

Adsorption of Selected Volatile Organic Compounds on a Carpet, a Wall Coating, and a Gypsum Board in a Test Chamber

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Abstract

The adsorption of vapours of different volatility and polarity on three materials widely used indoors (carpet, gypsum board, wall coating) has been investigated in small test chambers, in order to study methodological aspects and to estimate the importance of the phenomenon for human exposure assessments. The output of the models used, with rate constants describing two different sinks, is discussed. The experiments show that: a) adsorption seems to occur to at least two different sinks with different rate constants in the same material; b) generally adsorption increases with the boiling point of the compounds, but it depends also on other physicochemical properties, such as the chemical functionality, as well as on the sorbent material: e.g. the two alkanes n-decane and n-dodecane show a higher k_3/k_4 ratio on carpet than on gypsum board, whereas the opposite is observed for the two alcohols 2-butoxyethanol and 2-ethylhexanol.

KEY WORDS:

Adsorption, Indoor materials, Carpet, Gypsum board, Wall coating, Models, Test chambers, VOC.

Introduction

The adsorption of atmospheric pollutants on indoor materials has an impact on the exposure of occupants. Adsorption may lower the peak concentrations but the subsequent desorption will prolong the presence of indoor air pollutants.

Berglund et al. (1987) reported the emission of organic compounds from materials of a 7-year-old building, which they thought to be due to adsorption/desorption. A first qualitative study of volatile organic compounds (VOCs) adsorption on indoor materials (Seifert and Schmahl, 1987) has already evidenced the complex nature of this phenomenon. The adsorption of selected VOCs to homogeneous surface materials (carpet components) was studied in a quantitative way (Borazzo et al., 1990). Tichenor applied a sink model to the adsorption of two lipophilic compounds tested on a carpet (Tichenor et al., 1991) and identified the need for further studies and model development. Whereas all these studies were performed in a dynamic way in order to simulate real life conditions, the distribution of different VOCs between the vapour and the adsorbed state for various textile floor coverings was measured in a static system (Levsen and Sollinger, 1993).

This paper reports work aiming at the quantification of the phenomenon for selected VOCs and surface materials; the work includes testing and adaptation of an existing model. The adopted approach consisted in exposing the materials to constantly emitted vapours of the selected compounds into small test chambers and measuring their concentrations as a function of time, until a steady state was attained. The concentration-time data were the input for an existing model with five rate constants, two of them being known, the others characterizing

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a two-sink (one reversible and the other irreversible) adsorption phenomenon. For validation purposes, some experiments were carried out under static (no-flow) conditions (see below). A two-sink model analogous to the model describing the dynamic adsorption tests was developed to analyse the data of the static experiments.

Methods

The experiments were carried out in three environmental test chambers described elsewhere (Colombo et al., 1990): two chambers have glass walls (0.45 m³) and one chamber is of electropolished stainless steel (0.28 m³). The controlled parameters were temperature (23 ± 0.5 °C), relative humidity (from < 10% to 70 ± 5%, see below), air exchange rate (0 to 1 h⁻¹) and loading factor (1.1 and 1.8 m² · m⁻³, respectively for dynamic and static experiments). Air mixing in the chamber was achieved by fans. Vapours were introduced into the chambers at a constant rate using diffusion vials, maintained at constant temperature and weighed weekly: the coefficient of variation of the weight loss was < 2%. Vapour concentrations were determined by sampling 1 litre of chamber air on Tenax TA cartridges, thermal desorption with cryofocussing and capillary GC-FID analysis (De Bortoli et al., 1992).

