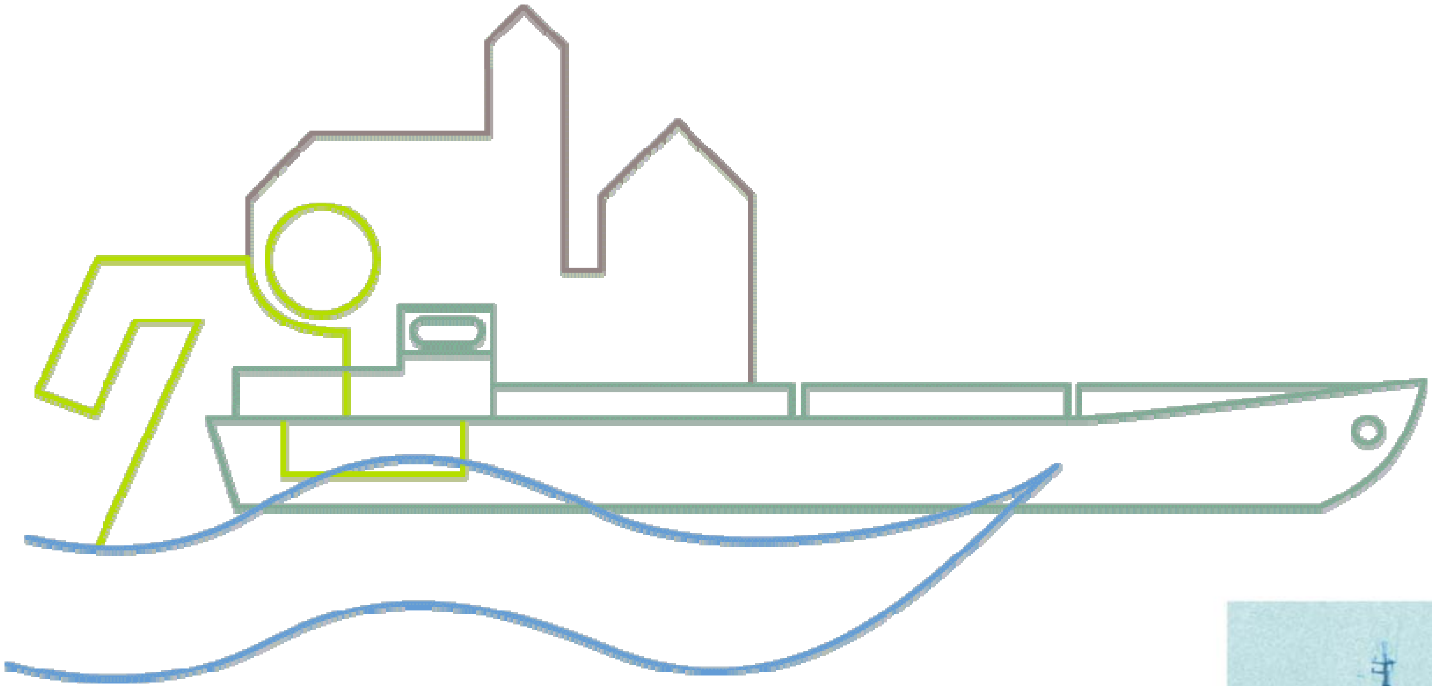
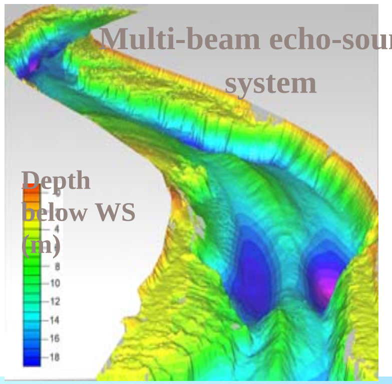


Welcome to the Federal Institute of Hydrology



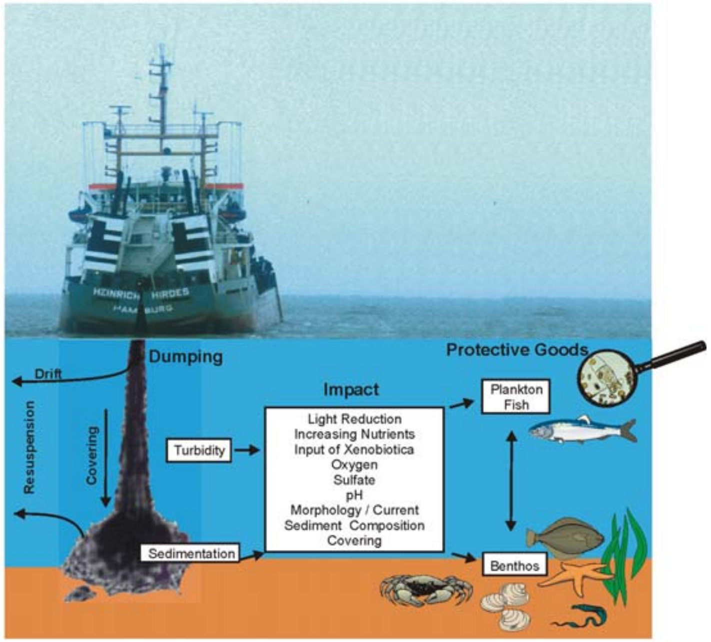
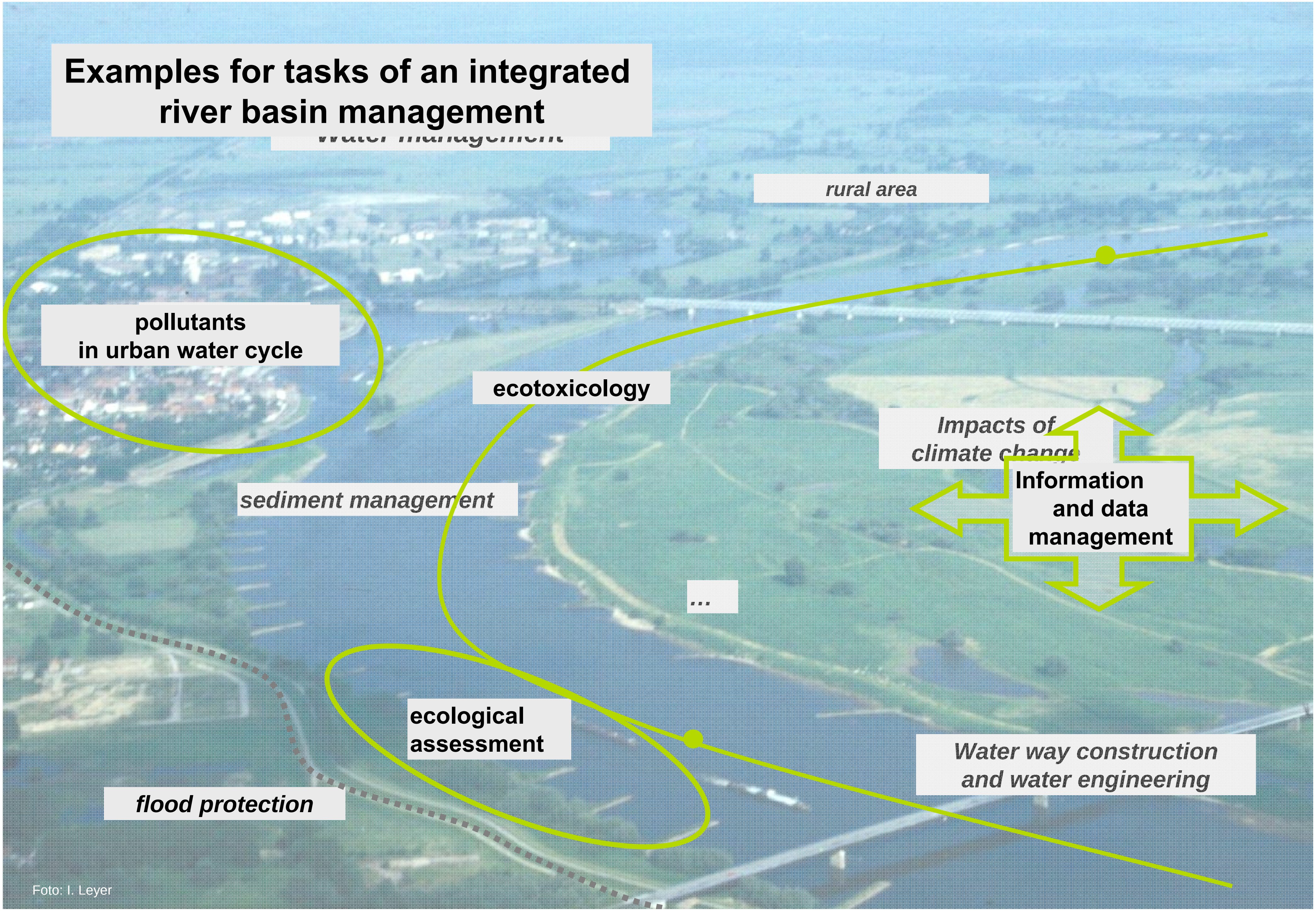
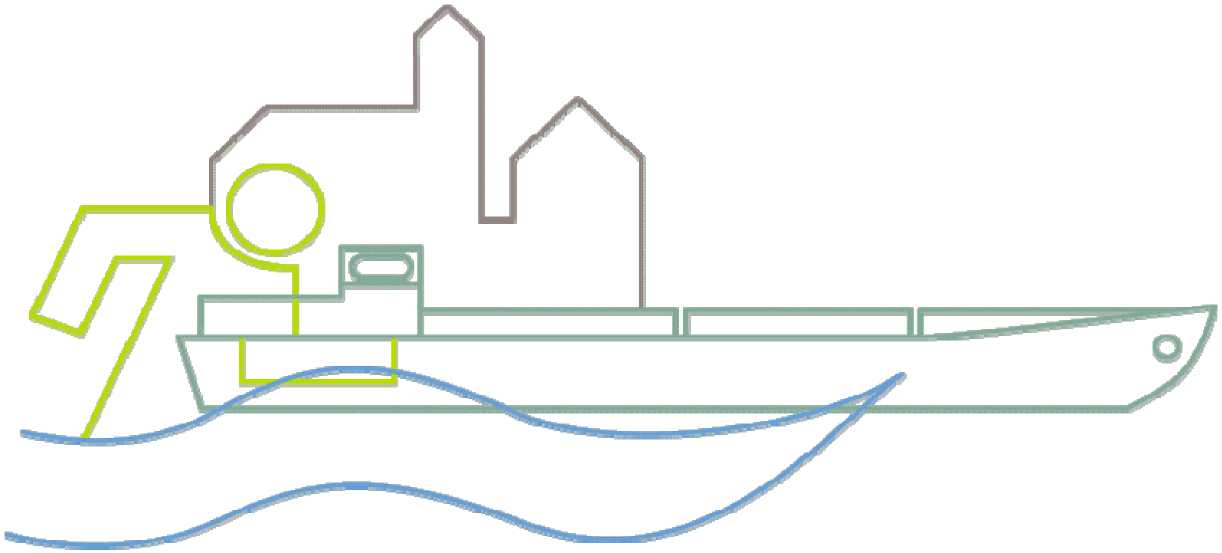



Foto: E.H. Stanley

Examples for tasks of an integrated river basin management





Occurrence and fate of emerging contaminants in the aqueous environment

A. Wick, J. Kormos, O. Marincas, M. Schulz, M. Schluesener, G. Fink, A. Joss, Z. Moldovan, H. Siegrist and T. A. Ternes

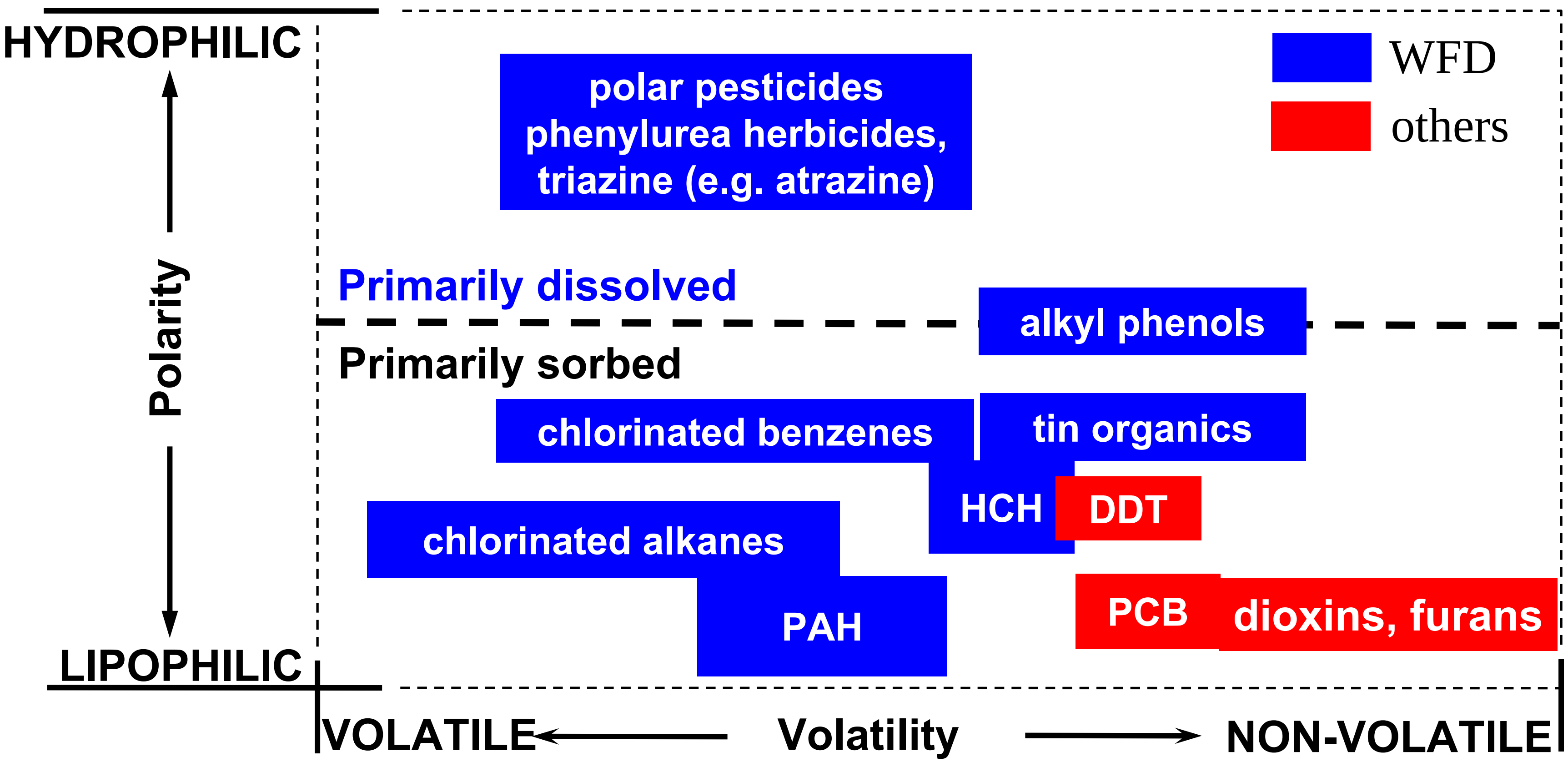
Chemicals used in the EU

- 100000 "old chemicals" until 1981
- > 4000 "new chemicals" since 1981

- 30000 chemicals > 1 t yr^{-1}
- 2900 chemicals > 100 t yr^{-1}
- 2600 chemicals > 1000 t yr^{-1}

