

# Modelling of Emissions of Total Volatile Organic Compounds in an Australian House

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## Key Words

Modelling · Total volatile organic compounds · Indoor air quality model · Emissions · Environmental chamber

## Abstract

A simplified indoor air quality (IAQ) model has been applied to predict IAQ in an Australian house, using environmental chamber measurements of source strengths, house ventilation and room size. Total volatile organic compounds (TVOCs) was used as the model pollutant in this study. The validity of the IAQ model was initially assessed by comparing model predictions with measurements in the house over a period of time. The root mean square error between the measured and predicted values was 0.039. This model explains 57% of the potential for error. The TVOC concentrations measured in the conventional house ranged from 60 to 162  $\mu\text{g}\cdot\text{m}^{-3}$ . These values are much lower than some published values (0.48–31.7  $\text{mg}\cdot\text{m}^{-3}$ ) for new houses in Scandinavian countries and in the USA. The low TVOC concentrations obtained in this study probably result from the high ventilation rates in this conventional house and the use of low TVOC emission materials.

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## Introduction

Models are needed to predict emissions of volatile organic compounds (VOCs) from indoor sources. There are several types of empirical models used to describe such emissions based on dynamic chamber testing [1]. Validation of such models involves tests in which samples are placed in test chambers and concentrations of total VOCs (or individual compounds) are measured at various times. The concentration and time data are then used to determine the parameters of empirical emission rate models. The first-order decay model is the one most commonly used [2–5]:

$$R = R_0 e^{-kt}$$

where  $R$  is the emission rate at time  $t$  ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ),  $R_0$  is the initial emission rate ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ) and  $k$  is the first-order decay constant ( $\text{h}^{-1}$ ).

Although the first-order decay model can be used to describe emission rates, it is often deficient in characterising the 'tail' of the emission curve for fast sources [4]. In addition, the first-order decay model does not provide a physical description of the emission process, nor does it separate the parameters describing the source from those describing the environment [6, 7].

The mass transfer models for indoor air pollution sources developed by other researchers [6, 8–10] provide

a good fit between modelled and measured VOC concentrations. However, due to the difficulty in estimating or measuring the large number of parameters required by these models, it was impossible to use these models in this study.

A double-exponential model was developed to predict emissions of VOCs from indoor sources [11–13]. The model predicts the measured data quite well in most cases. In this study, the emissions of total VOCs (TVOCs) from indoor materials measured in environmental chambers were fitted using a double-exponential empirical model [14, 15]. The emission parameters were estimated for each indoor material by non-linear least-squares regression of a data set.

In order to analyse the impact of emission sources on indoor air quality (IAQ), an integrated approach consisting of chamber studies, modelling and test house studies is necessary. The above-mentioned models are used only for the prediction of VOC emissions in environmental chambers. Models are also needed to predict IAQ in buildings, using environmental chamber measurements of source strengths, and using TVOCs or individual VOCs as model pollutant. Some studies have used empirical models to simulate IAQ from chamber measurements of source strengths in the USA and some Scandinavian countries [16–18]. Others have developed physically based models to predict emissions of pollutants in an indoor environment. Based on fundamental theory, some investigators considered external diffusion [19–25], while others have emphasised internal diffusion [9, 10, 26]. Although these physically based models can provide an insight into the controlling mechanisms, it is difficult to estimate or measure the large number of parameters required by these models. In fact, the applicability of most of these models is limited because there is no, or insufficient, experimental data available.

In the present study, TVOCs were used as the model pollutant. TVOC emissions from materials which were used indoor in the construction of a conventional house were tested in environmental chambers. The emission parameters for each indoor material were obtained from these chamber measurements. A simplified IAQ model was then used to predict TVOC concentrations in the conventional house over a period. These predictions were compared to measurements in the conventional house, as a means to assess the validity of the model. The correlation between chamber measurements and emission modelling results, and the field measurements and the corresponding modelled results, is statistically evaluated.

## Methods and Materials

The prediction of emissions of TVOCs from indoor sources was based on the results of environmental chamber testing of various products. In these experimental investigations, the change of TVOC concentrations with time for three paints, one adhesive and one wood product was measured in an environmental chamber with controlled temperature, relative humidity and air flow rate. The emissions quantified by chamber testing were then converted into indoor air concentrations by use of a model room approach [27].

### *The Environmental Chamber Test*

Before testing each indoor product, one chamber blank sample was analysed by gas chromatography/flame ionisation detection (GC/FID) to ensure the TVOC concentration in the chamber was below  $5 \mu\text{g}\cdot\text{m}^{-3}$ . Otherwise, the chamber was cleaned and tested again until this criterion could be met. To obtain specific and clear TVOC emission data, the paint and adhesive samples were prepared by brushing an amount of sample onto a  $7.5 \times 7.5 \text{ cm}^2$  metal plate. The wood product was prepared by cutting a sample piece measuring  $15 \times 15 \text{ cm}^2$ . The sample was weighed (Model 1801, Sartorius GmbH, Göttingen, Germany) and placed in the chamber immediately. Sample weight loss was determined by weight difference to the nearest 0.0001 g.

The experimental conditions for all emission measurements in the chamber were as follows: temperature  $23 \pm 1^\circ\text{C}$ , relative humidity  $50 \pm 5\%$ , air exchange rate  $0.885 \text{ h}^{-1}$ , chamber volume 13.56 litres, area of material  $7.5 \times 7.5 \text{ cm}^2$  (paints and glue) and  $15 \times 15 \text{ cm}^2$  (wood product), support material metal plate.

