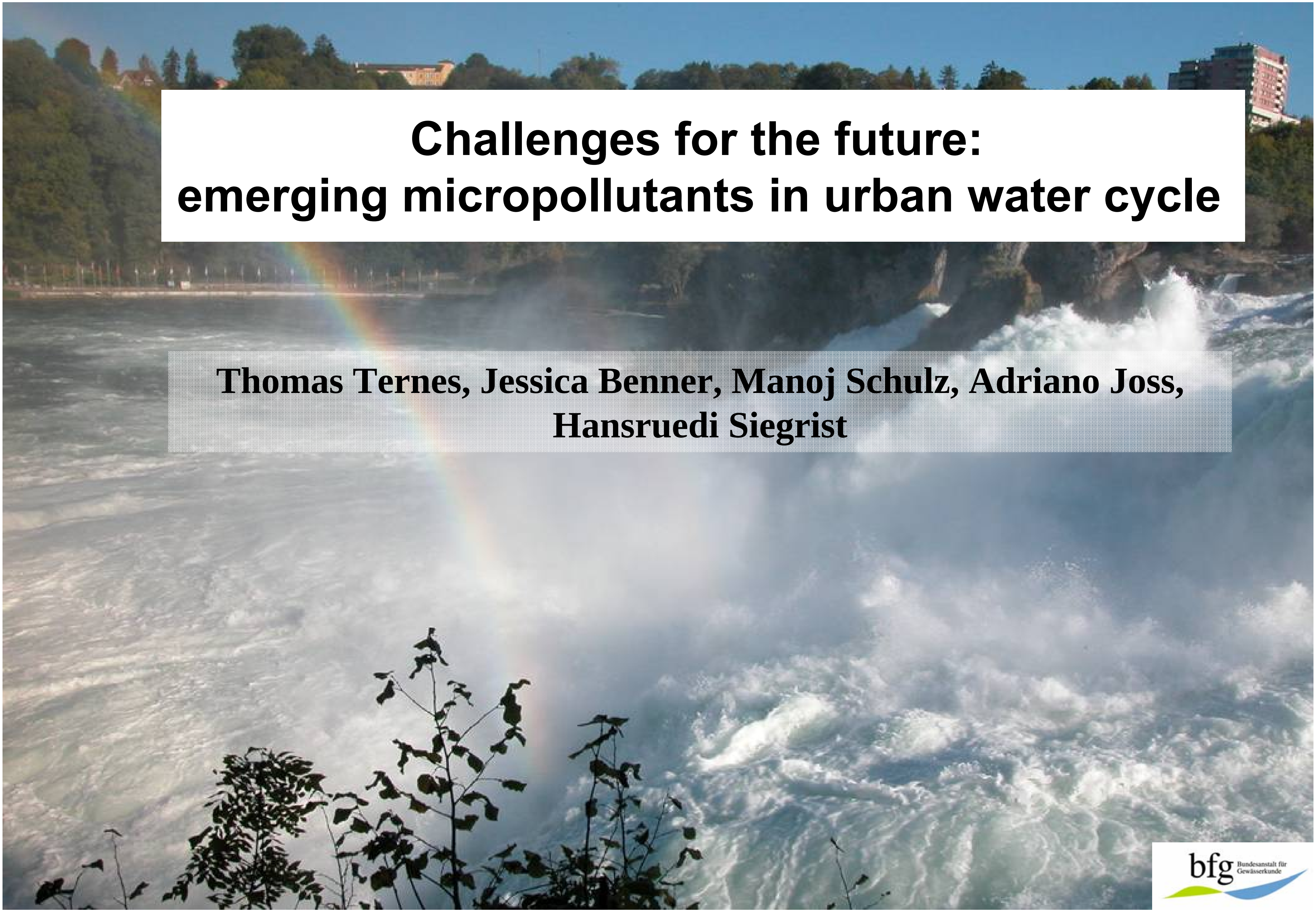
Challenges for the future: emerging micropollutants in urban water cycle

Thomas Ternes, Jessica Benner, Manoj Schulz, Adriano Joss, Hansruedi Siegrist



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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}

Predicted application and production quantities

Application quantities in Germany

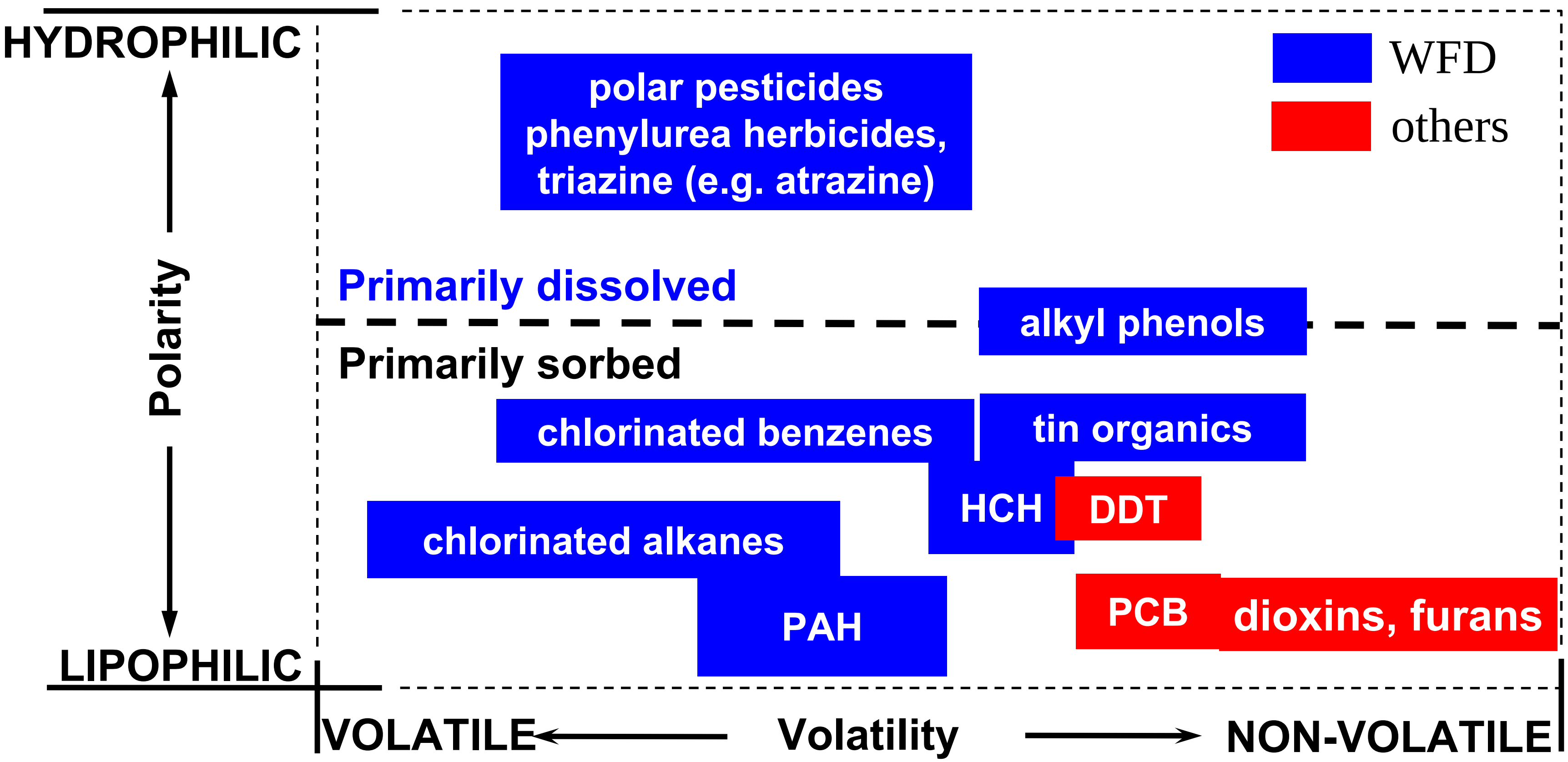
- Human-use pharmaceuticals (ca. 2800): about 6500 t yr^{-1} corresponds to 78 g cap^{-1} yr^{-1}
- Veterinary pharmaceuticals: about 1000 t yr^{-1}
- Pesticides (ca. 200): about 30000 t yr^{-1}
- Surfactants: 188629 t yr^{-1} (2.3 kg cap^{-1} yr^{-1})

Production quantities in Germany

- Personal care products: > 500000 t yr^{-1} (> 6.1 kg cap^{-1} yr^{-1})
- EDTA: 29560 t yr^{-1}

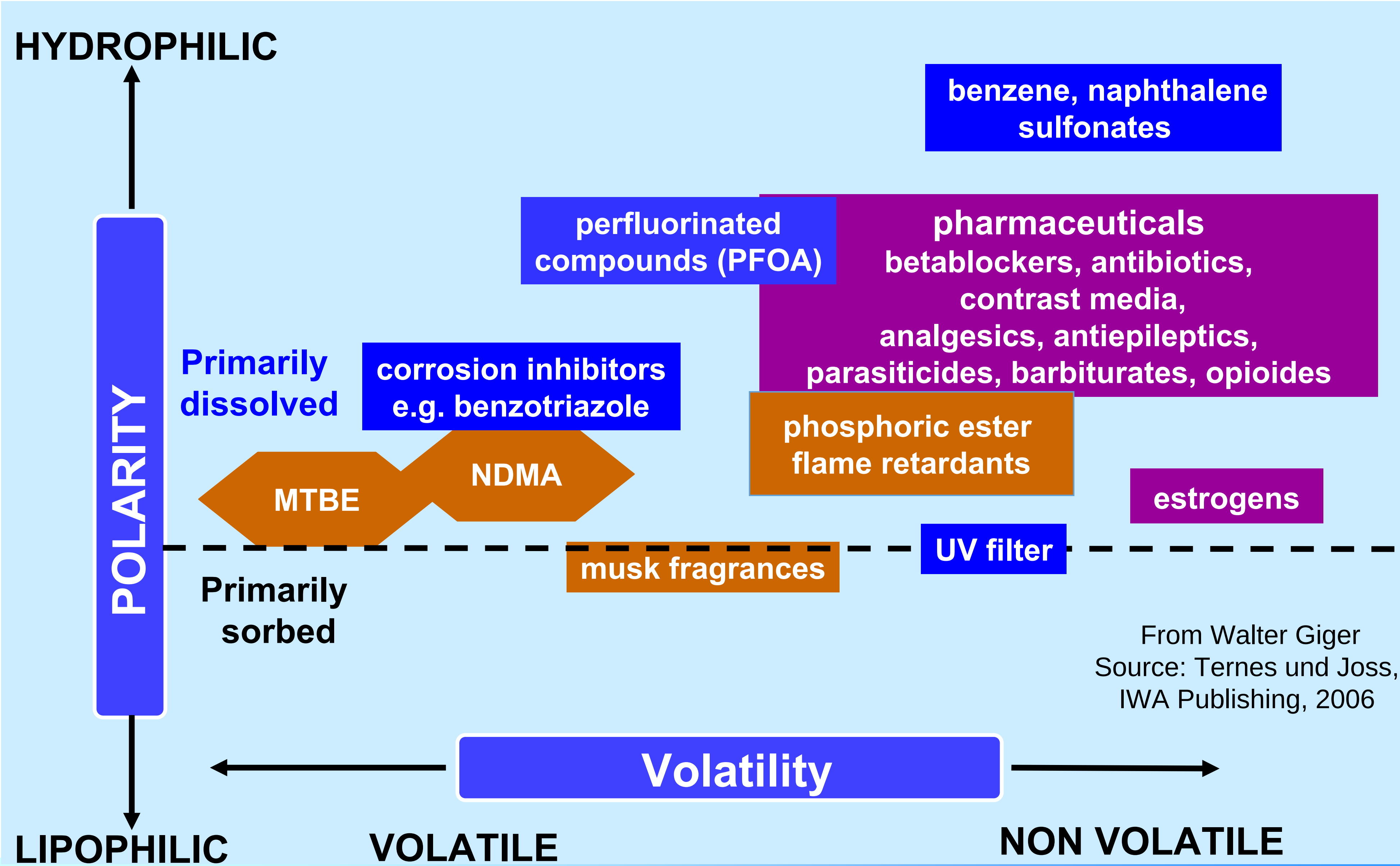
Organic pollutants already regulated (WFD, …)

based on ecotoxicological criteria



Source: Ternes and Joss (2006) IWA Publishing

Emerging contaminants detected in the environment



Environmental quality standards (EQS) of dissolved contaminants determined according to WFD

(based on ecotoxicological data)

	[1]AA-EQS-S	Annual average measured concentration in German rivers
Bisphenol A	0.79 ng/L	0.5 ng/L-270 ng/L
Diclofenac	100 ng/L	50-500 ng/L
EE2	0.03 ng/L	< 1 ng/L (WWTPs)

Discharged primarily via WWTPs

Source: Moltmann et al., 2007, German EPA report

[1]: **Suggested maximum annual average concentration**

Ecotoxicological effects of betablockers

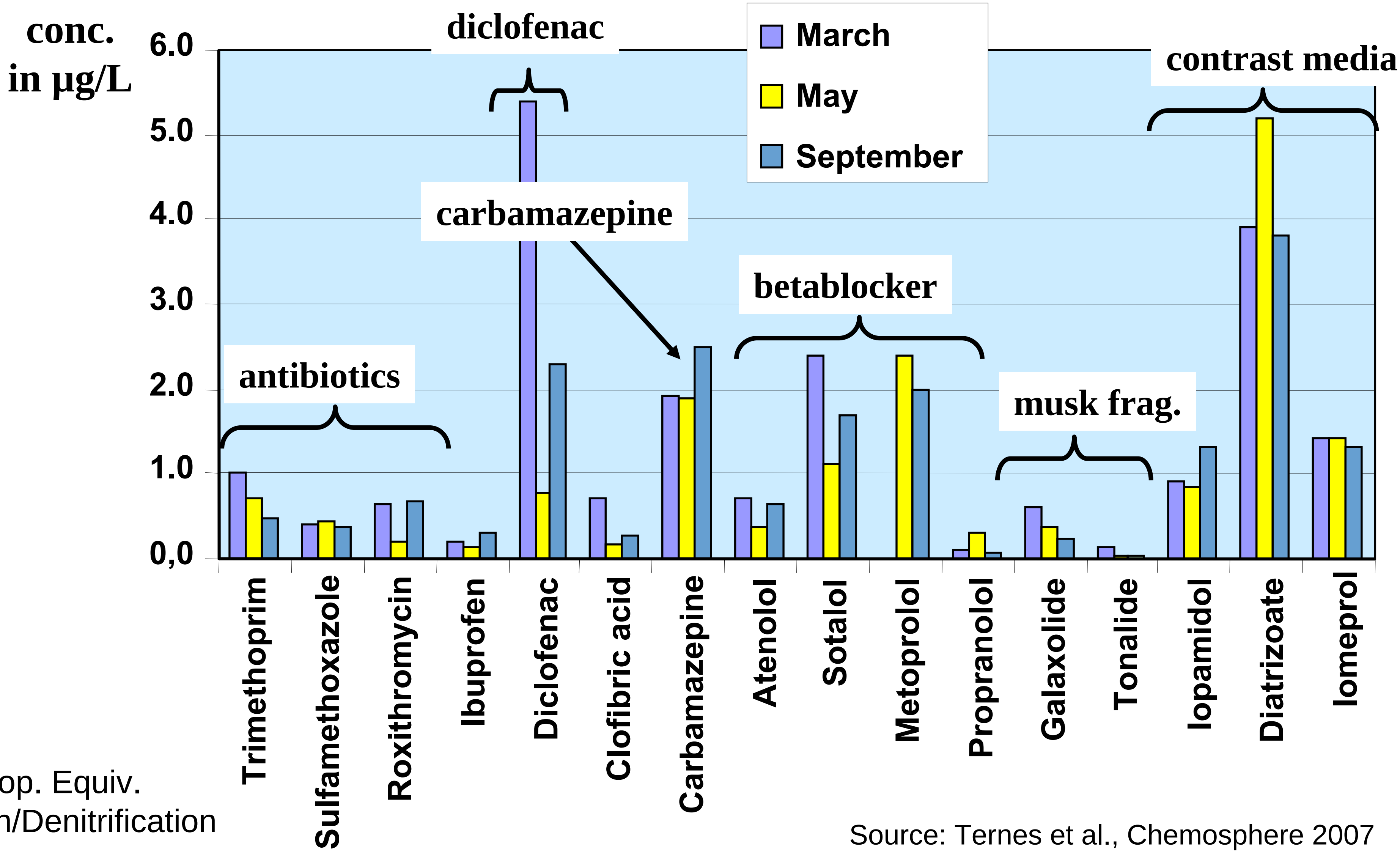
- 4-week exposure of 500 ng/L propranolol $\Rightarrow$ effects on reproduction and steroid levels in fish (Japanese medaka)[a]
- **More than additive effects** of betablocker mixtures[b]

  Theoretical Σ EC_{50} (*daphnia magna*) of propranolol, metoprolol and atenolol: 21.3 % inhibition, measured inhibition: 65 %

[a] Huggett, D. B. et al. *Arch. Environ. Contam. Tox.* **2002**, *43*, 229-235.

[b] Cleuvers, M. *Chemosphere* **2005**, *59*, 199-205.

