

# Long-term Emission of Volatile Organic Compounds from Waterborne Paints - Methods of Comparison

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## Abstract

The emission of volatile organic compounds (VOCs) from five different waterborne paints was measured in small climatic chambers under standard conditions over a one-year period. The aims of the study were to evaluate the time emission profiles and to develop methods for comparison of different paints. The paints were applied to tin-plated steel sheets. VOCs were sampled on Tenax TA and analysed by thermal desorption and gas chromatography. The chamber concentrations increased rapidly during the first few hours and then decreased as the emission rates dropped. A model expression including an exponentially decreasing emission rate of the paint film, the air exchange rate, and a normalization of the film thickness was fitted to the concentration versus time data. The time required to reach a given emission rate was estimated and found suitable for comparison of the emission of VOCs from the paints. It was found that data sampled within three weeks or less may be sufficient to predict the emission of VOCs up to one year. Reduction of long-term emissions may be achieved most efficiently by (1) substituting a more volatile VOC whose emis-

sion is controlled by evaporation for a less volatile VOC characterized by diffusion-controlled emission and (2) reducing the paint film thickness rather than reducing the initial VOC content of the paint.

## Introduction

Paints represent a major building material used indoors. They are used for ceilings, walls and woods. Mucous membrane irritation is among the most common complaints of the indoor environment (Valbjørn and Kousgaard, 1986; Skov et al., 1989; WHO, 1989). A higher tendency to eye irritation has been found in houses painted with waterborne wall paints than in houses painted with white-spirit-formulated wall paints (Valbjørn et al., 1983). Water was substituted for white spirit as the main solvent in paints during the 1970s in Denmark to ensure a safer occupational environment. Today more than 90% of construction paints are waterborne (Hansen et al., 1987).

The purpose of the work presented here was to monitor the time emission profiles of volatile organic compounds (VOCs) from waterborne paints and to develop a method for comparison of the VOC emission from the paints. The relevance of the film thickness of thin film sources (e.g. waterborne paints) has not been considered earlier when comparing chamber emission measurements related to the indoor air. The toxicological

## KEY WORDS:

Waterborne paints, Emission of volatile organic compounds, Model calculations, Nonlinear regression, Film thickness, Time to reach a given emission rate.

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properties of the VOCs emitted are not considered as they have been discussed elsewhere (Hansen et al., 1987; Van Faassen and Borm, 1991). The work presented here is a summary of a full report in Danish (Clausen et al., 1990).

## The Experiments

### Selection of Paints

Five common white-pigmented waterborne wall and ceiling paints (A-E) were selected according to the following criteria: widely used, high room loading, and type of binder. These are similar to the criteria used in an investigation of the occupational environment of painters (Hansen et al., 1987).

### VOC Measurements

Prior to chamber tests, the paints were examined by headspace techniques using thermal desorption and gas chromatography combined with mass spectrometry (Wolkoff, 1990a) or Fourier transform infrared spectroscopy (Clausen et al., 1990). Major VOCs, which on a rough estimate constituted about 90% of the emission, were selected for quantitative measurements in the later chamber tests. The measurements of the emissions were performed by chamber air sampling on Tenax TA, thermal desorption and subsequent analysis by capillary gas chromatography with flame ionization detection (Wolkoff, 1990b). Six to eight duplicate and two to four single air samples for each paint were taken over the one-year test period. The sampling flow was about 50 ml/min and the sampling volumes were from 177 ml to 4885 ml at the end of the test period.

The total concentration of VOCs (TVOC) was calculated as the sum of the concentrations of quantified VOCs and unidentified peaks calibrated as toluene. White spirit concentration was calculated as the sum of unidentified peaks calibrated as toluene. Undecane was used as a representative for white spirit during the entire test period.

### Chambers

The electropolished stainless steel chambers had a volume of 0.234 m<sup>3</sup> resulting in a chamber loading of 1.46 m<sup>2</sup>/m<sup>3</sup> for the paints. The test conditions were 23.0 ± 0.6 °C, 45 ± 3% RH, and an air exchange rate of 0.25 ± 0.013 h<sup>-1</sup>. The chambers fulfilled the requirements of a Nordic method (Nordtest, 1990).

### Sample Preparation

Each paint was applied to two tin-plated steel sheets (501 mm × 341 mm each) by means of a synthetic short haired paint roller in order to obtain a surface similar to a painted wall. Before application the steel sheets were cleaned with methylisobutylether and heated to 300 °C for 24 hours. The application reproducibility was checked by weighing the two sheets immediately before and after application.

### Chamber Tests

Before each insertion of paint samples the chambers were cleaned and the background concentrations of VOCs in the chambers were measured. Shortly after preparation, the two paint samples were placed in the chamber and test start (time = 0) was established when the door was closed. Paints A, B, and control samples (two cleaned, unpainted tin-plated steel sheets) were tested in three chambers for a continuous three-week period, after which paints C, D, and E samples were tested for a continuous four-week period. During the one-year test period, paints A and B samples were inserted into the chambers three times and paints C, D, and E samples twice. Between chamber measurements the samples were stored in an office at normal ambient temperature, humidity and air exchange. After the office storing the paint samples were conditioned for a week in the chambers prior to measurements. The tests fulfilled the requirements of a Nordic method (Nordtest, 1990). When the tests were terminated, the dry film

thickness on each of the two paint samples was measured 10 times by means of a Twin-tector Elcometer.

#### Data Treatment and Calculations

Before the model fitting the concentration versus time data were reduced. Concentrations less than three times the average background were omitted and only data sampled after 24 hours of emission were used because the emission before was stronger (discussed later). Thus only data sampled during the

first continuous test period in the chambers were used in the calculations. There was no further data reduction. The model expression was fitted to the data with STATGRAPHICS routine for nonlinear regression using the standard regression parameters of the program (STATGRAPHICS, 1987). The duplicate samples were used as two individual data points at the nonlinear regression. The pooled film thickness of the two samples of each paint was used in the calculations because no significant difference be-