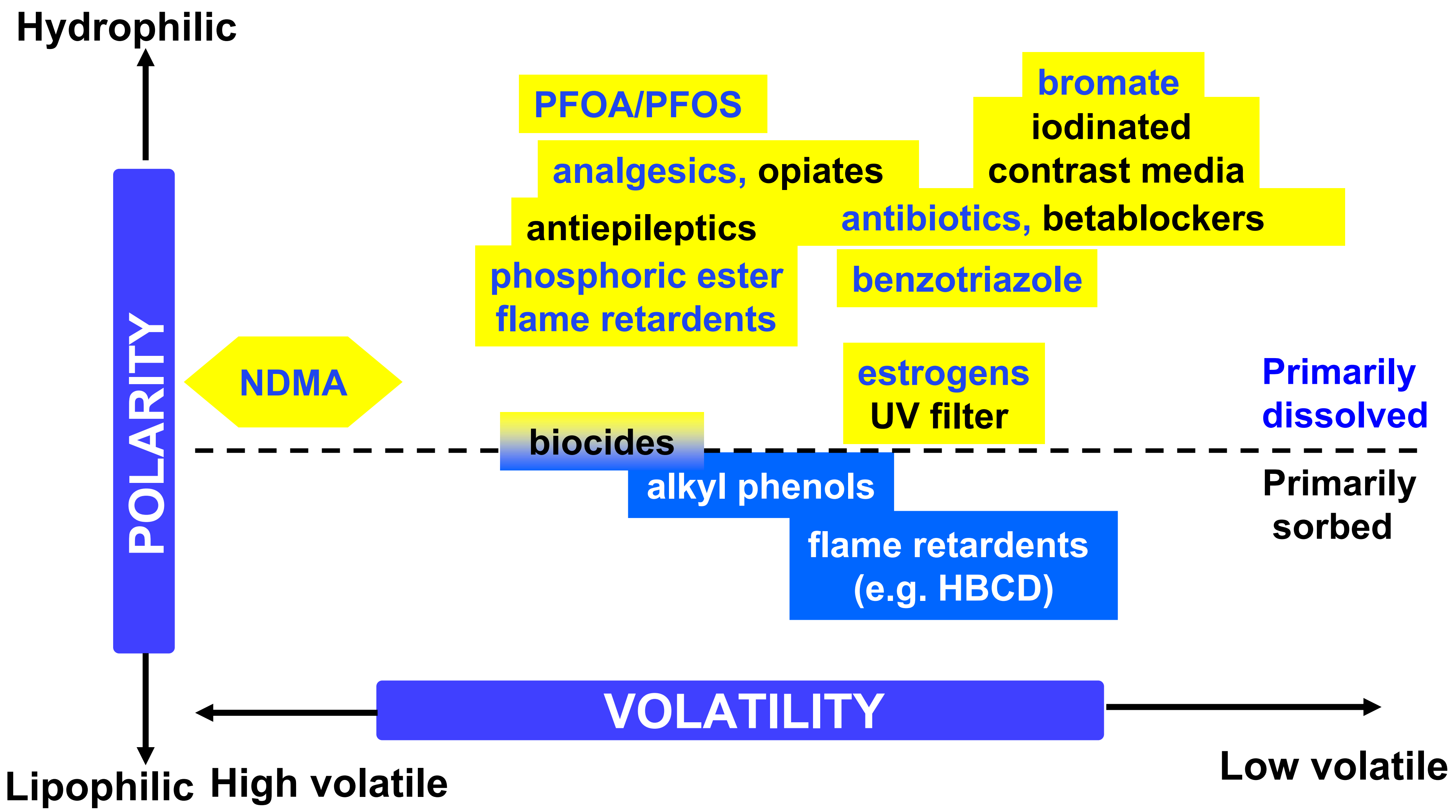
Organic pollutants already regulated (WFD, …)

based on ecotoxicological criteria

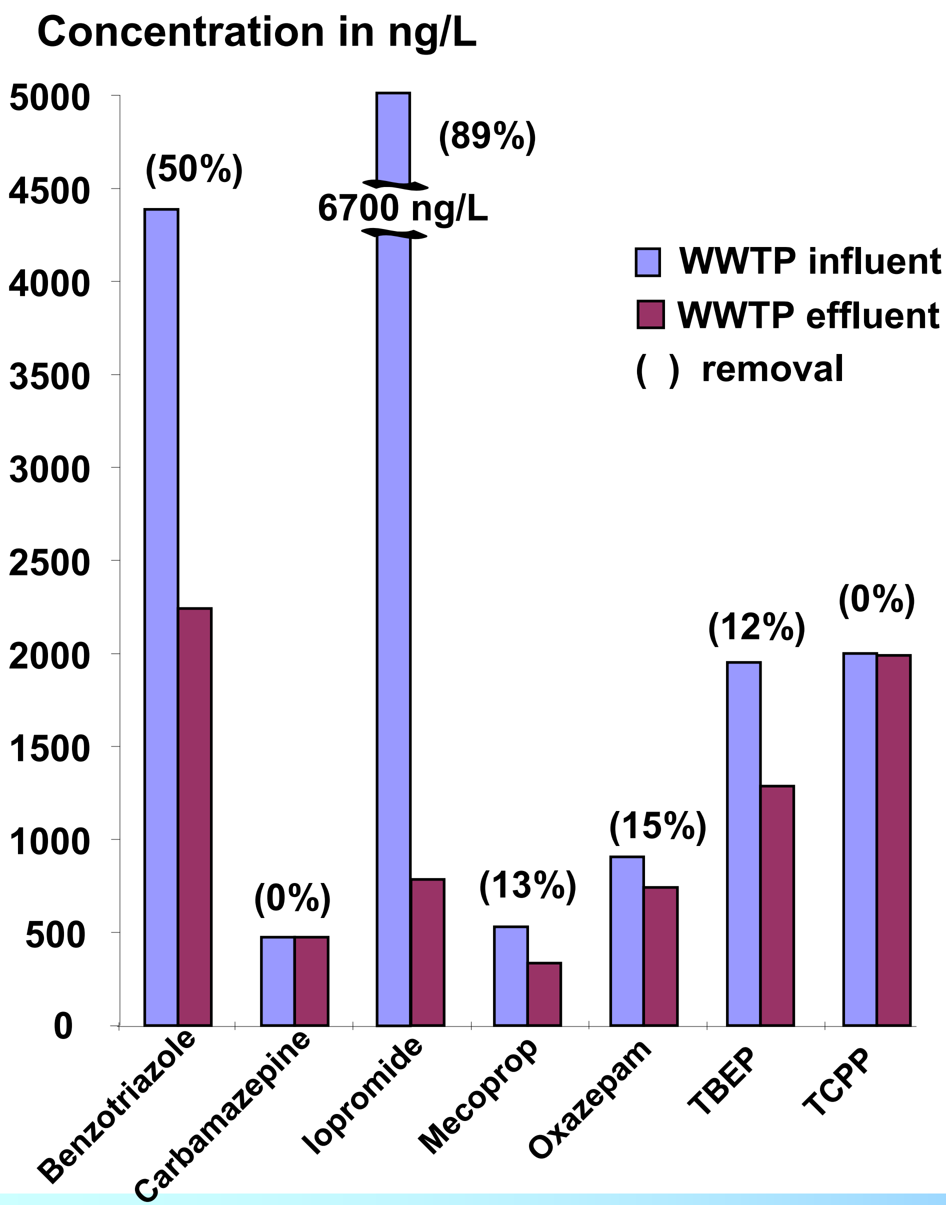


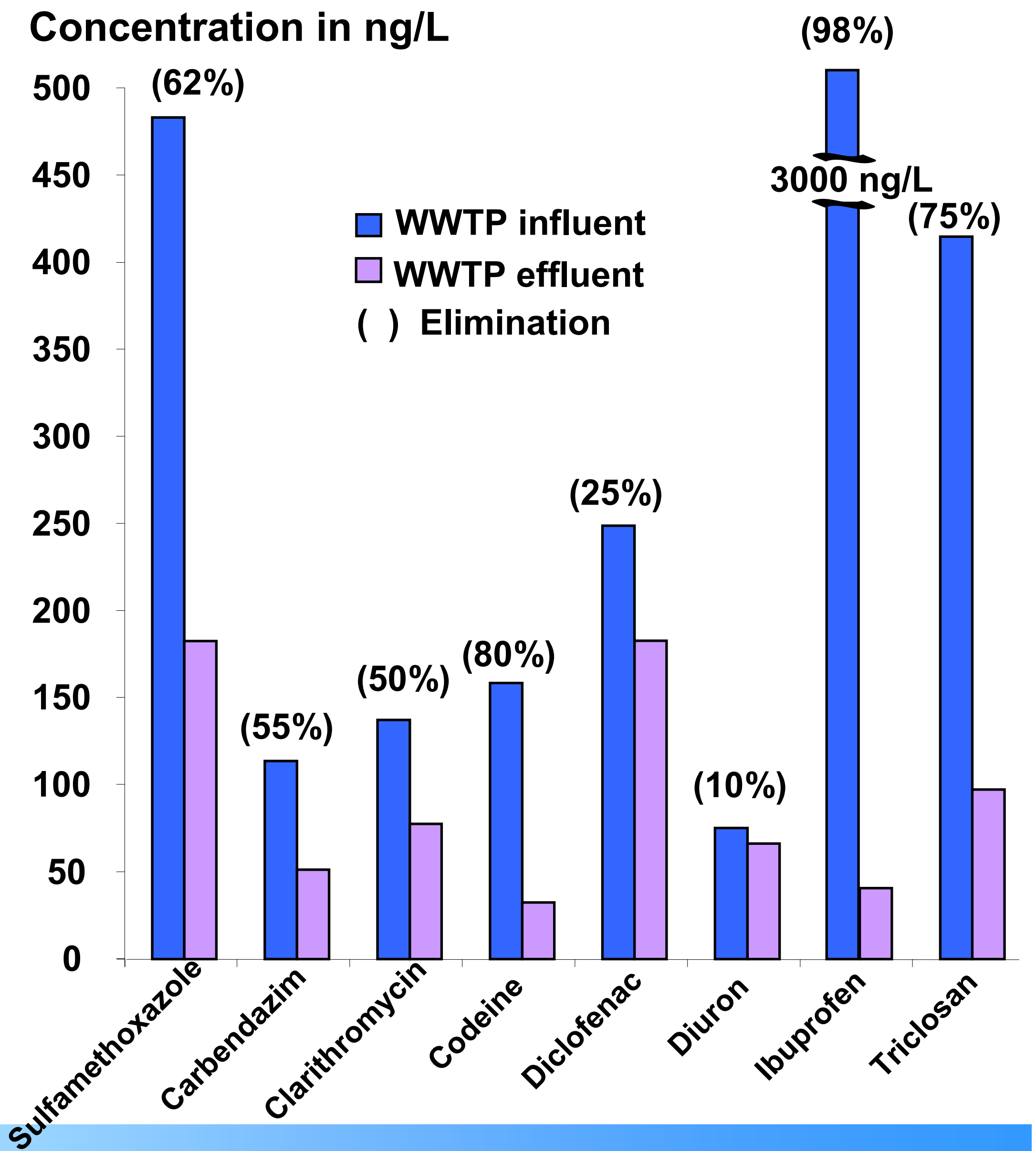
Source: Ternes and Joss (2006) IWA Publishing

Emerging pollutants measured by Neptune



Elimination of emerging pollutants in municipal WWTP





Sorption - „rapid“ batch experiments

secondary sludge + NaN_3 (0.2%)

↓

sampling after 2.5, 5 und 14 h

(triplicates)

