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Comparative analysis of formaldehyde and toluene sorption on indoor floorings and consequence on Indoor Air Quality

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Abstract

Indoor surfaces may be adsorptive sinks with the potential to change Indoor Air Quality. To estimate this effect, the sorption parameters of formaldehyde and toluene were assessed on five floorings by an experimental method using solid-phase microextraction in an airtight emission cell. Adsorption rate constants ranged from 0.003 to 0.075 m·h⁻¹, desorption rate constants from 0.019 to 0.51 h⁻¹, and the partition coefficient from 0.005 to 3.9 m, and these parameters vary greatly from one volatile organic compound/material couple to another indicating contrasted sorption behaviors. A rubber was identified as a sink of formaldehyde characterized by a very low desorption constant close to 0. For these sorbent floorings identified, the adsorption rates of formaldehyde are from 2 to 4 times higher than those of toluene. Two models were used to evaluate the sink effects of floorings on indoor pollutant concentrations in one room from different realistic conditions. The scenarios tested came to the conclusion that the formaldehyde sorption on one rubber (identified as a sink) has a maximum contribution from 15% to 21% for the conditions of low air exchange rate. For other floorings, the sorption has a minor contribution less than or equal to 5%, regardless of the air exchange rate.

KEYWORDS

emission cell, indoor materials, modeling, partition coefficient, sorption rate constants, SPME

1 | INTRODUCTION

Among indoor air pollutants, volatile organic compounds (VOCs) are of particular concern because of their abundance indoors and direct effects on human health, comfort, and productivity.^{1,2} The impact of VOCs consists of acute effects such as headaches and irritation of the nose and eyes³ and adverse respiratory effects such as asthma.⁴ Formaldehyde is even pointed out as carcinogenic and mutagenic.⁵

The interaction of VOCs with indoor surfaces (ie, sinks) could have a significant impact on Indoor Air Quality (IAQ).^{6,7} The mass transfer mechanisms can be adsorption,⁸ absorption like for a water-soluble compound to a moist surface,⁹ or reactions on the indoor surfaces.^{10,11} Contribution of these interactions to IAQ depends on

the affinity of compound for materials covering indoor surfaces as well as the humidity and temperature conditions.^{12,13} Materials can act as VOC sinks at first and then become emission sources on the long term when the environmental conditions are favorable to the reemission.

Most studies identified the sorption processes as the main interaction occurring between gas compounds and materials.¹⁴ They used most often an emission chamber^{6,8} or an emission cell¹⁵ in which the material was exposed to airflow with pollutant (adsorption phase) and without pollutant (desorption phase) alternatively. Langmuir model was successfully applied to describe the gaseous concentration patterns during the two phases and assess adsorption and desorption rate constants (k_{am} and k_{dm}).¹⁶ The interaction

with indoor materials has a significant impact on indoor concentration only in the case where the net removal rate associated to these sorption processes is comparable or greater than the rate at which the compound is removed by air exchange. k_{am} and k_{dm} constants are required parameters to assess the impact of specific compound-material interactions on indoor concentration and better understand the compound behavior indoors. Data on these constants are scarce in the literature and the conclusions about the importance of VOC/material interactions on IAQ differ widely from one study to another.^{16,17}

The experimental conditions used were often far from those of indoor environments with higher concentration levels and higher airflow at the material surface. It has not been proven that these differences in conditions do not influence the results of adsorption and desorption rate coefficients. These laboratory experiments were carried out at the material scale and required a measurement technique with high time resolution in order to describe the fast kinetics of changes in gaseous concentration caused by the sorption processes. Recently, the direct injection mass spectrometry (MS) such as SIFT-MS (selected ion flow tube MS) or PTR-MS (proton transfer reaction-mass spectrometer) was used as means of VOC measurements.^{18,19} Another way is the using of solid-phase microextraction (SPME) sampling performed in an airtight emission cell. The gaseous concentration pattern in the cell during the adsorption phase can be determined from successive measurements by SPME and lead to the assessment of adsorption and desorption rate constants. The applicability of this method was proven to investigate the sorption of formaldehyde on different types of indoor materials and the analytical solution of Langmuir model defined in the specific case of a closed system.¹⁷ The present study follows on from this work.

The objectives are to (a) assess and compare the sorption characteristics of a series of floor coverings regarding two compounds (toluene and formaldehyde) and (b) evaluate the contribution of flooring sorption on IAQ from different scenarios under typical indoor air conditions using modeling.

2 | MATERIAL AND METHODS

2.1 | Model and analytical solution for the assessment of adsorption and desorption rate constants (k_{am} and k_{dm})

The method is based on mathematical equations using the Langmuir model and mass balance applied to a closed system (airtight cell, no airflow) containing the material sample for the adsorption stage (after a fast injection of air loaded with VOC). The concentration of a pollutant i is assumed to be homogeneous in the cell air and the diffusion in the material is here not considered. The pollutant concentration decreases in the cell air as a function of sorption processes occurring between air and the surfaces (material and inner walls of cell).

The gas-phase concentration change can be defined by the general Equation⁶:

Practical Implications

- Indoor surfaces may be adsorptive sinks with the potential to change Indoor Air Quality (IAQ). The experimental method developed provides an assessment of adsorption and desorption rate constants (k_{am} and k_{dm}) which constitute the key parameters to describe material/air exchanges.
- Application of two predictive models to the realistic scenarios at the scale of a room demonstrates that sorption on floorings has the ability to modify the indoor concentrations under certain conditions of low air exchange rate.
- Data of sorption parameters obtained in this study can serve as inputs to improve the prediction of IAQ models.

$$\frac{dC_i}{dt} = k_{dc} \frac{A_c}{V} C_{sc} - k_{ac} \frac{A_c}{V} C_i + k_{dm} \frac{A_m}{V} C_{sm} - k_{am} \frac{A_m}{V} C_i \quad (1)$$

where C_i , the gas-phase concentration of compound in the cell ($\mu\text{g}\cdot\text{m}^{-3}$); A_m , the material surface (m^2); A_c , inner surface of the cell (m^2); V , the cell volume (m^3); k_{dc} , the desorption rate constant for inner surface of cell (h^{-1}); k_{ac} , the adsorption rate constant for inner surface of cell ($\text{m}\cdot\text{h}^{-1}$); k_{dm} , the desorption rate constant for the material surface (h^{-1}); k_{am} , the adsorption rate constant for the material surface ($\text{m}\cdot\text{h}^{-1}$); C_{sc} , the compound concentration on inner surface of cell ($\mu\text{g}\cdot\text{m}^{-2}$); and C_{sm} the compound-material-phase concentration ($\mu\text{g}\cdot\text{m}^{-2}$).

Equation (1) can be solved by resolution of first-order differential equation and mass balance considering two configurations: test with material and blank test (where the material is replaced by a disk of the same size and similar in nature to the cell). The solution process for Equation (1) which leads to the assessment of adsorption and desorption rate constants (k_{am} and k_{dm}) was detailed in a previous paper.¹⁷ The analytical solutions obtained for the constants are only briefly reiterated here.

