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Advanced treatment processes for micropollutant removal

Full-scale ozonation and PAC addition

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NEPTUNE Workshop, 21/22 April, Koblenz, Germany

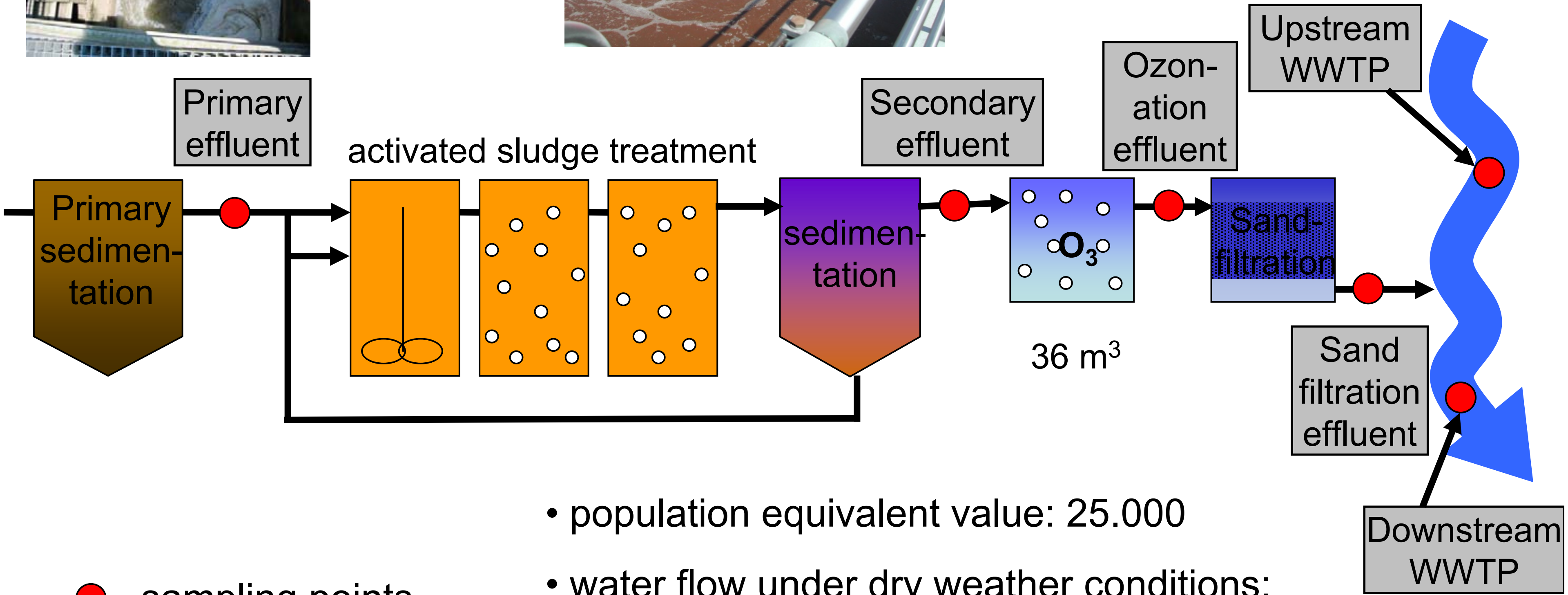
Overview

Two technical processes are mainly in discussion for extended micropollutant removal:

- **Ozonation:** addition of ozone after biological treatment to a short contact tank of about 20 minutes HRT followed by a biological filter or moving bed reactor to degrade the oxidation by-products.

- **Activated carbon adsorption:** PAC/flocculant addition to a contact/flocculation tank of about 30-60 minutes HRT followed by a clarifier or membrane separation, after the clarifier a filter is needed to reduce PAC loss. *Alternatives:* PAC addition directly to biology or filtration?

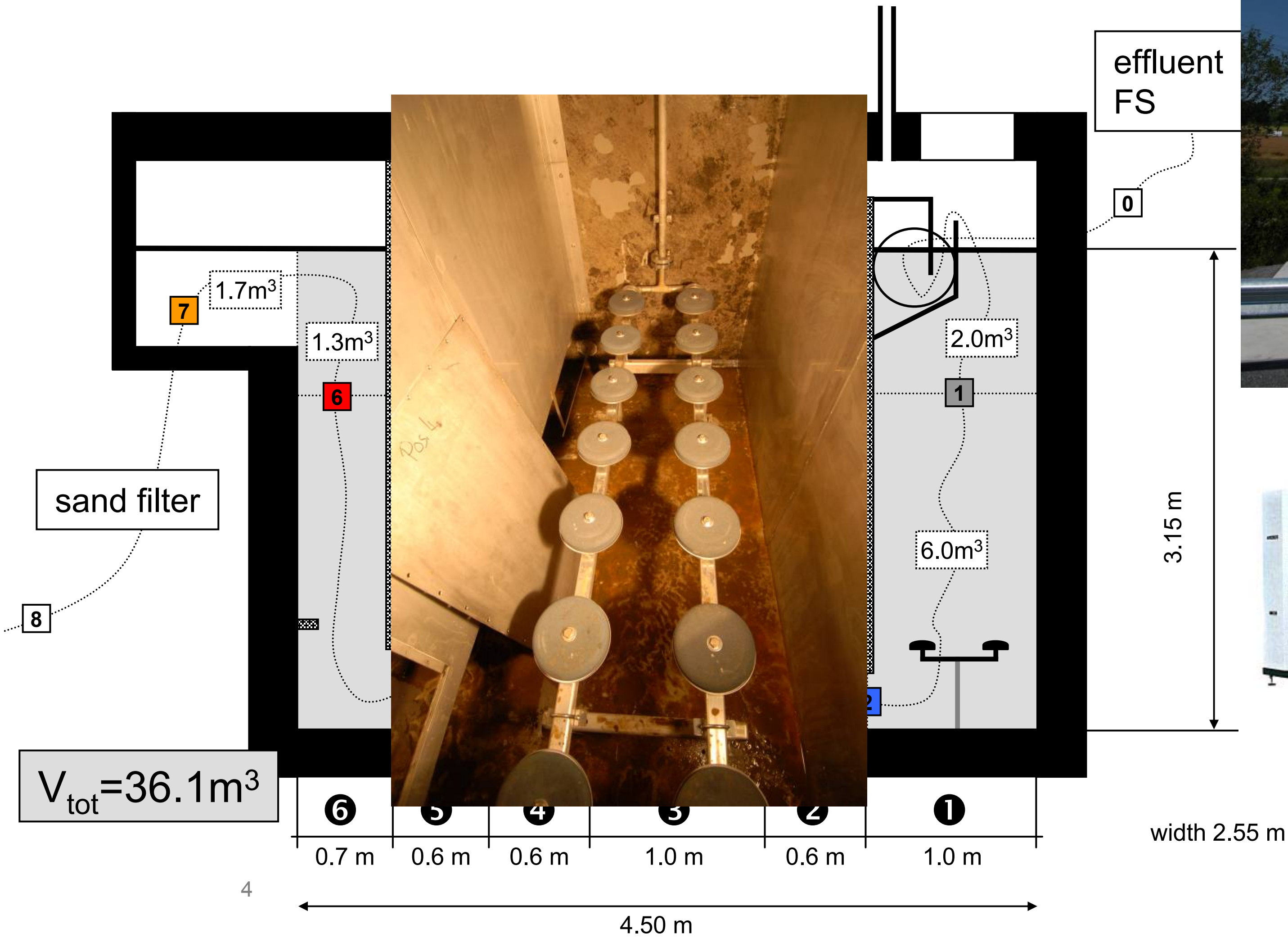
Full scale ozonation at WWTP Regensdorf



● sampling points

- population equivalent value: 25.000
- water flow under dry weather conditions: 30-120 L/sec ~ 50 % water flow of creek

Ozonation


effluent
FS
0
1
2.0m^3
6.0m^3
1.7m^3
1.3m^3
6
7
8
sand filter
V_{tot}=36.1m^3
❻ ❺ ❹ ❸ ❷ ❶
0.7 m
0.6 m
0.6 m
1.0 m
0.6 m
1.0 m
4.50 m
3.15 m
width 2.55 m

Full-scale ozonation

Ozone dosage

- Online measurement of ozone and DOC (as UV absorption)
- Control of ozone concentration by DOC measurements
- Ozone concentration: 0 – 1200 g /kg DOC ≈ 0 – 6 mg/L Ozone

Sampling

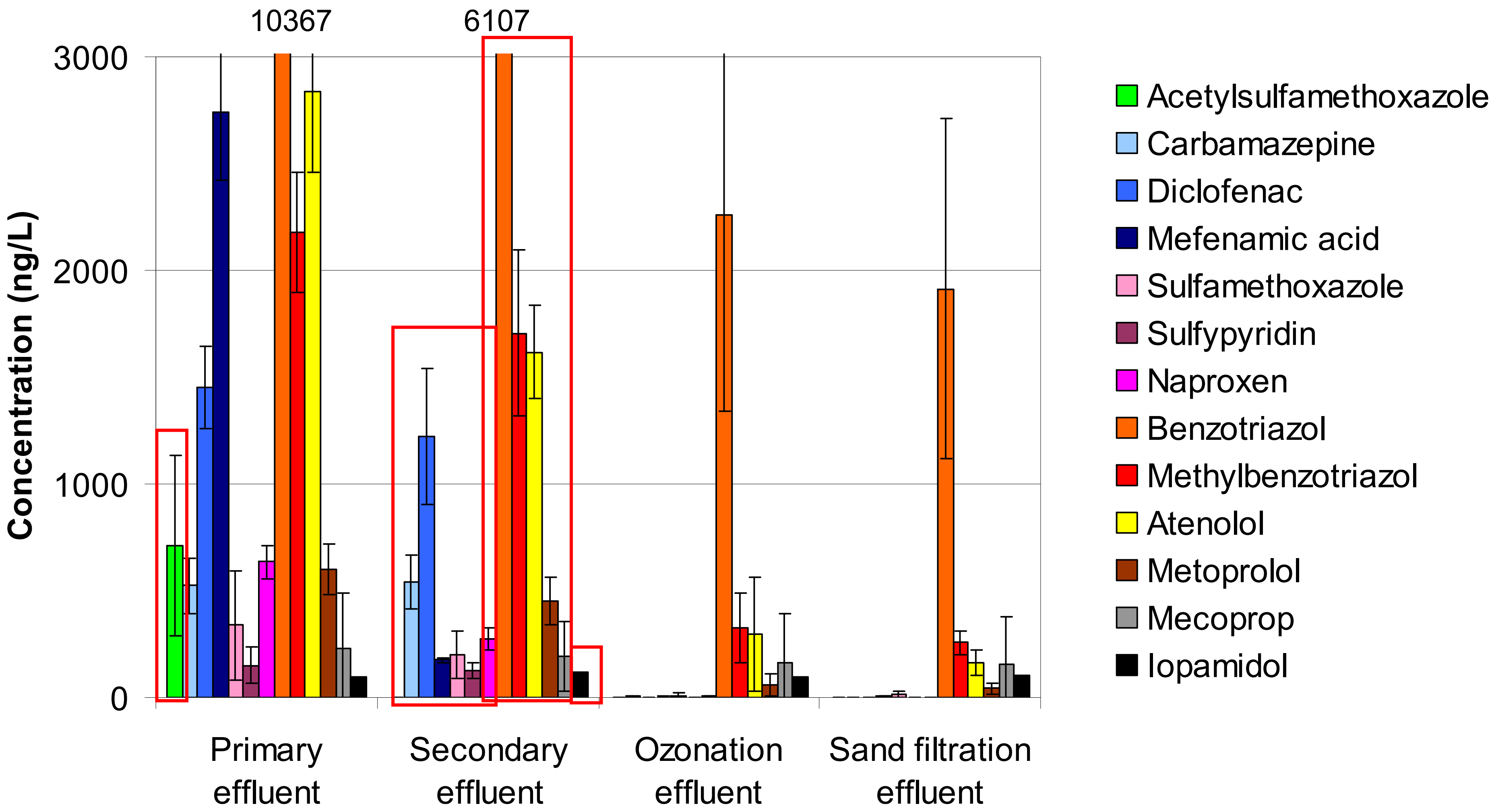
- 10 sampling compaigns
- 24h- or 48h-volume proportional composite samples
- Fitration on-site (0.7 µm glassfiber filters)

Analysis

- Micropollutants
- Ecotoxicity
- Pathogens

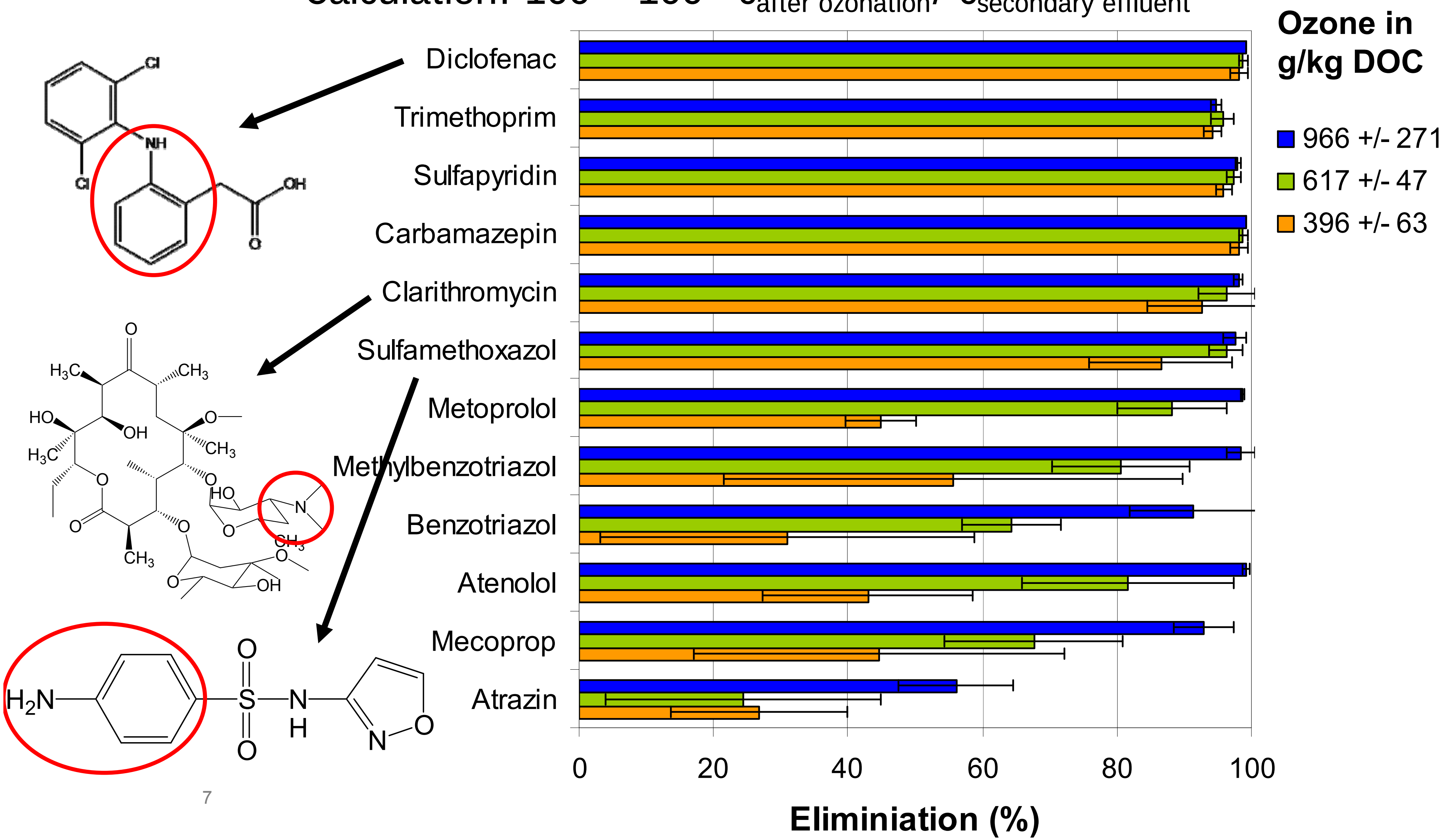
Elimination efficiency – micropollutants

5 sampling campaigns: 617 ± 47 g O_3 / kg DOC



Effect of ozone concentration on elimination efficiency

Calculation: 100 – 100 $*c_{after\ ozonation} / c_{secondary\ effluent}$



Elimination efficiency – micropollutants

	Number	Secondary Effluent >15 ng/L	Ozonation effluent (634 g O3/kg DOC) > 15 ng/L	Ozonation effluent (634 g O3/kg DOC) > 100 ng/L
Pharmaceuticals	14	12	3	Atenolol
Antibiotics	10	8	0	
X-Ray contrast media	6	6	not determined	
Biocides/Pesticides	12	8	3	Mecoprop
Corrosion inhibitor	2	2	2	(Methyl)-Benzotriazol
Endorine disruptors	4	1	1	Bisphenol A
Metabolites	5	1	1	

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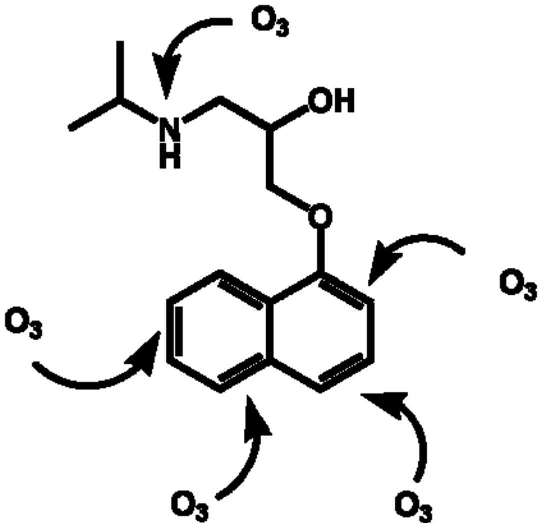
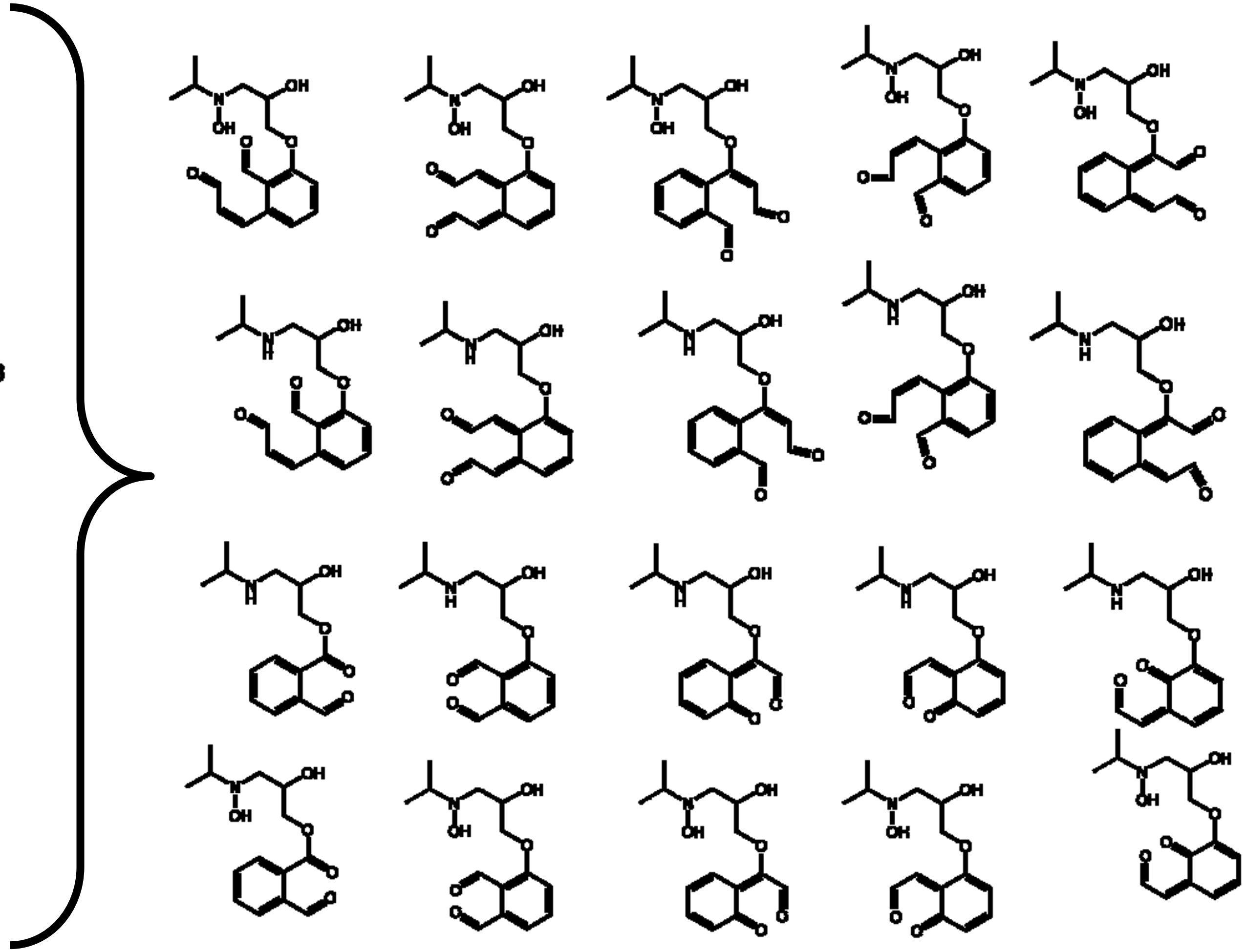
Isomers of propranolol OPs