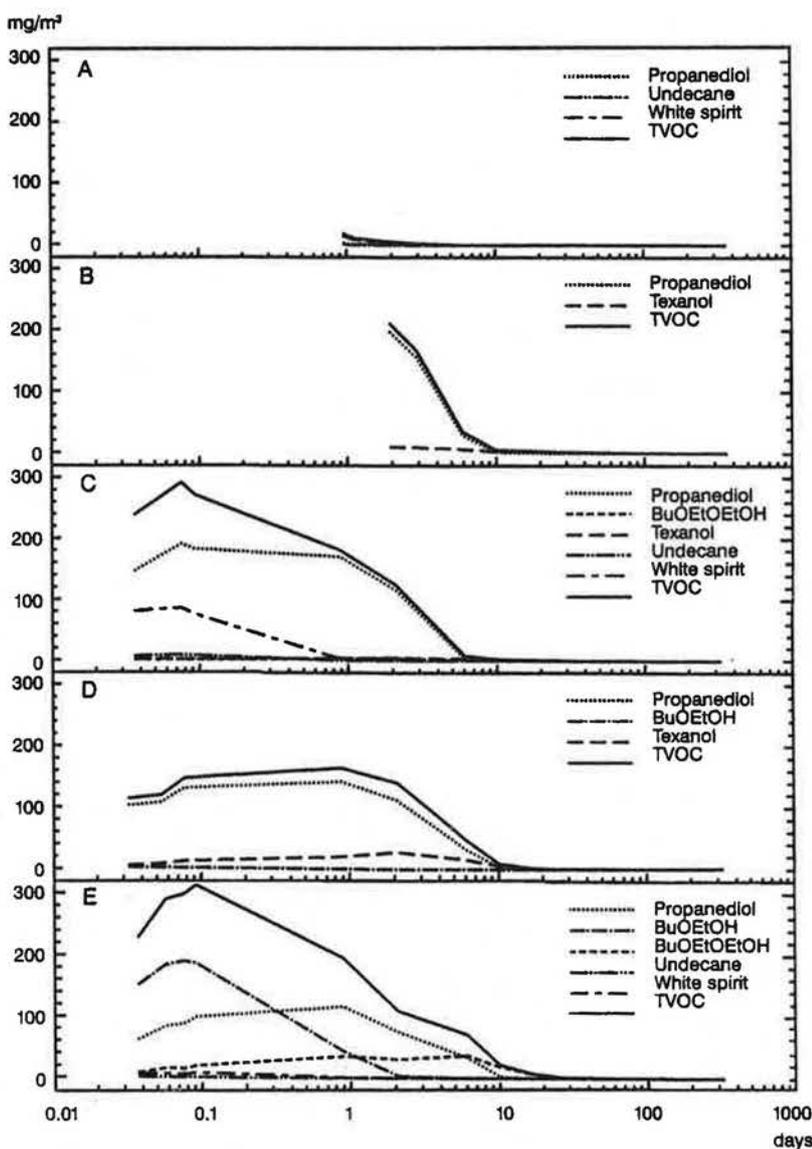


Fig. 1A. Chamber concentrations versus time (logarithmic scale) for the paints A-E in the range 0-300 mg/m<sup>3</sup>. Abbreviations of the VOC names are listed in Table 1.

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ples was found.

## Results

VOCs selected for quantitative measurements are shown in Table 1. It will be seen that some of the identified and selected VOCs were not stated in the recipes of the producers in spite of a relatively high content. Several explanations may be given. For example the white spirit content of paint E

may be due to use of white spirit as solvent in the production of the alkyd binder.

Figures 1A and 1B show the chamber air concentrations (each point estimated by single or duplicate measurements) as function of a logarithmic time scale. Generally the chamber air concentration increased during the initial hours following insertion of samples and decreased as the emission rate dropped. The high boiling VOCs Texanol and 2-(2-butoxyethoxy)ethanol, however, showed delayed maximum concentrations

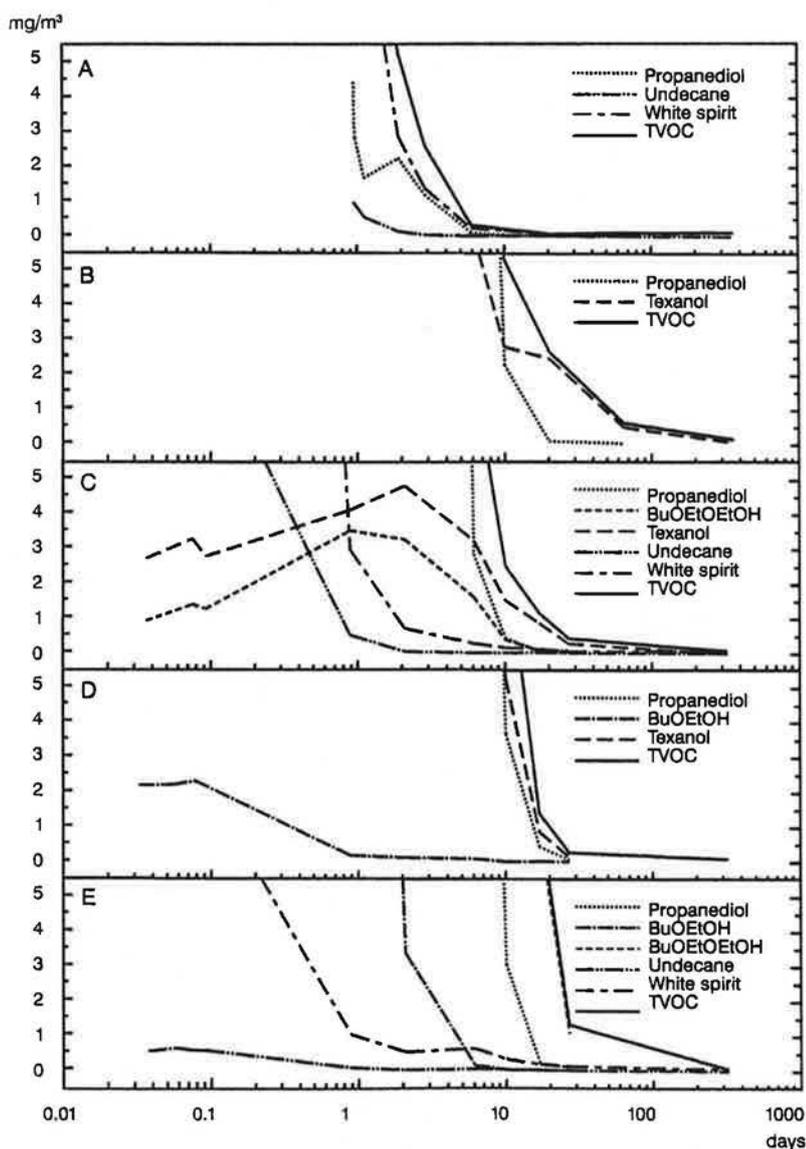


Fig. 1B. Chamber concentrations versus time (logarithmic scale) for the paints A-E in the range 0-5 mg/m<sup>3</sup>. The curves end when the succeeding measurement is below the detection limit. Abbreviations of the VOC names are listed in Table 1.

A. Chamber concentrations versus time (logarithmic scale) for the paints A-E in the range 0-300 mg/m<sup>3</sup>. Abbreviations of the VOC names are listed in Table 1.