First of all, the k_{ac} and k_{dc} constants are assessed from the results of blank tests. In our experiments, a glass cell is used. So, the material sample is replaced by a glass disk of the same size. Only the exchanges between air and the glass disk and inner walls of cell occur and are therefore considered. This leads to the following expressions of k_{ac} and k_{dc} ¹⁷:

$$k_{ac} = \frac{L'V}{A_c + A_m} \left(1 - \frac{C'_{ieq}}{C'_{i0}} \right) \quad (2)$$

$$k_{dc} = L' - k_{ac} \frac{A_c + A_m}{V} \quad (3)$$

with $L' = \ln \frac{C'_{i0} - C'_{ieq}}{C'_{i0} - C'_{ieq}}$, C'_{i0} is the gaseous concentration of pollutant i at the start of adsorption phase and C'_{ieq} is the gaseous concentration when a

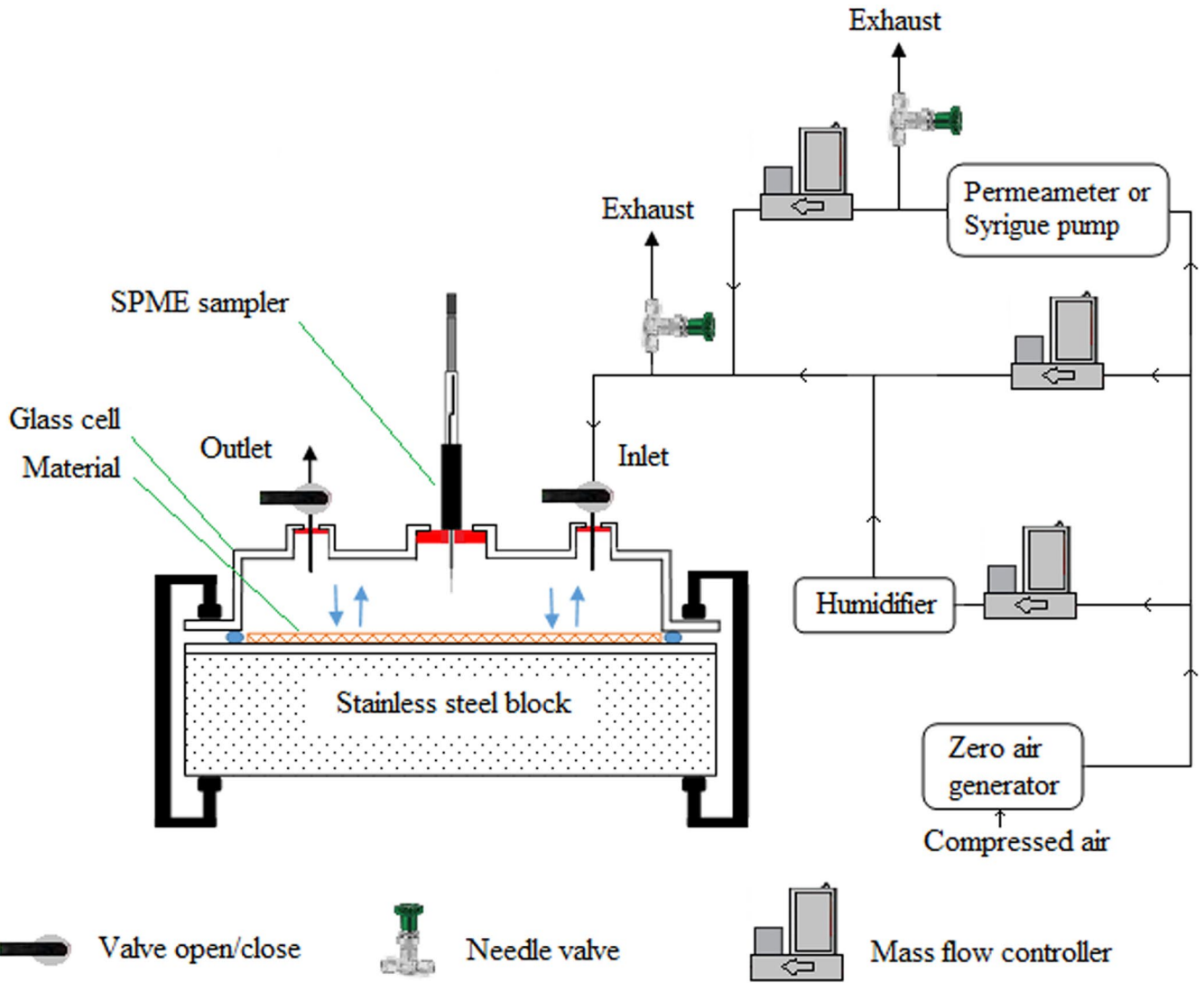


FIGURE 1 Diagram of experimental setup for assessing the material/air exchanges parameters for formaldehyde

steady state is reached at the end of adsorption phase for the blank test. By tracing $\ln \frac{C_{i0} - C_{ieq}}{C_i - C_{ieq}}$ as a function of t , the parameter L' can be determined from the slope of the best-fit line from the origin.

Secondly, the k_{am} and k_{dm} constants are then assessed from the results of tests with material and the knowing of k_{ac} and k_{dc} constants. The exchanges between air, the material sample, and the inner walls of cell are taken into account. The solution process leads to the following expressions of k_{am} and k_{dm} ¹⁷:

$$k_{am} = \frac{LV}{A_m} \left(1 - \frac{C_{ieq}}{C_{i0}} \right) - k_{ac} A_c \quad (4)$$

$$k_{dm} = \frac{L - k_{am} \frac{A_m}{V} - k_{ac} \frac{A_c}{V} - k_{dc} \frac{A_c}{A_c + A_m}}{1 - \frac{A_c}{A_c + A_m}} \quad (5)$$

with $L = \ln \frac{C_{i0} - C_{ieq}}{C_i - C_{ieq}}$, C_{i0} is the initial gaseous concentration of pollutant i and C_{ieq} is the gaseous concentration at the end of adsorption phase for the test with material. The parameter L is determined from the slope of the best-fit line $\ln \frac{C_{i0} - C_{ieq}}{C_i - C_{ieq}} = f(t)$ considering the initial part of the curve.

The ratio of sorption rate constants $\frac{k_{am}}{k_{dm}}$ can be determined from these results. It also corresponds to the material/air equilibrium partition coefficient K_e (m), that is the ratio of the material-phase concentration on the gas-phase concentration adjacent to material surface at the equilibrium state: $K_e = \frac{C_{sm}}{C_{ieq}}$. A high K_e value means that the material is a sink for the compound.

2.2 | Experimental device, test protocol, and SPME method

The target chemical compounds in this study were formaldehyde and toluene. Those are two VOCs characteristic of indoor air. The method uses a glass emission cell of 504 mL (Figure 1) and a suitable monitoring of formaldehyde and toluene concentrations by SPME which was developed by our laboratory and previously described.^{17,20,21} Here, the key points of this method are summarized briefly. The material is placed under the cell and covers the entire area, that is, 206 cm². The emission cell was supplied by

a gas generation/dilution system (Figure 1) using a permeameter (Calibrage, St Chamas, France) equipped by a paraformaldehyde permeation tube Dynacal® (VICI Metronics, Poulosbo, WA, United States) and a syringe pump (Harvard Apparatus, Les Ulis, France) as continuous generation means of formaldehyde and toluene, respectively.