The following materials were tested: 1) carpet, nylon fibre pile, SBR (stirene butadiene rubber) backing, 4 mm overall thickness, 1900 g · m⁻², used widely in rooms with heavy traffic; 2) blown vinyl wallcoating, 240 g · m⁻²; 3) gypsum board, cartoon finish on both sides, 12 mm thickness. These materials were chosen in view of their use as large surfaces in indoor environments and/or because of their suspected high adsorption capacity. The compounds for adsorption testing were selected on account of: a) their importance as indoor air pollutants; b) their wide volatility range; c) their lipophilic or hydrophilic character, a feature more important than polarity, according to our experience. The following were selected and used (in GC elution order): tetrachloroethene, 2-butoxyethanol, α -pinene, 1,2,4-trimethylbenzene, 1,4-dichlorobenzene, n-decane, 2-ethylhexanol, n-dodecane. Hexanal, aniline and nicotine, initially also selected, had to be discarded either because no constant source could be obtained or because of analytical difficulties.

All the dynamic experiments were carried out in the glass chambers, whereas the static experiments

were performed in the stainless steel chamber. However, the equivalence of the two chamber types has been confirmed in an interlaboratory comparison (De Bortoli and Colombo, 1993).

The basic experimental design was dynamic, i.e., with airflow through the chamber and continuous inlet of the compound vapours at a constant rate, starting from the introduction of the material (t_0 , i.e., $t = 0$); vapour sampling was carried out at fixed time intervals after t_0 , normally up to 48 hours, but also for longer periods (in one case 528 h). Steady-state concentrations in these experiments ranged from 0.05 to 1 mg · m⁻³. In order to confirm results of this type of experiment, some static tests were carried out. For these experiments compounds were injected at the beginning of an experiment as liquids with a microsyringe into the sealed chamber, where they vaporized, assisted by fan mixing of the air. The (decreasing) vapour concentrations were measured as a function of time (initial concentration c_0 at time t_0). In this case the volume of air samples was reduced to 0.5 litre. The tightness of the chamber was occasionally tested by injecting inert SF₆ tracer gas, the concentration of which showed a decay of $\approx 0.1\% \text{ h}^{-1}$.

The fitting model for the dynamic tests was adapted from the constant source full model of Dunn and Tichenor (1988), which includes one reversible sink. The analytical relationships in their Table 1 do not change if the "vapour pressure" term k_5 is interpreted as an "irreversible sink" effect, thus making the model capable of including two different sinks. This interpretation implies, however, a constant source emission rate and the deposition of the emitted compounds to a sink rather than the recondensation to the source. The Appendix reports the mathematical expressions for both the dynamic model and the model developed to describe the static experiments (in a more compressed form than in Dunn and Tichenor, 1988).

Whenever appropriate, the rate constants are: k_1 (known), the source emission rate; k_2 (known), the air exchange rate; k_3 , the rate of deposition to the reversible sink; k_4 , that of emission from this sink; k_5 , the rate of deposition to the irreversible sink. All of them are regarded as positive, the possible exception being k_5 in the dynamic tests, if small (within $\pm 5\%$) in comparison to k_2 . When small, the irreversible sink effect could simply mean an error in the airflow measurement.

The unknown constants (including c_0 for the static case) were estimated from the experimental data

by a non-linear least square regression program taken from Valkó and Vajda (1989), which was updated with sections for the data input and the instant plot of the fits. It allows for the simultaneous regression of both the equations of concentration (Equations 1 or 7) and of the entire sink. The latter is the whole mass existing in the two sinks at a given time, expressed by $w_{rev} + w_{irr}$ (Equations 2 + 3 or 8 + 9). In the dynamic case the experimental data for the entire sink were obtained by the trapezoid rule from the difference between the ideal (i.e., no sinks: $k_3 = k_5 = 0$ in Equation 1) and the experimental concentration data, taking into account the chamber airflow rate. In the static case, the data were obtained from the difference between experimental c_0 and experimental concentration data, taking into account the chamber volume. Use of the trapezoid rule is illustrated elsewhere (De Bortoli and Colombo, 1992).