J. Benner and T. Ternes, AOP5 Conference, Berlin, April 2009

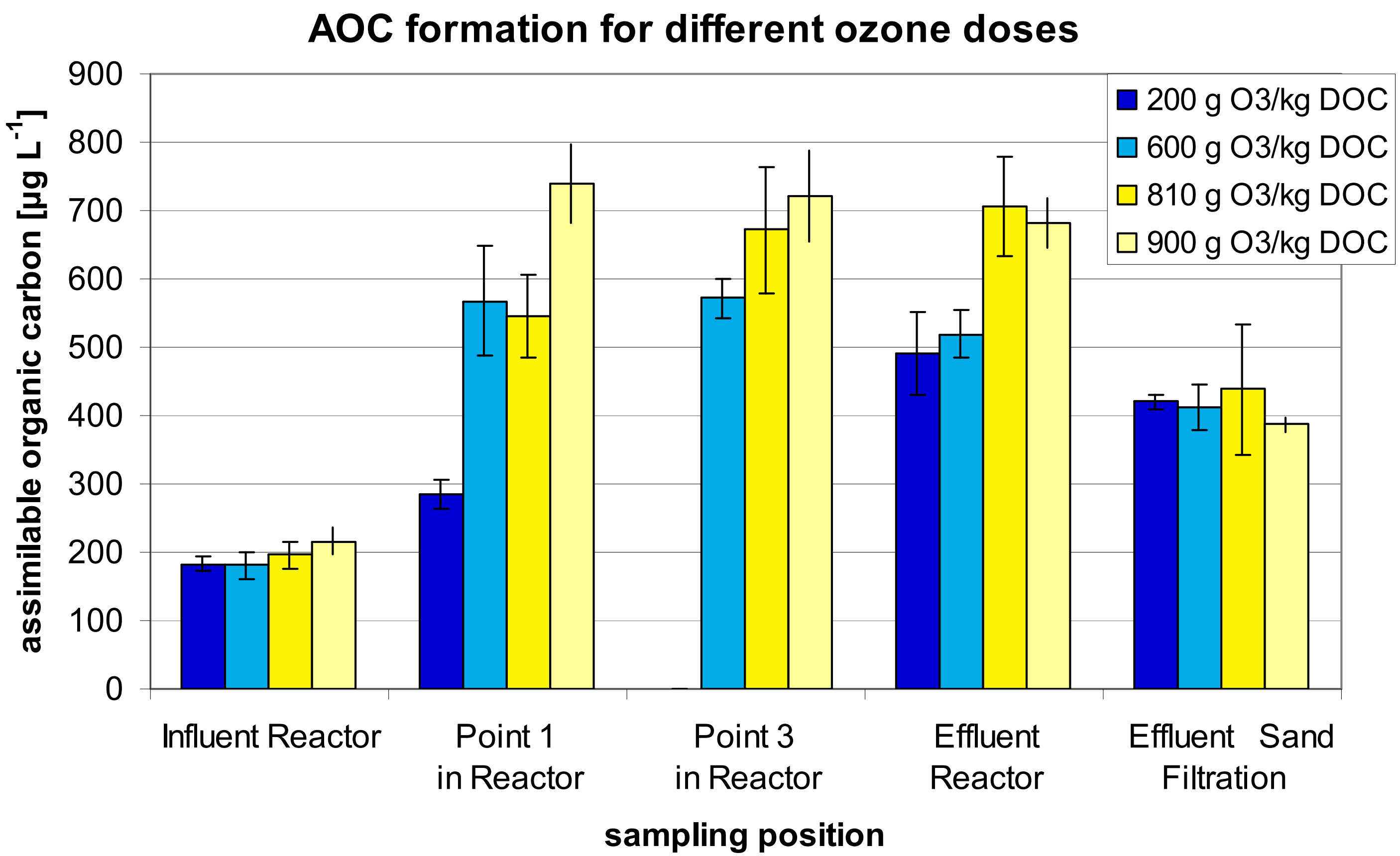


Propranolol



Some compounds with aldehyde moieties interact with DNA and show therefore genotoxic and carcinogenic properties

AOC formation in the ozone reactor



- **ozonation increases the assimilable organic carbon up to a factor of 3.5**
- **sand filtration decreases it subsequently to twice the influent concentration**

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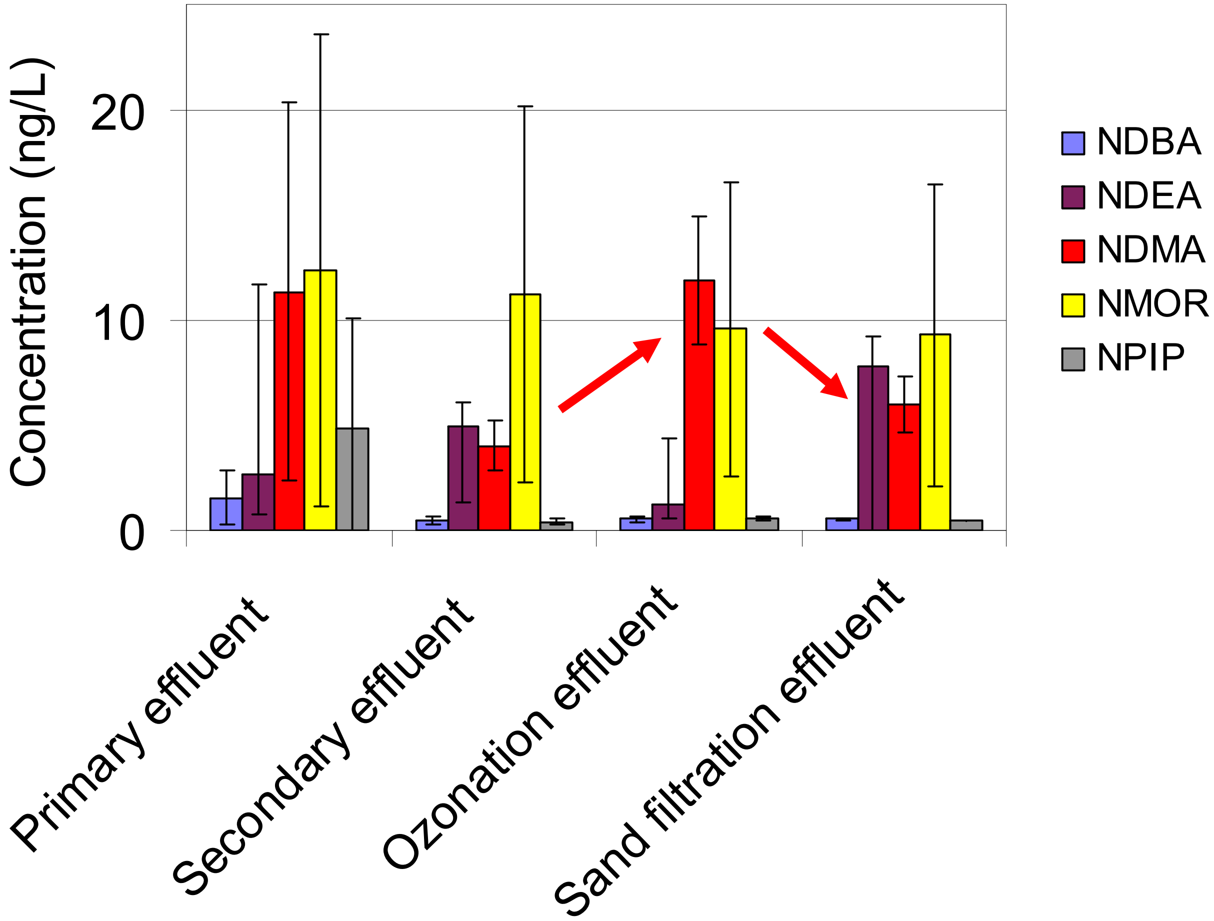
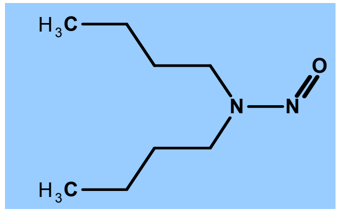
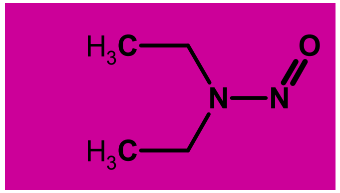
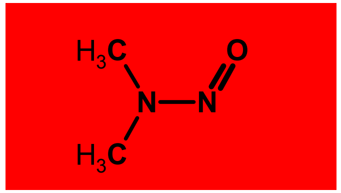
Nitrosamines
- by-products of the ozonation?

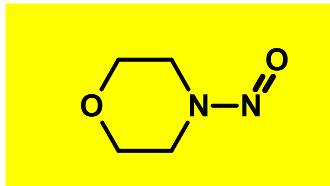
4 sampling compaigns: 400 – 700 g Ozone/kg DOC

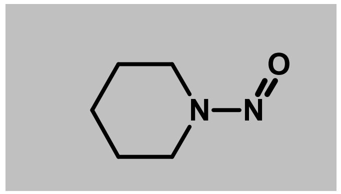




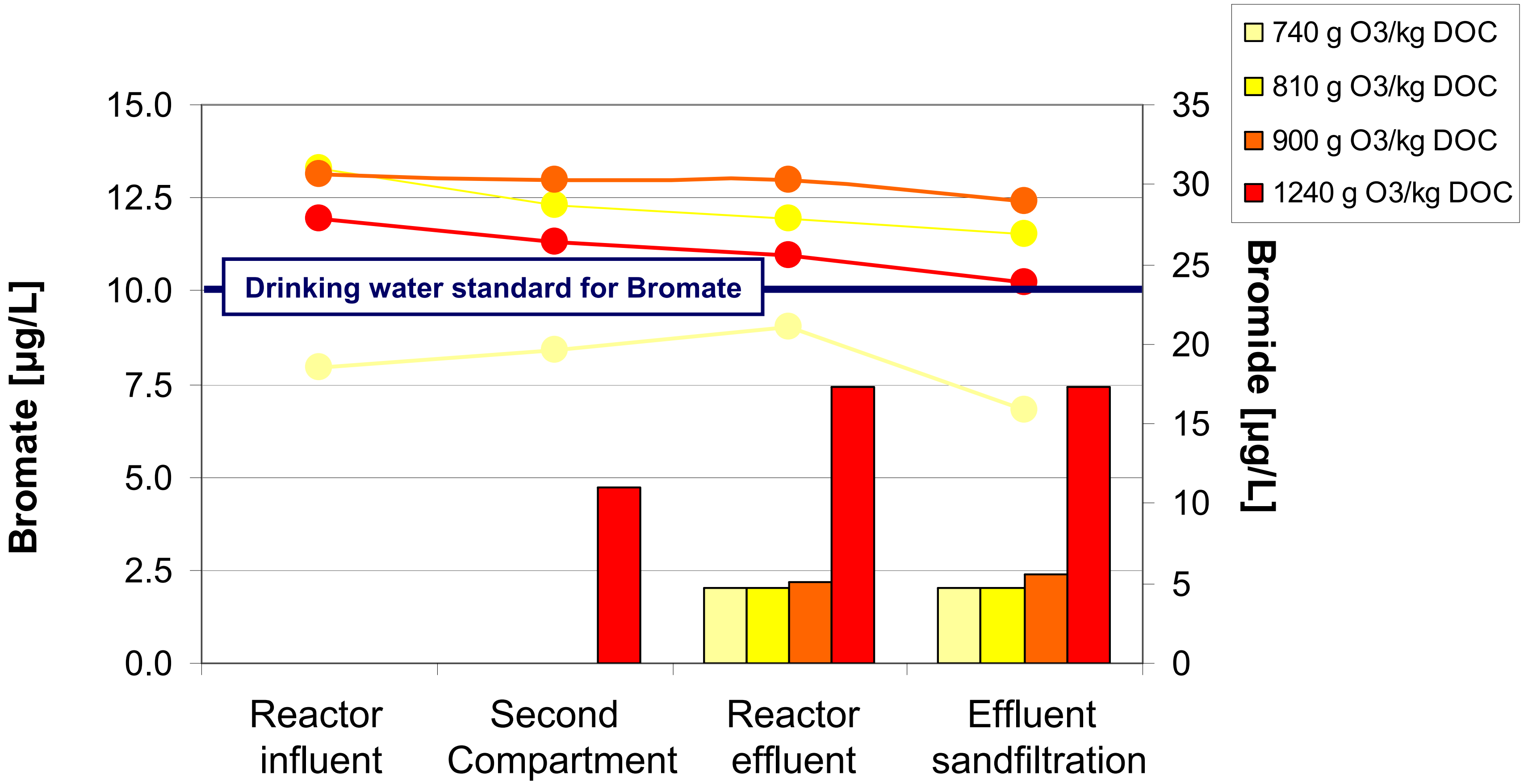








Bromate formation in ozone reactor

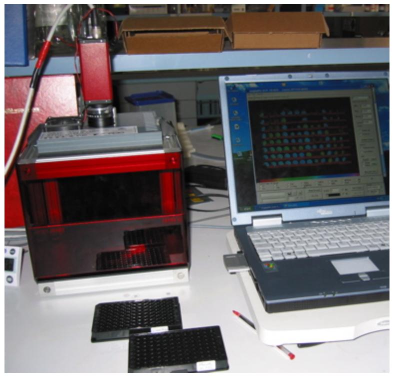


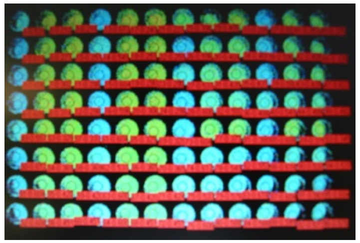
- **Bromate formation only for very high ozone dose (LOQ = 2 µg L^{-1})**
- **Concentration remains even below the drinking water standard!**

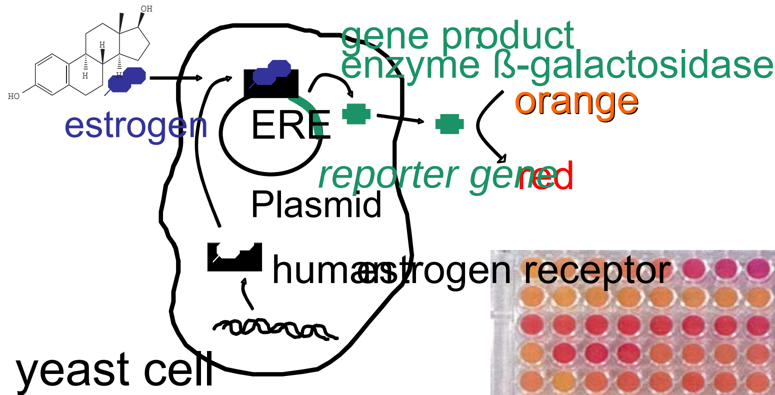
Elimination efficiency – toxic effects

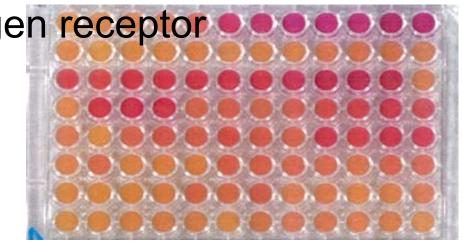
Testbattery

➢Bioluminescence test	non-specific toxicity
➢Algae test	inhibition of photosynthesis
➢Acetylcholinesterase test	neurotoxicity
➢Yeast estrogen screen (YES)	endocrine disruption

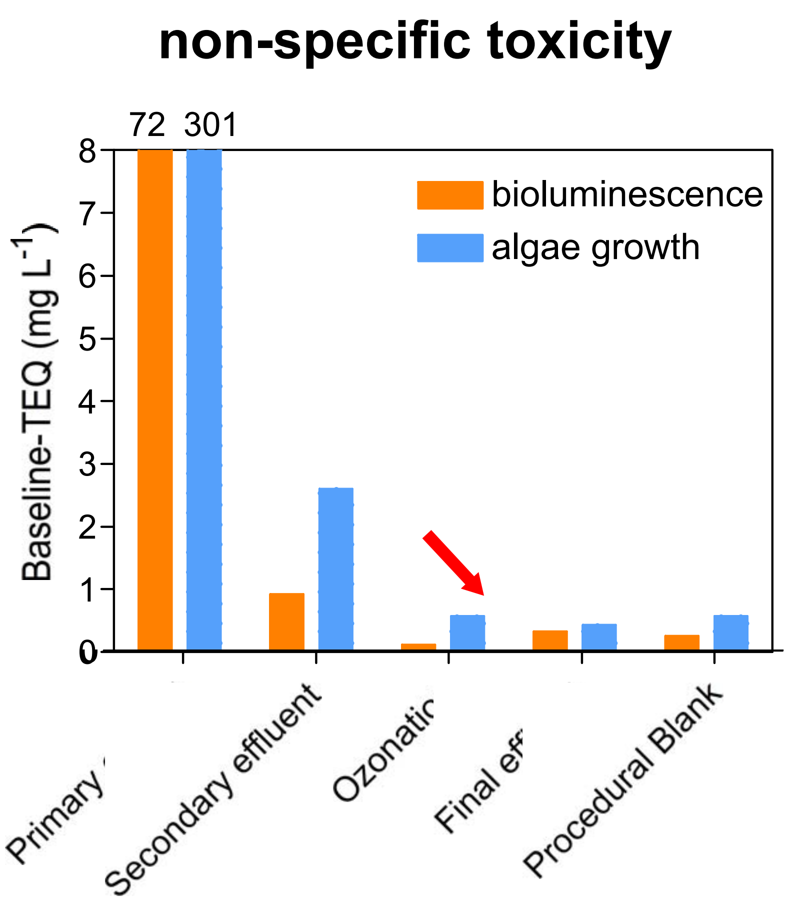


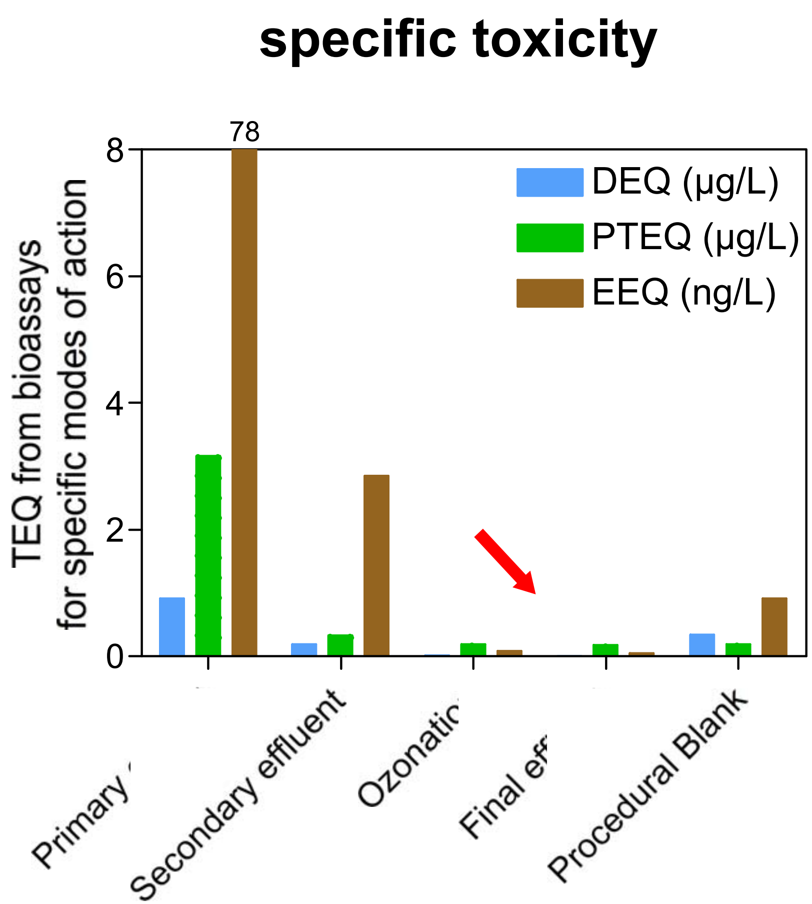






Elimination efficiency – toxic effects

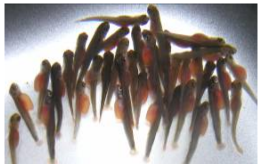




➔ Ozonation leads to a significant reduction of non-specific and specific toxicity

