Maintaining wood naturalness:
Production of Biocompatible wooden floors
and monitoring of Heavy Metals, VOC, and Radiation
Outline

• Introduction
• Sampling
• Materials and methods
• Results
• Conclusions
Introduction

• The wood floorings are perceived as natural and healthy materials.

• They are, however, a potential source of indoor VOC’s, which may worse the IAQ and human health. Other possible hazards are the presence of radioactive isotopes or heavy metals. It depends on HOW you manufacture it.

• A new generation of biocompatible wood floorings has been tested for the heavy metals, VOC’s emissions, radiations and related health impact, together with other brand floorings without evident low-emission attitude.

• The Alfapinene project is a 18 months research project ending in december 2016.
Introduction – Heavy metals

- Pigments, $Ti$, $Pb$, $Cr$, $Cu$..., 
- Presence may be naturally originated 
- Hazardous for children ingestion and adults inhalation 
- They are a challenge for a proper recycling
# Introduction - VOC

<table>
<thead>
<tr>
<th>VOC content</th>
<th>VOC emission</th>
<th>VOC concentration</th>
<th>VOC effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>[g/l]</td>
<td>[µg/m³] [mg/hm²]</td>
<td>[µg/m³]</td>
<td>Symptoms</td>
</tr>
<tr>
<td>ASTM 2369...</td>
<td>ISO 16000, EN 717, ASTM D6330, ASTM D6670...</td>
<td>Air changes, T, RH, heating, ventilation, air conditioning...</td>
<td>Gender, age, dose, frequency...</td>
</tr>
</tbody>
</table>
Introduction - VOC

• Are VOC good?

• **Negative effects:** headache, fatigue, skin irritation, nose congestion... The five «Ds» discomfort, dysfunction, disability, disease or death.

• **Positive effects:** heartbeat slowdown, cancer prevention and therapy, anti-inflammatory, antioxidants, decongestant, antimicrobials, help in drugs adsorption, anti-tussive, bronchodilators, mucolytic...

• **Important:** which molecule, route of exposure (inhalation...), magnitude (concentration), duration (how long?), frequency (how often?), timing (at what age?), gender, age, genetic, health, interactions...
Introduction - Radiation

RADIATION FROM CHERNOBYL

Kilo Becquerels (KBq) per square metre

- more than 1,480
- 185 to 1,480
- 40 to 185
- 10 to 40
- 2 to 10
- less than 2
- No data

- Chernobyl plant

Sampling

- 100 oiled wood floorings:
  - biocompatible floorings, made with vegetable raw materials.
  - other floorings without evident low-emission /eco-friendly attitude.
- 200 wood species in 350 specimens for heavy metals.
Biocompatible wood floorings:

- Organic, made with vegetable raw materials. Absence of chemical and petrol derivative product, or any potentially harmful for health.

- Fiemme valley – Italy is famous for its wood because it has luxuriant forests, where Stradivari used to come to bring the timber for his precious violins.
Sampling of natural air
Materials and methods - VOC

VOC analysis:
- On biocompatible wood floorings (headspace SPME-MS).
- On other wood floorings (headspace SPME-MS).
- Emissions from wood floorings (Preliminary tests with PID).
- Emissions from wood floorings (ISO 16000, 3 and 28 days).
- Natural “uncontaminated” air (Tenax vials and GC-MS).
- On VOC based pharmacy drugs (headspace SPME-MS).
Materials and methods - VOC

- The identification of the compounds has been done matching chromatograms with the NIST library.
- The health impact of the resulted compounds has been classified using databases from:
  - The International Agency for Research on Cancer (World Health Organization)
  - The AgBB (Committee for Health-related evaluation of Building Products)
  - Toxline
  - Medline
  - The Regulation EC n° 1272/2008
Materials and methods – Heavy metals

ED-XRF:
- Elements atomic mass > 12 a.m.u. (Mg) (no C, H, O...)
- Quali-quantitative analysis
- Handheld instrument with possible bench top and automation set-up.
- with pretty good accuracy
- Designed for metals, calibrated for wood
- No preparation, fast and cheap analysis

