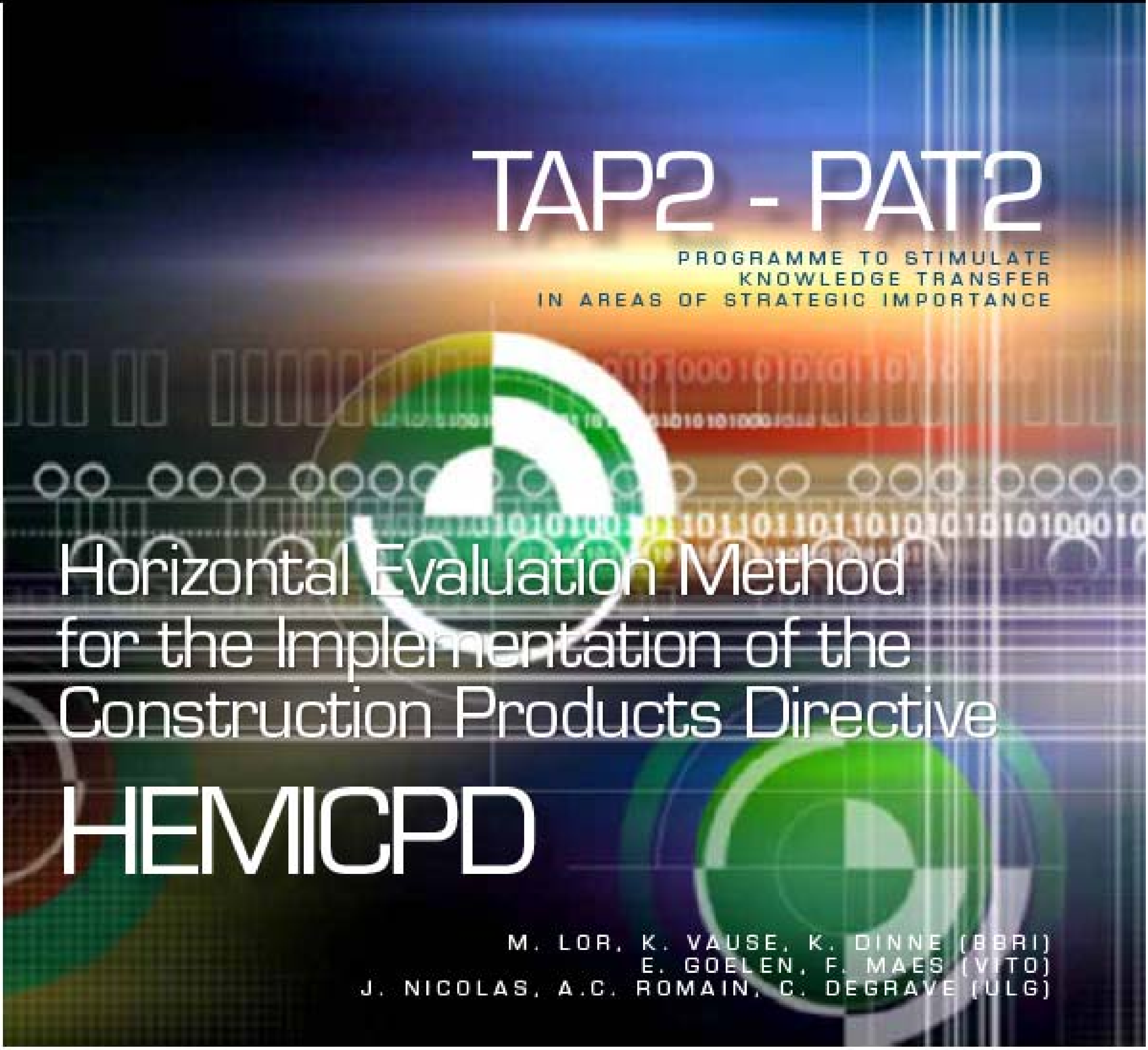

TAP2 - PAT2

PROGRAMME TO STIMULATE
KNOWLEDGE TRANSFER
IN AREAS OF STRATEGIC IMPORTANCE

Horizontal Evaluation Method for the Implementation of the Construction Products Directive

HEMICPD

M. LOR, K. VAUSE, K. DINNE (BBRI)
E. GOELEN, F. MAES (VITO)
J. NICOLAS, A.C. ROMAIN, C. DEGRAVE (ULG)

STANDARDISATION ○

TELECOMMUNICATIONS ○

SPACE SECTOR ○

CLEAN TECHNOLOGIES ○

NEW MATERIALS ○

PROGRAMME TO STIMULATE KNOWLEDGE TRANSFER IN AREAS OF STRATEGIC IMPORTANCE

TAP2

FINAL REPORT

HORIZONTAL EVALUATION METHOD FOR THE IMPLEMENTATION OF THE CONSTRUCTION PRODUCTS DIRECTIVE

HEMICPD

Promoters
Marc Lor
Belgian Building Research Institute (BBRI)
Lozenberg 7
1932 Sint-Stevens-Woluwe
Eddy Goelen
Flemish Institute for Technological Research (VITO)
Boeretang 200
2400 Mol
Jacques Nicolas
Université de Liège (ULg)
Avenue de Longwy 185
6700 Arlon

Authors
Marc Lor, Kevin Vause, Karla Dinne (BBRI)
Eddy Goelen, Frederick Maes (VITO)
Jacques Nicolas, Anne-Claude Romain, Christophe Degrave (ULg)

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Avenue Louise 231
Louizalaan 231
B-1050 Brussels
Belgium
Tel: +32 (0)2 238 34 11 – Fax: +32 (0)2 230 59 12
http://www.belspo.be

Contact person: *Anna Calderone*
Secretariat: +32 (0)2 238 34 80

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Résumé

A. Contexte

Un des objectifs de la directive européenne produits de construction (DPC) est l'harmonisation des spécifications techniques en matière de substances dangereuses pour les produits de construction. Il se peut que des produits de construction émettent ou contiennent des substances définies comme dangereuse dans les directives de la Commission européenne et dans les législations nationales. Dans le futur, les matériaux de construction ne pourront être placés sur le marché de l'Union Européenne que s'ils portent le marquage CE et s'ils sont conformes aux spécifications techniques harmonisées (deuxième génération) incluant les aspects de santé.

B. Objectifs

Le présent projet de recherche a pour objectif d'améliorer le flux de connaissances et d'informations concernant les activités de normalisation en matière de mesures de l'air intérieur, d'essais d'émissions à l'intérieur des bâtiments, de labélisation et de certification. Les moyens proposés sont une méthode d'évaluation et des méthodes de détermination normalisées à mettre en œuvre en Belgique pour harmoniser l'approche des émissions, dans l'air intérieur, par les matériaux de construction. Cette approche s'adaptera aux efforts actuels d'harmonisation au niveau européen.

C. Conclusions

- Les tendances internationales, tout comme les développements nationaux, indiquent l'importance croissante de tester les émissions provenant des matériaux de construction.
- L'harmonisation des schémas gouvernementaux pour évaluer les émissions de composés organiques volatils dans le cadre de la DPC est nécessaire pour obtenir la transparence.
- Le sujet des différentes valeurs limites dans différents pays est un problème difficile à résoudre.
- Il a été démontré qu'il était possible de réaliser une corrélation qualitative et quantitative avec la méthode de référence. Cette étude comparative doit cependant être étendue à plus de matériaux.
- L'influence importante de la procédure de quantification sur les résultats d'émission a été démontrée.

- La possibilité d'étudier la résistance des matériaux de construction à l'activité microbienne a été démontrée avec la technique intitulée « µ-chambre ».
- Une double méthodologie pour la détermination d'odeur des matériaux de construction a été développée : une méthode quantitative basée sur l'intensité et une méthode qualitative basée sur l'échelle hédonistique. En outre, la base pour le développement d'un nez électronique spécifique à l'évaluation des matériaux de construction a été établie.
- Un système d'évaluation possible en Belgique, basé sur les procédures AFSSET/AgBB/prEN15052 a été proposé avec deux modifications :
  - modification du temps de prélèvement (7 ou 10 jours)
  - « prescreening » avec une méthode alternative (< 20 L).

D. Apport du projet dans un contexte d'appui scientifique au transfert des connaissances et à l'innovation

Ce projet de recherche vise à mettre en œuvre l'exigence essentielle « hygiène, santé et environnement » de la Directive Produits de Construction. Outre son rôle d'information et de sensibilisation, il a un rôle de support dans le développement de nouveaux matériaux de construction innovants à faible niveau d'émission.

Le projet de recherche a également assuré une contribution de la Belgique dans le travail de validation du projet de norme "Emissions into indoor air - WI 351009 - Construction products - Assessment of emissions of regulated dangerous substances from construction products - Determination of emissions into indoor air" en cours de développement dans le groupe de travail 2 du CEN/TC 351.

De plus, cette recherche a mené au développement de nouvelles méthodes d'essai innovantes, adaptées aux exigences spécifiques des matériaux de construction.

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E. Mots-clés

DPC, substances dangereuses, air intérieur, CEN/TC 351, EOTA PT9, marquage CE, émissions des produits de construction

Samenvatting

A. Context

Eén van de doelstellingen van de Europese Richtlijn Bouwproducten (BPR) is de technische specificaties in verband met gevaarlijke stoffen voor bouwproducten te harmoniseren. Bouwproducten kunnen stoffen emitteren die als gevaarlijke stoffen gedefinieerd zijn in richtlijnen van de Europese Commissie en nationale regelgevingen. Bouwmaterialen gaan in de toekomst enkel nog op de markt gebracht worden indien ze overeenstemmen met de (tweede generatie) geharmoniseerde technische specificaties inclusief gezondheidsaspecten en CE-markering dragen.

B. Doelstellingen

Dit onderzoeksproject heeft tot doel de kennis- en informatiestroom te verbeteren ten opzichte van de normalisatie-activiteiten op vlak van binnenluchtmetingen, indoor emissietests door een evaluatiemethode en gestandaardiseerde bepalingsmethodes voor te stellen voor een geharmoniseerde benadering van de emissie door bouwmaterialen in de binnenlucht voor uitvoering in België. Deze benadering zal zich schikken naar de huidige pogingen tot harmonisatie op Europees niveau.

C. Besluiten

- Internationale tendenzen evenals evoluties op nationaal niveau tonen duidelijk aan dat bouwmateriaalemissietesten steeds belangrijker worden.
- Harmonisatie van overheidsschema’s om vluchtige organische emissies te bepalen en te beoordelen in de context van BPR is noodzakelijk om transparantie te bekomen.
- Het topic van verschillende limietwaardes in verschillende landen is een moeilijk op te lossen probleem.
- Naast de zogenaamde referentiemethode werd aangetoond dat alternatieve methodes mogelijk zijn om kwalitatieve en kwantitatieve overeenkomsten te bekomen. Niettemin is er een nood om deze vergelijkende studie uit te breiden naar meer materiaalgroepen.
- De belangrijke invloed van de kwantificatieprocedure op de emissieresultaten werd aangetoond.
- De mogelijkheid om de microbiële weerstand van materialen te onderzoeken met de zogenaamde μ-testkamer techniek werd aangetoond.

- Een tweedelige methodologie voor de geurbepaling van bouwmaterialen werd ontwikkeld met name een kwantificatie methode op basis van intensiteitsbepaling en een kwalitative methode op basis van “hedonic scale”. Eveneens werd de basis gelegd voor de ontwikkeling van een elektronische neus specifiek voor evaluatie van bouwmaterialen.
- Een mogelijk evaluatieschema voor België op basis van AFSSET/AgBB/prEN 15052 schema werd voorgesteld waarbij 2 wijzigingen werden voorgesteld:
  - tijdspadmodificatie (7 of 10 dagen)
  - prescreening met alternatieve methode (< 20 L).

D. Bijdrage van het project in een context van wetenschappelijke ondersteuning aan transfer van kennis en innovatie

Dit onderzoeksproject voor implementatie van de essentiële vereiste “hygiëne, gezondheid en milieu” (ER N°3) van de Richtlijn Bouwproducten heeft naast zijn informerende en sensibiliserende rol ook ondersteunend gewerkt in de ontwikkeling van nieuwe innovatieve weinig emitterende bouwmaterialen.

Het onderzoeksproject heeft ook Belgische input geleverd in het validatieproces van de draft standaard "Emissions into indoor air - WI 351009 - Construction products - Assessment of emissions of regulated dangerous substances from construction products - Determination of emissions into indoor air” in ontwikkeling in werkgroep 2 van CEN/TC 351.

Verder heeft dit onderzoek ook geleid tot de ontwikkeling van nieuwe innovatieve testmethodes aangepast aan de specifieke vereisten van bouwmaterialen.

E. Trefwoorden

BPR, gevaarlijke stoffen, binnenlucht, CEN/TC 351, EOTA PT9, CE markering, bouwmateriaalemissieproducttesten

Summary

A. Context

One of the objectives of the European Construction Products Directive (CPD) is to harmonize the technical specifications with regard to dangerous substances and construction materials. Construction products could emit or contain dangerous substances that have been defined as dangerous substances under Commission directives and national regulations. In the future construction products may only be placed on the market in the European Union if they accord with the (second generation) harmonized technical specifications including health aspects and bear the CE mark.

B. Objectives

The goal of this research project is to improve the flow of knowledge and information vis-à-vis normalisation activities in the domain of indoor air measurements, indoor product emission testing, labeling and certification by proposing an evaluation method and standardized assessment methods for a harmonized approach relating to emissions from building materials into indoor air for implementation in Belgium. This approach will comply with current European harmonizing efforts ongoing on European level.

C. Conclusions

- International tendencies as well as national developments indicate the growing importance of building material emission testing.
- Harmonisation of governmental schemes to assess volatile organic emissions in the context of the CPD is necessary to obtain transparency.
- The topic of different limit values in different countries is a difficult problem to solve.
- It was demonstrated that it is possible with alternative methods (µ-chamber and FLEC) to achieve a qualitative and quantitative correlation with the reference method. However there is a need to extend this comparative study to more materials.
- The important influence of the quantification procedure on the emission results was demonstrated.

- The possibility to investigate microbial resistance of building materials with the so called µ-chamber technique was demonstrated.
- A twofold methodology for the odour determination of building materials was developed: a quantitative method based on intensity and a qualitative method based on hedonic scale. Furthermore the basis for the development of an electronic nose specific for evaluation of building materials was laid down.
- A possible evaluation scheme for Belgium on the basis of AFSSET/AgBB/prEN15052 was proposed with two modifications:
  - time path modification (7 or 10 days)
  - prescreening with alternative method (< 20 L).

D. Contribution of the project in a context of scientific support to transfer of knowledge and innovation

This research project for implementation of the essential requirement “Hygiene, health and the environment” of the Construction Products Directive has besides its informative and sensitizing role also performed a supporting role in the development of new innovative low emission construction products.

The research project has also ensured a Belgian input in the validation work of the draft standard "Emissions into indoor air - WI 351009 - Construction products - Assessment of emissions of regulated dangerous substances from construction products - Determination of emissions into indoor air” in development in working group 2 of CEN/TC 351.

Furthermore this research project has lead to the development of new innovative test methods tailored to the specific needs of construction products.

E. Keywords

CPD, dangerous substances, indoor air, CEN/TC 351, EOTA PT9, CE marking, indoor building product emission

1. Programs that assess building materials to determine impacts on indoor air quality

Over the years a wide variety of organisations have developed a large number of labelling systems (protocols). Examples (non exhaustive list) are:

- German AgBB scheme
- French AFSSET protocol
- Austrian ecolabel
- GUT
- Emicode
- Green Label (Plus)
- Greenguard
- Nordic Swan
- M1 label
- Floorscore
- LQAI
- EU ecolabel (European flower)
- Green Seal
- Indoor Advantage
- Natureplus
- Indoor Air Comfort (Gold)
- Certipur

This proliferation was and is still due to a lack of harmonized standards for sampling, emission measurement and analytical procedures, the different construction traditions in different countries and the lack – or differing – regulations for health and environmental protection.

The different protocols that exist worldwide to evaluate building materials concerning indoor air quality with emphasis on VOC (volatile organic compound) emissions (can) differ in several ways:

- Differences in test methods (& sampling) and test parameters
- Differences in types of materials that are tested
- Differences in pollutants (target compounds) that are measured and reported
- Differences in quality assurance
- Differences in limit values

- Differences in legal status
- Differences in exposure scenario(s)
- Differences in restriction of carcinogenic VOCs
- Differences in sensory evaluation
- Differences in emission calculation procedures

For the HEMICPD project a state of the art report (work package 1) was written to serve as a guidance for the selection of the test- and analysis methods to be used for the determination of dangerous substances from building materials into indoor air.

Figure 1 : State of the art report

The state of the art report (published separately) is divided in nine main sections each dealing with a specific topic of relevance in the field of emissions into indoor air:

1. Product policy
2. Framework
3. Dangerous substances
4. Test- and analysis methods for (V)(S)VOCs and PM
5. Methods for odour determination
6. Methods for microbial resistance
7. **Test protocols and labels**
8. Emission data
9. Relevant construction materials

In chapter 7 of the state of the art report an overview (and comparison) is given of several programs existing worldwide that assess building materials to determine their impacts on the indoor air quality.

2. Test methods and materials

The principle of the building products emission tests is to determine the area specific emission rate of VOCs emitted from building products. The test is performed in an emission test chamber at constant temperature, relative air humidity, and area specific air flow rate. The air in the emission test chamber is fully mixed, and measurements of the VOC concentration in the air at the outlet are representative of the emission test chamber air concentrations.

Test chambers prevail in different chamber volumes. In general the "reference" emission test is executed in a test chamber with a volume of 1 m³, but other test chamber systems are possible.

All three partners are complementary equipped regarding emission measurements. The coordinator (BBRI) executes building product testing in a µ-test chamber and FLEC, VITO in a "medium-sized" test chamber and FLEC and ULg performs building product tests in a "real size" test chamber.
A short introduction to each test chamber is given below.

2.1. Overview of test chambers

2.1.1. µ-CTE

The µ-CTE system comprises six microchamber pots (up to 28 mm deep and ~45 mm in diameter) which allow surface or bulk emissions to be tested from up to six samples simultaneously.

Figure 2 : µ-chamber

When testing surface emissions, aluminium disk spacers are placed inside of the microchamber pots, underneath the sample. In this configuration, named cell mode, 12.82 cm^2 of the sample surface area is exposed to the gas flow and the volume above this surface is 3.2 cm^3. Materials for bulk emissions tests, as for them, may simply be weighed directly into an empty microchamber prior to sampling.

The volume of the microchamber available for bulk emissions testing is ~44 cm^3. Various accessories like inserts are available for liquid emissions analyses (e.g. VOCs emitted from varnishes, paints, detergents, etc.) and for permeation testing (e.g. evaluating the permeability of textiles or rubber gloves).

An international standard for the microchamber method is under development (ISO/DIS 16000-25) as well as a new ASTM work item “New Practice for Rapid Screening of VOC Emissions from Products Using Micro-scale chambers” (ASTM WK22044).

2.1.2. Field and Laboratory Emission Cell (FLEC)

In contrast to the large environmental test chambers VOC emission tests can also be done with smaller test cells: the µ-chamber (see above) and the FLEC. The FLEC (see photo below) is a small test cell (± 35 ml) which is placed onto the (flat) test material and is designed in such a way that the surface of the sample is a part of the test cell.

It is constructed of acid resisting stainless steel. The inner surface is hand polished and shaped like the mouth of a trumpet to optimise air velocity over the sampling surface and to eliminate sink effects. A controlled flow of purified and humidified air enters the cell from a baffle around the perimeter of FLEC passing over the test material at flow rates simulating real world conditions.

As the name implies, it can also be used to perform emission tests on building materials in dwellings or other test settings. An overall test procedure to determine area specific VOC emission rates is described in EN ISO 16000-10.

Figure 3 : FLEC with subunit

2.1.3. *Medium size test chamber (1 m³)*

The overall procedure for the use of a test chamber for evaluating VOC emissions from building materials has been laid down in the standard EN ISO 16000-9. Many measures are taken to ensure that the test chamber fulfils the conditions noted in the EN ISO standard. In that regard, it is possible to adjust the environmental parameters (temperature, relative humidity (R.H.), air speed, air exchange factor) to the specific needs of the emission test.

Figure 4 : 1 m^3 test chamber

The sample is placed in the inner test chamber: depending on the needed temperature, heated air circulates around this chamber so that the inner chamber reaches the temperature's set point. To establish relative humidity in the test chamber, the zero-air entering the chamber passes through a water reservoir. The air exchange rate is determined by the setting of the mass flow controller which controls the air flow going into the chamber. The air speed above the sample can be altered by changing the number of revolutions of the fan inside the chamber.

2.1.4. The FOG macro chamber (50 m³)

The macro chamber has a size of 4 m width, 4,8 m length and 2,6 m high. So the volume is 50.5 m³. Air flow and temperature are managed thanks to a control system. Humidity can be measured by two humidity probes; ground heating is used to obtain 23°C in the macro-room.

Figure 5 : 50 m^3 test chamber (outside view)

The fresh air firstly arrives from outdoor; it passes then through a dust filter, the cooling exchanger and finally the fan. There, temperature is led to +/-15°C to decrease the humidity level before air enters into the active charcoal. After this air purification, pure air is warmed up until +/-20°C by a heating resistor. It arrives in the test chamber through an aluminium perforated tube, used as diffuser. Then ambient air exits the chamber through another aluminium perforated tube and finally, goes outdoor.

Figure 6 : 50 m^3 test chamber (inside view)

2.2. Selection of test methods for VOC emission testing

From gathering and studying all available information – which was written down in state of the art report - in the field of (building)material emissions it was concluded that the following test and analytical methods/procedures for (V)(S)VOCs - (very)(semi)volatile organic compounds - will act as the starting point for the VOC experiments (Table 1):

	Procedure	Sampling time	What
FLEC	EN ISO 16000-10	3, 7 and 28 days	10 highest VOCs TVOC TSVOC Analysis: ISO 16000-6 Odour Aldehydes ISO 16000-3
µCTE	literature manual (ISO 16000-25)	3, 7 and 28 days	
Test chamber 1 m³	EN ISO 16000-9	3, 7 and 28 days	
Test chamber 50.5 m³	(EN ISO 16000-9)	3, 7 and 28 days	

Table 1 : Summary of used test and analytical methods

It's clear that the HEMICPD emission tests were based on the EN ISO 16000 series "Indoor air" and the new CEN/TC 351/WG2 standard under development by :

- using a 5% phenyl/95% methylpolysiloxane capillary GC column and

- adapting to the new dimensions of the reference room and
- using ISO 16000-3 only for formaldehyde and carbonyl compounds up to C4.

For the sampling, storage and preparation of test specimens the procedure described in EN ISO 16000-11 was followed.
For the operation of the test chambers – with the exception of the µ-CTE – and the test cell the procedures described in EN ISO 16000-9 and EN ISO 16000-10 were followed, respectively.
VOC sampling on Tenax TA is done after 3, 7 and 28 days. Odour sampling from the FLEC, 1 m³ and 50.5 m³ was done after 3 days.

For the VOC analysis the procedure described in ISO 16000-6 was followed. For the first series a semi-quantitative analysis (on the basis of 2-fluortoluene, expressed as 2-fluorotoluene equivalents) was done. This procedure is similar to the one described in ISO 16000-6 and also applied in the French AFSSET protocol. In further experiments done, determination has also been done quantitatively (with calibration curves for each compound) as described in the German AgBB procedure.
Formaldehyde and other aldehydes are measured as described in ISO 16000-3.

The following paragraphs describe more in detail the different aspects of test chamber experiments, starting from the test chamber parameters itself to the analysis of VOCs and aldehydes.

2.2.1. Experimental test chamber parameters

One of the objectives of the project was to do a comparative study of results obtained by emission experiments in the different sized test chambers. In order to compare emission results we have to calculate the area specific emission rate, which is independent of the volume, air flow,… of the different test chambers, in contrast to the concentration of a compound.

For an overview of the different test conditions in the test chambers, see Table 2.

Parameters	µ-CTE	FLEC	1 m³	50 m³
Sample Diameter (m)	0,040	0,15		
Chamber volume (m³)	3,2E-06	0,000035	1	50,5
Load factor (m²/m³)	400,6	505,7	0,4	0,42
Exchange rate (h^{-1})	469	514,3	0,498	1,05
Air flow rate (L/min)	0,025	0,3	8,3	883
Chamber temperature (°C)	23	23	23	23
Area specific air flow rate (exchange rate/load factor) (m³/m².h)	1,17	1	1,25	2,5

Table 2 : Overview of the test conditions in the different chambers

If the concentration is multiplied by the area specific air flow rate, we obtain the area specific emission rate, which expresses the emission rate (µg/h) per m². This value can be used to compare emission results originating from different sized test chambers, not only for individual compounds, but also for TVOC - total volatile organic compounds.

2.2.2. Sampling

In order to identify and quantify VOCs from building materials, known volumes of test chamber outlet air containing VOCs emitted by the specimen are passed through stainless steel tubes packed with 200 mg of Tenax TA. This porous polymer resin based on 2,6-diphenylene-oxide is able to adsorb chemicals from n-C_6 to n-C_{30}, it is thus well adapted for the determination of VOCs and is the choice of the ISO 16000-series. During the course of the project an alternative sorbent, Carbotrap 202, was tested (see 5.5).

As Tenax tubes may present impurities adsorbed from ambient air or chemicals which do not have reacted during the polymerization reaction of the solid phase (i.e. the precursors of Tenax), it is crucial to condition the tubes prior to sampling in order to avoid emission peaks from the tube itself. Conditioning involves the continuous flow of a carrier gas (nitrogen) while desorption tubes are heated at elevated temperatures.