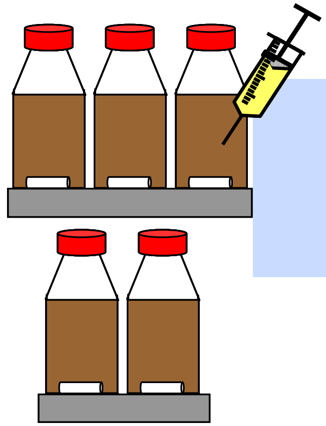
↓

centrifugation

water phase → Analysis by LC tandem MS

sludge → freeze-drying → Analysis by LC tandem MS

Analysis by LC tandem MS



spiking with
(15 µg L^{-1})

Sorption – rapid batch experiments

sludge/water-partition coefficients (K_d) for secondary sludge

psycho-active drugs:

K_d < 100 L kg_{SS}^{-1} (except doxepin: K_d = 140 L kg_{SS}^{-1})

betablockers:

K_d < 100 L g_{SS}^{-1} (except propranolol: K_d = 340 L kg_{SS}^{-1}) *Scheurer et al., in preparation*

predicting the ratio eliminated by sorption

$$\frac{X}{C} = \frac{K_d SP}{1 + K_d SP}$$

Ternes et al., Wat. Res.38, 4075-4084 (2004)

X: concentration (sorbed) [ng L^{-1}]

C: concentration (total) [ng L^{-1}]

SP: sludge production [g_{SS} L^{-1}]

sludge production: (~ 0.09 g_{SS} L^{-1})

⇨ **< 3% are eliminated by sorption**

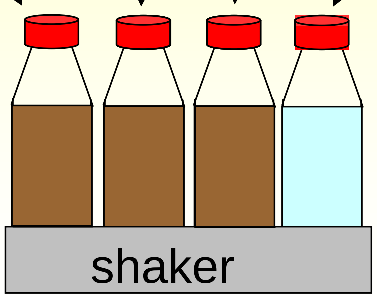
Sorption can be neglected for these target compounds

Sorption of biocides onto secondary sludge isotherm batch experiments

experiment I: sorption equilibrium

w/o NaN_3 | 0.2% NaN_3 | 1% NaN_3 | w/o sludge (control)

spiked with 10 µg L^{-1}

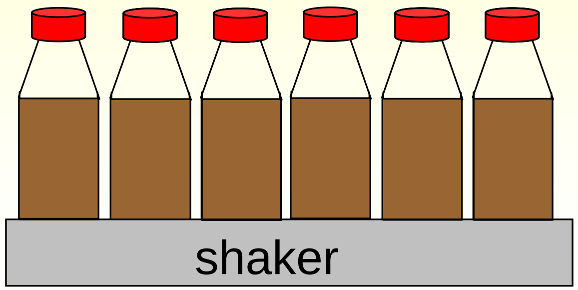


incubation times: 0, 0.75, 1.5, 3.2, 6, 24 h

addition of NaN_3 significantly influences the sorption affinities

experiment II: Freundlich isotherms

spiked with 6 different concentrations (0.1 – 30 µg L^{-1})



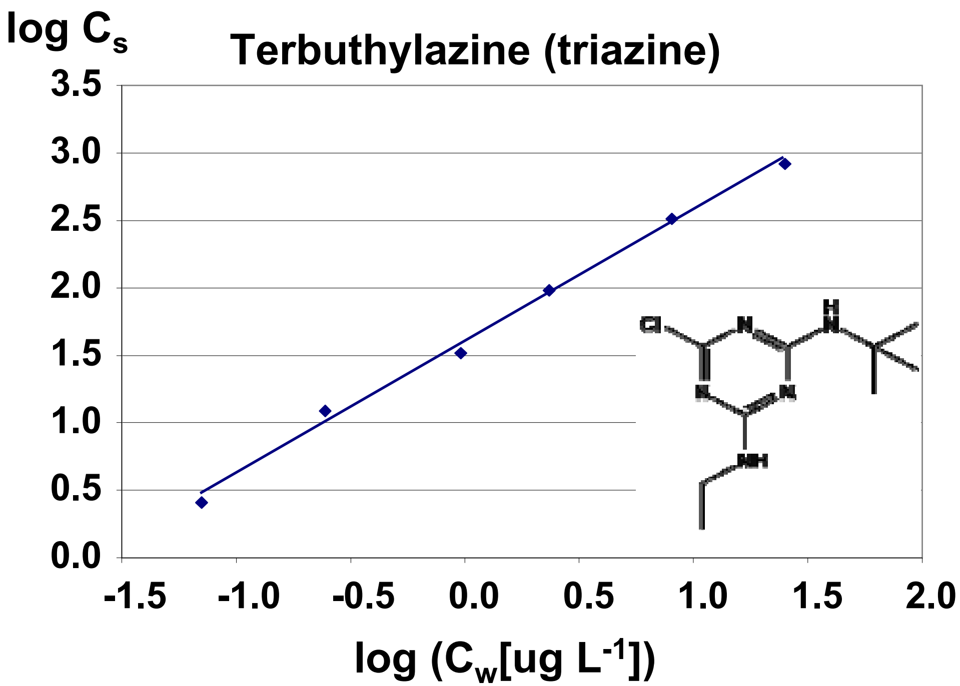
incubation time: **1.5 h**

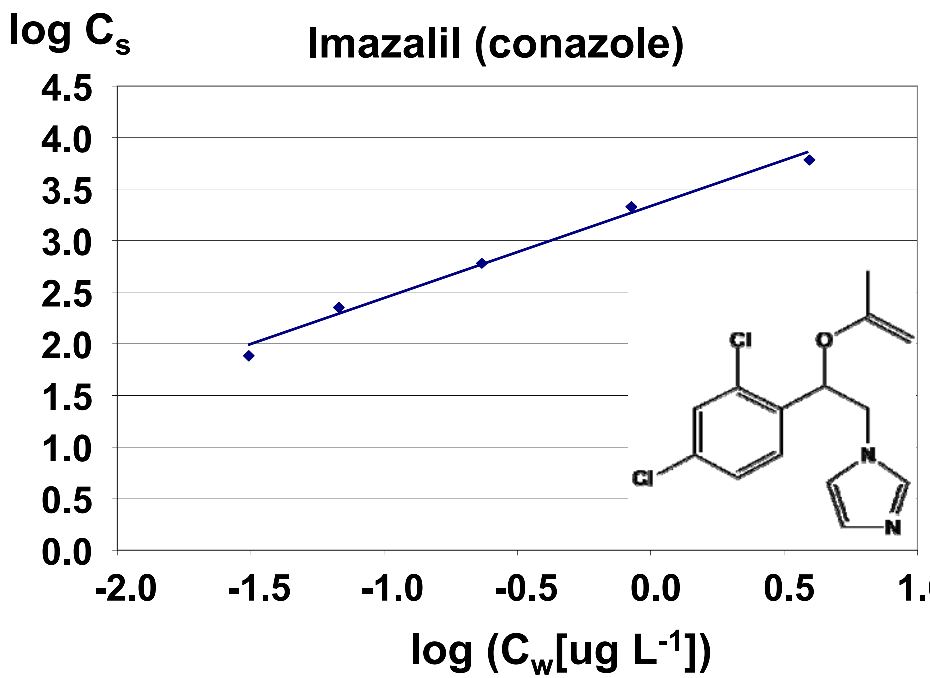
$$C_S = K_F\, C_W^{\,n}$$

$$\log C_S = \log K_F + n \log C_W$$

Freundlich sorption isotherms of triazines/conazoles

Approx. 40 compounds were investigated (e.g. triazines, phenyl urea herbicides, conazoles, antiseptics)





$R^2 = 0.996$

$n = 0.98 \pm 0.10$ (n = 0.98 +/- 0.10)

$K_F = 42$ +/- 10 L kg^{-1}

($K_d = 47$ +/- 14 L kg^{-1})

$R^2 = 0.989$

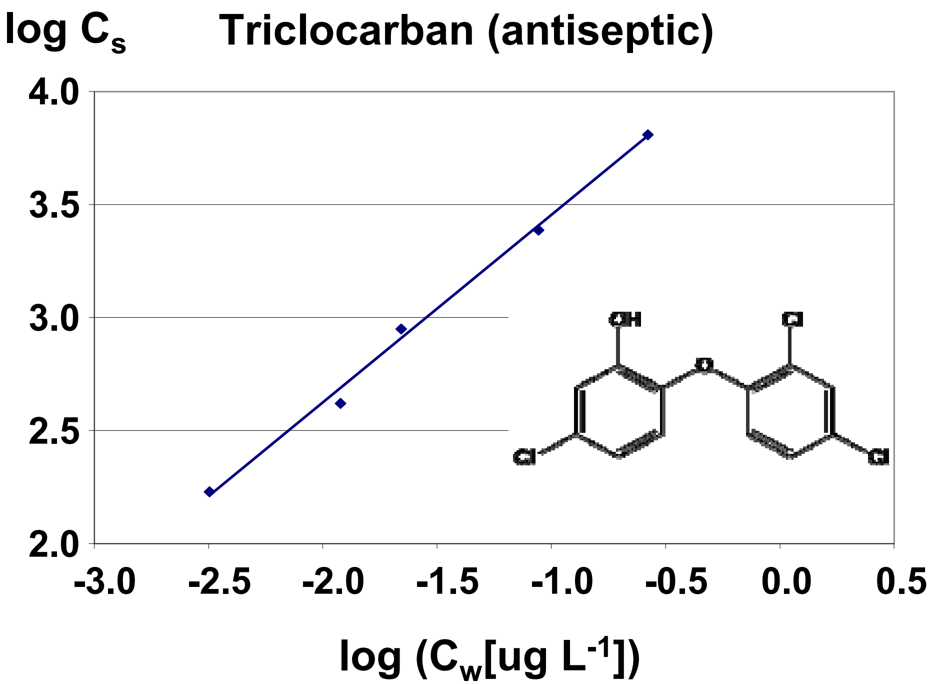
n = 0.89 +/- 0.17

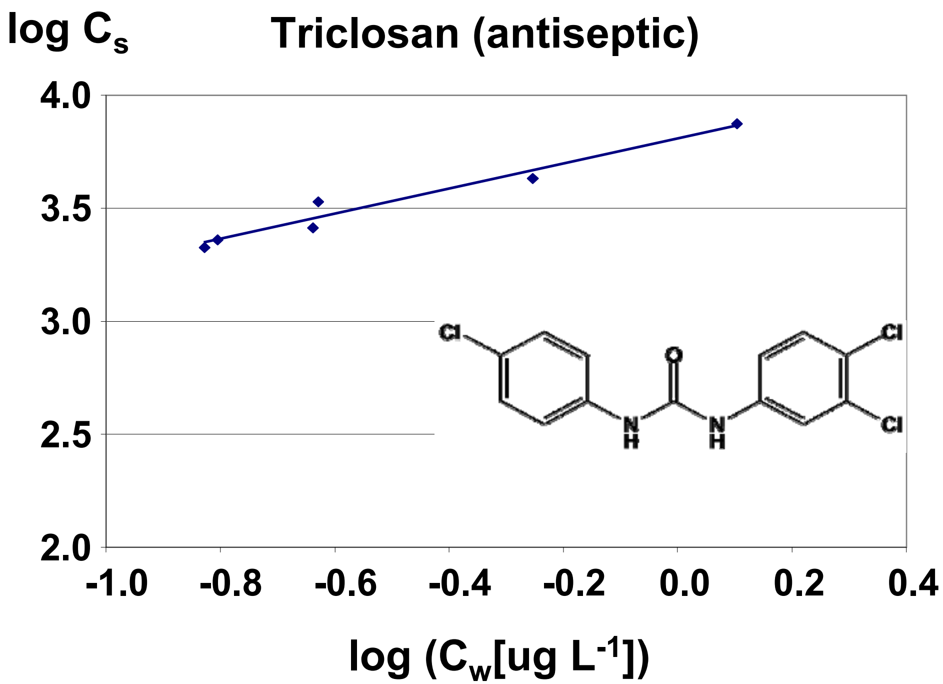
$K_F = 2282$ +/- 741 L kg^{-1}

($K_d = 3003$ +/- 243 L kg^{-1})

0.4 % ← **eliminated by sorption** → **23 %**

Freundlich sorption isotherms of antiseptics





$R^2 = 0.996$

n = 0.83 +/- 0.10

K_F = 19011 +/- 6535 L kg^{-1}

(K_d = 39761 +/- 4096 L kg^{-1})

$R^2 = 0.961$

n = 0.55 +/- 0.16

K_F = 6432 +/- 1396 L kg^{-1}

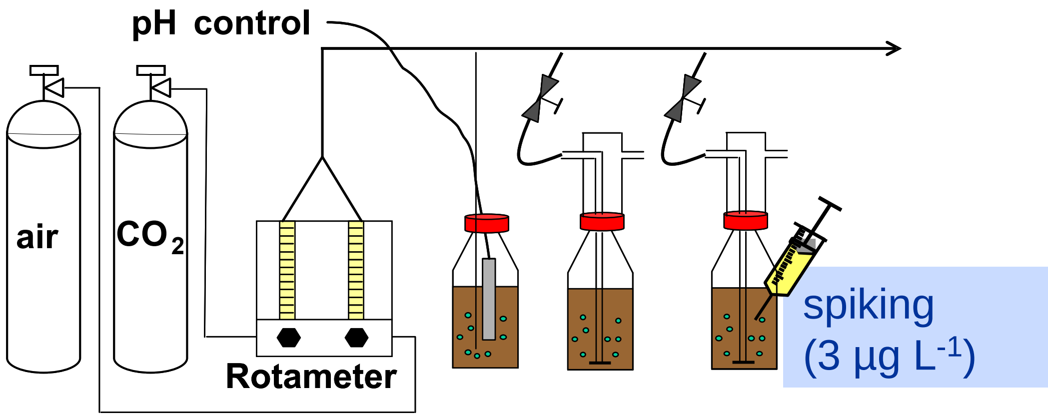
(K_d = 15944 +/- 621 L kg^{-1})