<u>Ozone dose</u>
600 g O_3 / kg DOC

Summary of *in vivo* biotests in EU-Neptune



Organism	Endpoint	FS	O	OS
Chironomus riparius	Mortality	[green]	[green]	[green]
	Emergence	[green]	[green]	[green]
Lumbriculus variegatus	Reproduction	[yellow]	[red]	[yellow]
	Biomass	[yellow]	[red]	[yellow]
Potamopyrgus antipodarum	Reproduction	[yellow]	[yellow]	[yellow]
Oncorhynchus mykiss	Development	[yellow]	[red]	[yellow]
	Biomass	[yellow]	[red]	[yellow]
	Vitellogenin	[red]	[green]	[green]

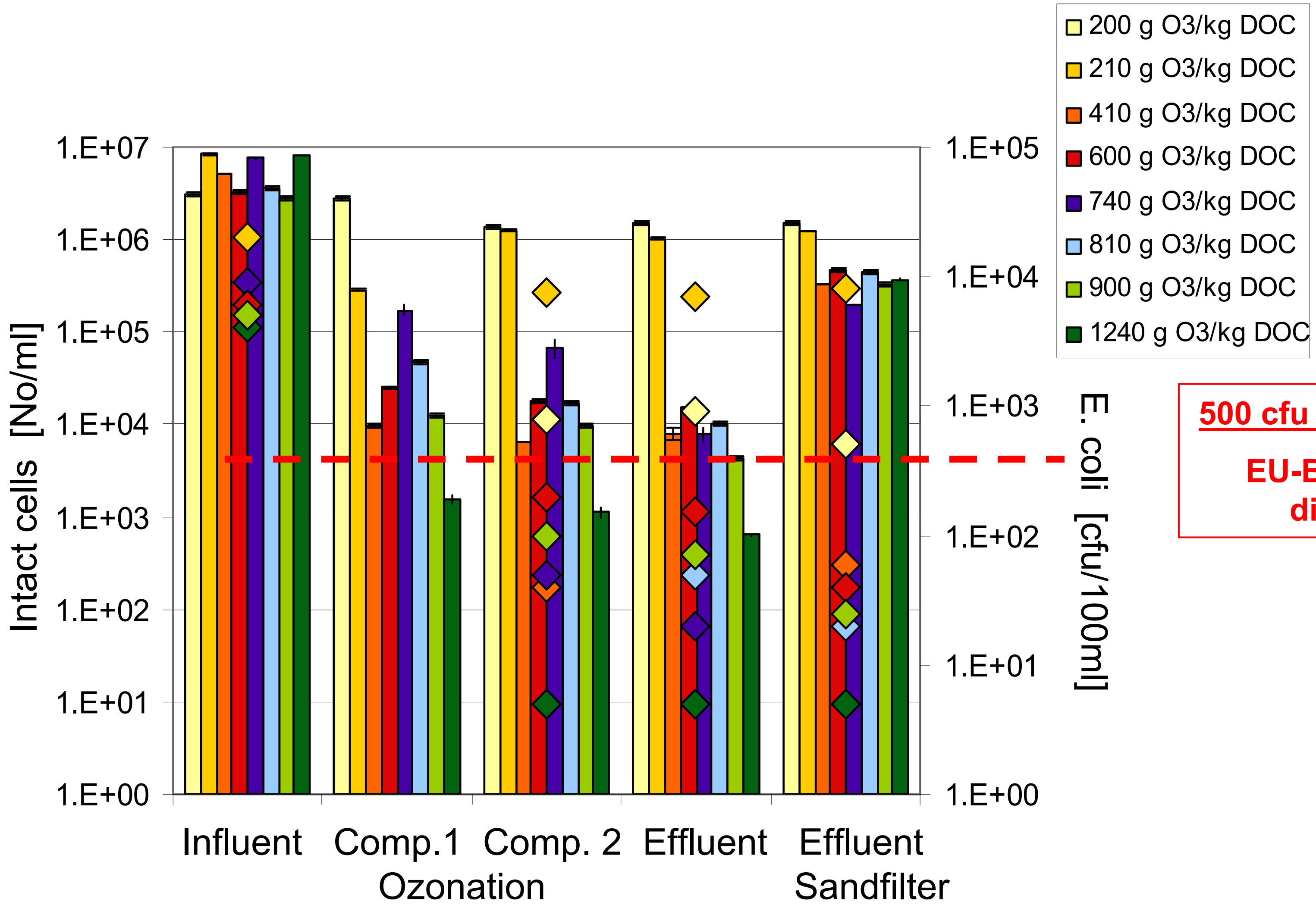
[green] **No effects compared to control**

[yellow] **Significant negative effects compared to control**

[red] **Significant negative effects compared to other treatments**

Source: Axel Magdeburg, Daniel Stalter, Mirco Weil, Thomas Knacker, Jörg Oehlmann unpublished Neptune data

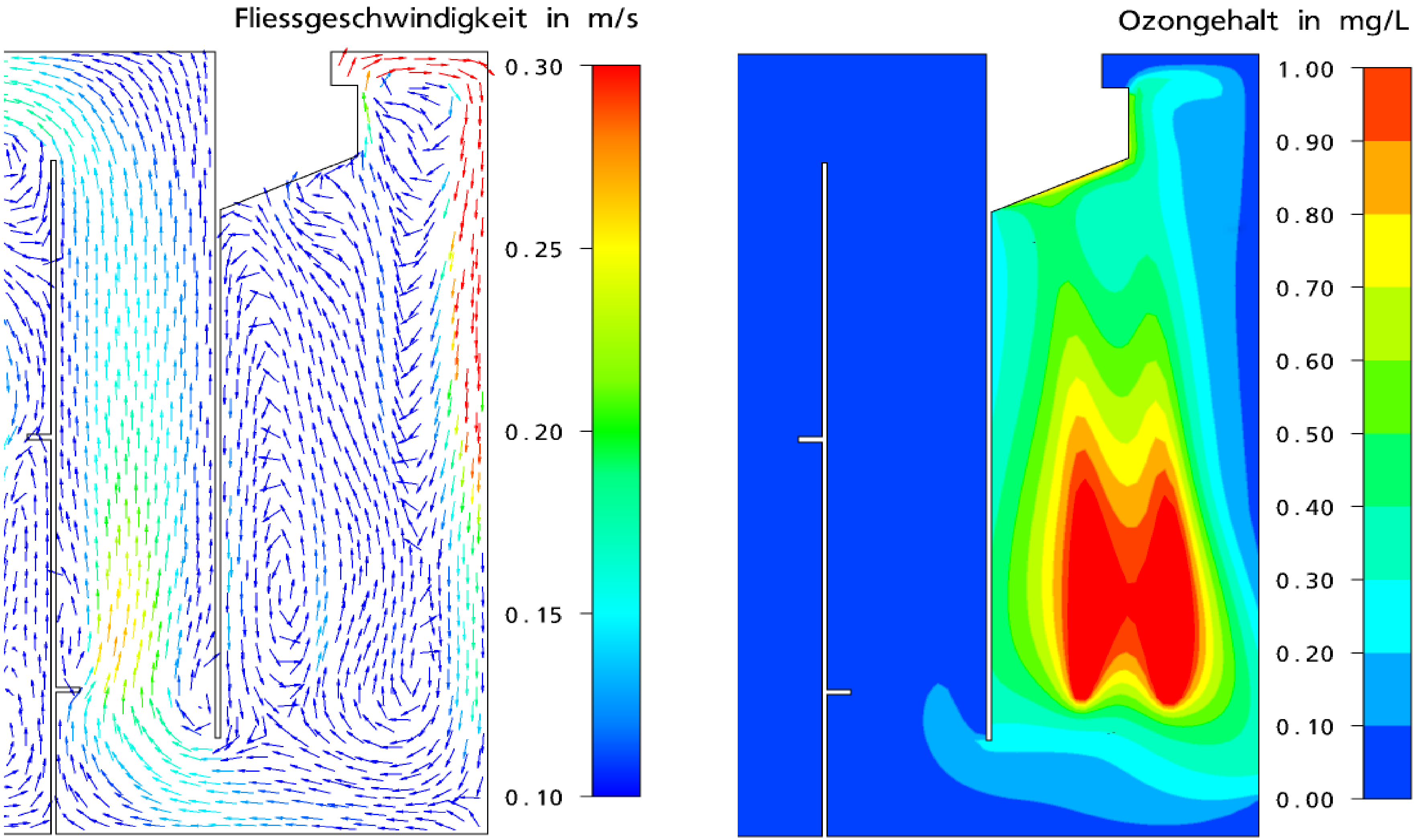
Desinfection efficiency of ozonation



500 cfu E.coli/100 ml

EU-Bath water directive

Short-circuiting in ozonation reactor

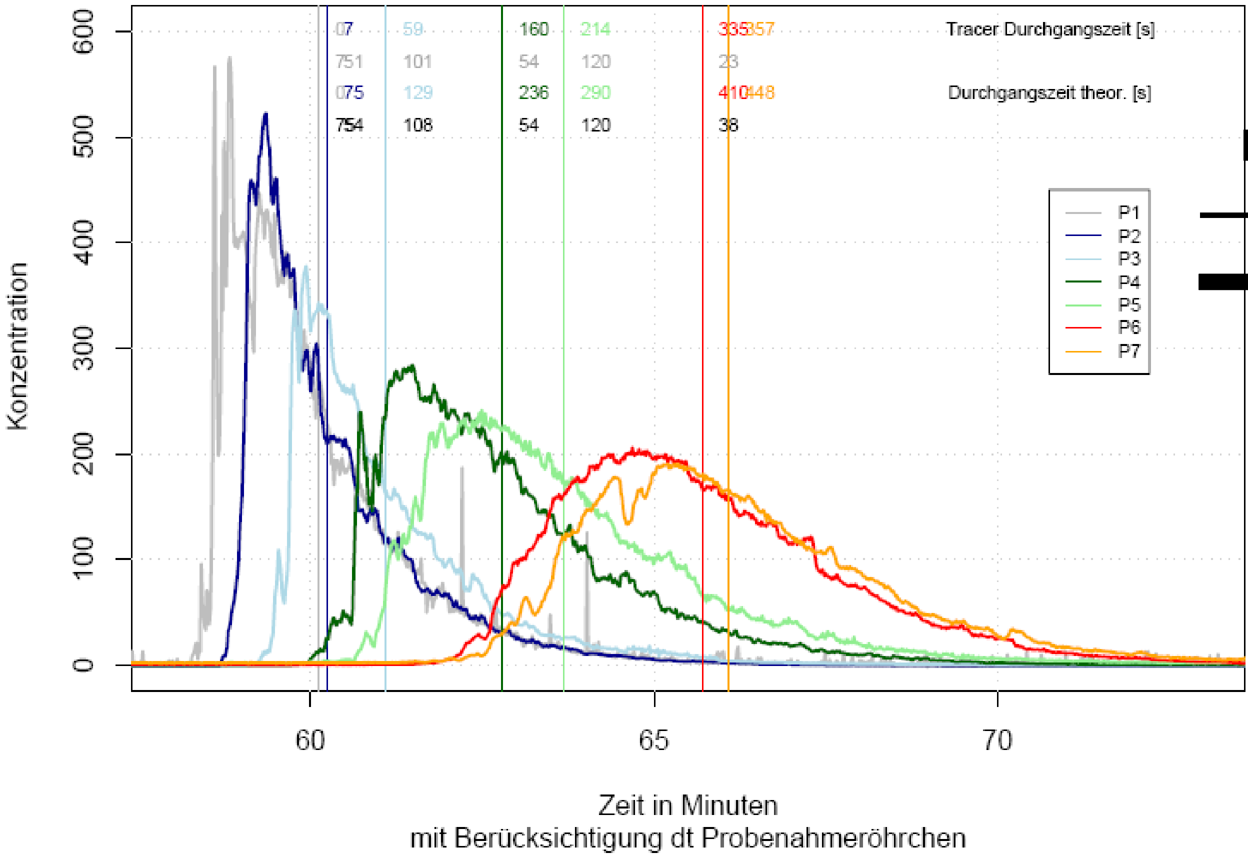


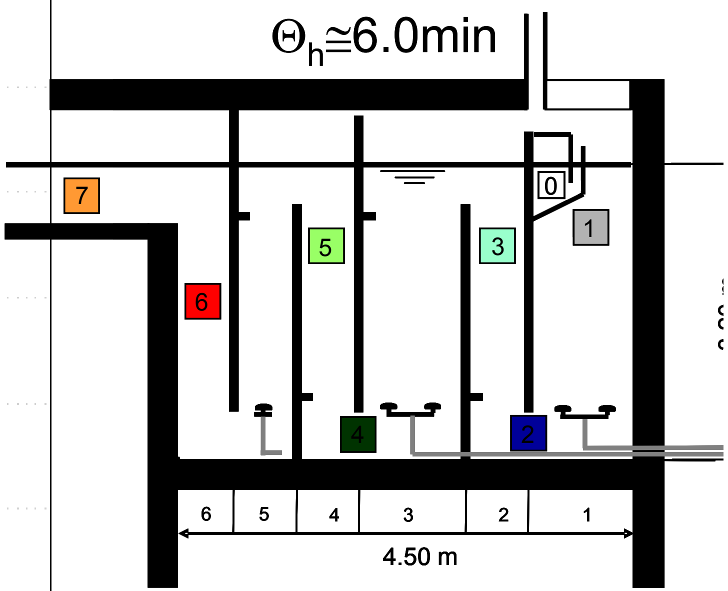
Three-dimensional CFD-simulation for Q = 0.15 m^3 sec^{-1}, and O_3-dosage = 5 g m^{-3}

Markus Gresch, Process Engineering, Eawag

Confirmation with tracer experiments

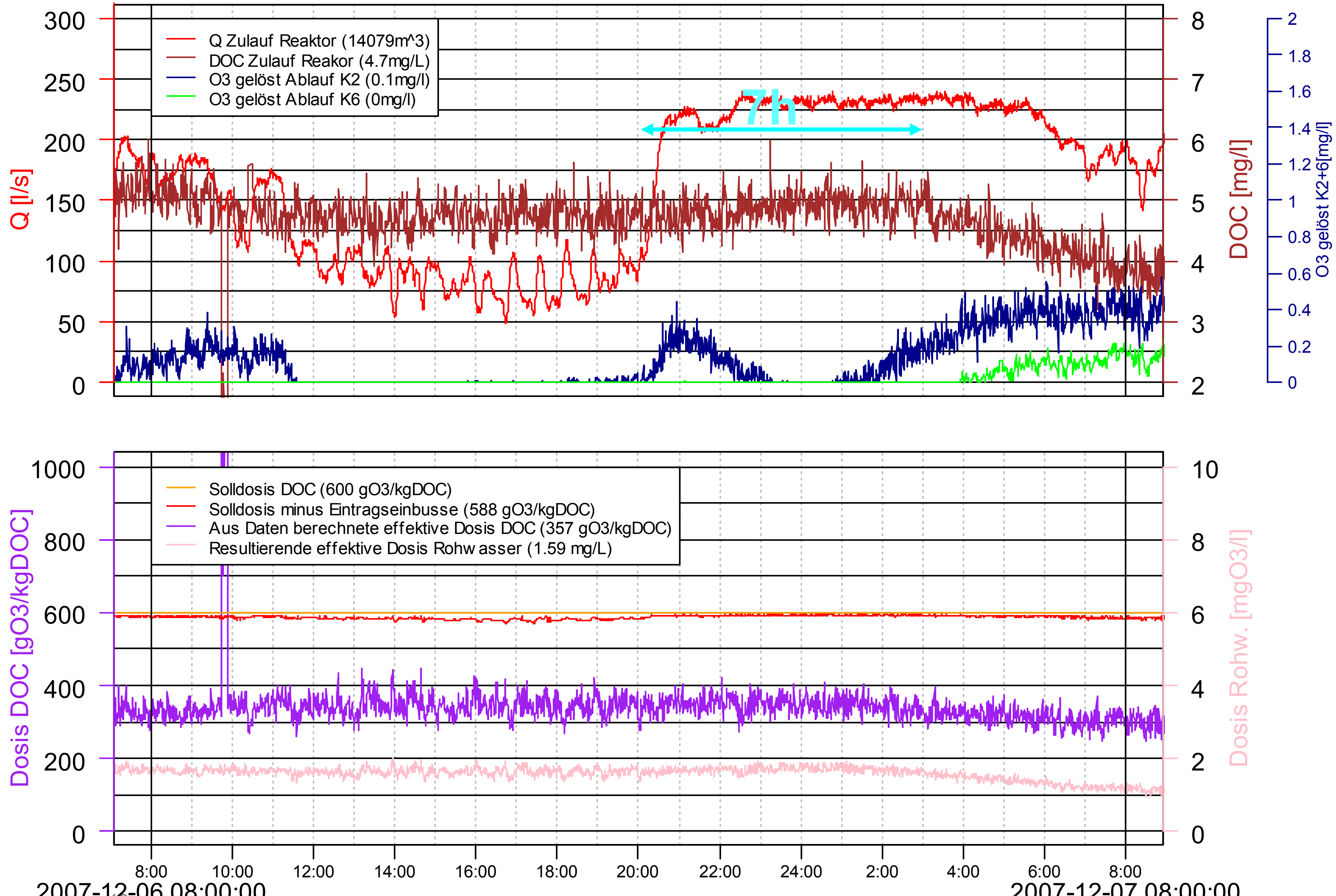
Tt1, Q 80l/s, 15m3/h





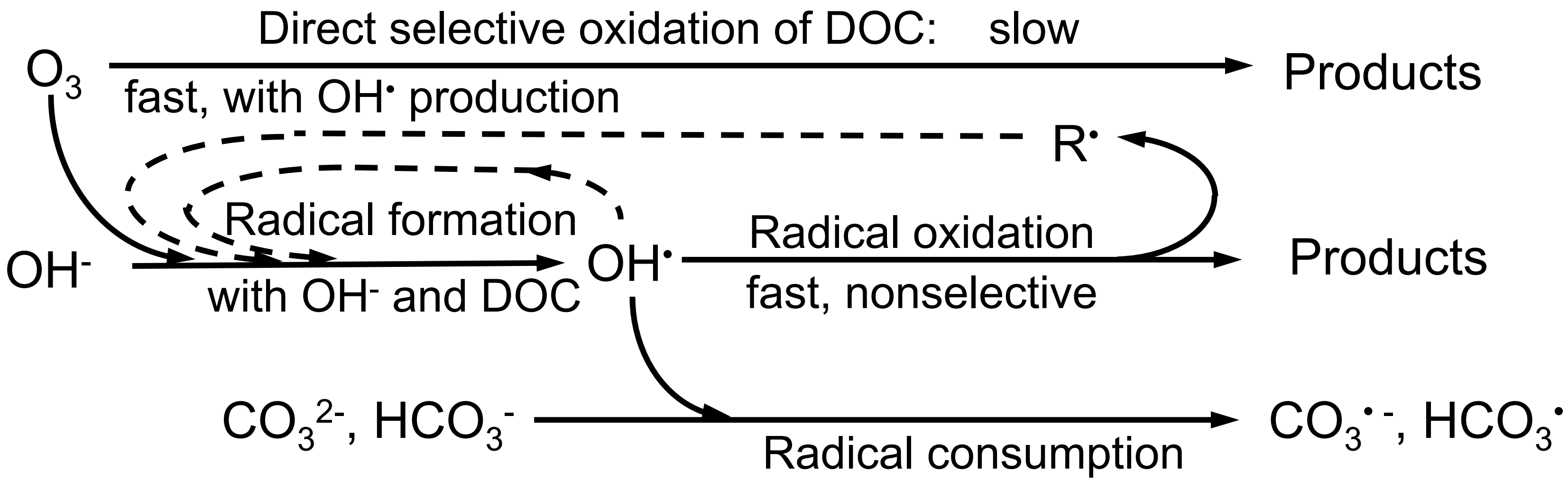
Ozonreaktor
0 = Zulauf Ozonreaktor
7 = Ablauf Ozonreaktor

Behavior during stormwater



Oxidation kinetics with ozone

Ozone decay depends on pH, alcalinity and DOC (Hoigné, 1988)



Oxidation of the micropollutant S with O_3 und OH radicals

$$- d[S]/dt = k_{O3} \cdot [O_3] \cdot [S] + k_{OH} \cdot [^{\bullet}OH] \cdot [S]$$

