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Identification of VOCs and formaldehyde from materials: development of methods - Applications

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Context:
VOCs and formaldehyde in indoor air

- Role in allergic diseases and health symptoms:
  - Carcinogenic properties established *e.g.* for benzene and formaldehyde *(IARC, 2004)* – $VGAI_{long\ term} = 10\ \mu g.m^{-3}$ *(ANSES, ex AFSSET)*

- Major sources = building materials, furniture:
  - **2nd National Plan for Health and Environment (2009 – 2013)**

  « To implement a label of the sanitary and environmental characteristics of the building materials and decoration products »

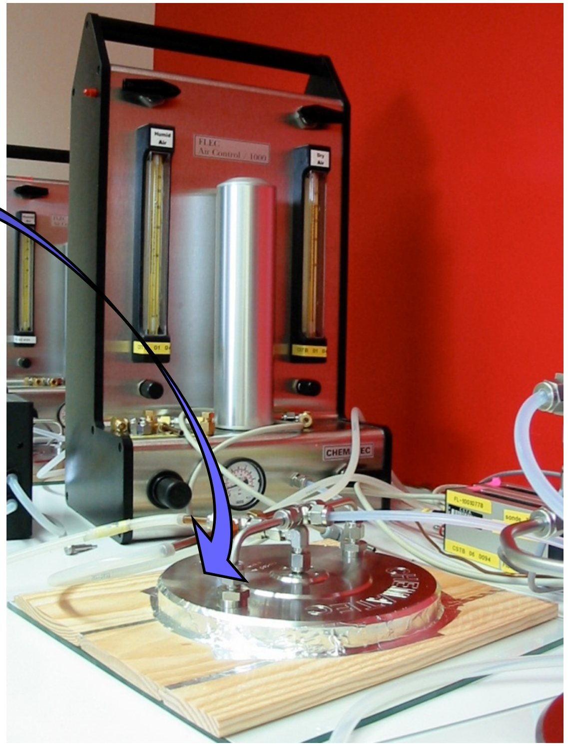
  Obligatory labelling of the products from january 2012

- **Protocols to control VOCs and formaldehyde emissions** from solid building materials proposed by the french sanitary agency *(AFSSET) (revised in 2009)*

Evaluation of new building materials

Standard methods (ISO 16000-9 and 16000-10, 2006)

- Emission test performed using environmental chamber or emission cell
  - Dynamic sampling (adsorbent tubes or DNPH cartridges) requires:
    - pump; flow controller; clean air supply, 50% RH
    - sampling time: 60 min
  - Analysis requires:
    - Specific thermal desorber on-line with GC (for VOCs)
    - Acetonitrile elution and HPLC-UV (for formaldehyde)



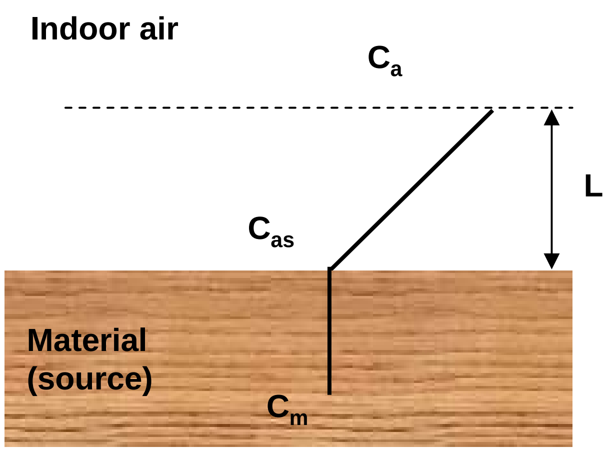
Not convenient for field studies (*i.e.* identification of sources in buildings) simple methods are needed.

Passive sampling was chosen instead of dynamic standard methods thanks to its easiness of use

Emission from material to indoor air

➡ The emission rate can be determined from first Fick law under steady state conditions:

$$T = -D\frac{dC}{dx} = -D\frac{C_a - C_{as}}{L}$$



T: emission rate ($\mu g.m^{-2}.s^{-1}$)

D: Diffusion coefficient ($m^2.s^{-1}$)

Ca: Concentration in indoor air ($\mu g.m^{-3}$)

L Thickness of the gas phase boundary layer (m)

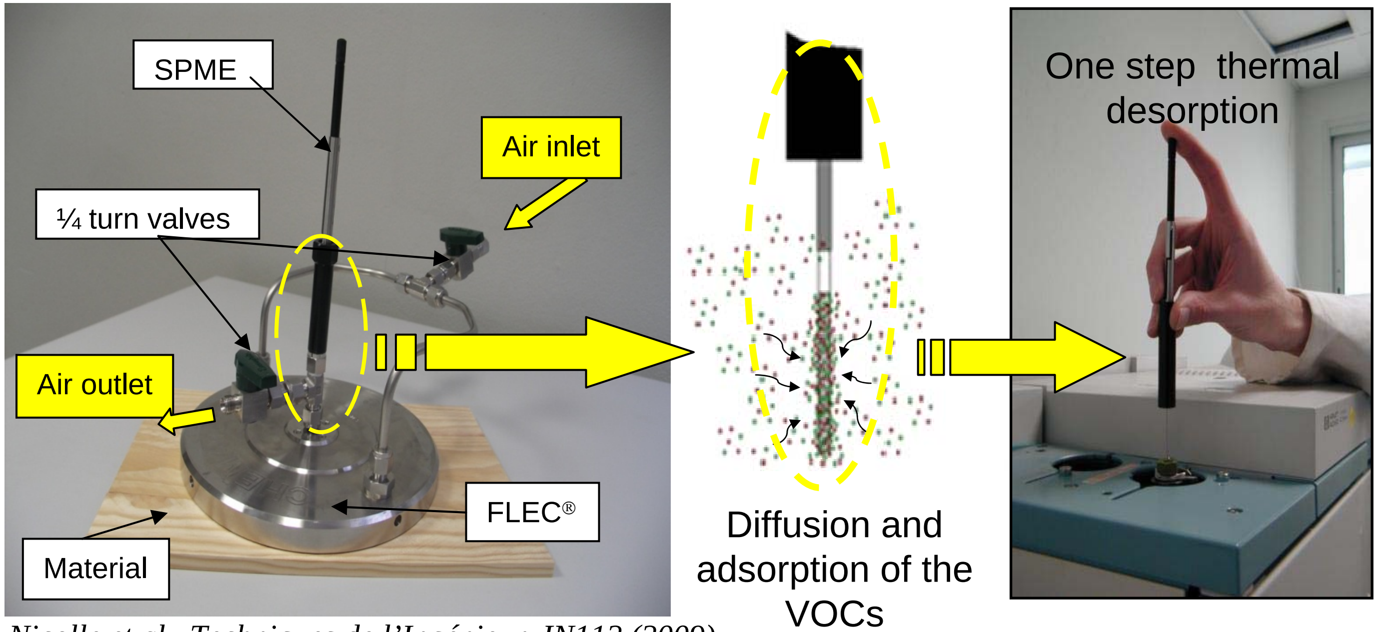
C_{as}: Gas phase concentration at the material surface ($\mu g.m^{-3}$)

