Micropollutants and ecotoxicity in municipal WWTP effluents – an overview

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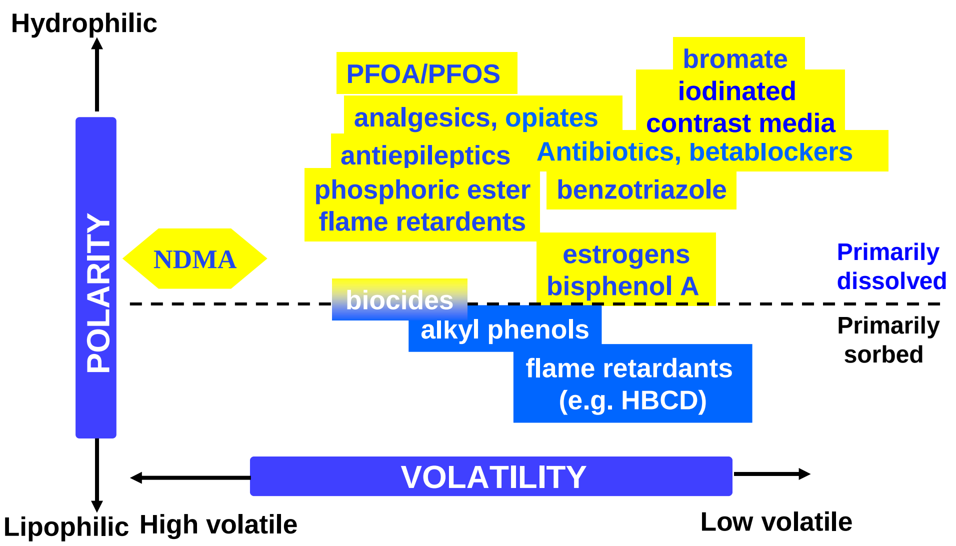
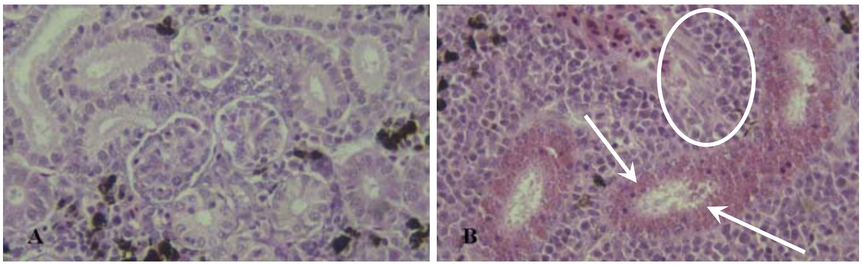
New emerging pollutants (measured by Neptune)



Diclofenac effects in fish

- Damage in kidney, gill and liver at ≥ 1 µg/L by the anti-inflammatory drug
- Example kidney: Protein accumulation, epithelial degeneration and interstitial proliferation



Oncorhynchus mykiss, control — *O. mykiss*, 100 µg diclofenac/L

Source: Schwaiger et al. (2004): Aquatic Toxicol. 68, 141-150

Processes to remove emerging pollutants in water treatment

Frequently transformation, sometimes mineralization

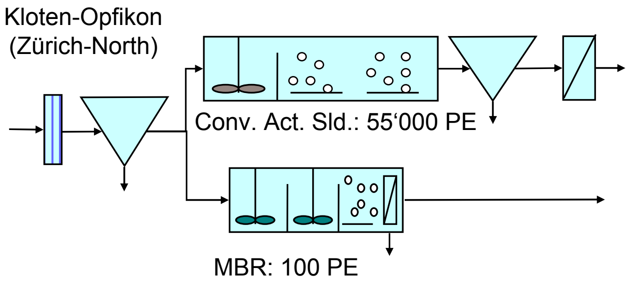
- **Biological degradation:** nitrification, denitrification
- **Chemical oxidation:** ozone, advanced oxidation
- **Photo(chemical)degradation:** UV/H_2O_2, sun light

