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Using the chemical mass balance model to estimate VOC source contributions in newly built timber frame houses: a case study

Herve Plaisance¹  · Pierre Mocho² · Nicolas Sauvat³ · Jane Vignau-Laulhere¹ · Katarzyna Raulin⁴ · Valerie Desauziers¹

Abstract Basing on the material emission data obtained in a test chamber, chemical mass balance (CMB) was used to assess the source apportionment of volatile organic compound (VOC) concentrations in three newly built timber frame houses. CMB has been proven to be able to discriminate the source contributions for two contrasted environmental conditions (with and without ventilation). The shutdown of the ventilation system caused an increase in the VOC concentrations due to the increased contribution of indoor surface materials like the door material and furniture explaining together over 65% of total VOCs. While the increase in formaldehyde concentration is mainly due to furniture (contribution of 70%), the increase in α -pinene concentration is almost exclusively attributable to the emission of door material (up to 84%). The apportionment of VOC source contributions appears as highly dependent on the position of source materials in the building (surface materials or internal materials) and the ventilation conditions explaining that the concentrations of compounds after the shutdown of ventilation system do not increase in equivalent proportion. Knowledge of indoor sources and its contributions in real conditions may help

in the selection of materials and in the improvement of construction operations to reduce the indoor air pollution.

Keywords Indoor air quality · Energy-efficient houses · Wood-based materials · VOC indoor concentrations

Introduction

Building and furniture materials are known as major indoor sources of volatile organic compounds (VOCs). Depending on the nature and abundance of these chemical species, they may be a potential risk to the health and well-being of building occupants (Tham 2016). Some studies showed that newly built or renovated buildings often exhibit high indoor VOC concentrations resulting to high emissions of new materials (Hodgson et al. 2000; Liang et al. 2014). VOC concentrations tend to gradually decrease over time in relation to the decay of emissions, but the contamination may persist over several months or even years depending on the source material, its place in the building, and the released compounds (Liang et al. 2014). Identification of indoor sources and assessment of their contribution to VOC concentrations are often complex due to the high number of sources in a building and the multi-pollutant nature of emissions. In the field of ambient air, research has demonstrated using chemical mass balance (CMB) that significant fractions of VOC are attributable to vehicle exhaust, gasoline vapor, and other area sources even in heavily industrialized zones (Mukund et al. 1996). Receptor models such as CMB were successfully applied for the verification of VOC emission inventories that are ultimately used in air quality management plans and photochemical modeling (McLaren et al. 1996; Harley et al. 1992).

There is fewer literature addressing the use of the CMB model to quantify the contributions of material emissions to

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indoor VOC concentrations for two main reasons: (1) the source profiles should be assessed individually because the variability in the source profiles is too large to define typical profiles for different material categories and (2) the temporal decrease in VOC amounts released from materials is a limiting factor in the definition of source profiles that are taken into account in CMB model. However, it can be assumed that the composition of emissions in mass fraction is fairly constant over the long term. Gokhale et al. (2008) used the CMB model to compare the source contributions of personal exposure to 25 VOCs in three microenvironments (home, workplace, and outdoors). They showed that the largest contribution is the home in the range from 42 to 73% with different dominant species between the three microenvironments. Other studies focused on the indoor-to-outdoor relationships of fine particulate matter using the CMB on data of organic molecular markers as polycyclic aromatic hydrocarbons, hopanes, and *n*-alkanes, as well as metals and some trace elements (Hasheminassab et al., 2014; Cattaneo et al. 2016; Kopperud et al. 2004). They showed that the indoor fine particulate matter comes mainly from outdoors and from sources such as the emission exhaust, industrial activities and heating (coal combustion), and mass burning (Hasheminassab et al., 2014; Olson et al. 2008; Junninen et al. 2009) in contrast to VOCs that have mainly an indoor origin (Gokhale et al. 2008). However, other sources such as cleaning (Hasheminassab et al., 2014), food cooking (Mugica et al. 2001; Gokhale et al. 2008), smoking (Dacunto et al. 2014), and indoor resuspension activities (Kopperud et al. 2004) were also emphasized. In these examples, the individual contributions of the material emissions to VOC concentrations were not considered. The goals of these studies were to distinguish the outdoor inputs from indoor contributions and to examine the impact of specific sources on indoor air.

This study examined the feasibility of applying the CMB model to assess the material emission contributions to VOC concentrations in three newly built timber frame houses. It was based on a full data set on the emissions of materials used in the construction of the three houses and field samples carried out in the unoccupied houses before delivery. This study is a continuation of the first article devoted to the change of VOC concentrations in these three houses during the construction process (Plaisance et al. 2017).

Materials and methods

Chemical mass balance (CMB) model

The CMB is a receptor model which provides a least square solution to a set of mass-balance equations expressing each receptor chemical concentration (C_i) as a linear sum of products of source profile abundances (i.e., the mass fraction of a

chemical species in the emissions from each source type) and source contributions. A source profile consists of a mass percentage for each VOC; the sum for all target VOCs is equal to 1. Each receptor chemical concentration may be written as follows:

$$\frac{C_i}{C_{tot}} = \sum_{j=1}^N a_{ij} \cdot S_j \quad i = 1, \dots, P \quad \text{and} \quad j = 1, \dots, N \quad (1)$$

where C_i is the observed concentration of the species i at the receptor, C_{tot} is the total VOC concentration at the receptor, a_{ij} is the mass fraction of the species i in emission of the source material j ($j = 1, \dots, N$), S_j is the source contribution, N is the number of source materials, and P is the number of VOC. If $P > N$, a set of P simultaneous linear equations is obtained from which the source contribution S_j may be calculated by the least square methods.