**Table 1.** VOCs selected for quantitative measurements.

Paint		A	B	C	D	E
VOC	abbreviation					
1, 2-propanediol	(Propanediol)	*	+	+	+	+
2-butoxyethanol	(BuOEtOH)	*			*	+
2-(2-butoxyethoxy)ethanol	(BuOEtOEtOH)			*		+
2, 2, 4-trimethyl-1, 3-pentanediol monoisobutyrate	(Texanol)		+	+	+	
white spirit	(White spirit)	+		+		*

\* = VOC found in the paint emission but *not* stated in the recipe

+ = VOC found in the paint emission and stated in the recipe

after 1-6 days for paints C, D and E, respectively (see Figures 1A and 1B). Among the selected VOCs, Texanol was the only compound detectable after one year. The emissions from paints B and C resulted in Texanol concentrations of 0.057 mg/m<sup>3</sup> after 360 days and 0.001 mg/m<sup>3</sup> after 324 days, respectively. The application reproducibility is demonstrated by the amount and film thickness of the paints on the two samples (see Tables 2 and 3). The differences found for the amount of paint on the two samples, however, were not reflected in the film thicknesses, the differences being insignificant.

**Table 2.** The amount of paint (grams) on the two paint samples.

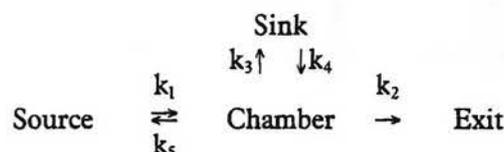
Paint	A	B	C	D	E
Sample 1	8.87	8.49	12.30	9.89	20.46
Sample 2	9.08	9.20	12.25	11.57	16.86

**Table 3.** Thicknesses of the paint films (micrometers) on the two paint samples and pooled film thicknesses together with the standard deviations (SD).

Paint	A	B	C	D	E
Sample 1	30.10	23.90	42.00	37.10	63.70
SD <sub>1</sub>	6.87	6.80	11.85	5.49	7.59
Sample 2	26.50	26.30	40.90	41.90	61.80
SD <sub>2</sub>	6.19	7.47	7.85	6.79	8.03
Mean <sub>pool</sub>	28.30	25.10	41.45	39.50	62.75
SD <sub>pool</sub>	6.63	7.06	9.80	6.49	7.66

## Derivation of Formulas

Models which mathematically try to decouple the true emission characteristics of an organic source from effects imposed by a climatic chamber have been developed (Dunn and Tichenor, 1987). These models assume that a climatic chamber consists of four (mathematical) compartments. These are the source, the homogeneous chamber air, an exit, and a sink. Rate constants describe the flow among these compartments as illustrated in the following scheme:



The so-called dilution model does not take into account sink and vapour pressure effects and therefore uses only the rate constants  $k_1$  and  $k_2$ . Using this model, the mass balance for the chamber over a small time increment  $dt$  can be expressed as shown in Equation 1 (see List of nomenclature):

$$V \cdot dC = A \cdot R \cdot dt - k_2 \cdot V \cdot C \cdot dt \quad (1)$$

It is assumed that the change in the concentration of a VOC in a thin film source can be approximated by a first order decay. The mass of a VOC per unit area of a given thin film source is proportional to the average concentration of the VOC in the source. It

can therefore be assumed that the loss of mass of an emitting VOC per unit area of the source is equal to a constant multiplied by the mass per unit area, i.e.:

$$dM_s/dt = -k_1 M_s \tag{2}$$

Given that  $M_s = M_0$  at  $t = 0$ , the solution to Equation 2 is:

$$M_s = M_0 \exp(-k_1 t) \tag{3}$$

The mass of the VOC per unit area of the source emitted to the chamber is:

$$M = M_0 - M_s = M_0 - M_0 \exp(-k_1 t) \tag{4}$$

Differentiation of Equation 4 with respect to time gives the emission rate of the source:

$$R = dM/dt = M_0 k_1 \exp(-k_1 t) \tag{5}$$

Given that  $C = 0$  at  $t = 0$ , the solution to the differential equation resulting from insertion of Equation 5 into Equation 1 is:

$$C = AM_0 k_1 (\exp(-k_1 t) - \exp(-k_2 t)) / (V(k_2 - k_1)) \tag{6}$$

**Emission of VOCs from Waterborne Paints**

The emission of VOCs from a waterborne paint film prior to film formation may be regarded as being controlled by evaporation, i.e. limited by diffusion through a boundary layer above the paint film (Kornum, 1980). The emission after film formation may be controlled either by evaporation or by internal diffusion in the paint film. This depends upon the VOC involved and the interactions which occur between different VOCs (Sullivan, 1975).

**Evaporation-Controlled Emission**

The evaporation-controlled emission may be characterized by an approximately homogeneous concentration of VOC in the paint film and an emission limited by diffusion in the

boundary layer (a stagnant air layer). The reduced time variable  $t/L$  has been used to correlate the evaporation-controlled concentration decrease of emitting VOCs in paint films for all times and film thicknesses (Hansen, 1974; Sullivan, 1975). The concentration of a VOC in a given paint film is proportional to the mass of the VOC per unit area of the paint film. Assuming that the change in mass of the VOC per unit area of the paint film can be approximated by a first order decay, substitution of  $k_{EI} t/L$  for  $k_1 t$  in Equation 3 ( $k_{EI}$  is assumed to be constant for all values of  $L$ ) would be expected to incorporate the effect of film thickness upon the evaporation-controlled emission:

$$M_s = M_0 \exp(-k_{EI} t/L) \tag{7}$$

Equation 7 is equivalent to Equation 3 and the expression for the emission rate can be derived in the same way as for Equation 5:

$$R = (M_0 k_{EI}/L) \exp(-k_{EI} t/L) \tag{8}$$

Defining  $M_0/L = M_{L0}$  and inserting into Equation 8 gives:

$$R = M_{L0} k_{EI} \exp(-k_{EI} t/L) \tag{9}$$

Given that  $C = 0$  at  $t = 0$ , the solution to the differential equation resulting from insertion of Equation 9 into Equation 1 is:

$$C = AM_{L0} k_{EI} (\exp(-k_{EI} t/L) - \exp(-k_2 t)) / (V(k_2 - k_{EI}/L)) \tag{10}$$