During the high-emission period of the emission test, air sample volumes of 1,000 ml were collected at a sampling rate of  $200 \text{ ml}\cdot\text{min}^{-1}$  to prevent overloading of the concentration column of the purge and trap unit [28]. The air sample volume was increased to a maximum of 1,500 ml as the emission rate decreased. VOCs were collected using adsorption tubes (Tenax-GR, 80/100 mesh). Immediately after sampling the tubes were tightly sealed and analysed with GC/FID. Samples were collected at progressively increasing intervals. The gas chromatograph (Varian Model 3700) was equipped with a modified thermal desorption cold trap injector and an FID. The samples were thermo-desorbed into the instrument for TVOC quantification. A film capillary (Alltech ECONO-CAP SE-54,  $30 \text{ m} \times 0.53 \text{ mm i.d.} \times 1.2 \mu\text{m}$ ) was employed for the separation of VOCs. The adsorbed sample was cryo-trapped at  $-80^\circ\text{C}$  and injected into the chromatograph. The temperature program was initially set at  $40^\circ\text{C}$  for 5 min, then increased at a rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$  to  $200^\circ\text{C}$ , which was held for 3 min. The injection temperature was  $200^\circ\text{C}$ ; the temperature of detector was  $230^\circ\text{C}$ . The concentration of TVOCs was calculated from the total area of the FID chromatogram using a toluene response factor.

The change of TVOC concentrations from each paint and adhesive sample against time was measured for approximately 24 h, and for about 1 week for the wood product, as emission rates were adequately described and predictable by this time. A series of toluene standards in methanol from 50 to  $500 \mu\text{g}\cdot\text{ml}^{-1}$  were prepared. A calibration curve was established by direct injection of  $0.5\text{-}\mu\text{l}$  aliquot portions of the toluene standards. An aliquot portion of  $0.1 \mu\text{l}$  of an appropriate standard toluene solution was injected into the adsorption tubes before thermal desorption as a quality control measure.

Some 10% of air samples were replicated for the indoor samples for each sample analysis run.

For these small chamber studies only one side of the wood material was exposed and the edges of the wood material were not sealed. The exposed area thus included both the face and the edge areas.

### The Conventional House

The field investigations were performed in a conventional house, which was constructed for aged persons. The house had two bedrooms, one bathroom, one lounge, one laundry and one kitchen. The internal and external walls were of brick. The house had just been completed and was unoccupied. The flooring of the house consisted of ceramic tiles. A water-based floor adhesive was used to adhere the floor tiles. The house had two air conditioners: one was in the lounge and another was in the main bedroom. The roof insulation was aluminium foil casing of layers of air. The house was well ventilated to avoid the accumulation of indoor allergens and moisture. Windows and doors were located to maximise cross ventilation. An electric heating system was used in the house to avoid the emission of combustion gases. The stove, oven and hot water systems used gas but moisture and cooking fumes were removed by hoods and extractor fans. There were no carpets or furniture in the house. The external environment was as unpolluted as could be expected in a suburb with no industry. The area and volume of this conventional house are listed in table 1.

The major sources of VOCs in indoor air are wet construction products (paints, adhesives, sealant) in new buildings and a mixture of wet household products and other materials in established buildings [29]. Investigations and measurements on the construction materials and products used in the conventional house showed that paints, 'hardboard' and adhesives were the main source of VOCs. The construction material 'hardboard' has a fine, wood fibre structure, densely bonded with phenolic resins. The smooth face surface provides an ideal base for paint finishing. The back surface is characterised by a fine, wire-screen texture. The material is used extensively in the building, packaging, furniture and general industrial manufacturing industries. The materials used in the conventional house are listed in table 2.

The conventional house was completed on January 6. Especially for this project, the builder was required to install VOCs emitting materials listed in table 2 on the last day of the completion of the house. The TVOC measurements were made between January 27 and February 8, starting 3 weeks after the end of the construction. This study, therefore, dealt with the measurements made during the subsequent ageing phase before the house was occupied. Over this period, seven detailed investigations were made at intervals of 2 days. The TVOC samples were taken at the same time of day.

### The TVOC Measurements

TVOCs were sampled on Tenax-GR as described above but from 5.0- to 6.0-litre air samples taken using an air sampler (Airchek, model 224-PCXR8 or model 224-52, SKC Inc., Eighty Four, Pa., USA) because of expected low TVOC concentrations in the conventional house. The sampling time was 5–6 min at a sampling rate of 1.0 litre·min<sup>-1</sup>. Samples were taken from the two bedrooms and the lounge and analysed using GC/FID immediately after sampling.

**Table 1.** Parameters for the conventional house

Volume m <sup>3</sup>	Walls area m <sup>2</sup>	Ceiling area m <sup>2</sup>	Painted areas m <sup>2</sup>	Floor area m <sup>2</sup>
167	178	72	26	60.5

**Table 2.** Indoor materials used in the conventional house

Products	Applied area, m <sup>2</sup>
Low odour acrylic undercoat	178
Low odour satin enamel	26
Satin advanced acrylic	72
Hardboard	37
PVA glue	60.5

### Ventilation and Temperature Measurements

Air exchange rates in the conventional house were measured at the same time the TVOC samples were taken by flooding with carbon dioxide (CO<sub>2</sub>) to 1,000 ppm while agitating the air with a fan. When this concentration was achieved the fan was turned off and the CO<sub>2</sub> concentration logged over time. From this data air exchange rates were estimated using the method described by Reindl [30] and Feher and Ambs [31].

