



# Are we about to upgrade wastewater treatment for removing organic micropollutants?



Adriano Joss, Hansruedi Siegrist, Eawag, Switzerland  
Arne Wick, Michael Schlüsener, Thomas Ternes, BfG, Germany

Neptune Workshop, 25 March 2010, Quebec



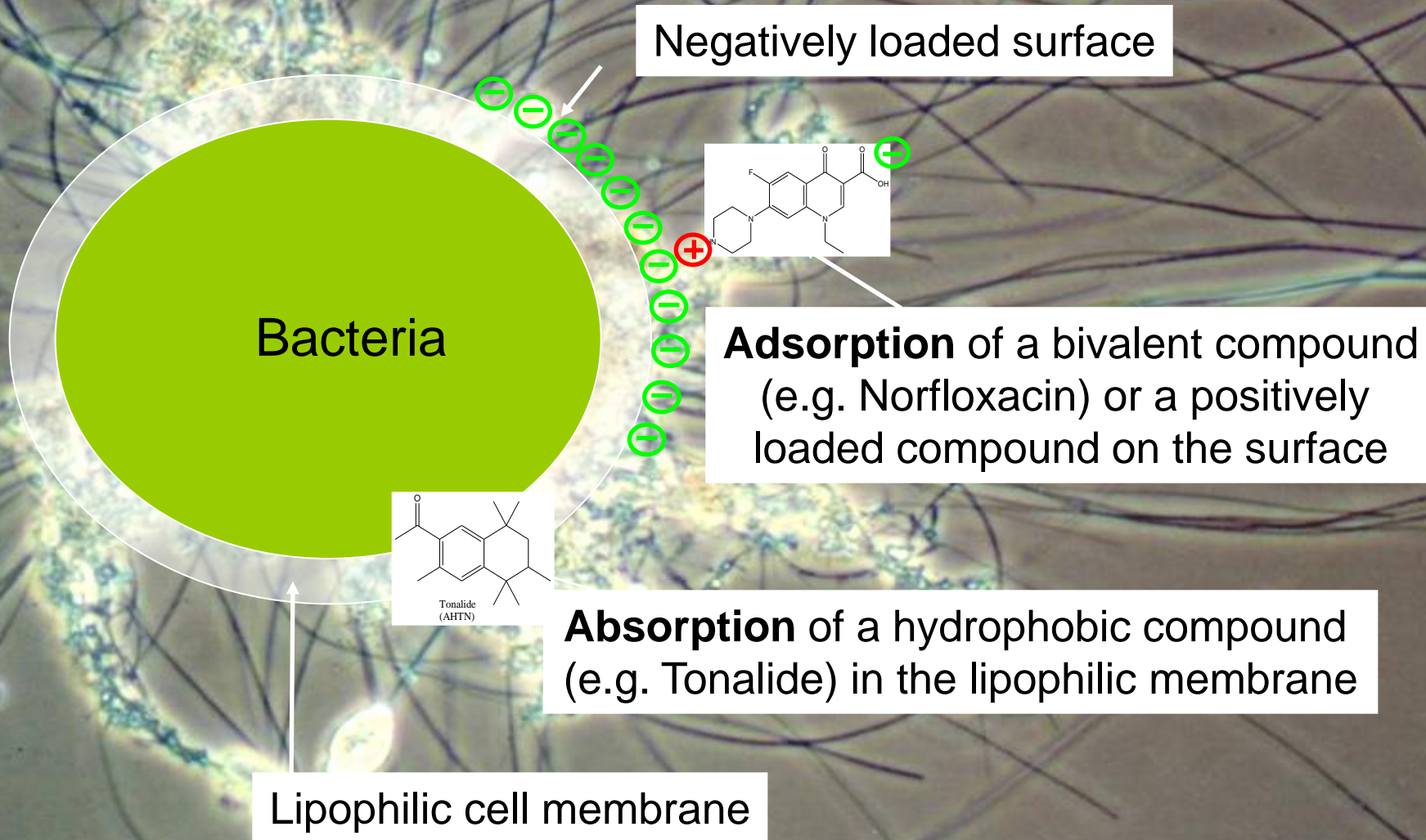
Neptune workshop: Technical Solutions for Nutrient and Micropollutants Removal in WWTPs

*Université Laval, Québec, March 25-26, 2010*

# Contents

- Sorption
- Biodegradation
- Transformation products
- Predicting environmental concentrations
  
- Conclusion

# Removal by sorption on activated sludge



# Sorption of micropollutants

## Sorbed concentration:

$$C_{\text{sorbed}} = K_d \cdot SS \cdot C_{\text{soluble}}$$

$K_d$  = Sorption coefficient [l/gSS]

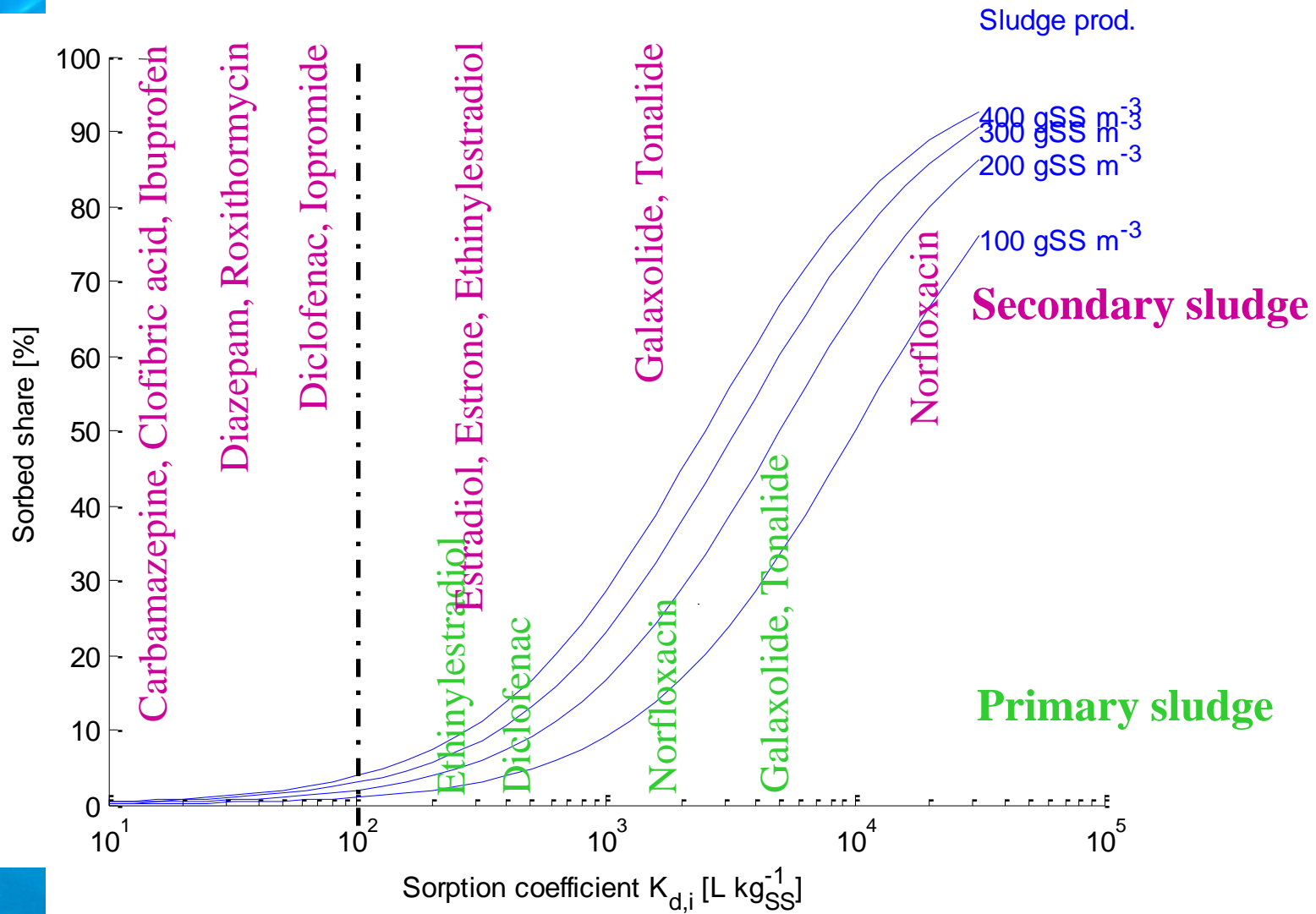
SS = Suspended solids or sludge production [g/l]

## Sorbed fraction:

$$\frac{C_{\text{sorbed}}}{C_{\text{soluble}} + C_{\text{sorbed}}} = \frac{K_d \cdot SS}{1 + K_d \cdot SS}$$

# Sorption of micropollutants on activated sludge

Pharmaceuticals



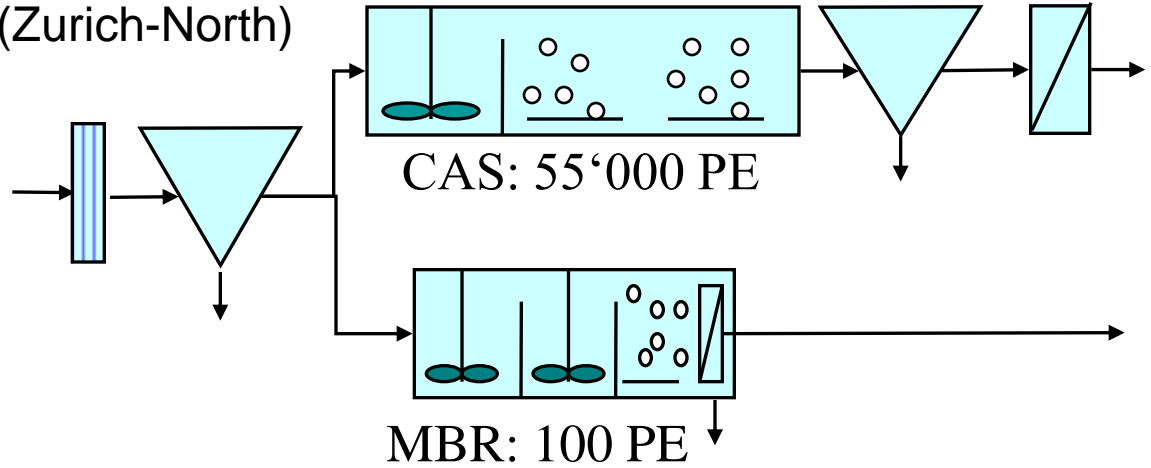
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- Sorption
- **Biodegradation**
- Transformation products
- Predicting environmental concentrations
  
