EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM FLOOR COVERINGS (PETROSOURCED, BIOBASED, OR DEPOLLUTANT) AND INFLUENCE OF AGEING

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FRAMEWORK OF THE STUDY

SAFEMATER PROJECT

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AIM OF THE STUDY

- Compare the VOCs emissions of various petrosourced, biobased and / or purifying products (flexible floorings), already implemented in buildings.
  - With unused materials
  - With aged materials

- Determine the VOCs emission profile during accelerated aging

Obtain experimental data in order to evaluate :
- if the new products are really less emissive than the petrochemical ones
- what is the effect of materials aging on their emissions

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SELECTED MATERIALS

PRODUCT/ REFERENCE	NATURE	CURRENT APPLICATION	CLASSIFICATION UPEC	INFORMATIONS
PVC 1	PVC	ERP	U4P3E2/3C2	Glued pose
PVC 2	PVC	ERP	U4P3E2C2	Glued pose Certification Floorscore
PVC 3	PVC	ERP	U4P3E2/3C2	Without phtalates Without glued pose **50% natural material**
PVC DECONT	Decontaminating PVC	Housing/ ERP	U4P3E2C2	Glued pose Decontaminating property
LINO 1	LINOLEUM	Housing/ ERP	U4P3E1/2C2	Glued pose **93% natural material**
LINO 2	LINOLEUM	ERP	U4P3E1/2C2	Glued pose **97% natural material**
RUBBER N	RUBBER	Housing/ ERP	U4P3E2/3C1	Without phtalates, PVC, chlorine Glued pose **Natural rubber**
RUBBER S	RUBBER	Housing/ ERP	U4P3E2C1/2	Glued pose Synthetic rubber

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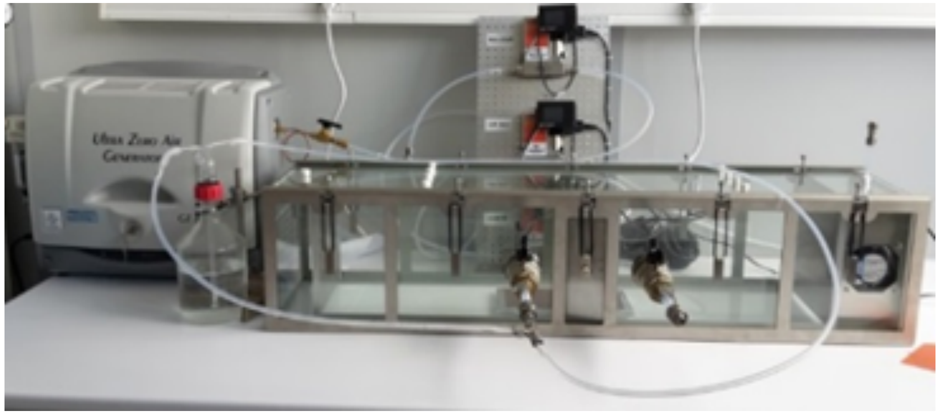
STANDARD TEST METHOD

Emission measurement according to standard NF EN ISO 16000-9



Test parameters :
T= 23 ± 2°C
HR= 50 ± 5%
Air exchange rate = 0.5 h^{-1}
Air speed = 0.25 $m.s^{-1}$
Surface/Volume=0.6 m^2/m^3

VOCs measurement

- **72 ± 2 hours and 28 ± 2 days after the test starting**
- **Air sampling and analysis methods for the determination of VOCs** :
  - TENAX sampling and ATD-GS-MS/FID analysis (ISO 16000-6)
  - DNPH analysis and HPLC-UV analysis (ISO 16000-3) :
    (formaldehyde and acetaldehyde)
  - Water bubbling and IC-Conductimetry analysis :
    (carboxylic acids C1-C3)

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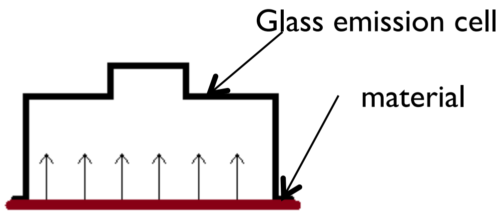
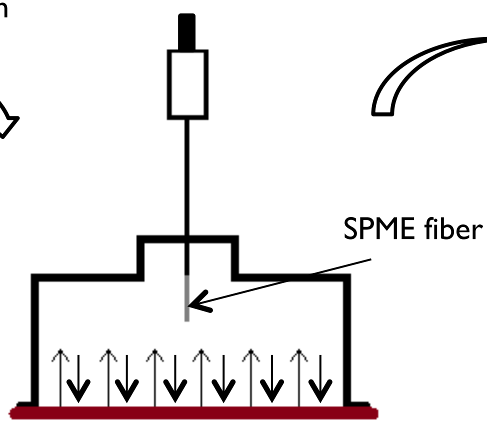
DOSEC-SPME METHOD

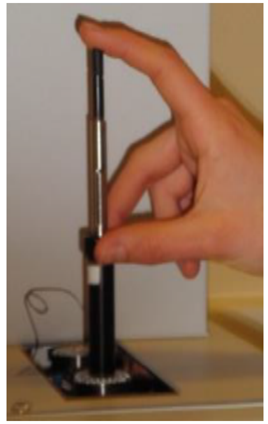
Material/air equilibrium



1- Material emission



2- VOC sampling
Solid-Phase Microextraction (SPME)
Fiber specially modified for formaldehyde analysis



3- SPME fiber thermal desorption and analysis by GC-MS-FID

1st Fick's law of diffusion
(stationnary conditions):

$$T=-DdC/dx=-Dy-y0/L$$

Determination of the concentration at the material surface: y_0

T : emission rate (µg.m^{-2}.s^{-1})
D : diffusion coefficient (m^2.s^{-1})
y : concentration in air (µg.m^{-3})
L : thickness of the boundary layer (m)
y_0 : concentration at the material/air interface (µg.m^{-3})

