



The urban biocide terbutryn: field investigations to explore release and reactive transport under environmental conditions

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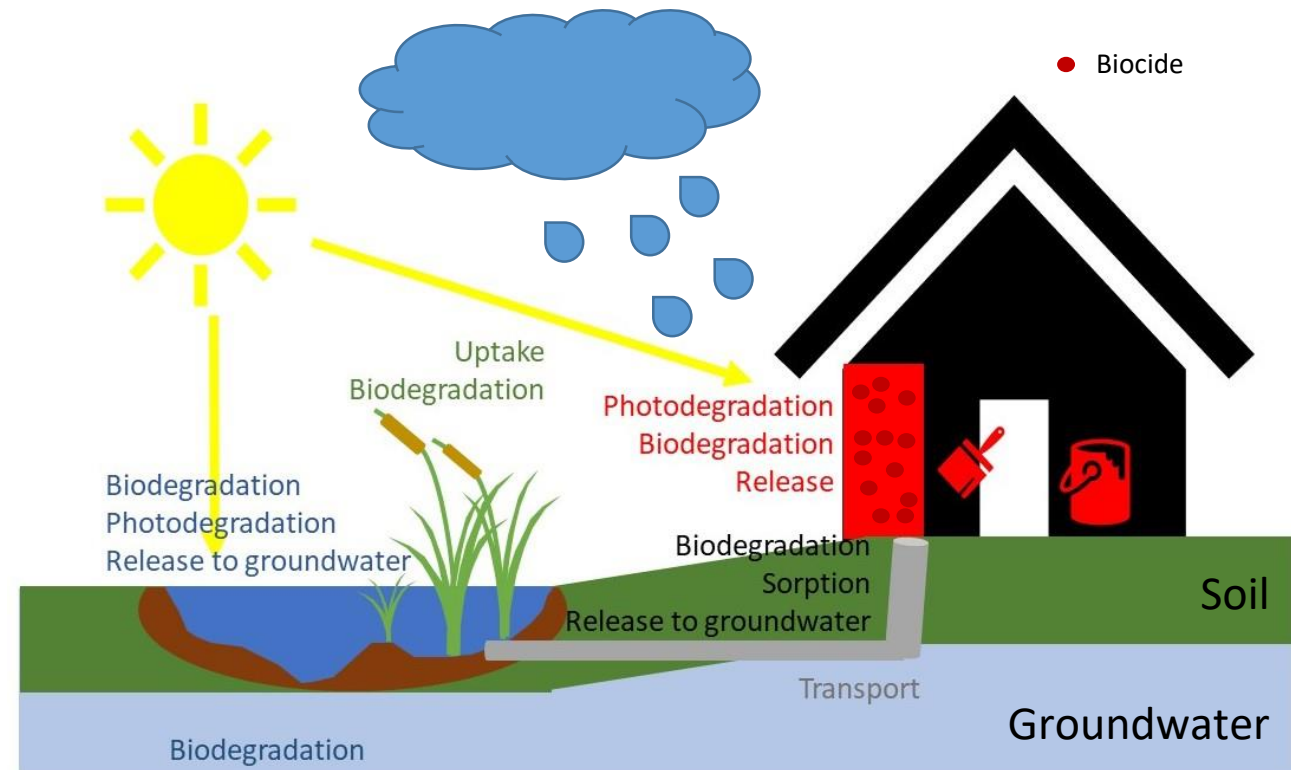
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Why studying urban biocides?

- Used in building materials like paint and render¹
- Prevent growth of algae, fungi,...
- Leaching into environment with **wind driven rain** ^{2,3,4}