Measurements of CO<sub>2</sub> were made using an ADC 225 MK 2 infrared gas analyser (Bacharach, Pittsburgh, Pa., USA) in absolute measurement mode and scaled 0–1,000 ppm. The analyser inlet was plumbed via 4-mm tubing to the centre of the room 1,200 mm above the floor. Outside the house, ambient CO<sub>2</sub> levels were measured 2 m above the ground. The operator set up the equipment and departed for 60 min while the instrument warmed up and respired CO<sub>2</sub> dissipated. The operator then avoided further CO<sub>2</sub> contamination of the experimental site. The analyser output was monitored with a Unidata Macrologger (Unidata, Perth) logging data at 1-min intervals.

Air temperature and relative humidity in the conventional house were measured by using thermo-hygrometers (High Accuracy Thermo-Hygro, Model 204-072, Radio Spares Components, Perth).

The whole conventional house was considered as a single, well-mixed compartment in this study. Because air mixing throughout the indoor space is relatively rapid compared to characteristic residence time, it is reasonable to assume that a particular room, floor or entire building is a single, well-mixed compartment [16].

### Modelling of TVOC Emissions in an Environmental Chamber

#### Modelling of TVOC Concentrations

The emission rates of TVOCs from the test materials were calculated using a double-exponential model [12, 13]:

$$E(t) = E_1 + E_2 = E_{10}e^{-k_1 t} + E_{20}e^{-k_2 t} \quad (1)$$

where  $E(t)$  = emission rate of TVOCs (mg·m<sup>-2</sup>·h<sup>-1</sup>),  $E_1$  = phase 1 (evaporation-dominated) emission rate (mg·m<sup>-2</sup>·h<sup>-1</sup>),  $E_2$  = phase 2

(diffusion-dominated) emission rate ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ),  $E_{10}$  = phase 1 initial emission rate ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ),  $k_1$  = phase 1 emission rate decay constant ( $\text{h}^{-1}$ ),  $E_{20}$  = phase 2 initial emission rate ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ), and  $k_2$  = phase 2 emission rate decay constant ( $\text{h}^{-1}$ ).

The corresponding TVOC concentration is given by:

$$c = L'E_{10}(e^{-k_1t} - e^{-N't})/(N' - k_1) + L'E_{20}(e^{-k_2t} - e^{-N't})/(N' - k_2) \quad (2)$$

where  $L'$  = material loading ( $\text{m}^2\cdot\text{m}^{-3}$ ),  $N' = Q'/V'$  = air flow rate through the chamber/chamber volume = air exchange rate in the chamber ( $\text{h}^{-1}$ ).

Equation (2) can be used to give a solution for an initial zero concentration and assumed constant ventilation rate, constant source rate, and single-zone well-mixed conditions.

The double exponential model was used to analyse the chamber data using a non-linear least squares best-fit routine [32]. From this the four emission parameters  $E_{10}$ ,  $E_{20}$ ,  $k_1$  and  $k_2$  may be obtained. The quality of the least squares fit and the uncertainties in the coefficients are assessed automatically by the MacCurveFit program used [32, 33]. This program uses an exponential peeling procedure to calculate the best estimates of the emission parameters [3, 32, 34].

Using known emission parameters from indoor sources, the TVOC concentrations can be simulated for specific material loading ( $L$ ) and air exchange rate ( $N$ ).

#### IAQ Model

The IAQ model was intended to be used to convert the concentrations of TVOCs or individual VOCs measured in an environmental chamber into the concentrations in buildings and residences. This study used TVOCs only as a model pollutant. To run the model it is necessary to have data on source strengths, air exchange and room size. The model can also be used to compare measurements of pollutant concentrations in buildings with model predictions based on emission parameters measured in the laboratory.

A generalised equation for IAQ models may be expressed in the form:

$$VdC/dt = Q(C_{\text{out}} - C) + S \cdot E(t) - R \quad (3)$$

where  $V$  = the volume of a house ( $\text{m}^3$ ),  $C_{\text{out}}$  = TVOC concentration outside of the house ( $\mu\text{g}\cdot\text{m}^{-3}$ ),  $C$  = TVOC concentration in the house ( $\mu\text{g}\cdot\text{m}^{-3}$ ),  $Q$  = the ventilation rate for the house ( $\text{m}^3\cdot\text{h}^{-1}$ ),  $S$  = the area of indoor source ( $\text{m}^2$ ),  $E(t)$  = the emission rate of TVOC by indoor source ( $\mu\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ), and  $R$  = sink rate of TVOCs ( $\mu\text{g}\cdot\text{h}^{-1}$ ).

Equation (3) is an isothermal formulation of a mass conservation relation. It is simplified as well as generalised, as it assumes one source strength and sink rate, and a single emission rate function.

Published studies indicated that 'dry sources' indoors such as carpets, vinyl wall coatings and gypsum boards normally have a capacity for adsorption of TVOCs [35-37]. In this study, although the hardboard is a kind of dry source,  $R = 0$  will still be assumed, as a first-order approximation, for the purposes of simplification. Equation (3) may then be then simplified as follows:

$$VdC/dt = Q(C_{\text{out}} - C) + S \cdot E(t) \quad (4)$$

In addition, the TVOC concentrations outside the conventional house were measured and found to be less than  $5 \mu\text{g}\cdot\text{m}^{-3}$ , and as a result  $C_{\text{out}}$  was assumed to be zero. Therefore, equation (4) can be simplified as:

$$(dC/dt) + Q \cdot C/V = (S/V) \cdot E(t) \quad (5)$$

where, from equation (1):  $E(t) = E_{10} e^{-k_1t} + E_{20} e^{-k_2t}$ .