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ACCELERATED AGING METHOD

Aging cycle with 3 successive operations:

1. Friction simulation: Abrasion by sandblasting
2. Cleaning simulation : water-soaked wipe
3. Simulation of solar exposure behing glass: photometric aging in QUV chamber (UVA-351, irradiance: 0,76 $W.m^{-2}$, T= 50°C)

Study of time evolution of VOCs emission:

- Total accelerated aging: 408h
- 7 intermediate measurements of y_0 after 24h, 48h, 96h, 144h, 216h, 288h, 408h

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TESTS ACCORDING TO NF EN ISO 16000-9 STANDARD

Tests with new and aged materials

- ➢ Check the criteria applied to building materials (Décret n° 2011-321 du 23 mars 2011 and Arrêté du 19 avril 2011)

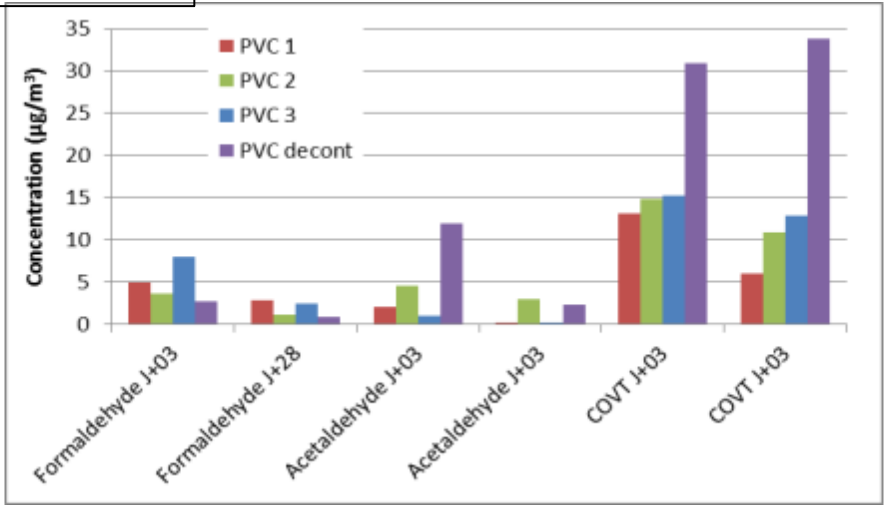
CLASSES	C	B	A	A+
Formaldéhyde	> 120	< 120	< 60	< 10
Acétaldéhyde	> 400	< 400	< 300	< 200
Toluène	> 600	< 600	< 450	< 300
Tétrachloroéthylène	> 500	< 500	< 350	< 250
Xylène	> 400	< 400	< 300	< 200
1,2,4-Triméthylbenzène	> 2000	< 2000	< 1500	< 1000
1,4-Dichlorobenzène	> 120	< 120	< 90	< 60
Ethylbenzène	> 1500	< 1500	< 1000	< 750
2-Butoxyéthanol	> 2000	< 2000	< 1500	< 1000
Styrène	> 500	< 500	< 350	< 250
COVT	> 2000	< 2000	< 1500	< 1000

- ➢ <u>Identify and quantify other VOCs characteristic of selected materials (VOCs screening)</u>