- Conclusion

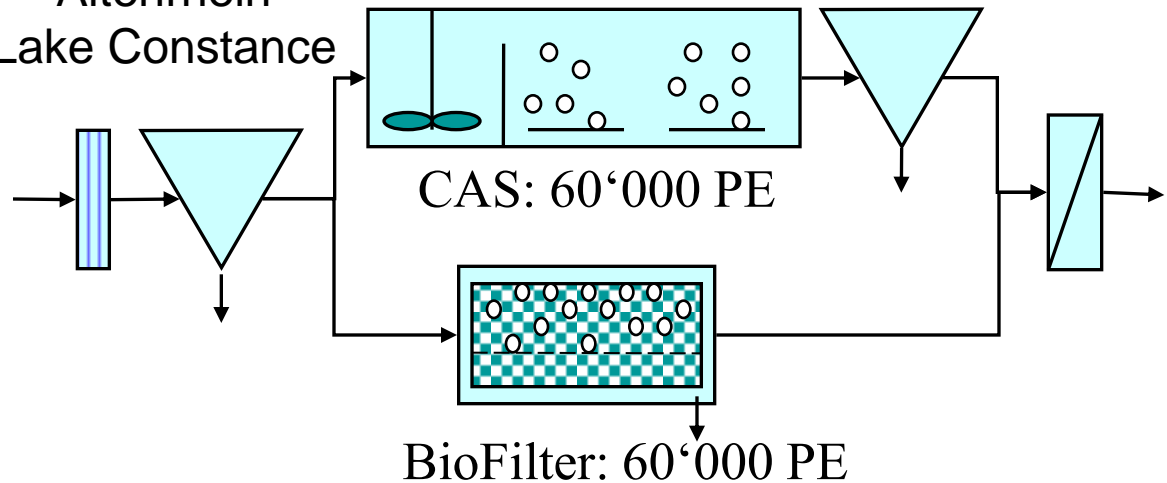
# Full scale sampling



Kloten-Opfikon  
(Zurich-North)



Altenrhein  
Lake Constance



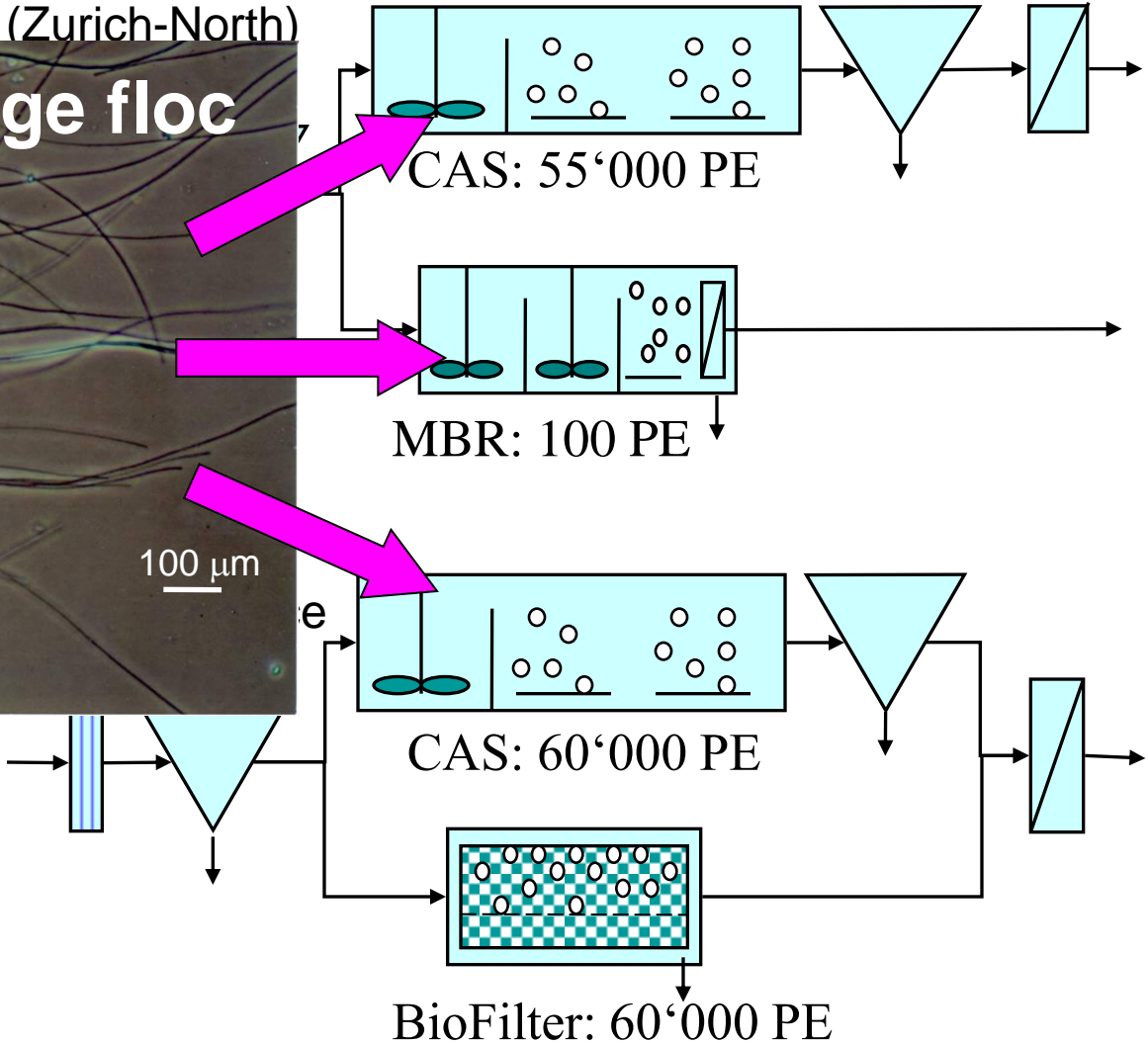
# Full scale sampling



Kloten-Opfikon  
(Zurich-North)



Activated sludge floc



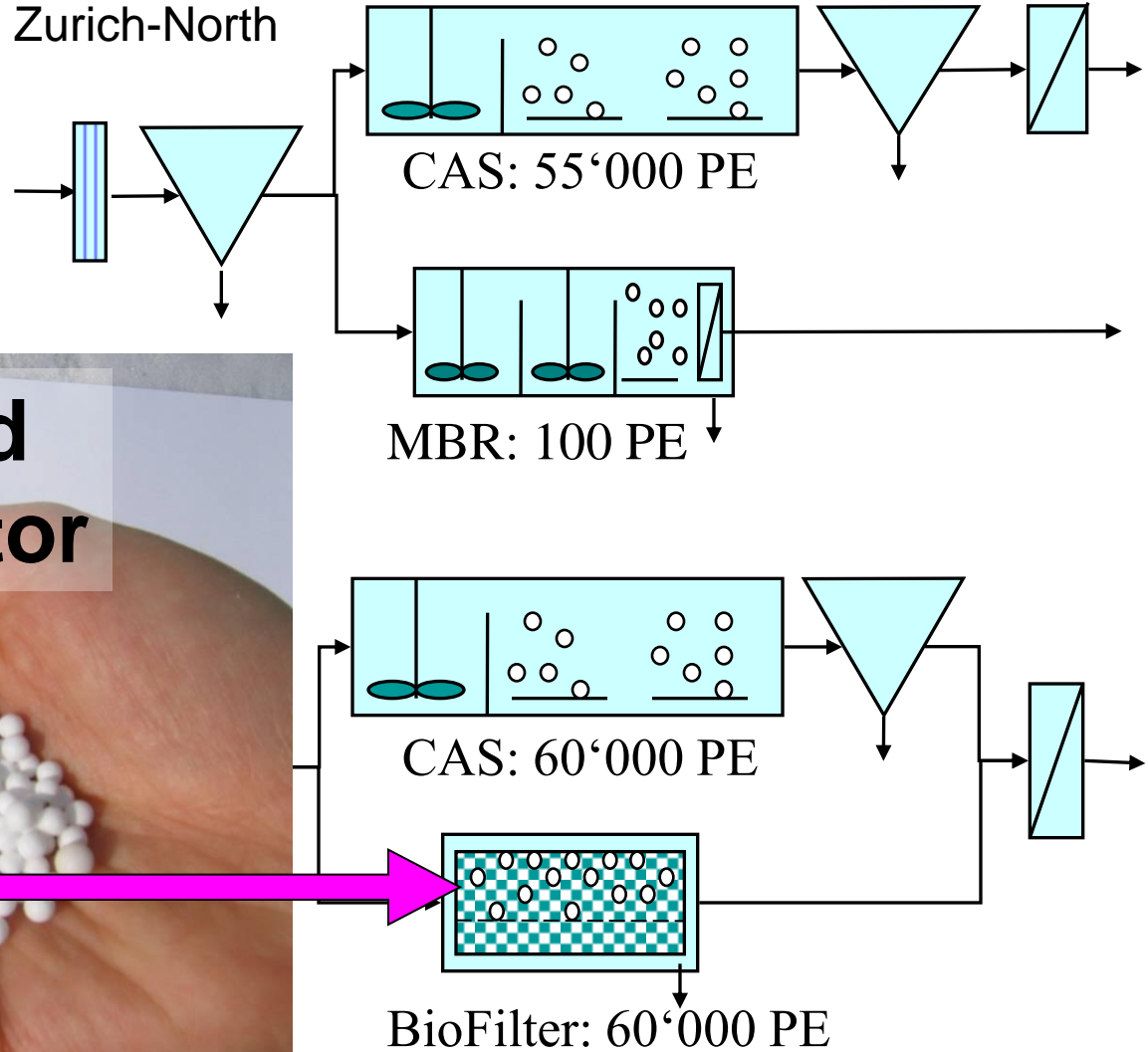
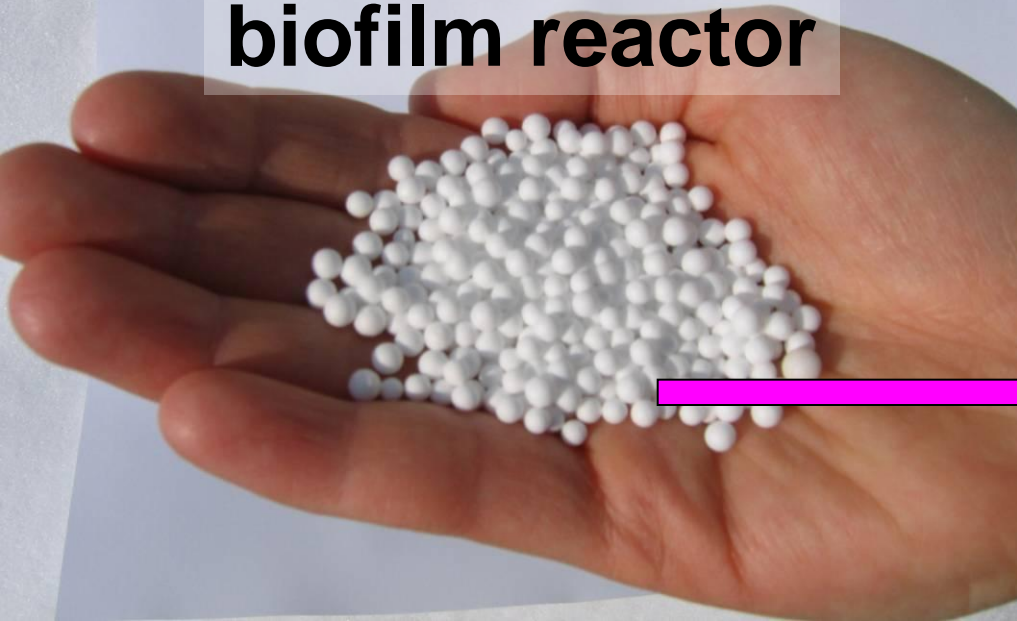


