Environmental monitoring of biocides in Europe.
Compartment-specific strategies

Workshop – 25/26 June 2015 Berlin

Benzalkonium runoff from roofs treated with biocides

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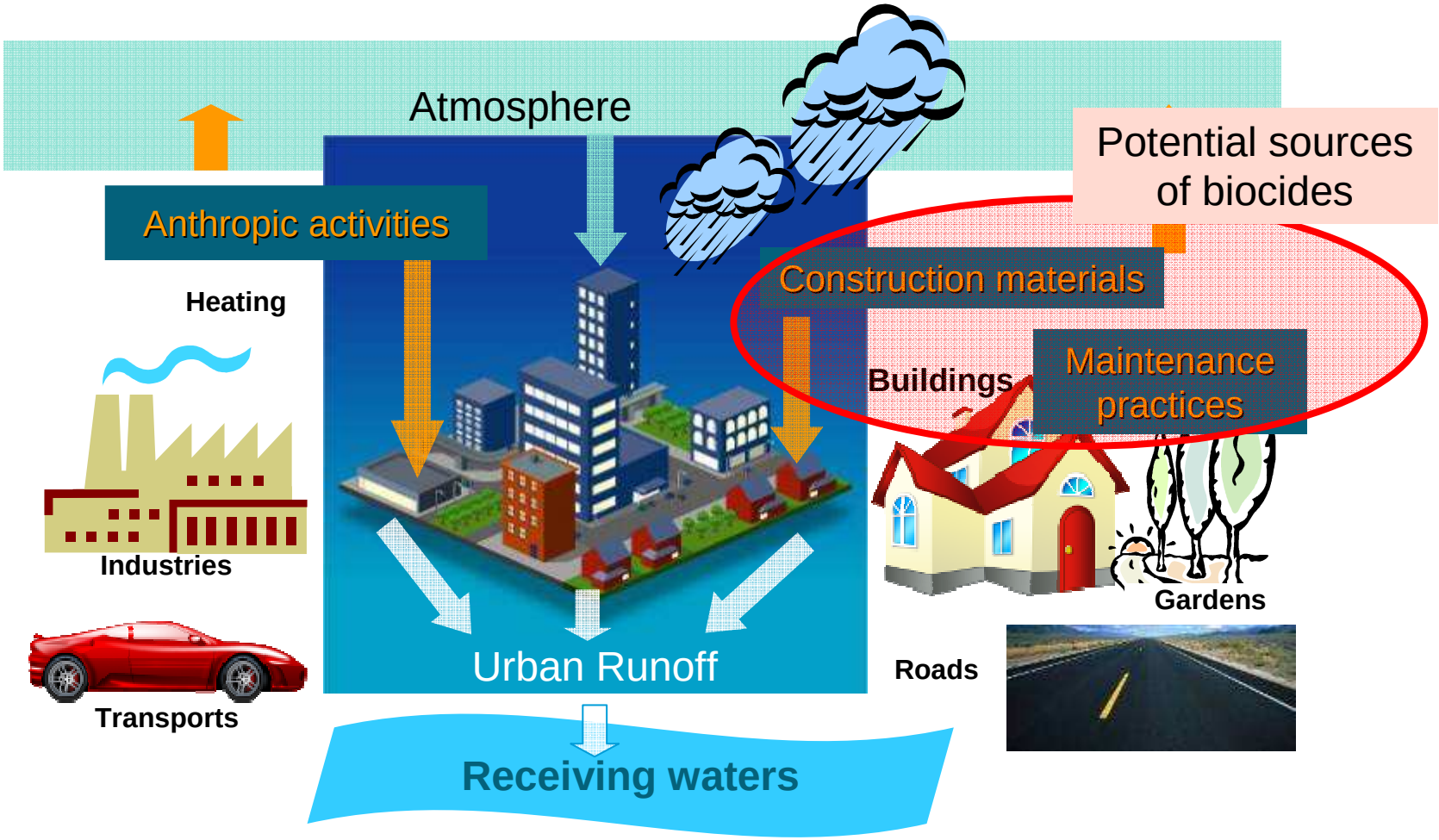
Context / Objectives

