

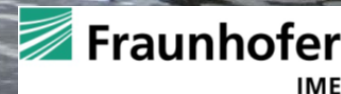
# Fate of triclosan and azole fungicides during wastewater treatment

*Project: Environmental impact of biocides  
Development of milestones of a monitoring  
program for measuring entries of biocides into  
the environment*

Jan Schwarzbauer, Ann-Kathrin Wluka

Heinz Rüdell

Katja Michaelis



- simple analytical multiparameter method
- application for various environmental compartments (WWTP, receiving waters, sewage sludge)
- transferable method

## Based on

Kahle et al. (2008) Azole Fungicides: Occurrence and Fate in Wastewater and Surface Waters

Wick et al. (2010) Multi-residue analysis of biocides, UV-filters and benzothiazoles in aqueous matrices and activated sludge by LC-MS/MS

# Sampling strategy

<b>WWTP</b>	<b>PE</b>
B5	10.000
B1	32.000
B2	50.000
N2	130.000
B3	200.000
N1	580.000
B4	1.000.000

## 7 WWTP

- 2 NRW (N1, N2 (municipal and industrial))
- 5 Bavaria (B1, B2, B3, B4, B5)

**Influent**

**Sewage water before biological treatment**

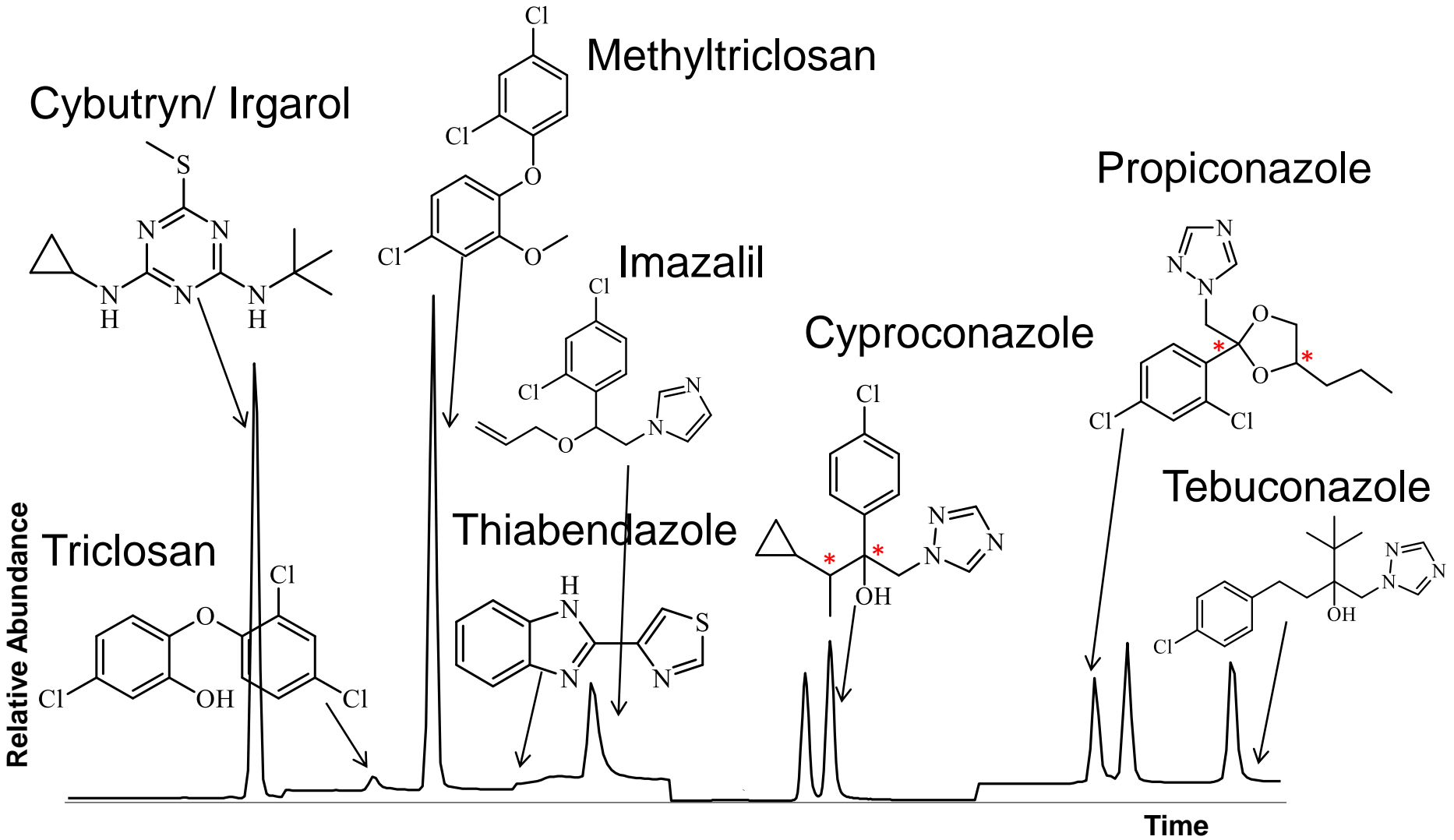