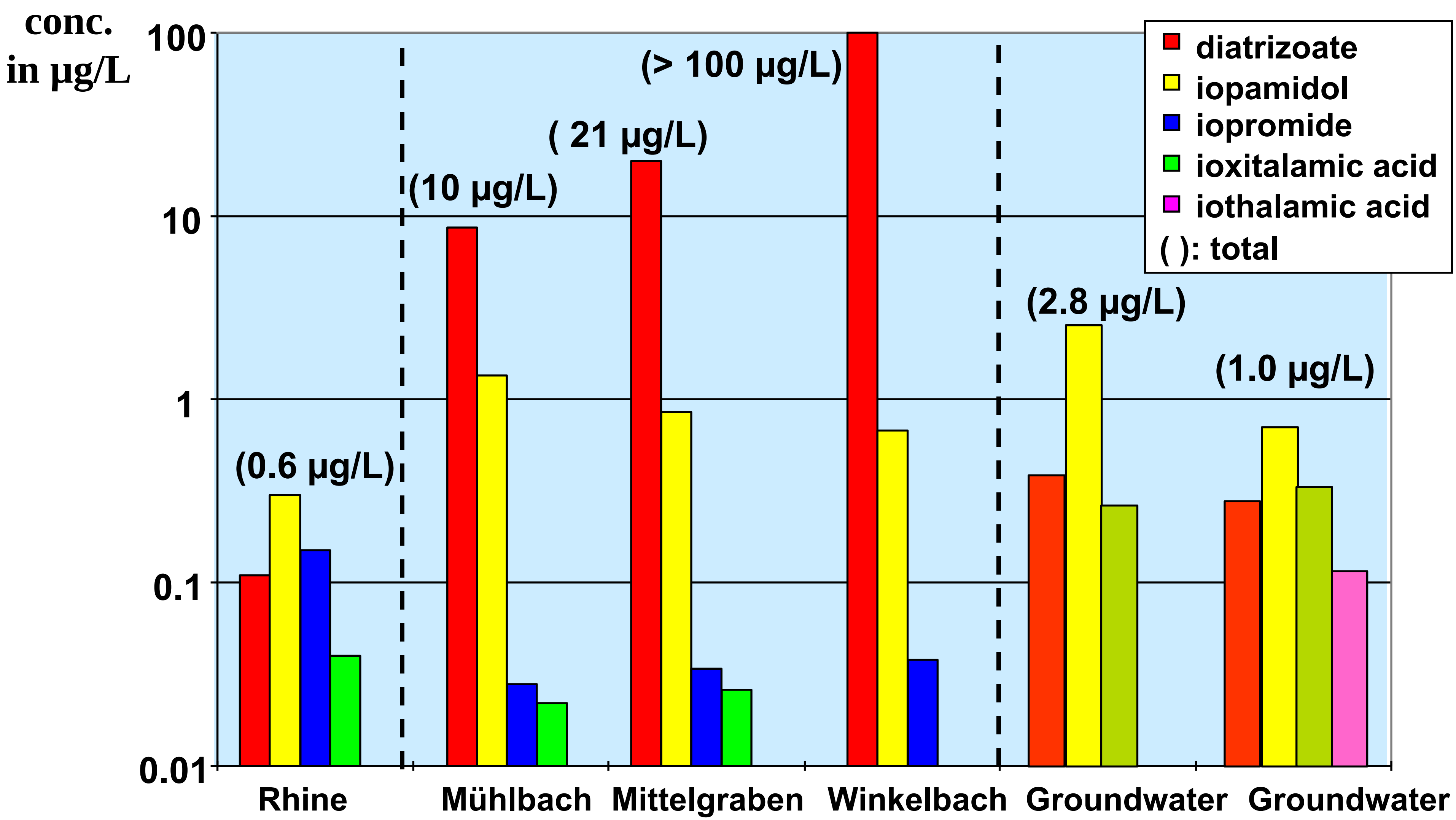
Pharmaceuticals in treated wastewater



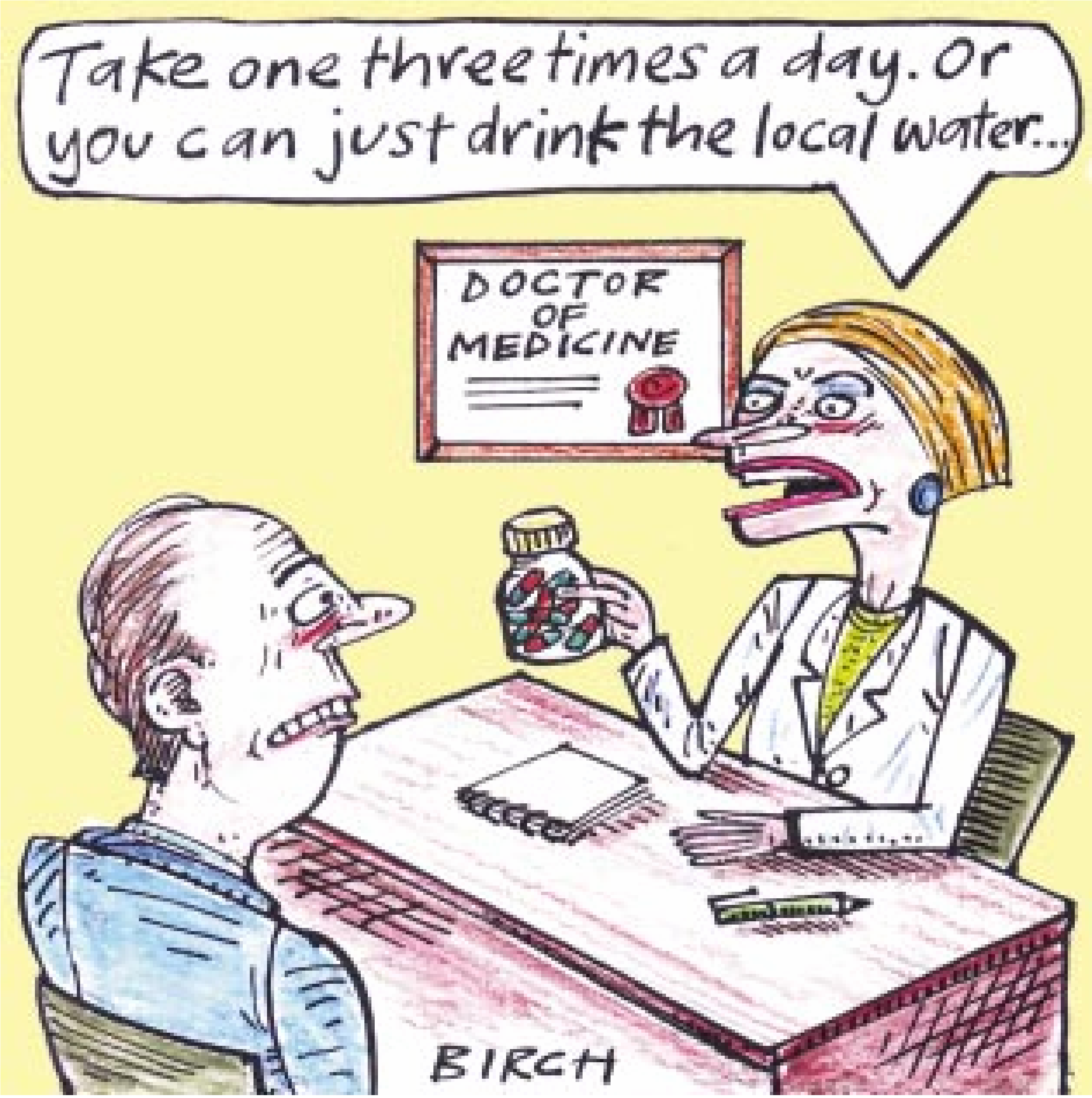
360‘000 Pop. Equiv.
Nitrification/Denitrification

Source: Ternes et al., Chemosphere 2007

Iodinated contrast media: found in surface water and groundwater



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



Nature, *424*, 3. Juli 2003, S. 5

from Walter Giger

Measures to remove emerging contaminants and their transformation products in the water cycle

Evironmental quality standards (EQS) of WFD

If EQS are exceeded (probably for diclofenac, isoproturon, EE2, bisphenol A, …) advanced measures have to be established, in order to guaranty the good ecological/chemical status of rivers and streams until 2015.

Processes for advanced municipal wastewater treatment to remove emerging pollutants

Frequently transformation, sometimes mineralization

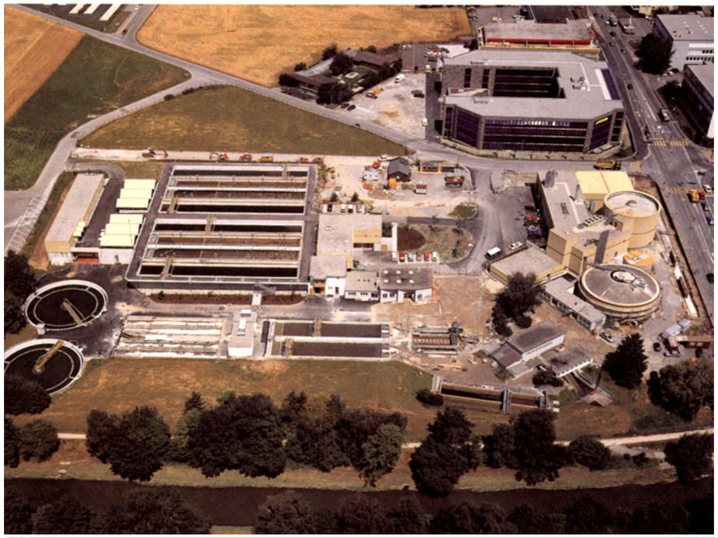
- **Biological degradation:** nitrification, denitrification
- **Chemical oxidation:** ozone, advanced oxidation
- **Photo(chemical)degradation:** UV/H_2O_2, sun light

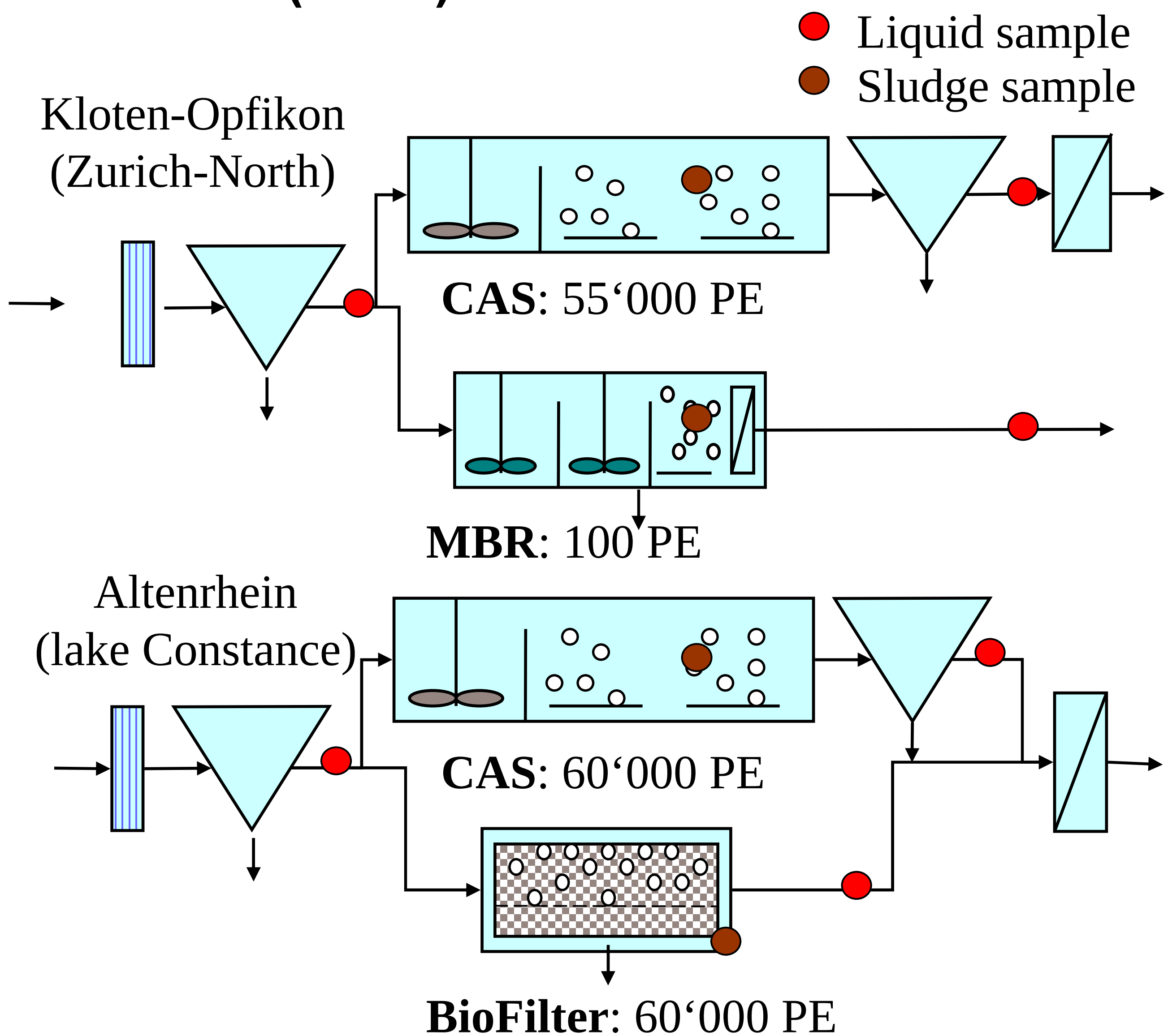
Quantitative removal

- **Sorption:** activated carbon (GAC, PAC)
- **Size exclusion:** dense membranes (nanofiltration, reverse osmosis)

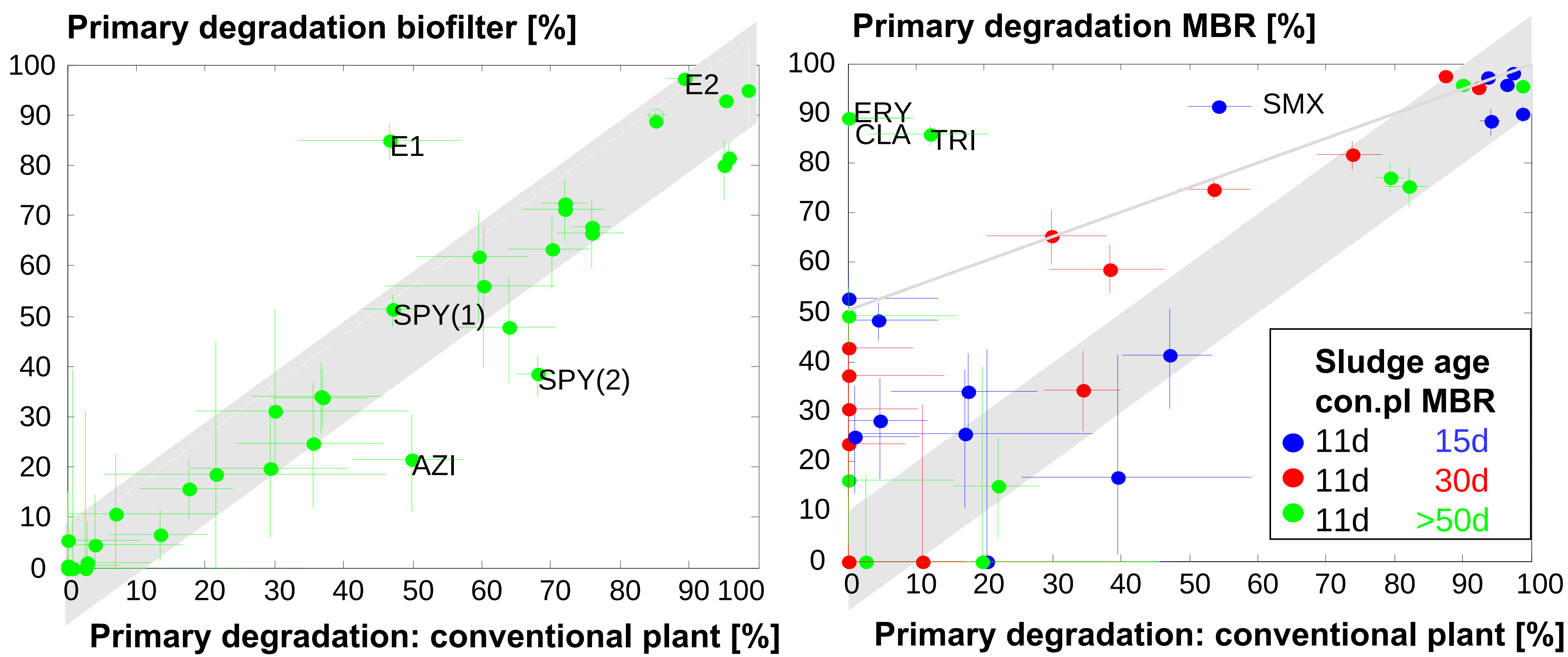
Biological degradation
(and sorption on sludge particle)

Comparison: biofilter, conventional activated sludge (CAS) and membrane bioreactor (MBR)





Comparison of primary degradation MBR, biofilter, conventional plant



Source: Joss und Siegrist, 2005, Eawag News

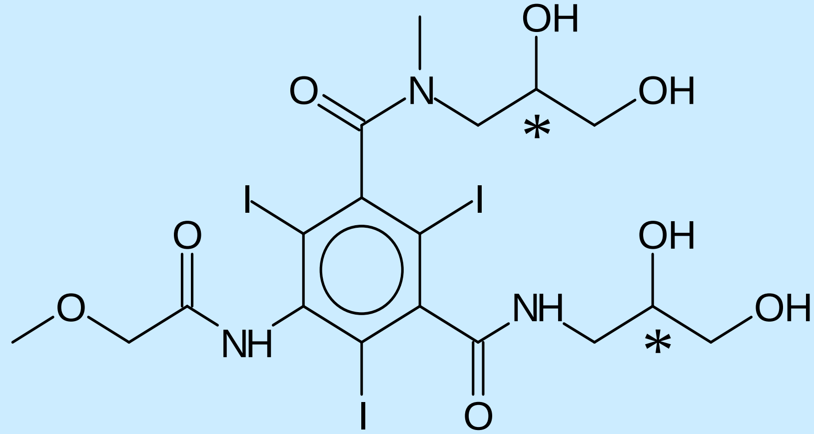
Iodinated X ray contrast medium Iopromide