The solution to Eq. (1) is obtained by an effective variance least square method that was developed and tested by Watson et al. (1984). The effective variance solution is derived by minimizing the weighted sums of the squares of the differences between the measured and calculated values of C_i and a_{ij} (Britt and Luecke, 1973; Watson et al. 1984). The solution algorithm is an iterative procedure which calculates a new set of S_j based on the S_j estimated from the previous iteration. Its feature is to have in solving equations a greater influence on chemical species with smaller values for uncertainty in both the source and receptor measurements than on species with higher values for uncertainty. More details on the fundamentals of CMB can be found in Hopke (1991). Model calculations were made using the US Environmental Protection Agency (EPA) version 8.2 of the CMB model which is available for download from the US EPA website (www.epa.gov/scram/chemical-mass-balance-cmb-model). The EPA-CMB 8.2 algorithm is given in Watson et al. (1984).

The application of the CMB model involves several assumptions: (1) source profiles are invariable between the ambient sampling and source sampling; (2) chemical species do not react with each other and they have no interaction with the indoor materials; (3) all sources having a significant contribution to the receptor have been identified and have had their emissions characterized; (4) compositions of source emissions are linearly independent and sufficiently different from each other; (5) measurement uncertainties are random, uncorrelated, and normally distributed; and (6) the number of sources is less than or equal to the number of species.

The degree to which these assumptions are met depends on the application and properties of compounds that are measured at the source and receptor. CMB tolerates reasonable deviations from these assumptions and provides various performance parameters and criteria for validating the application which are described later in the "Indoor VOC concentration

levels and source apportionment by CMB” section (ratio of source contribution on its uncertainty, squared correlation coefficient, sum of source contributions, chi-square value, and absence of collinearity). All these tests ensure an acceptable quality level in the CMB results, and deviations from the CMB model assumptions are converted to estimated uncertainties associated to the source contributions.

Target compounds and method for VOC measurements

The target VOCs in this study were the ten compounds listed in the French regulation for material emission labeling (Decree 2011-321, 23 March 2011) completed by four other compounds known as tracers of wood-based materials: α -pinene, 3-carene, *d*-limonene, and hexanal (Derbez et al. 2014; Hodgson et al. 2000). The target VOCs were therefore formaldehyde, acetaldehyde, benzene, toluene, tetrachloroethylene, xylenes, 1,4-dichlorobenzene, styrene, hexanal, α -pinene, 3-carene, *d*-limonene, 1,2,4-trimethylbenzene, and 2-butoxyethanol. The VOC concentrations were monitored by two active sampling methods using a BPE/DNPH cartridge (Sigma-Aldrich, Saint-Louis, MO, USA) for formaldehyde and acetaldehyde and a stainless steel cylindrical cartridge filled with 400 mg of 40–60 mesh Carbograp 4 (an adsorbent suitable for analysis of VOCs by thermal desorption). They were used to quantify the VOC concentrations for both the emission tests and field measurements. To ensure that no breakthrough occurs for the sampling conditions, a guard tube was added to the sampling device. The sampling flow rates were adjusted between 60 and 500 mL min⁻¹ according to samples with a mass flow meter and checked before and after each pumped sample with a gas flow meter (DryCal DC-Lite). Sampling duration varied from 10 min to 24 h depending on the concentration levels and sampling types (emission test or field sampling). The BPE/DNPH cartridges were then extracted and analyzed by HPLC according to the protocol described in a previous article (Vignau-Laulhere et al. 2015). The Carbograp 4 cartridges were analyzed with a thermal desorber (TD) (Turbomatrix from Perkin-Elmer, USA) interfaced with a gas chromatograph (GC) equipped with a flame ionization detector (FID) following the method previously described by Plaisance et al. (2008). Other details were also given in Plaisance et al. (2017) and Vignau-Laulhere et al. (2016) about these active sampling methods. In the sampling and analytical conditions chosen, the quantification limits for all target VOCs were less than 0.5 $\mu\text{g m}^{-3}$. In parallel to these active samples, another method based on a vacuum air sampling in a vial followed by a solid-phase microextraction (SPME) pre-concentration directly in vial, and GC-MS analysis was also carried out to ensure that there is no coelution in the GC analysis for the target VOCs. More details about this SPME method were given in Bourdin and Desauziers (2014), Desauziers et al. (2015), and Plaisance et al. (2017).

Description of houses, building materials, and field measurements

The test buildings are three energy-efficient timber frame houses located in France at the BOIS PE center (Egletons, Limoges University): a standard low-energy house (BBC) according to the 2012 French thermal regulation (RT2012, 2011), a passive house (BEPAS), and a positive-energy house (BEPOS) with solar panels on the base of the passive one. Those are one-storey houses of identical design with area of about 105 m² and equipped with an energy recovery ventilation.

The conventional energy consumptions according to RT2012 (2011) for five uses (heating, ventilation, domestic hot water, lighting, auxiliary pumps and fans) are 62.5 kWh m⁻² year⁻¹ of primary energy for BBC house and 42 kWh m⁻² year⁻¹ for the two others. Airtightness was measured by a Q₄Pa-surf test at 0.4, 0.32, and 0.35 m³ h⁻¹ m⁻² for BBC, BEPAS, and BEPOS houses, respectively. The ground floor consists of a large living room with an open kitchen, a toilet, and a garage. The floor comprises three bedrooms, a second toilet, and a bathroom. Air exhaust vents are located in the two toilets, bathroom, and kitchen while some air intakes are inside the bedrooms and living room. A suitable space under inner doors allows air exchange between rooms. The same standard materials were used in the construction of the three houses. They were chosen among the building materials with low VOC emissions according to the current French regulation (Decree 2011-321, 23 March 2011). Insulation layer widths inside the structural walls and ceiling of the BEPAS and BEPOS houses (220 and 460 mm) are thicker than those of the BBC house (120 and 370 mm). The BBC house has double-glazed windows whereas the BEPAS and BEPOS houses are equipped with triple-glazed windows with the same massive wood frame. VOC sampling was carried out in the main bedroom located upstairs of the test houses. Figure 1 shows the plan of the sampling room and the materials constituting its envelope (the wall, the interior partition, the floor, and the ceiling). The main bedroom was chosen for some reasons: the bedroom is the room where the future inhabitants will spend the most time in the house; some characteristics of this room (small in size, with a single air inlet vent and a limited number of materials constituting its envelope) simplify the investigation about the indoor sources that was performed in this study. As shown in Fig. 1, a large number of materials were used in construction and belonged to different categories: structural materials, adhesive, insulations, coverings, plasters, and paintings. Electrical and ventilation components, metallic stud, facade coating, and its support in wooden fiber were not tested. Because of their nature and location in the building, they are considered to have no contribution to indoor air composition.