Two passive sampling approaches:

✓ Determination of C_{as}: FLEC-SPME sampler

✓ Determination of T: Passive flux sampler for formaldehyde

FLEC-SPME sampler



Nicolle et al., Techniques de l'Ingénieur, IN112 (2009)

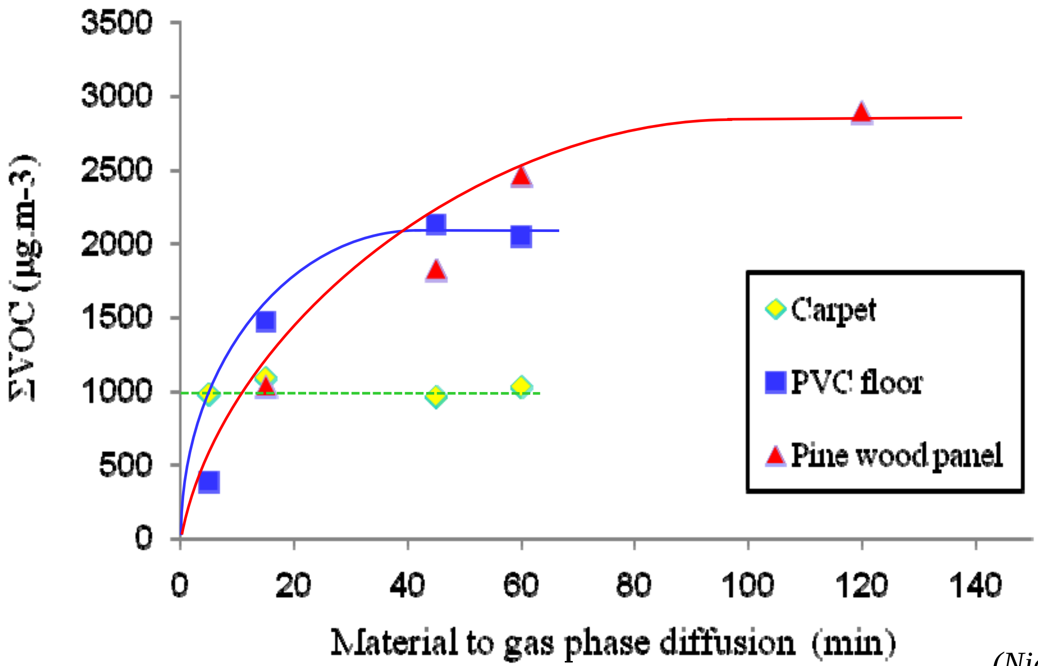
1) FLEC placed on the material, flushed by clean air (few sec.), valves closed

2) Passive sampling (1st step): VOCs diffusion from the material to the gas phase
   - **Until steady state (5- 60 min): determination of C*as*** (Gas phase concentration at the material surface)

3) Passive sampling (2nd step): VOCs diffusion from the gas phase to the fiber

Passive sampling: first step
Material to gas phase diffusion

- 3 materials studied: carpet, PVC floor, pine wood panel
- VOCs were let diffuse for 5 to 120 min before SPME sampling (20 min extraction)



(Nicolle et al., Talanta, 2009)

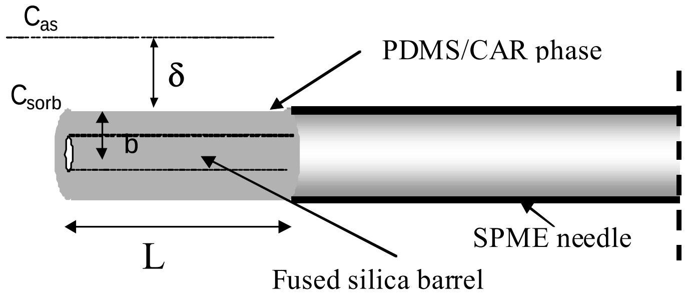
- ➡ Carpet: equilibrium reached rapidly (after 5 min)
- ➡ PVC floor: ≈ 35 min
- ➡ Pine wood panel: ≈ 60 min

Passive sampling: second step

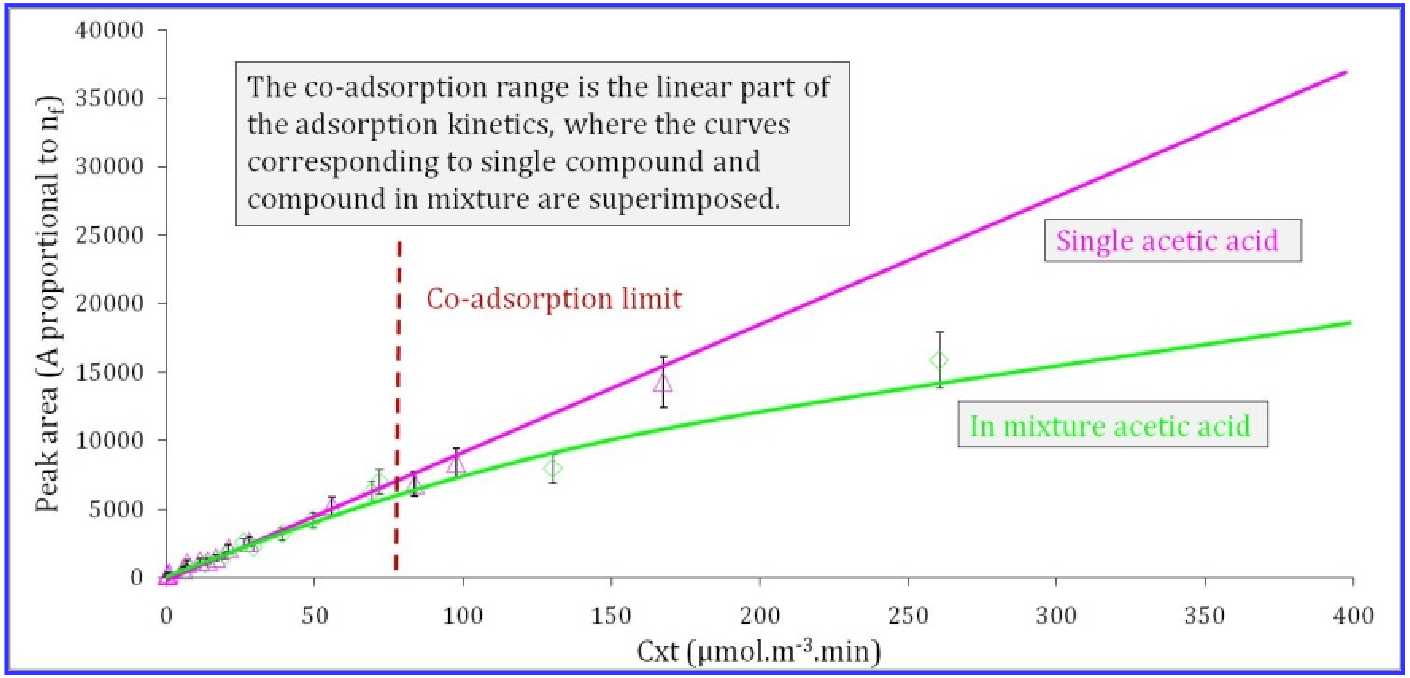
VOCs diffusion from the gas phase to the fiber