Annual consumption (Germany): ca. 130 t/a (1,5 g $cap^{-1}a^{-1}$)
> 95% excreted nonchanged

log K_{OW}: -2.33-(-2.05) (Steger-Hartmann et al., 1999)

K_d (activated sludge/digested sludge): 5.2-30 L/kg (Carballa et al., 2008; Ternes et al., 2005)

pK_a: 9.9 (Bayer-Schering)



Wastewater treatment plant Braunschweig

Irrigation of treated wastewater digested sludge
on 3000 h agricultural land since more than 50 years

Iopromide

influent: 18 µg/L, WWTP effluent: 3µg/L

Wells in irrigation area: <LOQ

Leaching of Iopromide in soil columns

Diploma thesis: J. Oppel

source: Oppel, J., Broll, G., Löffler, D., Meller, M., Römbke, J., Ternes, T.A..
Sci. Total Environ., 2004, 42, 7207-7217

Leaching of Iopromide with „disturbed” soil columns

Soil columns of air dried and
sieved soil (< 2mm), **BBA-guideline** IV 4-2

Saturation of the soil witht 0.01 M $CaCl_2$ solution
to the **max. water capacity**

393 mL 0.01 M $CaCl_2$ solution (ca. **200 mm** rain fall)
over **48 h** in the dark at 20 ± 2°C

Typical agricultural soil

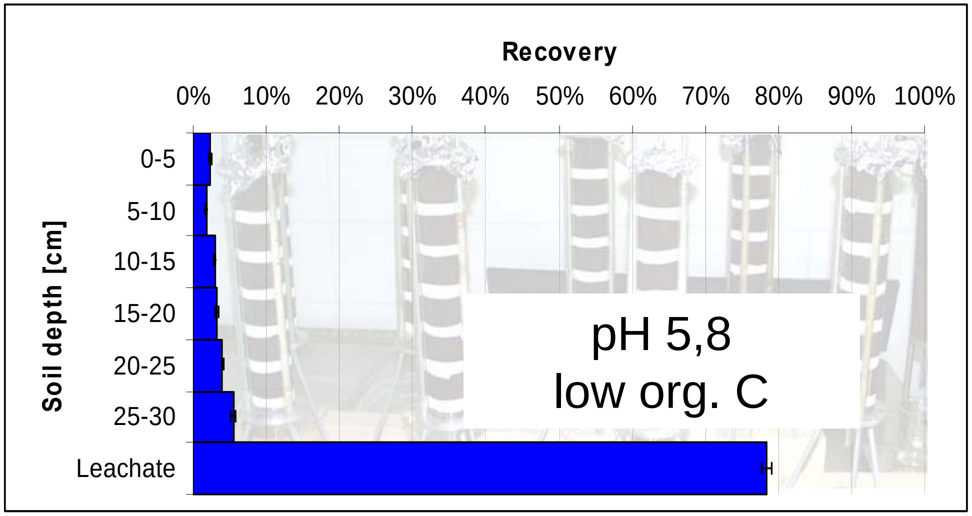
agricultural soil (winter wheat)

	LUFA 2.2	*Euro Soil 5*	*Neuenkirchen*
pH ($CaCl_2$)	**5.8**	**2.9**	**7.0**
C_{org} [%]	**2.3**	**6.3**	**1.3**

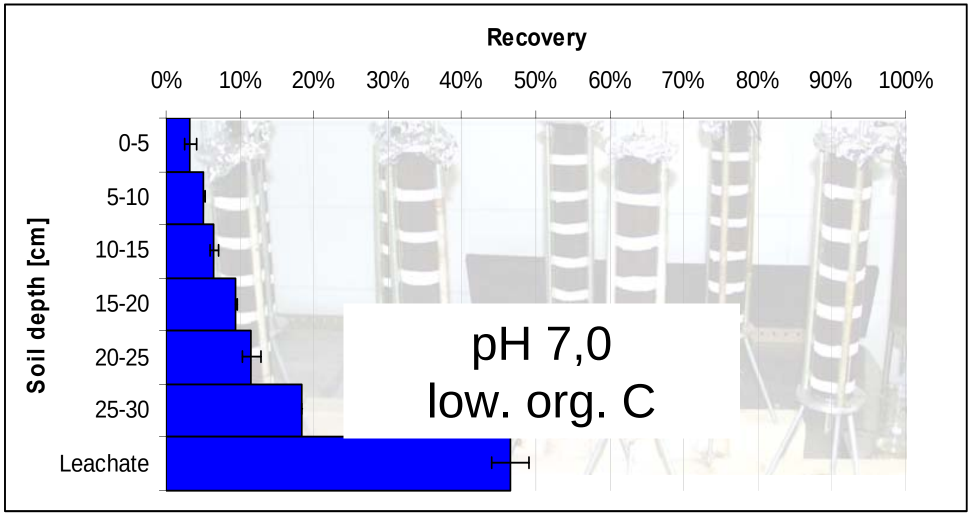
Source: Oppel et al., 2004

Leaching behavior: ^{14}C-Iopromide

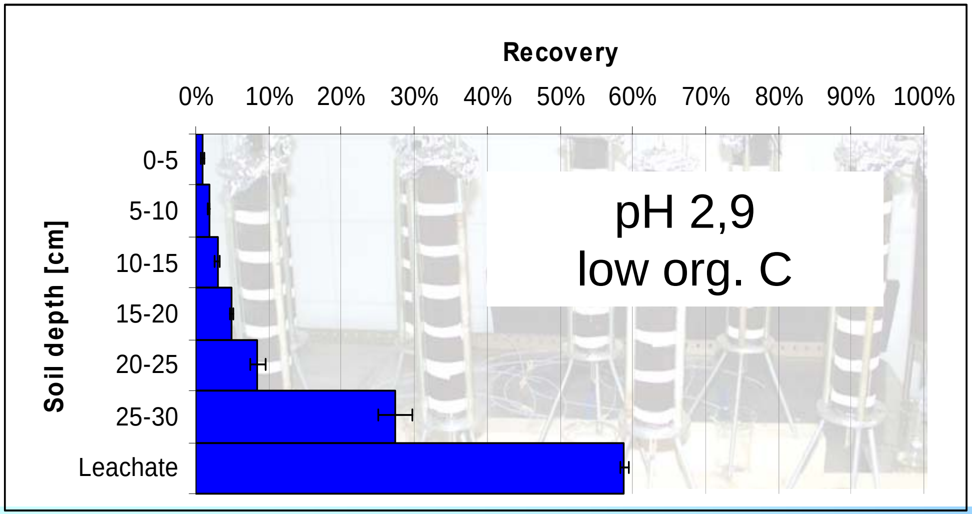
LUFA 2.2



Neuenkirchen



EuroSoil 5

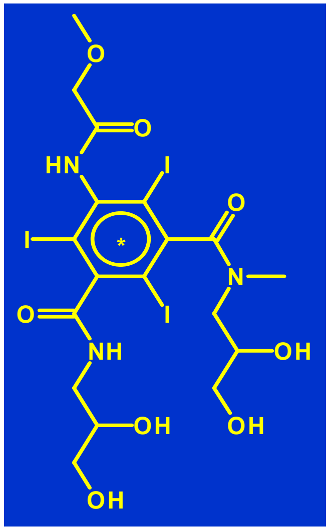


High leaching potential

log K_{OW} = -2.33

Source: Oppel et al., 2004

Formation of Iopromide transformation products (TPs) in the soil columns



	LUFA 2.2	*Euro Soil 5*
Iopromide LC tandem MS	0%	38 ± 7%
^{14}C-radioaktivity LSC	79 ± 1%	59 ± 3%

TLC radio det.	*LUFA 2.2*	*EuroSoil 5*
Iopromide	0%	50 ± 1%
TP 1	50 ± 2%	9 ± 4%
TP 2	18 ± 1%	-
TP 3	11 ± 3%	-
Sum	79%	59%

Source: Oppel et al., 2004

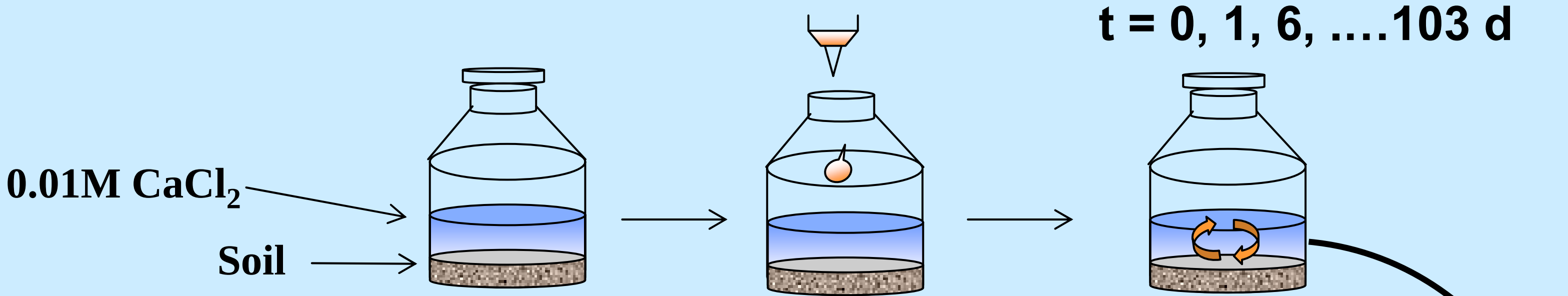
Identification of Iopromide transformation products

Diploma thesis: Manoj Schulz

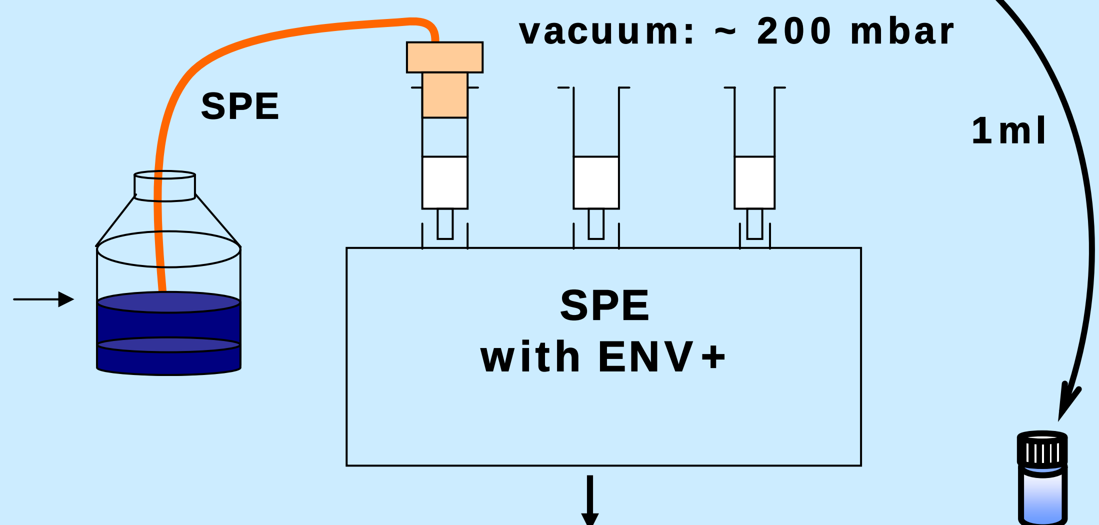
source: Schulz M., Löffler D., Wagner M., Ternes T.A., ES&T, 2008, 42, 7207-7217