TESTS ACCORDING TO ISO 16000-9 STANDARD

Tests with new PVC materials

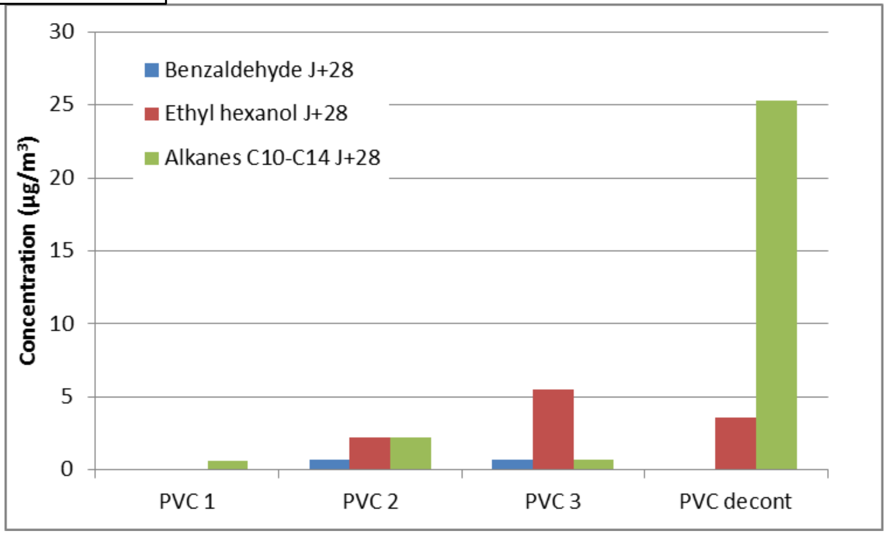
Labelling VOCs



All PVC materials are classified A+

Few labelling compounds identified

Specific VOCs



Very low emissions

Oxygenated VOCs and alkanes

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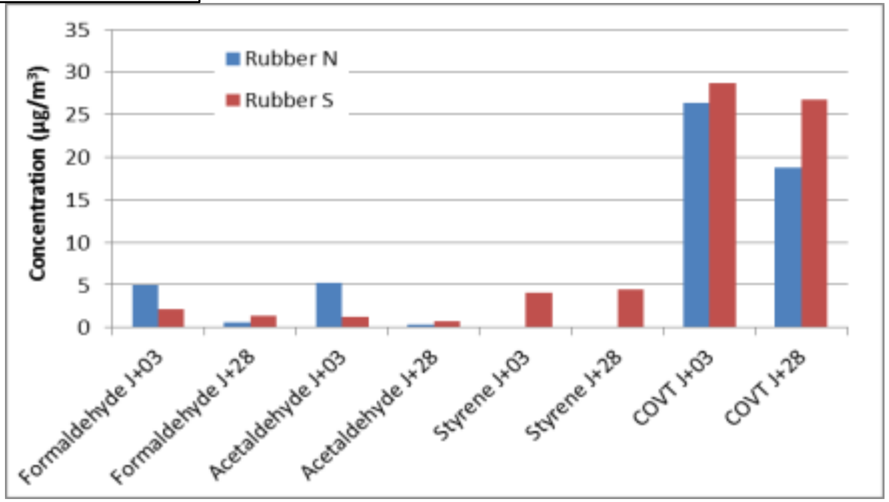
TESTS ACCORDING TO ISO 16000-9 STANDARD

Tests with new rubber materials

Labelling VOCs



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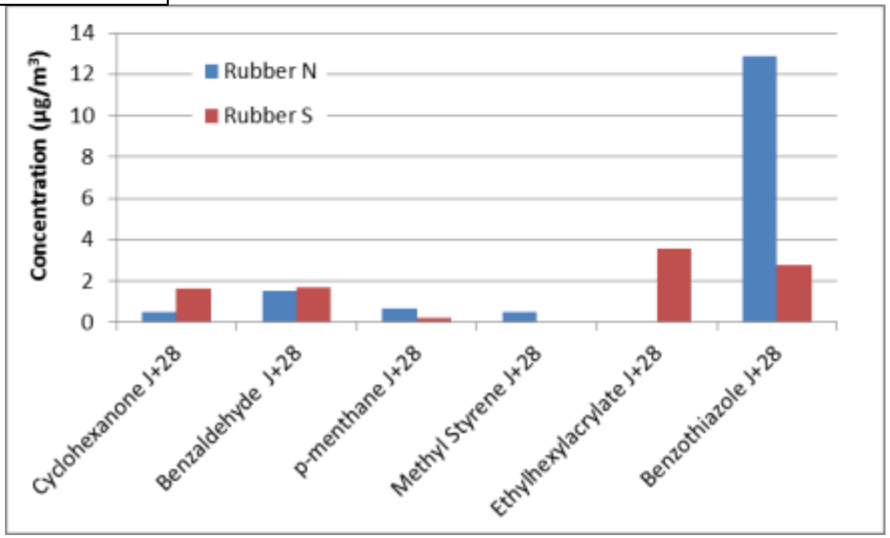

Very low emissions

Oxygenated VOCs and aromatics

A toxic compound (benzothiazole)

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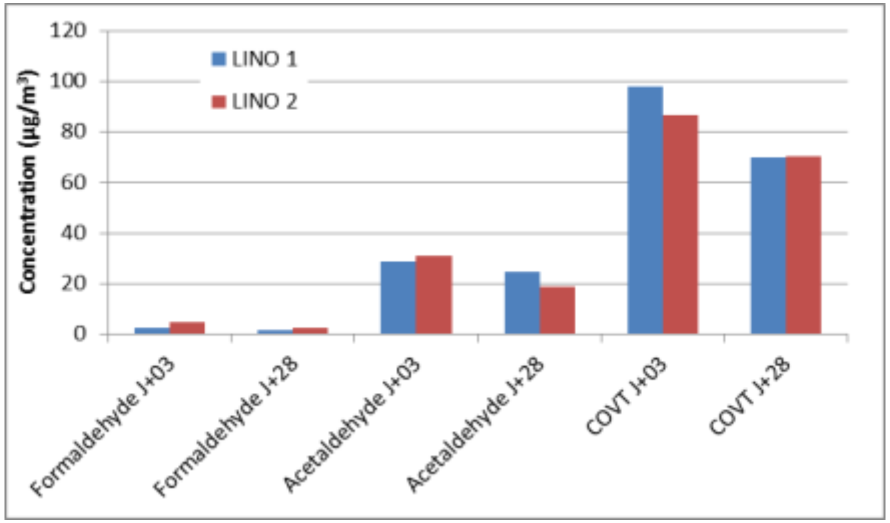
TESTS ACCORDING TO ISO 16000-9 STANDARD