- 1st Fick law of diffusion applied to SPME

$$n = \underbrace{2\pi * D * L \Big/ \ln(b+\delta/b)}_{k} \int (C_{as} - C_{sorb})\,dt$$



- At the beginning of sampling, C_{sorb} can be neglected (i.e.co-sorption) : $\boxed{n = K.\ C_{as}.t}$



(Nicolle et al., J. Chromatogr. A, 2008)

Analytical performances

	GC/MS			GC/FID				
	LOD in full scan mode (µg m^{-3})		RSD (%)	LOD with FID (µg m^{-3})		LOQ with FID (µg m^{-3})		RSD (%)
	Extraction time			Extraction time				
	5 min	20 min		5 min	20 min	5 min	20 min	
acetic acid	31	8.2	20	6	1.4	17	4	13
methyl vinyl ketone	6	1.5	5	15	3.9	47	12	13
methyl metacrylate	12	3.7	6	2	0.6	7	2	6
hexanal	13	3.2	4	10	2.4	29	7	16
styrene	12	2.8	3	3	0.7	8	2	8
α-pinene	3	0.8	2	4	1.0	12	3	5
benzaldehyde	7	1.7	14	10	2.4	29	7	12
n-decane	10	2.5	6	7	1.8	22	5	9
2-ethyl-1-hexanol	5	1.2	11	11	2.8	34	8	12

(Nicolle et al., J. Chromatogr. A, 2008)

- ➡ Good agreement with analytical objectives (LOD and LOQ ≈ µg.m^{-3} for 20 min)
- ➡ Short sampling times (5 min) useful for rapid evaluation of new materials

Application of the FLEC-SPME sampler
Study of a new office building

- Build in 2007 under traditionnal rules of building

  no mechanical ventilation

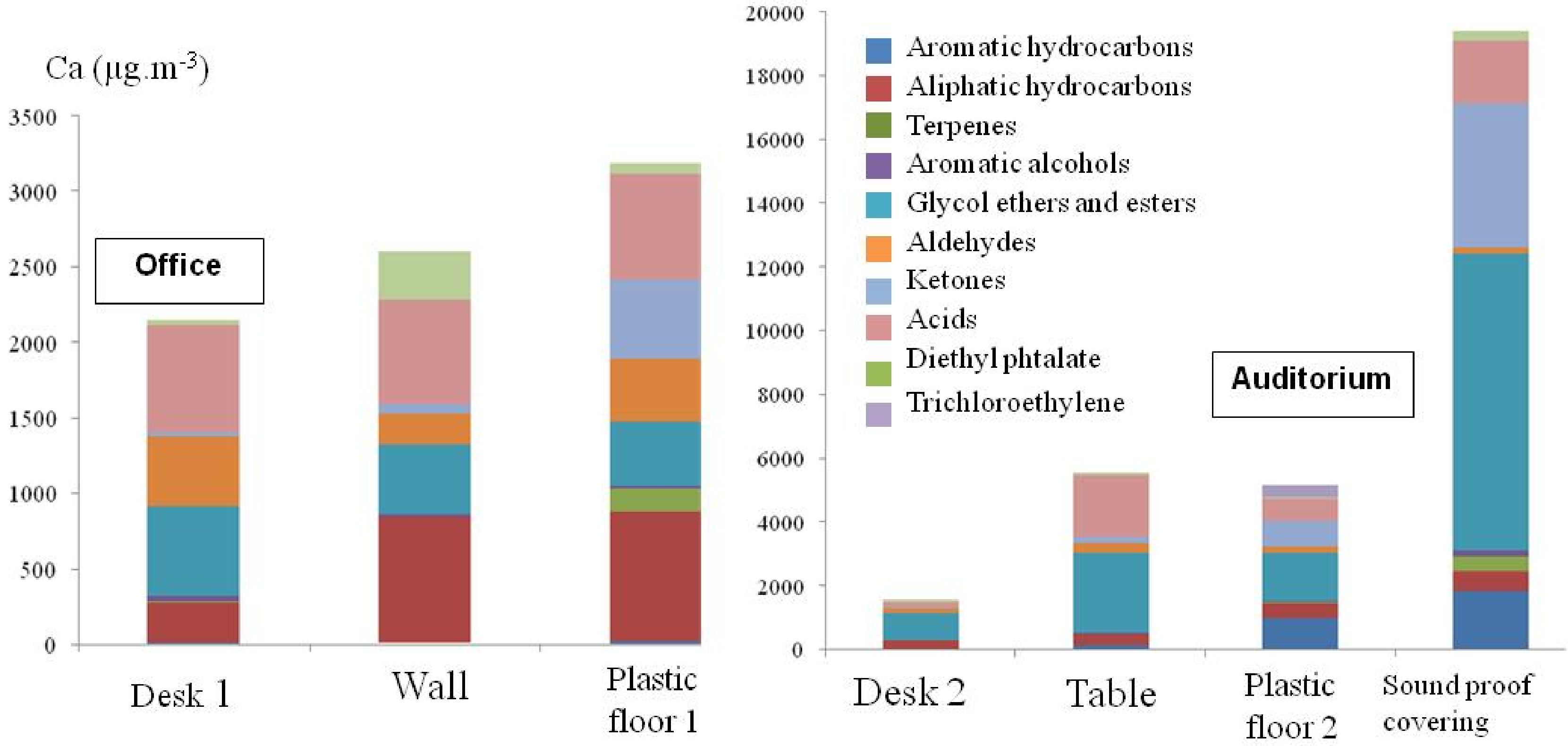
- Sampling campaign (9th july 2008) – T = 20°C; RH = 54%

