

Environmental Fate and Behavior of Transformation Products of Pesticides used in Urban Areas

First Estimation of the Release and Transformation of the Biocidal Active Substance OIT

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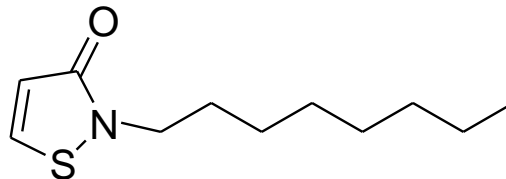
Biocidal Active Substances

Introduction

- Substances to **protect humans and products** against harmful organisms
- E.g. disinfectants, preservatives, coating agents, masonry preservatives

Studied Substance

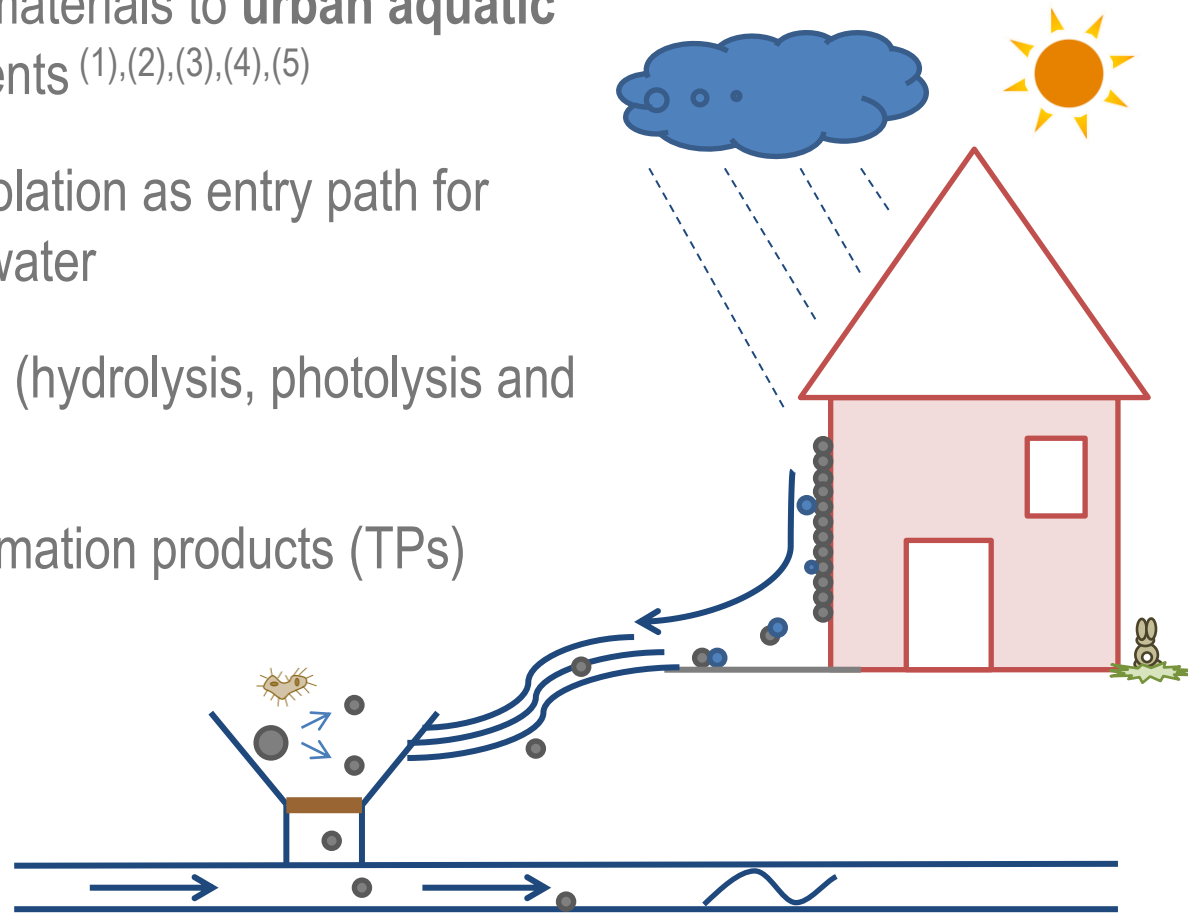
- **Octhilinone** (OIT) is a film preservative in water-based polymer resin paints
- **Fungicide** to prevent the growth of moulds and bacteria on facade paints