A flow-calibrated pump (or a pump with a flow-calibrated Mass Flow Controller) ensures the passing of the outlet air over the sampling tube during a certain time, so the total volume of air which has been sampled can be calculated. The concentrations of the compounds in the test chambers are calculated by dividing the analytical results (mostly in nanograms) by the sampling volume (mostly litres). The concentrations are thus expressed as ng/L or µg/m³.

Typical sampling rates and times are for the FLEC and 1 m^3 test chamber about 40 mL/min during 2 hours. Total volume is then about 5 L, described as maximum in ISO 16000-6. These volumes can be lowered if high emission is expected.

Formaldehyde and other carbonyl compounds are sampled on adsorbent tubes impregnated with 2,4-dinitrophenylhydrazine (DNPH).

2.2.3. VOC analysis

VOCs are extracted from the tube by thermal desorption and are transported with a carrier gas to a cold trap (focusing trap) where the VOCs are readsorbed. After flash-heating of this cold trap, the redesorbed VOCs are transferred to a GC (gas chromatography) where the VOCs are separated and finally are detected by a MS (mass spectrometer).

For an overview of the most important analytical parameters, see Table 3.

Tube desorption temperature (°C):	280
Tube desorption time (min):	15
Focusing trap:	General purpose hydrophobic cold trap
Focusing trap temperature:	+5 °C
Focusing trap desorption temperature (°C):	280
Focusing trap desorption time (min):	2
Desorption flow (mL/min):	20
Transfer line temperature (°C):	200
Column type:	AT 5ms; 60 m x 0,32 mm x 0,25 µ
Temperature program:	38 °C, 7 min; 5 °C/min until 250 °C; 5 min on 250 °C; 10°C/min until 300°C; 1 min on 300°C
Run time (min):	60
MS mode:	SCAN
MS transfer line temperature (°C):	300

Table 3 : Overview of the most important analytical parameters for VOC analysis

Before analysis the Tenax tubes are spiked with a known amount of 2-fluortoluene which acts as an internal standard to determine a semi-quantitative analysis and as a tool to check the stability of the MS in the sample sequence. TVOC is calculated as being the sum of VOCs quantified with the response factor of 2-fluorotoluene between hexane and hexadecane. The concentration is expressed in terms of fluorotoluene equivalents.

Furthermore the ten highest peaks are identified using the MS total ion chromatogram and compilation of mass spectra libraries. They are also determined semi-quantitatively and these data are used to compare the different test chambers. As mentioned earlier, other quantification strategies are also performed (see 5.1).

After sampling of the aldehydes on DNPH (2,4-dinitrophenylhydrazine), the formed hydrazones are desorbed with acetonitrile and analysed quantitatively by HPLC (high pressure liquid chromatography) with a DAD detector (diode array detector).

2.3. Analytical SVOC methods

2.3.1. Phthalates

Phthalates are used as plasticizers in consumer products, including surface materials in buildings. For instance they're used in PVC and vinyl chloride resins, which together have been suggested to be the major source of plasticizer exposure in residences.

Following phthalates were selected (ordered from lowest to highest boiling point):

- Dimethylphthalate (DMP; bp 284°C)
- Diethylphthalate (DEP; bp 299°C)
- Dibutylphthalate (DBP; bp 340°C)
- Bis(2-ethylhexyl)phthalate (DEHP; bp 385°C)
- Di-octylphthalate (DOP; bp 405°C)

Initially we tried to analyse the phthalates on the same analytical system as the VOCs, but it turned out some instrumental modifications had to be made to be able to successfully determine the phthalates.

Classical methods for VOCs using Tenax TA have not been used extensively for the enrichment of SVOCs (semivolatile organic compounds). This is especially due to some instrumental problems (problem of efficient thermal desorption and transfer of high boiling compounds to the GC/MS). Because of these temperature related instrumental problems we installed a second, upgraded thermal desorption apparatus with extra insulation, a heated GC inlet, a cold trap specifically designed for the analysis of high boilers and the possibility to maintain higher temperatures in the system.

The sorbent was also upgraded, from the standard Tenax TA to PDMS/Tenax. PDMS is well known as stationary phase in GC and is a good sorption material for concentrating SVOCs from air, allowing subsequential thermal desorption. The analytical method (Table 4) is based on Wauters et al., and can also be used to measure PAHs in indoor air.

Tube desorption temperature (°C):	300
Tube desorption time (min):	10
Focusing trap:	High boilers cold trap
Focusing trap temperature (°C):	10
Focusing trap desorption temperature (°C):	350
Focusing trap desorption time (min):	5
Desorption flow (mL/min):	30
Transfer line temperature (°C):	210
Column type:	Rxi- 5ms; 30 m x 0,25 mm x 0,25 µ
Temperature program:	75 °C 5 min; 25 °C/min until 225 °C; 5 °C/min until 295 °C
Run time (min):	25
MS mode:	SIM/SCAN
MS transfer line temperature (°C):	320

Table 4 : Overview of the most important analytical parameters for phthalate analysis

Calibration curves were made and linearities between 0.99 and 0.999 were obtained for amounts between 2 and 50 ng. The standards were injected onto the tubes as methanol solutions. Below is an example of a chromatogram with the 5 phthalates.

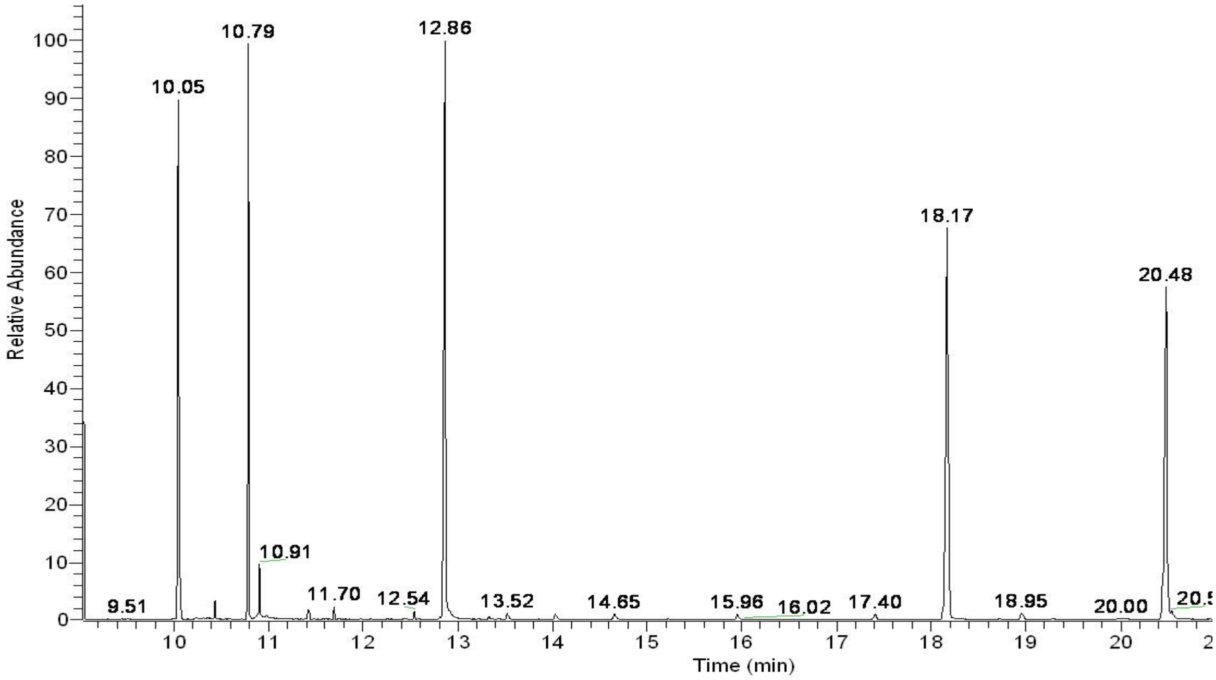


Figure 7 : Example of chromatogram with 5 phthalates

To investigate the emission of phthalates a 1 m³ test chamber experiment was executed of a PVC floor covering (under standard conditions). PDMS/Tenax was sampled after 6 days, during about 24 hours at a sampling flow of 200 mL/min what results in a total sampling volume of 288 liters (Afshari et al.). Only dimethylphthalate was detected, at a rather low concentration of 0.055 µg/m³ or 55 ng/m³.

2.3.2. *Brominated flame retardants*

Flame retardants (FR) have been used increasingly in consumer and building products in combination with a rapid increase in the use of plastics. Fire codes dictate the use of FR in such products as insulating materials, electronic and electrical goods, upholstered furniture, and carpets.

FR are added to a variety of polymers in the form of additives, or bound using a macromolecular reaction to reduce their flammability. In doing so the potential risk to Human health and the environment must be weighed against the reduction of fire hazard. The most frequently used organic FR are polybrominated (BFR) and organophosphoric compounds (POCs). Recently, special attention has been given to BFR.

An insulation material (XPS with a wooden backing) was inserted into the 1 m³ test chamber under standard conditions (23 °C, 50 % RH, 0.5/h), samples were taken 39 days after the start of the emission test. Active air sampling was done using glass tubes (22 x 100 mm) equipped with one polyurethane foam (PUF) plugs to which BFR adsorb. Sampling flow of about 1 L/min during 24 hours resulted in a total sampling volume of about 1.5 m³.

The samples are desorbed using a Soxhlet extraction with toluene and 1 µL of the extract is injected into the GC (DB-5HT column). High resolution MS detects the specific masses of the BFR.

A blank PUF cartridge was analysed to check the presence of BFR in the PUF itself. High amounts of some BFR were found, but they disappeared after a second extraction. Those PUF cartridges were used to sample the test chamber, however no BFR were present above the limits of quantification.

2.4. Microbial resistance

2.4.1. Motivation and objectives

The focus of this research project aims also at the development of a screening procedure for determining MVOCs (microbial volatile organic compound) based on thermal desorption and the so called µ-CTE test chamber. The assessment of MVOC production in buildings is important for two reasons:

- To determine whether these compounds have specific toxic properties and could be produced in sufficient amount to affect human health.
- To determine whether these are “signature” or marker compounds that investigators could use to determine if microorganisms are growing in a building.

One of the difficulties raised by this research is that many VOCs that microorganisms produce have also non-microbial origins or the original biological producer is not directly involved in the compound’s presence in the building (e.g. limonene and pinene are used in cleaning agents).

Currently, there is a lack of information concerning the use of VOCs as fingerprint or marker easily detectable to highlight fungal and/or bacterial activity.

This research is mainly focused on the study of VOC produced under defined lab conditions. It aims at learning whether field measurements can identify MVOCs that characterise indoor microbial growth.

In a first part, emission tests were conducted on the following fungi which were grown on an agar culture medium:

- Cladosporium cladosporoides
- Aspergillus versicolor
- Penicillium purpurogenum
- Stachybotrys chartarum

In the second part of this work, one specific fungus was selected to grow on damp building materials (e.g. a gypsum board or an OSB) on the basis of preliminary results obtained on agar. These measurements were conducted with the screening procedure developed in the first part of this study.

The following sections describe the newly developed µ-chamber screening procedure and give a description of the obtained results.

2.4.2. Methodology

For this test, taking into account a possible risk of contamination of the test chambers by moulds, stainless steel Microchamber pots were exclusively used for the incubation of microorganisms (on agar or on building materials) and for sampling MVOCs.

A mixture of agar was prepared and transferred into each individual Microchamber pots (see Figure 8). After solidification of the gel, the different strains of mould were injected into the culture medium. The test pots were closed with a Parafilm stretched and pierced on its surface to provide a humidification environment while minimizing the possible contamination by other fungi / bacteria.

Figure 8 : Preparation of mould cultures for testing MVOCs

The various pots were then placed in beakers containing demineralised and purified water which provides a relative humidity superior to 80 %. The beakers were finally sealed with Parafilm and stored in a conditioned lab (23 °C ± 2 °C and 0 % ± 5 % R.H.) until sampling. The blank reference, i.e. the agar medium that was not contaminated by mould, was in turn placed in the refrigerator during storage phases. MVOCs emissions by moulds on agar were tested according to the planning of sample measurements listed in Table 5. The blank reference was removed from the refrigerator three hours before taking the air sample so that the reference is in the same conditions of sampling as the various strains.

Sampling	Number of incubation days
1	2 days
2	3 days
3	7 days
4	10 days
5	14 days
6	21 days
7	30 days

Table 5 : Planning of screening tests of MVOC emissions on agar using the so called µ-CTE method

The following procedure was performed for each sampling:

- The µ-CTE is configured to work with an air flow of 100 mL/min.
- The Microchamber pots are removed from the beakers and the outside of the pot was dried with paper towels. The Parafilm is removed and the pots are placed into the µ-CTE device.
- Before the start of sampling a period of 30 minutes is observed in order to allow the establishment of a dynamic equilibrium within the µ-CTE.
- Sampling is done on Tenax TA cartridges placed in series on the output of the µ-CTE under the following conditions:

    - Temperature: 23 °C ± 2 °C
    - Relative humidity: 0 % ± 5 %
    - Sampling flow: 100 mL/min
    - Sampling duration: 30 minutes
    - Sampled volume: 3,0 L

2.4.3. Results of preliminary emission tests of MVOCs by moulds

2.4.3.1. Cladosporium

A culture medium was contaminated by two strains of *Cladosporium*, one per Microchamber pot. A visual inspection of mould growth over time (see Figure 9 and Figure 10) indicates a similar development of the two strains of *Cladosporium* in the selected test conditions. Moreover, no contamination by other strains (like *Aspergillus* or *Penicillium*, e.g.) is observed, after 2 or 10 days.


[redacted] [redacted] [redacted] [redacted]

Figure 9 : Development of Cladosporium microorganisms (strain 01) over time

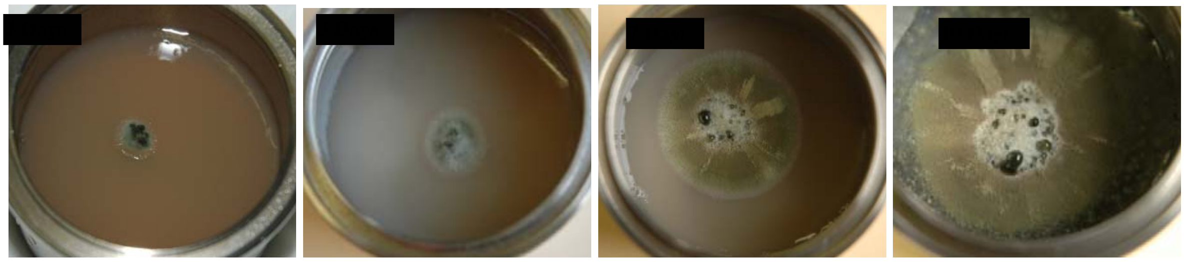

[redacted] [redacted] [redacted] [redacted]

Figure 10 : Development of Cladosporium microorganisms (strain 02) over time

After identification of all peaks present in the emissions of the system "*Cladosporium* on agar", and subtracting the peaks corresponding to the agar itself, two VOCs have been identified: 3-methyl-1-butanol (black line in Figure 11 and Figure 12) and butylated hydroxytoluene (grey line in Figure 11 and Figure 12). These compounds, present in low quantities in the samples, behave the same in both cases (see Figure 11 and Figure 12):

- The maximum concentration of 3-methyl-1-butanol is found at the beginning of the test, i.e. two days after the injection of *Cladosporium* moulds. The concentration of butylated hydroxytoluene, meanwhile, is zero at that time of the test.
- The concentration of 3-methyl-1-butanol decreases exponentially between day 2 and day 10. Between these two dates, *Cladosporium* grow to occupy the entire surface of the agar. Simultaneously, an increase of emissions of butylated hydroxytoluene is observed. The emitted quantity of the latter reaches a maximum at day 10 and decreases gradually thereafter.

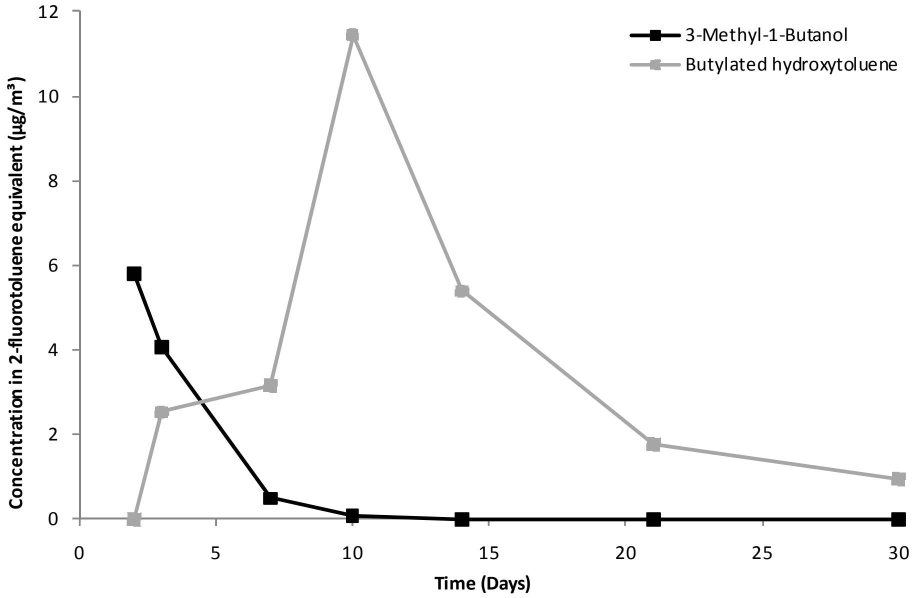


Figure 11 : Evolution of the principal MVOCs emitted by a strain of Cladosporium (strain 01)

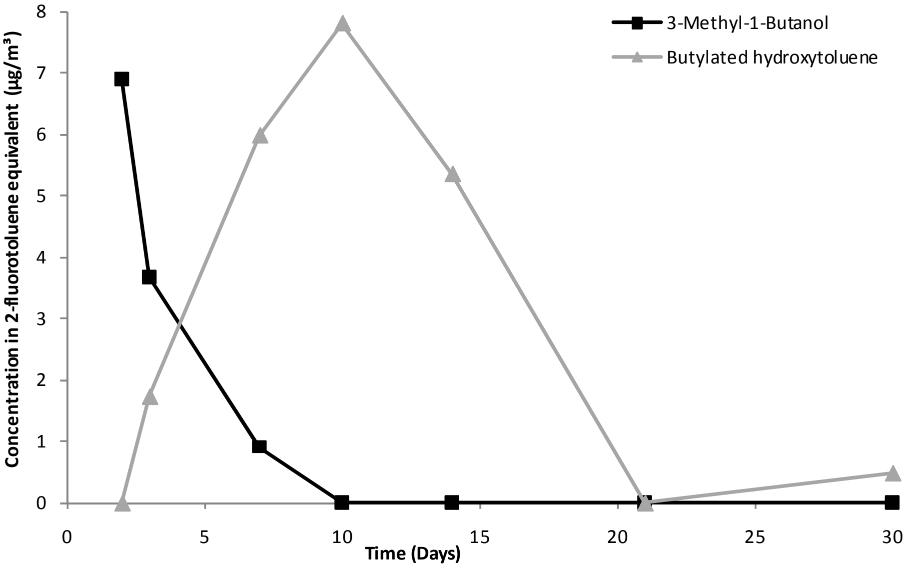


Figure 12 : Evolution of the principal MVOCs emitted by a strain of Cladosporium (strain 02)

2.4.3.2. Aspergillus

An agar medium was contaminated by injecting a strain of *Aspergillus*. A visual inspection of the mould growth over time (Figure 13) shows, with the selected experimental conditions, a slower development than for *Cladosporium*. At the macroscopic level, it appears that a contamination, different from *Aspergillus*, grew against a wall of the test chamber from day 10. An examination under optical microscope at the end of the test reveals a slight contamination by spores of *Penicillium*.


[redacted] [redacted] [redacted] [redacted]

Figure 13 : Development of Aspergillus microorganisms over time

The identification of volatile organic compounds specific to microorganisms (MVOCs) revealed the presence of four chemicals that can be classified in MVOCs in the emissions of “Aspergillus on agar”.

These compounds are: 3-methyl-1-butanol (black line in Figure 14), 1-octene-3-ol (light grey), butylated hydroxytoluene (grey) and 3-methyl-3 - butene-1-ol (dark grey) and are present in relatively low concentrations in samples. Their presence in air varies over time:

- 3-methyl-1-butanol is the only detected MVOC after 2 days of incubation on a culture medium. Its concentration is highest in early testing as it was the case with the emission results for *Cladosporium*.
- Over time, the concentration of 3-methyl-1-butanol decreases gradually while other MVOCs are emerging. This is mainly the case of 1-octene-3-ol whose concentration at day 30 is practically equal to the initial concentration of 3-methyl-1-butanol.

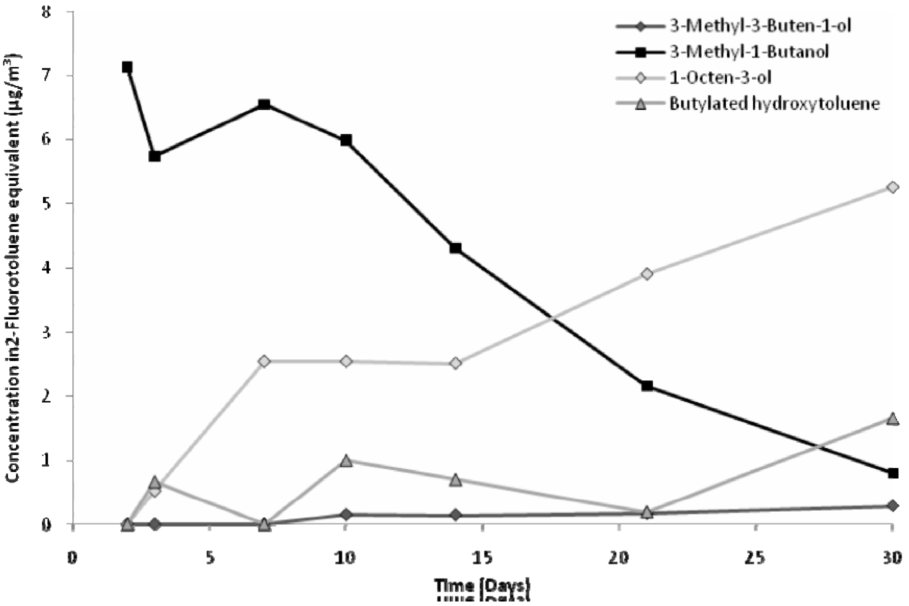
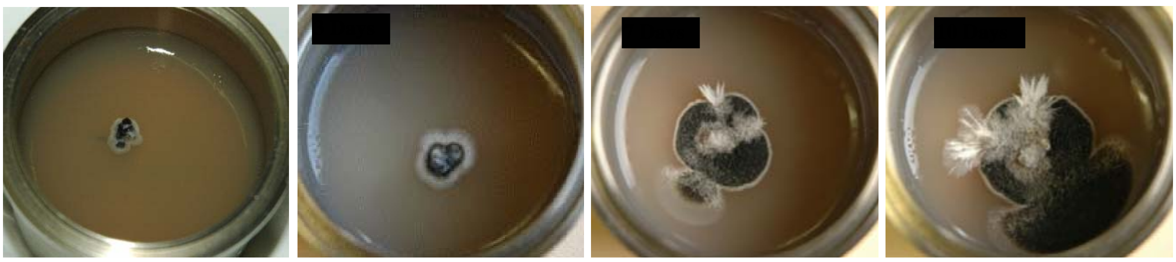


Figure 14 : Evolution of the principal MVOCs emitted by a strain of Aspergillus

2.4.3.3. Stachybotris

A strain of *Stachybotris* was injected on an agar medium. Before each sampling of emitted MVOCs, a visual examination of the microorganisms' development and a control of the system "*Stachybotris* on agar" were made (see Figure 15). This observation and a further examination at the end of the test with an optical microscope showed no environmental contamination by other microorganisms that the *Stachybotris* mould.



[redacted] [redacted] [redacted]

Figure 15 : Development of Stachybotris microorganisms over time

The chromatographic comparison of agar contaminated by *Stachybotris* and its blank allowed the isolation of the compounds emitted by *Stachybotris*. These identified MVOCs are four and are as follows: 3-methyl-1-butanol (black line in Figure 16), 1-octene-3-ol (light grey), butylated hydroxytoluene (grey) and 3-methyl-3-butene-1-ol (dark grey).

Unlike previous cases, the evolution of the emissions profile for *Stachybotris* does not follow any particular rule, except that once again 3-methyl-1-butanol is the only MVOC detected after 2 days of incubation. Its concentration decreases also gradually over time.

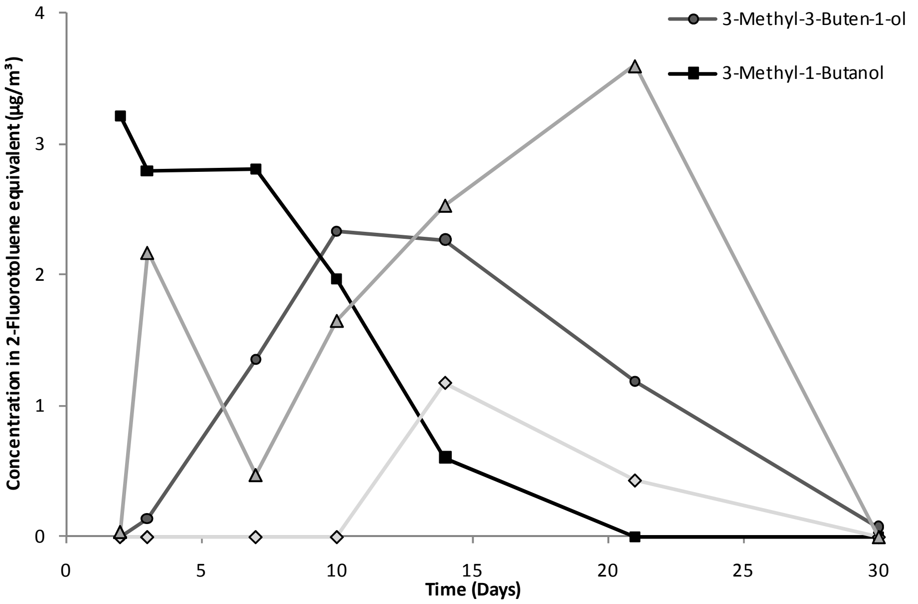


Figure 16 : Evolution of the principal MVOCs emitted by a strain of Stachybotris

2.4.3.4. Penicillium

A culture medium was contaminated with a strain of *Penicillium* by injection at the centre of the agar. A visual examination of the *Penicillium* development over time (Figure 17) shows a rapid growth of these moulds. Indeed, only 7 days after contaminating, the entire surface of the agar was fully covered with *Penicillium*.