The resulting estimates, with very few exceptions, were significantly different from zero at the 95% confidence level. Regressing both equations, rather than that of concentration only as is usually done, provides more significant parameter estimates (i.e., with smaller standard errors) and sometimes leads better towards optimum regression convergence. However, from routine checks, it is believed that regressing the sole concentration equation should in general yield quite acceptable and similar estimates. Once the unknowns are obtained, the relationships in the Appendix can provide compound mass budgets at any time.

Results and Discussion

Initially, several dynamic experiments were performed to test the reproducibility of the procedure, the influence of different relative humidities, and the effect of the hydrophilic or lipophilic character of the test compound. The results of these tests, carried out at an air exchange rate of $1.05 \pm 0.05 \text{ h}^{-1}$ with n-decane and 2-butoxyethanol in the empty chamber and in the chamber with carpet, are reported in Table 1.

The table shows that whilst the rate constants k_3 to k_5 vary considerably, the ratio k_3/k_4 varies much less. The relatively large differences found for the estimated constants are due essentially to the variability of the experimental data, as in any regression procedure. The ratio k_3/k_4 represents the ratio of the masses of a compound in the reversible sink and in the vapour phase of the chamber at steady state

Table 1 Adsorption parameters for n-decane and 2-butoxyethanol

Conditions	$k_1(\text{h}^{-1})$	$k_3(\text{h}^{-1})$	$k_5(\text{h}^{-1})$	k_3/k_4
<i>n-decane</i>				
empty chamber, 70% RH	0.36	0.75	0.03	0.48
empty chamber, 35% RH	0.83	1.06	-0.04	0.78
carpet, 35% RH	1.22	0.31	0.12	3.97
carpet, 70% RH	0.63	0.14	0.14	4.46
carpet, 35% RH	0.93	0.19	0.09	4.82
carpet, 35% RH	1.66	0.44	0.11	3.75
<i>2-butoxyethanol</i>				
empty chamber, 35% RH	0.11	0.09	0	1.26
empty ch., <10% RH	1.46*	7.96*	0.03	0.18
carpet, <10% RH	0.74	0.12	0.26	6.25
carpet, 35% RH	1.42	0.35	0.21	4.05
carpet, 75% RH	1.23	0.33	0.22	3.72
carpet, 35% RH	0.43	0.06	0	7.11

* multiply by 1,000

(from Equations 5 and 6 in the Appendix). As can be expected, the ratio is smaller for the empty chamber than for the chamber with carpet. Moreover, the values of k_5 for the two chamber conditions (with and without carpet) parallel in general those of k_3/k_4 , implying a more important irreversible sink in the chamber with carpet. The adsorption property of this carpet does not appear to be influenced by either the lipophilic or hydrophilic character of the test compounds, or by the relative humidity. In fact, if the mean and standard deviation of k_3/k_4 for the four experimental values available for carpet are calculated, one obtains 4.25 ± 0.48 and 5.28 ± 1.66 , for n-decane and 2-butoxyethanol respectively. This variability appears small if the entire procedure involved is considered.

To investigate whether k_5 really describes an irreversible adsorption, an experiment with n-decane on carpet was conducted for 528 h in the adsorption phase and then for the same period in the desorption phase, i.e., with the source removed and clean air flowing through the chamber. Whereas the dynamic model indicated the adsorbed vapours to be almost totally in the irreversible sink, in the desorption phase the whole accumulated mass was released, although very slowly. Hence, the model does not fully describe the phenomenon despite its general very good fit with the data.