**Diffusion-Controlled Emission**

The diffusion-controlled emission is limited by diffusion in the paint film. It is characterized by a concentration gradient across the paint film though the VOC concentration in the paint film in the initial state (immediately after application) is homogeneous. The reduced time variable  $t/L^2$  has been used to correlate the diffusion-controlled concentra-

tion decrease of emitting VOCs in paint films for all times and film thicknesses (Hansen, 1974; Sullivan, 1975). In the same way as for the evaporation-controlled emission, substitution of  $k_{D1}t/L^2$  for  $k_1t$  in Equation 3 would be expected to incorporate the effect of film thickness upon the diffusion-controlled emission:

$$M_s = M_0 \exp(-k_{D1}t/L^2) \quad (11)$$

Using the same method of derivation as for the evaporation-controlled emission, the emission rate can be expressed as:

$$R = (M_{L0}k_{D1}/L) \exp(-k_{D1}t/L^2) \quad (12)$$

Given that  $C = 0$  at  $t = 0$ , the solution to the differential equation resulting from insertion of Equation 12 into Equation 1 is:

$$C = (AM_{L0}k_{D1}/L)(\exp(-k_{D1}t/L^2) - \exp(-k_2t)) / (V(k_2 - k_{D1}/L^2)) \quad (13)$$

Estimates of  $M_0$  and  $k_1$ ,  $M_{L0}$  and  $k_{E1}$ , and  $M_{L0}$  and  $k_{D1}$  are obtained by fitting Equations 6, 10 and 13, respectively, by nonlinear regression to the concentration versus time data. Approximate confidence ellipses for the estimate pairs are obtained as described in the appendix.

#### Time Required to Reach a Given Emission Rate

Waterborne paint films are decreasing sources and at a certain time the emission will be insignificant. Therefore the time required to reach a given emission rate is more suitable for comparison of the paints with regard to the indoor air than the initial mass of an emitting VOC and the first order rate constant. The time required to reach an emission rate equal to  $R$  can be obtained by rearrangement of Equation 5:

$$t(R) = (\ln(M_0 \cdot k_1/R))/k_1 \quad (14)$$

The time required to reach an emission rate equal to  $R$  for the evaporation- and diffusion-controlled emission can be obtained by rearrangement of Equations 9 and 12, respectively:

$$t(R) = L(\ln(M_{L0} \cdot k_{E1}/R))/k_{E1} \quad (15)$$

$$t(R) = L^2(\ln(M_{L0} \cdot k_{D1}/R \cdot L))/k_{D1} \quad (16)$$

The effect of film thickness on the emission of paints is obvious and therefore has to be considered in comparisons of different emission measurements. The simplest way to compare the paints is to normalize the film thicknesses to  $1 \mu\text{m}$ . Inserting  $L = 1 \mu\text{m}$  film thickness into Equations 15 and 16 gives the time required to reach an emission rate equal to the emission rate when  $L = 1 \mu\text{m}$  ( $R_E$  and  $R_D$ ) of the evaporation- and diffusion-controlled emission, respectively:

$$t(R_E) = (\ln(M_{L0} \cdot k_{E1}/R_E))/k_{E1} \quad (17)$$

$$t(R_D) = (\ln(M_{L0} \cdot k_{D1}/R_D))/k_{D1} \quad (18)$$

Estimates of  $t(R)$ ,  $t(R_E)$ , and  $t(R_D)$  are obtained by inserting estimate values from Table 4 into Equations 14, 17 and 18, respectively, and choosing an appropriate value for  $R$ ,  $R_E$ , and  $R_D$ . Confidence limits are obtained as described in the appendix.

## Discussion

### Analysis of the Results

It was found that the model was not able to describe the emission of the paints in the entire test period. Fitting Equation 6 to the data of the first 24 hours of emission gave estimates of  $M_0$  which were from 0.4 to 3.2 times the estimates of the emission after 24 hours. The corresponding estimates of  $k_1$  were from 4 to 40 times the estimates of the emission after 24 hours. This stronger initial emission may be due to a more rapid diffusion in the paint film because of the more li-

Table  
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Paint

1,2-pr

 $M_0$  $k_1$  $M_{L0}$  $k_{E1}$  $M_{L0}$  $k_{D1}$ (N; r<sup>2</sup>)

2-but

 $M_0$  $k_1$  $M_{L0}$  $k_{E1}$  $M_{L0}$  $k_{D1}$ (N; r<sup>2</sup>)

un

 $M_0$  $k_1$  $M_{L0}$  $k_{E1}$  $M_{L0}$  $k_{D1}$ (N; r<sup>2</sup>)

white

 $M_0$  $k_1$  $M_{L0}$  $k_{E1}$  $M_{L0}$  $k_{D1}$ (N; r<sup>2</sup>)

TV

 $M_0$  $k_1$  $M_{L0}$  $k_{E1}$  $M_{L0}$  $k_{D1}$ (N; r<sup>2</sup>)

N

r<sup>2</sup>

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**Table 4.** Emission parameters estimated by nonlinear regression for the five paints (A-E).

Paint	A	B	C	D	E
<i>1,2-propanediol</i>					
$M_0$	40	4259	2262	2621	2078
$k_1$	0.02	0.016	0.018	0.012	0.012
$M_{L0}$	1.40	170	55	66	33
$k_{E1}$	0.56	0.42	0.75	0.47	0.73
$M_{L0}$	1.40	170	55	66	33
$k_{D1}$	16	11	31	19	46
(N; $r^2$ )	(7;44)	(8;98)	(6;97)	(11;99)	(9;99)
<i>2-butoxyethanol</i>					
$M_0$				5	374
$k_1$				0.0057	0.089
$M_{L0}$				0.13	6
$k_{E1}$				0.22	6.6
$M_{L0}$				0.13	6
$k_{D1}$				8.8	351
(N; $r^2$ )				(7;11)	(9;99.9)
<i>undecane</i>					
$M_0$	10		4.3		
$k_1$	0.10		0.092		
$M_{L0}$	0.35		0.10		
$k_{E1}$	2.9		3.8		
$M_{L0}$	0.35		0.10		
$k_{D1}$	82		159		
(N; $r^2$ )	(7;99)		(4;99)		
<i>white spirit</i>					
$M_0$	127		24		11
$k_1$	0.072		0.050		0.024
$M_{L0}$	4.5		0.57		0.18
$k_{E1}$	2.1		2.1		1.5
$M_{L0}$	4.5		0.57		0.18
$k_{D1}$	58		87		93
(N; $r^2$ )	(7;99)		(4;98)		(3;65)
<i>TVOC</i>					
$M_0$	157	4609	2485	3502	4104
$k_1$	0.057	0.016	0.017	0.010	0.0092
$M_{L0}$	5.6	184	60	89	65
$k_{E1}$	1.6	0.41	0.72	0.40	0.58
$M_{L0}$	5.6	184	60	89	65
$k_{D1}$	46	10	30	16	36
(N; $r^2$ )	(7;95)	(10;98)	(10;99)	(11;99)	(11;97)

N = numbers of observations;  
 $r^2$  = squared correlation coefficient

quid-like state of the drying paint film and the high content of water which is an efficient plasticizer (Hansen, 1982). Therefore

data sampled before 24 hours of emission were omitted in the model calculations. Furthermore, all concentration data less than three times the average background were rejected on grounds of principle, though fitting Equation 6 to the reduced data sets and to data sets containing all data from 24 hours and up to one year gave the same estimate values in nearly all cases. Where this was not the case some of the duplicate samples had relative standard deviations (RSD) > 30% or the background level was high. This indicates that the model may be able to describe the emission of VOCs from waterborne paints in small chambers from 24 hours and up to one year and that emission data for only three weeks or less are sufficient to predict the one-year emission.