  Offices and corridors : equipped with the same building materials (plastic floor and painted walls)

  Auditorium: plastic floor , walls partially covered by a sound proof material

Office	Auditorium
26 m^3	330 m^3
West	South (without window)
Materials analysed by FLEC-SPME	
Painted wall	Sound proof covering
Plastic floor (1)	Plastic floor (2)
Desk (1)	Desk (2) + table
Air analysed by SPME	
indoor	indoor
outdoor	

VOCs emitted by the materials



- ➢ Qualitative and quantitative profiles quite different
- ➢ Emitted concentrations in the auditorium considerably higher than in the office

Identification of VOCs sources
Auditorium

VOCs	Outdoor air ($\mu g.m^{-3}$)	Indoor air ($\mu g.m^{-3}$)	Desk ($\mu g.m^{-3}$)	Table ($\mu g.m^{-3}$)	Floor ($\mu g.m^{-3}$)	Sound proof covering ($\mu g.m^{-3}$)
Toluene	41.2	149.3	< LOQ	25.0	543.0	50.2
Ethylbenzene	16.7	53.0	/	7.7	12.4	119.0
Xylenes (*p*, *m*, *o*)	21.5	311.0	/	111.9	444.3	1575.0
Hexanal	/	93.0	176.1	123.1	84.7	/
Cyclohexanone	/	109.3	< LQ	22.3	529.2	4431.2
Acetone	0.3	3.3	12.0	199.9	303.3	97.3

- TEX mainly come from the plastic floor and the wall covering
- Hexanal, from the desk and tables
- Cyclohexanone, from the wall covering

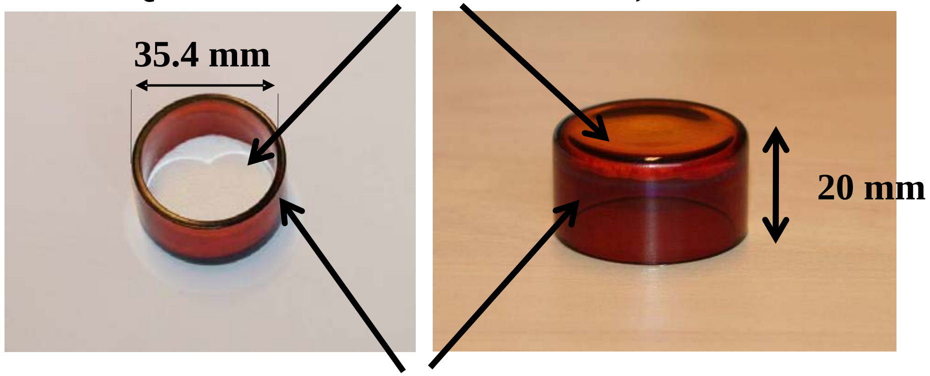
Identification of VOCs sources

Office

VOCs	Outdoor air (µg.m^{-3})	Indoor air (µg.m^{-3})	Desk (µg.m^{-3})	Wall (µg.m^{-3})	floor (µg.m^{-3})
Toluene	41.2	41.2	< LQ	< LQ	13.3
Ethylbenzene	16.7	21.5	/	/	< LQ
Xylenes (*p*, *m*, *o*)	21.5	102.2 ??	< LQ	4.8	7.6
Hexanal	/	73.0	62.8	143.8	298.6
Cyclohexanone	/	54.3 ??	< LQ	/	11.1
Acetone	0.3	2.8	31.3	62.9	513.4

- Outdoor air seems to be the major source of toluene and ethylbenzene
- Hexanal mainly comes from the floor and walls
- Data are not sufficient to explain xylenes and cyclohexanone

Passive flux sampler for Formaldehyde

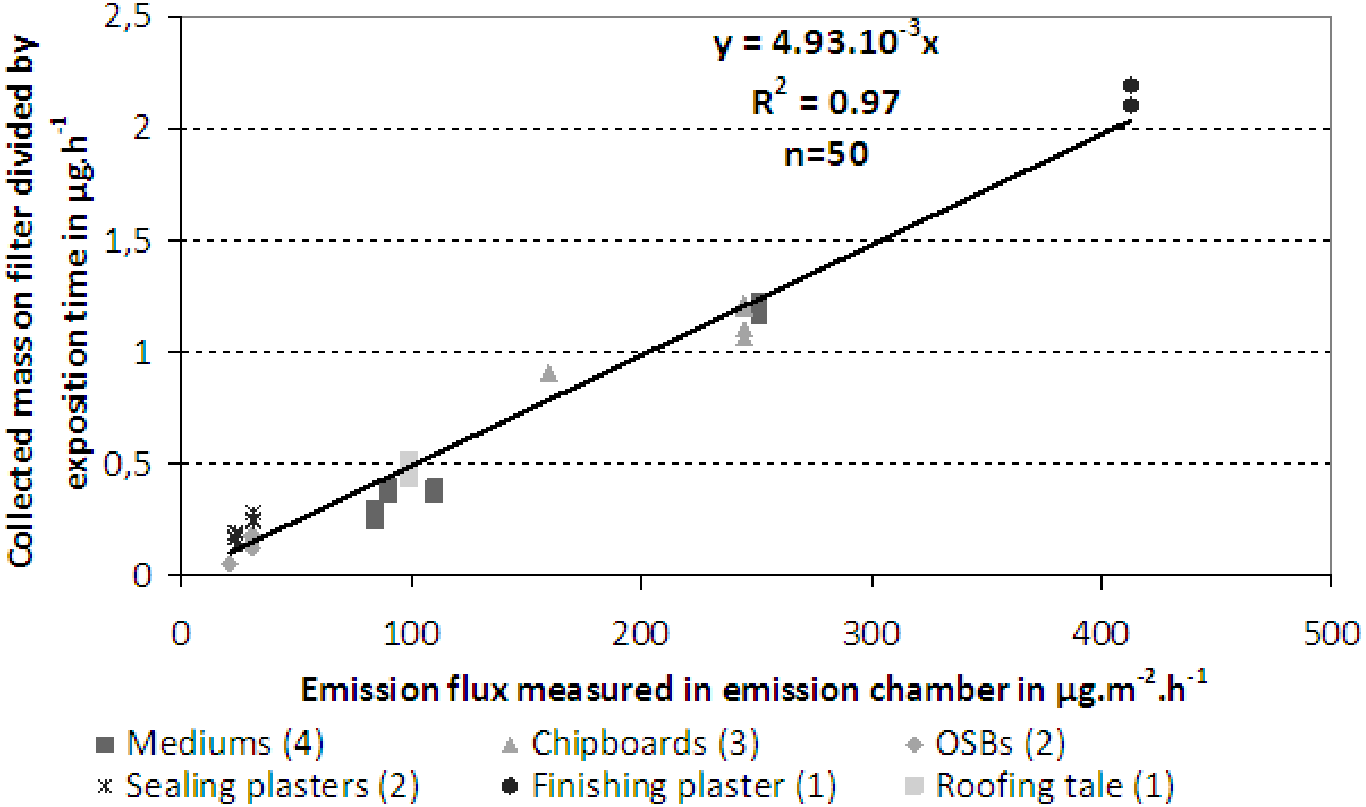


- Exposure time (*t*): 4 to 8 hours
- Acetonitrile elution
- HPLC-UV analysis

- The mass *m* (µg) of formaldehyde sampled is proportional to the emission rate *T* for a diffusion length of 20 mm (Theoretical basis and trials are shown in Shinohara et al., Atm. Env., 2007 and Blondel and Plaisance, Analytical Methods, 2010).

