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Documentation of Field and Laboratory Emission Cell "FLEC": Identification of Emission Processes from Carpet, Linoleum, Paint, and Sealant by Modeling*

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Abstract

Time versus concentration data of selected volatile organic compounds (VOCs) emitted from four pre-conditioned building materials were measured in the Field and Laboratory Emisssion Cell (FLEC) at three air exchange rates, 171, 342, 684 h^{-1}, respectively, during a period of 240 hours. The materials were a carpet, a linoleum, a water-borne paint, and a sealant. Modeling of the time versus concentration data for two air exchange rates showed that the emission of VOCs from the carpet were best described with a diffusion model in which the diffusion coefficient depends on the concentration gradient for all data (exponential diffusion model), while a reduced data set eliminating initial events also could be described with a first order decay incorporating a sink effect. The paint emission data of the polar semi-VOC, Texanol, could be described with a first order decay model incorporating a sink effect for all three air exchange rates. The emission rate constant doubled by doubling the air exchange rate. The emission data for VOCs from the sealant were best described for all three air exchange rates by the exponential diffusion model. The best model correlation fit was obtained for hexane, but satisfactory results were also obtained for 2-ethylhexanol and dimethyloctanols. The decay results of linoleum did not allow for modeling leading to the conclusion that an internal concentration gradient had not yet been established under the experimental conditions.

KEY WORDS:
Building materials, Emission testing, Emission processes, Field and laboratory emission cell (FLEC), Modeling, Volatile organic compounds (VOCs).

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Introduction

Effective source control indoors requires an understanding of the various emission processes controlling the building material emission over both short and long time intervals. In order to develop healthier building materials, there is a need to establish the link between emission testing over time and human response so that not only building material manufacturers can produce better materials, but also building designers and architects are able to specify the best available materials, thus reducing the probability of discomfort problems over time, like sick building syndrome (SBS) symptoms, in particular in new buildings (Levin 1992).

Recently, the Field and Laboratory Emission Cell (FLEC) was developed for emission testing of volatile organic compounds (VOCs) (Wolkoff et al. 1991). The FLEC has two purposes: it can provide VOC emission data of material surfaces in the field for problem solving, apportionment studies, and be used in the laboratory as an emission chamber. The principle is that the steel top is placed on the surface material specimen and the material itself becomes the bottom part of the cell.

This paper describes testing of four pre-conditioned typical Danish building materials to investigate the influence of the air exchange rate and to identify the emission processes to be used for long-term modeling of the emitting VOCs (Wolkoff and Nielsen 1993). In principle, the emission may proceed by two processes (Dunn and Tichenor 1988). These are 1) evaporation directly from the material surface and 2) diffusion within the material as the limiting step for selected VOCs, or a combination thereof. This study was performed jointly with testing using other climatic chambers with the same

type of preconditioned materials (Gunnarsen et al., 1993a,b).

Experimental

Materials

The four materials investigated were received from manufacturers, see Table 1. The carpet and the linoleum were wrapped in aluminum foil for storage. The paint and sealant were allowed to dry for one week in a well-ventilated room and afterwards wrapped in aluminum foil. Materials were cut or prepared into triplicate samples for linoleum, paint and sealant. Only two carpet samples were used. The materials were conditioned for about 7 days in a well-ventilated room and ambient temperature prior to testing (Gunnarsen et al., 1993a).

Method

The FLEC is made of stainless steel. The inner surface is lathe made and handpolished. The cell is circular with a diameter of 150 mm providing a maximum test material surface area of 177 cm^2 and a volume of 35 ml. For sealing of FLEC an emission free silicon rubber foam is used. The FLEC is handled according to the protocol described previously (Wolkoff et al., 1991).

