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C. Radulescu-Bouilly, Francis Allard, Patrice Blondeau, Bernard Collignan, R. Popescu, et al. A physically- based analysis of the Interactions between humidity and VOCs in building materials. Healthy Buildings 2006, Jun 2006, Lisboa, Portugal. hal-00312657

HAL Id: hal-00312657

<https://hal.science/hal-00312657v1>

Submitted on 7 Jun 2023

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A Physically- Based Analysis of the Interactions between Humidity and VOCs in Building Materials

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Summary: *The present paper investigates the different ways humidity may interact with VOCs in building materials. It aims to help in interpreting the results of experiments dealing with the influence of humidity on the reversible sink effect of materials, and/or the VOC emission from walls and furnishings. Three kinds of interactions have been considered: competition for adsorption at the pore surfaces of the materials, as well as change in the diffusion properties and possible absorption / desorption of VOCs due to capillary condensation of water vapour in the micropores of the materials. After briefly presenting the fundamentals of diffusion, capillary condensation, adsorption/desorption and absorption/desorption in porous media, the potential influence of each of these interactions on the VOC transport in building materials has been evaluated for various materials from existing experimental data. The results show that the influence of humidity strongly depends on the porosity and pore size distribution of the materials, as well as the physical properties of the VOCs. Moreover, the VOC mass fluxes at the material surface may vary in a non-linear way with increasing humidity due to changes from one leading interaction phenomenon to another.*

Keywords: *humidity, VOCs, adsorption, absorption, diffusion, porous media, emission, sink effect, solubility, capillary condensation*

1 Introduction

During the past 15 years, many experimental studies have dealt with the influence of environmental parameters (temperature, humidity, air velocity, ...) on the VOC emissions and reversible sink effect of materials [1-3]. While globally leading to a consensus on the influence of parameters such as temperature, they also lead to different and sometimes divergent conclusions regarding the influence of humidity. For instance, when measuring the VOC emissions from a water-based acrylic paint and a polyurethane plastic finish varnish, Haghghat and De Bellis [1] came to the conclusion that, during the first stage of the emission process, TVOC emissions from the paint were higher at 32% relative humidity (RH) than at 62% RH. On the other hand, the TVOC emissions from the varnish proved to increase with increasing humidity. Nevertheless, in this latter case, the authors also noticed that unlike the TVOC, individual compounds such as toluene, m,p-xylene and 1,3,5 trimethylbenzene showed higher emission rates at 32% RH than at 62% RH. This illustrates, if necessary, that at the microscopic level, humidity probably brings various interaction phenomena into play. The fact that the strength of these interactions could depend on the material and VOC systems tested, as well as the VOC concentrations and

humidity level considered, may explain the non-linearities observed macroscopically when dealing with the influence of humidity on the VOC mass transports at the material surface.

The present study aims to serve as a first step in the understanding and modelling of these complex interactions. It particularly focuses on porous structural or covering materials used in buildings, the pore size distribution (PSD) of these materials being a key parameter of the analysis. Indeed, it determines capillary condensation in the pores of the material in a way which is described in the first paragraph of the paper. As gaseous contaminants, and especially VOCs, are soluble in liquids to a greater or lesser degree [4], the pores that are filled with liquid water will give rise to absorption / desorption mass transports inside the material, with the consequence to increase its mass capacity. In addition, the pores that are filled with liquid water no longer contribute, or contribute differently, to the porous diffusion of gases in the material. Therefore, the effective diffusivity of VOCs may be decreased significantly when humidity increases. These two points are addressed in paragraphs 2 and 3, respectively. Finally, in the pores where capillary condensation doesn't occur, water vapour can be considered as a competitor of VOCs for adsorption

on the active sites of the pore surfaces. This question is discussed in paragraph 4.