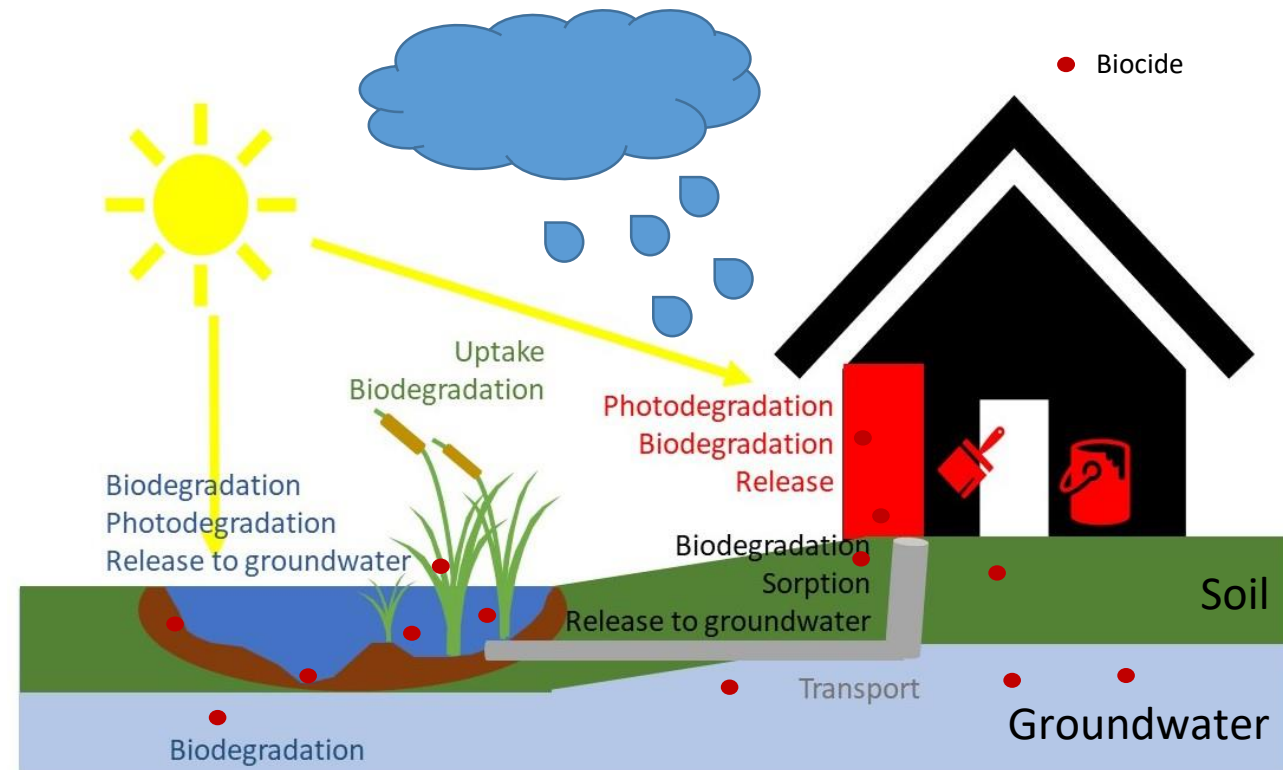
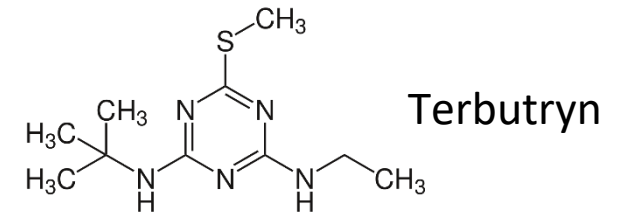


¹ Gartiser et al., 2015, ² Bollmann et al., 2016, ³ Burkhardt et al., 2012, ⁴ Wittmer et al., 2011, Picture: www.hausinfo.ch/

Why studying urban biocides?

- Used in building materials like paint and render¹
- Prevent growth of algae, fungi,...
- Leaching into environment with **wind driven rain** ^{2,3,4}
- **Terbutryn** is of major concern!
 - Prohibited in agriculture ⁵
 - PNEC towards aquatic organisms: 3 - 34 ng/L ^{6,7}
 - Concentrations up to 5.6 µg/L (rivers) and 7.6 ng/L (groundwater) ^{8,9}
 - Transformation products “probably toxic”¹⁰

Reaction pathways from façade to soil and surface water still unknown

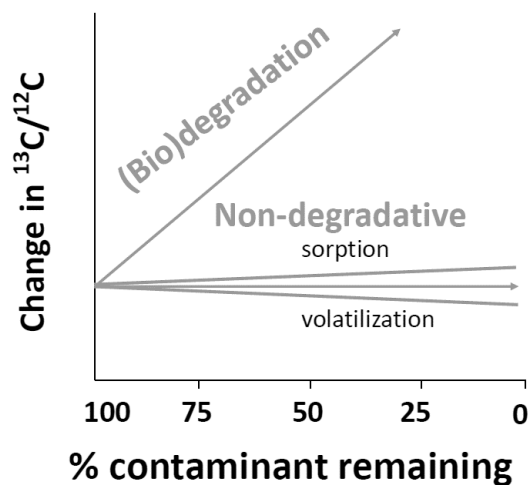
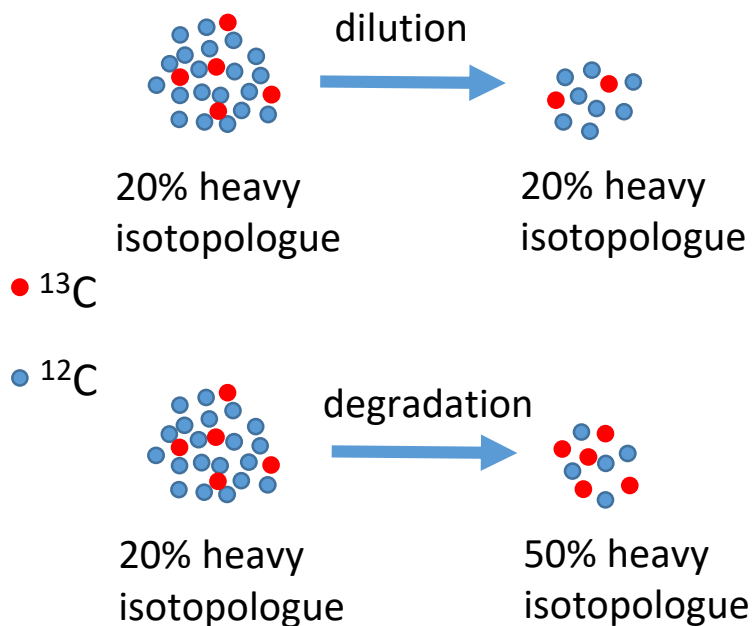




