		0.227*	0.223		
	0.229	0.226*	0.226 (92.4)		0.227*	0.225	0.225	
	27.4	27.1*	29.3		27.3*	27.0	27.0	37.8

¹ 1st row of each compound: initial and steady state emission rates (mg h^{-1}), respectively, for decreasing and pseudo constant mass compounds.

² 2nd row of each compound: mean emission rates (mg h^{-1}) over the test period calculated excluding the mass present in sink, if any; figures in brackets give the same quantity as percentage of the total mean emission rate (which includes the mass in sink).

³ 3rd row of each compound: total mass (mg) emitted during the test period including amount present in sink, if any, at the end of the test.

The equations required by the physical model for computing the above values may be found in Dunn and Tichenor (1988). Those for the empirical one are given in the text: Eqs. (1), (2) and (3) refer to the basic model, decreasing mass simplified and pseudo constant mass simplified submodels, respectively; whereas concentration (and, therefore, the mass of vapour in chamber) is directly provided, their integration over the test period, times the chamber airflow rate, is required to compute the mass released at the chamber outlet; Eq. (4) is used with the appropriate concentration equation to compute initial and steady state emission rates.

The asterisks indicate the best model on the basis of the extra-sum-of-squares principle at 5% significance level.

² From the sum of the trapezoid areas resulting from the linear interpolation of the experimental concentration-time values times the chamber airflow rate, plus the experimental residual mass of vapour in chamber.

³ Non realistic results with some models due apparently to a very fast concentration rise and insufficient number of data in that region.

⁴ From the weight of the vial before and after the experiment.

spectively (corresponding to airflow rates of 7.5 and 3.94 l min^{-1}).

Fitting Models to Data

Model coefficients were estimated by non-linear least squares regression of the experimental data sets using SAS procedure NLIN (SAS Institute Inc., 1985) on a mainframe computer.

This procedure, similar to routines from other software packages commercially available, iteratively minimizes the residual sum of squares for the equation under process and requires reasonable initial guesses of its coefficients for optimal convergence to final values. For this purpose the option of SAS procedure NLIN was used to specify a grid of initial guesses, i.e. several values for each coefficient. The set of values giving the smallest initial residual

sum of squares is automatically used to start the regression routine. Although in general this makes the task of guessing easier, it does not guarantee convergence, especially when several coefficients need to be estimated. Moreover, this option is not usually offered in personal computer packages, due to the computing time necessary to explore a reasonable sized grid. Guessing properly is important in terms of user friendliness and will be discussed in greater depth later.

Non-linear regression routines also require the specification of the equation to regress and usually of its partial derivatives with respect to the coefficients to estimate. Dr J.E. Dunn kindly provided us with detailed information for operating his physical submodels and with a diskette containing the elaborate SAS statements needed for them. Due to its

algebraic simplicity, setting up the NLIN procedure for the empirical model did not pose any particular problem.

Results and Discussion

The concentrations of "total VOC" (i.e. the integrated response of the FID detector, converted to toluene-equivalent concentration) and of the most abundant individual compounds were measured as a function of time and fitted by the above-mentioned models.

Table 2 (presented as 2a and 2b) reports the meaning and value of the most significant emission results obtained from the equations of the examined models. Void entries mean that in some instances, despite numerous attempts with a variety of guesses, SAS procedure NLIN did not meet its normal convergence criterion in 200 iterations or less. In those cases procedure NLIN only "assumed" convergence, yielding coefficient estimates affected by very large standard errors, indicating possible overparametrization of the model. Void entries for the "Trapezoid rule" and "Compound weight loss" columns are due to obvious reasons.

Table 2 shows that there were no substantial differences between the values of the initial or steady state emission rates of the physical and of the empirical model in general (1st row of values of each compound of the table) whether they were obtained by the "best" (in the sense of the extra-sum-of-squares principle) or by the most complex model available.