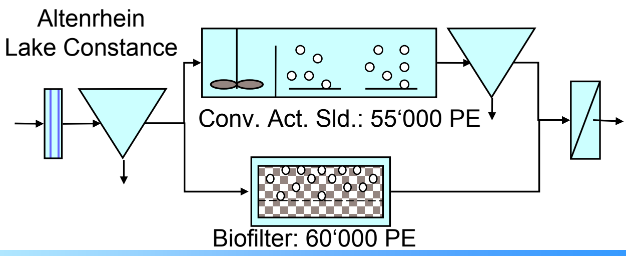
Quantitative removal

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

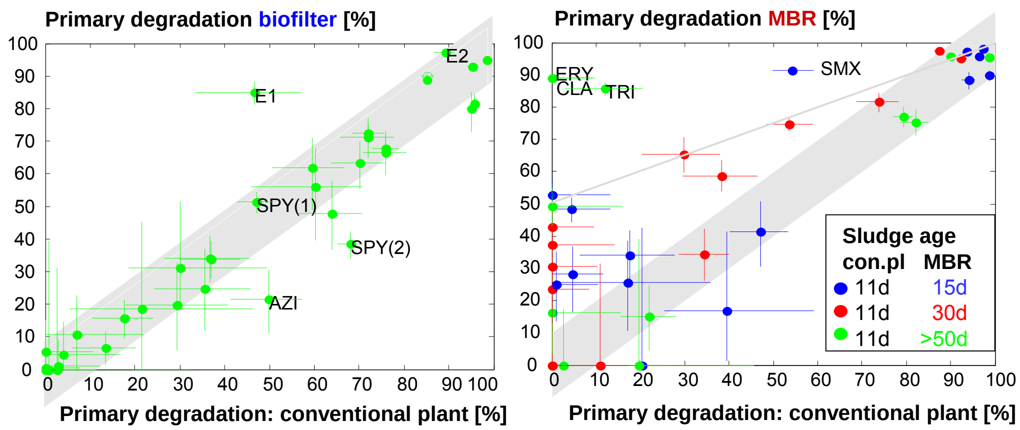
Biological degradation
(and sorption on sludge particle)

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



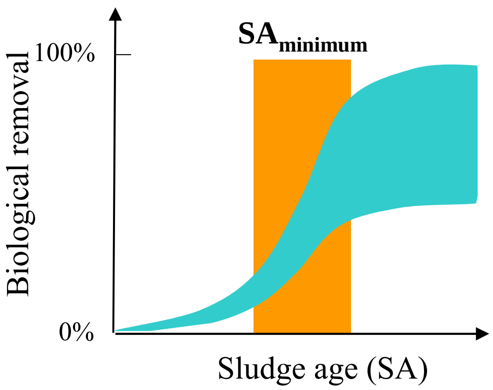


Comparison of primary degradation MBR, biofilter, conventional plant



Source: Joss und Siegrist, 2005, Eawag News

Biological degradation - sludge age



The **biological removal depends** on:

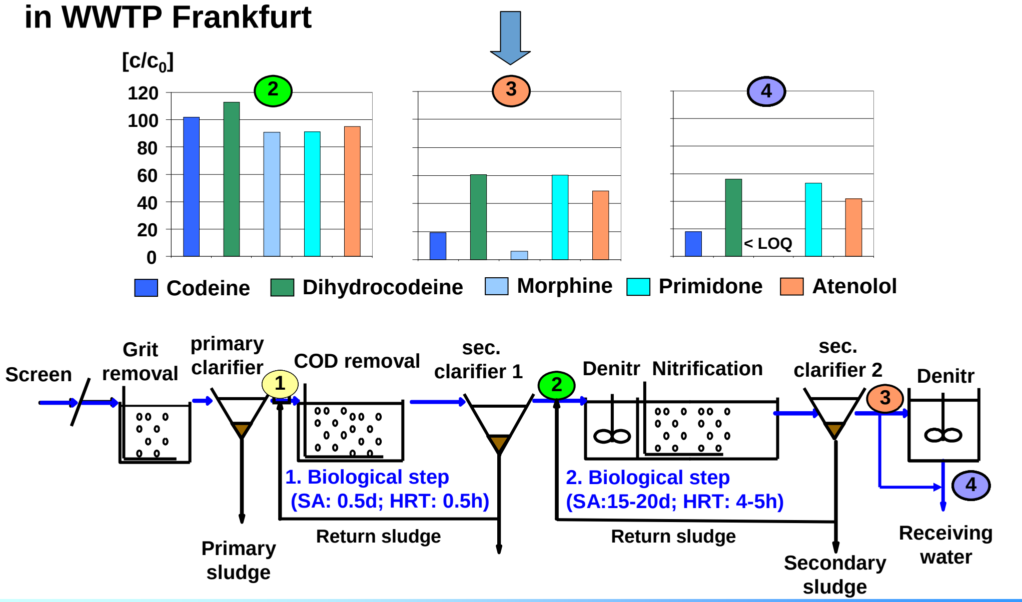
- **Substance properties**
- **Sludge age (SA)**
- Temperature
- etc.