Tests with new linoleum materials

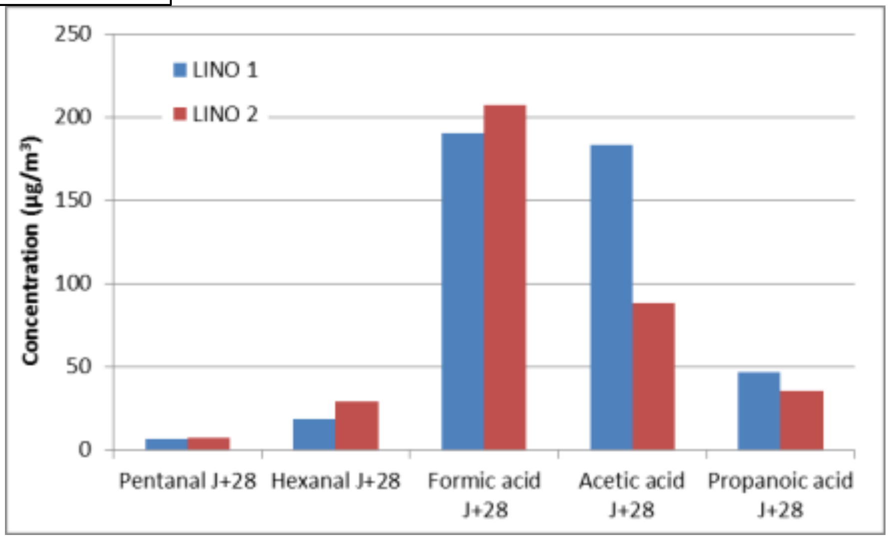
Labelling VOCs



All linoleum materials are classified A+

Few labelling compounds identified

Specific VOCs



Low emissions

Oxygenated VOCs: Aldehydes, ketones, carboxylic acids

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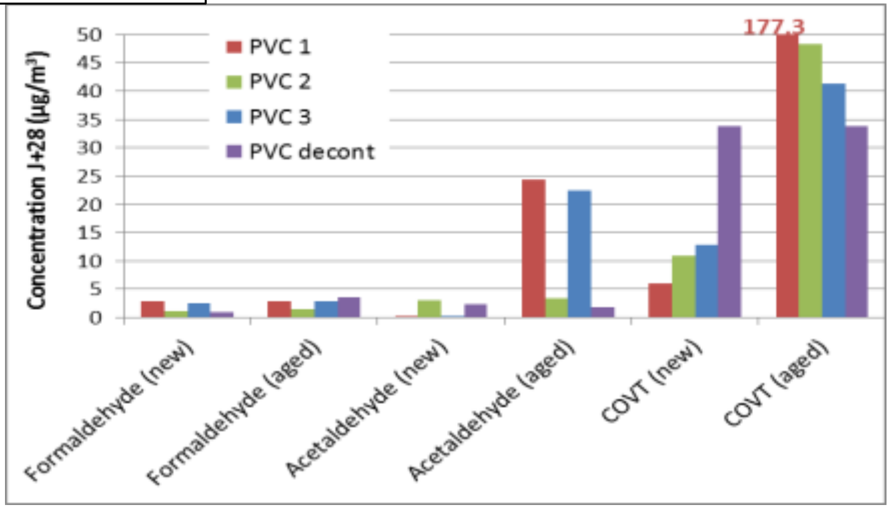
TESTS ACCORDING TO ISO 16000-9 STANDARD

Tests with aged PVC materials

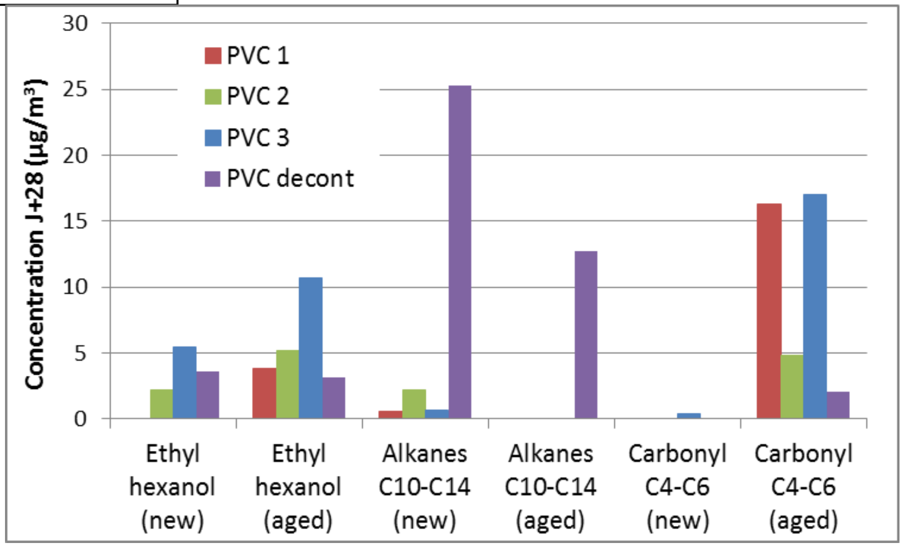
Labelling VOCs



All PVC materials are classified A+ after aging

PVC decontaminant less impacted by aging

Specific VOCs



Very low emissions

Increase of carbonyl VOCs after aging

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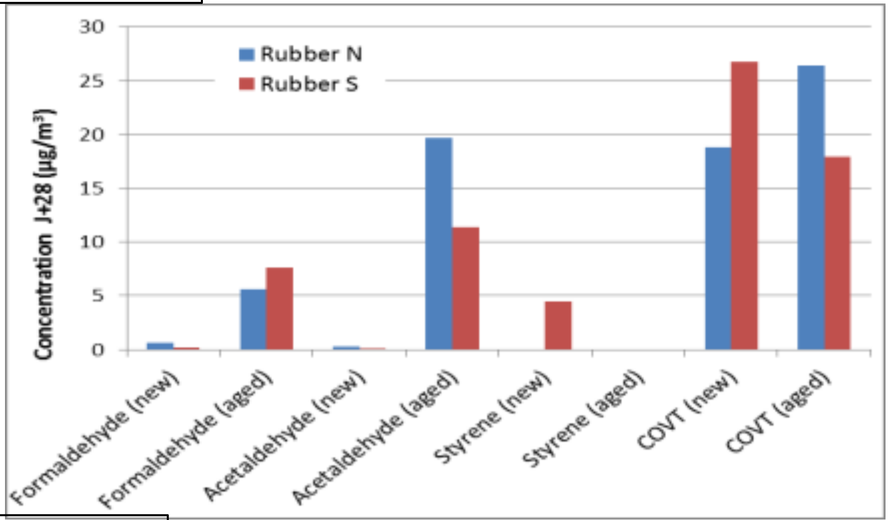
TESTS ACCORDING TO ISO 16000-9 STANDARD