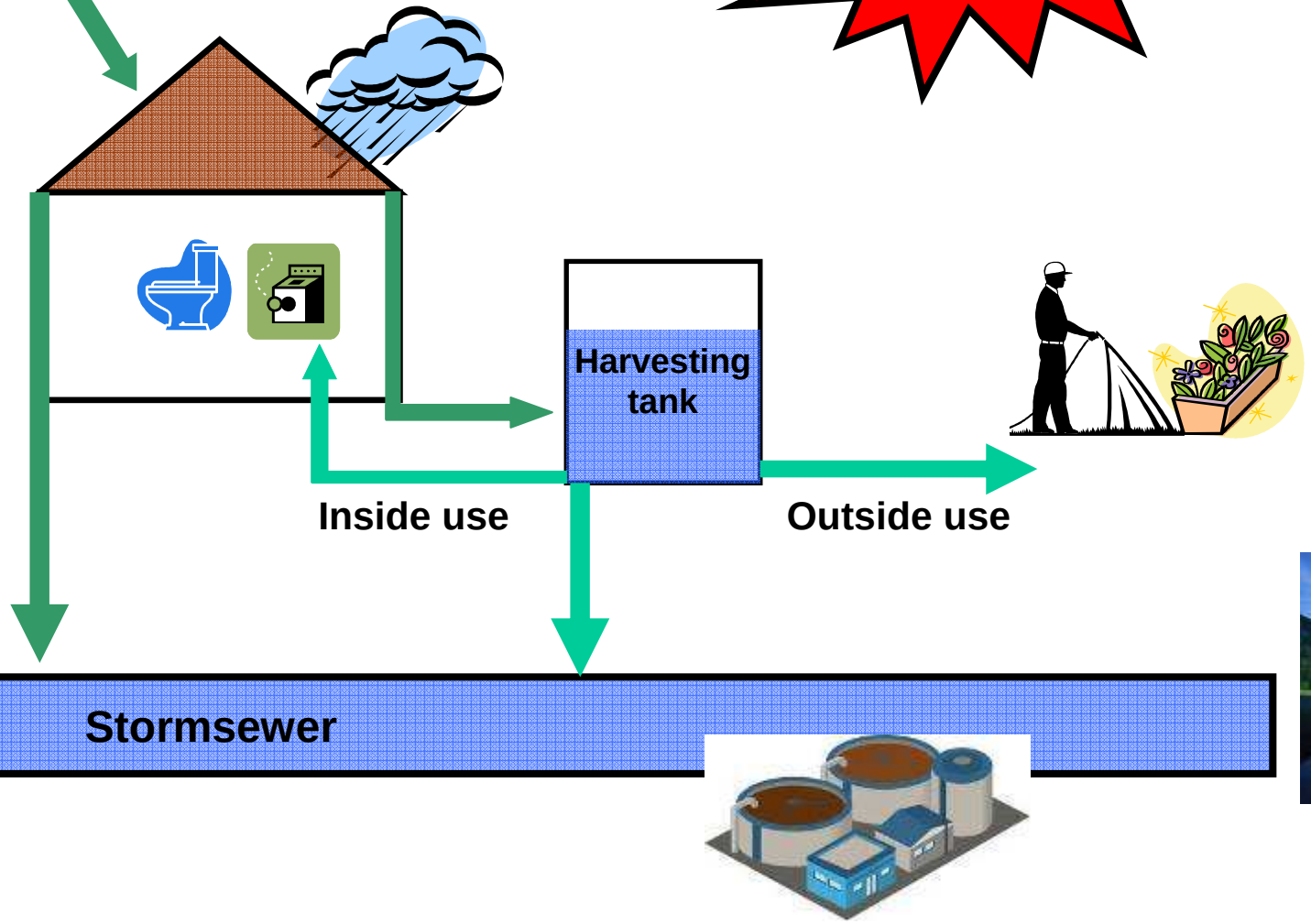
- Sources of stormwater contamination



Context / Objectives

Biocide products for roof cleaning

Runoff loads?
Risks?



Lakes, rivers

Methodology

Roof treatment typology

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

Runoff monitoring

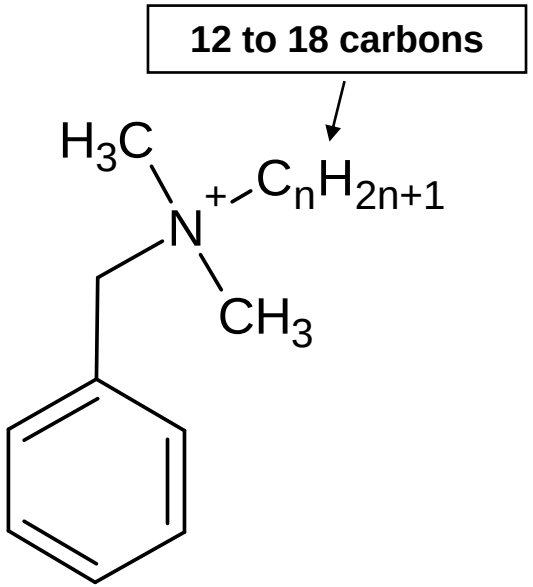
- Biocide runoff under real meteorological conditions **(Semi-field tests)**
- Major factors influencing the wash-off **(Lab studies under simulated rainfall)**