k_{biol}

SA_{min}	biodegradable
2 - 5 d	Bezafibrate Ibuprofen
5 -15 d	Naproxen 17α-Ethinylestradiol Iopromide Roxithromycin
	no biodegradation
< 20d	Carbamazepine Diazepam

Kreuzinger et al., 2004, Wat. Sci. Tech.
Ternes et al., 2004, Env. Sci. Technol.

Removal of Atenolol and psycho-active drugs in WWTP Frankfurt



Model assumptions for elimination in a fully mixed nitrification system

$C_{sorbed} = K_d \cdot SP \cdot C_{i,out}$

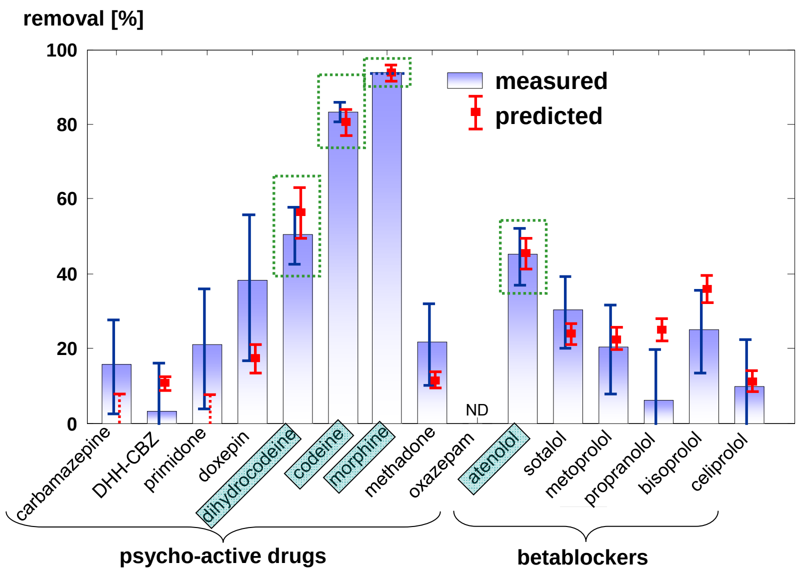
influent conc. $C_{i,in}$ → **nitrification (totally mixed)** → effluent conc. $C_{i,out}$,

$C_{biodegraded} = k_{biol}(T, SA) \cdot SS \cdot HRT \cdot C_{i,out}$

$$C_{i,out}/C_{i,in} = 1/(1 + K_d \cdot SP + k_{biol}(T, SA) \cdot SS \cdot HRT)$$

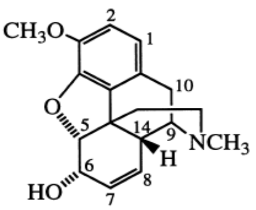
SS = sludge concentration in reactor
SP = sludge production per m³ of wastewater

Modelling of the removal in the second biological step



Biological transformation

Example: Codeine

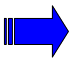


Codeine

- used as analgesic and cough supressant
- 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

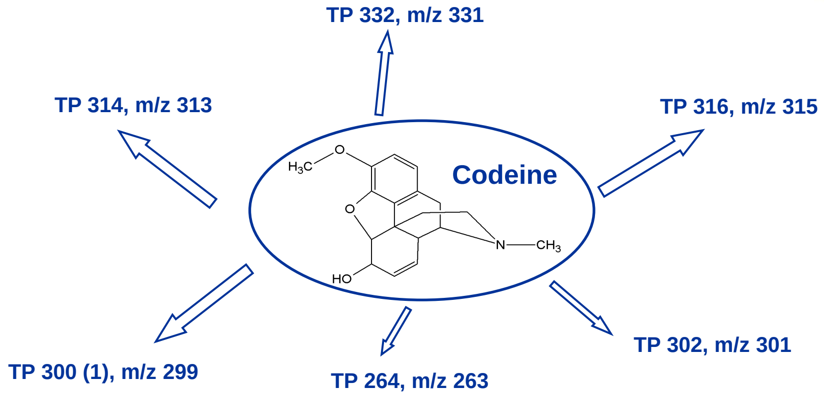
capsule of the opium poppy
(*Papaver somniferum L.*).

up to 90% is removed in WWTPs by primary degradation



formation of transformation products (TPs) ?