1 Capillary condensation in porous materials

Gas condensation is usually thought to occur when the pressure (concentration) of the species approaches its saturated vapour pressure, P_s (Pa). However, due to surface tension phenomena, condensation in a pore of radius r (m) will occur at a lower pressure, P_r (Pa), which is related to P_s by the Laplace equation [5]:

$$\ln \frac{P_r}{P_s} = - \frac{2\gamma \cos \theta V_L}{rRT}, \quad (1)$$

where γ (N/m) is the surface tension, θ the contact angle of the condensed liquid meniscus in the pore, V_L ($\text{m}^3 \cdot \text{mol}^{-1}$) the molar volume of the liquid, R ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) the universal gas constant, and T (K) the temperature.

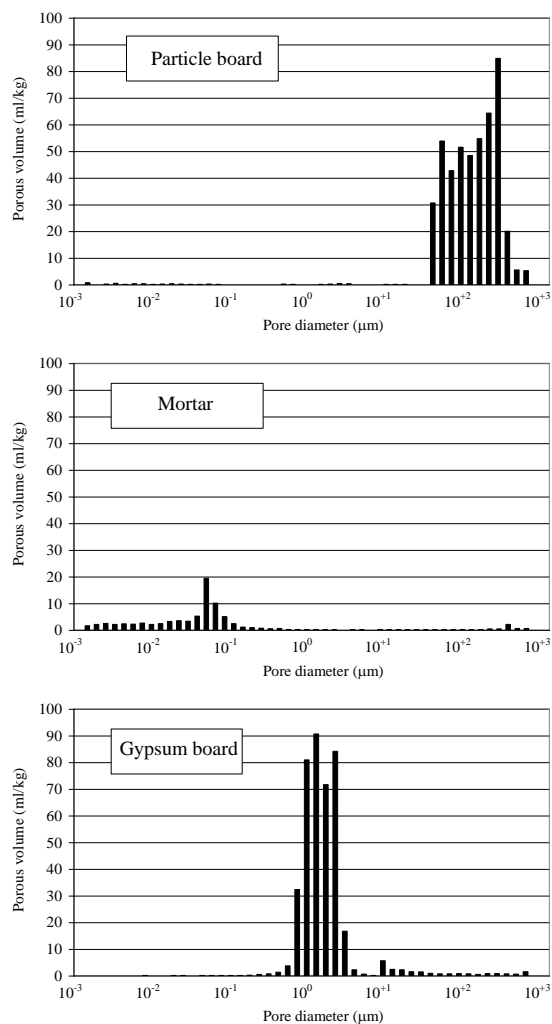


Fig. 1 : Pore size distribution (PSD) of mortar, particle board and gypsum

Eq. (1) can be used to determine the pore size distribution of materials by measuring the volume of mercury (non-wetting material: $\theta = 140^\circ$) penetrating the pores of radius r_i when an increasing pressure P_i (Pa) is applied. Figure 1 shows the PSD of 3 materials that were determined based on this technique [6], and considered in the present study.

For the purpose of this study, Eq. (1) was also used to determine the critical pore radius r_{crit} (m) under which capillary condensation of water vapour will occur for a uniform relative humidity in the pore air phase ($\equiv P_r$). Then, the (liquid) water content of the materials was determined from the PSD by summing the void volume of all pores having a radius $r < r_{crit}$ (Fig. 2). All the parameters were evaluated at $T = 20^\circ\text{C}$ ($P_s = 2340$ Pa), $\gamma = 72.8 \times 10^{-3}$ N/m, and $V_L = 1.8 \times 10^{-5}$ $\text{m}^3 \cdot \text{mol}^{-1}$. As no data for the contact angle could be found in the literature, a value of 10° was considered. Although being very uncertain, this parameter proved to have a negligible influence on the computed radius up to 70° , this upper value being very unlikely for a wetting liquid such as water. Relative humidities lower than 60% were found to lead to negligible amounts of condensed water and are thus not represented on Fig. 2. The latter shows that the water content of the materials logically increases with increasing relative humidity in the air phase. Overall, Fig. 2 shows that mortar having a significant volume of submicronic pores (see Fig. 1), its water content is much higher than those of gypsum and particle board. This will prove to be important when discussing the role of humidity in the next paragraphs.