**Treated effluent**

**Sewage sludge**

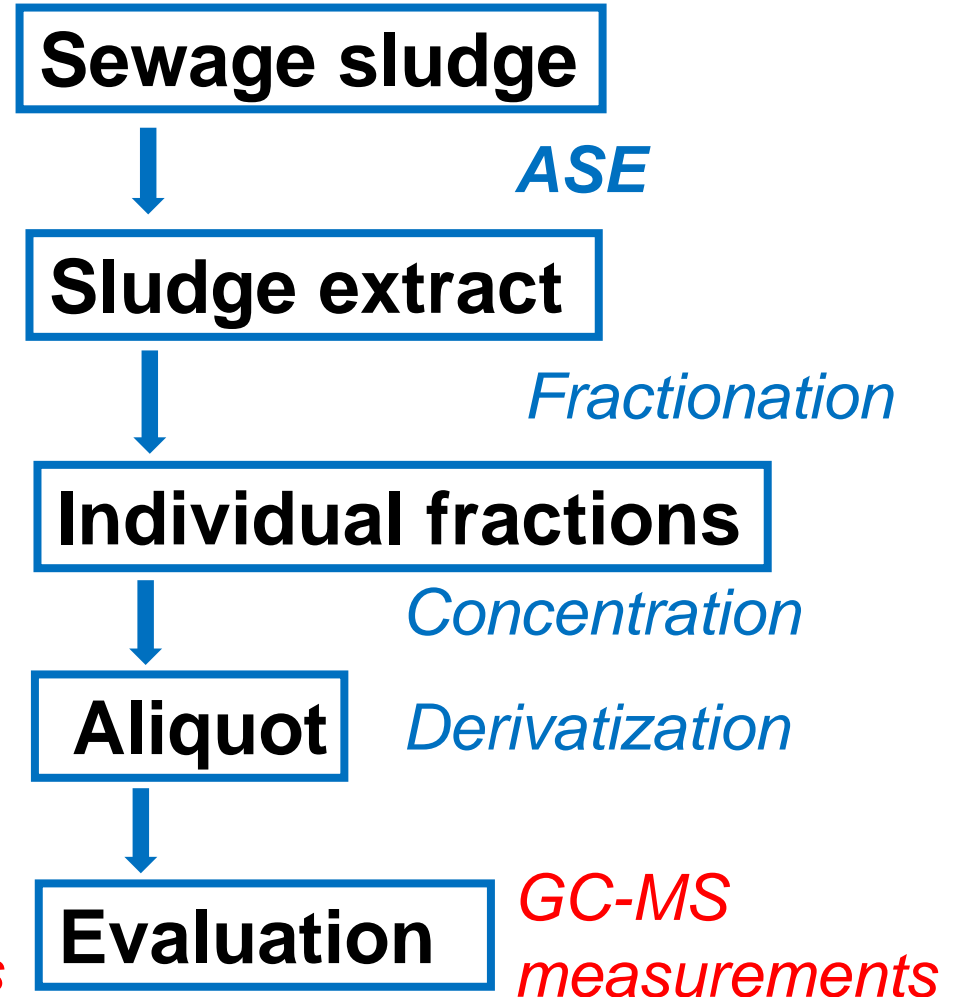
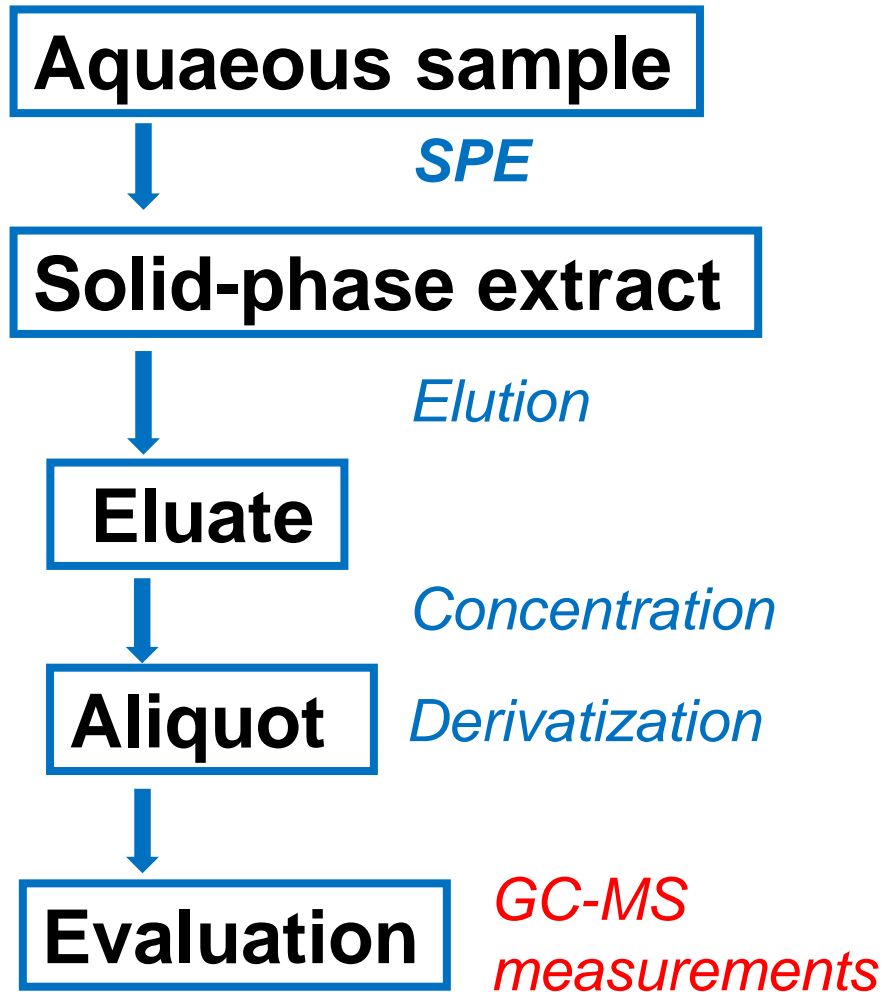
**1 sample upstream**

**3 samples downstream (0m, 500m, 1000m)**

# Spectrum of target biocides



# Analytical methods



## GC-MS

- full spectrum detectable (8/8), multiparameter
- simple system
- widely used and easily transferable

- sample preparation including derivatization
- only organic solvents

## LC-MS

- commonly used for polar chemicals
- solubility in polar solvents including water
- fast measurements
- no derivatization needed