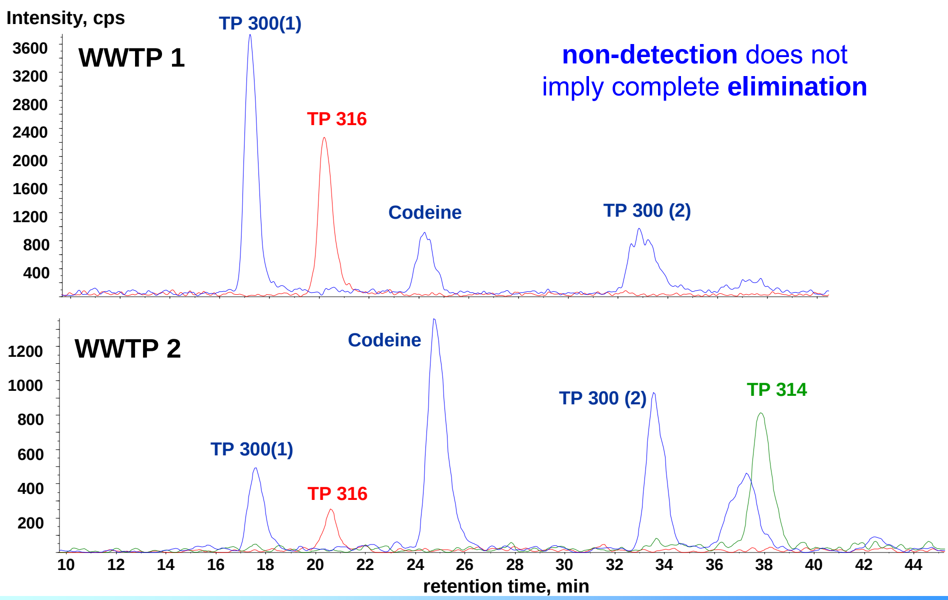
Identified TPs of Codeine

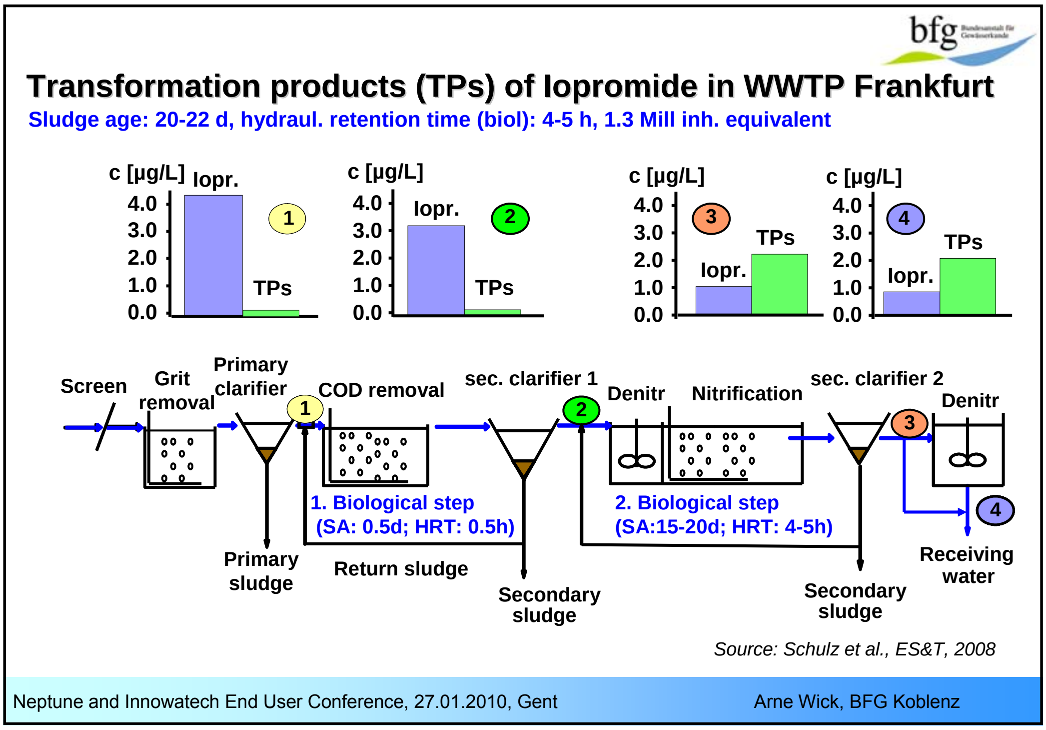


in most cases basic structure unchanged

typical reactions observed:
• double bond shift
•hydroxylation
•demethylation

Occurrence of Codeine TPs in WWTP effluents

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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
c [µg/L]
Iopr.
TPs
1
2
3
4
4.0
3.0
2.0
1.0
0.0
Screen
Grit removal
Primary clarifier
COD removal
sec. clarifier 1
Denitr
Nitrification
sec. clarifier 2
Denitr
1. Biological step
(SA: 0.5d; HRT: 0.5h)
2. Biological step
(SA:15-20d; HRT: 4-5h)
Primary sludge
Return sludge