The FLEC was placed on the material surface at time 0 and under similar conditions as described previously (Wolkoff et al., 1991, 1993). The FLEC subunit was used for the carpet. The sealant was applied on to a circular aluminum plate (o.d. = 200 mm, depth = 20 mm) with a circular square cross section (i.d. = 21 mm, o.d. = 33 mm, depth = 10 mm). The FLEC was supplied with clean and humidified air ($50 \pm 3\%$) from an air supply control unit (Wolkoff et al., 1993). All experiments were carried out in the laboratory at ambient temperature (22.0 ± 1.5°C). Except for the carpet (only two), three air supply flows at 100 ± 1.5 ml/min, 200 ± 2 ml/min, and 400 ± 4 ml/min were used, which corresponds to 171, 342, and 684 air exchange rates per hour. The air flow supply was re-adjusted before each air sampling to the set value.

Sampling was carried out with Tenax TA tubes using Alpha-1 pumps and analyzed by combined thermal desorption (Perkin-Elmer ATD 400 desorber with a 50 tube carousel) and gas chromatography (Hewlett Pachard 5890 gas chromatograph) with a FID detector using a HP 5895A Workstation. Further details are given in previous papers Wolkoff et al. (1991, 1993) and Wolkoff and Nielsen (1993). The sampling volume was 1.80 l sampled over 45 min. All results were reported as the mean of duplicate air samples.

Four point calibration curves were obtained for each VOC by injection of methanol solutions with weighed amounts of pure VOCs into clean tubes followed by purging. The calibration curve for 3,7-dimethyloctanol was used for determination of the isomeric mixture of dimethyloctanols emitted from the sealant using the sum of their GC FID areas. Weighed decane standards were run after each third sample for overall system control of analysis.

Modeling

The time versus concentration data for the selected VOCs were fitted to a first order decay model (Dunn and Tichenor 1988), and a first order decay model accounting for a sink effect, but neglecting vapor pressure effects (Dunn and Tichenor 1988). The mathematical equation of the latter model is shown below in Equation 1. In addition, the high air exchange rate in the FLEC made it possible to use a newly developed diffusion model accommodating for an exponentially concentration dependent diffusion coefficient within the material (exponential diffusion model) (Clausen et al., 1993). Its mathematical equation is shown below in Equation

Table 1 List of four building materials and FLEC climatic conditions

Material	FLEC conditions		
	air exchange h^{-1}	specimen test area cm^2	air velocity[a] cm/s
Carpet with polyamide fibers (height = 5.4 mm) and latex backing (thickness = 3.2 mm)	171, 340	177	0.35, 0.7
Linoleum, thickness = 3.0 mm	171, 342, 684	177	
Waterborne paint, thickness = 75 ± 27 µm	171, 342, 684	177	0.35, 0.7, 1.4
Silicone based sealant, width = 12 mm, depth = 10 mm	171, 343, 684	7.2	

[a] Calculated, based on chamber volume and flow rates.

Table 2 Emission characteristics of four materials at different air exchange rates

Material: VOCs	N[a] (h^{-1})	Reduced data points	Best model	Corr. r^2	k_1 (h^{-1}) k/l (m^2/mg)	$R_0 - F_0$ $mg(m^2 \times h)$
Carpet:			first order decay			R_0
2-ethylhexanol	171	3		–	0.0039	1.431
	384	3		–	0.0051	2.514
2-nonenal	171	1		0.996	0.0060	2.220
	384	0		0.88	0.0064	2.803
					(k/l)	F_0E-2
	171	1	exp. conc. dependent	0.999	0.378	2.38
	384	0	diffusion	0.93	0.306	2.88
Paint:						R_0
Texanol[b]	171	0	first order decay		sensitive	
	382	0	with sink	0.96	0.00794	0.0823
	684	0		0.98	0.01477	0.0666
Sealant:					(k/l) E-4	F_0
hexane	171	1		0.98	6.36	13.46
	343	1		0.98	8.66	16.39
	684	1	exp. conc. dependent	0.99	6.89	10.88
2-ethylhexanol	171	2	diffusion	0.92	21.6	1.021
	343	2		0.92	17.0	1.293
	684	2		0.79	10.9	1.604
dimethyloctanols[c]	171	2		0.88	0.50	9.257
	343	1		0.92	0.93	14.28
	684	1		0.90	1.32	18.93

[a] Air exchange rate. [b] 2,2,4-trimethyl-pentan-1,3-diol monoisobutyrates. [c] Sum of isomeric dimethyloctanols.