# Full scale sampling



Klotten-Opfikon  
Zurich-North

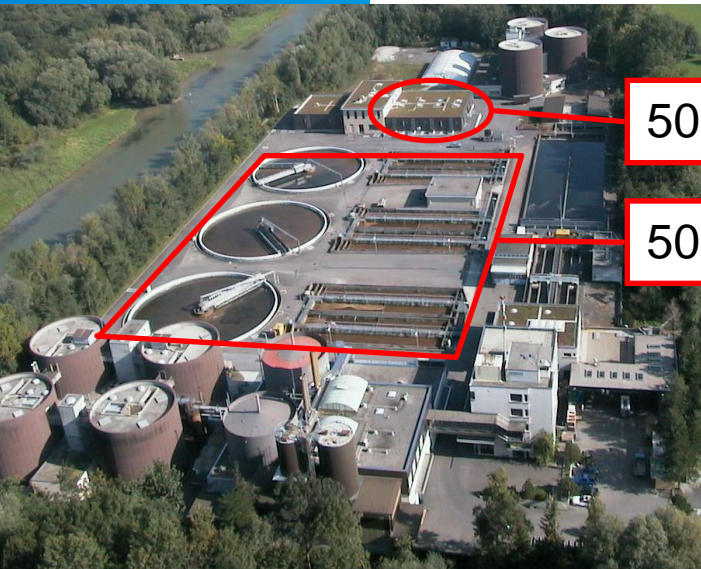
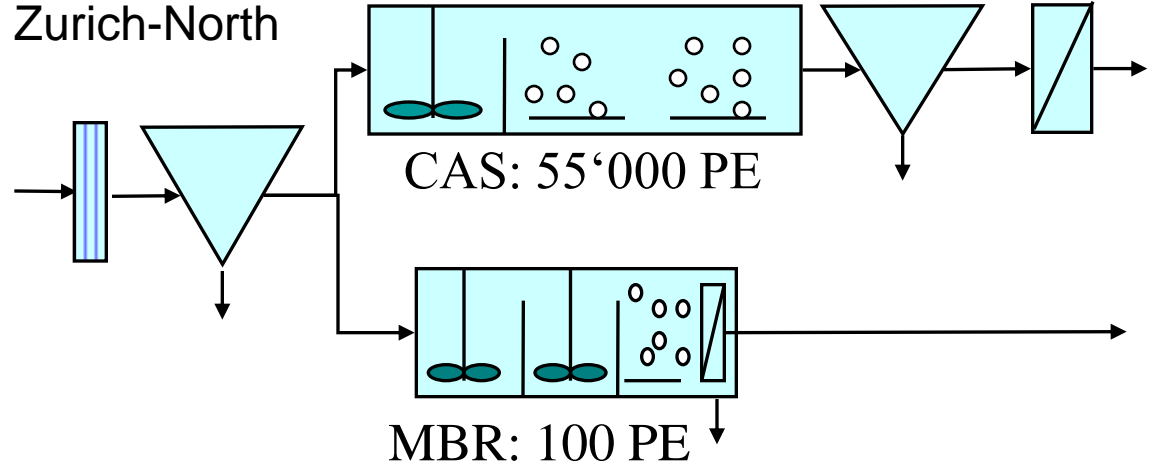
**Submerged  
biofilm reactor**