Secondary sludge
Secondary sludge
Receiving water
Source: Schulz et al., ES&T, 2008
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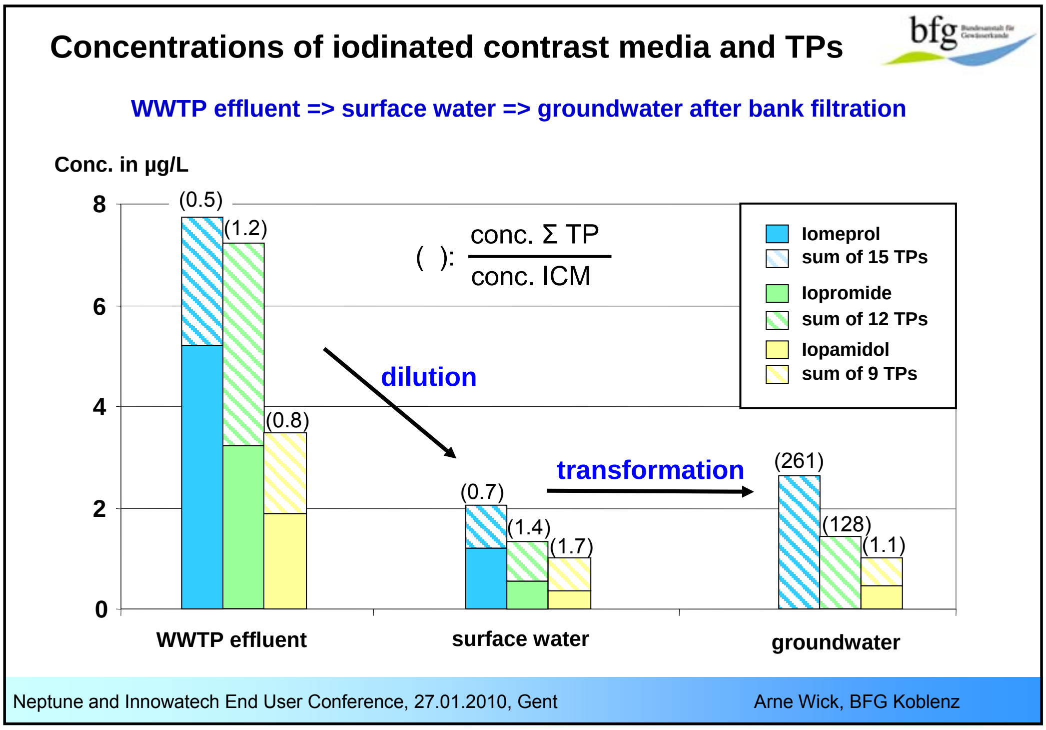
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Concentrations of iodinated contrast media and TPs
WWTP effluent => surface water => groundwater after bank filtration
Conc. in µg/L
8
6
4
2
0
(0.5)
(1.2)
(0.8)
( ): conc. Σ TP / conc. ICM
dilution
transformation
(0.7)
(1.4)
(1.7)
(261)
(128)
(1.1)
Iomeprol
sum of 15 TPs
Iopromide
sum of 12 TPs
Iopamidol
sum of 9 TPs
WWTP effluent
surface water
groundwater
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Oxidative transformation