Compound specific isotope analysis as a tool to differentiate degradation pathways

Background: CSIA

- Each element in a compound has a distinct isotopic ratio
- Isotopic ratio can shift in systematic way (e.g. biodegradation / photodegradation)¹
- Non-degradative processes usually don't cause isotope fractionation¹



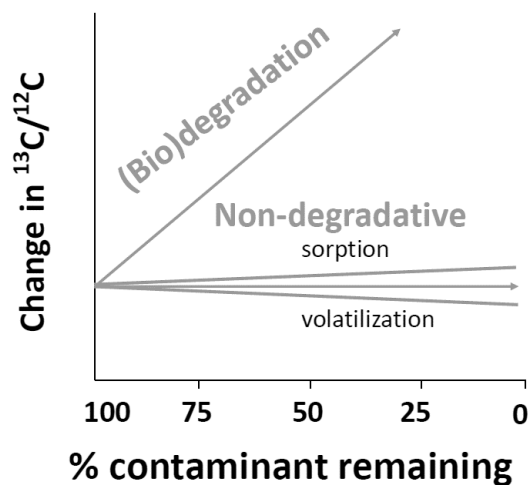
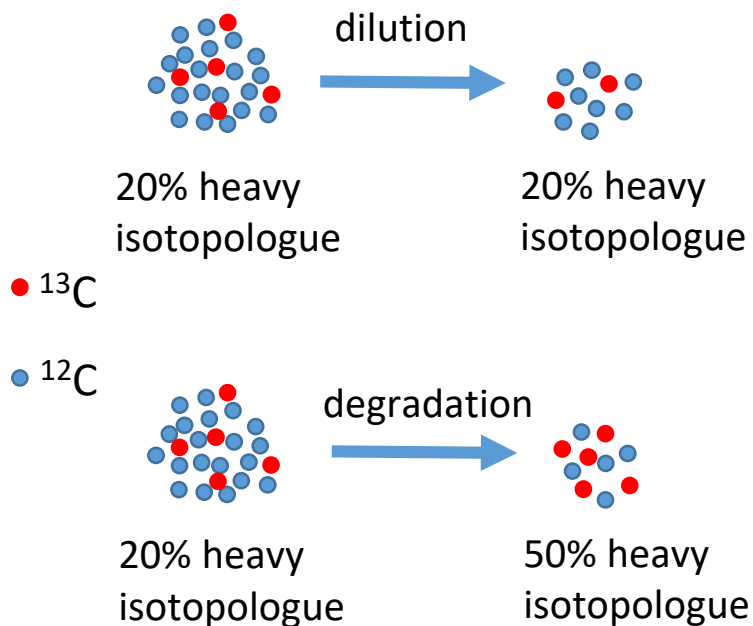
¹ Elsner & Imfeld (2016)



Compound specific isotope analysis as a tool to differentiate degradation pathways

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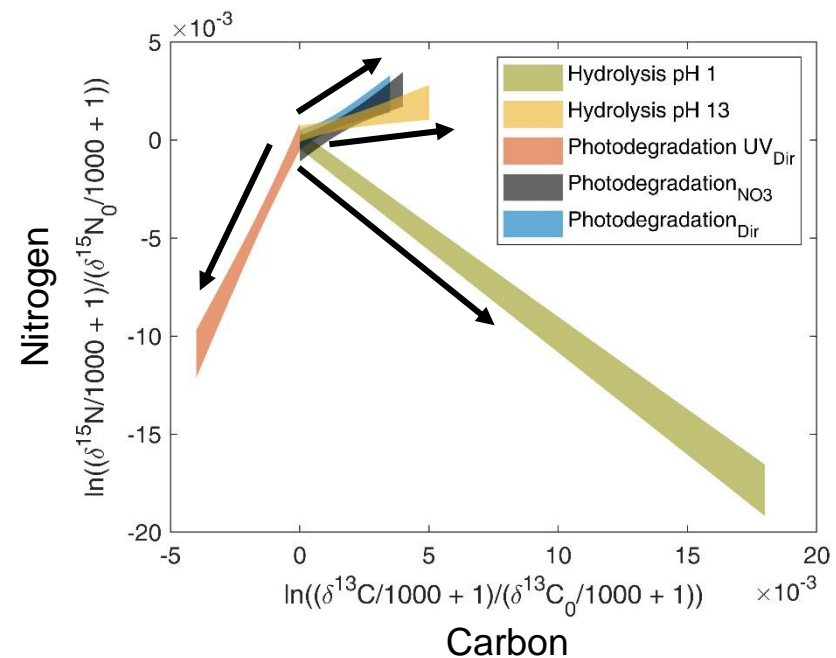
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CSIA of terbutryn