2. The rate constants k_1 (h^{-1}) or k/l and the initial emission factor R_0 or F_0 (exponential diffusion model) were determined according to the equations by non-linear regression using the program STATGRAPHICS (1987). For some of the polar VOCs it was necessary to use a reduced data set (see Table 2) for the exponential diffusion model due to sink effects (see Figures 1, 2, 7, 9, 10 and Table 2). This implies that data before the decay were omitted in the modeling. The equations used for modeling are shown below:

$$C = AM_0k_1\{(k_4-k_1)\exp(-k_1t)/[(r_1-k_1)(r_2-k_1)] - (k_2+k_3-r_2)\exp(-r_1t)/[(r_1-r_2)(r_1-k_1)] + (k_2+k_3-r_1)\exp(-r_2t)/[(r_1-r_2)(r_2-k_1)]\}/V \quad (1)$$

where,

C = chamber air VOC concentration (mg/m^3),
A = area of source (m^2),
M_0 = initial (S)VOC mass in the source (mg/m^2),
k_1 = first order rate constant (h^{-1}),
t = time (h),
k_2 = air exchange rate (h^{-1}),
V = chamber volume (m^3).
$r_2, r_1 = \{k_2+k_3+k_4 \pm [(k_2+k_3+k_4)^2 - 4k_2k_4]^{1/2}\}/2$
k_3, k_4 = first order rate constants describing the sink effects (h^{-1}).

$$C = A/(V \cdot k_2)/(k/L)t + F_0^{-1}), \text{ when } t \gg 1/k_2 \quad (2)$$

where,

k/L = material specific constant divided by the material thickness (m^2/mg),
F_0 (= initial emission rate ($mg/(m^2 \cdot h)$)

Results and Discussion

The time versus concentration profiles of selected VOCs for the materials are shown in Figures 1–10. Additionally, the main results of the emission testing and modeling results thereof are summarized in Table 2. Figures 11–13 show the model fit of selected VOCs for the carpet, paint, and sealant, respectively.

Maximum chamber concentrations were generally reached within two hours at an air exchange rate = 342 h^{-1} for unpolar VOCs or VOCs having a low b.p., while polar and high boiling VOCs required 25–75 hours at the lowest air exchange rate (171 h^{-1}), see Figures 1–8.

Carpet

Comparison of different modeling results of concentration versus time data obtained at the two lowest air exchange rates showed that the emission pro-