As indicated by the squared correlation coefficients ( $r^2$ ) in Table 4, Equation 6 fitted in nearly all cases with  $r^2 > 95\%$  to both single VOCs and TVOC data though the TVOC emission may be described by a sum of exponential functions as Equation 5. The relatively good fit of the TVOC data compared to the single VOCs is presumably due to the fact that the emissions were dominated by one VOC or that the major VOCs had approximately the same  $k_1$  values. In the cases where the fits had  $r^2 < 95\%$  some of the duplicate samples had a RSD > 30% or the number of observations was small.

The model did not fit to the reduced data sets of the high boiling VOCs Texanol and 2-(2-butoxyethoxy)ethanol. The model, however, fitted well to data beyond the delayed peaks of the emission (see Figures 1A and 1B). Sink effects may be the reason for the delay. Fitting the sink model (Dunn and Tichenor, 1987) to the data sets, however, was unsuccessful because of insufficient data. Figure 2 shows a theoretical example of the influence of sink effects on the emission curve profile based on the sink model. The full line curve was calculated without sink effects ( $k_1 = 0.02$ ,  $k_2 = 0.25$ ) and the dotted curve was calculated with sink effects ( $k_1 =$

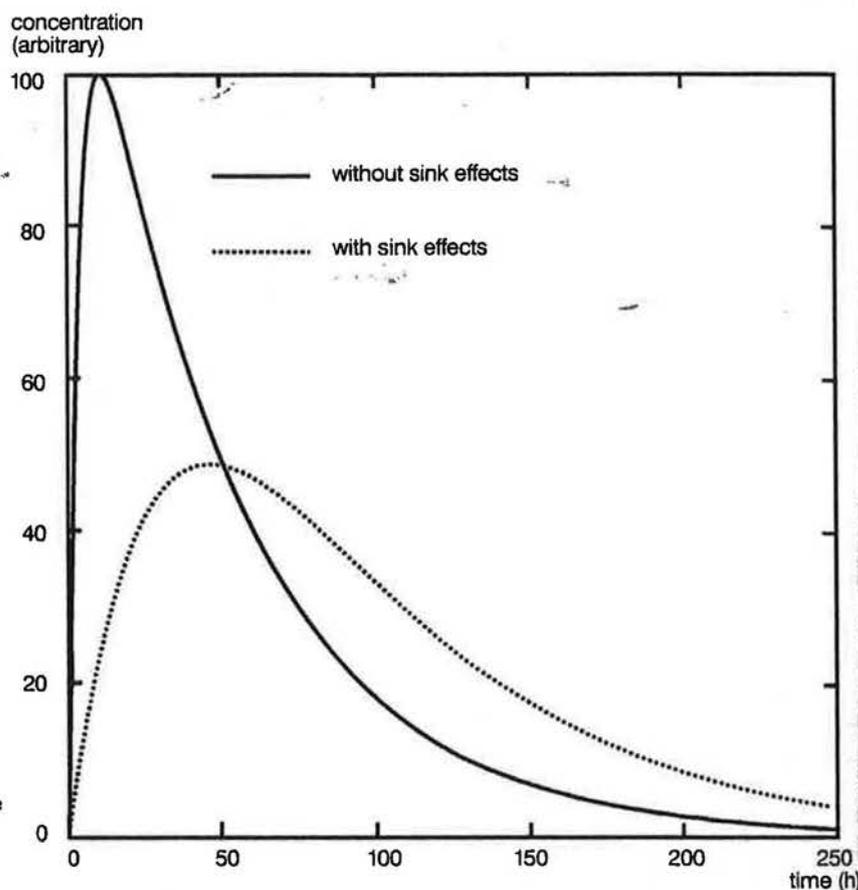


Fig. 2. Theoretical example of the influence of sink effects on the emission curve profile of the same source.

0.02,  $k_2 = 0.25$ ,  $k_3 = 100$ ,  $k_4 = 10$ ). The result is a much lower and delayed summit of the curve just as the experimental results showed for Texanol and 2-(2-butoxyethoxy)ethanol. It was also found difficult to remove these VOCs from the chambers after testing, thus supporting the postulated sink effects. They were therefore omitted from further analysis because of insufficient data to estimate the sink effects.

The other VOCs in this investigation are believed to have no sink effects of significance for the estimated values of  $M_0$  and  $k_1$ . Sink effects where the ratio  $k_3/k_4$  is up to 0.76 have been found for methyl ethyl ketone, butyl propionate and a  $C_8$  alcohol under similar conditions (Dunn and Tichenor, 1987). Theoretical calculations showed that sink effects of that magnitude do not alter emission curve profiles markedly or

alter  $M_0$  and  $k_1$  found by fitting Equation 6 which does not take sink effects into account. The same type of calculation showed that the magnitude of the vapour pressure effect found for the above-mentioned three VOCs under similar conditions (Dunn and Tichenor, 1987) was not of significance for the estimated values of  $M_0$  and  $k_1$ .

#### Comparison of the Emission of VOCs from Waterborne Paints

The estimated values of  $M_0$  and  $k_1$ ,  $M_{L0}$  and  $k_{EL}$ , and  $M_{L0}$  and  $k_{DL}$  found by nonlinear regression are listed in Table 4. Theoretical  $M_0$  or  $M_{L0}$  is the initial mass of VOC in the paint film (per area and volume, respectively), i.e. the amount of VOC used in the formulation of the paint. For waterborne paints, however,  $M_0$  and  $M_{L0}$  give only hypothetical values of the initial mass because the initial

emission is stronger than that found later. Therefore  $M_0$  and  $M_{L0}$  are underestimated and equal to the initial mass if  $k_1$ ,  $k_{E1}$  or  $k_{D1}$  was constant from  $t = 0$ . The rate constants

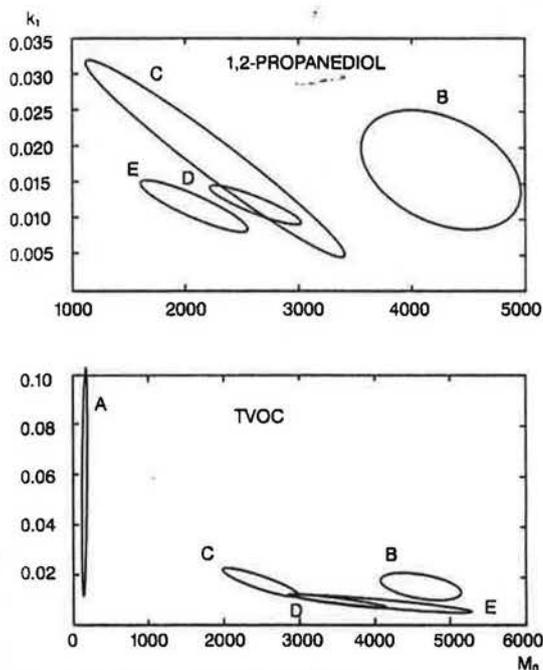


Fig. 3. 95% confidence ellipses for  $M_0$ ,  $k_1$ .