[redacted] [redacted] [redacted] [redacted]

Figure 17 : Development of Penicillium microorganisms over time

The profile of MVOCs emitted by the *Penicillium* moulds growing on agar (Figure 18) shows again a predominance of 3-methyl-1-butanol after 2 days of incubation. However, instead of decreasing from that date, the concentration of this compound increases up to day 7 and begin decreasing slowly from a week of incubation.

At the same time, other MVOCs are emerging in the emissions from Penicillium: 3-methyl-3-butene-1-ol, 1-octene-3-ol and especially butylhydroxytoluene which is the MVOC with the highest concentration in the long term.

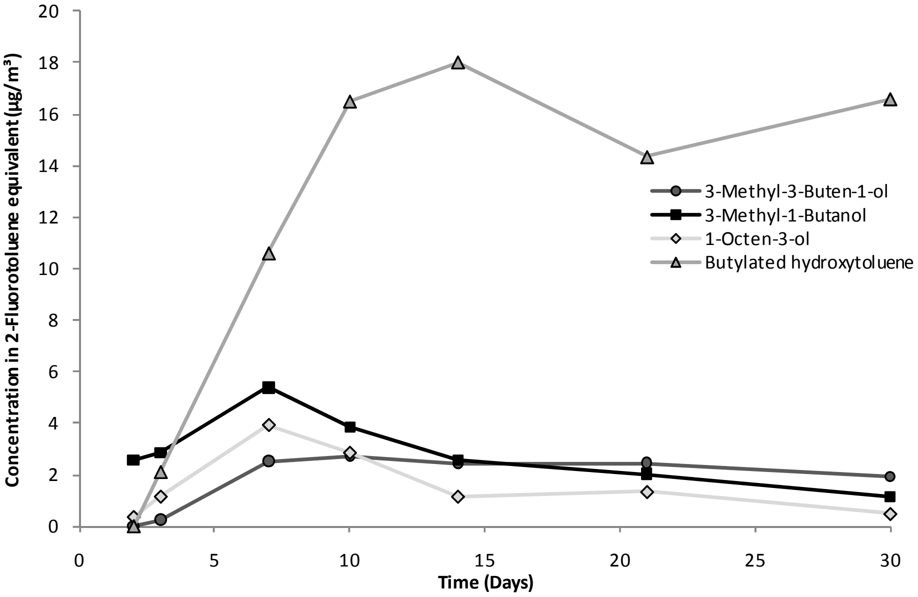


Figure 18 : Evolution of the principal MVOCs emitted by a strain of Penicillium

The concentration in air of the latter is increasing until it reaches nearly five times the initial concentration of 3-methyl-1-butanol. In this test, the maximum concentration of butylated hydroxytoluene is reached after 14 days of incubation.

The presence of 1-octene-3-ol in the emissions, as for it, is maximal after 7 days. This corresponds to the moment when *Penicillium* can no longer grow on the surface of the agar. To continue growing, *Penicillium* must thus change their metabolism and enter the medium.

2.4.3.5. Conclusions of preliminary tests of MVOC emissions by fungi

Various volatile organic compounds have been identified through this preliminary test despite a high emission profile from the blank reference, i.e. the agar medium used. In all four studied cases, two MVOCs are always present and helped to highlight a fungi activity. These two MVOCs are 3-methyl-1-butanol and butylated hydroxytoluene.

Changes of MVOCs over time for the four moulds may suggest that the identified compounds are chemical markers which could correspond to different stages of microorganisms' development. For example, in the case of Cladosporium, the butylated hydroxytoluene is not measurable in the early development of moulds, then the concentration of this VOC increases gradually until day 10 where its concentration reached a maximum. This date corresponds visually to the maximum stage of development at the surface (aerobic). From day 10, Cladosporium would be forced to change their metabolism to continue growing within the agar (anaerobic).

2.4.3.6. Tests on building materials

For this second series of tests, Penicillium was selected to contaminate a building material. The reason for this is the MVOCs point of view. Indeed, Penicillium is the fungus that produces the highest quantity of MVOCs when it grows on agar, especially after several weeks of incubation. It can be assumed that MVOC emissions on a building material will follow a similar pattern and/or will be easier identified. Since Penicillium grows readily on materials like OSB, it was natural to choose an OSB board as a support for the development of that fungus.

Nine OSB disks were cut from the same board. Two of them were used as references and were just placed into microchamber pots which are in turn placed in a beaker with a small quantity of pure water to ensure a good relative humidity level. A solution containing Penicillium strains was dropped on the other seven disks that were placed into the microchamber pots configured in “cell mode”. MVOC emissions from Penicillium on OSB samples were tested in two times: first a reference with four contaminated samples followed by the second reference with the remaining samples.

Table 6 lists the planning of measurements proposed for this test.

Sampling	Number of incubation days
1	2 days
2	3 days
3	7 days
4	10 days
5	14 days
6	21 days
7	35 days

Table 6 : Planning of screening tests of MVOC emissions from Penicillium on OSB using the so called µCTE method

The procedure described previously for the determination of MVOCs on agar was performed for each sampling. Terpenes form the main family of emitted VOCs by the samples, whether they are blank references or OSB samples contaminated by Penicillium. Among these terpenes, the most present are α-Pinene (R.T. = 16.43 min) and β-Pinene (R.T. = 18.22 min). Camphene (R.T. = 17.05 min), 3-Carene (R.T. = 19.56 min) and D-Limonene (R.T. = 20.27 min) were also easily identified.

The chromatograms obtained for the different sampling dates have been investigated exhaustively. Among all identified VOCs, only the 1-hexanol proves to be present in the emissions from all contaminated samples and not in the emission profiles from the blank reference.

Figure 19 below shows the presence of 1-hexanol in the emissions of the seven contaminated samples and its absence in those of the blank references.

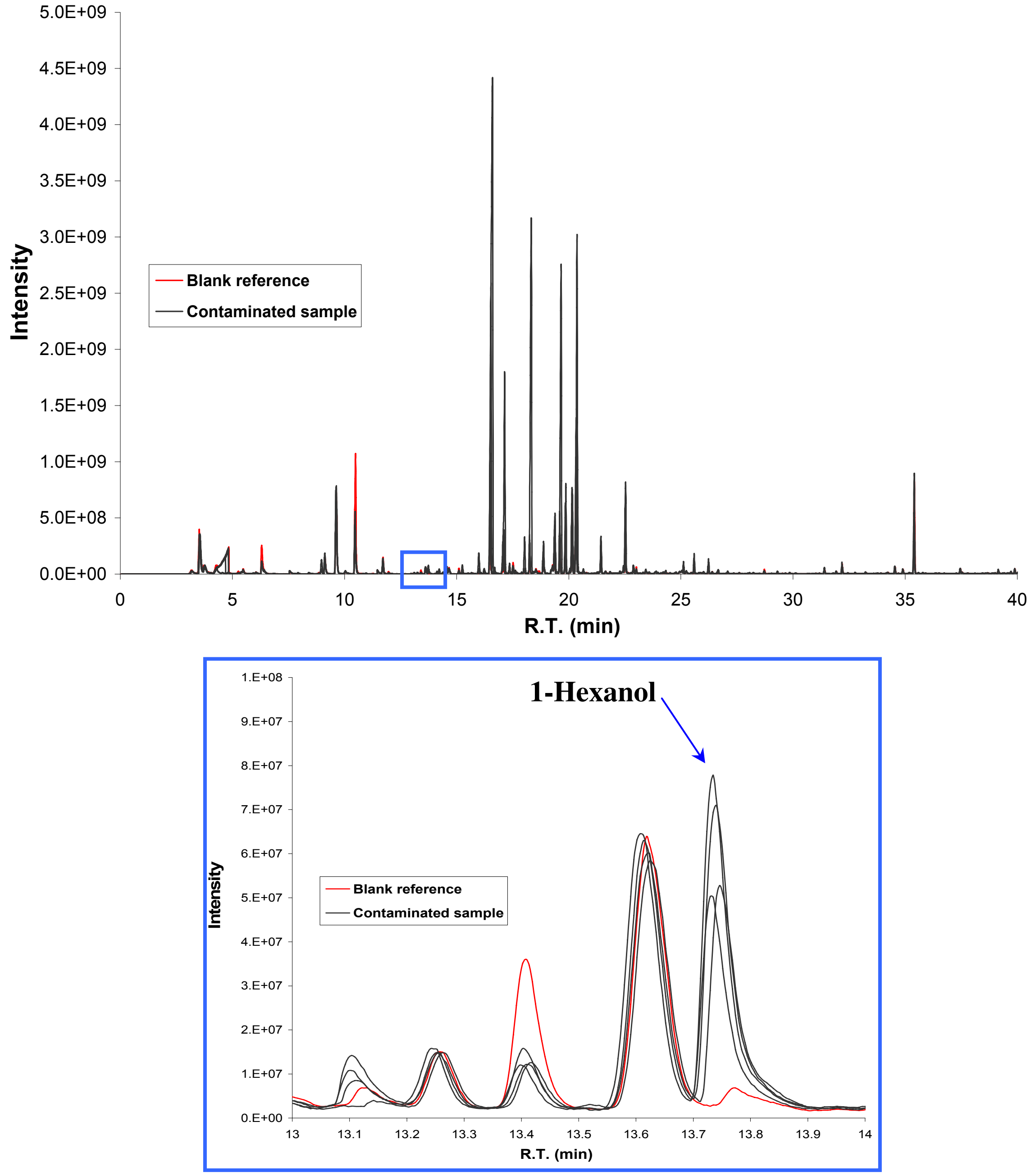


Figure 19 : Comparison of the chromatograms of the contaminated OSB samples and the blank reference

Although 1-hexanol is present in very low concentrations in the emissions from *Penicillium* on OSB, this compound can be identified with certainty as a MVOC. Indeed, the comparison of the peak area of 1-hexanol with the corresponding surface in the blank reference shows that the ratio of these surfaces is always higher than the detection limit (which is equal to 3 times the area of peak in the chromatogram of the blank). A minimum ratio of 4:1 is found in all of the analyses carried out and that ratio rose up to more than 10:1 in some cases (see Figure 20).

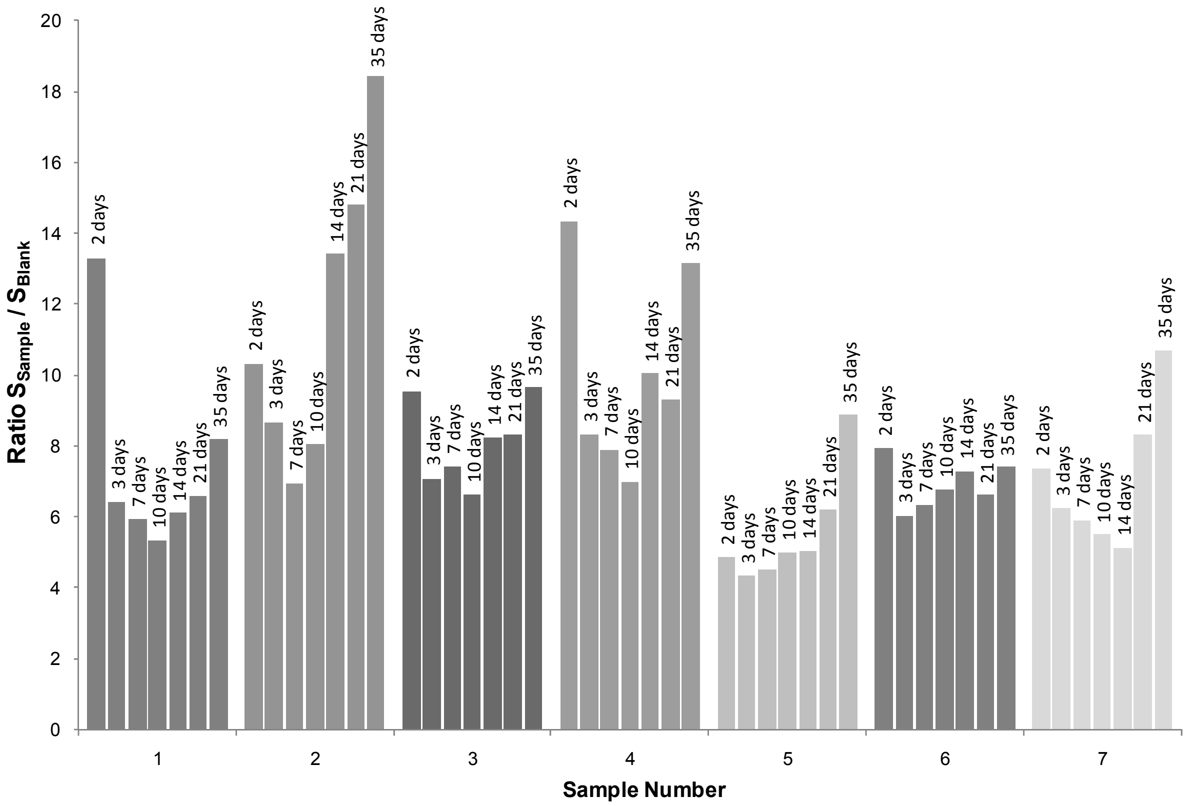


Figure 20 : Comparison of the 1-hexanol peak area for the contaminated sample and the blank reference

The concentration of 1-hexanol was calculated in 2-fluorotoluene equivalents and its evolution was studied over time as illustrated in Figure 21. The solid line represents the average of measurements obtained for OSB samples contaminated with a strain of Penicillium. The dashed lines show the experimental maximum deviations. Based on these results, 1-hexanol is already present just two days after contamination of the substrate. The concentration of this compound decreased slightly between day 3 and day 10, then it rises gradually until the end of the test.

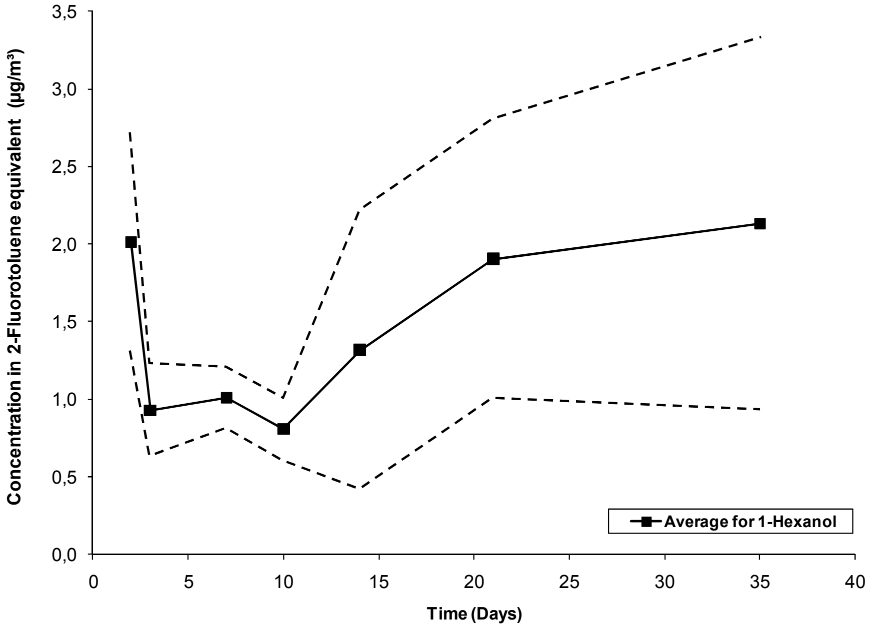


Figure 21 : Evolution of the 1-hexanol concentration in function of time for the contaminated OSB sample

3. Analysis of chamber VOCs emission data

3.1. Qualitative comparison

3.1.1. Motivation and objective

One of the objectives of this project was to study the influence of different emission chambers on VOCs emission data to develop alternative methods. In addition to the "chamber" influence, the "sampling day" and the "material type" effects have to be considered. To study these influences, chromatograms have been compared. An example of chromatograms obtained with the different techniques is shown in Figure 22.

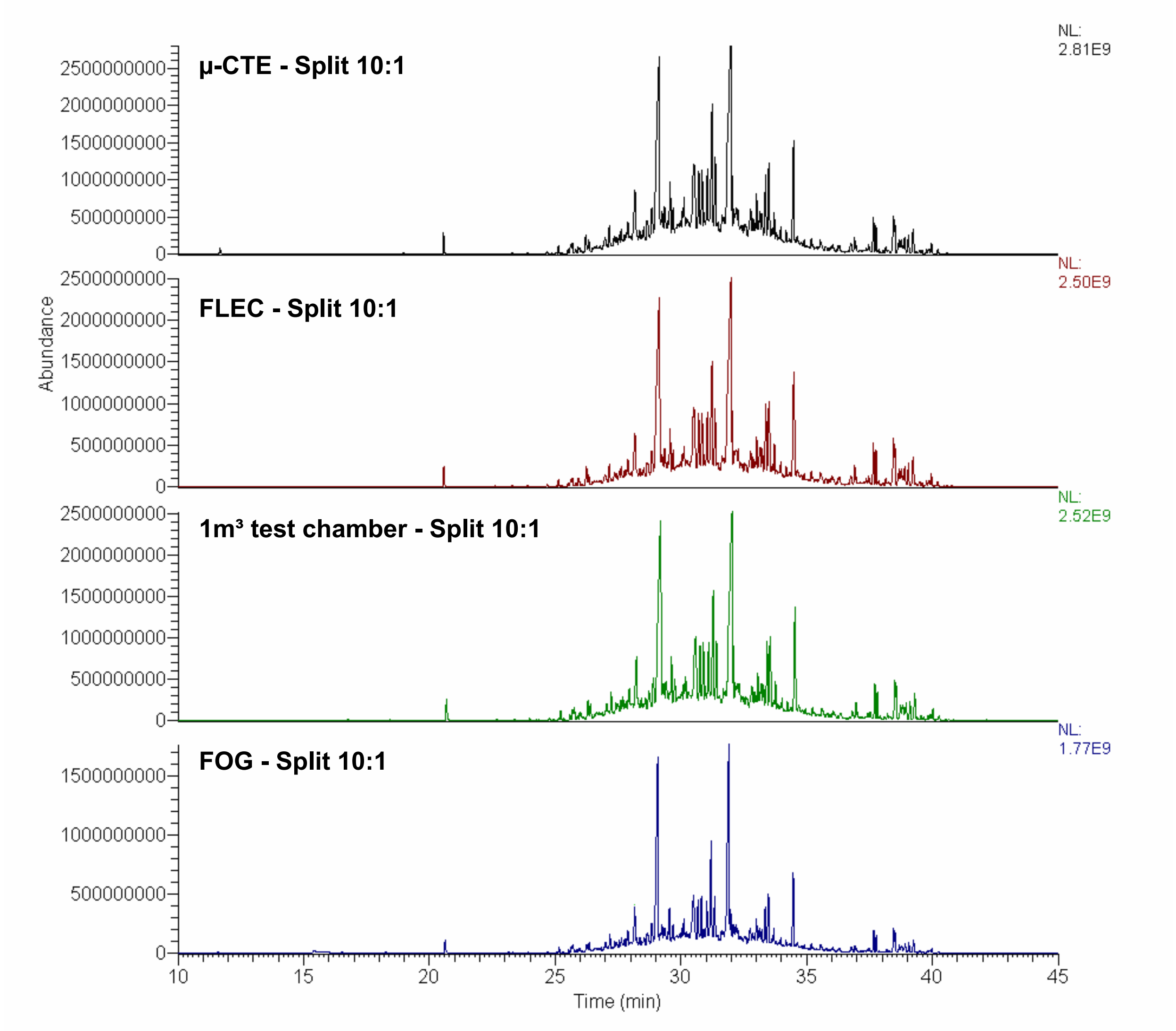


Figure 22 : **Qualitative comparison of results obtained (after 3 days) for a highly emissive PVC floor covering using various techniques**

But the integration of these three influences makes it difficult to compare the different results and the interpretation of emission data. Indeed, exhaustive analysis of the VOCs materials emission generates chromatograms with about one hundred various chemical compounds. For instance, and for one material, 18 chromatograms comparisons are imposed when combining the different occurrences for "chambers" and "sampling days". In this project, a global data processing has been proposed and tested to compare the numerous VOC emission data. These global methods, applied for many variables, are called multivariate data techniques. The multivariate data treatment is the support of chemometrics and is also frequently used in the environmental science but doesn't yet appear in indoor publications concerning chemical analyses treatment.

3.1.2. Methodology

In particular, a statistical method called principal component analysis (PCA) has been used on the HEMICPD emission data. To compare the chambers, a methodology has been conceived. 4 floor covering materials have been selected (material 1: PVC floor covering, material 2: PVC floor covering, material 3: Carpet, material 4: Linoleum). Samples of each material have been distributed to each chamber at the same time and the tests have been realised simultaneously to guarantee that the samples have the same age.

VOC’s sampling on Tenax has been performed after 3, 7 and 28 days in each chamber by each partner. The tubes have been sent to one partner (laboratory), randomly by material for TD-GC/MS analyses. Exhaustive analyses of the chromatograms have been made.

3.1.3. Input variables

Instead of VOC’s compounds, the **chemical families** have been considered. Several motivations explain this choice:

- All GC peaks are not recognizable and so the totality of the compounds are not identifiable;
- It is difficult to identify the isomers: for instance in the hydrocarbons families, there are a lot of isomers (i.e. uncertainty on the name 1-methyl-…. or 3-methyl-….?);
- Identifying correctly a chemical family to which a compound belongs is easier than recognising the exact name of the compound;

- Reduction of the variables (for a statistical analysis, many variables require ideally many data).

Variables used and database

As results, 10 chemical families specific of the 4 materials tested have been used to perform the chamber comparison: carboxylic acids, alkanes, alkenes, aromatics, ketones, aldehydes, alcohols, ethers, HAPs (polycyclic aromatic hydrocarbons) and cycloalkanes.

To create the family group, it is fundamental to consider compounds present in every sample. A database, merging all the identified compounds with a chemical family has been creating. The same database has to be used for each sample.

Data set

A total of 39 reliable observations have been used (Table 7). The values express the relative abundance of each chemical family, in percentage, for every chromatogram, with a total, for the 10 families, of 100%.

Chamber	Day	Sample	Organic acid	Alkane	Alkene	Alcohol	Aldehyde	Aromatic	Ketone	CycloAlkane	Ether	HAP
1 m^3	3	sample 1	4	21	2	3	7	48	2	5	8	0
1 m^3	28	sample 1	2	34	2	4	2	43	2	5	5	1
50 m^3	3	sample 1	2	30	4	4	21	26	2	8	2	1
50 m^3	7	sample 1	14	30	4	4	14	16	8	8	2	0
50 m^3	28	sample 1	3	38	3	1	13	13	2	23	4	0
Flec	3	sample 1	5	30	2	7	5	29	1	10	10	0
Flec	7	sample 1	4	29	1	9	7	31	3	7	10	0
Flec	31	sample 1	1	29	2	8	3	37	2	9	10	0
Flec	3	sample 2	0	79	0	1	0	9	2	6	1	3
Flec	7	sample 2	0	76	0	1	0	12	2	5	1	3
Flec	28	sample 2	0	76	0	1	0	12	2	5	1	3
50 m^3	3	sample 2	0	82	1	1	0	6	0	7	1	3
50 m^3	7	sample 2	0	77	0	1	0	9	2	6	1	2
50 m^3	28	sample 2	0	67	0	0	0	24	0	5	1	3
1 m^3	3	sample 2	0	80	0	1	0	8	0	6	1	3
1 m^3	7	sample 2	0	77	0	1	0	11	0	6	1	4
1 m^3	28	sample 2	0	70	0	1	0	22	0	5	1	2
micro	3	sample 2	0	56	0	2	0	36	1	3	1	1
1 m^3	3	sample 3	0	17	31	12	7	21	2	8	1	1
1 m^3	7	sample 3	1	17	23	10	11	24	3	10	1	0
1 m^3	28	sample 3	1	18	18	9	16	22	2	11	1	2
50 m^3	3	sample 3	0	60	8	5	6	7	4	8	2	1
50 m^3	7	sample 3	1	36	16	3	9	13	10	9	0	2
50 m^3	28	sample 3	0	12	11	1	4	66	2	2	0	1
Flec	3	sample 3	1	25	26	8	12	13	2	10	0	2
Flec	7	sample 3	2	25	31	10	5	14	0	8	0	6
Flec	28	sample 3	1	19	24	1	12	19	4	20	0	0
Flec	3	sample 4	19	0	7	0	70	4	0	0	0	0
Flec	7	sample 4	26	0	11	0	63	0	0	0	0	0
Flec	28	sample 4	27	0	8	0	65	0	0	0	0	0
50 m^3	3	sample 4	8	0	0	0	25	0	0	0	0	0
50 m^3	7	sample 4	8	0	0	0	26	0	0	0	0	0
50 m^3	28	sample 4	4	0	0	0	9	0	0	0	0	0
1 m^3	3	sample 4	13	0	7	0	55	10	15	0	0	0
1 m^3	7	sample 4	8	0	4	0	69	8	12	0	0	0
1 m^3	28	sample 4	11	0	16	0	56	5	12	0	0	0
micro	3	sample 4	11	5	4	5	76	0	0	0	0	0
micro	7	sample 4	21	4	6	0	70	0	0	0	0	0
micro	28	sample 4	0	4	6	0	90	0	0	0	0	0

Table 7 : Example of a chemical families data set for chambers comparison by PCA

3.1.4. Results

First, four variables (TVOCs, TSVOCs, SER_{TVOCs}, SER_{TSVOCs}) (SER: specific emission rate) are considered to classify the data. Material 2 behaves different than the 3 others samples (see Figure 23). The materials 1, 3 and 4 are well separated independently of the laboratory performing the analysis and the sampling day.

