

# Adsorption/desorption of volatile organic compounds by uncoated cork parquet

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## ABSTRACT

Building materials are recognized to be the cause for indoor air contamination as emitters of volatile organic compounds. However, building materials can also act as sorbents of volatile organic compounds (VOCs) present in the surrounding atmosphere, entraining a variation of the respective concentrations in the indoor air with time. The behaviour of uncoated cork parquet in terms of adsorption/desorption of VOCs was studied using a standardized test chamber. A textile carpet, one of the more studied materials, was included in this work for comparison. Two types of experiments were carried out: adsorption from the atmosphere containing a known VOC concentration, followed by desorption, after removing the VOCs source. Five VOCs with different characteristics were the object of this study: 2-(2-ethoxyethoxy)ethanol, limonene, dodecane, tetradecane and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. The empirical expression of van der Wal was applied to the data obtained in the desorption phase. Cork parquet showed to have an adsorption capacity lower than carpet for all the compounds studied, except for 2-(2-ethoxyethoxy)ethanol.

## INDEX TERMS

VOC; Adsorption; Desorption; Modelling

## INTRODUCTION

Building materials are recognized to be contributors for indoor air contamination, as they are able to emit volatile organic compounds (VOCs). However, building materials can also act as sorbents of VOCs present in the surrounding atmosphere, causing a temporary decrease of the respective concentrations in the indoor air. Tirkkonen and Saarela (1997) have conducted studies in dwellings and demonstrated that painted walls adsorb compounds primarily emitted by the floor. Later desorption gives rise to an increase of the time of residence of those compounds in the indoor air, although at lower concentration values. Sorption properties of building materials shall be taken into consideration when models to preview VOC concentrations in real spaces are to be developed, associated with all the parameters involved. Modelling of adsorption/desorption phenomena is very difficult, given the complexity due to the involvement of several parameters, namely the characteristics of the VOCs (polarity, vapour pressure) and materials (porosity, specific area, etc.) and the affinity between each pair material/compound; and the influence of the environmental parameters (temperature, relative humidity, etc.). Some methods have been developed for the study of the adsorption of VOCs by building materials: test chamber, microbalance, Climpaq (e.g. Dunn and Tichenor, 1988; Kirchner *et al.*, 1999, Meninghaus *et al.*, 2000). Some experiments with test chambers were carried out with different materials and compounds (e.g. van der Wal and Hoogeveen, 1994; De Bortoli *et al.*, 1996, Jorgensen *et al.*, 1999; Won *et al.*, 2001). De Bortoli *et al.* concluded that the adsorption depends on the specific pair material-compound. For instance, for 2-

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buthoxyethanol these authors observed that the adsorption decreased by the order gypsum board > vinyl > carpet. Otherwise for *n*-dodecane, the decreasing order was carpet > vinyl > gypsum board.

Literature shows that most sorption studies regard textile carpets of different types, although adsorption properties of other materials like gypsum board, vinyl, PVC, curtain textile, fibreboard, wood flooring, glass, glass wool and acoustic tiles have also been reported. To our knowledge, the adsorption properties of cork-based materials have not been studied before, and that is why they constitute the aim of the present work. As cork is a good thermal insulator and natural material, it has been very much used as a cladding material of indoor surfaces. A textile carpet was also studied, in parallel, for comparison. Five compounds with different characteristics with respect to volatility and polarity, 2-(2-ethoxyethoxy)ethanol (2-EEE), limonene, *n*-dodecane, *n*-tetradecane and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB), were selected.

## METHODS

Small test chambers that fulfil the requirements (Silva *et al.*, 2003) defined by European Standard ENV 13419-1 (1999) were used. The values of temperature, 22°C, relative humidity, 44%, air exchange rate, 0.86 h<sup>-1</sup>, and air velocity at the material surface, 0.17 m s<sup>-1</sup>, were maintained constant throughout the study. Two types of experiments were carried out: adsorption from the air containing known VOC concentrations, followed by desorption, after removing the VOC sources. For the study of VOC adsorption, emission sources of different VOC (known volume of each VOC in a glass container) were introduced in the test chamber. The capacity and diameter of the containers and the volume of the VOC in the liquid phase varied according to the volatility of the compound under study. The mass of the VOC evaporated during the experiment was determined by gravimetry (Mettler Toledo, 0.01 mg). From the mass lost, the emission rate (ER) of the compound was calculated. The desorption experiment began just after the adsorption experiment was finished, that is, when the container with the liquid VOC was removed from the test chamber.