- *T* can be calculated from a calibration curve: $m/t = f(T)$

Passive flux sampler performances



- A linearity of the sampler response in a large range of emission rates (from 1 to 413 µg.m^{-2}.h^{-1})
- A detection limit of 1.2 µg.m^{-2}.h^{-1} for 6 hour sampling time
- A precision of replicate measurements around 7.2% (expressed in RSD) for 6 replicate measurements

Application of passive flux sampler for Formaldehyde: Investigation in 24 unoccupied student rooms of three residences

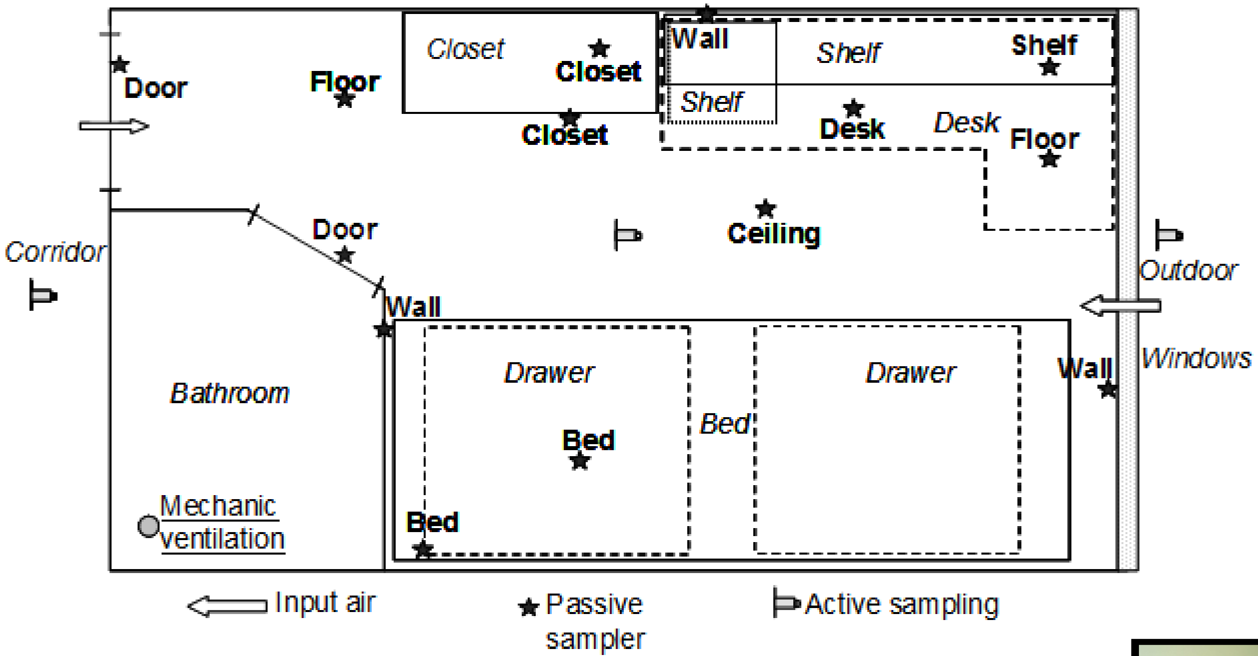
➡ Objectives:

- to quantify the emission rates from all the indoor materials present in the rooms and to identify the main indoor sources,
- to estimate the contributions of these indoor sources to the indoor formaldehyde concentration,
- to examine the relations between the indoor formaldehyde concentration and the housing and environmental factors and indoor emissions.
- to test a mass balance model using the emission rates as basis data to predict indoor formaldehyde concentrations.

➡ Instrumentation and measurement protocol:

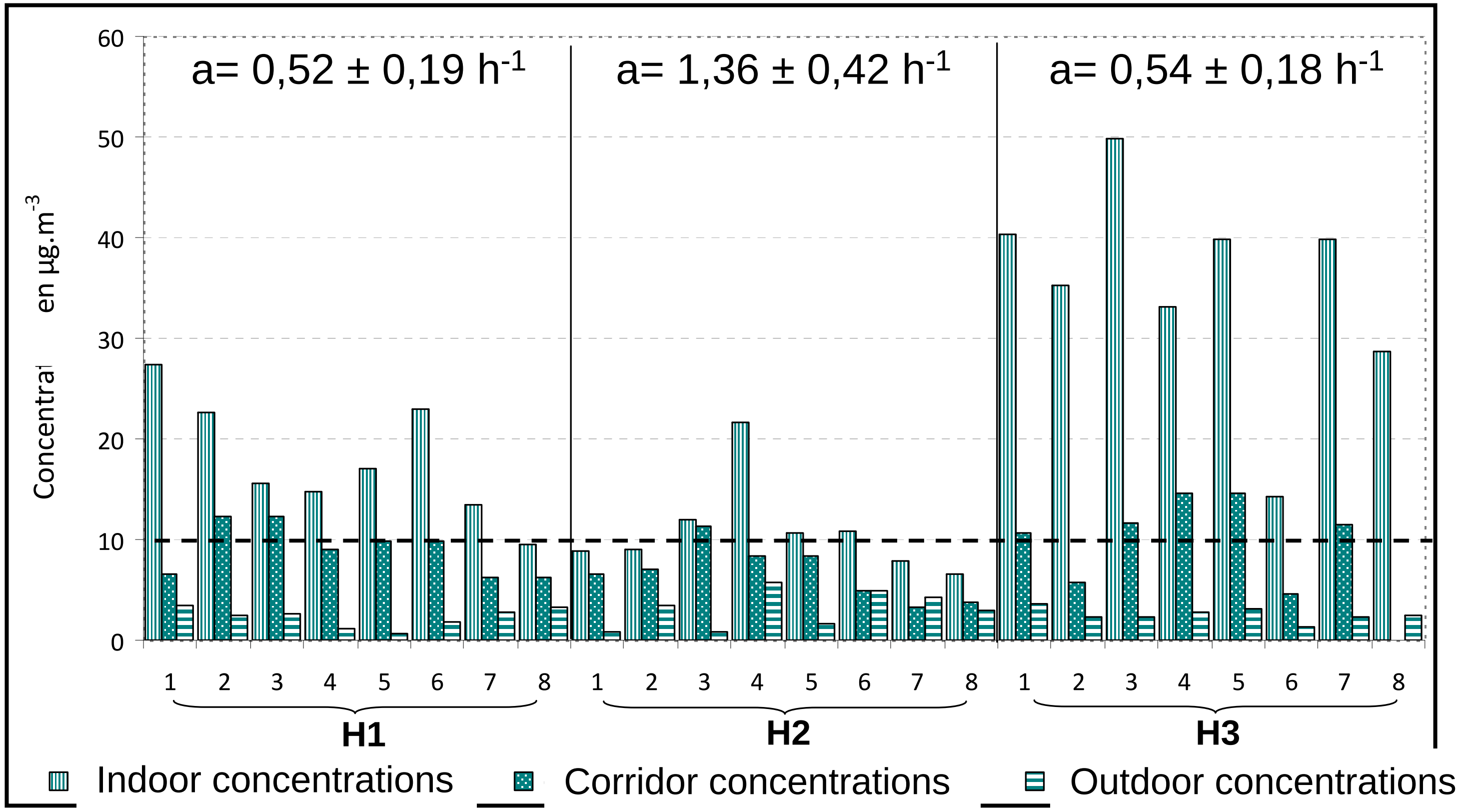
- **Formaldehyde emission rates** of all the materials present in the indoor environment (the floor, walls, ceiling and furnishing) were measured with 13 to 15 passive flux samplers (6h sampling time)
- **Formaldehyde concentrations** were simultaneously measured by the conventional active sampling using DNPH cartridges on three points: the room, the corridor adjacent to the room and outdoors
- **Air exchange rate** was determined before each sampling by the injection of CO_2 in the room and follow-up of its decay according to the standard method as described in He et al., (2004)
- **Temperature and relative humidity** were continuously measured for each trial
- **Surface area of each material** was systematically measured to calculate the total amount of FA emitted per material (expressed in $\mu g.h^{-1}$).

Rooms and location of sampling points



	Area (m²)	Volume (m³)	S furnishing/ S building
H 1	11,2	26,5	0,8
H 2	9,3	23,1	0,6
H 3	10,0	24,1	0,8

Indoor, outdoor and corridor concentrations



	Mean±Standard Deviation (Min-Max) in µg.m^{-3}			Overall Mean (µg.m^{-3})	Median (µg.m^{-3})	Kruskal-Wallis Test
	H 1 (n=8)	H 2 (n=8)	H 3 (n=8)			
Indoor	17.9 ± 5.9 (9.5 - 27.3)	10.9 ± 4.6 (6.6 - 21.6)	35.2 ± 10.5 (14.3 - 49.9)	**21.3 ± 12.6**	**16.3**	**p=0.0003**
Corridor	9.0 ± 2.5 (6.2- 12.3)	6.7 ± 2.7 (3.2 - 11.3)	10.5 ± 4.0 (4.6 - 14.6)	**8.7 ± 3.3**	**8.4**	**p=0.0934**
Outdoors	2.3 ± 1.0 (0.7 - 3.5)	3.1 ± 1.8 (0.9 - 5.7)	2.5 ± 0.7 (1.3 - 3.6)	**2.6 ± 1.2**	**2.6**	**p=0.6143**

Emission rates of indoor sources

	Mean ± Standard Deviation (Min-Max)			Kruskal-Wallis Test
	H 1 (n=8)	H 2 (n=8)	H 3 (n=8)	
Flooring	2.3 ± 1.5 (1.2 - 5.5)	1.4 ± 0.7 (1.2 - 2.4)	5.3 ± 3.5 (2.5 - 13.0)	**p=0.0009**
Ceiling and Walls	3.6 ± 1.7 (1.2 - 6.3)	3.2 ± 2.0 (1.2 - 7.1)	8.8 ± 2.8 (4.1 - 12.1)	**p=0.0029**
Door	4.0 ± 2.0 (1.2 - 6.4)	2.6 ± 1.6 (1.2 - 5.5)	7.0 ± 4.2 (1.2 - 14.7)	**p=0.0279**
Bed	3.3 ± 1.8 (1.2 - 6.7)	2.8 ± 1.7 (1.2 - 5.8)	87.3 ± 37.5 (21.3 - 131.3)	**p=0.0004**
Other furniture	2.8 ± 0.9 (1.2 - 3.6)	3.4 ± 0.6 (2.8 - 4.4)	2.9 ± 1.9 (1.2 - 7.0)	**p=0.1959**
Total ($\mu g.h^{-1}$)	322.7 ± 120.0 (122.4 – 474.0)	309.2 ± 155.4 (160.9 – 603.5)	773.2 ± 210.1 (310.7 – 984.2)	

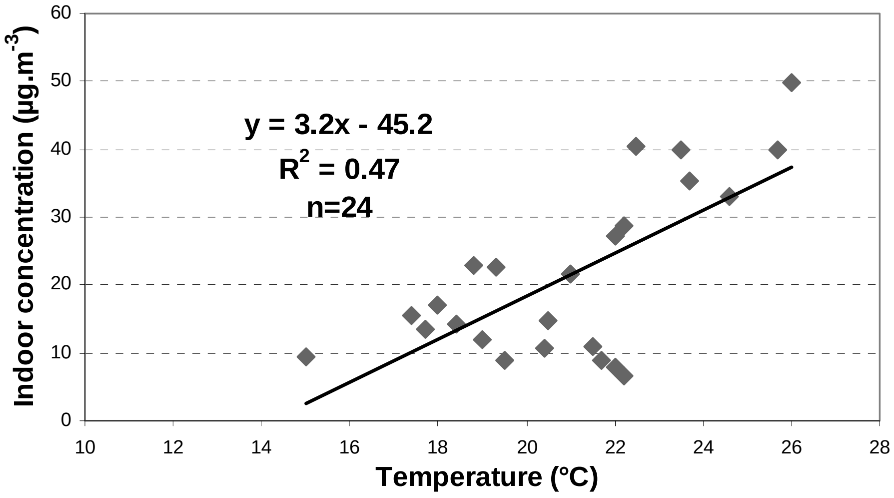
Influence of environmental and housing factors on indoor formaldehyde concentration