Given that  $C = 0$  when  $t = 0$ , the solution to equation (5) is:

$$C = LE_{10}(e^{-k_1t} - e^{-Nt})/(N - k_1) + LE_{20}(e^{-k_2t} - e^{-Nt})/(N - k_2) \quad (6)$$

where  $C$  = TVOC concentration in the conventional house ( $\mu\text{g}\cdot\text{m}^{-3}$ ),  $N$  = air exchange rate in the conventional house ( $\text{h}^{-1}$ ),  $L = S/V$  = material loading ( $\text{m}^2\cdot\text{m}^{-3}$ ),  $V$  = volume of the conventional house ( $\text{m}^3$ ),  $S$  = area of the object in the conventional house ( $\text{m}^2$ ),  $E_{10}$ ,  $E_{20}$ ,  $k_1$  and  $k_2$  = source emission parameters.

The resulting concentration of TVOCs from various sources was, in this first-order approximation, obtained by simple summation of the  $C$  values such that TVOC concentration in the conventional house equals  $\Sigma C$ . This simple summation of estimated concentrations from each source assumed that there was no effect on emission rates from indoor VOC concentrations from other sources.

Where air quality in a building was to be evaluated, the actual values were inserted in the IAQ model equation (6). In this way, the concentration of TVOCs in the indoor air from a single source and the total concentration of TVOCs from several sources could be calculated.

#### Model Evaluation

The correlation between chamber measurements and emission modelling results, and the field measurements and the corresponding modelled results, was statistically evaluated by using techniques outlined by Stunder and Sethu Raman [38] and Hanna [39]. These techniques included both residual analysis which allows a quantitative estimate of  $(\bar{C}_p - \bar{C}_m)$  and correlation which allows a measure of agreement between measured TVOC concentration ( $C_m$ ) and predicted concentration ( $C_p$ ). Here,  $\bar{C}_p$  is the mean of predicted concentrations, and  $\bar{C}_m$  is the mean of measured concentrations.

This study used correlation coefficient ( $R$  or  $R^2$ ), an index of agreement ( $d$ ) and the RMSE to interpret model accuracy. The index of agreement can be interpreted as a measure of how error-free a model predicts a variable. RMSE is composed of systematic RMSEs and unsystematic RMSEu. Difference measures provide the most rigorous and useful information regarding overall model performance. However, models contain both systematic and unsystematic errors. Systematic errors result from causes which occur consistently. Unsystematic errors consist of a number of small effects such as the imprecision of a constant. The best model therefore has a systematic difference of zero since it should explain most of the systematic variation in observed values  $C_m$ , while the unsystematic difference should approach the RMSE. The value of RMSE should be minimised so that the model is predicting at peak accuracy. A large value of RMSEu may indicate that the model is as good as possible under the present conditions [38].

Therefore, the statistical descriptive relative error measure which indicates the degree to which  $C_p$  approaches  $C_m$  can then be expressed as:

$$d = 1 - [\Sigma(C_{pi} - C_{mi})^2 / \Sigma(|C_{pi}'| + |C_{mi}'|)^2] \quad (7)$$

$$0 \leq d \leq 1, i = 1, 2, \dots, n$$

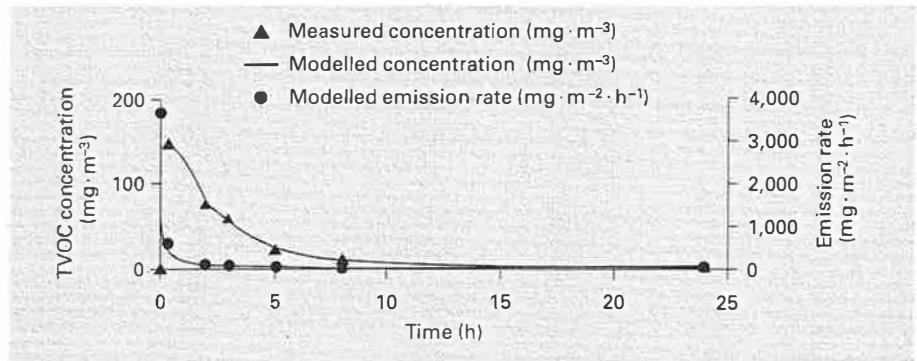
where  $C_{pi}' = C_{pi} - \bar{C}_m$  and  $C_{mi}' = C_{mi} - \bar{C}_m$ .

The index  $d$  therefore allows for sensitivity toward differences in  $C_m$  and  $C_p$  as well as proportionality changes. A value of 1.0 indicates perfect agreement between  $C_m$  and  $C_p$  values.