For the purpose of sorption tests, two standard atmospheres were generated, the one without VOC and the other one with a selected VOC concentration of 300-500 $\mu\text{g}\cdot\text{m}^{-3}$ at the stable conditions of relative humidity and temperature ($50 \pm 3\%$ at $T = 23 \pm 2^\circ\text{C}$).

The test protocol consists of two successive phases: emission and adsorption steps.

Prior to the emission phase, the material was conditioned for 3 days under very low clean airflow ($8 \text{ mL}\cdot\text{min}^{-1}$) at $50 \pm 3\%$ relative humidity and $23 \pm 2^\circ\text{C}$. The cell was then closed and the gaseous VOC concentration change was described from successive measurements by SPME. This phase was extended until a steady concentration was reached in the cell.

After the emission step, the adsorption phase was completed. A high flow rate ($1.1 \text{ L}\cdot\text{min}^{-1}$) of humidified air (50% RH) containing 350-500 $\mu\text{g}\cdot\text{m}^{-3}$ of VOC was injected in the cell for 3 min. The cell was then closed and adsorption kinetic was recorded from successive measurements by SPME. The extraction time was gradually increased from 1 to 6 min during the adsorption phase to respect the quantification range of the method.

A PDMS-DVB (polydimethylsiloxane-divinylbenzene) SPME fiber (Sigma-Aldrich, Saint-Quentin Fallavier, France) was used as sampling media. For analysis of formaldehyde in gas chromatography (GC), the compound was derivatized on the SPME fiber according to a method previously developed by our laboratory.^{20,22} After exposition of the fiber into the emission cell, it was then directly desorbed into the injection port of GC coupled to MS and flame ionization detector (FID) for analysis. For quantification, the analysis by FID was favored because of the greater

calibration stability over time. Analytical conditions and the protocol for GC analysis of formaldehyde were given by Bourdin and Desauziers.²⁰

Volatile organic compound amount sorbed on the fiber is directly proportional to the product of its air concentration and the exposure time.^{23,24} Therefore, for calibration of SPME method, a relationship between the peak area obtained by SPME and the product of concentration and exposure time was achieved. To this end, standard atmospheres were generated at least two concentration levels and $50 \pm 3\%$ relative humidity and $23 \pm 2^\circ\text{C}$ and measurements by SPME were performed in static mode (closed cell) with variable exposure time from 1 to 10 minutes. Then, the concentrations of standard atmospheres were measured by two active sampling methods using a BPE/DNPH cartridge (Sigma-Aldrich, Saint-Louis, MO, USA) for formaldehyde and a stainless steel cylindrical cartridge filled with Carbograph 4 (TERA Environnement, Crolles, France) for toluene. Details about these active sampling methods and associated analytical protocols were given in our previous articles.^{25,26} Performance of SPME method under the conditions of use are presented in Section 3.1.

2.3 | Test materials

Five different floor coverings (2 PVC, 2 rubbers, and 1 linoleum) were tested as sorptive materials. Information about the materials is given in Table 1. The tested floorings have a close density from 1100 to 1700 $\text{kg}\cdot\text{m}^{-3}$, but they are composed of several superposed layers of different materials for some of them. Materials have a non-porous smooth surface or finely textured in the case of linoleum.

Before the test, the materials were stored in the laboratory away from light for over six months. The material sample was cut, placed in the cell and conditioned for 3 days under clean airflow ($8 \text{ mL}\cdot\text{min}^{-1}$) at $50 \pm 3\%$ relative humidity and $23 \pm 2^\circ\text{C}$ before each emission-adsorption experiment.

TABLE 1 Information about the tested materials

Material	Commercial name and Supplier	Description	Sample size	Density ($\text{kg}\cdot\text{m}^{-3}$)
PVC 1	Grabo Diamond Graboplast (Hungary)	<ul style="list-style-type: none"> Commercial flexible PVC flooring packaged in roll Three-layer media 	Disk of 206 cm^2 with 0.2 cm thickness	1412
PVC 2	Acczent Excellence 4 Tarkett (France)	<ul style="list-style-type: none"> Commercial flexible PVC flooring packaged in roll Two-layer media 	Disk of 206 cm^2 with 0.2 cm thickness	1502
Rubber 1	Noraplan Eco Nora (France)	<ul style="list-style-type: none"> Commercial flexible rubber flooring packaged in roll Single media 	Disk of 206 cm^2 with 0.2 cm thickness	1656
Rubber 2	Granito Artigo (France)	<ul style="list-style-type: none"> Commercial flexible rubber flooring packaged in roll Single media 	Disk of 206 cm^2 with 0.2 cm thickness	1383
Linoleum	Veneto XF ² Tarkett (France)	<ul style="list-style-type: none"> Commercial flexible linoleum flooring packaged in roll Jute hessian upside down Two-layer media 	Disk of 206 cm^2 with 0.25 cm thickness	1108

2.4 | IAQ models and simulations

Two mass balance models were used to evaluate the contribution of flooring sorption on IAQ in one room from different realistic scenarios.

In these models, the gas concentration change in a well-mixed room was described as a differential equation in which three production processes (indoor emission, desorption by flooring, and flow of outdoor compounds incoming into the room by ventilation) and two loss processes (adsorption by flooring and flow of indoor compounds out of the room by ventilation) were considered. The potential input of secondary pollutants produced by reactivity and the diffusion in the material was not considered in this simple approach.

A first model (M_1) is based on mathematical equations using the Langmuir model and mass balance applied to an open system flowed through by air and containing a sorbent material (flooring) and a material source with a constant emission rate. The concentration changes in the room can be described by the two following Equation⁶:

$$\frac{dC_i}{dt} = \frac{R(t)}{V} + NC_0 - NC_i + k_{dm} \frac{A_m}{V} C_{sm} - k_{am} \frac{A_m}{V} C_i \quad (6)$$

$$\text{and } \frac{dC_{sm}}{dt} = k_{am} C_i - k_{dm} C_{sm} \quad (7)$$

where C_i , the gas-phase VOC concentration inside the room ($\mu\text{g}\cdot\text{m}^{-3}$); $R(t)$, the emission rate of source ($\mu\text{g}\cdot\text{h}^{-1}$); V , the room volume (m^3); N , the air exchange rate (h^{-1}); C_0 , the gas-phase concentration of air coming from outdoors by ventilation; k_{am} , the adsorption rate constant ($\text{m}\cdot\text{h}^{-1}$); k_{dm} , the desorption rate constant (h^{-1}); A_m , the material surface (m^2); and C_{sm} , the surface concentration ($\mu\text{g}\cdot\text{m}^{-2}$).

A second model (M2) is an updated version of previous model (M1) proposed by Tichenor et al⁶ and Rizk et al¹⁶ in order to take into account of the concentration gradient developing in the boundary layer above the material surface. In this case, the diffusion in gas-phase between the material surface and the bulk air is considered.