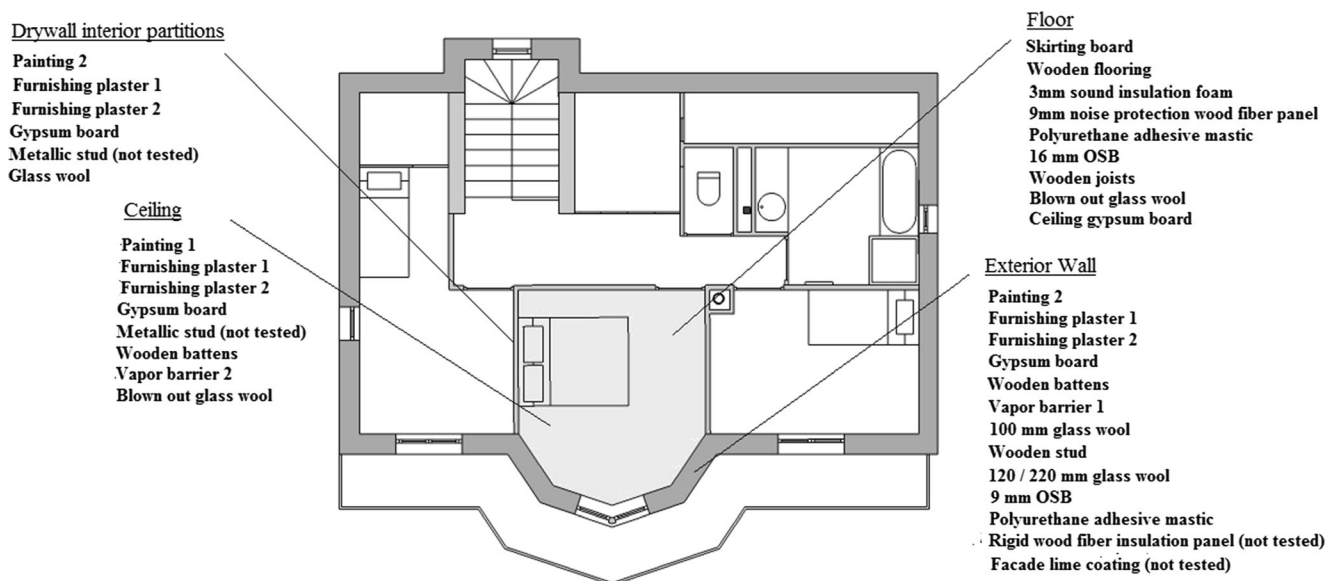


Fig. 1 Sampling room (in gray tone) and location of materials constituting the room envelope. The materials are listed from inside to outside

Most of these materials ($n = 20$) were assessed by the chamber tests to determine their VOC emissions as described in the following section.

The air exchange rate (AER) in the studied room is conditioned by the input flow rate set point fixed to the ventilation system. The door undercut provides output flow. The AER was assessed using CO₂ concentration decay method (ASTM E 741-11, 2011) at 0.7 h⁻¹ under normal ventilation conditions (supply of input air from a fixed rate at 20 m³ h⁻¹ by ventilation) and 0.1 h⁻¹ without ventilation.

Indoor VOC measurements were carried out in the three houses using the same methods as those of emission tests, i.e., active sampling with BPE/DNPH cartridges for formaldehyde and acetaldehyde and Carbograph 4 cartridges for the other target VOCs. The sampling duration was 2 h with the flow rate adjusted to 300 mL min⁻¹ and checked before and after each pumped sample with a gas flow meter (DryCal DC-Lite). The description of measurements series as well as the environmental conditions during the sampling is given in Table 1. VOC concentrations in outdoor air were also measured at each series by means of the vacuum vial-SPME method developed by our laboratory

and described in the “Target compounds and method for VOC measurements” section. It was used to determine the VOC profile of the outdoor air considered here as a source.

Methods for assessment of material emissions

The emissions of materials constituting the envelope of the sampled room (main bedroom) were assessed by the emission chamber tests. The materials used in the building including both wet and dry products are reported in Fig. 1. The door and furnishing materials could not be tested in the chamber: their emission profiles were set up from the on-site measurement of VOC concentrations at the material surface by means of an emission cell called DOSEC followed by a SPME sampling. This method was described in previous articles for the target VOCs (Desauziers et al. 2015).

For the chamber tests, dry materials were cut in order to obtain a sample with an exposed area of 120 cm². Wet materials were spread on a glass plate of 4.5 by 3 cm. Due to higher VOC emission levels, samples of smaller areas were chosen for wet products: 27 cm² for the two furnishing plasters and 2.8 cm² for polyurethane adhesive mastic and paintings. After

Table 1 Description of field measurements and environmental conditions in houses

House and sampling series number	Sampling date	Temperature (°C) mean [min_max]	Relative humidity (%) mean [min_max]	Ventilation and air exchange rate estimated (AER, h ⁻¹)
BBC_8	12/08/2014	19.7 [19.2_20]	38.3 [36.5_41.1]	Ventilation on; AER = 0.7
BEPOS_9	02/11/2015	25.6 [25.3_25.8]	28.9 [23.6_39]	Ventilation on; AER = 0.7
BEPAS_9	02/12/2015	23.9 [21.5_25.4]	33.2 [25.1_42]	Ventilation on; AER = 0.7
BEPAS_10s	06/15/2015	23.9 [22.5_24.6]	56.4 [53.7_59]	Ventilation off; AER = 0.1
BEPAS_10a	06/16/2015	23.2 [21.1_24.5]	55.4 [52_59]	Ventilation on; AER = 0.7

Table 2 Emission rates (expressed in $\mu\text{g m}^{-2} \text{h}^{-1}$) obtained after a conditioning of 3 days for the 20 tested materials constituting the envelope of the sampled rooms