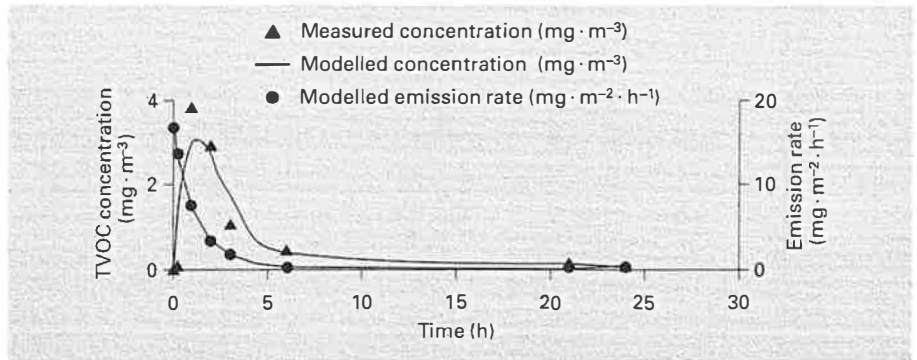
The systematic mean square error is the error caused by model additive or proportional problems and can be expressed as:

$$\text{RMSEs} = [\Sigma(\bar{C}_{pi} - C_{mi})^2/n]^{1/2}, i = 1, 2, \dots, n \quad (8)$$

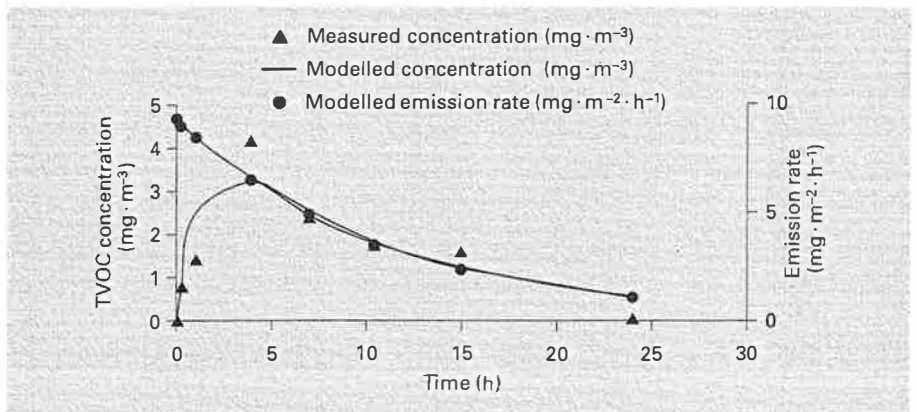
**Fig. 1.** The TVOC concentration and emission rate from satin enamel paint with time after application.



**Fig. 2.** The TVOC concentration and emission rate from acrylic undercoat with time after application.



**Fig. 3.** The TVOC concentration and emission rate from satin advanced acrylic with time after application.



where  $\hat{C}_{pi} = a + b \cdot C_{mi}$ , and  $a$  and  $b$  are regression coefficients. The unsystematic mean square error is:

$$RMSE_u = [\sum (C_{pi} - \hat{C}_{pi})^2 / n]^{1/2} \quad (9)$$

The total RMSE is written as:  $RMSE = (RMSE_s^2 + RMSE_u^2)^{1/2}$ .

In addition to RMSEs, RMSEu and  $d$ , calculation of summary measures such as  $\bar{C}_m$ ,  $\bar{C}_p$ ,  $S_m^2$  and  $S_p^2$  along with simple linear regression will be of use [38]. Here,  $S_m^2$  and  $S_p^2$  are squared standard deviations for measured values and for predicted values, respectively.

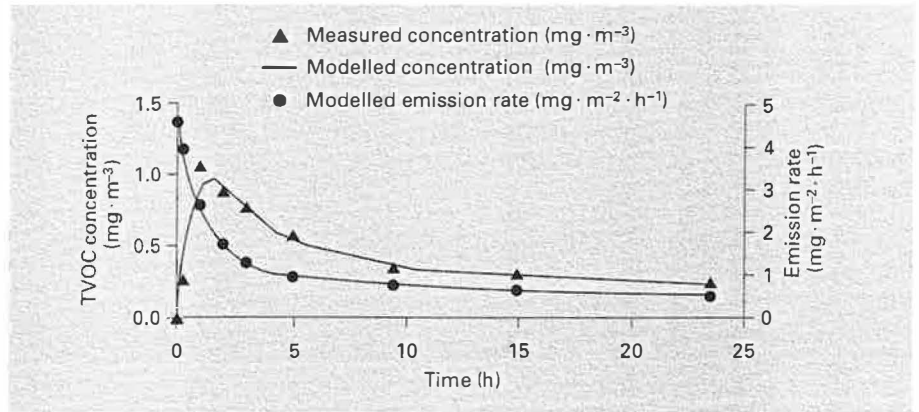
Hanna [39] stated that the total model error or uncertainty can be defined as  $(C_p - C_m)^2$ , where the bar indicated an average over a certain number of pairs of  $C_p$  and  $C_m$  observed at various points and/or times. Therefore, this study also evaluates the uncertainty of models by using  $(C_p - C_m)^2$ .