Release and Behavior of Biocides

Introduction

- **Leaching** from outdoor materials to **urban aquatic environment** by rain events (1),(2),(3),(4),(5)
- **Urban stormwater** percolation as entry path for biocides into the groundwater
- **Degradation processes** (hydrolysis, photolysis and biodegradation)
 - Formation of transformation products (TPs)



References: (1) Burkhardt et al. 2012; (2): Schoknecht et al. 2009; (3): Wangler et al. 2012; (4): Jungnickel et al. 2008; (5): Breuer et al. 2012).

Research Objective

Introduction

- Measured concentration in suburban areas in Denmark after heavy rain event: **5 - 50 ng/L** ⁽⁶⁾
- Considered Predicted No Effect Concentration (PNEC) = **13 ng/L** ⁽⁷⁾
- UV-irradiation of OIT lead to **7 TPs** ⁽⁸⁾

Identification of **transformation pathway** of OIT

Detection of TPs in urban rainwater discharge and groundwater

Contribution to an environmental **hazard assessment**

References: (6): Bollmann et al. 2014; (7): Burkhardt et al. 2009; (8): Bollmann et al. 2017

Experimental Approach

Methods



Photolysis
Xenon Arc Lamp

OECD 316; 8 hours

Initial Substance

Transformation Products



Biodegradation
Closed Bottle Test

OECD 301 D; 28 days



Toxicity

Luminescent Bacteria Test

acute & chronic toxicity, cell reproduction

Environmental Samples

Solid Phase Extraction/LC-MS/MS

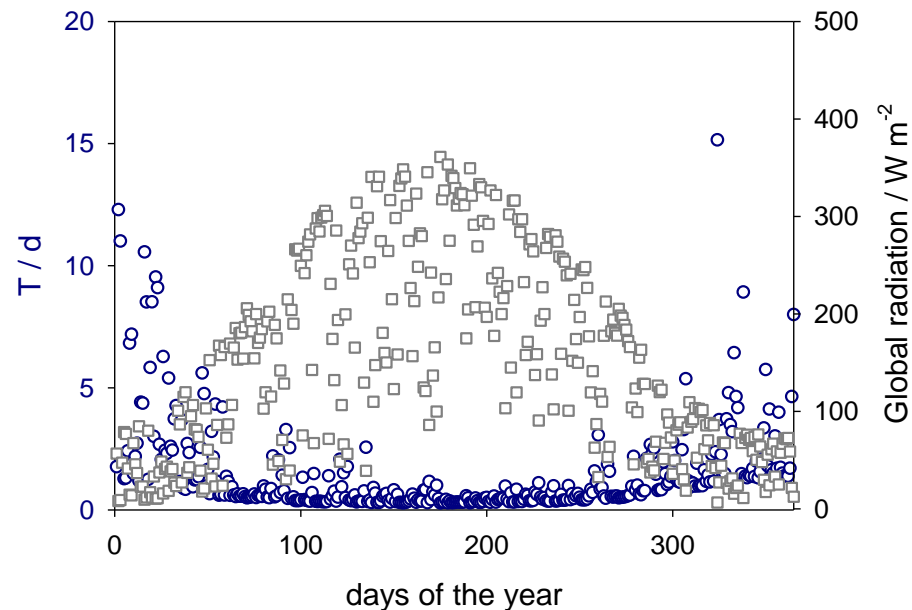
40 samples (urban catchment)



Kinetic of Photolytic Processes

Results

- **Photolytic efficiency:** quantum yield $\Phi = 0.01$
- **Global radiation** (Germany, Freiburg: 48.0004 N, 7.5055 E)
- **Lifetimes (τ)** of 0.3 (summer) to 15 days (winter)