60 % ⇐ **eliminated by sorption** ⇒ **78 %**

Batch experiments – primary transformation

sludge diluted with effluent (1:10)

control: effluent w/o sludge



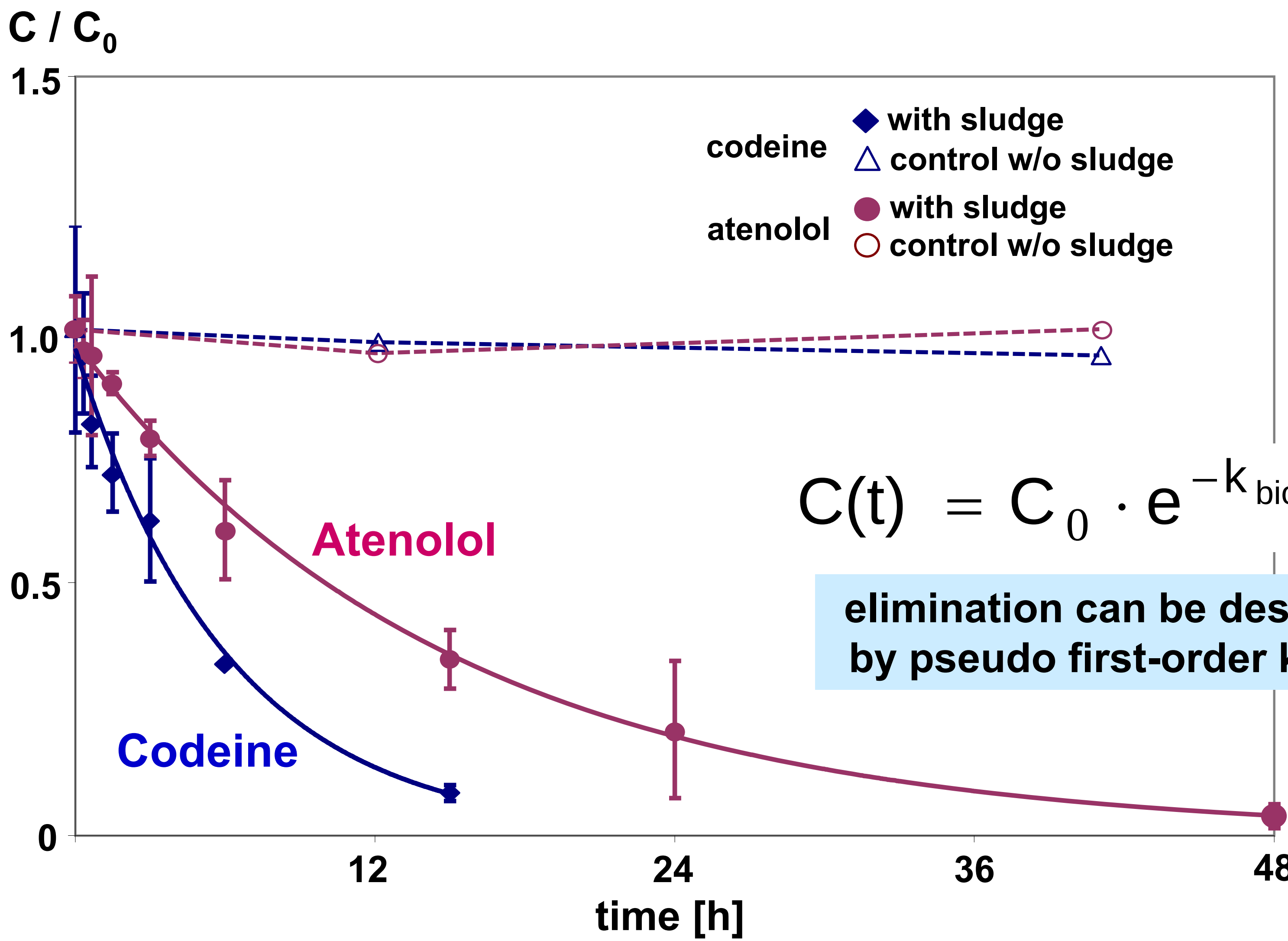
oxic conditions + stable pH (7.2 ± 0.2)
by bubbling air and CO_2

48 h incubation, continuous sampling (triplicates)

⇩

samples acidified to pH 3 for inhibition of the microbial activity

Batch experiments
primary transformation of Codeine/Atenolol



$$C(t) = C_0 \cdot e^{-k_{biol} \cdot SS \cdot t}$$

elimination can be described by pseudo first-order kinetic

Model for primary degradation

Model assumptions

- biol. treatment tank can be modeled as a cascade of ***n*** completely stirred reactors (CSTR) (n=1-3)
- sorption negligible

$$\text{elimination [\%]} = 1 - \frac{1}{(1+R)\cdot\left[1+\left(k_{biol}\cdot T_{corr}\cdot SS\cdot\frac{HRT}{n\cdot(1+R)}\right)\right]^{n} - R}$$

biol. transformation constants (k_{biol})

hydraulic retention time (HRT)

temperature correction (T_{corr})

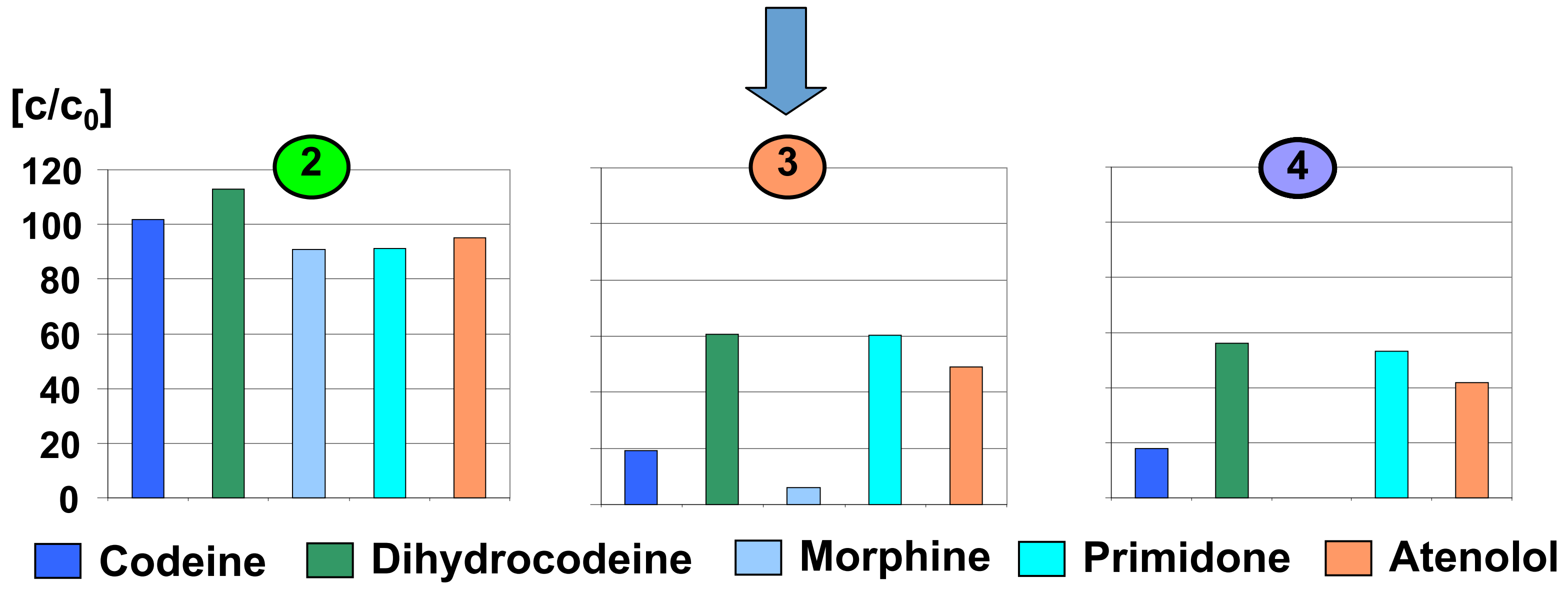
suspended solids (SS)

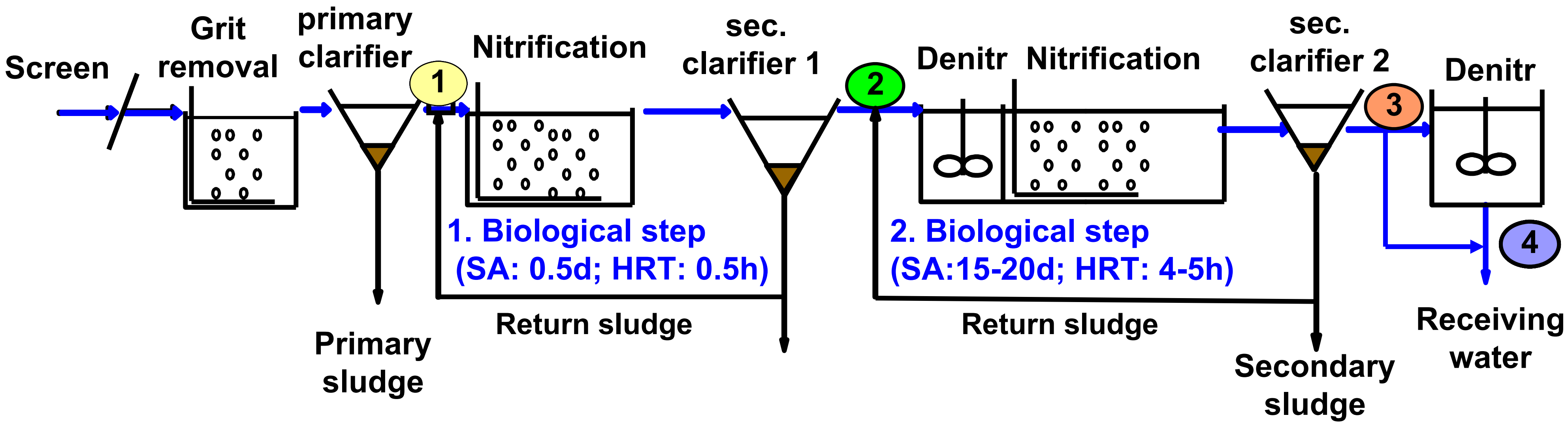
sludge recycle (R)

number of compartments (n)

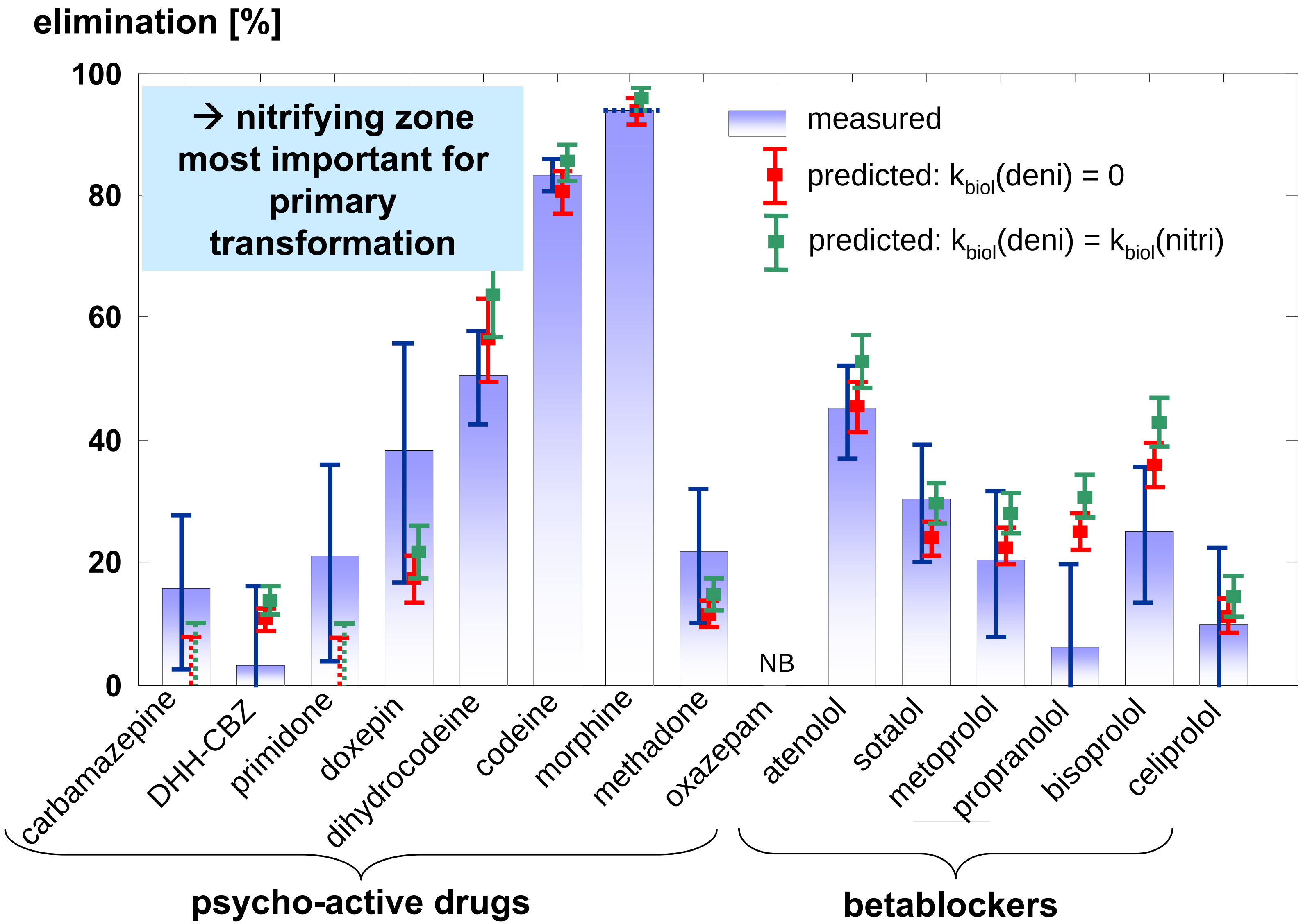
Source: Joss et al.,
Wat. Res.40, 1686-1696 (2006)