Tests with aged rubber materials

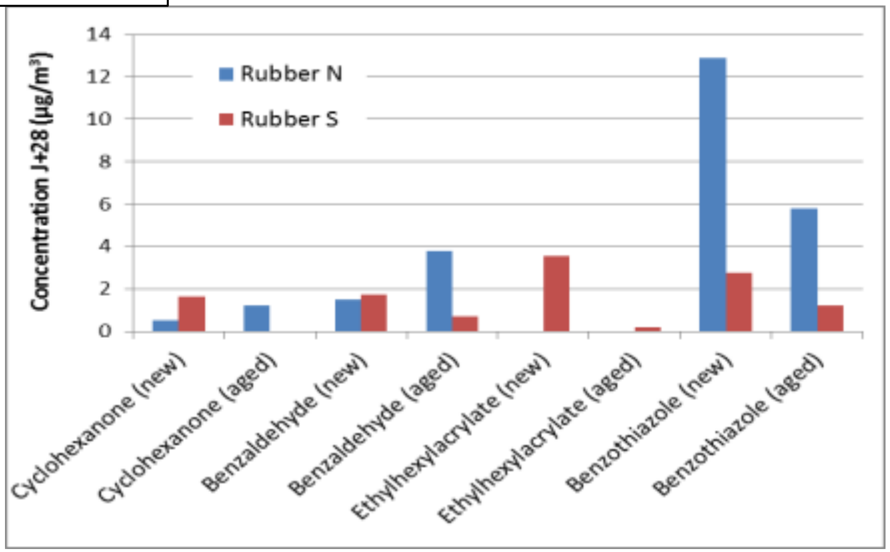
Labelling VOCs



All rubber materials are classified A+ after aging

Low impact of aging: Small increase of aldehydes

Specific VOCs



Very low emissions

Decrease of the toxic compound (benzothiazole)

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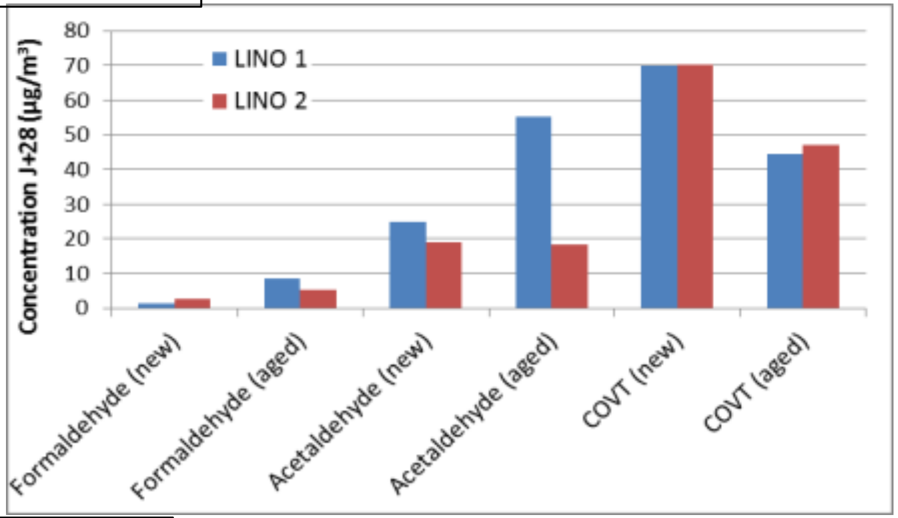
TESTS ACCORDING TO ISO 16000-9 STANDARD

