Benzalkonium runoff from roofs treated with biocides

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Context / Objectives

- Sources of stormwater contamination
Context / Objectives

Biocide products for roof cleaning

Runoff loads? Risks?

Inside use

Outside use

Harvesting tank

Stormsewer

Lakes, rivers
Methodology

Roof treatment typology

- Roof treatment practices (survey among private / professionals)
- Treatment products, biocides, toxicity data (documentary research)

Runoff monitoring

- Biocide runoff under real meteorological conditions (Semi-field tests)
- Major factors influencing the wash-off (Lab studies under simulated rainfall)

Potentiel effects

- At local scale (tests)
- Stormwater contamination at catchment scale (modeling)
Treatment Typology

- **Most frequent treatment:** de-mossing
  - 1 / 4 private house owners already did it
  - Every 5 years on average
  - Professionnals or DIY
- **Biocide used:** benzalkonium chloride
  - Numerous trademarks
- **Normal dosage:** 4 to 7g/m²

![Alkyldimethylbenzylammonium or benzalkonium](image)

EC$_{50}$ *Fishies* = 280µg/L (Sütterlin, 2008)
EC$_{50}$ *Invertebrates* = 5.9µg/L (USEPA, 2006)
Semi field testing

- 12 test roof frames

<table>
<thead>
<tr>
<th>Materials</th>
<th>De-mossing treatment</th>
<th>Aspect</th>
<th>Exposition</th>
<th>Surface</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic Tiles (Cl)</td>
<td>No (controls)</td>
<td>Old</td>
<td>S</td>
<td>~1m²</td>
<td>40°</td>
</tr>
<tr>
<td>Concrete Tiles (Co)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yes</td>
<td>Old</td>
<td>N, S, E, W</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yes</td>
<td>New</td>
<td>N</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- 13 month follow up after biocide treatment
  - First 5 successive rain events (50 mm, 1 month)
  - 4 rain events later on
**Semi-field testing**

**Old tiles**
\[ y = 27.3e^{-0.012x} \]
\[ R^2 = 0.99 \]

**New tiles**
\[ y = 6.18e^{-0.012x} \]
\[ R^2 = 0.98 \]

- Very high concentrations in the first runoff events
- Rapid first order decrease
- Persistent emissions even after 13 month

Emission level depends on the tile material
But not on the exposition
Semi-field testing - mass balance after 13 month

Initial mass spread

Total mass leached

Residual mass in the roof material

Mass Balance

Product dilution and analysis

Regression

Integration

Extraction and analysis

Graphs showing the relationship between cumulated rain depth (mm) and mass of benzalkonium washed off (mg/m²). The regression equation is given as $y = 3.36 - 0.012x$ with $R^2 = 0.988$.
- Benzalkonium trapped in material negligible compared to mass spread (0.5 - 2%)

- Mass washed off dominant for both concrete and clay

- Low recovery (especially for clay) → could indicate biodegradation processes

<table>
<thead>
<tr>
<th></th>
<th>Concrete</th>
<th>Ceramic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass spread (mg/m²)</td>
<td>5900 ± 300</td>
<td></td>
</tr>
<tr>
<td>Residual concentration (mg/m²)</td>
<td>130 ± 17</td>
<td>30 ± 16</td>
</tr>
<tr>
<td>Benzalkonium washed off by the rain Min. - Moy. - Max. (mg/m²)</td>
<td>980 - 1690 - 2540</td>
<td>65 - 150 - 300</td>
</tr>
<tr>
<td>Total benzalkonium recovery</td>
<td>25% &lt; P &lt; 38%</td>
<td>2% &lt; P &lt; 4%</td>
</tr>
</tbody>
</table>
Lab studies under simulated rainfall

- Identification of main factors controlling benzalkonium runoff

Simulated rainfall

*Influence of dosage (mass and concentration of biocide product), material, rain intensity on benzalkonium runoff*

<table>
<thead>
<tr>
<th>Material</th>
<th>Mass of biocide spread</th>
<th>Conc. of biocide product</th>
<th>Rain intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>Natural ceramic</td>
<td>N</td>
<td>Y/N</td>
<td>-</td>
</tr>
<tr>
<td>Siliconated ceramic</td>
<td>Y</td>
<td>Y/N</td>
<td>-</td>
</tr>
</tbody>
</table>

Y : important effect  O/N : few effect  N : no effect

Emission patterns depend on the surface treatment of tiles

- Impervious surface: fast leaching proportional of the mass spread
- Pervious surface: product penetration and long term emission
Stormwater contamination at catchment scale

Sucy en Brie catchment

<table>
<thead>
<tr>
<th>Total area (km²)</th>
<th>Imperviousness (%)</th>
<th>Road area (km²)</th>
<th>Roof area (km²)</th>
<th>Number of treatable roofs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>30</td>
<td>0.325</td>
<td>0.315</td>
<td>2850</td>
</tr>
</tbody>
</table>

Roof material market study by MSI Etude (2006)

Concrete (15 %)

Clay (52 %)

430 roofs

MSI Etude (2006)

1500 roofs
Stormwater contamination at catchment scale

Structure of the model

Precipitation
- Monthly rainfall (mm)
- 6 years

Treatment module:
- Month of treatment (0 if roof not treated)
- Mass spread (mg.m⁻²)

Emission module:
- Mass leached for each roof during each month (mg.m⁻²)

Monthly mass and concentration downstream the watershed

Stochastic approach
Based on survey data
\[ M_{\text{spread}} \sim N(\mu = 7500; \sigma = 2500) \]
\[ M_{\text{spread}} \geq 5000 \text{mg.m}^{-2} \]

Based on field and lab. data
\[ M(h) = M_0 \times \left(1 - e^{-h/h_1}\right) \]
\( h_1 = 80 \text{mm} \)
concrete: \( M_0 = 0.29 M_{\text{spread}} \)
ceramic: \( M_0 \in U(300:500) \)

\( \times 1000 \text{ runs} \)
- Strong annual pattern linked to treatment periods
- Rapid decrease in periods without treatment
- Strong uncertainty due to variability in treatment practices
Comparison to measured stormwater concentrations at the outlet of Sucy catchment

<table>
<thead>
<tr>
<th></th>
<th>Model</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Monthly conc. (µg/L)</td>
<td>Total conc. (µg/L)</td>
</tr>
<tr>
<td>16/07/2011</td>
<td>13 to 35</td>
<td>28</td>
</tr>
<tr>
<td>19/07/2011</td>
<td>7</td>
<td>0.29</td>
</tr>
<tr>
<td>18/10/2011</td>
<td>17 to 50</td>
<td>28</td>
</tr>
</tbody>
</table>

Modeled values are consistent with measurements

but

Measured benzalkonium almost at 100% in particulate phase
Conclusion

- Roof treatment using benzalkonium biocides: a widespread practice

- **Huge runoff contamination** after a treatment (several mg/L)
  - Concentration $1,000 \times EC_{50}$
  - Fast decrease of contamination but concentration $> EC50$ even after 100s of mm

- Potential impacts at local scale (small ponds, harvesting tanks, ...):
  - For harvesting: disconnect during the first months after a treatment

- At catchment scale
  - For separative sewers $\rightarrow$ Dilution factor 2 to 10 to avoid short term toxicity
Thank you for your attention