The mathematical equations to model the concentration changes in the room become¹⁶:

$$\frac{dC_i}{dt} = \frac{R(t)}{V} + NC_0 - NC_i + \frac{k_{dm} h_m}{h_m + k_{am}} \frac{A_m}{V} C_{sm} - \frac{k_{am} h_m}{h_m + k_{am}} \frac{A_m}{V} C_i \quad (8)$$

$$\text{and } \frac{dC_{sm}}{dt} = \frac{k_{am} h_m}{h_m + k_{am}} C_i - \frac{k_{dm} h_m}{h_m + k_{am}} C_{sm} \quad (9)$$

with h_m the convective mass transfer coefficient of compound through the boundary layer over the material ($\text{m}\cdot\text{s}^{-1}$).

Comparing Equation (6) with (8) and (7) with (9), this model is similar to the previous one but with apparent sorption coefficients k'_{am} and k'_{dm} defined as:

$$k'_{am} = \frac{k_{am} h_m}{h_m + k_{am}} \quad (10)$$

$$k'_{dm} = \frac{k_{dm} h_m}{h_m + k_{am}} \quad (11)$$

For the estimation of convective mass transfer coefficient (h_m), empirical relations were applied according to Bourdin et al²¹ In the case of laminar flow, there is:

$$\text{Sh} = 0.664 \text{Re}^{1/2} \text{Sc}^{1/3} \quad (12)$$

where $\text{Sh} = h_m L_c / D$ is Sherwood number, $\text{Sc} = \nu / D$ Schmidt number, $\text{Re} = UL_c / \nu$ Reynolds number, ν is the kinematic viscosity of the air ($\text{m}^2\cdot\text{s}^{-1}$), U is the air velocity over the material ($\text{m}\cdot\text{s}^{-1}$), D is the molecular diffusion of the compound in the air ($\text{m}^2\cdot\text{s}^{-1}$), and L_c is the characteristic length of the material/fluid system (m)

These Equations (10-12) allow to estimate the apparent sorption coefficients k'_{am} and k'_{dm} used in the model (M2).

The general equations of two models ([6]-[9]) are simultaneously solved using a Microsoft Excel solver and finite-element calculations and considering the initial conditions defined in Section 3.3.

3 | RESULTS AND DISCUSSION

3.1 | Performance parameters of SPME method

In order to satisfy the sorption experiments, a calibration on a wide range of exposure dose up to $500 \mu\text{g}\cdot\text{m}^{-3}\cdot\text{min}$ was required for the quantification of two compounds. To check the linearity and stability over time, two calibration series with two different concentration levels (around 20 and $50 \mu\text{g}\cdot\text{m}^{-3}$) and several exposure times (from 1 to 10 min) were carried out before and after the sorption experiments for both compounds (Figure 2). These results confirm good linearity between the SPME response obtained by FID and the product of concentration and the exposure time with a squared correlation coefficient greater than 0.99. None deviation was observed between the two calibrations showing a long-term stability. Note that the sensibility of the method (slope of calibration curve) is twelve times higher for formaldehyde than for toluene. This could be due to the derivatization reaction and the formation of formaldehyde oxime which obviously has a FID response higher than toluene.

The limits of detection (LOD) and quantification (LOQ) were calculated as three times and ten times the standard deviation of the blank (non-exposed fiber) for formaldehyde. In absence of blank value for toluene, LOD and LOQ were assessed considering the standard deviation of low concentration close to detectable level. As shown in Table 2, the blank value contributes to rising LOD and LOQ for formaldehyde. Accordingly, all the formaldehyde measurements were systematically subtracted from the blank value average.

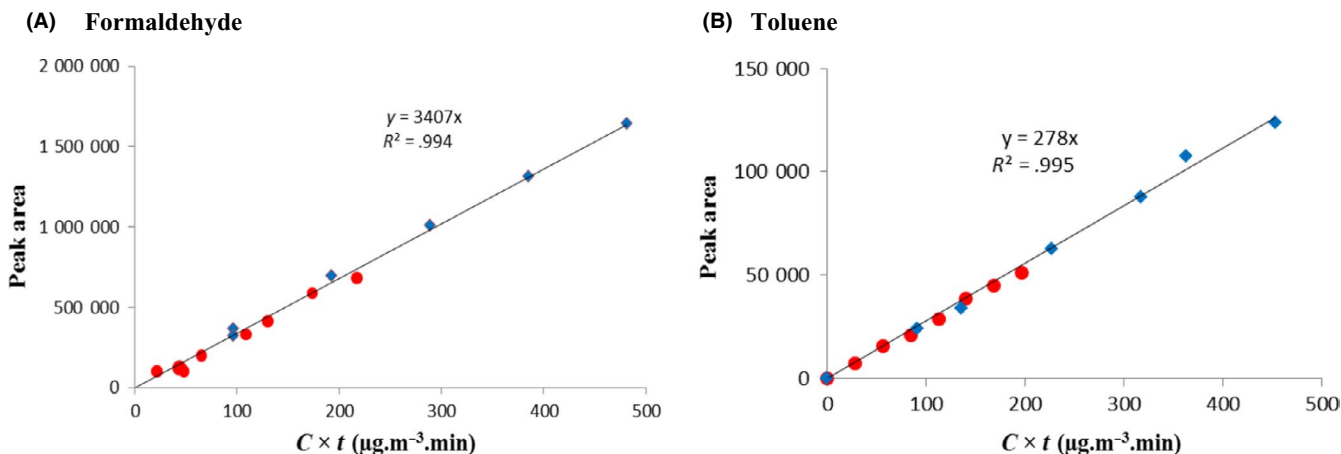


FIGURE 2 Calibration curve obtained in GC-FID, $A = f(C \times t)$, for formaldehyde by combining the data of two calibration series before and after the sorption experiments (circles and diamonds, respectively). FID, flame ionization detector; GC, gas chromatography

Limits of detections are suitable for the experiments gradually increasing the extraction time during the adsorption phase to respect the quantification range of the method.

Reproducibility was investigated at several concentration levels and extraction times (2, 4, and 5 min) using different SPME fibers (Table 3). The relative standard deviations (RSD) were less than 5% with the exception of the series for formaldehyde at low concentration which reached 15%. The step of PFBHA loading on the SPME fiber tends to degrade the measurement accuracy for formaldehyde. The fast decay in concentration during the adsorption phase required the use of six to seven different SPME fibers. The measurements were also multiplied at the end of the adsorption phase (low concentration level) in order to improve the measurement accuracy in this final part of concentration pattern.

3.2 | Toluene and formaldehyde sorption on glass cell (blank test)

The method uses a glass cell. Therefore, there is a need to know the sorption of two compounds on glass. To this end, the cell was placed directly on a glass disk. In this configuration, all inner surfaces in contact with air are made of glass. The results are summarized in Table 4. Gaseous concentration patterns obtained during the adsorption phase as well as the associated sorption model curves are shown in Figure 3.

A sorption effect imputable to the inner glass walls of cell was observed for the two compounds. The magnitude of this effect was much higher for formaldehyde than for toluene with a thirty times higher adsorption rate constant. The adsorption and desorption constants of the glass cell have to be taken into account in the calculation of material constants for formaldehyde (Equations 4 and 5). In the case of toluene, the sorption on the cell walls has a marginal effect (less than 10%) on the determination of material constants

given the sorption kinetics obtained for the materials (shown in the following section).