- Degradation leads to distinct fractionation pattern dependant on degradation pathway
 - Reaction specific!
- No isotope fractionation during biodegradation

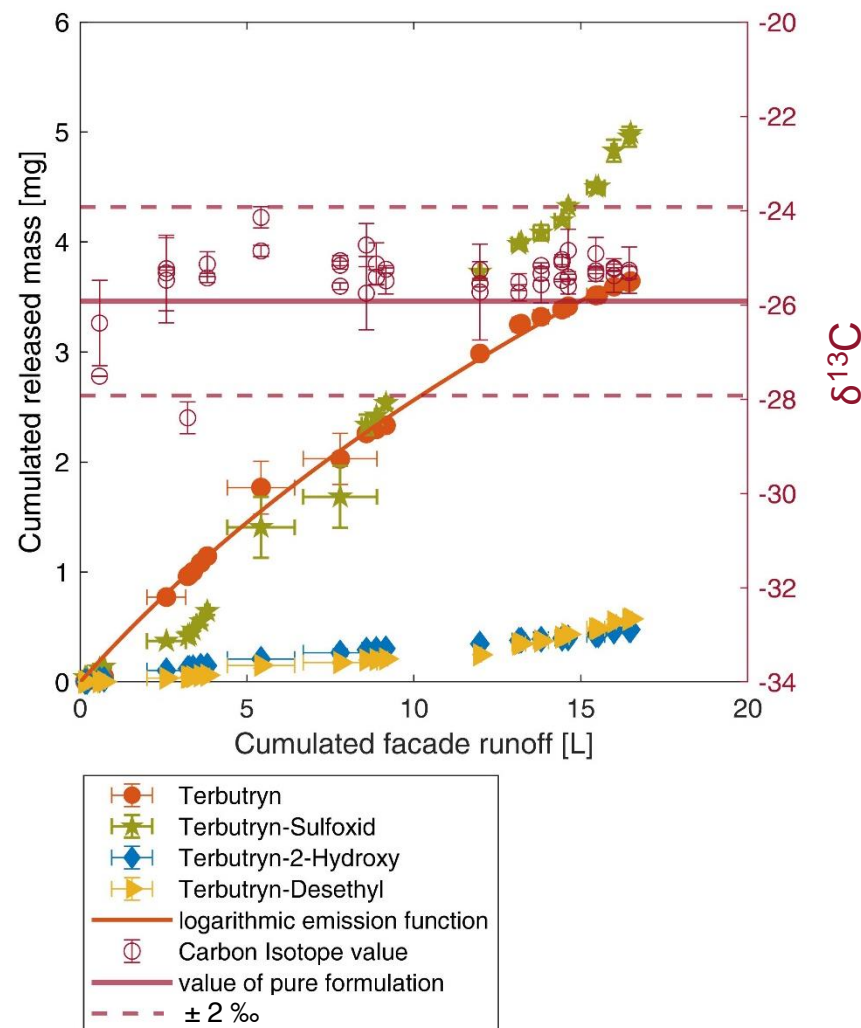


Reactive transport of urban biocides: Leaching from facades



- Release? Degradation? Applicability of CSIA to follow terbutryn degradation in the field?
- Facades built according to construction guidelines
- Encapsulated terbutryn in paint