After this interesting first result, PCA on chemical families' data has been performed in order to give information on several questions:

1. Are the 4 materials well identified?
2. Is there an influence of the emission test chamber?
3. Which chemical families are specific of the materials?

In the PCA space, a chromatogram is a dot in a 2 or 3 dimensional plot. If the points are close, they are similar and indicate that they have the same chromatograms profiles.

1. Are the 4 materials well identified?

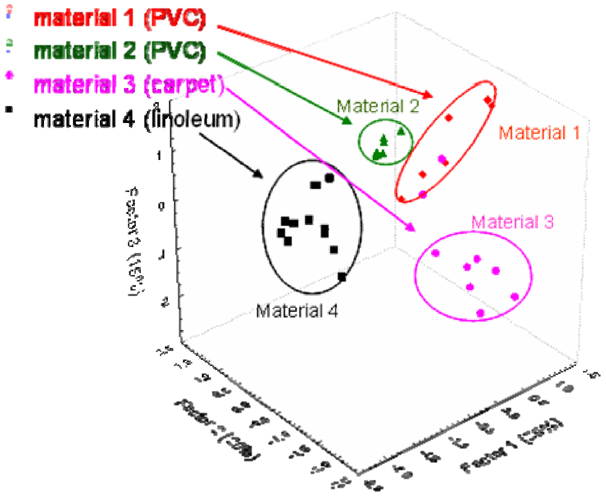


Figure 23 : PCA results, comparison of 4 floor covering materials for different test methods

The dots of the same materials are close and form a cluster. The two PVC groups are understandably close. The carpet is separated from the 3 others.

This result indicates that there is a good identification of the materials in all the chambers independently of the laboratory performing the analysis, the sampling days and the methodology.

2. Is there an influence of the emission chambers?

The plot above is used (Figure 23). The data set is the same but here the label classifies the different chambers.

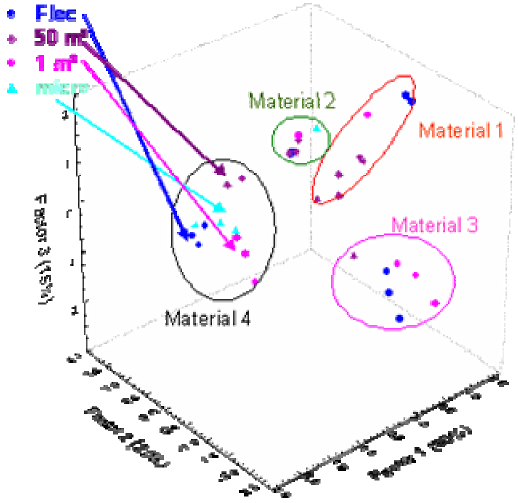


Figure 24 : **PCA results, comparison of floor covering materials by PCA (no influence of the test chambers)**

This figure indicates that there is no separation of the data (chromatograms-chemical family profiles) due to the different test chambers.

3. Which are the chemical families specific of the materials?

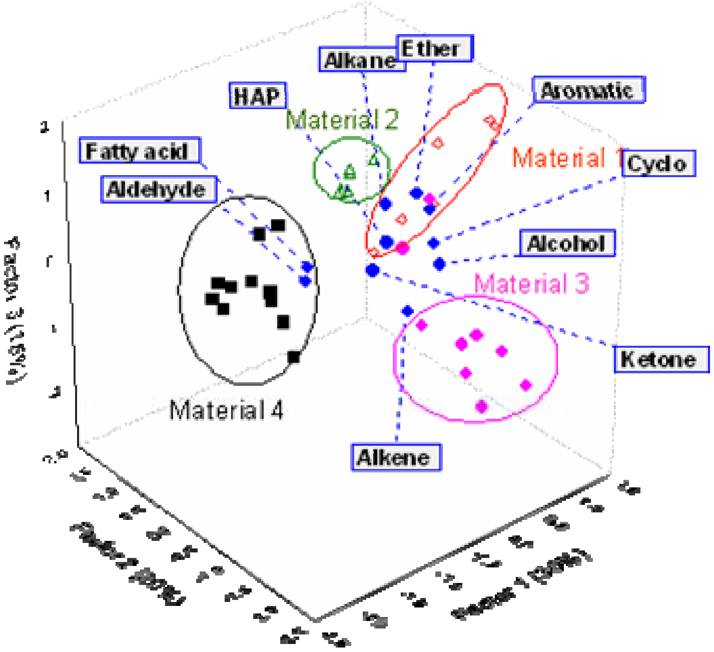


Figure 25 : Characterization of the chemical profile of the different materials by PCA loadings

The addition of the loadings (the chemical families) on the PCA plot gives an explanation about the material separation (see Figure 25). Sample 2 is characterised for instance by alkanes and sample 4 by fatty acids, aldehydes, aromatics, alcohols etc. For the sample 4, data analysed in the 50 m³ chamber are differentiated by a higher proportion of aromatics and alcohols.

3.1.5. Outcomes

The PCA results highlight that the type of chamber doesn't influence the qualitative and chemical families' relative abundance information. Each chamber generates the same chemical profile for the same material independently of the sampling day and the chamber volume.

Even the results, obtained in a real size chamber in less controlled conditions, are similar to the ones realised in a standardized emission chamber. It is a good starting point to evaluate the possibility to extrapolate the lab results to the field observations.

Multivariate data processing, like PCA, presents many advantages: easy tool to evaluate, in one shot, the analysis results and various parameters for indoor air chemical analysis. PCA highlights, in one shot, differences or similarities between data sets, reduces numerous variables to two or three while keeping a maximum of information. It's a tool to compare fast, easily and objectively the whole data set taking into account samples, chambers and days.

This part of the project has also pointed out that it is imperative, for a comparative approach, to create a data base common for all the tests.

The results show also that a pre-screening chamber would give the same VOC's profile results than a more complex one. A selection of a chamber, rapid, less material consumption, easy to manipulate and control (simple), able to manage different tests simultaneously is conceivable. For instance, "Flec" type chamber could be a good compromise, all the more VOC analyses and sensory tests are both realisable (see chapter 4, olfactory tests).

3.2. Semi-Quantitative comparison

3.2.1. The FLEC procedure (EN IS0 16000-10) versus the reference (1 m^3) test chamber (EN ISO 16000-9)

As already reported in the literature (see References list), data from chambers and cells are generally well correlated (i.e. results are within 25 % difference). This is especially the case for dry products (e.g. floor coverings) where the dominating emission mechanism from the material is diffusion. As emissions via internal diffusion are broadly independent of surface velocity, it is possible to compare meaningfully area specific emission rates (SERa) from the FLEC with that obtained using the 1 m³ test chamber.

In the HEMICPD project a comparison between the reference test chamber and the FLEC cell was made after 3 days. The selected building materials for the establishment of a correlation were linoleum and PVC floor coverings. These ones were both prepared according to EN ISO 16000-11 and placed in the two test chambers at the same date.

Sampling was carried out following the EN ISO 16000-9 and -10 procedures. Results obtained for TVOC and the main emitted compounds are shown in Figure 26.

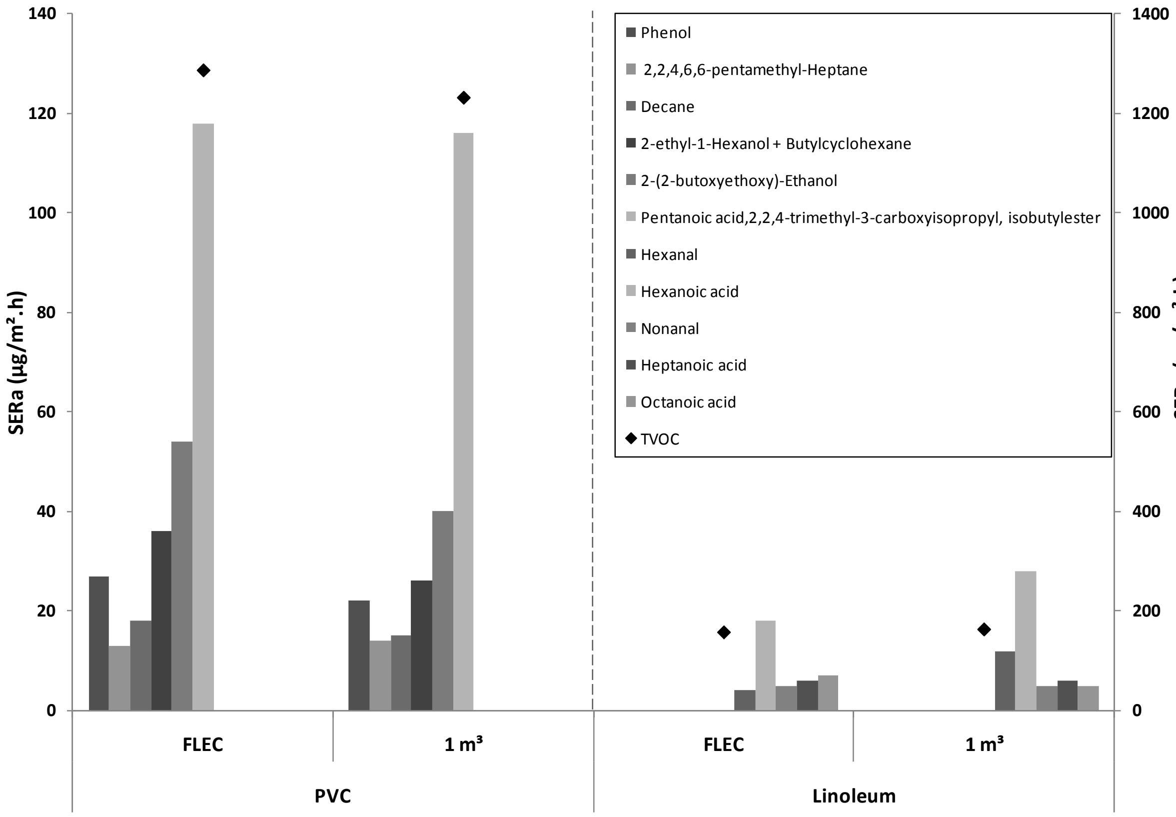


Figure 26 : Quantitative comparison between the FLEC cell and the reference test chamber for two different floor coverings tested after 3 days

Results of area specific emission rates obtained in this study show a satisfactory correlation (<25 % difference) between the cell and the test chamber, especially for TVOC for which the difference is lower. The next step is to extend the correlation to µ-CTE results for several building materials. To this end, various sampling methods were developed for the µ-CTE and were compared to the experimental procedure used for the FLEC.

3.2.2. The µ-CTE method compared to the FLEC (EN ISO 16000-10)

After obtaining good qualitative results with the PCA analysis and showing a satisfactory correlation between FLEC and the 1 m³ test chamber results, the next step is to determine µ-CTE parameters to provide comparable results with other chambers and to show that the microchamber method could be used for screening the VOCs emissions.

To assess the applicability of the µ-CTE as an indirect method for measuring emissions of VOCs from construction products, three floor coverings (PVC, wall-to-wall carpet and linoleum) and an insulating material were tested using three methods, i.e. a µ-CTE method, the EN ISO 16000-9 for 1 m³ and the EN ISO 16000-10 for FLEC measurements. The samples were prepared according to EN ISO 16000-11 by cutting discs having the microchamber's diameter.

For the first tests, the µ-CTE was operated with the so-called "procedure 1". This procedure was based on publications about the use of the microchamber (Schripp et al; Hugues et al) and aims at providing fast results concerning the emissions from tested materials.

In the "procedure 1", an inlet air flow of 100 mL/min was selected and a sampling of 1L air was performed. Specimens of a PVC floor covering were stored in the lab (controlled conditions of temperature and R.H.) until the day of testing. Sampling occurred 40 min after placing samples in the microchamber pots parameterised in cell mode thanks to aluminium spacers. Results from this first comparison with 1 m³ test chamber data are shown in the Figure 27.

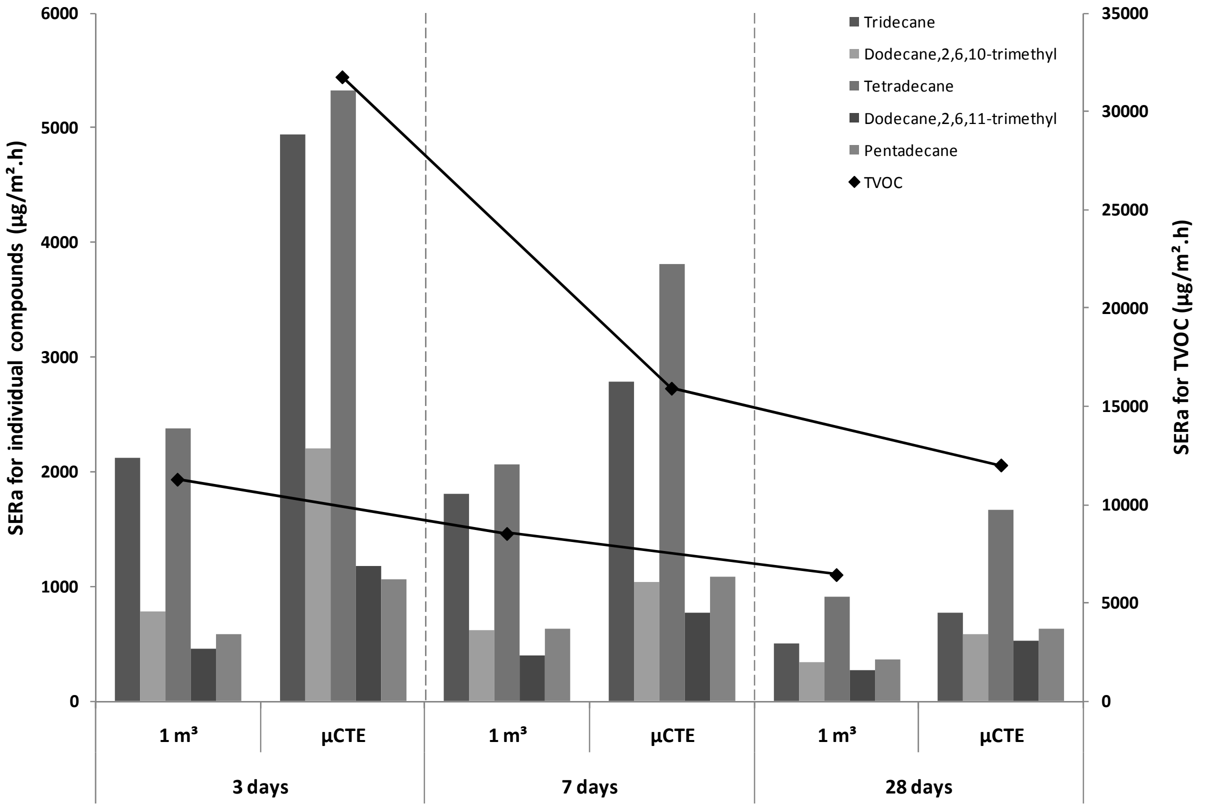


Figure 27 : **Quantitative comparison of emission profiles obtained for a sample of a high emissive PVC floor covering tested with the 1 m^3 test chamber and the µ-CTE with "procedure 1"**

Results from µ-CTE are obviously too high using this procedure to have a good correlation with standardised methods. This could be due to an insufficient air flow over the material while it is placed in lab. A second procedure was then proposed where the various tested materials were, as described in ISO 16000 series, placed immediately after unwrapping instead of being conditioned in laboratory as it was the case for the "procedure 1" used with the µ-CTE.

In the case of this second procedure, a linoleum floor covering was selected to be tested for comparing µ-CTE method with the EN ISO 16000-9 procedure. All of the parameters (temperature, humidity, sample flow and volume) were the same as for "procedure 1", the difference being that samples were placed in the µ-CTE at day 0 up to day 28. Results obtained using "procedure 2" are shown in Figure 28.

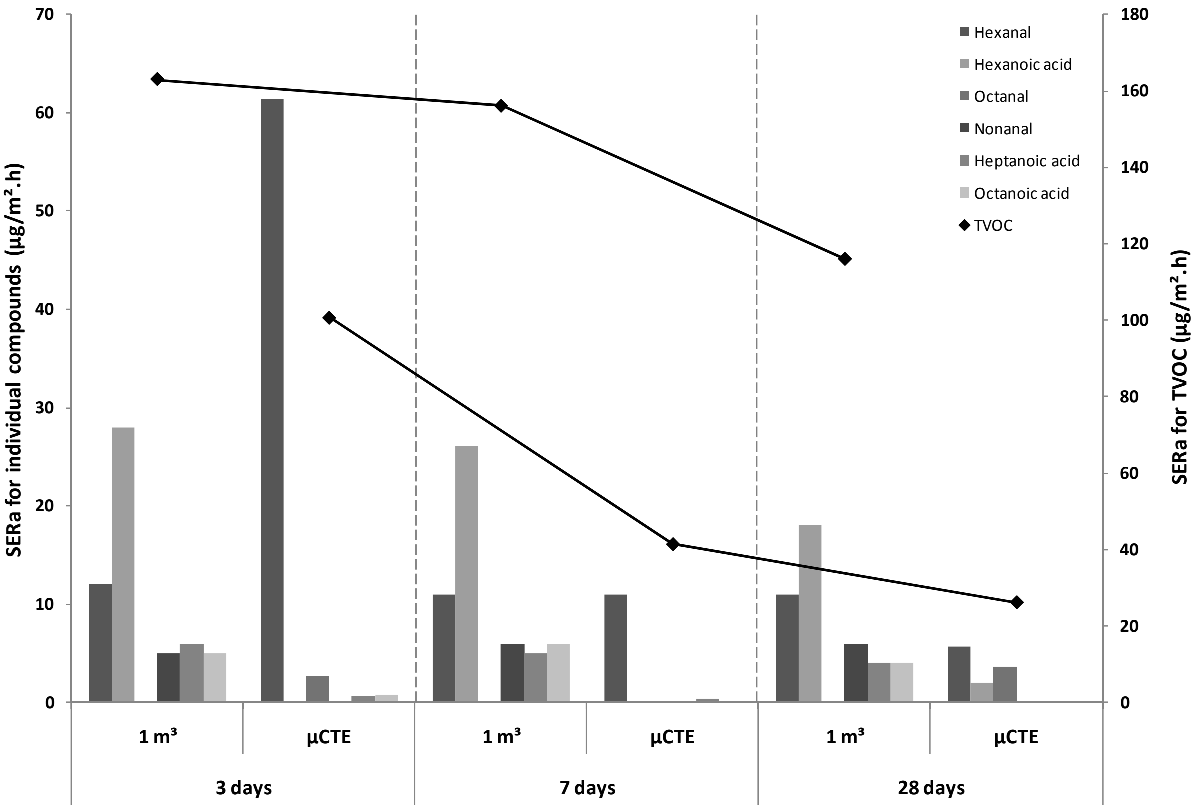


Figure 28 : **Quantitative comparison of emission profiles obtained for a sample of linoleum floor covering tested with the 1 m^3 test chamber and the μ-CTE with “procedure 2”**

In the latest developed procedure (i.e. “procedure 3”) for sampling with the μ-CTE, the microchamber was configured to work with an area specific air flow rate similar to the one used for other sampling methods (Table 8). Furthermore, the materials are placed in the microchamber pots on day 0 and were not removed from it till the end of the test. The μ-CTE is equipped with two different restrictors allowing selection of a low-flow (10-70 mL/min) or a high flow (50-500 mL/min). In this part of the project, the low-flow range was used exclusively.

Parameters	Values			
	μ-CTE	FLEC	1 m^3	50 m^3
Vchamber (m^3)	3.2 x10^{-6}	3.5 x 10^{-5}	1	50,53
Exch. Rate (h^{-1})	1875	514	0,5	0,5
L (m^2/m^3)	406	507	0,4	0,42
Q = n/L (m^3/m^2.h)	4,7	1,0	1,2	1,2

➡

Parameters	Values			
	μ-CTE	FLEC	1 m^3	50 m^3
Vchamber (m^3)	3.2 x10^{-6}	3.5 x 10^{-5}	1	50,53
Exch. Rate (h^{-1})	469	514	0,5	0,5
L (m^2/m^3)	406	507	0,4	0,42
Q = n/L (m^3/m^2.h)	1,2	1,0	1,2	1,2

Table 8 : **Sampling parameters changes from the first μ-CTE method (early in the project) to the newly developed procedure.**

Sampling was done on Tenax TA cartridges placed in series on the output of the μ-CTE under the following conditions:

- Temperature: 23 °C ± 2 °C;
- Relative humidity: 0 % ± 5 %;

- Sampling flow: 25 mL/min ± 0.2 mL/min;
- Sampling duration: 80 minutes;
- Sampled volume: 2,0 L.

3.2.2.1. Tests on floor coverings

Emissions from each floor covering were sampled with the FLEC and the µ-CTE at the same time to ensure that the obtained results are comparable. VOCs' sampling on Tenax was carried out in duplicate after 3 and 28 days with each sampling device. The sampled tubes were all analysed by TD-GC/MS by the same lab. Exhaustive analyses of the chromatograms have been made.

Figure 29 shows the results obtained for the PVC sample tested after 3 days. The range of concentrations in 2-fluorotoluene equivalents for individual compounds goes from 2 µg/m³ to 200 µg/m³.

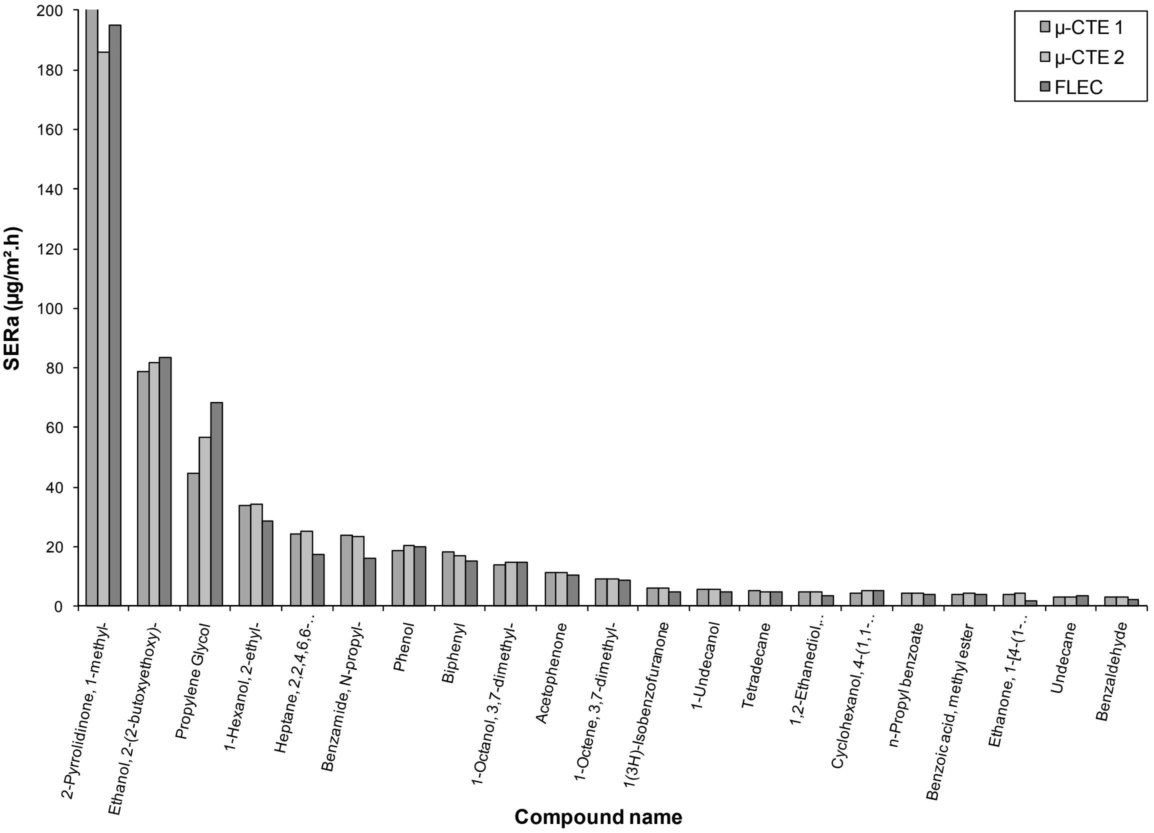


Figure 29 : Comparison of individual emissions from a sample of PVC floor covering tested after 3 days with the FLEC and µ-CTE procedures

A good correlation is obtained between the results with the µ-CTE method and those from the FLEC, as well for compounds present in high concentration as for those at trace level.

Figure 30 presents the quantitative comparison of TVOCs calculated in 2-fluorotoluene equivalents for the PVC floor covering tested after 3 days with the µ-CTE and the FLEC methods.