3.3 | Toluene and formaldehyde sorption on floor coverings

Five floor coverings (2 PVC, 2 rubbers, and 1 linoleum) were analyzed twice according to the protocol described in Section 2.2. Two sorption kinetics of one material (Rubber 1) are shown in comparison with those of blank test (Figure 4), and all results on the sorption parameters for the five materials are detailed in Table 5 and Figure 5.

A satisfying reproducibility of the measured sorption parameters was obtained with deviation from the mean of less than 20%, except for a few cases like PVC1/formaldehyde interaction where no sorption effect was observed (k_{am} close to 0). As shown in Figure 4, the sorption kinetic of formaldehyde is much faster than those of toluene. The trend was found in the overall sorption tests except for PVC1 and is as a result of adsorption

TABLE 2 Blank values and limits of detection (LOD) and quantification (LOQ) obtained from the analysis of 25 blanks (non-exposed fibers) for formaldehyde and 7 replicates at $18 \mu\text{g}\cdot\text{m}^{-3}$ and a 1 min extraction (lowest time) for toluene

	Extraction time		
	1 min	5 min	10 min
Formaldehyde			
Concentration equivalent to mean of blank values ($\mu\text{g}\cdot\text{m}^{-3}$)	37	7.4	3.7
LOD ($\mu\text{g}\cdot\text{m}^{-3}$)	21	4.2	2.1
LOQ ($\mu\text{g}\cdot\text{m}^{-3}$)	70	14	7
Toluene			
LOD ($\mu\text{g}\cdot\text{m}^{-3}$)	13.5	2.7	1.4
LOQ ($\mu\text{g}\cdot\text{m}^{-3}$)	45	9	4.5

	Extraction time	Concentration ($\mu\text{g}\cdot\text{m}^{-3}$) Mean \pm standard deviation	RSD (%)
Formaldehyde			
Series of 7 measures with multiple fibers	5 min	26.3 \pm 3.9	15
Series of 7 measures with multiple fibers	2 min	124.8 \pm 3.6	2.9
Toluene			
Series of 6 measures with multiple fibers	4 min	24.5 \pm 1.2	4.9
Series of 6 measures with multiple fibers	5 min	54.3 \pm 1.5	2.7
Series of 6 measures with multiple fibers	2 min	94.1 \pm 3.0	3.2

Abbreviation: SPME, solid-phase microextraction.

TABLE 3 Reproducibility (RSD) obtained by analysis of standard atmospheres with different SPME fibers for various concentration levels and extraction times. The experimental conditions were maintained at $50 \pm 3\%$ relative humidity and $23 \pm 2^\circ\text{C}$

TABLE 4 Average and range of equilibrium gas-phase concentration for the emission phase and sorption coefficients for the glass cell without material—results of Langmuir isotherm model

	Emission phase	Adsorption phase			
	C_{ieq0} ($\mu\text{g}\cdot\text{m}^{-3}$)	k_{ac} ($\text{m}\cdot\text{h}^{-1}$)	k_{dc} (h^{-1})	K_e (m)	R^2
Blank test for toluene (n = 2)	<4.5	0.001 [0.001_0.001]	0.39 [0.37_0.41]	0.003 [0.003_0.004]	0.93
Blank test for formaldehyde (n = 5)	<7	0.032 [0.025_0.04]	0.325 [0.29_0.355]	0.10 [0.08_0.12]	0.98

Note: n, number of replicates. Minimum and maximum are enclosed in brackets.

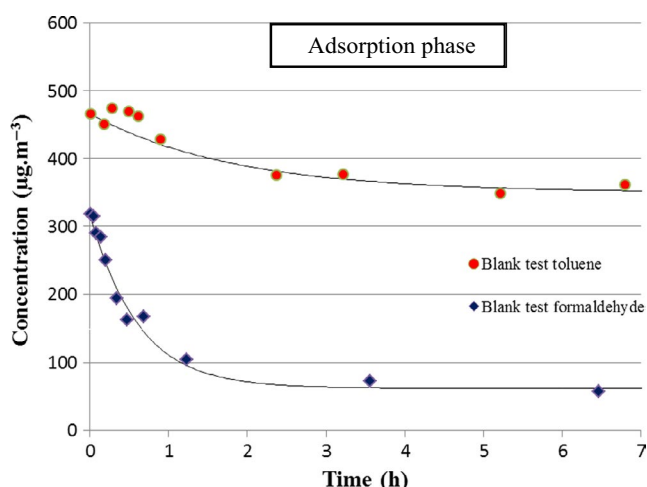


FIGURE 3 Gaseous toluene and formaldehyde concentration patterns and the associated sorption model curves for the blank tests (without material)

rate constants three times higher for formaldehyde than for toluene (Table 5 and Figure 5). It is noted that the low adsorption and desorption rate constants for toluene are homogeneous reflecting a low non-specific sorption. Conversely, there are much larger differences in the adsorption and desorption constants of

formaldehyde that show contrasted sorption behaviors depending on the materials. For PVC1, the adsorption rate constant (k_{am}) as well as the K_e value are close to 0. Formaldehyde is not adsorbed on the surface of this material. With a K_e value exceeding 3 m, Rubber 1 represents a formaldehyde sink due to its very low desorption constant close to 0. A low concentration of $14 \mu\text{g}\cdot\text{m}^{-3}$ is recorded at the end of adsorption phase for this material showing its strong adsorbent character (Figure 4A). This high K_e value for Rubber 1 is comparable to those of carpets identified by Won et al²⁷ as adsorptive reservoirs for VOCs. We can observe that the sorption behavior does not seem to depend on belonging to a family of materials but rather on specific characteristics of each material. Indeed, the formaldehyde sorption characteristics of the two PVCs on the one hand and the two rubbers on the other hand are not similar. For this reason, it is difficult to compare these data with literature. However, existing experimental studies identified many materials (gypsum wallboard, calcium silicate, plastic flooring) with high K_e values for formaldehyde (from 3 to 40 m) indicating a strong tendency to sorption of this compound on interior surfaces.^{13,18,19,28,29}

Previous studies showed that vapor pressure is a reasonably good predictor of the adsorption capability of VOCs spanning the mostly chemical classes on the materials.³⁰ Formaldehyde is a compound more volatile than toluene, its partition coefficient K_e should be lower