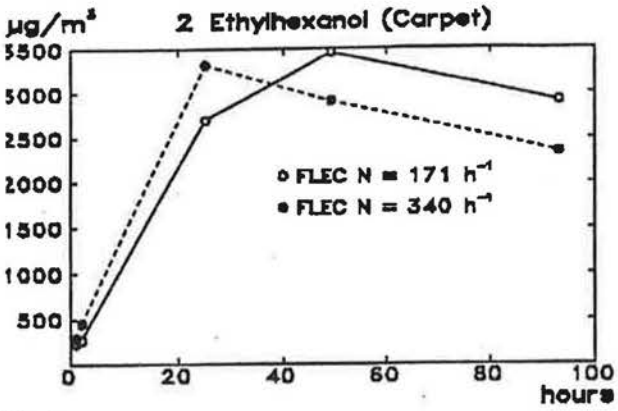

Fig. 1

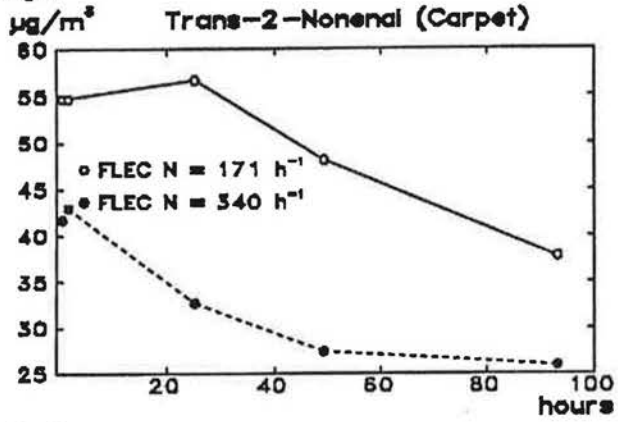

Fig. 2

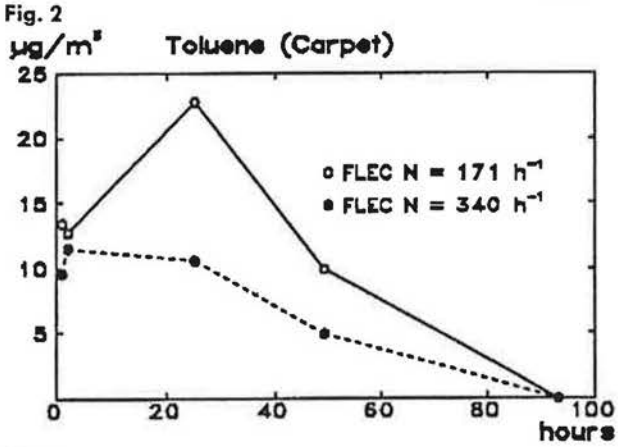

Fig. 3

Figs. 1–3 Time *vs* concentration profiles of VOCs from carpet at two air exchange rates, respectively.