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 (CAS: 8001-54-5)

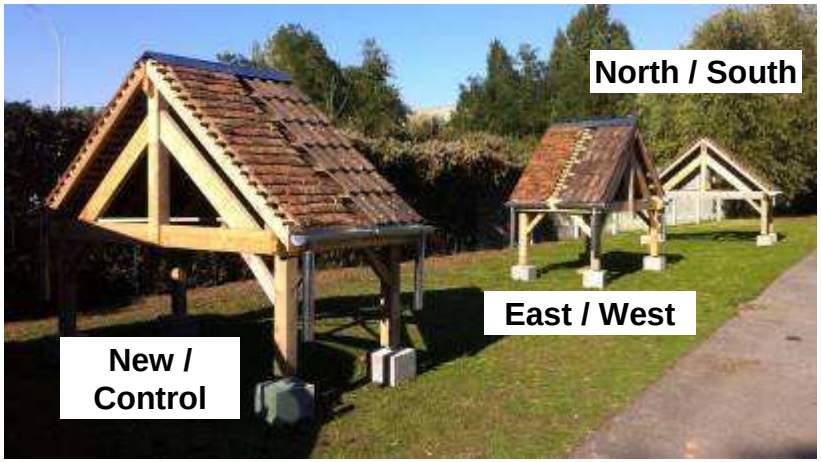
EC50*Fishies* = 280µg/L (Sütterlin, 2008)
EC50*Invertebrates* = 5.9µg/L (USEPA, 2006)