Reactive transport of urban biocides: Leaching from facades

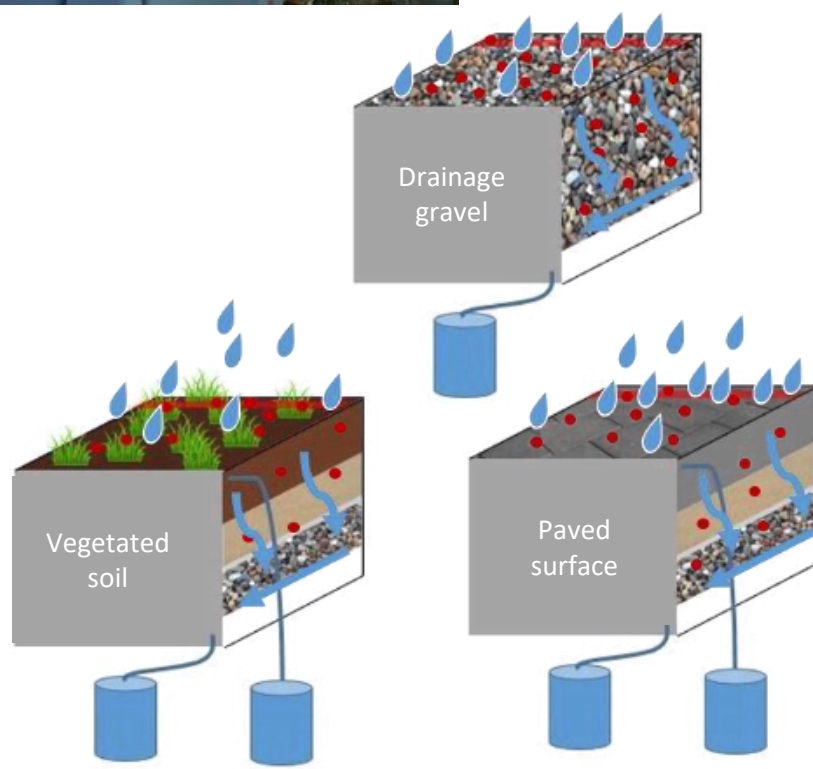


- leaching over 200 days (April – October)
- Less than 1 % of terbutryn released
- Release decreases over time
- Increasing release of terbutryn-sulfoxide → degradation already on facades
- No isotope fractionation
 - Photodegradation only at outer layer
 - Diffusion of non-degraded terbutryn to surface
→ dilution of “degraded fraction”

Reactive transport of urban biocides: lysimeter experiment

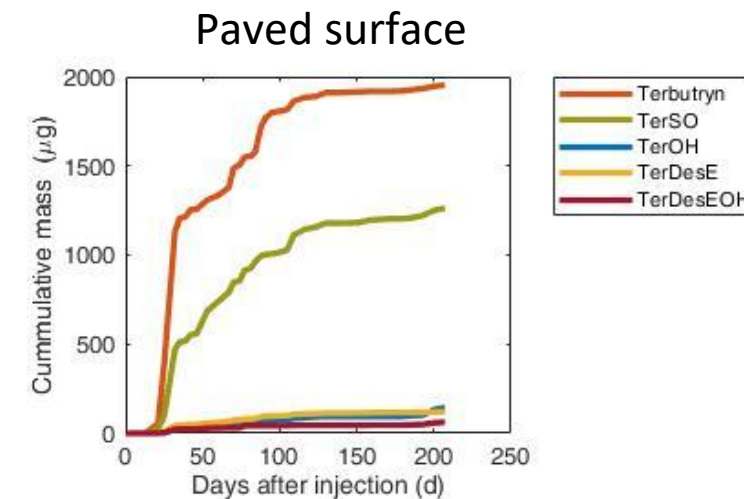
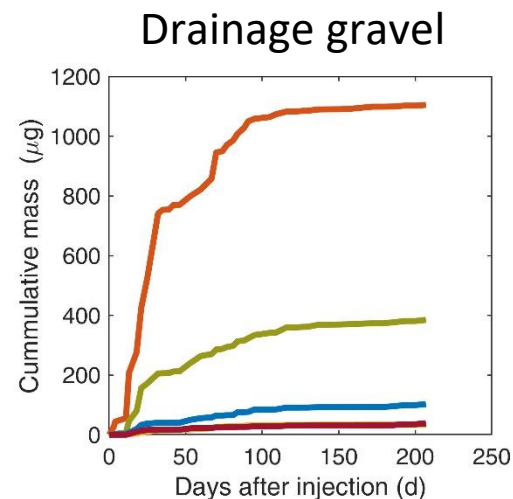
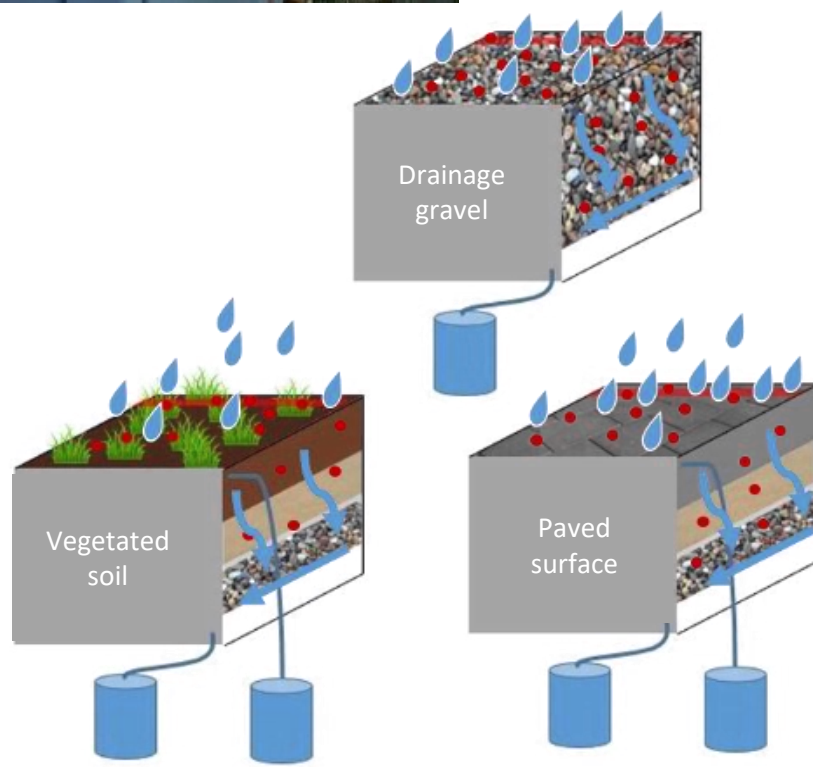


- Reactive transport and release towards groundwater?
 - Extent of degradation?
 - Formation of transformation products?
 - Applicability of CSIA ?