Set-up:
- Oxford Instruments X-MET 5100 ED-XRF
- X-ray source: 45 kV 40 μA,
- Sensitivity: from few to 1 000 000 mg/kg (e.g. Cl 2000 mg/kg Cd 4 mg/kg)
- Measurement set-up: bench top position, 40cm air background
- 6 replicas of 600 s measures per specimen

automatic process: 6 spec., 36 meas., 6 hours
Materials and methods - Radiation

- Pocket geiger type 6;
- 100 mm² First Sensor A.G. X100-7 PIN Ionizing radiation detector;
- X γ rays radiation (β removing the internal shield;
- High sensitive sensor;
- Measuring range (Cs\(^{137}\)) 0.05uSv/h ~ 10mSv/h 0.01cpm ~ 300Kcpm;
- USB, microcontrollers (e.g. Arduino), Android, IOS compatible;
- 10 minutes measurements;
- Certification Dutch Metrology Institute;

www.radiation-watch.org
Results – Heavy metals in wooden flooring
Results – Heavy metals in natural wood

Chemical element: Ca, Cr, Mn, Ni, Cu, Zn, Br, Sr, Ag, Cd, Pb

Average concentration [mg/kg]
Results - VOC

- International Agency for Research on Cancer (World Health Organization), about 1000 entries: none found
- The AgBB red list (Committee for Health-related evaluation of Building Products), about 800 entries: none found
- Toxline: both positive and negative health effects for the monoterpenes like α-pinene, camphene, β-pinene, cineole, limonene, camphor, eucalyptol and thujone.
Results

VOC Emissions SPME [%]

- α-Pinene
- β-Pinene
- Limonene
- Camphene
- γ-Terpinene
- β-Phellandrene
- Acetic acid
- Hexanal
- Supraene
- o-Cymene
- Terpinolene
- Borneol
- Longifolene
- Terpineol
- 3-carene
- m-Cymene
- Fenchol
- α-Terpinene
- (±)-Camphor
- l-Verbenone
- β-Myrcene
- Camphor
- Tricyclene
- Pentanal
- Other floorings

Other floorings

89% of total emitted VOC
61%

81%
77%
Results - radiation

beta radiations emitted from wooden floors

\[
\text{world «normal» } \frac{2.4 \, \mu Sv/\text{year}}{8760 \, \text{h/year}} = 0.274 \, \mu Sv/h
\]
Results - radiation

Radiations from stone and wood floorings

- Red granite
- Pink granite
- Wood floorings
- "Normal environment"

Frequency (n) vs. uSv/h
Conclusions

• The biocompatible floorings made with vegetable raw materials present no trace of heavy metals, radiation, petroleum-derived compounds. The detected VOC are naturally occurring in wood, and show no evident threat to human health.

• A bibliographic search suggests that some of the VOC emitted by the biocompatible floorings are the same molecules naturally emitted by conifers forests, or found in VOC based pharmacy drugs. (Scientific validation is ongoing).

• The other floorings VOC emissions are completely different, showing molecules with evident human hazard (toluene).

• Actual indoor concentrations are ongoing.
Conclusions

Final OPEN question:
Are the natural-based VOC emitted from these wooden based materials contributing to increase the indoor discomfort, are they neutral or are they improving the air quality?
Acknowledgements

Research funders:

- D.K.Z. srl – Fiemme 3000: Marco Felicetti, Vittorio Monsorno, Luca De Marco
- Fondazione Caritro

SPME analysis:

- Marco Michelozzi, Luca Calamai, CNR-IBBR


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Questions?
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Addendum
How does end life wood looks like?
Test 5: maximum detection thickness

**Cubes**
- 3 anatomical directions of wood,
- 5 wood species

**Wedges**
- 3 anatomical directions of wood,
- 2 specimens for anatomical direction,
- 1 wood specie (*Fagus Sylvatica*)
- 22 measurements along the changing thickness
- 11 replicas
- total of 1452 measurements

Graphs showing the relationship between wood density and the maximum thickness of Cu detection for different anatomical directions:**
- **Radial:** $y = -0.023x + 34.23$, $R^2 = 0.935$
- **Axial:** $y = -0.025x + 32.79$, $R^2 = 0.841$
- **Tangential:** $y = -0.023x + 33.26$, $R^2 = 0.924$
## Test 6: Set-up and radiation leaks