	Mass (g)	Area (cm^2)	FA	Ac	He	Be	To	1,4dC	EB	m/p-X	Sty	TMB	α -P	3-Ca	d-Li	2-Bu
Glass wool (interior partitions)	4.1	163	1.9	7.4												
Gypsum board	41	122	2.6	5.9												
16-mm OSB	43	122	3.3	7.2	0.78											
9-mm OSB	32	123	6.9	4.9	12.7						0.79		1.9	0.80	0.72	
PU adhesive mastic	0.16	2.8	11.6	1.9	0.54		2.6		995	2447	9.9					
Wooden studs/joists	29	125	3.6		25.3								2.6		1.3	
Wooden flooring	30	122	134	4.2	4.4		0.78	0.99			0.88		1.6	0.81	0.59	
Skirting board	32	121	17.8	4.0	1.5											
Wooden battens	51	122	0.92	0.63	1.29											
9-mm noise protection panel	11.9	123	5.3	4.1	3.4			0.6						10.1	5.1	5.5
3-mm sound insulator	0.75	119	5.0									2.37				
Vapor barrier 1 (walls)	1.12	120	0.61									1.50				
Vapor barrier 2 (ceiling)	0.73	120	3.0	2.4								1.26				
100-mm glass wool	4	161	5.0													
120-/220-mm glass wool	4.10	163	0.90													
Blown out glass wool	4.70	135	1.11		7.1											
Painting 1	0.15	2.8	107	45	16.5	0.5				1.77	2.1				1.6	2.3
Painting 2	0.07	2.8	69	32					3.5	1.33	12.3				9.9	2.8
Furnishing plaster 1	1.74	27	29	3.8	0.60											
Furnishing plaster 2	3.6	27	6.0	2.6	1.15											

No value: compound undetected or emission rate $\leq 0.5 \mu\text{g m}^{-2} \text{h}^{-1}$

FA formaldehyde, Ac acetaldehyde, He hexane, Be benzene, To toluene, 1,4dC 1,4-dichlorobenzene, EB ethylbenzene, m/p-X m-/p-xylene, Sty styrene, TMB 1,2,4-trimethylbenzene, α -P α -pinene, 3-Car 3-carene, d-Li d-limonene, 2-Bu 2-butoxyethanol

Table 3 Concentrations (expressed in $\mu\text{g m}^{-3}$) at the surface of two materials (door and furnishing) by on-site measurements with DOSEC emission cell coupled to a SPME sampling

	FA	Ac	He	Be	To	1,4dC	EB	m/p-X	Sty	TMB	α -P	3-Car	d-Li	2-Bu
Door	9.8	64	54								125	0.55	3.1	
Furnishing	68	33	7.0								2.1	1.01	0.56	

No value: compound undetected or emission rate $\leq 0.5 \mu\text{g m}^{-2} \text{h}^{-1}$

FA formaldehyde, Ac acetaldehyde, He hexane, Be benzene, To toluene, 1,4dC 1,4-dichlorobenzene, EB ethylbenzene, m/p-X m-/p-xylene, Sty styrene, TMB 1,2,4-trimethylbenzene, α -P α -pinene, 3-Car 3-carene, d-Li d-limonene, 2-Bu 2-butoxyethanol

spreading on the glass plate, the sample was dried under air-flow at ambient temperature until its weight stabilizes.

Each selected material was then tested individually in the emission chamber to assess emissions of target VOCs after 3 days. The experimental device and procedure for these tests were already described in a previous article (Plaisance et al. 2017). The test conditions were as follows: an air exchange rate of 0.5 h^{-1} , temperature maintained at $20 \pm 2 \text{ }^\circ\text{C}$, and the relative humidity at $50 \pm 5\%$. Considering material sample surfaces, loading factors were $0.5 \text{ m}^2 \text{ m}^{-3}$ for wet materials, $0.11 \text{ m}^2 \text{ m}^{-3}$ for the two furnishing plasters, and $0.012 \text{ m}^2 \text{ m}^{-3}$ for polyurethane adhesive mastic and paintings.

The results are expressed in emission rates (in $\mu\text{g m}^{-2} \text{h}^{-1}$) and calculated by means of the following equation:

$$F = C \times a \times \frac{V}{S} \quad (2)$$

Where $F (\mu\text{g m}^{-2} \text{h}^{-1})$ is the VOC emission rate, $C (\mu\text{g m}^{-3})$ is the VOC concentration measured in the emission test chamber, $V (\text{m}^3)$ is the chamber volume, $S (\text{m}^2)$ is the area of material sample, and $a (\text{h}^{-1})$ is the air exchange rate in the test chamber.

To ensure the cleaning of the emission chamber between successive tests, a systematic flushing of empty emission chamber was carried out with clean air at a high flow rate (2 L min^{-1}) for at least 24 h. The background concentrations in the emission chamber were regularly assessed during the test program. No contamination was detected.

Results and discussion

VOC source profiles

Twenty materials constituting the envelope of the sampled rooms were assessed by means of the emission chamber tests