Removal of Atenolol and psycho-active drugs in WWTP Frankfurt



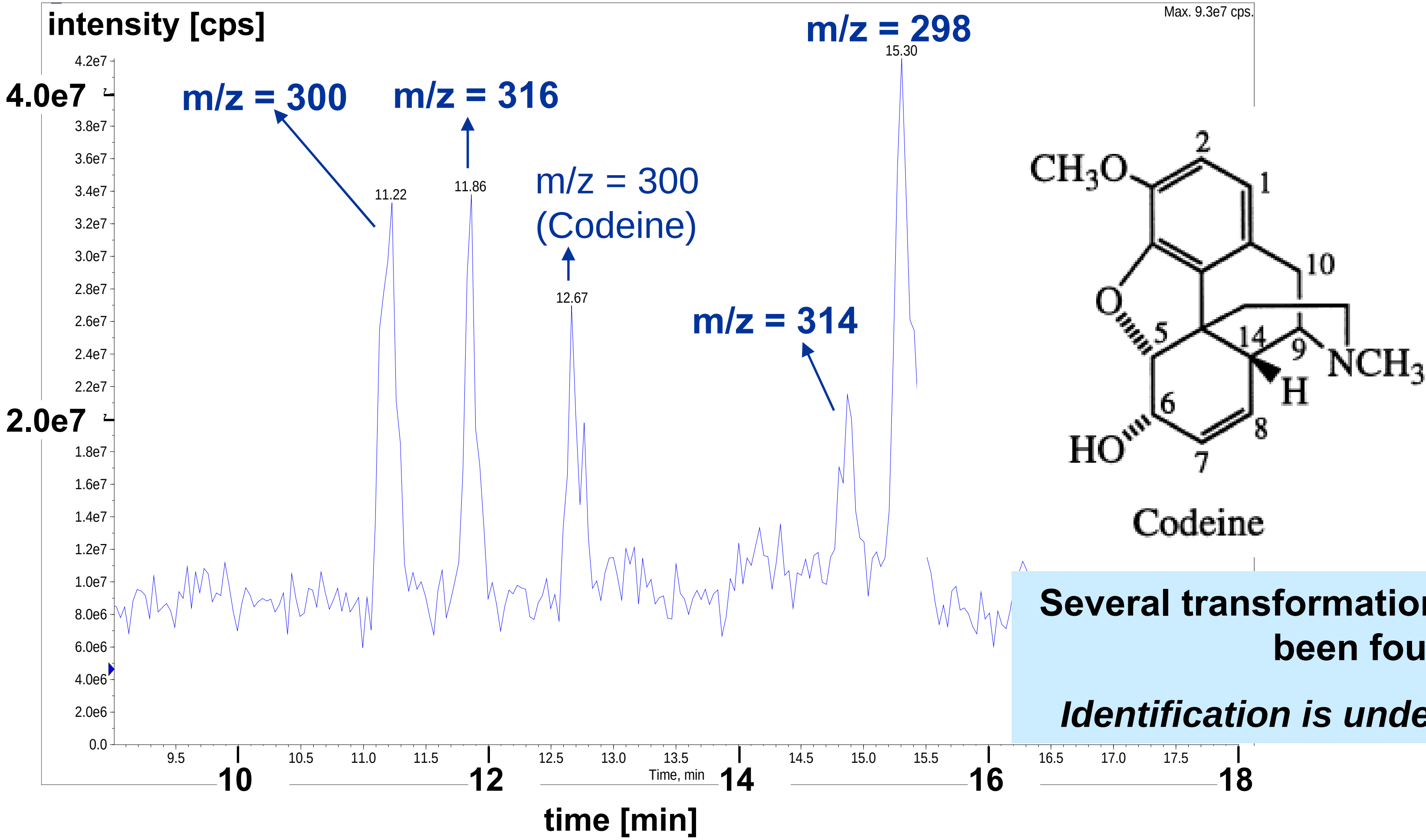


Modelling of the removal in the second biological step



Transformation products of codeine

After 10 days incubation of **codeine** in contact with secondary sludge

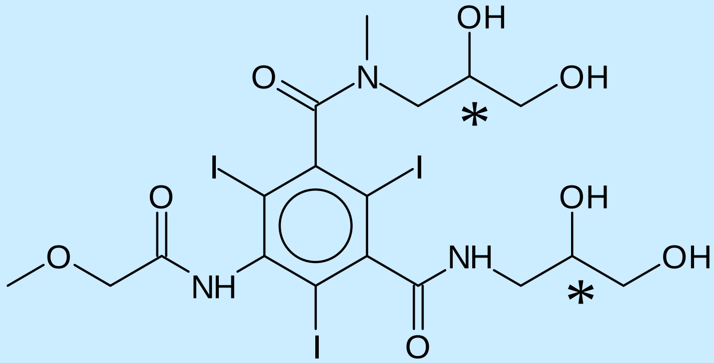


Codeine

Several transformation products have been found

Identification is under investigation

Iodinated X ray contrast media

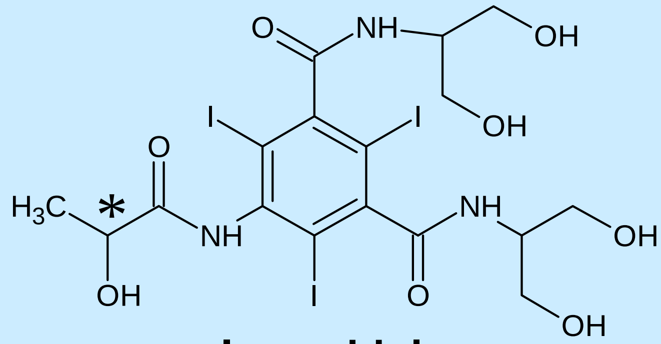


Iopromide

log K_{OW}: -2.33

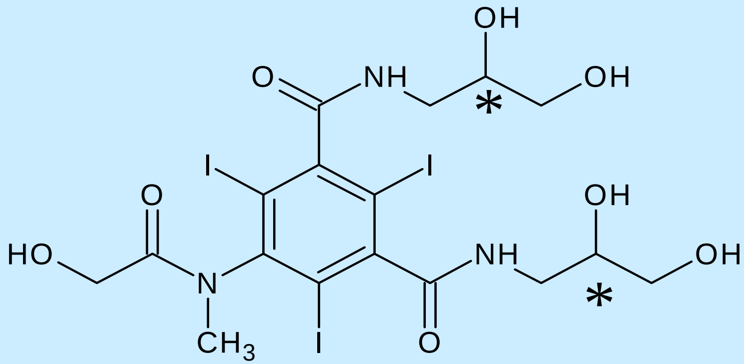
K_d: 5.2-30 L/kg

(activated/digested sludge)



Iopamidol

log K_{OW}: -2.42

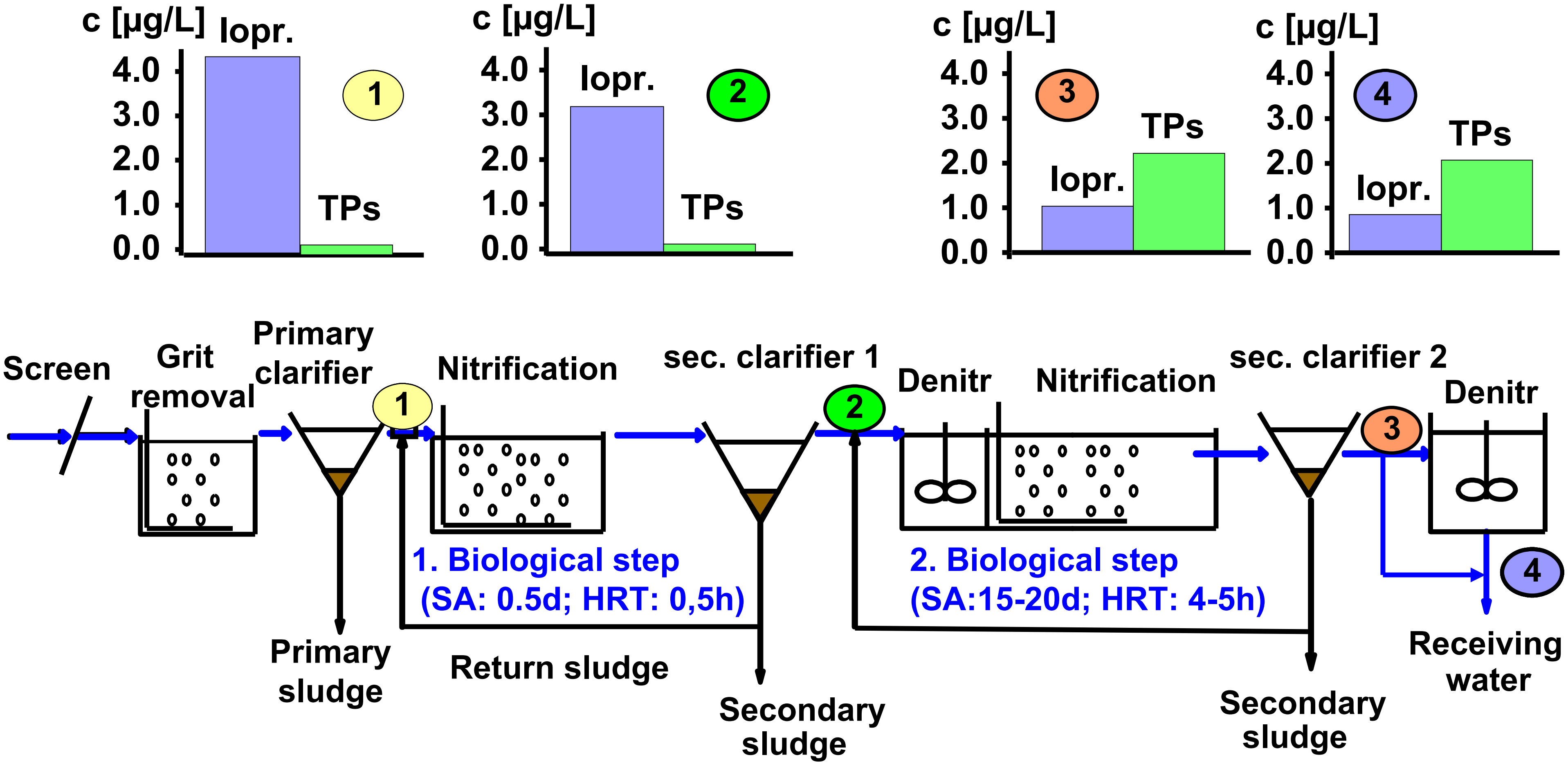


Iomeprol

(source: Steger-Hartmann et al., 1999; Carballa et al., 2008; Ternes et al., 2005)

Transformation products (TPs) of Iopromide in WWTP Frankfurt

Sludge age: 20-22 d, hydraul. retention time (biol): 4-5 h, 1.3 Mill inh. equivalent



Source: Schulz et al., ES&T, 2008

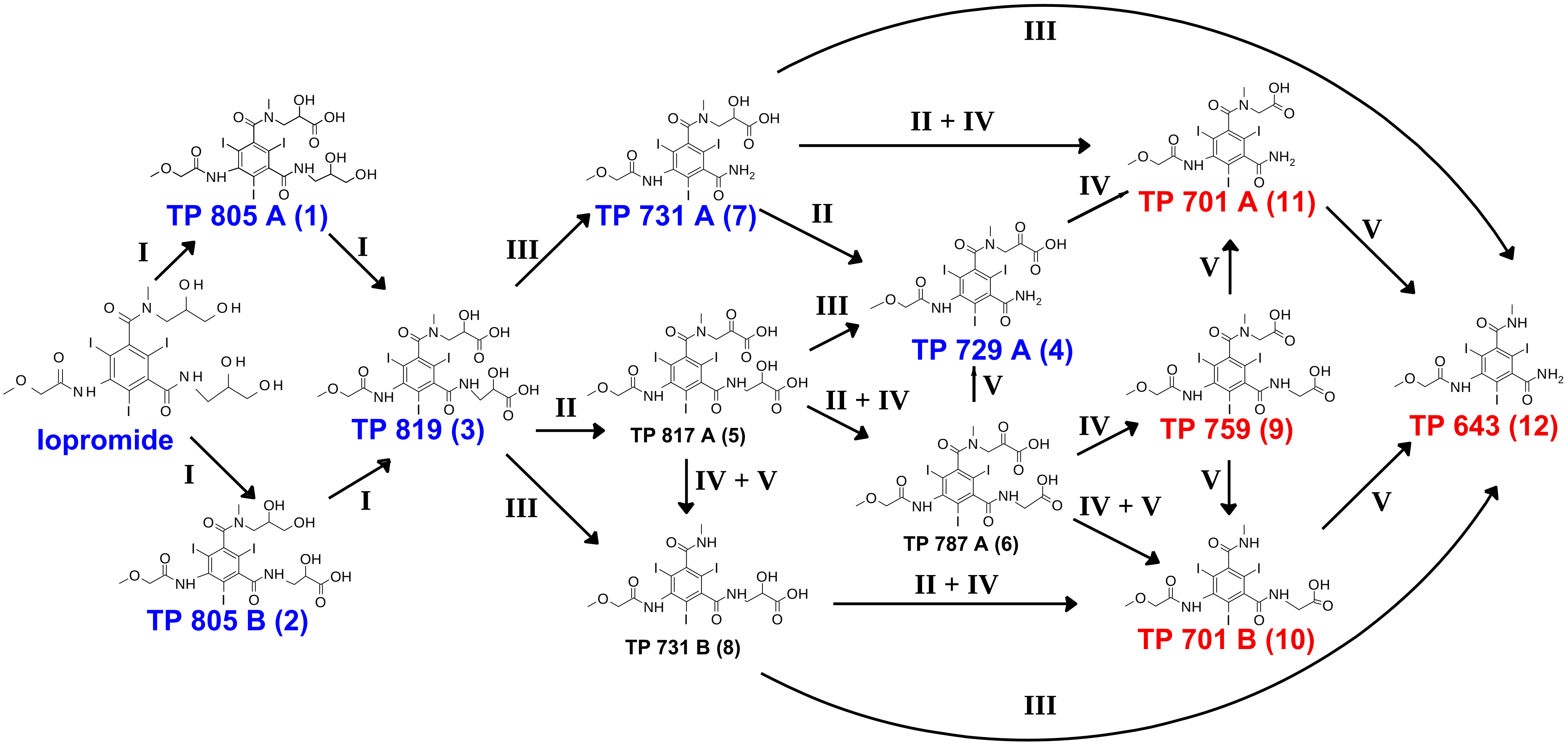
Potential aerobic degradation pathways of Iopromide