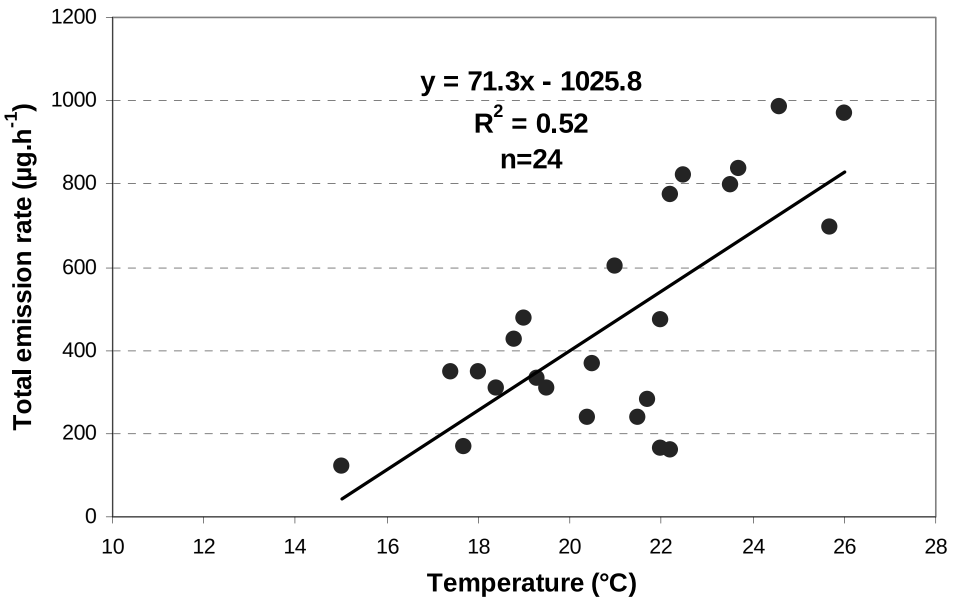
- Data analysis by multiple regression defining the indoor concentration (C_{ind}) as a function of factors and their interaction:

$$C_{ind}\ (\mu g.m^{-3}) = 25{,}614 \times (T) + 12{,}555 \times (1/a) + 15{,}219 \times (T \times HR) + 22{,}028 \qquad R^2=0{,}82$$

The factors T, HR and 1/a are standardized varying between -1 and +1

- Correlation Analysis: Indoor Concentration/T and Total Emission/T:





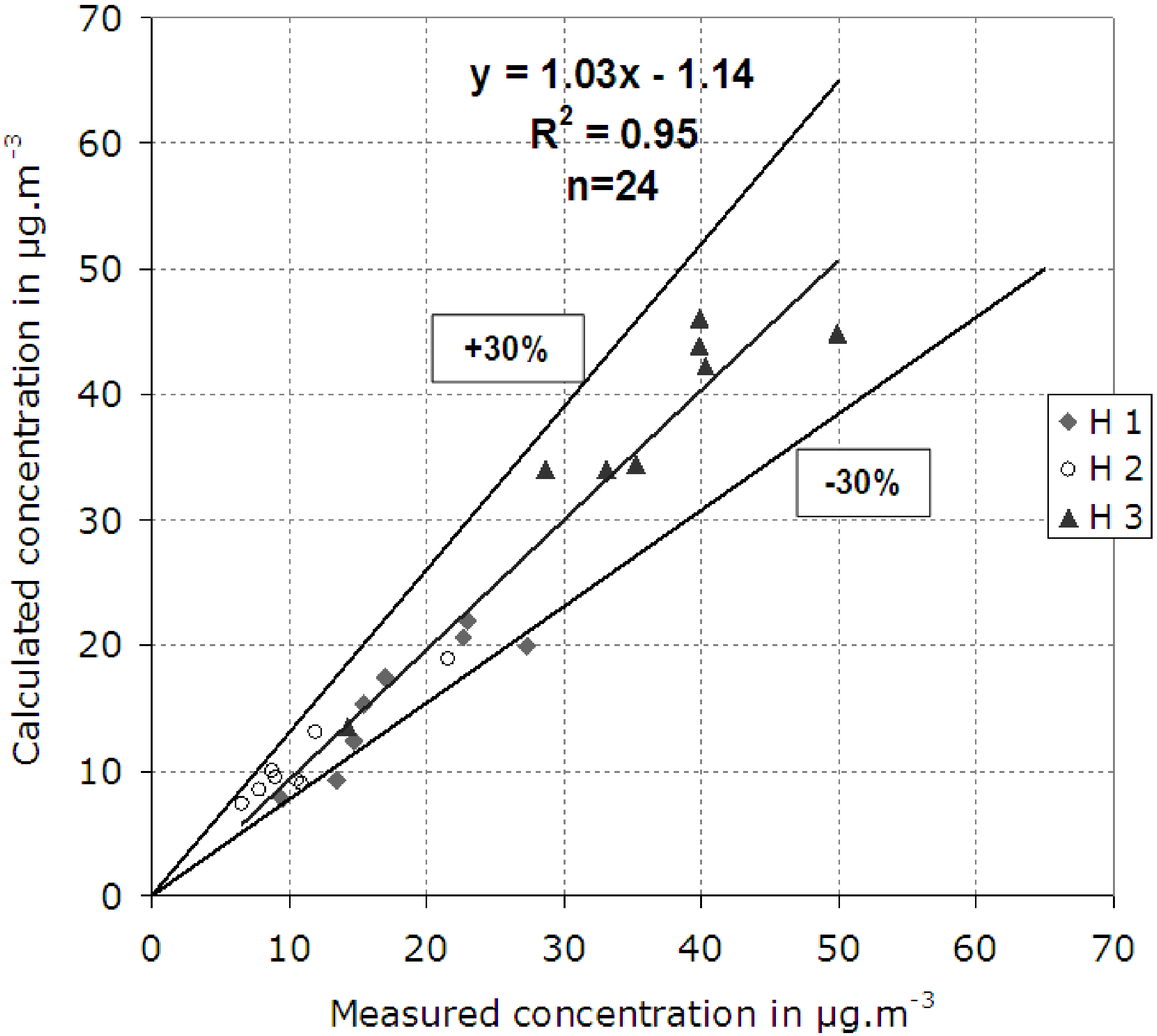
A one-compartment mass balance model to calculate the indoor concentrations

$$C_{ind} = \underbrace{\left(\frac{xa\ P}{xa+k} C_{out} + \frac{(1-x)a\ P}{(1-x)(a+k)} C_{Cor}\right)}_{\text{Outdoor + Corridor Component}} + \underbrace{\frac{Q}{V}\frac{1}{a+k}}_{\text{Indoor Component}}$$