Four dynamic experiments, one with the empty chamber and three with one of the test materials, were performed using a mixture of all eight test compounds. Table 2 reports the results of these experiments. The ratios k_3/k_4 are represented in Figure 1. Interestingly, the ratio k_3/k_4 for tetrachlo-

Table 2 Adsorption and desorption constants for the compounds and materials tested (h^{-1})

Compounds (ordered by b.p.)	Empty chamber			Carpet			Blown vinyl			Gypsum board		
	k_3	k_4	k_5	k_3	k_4	k_5	k_3	k_4	k_5	k_3	k_4	k_5
tetrachloroethene	332	1410	0.15	1.04	0.91	0.17	2.04	7.13	0.17	0.21	0.04	0.06
α -pinene	56.4	196	0.18	0.74	0.68	0.23	0.36	0.41	0.24	1.19	0.98	0.13
1,2,4-trimethylbenzene	0.98	2.56	0.17	1.34	0.21	0.32	1.68	0.60	0.21	1.33	0.54	0.14
2-butoxyethanol	2200	9610	0.22	1.39	0.24	0.27	2.78	0.87	0.54	1.22	0.13	1.28
n-decane	91.2	332	0.17	1.14	0.28	0.28	1.13	1.01	0.17	1.24	0.40	0.08
1,4-dichlorobenzene	6060	8130	0.52	2.46	0.20	0.71	3.26	0.49	0.64	1.64	0.31	0.23
2-ethylhexanol	1.25	1.47	0.24	0.85	0.11	0.26	2.68	0.38	0.23	1.37	0.11	0.76
n-dodecane	0.53	0.59	0.21	2.05	0.13	0.85	3.29	0.40	0.20	2.00	0.16	0.09

Table 3 Concentrations ($mg \cdot m^{-3}$) and masses adsorbed in the sinks (mg) at the end of the experiment as obtained through the model

Compounds (ordered by b.p.)	Empty chamber			Carpet			Blown vinyl			Gypsum board		
	conc.	sink 1	sink 2	conc.	sink 1	sink 2	conc.	sink 1	sink 2	conc.	sink 1	sink 2
tetrachloroethene	0.288	0.03	0.90	0.283	0.15	1.01	0.312	0.04	1.72	0.351	0.73	0.61
α -pinene	0.234	0.03	0.89	0.224	0.11	1.07	0.245	0.10	1.85	0.269	0.15	1.16
1,2,4-trimethylbenzene	0.348	0.06	1.24	0.307	0.86	1.90	0.363	0.46	2.36	0.386	0.43	1.76
2-butoxyethanol	0.137	0.01	0.64	0.131	0.34	0.68	0.156	0.22	2.61	0.078	0.32	3.12
n-decane	0.244	0.03	0.86	0.223	0.40	1.23	0.268	0.13	1.42	0.290	0.40	0.76
1,4-dichlorobenzene	0.048	0.02	0.52	0.041	0.23	0.54	0.105	0.32	2.04	0.126	0.30	0.91
2-ethylhexanol	0.093	0.04	0.47	0.089	0.33	0.44	0.105	0.34	0.72	0.070	0.40	1.58
n-dodecane	0.079	0.03	0.34	0.052	0.37	0.81	0.089	0.33	0.51	0.099	0.55	0.24

N.B. Sink -1 is called "reversible" and sink -2 is called "irreversible" in the text. Concentrations and sink -1 values were in practice identical to the steady-state values.

roethene on carpet (1.15), if divided by the loading factor ($1.1 \text{ m}^2 \cdot \text{m}^{-3}$), gives a result of 1.05 m which compares well with the formally equivalent value of k_c ($0.89 \pm 0.19 \text{ m}$) in the paper by Tichenor (Tichenor et al., 1991) for the adsorption of the same compound on a nylon carpet.

Table 3 provides, according to the model, the amounts (mg) of the tested compounds partitioned between the two sinks at the end of the experiments. As an alternative to the masses deposited in the two sink compartments, one could have reported "recovery" values. The "recovery" is defined as the sum of the masses in the two sinks divided by the total mass, i.e. the sum of the mass exhausted from the chamber, the (small) mass remaining in the chamber air and the mass in the sinks. We have deemed it more interesting, from the point of view of human exposure, to report the mass deposited. However, just to give an idea, the "recovery" of the eight compounds in the experiments reported in Table 3 ranges between 67% (1,4-dichlorobenzene) and 88% (tetrachloroethene) for the empty chamber; between 47% (n-dodecane) and 85% (tetrachloroethene) for carpet; between 60% (1,4-dichlorobenzene) and 86% (tetrachloroethene) for

blown vinyl; and between 41% (2-butoxyethanol) and 89% (tetrachloroethene) for gypsum board.