# Full scale sampling

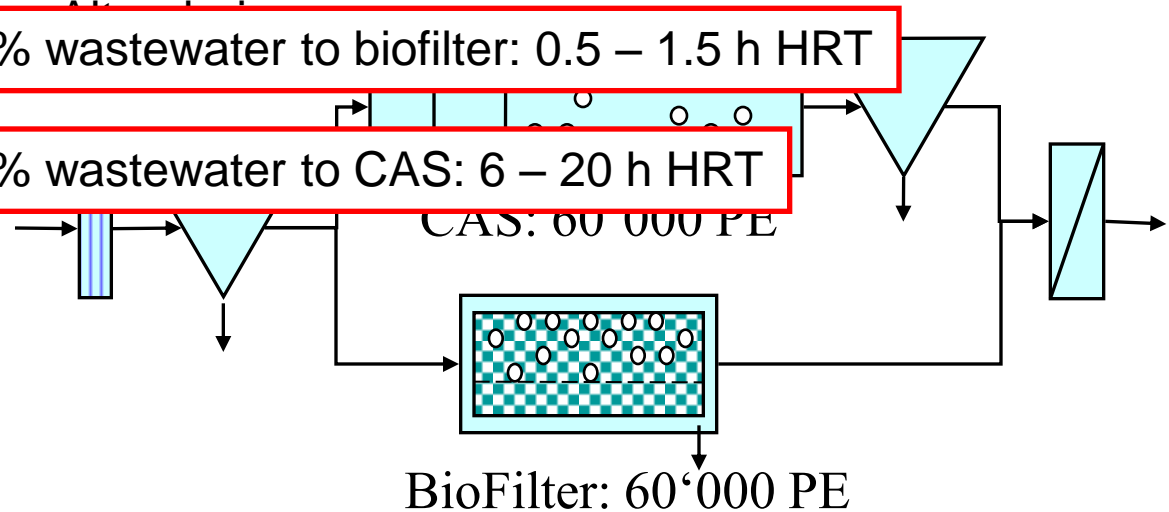


Kloten-Opfikon  
Zurich-North



50% wastewater to biofilter: 0.5 – 1.5 h HRT

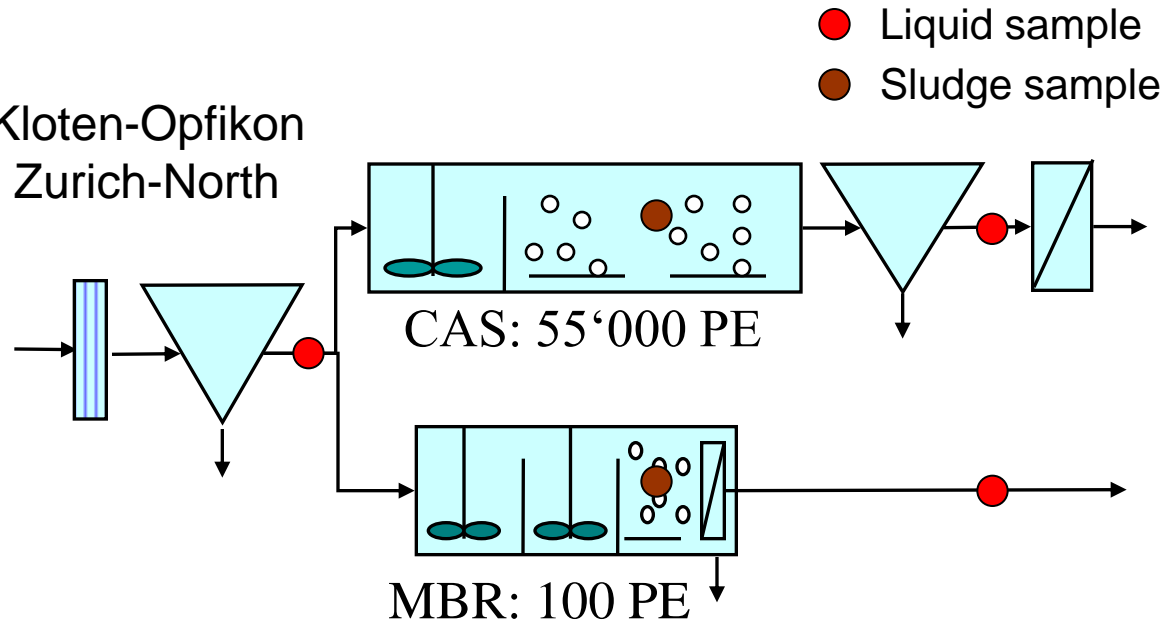
50% wastewater to CAS: 6 – 20 h HRT



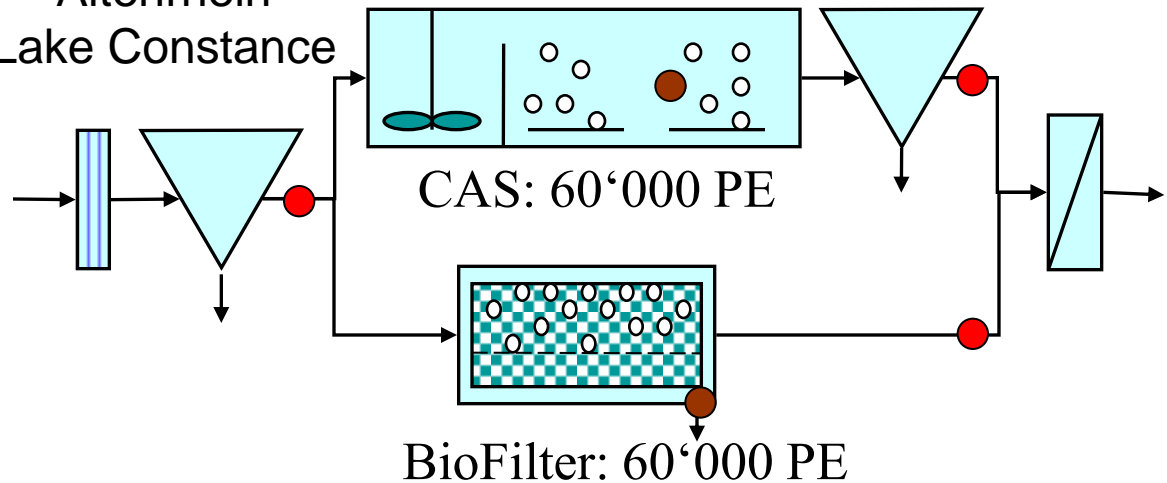
# Full scale sampling



Kloten-Opfikon  
Zurich-North

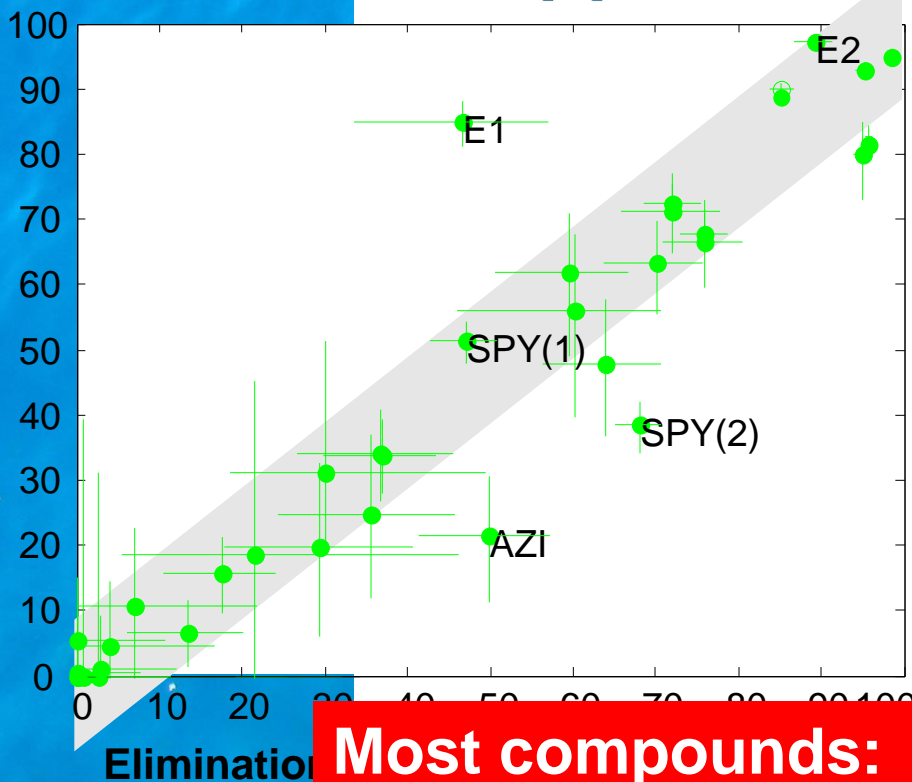


Altenrhein  
Lake Constance

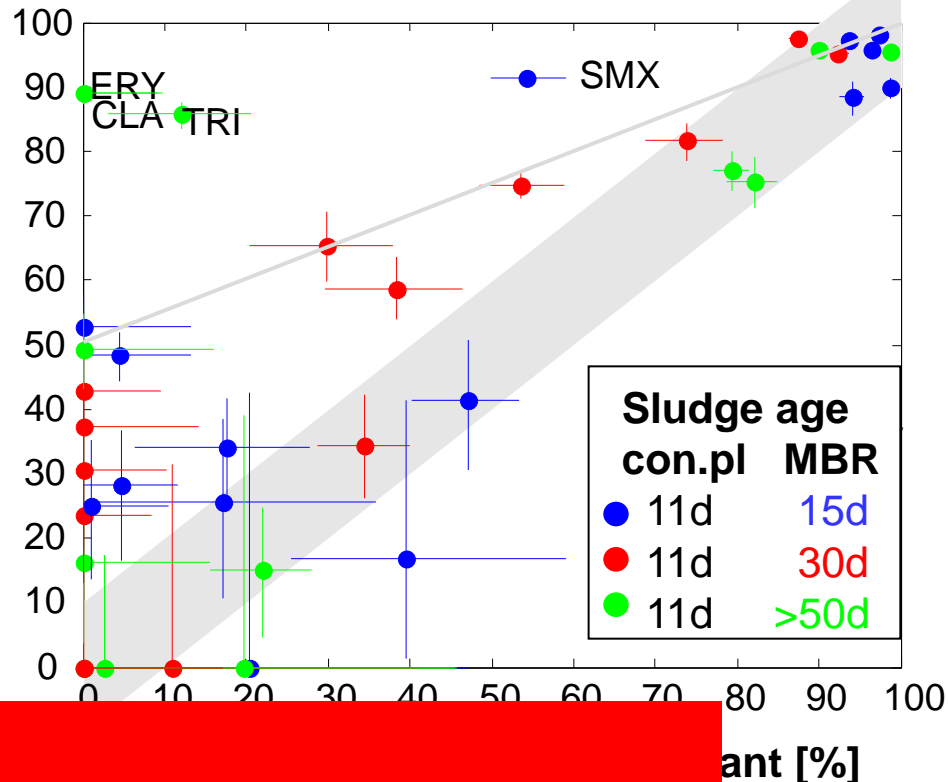


# Comparison of elimination in MBR, biofilter and conventional plant

Elimination in biofilter [%]



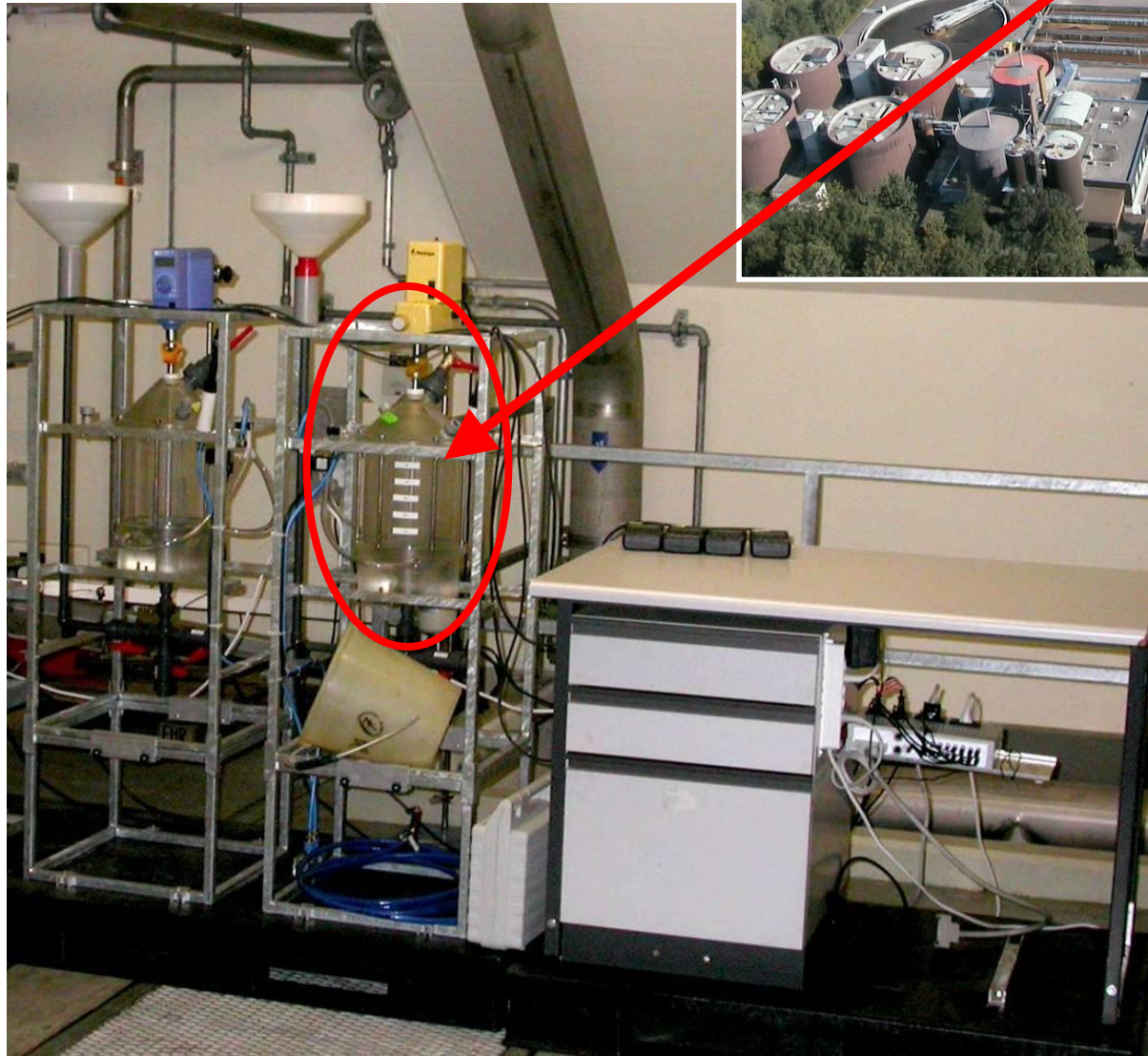
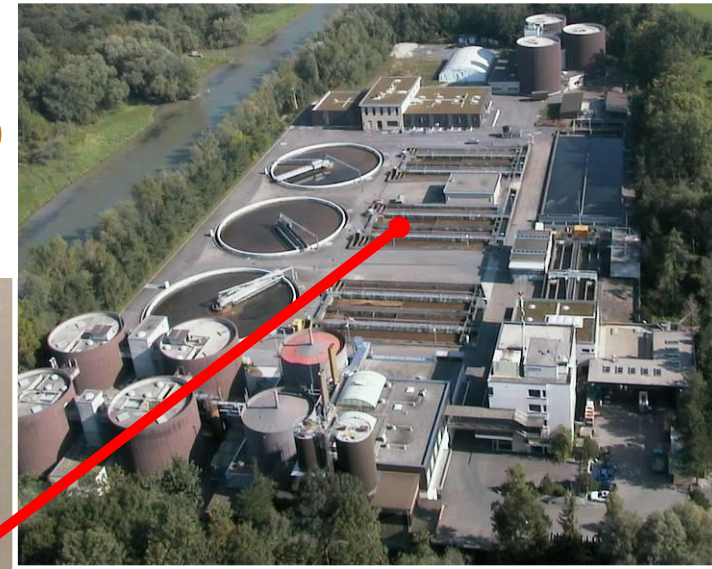
Elimination in MBR [%]



**Most compounds:**  
a) different treatment, comparable removal  
b) only partially removed

# Batch experiment

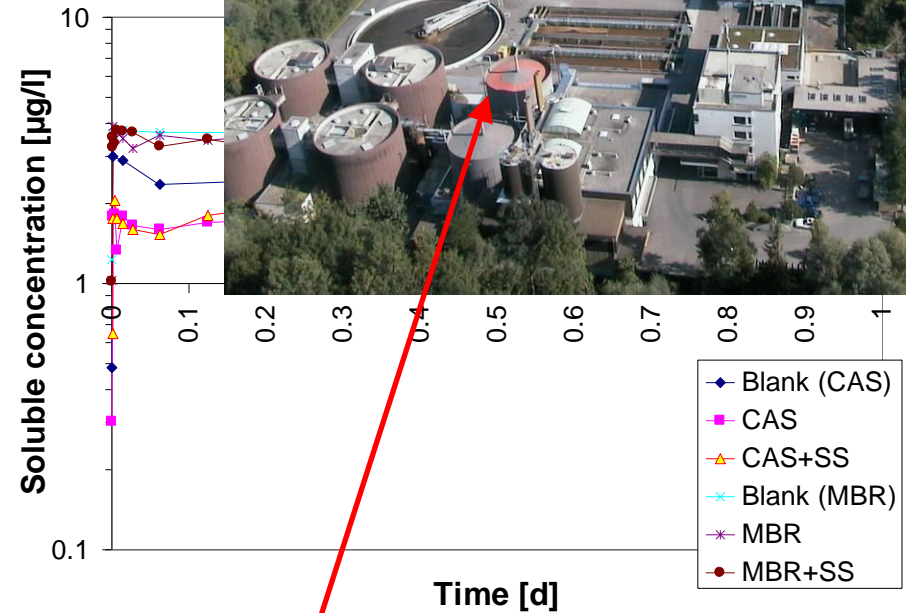
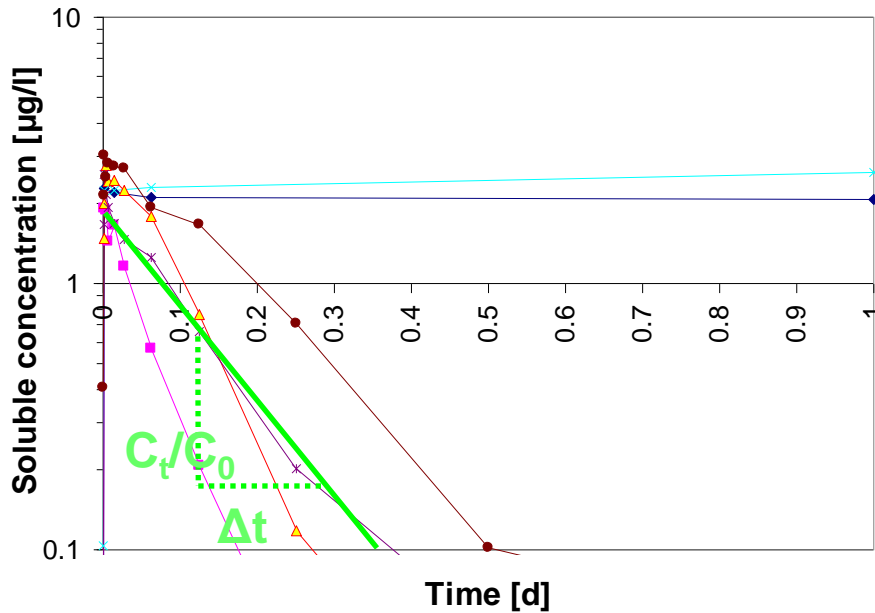
## Test degradation in lab