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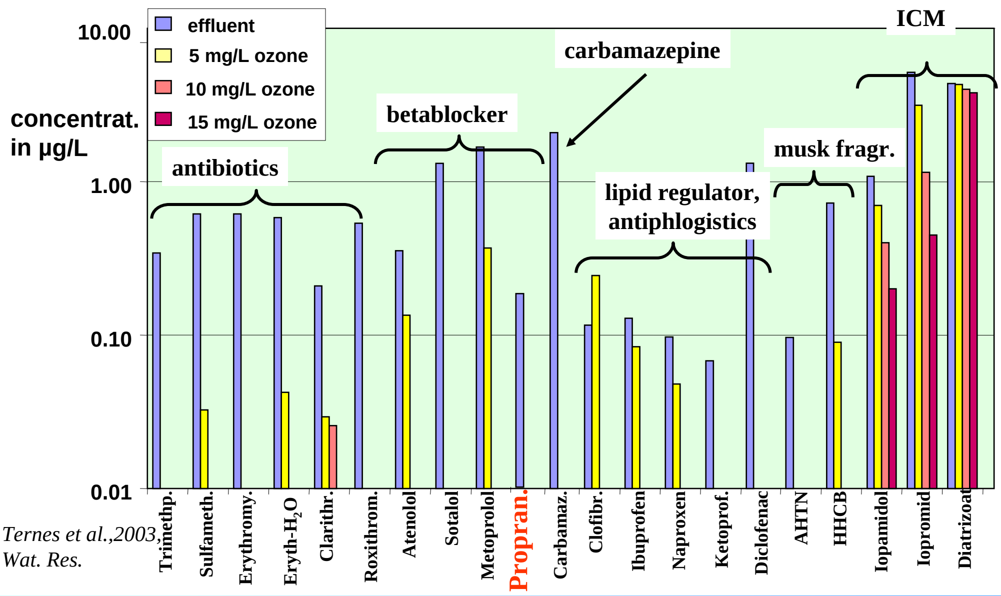
Ozonation of Braunschweig effluent



Ternes et al.,2003, Wat. Res.

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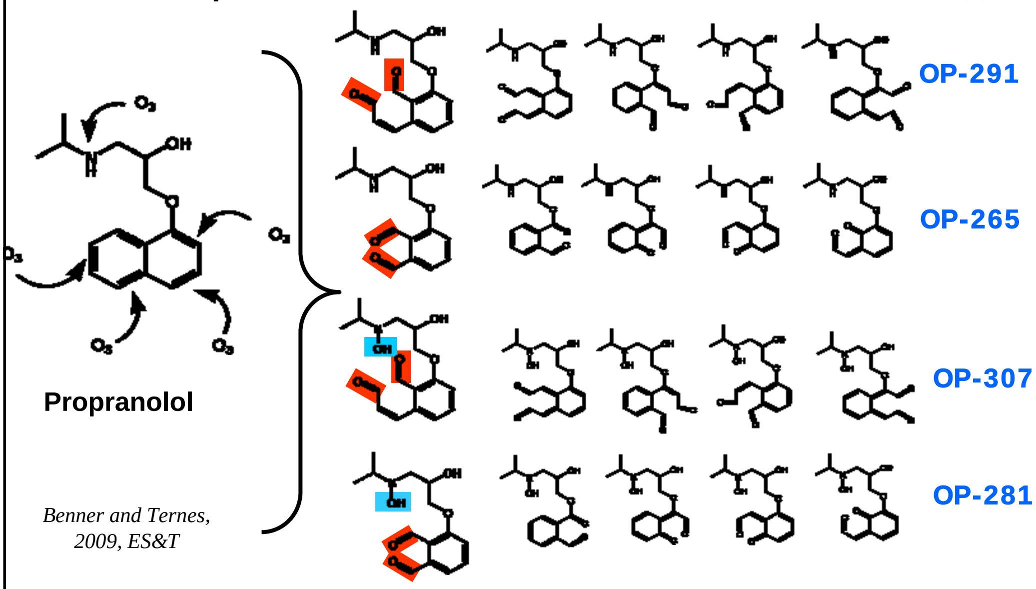
OPs of Propranolol