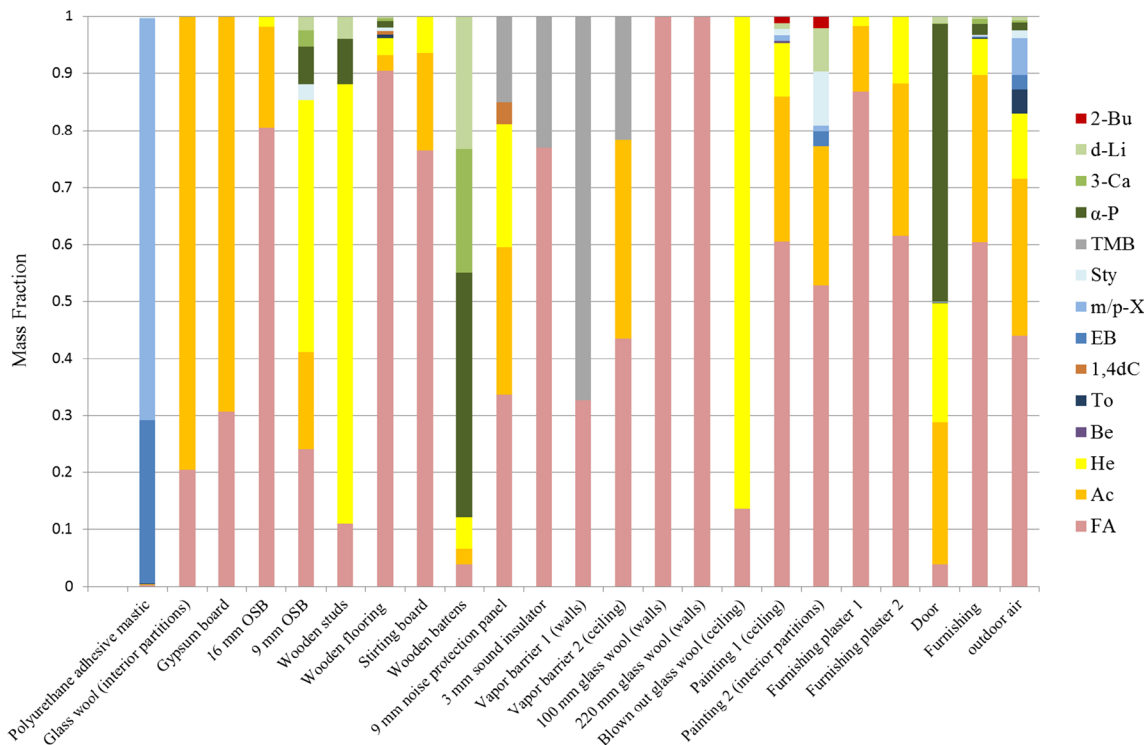


Fig. 2 VOC source profiles assessed and taken into account in CMB

as described in the “Methods for assessment of material emissions” section. Table 2 presents the emission rates expressed in $\mu\text{g m}^{-2} \text{h}^{-1}$ obtained for these materials. These results reveal three main trends: (1) polyurethane adhesive mastic used as sealing material in the construction is a major source of *m*-/*p*-xylenes and ethylbenzene with emissions from 995 to 2447 $\mu\text{g m}^{-2} \text{h}^{-1}$ for ethylbenzene and *m*-/*p*-xylenes, respectively, whereas the other materials have low emissions or below the quantification limit for these two aromatic compounds; (2) the twenty materials are mostly sources of aldehydes, with a predominance of formaldehyde in emissions ranging from 0.9 to 134 $\mu\text{g m}^{-2} \text{h}^{-1}$; (3) terpenes known to be wooden tracers are minor compounds in the composition of emissions.

These emission results initially expressed in microgram per square meter per hour were converted into mass fraction (varying from 0 to 1) in order to agree with source profiles processed by CMB.

The emission compositions of two materials (door and furnishing) that could not be tested in the emission chamber were documented from the VOC concentrations measured by on-site sampling at their surface using the DOSEC-SPME method (Desauziers et al. 2015). They are shown in Table 3. These two materials are also sources of aldehydes; the door has a high emission of α -pinene. These results were also expressed in mass fraction. Figure 2 gathers the 22 material emission profiles as well as that of outdoor air defined using the field data and considered in CMB as a VOC source. It confirms that aldehydes are the major compounds in most source profiles. Terpenes are dominant in the source profiles of some wood-based materials like the wooden battens and door whereas *m*-/*p*-xylenes and ethylbenzene are associated with the emission of polyurethane adhesive mastic. Wood species used are *Picea abies* for studs, battens, and joists and *Pinus pinaster* for the door. Trimethylbenzene appears in source profiles of plastic materials like the vapor barriers and sound insulator.

Indoor VOC concentration levels and source apportionment by CMB

Table 4 shows the VOC concentrations found in the three houses under normal conditions of ventilation ($\text{AER} = 0.7 \text{ h}^{-1}$). Similar compositions and concentration levels were recorded under normal ventilation conditions with aldehydes as the major compounds. With the ventilation on, the concentration levels were kept low ranging from 0.5 to 15 $\mu\text{g m}^{-3}$ according to the compound. Note that the order of abundance in VOC compositions of the three houses (formaldehyde > acetaldehyde > hexanal > α -pinene) is the same as that found in the material emissions. These four latter compounds represent more than two thirds of the mass chemical compositions

Table 4 Concentrations (expressed in $\mu\text{g m}^{-3}$) measured in the three houses by the active sampling methods

House and no. series	TVOC	FA	Ac	He	Be	To	1,4dC	EB	m/p-X	Sty	TMB	α -P	3-Car	d-Li	2-Bu
BBC_8	36	6.2 ± 1.2	6.3 ± 1.3	5.7 ± 1.1			1.24 ± 0.2		0.76 ± 0.2	0.51 ± 0.1	6.3 ± 1.3	5.9 ± 1.2	2.1 ± 0.4	0.82 ± 0.2	
BEPOS_9	53	13.4 ± 2.7	4.6 ± 0.9	8.8 ± 1.8	0.76 ± 0.2	0.69 ± 0.1	1.92 ± 0.4	0.89 ± 0.2	3.4 ± 0.7	1.90 ± 0.4	1.03 ± 0.2	8.5 ± 1.7	3.0 ± 0.6	2.7 ± 0.5	1.18 ± 0.2
BEPAS_9	36	11.5 ± 2.3	5.9 ± 1.2	5.7 ± 1.1	0.72 ± 0.1	0.78 ± 0.2	1.35 ± 0.3	0.57 ± 0.1	1.53 ± 0.3	1.06 ± 0.2	0.57 ± 0.1	3.75 ± 0.8	1.3 ± 0.3	1.61 ± 0.3	
BEPAS_10s	269	48 ± 9.6	48 ± 9.5	63 ± 12.6		2.6 ± 0.5	1.8 ± 0.4	5.9 ± 1.2	9.9 ± 2.0			69.6 ± 14	17.9 ± 3.6	1.98 ± 0.4	
BEPAS_10a	77	12.4 ± 2.5	29 ± 5.8	12.8 ± 2.6		0.96 ± 0.2	1.13 ± 0.2	2.0 ± 0.4	4.9 ± 1.0			8.5 ± 1.7	3.0 ± 0.6	2.7 ± 0.55	