Semi field testing

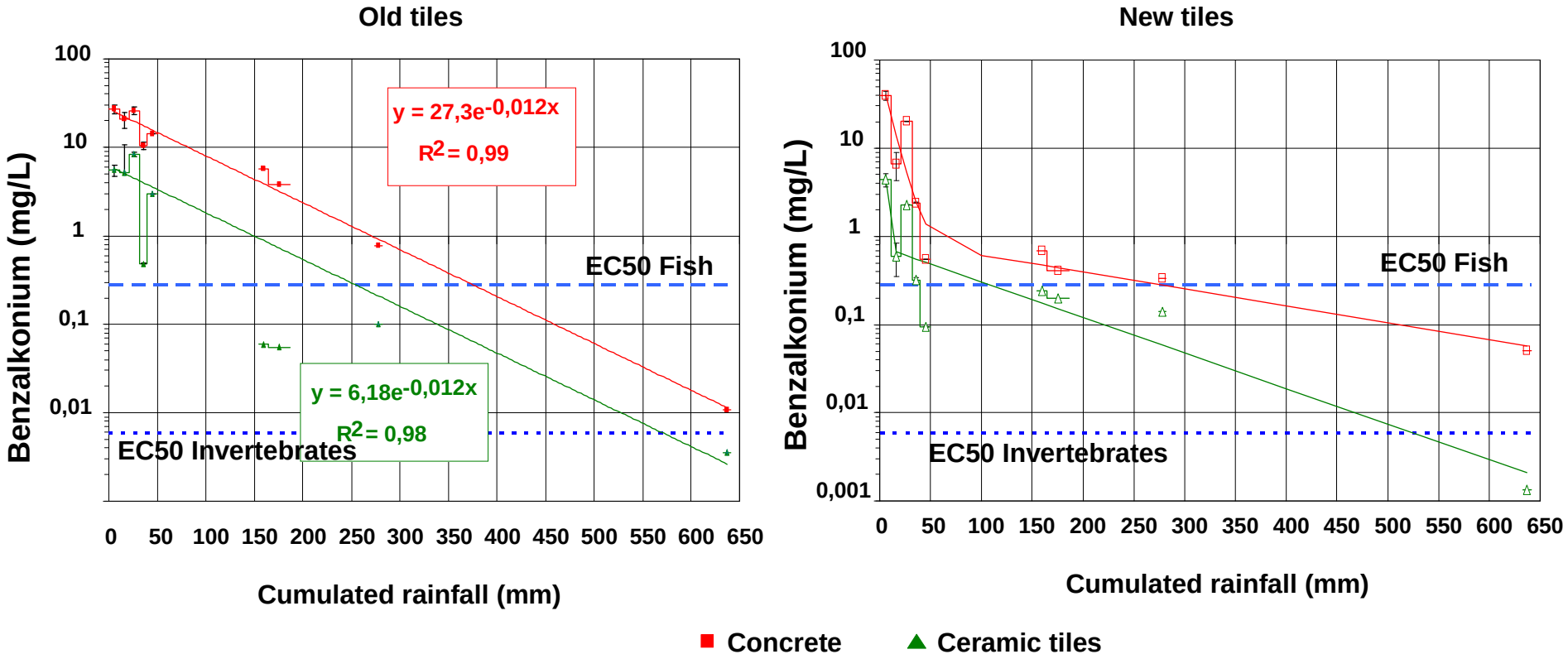
- 12 test roof frames

Materials	De-mossing treatment	Aspect	Exposition	Surface	Slope
Ceramic Tiles (Cl) Concrete Tiles (Co)	No (controls)	Old	S	~ 1m²	40°
	Yes	Old	N, S, E, W		
	Yes	New	N		

- 13 month follow up afer biocide treatment
  - First 5 successive rain events (50 mm, 1 month)
  - 4 rain events later on



Semi-field testing



Emission level depends on the tile material
But not on the exposition

Very high concentrations in the first runoff events
Rapid first order decrease

Persistent emissions even after 13 month

Semi-field testing – mass balance after 13 month

Initial mass spread

—

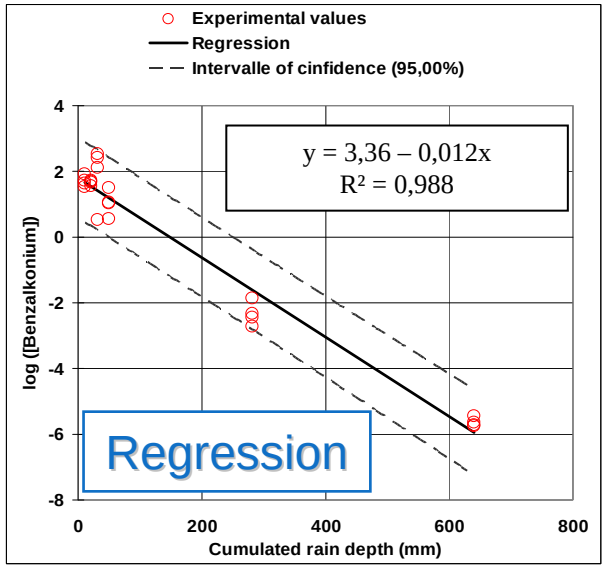
Total mass leached

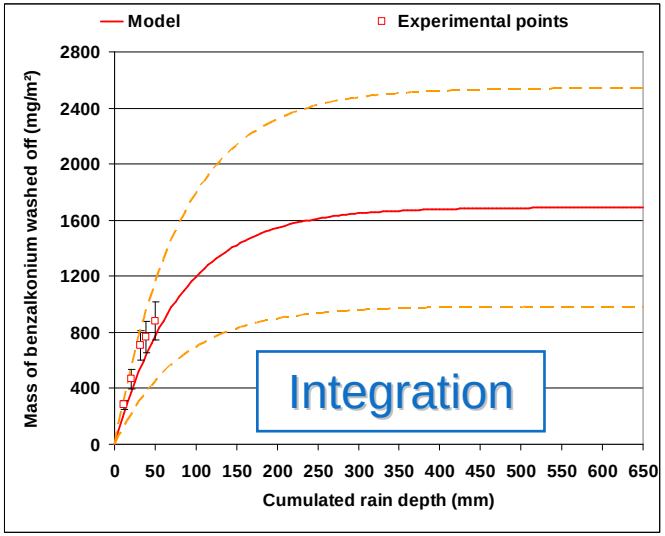
+

Residual mass in the roof material

= **Mass Balance**

Product dilution and analysis





Extraction and analysis

Semi-field testing – mass balance after 13 month

- 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

	Concrete	Ceramic
Mass spread (mg/m^2)	5900 ± 300	
Residual concentration (mg/m^2)	130 ± 17	30 ± 16
Benzalkonium washed off by the rain Min. - Moy. - Max. (mg/m^2)	980 - 1690 - 2540	65 - 150 - 300
Total benzalkonium recovery	*25% < P < 38%*	*2% < P < 4%*