In the presence of the material under study (0.222 m<sup>2</sup> of uncoated cork parquet) five VOCs, 2-(2-ethoxyethoxy)ethanol (purum, >98% (GC) Fluka), limonene (purum, ~98% (GC) Fluka), *n*-dodecane, *n*-tetradecane (~99% Sigma) and TXIB (99% Aldrich), were introduced individually in the test chamber, each one in its glass container (VOC source), and the respective levels in the chamber atmosphere were monitored for 120 h. Just after removal of the VOC sources, another monitoring period of 120 h was carried out. Similar experiments were carried out, in parallel, in the absence of the building material; that is, with the chamber empty. The set of experiments was repeated for 0.205 m<sup>2</sup> of textile carpet 100% polyamide. The bottom surface of the materials was wrapped with aluminium foil and its edges were covered with low emission self-adhesive aluminium tape, before being introduced in the test chamber. In all cases, the moment of closing the test chamber was the starting time of exposure.

For air sampling, Tenax TA, 60/80 mesh, from Supelco, was used as adsorbent in stainless steel tubes. Personal air pumps, from Casella, with flow rates in the range 60–135 ml min<sup>-1</sup>, were used to collect the samples. The volume of sampled air varied between 1.0 and 5.0 l. After the sampling, the Tenax tubes were immediately closed and the VOCs were analysed within a week. For the analysis, a thermal desorption system (from Dani, model SDT 33.50) online with gas chromatography (from Hewlett Packard, model HP 5890), coupled to a mass selective detector (MSD HP5972), for VOC identification, and flame ionization detection, for VOC quantification (CG/MSD/FID), was used. For quantification, the response factor of the specific compounds was used.

An empirical expression (Eqn (1)) from van der Wal and Hoogeveen (1994) was applied to the VOC concentrations obtained in the phase of desorption, where  $C$  is the VOC concentration ( $\text{mg m}^{-3}$ ),  $C_0$  is the initial VOC concentration of desorption phase ( $\text{mg m}^{-3}$ ),  $t$  is the time,  $k$  a decay constant ( $\text{h}^{-1}$ ) and  $n$  an adimensional constant. The total desorbed mass ( $M$ ) of VOC, which is a measure of the adsorption capacity of the surrounding material, was calculated through Eqn (3), where both integrals represent the surface areas under, respectively, the fitted curve and the 'ideal' curve, i.e. the ideal behaviour in the absence of adsorption (see Eqn (2), where  $k_2$  ( $\text{h}^{-1}$ ) is the air exchange rate):

$$C / C_0 = e^{-kt^n} \quad (1)$$

$$C / C_0 = e^{-k_2t} \quad (2)$$

$$M / qC_0 = \int e^{-kt^n} dt - \int e^{-k_2t} dt \quad (3)$$

## RESULTS

### Cork

The results obtained in the adsorption phase for the test chamber containing the cork material are illustrated in Figure 1 for 2-EEE, as well as the ideal curve expected (absence of sink). After 120 h of exposure, the equilibrium was attained for all the compounds. The empirical expression of van der Wal was applied to the desorption data (Figure 1 and Table 1). The values for the decay constant ( $k$ ) obtained were in general higher in the empty chamber than in the presence of cork. The desorbed mass was bigger in the presence of the cork than for the case of the empty chamber, although relatively low values of  $M/C_0$  were obtained for limonene and dodecane. Table 2 shows the results obtained after the subtraction of the mass desorbed from the empty chamber.

**Table 1** Results of parameters  $k$  ( $\text{h}^{-1}$ ) and  $n$  of the empirical expression of van der Wal and Hoogeveen (1994) and calculated values of  $M/C_0$  ( $\mu\text{g per } \mu\text{g m}^{-3}$ ) and  $M$  ( $\mu\text{g}$ ) (where  $M$  is the total mass desorbed and  $C_0$  the initial concentration)

Compound	$k$	$n$	$r^{2a}$	$M/C_0$	$M$	$k$	$n$	$r^{2a}$	$M/C_0$	$M$
	Empty chamber					Cork				
2-EEE	1.26	0.33	0.999	0.42	74	0.80	0.25	0.924	3.34	401
Limonene	2.64	0.27	0.999	—	—	1.96	0.27	0.999	0.086	197
Dodecane	2.75	0.26	0.999	—	—	1.68	0.26	0.999	0.29	192
Tetradecane	2.75	0.26	0.996	—	—	1.00	0.26	0.987	1.95	119
TXIB	0.65	0.39	0.985	1.80	706	0.25	0.54	0.995	4.24	1297
	Empty chamber					Carpet				
2-EEE	2.29	3.02	1	—	—	1.38	4.57	0.999	—	—
Limonene	1.72	0.26	0.998	0.23	578	0.38	0.41	0.979	4.31	9318
Dodecane	1.70	0.22	0.995	0.49	316	0.53	0.19	0.995	8.80	4171
Tetradecane	1.02	0.21	0.989	2.63	142	0.56	0.11	0.921	11.36	409
TXIB	1.13	0.21	0.999 <sup>b</sup>	2.12	869	0.11	0.67	0.815	6.29	1352