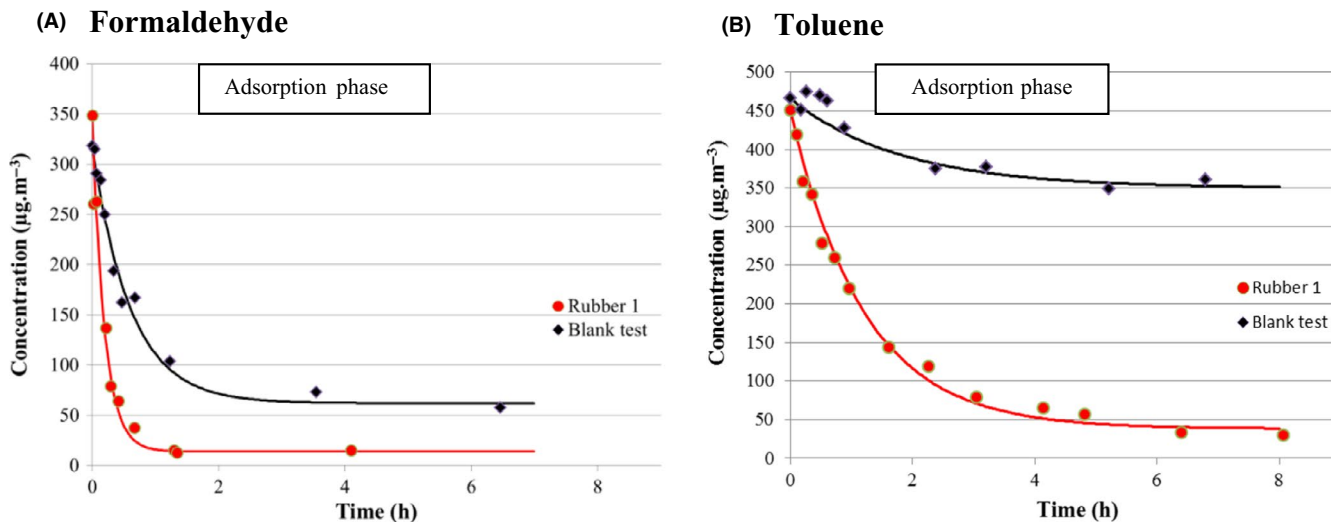


FIGURE 4 Gaseous formaldehyde and toluene concentration patterns during the adsorption phase and the associated sorption model curves for the tests on one flooring (Rubber 1) in comparison with those of blank tests (without material)

TABLE 5 Average and range of equilibrium gas-phase concentration at the emission phase and sorption coefficients for material tests—results of Langmuir isotherm model

	Emission phase	Adsorption phase				R^2
	C_{ieq0} ($\mu\text{g}\cdot\text{m}^{-3}$)	k_{am} ($\text{m}\cdot\text{h}^{-1}$)	k_{dm} (h^{-1})	K_e (m)		
Formaldehyde						
PVC 1 (n = 2)	23 [19_27]	0.003 [0_0.007]	0.51 [0.24_0.78]	0.005 [0_0.01]	0.98	
PVC 2 (n = 2)	19.3 [17_22]	0.06 [0.059_0.065]	0.41 [0.33_0.49]	0.15 [0.13_0.17]	0.97	
Rubber 1 (n = 2)	7.3 [5.2_9.5]	0.075 [0.073_0.077]	0.019 [0.017_0.021]	3.9 [3.4_4.5]	0.98	
Rubber 2 (n = 2)	16.5 [9_24]	0.063 [0.050_0.076]	0.24 [0.23_0.24]	0.26 [0.21_0.31]	0.97	
Linoleum (n = 2)	22.9 [21_24]	0.059 [0.057_0.06]	0.9 [0.88_0.93]	0.065 [0.061_0.068]	0.98	
Toluene						
PVC 1 (n = 2)	<4.5	0.018 [0.015_0.02]	0.08 [0.07_0.09]	0.22 [0.21_0.23]	0.98	
PVC 2 (n = 2)	<4.5	0.018 [0.016_0.02]	0.08 [0.07_0.09]	0.23 [0.22_0.24]	0.99	
Rubber 1 (n = 2)	<4.5	0.019 [0.017_0.02]	0.08 [0.07_0.095]	0.23 [0.21_0.24]	0.99	
Rubber 2 (n = 2)	<4.5	0.027 [0.023_0.03]	0.08 [0.06_0.1]	0.35 [0.31_0.38]	0.98	
Linoleum (n = 2)	<4.5	0.018 [0.018_0.019]	0.23 [0.22_0.23]	0.079 [0.077_0.08]	0.99	

Note: n, number of replicates. Minimum and maximum are enclosed in brackets.

than that of toluene for the same material. This rule is not verified in the case of Rubber 1 suggesting that other processes than the deposition and vaporization are involved in mass transfer of formaldehyde to this material. This singular sorption behavior of formaldehyde was already identified by the field experiments and modeling carried out in the rooms.^{7,31} They estimated an overall removal rate constant of $0.09 \pm 0.02 \text{ m}\cdot\text{h}^{-1}$ in the unoccupied rooms. This high value obtained at the room scale is comparable to the adsorption rate constants ranged from 0.05 to 0.08 $\text{m}\cdot\text{h}^{-1}$ found for the four materials having a sorption ability of formaldehyde (Table 5). This suggests that the high removal of formaldehyde detected indoors can potentially be explained by the sorption occurring on the material surfaces.

The formaldehyde sorption mechanisms are not well described in the literature. Some studies^{13,18,19,28} showed that the

formaldehyde sorption on the porous materials like wallboards and carpets is increased under high humidity conditions. Some of these authors suggested that formaldehyde may be transferred in water film formed on the material surfaces in relation to the highly water-soluble nature of compound.¹³ Other authors¹⁸ pointed out that the materials with the surface oxygen functionalities like OH groups in the case of gypsum board have an increased sorption capability of formaldehyde. Ye et al¹² showed that the mass transfer of formaldehyde in some selected polymers can be partially irreversible. The study revealed the formation of aliphatic acids on the polymer surface exposed to formaldehyde suggesting that there is an irreversibility of the adsorption process that could be due to oxidation. The authors concluded that the observed mass transfer irreversibility could be caused by formaldehyde molecules binding or