The data in Tables 2 and 3 and in Figure 1 deserve the following comments. The adsorption of the three materials and of the empty chamber may be compared through the mean k_3/k_4 ratio for the eight compounds; this shows that: empty chamber \ll blown vinyl $<$ gypsum board and carpet. If the mean k_5 values are compared, the order is the same, but the differences are smaller. Another comment concerns the differences among compounds: they are due to the chemical functionality of the compound and, if this is the same, to the boiling point. So the two alkanes n-decane and n-dodecane show a higher k_3/k_4 ratio on carpet than on gypsum board, whereas the opposite is observed for the two alcohols 2-butoxyethanol and 2-ethylhexanol.

Figure 2 is an example of the experimental data which are the input to the dynamic model. The effect induced by the carpet is evident as well as that of the empty chamber itself: steady-state concentrations lower than those ideally expected and due to a non-zero k_5 value, are evident. This Figure displays also the fit distortions provoked by the adoption of a model including only the reversible

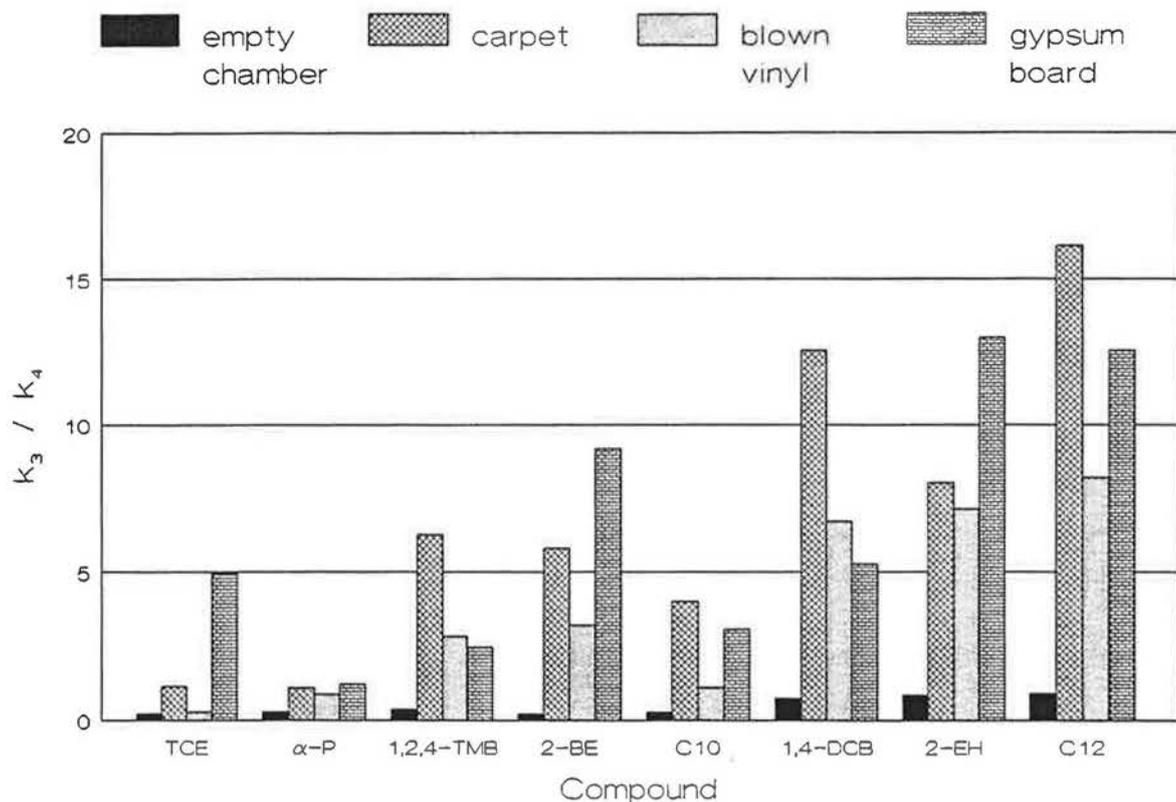


Fig. 1 Ratio of the adsorption (k_3) to the desorption (k_4) constant for the different compounds and materials (TCE = tetrachloroethene; α -P = α -pinene; 1,2,4-TMB = 1,2,4-trimethylbenzene; 2-BE = 2-butoxyethanol; C10 = n-decane; 1,4-DCB = 1,4-dichlorobenzene; 2-EH = 2-ethylhexanol; C12 = n-dodecane).

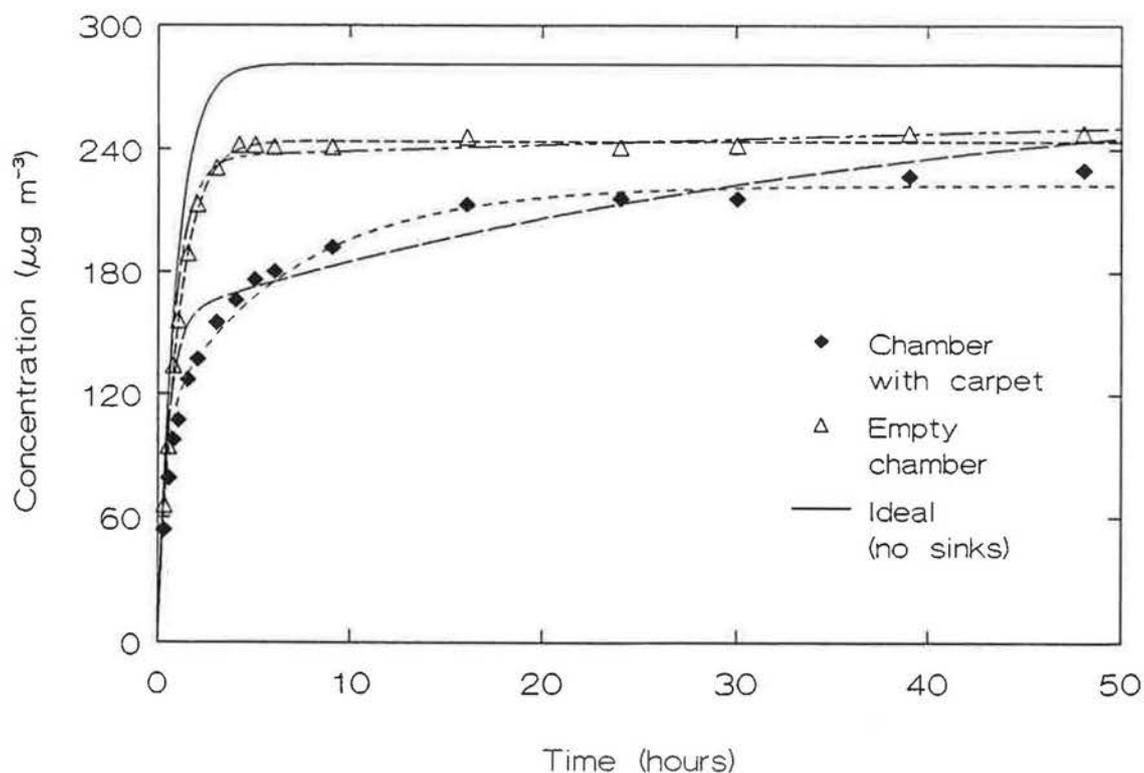


Fig. 2 Concentration versus time curves for n-decane under dynamic conditions: best-fits on empty chamber data by model including one sink only (---) and two sinks (-.-.); best fits on carpet data by model including one sink only (---) and two sinks (-.-.).