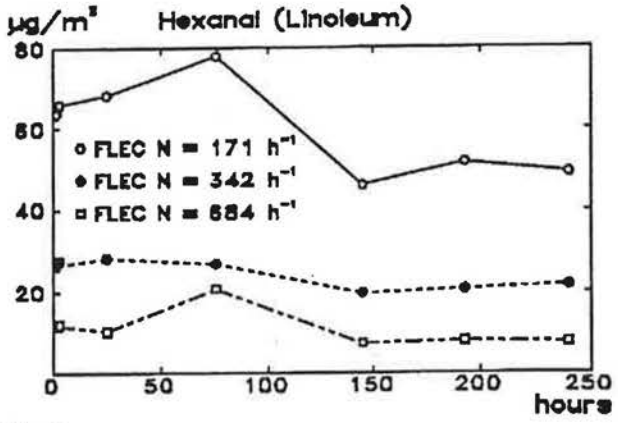

Fig. 4

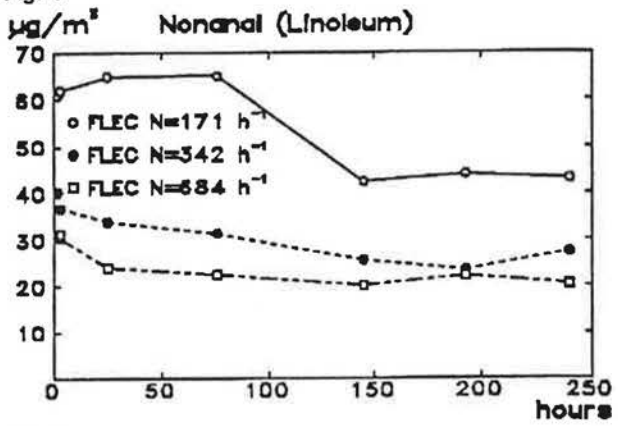

Fig. 5

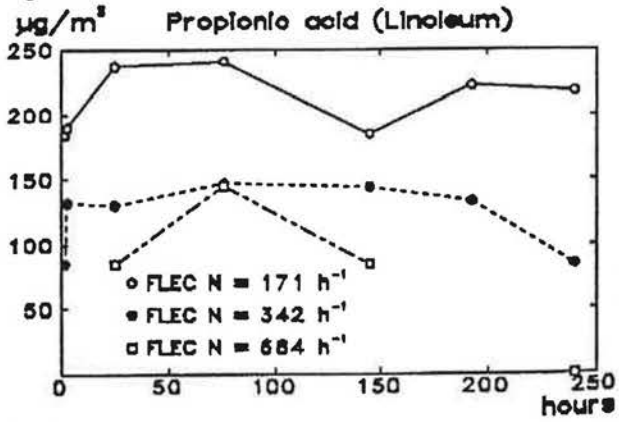

Fig. 6

Figs. 4–6 Time *vs* concentration profiles of VOCs from linoleum at three air exchange rates, respectively.

cess of the carpet was best described by the exponential diffusion model, in particular for 2-nonenal, rather than a first order decay model with sink. Using a first order model with sink effect for 2-ethylhexanol resulted in 25% increase of the k_1 value at highest air exchange rate. It is possible, however, that the data would be even better described with an exponential diffusion model including a sink effect. Such a model has not yet been developed. Noteworthy, is the larger 2-ethylhexanol concentration at the highest air exchange rate (see Figure 1), a lower concentration would have been expected. A rationale could be a combination of a sink effect and that the higher air exchange rate enhances transfer from the nylon fiber layer to the chamber due to an increased concentration gradient in the boundary layer. These results agree with conclusions recently obtained in a study of a carpet

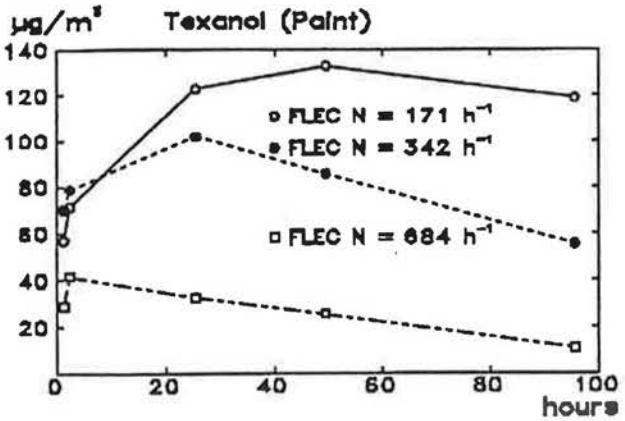

Fig. 7 Time *vs* Texanol concentration from paint at three different air exchange rates.

(Sollinger et al., 1993). It is remarkable that 2-ethylhexanol exhibited a sink effect which was reflected in the delayed peak concentration compared to the same VOC, though at much lower concentrations, emitted from the sealant. The decay behavior of toluene (see Figure 11) could be explained as desorption from the nylon fibers. Its origin is likely by adsorption from the environment during storage, because toluene is normally not found to a great extent in Danish carpets.

Linoleum

The results of linoleum did not allow for modeling (see Figures 4–6). The results indicated that a concentration gradient in the pre-conditioned material had not yet been established and/or chemical reactions occurred. However, in a recent work satisfactory model fits using the exponential diffusion model has been obtained for four linoleum products (Jensen et al., 1993) as similarly obtained for a PVC flooring material (Clausen et al., 1993).