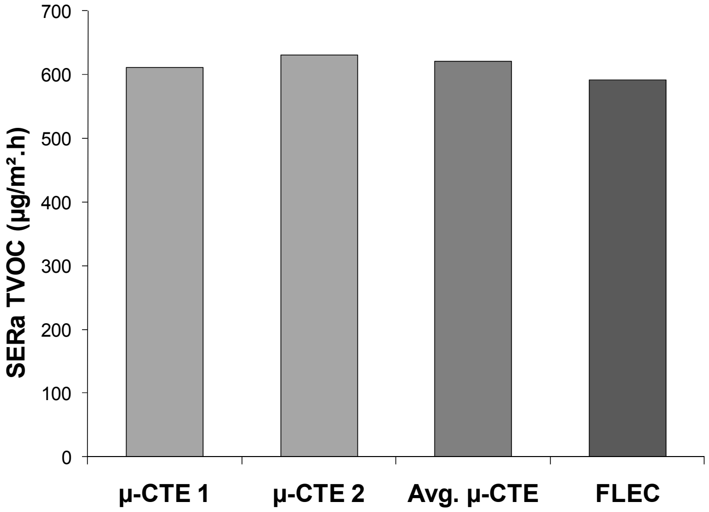


Figure 30 : **Comparison of TVOCs emitted by a sample floor covering tested after 3 days with the FLEC and µ-CTE procedures**

These results show a good correlation between these two sampling methods with a maximum deviation of less than 25 % for TVOC. This is promising for the use of the microchamber as an indirect method for the screening of VOCs emitted by building materials.

The second tested floor covering was a linoleum. This material was sampled with the same procedure as the PVC floor covering in order to evaluate the performance of the new µ-CTE method. The results obtained for the principal emitted compounds were calculated in 2-fluorotoluene equivalents and are shown in Figure 31.

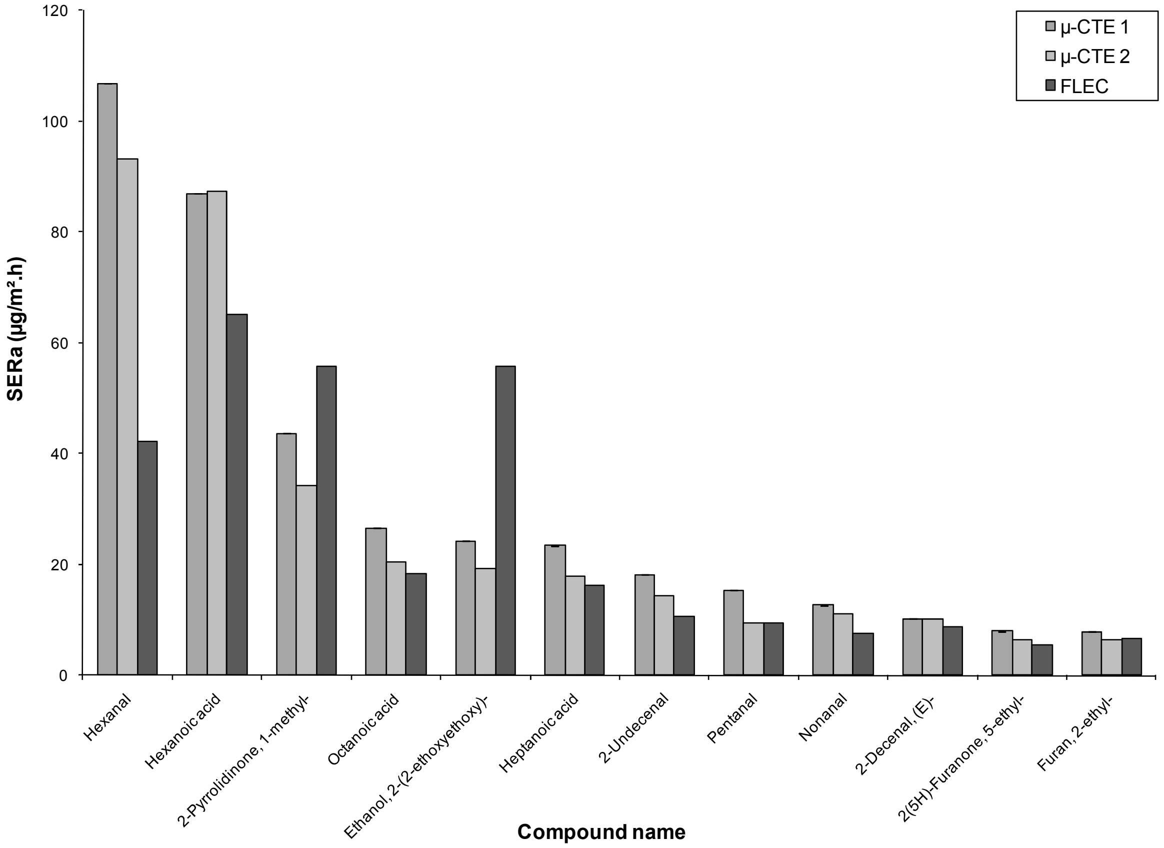


Figure 31 : Comparison of individual emissions from a sample of linoleum floor covering tested after 3 days with the FLEC and µ-CTE procedures.

Among these twelve studied VOCs, a correlation with a standard deviation < 20 % is observed for eight of them: Hexanoic acid, Octanoic acid, Heptanoic acid, 2-Undecenal, Pentanal, 2-Decenal, (E)-, 2(5H)-Furanone, 5-ethyl- and Furan, 2-ethyl-. For the other compounds a higher standard deviation is observed.

For these eight compounds, as well as for TVOC (see Figure 32 below), the results from the µ-CTE 2 are closer to the results from the FLEC than those obtained with the µ-CTE 1. This could be a consequence of a possible – but not so significant – inhomogeneity of the linoleum floor covering.

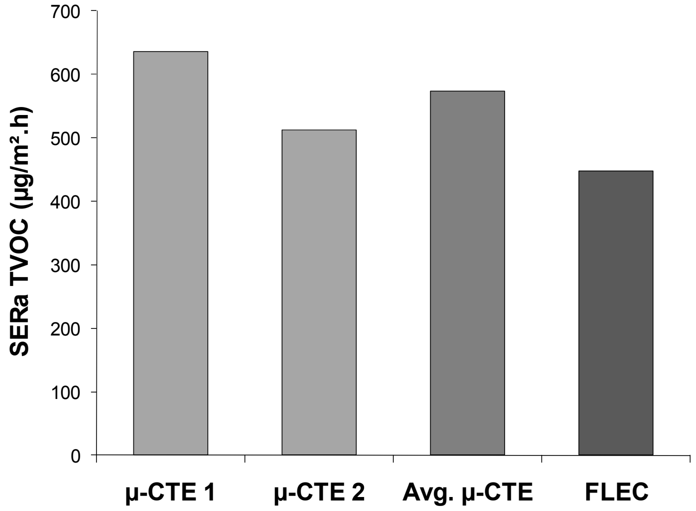


Figure 32 : Comparison of TVOCs emitted by a sample of a linoleum floor covering tested after 3 days with the FLEC and the µ-CTE procedures

Finally, a wall-to-wall carpet was tested to compare the µ-CTE method with the standardized EN ISO 16000-10 procedure. As this material emits low concentrations of VOCs compared to the tested linoleum and PVC floor coverings, only TVOC results are presented here (Figure 33); the individual concentrations of detected compounds ranging only from 2 µg/m³ to 5 µg/m³.

The standard deviation calculated between the average of the µ-CTE results and the one from FLEC sampling is 3%, what proves that a good correlation between these two sampling methods can be achieved for floor coverings.

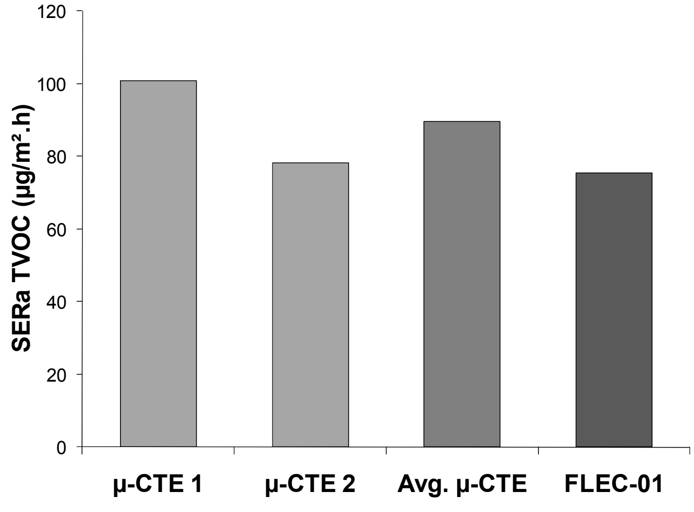


Figure 33 : Comparison of TVOCs emitted by a sample of a wall-to-wall carpet floor covering tested after 3 days with the FLEC and the µ-CTE procedures

3.2.2.2. Tests on an insulation material

An insulation material (XPS with a wood wool backing) was selected to perform a repeatability test using the µ-CTE and for the comparison of the obtained results with a standardised method (ISO 16000-10).

Circular test specimens are cut from the insulating material to fit into the microchamber pots. They are then placed into a microchamber and the sampling flow is parameterised on 25 mL/min to ensure a specific air flow rate *q* in the same range as for the 1 m³ test chamber and the FLEC. The environmental conditions are kept constant the entire test (23 °C, 0 % R.H.). Samples were taken at 3, 7 and 28 days after the start of the emission test.

For FLEC measurements, two specimens were prepared according to EN ISO 16000-11. The first one was directly used with the FLEC, acting as a wall of the cell. The second one, as for it, was cut into a disk to fit the subunit, an accessory for the FLEC which can be regarded as a small test chamber open on its top. Given the porosity of the insulation material, results obtained with the subunit are expected to be higher than without the use of a subunit.

An exhaustive identification was done on the chromatograms and the concentration of individual compounds was calculated and expressed as 2-fluorotoluene equivalents. TVOC determined for the various sampling dates and instruments is given in Figure 34. Although a difference of a factor 2 between the microchamber pots n°2 and n°3 (called µ-CTE 2 and µ-CTE 3 in the figure) after 3 days, the average value obtained for the µ-CTE measurements is identical to those for FLEC, whether with and without the subunit. The results are still comparable between the FLEC (with subunit) and the µ-CTE after 7 days.

Concerning results without the subunit the concentration of TVOC decreases more slowly. The evolution of values determined for the main compounds – pentane and styrene (Figure 35 and Figure 36) – show that in certain cases the use of an accessory like the subunit is required in order to take into account the nature of the material. In the present case, a lack of air tightness (leaks >> 5 %) is observed due to the porosity of the material, showing that it is preferable to make use of the subunit.

Results between the two sampling devices differ a little for the test conducted after 28 days: the concentration for samples measured with the µ-CTE is not significantly different from those obtained after 7 days while for air samples from the FLEC with subunit a decrease from 78 µg/m³ to 18 µg/m³ is observed.

Nevertheless, this study shows that the values obtained using the microchamber as an indirect method are acceptable to achieve a pre-screening on building materials.

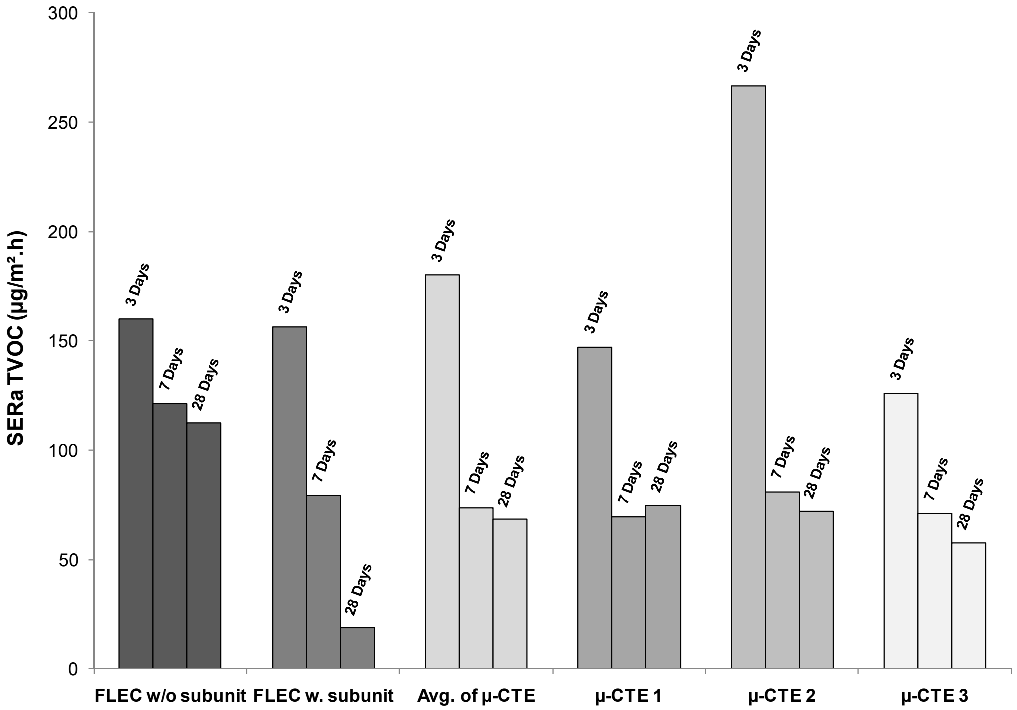


Figure 34 : Comparison of TVOCs emitted by a sample of an XPS insulating board with a wood backing using the FLEC and the µ-CTE methods

The two main compounds emitted by this insulation material, namely pentane (VVOC) and styrene (VOC), have also been studied over time. A comparison of data from the µ-CTE sampling and those from FLEC are shown in Figure 35 and Figure 36. It can be observed that the concentration of pentane calculated for the µ-CTE (all the microchamber pots together) is 2 to 3 times higher than the result for the same material tested with the FLEC. The opposite is observed for styrene (Figure 36). In the latter case, these are the values determined for the sample tested with the FLEC that are much higher than those from the use of the µ-CTE. However, for pentane as for styrene, the evolutions over time of these compounds are similar with both sampling methods.

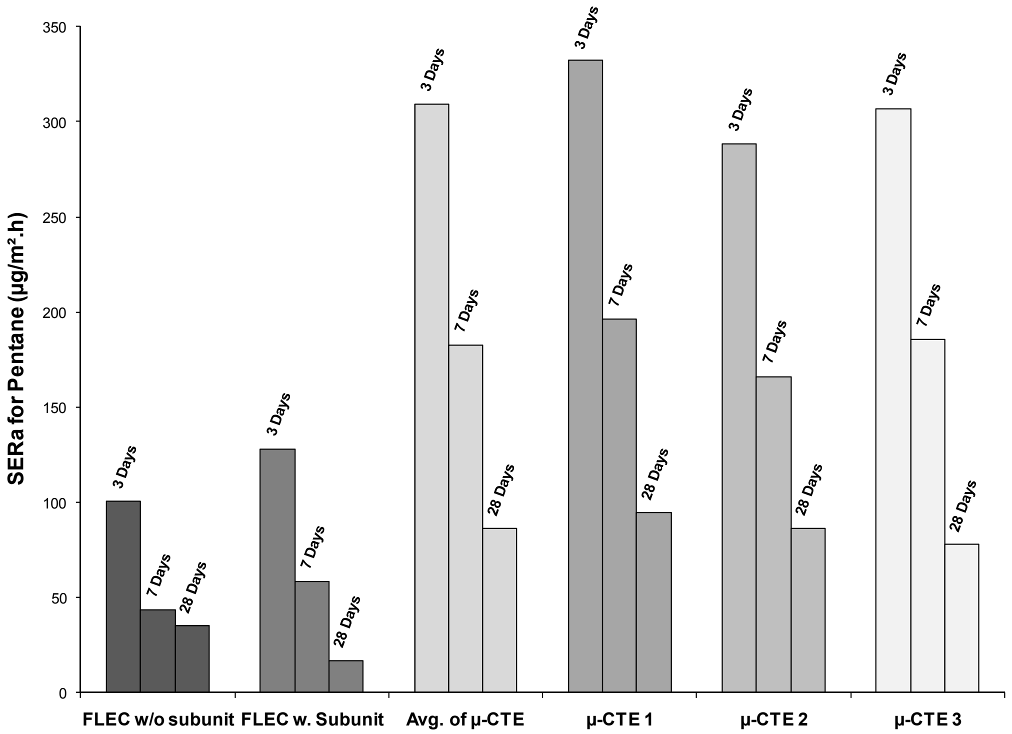


Figure 35 : **Comparison of pentane emissions (sampling with FLEC and u-CTE) from a sample of insulation material**

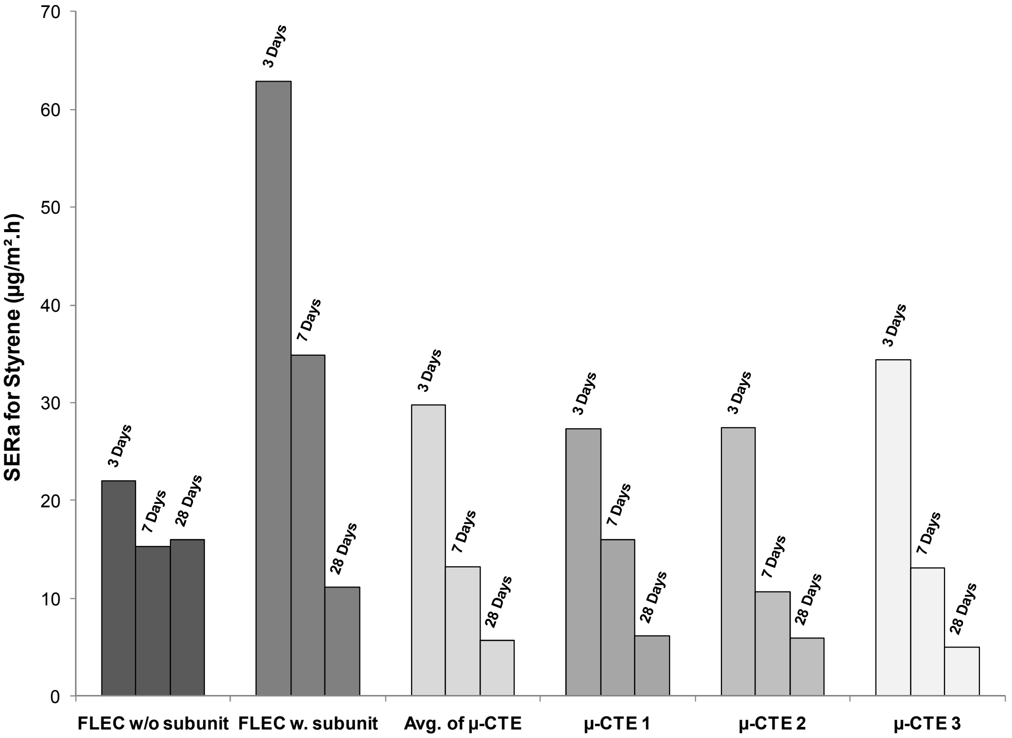


Figure 36 : **Comparison of styrene emissions (sampling with FLEC and µ-CTE) from a sample of insulation material**

3.2.2.3. Conclusions

Firstly, it has been shown that the microchamber data were reproducible for all four tested materials (PVC floor covering, linoleum, wall-to-wall carpet and insulation material). As already reported by P. Hugues et al., this sampling instrument is really convenient and is less reliant on the expertise of the user.

This project has also shown that the µ-CTE gives semi-quantitative results with a pretty good correlation compared to those obtained using with the FLEC, making the Micro-Chamber Thermal Extractor a suitable tool for screening materials in order to have an idea of the concentration range for emitted VOCs.

Indeed, even in the case of the XPS insulation material – where pentane and styrene concentrations were not the same – the emission profiles of these two main compounds using the µ-CTE and the FLEC behave the same over time.

4. Olfactory tests

4.1. Selection and development of a sensory method

4.1.1. Context

The state of the art report highlights the diversity in the existing sensory methods (see separate state of the art report, chapter 5).

At present, sensory evaluation is not yet integrated in all labels and standards. The measurement uncertainties and poorly reproducible results describe this fact. A lack of harmonisation is observed and explained partially the weaknesses of a sensory evaluation

In the sensory methods, the sampling strategy, the panel selection and the data processing are as important as measurement itself. In this project, attention is given to the measurement sequence (from the sampling to the data processing).

The odour perception can be determined by four major dimensions: concentration - detection threshold, intensity, quality and hedonic tone.

4.1.2. HEMICPD sensory methodology

After comparison and interpretation of the weaknesses and the strengths of the several existing methods, a methodology has been elaborated. Previous experience in off-odour measurements for environmental field investigations was useful to understand and to develop the scientific concepts.

Odour dimensions selection

The intensity and the hedonic tone (plus the acceptability) have been selected to evaluate building materials.

- For material tests, intensity is more significant than the odour concentration. The odour concentration of materials is weak (in regard to environmental outdoor odour) and of the same magnitude as the instrument detection limit. Tests realised on flooring materials, in the ULg olfactometric laboratory with the EN 13725 standard method, have proven this statement. Intensity is more adapted for low odour emissions typical of building materials, more indicative of “annoyance” (quality and quantity dimensions) and largely used in indoor investigations.

- The hedonic tone gives information on the odour material acceptability and is important to qualify the material.

Contrary to the odour concentration, there is no European standard for the intensity and the hedonic tone. However recently, an international working group (ISO 146-6 WG 14: ISO 16000-28) has emerged to work on "Indoor air: sensory evaluation of emissions from building materials and products".

Measurement methods

For the intensity, the "comparative scale" method has been preferred to the magnitude estimation method. The magnitude method is simply a numeric scale without reference chemical. The comparative scale guarantees better reproducibility between the measurements and higher homogeneity between panel members. The selected reference gas is n-butanol.

Comparison between odour delivery static method (headspace sniffing in glass vials without flow) and dynamic method (sniffing at the exit of a funnel with controlled flow) has been performed. The dynamic method had a better reproducibility and has been chosen.

The hedonic tone has been valuated by a nine level scale according to VDI 3882-2 standard (Figure 37).

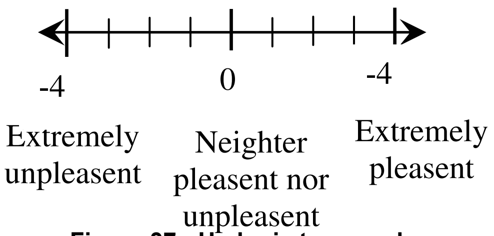


Figure 37 : Hedonic tone scale

Instrumentation

The ULg olfactometric laboratory is equipped to measure the odour concentration. In this project, a specific instrument (called "Perceptor") has been developed in respect to the ASTM E544 standard (Practices for Referencing Suprathreshold Odor Intensity, 99, 2004) to evaluate the intensity.

The instrument is based on the simultaneous presentation to expert panellists of 8 n-butanol concentration levels in geometric progression. It comprises two parts, an air supply system and an odorant vaporization-dilution system. The synthetic odourless air functions both as a carrier gas and as a diluent for n-butanol vapour.

The vaporization chamber is made of a horizontal glass vessel containing liquid butanol. A part of the air flow passes over the headspace and converts the saturated vapour to a gas mixture. It is mixed again with the other portion of the air, flowing through the bypass capillary.

This mixture goes to the stimulus-flow splitter, which is made of 8 stainless steel capillaries distributing the diluted n-butanol to 8 sniffing ports. The different dimensions of the capillaries (lengths and inside diameters) are such that each port receives a different flow of n-butanol.

A second air supply system acts as make-up air. It is connected to a second splitter made of capillaries of dimensions such that they supply to each port the complementary flow in order to assure that the total flow from each of the ports is always the same (150 mL/min).

The result is a stimulus presentation system with eight ports, with each concentration differing from the preceding one by a factor of two. These eight concentrations of n-butanol flow continuously from eight sniffing ports with the same flow rate.

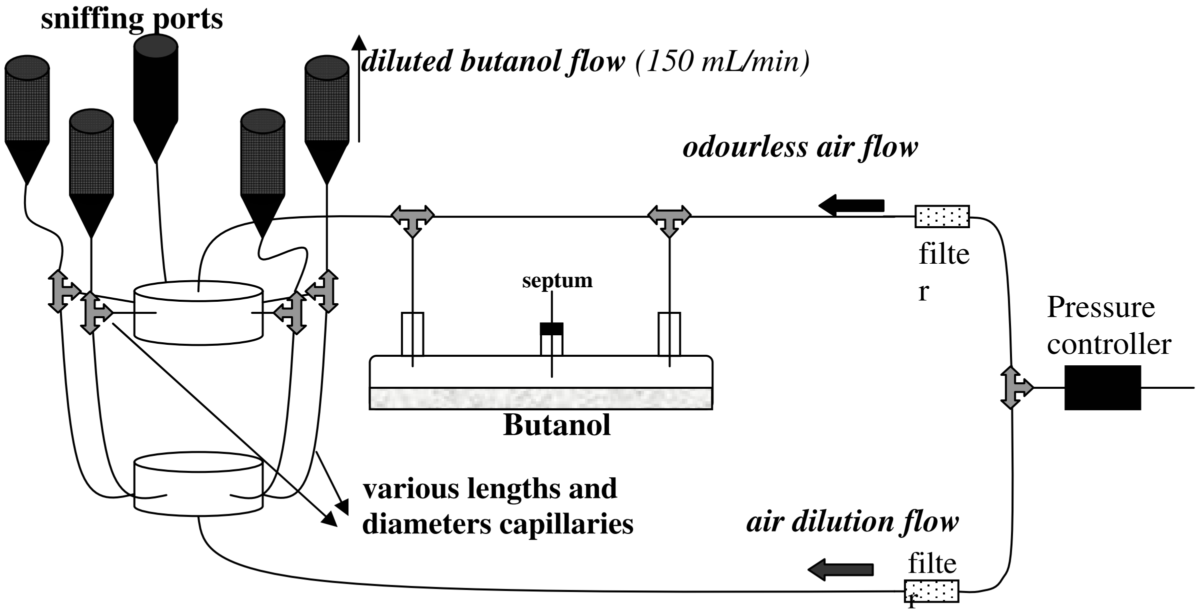


Figure 38 : "Perceptor" principle (in this figure, only 5 ports are shown)

Sampling

It is important, for the reliability, to sniff the sample by the same way as the reference chemical. In order to have a high control of the odour delivery, the dynamic method has been chosen (see previous paragraph).