# Batch experiment with



Ibuprofen



- ◆ Blank (CAS)
- CAS
- ▲ CAS+SS
- ◆ Blank (MBR)
- \* MBR
- MBR+SS

Relative removal rate constant

$$\frac{\log C_t - \log C_0}{\Delta t} = k_{biol} \cdot SS$$

→ Removal (pseudo) first order

$$\Rightarrow \frac{dC_t}{dt} = k_{biol} \cdot SS \cdot C_t$$

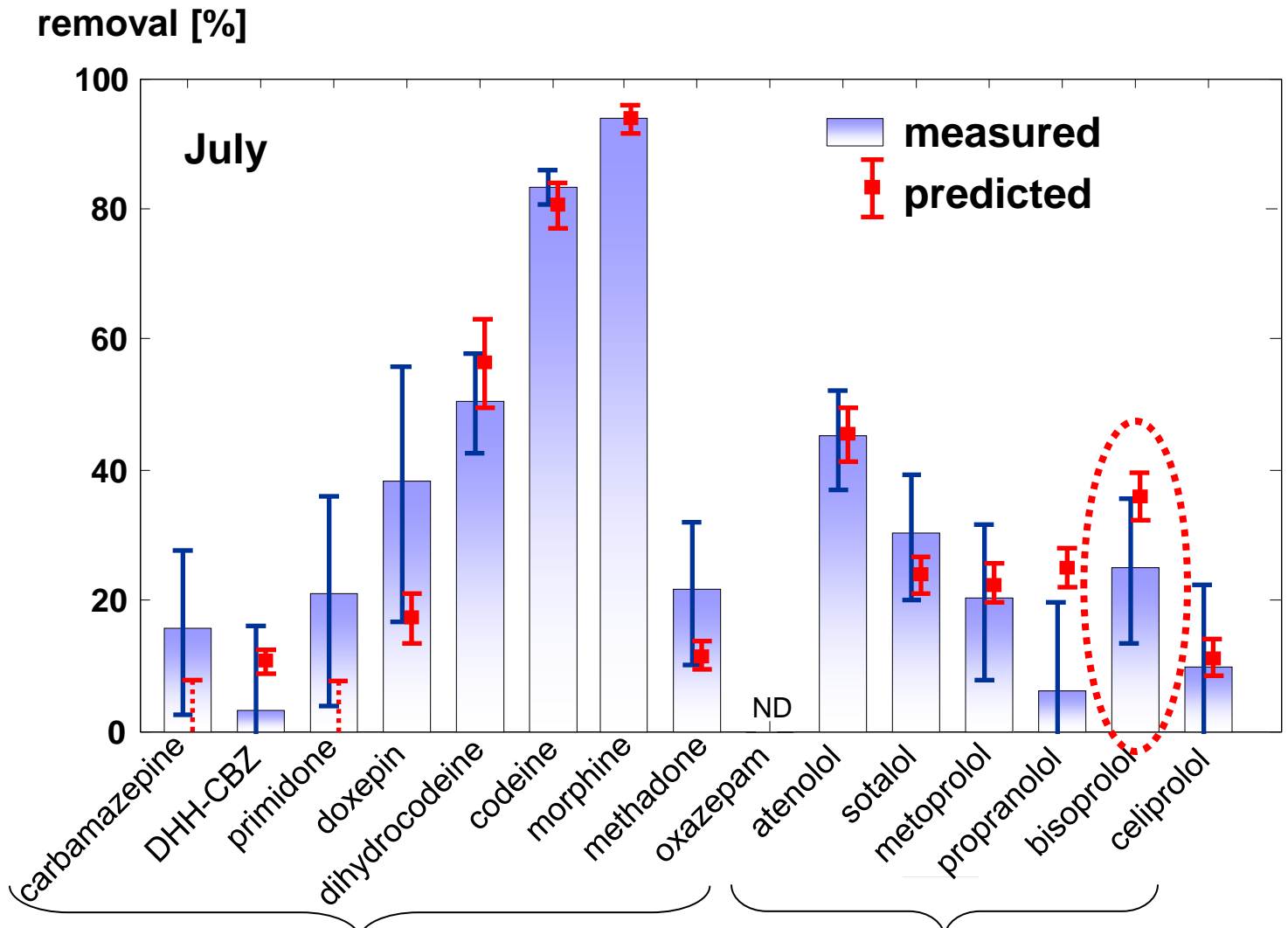
Reaction rate  
[ $\mu\text{g} \cdot \text{m}^{-3} \cdot \text{Reaktor} \cdot \text{d}^{-1}$ ]

Substance conc.  
[ $\mu\text{g} \cdot \text{m}^{-3} \cdot \text{Reaktor}$ ]

Rate constant  
[ $\text{L} \cdot \text{gSS}^{-1} \cdot \text{d}^{-1}$ ]

Sludge concentration  
[ $\text{gSS} \cdot \text{L}^{-1}$ ]

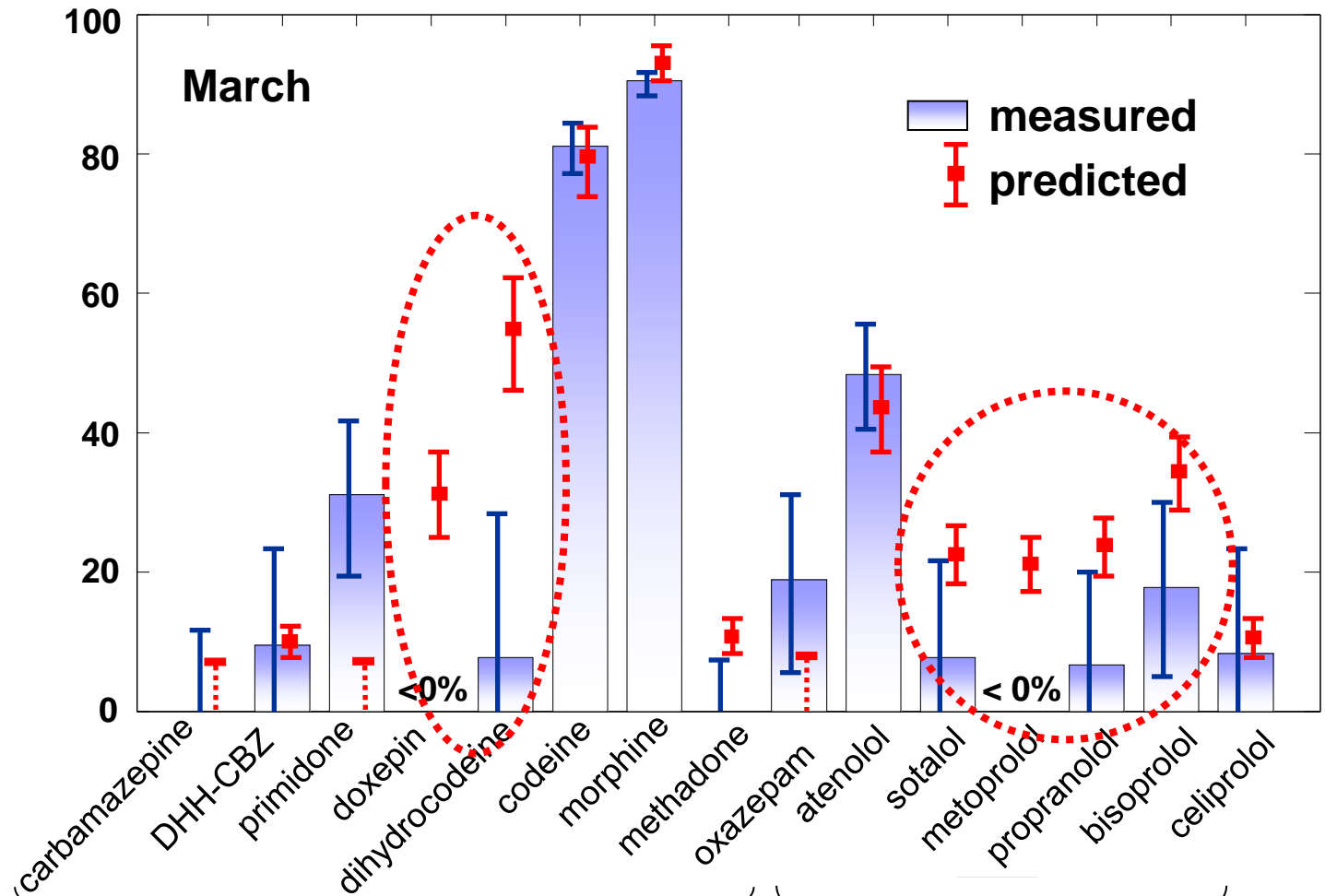
# Modelling removal in the second biological step



**Model fits most but not all compounds**

# Modelling removal in the second biological step

removal [%]