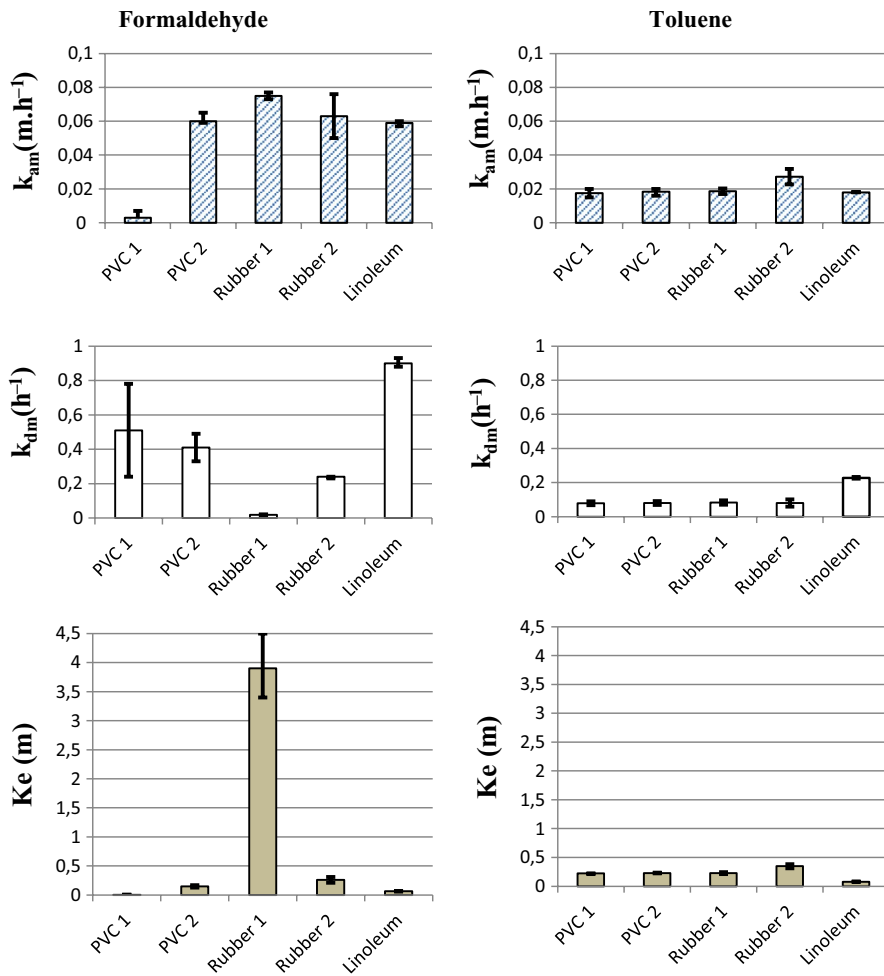


FIGURE 5 Average of k_{am} , k_{dm} and K_e values assessed for formaldehyde and toluene sorption on the five floorings. Error bars correspond to min-max

TABLE 6 Parameters for the determination of VOCs and the conditions used in the numerical modeling

	Formaldehyde	Toluene
Characteristic parameters		
Diffusion coefficient in air (m ² .h ⁻¹)	0.0601	0.0295
Concentrations of inlet air (μg.m ⁻³)	3	3
Initial surface concentration (μg.m ⁻²)	From 0.02 to 11.7 ^a	From 0.2 to 1.0 ^a
Convective mass transfer coefficient (m.h ⁻¹)	From 0.09 to 0.4 ^b	From 0.055 to 0.25 ^b
Realistic room conditions		
Volume of the room (m ³)	30	
Size of the room (m × m × m)	4 × 3 × 2.5	
Area of sorbent material (m ²)	12	
Air exchange rates (h ⁻¹)	0.05, 0.1, 0.5 and 1	
Indoor source emission (μg.h ⁻¹)	20	

Abbreviation: VOC, volatile organic compound.

^aCalculated from data of C_{ieq0} and K_e given in Table 5.

^bCalculated using the Equation (12) for the characteristic parameters and conditions given in Table 6.

reacting with the polymer matrix by chemisorption and that at least a part of the chemisorption processes were reversible. According to these studies, several sorption pathways for formaldehyde seem to coexist.

3.4 | Contribution of floorings sorption on IAQ

Data obtained about sorption parameters have been considered to assess the impact of these five flooring materials on the indoor concentrations in realistic room conditions using the models (M1 and M2). These numerical simulations were performed basing on the parameters and conditions described in Table 6. The concentrations were predicted after introduction of a source having a constant emission rate of 600 μg.h⁻¹ (corresponding to a material of 3 m² with an emission rate of 200 μg.m⁻².h⁻¹). Different air exchange rates from 0.05 to 1 h⁻¹ were considered. The concentrations of inlet air were chosen as those usually recorded in outdoor air³² and the initial surface concentrations C_{sm0} (μg.m⁻²) were calculated using the material/air equilibrium partition coefficients K_e (m) and the gas-phase concentrations C_{ieq0} (μg.m⁻³) recorded at the end of adsorption phase. The convective mass transfer coefficient of formaldehyde is 1.6 times higher than that of toluene in the studied conditions which

FIGURE 6 Variations of formaldehyde concentration predicted by the two models for a room with Rubber 1 and at a low air exchange rate of 0.05 h^{-1} compared to the case without sink (A) and contributions of sorption on Rubber 1 to mass balance of formaldehyde in the room (B)

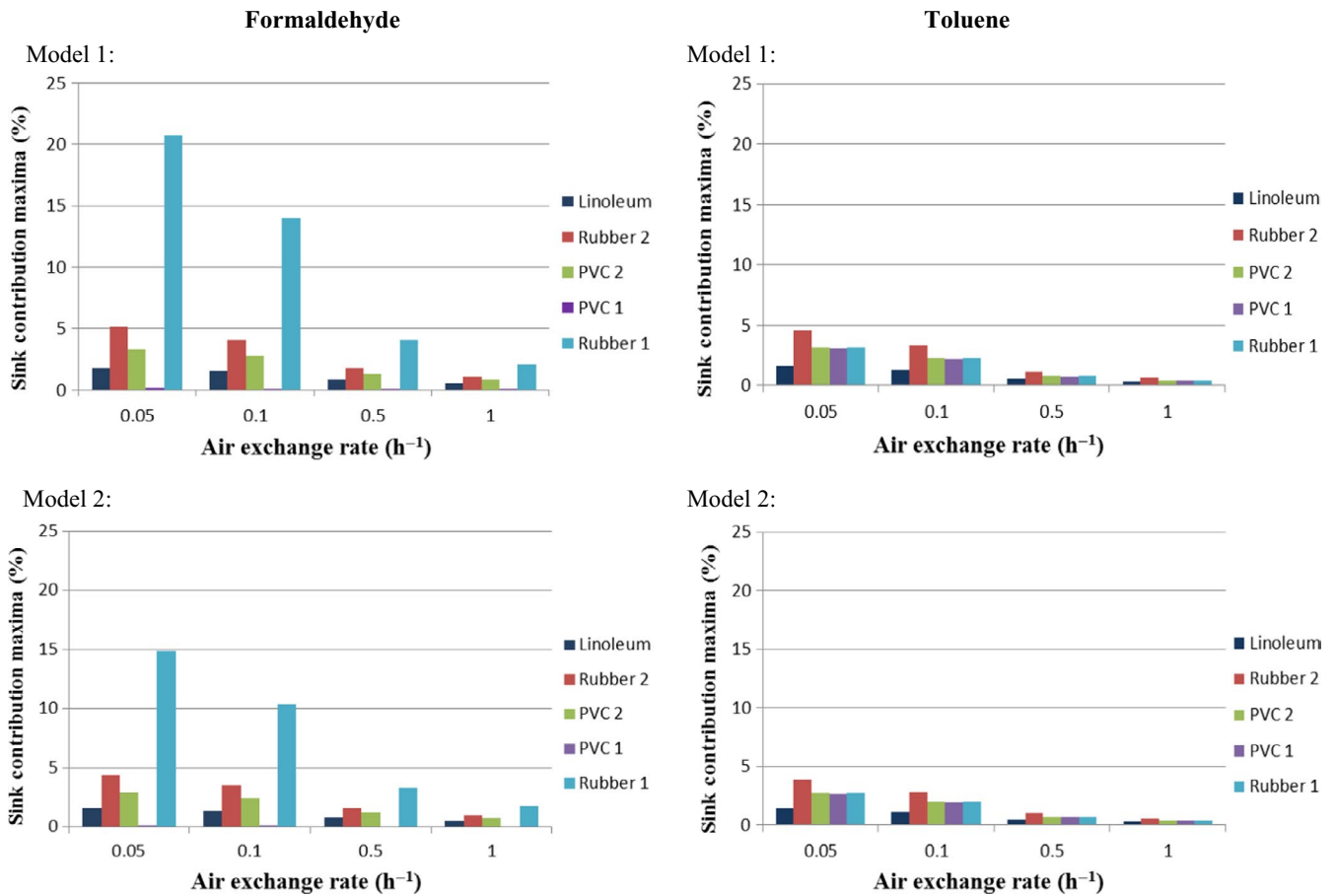
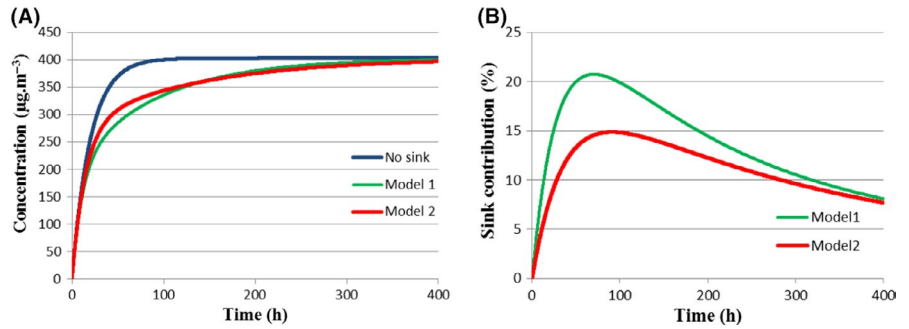