## Results

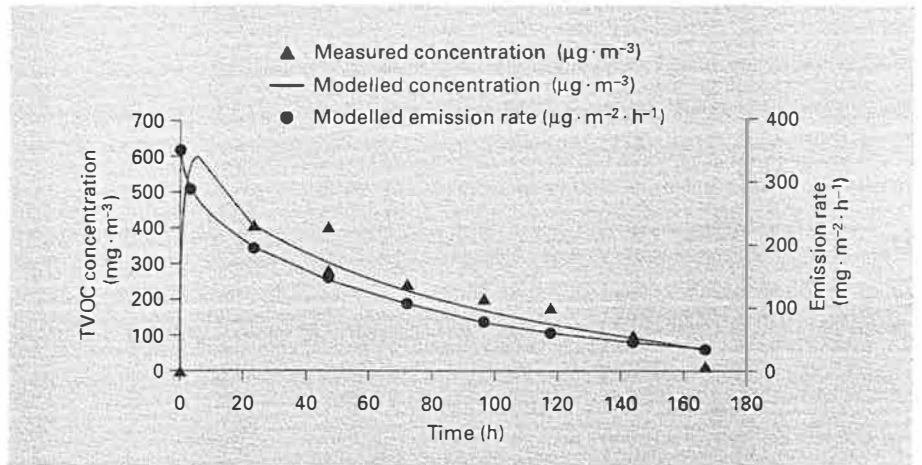
### *Emission Parameters for the Products Applied Indoors*

Figures 1–5 represent the change of TVOC concentrations for the products applied listed in table 2 against as time measured in environmental chambers. These figures show that TVOC concentration in the chamber for the applied products increases with time passing through a maximum value and then decreases towards an equilibrium value or undetectable.

**Fig. 4.** The TVOC concentration and emission rate from PVA glue with time after application.



**Fig. 5.** The TVOC concentration and emission rate from hardboard.



**Fig. 6.** Predicted and measured total concentrations of TVOCs in the unoccupied conventional house. Day zero is the start of the TVOC measurements.

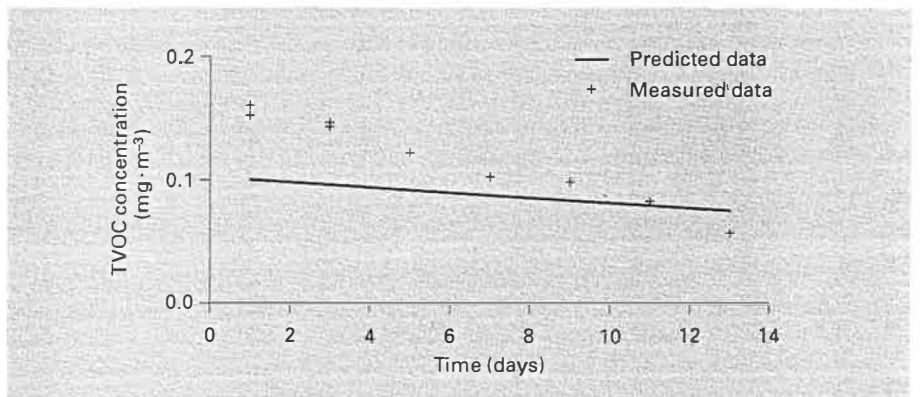


Table 3 lists the model-derived emission parameters from these products used indoor. With known emission parameters, the TVOC concentrations in an indoor environment can be estimated. The squared correlation coefficients ( $R^2$ ) for the products range from 0.810 to 0.996. The sum of squared error (SSE) between the measured and predicted TVOC concentrations ranges from 0.0402

to 71.42. A value of zero for SSE indicates a perfect fit. PVA glue and hardboard have a value close to zero. The satin enamel has the largest SSE value.

To better understand about the degree of error, a listing of the various summary measures, regression coefficients and difference measures are presented in table 4. The  $\bar{C}_m$  vs.  $\bar{C}_p$  summary measures indicate that on the average,

**Table 3.** Emission parameter model derived for the indoor products

Product	$E_{10}, \text{mg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$	$k1, \text{h}^{-1}$	$E_{20}, \text{mg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$	$k2, \text{h}^{-1}$	$R^2$	SSE
Satin enamel	$3,482 \pm 2,704^a$	$8.38 \pm 9.32$	$181.2 \pm 75.8$	$0.33 \pm 0.11$	0.996	71.42
Acrylic undercoat	$16.39 \pm 5.75$	$0.793 \pm 0.484$	$0.249 \pm 1.71$	$0.000953 \pm 0.21$	0.815	2.94
Satin acrylic	$9.23 \pm 2.08$	$0.093 \pm 0.045$	– <sup>b</sup>	– <sup>b</sup>	0.810	2.20
PVA glue	$3.545 \pm 0.65$	$0.767 \pm 0.304$	$1.022 \pm 0.40$	$0.0306 \pm 0.03$	0.958	0.0402
Hardboard	$0.259 \pm 0.031$	$0.0123 \pm 0.015$	$0.093 \pm 0.031$	$0.246 \pm 0.186$	0.942	0.830

<sup>a</sup> The uncertainty in the coefficient = the standard error of the estimate.

<sup>b</sup> The term is not in the model.

**Table 4.** Quantitative measures of model performance for indoor materials used in the conventional house

Product	Summary measures				Model uncertainty	Linear regression		Difference measures			
	$\bar{C}_m$	$\bar{C}_p$	$S_m$	$S_p$	$(C_p - C_m)^2$	a	b	RMSE	RMSEs	RMSEu	d
Satin enamel	52.98	52.93	55.26	54.62	11.91	0.687	0.986	3.45	0.71	3.38	0.999
Acrylic undercoat	1.24	1.35	1.50	1.20	0.42	0.466	0.712	0.68	0.41	0.54	0.931
Satin acrylic	1.71	1.79	1.30	0.98	0.34	0.643	0.669	0.58	0.40	0.42	0.922
PVA glue	0.56	0.56	0.31	0.28	0.005	0.073	0.884	0.071	0.035	0.062	0.983
Hardboard	0.22	0.20	0.13	0.10	0.0025	0.017	0.817	0.05	0.033	0.038	0.951

the satin enamel and hardboard underpredict concentration values, and acrylic undercoat and satin acrylic overpredict. The PVA glue prediction fits the experimental values very well. A comparison of  $S_m$  and  $S_p$  gives a relative indication of how well a model is reproducing the observed variance. From table 4, therefore, it seems that the PVA glue and hardboard are best at fitting the observed variability.