- Three types of materials
- Spiked with mixture of urban biocides
- Sampling at 40 cm depth, extraction (SPE) and analysis (LC-MS/MS)

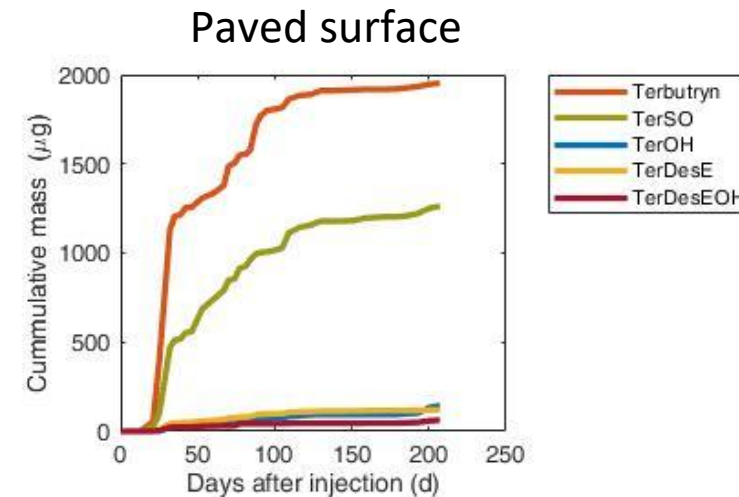
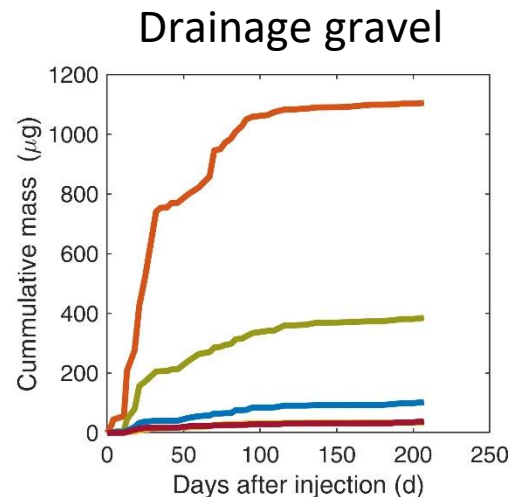
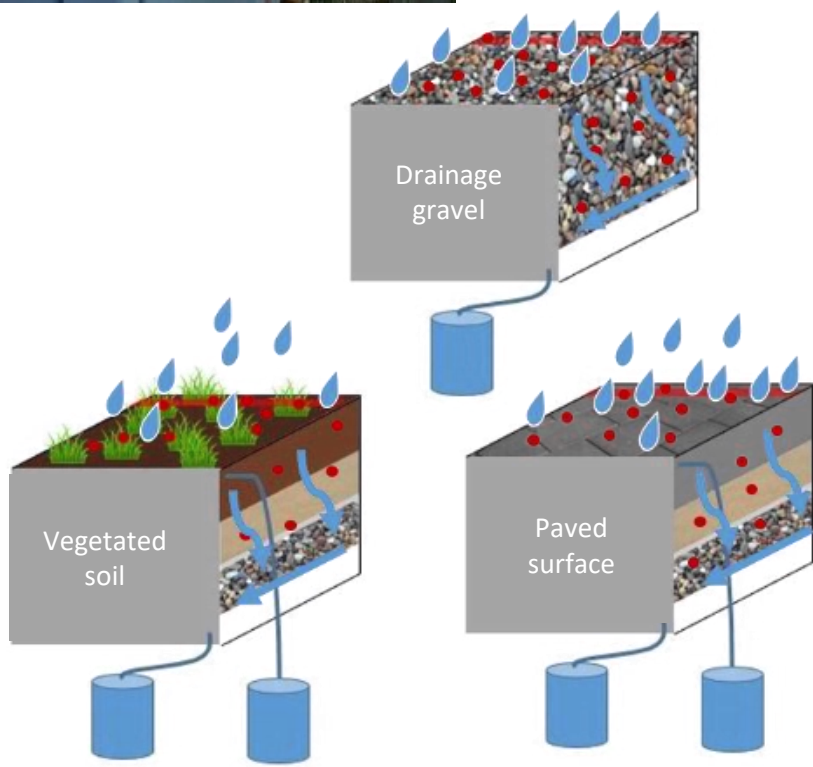
☀ ☁ Reactive transport of urban biocides: lysimeter experiment



How much terbutryn leached within 207 days?