<table>
<thead>
<tr>
<th>case</th>
<th>orientation</th>
<th>Specimen (1 cm spruce)</th>
<th>protection</th>
<th>background</th>
<th>distance of measurement [m]</th>
<th>emissions μSv/h</th>
<th>maximum exposure [hours/year]</th>
<th>Operations</th>
<th>Max specimen size [cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>upward</td>
<td>no</td>
<td>cabinet</td>
<td>Air</td>
<td>x</td>
<td>0,1</td>
<td>10000</td>
<td>low</td>
<td>60x60x30</td>
</tr>
<tr>
<td>2</td>
<td>upward</td>
<td>no</td>
<td>shield cap</td>
<td>Cap</td>
<td>x</td>
<td>0,1</td>
<td>10000</td>
<td>average</td>
<td>8x4x2,5</td>
</tr>
<tr>
<td>3</td>
<td>down-ward</td>
<td>no</td>
<td>enclosure</td>
<td>Plate</td>
<td>x</td>
<td>0,1</td>
<td>10000</td>
<td>good</td>
<td>40x40x20</td>
</tr>
<tr>
<td>4</td>
<td>down-ward</td>
<td>yes</td>
<td>none</td>
<td>Plate</td>
<td>x</td>
<td>12</td>
<td>83</td>
<td>good</td>
<td>Unlimited</td>
</tr>
<tr>
<td>5</td>
<td>upward</td>
<td>yes</td>
<td>none</td>
<td>Air</td>
<td>x</td>
<td>29</td>
<td>34</td>
<td>good</td>
<td>Unlimited</td>
</tr>
<tr>
<td>5a</td>
<td>upward</td>
<td>yes</td>
<td>none</td>
<td>Air</td>
<td>x</td>
<td>3</td>
<td>333</td>
<td>good</td>
<td>Unlimited</td>
</tr>
<tr>
<td>5b</td>
<td>upward</td>
<td>yes</td>
<td>none</td>
<td>Air</td>
<td>x</td>
<td>0,1</td>
<td>10000</td>
<td>good</td>
<td>Unlimited</td>
</tr>
<tr>
<td>6</td>
<td>horizontal</td>
<td>yes</td>
<td>none</td>
<td>Air</td>
<td>x</td>
<td>70</td>
<td>14</td>
<td>average</td>
<td>Unlimited</td>
</tr>
<tr>
<td>6a</td>
<td>horizontal</td>
<td>yes</td>
<td>none</td>
<td>Air</td>
<td>x</td>
<td>14</td>
<td>71</td>
<td>average</td>
<td>Unlimited</td>
</tr>
<tr>
<td>6b</td>
<td>horizontal</td>
<td>yes</td>
<td>none</td>
<td>Air</td>
<td>x</td>
<td>0,3</td>
<td>3333</td>
<td>average</td>
<td>Unlimited</td>
</tr>
</tbody>
</table>
Introduction

PARADOX: Certain VOC are freely sold and largely used
Introduction

PARADOX: Certain VOC have positive effect on health
Introduction

PARADOX: Certain VOC are carcinogenic/hazardous and limited/banned
### Results

**Comparison of two floors**

<table>
<thead>
<tr>
<th>Compound name</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>25.71</td>
</tr>
<tr>
<td>Pentane</td>
<td>12.52</td>
</tr>
<tr>
<td>Ethyl ether</td>
<td>6.88</td>
</tr>
<tr>
<td>Plinol C</td>
<td>5.62</td>
</tr>
<tr>
<td><strong>Limonene</strong></td>
<td></td>
</tr>
<tr>
<td>CO2</td>
<td></td>
</tr>
<tr>
<td>Silane, trichlorodecyl-Cyclotrisiloxane, hexamethyl</td>
<td></td>
</tr>
<tr>
<td>Lilac alcohol B</td>
<td></td>
</tr>
<tr>
<td><strong>1R-α-Pinene</strong></td>
<td></td>
</tr>
<tr>
<td>1,3-Cyclohexanediol, 2-methyl</td>
<td></td>
</tr>
<tr>
<td>p-Trimethylsilyloxyphenyl-b</td>
<td></td>
</tr>
<tr>
<td>Hexanal</td>
<td></td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td></td>
</tr>
<tr>
<td>Octane</td>
<td></td>
</tr>
<tr>
<td>2-Furanmethanol, 5-ethenyl</td>
<td></td>
</tr>
<tr>
<td>Cyclohexanol, 1-methyl-4-(1-methylethyl)-</td>
<td></td>
</tr>
<tr>
<td>Propylene Carbonate</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
</tr>
<tr>
<td>1-Pentanol</td>
<td></td>
</tr>
<tr>
<td>Nonane</td>
<td></td>
</tr>
<tr>
<td>1,6-Anhydro-2,4-dideoxy-β-</td>
<td></td>
</tr>
<tr>
<td>β-Pinene</td>
<td></td>
</tr>
<tr>
<td>3-Octen-2-ol</td>
<td></td>
</tr>
</tbody>
</table>