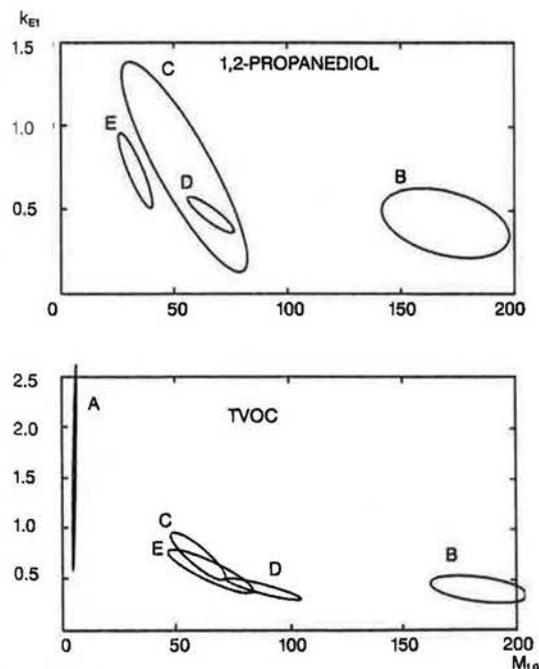


Fig. 4. 95% confidence ellipses for  $M_{L0}$ ,  $k_{E1}$ .

$k_1$ ,  $k_{E1}$  and  $k_{D1}$  are related to the diffusivity of the VOCs in the paint film matrix or in the boundary layer depending upon the type of emission. Table 4 shows that the rate constants have a tendency to be positively correlated to the volatility of the VOCs.

Confidence regions of the estimate pairs of the initial mass and the rate constant can be used to compare the emission of the paints. These confidence regions can be approximated by ellipses (see appendix). Comparison was only possible for 1,2-propanediol and TVOC because some of the confidence ellipses of the other VOCs had negative values. The confidence ellipses are shown in Figures 3, 4 and 5 for  $M_0$  and  $k_1$ ,  $M_{L0}$  and  $k_{E1}$ , and  $M_{L0}$  and  $k_{D1}$ , respectively. Figure 3 shows that the 1,2-propanediol emission (not corrected for film thickness) is significantly different for paints B, E and C or D (C and D are indistinguishable). The TVOC emission from paints A and B is significantly different from C, D or E which are indistinguishable.

The film thickness has to be considered in comparing the paints because it affects the

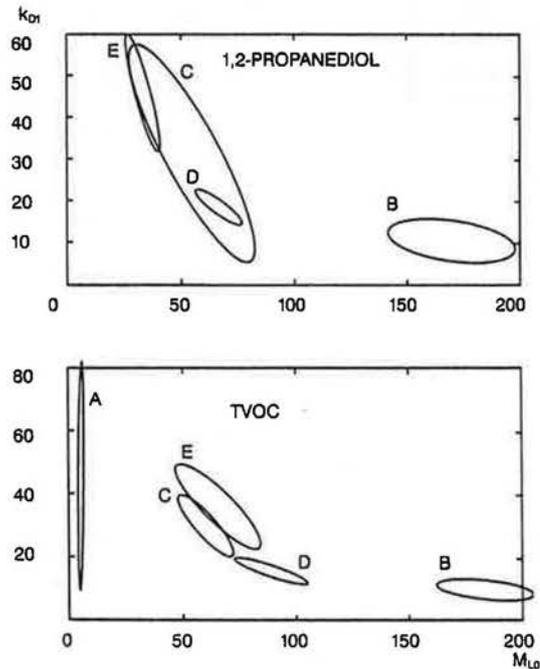
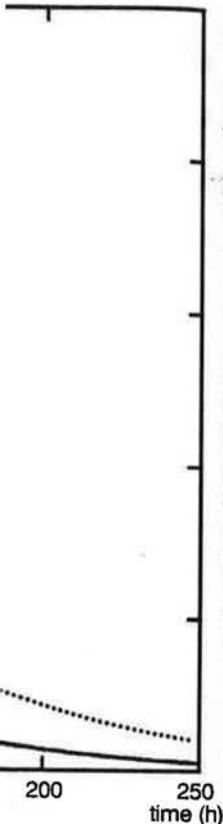


Fig. 5. 95% confidence ellipses for  $M_{L0}$ ,  $k_{D1}$ .

ints



fitting Equation 6  
k effects into ac-  
calculation showed  
vapour pressure ef-  
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tions (Dunn and  
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ision of VOCs

and  $k_1$ ,  $M_{L0}$  and  
by nonlinear re-  
4. Theoretical  $M_0$   
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C used in the for-  
waterborne paints,  
only hypothetical  
because the initial

emission. In this investigation only one layer of paint has been applied and the film thicknesses ranged from 25  $\mu\text{m}$  to 63  $\mu\text{m}$  as shown in Table 3. In practice, however, paints are applied in one, two or three layers depending on the covering power. The simplest way to compare the paints is therefore to normalize the film thicknesses to 1  $\mu\text{m}$ . This implies that any change in chamber concentration resulting from a change in film thickness or other factors does not change the rate constant. The type of emission of single VOCs is unknown. It is therefore necessary to compare the estimates of both the evaporation- and diffusion-controlled emission. The 1,2-propanediol emission of paint B (normalized to a film thickness of 1  $\mu\text{m}$ ) as shown in Figures 4 and 5 differ significantly from paints C, D or E which are indistinguishable. The TVOC emissions from paints A and B differ significantly from C, D or E which are also indistinguishable. In this case normalization of film thickness has no important effect on the conclusions, though paint B differs more from the others.