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

reaction III: cleavage of amide-methylen bond

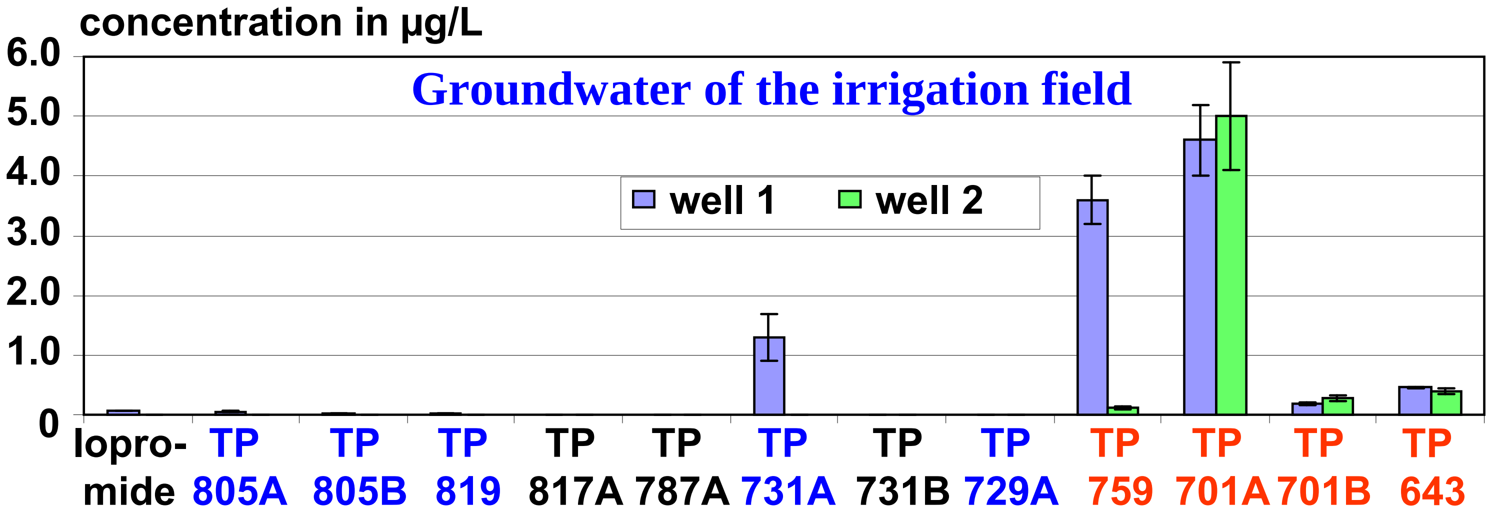
reaction IV: oxidative decarboxylation

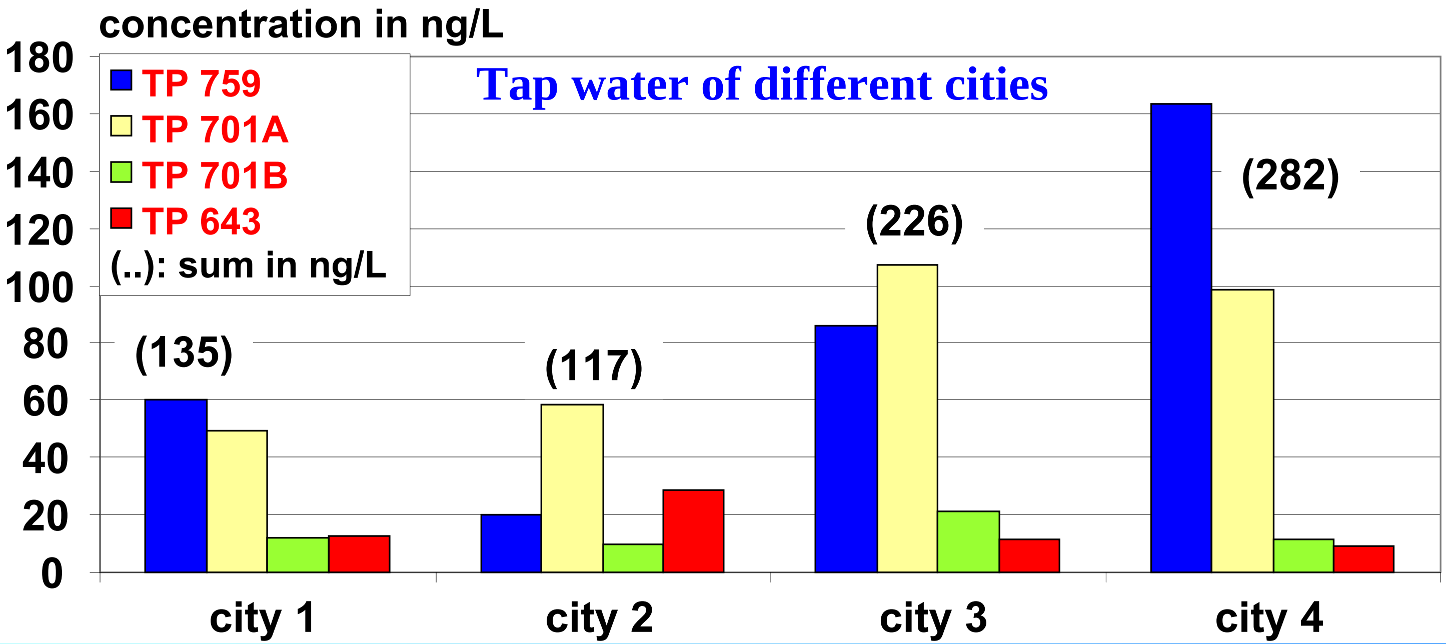
reaction V: deacetylation



Source: Schulz et al., ES&T, 2008

Occurrence of iopromide TPs





Source: Schulz et al., EST, 2008

Conclusions

Occurrence of emerging compounds

Pharmaceuticals, biocides and other polar emerging contaminants are ubiquitously present in WWTP effluents and surface waters as well as certain substances in groundwater and drinking water

Modelling of sorption and primary degradation in WWTPs

Removal by sorption and primary biodegradation of emerging contaminants can be predicted by batch experiments

Relevance of transformation products (TPs)

- Frequently primary degradation is the main removal process in WWTPs, but it is not leading to mineralization
- TPs formed in WWTPs can be polar and persistent
- Currently the formation of TPs cannot be sufficiently predicted by models
- A toxicological risk assessment of TP is currently impossible

! The known TPs and target compounds are only the top of an iceberg !