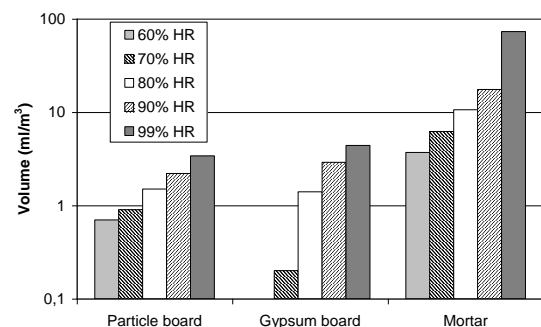


Fig. 2: Water content of particle board, gypsum and mortar as a function of relative humidity

2 Influence of humidity on VOC absorption

In porous materials, the diffusing gases accumulates in the air-phase of the pores, at the pore surfaces due to adsorption transports, and, when capillary condensation occurs, in liquid water due to absorption transports. For a uniform pore air-phase concentration C ($\text{g}/\text{g}_{\text{air}}$), the unit mass of

VOC contained in the porous volume, M_{air} ($\text{kg}/\text{m}^3_{\text{mat}}$), is given by :

$$M_{air} = \rho_{air} \varepsilon C \quad (2)$$

where ρ_{air} (kg/m^3) is the air density and ε ($\text{m}^3_{\text{air}}/\text{m}^3_{\text{mat}}$) the total porosity of the material. The unit mass of VOC which is adsorbed at the pore surface, M_{ads} ($\text{kg}/\text{m}^3_{\text{mat}}$), depends on the sorbed-phase concentration of the chemical, C_s ($\text{kg}/\text{kg}_{\text{mat}}$), and the material density ρ_{mat} (kg/m^3):

$$M_{ads} = \rho_{mat} C_s \quad (3)$$

Assuming a linear adsorption isotherm, Eq. (3) transforms into :

$$M_{ads} = \rho_{mat} K C \quad (4)$$

where K ($\text{kg}_{\text{air}}/\text{kg}_{\text{mat}}$) is the partition coefficient of the VOC and material system.

Finally, the unit mass of VOC which accumulates in the pores due to absorption in condensed water, M_{abs} ($\text{kg}/\text{m}^3_{\text{mat}}$), is given by :

$$M_{abs} = \varepsilon_{liq} C_{liq} \quad (5)$$

where ε_{liq} ($\text{m}^3_{\text{water}}/\text{m}^3_{\text{mat}}$) is the humidity content of the material for a uniform relative humidity RH in the material (see Fig. 2), and C_{liq} ($\text{kg}/\text{m}^3_{\text{liq}}$) is the VOC aqueous-phase concentration. For dilute solution, Henry's law applies, and Eq. (5) transforms into :

$$M_{abs} = \varepsilon_{liq} H C \quad (6)$$

where H ($\text{kg}_{\text{air}}/\text{m}^3_{\text{water}}$) is the Henry's constant (solubility in water) of the VOC.

The elemental mass capacities of particle board, gypsum and mortar were determined from Eqs. (2), (4) and (6) for various uniform relative humidities in the pore air phase, and three VOCs: acetone ($\text{C}_3\text{H}_6\text{O}$, ketone), formaldehyde (HCHO, aldehyde), and tetrachloroethylene (C_2Cl_4 , halogenated aliphatic hydrocarbon). The total porosities, ε , of particle board, gypsum and mortar, were taken as 25.8%, 29.5% and 22.6%, respectively [6]. The Henry's constants H and partition coefficients K considered are summarised in Table 1. Henry's constants were taken from Sander [4]; it can be noted that whilst the solubility of tetrachloroethylene in water is very low, formaldehyde counts among the most soluble chemicals in water. The partition coefficients of acetone in gypsum and particle board were taken

from Tiffonnet and al [7]. The partition coefficient of tetrachloroethylene in gypsum was determined experimentally using the facility and protocol described in reference [7]. Finally, the partition coefficient of formaldehyde in gypsum was taken from Silberstein [8]. In the absence of experimental data for mortar, as well as for tetrachloroethylene and formaldehyde in particle board, the partition coefficients of the species in gypsum were considered. These values are thus very uncertain.