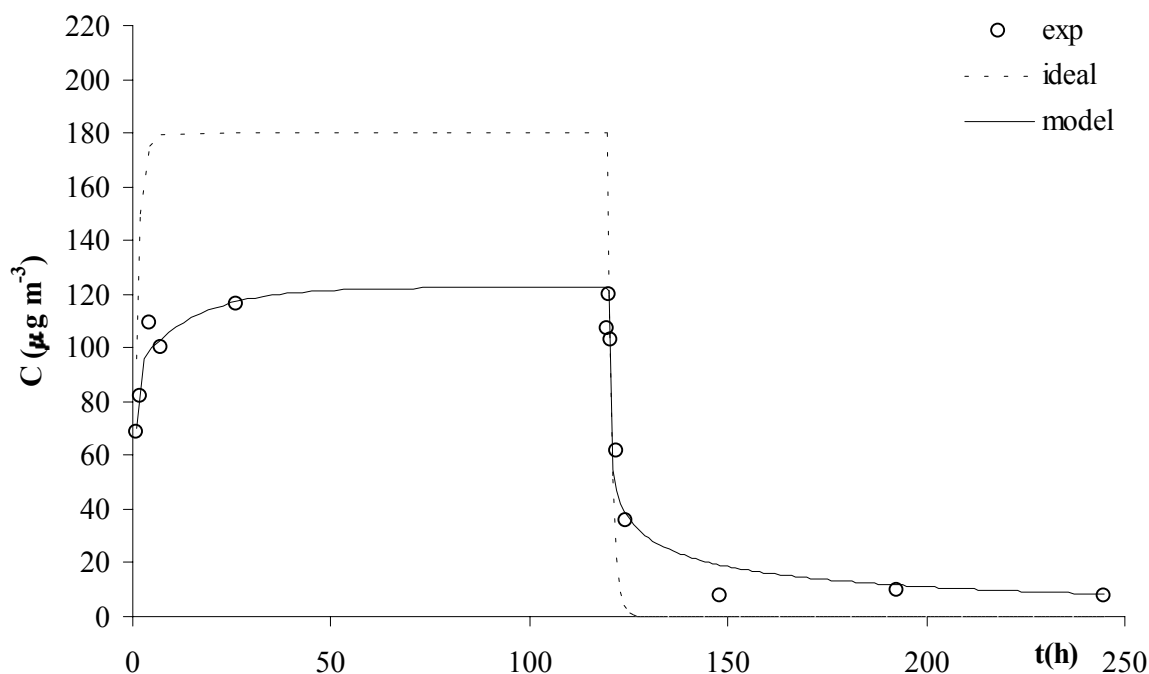
<sup>a</sup>Correlation coefficient of the adjustment.

<sup>b</sup>Three points rejected.

### Carpet

The results obtained in the adsorption phase for the test chamber containing the carpet are present in Figure 2, for limonene. It was observed that after 120 h of exposure the equilibrium was attained for all the compounds. Relatively to the desorption phase (see Table 1 and Figure 2), the values of the decay constant ( $k$ ) were in general higher in the empty chamber than in

the presence of carpet. The desorbed mass was bigger in the presence of the carpet than for the empty chamber. In the case of 2-EEE the values of concentration after 28 h were below the limit of detection for both cases, so it can be concluded that adsorption was weaker in these particular cases. Table 2 presents the results after the subtraction of the mass desorbed from the empty chamber.



**Figure 1** Variation of the concentration of 2-ethoxyethoxyethanol as a function of time during both dynamic adsorption and desorption study for uncoated cork parquet. Model fitting (Dunn and Tichenor, 1988; van der Wal and Hoogeveen, 1994) and ideal behaviour (no sink) are also shown.

**Table 2** Comparison of the calculated values of  $M/C_0$  ( $\mu\text{g per } \mu\text{g m}^{-3}$ ) for cork and carpet after subtraction of the mass desorbed from the empty chamber