No value: compound undetected or emission rate $\leq 0.5 \mu\text{g m}^{-2} \text{h}^{-1}$

TVOC sum of 14 target VOC concentrations, FA formaldehyde, Ac acetaldehyde, He hexane, Be benzene, To toluene, 1,4dC 1,4-dichlorobenzene, EB ethylbenzene, m/p-X *m*-/*p*-xylene, Sty styrene, TMB 1,2,4-trimethylbenzene, α -P α -pinene, 3-Car 3-carene, d-Li *d*-limonene, 2-Bu 2-butoxyethanol

Table 5 Summary of CMB results for the data sets from three houses

	R^2	χ^2	Measured total mass ($\mu\text{g m}^{-3}$)	Calc total mass (%)	Source relative contributions (\pm standard deviation) (% of measured total mass)												
					Outdoor air	Wooden battens	Door	9-mm OSB	Gypsum board	Vapor barrier I	Painting 2	Wooden flooring	Noise protection panel	Polyurethane adhesive mastic	Blown out glass wool	120-/220-mm glass wool	Furniture
BBC 8	0.93	1.85	35.8 \pm 7.2	100.1 \pm 9.7	16.1 \pm 4.5	8.3 \pm 2.6	18.8 \pm 8.1	25.0 \pm 8.0	6.3 \pm 6.0	25.4 \pm 6.9							
BEPOS 9	0.9	3.8	52.8 \pm 10.6	89.5 \pm 8.4	24.7 \pm 5.2	23.0 \pm 4.3	—	—	—	2.9 \pm 0.8							
BEPAS 9	0.87	3.6	36.4 \pm 7.3	98.4 \pm 9.3	34.4 \pm 5.5	13.9 \pm 3.0	—	13.2 \pm 8.9	—	—							
BEPAS 10s	0.82	4.0	268.8 \pm 53.8	91.7 \pm 9.8	8.4 \pm 2.7	—	44.9 \pm 9.6	—	—	—							
BEPAS 10a	0.89	2.6	77.2 \pm 15.4	100.9 \pm 11.1	15.1 \pm 4.3	15.3 \pm 3.3	8.1 \pm 6.4	—	—	—							

Source relative contributions (\pm standard deviation) (% of measured total mass)															
	Painting 2	Wooden flooring	Noise protection panel	Polyurethane adhesive mastic	Blown out glass wool	120-/220-mm glass wool	Furniture	Glass wool (interior partitions)							
BBC 8	—	—	—	—	—	—	—	—							
BEPOS 9	17.4 \pm 6.6	—	—	1.9 \pm 1.4	—	7.2 \pm 6.6	—	—							
BEPAS 9	11.3 \pm 6.5	13.2 \pm 8.9	12.4 \pm 3.1	—	12.5 \pm 4.9	—	—	—							
BEPAS 10s	—	—	—	4.7 \pm 1.2	12.7 \pm 6.7	—	21.0 \pm 7.2	—							
BEPAS 10a	—	—	10.0 \pm 4.0	6.5 \pm 1.8	10.4 \pm 4.9	—	—	35.4 \pm 10.5							

acetaldehyde, hexanal, α -pinene, and 3-carene observed after the shutdown of ventilation system are mainly due to emissions of these two materials. The specific origin of these VOCs will be stated in the following section. The shutdown of the ventilation system tends to favor the inputs from the indoor surface materials. After restarting the ventilation and after a time period of 20 h (BEPAS 10a), the source contributions approach to that found in the house under the normal ventilation conditions without going back to the same apportionment (Fig. 4).

Source contributions to main individual VOC concentrations

The CMB model also provides the source contributions to individual VOC concentrations. These results are given in Fig. 4 for the formaldehyde, acetaldehyde, hexanal, and α -pinene concentrations measured in the BEPAS house under the normal ventilation conditions (BEPAS 9) and without ventilation (BEPAS 10s). This comparison may indicate for each of these compounds which sources are responsible for the increase in concentration observed during the day without ventilation. Increases in concentrations are not caused by the same sources. For formaldehyde, the main contributor is furniture with a part of 70% of its concentration attributable to this source. Furniture is made of particle board and medium-density fiberboard containing urea-formaldehyde resins known to be sources of formaldehyde (Baumann et al. 2000; Plaisance et al. 2014).

Increase in acetaldehyde concentration would be mainly due to the door material (to more than 63%) and, to a lesser degree, to furniture (to 35%). For hexanal, two main sources (door material and glass wool of ceiling) contribute in equivalent proportion (40 and 47%, respectively). Increase in α -pinene concentration is almost exclusively due to the emission of door material (up to 84%). Door material is *P. pinaster*. Manninen et al. (2002) and Hyttinen et al. (2010) reported that α -pinene, 3-carene, and hexanal are the most abundant individual compounds in the emission of wood pine. They represent 40–48% of the total VOC emission for α -pinene, 8–37% for 3-carene, and 4–15% for hexanal. This is in agreement with our results of CMB which identify the door made of pine wood as the main source contributing to the increase in α -pinene concentration for the day without ventilation.