Water-borne paint

The emission of Texanol, a high boiling VOC, could be described with a first order decay model incorporating a sink effect for air exchange rates 342 and 684 h^{-1} ($r^2 \geq 0.98$). The data for the lowest air exchange did not allow for satisfactory modeling because the regression analysis was too dependent on initial estimates. The results showed, however, that the rate constant (k_1) doubled by increase of the air exchange rate from 342 to 684 h^{-1} (see Table 2), and the initial mass R_0 was reduced. This suggests that the emission process is evaporation controlled in accordance with a recent study by Clausen (1993; see also Clausen et al., 1991) and that the emission depends on the thickness of the boundary layer. Similar increases of k_1 by enhanced air exchange rate at short times have been demonstrated for some wet materials, a wood stain, polyurethane varnish, and a sealant but less so for a floor wax (Tichenor, 1989; Tichenor and Guo, 1991). Sink effects have been found to be important parameters to be considered (Tichenor et al., 1991). The concentrations of 1,2-propandiol and butanol were too low to model.

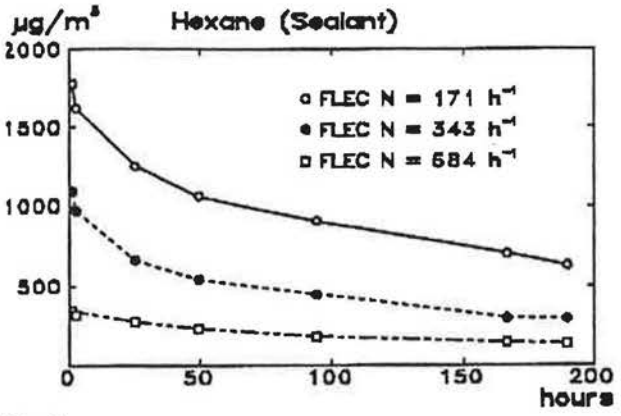

Fig. 8

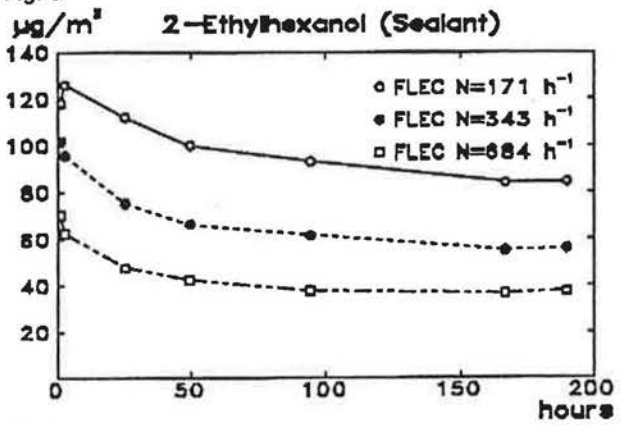

Fig. 9

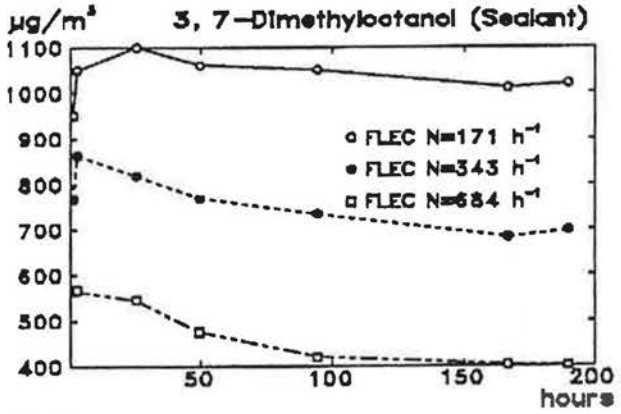

Fig. 10

Fig. 8–10 Time *vs* concentration profiles of VOCs from sealant at three air exchange rates.

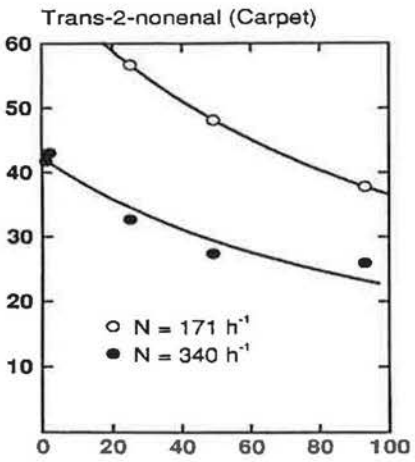

Fig. 11 Exponential diffusion model fit of trans-2-nonenal with FLEC data from carpet.