Table 1: Henry's and partition coefficients considered for the study

	HCHO	C_2Cl_4	$\text{C}_3\text{H}_6\text{O}$
Henry's constant ($\text{mol}\cdot\text{l}^{-1}\cdot\text{atm}^{-1}$)	5700	0.6	24
Partition coefficient in gypsum ($\text{g}/\text{g}_{\text{air}}$)	5.5	0.094	0.69
Partition coefficient in particle board ($\text{g}/\text{g}_{\text{air}}$)	5.5 ^(*)	0.094 ^(*)	1.8
Partition coefficient in mortar ($\text{g}/\text{g}_{\text{air}}$)	5.5 ^(*)	0.094 ^(*)	0.69 ^(*)

^(*)Not a measured value – in the absence of data, assumed to be the same as for gypsum

Fig. 3 presents the computed elemental unit masses of the selected VOCs in gypsum for a uniform VOC concentration of $1 \text{ mg}/\text{m}^3$. By definition, pores that are filled with water are free of air and no longer contribute to adsorption transports. Therefore, in theory, the partition coefficients determined for dry conditions, as well as the total air porosity of the materials should be decreased to account for the reduction in air porosity and pore surface area available for adsorption. However, the aqueous volume was found to account for only 0.05% of the total porous volume at the most, and these interactions were thus not considered. Due to the lack of experimental data on the adsorption isotherm of water vapour, neither was considered here the possible decrease in the adsorption capacity of the three materials investigated (this problem is addressed in paragraph 4). Finally, M_{ads} and M_{air} have constant values corresponding to dry conditions.

As it can be noted from Fig. 3, M_{abs} logically increases with humidity but, due to the limited amount of water condensed in gypsum, it remains at least one order of magnitude lower than M_{ads} whatever the humidity level and the VOC. Things are rather different in the case of mortar and formaldehyde: Fig. 4 shows that, although the unit water volume remains low compared to the total porosity of the material, M_{abs} can account for 10% of M_{ads} at 60% RH, and may be of the same order of magnitude as M_{ads} at higher humidities. Of course, this result has to be taken with the greatest caution due to the large uncertainty on the partition coefficient considered. In addition, some people

will argue that formaldehyde is much soluble in water than many other VOCs found indoors. This is true, but one must keep in mind that the partition coefficient considered here ($5 \text{ g}_{\text{air}}/\text{g}_{\text{mat}}$) is also very high compared to the partition coefficients of other material / VOC systems (see measured data of Table 1 for instance). Therefore, one can imagine that at humidity levels representative of what is commonly measured indoors, the contribution of absorption transports might even be greater than the one of adsorption transports.

Finally, the conclusion is that humidity might tremendously increase the water soluble-species mass capacity of any kind of polydispersed material having micropores. Practically, this means that humid conditions will tend to limit their emission during the first stage of the emission process (but the emission period will be longer!). On the contrary, humid conditions will tend to strengthen the reversible sink effect of such materials and VOCs.

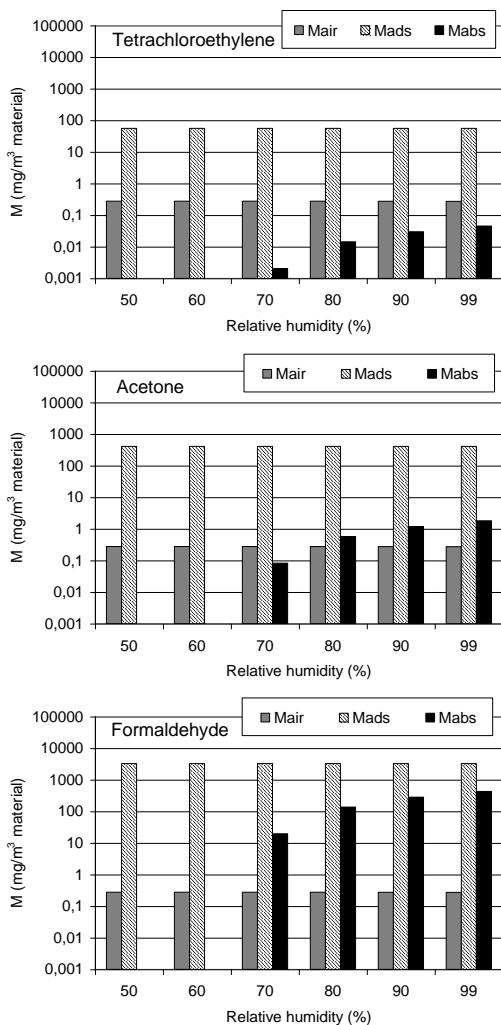


Fig. 3 : Computed elemental unit masses in gypsum for a uniform VOC air phase concentration of $1 \text{ mg}/\text{m}^3$