From Liu et al., Atm. Env. 2006

- C_{ind} : Indoor concentration ($\mu g.m^{-3}$)
- C_{out} : Outdoor concentration ($\mu g.m^{-3}$)
- V : Volume of room (m^3)
- P: Fraction of outdoor contaminants that penetrates the shell (unitless) (1 = 100% penetration)
- a: Air exchange rate (h^{-1}), x: Fraction of air exchange rate coming from outdoors
- k: net rate of removal processes other than air flow (h^{-1}). A k value of 0.36 h^{-1} determined experimentally for formaldehyde by Traynor et al., (Atm. Env.1982) was confirmed by a series of trials carried out in three student rooms (Blondel and Plaisance, Thesis, 2010)
- Q : Taux d'émission des sources intérieures en $\mu g.h^{-1}$

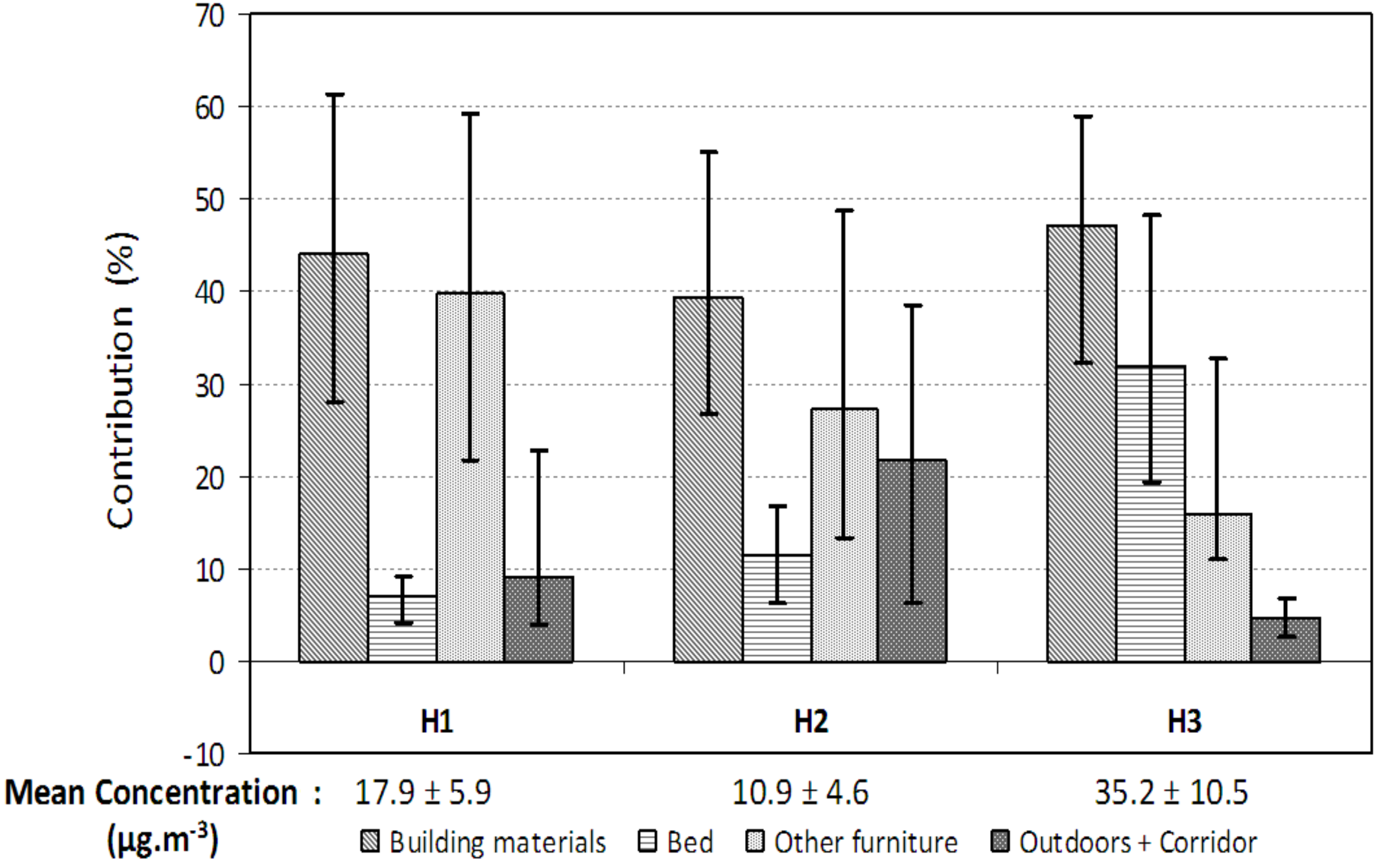
Comparison
modelled indoor concentrations / measured concentrations



Source contributions to the formaldehyde indoor concentration (%) (± min-max)

$$\%C_i = \frac{Q_i}{V(a+k)} \frac{100}{C_{Ind}}$$ for the source i

$$CR_{out+cor} = \left(\frac{xa\ P}{xa+k} C_{out} + \frac{(1-x)a\ P}{(1-x)(a+k)} C_{Cor}\right) \times \frac{100}{C_{Ind}}$$ for the corridor and outdoors



Recommendations for the improvement of indoor air quality in the rooms

		Air exchange rate (h^{-1})	Indoor sources	Indoor concentrations mean (min – max) ($\mu g.m^{-3}$)
H1	**Scenario 1**	Increase a: 0.52→1	-	17.9 (9.5 - 27.3) → **10.7 (5.9 - 16.3)**
	Scenario 2	-	Removal all furniture	17.9 (9.5 - 27.3) → **8.7 (4.8 - 14.3)**
	Scenario 3	Increase a: 0.52→1	Removal all furniture	17.9 (9.5 - 27.3) → **6.3 (4.1 - 11.3)**
H3	**Scenario 1**	Increase a: 0.54→1	-	35.2 (14.3 - 49.9) → **24.9 (8.4 - 27.1)**
	Scenario 2	-	Removal all furniture	35.2 (14.3 - 49.9) → **17.6 (8.2 - 27.1)**
	Scenario 3	Increase a: 0.54 →1	Removal all furniture	35.2 (14.3 - 49.9) → **12.6 (5.3 - 18.6)**

Conclusions

➡ These two applications show:

- the potential of passive sampling methods for the characterization of material sources of VOCs and formaldehyde (FA),
- the suitability of these passive sampling methods for field measurements as alternatives to the dynamic devices involved in standard methods,
- the interest for the diagnostic of indoor air quality and health risk assessment
- the possibility to define strategies for the efficient reduction of indoor concentrations.

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- GIP Cereste
- GEM'Air