Degradation of iopromide in soil/water-systems

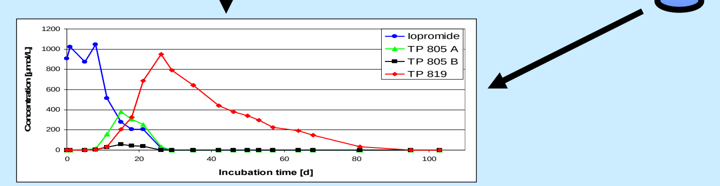
- Batch-experiments



- separation
- SPE

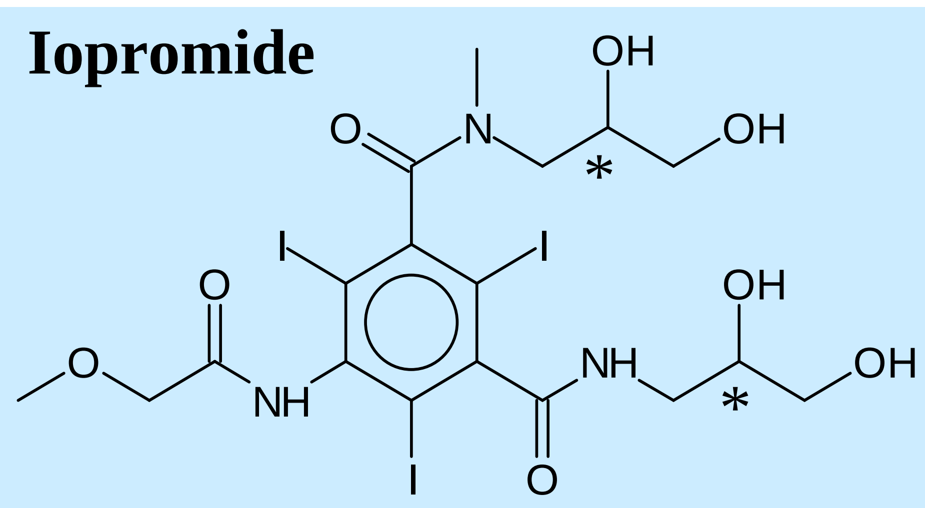


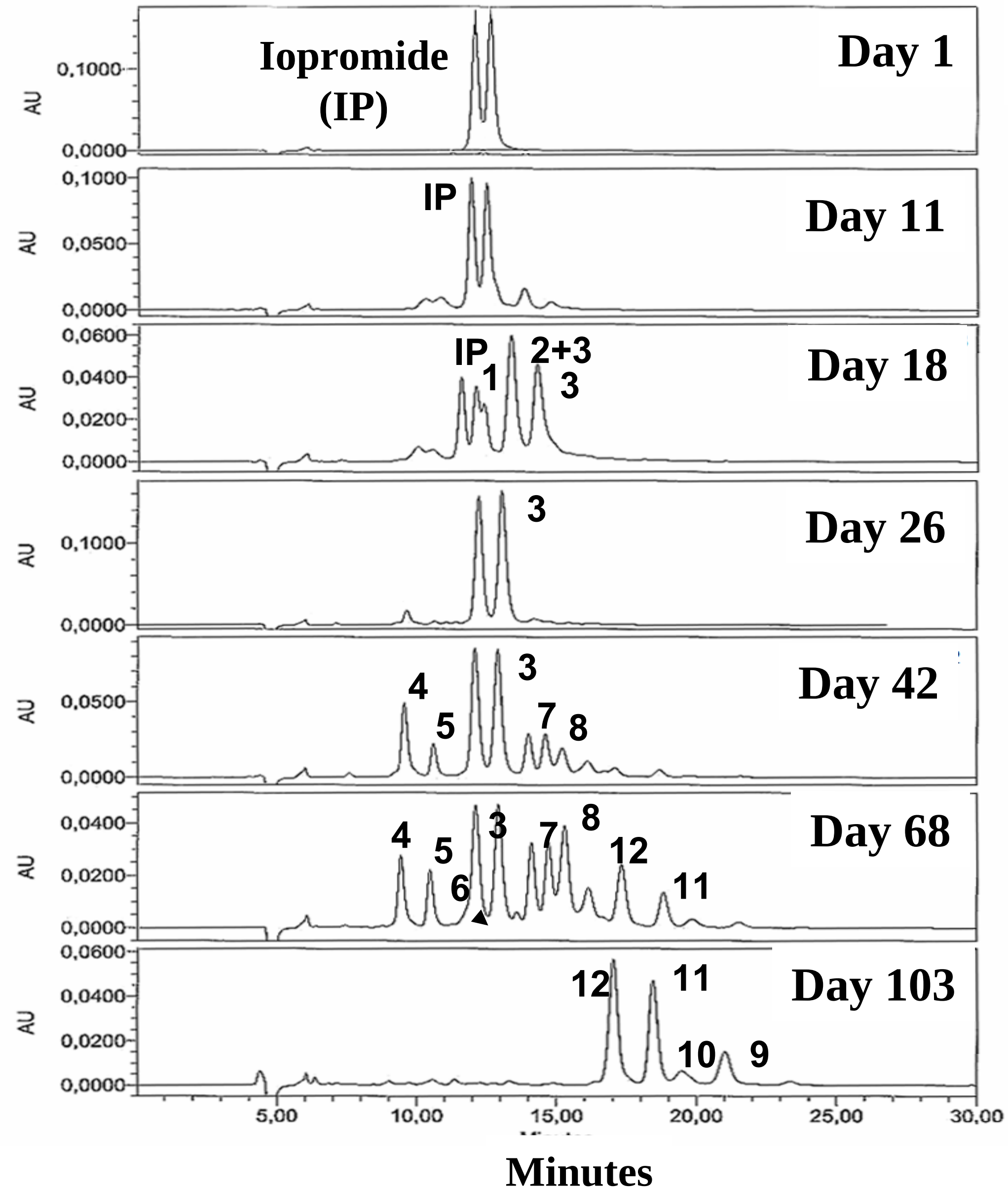
- detection:
- LC-tandem MS or LC/UV



Formation of 12 iopromide TPs in water/soil-systems

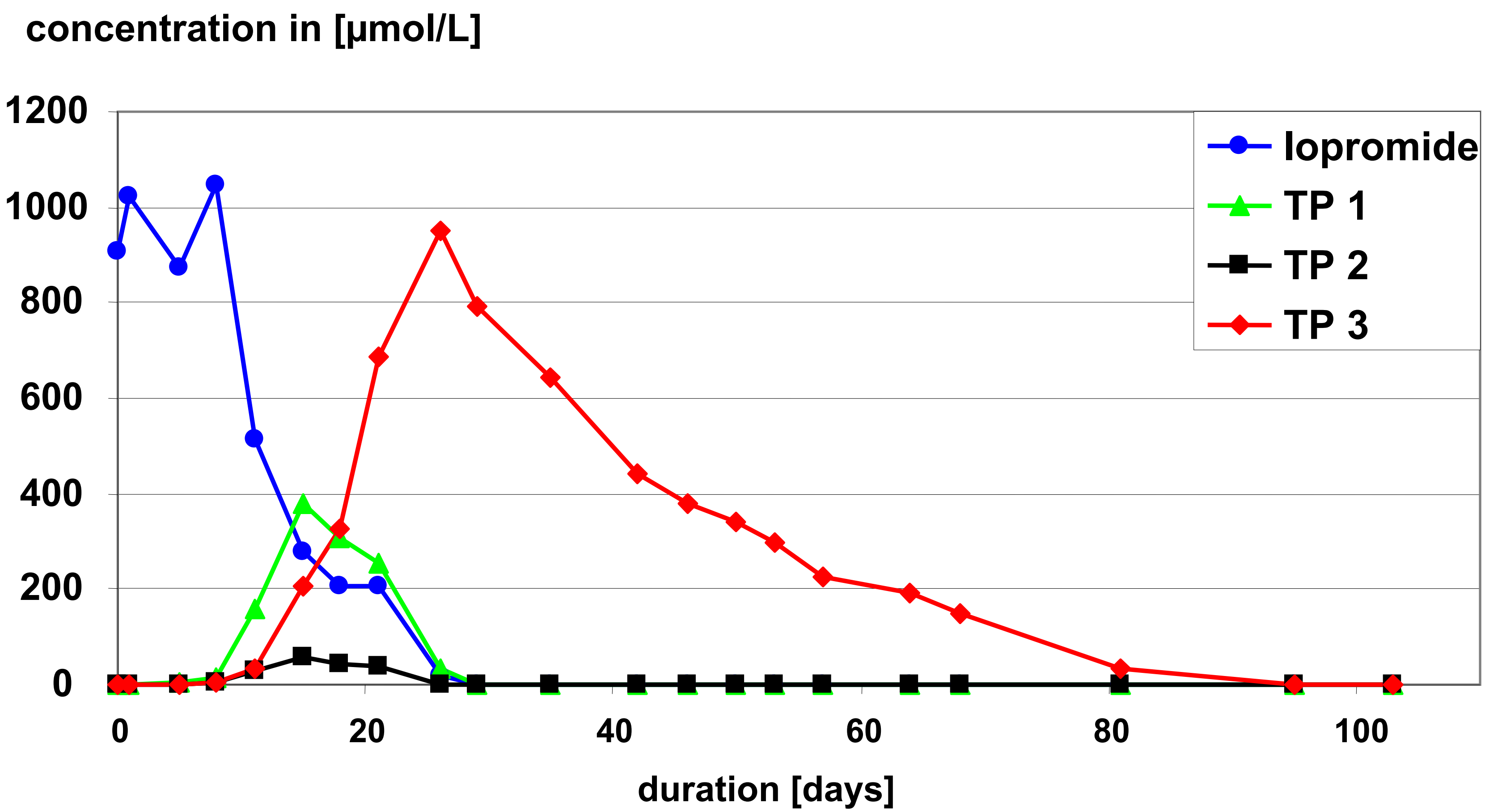
detection via HPLC/UV





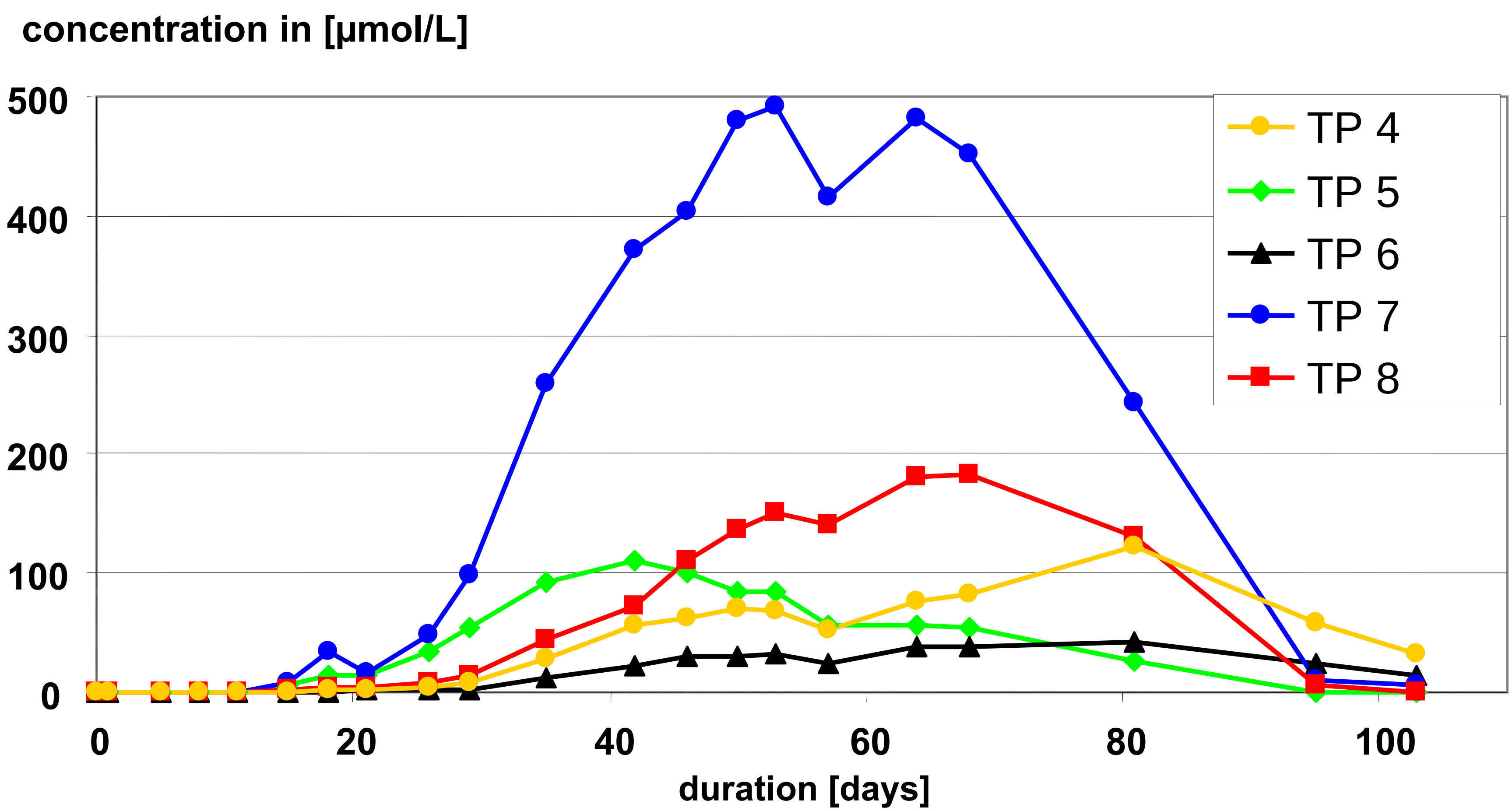
Iopromide transformation

Phase I



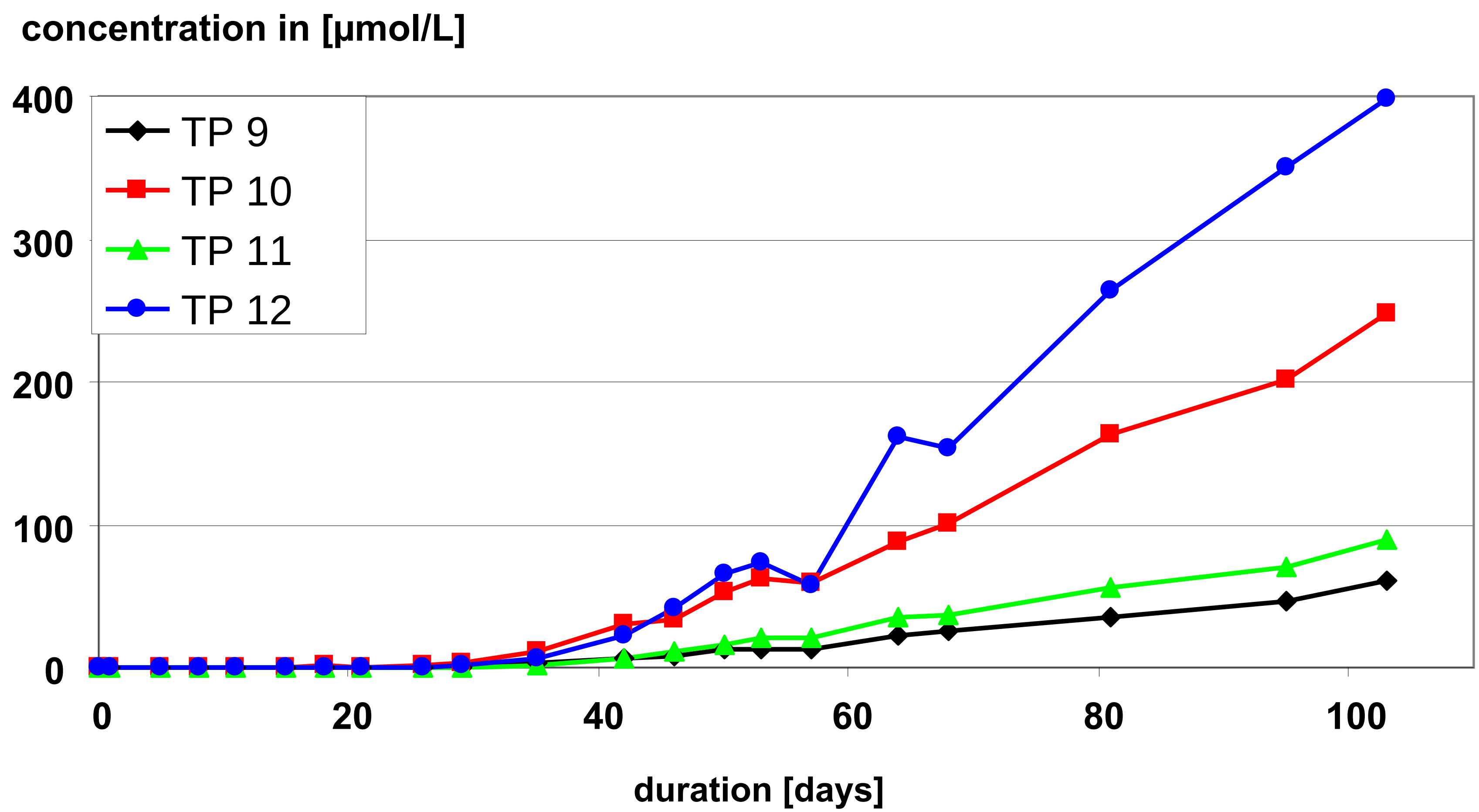
Iopromide transformation

Phase II

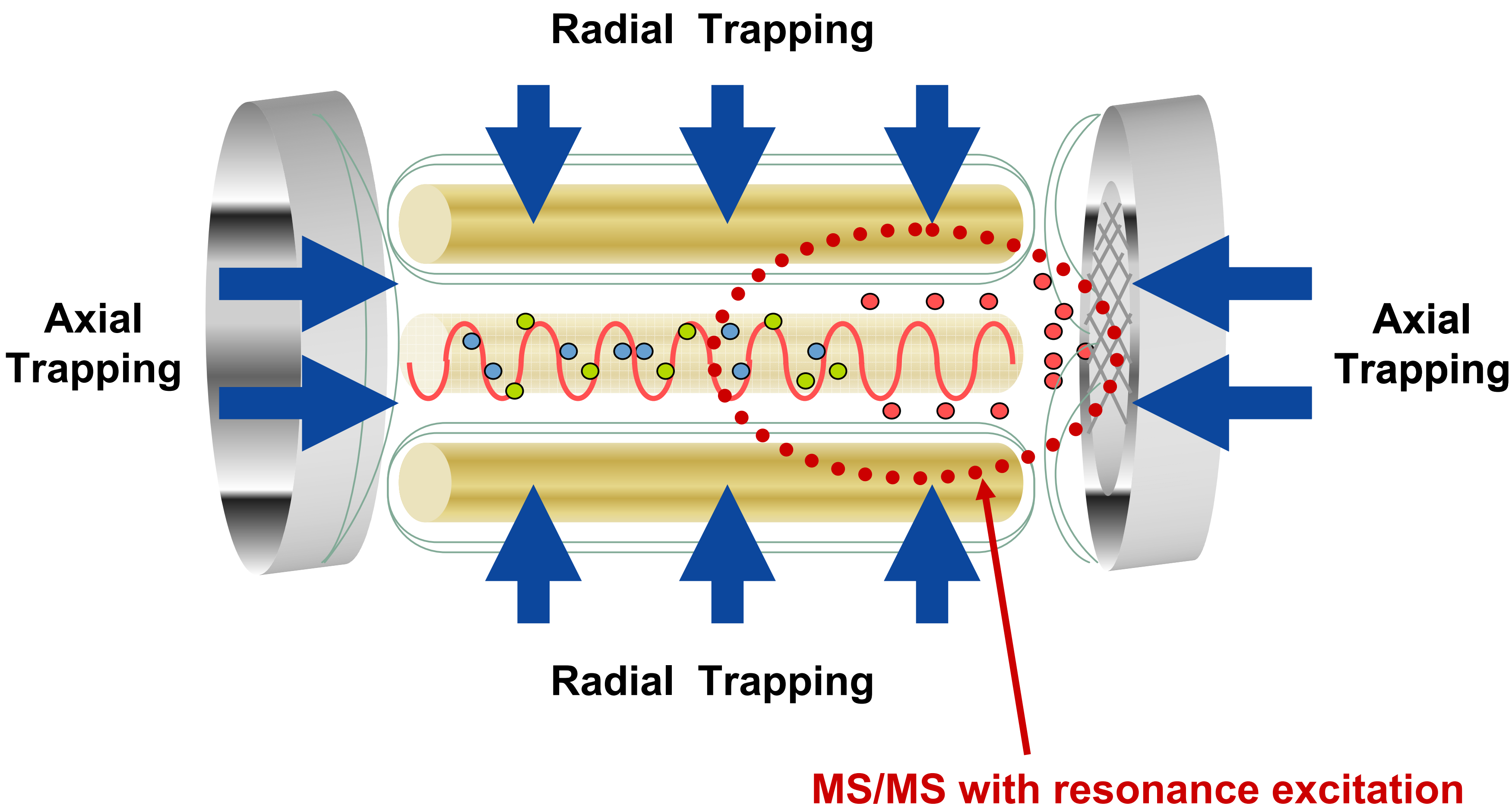


Iopromide transformation

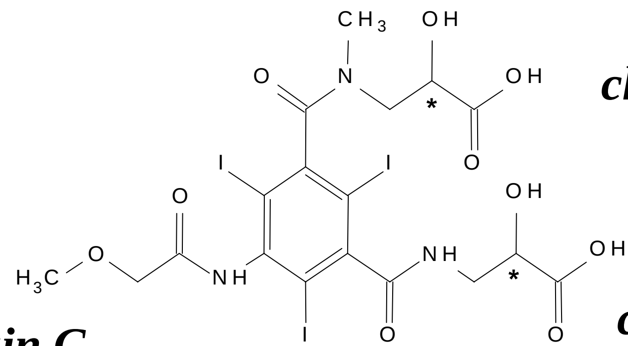
Phase III