The 2nd row of values of each compound of Table 2 reports mean emission rates, i.e. the emitted mass divided by the test duration, all computed by including only the mass released at the chamber outlet and the residual vapour in the chamber. Therefore these results, including those from the Sink and Full models, may be compared with those obtained from the observed values by means of the trapezoid rule, which implies the same quantities. Quite often, the extra-sum-of-squares principle did not identify as best that model, either physical or empirical, which yielded the mean emission rate nearest to the trapezoid rule result, i.e. that model which adhered best to the experimental concentration profile. In this respect the most complex available model performed best in general, although it resulted as being the "best" model in some cases only.

The least squares linear relationships between model and trapezoid rule results for mean emission rate values (2nd row), which should ideally exhibit

an intercept of zero and a slope of one, are reported below and confirm the above statement. In fact, within the same kind of model and passing from the "best" to the most complex one, both the intercept and slope tend to improve, approaching zero and one, respectively.

"Best" physical	= -0.00573 + 1.0218
	Trapezoid
Most complex physical	= 0.00116 + 0.9794
	Trapezoid
"Best" empirical	= 0.00281 + 0.9407
	Trapezoid
Most complex empirical	= 0.00153 + 0.9823
	Trapezoid

If, to avoid the leverage effect of high values, only results less than 0.05 mg h⁻¹ are considered, one similarly obtains:

"Best" physical	= -0.00027 + 0.9061
	Trapezoid
Most complex physical	= -0.00013 + 0.9519
	Trapezoid
"Best" empirical	= -0.00057 + 0.9093
	Trapezoid
Most complex empirical	= 0.00006 + 0.9670
	Trapezoid

Examples of fits are given in Figures 1 and 2 for a decreasing and a pseudo constant mass compound, respectively.

It should be mentioned that in a few instances all physical (see Table 2a, total VOC and benzylalcohol for test No. 2) and empirical models (see Table 2a, benzylalcohol for test No. 2) gave results which were rather inconsistent with the trapezoid rule.

The 3rd row of values of Table 2 reports for each compound the total mass emitted during the test period including, besides the mass released at the chamber outlet and the residual vapour in the chamber, the amount present in the sink at the end of the test, where a sink is part of the model.

In practice, all decreasing mass compounds were entirely exhausted by the end of the experiment. Therefore for these compounds the values in the 3rd rows of Table 2a should also correspond to the total mass introduced into the chamber at the start of the experiment. Since in test No. 2 the same product was investigated as in test No. 3 but double the amount was applied to a surface twice as large (see Table 1), the total masses of total VOC and of the

Table 3 Total emitted mass ratios for the compounds of tests No. 2 and 3

Compound	Model				
	"Best" physical	Most complex physical	"Best" empirical	Most complex empirical	Trapezoid rule
Total VOC	0.97	1.15	1.75	2.22	2.19
Dicyclopentadiene alcohol	1.36	1.75	2.80	2.80	2.63
Benzylalcohol	2.43	3.16	1.95	2.28	2.64
Menthol	0.92	1.32	1.39	1.39	1.39
Mean value	1.42	1.85	1.97	2.17	2.21

single compounds emitted in these two tests should have been roughly in the ratio of 2. Table 3 summarizes these ratios for the "best" and most complex physical and empirical models and also for the trapezoid rule. In the case of the pseudo constant mass compounds, the total emitted mass by model can be directly compared in Table 2b to the corresponding weight loss.

The ratios in Table 3 differ rather widely from the expected value of 2 and do not show a clear pattern even if, as a whole, they seem to favour the empirical model.

The results of the pseudo constant mass compounds in Table 2b are conflicting: there is excellent agreement with test No. 5 ($N = 1 \text{ h}^{-1}$) but a rather large, unexplained difference with test No. 6 ($N = 0.525 \text{ h}^{-1}$).

Conclusions

The results presented in the previous section may be considered to be an accurate account of what can be

obtained at present in emission tests using small environmental chambers. Based on these results, neither the physical nor the empirical model seem to show decisive advantages in terms of accuracy of emission estimates.

Both models, however, need further consideration.