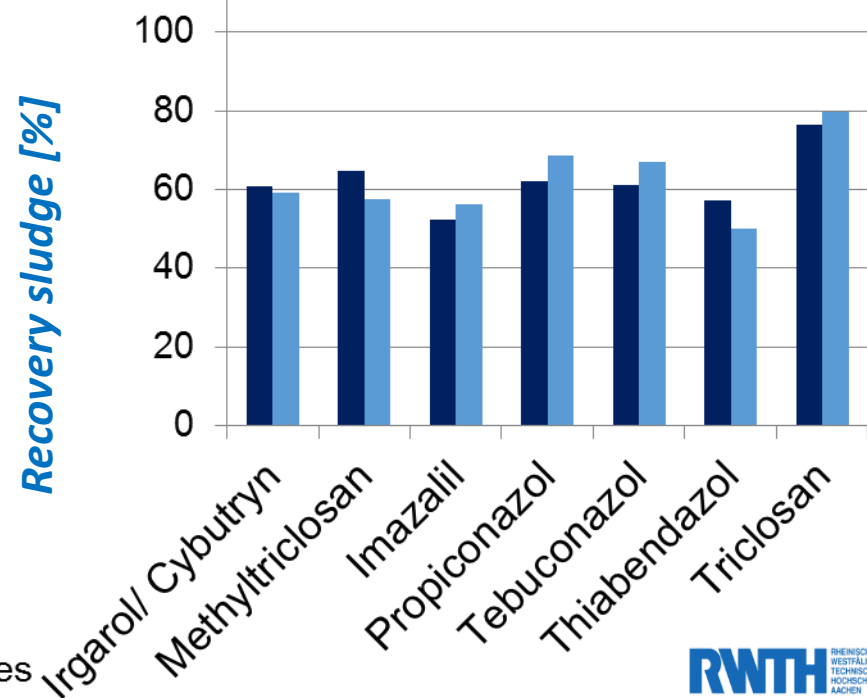
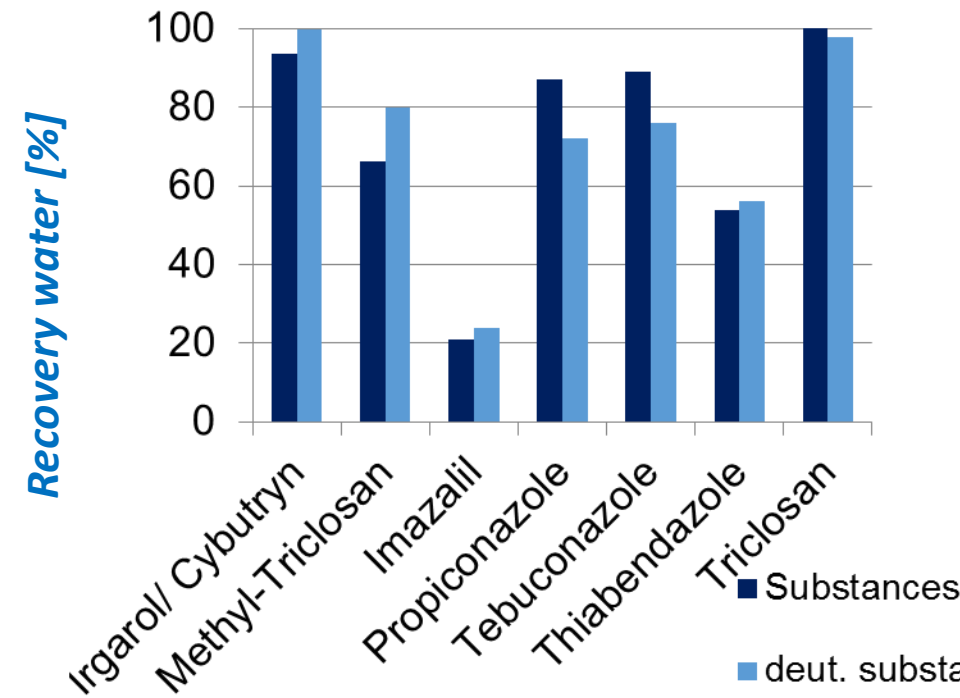
- 5 target analytes detectable (5/8)