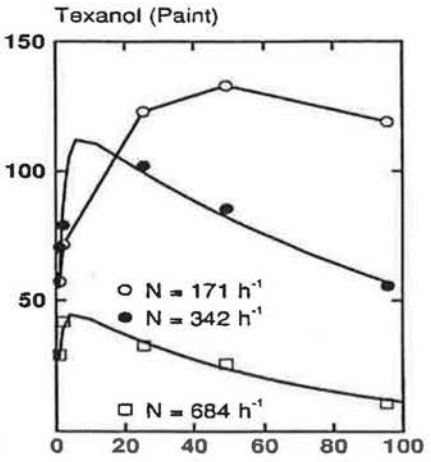

Fig. 12 First order decay inclusive sink effect model fit of Texanol FLEC data from paint.

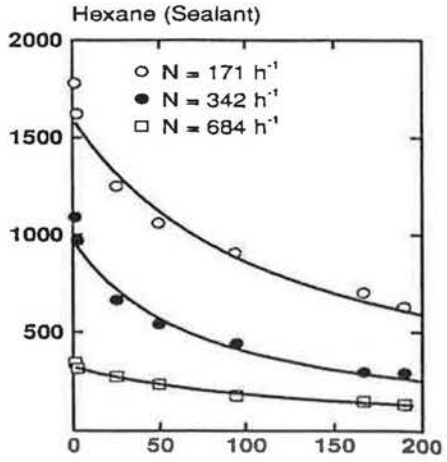

Fig. 13 Exponential diffusion model fit of hexane FLEC data from sealant.

Sealant

The exponential diffusion model was applied for the sealant, because initial trials with a first order decay model did not result in satisfactory fits. Excellent fitting ($r^2 \geq 0.98$) was obtained for hexane omitting the first data point (see Figure 13). Similarly, satisfactory fits were obtained for 2-ethylhexanol ($r^2 \geq 0.79$) omitting the first two data points, and for dimethyloctanols ($r^2 \geq 0.88$), both polar high boiling VOCs. The k/l ratio for hexane was not markedly affected by the air exchange rate, but some variation was found for the two polar VOCs (see Table 2). One rationale could be that the unpolar, low boiling hexane establishes a concentration gradient within the material relatively faster than the more polar, high boiling VOCs.

It is possible that the emission for the sealant and carpet could be even better described by a diffusion model accommodating for both an exponentially concentration dependent diffusion coefficient within the material in addition to a sink effect.

Conclusion

The purpose of this study has been to identify emission processes from four different building materials. Knowledge of these emission processes over a long time is a prerequisite to be able to transfer emission data to real-life indoor conditions and link health end points thereto (Wolkoff and Nielsen, 1993).

The emission profiles for selected VOCs from a paint, a thin film material, showed that the emission constant was strongly dependent on the air exchange rate. Because of the geometry of the FLEC it is likely that the air velocity over the material surface plays an important role. The emission rate constants (k/l) for the thick film materials, like the carpet and the sealant, however, showed lesser dependence on the air exchange rates applied. The question is whether the air exchange rates (or air velocities) applied in FLEC (see Table 1) are compatible with real life conditions. Matthews et al. (1989) have measured air velocities in occupied domestic environments. They found that a major proportion of air velocities maximized at 0–2.5 cm/s and Kovanen et al. (1987) found 9 cm/s, which is in the same order of the calculated air velocities based on the chamber volume and flow rates for the FLEC experiments, see Table 1.

A comparison of present results with other FLEC studies using shorter conditioning times (Wolkoff and Nielsen 1993) indicates that the preconditioning of materials prior to emission testing is an important parameter for future emission testing simulating real life conditions.

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