Fragmentation: using a linear trap of 4000 Q TRAP™



MS fragmentation of TP 3



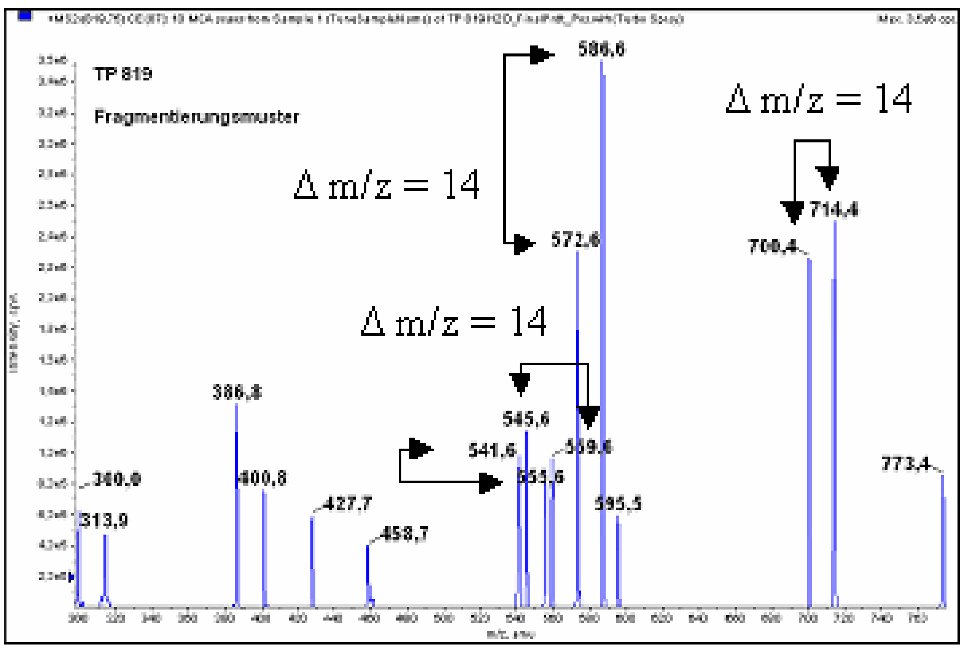
chain A

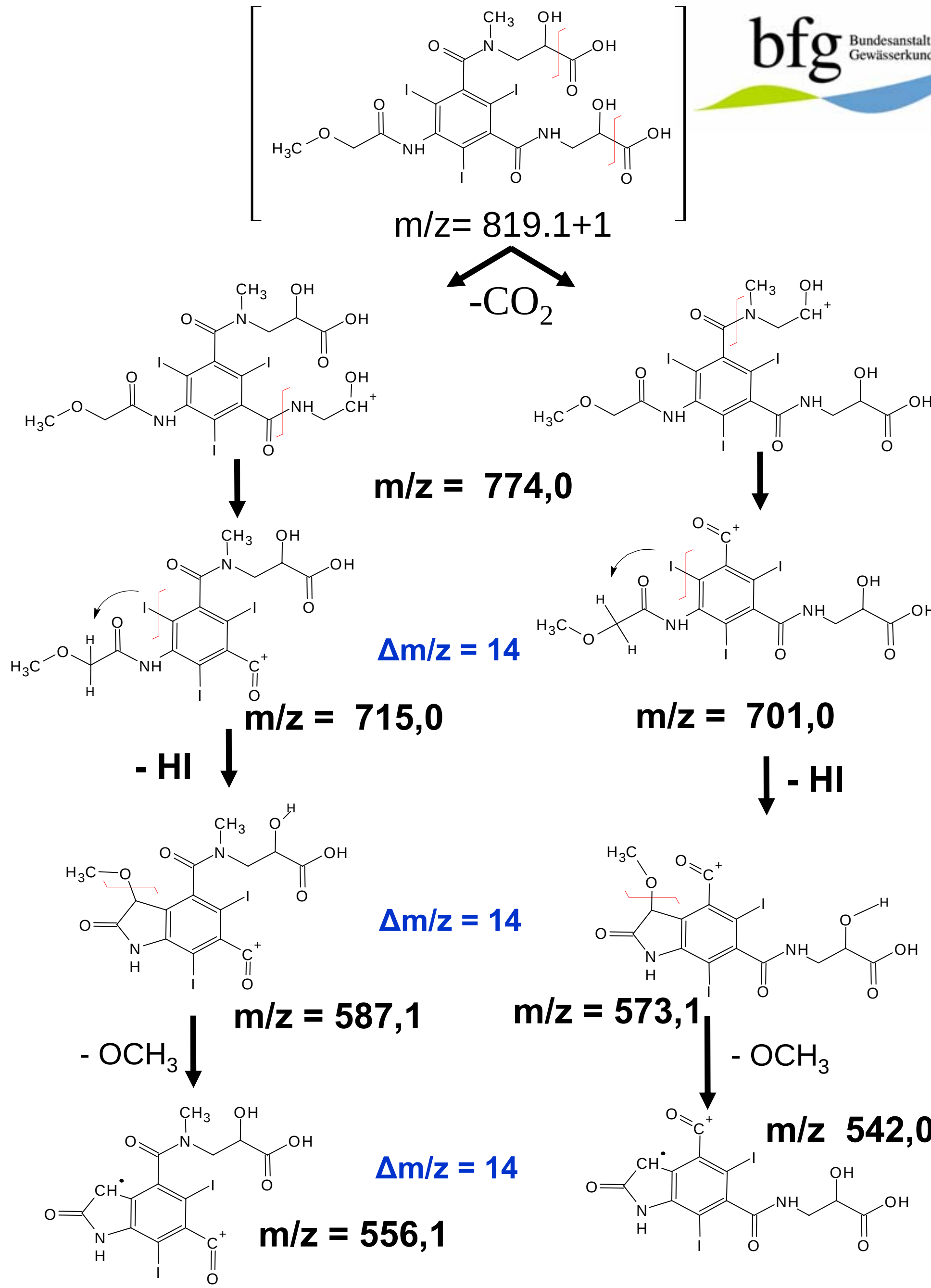
chain B

chain C

TP 3

Product Ion Scan (MS²)





[13]C-NMR (176 MHz) of TP 10 (TP 701)

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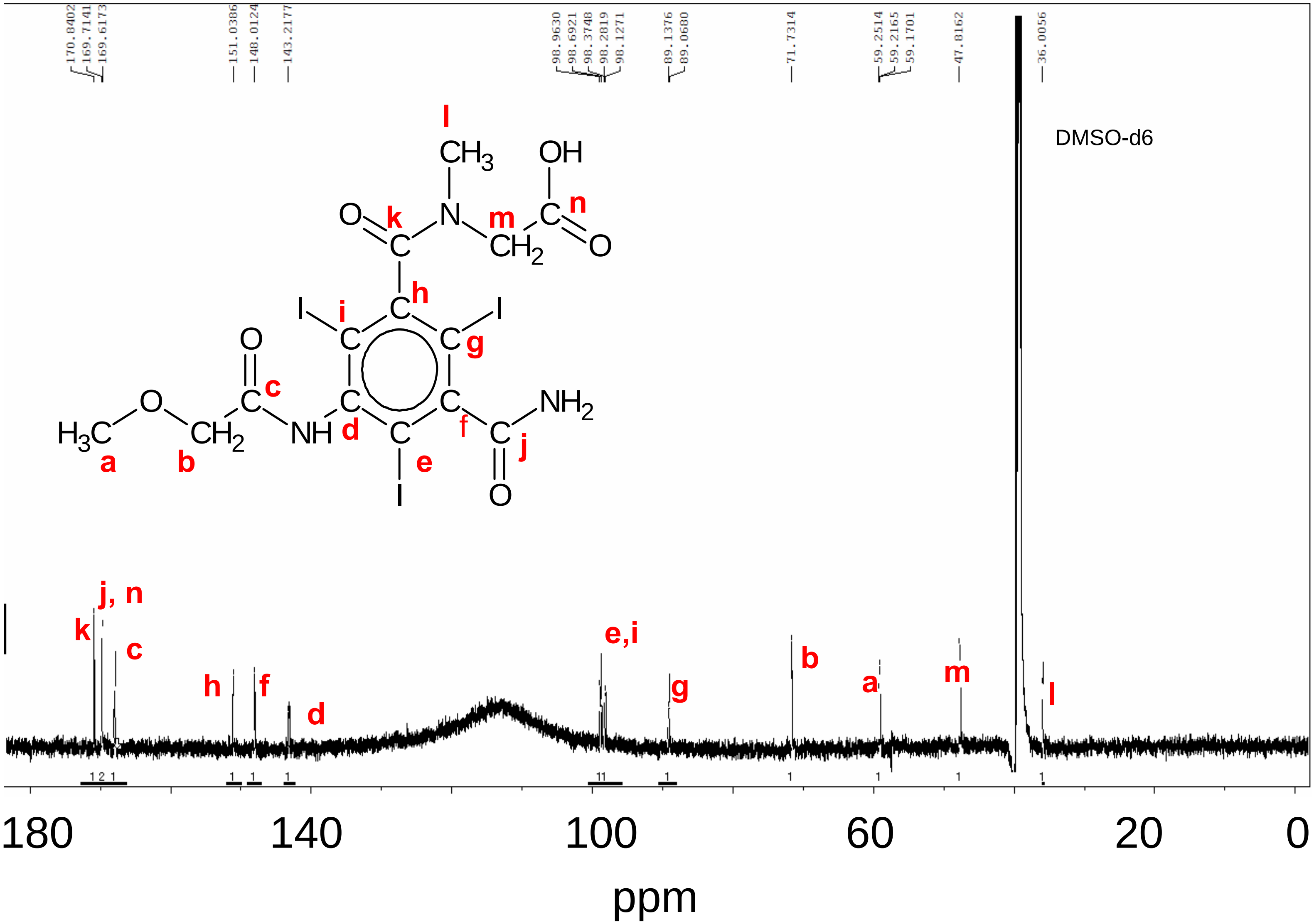
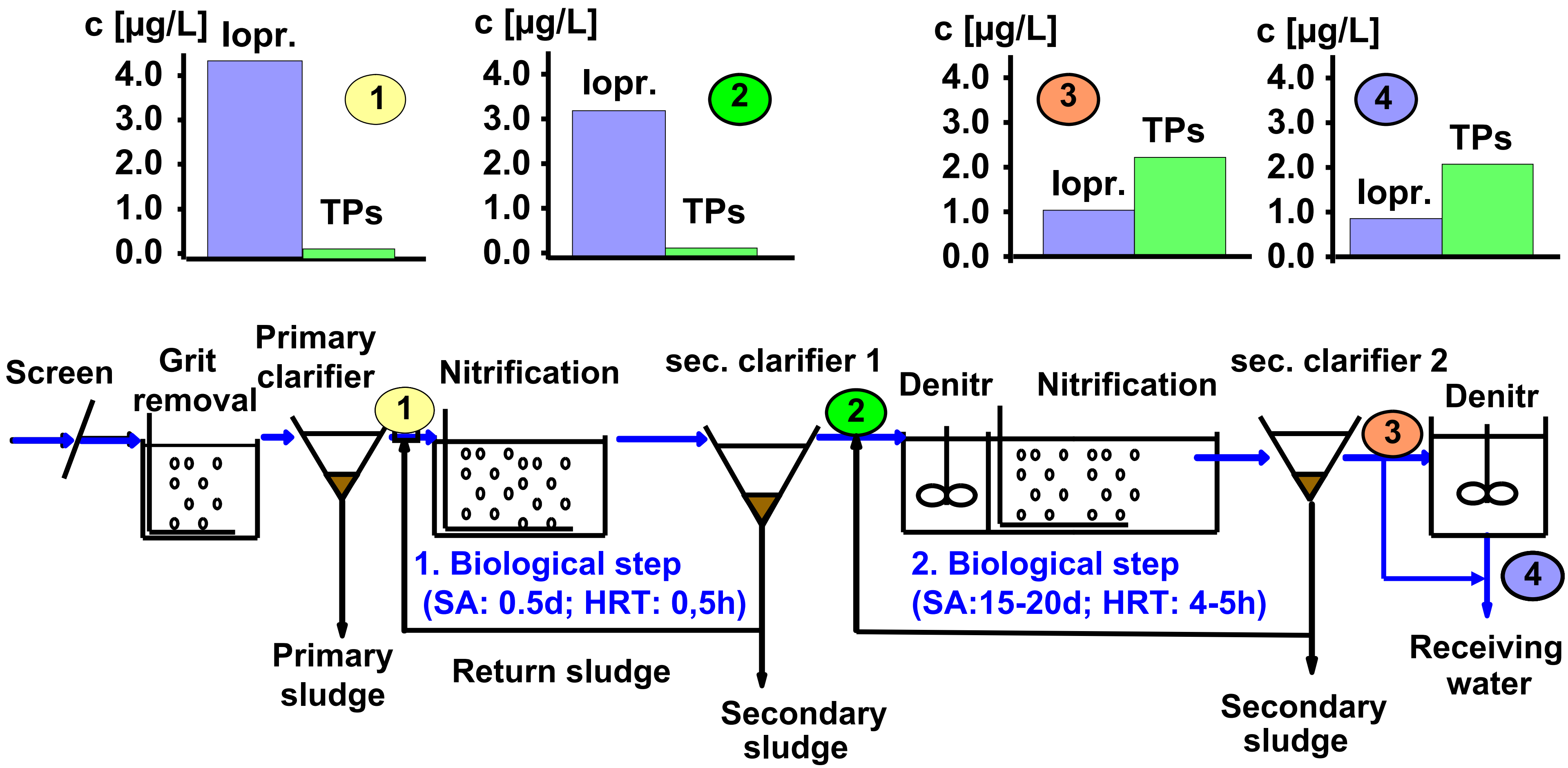


Transformation products (TPs) of Iopromide in WWTP Frankfurt

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



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

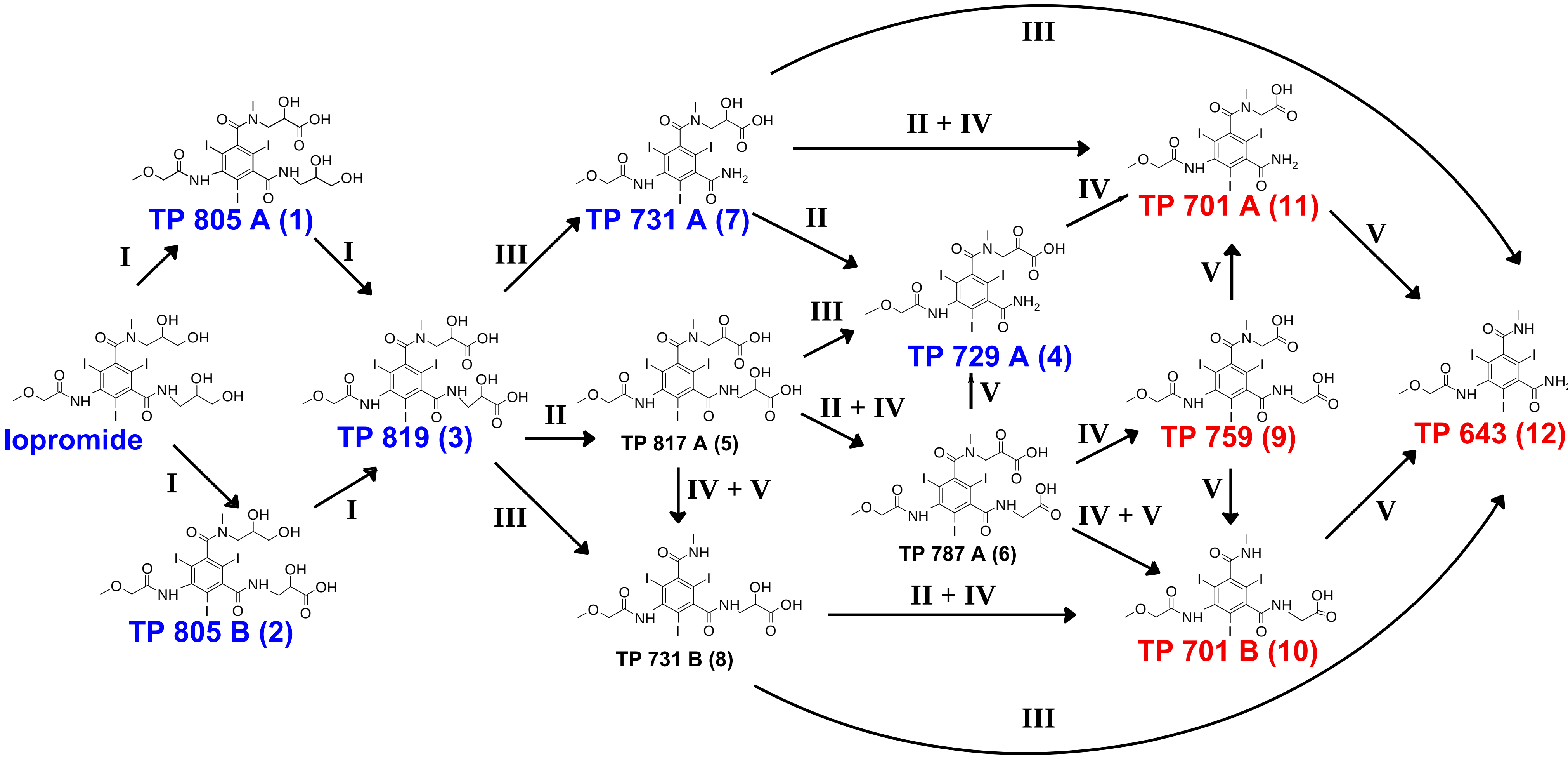
Potential aerobic degradation pathways of Iopromide