$< 1 - 10^9\ M^{-1}s^{-1}$
- double bonds
- Activated aromatics
- amines

Dose dependent
low to high conc.
DOC↑ pH↑ $[O_3]$↓

$10^8 - 10^{10}\ M^{-1}s^{-1}$
unspecific

low to very low concentration
DOC↑ alk↑ [OH]↓

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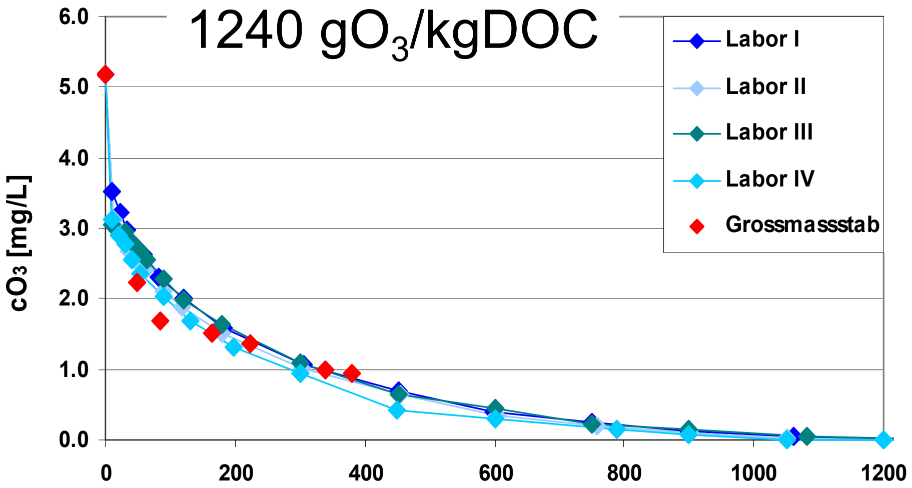
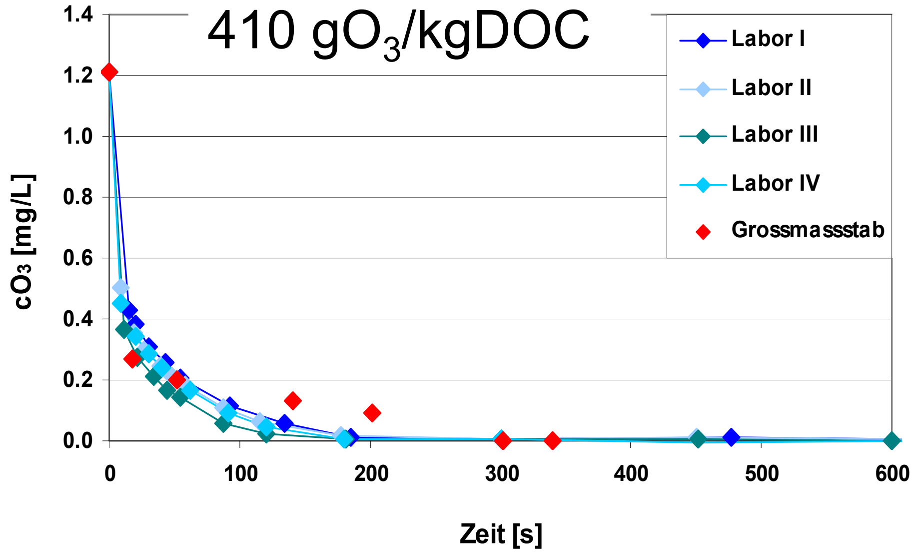
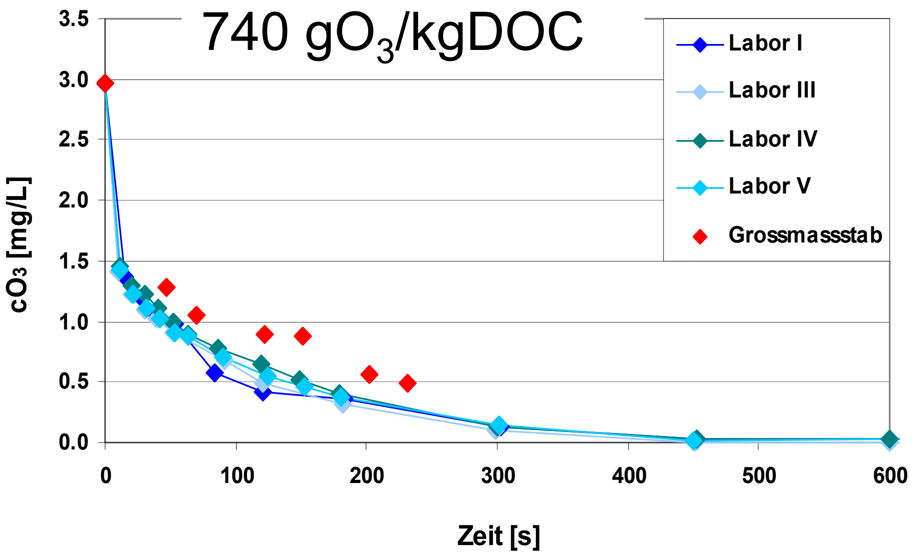
Ozone decay in treated wastewater at 21°C and pH = 7 for







About 1-2 $gO_3\ m^{-3}$ is quickly consumed for $OH^{\bullet}$ radical production due to amino compounds and activated aromatics.
(Diss. ETH No.16266, M. Buffle)

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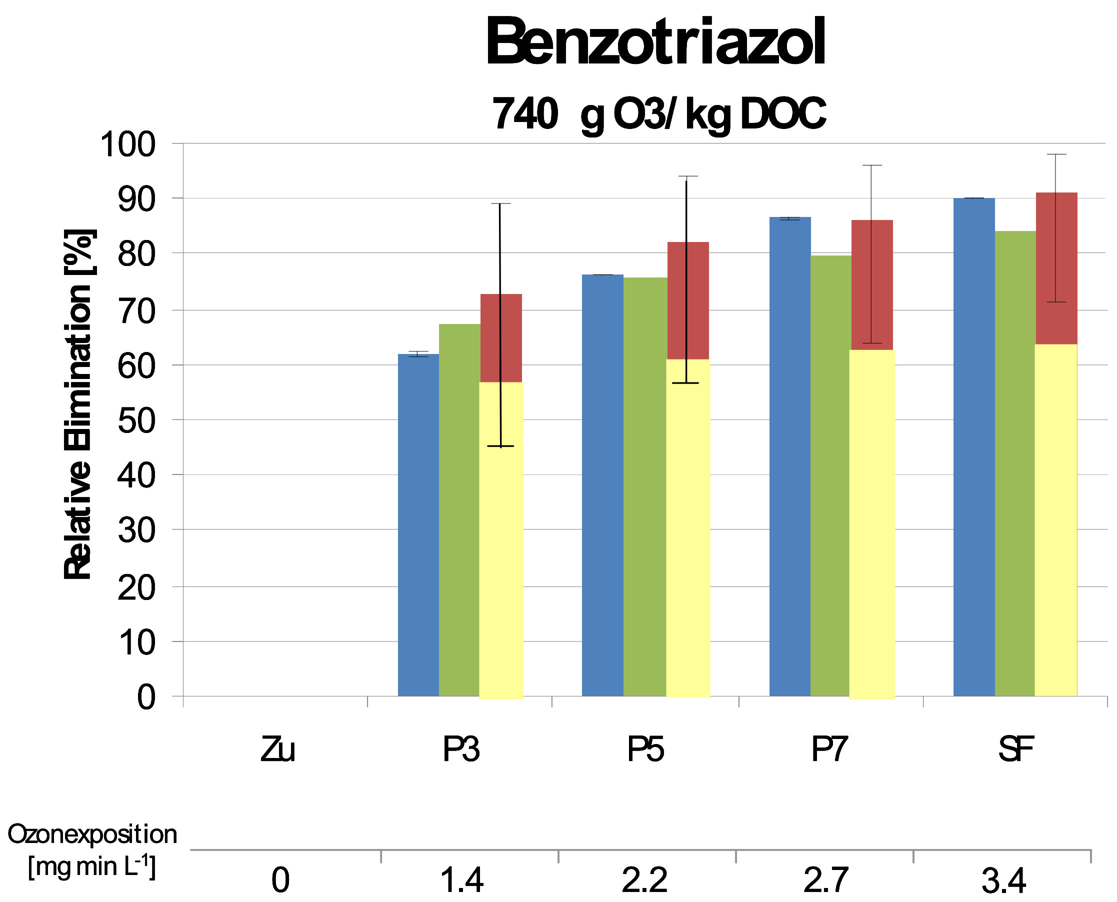
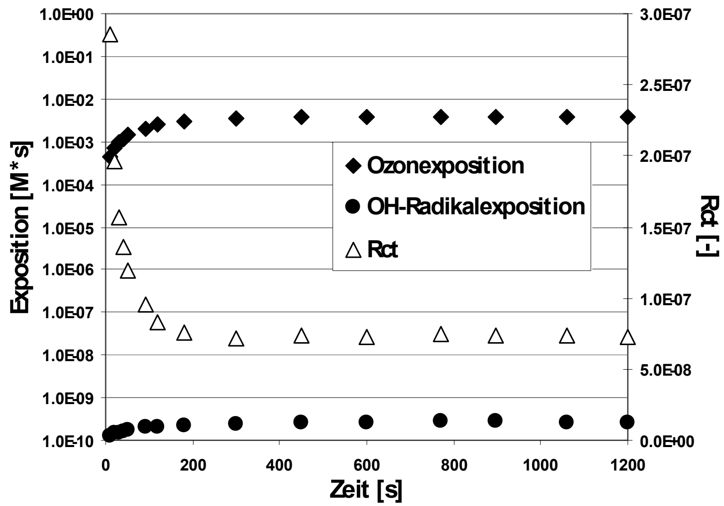
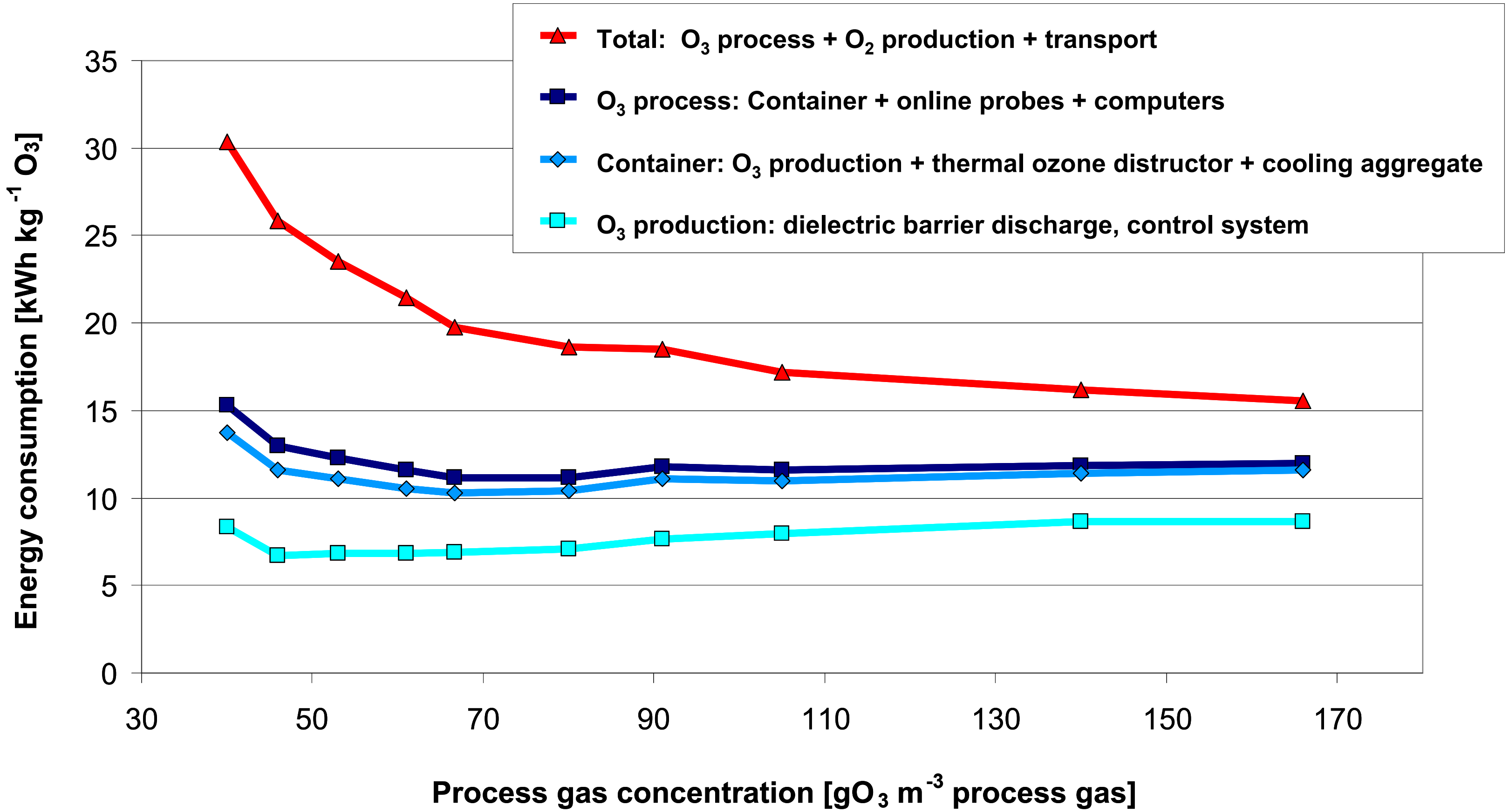
Effect of O_3 and $OH^{\bullet}$





Energy consumption for O_2 and O_3

Energy consumption (15m³ process gas h⁻¹)



Conclusions to ozonation

- Full scale reactor in Regensdorf proves ozonation to be an efficient technique for the elimination of micropollutants and disinfection
- 0.6-0.8 g Ozone/g DOC is sufficient to significantly reduce (80-100%) the selected micropollutants
- Ozonation reduces both specific and non-specific in vitro ecotoxicity
- In-vivo tests are not correlating with elimination of micropollutants (except for vitellogenin production)
- The embryo test with rain bow trouts showed a considerable developmental retardation after ozonation but not after filtration (formation of by-products that are again degraded in filtration?)
- Sandfiltration seems appropriate as an additional barrier for the elimination of products formed during ozonation e.g. NDMA but especially AOC
- Bromate formation is not of concern in wastewater with such low bromide concentrations

Conclusions to ozonation

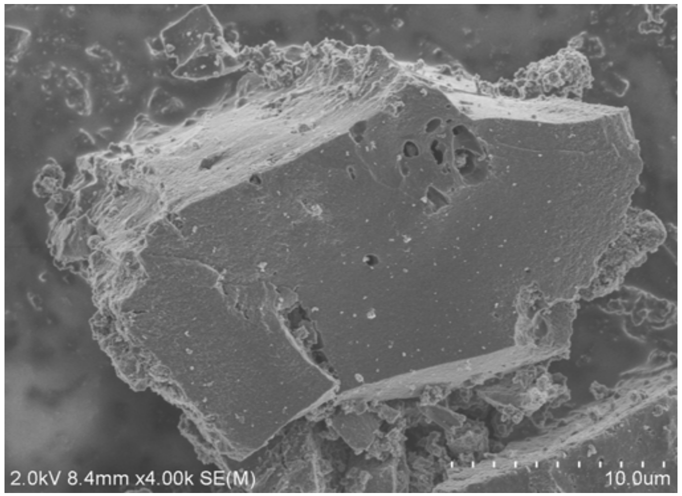
- E.coli is reduced significantly and bathing water quality reached with 0.6 g_{O3}/g_{DOC}, 0.9 g_{O3}/g_{DOC} reaches the requested CT-value of 10 min·mg_{O3}/l
- HRT should be about 20 minutes during dry weather to prevent ozone loss during stormwater (HRT > 5 minutes)
- Short circuiting in the ozonation chamber should be avoided
- Ozone decay increases with increasing pH and DOC
- Energy consumption for 1 kg ozone incl. pure oxygen production and transport to WWTP is about 15-17 kWh
- For 0.8 gO_3/gDOC and 5-10 gDOC m^{-3} wastewater electrical energy consumption is 0.06 - 0.13 kWh m^{-3} (20-40% of nutrient removal WWTP)

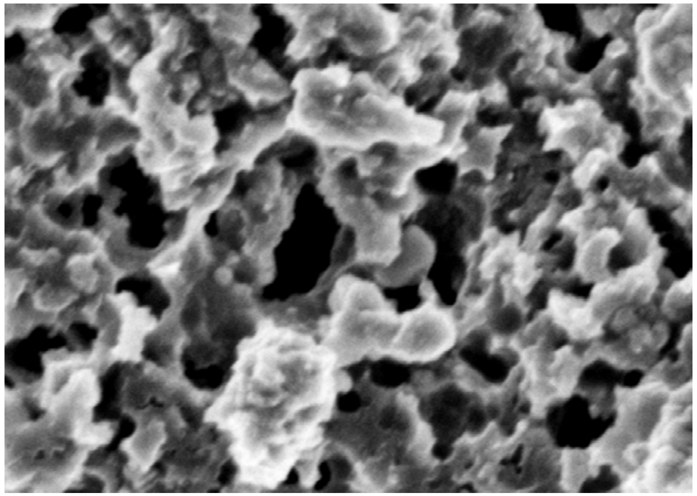
PAC addition processes

- PAC/flocculant addition to a contact/flocculation tank with clarifier for PAC recycling. After the clarifier a filter is needed to reduce PAC loss.
- PAC addition to a reactor with membrane separation.

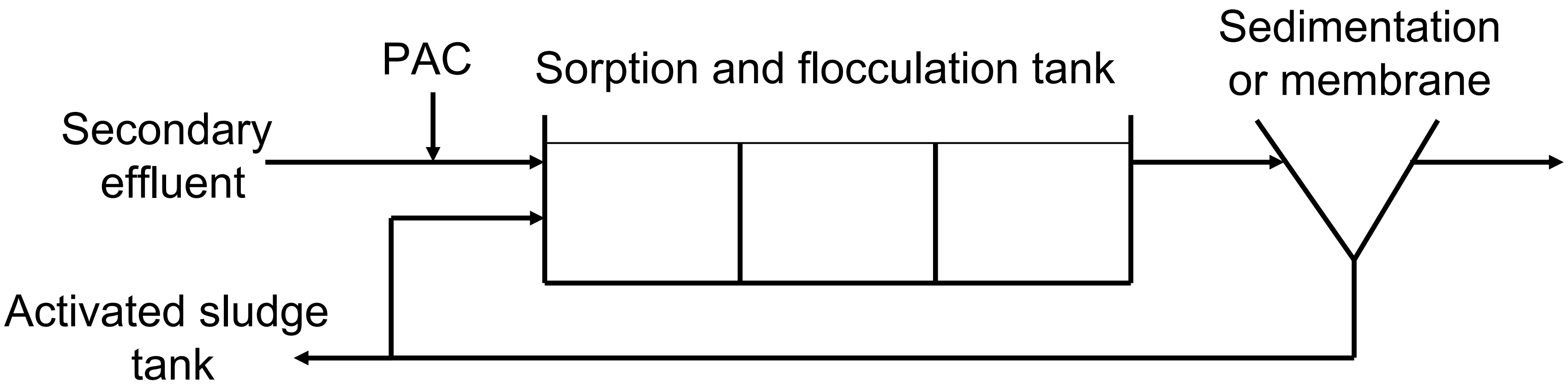
Alternatives:

- PAC addition directly to biology: more PAC, inhibitions?
- PAC addition directly to filtration: PAC loss to effluent?