Thank to my research group at BfG

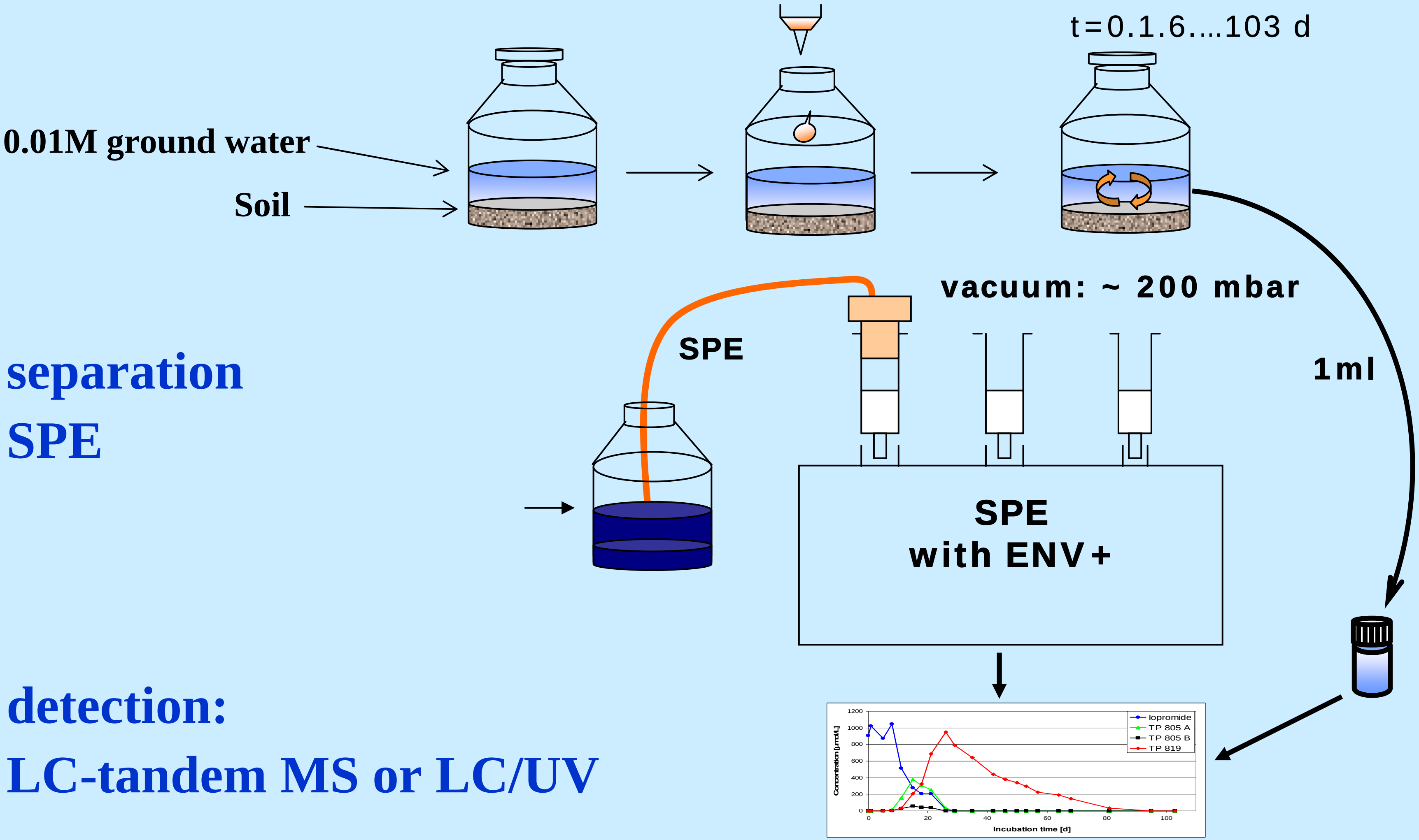
Financial Support

EU for funding Neptune and Keybioefffects

from the Sixth Framework Programme

Degradation of iopamidol/iomeprol in soil/water-systems

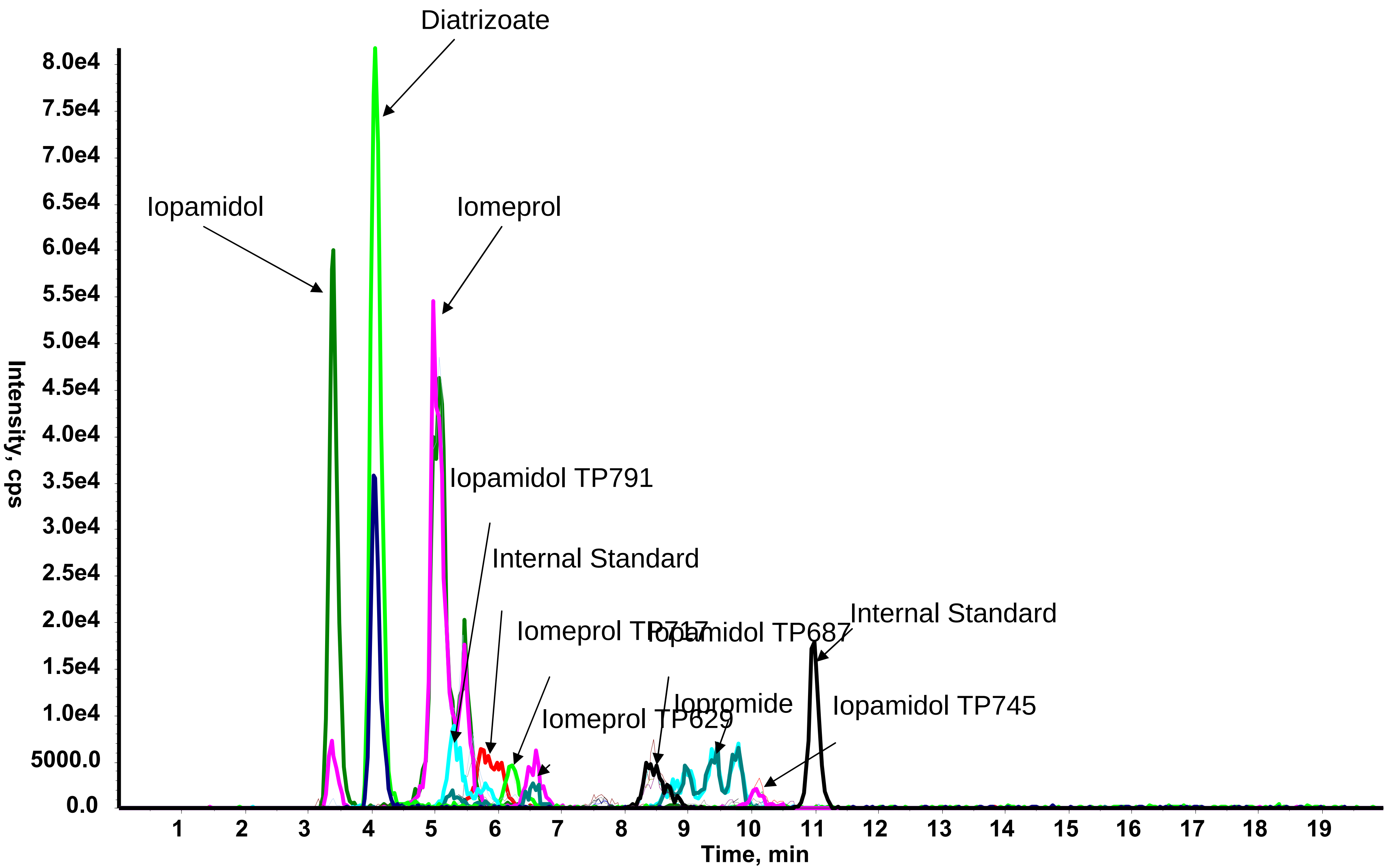
- **Batch-experiments**



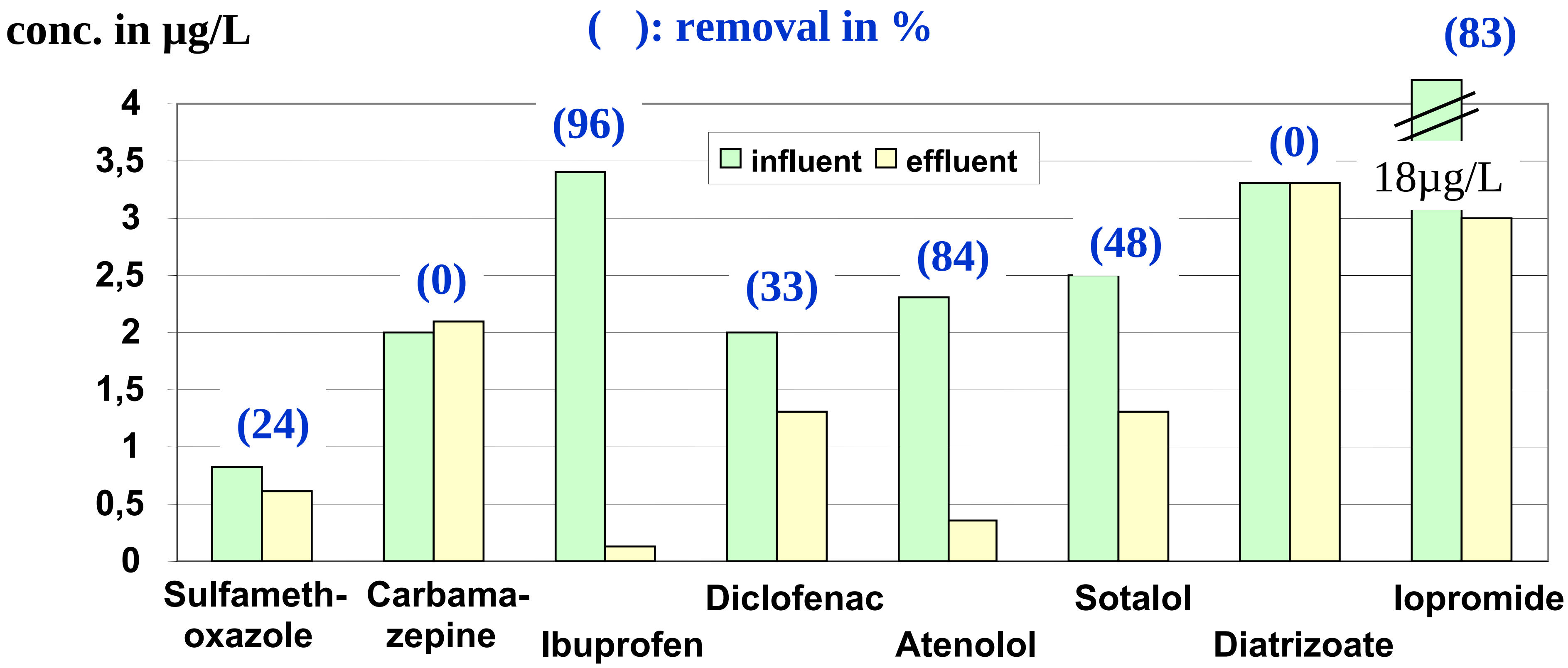
- **separation**
- **SPE**

- **detection:**
- **LC-tandem MS or LC/UV**

WWTP effluent sample



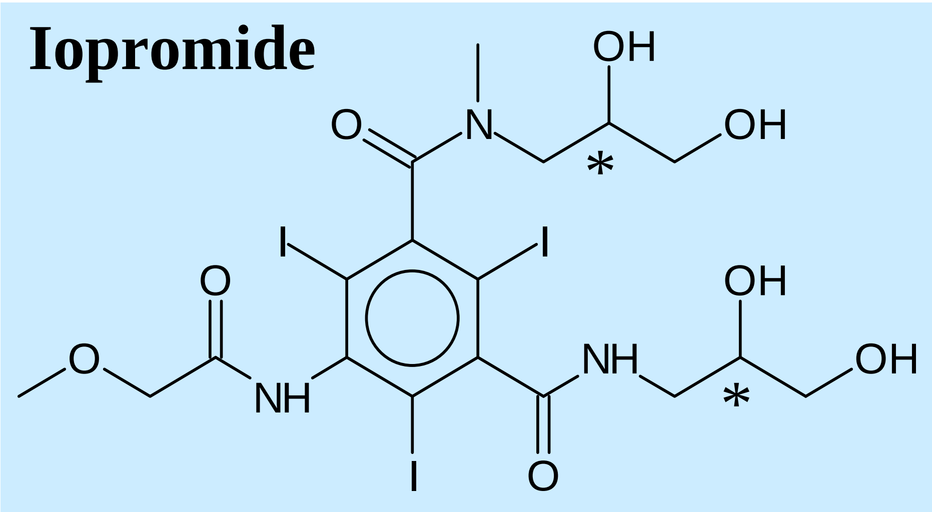
Removal in a municipal Wastewater treatment plant

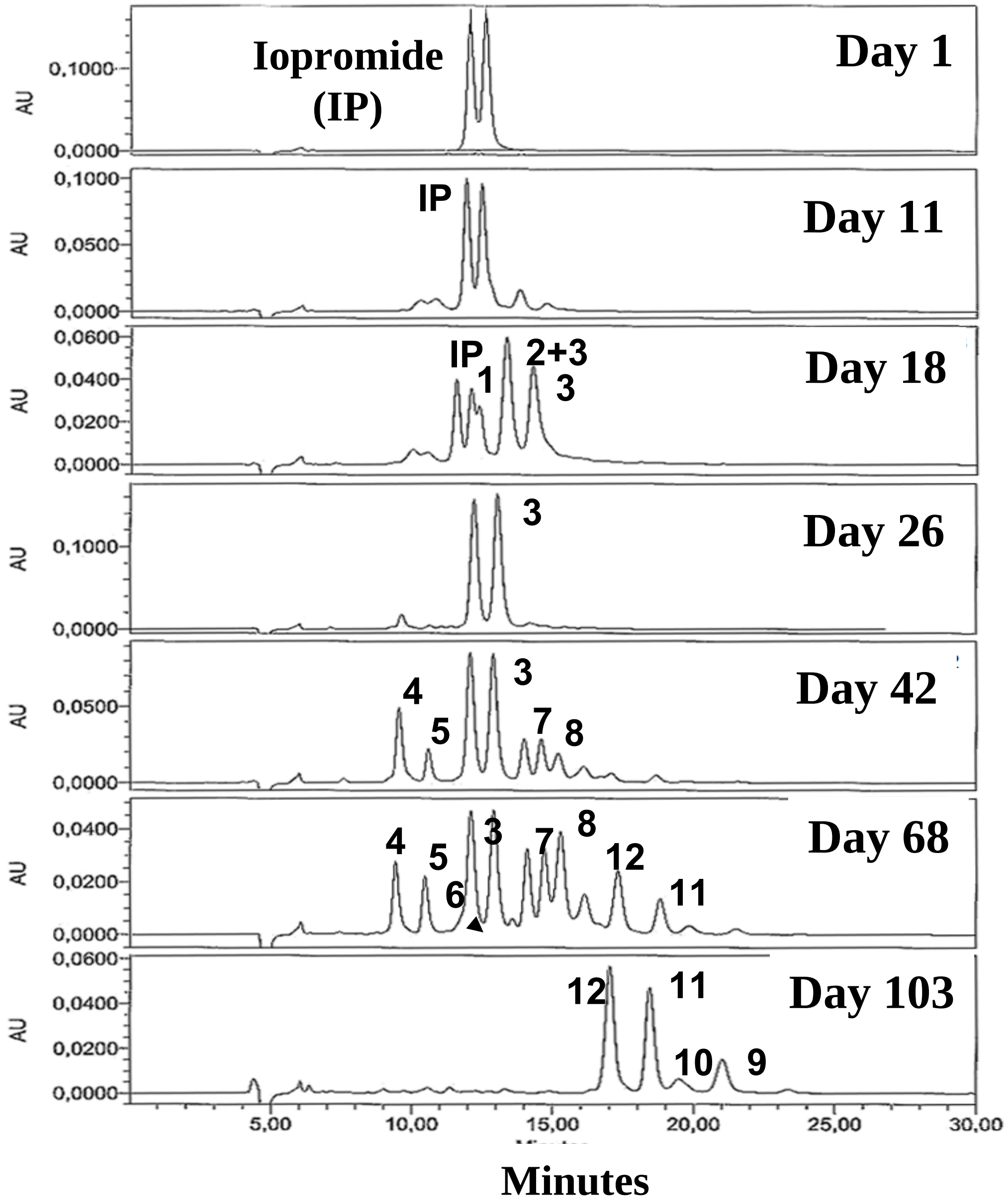


Ternes et al., Chemosphere, 2007, in press

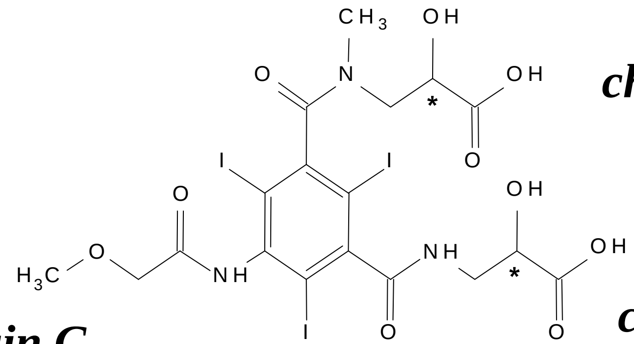
Formation of 12 iopromide TPs in water/soil-systems