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

reaction III: cleavage of amide-methylen bond

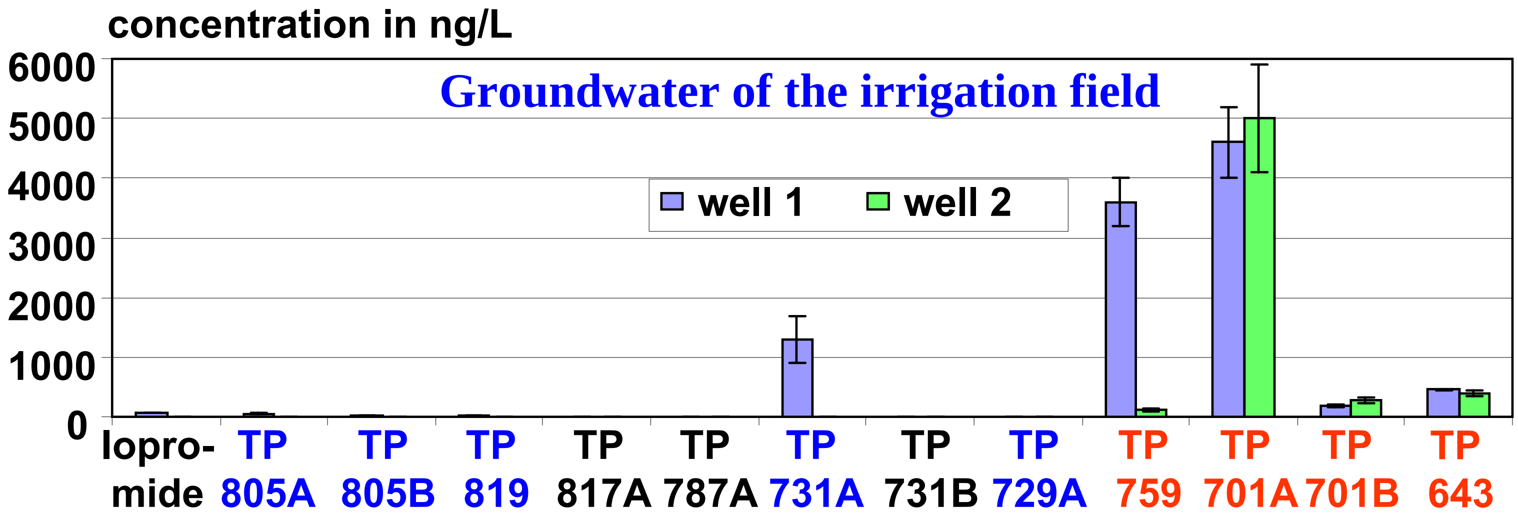
reaction IV: oxidative decarboxylation

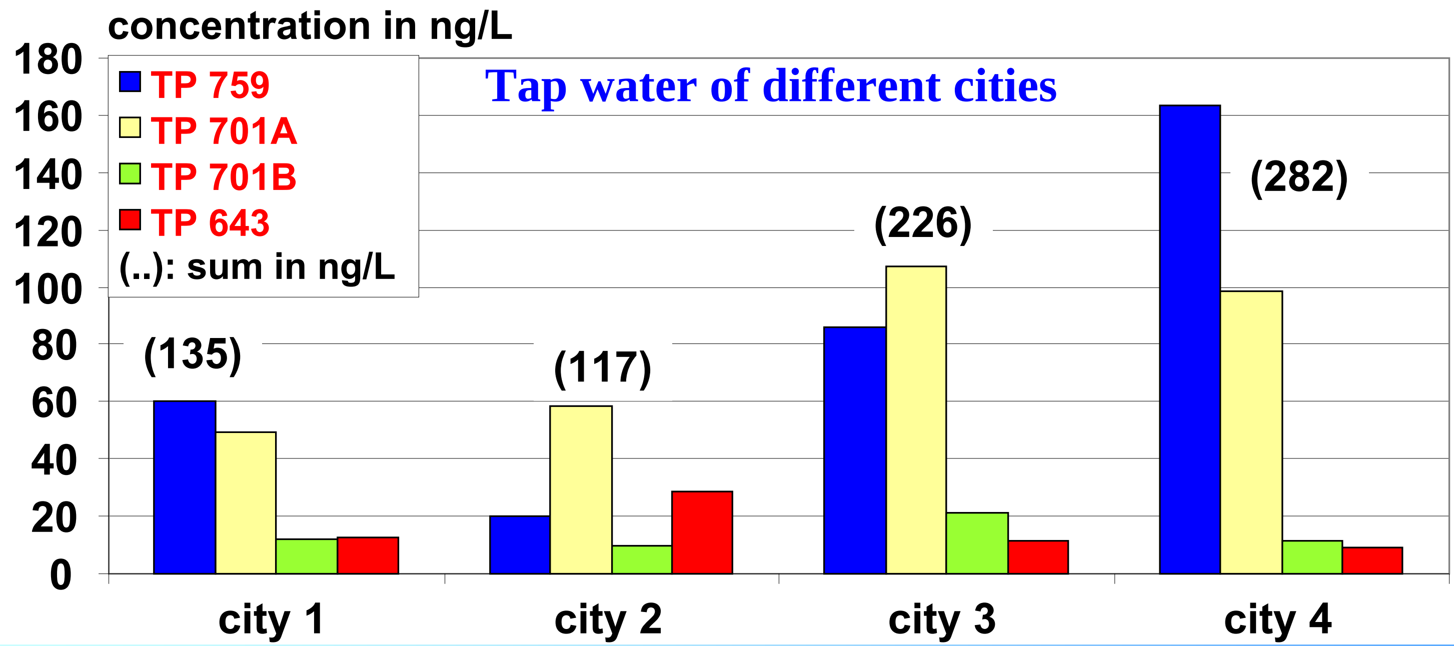
reaction V: deacetylation



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

Occurrence of iopromide TPs





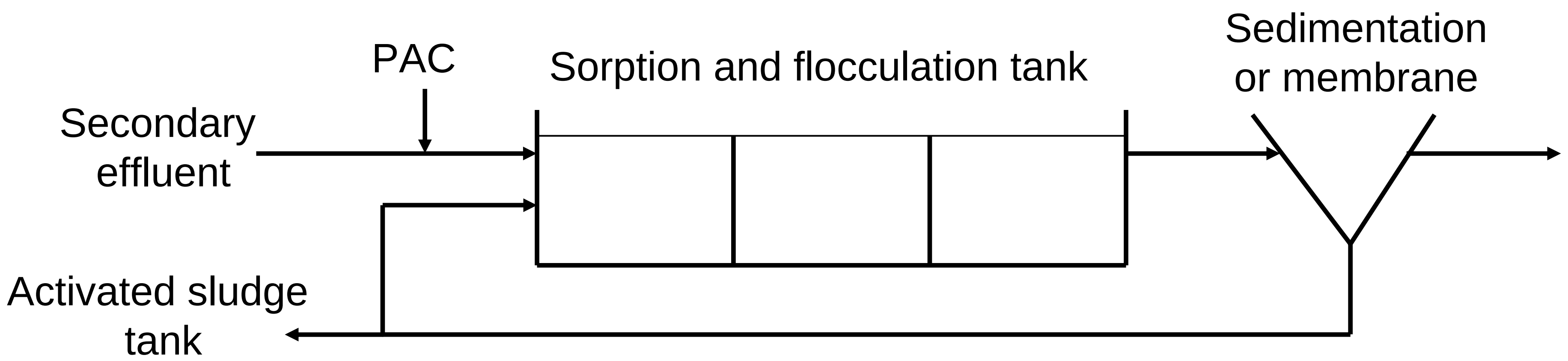
Source: Schulz et al., EST, 2008

Sorption onto activated carbon

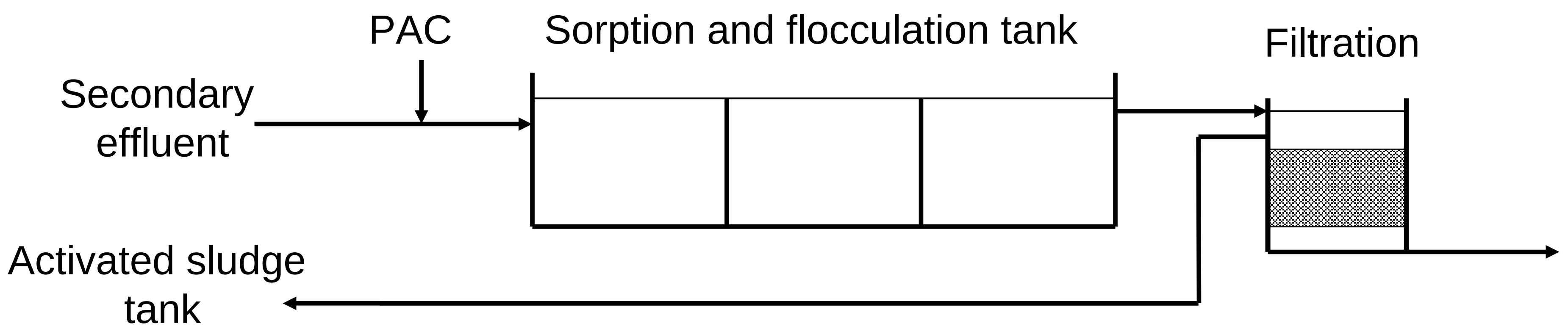
source: unpublished data of Neptune project

PAC addition with/without sludge recycling

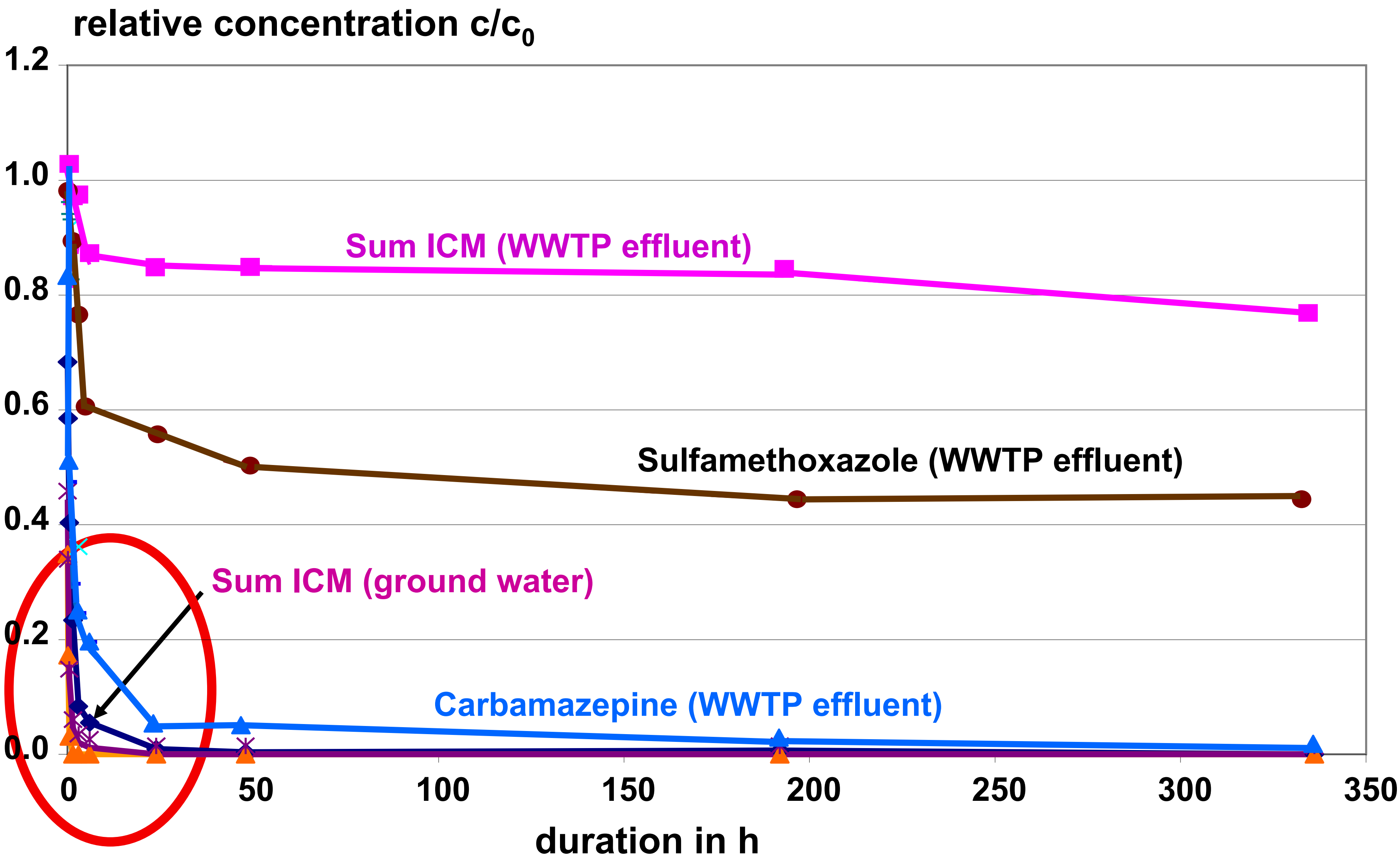
With sludge recycling: SA_{PAC} >> HRT



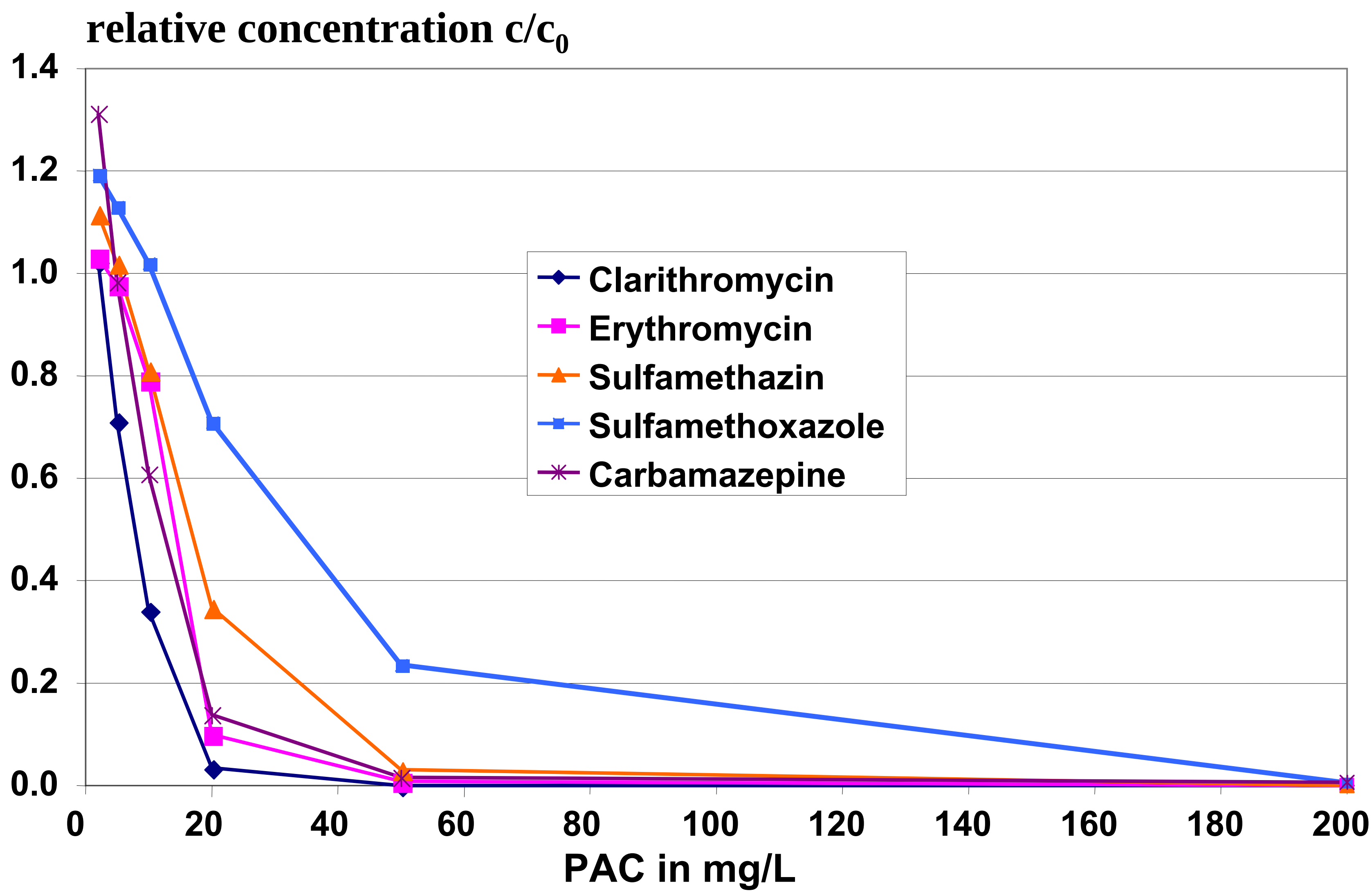
Without sludge recycling: SA_{PAC} = HRT



Sorption on powdered activated carbon (PAC=20 mg/L) in WWTP effluent (12 mg/L TOC) and ground water (0,3 mg/L TOC)



Sorption of antibiotics with PAC in WWTP effluent (12mg/L TOC)



Oxidative transformation

Dissertation: Jessica Benner

source: Benner J., von Gunten, U., Ternes T.A., ES&T, under revision

Ozonation of effluents: Braunschweig and Kloten-Opfikon

Convent. activated sludge (CAS)