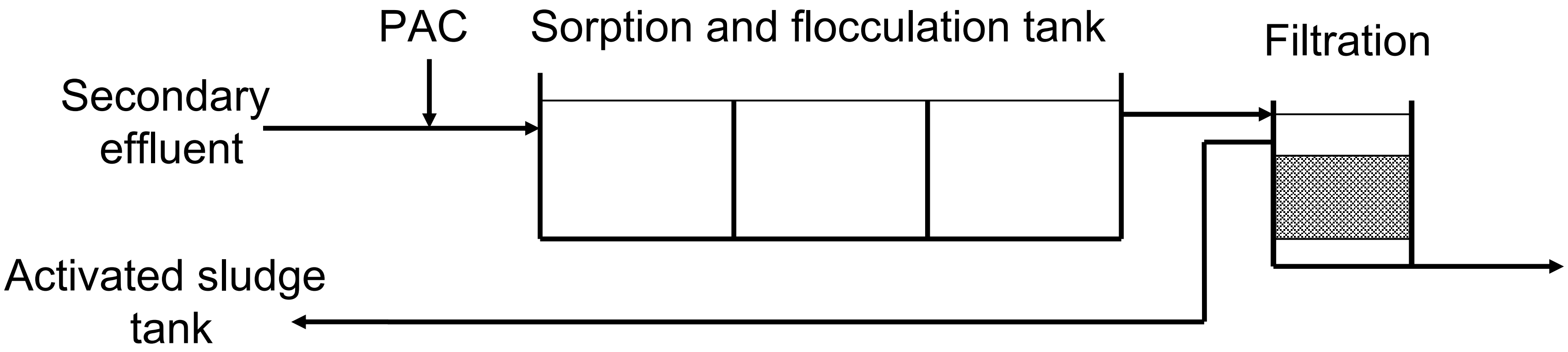




PAC dosage with/without sludge recycling



With sludge recycling: $SA_{PAC} >> HRT$



Without sludge recycling: $SA_{PAC} > HRT$

Micropollutant Sorption Model

Freundlich Isotherm: $C_S = K_F \cdot C_W^{1/n}$ with $n = 1 \ldots 4$

Sorption kinetics: $r_{sorb} = k_s \cdot (C_W - (C_S/K_F)^n) \cdot PAC_{tank}$

Example: PAC_{dos} = 10 mg/l, C_{in} = 1 µg/l

K_F = 0.5 l/mgPAC,

n = > 1, sorption decreases with increasing micropollutant concentration

k_S = 0.1 l/mg$_{PAC}$/h, $k = k_S \cdot PAC_{tank}$

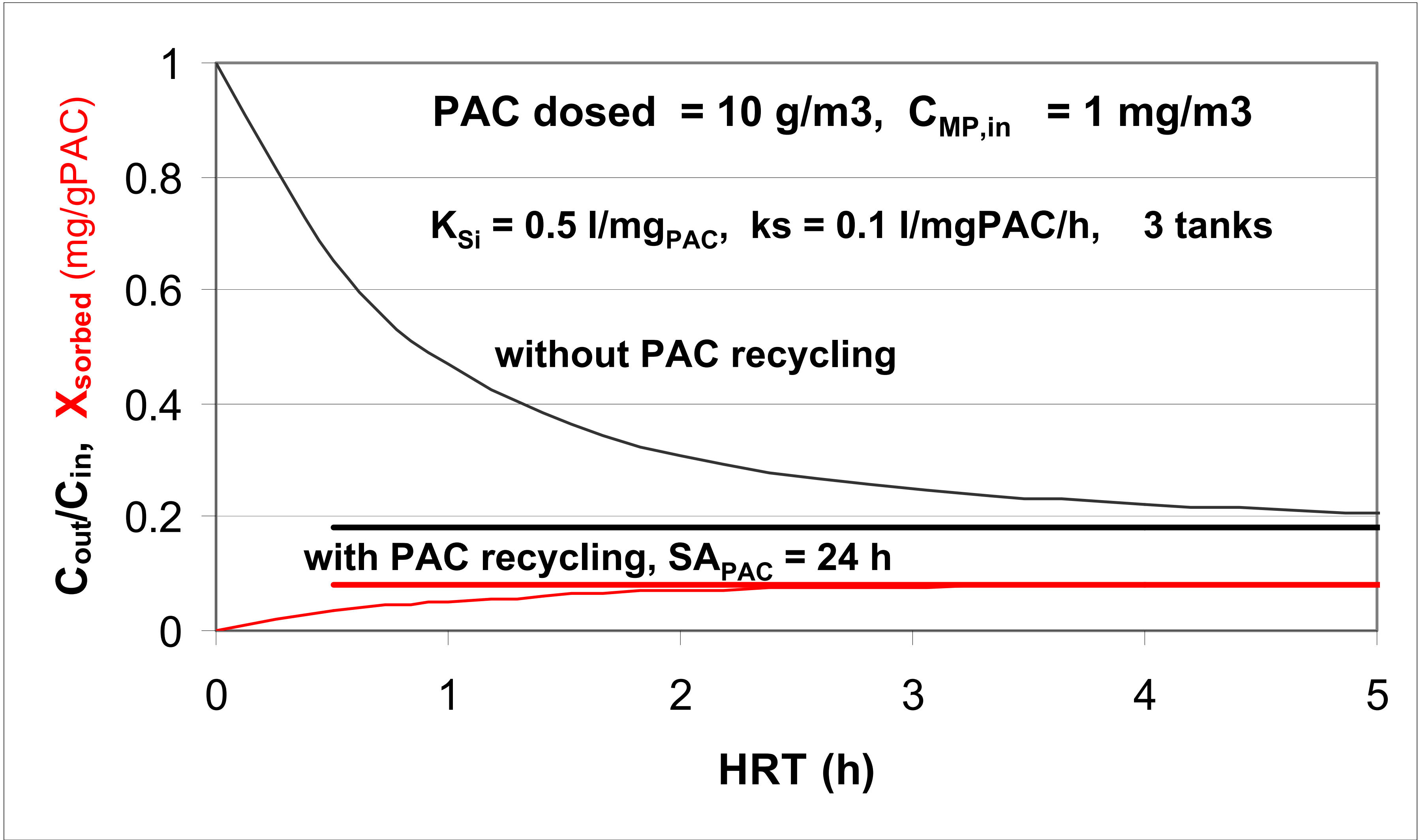
SA_{PAC} = 24 h

HRT_{tot} = 0.5 – 5 h

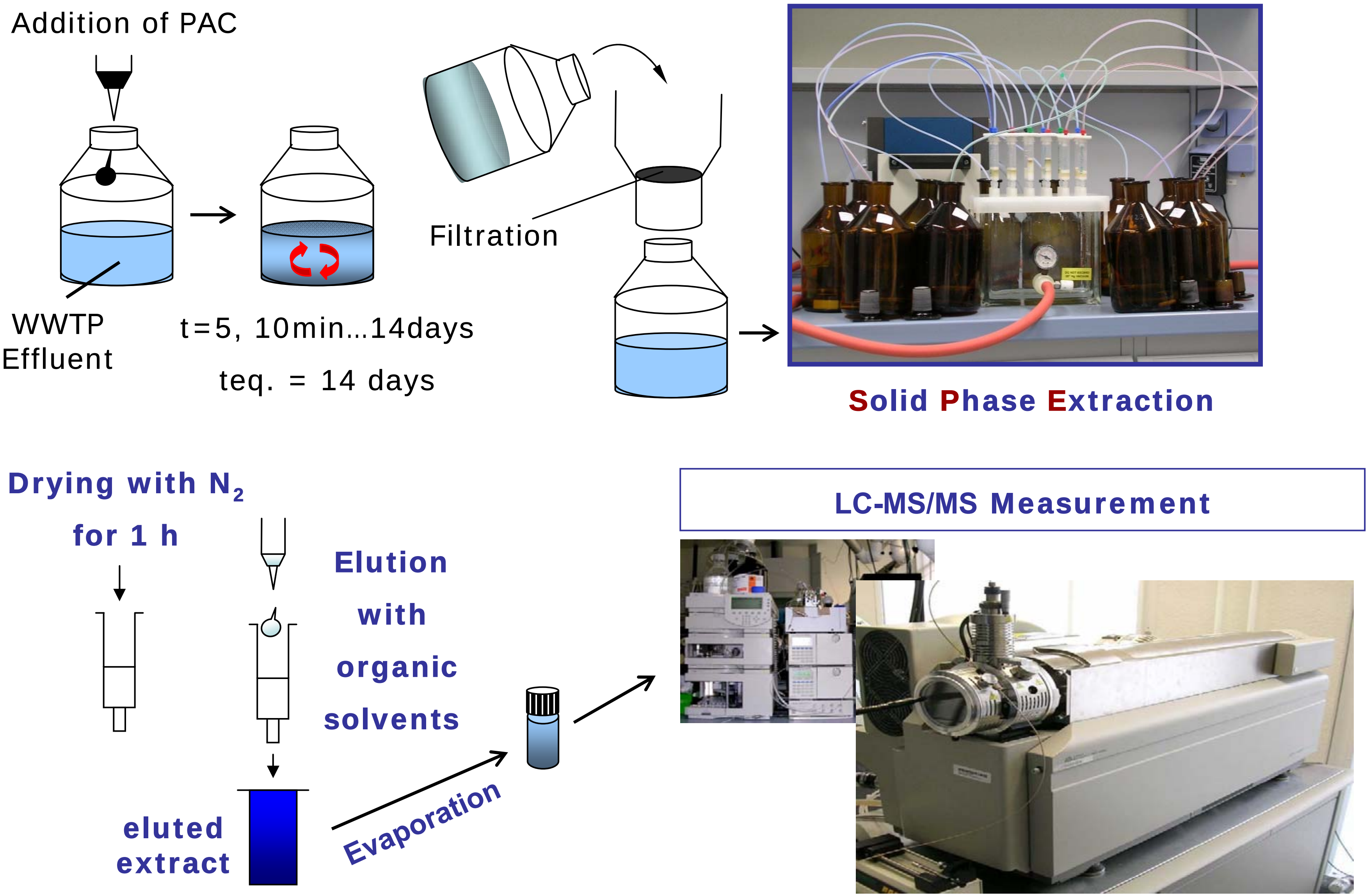
Cascade of 3 tanks

Not included: Competition with DOC: $K_F = K_{F,0} \cdot \exp(-k_{DOC} \cdot SA_{PAC})$

Result of Freundlich Isotherm Model



OECD test 106 – to measure Freundlich Isotherms and sorption kinetics



Test material

Test PAC

Typ:	Norit SAE Super
BET:	1.150 m²/g
Grain size D50:	15 µm
Bulk density:	425 kg/m³
Iodine number:	1.050

Test Effluent

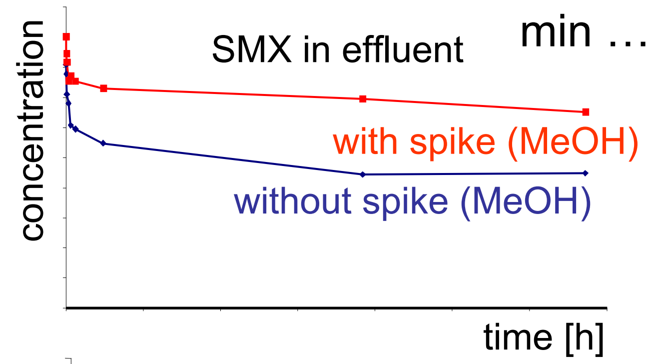
Filtrated STP effluent from WWTP Koblenz

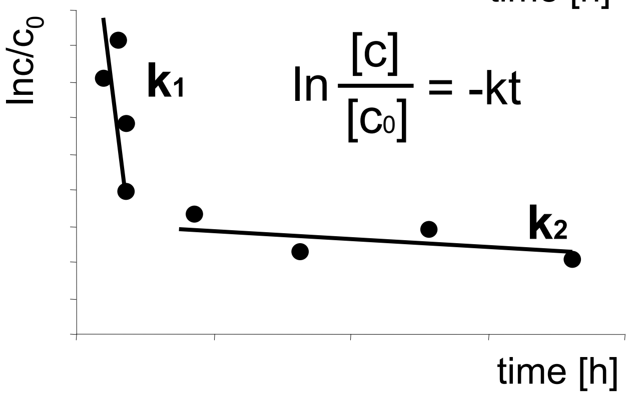
DOC: 12mg/l, pH: 6.8

Sorption test - interpretation

- Sorption kinetics

  PAC = 20mg/L, t = 5,10,30,90,180 min …14 days

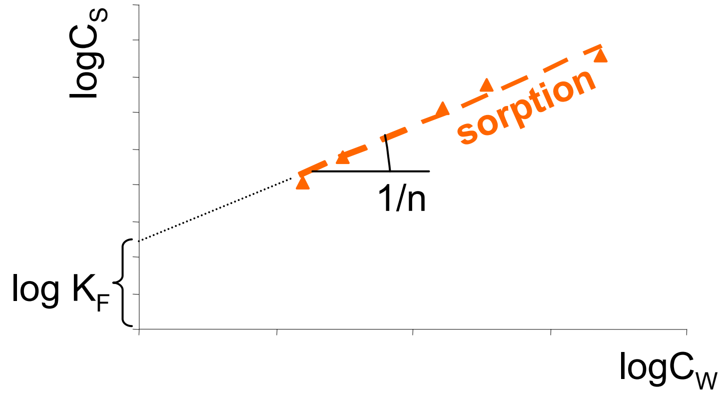




- Sorption isotherms

  PAC = 2,5,10,20,50,200 mg/L

  t = 24h and 14 days



FREUNDLICH:

$$C_S = K_F \cdot C_W^{1/n}$$

$$\log C_s = 1/n \cdot \log C_W + \log K_F$$

$$C_S = (C_{W,0} - C_W)/PAC$$

First evaluation of kinetics

k_1- and k_2 values for selected pharmaceuticals (PAC = 20mg/L)

Compound	with spike (1µg/L)		without spike	
	k_1 [h^{-1}]	k_2 [h^{-1}]	k_1 [h^{-1}]	k_2 [h^{-1}]
Sulfamethoxazole	0.11	0.001	0.11	(0.0004)
Carbamazepine	0.28	0.006	0.59	0.007
Clarithromycin	0.30	0.007	0.69*	1.78*
Erythromycin	0.15	0.007	0.40	0.007
Roxithromycin	0.21	-**	0.55	-**

* only three points in graph

** values for the last points < LOQ

Results from Batch Experiments

Plot of the Freundlich Isotherms: $\log C_S = 1/n \cdot \log C_W + \log K_F$ is yet not possible due to a lack of data points

Isotherms after 24h with additional spike (1µg/L)

Sample Name	ng/L				
	Clarithromycin	Erythromycin	Roxithromycin	Sulfamethoxazole	Carbamazepine
2mg/L	1331	1444	1281	2625	3938
5mg/L	925	1369	1061	2488	2950
10mg/L	445	1108	636	2244	1825
20 mg/L	45	139	94	1561	416
50mg/L	< LOQ	12	< LOQ	519	48
200mg/L	< LOQ	< LOQ	< LOQ	12	19
LOQ	***10***	***10***	***10***	***10***	***10***

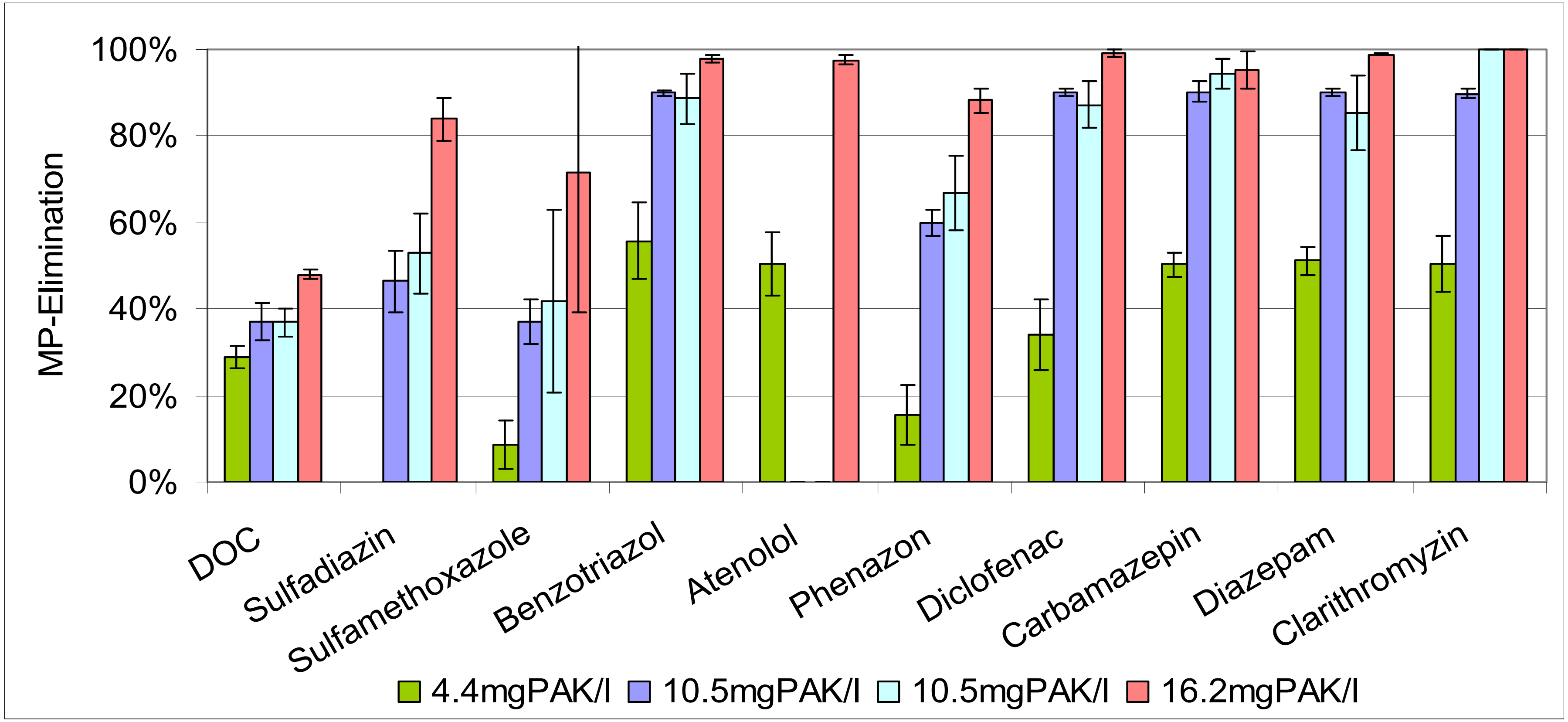
Isotherms after 14 days with additional spike (1µg/L)

Sample Name	ng/L				
	Clarithromycin	Erythromycin	Roxithromycin	Sulfamethoxazole	Carbamazepine
0.2 mg/l	2990	427	2280	2120	2310
0.5 mg/l	2106	408	2290	2006	2310
1 mg/l	3040	553	2980	2100	2144
2 mg/l	2200	383	2019	2013	2270
5 mg/l	1035	366	1191	2130	1735
10 mg/l	269	156	299	1859	710
50 mg/l	< LOQ	< LOQ	< LOQ	147	< LOQ
200 mg/l	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
LOQ	***10***	***10***	***10***	***10***	***10***

Eawag Pilot-scale experiments with SBR

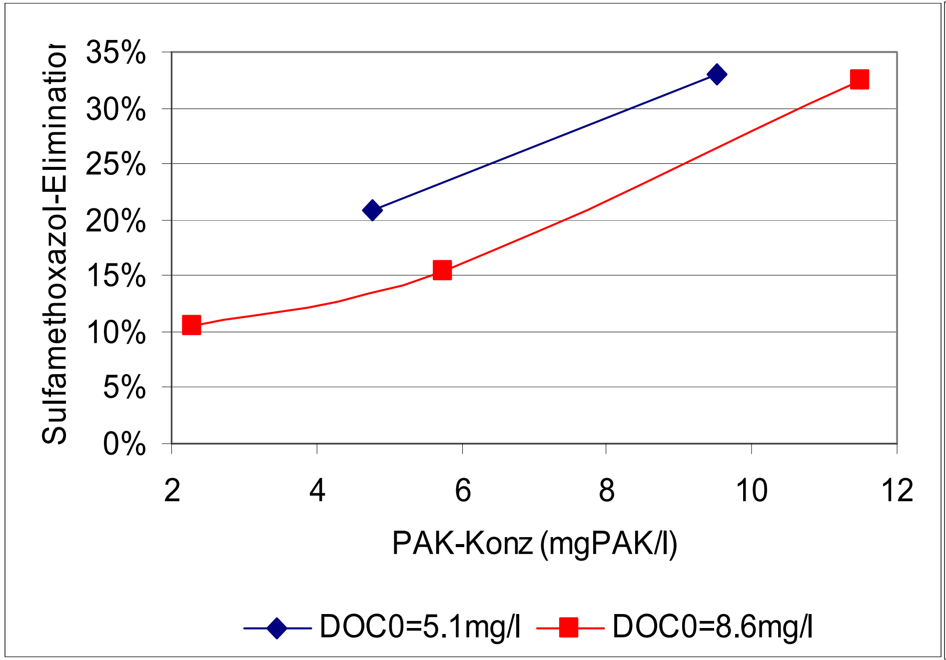
$SRT_{PAK,SBR}$ = 2.4d Mixing phase 30% of SBR cycle: $SRT_{PAK,eff}$ = 0.7d)

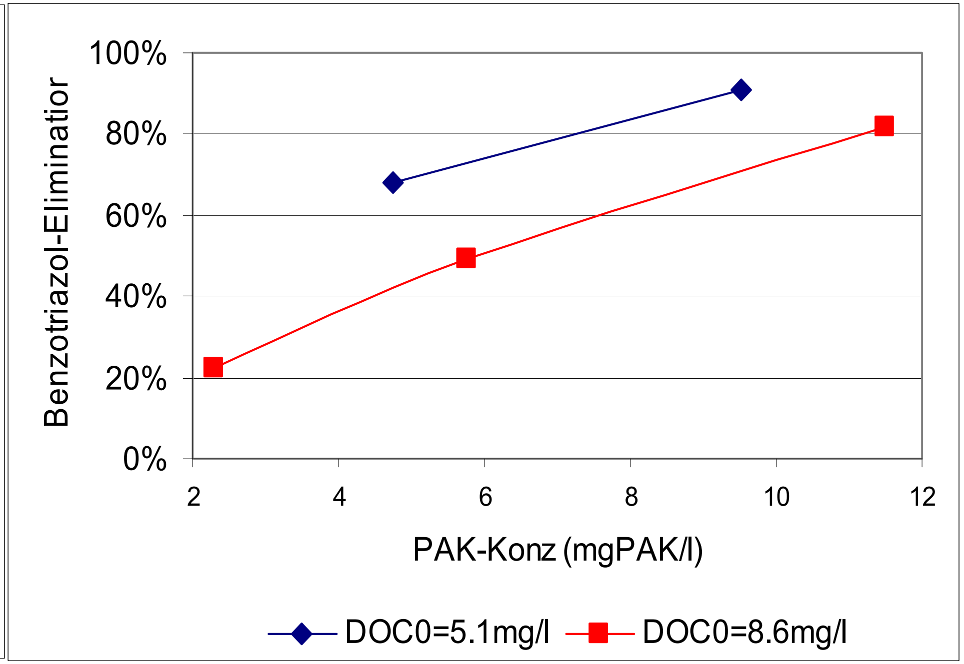
DOC = 6-8 mg/l,   Al dosage = 6-9 mg/l, after PAC dosage