Lab studies under simulated rainfall

- Identification of main factors controling benzalkonium runoff

Simulated rainfall

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

Material	Mass of biocide spread	Conc. of biocide product	Rain intensity
Concrete	**Y**	**Y**	N
Natural ceramic	N	Y/N	-
Siliconated ceramic	**Y**	Y/N	-

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

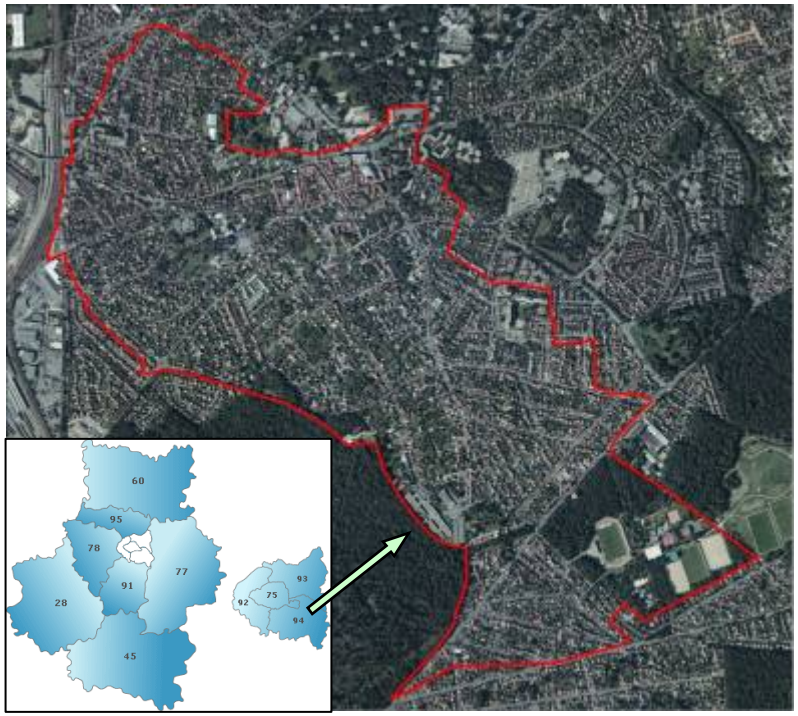
Emission patterns depend on the surface treatment of tiles

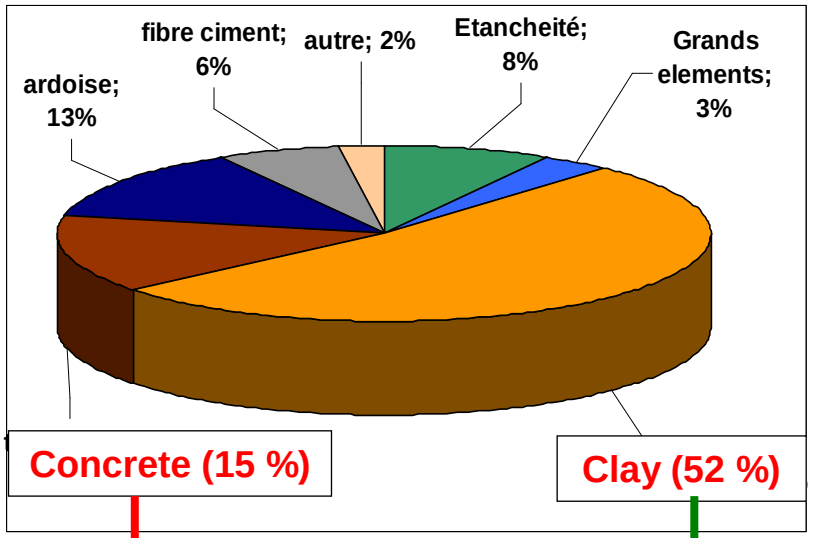
➔ Impervious surface : fast leaching proportinal of the mass spread
➔ Pervious surface : product penetration and long term emission

Stormwater contamination at catchment scale

Sucy en Brie catchment

Total area (km^2)	Imperviousness (%)	Road area (km^2)	Roof area (km^2)	Number of treatable roofs
2.1	30	0.325	0.315	2850





Roof material market study by MSI Etude (2006)