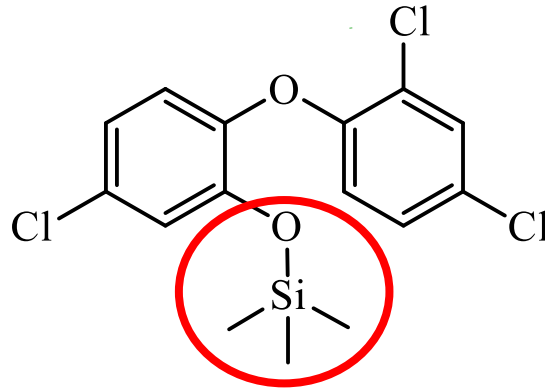
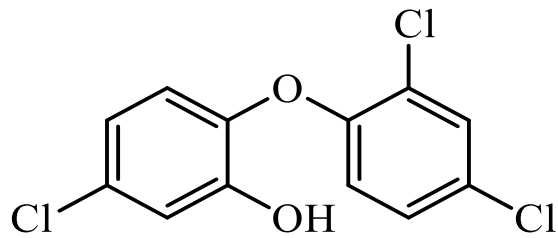
# Sensitivity Recovery

LOQ	GC-MS	LC-MS (Source: APCI)	
Substance	[ng/L]	[ng/L]	PNEC [ng/L]
Triclosan	15	not detectable	50
Methyltriclosan	0.4	not detectable	15
Irgarol/Cybutryne	0.5	13.8	2.5
Imazalil	7.1	18.2	200
Thiabendazole	45	not detectable	1,200
Cyproconazole	2.8	68.5	2,100
Tebuconazole	4.9	80.6	1,000
Propiconazole	2.9	64.9	6,800

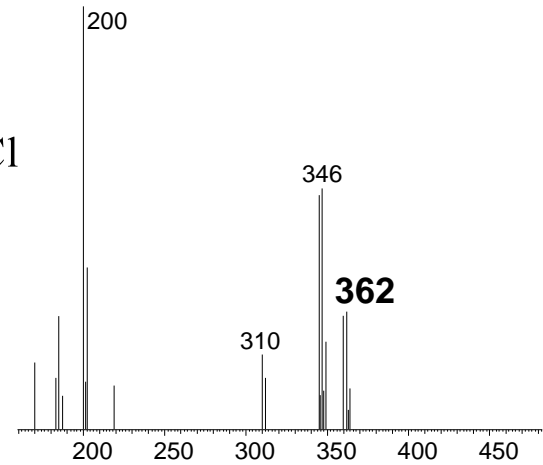
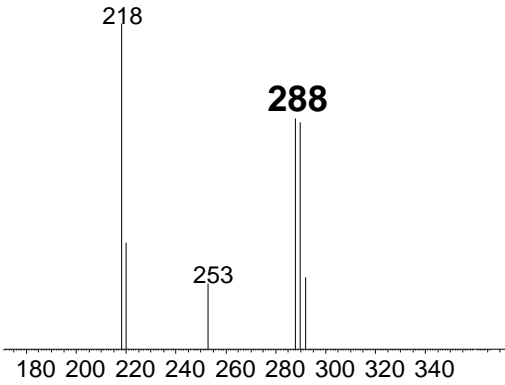