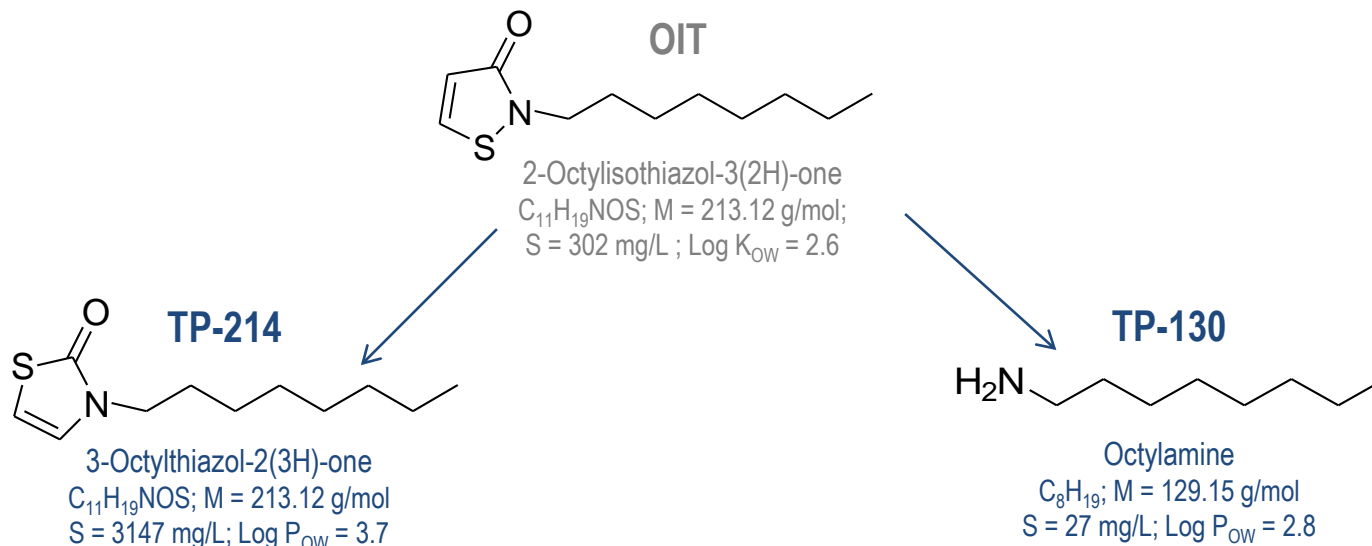
➤ OIT is photolytic degradable in the **environment** with low lifetimes