The analysis of RMSE from table 4 indicates that the hardboard has the least overall RMSE. However, the hardboard has almost the same value for RMSEs and RMSEu implying that it does not fit the criteria of the systematic error. The PVA glue has, however, the smallest SSE and comparatively small systematic error.

The index of agreement (d) suggests that the percentage of the potential for error in predicting concentrations has been explained by the model [38]. For the five products noted in tables 2 and 3, the d values range from 0.922 to 0.999. However, interpretation of the index d should not be given too much weight since d becomes unstable when the denominator is small.

The values of  $(C_p - C_m)^2$  in table 4 indicate that satin enamel has the largest uncertainty while the PVA glue and the hardboard have the smallest uncertainty.

### *Comparison of On-Site Measurements and IAQ Model Prediction*

#### *The IAQ Model*

The obvious advantage of the IAQ model (equation 6) is its simplicity. From the model predictions, the relative source strength of sources of indoor TVOCs can be estimated, and the effects of ageing of sources and house ventilation rates on the emission and especially the time needed for the emission in new houses to decrease to an acceptable level before the houses are occupied can be evaluated. With the results of modelling, the average acceptable emission rate of TVOCs from building materials can also be estimated. Also, the results obtained from this model can be validated by comparison with actual measurements.

Table 2 lists the type and the areas of products applied in the conventional house. The modelled emission parameters derived for each source are given in table 3. The measured and modelled concentrations of TVOCs in the conventional house are shown in figure 6, which suggests that all major sources of TVOCs are included in the model. In this figure, day zero ( $t = 0$ ) in the IAQ model is the start of the TVOC measurements, which was on the 21st

**Table 5.** Quantitative measures of the IAQ model performance

Model	Summary measures				Linear regression		Difference measures				Model uncertainty ( $C_p - C_m$ ) <sup>2</sup>
	$\bar{C}_m$	$\bar{C}_p$	$S_m$	$S_p$	a	b	RMSE	RMSEs	RMSEu	d	
IAQ	0.123	0.092	0.034	0.0087	0.061	0.253	0.039	0.039	0.0012	0.57	0.0015

day (508 h), after the end of the construction of the house. The final TVOC measurement was made on the 33rd day (796 h) after the end of the construction of the house.

The squared correlation coefficient ( $R^2$ ) between the measured and predicted TVOC concentrations in the conventional house was 0.981. However, distinctions between the type or magnitudes of variables are not indicated by the value of  $R$ . The single use of  $R$  and  $R^2$  may mislead in interpreting model accuracy. Therefore, table 5 lists the various summary measures, regression coefficients and difference measures for the measured and predicted TVOC concentrations.

The values of  $\bar{C}_m$  and  $\bar{C}_p$  in table 5 indicate that the IAQ model underpredicts TVOC concentration values. The large difference between the two deviation quantities  $S_m$  and  $S_p$  shows that the model does not reproduce well the observed variance. Also, the analysis of the RMSE indicates that the IAQ model does not fit the criterion of the systematic error, and the systematic error (RMSEs) itself is close to the overall RMSE, which implies that this model might contain numerous systematic errors. The index of agreement (d) suggests that only 57% of the potential for error has been explained by the model.

#### *Measurements Made in the Conventional House*

Three sets of duplicate samples were collected in the conventional house. Reproducibility, expressed as the difference between duplicates divided by the mean, averaged 3.6% for the total organic compounds analysed by gas chromatography.

The ventilation was measured in the conventional house in the summer season. These measurements showed that the conventional house was ventilated with fresh air at an average rate of  $1.60 \pm 0.25 \text{ h}^{-1}$  (ach). These measurements were sufficiently consistent for the variation inherent in the model calculations.

The average temperature and humidity of the unoccupied conventional house during the period of TVOC measurements were 27.9 °C and 35.7% RH, respectively.

## Discussion

A measurement of TVOCs is frequently used to assess IAQ, because the interpretation of one single parameter is simpler and faster than an interpretation of the concentrations of several dozens of the VOCs typically detected indoors. However, with regard to the reliability of TVOC measurements for estimating IAQ, they should be used with caution and only under certain circumstances, when data from IAQ surveys are examined. The emission decay time constants in this study indicated that 508 h after painting, only the emission from the acrylic undercoat was an important contributor to the concentration of TVOCs and was the dominant source at this time. In such a case, when a single source dominates, separation and identification of contributions from individual VOCs is not necessary.

The sources of TVOCs in the conventional house were comparable to those reported in published papers. Mølhave et al. [18] reported that the main sources in two Danish apartments were water-based paints, particleboard and varnished beech wood floor. A study by Rothweiler et al. [40] found that paints and sealing wax were the main sources of VOCs in new and renovated buildings. Ekberg [41] reported that adhesives, paint and wood-based materials were the main sources of VOCs in indoor air.

The main pollution sources in the conventional house were paints and adhesives. All these were all water-based except the paint used for the cupboards. These 'wet' sources had been identified as low VOC emission materials [14, 15]. There was no other obvious pollution source, such as carpets, in the conventional house.