Tests with aged linoleum materials

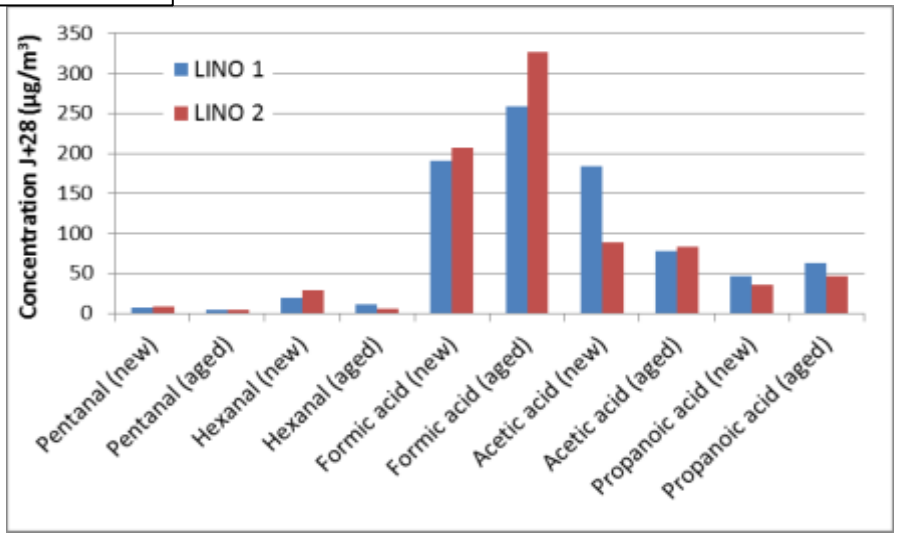
Labelling VOCs



All linoleum materials are classified A+ after aging

Few labeling compounds identified

Specific VOCs



Low emissions

Same oxygenated VOCs identified after aging

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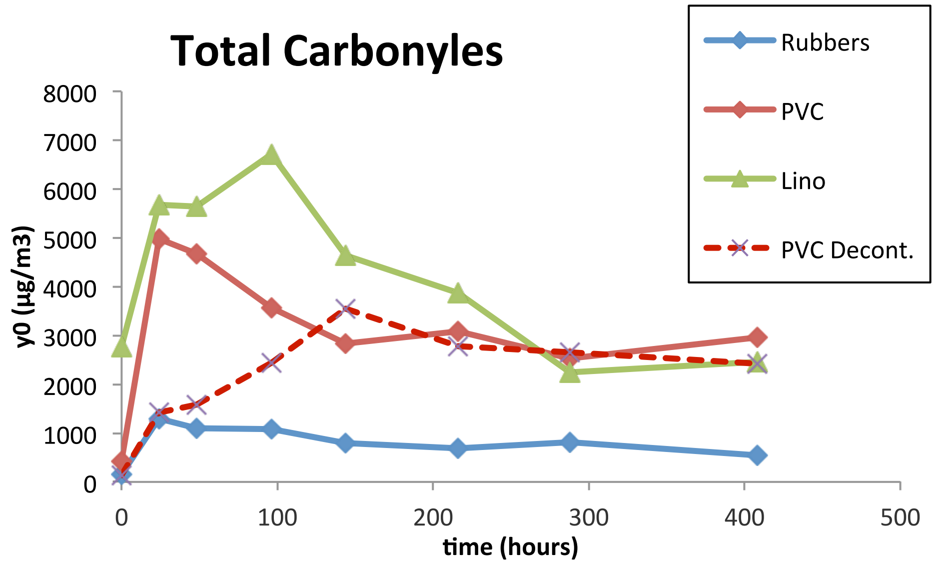
IMPACT OF AGING ON VOCS EMISSIONS
Carbonyl compounds

Mean of the sum of the alkanals surface concentrations (y_0) for each type of flooring



- Linear carbonyl compounds are the major VOCs emitted by all the floorings during aging, due to photo- and thermal oxidation degradation of the polymers
- Natural products (linos) or 50% natural plastic (PVC 3) are the most emissive
- Decontaminating PVC shows a slower degradation kinetics than other materials but the same stable emission level than for other PVC is obtained after 200 h.

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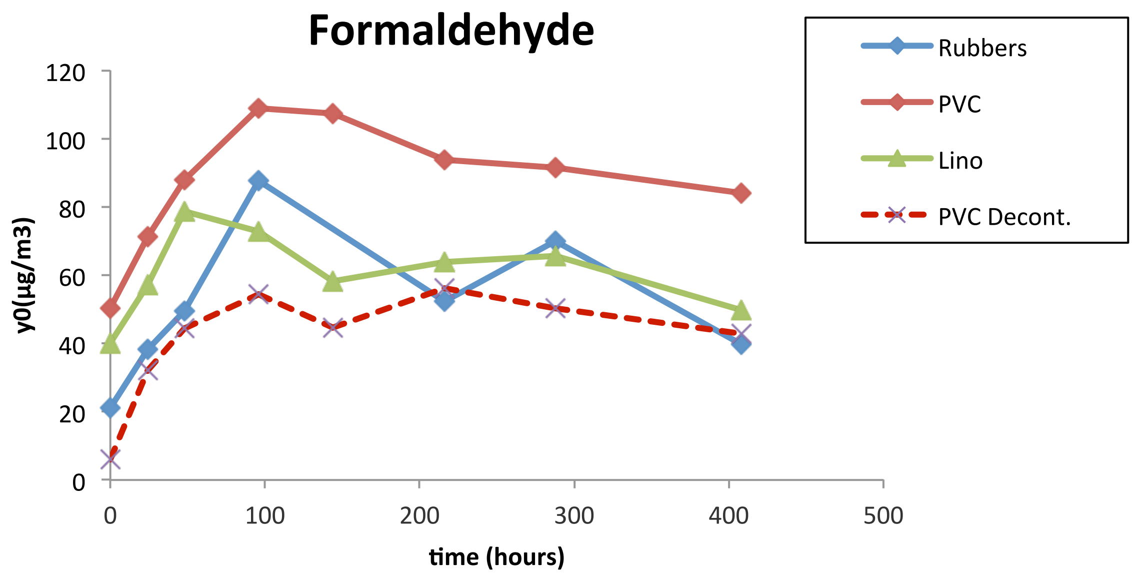
IMPACT OF AGING ON VOCS EMISSIONS
Carbonyl compounds – Focus on Formaldehyde

Mean of the formaldehyde surface concentrations (y_0) for each type of flooring



- Kinetics profiles show that formaldehyde is an oxidation by-product of the polymers: an increase of y_0 is observed up to100h followed by a slow decrease.
- After 400h, y_0 still range from 40 to 80 µg/m^3
- Decontaminating PVC shows the lower level whereas other PVC are the most emissive plastics