Development of TPs

Results

TPs during **photolysis** of OIT

- **Mobility: TP-130 > OIT > TP-214**



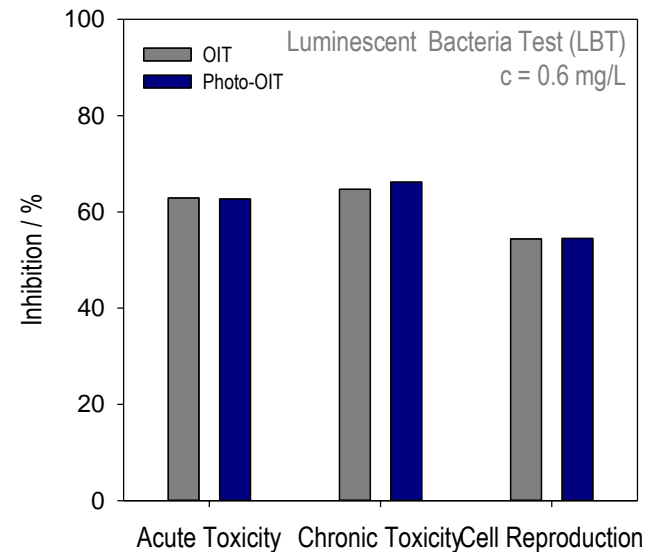
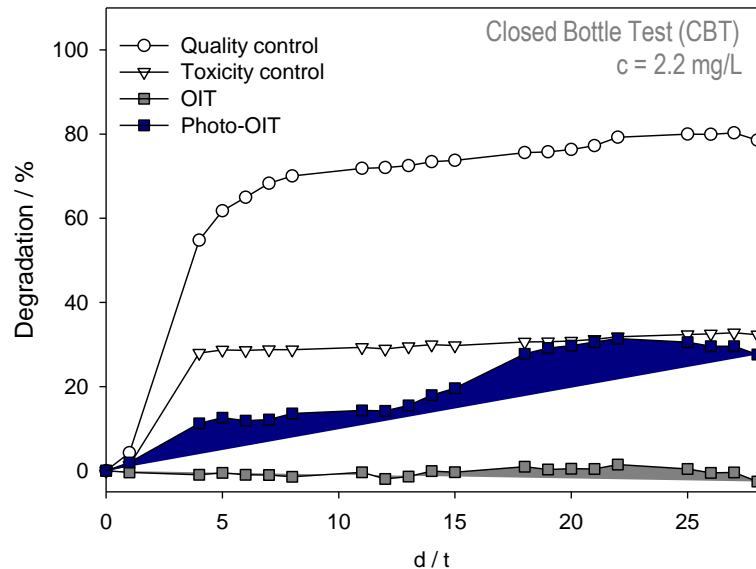
- **Already known TPs ⁽⁸⁾ with unknown properties on environmental fate and behavior**

(8): Bollmann et al. 2017

Estimation of the Behavior of TPs

Results

- OIT is probably not readily biodegradable
- OIT shows high toxic effects ($EC_{50} = 0.45 \text{ mg/L}$)



➤ **Higher biological activity and unchanged toxicity of the photolytic mixture**

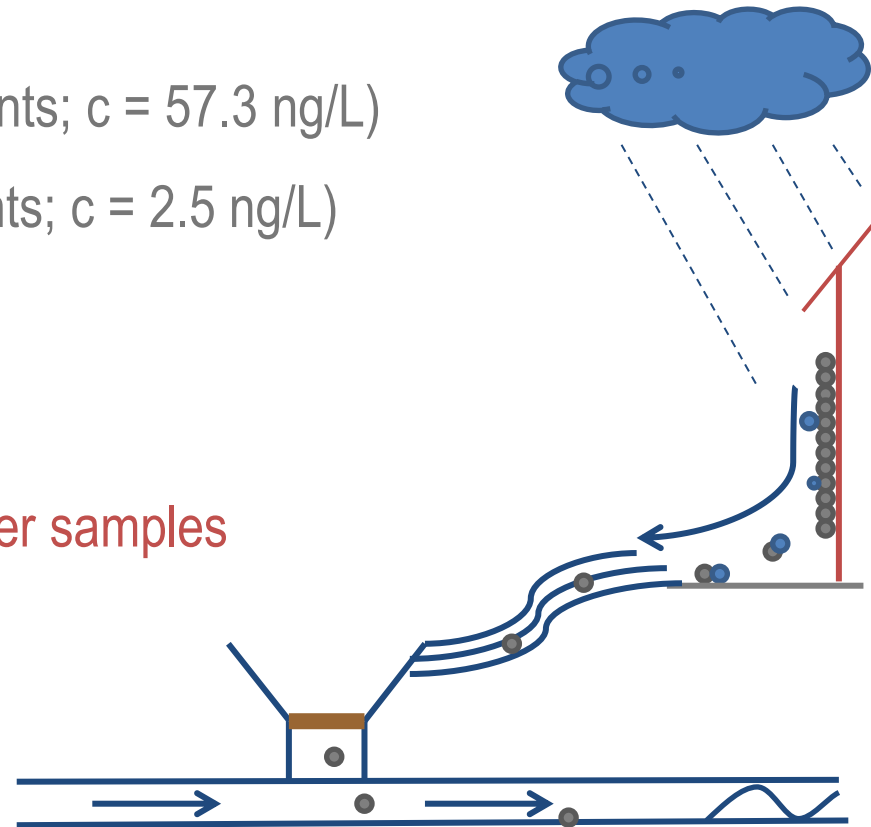
Environmental Samples

Results

Measurement of the **entry path** of OIT and its TPs in an urban catchment (Germany, Freiburg, 2016)