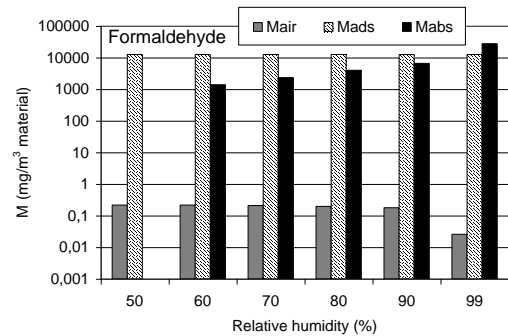


Fig. 4 : Computed elemental unit masses of formaldehyde in mortar for a formaldehyde air phase concentration of $1 \text{ mg}/\text{m}^3$

3 Influence of humidity on the VOC effective diffusivity in materials

Diffusion transport of gases in porous building materials involves a complex variety of processes including molecular, Knudsen and possible surface diffusion within the porous interstices [9]. All these processes can be modelled analogously by defining an effective diffusivity, D_e (m²/s), of the diffusing VOC in the material.

The influence of pores filling with water on D_e was investigated using a method based on porosimetry tests [6]. This method uses both the VOC molecular diffusivity in air and the PSD of the material as input of a mathematical model that computes the effective diffusivity of the corresponding VOC/material system. Comparison of the results obtained this way with experimental data coming from diffusion-cell methods concluded to a good agreement [6]. Assuming that pores that are filled with water no longer contribute to the diffusion transports, the VOC effective diffusivities at relative humidity RH were computed using as input of the model the size distribution of pores having a radius greater than the corresponding r_{crit} (see paragraph 1). As a representative example of the results obtained, Fig. 5 presents the computed effective diffusivities of acetone in particle board, mortar and gypsum as a function of relative humidity. It shows no influence of humidity on the diffusivities in particle board and gypsum, but a significant decrease in the acetone diffusivity in mortar with humidities increasing from 50% RH (-30% from 50% to 80% RH). Diffusion having a strong influence on the mass transports in thick materials, there's therefore no doubts that humidity can also influence the VOC emission profiles or the sink effect this way.

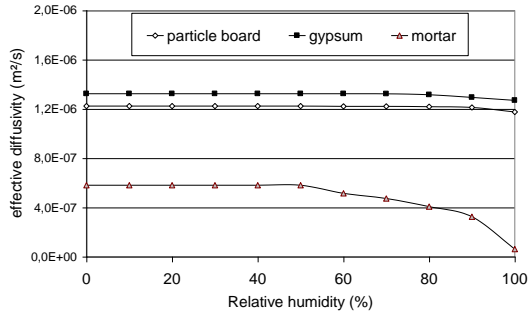


Fig. 5 : Effective diffusivity of acetone as a function of relative humidity

4 Influence of humidity on VOC adsorption

The third way humidity can influence the VOC transport in porous building materials is through the competition for adsorption on the active sites of the pore surfaces. In the case of VOC mixtures in dry conditions, this competition between species can be neglected considering that air-phase individual VOC concentrations are small - from ppb to few ppm - on the one hand, and the very large effective surface area available for adsorption – pore surface areas of 1285, 1750 and 14 385 m²/kgmat were estimated from the mercury intrusion porosimetry tests for gypsum, particle board and mortar, respectively - on the other hand. However, water vapour concentrations being several orders of magnitude higher than VOC concentrations, humidity might prove to have a significant influence on the sorption properties of VOCs in materials. This question was addressed by using the extended Langmuir equation as a multi-component adsorption isotherm model [10]:

$$C_{s,i} = \frac{C_{s,i}^0 K_{L,i} C_i}{1 + \sum_{j=1}^n K_{L,j} C_j} \quad (7)$$

where $C_{s,i}$ is the sorbed-phase concentration of species i , C_j the individual air-phase concentrations of all the species in the mixture, and C_s^0 and K_L the parameters of the Langmuir adsorption isotherm model for individual compounds :

$$C_{s,i} = \frac{C_{s,i}^0 K_{L,i} C_i}{1 + K_{L,i} C_i} \quad (8)$$

As mentioned previously, given the range of contaminant concentrations found indoors, the adsorption isotherms of VOCs are most of time assumed to be linear, and thus described by their partition coefficient K . On the other hand, the adsorption isotherms of water vapour show strong non-linearities [11] and require that BET-like

models be used [10]. Finally, the problem of applying Eq. (7) is that these linear and BET-like isotherms must first be fitted to Eq.(8) in order to draw the equivalent C_s^0 and K_L .

As no data on the adsorption isotherms of water vapour on particle board, gypsum and mortar could be found in the literature, the influence of humidity on the adsorption properties of VOCs was investigated by considering the air-phase concentrations of various VOCs measured indoors in the frame of the Expolis study [12], and plywood as a representative material. The adsorption isotherm of water vapour on plywood was taken from reference [13] while the VOC partition coefficients were taken or predicted from Bodalal and co-workers' measured data [14] or proposed correlations [15]. Fig. 6 presents the computed unit masses of adsorbed benzene, o-xylene and styrene as a function of humidity. It shows that the sorbed-phase concentrations at 80% RH can be up to 30% lower than in dry conditions. Sorbed-phase concentrations for humidities greater than 80% were not represented since the Langmuir adsorption isotherm model cannot correctly fit the last part of the water vapour adsorption isotherm.

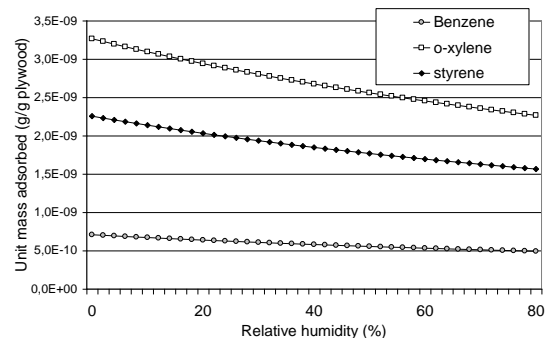


Fig. 6 : Sorbed-phase concentrations of benzene, o-xylene and styrene in plywood as a function of humidity

Practically, the reduction in the adsorption capacity of the materials with increasing humidities would tend to promote (accelerate) the VOC emission to the bulk air phase of the room, and/or to reduce the sink effect induced by materials.

5 Conclusion

The study presented here was a first attempt in explaining why and how humidity can influence the VOC emission from materials, or the sink effect induced by building materials and furnishings. It was shown that humidity may interact with VOCs in several ways inside porous materials. Especially, in the case of microporous materials– mortar is unlikely to be in direct contact with the indoor air but must be viewed here as representative of such materials used indoors - humidity can contribute to increase the mass capacity of materials due to the

VOC absorption in liquid water filling the smallest pores. On the other hand, a higher humidity indoors will tend to decrease the VOC mass capacity of materials due to the competition for adsorption at the spore surfaces. Finally, depending on the material, the VOC and the humidity level considered, increasing the indoor humidity can either strengthen or decrease the material emission and/or sink effect.

As humidity also influences the VOC diffusivity, one can imagine that a slight change in relative humidity can also contribute to change from one leading elemental interaction phenomenon to another. This could notably explain the non linearities in the phenomena observed experimentally when dealing with the role of humidity on the VOC emissions and/or sink effect. More experimental data is needed to confirm the trends highlighted here. Further researches on the role of humidity also include the consideration of reactivity phenomena such as the hydrolysis of VOCs, that was shown to be important in some materials [16].

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