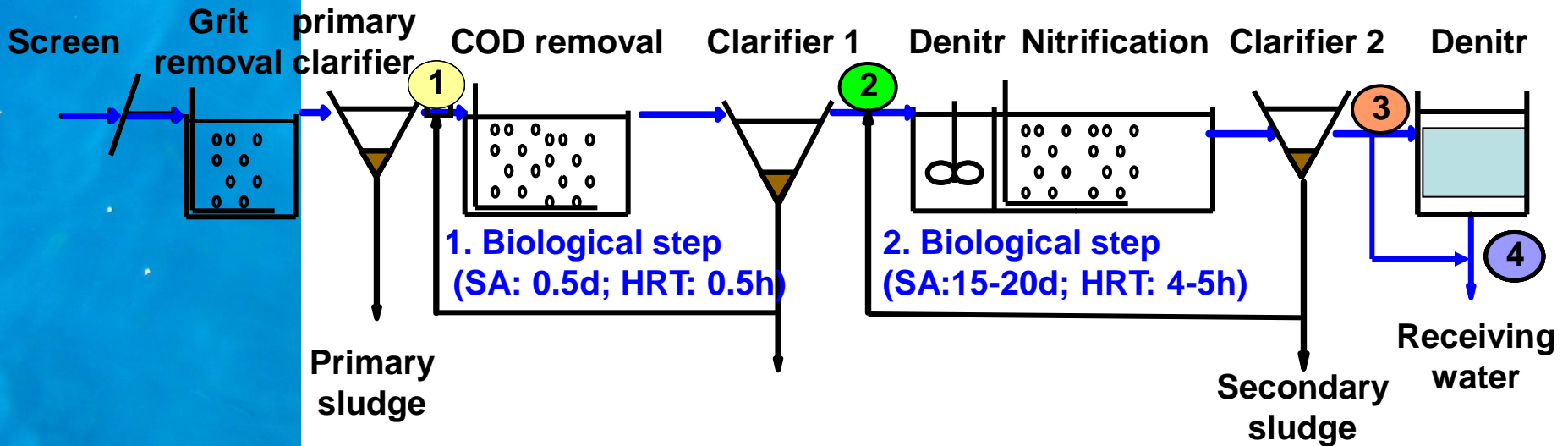
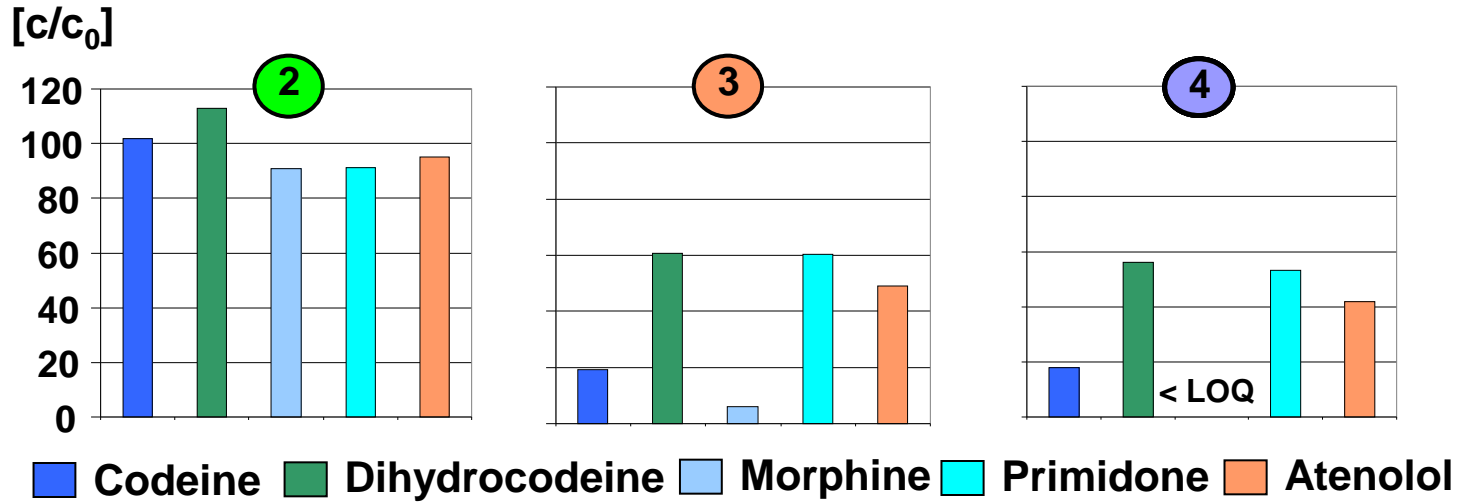
**Model fits most but not all compounds**



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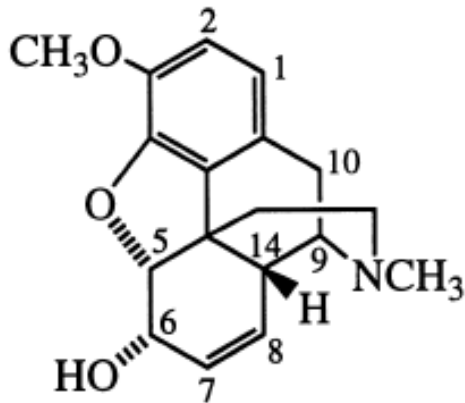
- Sorption
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- **Transformation products**
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# Removal of atenolol and psychoactive drugs in WWTP Frankfurt



# Biological transformation

## Example: Codeine



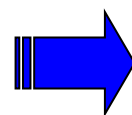
Codeine

- used as analgesic and cough suppressant
- most widely used opiate in the world
- opium contains 0.2 to 6% codeine
- mainly produced from morphine by methylation of the hydroxy group at the aromatic ring



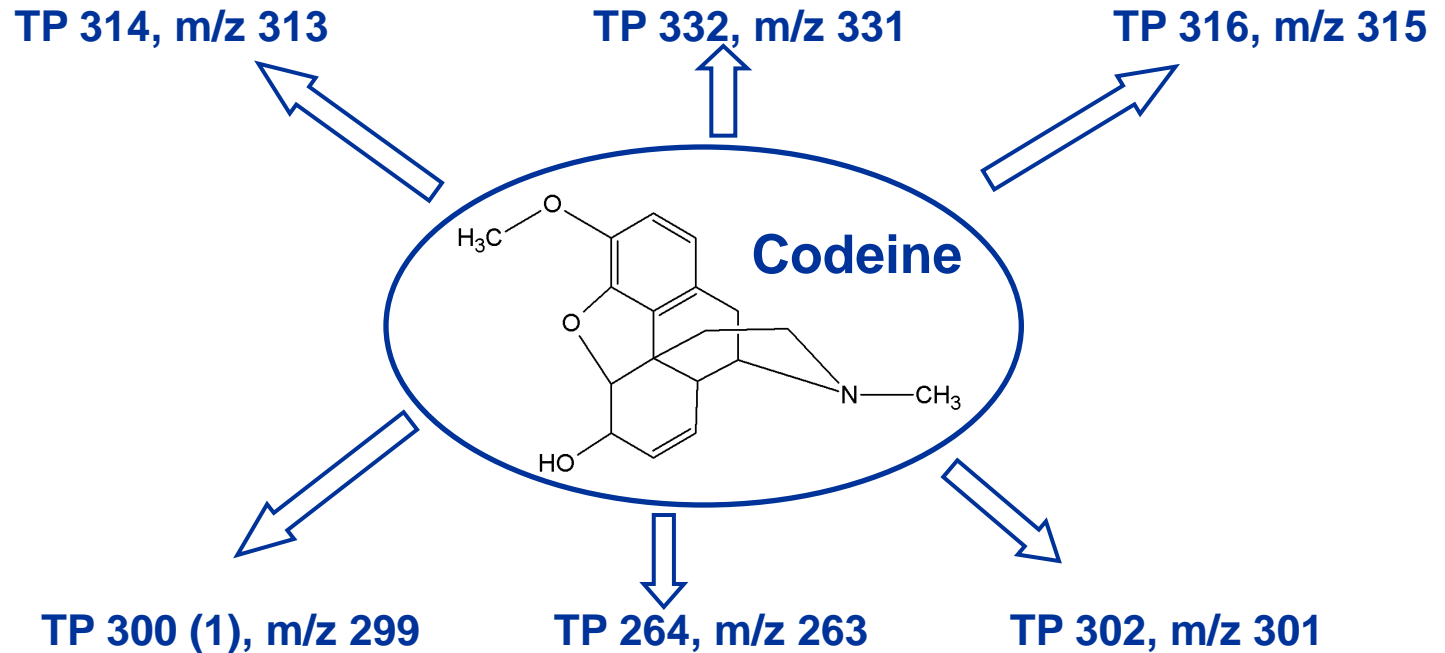
capsule of the opium poppy (*Papaver somniferum* L.).

up to 90% is removed in WWTPs by primary degradation



formation of transformation products (TPs) ?

# Codeine transformation products



**in most cases basic structure unchanged**

typical reactions observed:

- double bond shift
- hydroxylation
- demethylation

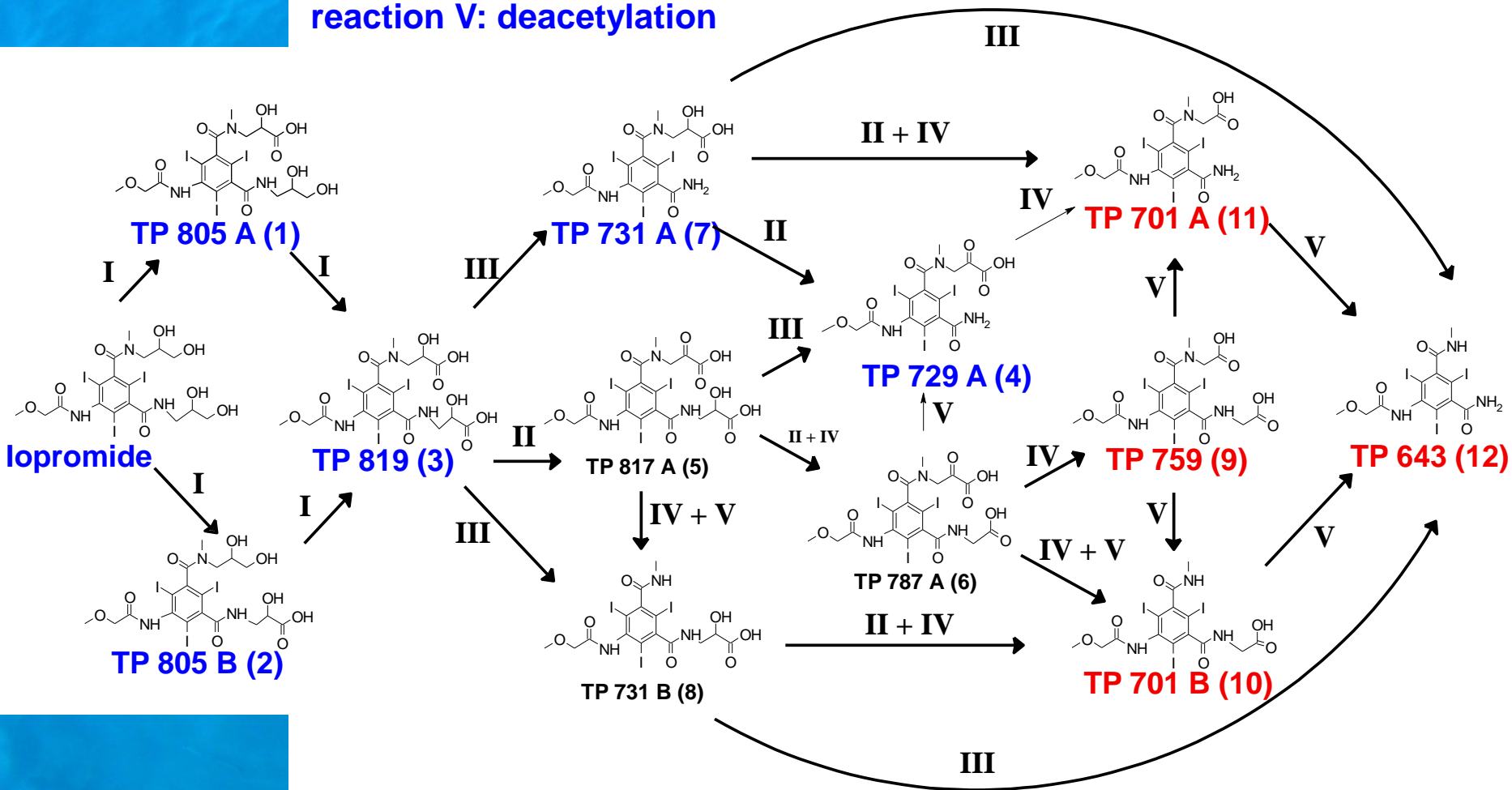
# Iopromide: potential aerobic degradation pathways