# Derivatization

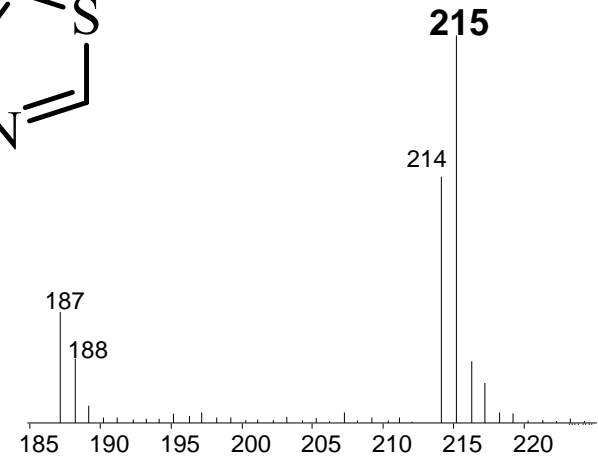
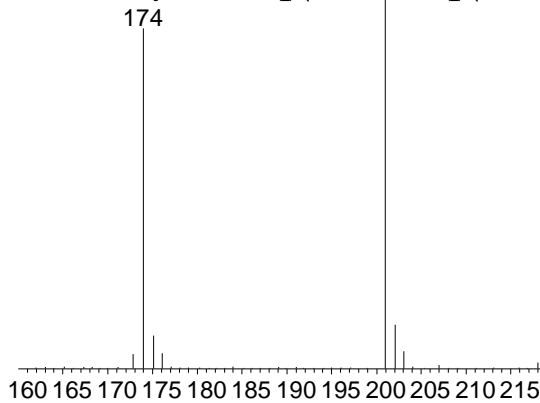
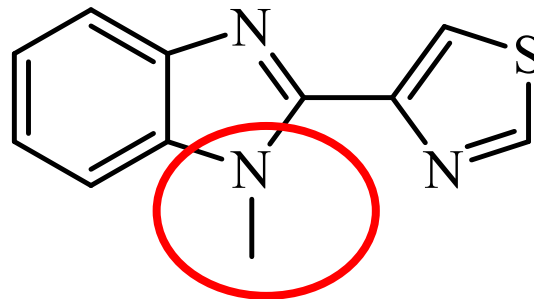
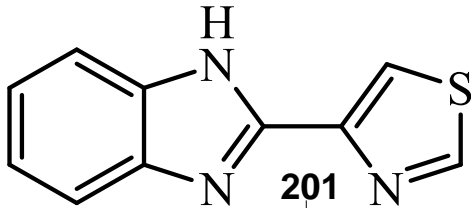
Silylation  
+BSTFA, 80°C



Relative Abundance



Methylation  
+Diazomethane, 0°C





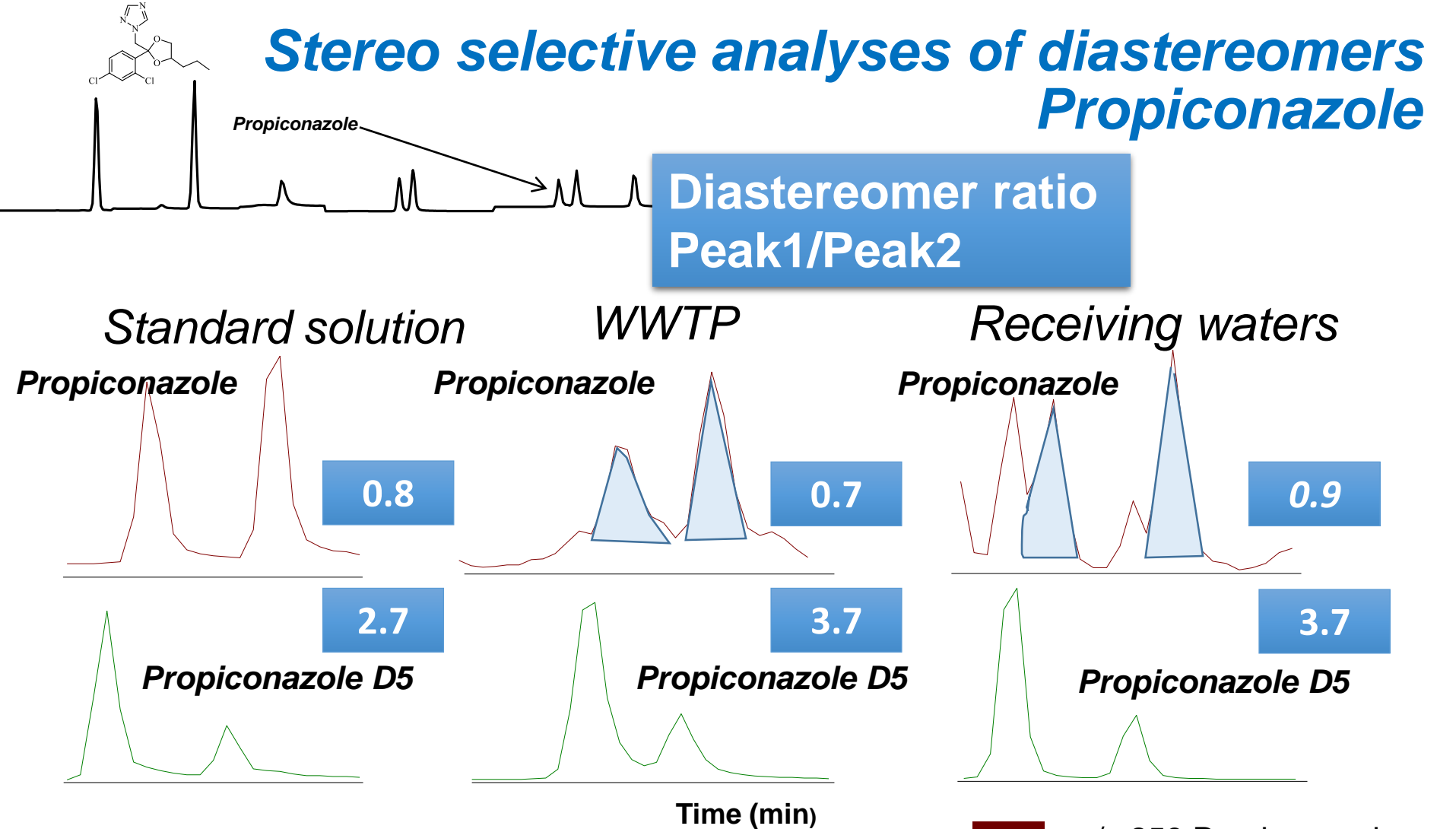
# WWTP and surface water [ng/L]