Although the conventional houses were just 3 weeks old when they were investigated and monitored, the results indicated that the TVOC concentrations were low compared to those found in other studies. The range of TVOC concentrations measured was only 60–162  $\mu\text{g}\cdot\text{m}^{-3}$ . Two-month-old houses investigated in Switzerland by Rothweiler et al. [40] had TVOC concentrations which ranged from 1.6 to 31.7  $\text{mg}\cdot\text{m}^{-3}$ . In the Danish twin apartment study by Mølhave et al. [18] two new apart-



**Table 6.** Air exchange rates in different countries

Country	Air exchange rate ach
Norway, Sweden, Finland, Denmark, Iceland, Canada	0.5
Germany, The Netherlands, New Zealand	0.8
United Kingdom, USA	0.5–1.0

ments were investigated 32 days after their completion and then continuously monitored for 12 months. They found that the TVOC concentrations ranged from about 0.1 to 3.8 mg·m<sup>-3</sup> for an unoccupied apartment and 0.8 to 4 mg·m<sup>-3</sup> for an occupied apartment. Other published values include a range of 0.48–31.7 mg·m<sup>-3</sup> for new houses in Scandinavian countries [40, 42] and 0.19–9.4 mg·m<sup>-3</sup> in a study of both new and old houses in Italy [43]. The concentrations obtained in the present study are even lower than those measured by Wallace et al. [44], who found that in 50% of residences studied in the United States TVOC concentrations were higher than 1 mg·m<sup>-3</sup>.

The low TVOC concentrations we measured probably resulted not only from the use of low TVOC emission materials but also the high ventilation rates in the houses. These ventilation rates were measured over a 2-week period during the summer season and for the purposes of this work dealt with the conventional house as a single compartment. This assumption is acceptable given the variation inherent in the model calculations. The average ventilation rate measured in the conventional house was 1.60 ach, which is higher than that reported for similar buildings in other countries. This is comparable to the findings of Biggs et al. [45] and Biggs and Bennie [46], who reported that the mean air exchange rates through contemporary houses in Australia in areas with a Mediterranean climate were approximately double the values reported previously from The Netherlands and Germany, where air exchange rates of approximately 0.8 ach were measured. Brown [47] has summarised information about air exchange rates in different countries (table 6).

Related to this, Biggs et al. [45] and Biggs and Bennie [46] also reported that the mean air exchange rates through contemporary houses in Australia with a Mediterranean climate for 50 Pa pressure difference were 12.2–26.3 ach, which at the highest rate is approximately double the values previously reported from New Zealand, The Netherlands and the UK (11.0–13.9 ach), and approximately 6 times greater than the ventilation rates reported from Sweden and Canada (3.7–4.4 ach).

Model evaluation studies suggest that the data input error is often a major contributor to total uncertainty. The impact of the model input data on the concentrations calculated using the model is normally examined by the sensitivity analysis of the model. In this study, the source emission parameters ( $E_{10}$ ,  $E_{20}$ ,  $k_1$  and  $k_2$ ) for the five products are modelled from chamber measurements and then input into the IAQ model to calculate TVOC concentrations in the conventional house. The uncertainties in the four parameters for the five products are quite large, which causes large errors in the prediction of the house concentration (table 3). The large uncertainties in the source emission parameters may result from the insufficient sampling data. The same value of the RMSEs and RMSE in table 5 indicates that a systematic error exists in the prediction.

In addition to the uncertainties in the source emission parameters, the low index of agreement ( $d$ ) in the house may result from several sources: (a) sink/re-emission effect; (b) substrate effect; (c) superposition of responses for individual sources; (d) an environmental effect involving dependency on temperature and relative humidity.

The model calculations of the levels of indoor TVOCs were based on chamber emission measurements of the individual samples of building materials that had been used for construction of the conventional house. However, in the construction of the house, all building materials were used together. The interaction between the various emissions and the building materials could cause adsorption and sink effects. That is, VOCs emitted from one material are adsorbed into other materials that act as sinks and later may re-emit the adsorbed VOCs with decay [48]. These sink/re-emission effects may be one of the reasons that most TVOC concentrations measured in the conventional house were higher than those predicted. In this study, the sink/re-emission effect could not be qualified, but future examinations should include such an effect in the analyses.

The change of substrate, temperature and relative humidity in the conventional house may have effects on the emission parameters  $E_{10}$ ,  $E_{20}$ ,  $k_1$  and  $k_2$  of the applied

materials. A diffusion barrier, like flooring tiles in the house, may have an effect on predicted emissions of the adhesive adhering to them when compared to chamber measurements of adhesives applied to a metal plate with no diffusion barrier. Furthermore, the different temperature and relative humidity in the house compared to the chamber could cause modelled concentrations to be different from the measured TVOC concentrations.

The discrepancies between the model predictions and the field data are also probably due to the semi-empirical nature of the IAQ model, which oversimplifies the emission process. In this study, the laboratory data that measures dynamic emission rates for only 1 day or 1 week were extrapolated to model predictions for the conventional house for up to 33 days. This kind of extrapolation may be deficient when using empirical models. The empirical model used in this study lacks a physical basis and

provides no insight into the controlling mechanisms [10]. It does not allow thorough separation of factors related to the source from factors related to the environment. Physically based models, however, address these issues directly and could be used to speculate about the above questions. Therefore, a physical model based on mass transfer fundamentals, which takes into account the characteristics of physical and chemical processes, is needed to represent fully the long-term behaviour of TVOC emissions in the conventional house.

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