- Rainwater discharge (1/10 sampling points; $c = 57.3$ ng/L)
- Swale-trench-system (1/9 sampling points; $c = 2.5$ ng/L)
- Up- and downstream of groundwater (7/20 sampling points; $c_{\text{mean}} = 0.7$ ng/L)

- TP-214 **measurable** only in groundwater samples
- TP-130 **not detectable**

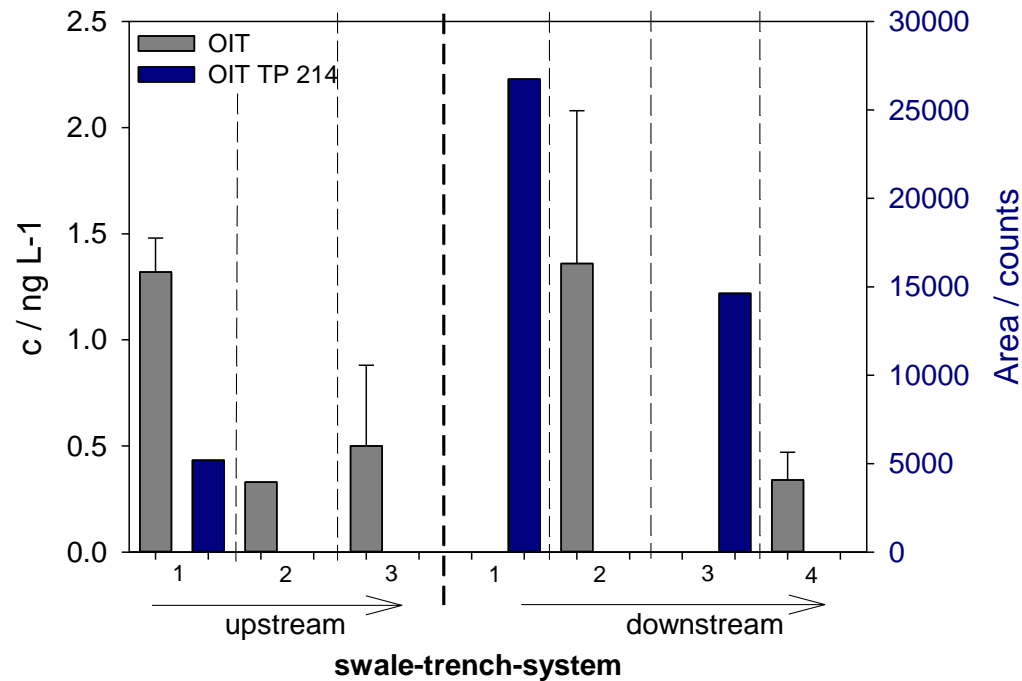


Environmental Samples

Results

Measurement of **groundwater samples** (Germany, Freiburg)

➤ Up- and downstream of an infiltration system



Gained Knowledge & Further Issues

Conclusion

- **First detection** of OIT-TPs in groundwater
 - Rainwater infiltration as an possible **entry path** of OIT-TPs
- **Higher biological activity** and **unchanged toxicity** of TP
- **Potential risk to human and environment** due to the entry to groundwater
- **Risk assessment** needs to be specified with regard to environmental relevant TP