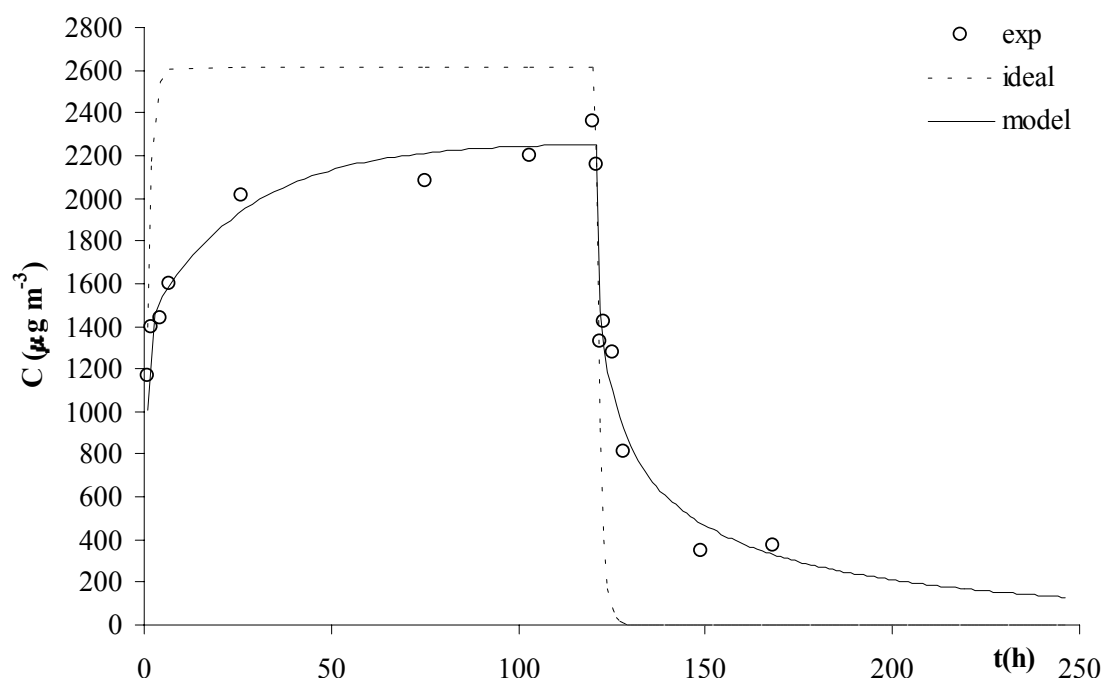
Compound	$M/C_0$	
	Cork	Carpet
2-EEE	2.72	—
Limonene	0.09	4.04
Dodecane	0.29	8.13
Tetradecane	1.95	7.42
TXIB	1.93	2.25

## DISCUSSION

### Comparison between Cork and Carpet

In the case of 2-EEE the mass desorbed from the cork was higher than that from the carpet. For limonene, *n*-dodecane and *n*-tetradecane the mass desorbed from the carpet was much higher than that from the cork. In the case of TXIB the values were similar while a little higher for the carpet. Considering the volatility of the compounds (*n*-dodecane versus *n*-tetradecane) an increase of the adsorption with decrease of volatility was verified for cork; however, in the case of the carpet this effect was not observed. Studies about adsorption in different materials show an increase of adsorption with decrease of volatility of *n*-alkanes (Levsen *et al.*, 1993; Wouda *et al.*, 1997), although a decrease of this variation with the

increase of the number of carbon chain can be observed. Relatively to an eventual effect of polarity in the adsorption (*n*-tetradecane versus 2-(2-ethoxyethoxy)ethanol), the increase of polarity seems to favour the adsorption in the case of cork.



**Figure 2** Variation of the concentration of limonene as a function of time during both dynamic adsorption and desorption studies for textile carpet. Model fitting and ideal behaviour (no sink) (Dunn and Tichenor, 1988; van der Wal and Hoogeveen, 1994) are included.

### Comparison between Results for Carpet between the Present Study and Previous Works

The comparison of the values of desorbed mass obtained for limonene and dodecane in the present study (4.0 and 8.1  $\mu\text{g}$  per  $\mu\text{g}/\text{m}^3$ , respectively) with those obtained by Wouda *et al.* (1997) (13 and 16  $\text{mg}$  per  $\text{mg}/\text{m}^3$ , respectively) for a carpet shows higher adsorption values for both compounds by the carpet used by Wouda *et al.*. The sorption capacity of the carpet for dodecane relatively to limonene is about 2.0 in the present study against 1.2 in the study of Wouda *et al.* (1997). These differences can result from the nature of the carpets in the two cases: 100% polyamide in this study versus polypropylene carpet in Wouda *et al.* (1997) study.

### CONCLUSION AND IMPLICATIONS

It is shown that cork and carpet have different behaviours relatively to the compounds studied. Carpet presents a higher adsorption than cork, especially for limonene, dodecane and tetradecane. The larger contact surface area provided by fibres is responsible by the higher sorption capacities of carpet. Cork showed to have some sorption capacity for 2-(2-ethoxyethoxy)ethanol, tetradecane and TXIB, although weak. A systematic relationship between the properties of the compounds (volatility and polarity) and the respective adsorption for the studied materials could not be found.

The difficulties and uncertainties shown and also reported in the literature can only encourage the continuation of this type of studies as adsorption properties of all possible pairs material/compound are necessary to validate models developed to preview concentrations in real spaces in association with ventilation strategies.

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