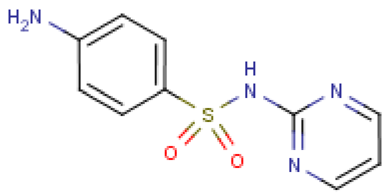
For comparison Carbamazepine elimination by direct dosage of PAC to an activated sludge system (8-12 mgDOC/l): η = 77% for 20 and η = 90% for 40 mgPAC/l,

Eawag Batch experiments: Effect of DOC



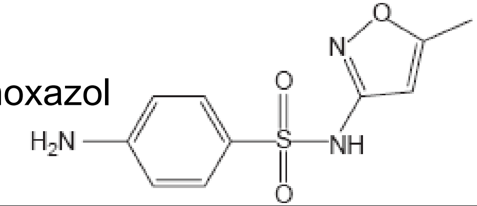


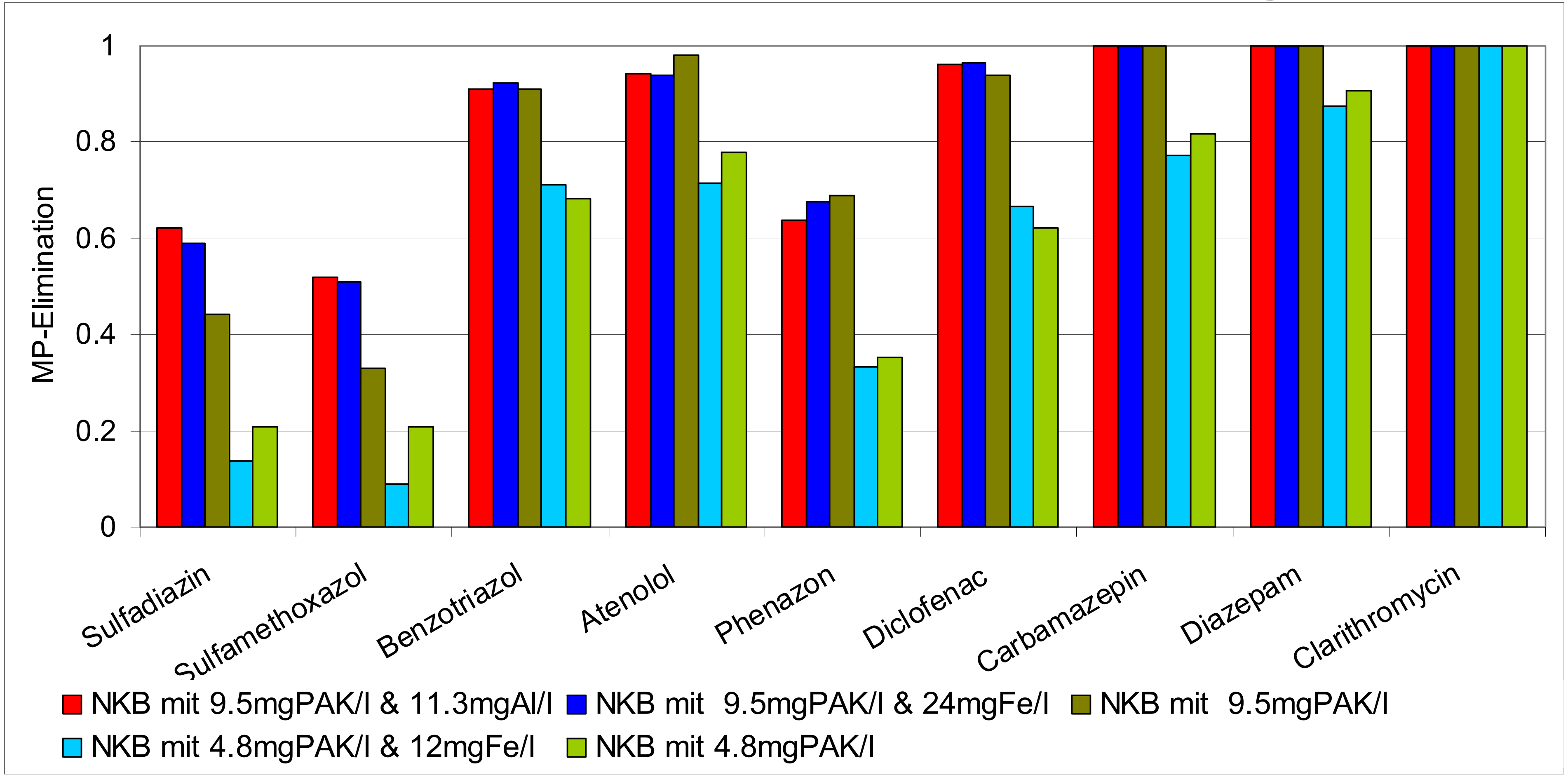
Batch experiments: Effect of flocculant



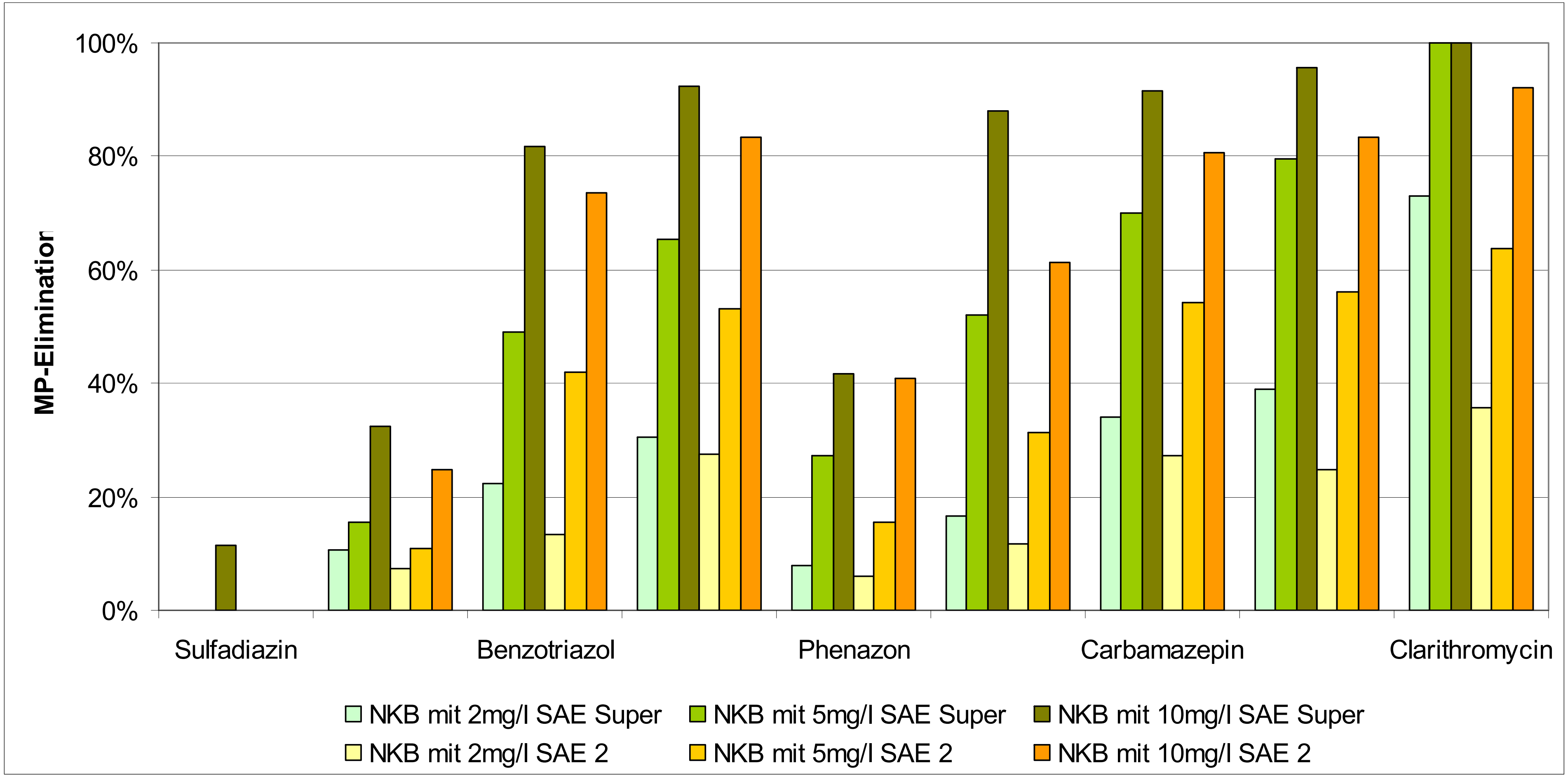
Sulfadiazin

Sulfamethoxazol

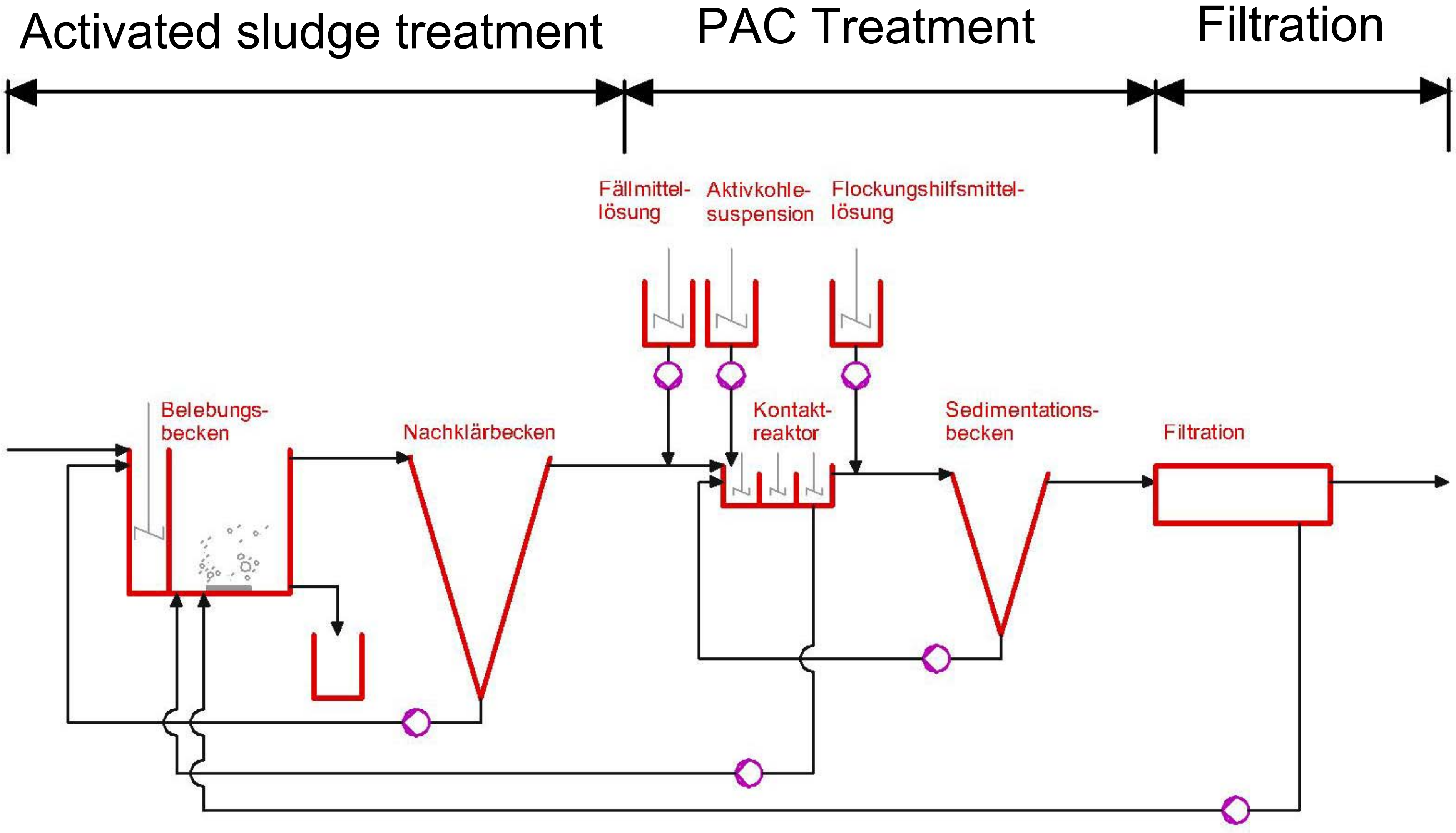




Comparison of Norit SAE super and Norit SAE 2 (recommended for micropollutant removal)

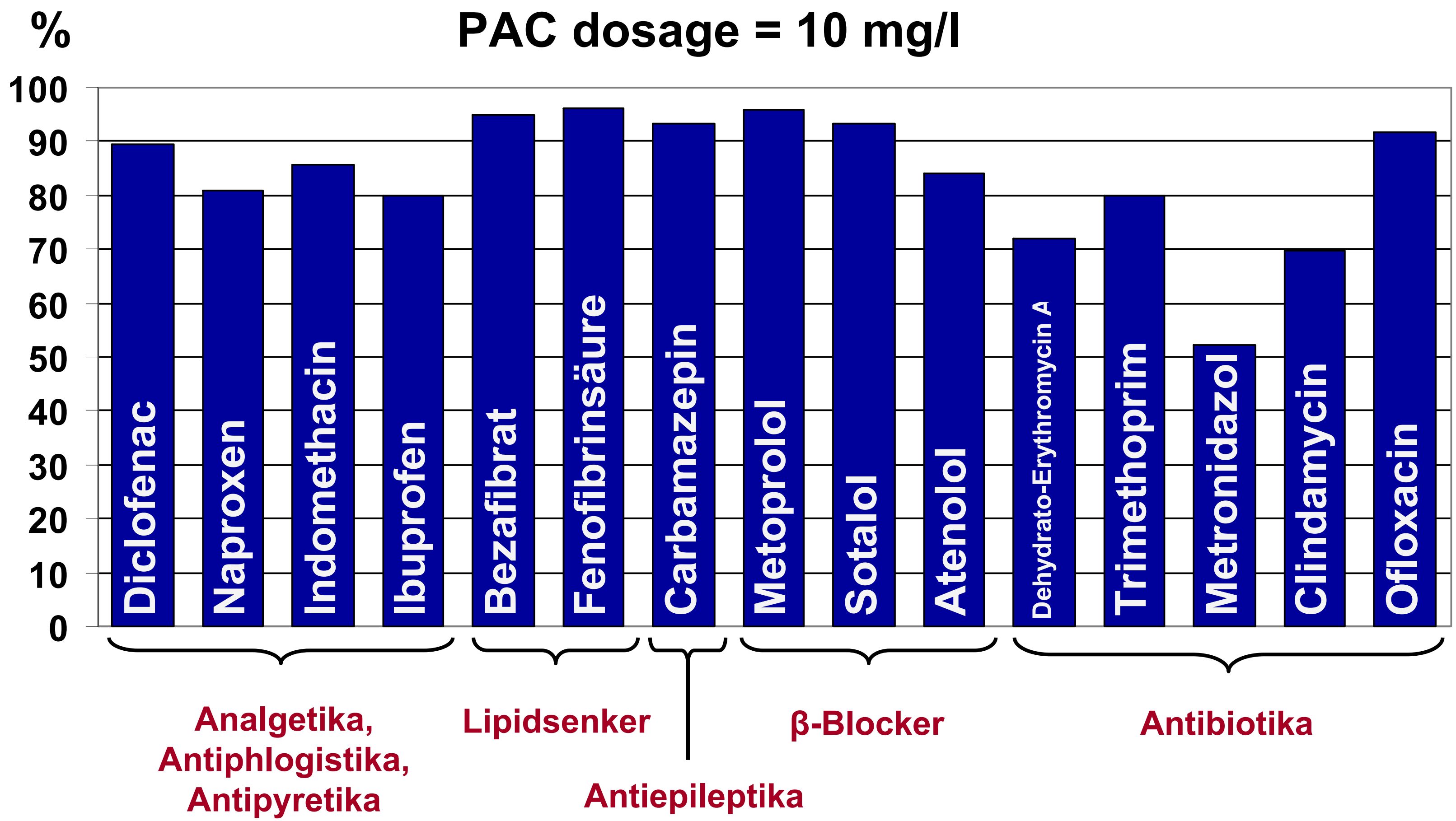


Pilot-scale Experiments at WWTP Ulm



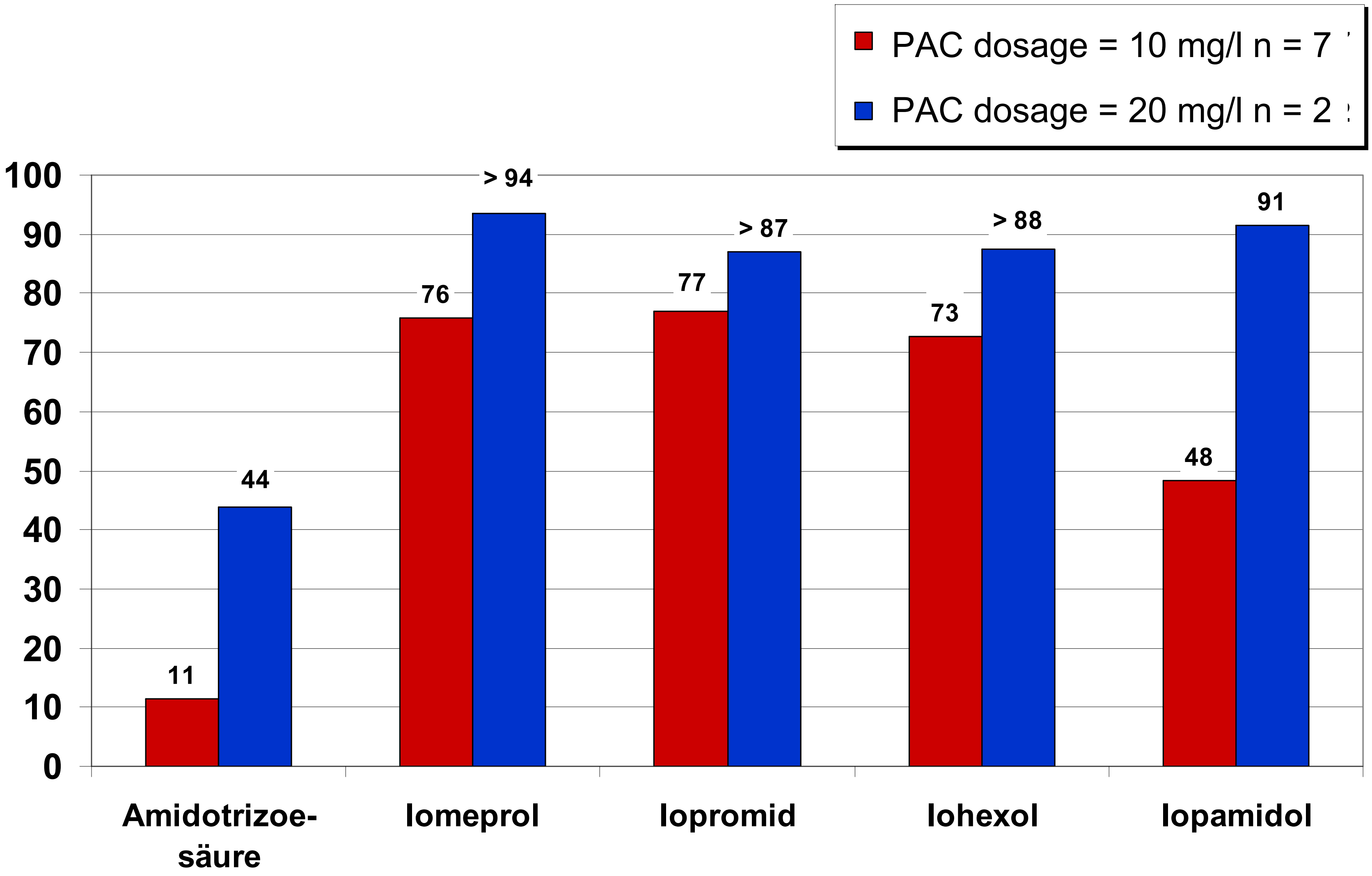
Source: **Hochschule Biberach • WWTP Steinhäule, Ulm**