	Upstream	Influent	Bef. biol. treatment	Effluent	Downstr. 0m	Downstr. 500m	Downstr. 1000m
	<b>B3</b>	<b>B3</b>	<b>B3</b>	<b>B3</b>	<b>B3</b>	<b>B3</b>	<b>B3</b>
<i>Imazalil</i>	<LOQ	<b>980</b>	<b>910</b>	<b>820</b>	<b>190</b>	<b>110</b>	<b>60</b>
<i>Cyproconazole</i>	<LOQ	<b>41</b>	<b>9</b>	<b>5</b>	<b>4</b>	<LOQ	<LOQ
<i>Tebuconazole</i>	<LOQ	<b>29</b>	<b>10</b>	<b>8</b>	<b>6</b>	<b>5</b>	<b>5</b>
	<b>B4</b>	<b>B4</b>	<b>B4</b>	<b>B4</b>	<b>B4</b>	<b>B4</b>	<b>B4</b>
<i>Imazalil</i>	<LOQ	<b>190</b>	<b>110</b>	<LOQ	<LOQ	<LOQ	<LOQ
<i>Propiconazole</i>	<LOQ	<b>46</b>	<b>29</b>	<b>12</b>	<b>5</b>	<b>4</b>	<b>3</b>
<i>Tebuconazole</i>	<LOQ	<b>93</b>	<b>90</b>	<b>62</b>	<b>7</b>	<b>6</b>	<b>6</b>
	<b>B5</b>	<b>B5</b>	<b>B5</b>	<b>B5</b>	<b>B5</b>	<b>B5</b>	<b>B5</b>
<i>Cyproconazole</i>	<LOQ	<b>15</b>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<i>Propiconazole</i>	<LOQ	<b>11</b>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

# Sludge samples [ng/g]

	N1	N2	B1	B2	B3	B4	B5
<b>Cybutryne/ Irgarol</b>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<b>Methyltriclosan</b>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<b>Imazalil</b>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<b>Cyproconazole</b>	<LOQ	<LOQ	<b>17</b>	<b>380</b>	<b>18</b>	<LOQ	<b>8</b>
<b>Propiconazole</b>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<b>Tebuconazole</b>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<b>Thiabendazole</b>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
<b>Triclosan</b>	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

# Stereo selective analyses of diastereomers Propiconazole



- Final steps: measurements and evaluation
- Indication: no significant microbial degradation of propiconazole

- combination of monitoring sites
- appropriate analytical method for target biocides
- sporadically contamination
- dominant contamination in water phase
  - 4 azole fungicides (<PNEC) detectable
- less contamination in sewage sludge
  - 1 azole fungicide (cyproconazole) detectable
- diastereomers: propiconazole and cyproconazole
  - stereo selective analyses provides an interesting tool

# Thank you for your attention!