This compared analysis shows that the increase in VOC concentrations following the shutdown of ventilation system mainly involves the contribution of indoor surface materials. The apportionment of VOC source contributions appears as highly dependent on the position of source materials in the building (surface materials or internal materials) and the ventilation conditions which explains that the concentrations of compounds after the shutdown of ventilation system do not increase in equivalent proportion. Indeed, in our example, the

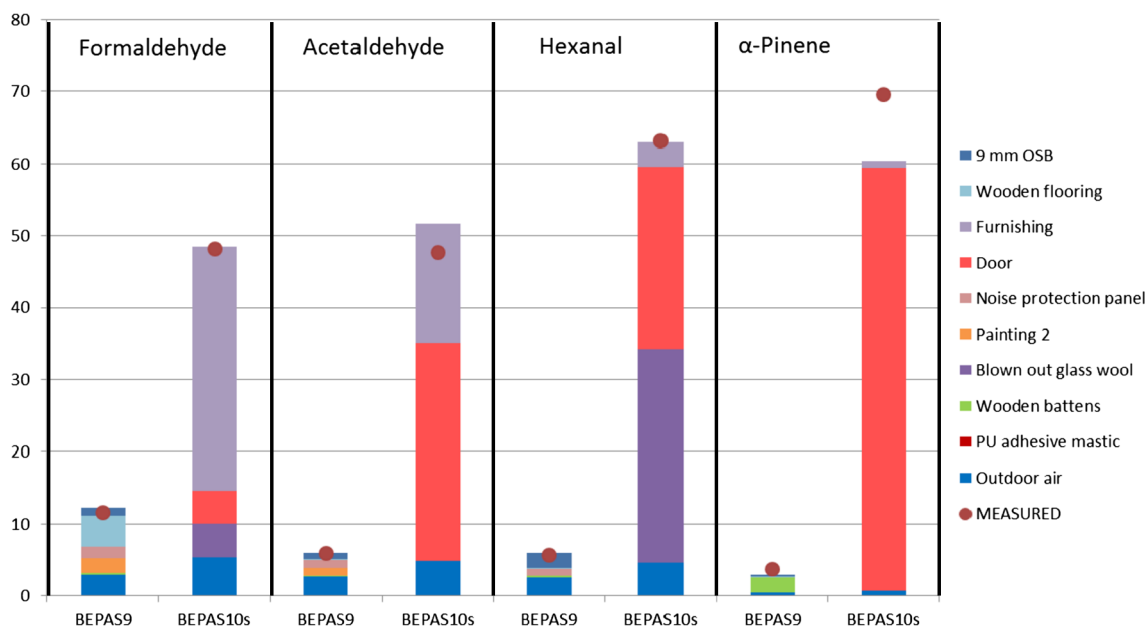


Fig. 4 CMB model results relative to source contributions to four major VOC concentrations in BEPAS house

formaldehyde concentration is multiplied by 4 while that of α -pinene is increased by a factor of 19.

These results underline the importance of ensuring that the ventilation is operating correctly as well as of the choice of low-emission materials particularly those constituting indoor surfaces.

Conclusions

The CMB model was used to assess the source apportionment of VOC concentrations in three newly built timber frame houses based on the material emission data obtained in the test chamber. The main results of this study were as follows: (1) Most emission profiles are dominated by aldehydes with the exception of wood-based materials that are sources of both terpenes and hexanal, polyurethane adhesive mastic is associated to high emissions of ethylbenzene and xylenes, and the plastic materials have emission profiles with trimethylbenzene; (2) The ability of the CMB model to discriminate and to estimate the source contributions in indoor environments is shown especially when changing the source apportionment of VOC concentrations; (3) Under normal conditions of ventilation, the CMB model identifies a large number of indoor materials as contributing to the VOC composition in the three houses. Outdoor air represents a contribution from 16 to 35%. After the shutdown of ventilation system, the apportionment of source contributions is highly modified. The contributions of indoor surface materials (furnishing and door material) become a majority part and that of outdoor air decreases below 8%; (4) The analysis of source contributions relative to four main VOC concentrations

shows that the increase in concentrations of these VOCs following the shutdown of ventilation system is not due to the same sources. While the increase in formaldehyde concentration is mainly due to furniture (contribution of 70%), the increase in α -pinene concentration is almost exclusively attributable to the emission of door material (up to 84%). The apportionment of VOC source contributions appears as highly dependent on the ventilation conditions and on the position of source materials in the building (surface materials or internal materials) which explains that the concentrations of compounds after the shutdown of ventilation system do not increase in equivalent proportion.

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References

- ASTME 741–11 (2011) Standard test method for determining air change in a single zone by means of tracer gas dilution. ASTM International, West Conshohocken
- Badol C, Locoge N, Galloo JC (2008) Using a source-receptor approach to characterize VOC behaviour in a French urban area influenced by industrial emissions part II: source contribution assessment using the chemical mass balance (CMB) model. *Sci Total Environ* 389:429–440
- Baumann MGD, Lorenz LF, Batterman SA, Zhang GZ (2000) Aldehyde emissions from particleboard and medium density fiberboard products. *For Prod J* 50:75–82
- Bourdin D, Desauziers V (2014) Development of SPME on-fiber derivatization for the sampling of formaldehyde and other carbonyl compounds in indoor air. *Anal Bioanal Chem* 406:317–328
- Britt HI, Luecke RH (1973) The estimation of parameters in nonlinear implicit models. *Technometrics* 15:233–247