**VOC emissions [%]**

- **Flooring type**
  - Other wood flooring, code 102, (oiled oak on plywood)
  - Fiemme 3000 biocompatible wood flooring, code 64

**Floors**

- Natural origin VOC
- Petroleum-derived VOC
## Results

Actual indoor concentrations preliminary tests:

- Climatized standard glass chamber
- Parallel measurements: TVOC emissions with PID analyzer + VOC qualification from SPME GC-MS
- Example:
  - PID detects TVOC: 330 ppb of isobutylene
  - SPME provides a list of compounds and proportions

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS number</th>
<th>SPM E Area (%)</th>
<th>Response Factor PID</th>
<th>Molecular Weight g/mol</th>
<th>Concentration of single VOC ppb</th>
<th>Concentration of single VOC μg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Pinene</td>
<td>80-56-8</td>
<td>32,4</td>
<td>0,27</td>
<td>136,237</td>
<td>28</td>
<td>158</td>
</tr>
<tr>
<td>β-Pinene</td>
<td>127-91-3</td>
<td>16,0</td>
<td>0,17</td>
<td>136,237</td>
<td>14</td>
<td>79</td>
</tr>
<tr>
<td>Limonene</td>
<td>138-86-3</td>
<td>10,5</td>
<td>0,9</td>
<td>136,237</td>
<td>9</td>
<td>51</td>
</tr>
<tr>
<td>Terpinolene</td>
<td>586-62-9</td>
<td>7,3</td>
<td>0,6</td>
<td>136,237</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>Terpineol</td>
<td>98-55-5</td>
<td>1,1</td>
<td>0,8</td>
<td>154,25</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>3-Carene</td>
<td>13466-78-9</td>
<td>0,7</td>
<td>0,5</td>
<td>136,1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>64-19-7</td>
<td>0,6</td>
<td>36</td>
<td>60,052</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td><strong>TOTAL VOC</strong></td>
<td></td>
<td><strong>60</strong></td>
<td></td>
<td></td>
<td><strong>335</strong></td>
<td></td>
</tr>
</tbody>
</table>
## Results

- **Actual indoor concentrations:**

<table>
<thead>
<tr>
<th></th>
<th>Concentration</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preliminary tests TVOC emissions</td>
<td>15 – 350 μg/m³</td>
<td>3 days</td>
</tr>
<tr>
<td>Preliminary tests TVOC emissions</td>
<td>2 – 30 μg/m³</td>
<td>28 days</td>
</tr>
<tr>
<td>UNI EN ISO 16000-9</td>
<td><em>measurements are still ongoing</em></td>
<td></td>
</tr>
</tbody>
</table>

- Comparison with the natural air VOC: Limonene, α-Pinene, Ocimene, Acetic acid, Acetone, Phenol... Benzene!

- Comparison with the pharmacy VOC: measurements are still ongoing.
Radiation screening distribution

<table>
<thead>
<tr>
<th>Value</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.030</td>
<td>min.</td>
<td>μSv/h</td>
</tr>
<tr>
<td>0.077</td>
<td>max.</td>
<td>μSv/h</td>
</tr>
<tr>
<td>0.036</td>
<td>5° perc.</td>
<td>μSv/h</td>
</tr>
<tr>
<td>0.051</td>
<td>Mean</td>
<td>μSv/h</td>
</tr>
<tr>
<td>0.051</td>
<td>Median</td>
<td>μSv/h</td>
</tr>
<tr>
<td>0.066</td>
<td>95° percentile</td>
<td>μSv/h</td>
</tr>
</tbody>
</table>