Various sampling tools have been tested:

- <u>Desiccator</u>

  A piece of material is placed in a familiar desiccator but there is no regulated flow and a high variability is reported.
- <u>Plastic bags (in Tedlar)</u>

  It requires a high air volume (at least 20 litres) in the bag and a large size emission chamber. A sampling step is obligatory. A delivery system under pressure is necessary in order to compress the bag and generate the odour flow. Moreover a fastidious cleaning procedure of the bag is necessary to decrease its own odour. Even after cleaning, the bag is not completely odourless and can interfere when low odour intensity material is sampled.
- <u>Outlet of medium and large emission chambers (1 m^3 and 50 m^3)</u>

  The panellists sniff, on line, the exhaust of the emission chamber. It is easy to realise even if it imposes to locate the "perceptor" next to the chamber. There is no need to have additional odour sampling systems. However, it requires having emission chambers of great size. A major disadvantage is the flow difference between the emission chamber and the perceptor.
- <u>Smaller emission chamber like the "Flec" system</u>

  The advantages are the same as for the medium and large chambers. Moreover, it is easier to regulate a similar flow between the chamber and the perceptor. "Flec" is used together with a subunit part. The system is small, easy to manage and permit to carry out olfactory tests and physicochemical analyses with the same chamber. Temperature and humidity are also regulated.

Finally, among the various tested sampling tools, the FLEC system has been selected for the sensory method.

Sampling procedure (Figure 39)

It’s important to clean the FLEC and the subunit with methanol to eliminate any traces of impurities that could influenced the test. It’s also advised to put the FLEC in an oven at 60°C for a couple of hours.

The material to be tested is placed in the subunit and the FLEC is put on the top of the subunit. The bottom of the FLEC leaves an area of 177 cm² open for the test material.

The supply air (dilution/humidification unit) is connected in the top of the FLEC cell. The total flow is adjusted. The relative humidity is regulated at 50 % and the temperature at 23°C. The air is distributed through a narrow slot to the entire cell and collected again in the centre.

The contamination of the cell from the outside is avoided by a positive pressure within the cell.

The funnel (sniffing port) is connected to the FLEC output, placed on the top of the cell. The air flow is kept for at least a day before performing the test.

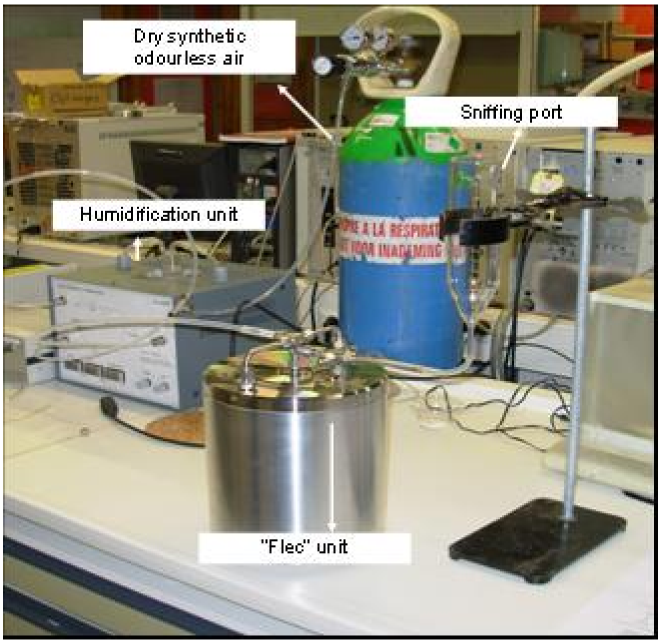


Figure 39 : Odour sampling procedure

Panel requirements

- The number of panellists should be eight or more, to permit elementary statistical tests on their judgments.
- Precautions must be taken in the selection of the panellists. They are issued from the certified panel of the ULg olfactometric laboratory. This panel is tested according to the EN 13725 standard (with butanol).

- An individual with insufficient sensitivity should not be a panellist. Also, some individuals that have been observed to experience difficulty in matching odour intensities shouldn't be used.

Odour Test

The odour test consists of two parts, the Acceptability measurement and the Intensity measurement.

To the participants a questionnaire is given (Figure 40) that they must fill in, according to their perception. The questionnaire has 3 questions regarding acceptability and 2 questions regarding the intensity of the odour.

For the intensity measurement, the participants are confronted with a 1-butanol reference scale (Perceptor), and they are asked to identify, within the butanol scale, the concentration that resembles the sample intensity the most. They are instructed to smell the unknown sample and then to smell the scale, beginning with its weakest end. The odour of the sample is, by this way, matched, ignoring differences in odour quality, against the odour intensity reference scale of 1-butanol. Participants report that point in the reference scale which, in their opinion, matches the odour intensity of the unknown. The participants are also advised that they may report a match between two adjacent points (for example 4.5, i.e., it's stronger than scale point n° 4, but weaker than scale point n° 5). They should also be advised that the odour may also be weaker than the weakest point of the scale, or stronger than the strongest point of the scale.

NAME ________________________________ DATE ____________ SAMPLE ________

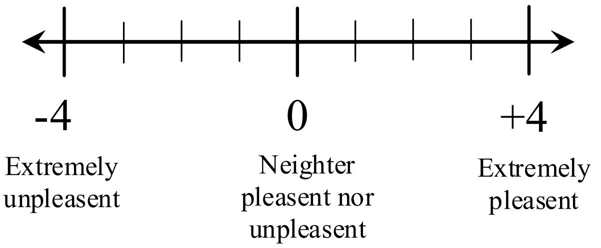
1. How do you describe the odour?

GOOD ☐
PLEASANT ☐
SATISFACTORY ☐
UNPLEASENT ☐
DISGUSTING ☐

2. Imagine you would have to stay in a room with this odour for an entire day, how would you considerer the odour?

Acceptable ☐ Not Acceptable ☐

3. Mark on point on the scale, which corresponds to the odour sample perception:



4. Would you considerer the sample:

NO ODOUR ___
SLIGHT ODOUR ___
MODERATE ODOUR ___
STRONG ODOUR ___
VERY STRONG ODOUR ___
OVERPOWERING ODOUR ___

5. Which of the eight point scale is similar to the odour sample?

1 ☐ 2 ☐ 3 ☐ 4 ☐ 5 ☐ 6 ☐ 7 ☐ 8 ☐
0.5 ☐ 1.5 ☐ 2.5 ☐ 3.5 ☐ 4.5 ☐ 5.5 ☐ 6.5 ☐ 7.5 ☐ 8.5 ☐

Figure 40 : Odour questionnaire

4.2. Sensory measurements on building materials

The previous sampling tools tests, the development of the "perceptor'" and the elaboration of the methodology are important outputs for the sensory part of the project.

4.2.1. Intensity versus hedonic tone (and acceptability)

After tool and methodology development, sensory tests, with the elected procedure, have been performed on 6 flooring materials after 3 days in the "FLEC system": 2 PVC floor coverings, 2 linoleums, 1 carpet and 1 versatile rubber flooring, older than the other materials (Figure 41).

Figure 41 : Materials sampled used for the sensory tests

Figure 42 shows Intensity/Hedonic tone relation for these materials. For this type of building materials, high odour intensity corresponds to unpleasantness odour (negatives values). Weak intensities and pleasantness's are reported for the two PVC materials. Moreover, for these materials, the acceptability percentages are respectively 100% and 80%.

The acceptability percentages for the other materials are less than 25% except for the carpet (78%).

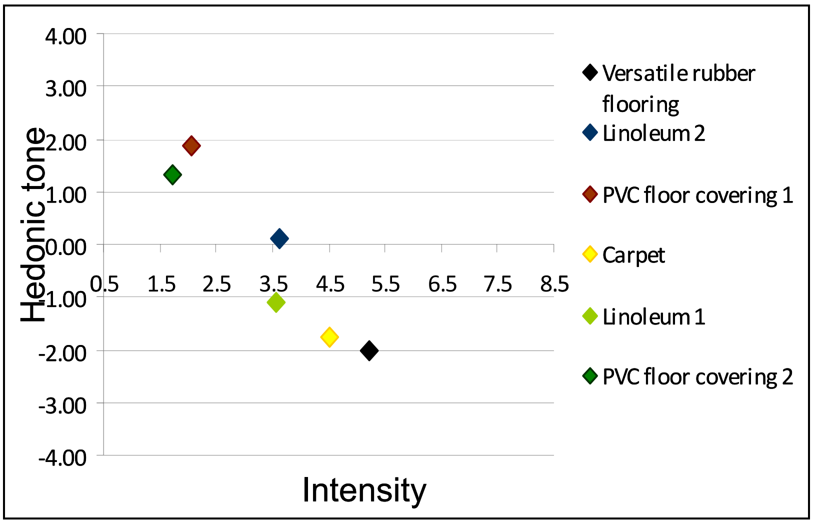


Figure 42 : Hedonic tone/intensity relation for 6 flooring materials

4.2.2. Relation VOC - odour

There are no systematic relations between VOC levels and odour perception:

- the less odorous materials (PVC) are also the ones with the higher level of total VOC (TVOC for one PVC material up to 10720 µg/(m²h) after 3 days)
- the linoleum had a strong odour with a low level of total VOC (TVOC after 3 days = 94 µg/(m²h)).

The explanation lies in the chemical family composition of the emission. The PVC emission contains mainly alkanes compounds (non odorous family) whereas the linoleum contains also odorous chemical families like carboxylic acids and aldehydes.

4.3. Preliminary tests with an E-nose

4.3.1. Context

An electronic nose (E-nose) is an array of non-specific chemical sensors, controlled and analyzed electronically, which was initially developed to mimic the action of the mammalian nose by recognizing patterns of response to vapours. The used gas sensors may be of different types. The sensors are not specific to any one vapour; they are included in an array of different sensors, each with a different sensitivity to chemical families. So, gases and gas mixtures can be identified by the pattern of response of the array. Most existing chemical sensors are designed to detect specific molecules, but array-based sensing uses non-specific sensors in which the pattern and magnitude of response are used to identify and quantify more globally the presence of contaminants. They are trained to identify different gaseous ambiences from their specific signal patterns. Contaminants are identified and quantified after model calibration through a suitable pattern recognition technique (statistical multivariate procedure, neural network,…).

Electronic noses are widely applied in different domains, such as food processing quality control, medical diagnosis, detection of explosives, identification of fragrances, etc. E-nose is even applied for environmental monitoring and the research group "Environmental Monitoring" at ULg was one of the pioneers in that field.

Applications of electronic noses go now far beyond the detection of odorant gas mixtures and they are applied to monitor various VOC's whether they smell or not. In that context, the monitoring of indoor air quality with E-nose is only a recent emergent application. Rather few scientific papers present original works dealing with air quality in dwellings (see separate state of the art report, chapter 5).

4.3.2. E-nose tests for building materials application

In this project, the ability of the E-nose technology to measure material emission has been evaluated and can prove to be a good instrument for indoor air applications.

Selection of gas sensors

First E-nose measurements have been performed on four flooring samples. The aim was to evaluate the ability of the selected chemical sensors of the lab-made E-nose to detect and to classify flooring materials.

A small round piece of the four flooring materials are put in closed glass vessels under a relative humidity of 50 %. After equilibrium of the headspace, a gas aliquot of 10 mL is spiked in the E-nose sensor chamber (Figure 43). The measurements are made randomly with 5 (or 4) replicates.

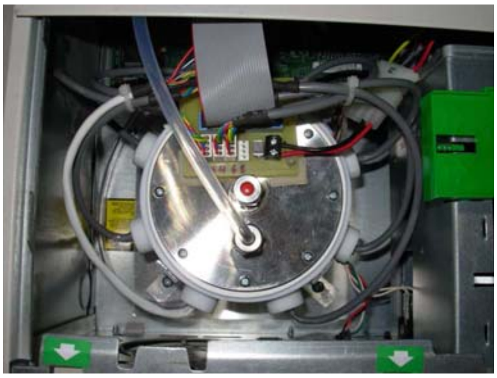
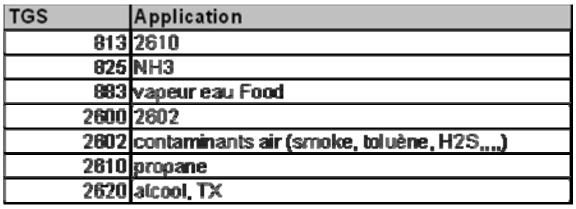


Figure 43 : E-nose sensor chamber

These preliminary results show that the sensors used (Table 9) are able to discriminate the 4 samples.



TGS	Application
813	2610
825	NH3
883	vapeur eau Food
2600	2602
2602	contaminants air (smoke, toluène, H2S,...)
2610	propane
2620	alcool, TX

Table 9 : List of selected gas sensors for the E-nose

The more sensitive sensors were the TGS 825, 2600, 2602 and 2610. The TGS 813 and 2620 were only sensitive to sample 4 and the TGS 883 didn't react.

First results of emissions identification

A multivariate data analysis (principal component analysis, PCA) has been realised on the acquired data set, in order to evaluate the E-nose ability to identify the various samples.

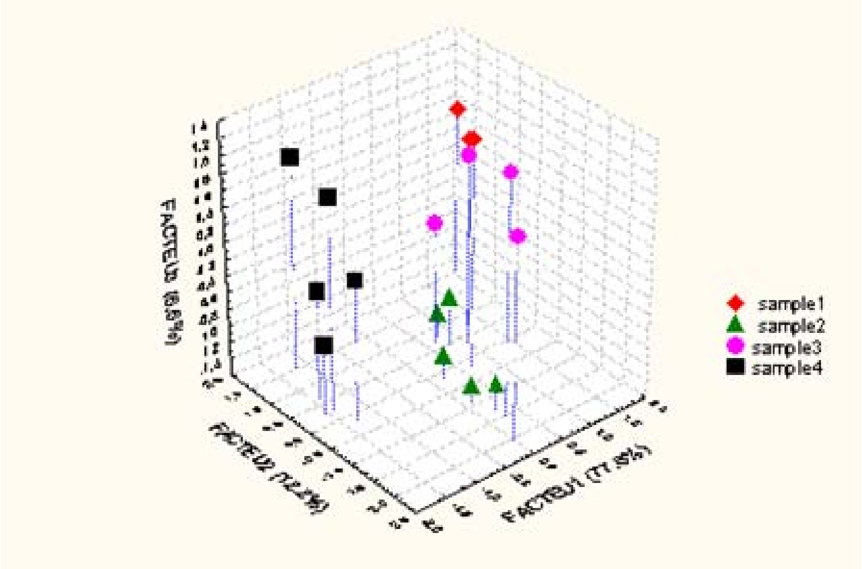


Figure 44 : Classification results for four floorcovering samples emissions with an E-nose (PCA)

This figure reveals that the E-nose system was able to identify the various materials based on their respective emissions. This result is only qualitative but it shows that it is possible to use this technology to measure rapidly the VOC's materials emission.

Unfortunately the sensors sensitivity to these material emissions was low. For instance, there are no significant responses for the lowest emissive materials (samples 1 and 3). The results need to be improved by a new methodology in order to concentrate the gas sample in the sensor chamber.

A quantification step (correlation between E-nose responses and odour intensity or total VOC's level) still needs to be developed.

First results of VOC continuous measurement during 28 days

The instrument was placed in the 50 m³ chamber in order to monitor the emission of a flooring material during 28 days.

Figure 45 shows that the sensors resistance increases with time. The resistance is inversely proportional to the VOC concentrations. Then a continuous increase indicates a continuous diminution of the VOC emission for this material.

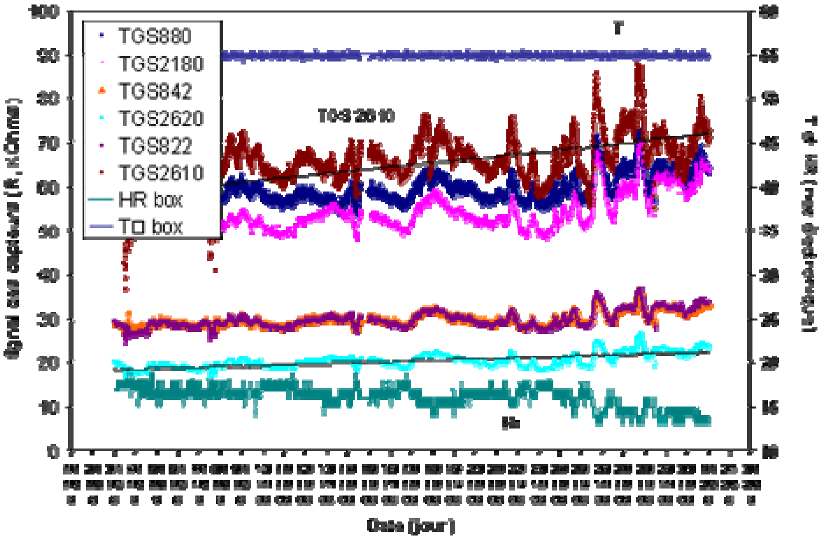


Figure 45 : Monitoring of a flooring material emission during 28 days with an E-nose

4.4. Conclusions

During this project, a sensory tool has been built to measure the odour intensity. Additionally, a methodology has been developed to evaluate the various sensorial dimensions for building materials.

The results have shown that there is no systematic relationship between total VOC emissions and odour intensity. The VOC content is not enough to determine the odour annoyance generated by a building material. To consider the odour impact, sensory evaluation of the building materials must be realised.

Moreover, for a realistic evaluation of the building materials odour, three aspects of the odour must be evaluated: the intensity, the hedonic tone and the acceptability. The first results show that some materials with high odour intensity are sensory acceptable by the individuals. Because, even if an intensity measurement is more robust than acceptability evaluation, attention is required in the interpretation of high intensity values.

The E-nose technology has been evaluated for the indoor application. Preliminary tests have been performed with lab made E-nose. These first results show the potentiality of the electronic-nose to distinguish between low emissive and high emissive materials and to monitor the emission in a room during several days.

5. Influence of test method parameters

5.1. Quantification procedure

The goal of a routine emission test according to a certain test protocol is to compare the concentrations of the compounds with the limit values laid down in the protocol.

Different quantification strategies can be used to calculate the concentrations, for example in ISO 16000-6 compounds are quantified using their individual response factors when reference compound is available. In other cases quantification is given as a toluene equivalent.

In the AgBB protocol on the other hand, identified substances with LCI (lowest concentration of interest) values as well as carcinogens have to be quantified using their individual calibration factors. Identified substances without LCI values and non-identified ("unknown") substances are quantified on the basis of toluene equivalents.

In this project, three different strategies can be distinguished, the previous two and an intermediate solution:

- The semi-quantitative approach where the concentration of each compound is expressed as the internal standard, 2-fluortoluene. This is the same procedure as used to determine TVOC (Semi method);
- Another semi-quantitative approach, as described in ANSI/BIFMA M7.1-2007, where a compound is quantified using the response factor of the reference compound of the chemical class they both belong to (ANSI (American National Standards Institute) method);
- The real quantitative approach where each compound is quantified according to a calibration curve using its own response factor (LCI method).

In the ANSI/BIFMA approach the quantification of the compounds are based on the response factors of the following reference compounds corresponding to each chemical class:

- Aromatics: toluene
- Aliphatic hydrocarbons: n-decane
- Cycloalkanes: cyclohexane
- Terpenes: aplha-pinene
- Alcohols: 1-butanol
- Glycols/glycol ethers: 2-butoxyethanol

- Aldehydes: hexanal
- Ketones: methylisobutylketone
- Halocarbons: 1,1,1-trichloroethane
- Esters: butylacetate
- Others: toluene

The ANSI and LCI methods require calibration standard mixtures of at least 3 different concentrations (4 were chosen) to be analysed with each set of samples to update the calibration.

The chosen quantification method is of big importance on the calculated concentrations as will be proven below by means of 4 emission tests (OSB plate, waterbased paint, plaster and floor covering glue in a 1 m³ test chamber; L= 0.4 m²/m³; n= 0.5/h).

Sampling was done on Tenax after 1, 3 and 28 (29) days and the 1-day sample was screened for the presence of LCI compounds. If the found compounds were not available in the lab, they were bought and try-outs of calibration curves were executed before the sampling of day 28 (29).

This is where the ANSI method has an advantage: you only have to buy once the reference compounds and the compounds in the calibration curves are always the same, in contrast to the LCI method where the 1-day screening decides which calibration curves have to be set up.

5.1.1. OSB results

Figure 46 shows the emission results (duplo results, hence the error bars) with the different quantification methods after 29 days.

LCI: LCI method
ANSI: ANSI method
Semi: Semi-quantitative method

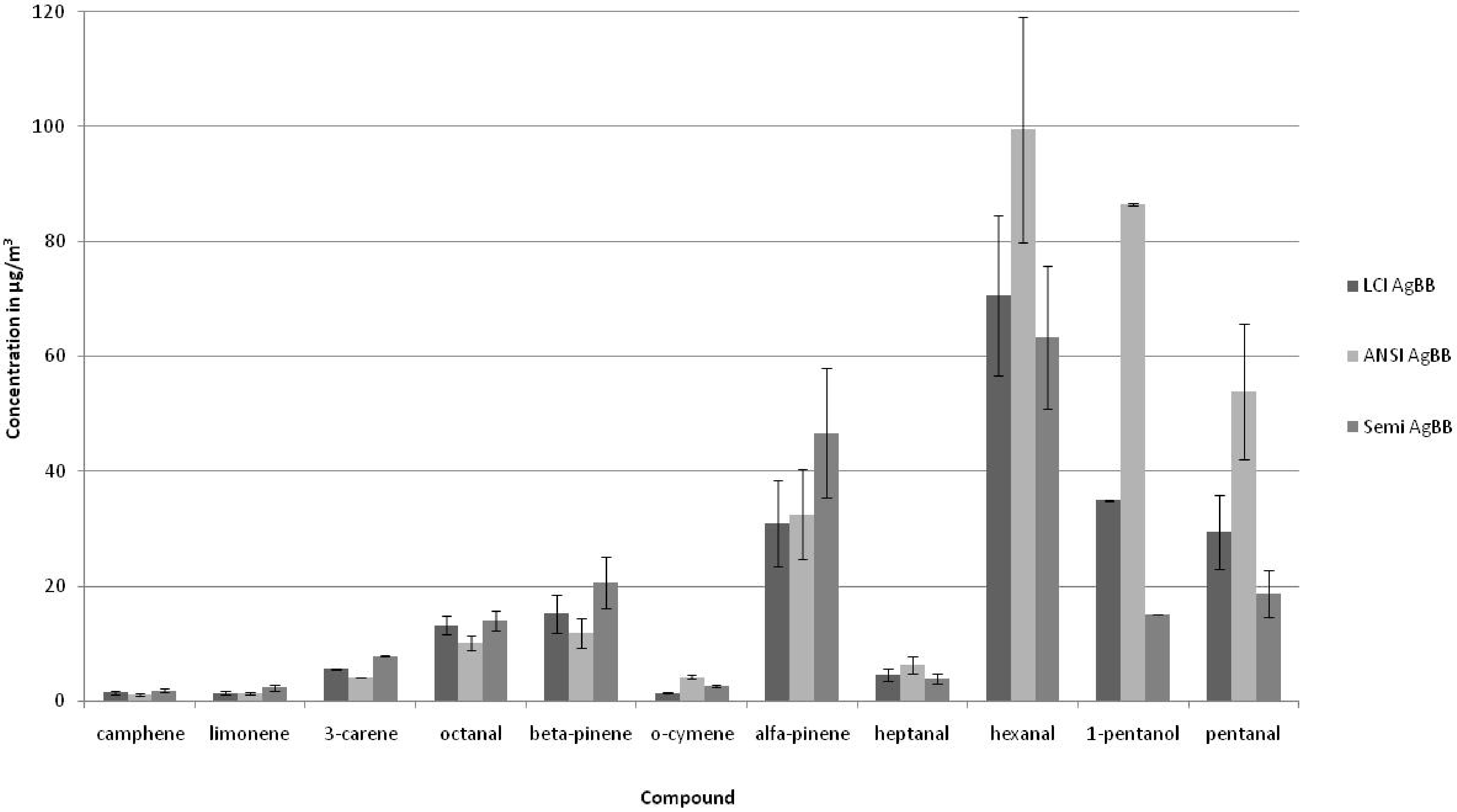


Figure 46 : Emission results after 29 days of an OSB material with the different quantification methods

The differences in concentrations for one compound between the three methods depend on the individual responses of each compound on the mass detector.
For example if the peak area for a certain amount of alpha pinene is higher than the same amount of 2-fluortoluene, the result will be an overestimation of the concentration of pinene when using the semi-quantitative determination because then the pinene is calculated using the response of 2-fluortoluene.

Also within a chemical family there is a difference in response, that is why the ANSI result can differ from the LCI result. In this case, the concentrations are far off the LCI values, but it’s obvious that with higher emitting materials it is important which quantification method is used to decide whether the material succeeds the protocol’s criteria or not.

5.1.2. Waterbased paint results

The results for the water-based paint experiment are shown in Figure 47.

The concentrations are very low, only up to a few µg/m³. In the 1-day screening sample, butylacrylate was identified but totally not present in the 28-days sample.