	Terbutryn leached [%]	Terbutryn TPs leached [%]	Total leached [%]
Gravel	7.4	3.8	11.2
Pavement	13.0	10.5	24.5
Grass	0.1	0.3	0.4

Reactive transport of urban biocides: lysimeter experiment



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Where is the remaining fraction?

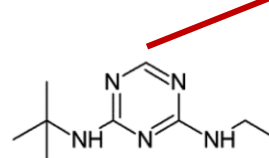
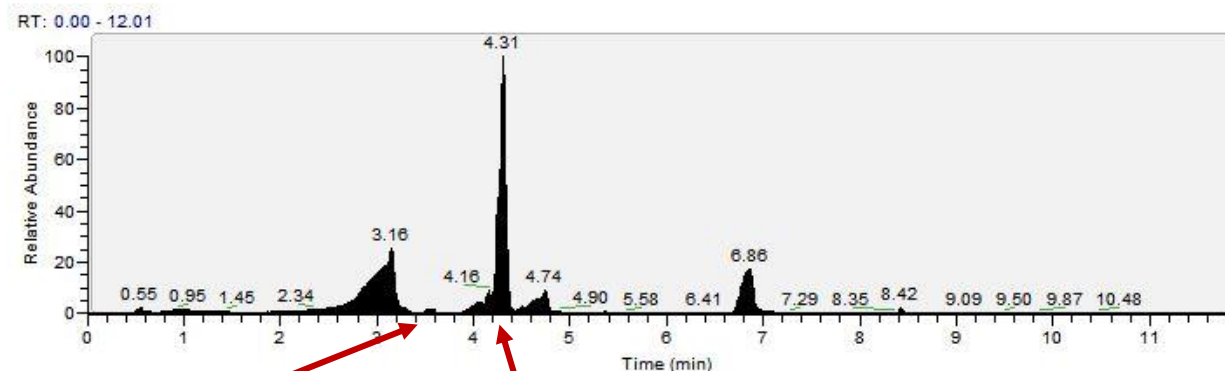
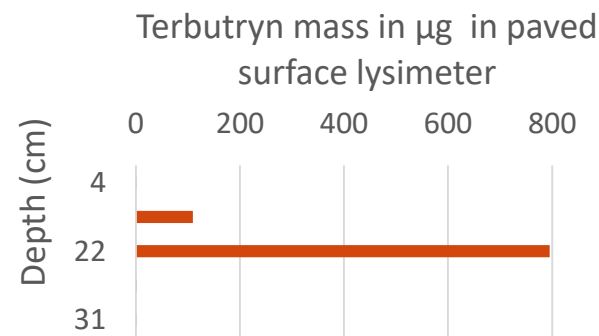
Reactive transport of urban biocides: lysimeter experiment

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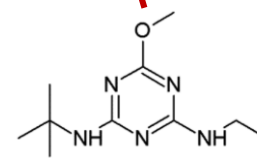
1. **Sorbed to the material** → extractions of materials reveal sorption of terbutryn → potential of desorption after long time periods

2. Leaching of transformation products that were not targeted in this study (semi-targeted approach)

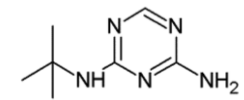
Note: no isotope fractionation was observed (in agreement with laboratory experiments)