#### Comparison of the Emission from Waterborne Paints from the Point of View of Indoor Air

The estimates of the time required to reach a given emission rate,  $t(R=0.1)$ ,  $t(R_E=0.1)$ ,

and  $t(R_D=0.1)$ , and their corresponding confidence intervals of the TVOC emission of the five paints are presented in Figures 6-8. The value of 0.1 of the emission rates is chosen arbitrarily. Figure 6 shows that  $t(R)$  of paint A is significantly smaller than that of all the other paints which are indistinguishable. Paint A has the smallest value and paint E the largest. It is necessary to compare the estimates of both the evaporation- and diffusion-controlled emissions as mentioned earlier. Figures 7 and 8 show that paints A and C have significantly smaller values than paint B. Paints D and E do not differ significantly from paints A or B, while paints C-E are indistinguishable. Paint A still has the smallest value while paint B now has the largest value.

Comparison of the paints using estimates of the time required to reach a given emission rate will, however, be on a relative scale with respect to absolute concentrations in the indoor air because sink effects in houses and stainless steel chambers are likely to be different.

Using the criterion that the best paint with regard to indoor air quality is the one which reaches the lowest possible emission rate within the shortest time, paint A is the best and paint B the worst.

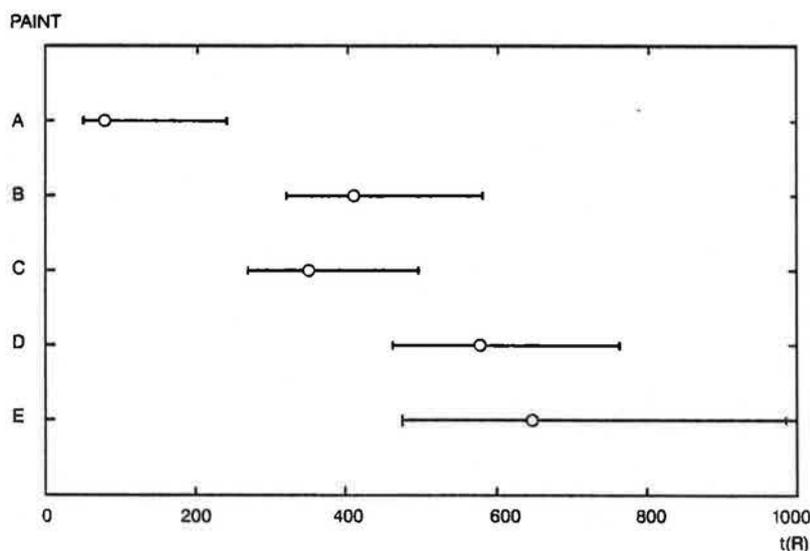


Fig. 6. Estimates of  $t(R)$  (indicated by o) and 95% confidence limits for the TVOC emission.

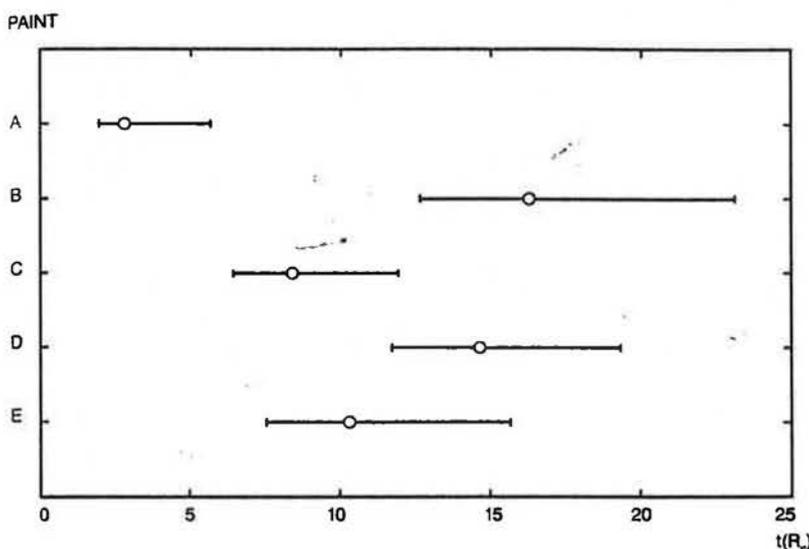


Fig. 7. Estimates of  $t(R_e)$  (indicated by o) and 95% confidence limits for the TVOC emission.

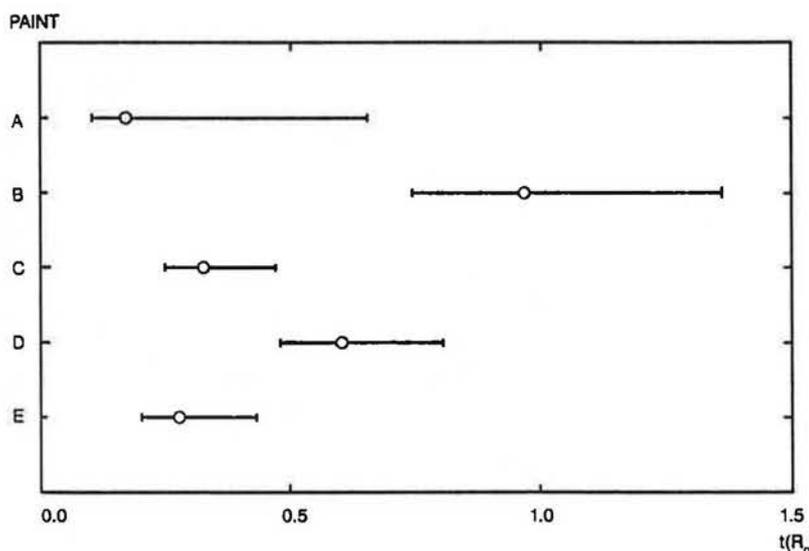


Fig. 8. Estimates of  $t(R_0)$  (indicated by o) and 95% confidence limits for the TVOC emission.

The problem with this criterion of comparison is that the maximum air concentrations of VOCs emitted from a paint in a room are reached a few hours after application (Hansen et al., 1987). The faster the emission rate, the higher the maximum concentration. Therefore the indoor air quality is complementary to the occupational environment.

Factors that influence the time required to reach a given emission rate may be illustrated by using Equations 17 and 18 for the eva-

poration- and diffusion-controlled emission, respectively. The value of  $t(R)$  may be reduced by a reduction of the film thickness,  $L$ , by a reduction of the initial amount of VOC,  $M_{L0}$ , and by an increase in the value of  $k_{E1}$  or  $k_{D1}$ . The value of  $t(R)$  may also be reduced by a shift from diffusion- to evaporation-controlled emission. This may be obtained by an increase of the diffusivity in the paint film which depends on the physical/chemical properties of the paint film matrix and the emitting VOC. Table 5 shows some

estimates of  $t(R)$  (indicated by o) and 95% confidence limits for the TVOC

**Table 5.** The effect of different factors on the time to reach a given emission rate,  $t(R)$ , illustrated by fictive theoretical examples.