detection via HPLC/UV





MS fragmentation of TP 3



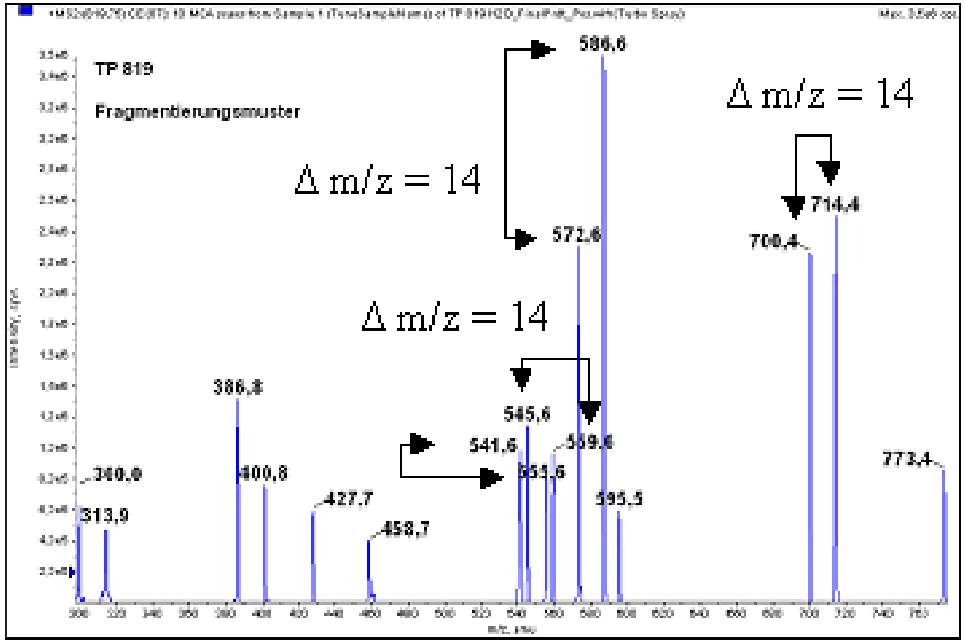
chain A

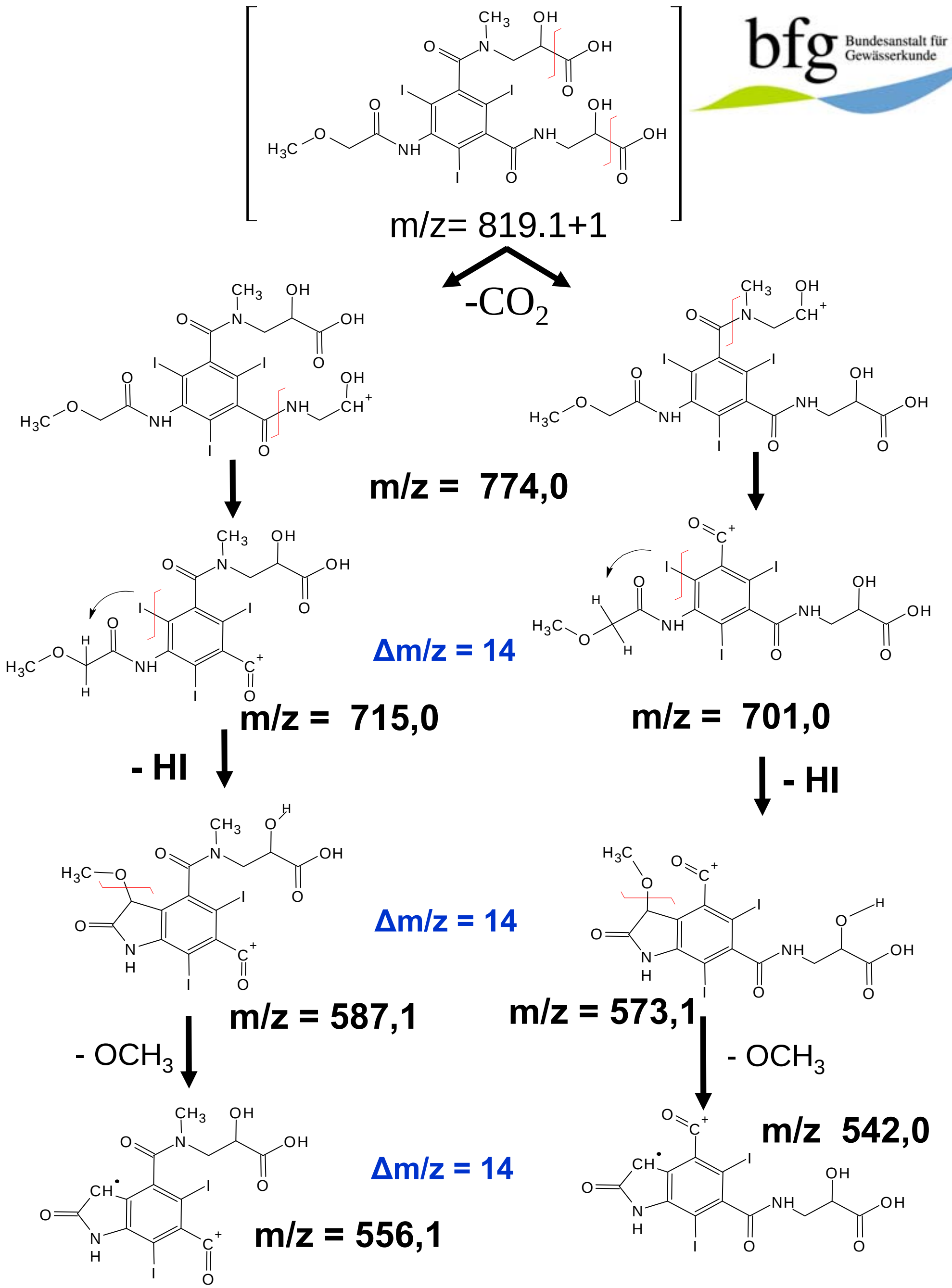
chain B

chain C

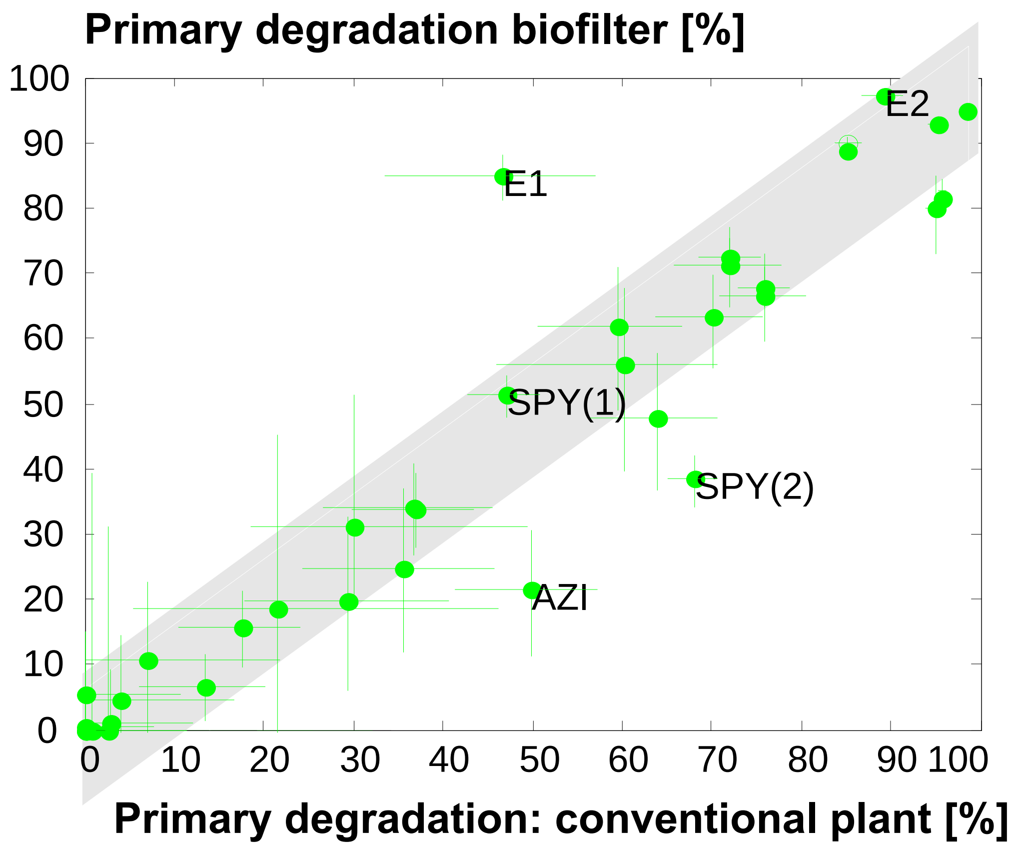
TP 3

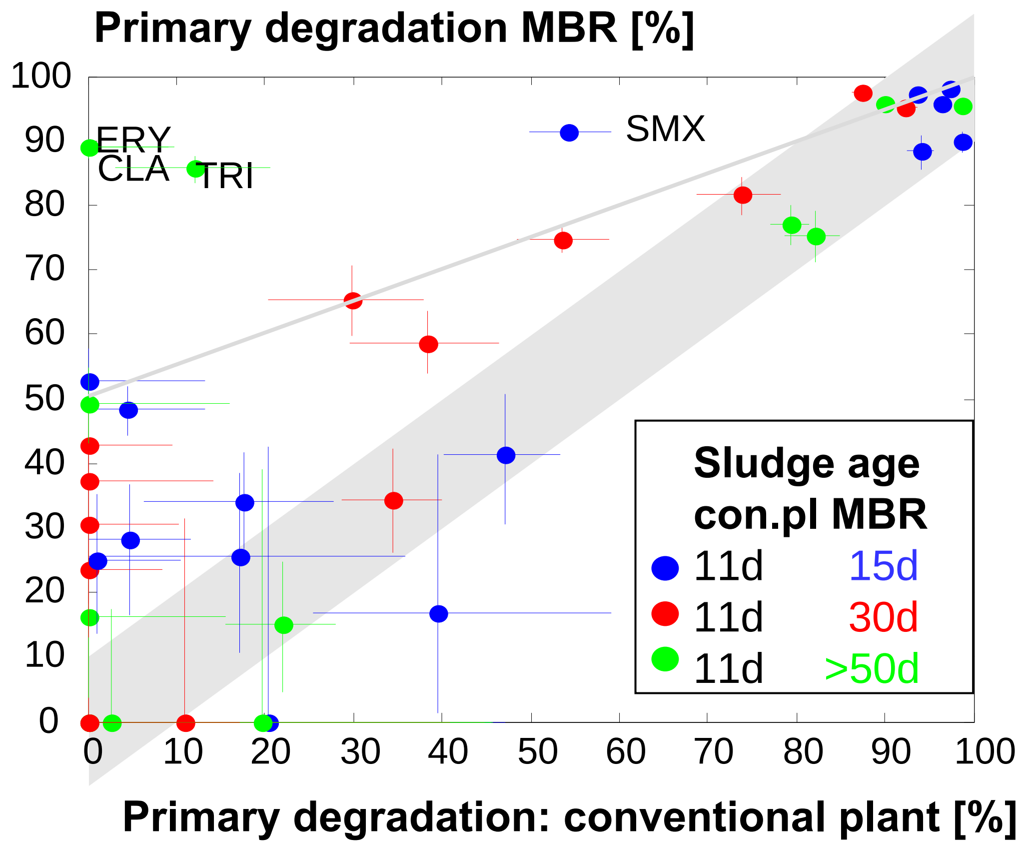
Product Ion Scan (MS²)





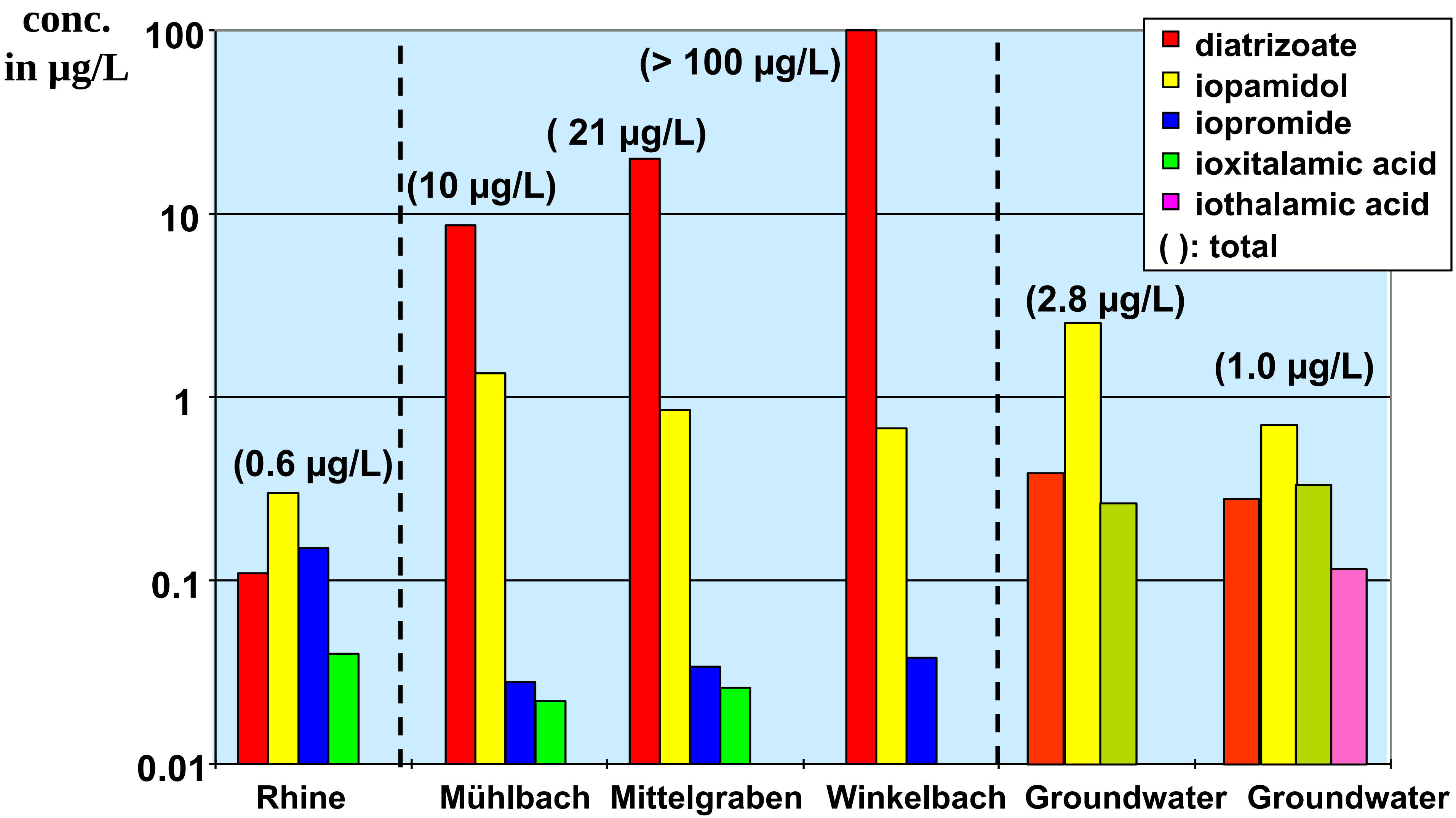
Comparison of primary degradation MBR, biofilter, conventional plant





Source: Joss und Siegrist, 2005, Eawag News

Iodinated contrast media: found in surface water and groundwater



Ternes & Hirsch, Environ. Sci. Techn. (2000) 34, 2741-2748