Elimination of selected Pharmaceuticals



Source: **Hochschule Biberach • WWTP Steinhäule, Ulm**

Elimination of contrast media (%)



Quelle: **Hochschule Biberach • WWTP Steinhäule, Ulm**

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Comparison of elimination efficiency of PAC addition to activated sludge versus post treatment

	Roxithromycin	Diclofenac	Carbamazepine	DHH	Iomeprol
PAC into the effluent (20 mg/l)					
and sandfiltration	67%	58%	89%	54%	37%
and membranefiltration	85%	63%	87%	77%	60%
PAC into the biol. step (20 mg/l)	80%	59%	77%	68%	88%
reference	*57%*	*29%*	-	*29%*	*90%*
Ozonation (0.7 mg O3/mg DOC)	95%	> 99%	> 99%	82%	61%

DOC = 9-11 mgC/l,
Sandfiltration: HRT in contact tank = 1h, PAC in Sandfilter = 1 d
Membranefiltration: PAC in Membrane tank = 6d
Activated sludge: SRT PAC = 20-25 d

EU Project Neptune: M. Schluessener, T.Ternes, G. Fink, BfG; S. Ante, S. Ellerhorst, DPU

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Ozone versus PAC addition
Comparison of energy and cost

Treatment	Dosage [mg L^{-1}]	Electrical energy [kWh m^{-3} ww]	Primary energy [kWh m^{-3} ww]	Annual Costs[c]	
				30'000 p.e. [€ m^{-3} ww]	500'000 p.e. [€ m^{-3} ww]
O_3	3[a] - 10	0.05[b] - 0.15	0.15 - 0.45	0.07[d] - 0.1	0.02[d] - 0.03
O_3 incl. sand filter	3[a] - 10	0.1 - 0.2[e]	0.3 - 0.6	0.15[d] - 0.2	0.05[d] - 0.07
PAC	10 - 20	0.005[f]	0.35 - 0.7[g]	0.15 - 0.2	0.06 - 0.08
PAC incl. sand filter	10 - 20	0.05[e,f]	0.5 - 0.8[g]	0.25 - 0.3	0.09 - 0.11

[a] Ø Operating conditions @ WWTP Regensdorf (5mg DOC L^{-1} ≅ 600g O_3 kg^{-1} DOC)

[b] Measured @ WWTP Regensdorf (production of O_3 (incl. O_2), thermal residual-O_3 destructor, control system, cooling aggregate ≅ 15kWh kg^{-1} O_3)

[c] Detailed, realistic cost study by Hunziker Ltd. (~300L c^{-1} d^{-1} ⇒ 100m^3 c^{-1} y^{-1})

[d] extrapolated from O_3 5-10mg L^{-1}

[e] Sand filter (experience from conventional treatment)

[f] Mixing (experience from conventional treatment)

[g] Primary energy consumption of PAC (no regeneration) 3.5 kg carbon needed for 1 kgPAC: 3.5kgC/kgPAC x 2.7kgCOD/kgC x 14MJ/kgCOD / 3.6MJ/kWh = 35kWh/kgPAC

Conclusions for PAC addition

- PAC dosage 10-20 mg/l depending on background DOC
- 60-90% elimination of pharmaceuticals with 10 mgPAC/l
- Sorption efficiency of PAC reduced with increasing DOC
- DOC reduction 30-40% with 10 mg DOC, increases with increasing flocculant concentration
- Flocculant has no substantial effect on sorption efficiency
- Additional clarifier (HRT = 1 h) for PAC recycling and Filtration needed to prevent PAC loss in effluent
- Increase of sludge production about 5-10%
- About 3 kg primary product needed for 1 kg of PAC => primary energy: 130 mJ/kgPAC = 35 kWh/kgPAC
- Investment and operation costs including filtration are 0.05 – 0.2 € m^{-3} for ozonation and 0.1-0.3 for PAC (5-30€/p/y based on 100 m3 wastewater/p/y)

Thank you for your attention

Acknowledgement:

BAFU, Switzerland

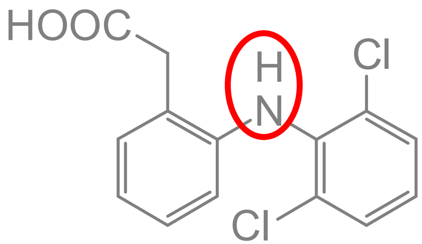
AWEL, Zürich

WEDECO, WABAG, BMG Engineering

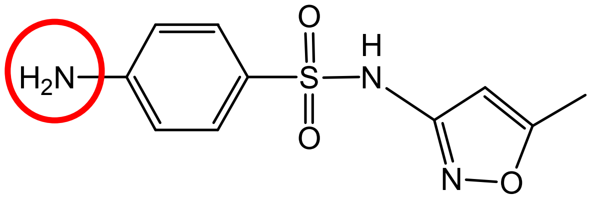
Staff of WWTP Regensdorf

This study was part of the **EU Neptune project** (Contract No 036845, SUSTDEV-2005-3.II.3.2), which was financially supported by grants obtained from the EU Commission within the Energy, Global Change and Ecosystems Program of the Sixth Framework (FP6-2005-Global-4)

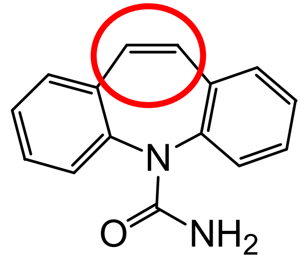
Pharmaceuticals with high ozone reactivity



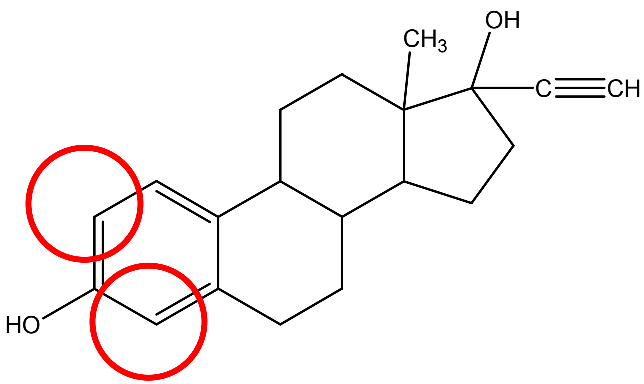
Diclofenac



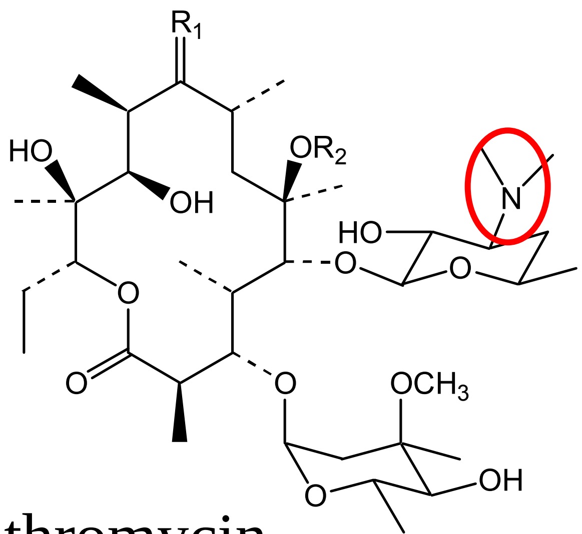
Sulfamethoxazole



Carbamazepine



17 α-Ethinylestradiol



Roxithromycin

Oxidation kinetics with ozone

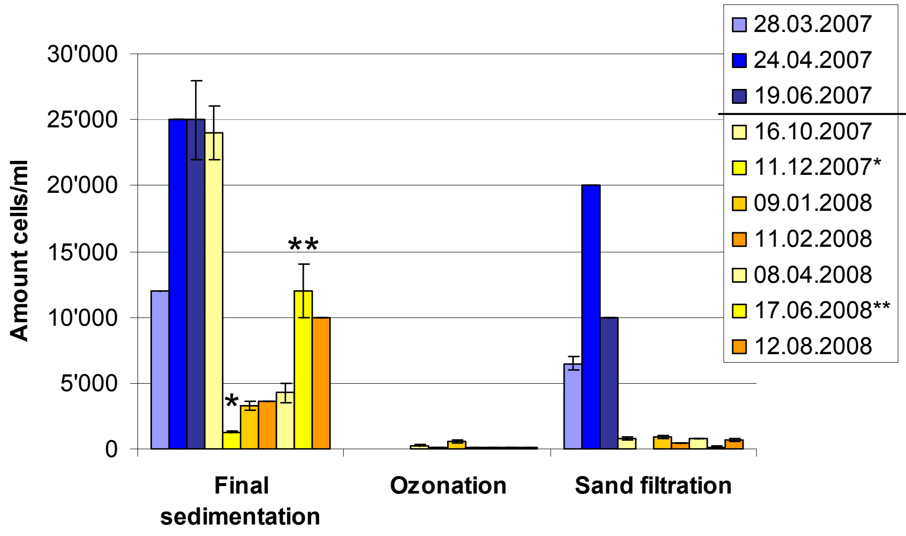
TABLE 3. Second-order rate constants for the reaction of O_3 and $^{\bullet}OH$ with selected pharmaceuticals

compound	pK_a	appar. k_{O3} ($M^{-1}\ s^{-1}$)	k_{OH} ($10^9\ M^{-1}\ s^{-1}$)
bezafibrate	3.6	590 ± 50	7.4 ± 1.2
carbamazepine		~ 3×10^5	8.8 ± 1.2
clofibric acid		< 20	4.7 ± 0.3
diazepam		0.75 ± 0.15	7.2 ± 1.0
diclofenac	4.2	~ 1×10^6	7.5 ± 1.5
17α-ethinylestradiol	10.4	~ 3×10^6	9.8 ± 1.2
ibuprofen	4.9	9.1 ± 1	7.4 ± 1.2
iopromide		< 0.8	3.3 ± 0.6
naproxen	4.5	2×10^5	9.6 ± 0.5
sulfamethoxazole	5.7	2.5×10^6	5.5 ± 0.7
roxithromycin	8.8	7×10^4	nd

Huber et al. (2005) Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: a pilot study, Env.Sci.&Techn., 39, 4290-4299.

Elimination efficiency - hygienization

Total cell count WWTP Regensdorf



Blue: before ozonation

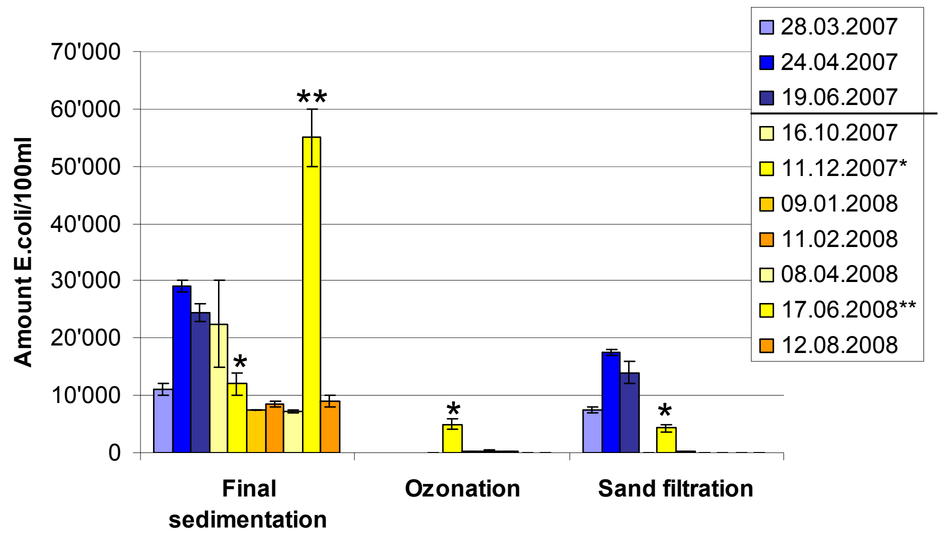
Yellow: with ozonation

*Sampling during rain event

**Sampling after rain event

Average values for two samplings within 15min, error bars show minimum and maximum values.

E. coli WWTP Regensdorf



WWTP Regensdorf

→ significant reduction of total cell counts in the wastewater by ozonation, slight regrowth in rapid sand filter

→ nearly complete elimination of E.coli in the wastewater

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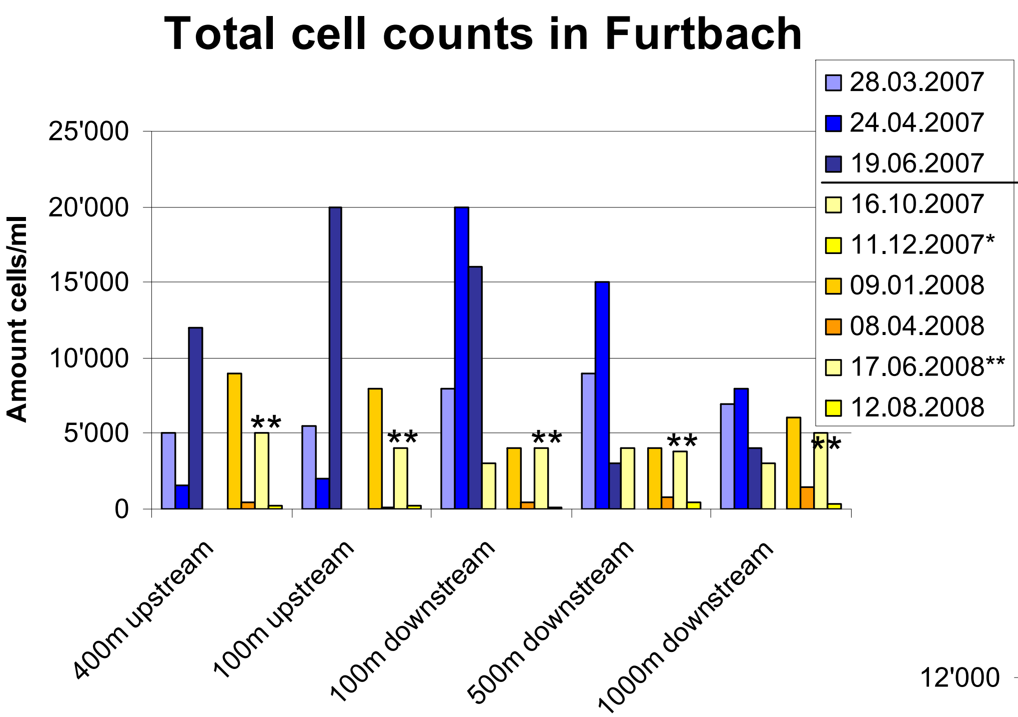
Elimination efficiency - hygienization

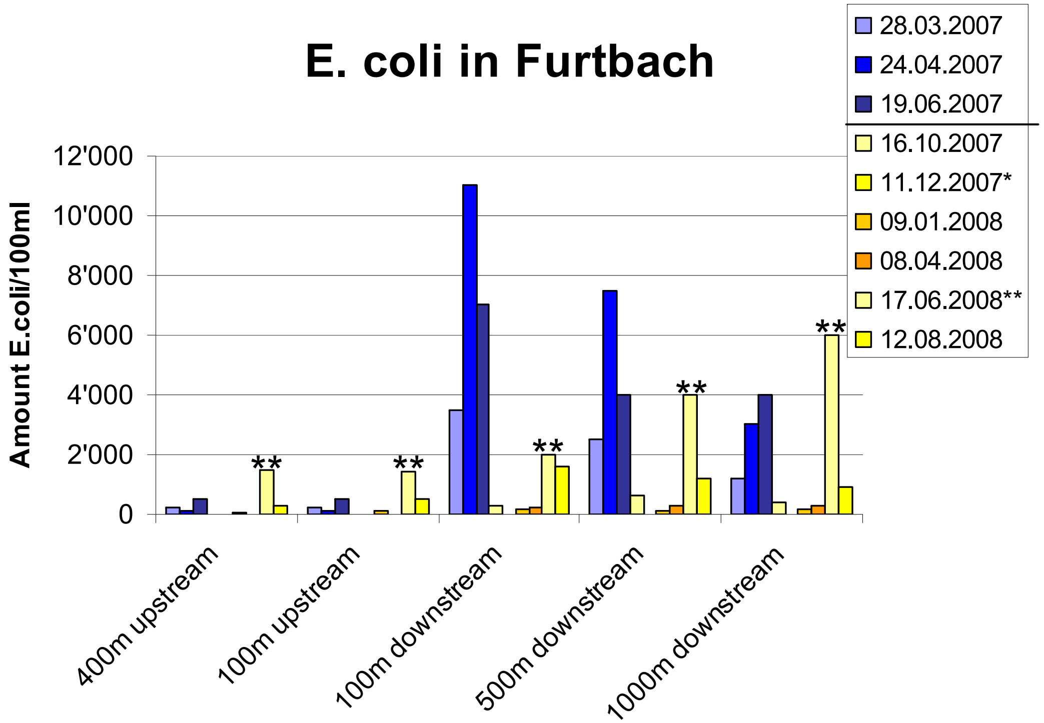


Blue: before ozonation

Yellow: with ozonation

*Sampling during rain event

**Sampling after rain event

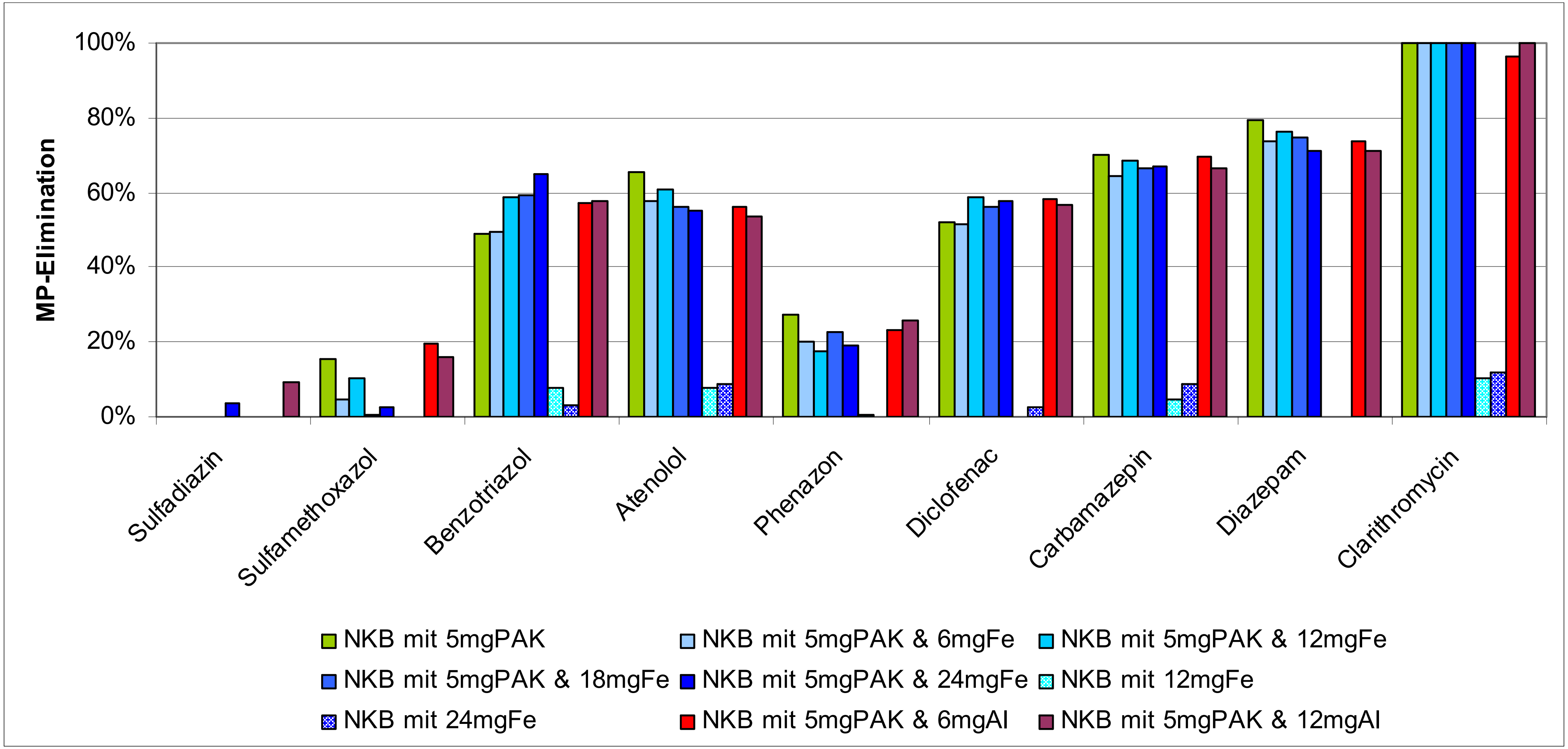


Receiving water: Furtbach

→ **slight decrease of total cell amount in river downstream of the WWTP**

→ **nearly complete elimination of E.coli release to receiving waters**

Batch experiments: Effect of flocculant

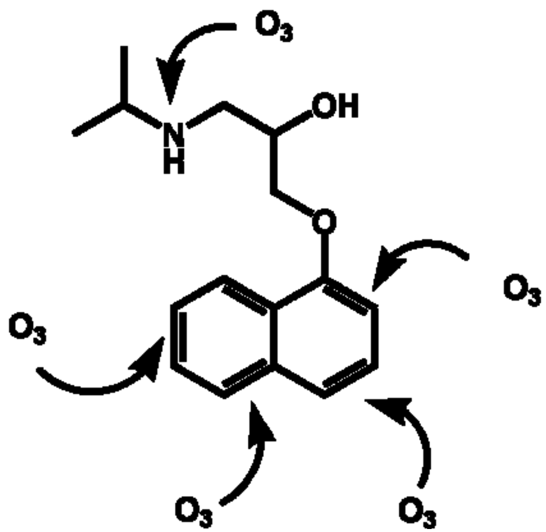


Ozonation of beta blockers: Kinetic studies and identification of oxidation products