References

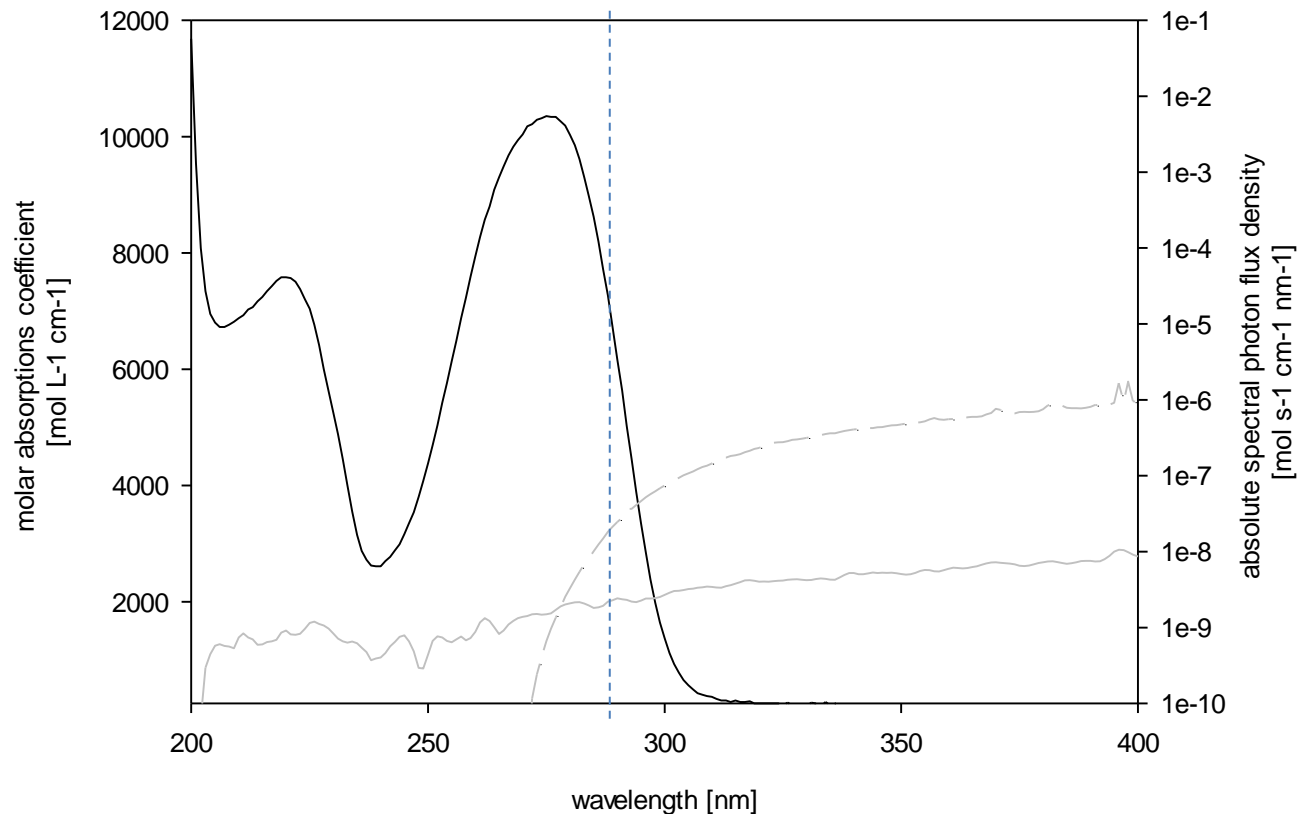
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Annex I

Emission spectra of used lamps and absorption spectrum of OIT



Annex II

Quantum yields ϕ were calculated following equation (1) by means of the experimental received rate constant k (s^{-1}) and the molar absorption coefficient ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$) of the substance as well as the absolute light intensity I_{abs} ($\text{mol s}^{-1} \text{L}^{-1} \text{nm}^{-1}$) of the xenon lamps.

$$\phi = (k) / (\sum(200\text{nm} - 400\text{nm}) \cdot (I_{(0,\lambda)} \cdot \epsilon_{\lambda}) \cdot \ln(10)) \quad (1)$$

The transfer of data acquired in laboratory to environmental rate constants was calculated as follows:

$$k_{\text{env}} = I_{\text{solar}} \cdot \ln(10) \cdot 1000 / 6.02 \cdot 10^{23} \cdot \phi \cdot \epsilon \quad (2)$$

Lifetimes are calculated by equation (3)

$$\tau = 1/k \quad (3)$$