FIGURE 7 Maximum contributions of sorption on floorings to mass balance of formaldehyde and toluene in the room according to the air exchange rate

could lead to greater differences between the results of the two models for formaldehyde.

As shown in Figure 6A, Rubber 1 modifies significantly the evolution of formaldehyde concentrations at a low air exchange rate of 0.05 h^{-1} for the two models in comparison with the case of room without sink. The sink contribution in proportion to total formaldehyde amount introduced in the room (Figure 6B) increases up to a maximum reached after 70-85 h depending on the model and then slowly decreases as a result of air exchange rate contribution. Considering the gas diffusion process through the boundary layer over the material (Model 2) tends to reduce the sink contribution with a maximum of 15% compared to 21% reached using Model 1.

Figure 7 gathers the maxima of sink effect for different VOC/material couples and air exchange rates using the two models. It confirms that Rubber 1 acts as a sink of formaldehyde in realistic room conditions mainly when the air exchange rate is low below 0.1 h^{-1} . These situations correspond to the rooms with natural ventilation.^{26,33} For the other floorings, the sorption has a minor contribution less than or equal to 5%, regardless of the air exchange rate.

Total amount of formaldehyde sorbed on Rubber 1 when a steady state is reached is 18 mg at 0.05 h^{-1} and 9.5 mg at 0.1 h^{-1} . Assuming that the sorption is a totally reversible process and a fast release of sorbed formaldehyde from Rubber 1 due to conditions favorable to the reemission, this could increase the indoor concentration until 45

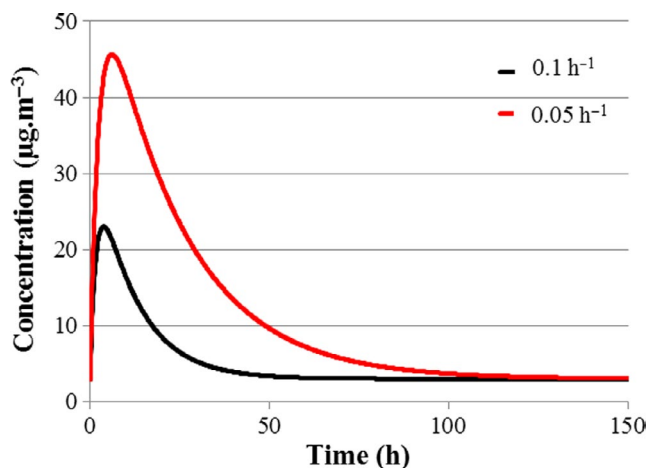


FIGURE 8 Modeled concentrations when a release of sorbed formaldehyde from Rubber 1 occurs under air exchange rates of 0.05 and 0.1 h⁻¹

and 23 µg·m⁻³ for air exchange rates of 0.05 h⁻¹ and 0.1 h⁻¹, respectively. Figure 8 gives the modeled concentration patterns obtained when reemission occurs under these low air exchange rates. These simulations consider the convective mass transfer coefficient of formaldehyde on the material and in the absence of indoor source. Results show that the release of sorbed formaldehyde from Rubber 1 can potentially contribute to a substantial increase of formaldehyde concentration indoors.

4 | CONCLUSIONS

This study compares the sorption characteristics of formaldehyde and toluene on different types of floor coverings under static conditions using an airtight emission cell coupled to SPME sampling. Compared to the available methods of determining these parameters described in the literature, this method has the following advantages: (a) an analytical solution assessing the adsorption and desorption rate constants simultaneously from only data of the adsorption phase; (b) taking into account of sorption on the inner walls of cell in the calculation of the material sorption parameters; and (c) an assessment of these sorption parameters under experimental conditions close to those encountered in indoor environments.

Basing on the material/air equilibrium partition coefficient (K_e) as well as the adsorption coefficient (k_{am}), the sorption of formaldehyde on the tested materials is overall higher than that of toluene. However, contrasted sorption behaviors were obtained ranging from a material (one PVC) having no sorption to a material (one rubber) identified as a sink of formaldehyde characterized by a very low desorption rate close to 0. For toluene, the sorbed amounts are low and the process tends to be reversible. At the scale of room, the simulations show that only the sorption of one rubber (identified as a sink) has a significant impact in mass balance of formaldehyde indoors with a contribution exceeding 10% for the cases of low air

exchange rates below 0.1 h⁻¹. The amount of formaldehyde sorbed on this rubber is sufficiently high to mitigate peak formaldehyde concentrations and could increase the indoor concentrations of a few tens µg·m⁻³ in the cases of reemission. For the other VOC/material couples, the sorption has a minor contribution less than or equal to 5%, regardless of the air exchange rate. This study demonstrates that the VOC sorption on floorings has a significant impact on IAQ under realistic indoor conditions and highlights the need to take into account its contribution in the IAQ modeling.

A sorbent material like the rubber can be considered as a buffer reservoir which can either improve IAQ because of its ability to sorb formaldehyde or lead to degradation of IAQ when the environmental conditions are favorable to the reemission. For example, the material/air equilibrium partition coefficient K_e can decrease as a result of a rise in ambient temperature and lead to release sorbed formaldehyde. Sorbent materials overall increase the persistence of contaminants indoors. For that reason, we do not recommend using sorbent materials as a means of improving IAQ.

Further investigations will be carried out to identify the physicochemical properties and surface mechanisms involved that can explain differences in sorption behavior of materials. This will be the subject of a subsequent paper.

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AUTHOR CONTRIBUTION

Herve Plaisance: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Funding acquisition (equal); Investigation (lead); Methodology (lead); Resources (equal); Validation (lead); Writing-original draft (lead); Writing-review & editing (lead). **Pierre Mocho:** Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Validation (equal). **Valerie Desauziers:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (lead); Methodology (equal); Project administration (lead); Resources (lead); Validation (equal).

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