While for intrinsic reasons the results of the physical model are always formally correct, e.g. predicted concentrations and emission rates are never negative, in quantitative terms they are sometimes shown to be unrealistic. The model may not take the real physical processes controlling the emission into full consideration, especially in complex circumstances. However, further sophistication of it will not improve the situation. Generally, it is convenient to start the fitting procedure by the simplest submodel which, almost irrespective of the value of the initial guesses, usually converges smoothly. Coefficient estimates obtained in this way may then be used as guesses for fitting a submodel of the next

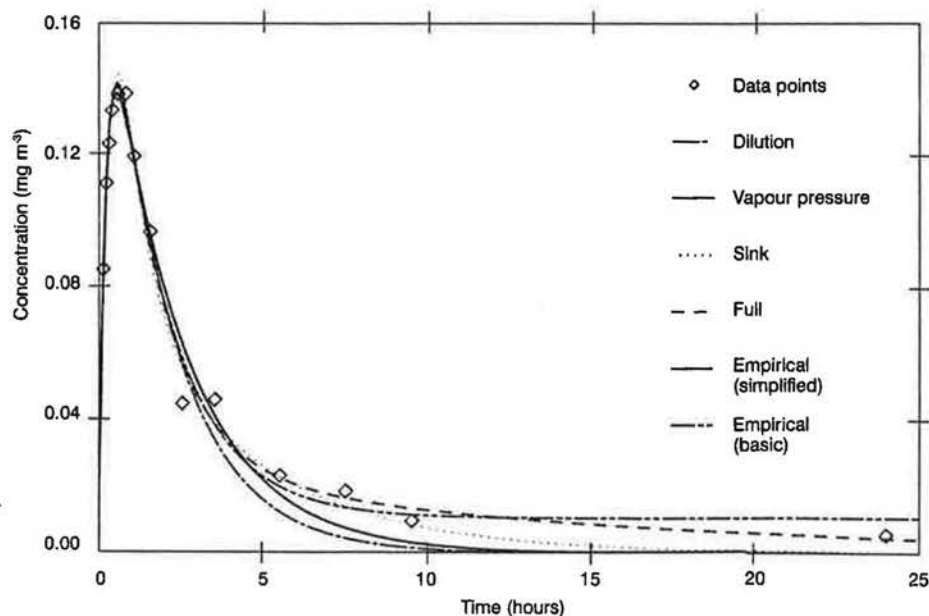


Fig. 1 Model best fits of dicyclopentadiene alcohol emitted in test No. 2 (curves of Vapour pressure and of simplified Empirical model are superimposed)

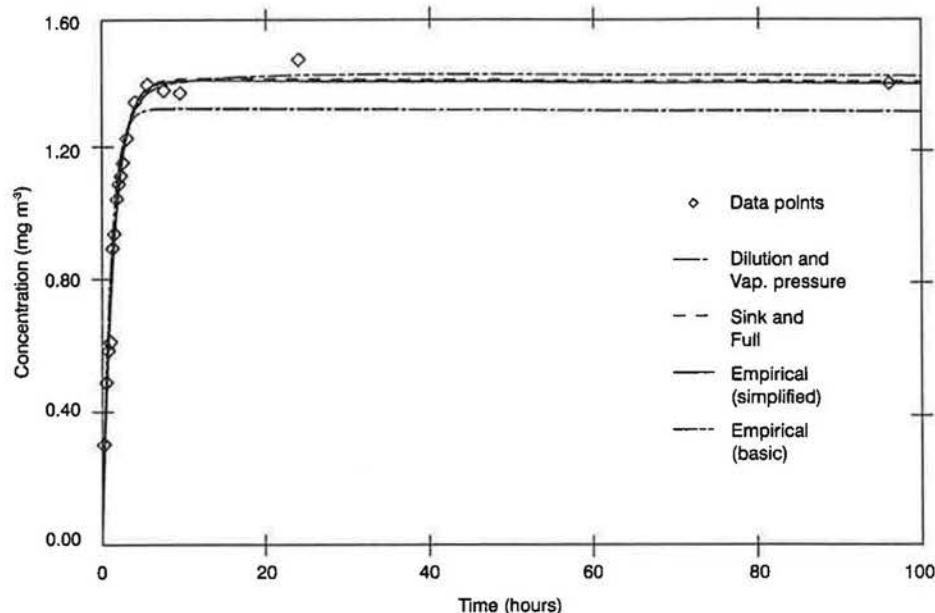


Fig. 2 Model best fits of toluene emitted in test No. 5 (identical results for Dilution and Vapour pressure and for Full and Sink models)