reaction I/II: oxidation prim./sek. hydroxyl moieties

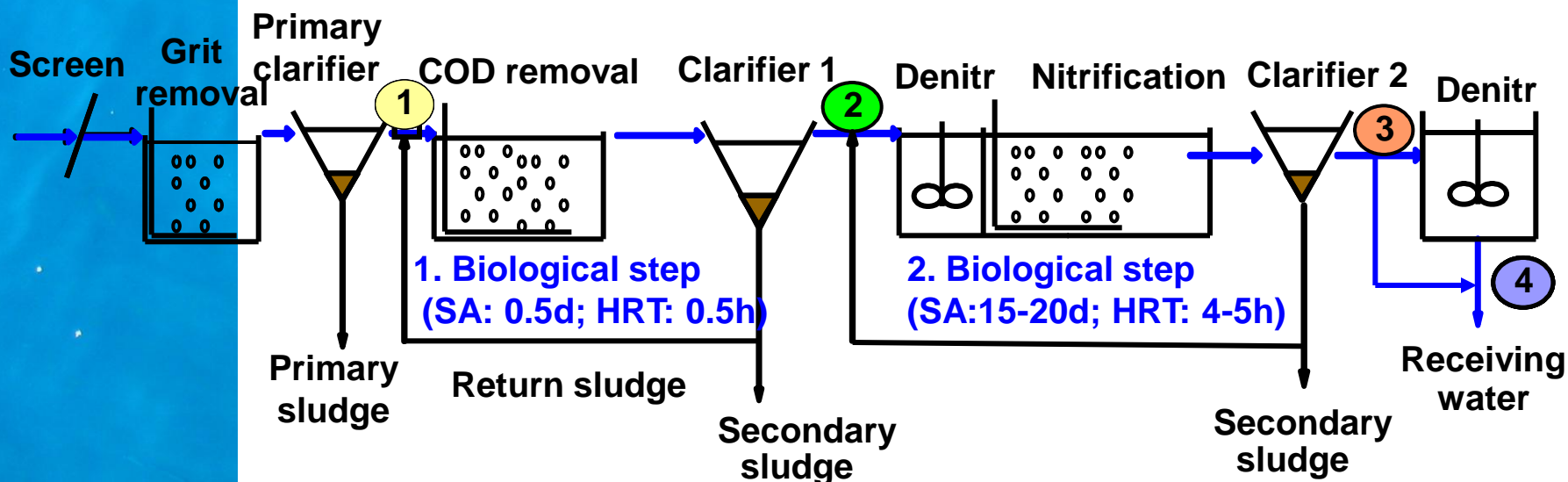
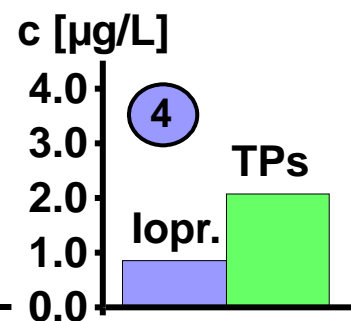
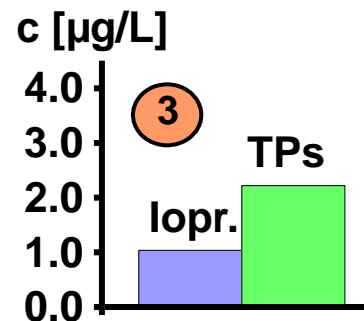
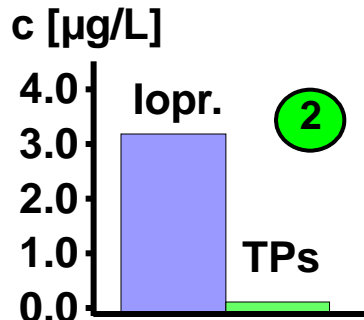
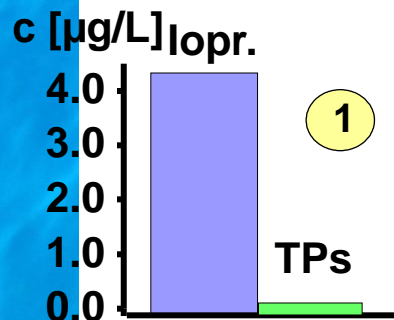
reaction III: cleavage of amide-methylen bond