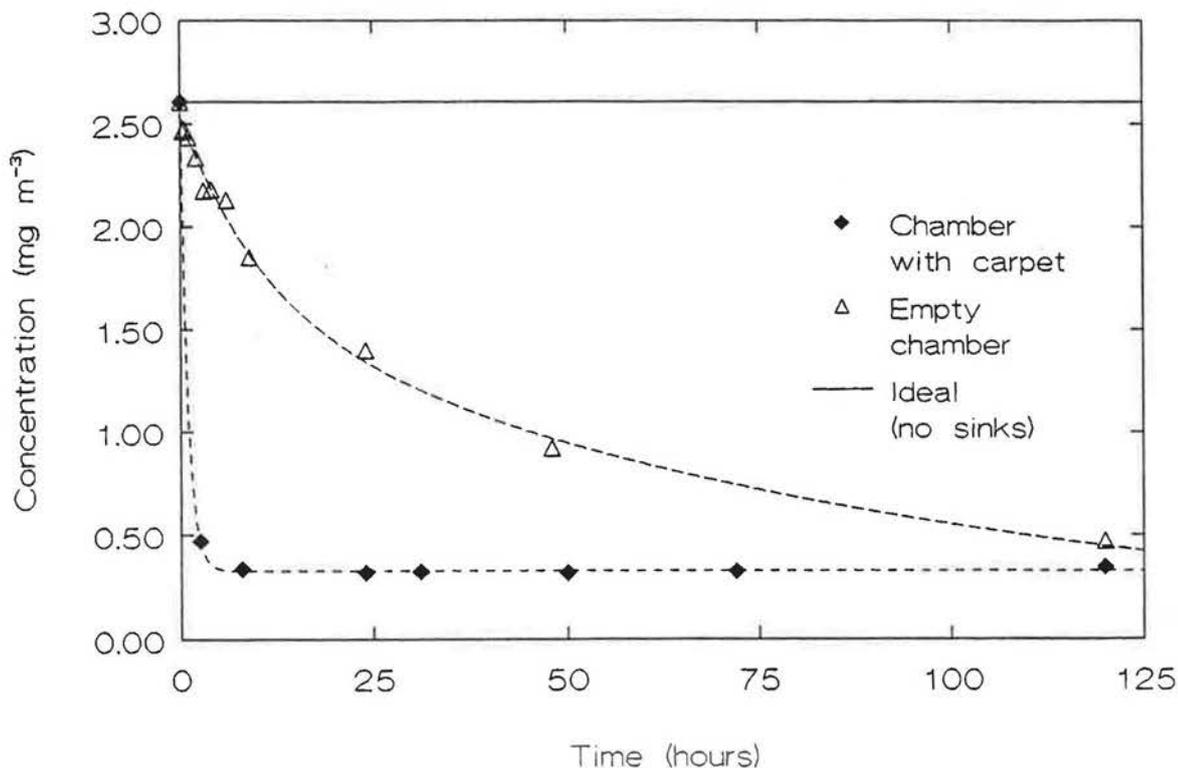


Fig. 3 Concentration versus time curves for *n*-decane under static conditions: best-fits by model including both reversible and "irreversible" sinks.

sink ($k_5 = 0$). Curves of this type led us to include an "irreversible" sink term into the model which, as mentioned above, appears in reality to be a slowly reversible one.