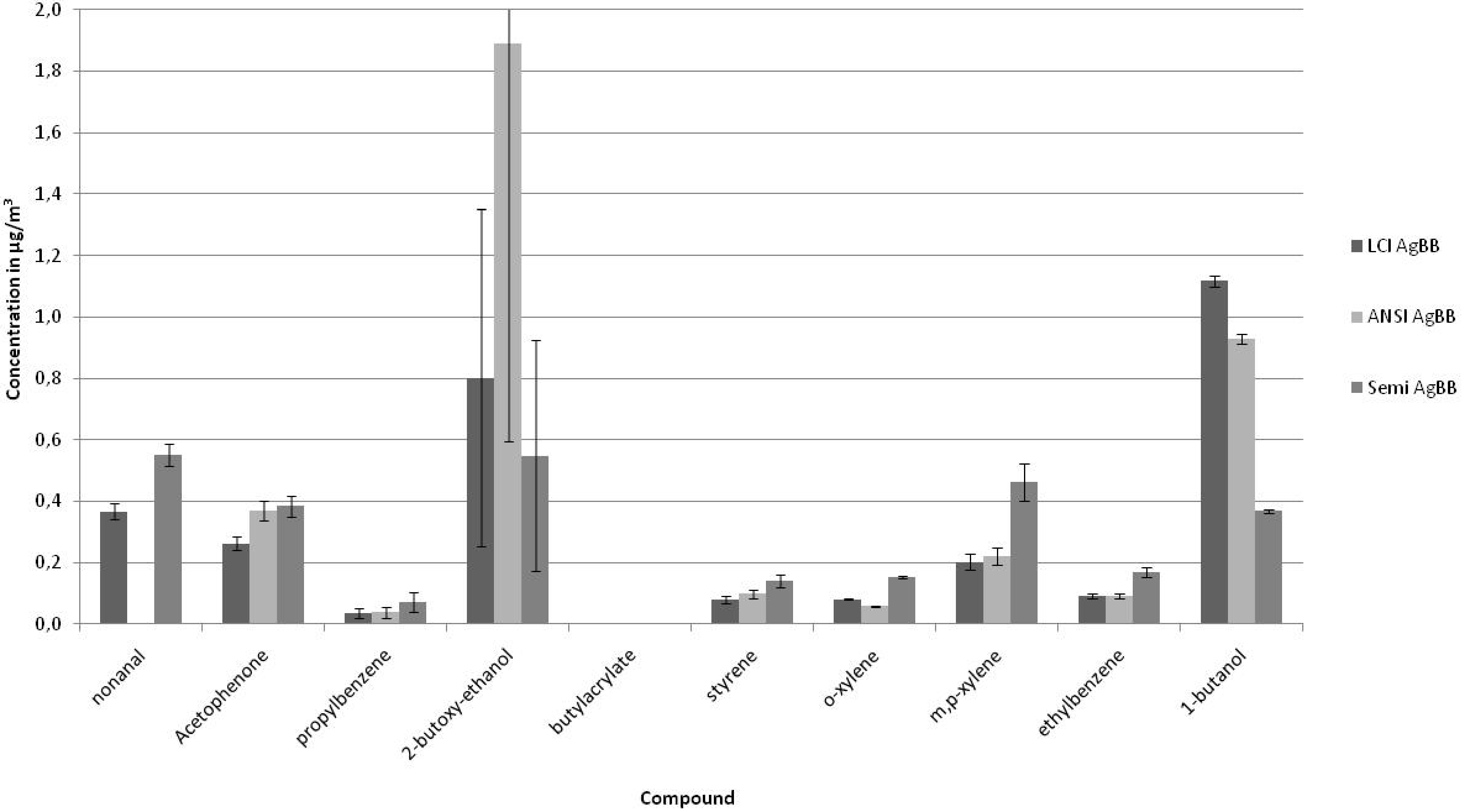


Figure 47 : Emission results after 28 days of a waterbased paint with the different quantification methods

5.1.3. Plaster

In all samples the concentrations were very low, on the same level as the blank value for the system. There wasn't any particular compound in the chromatogram which could be assigned as originating from the plaster.

5.1.4. Floor covering glue

The emission experiment of the floor covering glue has been done twice, for the emissions were so high we had to adapt the analytical settings of the thermal desorption and GCMS systems for the analysis of the second experiment.

As the emissions were so high we selected the highest compounds for the comparison of the quantification methods; 2 esters and 11 alkanes. The alkanes caused some troubles: not only the identification was rather complicated (most of them were isomeres), but some of them were not commercially (or too expensive) available as a pure compound. That's why we decided to use an alternative quantification method: the number of carbon atoms in the alkanes were counted and the compounds were expressed as the corresponding n-alkane with the same number of alkanes. So it was impossible to compare the different quantification methods for this sample.

Mind the concentration level in the Figure 48.

Note: more emission experiments were performed, but with sample 5 (floor covering glue + floor covering) we encountered the same issue as with sample 4; and the emissions of samples 6 (MDF) and 7 (thermal and acoustical insulation material) were too low.

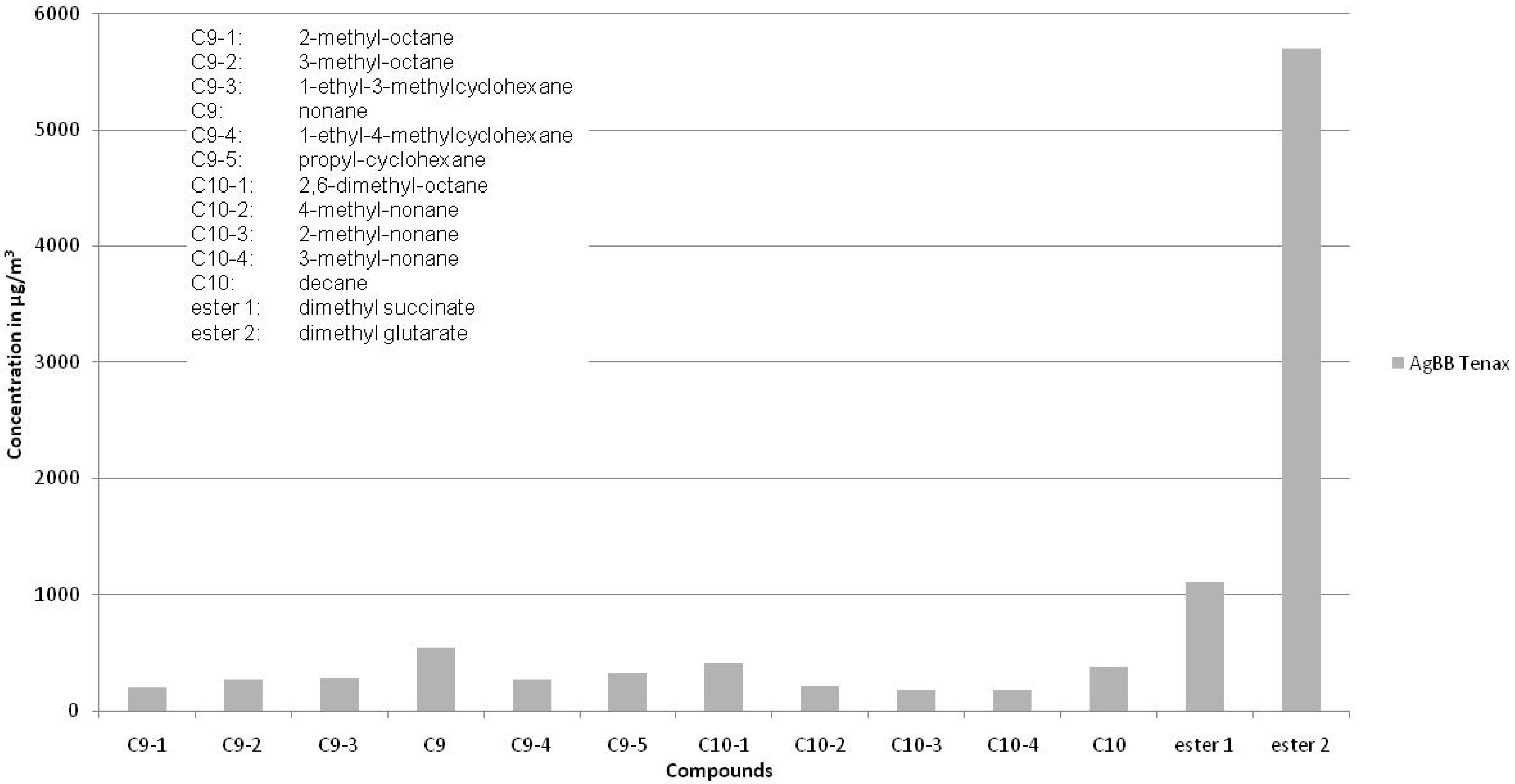


Figure 48 : Emission results after 28 days of a floor covering glue

5.2. Influence of loading factor

To check the influence of the loading factor on the emission results we conducted some emission experiments simultaneously in different test chambers (1m³ and 0.72 m³) according to two well known European test protocols with a different loading factor for a wall material.

In the following table the difference in loading factors between AgBB (2008) and the AFSSET (2006) protocol is shown for the different types of building materials.

Type of material	AgBB	AFSSET
floor, ceiling	0.4	0.4
walls	1.0	1.38
small surfaces	0.05	0.1
very small surfaces	0.007	0.012

Table 10 : Loading factors (m²/m³) for different materials for AgBB and AFSSET protocol

The test according to the AgBB protocol was done in the 0.72 m³ test chamber (loading factor: 1.0 m²/m³); the test according to AFSSET was done in the 1 m³ test chamber (loading factor: 1.38 m^2/m^3). The air exchange rates were in both cases the same, 0.5/h.

It’s obvious that the difference in loading factor will influence the concentrations in the test chambers (with AFSSET there is more material to be tested per m³), that is the reason the TVOC SER values will be compared. Three materials were sampled after 1, 3 and 28 (29) days on Tenax TA to check this influence: OSB (Figure 49), water-based paint (Figure 50) and plaster (results again not usable because of the very low emissions).

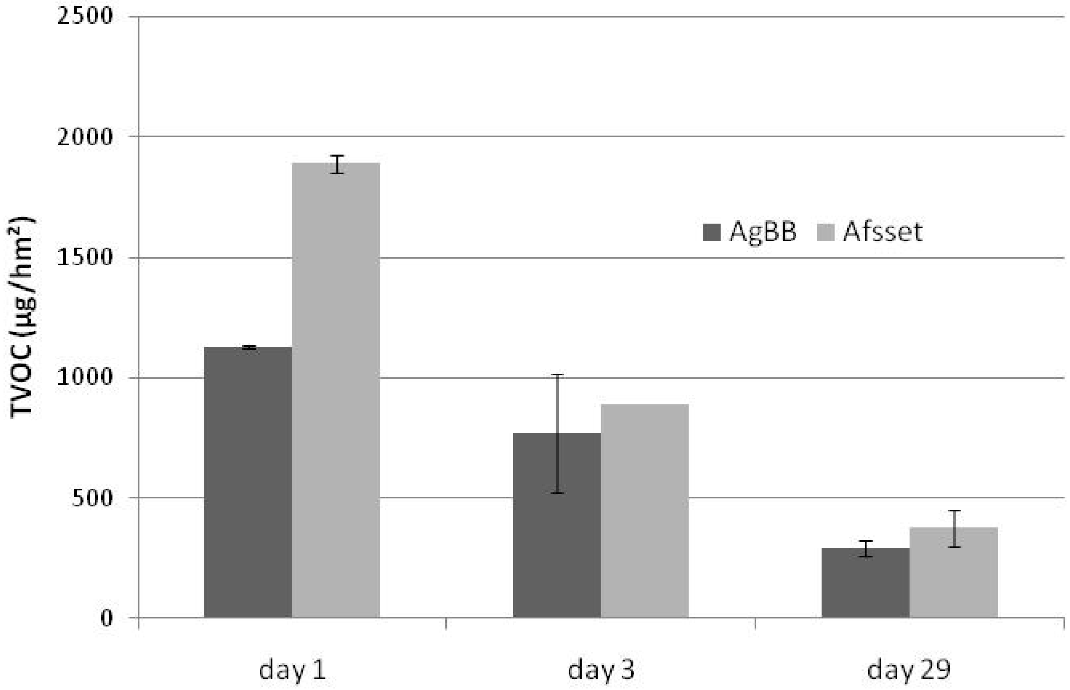


Figure 49 : TVOC$_{SER}$ emission results from an OSB material with different loading factors

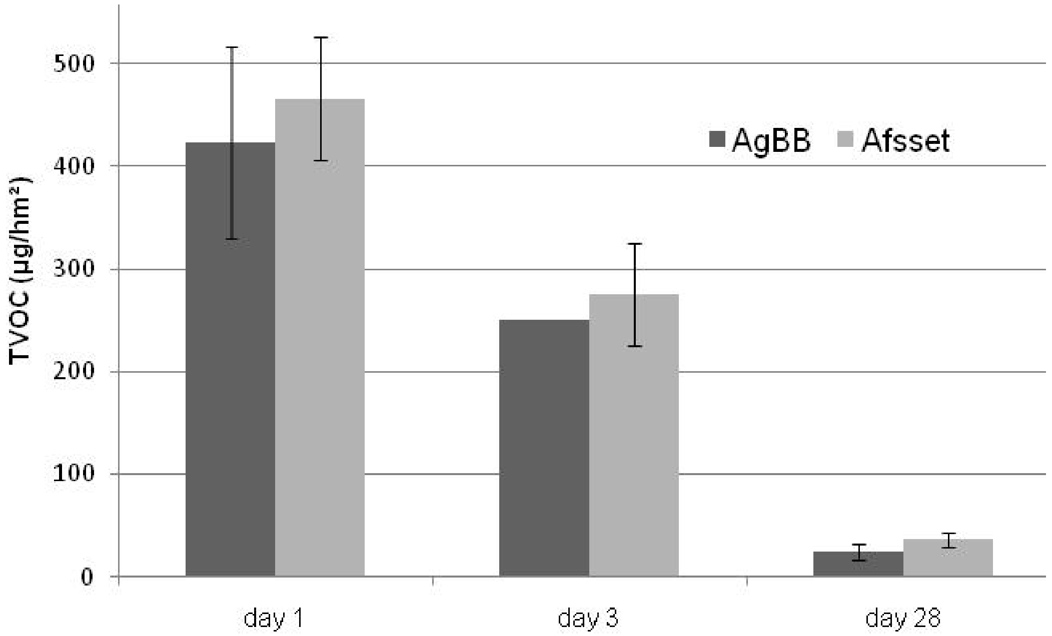


Figure 50 : TVOC$_{SER}$ emission results from a waterbased paint with different loading factors

On 5 out of 6 sampling times, the TVOC values are comparable. The only difference is situated at day 1 of the OSB emission experiment, probably due to equilibrium issues. In fact day 1 is not a mandatory sampling time in both protocols because it's relatively fast after the input in the test chambers.

Thus for TVOC$_{SER}$, the difference in concentration is directly related to the difference in loading factor since the SER is quasi unaffected. Looking more into detail in the individual SERs (Figure 51), it seems that for some pollutants there's a tendency that the AFSSET SERs are slightly higher than the AgBB SERs.

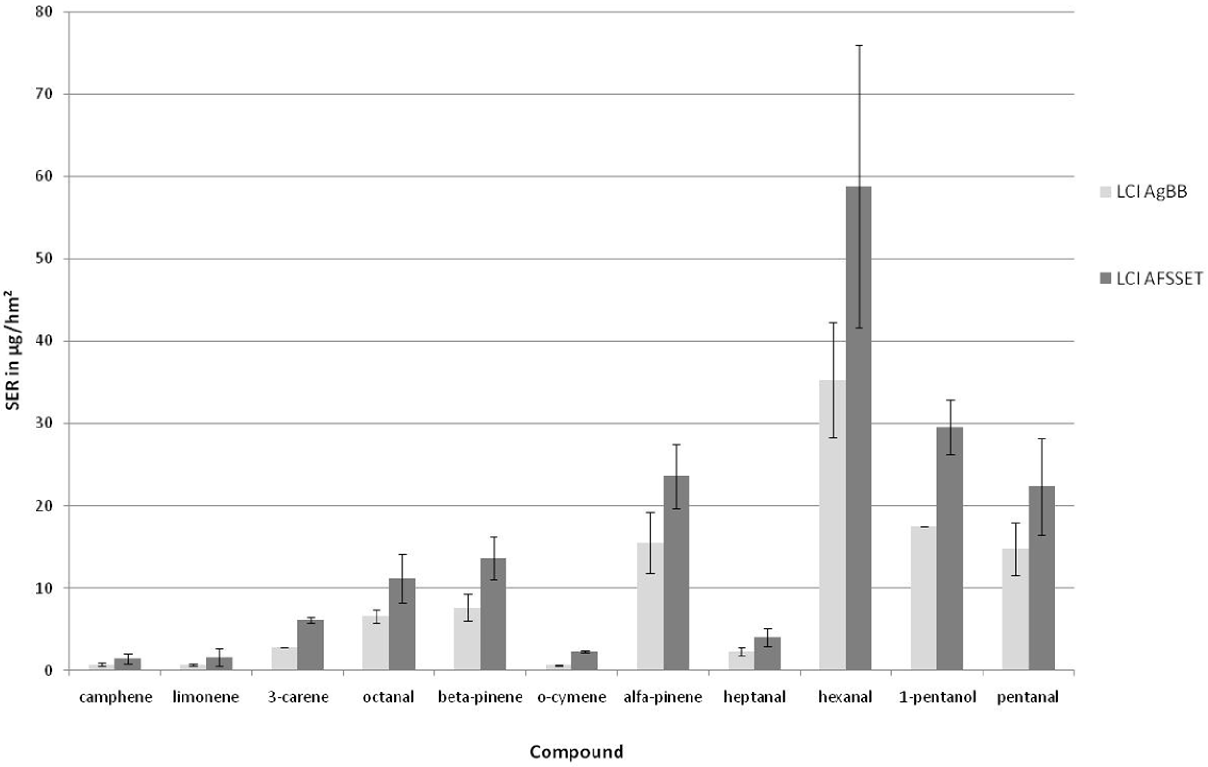


Figure 51 : Individual emission results from a sample of OSB with different loading factors (according to the AFFSET (2006) and AgBB protocol)

5.3. Influence of temperature and relative humidity

All test protocols establish test parameters: test conditions which have to be set up in order to perform the emission test. For temperature and humidity the test chamber must be able to control the set values of 23°C and 50 % RH. Almost all protocols use these two values, but some emission experiments were conducted to investigate the influence of temperature and humidity on the emission results.

In a first stage we conducted emission tests of a floor covering material with alternating climatical conditions (see Figure 52). The 1 m³ test chamber was sampled after 3 days, and the TVOC concentration was used to seek a possible influence of the climatical conditions.

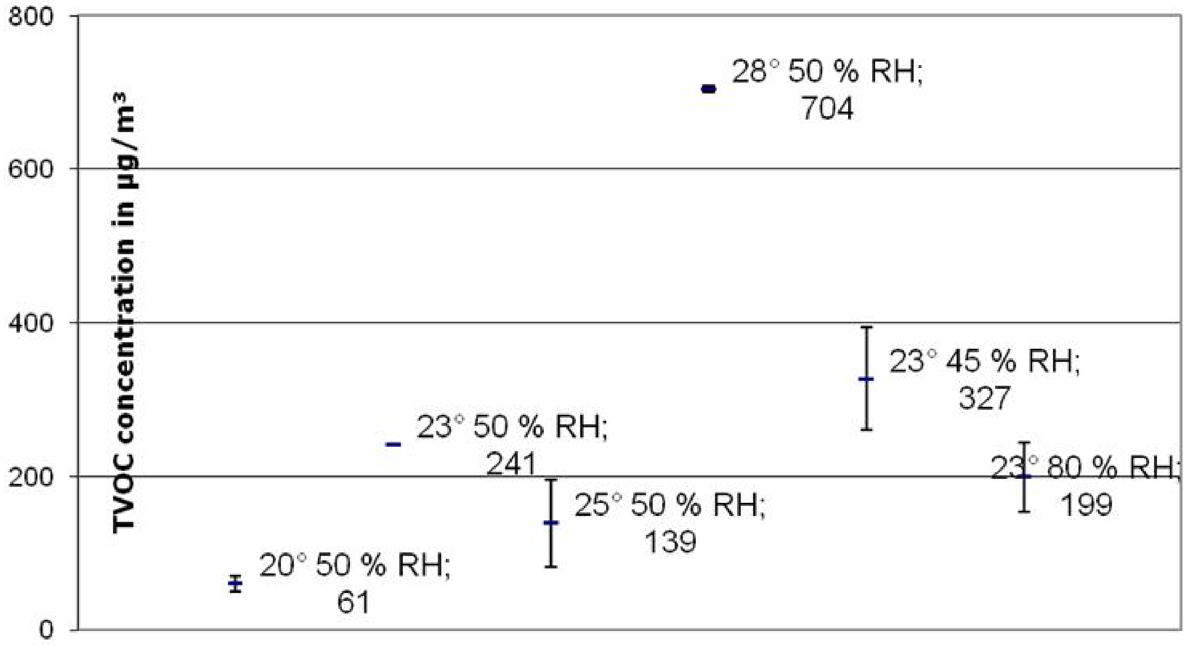


Figure 52 : Influence of T and RH on the emission (TVOC) behaviour of an OSB material

There seems to be an influence of the temperature: at 50 % RH, the TVOC value rises as the temperature rises, except for the 25°C test which could not confirm this trend.

The humidity is of lesser effect: at 23°C, the TVOC results at three different humidities are clustered together, although it seems that the TVOC emissions are lower at higher humidities.

An overall remark of these combination of tests was the rather low emission of the floor covering (emission concentrations are about 2 times higher than the combined blank value the analytical system/test chamber), so it was decided to repeat the tests, but with a higher emitting material which makes it more feasible to search for eventual influences.

So the same kind of tests was done on a OSB material. During those tests the test chamber suffered with some background problems, for that reason we checked the possible influence on a compound typically emitted from the OSB material, namely alpha-pinene.

Below (Figure 53) is an overlay of chromatograms with the peak areas of pinene for the different climatical conditions. The four peaks represent the following climatical conditions: at 50 % RH: 20, 23 and 28°C; and at 23°C: 25 % RH. There is no significant difference in the peak areas, so the temperature and humidity have no effect on the pinene emission for the OSB material investigated.

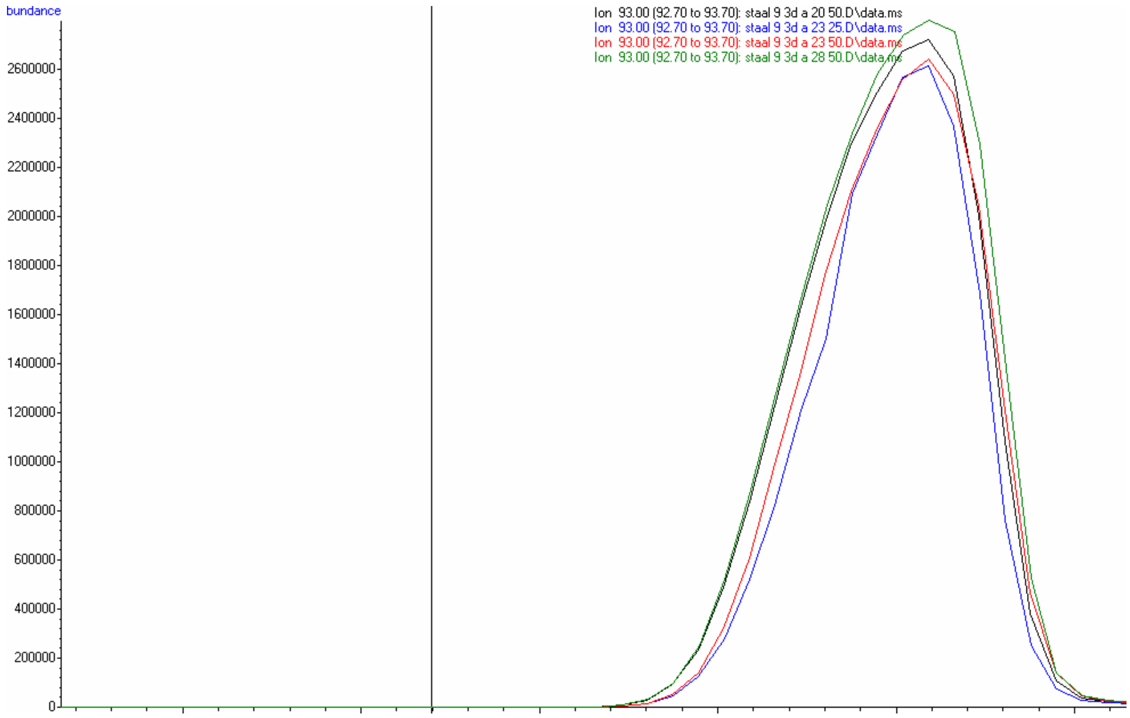


Figure 53 : Overlay of chromatograms with the peak area of alpha-pinene for the different climatic conditions

These findings were confirmed by some literature research: it's not feasible to set up a model which describes the influence of temperature on the emission results due to the chemical diversity of pollutants and building materials (Wolkoff, P.).

Formaldehyde do increase when temperature rises with wooden building materials. With a floor covering, there's no increase in alkylbenzenes when temperature is higher, in contrast to some SVOCs (Järnström, H.).

5.4. Influence of "upstream the test chamber"

The "upstream the test chamber" series of experiments are threefold and investigate the possible influence of events that occur with the building material before it is inserted in the test chamber:

- Frequency of sampling: the goal of this test is to investigate whether different batches of the floor covering (with different fabrication dates) show different TVOC emission results. In order to compare the emission results we tested 2 batches, one arrived at VITO in February 2008, the other in July 2008. The July test was compared to the February test for the frequency of sampling-experiment, and the former served as a reference test for the storage time-experiment (see below).