L ( $\mu\text{m}$ )	$M_{L0}$ ( $\text{mg}\cdot\text{m}^{-2}\cdot\mu\text{m}^{-1}$ )	$k_{E1}$ ( $\mu\text{m}\cdot\text{h}^{-1}$ )	$k_{D1}$ ( $\mu\text{m}^2\cdot\text{h}^{-1}$ )	$t(R=0.1)$ (h)
60	150		10	1988
60	15		10	1159
20	150		10	265
60	150	2.1		113
20	150	2.1		77

L = film thickness,  $M_{L0}$  = initial amount of VOC (concentration),  $k_{E1}$  and  $k_{D1}$  = rate constants of evaporation- and diffusion-controlled emission, respectively.

fictive examples of the effect of the different factors upon  $t(R)$  using parameter values found in this work. The worst case example is a thick film of a paint containing a large amount of a VOC which is slowly emitted by diffusion control. The best case example is a thin film of a paint containing a VOC which is emitted quickly by evaporation control. Table 5 shows that a tenfold reduction of the initial amount of VOC has only a relatively small influence upon the value of  $t(R)$ . Reduction of the initial content of VOC, however, will reduce the maximum air concentration of VOC a few hours after application of a paint.

### Conclusion

A model including an exponentially decreasing emission rate of the paint film and the air exchange rate was found suitable to describe the emission of VOC from waterborne paints in small climatic chambers. Data sampled within three weeks or less are probably sufficient to predict the emission up to one year.

The results indicate that comparison of emissions of decreasing thin film sources such as waterborne paints requires normalization of film thickness, otherwise incorrect conclusions may be drawn.

Estimates of time to reach a given emission rate are found suitable for a relative

comparison of the emission of VOCs from waterborne paints with regard to indoor air.

Reduction of long-term emissions may be obtained most efficiently by substituting a more volatile VOC whose emission is controlled by evaporation for a less volatile VOC characterized by diffusion-controlled emission and/or by reducing the paint film thickness rather than reducing the initial VOC content of the paint.

These approaches of comparison may also be applied to other thin film sources such as adhesives, varnish, etc. It is recommended that sufficient data be sampled to estimate sink and vapour pressure effects.

### List of nomenclature

- A = area of source ( $\text{m}^2$ )
- C = chamber air concentration ( $\text{mg}\cdot\text{m}^{-3}$ )
- $k_1$  = rate constant of emission ( $\text{h}^{-1}$ )
- $k_2$  = air exchange rate ( $\text{h}^{-1}$ )
- $k_{D1}$  = rate constant of diffusion-controlled emission for  $L = 1 \mu\text{m}$  ( $\mu\text{m}^2\cdot\text{h}^{-1}$ )
- $k_{E1}$  = rate constant of evaporation-controlled emission for  $L = 1 \mu\text{m}$  ( $\mu\text{m}\cdot\text{h}^{-1}$ )
- L = paint film thickness ( $\mu\text{m}$ )
- M = mass of the VOC emitted to the chamber ( $\text{mg}\cdot\text{m}^{-2}$ )
- $M_0$  = initial mass in the source of the emitting VOC ( $\text{mg}\cdot\text{m}^{-2}$ )
- $M_{L0}$  =  $M_0/L$  = initial specific mass (concentration) in the source of the emitting VOC ( $\text{mg}\cdot\text{m}^{-2}\cdot\mu\text{m}^{-1}$ )
- $M_s$  = mass in the source of the emitting VOC ( $\text{mg}\cdot\text{m}^{-2}$ )
- R = source emission rate ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ )
- $R_0$  = initial source emission rate ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ )
- $R_D$  = emission rate of diffusion-controlled emission for  $L = 1 \mu\text{m}$  ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ )
- $R_E$  = emission rate of evaporation-controlled emission for  $L = 1 \mu\text{m}$  ( $\text{mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ )
- t = time (h)
- $t(R)$  = time to reach an emission rate equal to R (h)

$t(R_D)$  = time to reach an emission rate equal to  $R_D$  (h)

$t(R_E)$  = time to reach an emission rate equal to  $R_E$  (h)

$V$  = chamber volume ( $m^3$ )

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## Appendix

### Estimation of the approximate confidence ellipses

It is assumed that the distribution of the estimate vector  $\mathbf{x} = (\hat{M}_0, \hat{k}_1)$  in the nonlinear model is bivariate normal with the covariance matrix  $\Sigma$  i.e.  $\mathbf{x} \in N_2(\mu, \Sigma)$  where  $\mu = (M_0, k_1)$ .

The asymptotic estimate of  $\Sigma$  is denoted  $S$ . This matrix is estimated by the STATGRAPHICS program.

The distribution of  $S$  is approximately a Wishart distribution which, in the general case (i.e. where  $\mathbf{x}$  is  $p$  dimensional), has the parameters  $n-p$  and  $1/(n-p) \Sigma$  where  $n$  is the number of observations and  $p$  is the number of parameters in the nonlinear model i.e.

$$S \in W(n-p, 1/(n-p)\Sigma) \text{ or } (n-p)S \in W(n-p, \Sigma).$$

The distribution of  $(n-p)(\mathbf{x}-\mu)'((n-p)S)^{-1}(\mathbf{x}-\mu) = (\mathbf{x}-\mu)'S^{-1}(\mathbf{x}-\mu)$  is then a  $T^2$  distribution with parameters  $(p, n-p)$  (Mardia et al., 1980).

The distribution of  $T^2(p, n-p)$  is equal to the distribution  $(n-p)p/(n-2p+1)F(p, n-2p+1)$  where  $F(p, n-2p+1)$  is a  $F$ -distribution with  $(p, n-2p+1)$  degrees of freedom (Mardia et al., 1980). The same applies to the estimate vectors  $\mathbf{x} = (\hat{M}_{LO}, \hat{k}_{EI})$  or  $\mathbf{x} = (\hat{M}_{LO}, \hat{k}_{DI})$ .

A  $100(1-\alpha)$  percent confidence region for  $\mu = (M_0, k_1)$  consists thus of all the  $\mu$  vectors satisfying the inequality

$$(\mathbf{x}-\mu)'S^{-1}(\mathbf{x}-\mu) \leq (n-p)p/(n-2p+1)F(p, n-2p+1)_{1-\alpha}$$

where  $F(p, n-2p+1)$  is the  $(1-\alpha)$  fractile in the  $F$ -distribution. Note that for  $p=2$  the region is an ellipse.

Let  $g(\mu)$  be a function of  $\mu$ . An approximate  $100(1-\alpha)$  percent confidence interval for  $g(\mu)$  can be calculated by inserting all vectors of  $\mu$  defining the border of the confidence region of  $\mu$  given above in  $g(\mu)$ .

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