In order to determine the ratios k_3/k_4 and the rate constant k_5 independently, experiments under static conditions were carried out with and without carpet in the chamber. The static model was used to determine the rate constants k_3 to k_5 . The k_3/k_4 values, if divided by the different loading factors (1.1 and $1.8 \text{ m}^2 \cdot \text{m}^{-3}$ for the dynamic and the static case, respectively), agreed well for most compounds, whereas the k_5 values were somewhat lower, although always significantly different from zero. Figure 3 is an example of experimental and model results for *n*-decane. For this compound a corrected mean k_3/k_4 value of 3.45 ± 0.70 ($n=3$) resulted, compared to a mean value of 3.73 ± 0.42 ($n=4$) for the dynamic experiments.

Conclusions

This work shows that adsorption of VOCs on indoor materials is not a simple phenomenon and much additional research is necessary in order to understand and describe it. More than one sink ap-

pears to be present on the same material, with different adsorption/desorption rates: the models used do not describe the observations completely, although the ratios k_3/k_4 appear to be a reasonable measure of the steady-state vapour/adsorbed phase distribution of the test compounds in most experiments. The adsorption of most compounds is remarkable on the materials studied and tends to increase with their boiling point. However, other physico-chemical properties of the adsorbed compounds and the nature of the adsorbing materials also play an important role (see, for example, the two alcohols on gypsum board and 1,4-dichlorobenzene on carpet).

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Appendix

Chamber concentration (c), mass in reversible sink (w_{rev}), in irreversible sink (w_{irr}) and to chamber exit (w_{exit}) as a function of time (t).

$$c = k_1[(r_1 - k_2)E_1 - (r_2 - k_4)E_2]/[(r_1 - r_2)V] \quad (1)$$

$$w_{rev} = k_1 k_3 (E_1 - E_2)/(r_1 - r_2) \quad (2)$$

$$w_{irr} = k_1 k_5 [r_1 E_1 - (r_1 - k_3 - k_4)E_2 + (r_2 - k_4)E_2]/[(r_1 - r_2)(k_2 + k_5)] \quad (3)$$

$$w_{exit} = k_1 k_2 [r_1 E_1 - (r_1 - k_3 - k_4)E_2 + (r_2 - k_4)E_2]/[(r_1 - r_2)(k_2 + k_5)] \quad (4)$$

$$r_1, r_2 = \{k_2 + k_3 + k_4 + k_5 \pm [(k_2 + k_3 + k_4 + k_5)^2 - 4k_4(k_2 + k_3)]^{1/2}\}/2$$

$$E_1 = (1 - e^{-r_1 t})/r_1 \quad E_2 = (1 - e^{-r_2 t})/r_2$$

Steady state ($t \rightarrow \infty$):

$$c = k_1/(k_2 + k_3) \quad (5)$$

$$w_{rev} = k_1 k_3 / (k_2 + k_3) k_4 \quad (6)$$

Static model ($t = 0$),

$$c = c_0[(r_1 - k_4)E_1 - (r_2 - k_4)E_2]/(r_1 - r_2) \quad (7)$$

$$w_{rev} = c_0 k_3 V (E_1 - E_2)/(r_1 - r_2) \quad (8)$$

$$w_{irr} = c_0 k_5 V [(r_1 - k_3 - k_4)(1 - E_1) + (r_2 - k_4)(1 - E_2)]/(r_1 - r_2) \quad (9)$$

$$r_1, r_2 = \{k_3 + k_4 + k_5 \pm [(k_3 + k_4 + k_5)^2 - 4k_4 k_5]^{1/2}\}/2$$

$$E_1 = e^{-r_1 t} \quad E_2 = e^{-r_2 t}$$

Steady state, occurring if $k_5 = 0$, only ($t \rightarrow \infty$):

$$c = c_0 k_4 / (k_3 + k_4) \quad (10)$$

$$w_{rev} = c_0 k_3 V / (k_3 + k_4) \quad (11)$$

Units

c, c_0 : mass units m^{-3} ; t : h; V (chamber volume): m^3
 k_i : mass units h^{-1} ; $k_{i(i=2,3,4,5)}$: h^{-1} ; $w_{i(i=rev,irr,exit)}$: mass units