reaction IV: oxidative decarboxylation

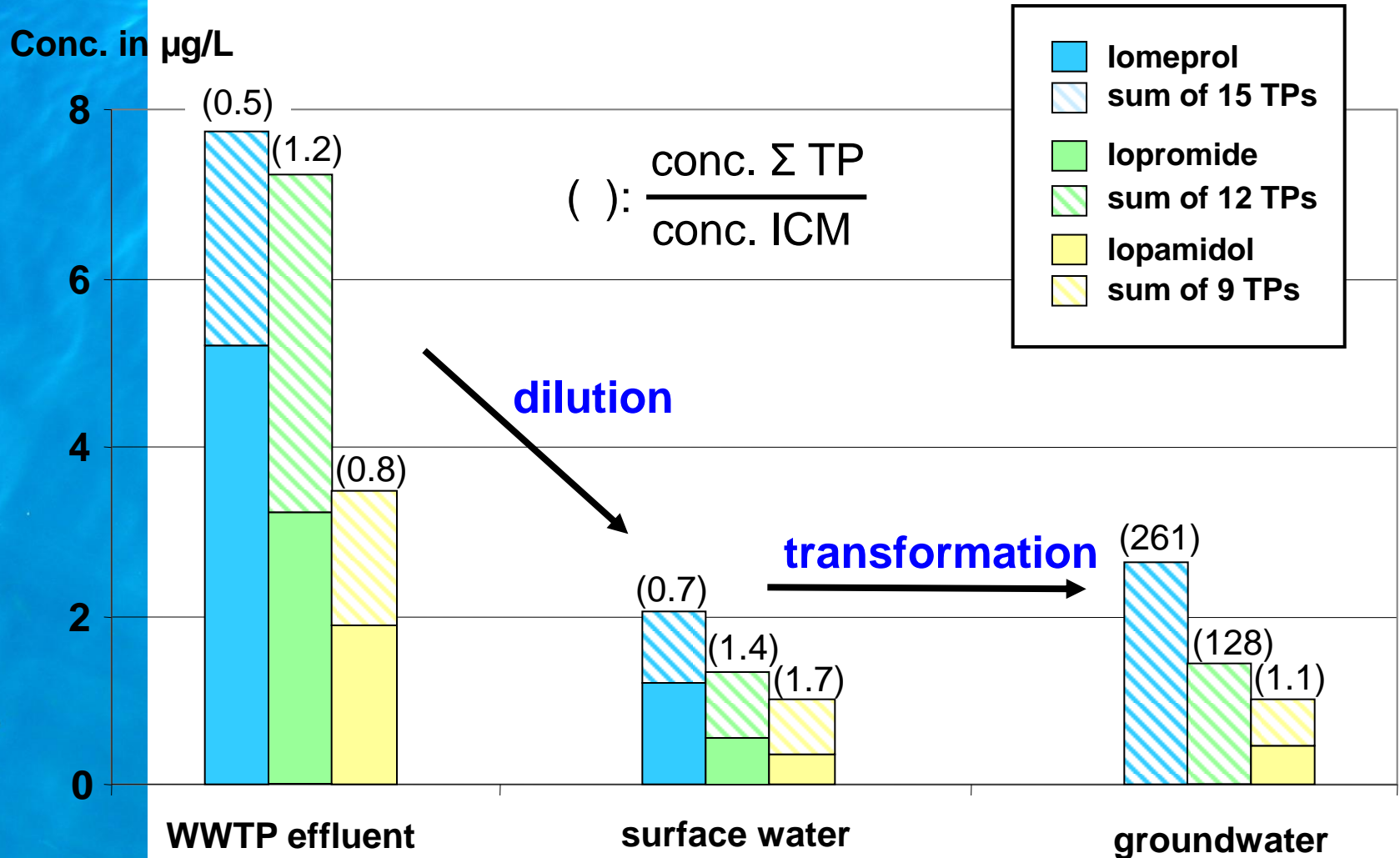
reaction V: deacetylation



# Transformation products (TPs) of Iopromide in WWTP Frankfurt



# Transformation of iodinated contrast media

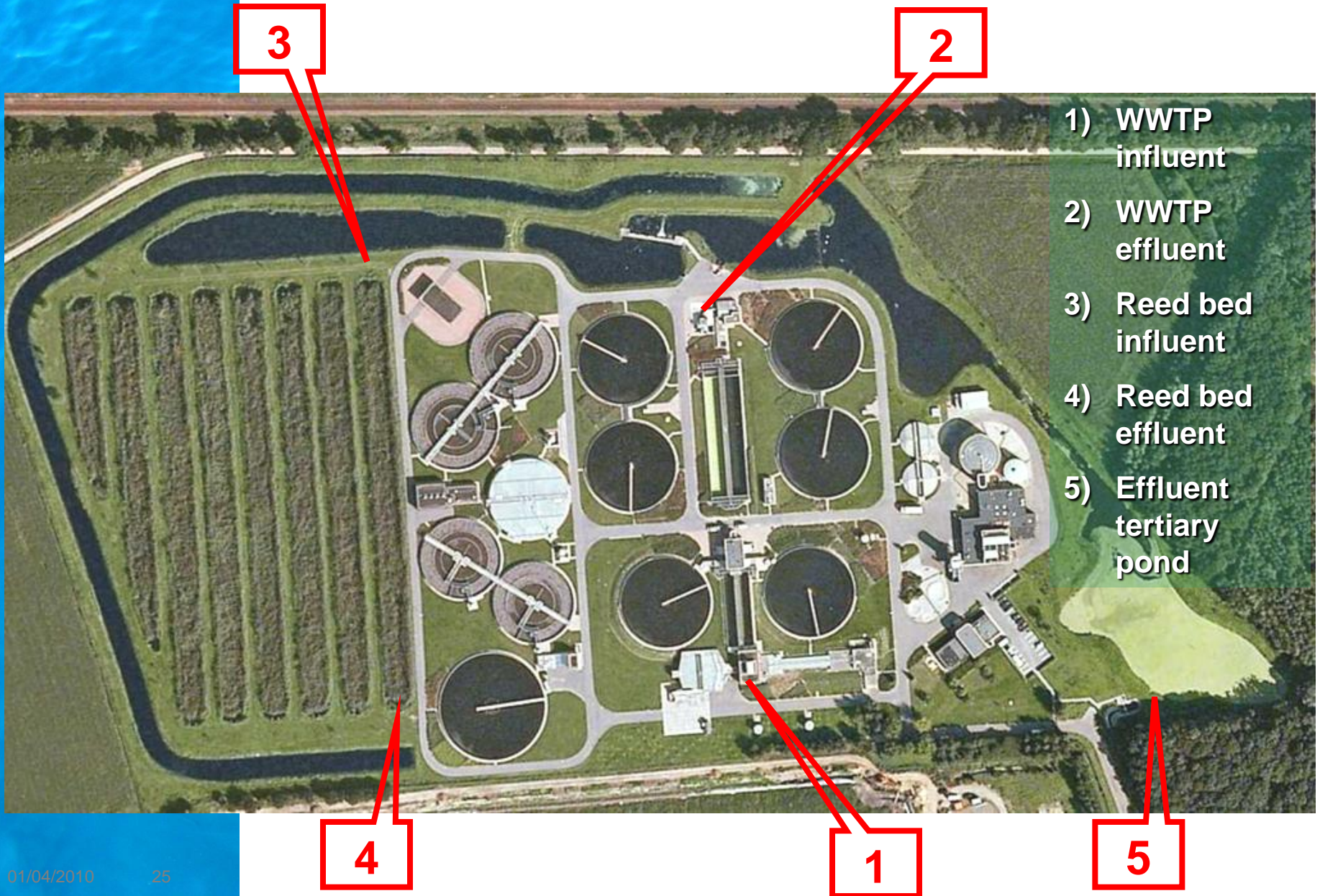


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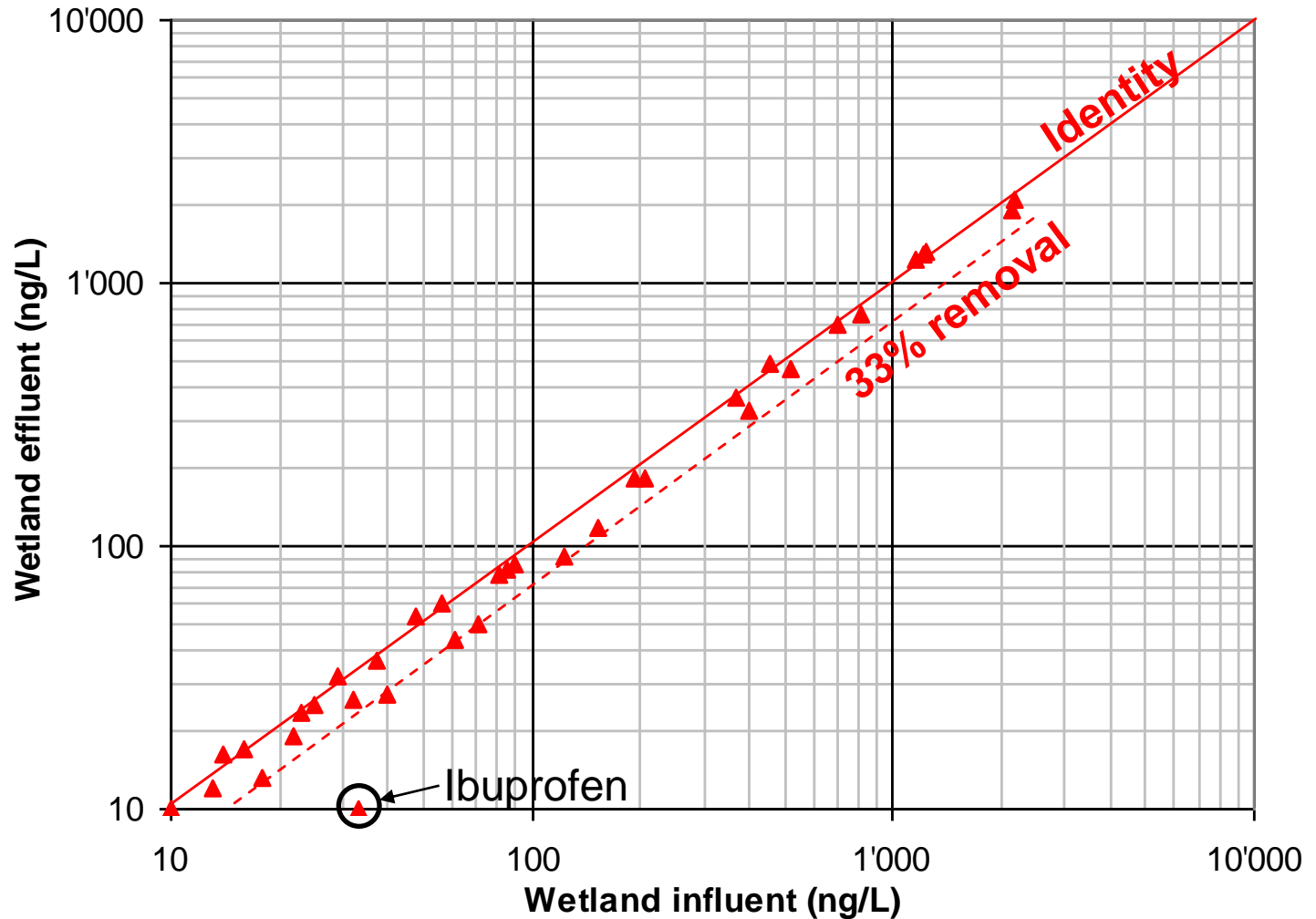
# Wetland van Cuijk



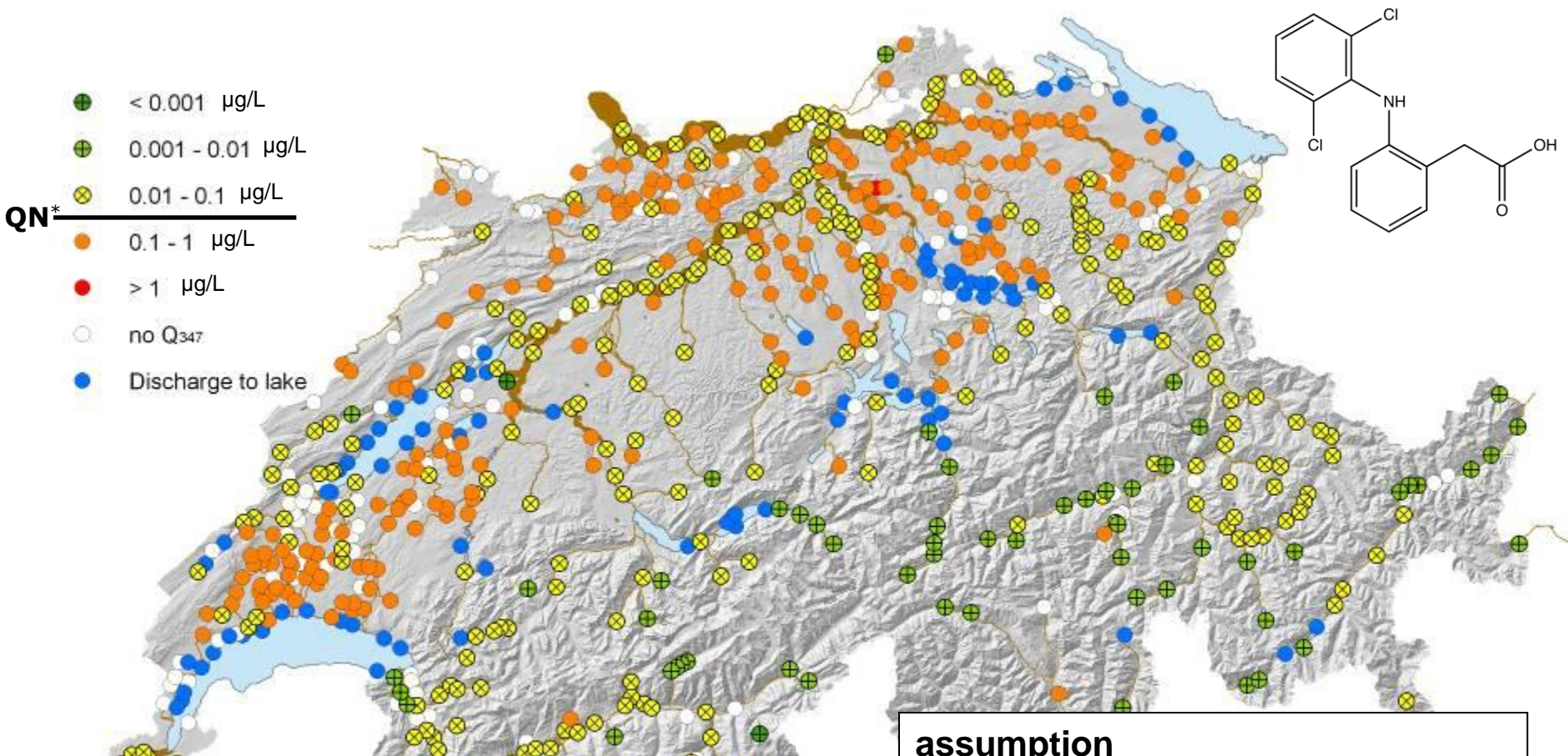
- 1) WWTP influent
- 2) WWTP effluent
- 3) Reed bed influent
- 4) Reed bed effluent
- 5) Effluent tertiary pond

## Wetland van Cuijk

- 4 days hydraulic residence time
- $0.17 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$  hydraulic loading



# Diclofenac: predicted concentrations in Swiss surface waters based on the dilution factor (environmental quality standard: 0.1 µg/L)



**A simple model allows identifying hot spots for advanced treatment**

- consumption: 4 t/a
- 5% (Dicl. + meta) in wastewater
- elimination in WWTP: Ø 25%
- no degradation in surface water

Data: Eawag/FOEN 2006/07  
Basis: Vector25@swisstopo (2004)  
DHM25@swisstopo (2004)

0 25 50 100 km

## Conclusions

- **Sorption to sludge:** relevant for few compounds
- **Degradation** achieves only partial removal
  - First order kinetic does not always fit
- **Transformation products** of similar chemical structure often formed
  - Does elimination result in **detoxification**?
- **Wetlands** achieve little micropollutant removal
- **Environmental concentrations:** estimation based on consumption and dilution
  - Identify spots for advanced treatment

# Thank you for your attention ...

... and the European Commission for financing  
NEPTUNE, 6<sup>th</sup> Framework Programme