2 columns (2 x 140 litre) for ozonation

contact time: ~ 8-9 min

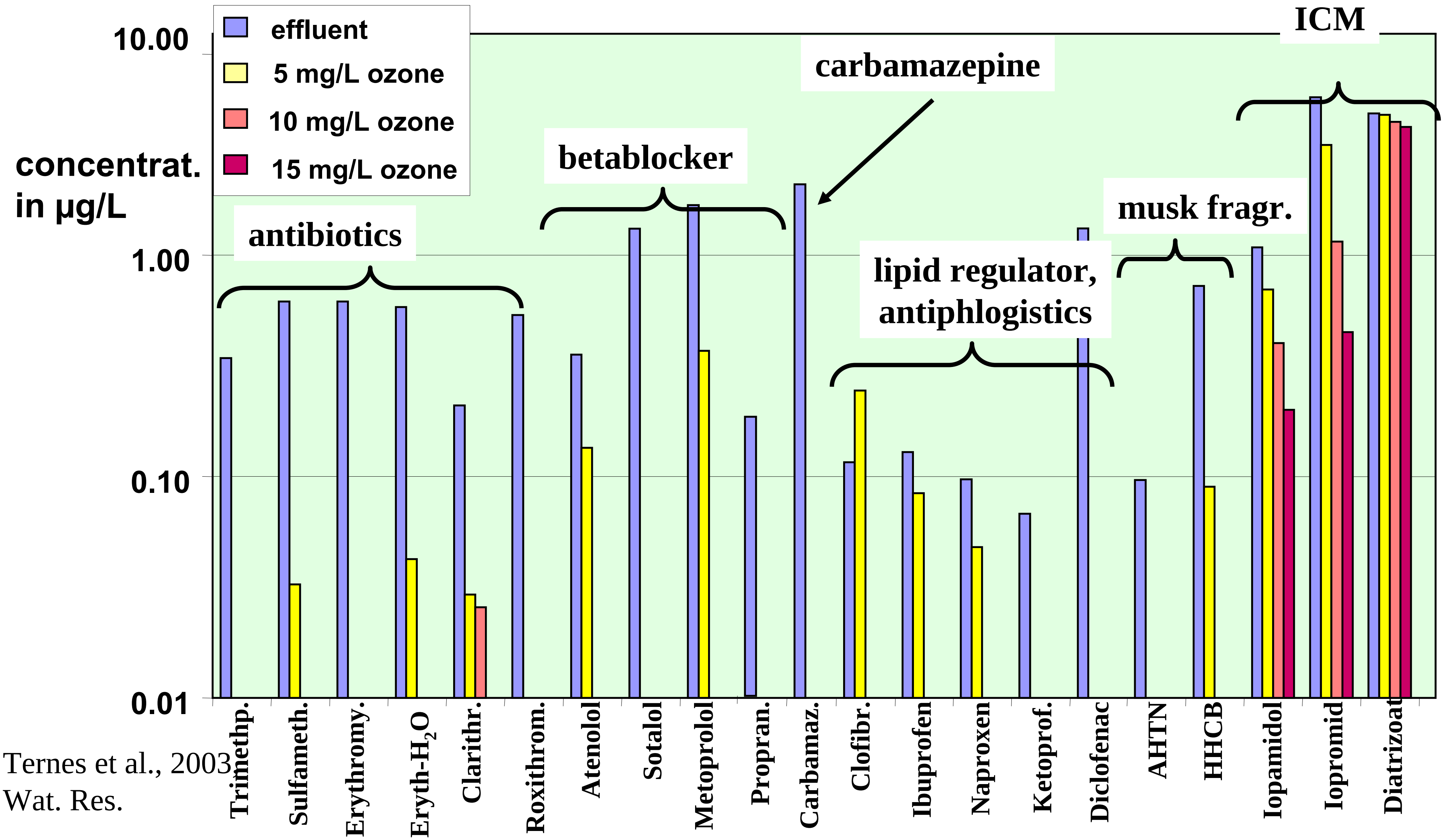
Pharma. dosage: ~ 2 mg/L/without

Ozone doses: **0.5, 1, 2, 3.5, 5, 10, 15 mg/L**

DOC: 6 - 8 mg/L (Kloten-Opfikon)

DOC: 23 mg/L (Braunschweig)

Ozonation of Braunschweig effluent (DOC: 23 mg/L)



Ternes et al., 2003
Wat. Res.

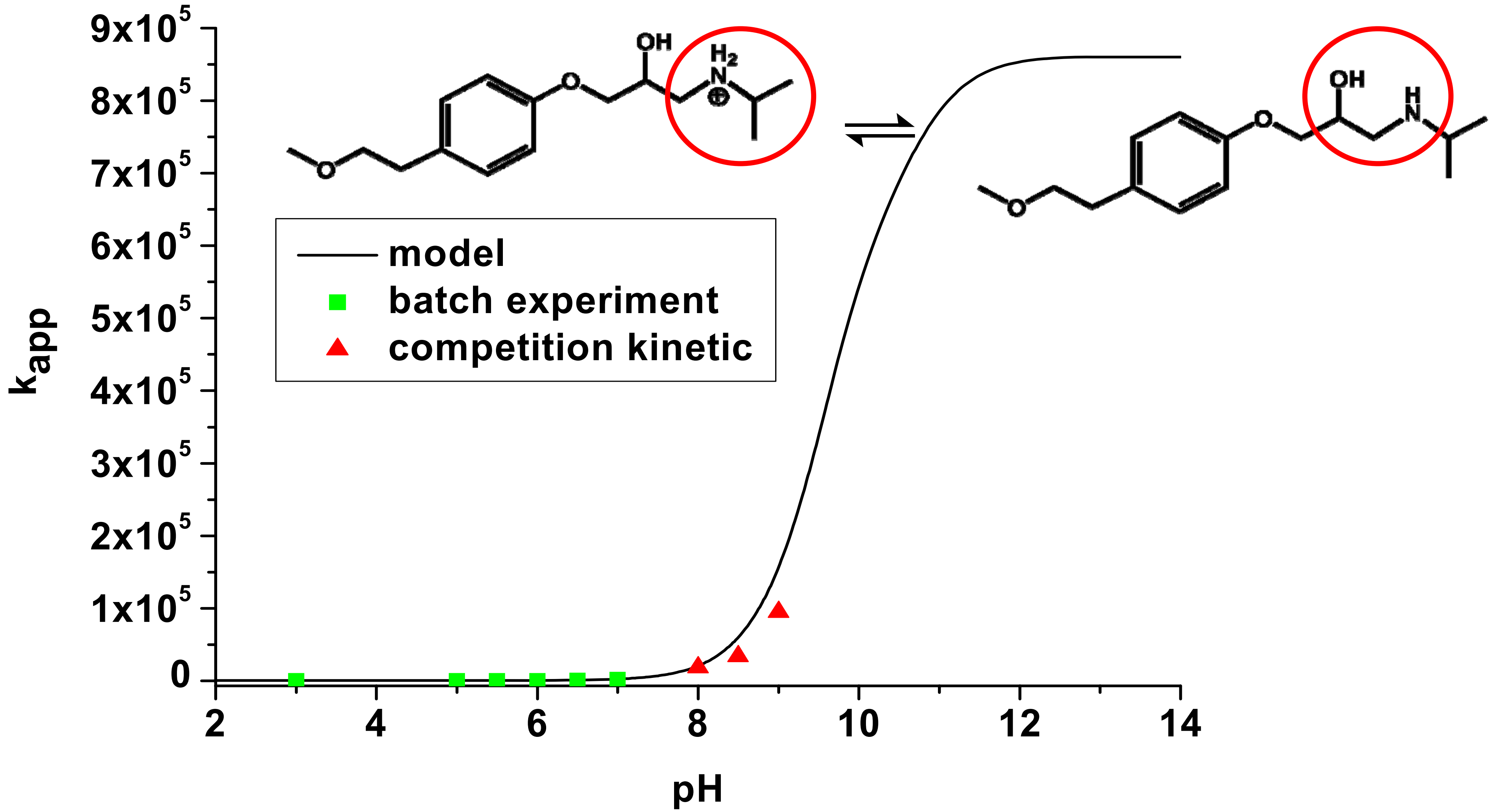
Rate constants k_{O_3} and $k_{\bullet OH}$

Substance	pKa	k_{O3} [$M^{-1}s^{-1}$] pH 7	$k_{\bullet OH}$ [$M^{-1}s^{-1}$] pH 7
Acetbutolol	9.2	$(1.9 \pm 0.6) \cdot 10^3$	$(4.6 \pm 0.7) \cdot 10^9$
Atenolol	9.6	$(1.7 \pm 0.4) \cdot 10^3$	$(8.0 \pm 0.5) \cdot 10^9$
Metoprolol	9.7	$(2.0 \pm 0.6) \cdot 10^3$	$(7.3 \pm 0.2) \cdot 10^9$
Propranolol	9.5	$1 \cdot 10^5$	$(1.0 \pm 0.2) \cdot 10^{10}$
17α-ethinylestradiol[3]	10.4	$3 \cdot 10^6$	$(9.8 \pm 1.2) \cdot 10^9$
Atrazine[4]	1.6	6	$2.4 \cdot 10^9$

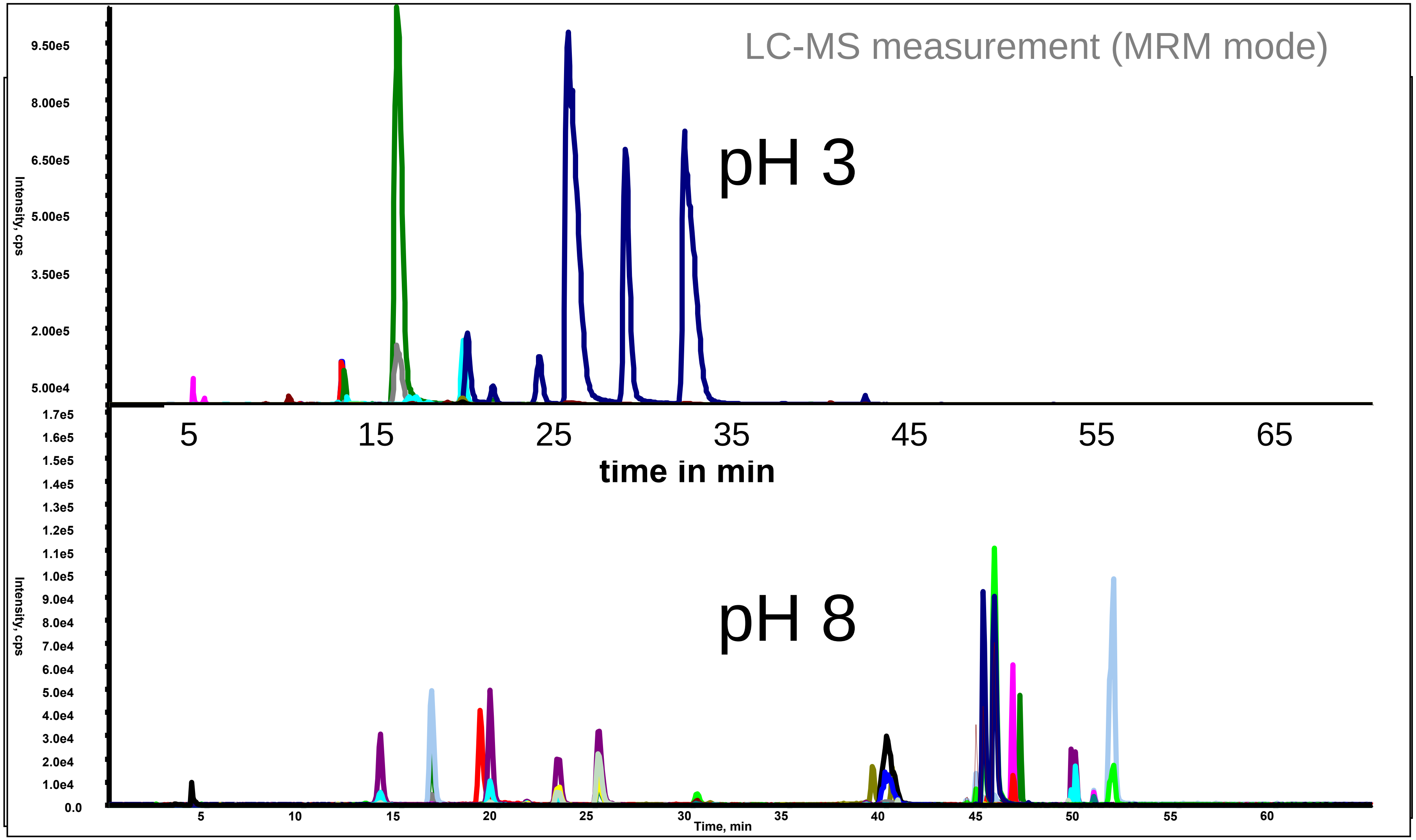
[3] Huber et al., *Environ. Sci. Technol.* 2003, *37*, 1016-1024.

[4] Acero et al., *Environ. Sci. Technol.* 2000, *34*, 591-597.

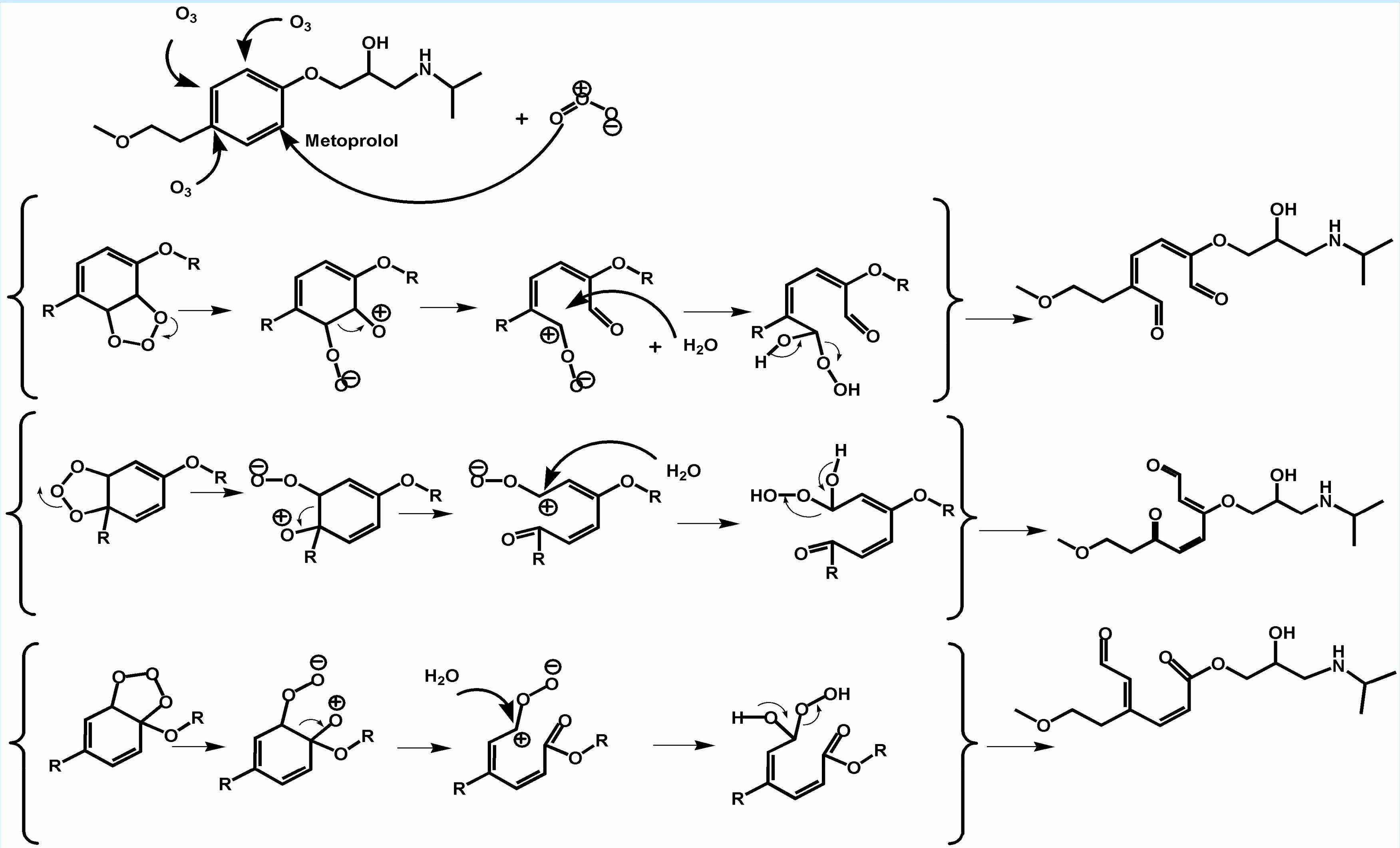
k_{O_3} pH dependence of metoprolol



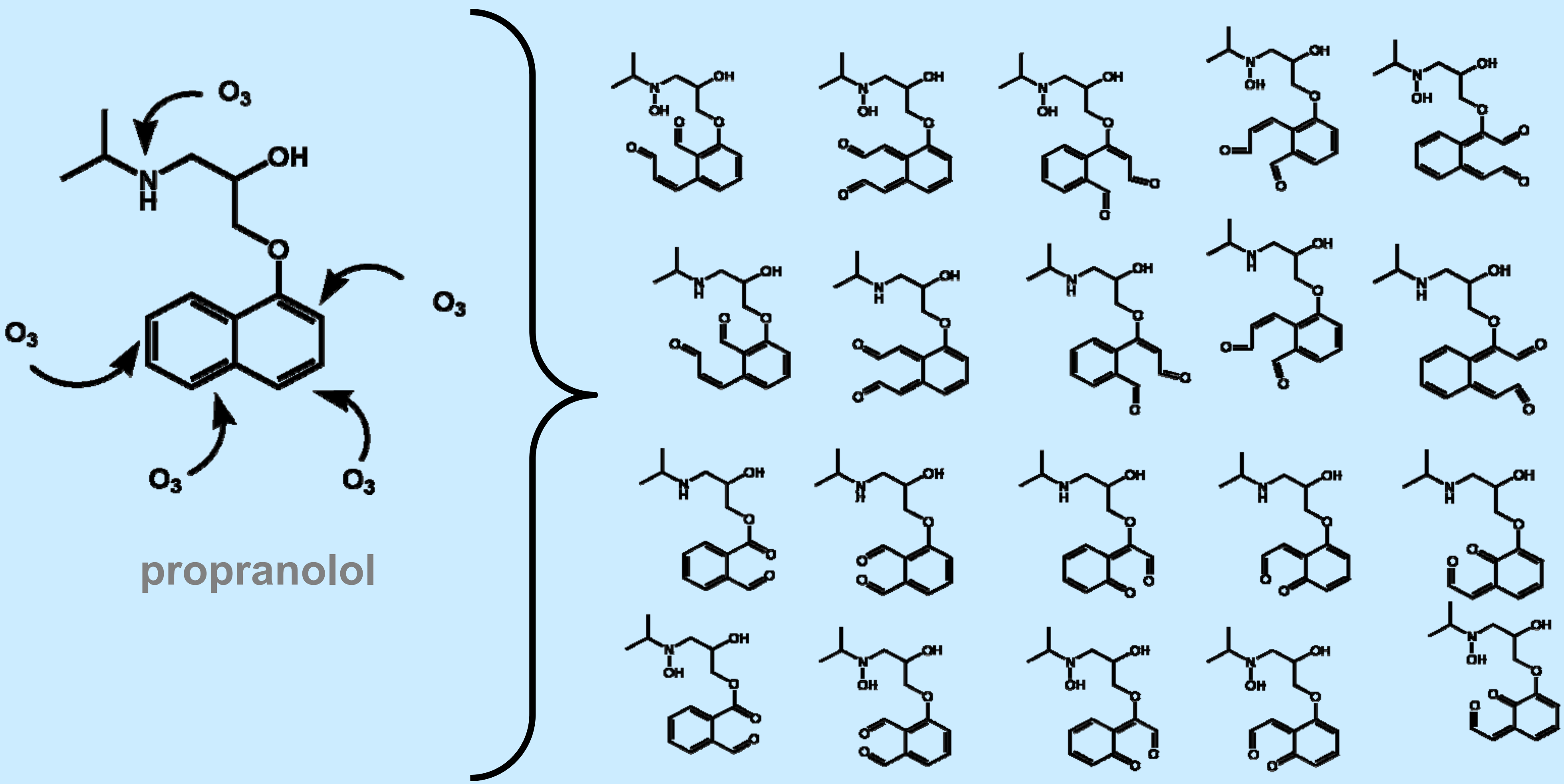
Oxidation products of metoprolol and propranolol