After the frequency of sampling test we divided the July batch in 2 pieces: one piece was stored in a office desk, and the other was stored in the lab (temperature controlled).

- Storage time: experiment to check the influence of storage time on the TVOC emissions. Therefore the lab-stored sample was kept for 5 weeks, and after this period a 3-day TVOC experiment was conducted. These results are compared with the July reference test.
- Storage place: immediately after the storage time-experiment the desk-stored sample was placed for 3 days in the test chamber. In this test the possible influence of the place where the sample is stored can be checked when it is evaluated with regard to the storage time-experiment.

The results of these 3 tests (frequency of sampling, storage time and storage place; standard test conditions: 23 °C, 50 % RH and an air exchange rate of 0.5) are shown in Figure 54 as an overview together with the results of the climatic conditions tests to see all the TVOC emissions resulting from the test chamber experiments.

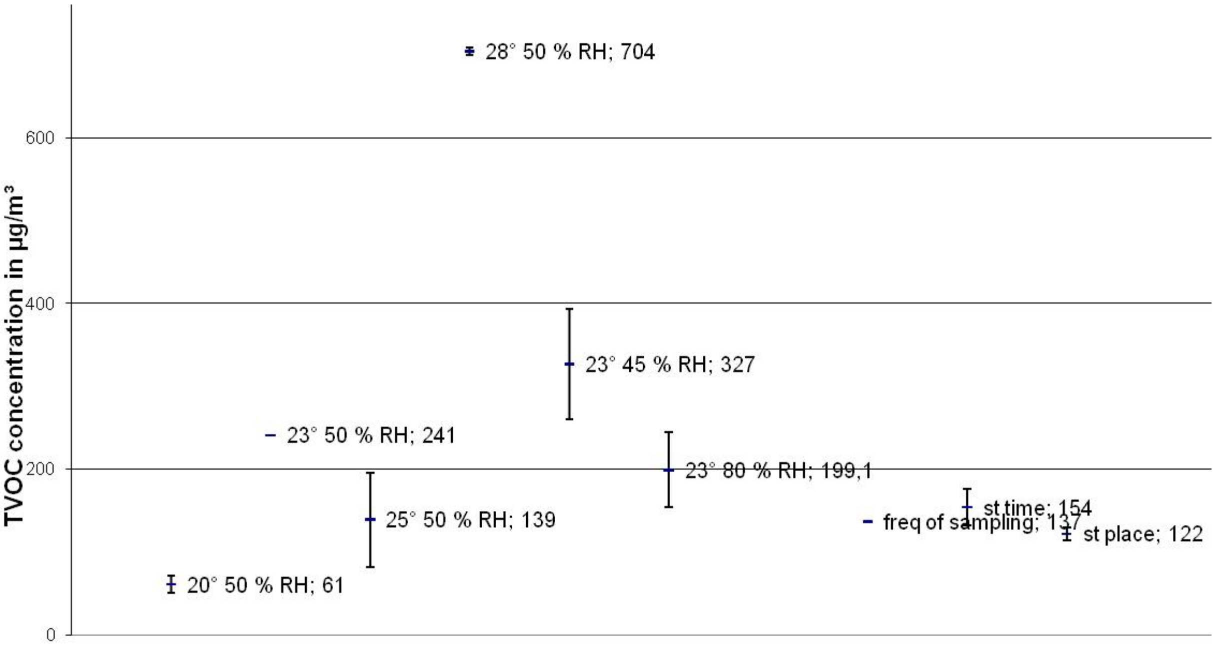


Figure 54 : Overview of the influence of climatic and "upstream the test chamber" conditions on the TVOC concentration

It's concluded that the July batch has a lower TVOC emission than the February batch (137 µg/m³ against 241 µg/m³). The three "upstream the test chamber" experiments have TVOC emissions in the same order of magnitude so that the conclusion is that there's no evidence of an influence of the (tested) storage time and storage place on the TVOC emission for the floor covering material investigated.

5.5. Influence of sorbent

The Tenax TA sorbent is widely used as standard sorbent for indoor air sampling analysed with thermal desorption. As an alternative sorbent Carbotrap 202 was selected, which has a slightly broader volatility range. It is a multisorbent tube and it contains Carbotrap B and Carbotrap C.

Sorbent	Tubes conditioned at	Max. suggested T	Desorption temperature	Volatility range
Tenax TA	335 °C	350 °C	300 °C	n-C6 to n-C30
Carbotrap 202	350 °C	400 °C	330 °C	n-C5 to n-C30

Table 11 : Sorbents used

During 3 emission tests (floor covering, floor covering + glue and thermal and acoustical insulation material) in the two different test chambers according to the AgBB and AFSSET protocols, we sampled on both sorbents to compare the TVOC value resulting from the analysis, see Figure 55 and Figure 56. The loading factor (0.4 m²/m³) and the air exchange rate (0.5 /h) were the same in both test chambers.

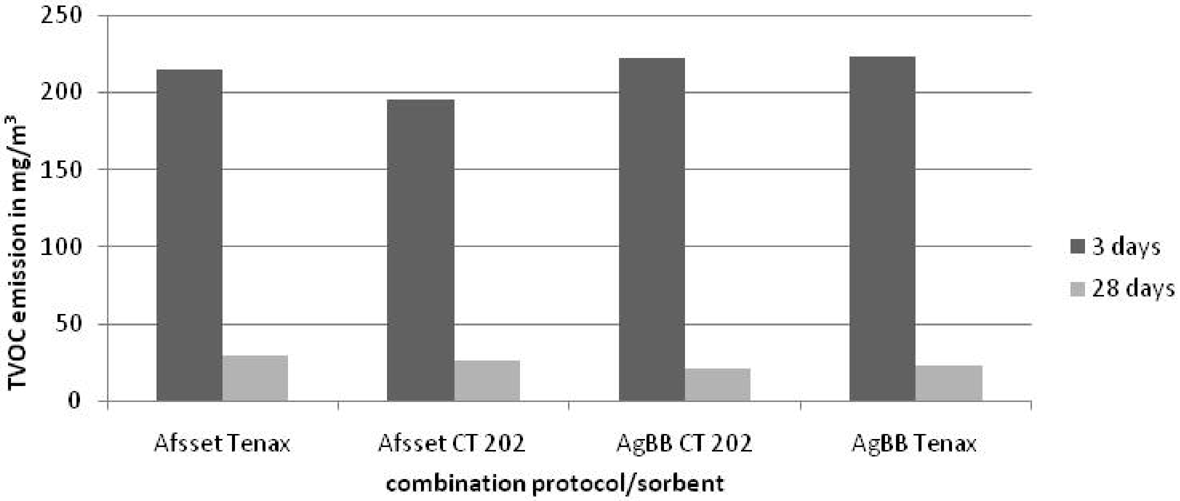


Figure 55 : Comparison of the TVOC value for different sorbents and different protocols for a floor covering glue emission test

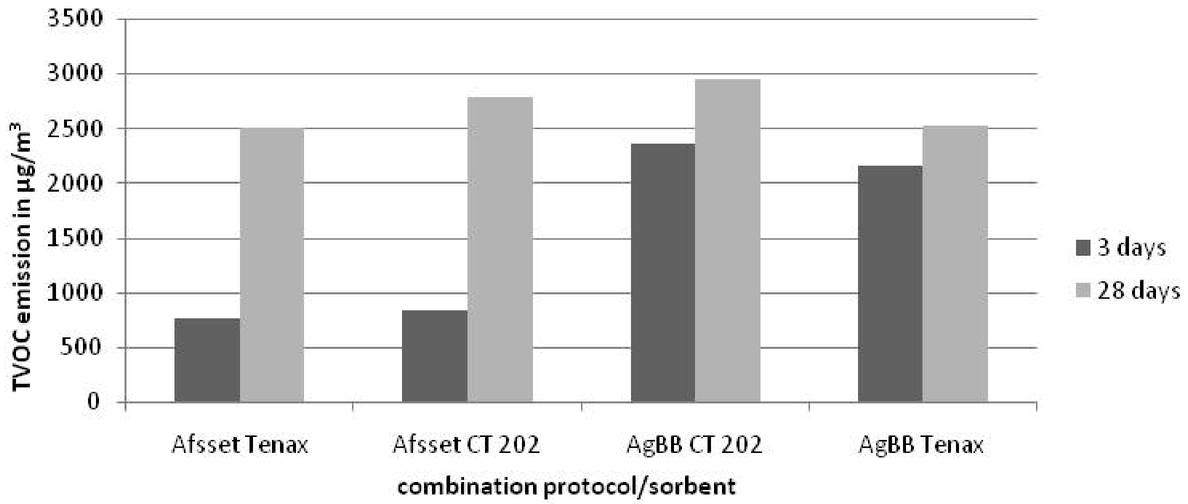


Figure 56 : Comparison of the TVOC value for different sorbents and different protocols for a (floor covering + glue) emission test

Figure 55 shows that there is no significant difference between the TVOC values for the different sorbents and for the different protocols.

Figure 56 shows that, again, there is no difference between the sorbents, but the different protocol yield different TVOC results, especially for the 3 days-sample. This is probably due to the use of a sealing box (in which the sample is inserted to prevent emissions from the sides) in the AFSSET protocol, but that was not used in the AgBB protocol. In that way, compounds were able to diffuse from the sides into the test chamber air in the AgBB protocol, where they are more retained by the floor covering itself in the sealing box. After 28 days however the TVOC values are more or less the same.

Also notice the very high emission (y-axis in mg/m³) from the glue after 3 days, which is much less after 28 days.

The combination experiment show much lower emissions, but they rise from 3 to 28 days, due to the retaining effect from the floor covering in the beginning of the experiment.

5.6. Influence of ozone on emission concentrations

To examine the influence of ozone on the emission concentrations we did experiments on two samples, OSB and a floor covering-subfloor combination. Both samples were tested with and without ozone. The ozone was added with a ozone generator, concentrations were monitored at the outlet of test chamber. Sampling was performed at about 24 hours on Tenax (TVOC and LCI compounds semi-quantitatively) and DNPH. Furthermore a portable PID (photo-ionization detector) monitor measured online the TVOC concentration and the dust (PM) concentration was determined with a Grimm dust monitor (The operation of the Grimm device is explained in detail in the separate state of the art report, section 5.3).

Exp 1: OSB with ozone (start concentration: 200 ppb)
Exp 2: OSB without ozone
Exp 3: flooring combination with ozone (start concentration: 157 ppb)
Exp 4: flooring combination without ozone

The course of the ozone concentrations are shown in Figure 56.

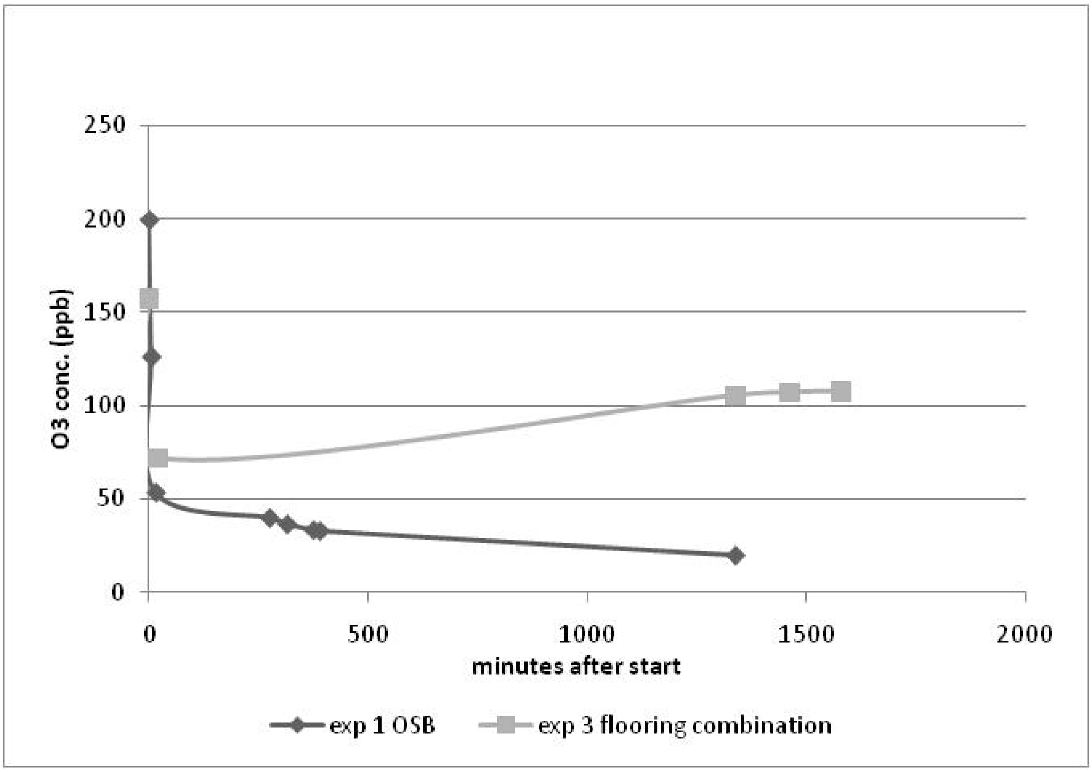


Figure 57 : Ozone concentrations in the course of the ozone experiments

After a sudden drop in concentration in the beginning of both experiments the ozone concentrations stabilizes rather fast. With the flooring combination, the concentration tends to rise near the end of the experiment. Is this drop of concentration due to the ozone degradation because of the unstable nature of ozone, or is the ozone reacting with the compounds emitted from the samples? Figure 58 shows the TVOC concentrations in all 4 experiments.

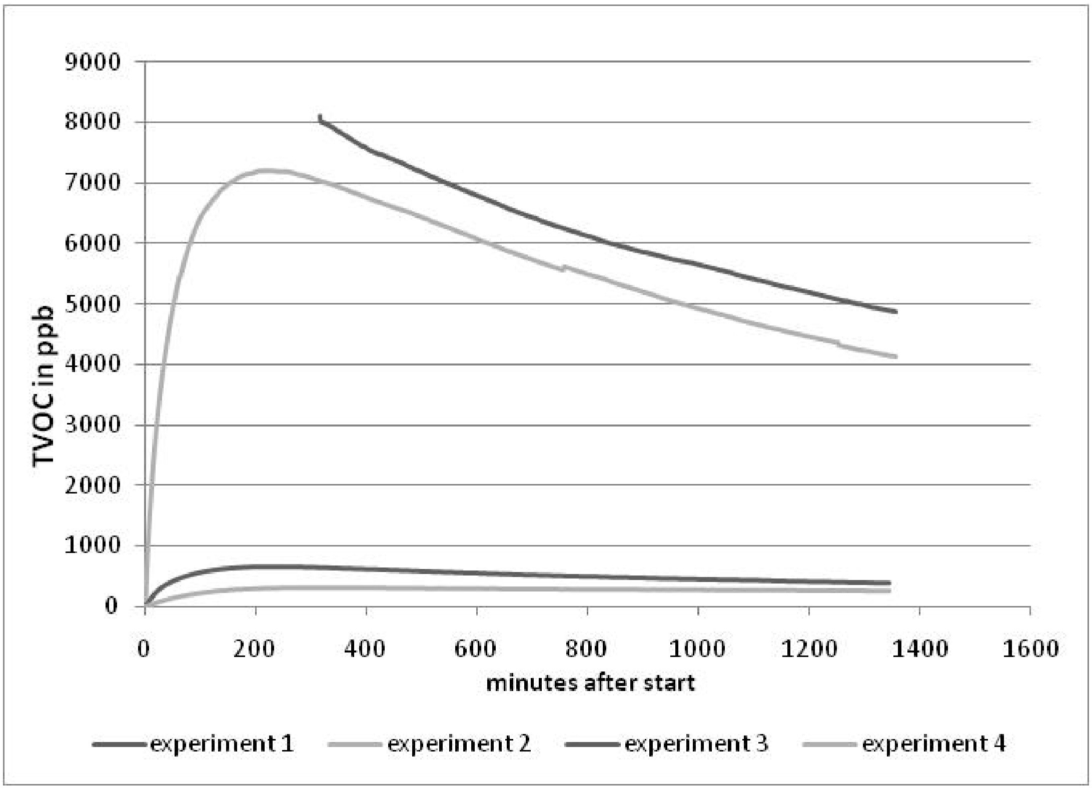


Figure 58 : TVOC concentrations in the four experiments

With both materials, the TVOC concentrations are slightly higher in the presence of ozone. It's possible that due to the presence of ozone compounds are generated with a different response on the PID monitor.

Typical reactions of ozone are reactions with compounds containing C=C bonds, most of these reactive chemicals are terpenes (e.g. α-pinene, limonene,...). Reaction products consist mostly of aldehydes (formaldehyde) or ketones (Nicolas et al.). It's also known that ultrafine particles are formed during the reaction of ozone with terpenes (California Air Resources Board, 2006). Our applied methodology allowed us to check whether these findings could be confirmed.

In Figure 59 the concentration of the compounds which can react with ozone and can be formed are summarized for the both emission tests, with and without ozone.

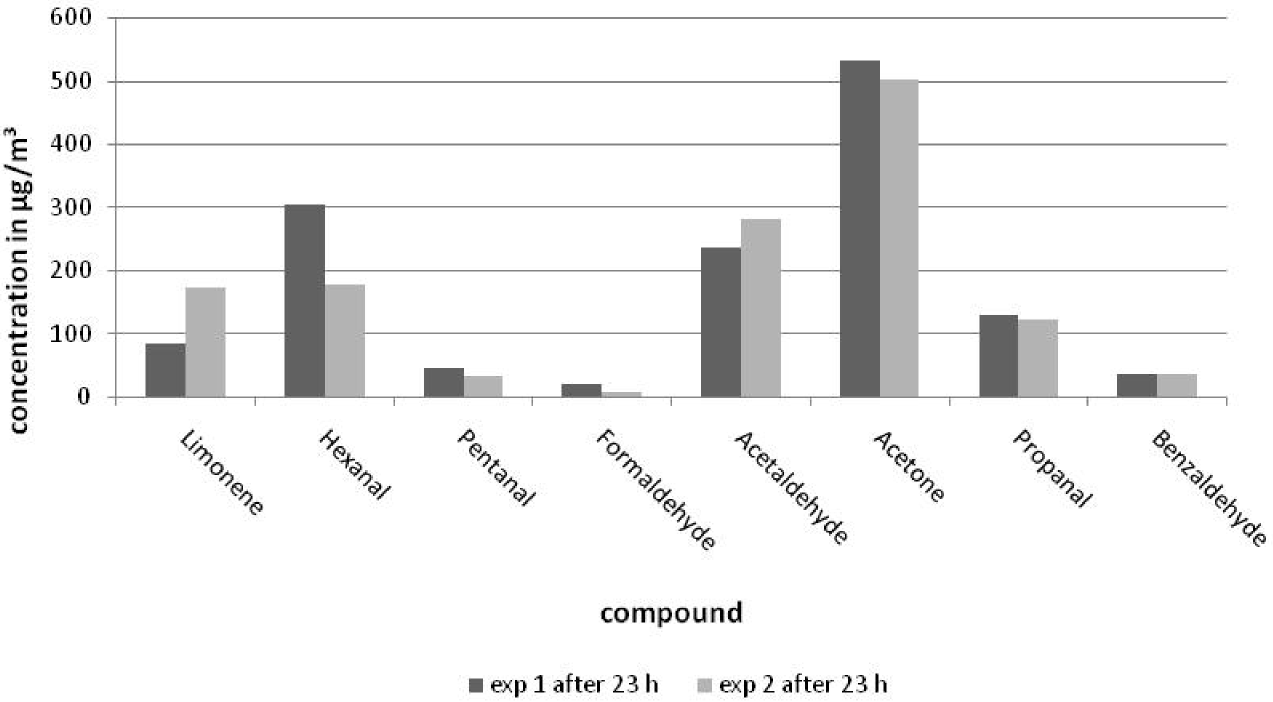


Figure 59 : Concentrations of selected compounds from OSB emission tests with (exp 1)/without (exp 2) ozone

The limonene concentration level with the ozone present is the half of the value when the ozone is not present. This could not be determined with the other terpenes. As a result, the formaldehyde and hexanal concentration is higher with ozone present. So the ozone has some influence on the OSB emission results. The flooring combination, with no terpenes emitted, does not show the same behaviour.

Figure 60 shows the PM concentrations in experiment 1, OSB with ozone.

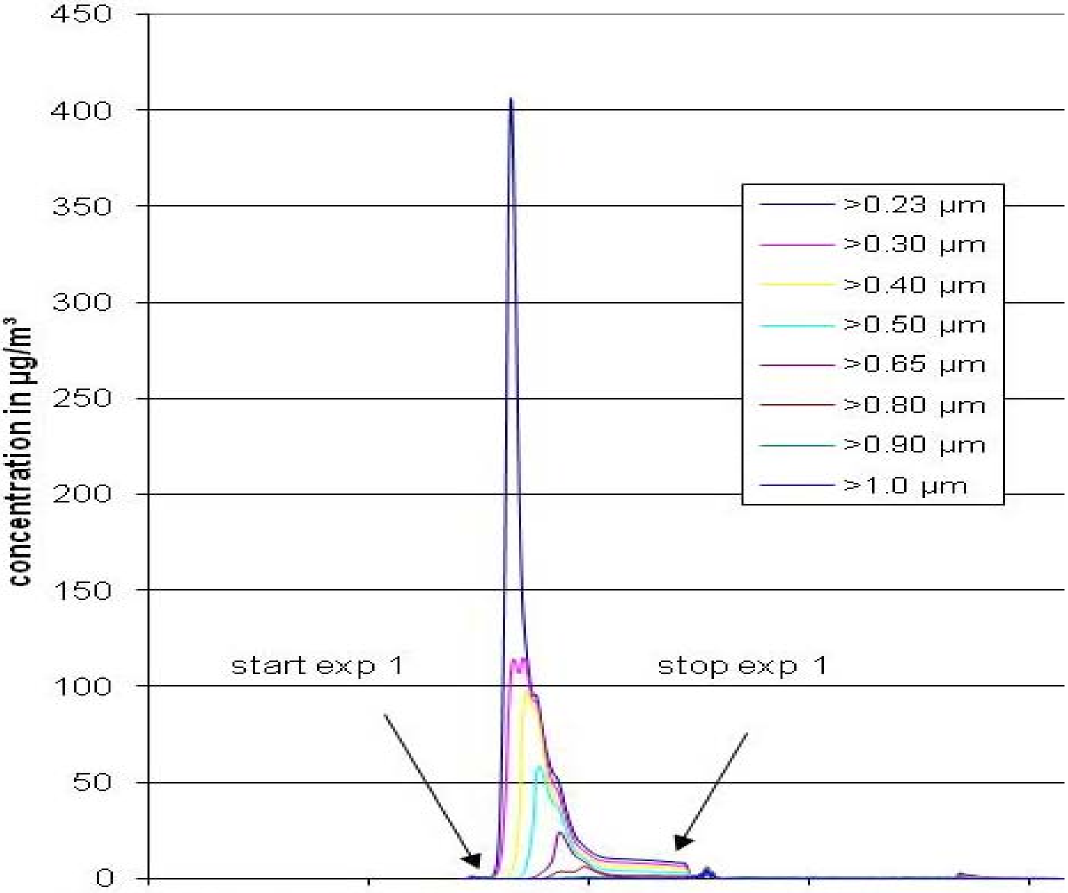


Figure 60 : Grimm PM concentrations during OSB emission test with ozone

Shortly after exposure to ozone, PM peaks appear and in particular the PM fractions with the smallest diameters are most abundant. The Grimm measures from PM0.23 – PM20, but only PM0.23-PM1 is present. In the 3 other experiments no PM concentrations whatsoever were measured. So in the presence of terpenes and ozone, fine PM fractions are generated.

6. Possibilities for testing building materials in Belgium – national approach

International tendencies indicate the growing importance of building material emission testing and the need for harmonization of the different approaches. The HEMICPD project wants to contribute to this ongoing harmonization exercise.

The different building material emission testing protocols can be classified in three types:

1. Limitation of TVOC and a limited number of VOCs: examples are Finnish M1 and Austrian ecolabel;
2. Limitation of all VOCs with low irritation and odour thresholds: for example the Danish ICL;
3. Limitation of (a large number) VOC emissions by setting limit values depending on their specific toxicological properties: examples are the German AgBB scheme and the French AFSSET protocol.

Type 3 is becoming the most popular approach and is also proposed for the "Belgian umbrella" evaluation scheme with following additions/modifications:

- Backbone is the new CEN/TC 351/WG2 standard under development;
- Apply a pre-screening procedure following the French/German/prEN15052 approach with an alternative method (< 20L) such as µ-chamber, FLEC or equivalent technique. This allows to differentiate between "ok" products and products that need further testing;
- For a health relevant assessment a safety margin can be used (for instance R= 0.5) with "adapted LCI values" as done for instance in the study "Determination of criteria for floorings and flooring adhesives, used in daycare centres for children on the basis of a risk-analysis related to the health of children" performed for the FPS Environment and Public Health (former national Belgian Ministry) in the contect of CPD implementation;
- Applying these faster and less expensive techniques leaves more "room" for try outs for product optimalisation, to consider other "upcoming" pollutant groups (PM, SVOC,…) and to incorporate the effect of interferences (ozon,…);
- Time path modification: allowing to stop the emission test earlier for instance after 7 days – with half the requirements of day 28: TVOC, TSVOC, T carc, Ci without LCI, LCI compounds – when no significant increase of individual substances occurs (this is additional work to be addressed in other research project). Scientific data illustrate the feasibility hereof. This modification will further improve the cost efficiency and response time.

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