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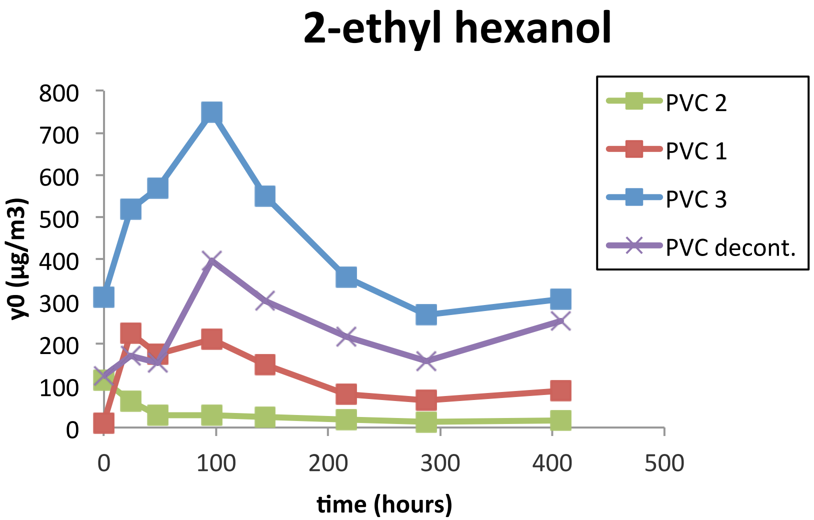
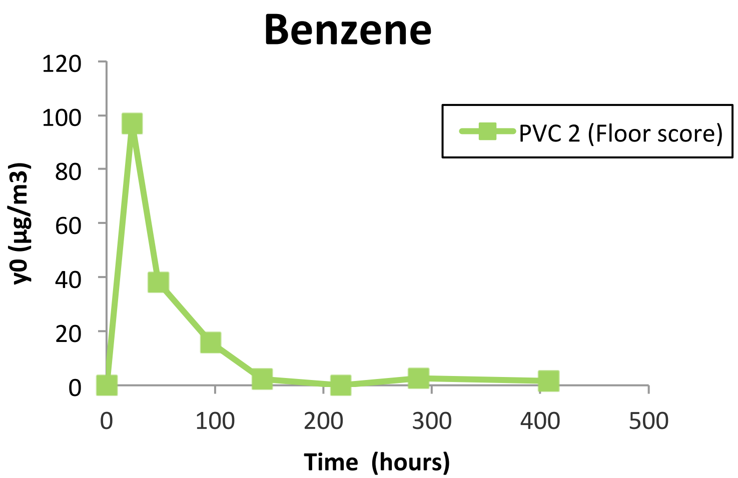
IMPACT OF AGING ON VOCS EMISSIONS
PVC – Specific VOCs





For all PVC materials:

- **2-ethyl hexanol:** hydrolysis of 2-ethylhexyl- moiety of plasticizers (i.e. DEHP, 2-ethylhexyl adipate)

For PVC 2 only:

- **Benzene**: emission after the first aging cycle, and rapid decrease

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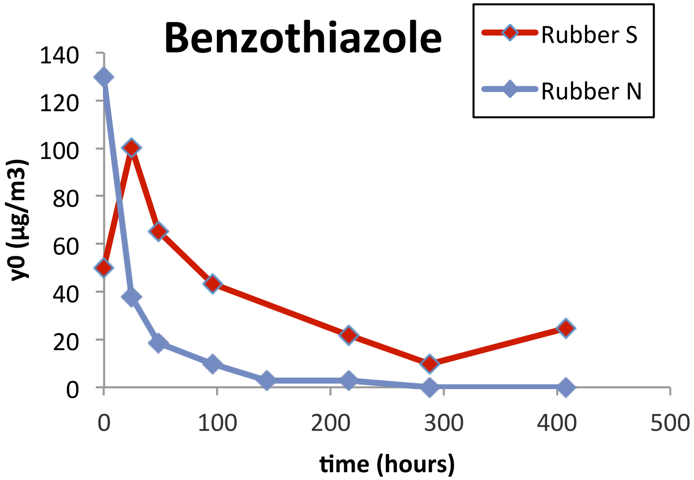
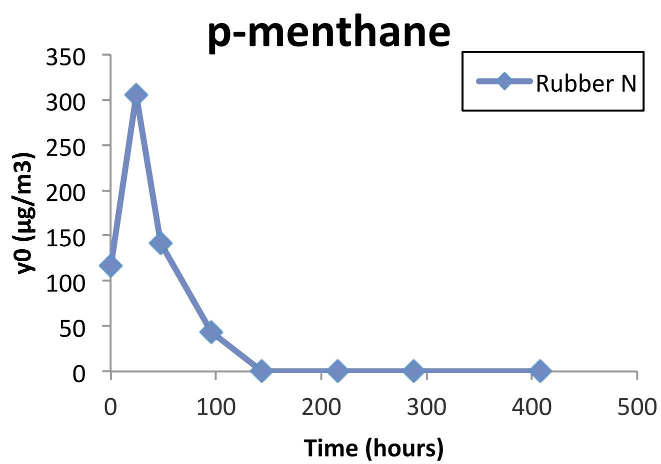
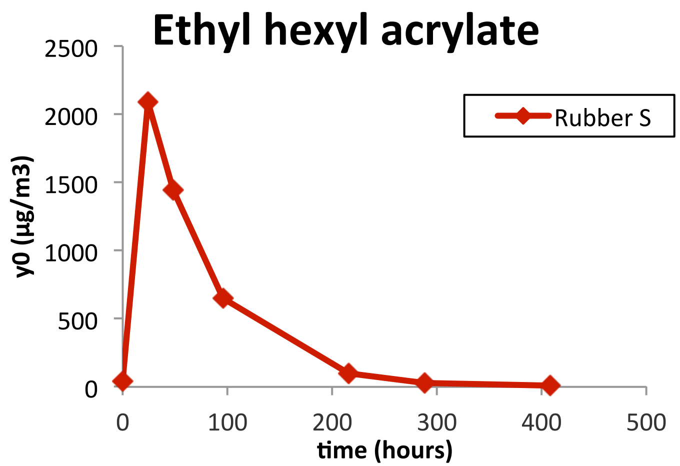
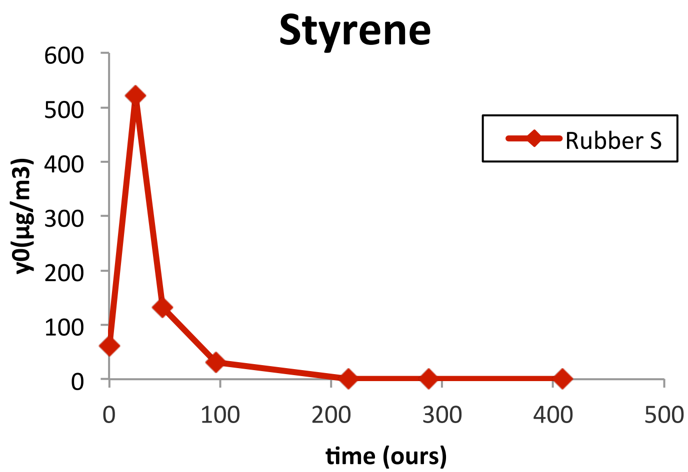
IMPACT OF AGING ON VOCS EMISSIONS RUBBERS – Specific VOCs