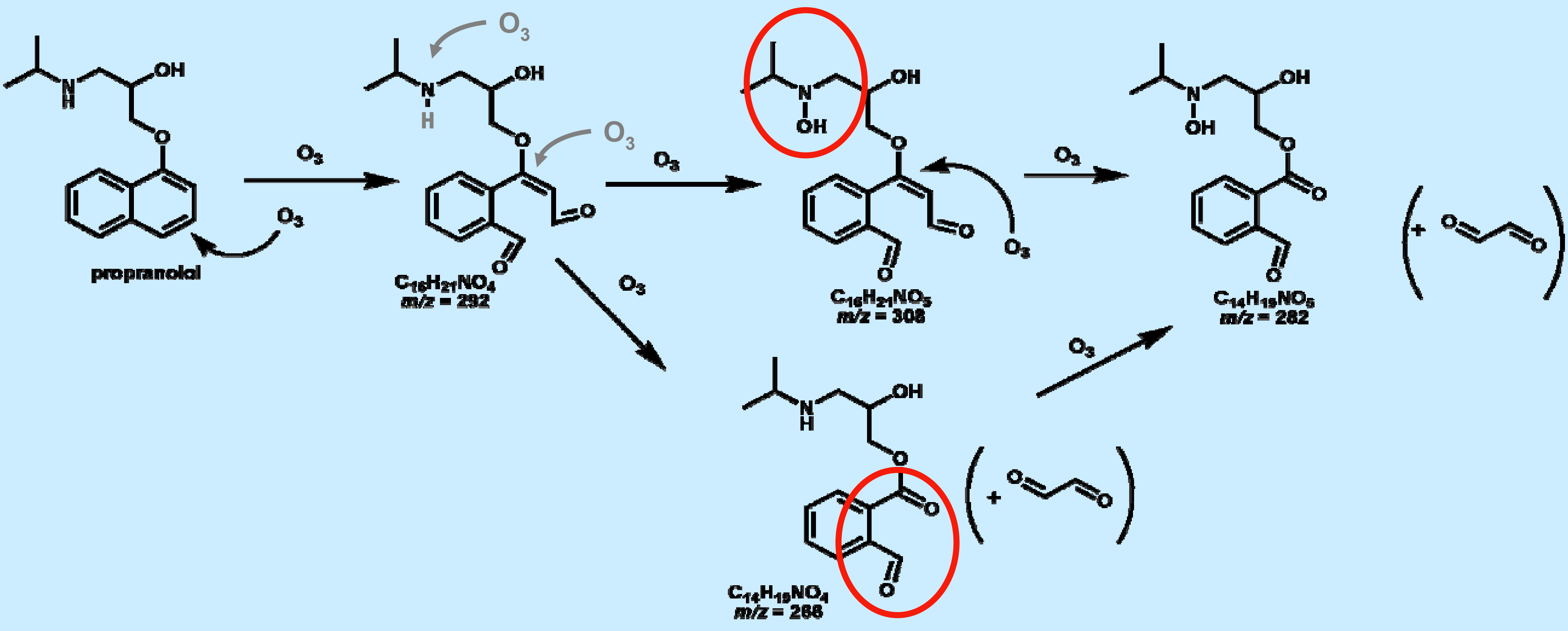
Formation of aldehyde moieties m Metoprolol OP 300 at pH 3



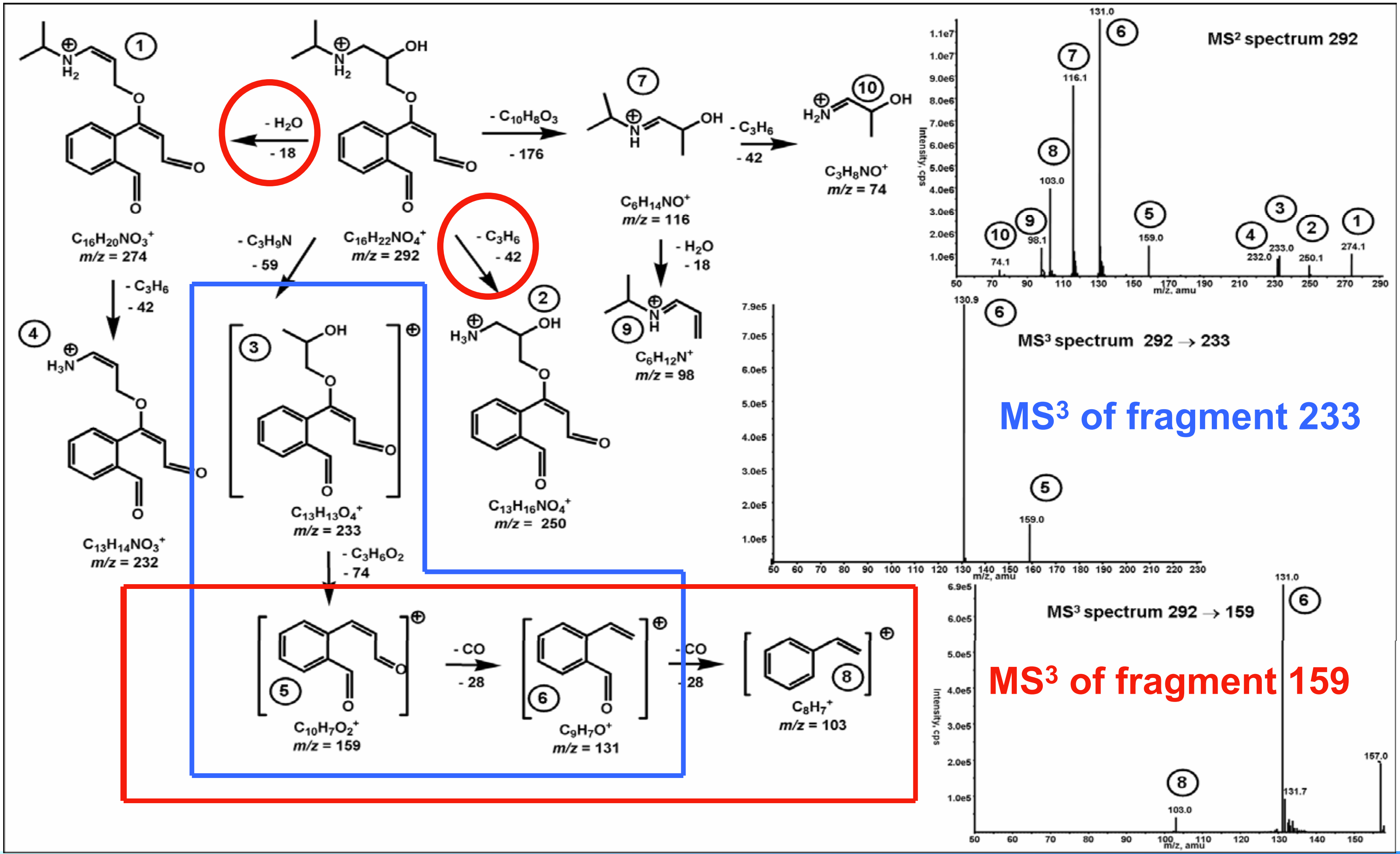
Isomers of propranolol OPs



Proposed OP formation of propranolol at pH 8



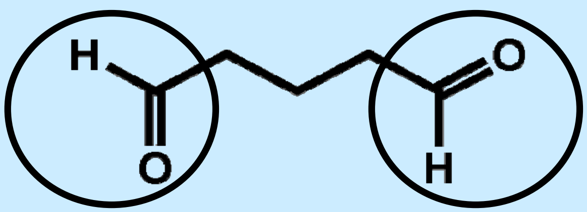
Identification of propranolol OP 292



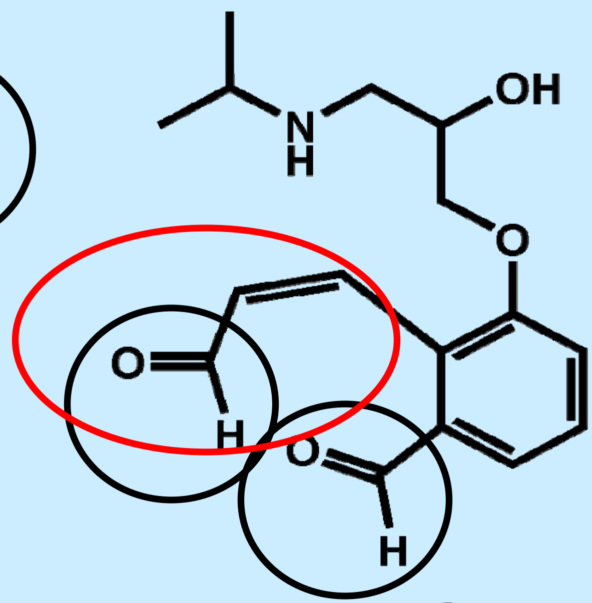
Reported genotoxicity of aldehydes

Compounds with aldehyde moieties

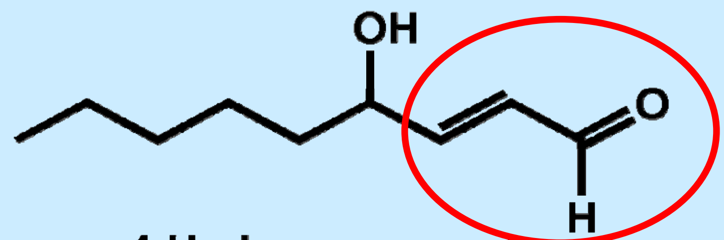
- interact with DNA [a] (e.g. DNA-protein cross linking)
- show genotoxic and carcinogenic properties



glutaraldehyde



propranolol OP-291



4-Hydroxynonenal

[a]Kuchenmeister, F. et al. *Res.-Gen. Tox. Environ. Mut.* **1998**, *419*, 69-78.
[b]Eckl, P. M. et al. *Mut. Res.* **1993**, *290*, 183-192.

Number of resistences in enteroccoci detected

Sampling site	Number resistences of 1 colony					Br^-	BrO_3^-
	5	6	7	8	9	µg/L	µg/L
„urban“ influent	+	+	-	-	-		
„rural“ influent	-	-	+	+	-		
WWTP effluent	+	+	+	-	-	850	< 15
ozone (8 g/m³)	-	-	-	-	-	850	< 15
ozone (15 g/m³)	-	-	-	-	-	780	25

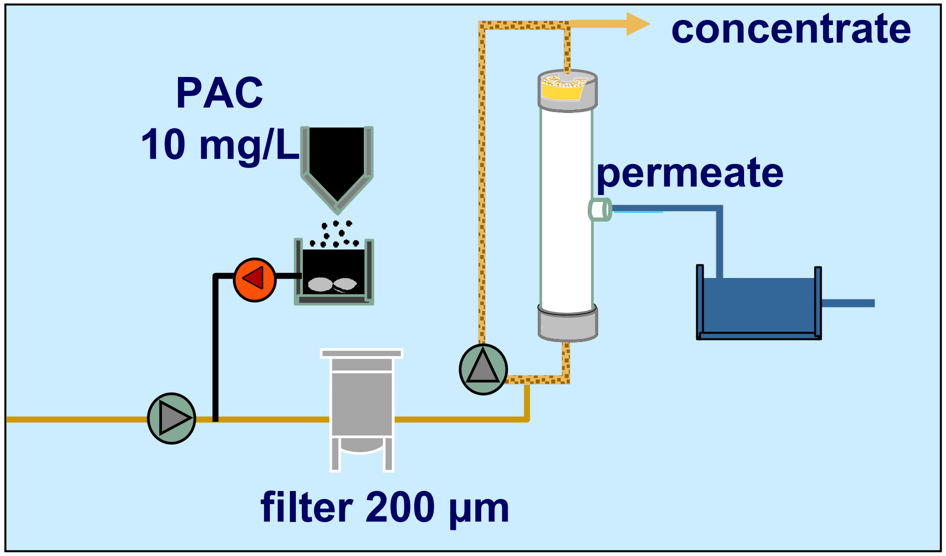
Resistences 7,8: Amoxicillin, Clavulanic acid, Ciprofloxacin, Erythromycin, Imipenem, Tertacyclin, Sulfamethoxazole/Trimetoprim, Gentamycin (8)

No resistences found: Vancomycin, Linezolide, Synercide

Cooperation:
University Mainz,
Kohnen, Schön-Hölz

Membranes

Cristal®-process and Nanofiltration/RO



Ground water spiked (1 µg/L): carbamazepine, iopromide, ibuprofen, sulfamethoxazole, roxithromycin

Cristal®-process (UF/PAC): Addition 10 mg/L PAC, elimination > 98 % except antibiotic sulfamethoxazole and iopromide (95 %)

UF nano filtration/reverse osmosis (parallel: NF90, XLE, BW30)
elimination > 98 % for all substances

Kooperation: Marie-Laure Janex-Habibi, Cirsee Environment, Paris

Contamination of RO membrane concentrate

removal of organic contaminants > 95%

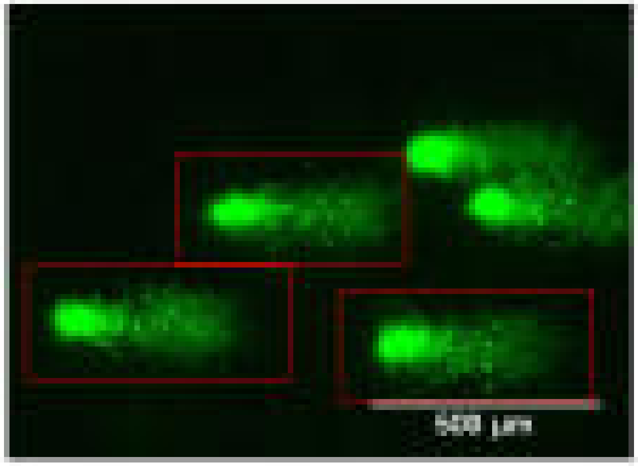
TOC	
WWTP effluent	**RO-concentrate**
11.6 mg/L	**45.8 mg/L**

Mean concentration factor

concentrate/effluent ⇨ 3-4

source: Benner et al., 2008, Water Res.

Positive effects of the Comet assay after ozonation of membrane concentrate



cooperation
Georg Reifferscheid, BfG

Options for advanced wastewater treatment

		Energy kWh m^{-3}	Costs € m^{-3}	By products
Piloting result	**Ozonation**	0.1 – 0.3	0.05 – 0.10	Toxicology unknown
Literature, lab scale	**RO desalination up to 50 bar**	2 – 4	0.2 – 0.3	up to 50% concentrate
	RO/NF low salt 5 – 30 bar	0.5 – 3	0.1 – 0.25	volume of concentrate?
	Activated carbon (PAC)	<< 0.05	0.10 – 0.20	none

Feasible costs: ≤ 25 €/person/year
(100 m^3/(person·year)

Conclusions

Which „relevant“ emerging pollutants“ has to be considered?

Criterium 1: ecotoxicological or human toxicological relevance

Criterium 2: potential to contaminate ground water and drinking water

Criterium 3: biological TP fulfilling criteria 1,2

How to determine the success of a measure?

- **Non-detection of a pollutant (sorption, degradation, size exclusion)**
- **Elimination of relevant TPs (biological, chemical)**
- **Models to transfer the results to other emerging pollutants or conditions**

Which measures are economically and ecologically appropriate?

- **Minimizing the direct risiks for humans and the enviromnment**
- **Taking into account the global impacts of the measure (green house effect)**
- **Costs should be justified by a success control (criteria: 1-3)**

bfg Bundesanstalt für Gewässerkunde

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Thank you for your attention