430 roofs

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

$$M_{spread} \in \mathrm{N}(\mu = 7500; \sigma = 2500)$$

$$M_{spread} \geq 5000 mg.m^{-2}$$

Based on field and lab. data

$$M(h) = M_0 \times \left(1 - e^{-h/h_1}\right)$$

$$h_1 = 80mm$$

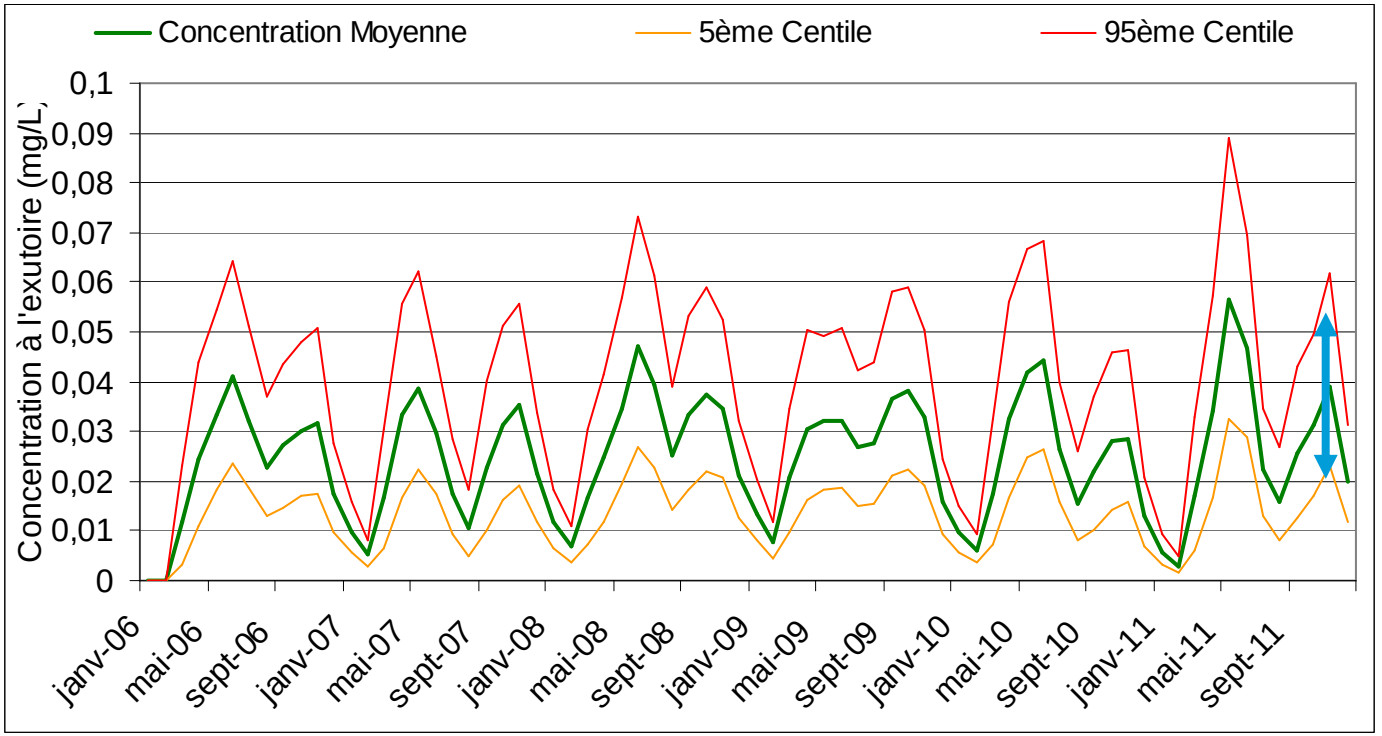
$$concrete : Mo = 0.29 Mspread$$

$$ceramic : Mo \in U(300;500)$$

×1000 runs

Stormwater contamination at catchment scale

- Simulated stormwater concentration ranges at the outlet of Sucy catchment



- Strong annual pattern linked to treatment periods

- Rapid decrease in periods without treatment

- Strong uncertainty due to variability in treatment practices

Stormwater contamination at catchment scale

- Comparison to measured stormwater concentrations at the outlet of Sucy catchment

	Model	Measurements		
	Monthly conc. (µg/L)	Total conc. (µg/L)	Dissolved conc. (µg/L)	Particulate conc. (mg/kg)
16/07/2011	13 to 35	28	0.13	50
19/07/2011		7	0.29	73
18/10/2011	17 to 50	28	0.28	84

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 x 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 → Dilution factor 2 to 10 to avoid short term toxicity


Thank you for your attention
Bench « North / South »