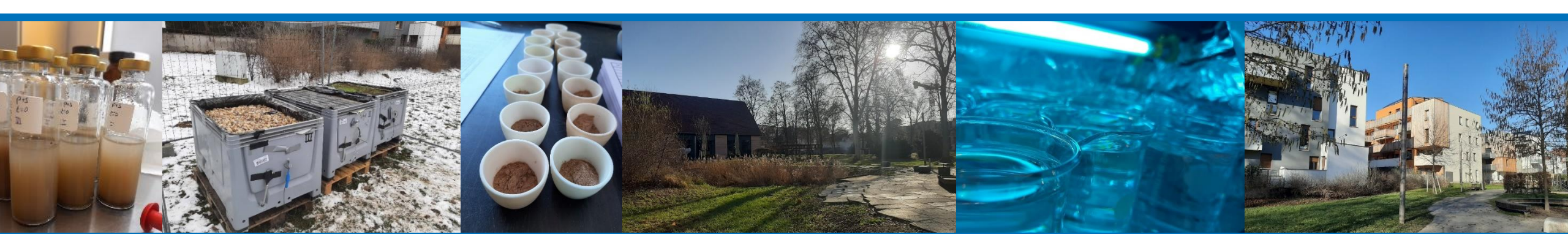
TerDesS



MEBT

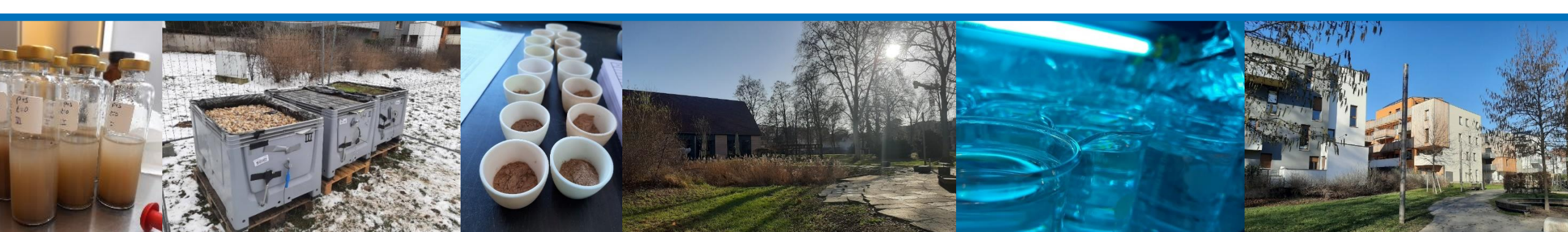


TerDesSDesE



Take home messages

- Only slow terbutryn degradation in environment
- Leaching from facades and towards groundwater for long time periods
- Formation of transformation products → toxic?
- CSIA as tool to follow degradation and differentiate degradation pathways:
 - in laboratory ✓
 - in the environment (✓)



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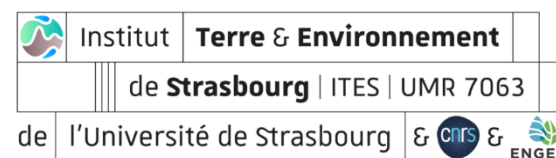
Eric Pernin

Francois Wallon

Comments? Suggestions? Questions?
Contact me!

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or



References

- Gartiser, Stefan, et al.** "Reduction of environmental risks from the use of biocides: Environmental sound use of disinfectants, masonry preservatives and rodenticides." (2015): 1-91, Annex IV
- Bollmann, Ulla E., et al.** "Leaching of terbutryn and its photodegradation products from artificial walls under natural weather conditions." *Environmental science & technology* 50.8 (2016): 4289-4295.
- Burkhardt, M., et al.** "Leaching of biocides from façades under natural weather conditions." *Environmental science & technology* 46.10 (2012): 5497-5503.
- Wittmer, Irene K., et al.** "Modelling biocide leaching from facades." *Water research* 45.11 (2011): 3453-3460.
- Bollmann, Ulla E., et al.** "Biocides in urban wastewater treatment plant influent at dry and wet weather: concentrations, mass flows and possible sources." *Water research* 60 (2014): 64-74.
- Burkhardt, Michael, et al.** "Biocides used in building materials and their leaching behavior to sewer systems." *Water Science and Technology* 56.12 (2007): 63-67.
- Luft, Agnessa, Manfred Wagner, and Thomas A. Ternes.** "Transformation of biocides irgarol and terbutryn in the biological wastewater treatment." *Environmental science & technology* 48.1 (2014): 244-254.
- Kresmann, Simon, et al.** "Ecotoxicological potential of the biocides terbutryn, octhiline and methylisothiazolinone: underestimated risk from biocidal pathways?." *Science of the Total Environment* 625 (2018): 900-908.
- Burkhardt, M., et al.** "Biocides in building facades-ecotoxicological effects, leaching and environmental risk assessment for surface waters." *Umweltwissenschaften und Schadstoff-Forschung* 21.1 (2009): 36-47.
- Quednow, Kristin, and Wilhelm Püttmann.** "Monitoring terbutryn pollution in small rivers of Hesse, Germany." *Journal of Environmental Monitoring* 9.12 (2007): 1337-1343.
- Hensen, Birte, et al.** "Entry of biocides and their transformation products into groundwater via urban stormwater infiltration systems." *Water research* 144 (2018): 413-423.
- Hensen, Birte, Oliver Olsson, and Klaus Kümmerer.** "A strategy for an initial assessment of the ecotoxicological effects of transformation products of pesticides in aquatic systems following a tiered approach." *Environment international* 137 (2020): 105533.
- Hartenbach, Akané E., et al.** "Carbon, hydrogen, and nitrogen isotope fractionation during light-induced transformations of atrazine." *Environmental science & technology* 42.21 (2008): 7751-7756.
- Masbou, Jérémy, et al.** "Carbon and nitrogen stable isotope fractionation during abiotic hydrolysis of pesticides." *Chemosphere* 213 (2018): 368-376.
- Urbanczyk, Michal M., et al.** "Influence of pigments on phototransformation of biocides in paints." *Journal of hazardous materials* 364 (2019): 125-133.
- Hensen, B., O. Olsson, and K. Kümmerer.** "The role of irradiation source setups and indirect phototransformation: Kinetic aspects and the formation of transformation products of weakly sunlight-absorbing pesticides." *Science of the Total Environment* 695 (2019): 133808.
- Meyer, Armin H., Holger Penning, and Martin Elsner.** "C and N isotope fractionation suggests similar mechanisms of microbial atrazine transformation despite involvement of different enzymes (AtzA and TrzN)." *Environmental science & technology* 43.21 (2009): 8079-8085.