level of complexity. However, it is difficult to optimize all the necessary guesses and for the complex submodels (i.e. Sink and Full) it becomes a frustrating task to try to achieve convergence.

An objective criterion of submodel choice such as the extra-sum-of-squares principle often appears inadequate. If the distribution of residuals is adopted as rationale for the choice, almost invariably the most complex submodel is selected, as is illustrated, e.g., by Figures 1 and 2. Considering the findings from Tables 2 and 3 however, this choice may be ambiguous as it is not clear whether the better fit reflects a better interpretation of the physical processes governing the emission or simply the effect of additional adjustable coefficients.

Other ambiguities can be shown to arise in computing emission rates if an irreversible sink (i.e. a sink which sorbs without re-emitting) exists in the chamber. Scientifically speaking, however, the physical model represents the right approach to understanding the emission process.

The empirical model does not rely explicitly on physical effects and has limitations typical of these models. They have already been discussed (Colombo et al., 1990) with emphasis on the effect of disregarding sinks and on the possibility of obtaining a sometimes slightly negative result for $A - C$, the steady state concentration.

Depending on the shape of the concentration vs. time curve, this model in some region past the maximum can give a slightly negative emission rate rather than a small, positive one for the compounds

which decay to zero concentration over time. It does, however, have the advantage of applying itself to diffusion-limited thick sources and fitting more easily in general. The SAS option for using a grid of initial guesses is not required for this model. Extensive tests also carried out by a non-SAS regression routine implemented on a personal computer showed that efficient guesses for A and C are usually the concentration maximum and the difference between the maximum and the steady value, respectively. Moreover, if c_1 is the first concentration value measured at time t_1 near the origin of the concentration curve, then a reasonable guess for B is $2c_1/(t_1 c_{\max})$. For rapidly emitted compounds, an efficient guess for D generally lies at N , the chamber air exchange rate, whereas for slower emitted compounds, e.g. those from diffusion-limited sources such as boards, plywoods, etc., D is more suitably set at $0.1N$ or even at $0.01N$. Experience suggests limiting the use of the simplified model to instances in which $A - C$ is negative and to pseudo constant mass compounds, provided the extra-sum-of-squares principle is satisfied: otherwise the basic one is always the model of choice.

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References

- Colombo, A., De Bortoli, M., Pecchio, E., Schauenburg, H., Schlitt, H. and Vissers, H. (1990) "Chamber testing of organic emission from building and furnishing materials", *The Science of the Total Environment*, **91**, 237-249.
- Colombo, A., De Bortoli, M., Knöppel, H., Schauenburg, H. and Vissers, H. (1991) "Small chamber tests and headspace analysis of volatile organic compounds emitted from household products", *Indoor Air*, **1**, 13-21.
- Draper, N.R. and Smith, H. (1981) *Applied Regression Analysis*, 2nd edition, New York, Wiley.
- Dunn, J.E. and Tichenor, B.A. (1988) "Compensating for sink effects in emission test chambers by mathematical modeling", *Atmospheric Environment*, **22**, 885-894.
- Kinniburgh, D.G. (1986) "General purpose adsorption isotherms", *Environmental Science and Technology*, **20**, 895-904.
- SAS Institute Inc. (1985) *SAS User's Guide: Statistics*, Version 5 edition, Cary, NC.
- Tichenor, B.A. (1989) *Indoor air sources: using small environmental test chambers to characterize organic emissions from indoor materials and products*, U.S. Environmental Protection Agency, Rep. EPA-600/8-89-074, Air and Energy Engineering Research Laboratory, Research Triangle Park, NC.