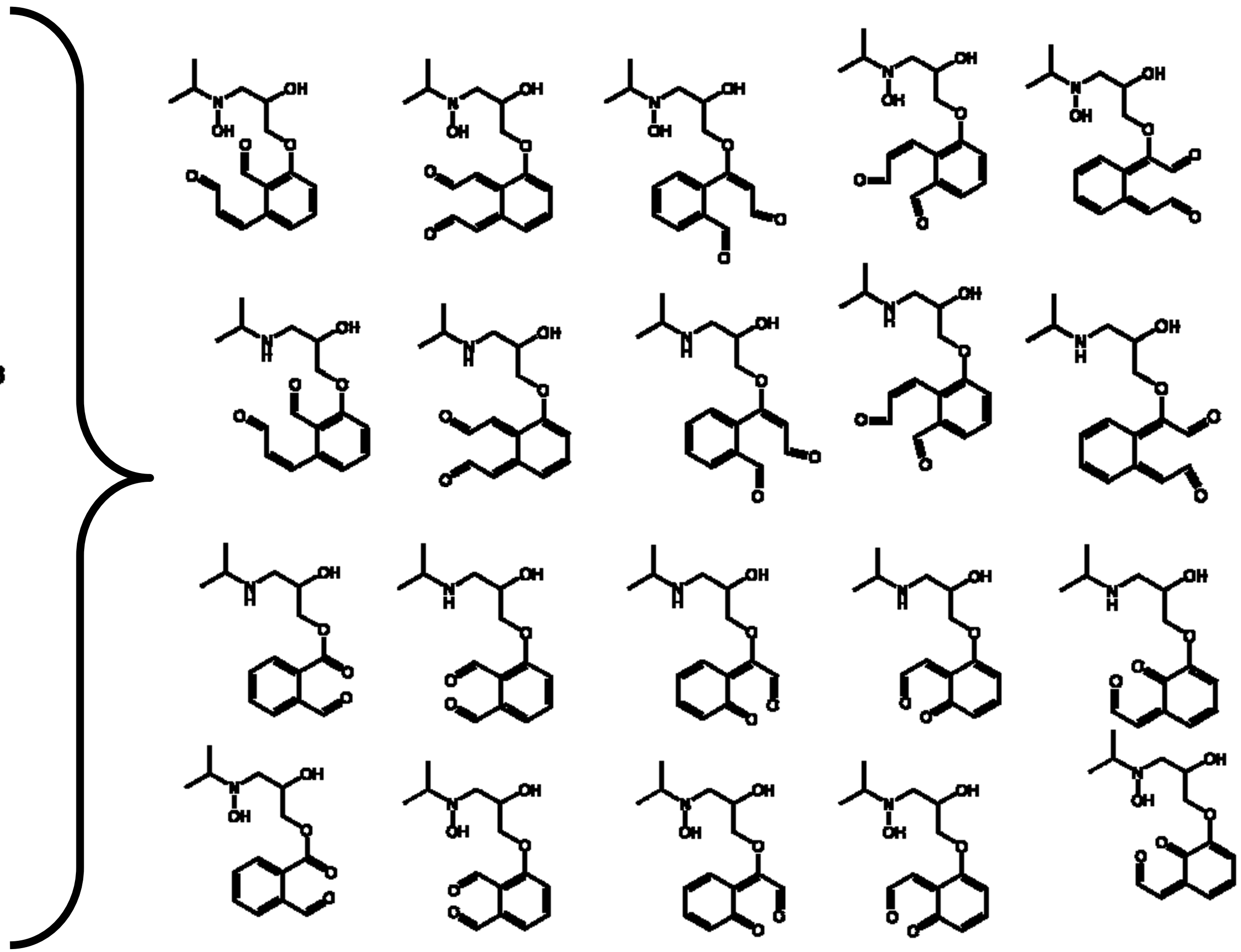
J. Benner, U. von Gunten and T. Ternes

Isomers of propranolol OPs

T. Ternes, AOP5 Conference, Berlin, April 2009

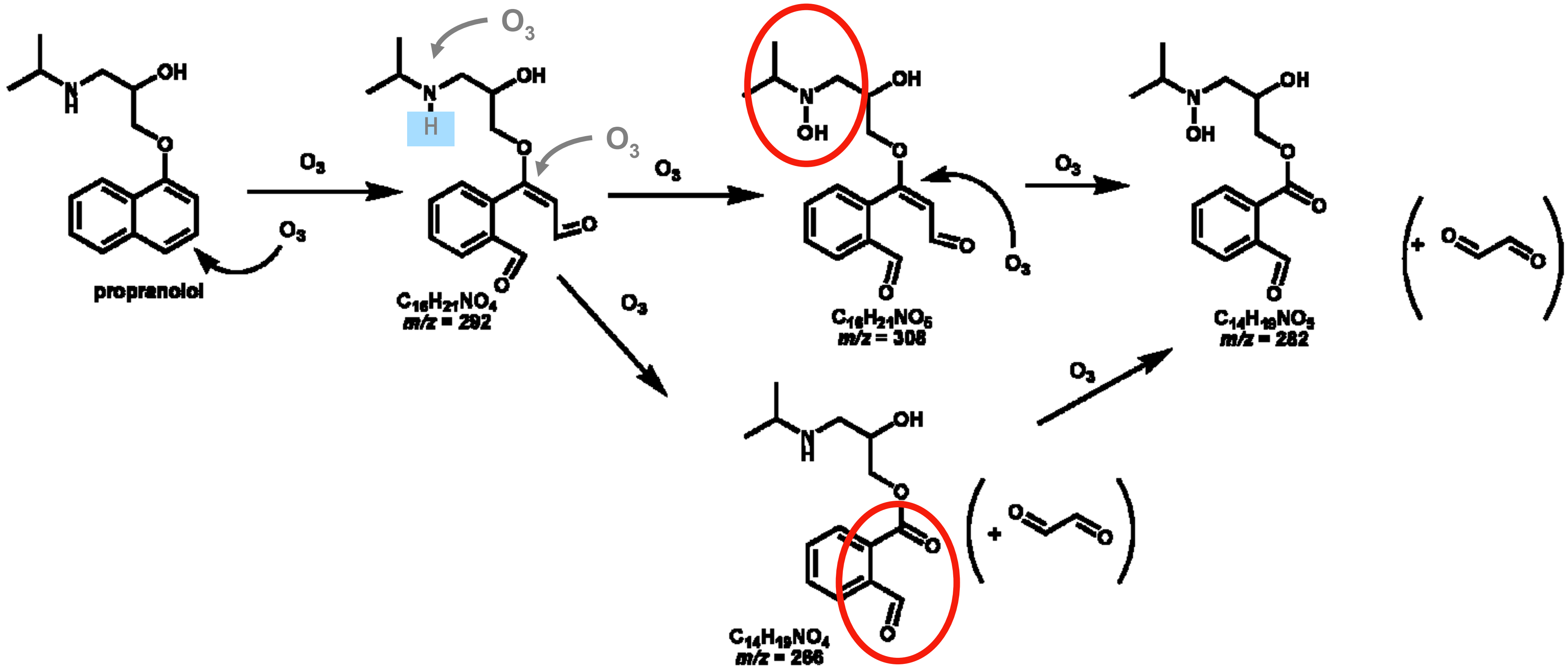


Propranolol

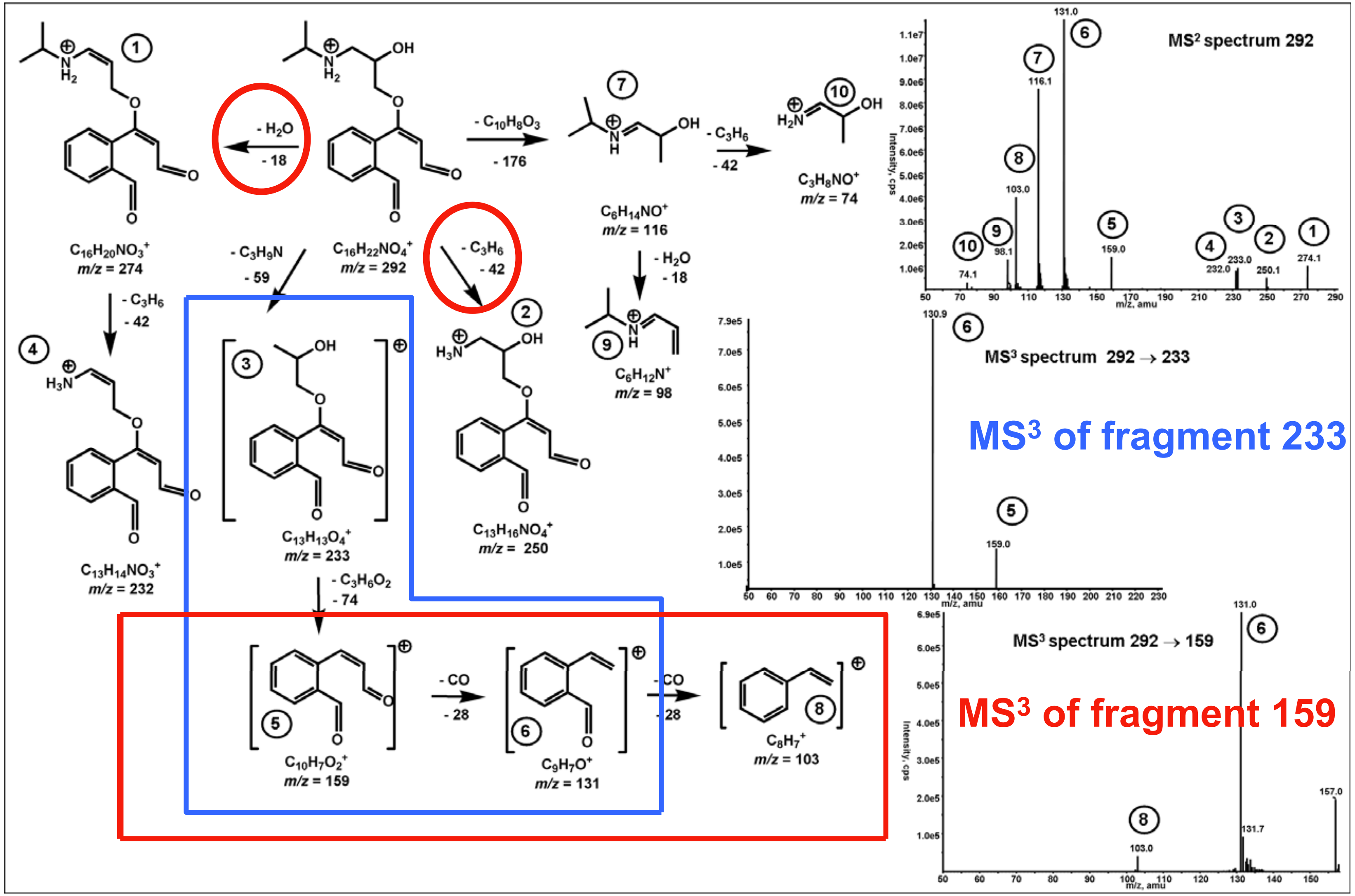


Some compounds with aldehyde moieties interact with DNA and show therefore genotoxic and carcinogenic properties

Proposed OP formation of propranolol at pH 8



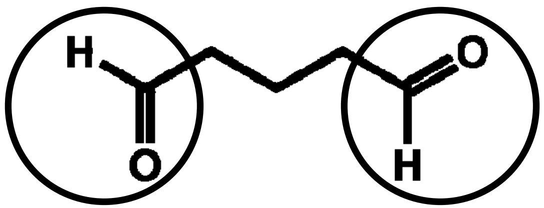
Identification of propranolol OP 292



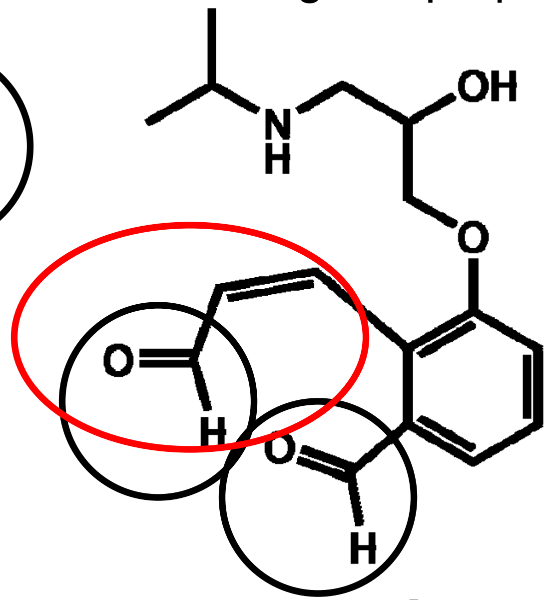
Reported genotoxicity of aldehydes

Some compounds with aldehyde moieties:

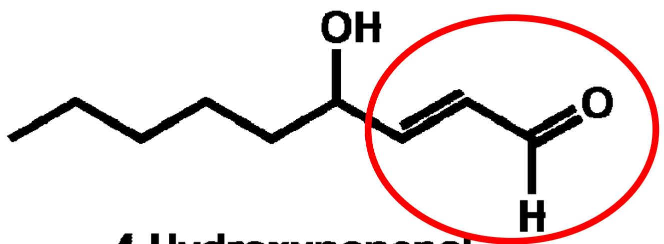
- interact with DNA [a]
  - e.g. DNA-protein cross linking
- show genotoxic and carcinogenic properties



glutaraldehyde



propranolol OP-291

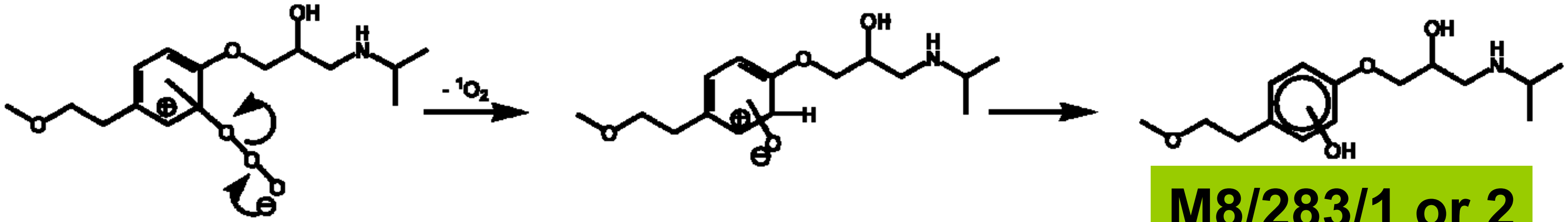


4-Hydroxynonenal

[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.

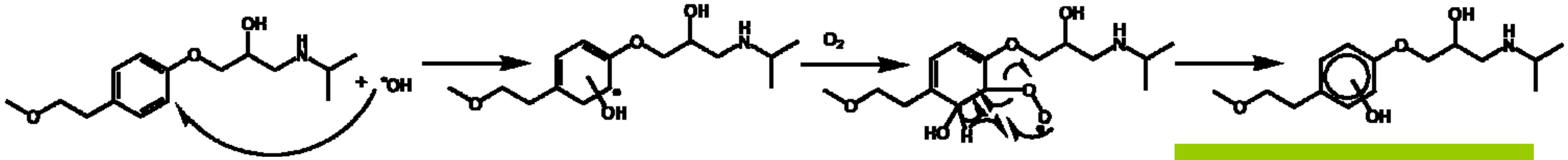
Formation of hydroxylated products of metoprolol

Ozone reaction[a]: release of singlet oxygen



M8/283/1 or 2

OH radical reaction[b]:



M8/283/1 or 2

(a) Boncz, M. A. et al. *Wat. Sci. Techn.* **1997**, *35*, 65-72.
(b) Song, W. H. et al. *E S & T* **2008**, *42*, 1256-1261.

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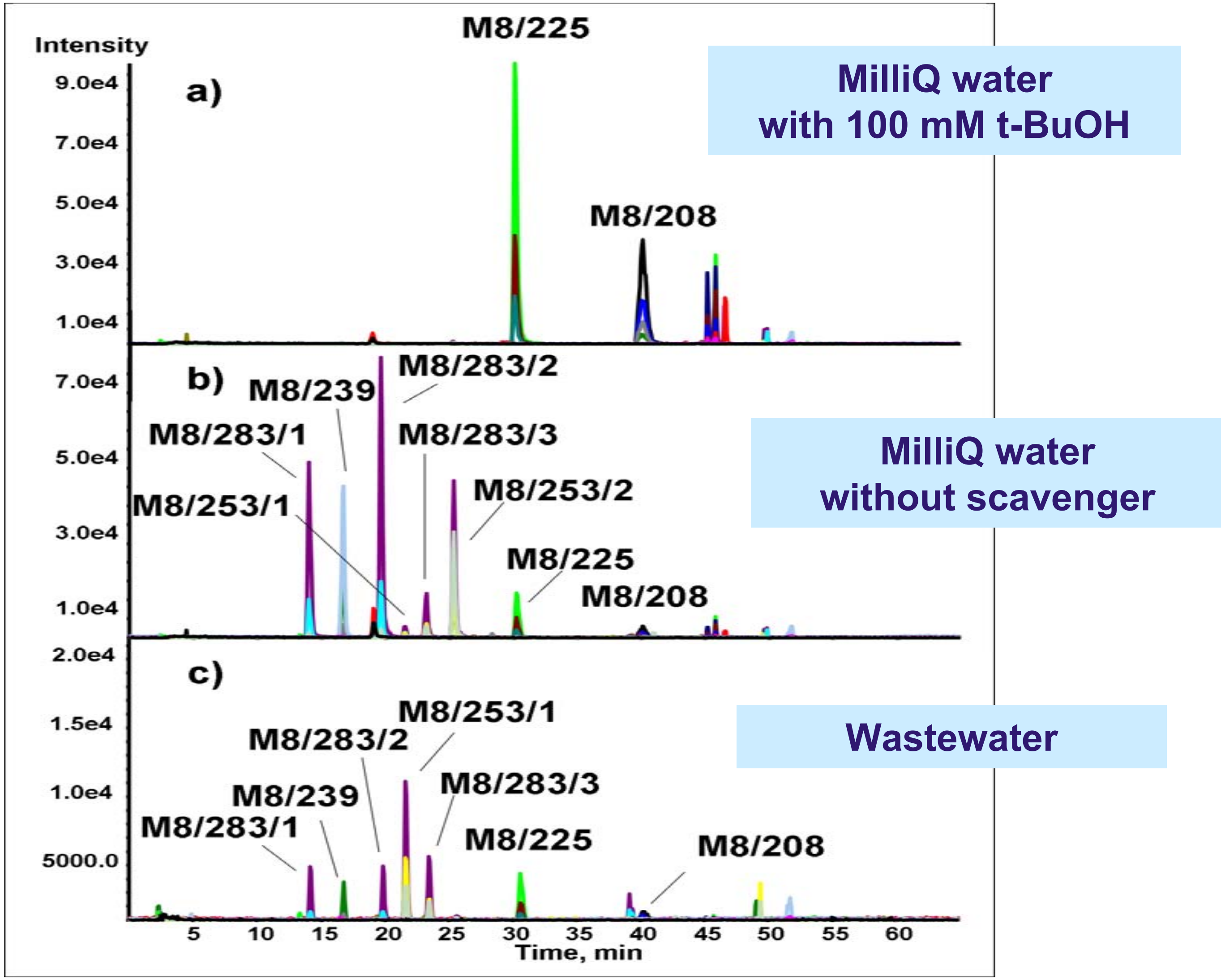
Ozonation of Milli-Q water and wastewater at pH 8 spiked with 10 µM metoprolol



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Conclusions

- Beta blockers are reactive towards ozone
  - moderate up to fast reaction kinetics
  - pH dependent k_{O3}
- Higher number of OPs are formed by ozone or OH radical attack
- Formation of aldehydes and phenolic moieties
- Metoprolol: pH and t-BuOH changed signifcantly the OP formation (much less for propranolol)
- In spiked wastewater identified OPs were formed

PAC to Sanfilter / Membranefiltration