- Similar kinetics profiles for additives and polymerization residues
- Emission of toxic compounds

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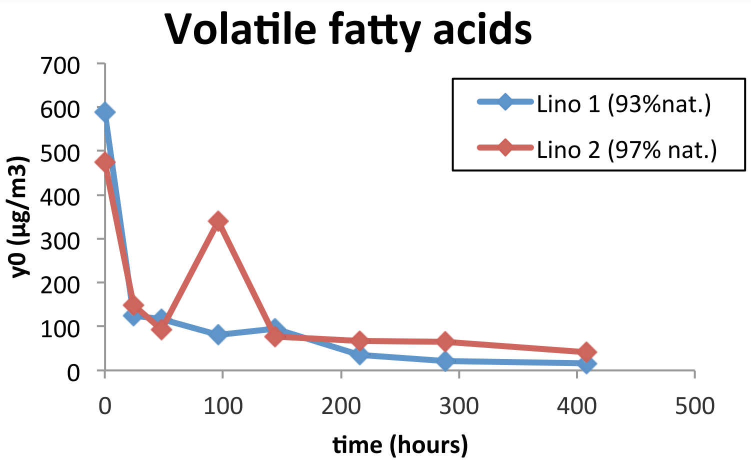
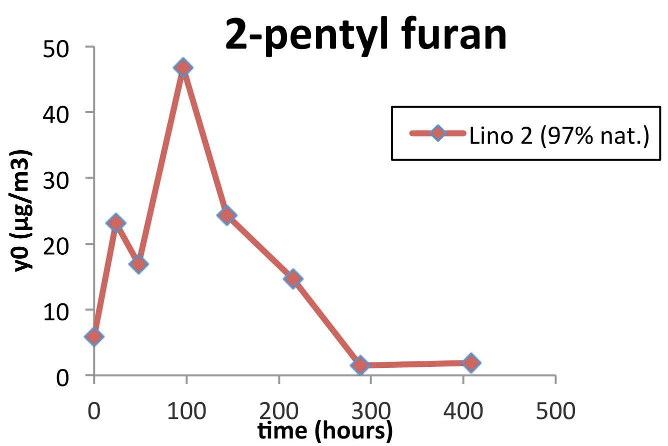
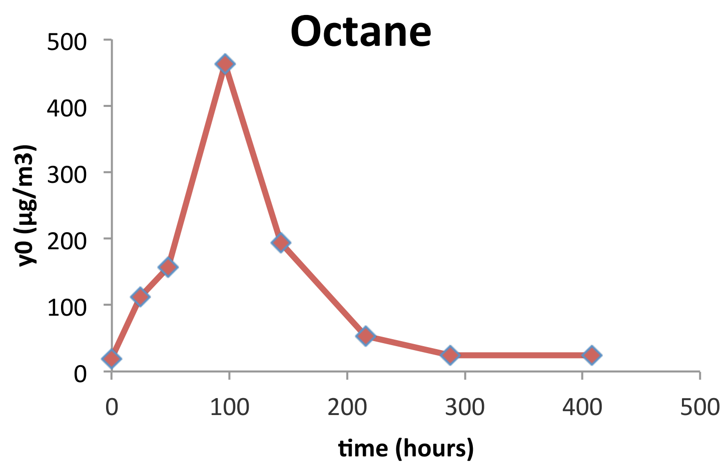
IMPACT OF AGING ON VOCS EMISSIONS LINOLEUMS – Specific VOCs







- Volatile fatty acids were detected in the 2 linoleums (secondary oxidation by-products)
- Octane and 2-pentyl furan are only detected in Lino 2: known to be emitted by oxidised linoleic acid (component of linseed oil)

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CONCLUSION

Emission tests according to the standard method with new materials and after aging:

- **PVC** New: Low emission of oxygenated compounds and alkanes.
  Petrochemical PVC are the less emissive

  Aged: Increase of carbonyl compounds.
  Decontaminant PVC are the less emissive
- **RUBBERS** New: Low emission of oxygenated compounds and aromatics.
  Aged: Small increase of carbonyl compounds.
  Decrease of toxic compounds.
- **LINOLEUM** New: Aldehydes, ketones and carboxylic acids emissions.
  Aged: Same compounds identified after aging.
  Comparable emissions for the 2 materials

Artificial aging:

- High emission of carbonyl compounds, issued from photo- thermal oxidation (y_0 up to 7000 µg/m^3)
- Formation of formaldehyde with slow y_0 decrease ($40<y_0<80$ µg/m^3 after 400 h aging)
- Identification of toxic compounds (emitted from PVC and Rubbers)

Perspective: temporal correlation between artificial and natural aging

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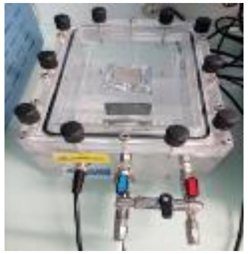
PERSPECTIVES

The study presented is supplemented by other investigations

Goals

- **Laboratory study - Comparison of materials**
  - ✓ Emission tests
  - ✓ Adsorption test
  - ✓ Influence of aging



- **Experimental platform study**
  - ✓ Effect of change of scale
  - ✓ Impact on air quality

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THANK'S FOR YOUR ATTENTION

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