- Cattaneo A, Fermo P, Urso P, Grazia-Perrone M, Piazzalunga A, Tarlassi J, Carrer P, Cavallo DM (2016) Particulate-bound polycyclic aromatic hydrocarbon sources and determinants in residential homes. *Environ Pollut* 218:16–25
- Dacunto PJ, Cheng KC, Acevedo-Bolton V, Jiang RT, Klepeis NE, Repace JL, Ott WR, Hildemann LM (2014) Identifying and quantifying secondhand smoke in source and receptor rooms: logistic regression and chemical mass balance approaches. *Indoor Air* 24:59–70
- Derbez M, Berthineau B, Cochet V, Lethrosne M, Pignon C, Riberon J, Kirchner S (2014) Indoor air quality and comfort in seven newly built energy-efficient houses in France. *Build Environ* 72:173–187
- Desauziers V, Bourdin D, Mocho P, Plaisance H (2015) Innovative tools and modeling methodology for impact prediction and assessment of the contribution of materials on indoor air quality. *Heritage Sci* 3:28
- Fujita EM, Watson JG, Chow JC, Lu Z (1994) Validation of the chemical mass balance receptor model applied to hydrocarbon source apportionment in the southern California air quality study. *Environ Sci Technol* 28:1633–1649
- Fujita EM, Watson JG, Chow JC, Magliano KL (1995) Receptor model and emissions inventory source apportionments of non-methane organic gases in California's San Joaquin Valley and San Francisco bay area. *Atmos Environ* 29:3019–3035
- Gokhale S, Kohajda T, Schlink U (2008) Source apportionment of human personal exposure to volatile organic compounds in homes, offices and outdoors by chemical mass balance and genetic algorithm receptor models. *Sci Total Environ* 407:122–138
- Harley R, Hannigan MP, Cass GR (1992) Respeciation of organic gas emissions and detection of excess unburned gasoline in the atmosphere. *Environ Sci Technol* 26:2395–2408
- Hasheminassab S, Daher N, Shafer MM, Schauer JJ, Delfino RJ, Sioutas C (2014) Chemical characterization and source apportionment of indoor and outdoor fine particulate matter (PM_{2.5}) in retirement communities of the Los Angeles Basin. *Sci Total Environ* 490:528–537
- Hellén H, Hakola H, Laurila T (2003) Determination of source contributions of NMHCs in Helsinki (60 °N, 25 °E) using chemical mass balance and unmix multivariate receptor models. *Atmos Environ* 37:1413–1424
- Hodgson AT, Rudd AF, Beal D, Chandra S (2000) Volatile organic compound concentrations and emission rates in new manufactured and site-built houses. *Indoor Air* 10:178–192
- Hopke PK (1991) Receptor modeling for air quality management. Elsevier Science Publishers, Amsterdam, The Netherlands, Vol 7
- Hyttinen M, Masalin-Weijo M, Kalliokoski P, Pasanen P (2010) Comparison of VOC emissions between air-dried and heat-treated Norway spruce (*Picea abies*), scots pine (*Pinus sylvestris*) and European aspen (*Populus tremula*) wood. *Atmos Environ* 44:5028–5033
- Junninen H, Monster J, Rey M, Cancelinha J, Douglas K, Duane M, Forcina V, Muller A, Lagler F, Marelli L, Borowiak A, Niedzialek J, Paradiz B, Mira-Salama D, Jimenez J, Hansen U, Astorga C, Stanczyk K, Viana M, Querol X, Duvall RM, Norris GA, Tsakovski S, Wahlin P, Horak J, Larsen BR (2009) Quantifying the impact of residential heating on the urban air quality in a typical European coal combustion region. *Environ Sci Technol* 43:7964–7970
- Kopperud RJ, Ferro AR, Hildemann LM (2004) Outdoor versus indoor contributions to indoor particulate matter (PM) determined by mass balance methods. *J Air Waste Manage Assoc* 54:1188–1196
- Liang W, Wang C, Yang C, Yang X (2014) Volatile organic compounds in different interior construction stages of an apartment. *Build Environ* 81:380–387
- Manninen AM, Pasanen P, Holopainen JK (2002) Comparing the VOC emissions between air-dried and heat-treated scots pine wood. *Atmos Environ* 36:1763–1768
- McLaren R, Singleton DL, Lai JYK, Khouw B, Singer E, Wu Z, Niki H (1996) Analysis of motor sources and their contribution to ambient hydrocarbon distributions at urban sites in Toronto during the southern Ontario oxidants study. *Atmos Environ* 30:2219–2232
- Mukund R, Kelly TJ, Spicer CW (1996) Source attribution of ambient air toxic and other VOCS in Columbus, Ohio. *Atmos Environ* 30:3457–3470
- Mugica V, Vega E, Chow J, Reyes E, Sanchez G, Arriaga J, Egami R, Watson J (2001) Speciated non-methane organic compounds emissions from food cooking in Mexico. *Atmos Environ* 35:1729–1734
- Olson DA, Turlington J, Duvall RV, Vidow SR, Stevens CD, Williams R (2008) Indoor and outdoor concentrations of organic and inorganic molecular markers: source apportionment of PM_{2.5} using low-volume samples. *Atmos Environ* 42:1742–1751
- Plaisance H, Leonardis T, Gerboles M (2008) Assessment of uncertainty of benzene measurements by Radiello diffusive sampler. *Atmos Environ* 42:2555–2568
- Plaisance H, Blondel A, Desauziers V, Mocho P (2014) Hierarchical cluster analysis of carbonyl compounds emission profiles from building and furniture materials. *Build Environ* 75:40–45
- Plaisance H, Vignau-Laulhere J, Mocho P, Sauvat N, Raulin K, Desauziers V (2017) Volatile organic compounds concentrations during the construction process in newly-built timber frame houses: source identification and emission kinetics. *Environ Sci: Processes Impacts* 19:696–710
- RT2012 (2011) Un saut énergétique pour les bâtiments neuf. Ministère de l'Ecologie, du Développement durable, des Transports et du Logement, Paris, France, www.developpement-durable.gouv.fr
- Tham KW (2016) Indoor air quality and its effects on humans—a review of challenges and developments in the last 30 years. *Energy Buildings* 130:637–650
- Vega E, Mugica V, Carmaona R, Valencia E (2000) Hydrocarbon source apportionment in Mexico City using the chemical mass balance receptor model. *Atmos Environ* 34:4121–4129
- Vignau-Laulhere J, Plaisance H, Mocho P, Raulin K, Bigay Y, Desauziers V (2015) Performance of the Radiello diffusive sampler for formaldehyde measurement: the influence of exposure conditions and ozone interference. *Anal Methods* 7:5497–5503
- Vignau-Laulhere J, Mocho P, Plaisance H, Raulin K, Desauziers V (2016) Assessment of diffusion parameters of new passive samplers using optical chemical sensor for on-site measuring formaldehyde in indoor air: experimental and numerical studies. *Anal Bioanal Chem* 408:2147–2157
- Watson JG, Cooper JA, Huntzicker JJ (1984) The effective variance weighting for least square calculations applied to the mass balance receptor model. *Atmos Environ* 18:1347–1355
- Watson JG, Robinson NF, Chow JC, Fujita EM, Lowenthal DH (1998) CMB 8 User's manual, Report EPA-454/R-01, U.S. EPA, United States
- Watson JG, Chow JC (1991) Chemical mass balance. In: Hopke PK, editor. Receptor modeling for air quality management 7ème edn: p. 83–112