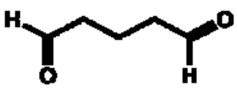


Reported genotoxicity of aldehydes

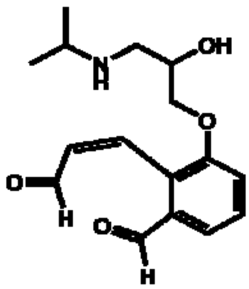
Compounds with aldehyde moieties:

a) interact with DNA [a] (e.g. DNA-protein cross linking)

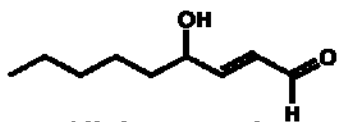
b) genotoxic and carcinogenic properties



glutaraldehyde



propranolol OP-291



4-Hydroxynonenal

illustrates the **importance** of investigating **TP formation**

[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.

Sorption onto activated carbon

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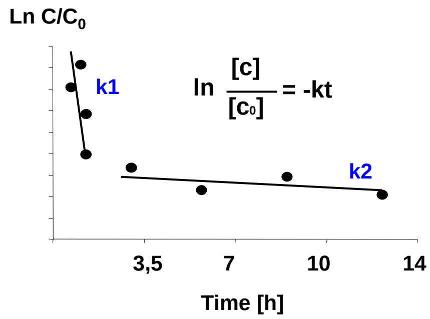
Sorption tests in laboratory

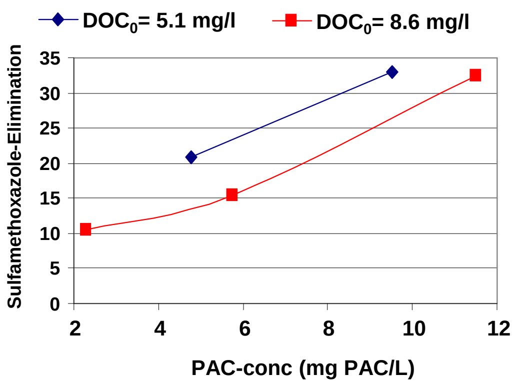
Sorption kinetic
PAC = 20 mg/L, t = 5, 10, 30, 90, 180min, …14 d

Sulfamethoxazole (SMX) in WWTP effluent



Duration till equilibrium t_{eq}
→ Kinetic coefficients k1 und k2

Elimination of SMX in%



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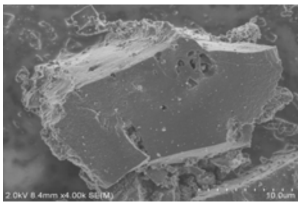
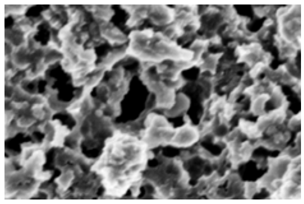
PAC addition processes

- **PAC/flocculant addition to a contact/flocculation tank with sedimentation + additional filtration unit (e.g. sand filtration) for PAC recycling**
- **PAC addition to a reactor with membrane separation.**

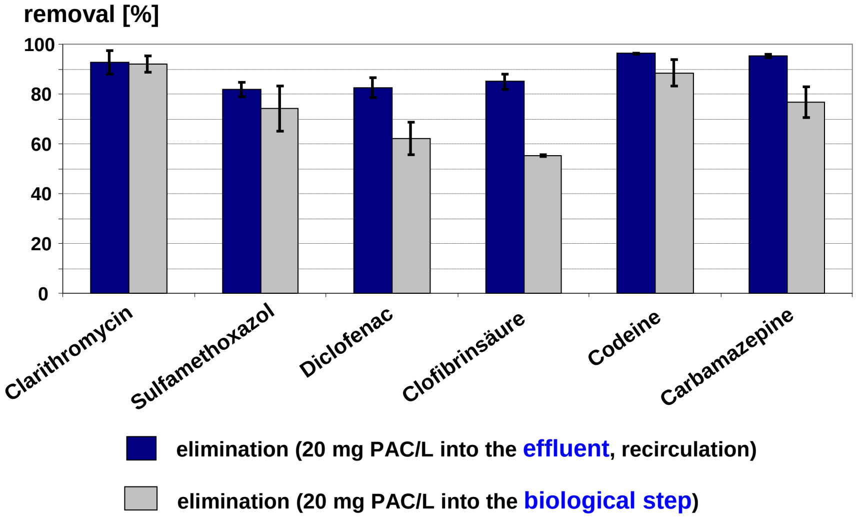
Alternatives:

- **PAC addition directly to biology: no additional reaction tank but higher DOC → more PAC, inhibition of microbial removal?**
- **PAC addition to a flocculation tank followed by sand filtration: PAC loss to effluent?**





Comparison of PAC addition into the biol. step and into the effluent



In-vivo **and *in-vitro* biotests to evaluate ozonation and PAC addition to pilot plant in Neuss, Germany**

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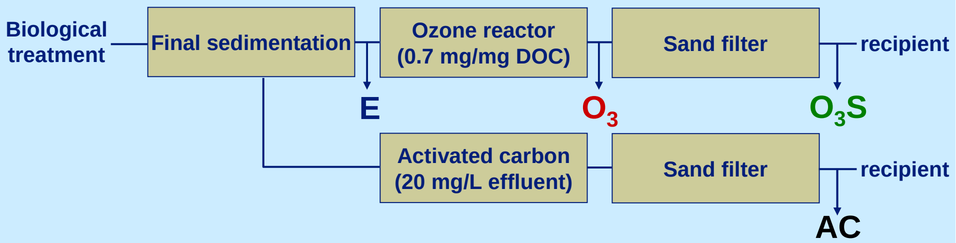
In vivo biotests for wastewater

- Case study WWTP Neuss (120,000 PE)
- Pilot treatment plant with ozonation and powdered activated carbon treatment in parallel lines; samples tested :
  - Effluent after final sedimentation (E)
  - After ozone reactor (O_3)
  - After sand filter (O_3SF)
  - After activated carbon treatment (AC)
  - Control (C)



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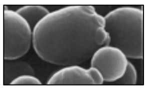
Summary: Estrogenicity



Species	Endpoint	E	O_3	O_3S	AC
Saccharomyes cerevisiae (YES)	estrogenicity	■ (red)	■ (green)	■ (green)	■ (green)
Potamopyrgus antipodarum	reproduction	■ (red)	■ (green)	■ (green)	■ (green)
Oncorhynchus mykiss (FELST)	vitellogenin	■ (red)	■ (green)	■ (green)	

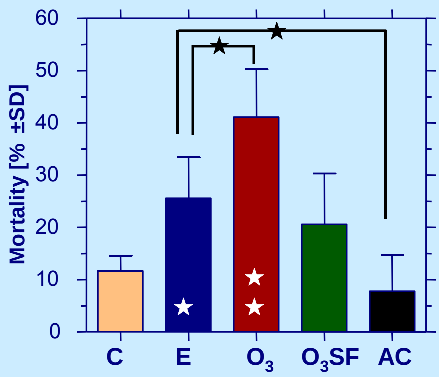
■ (red) Significant **negative** effects compared to **control**

■ (green) Significant **positive** effects compared to **E** (effluent final sedimentation)

Toxicity *in vivo* at WWTP Neuss: Fish

- Significantly enhanced mortality in Effluent and after Ozonation

(FELST)

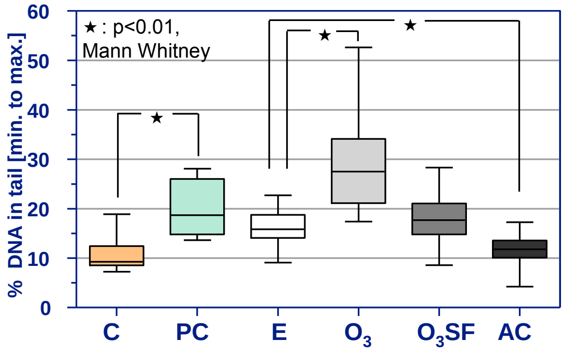


Magdeburg et al.: in prep.

Significant vs. C: ★ = p < 0.05-0.001; Fisher's exact test

Genotoxicity, *in vivo* (comet assay)

- **Increased DNA damage after the ozone reactor and decrease on E-level after the sand filter**
- **Activated carbon treatment reduces DNA damage below initial state**



Magdeburg et al.: in prep.

ozonation should not be applied w/o a barrier for by-products

Summary: *In vivo* tests

	Species	Endpoints	O_3	O_3S	AC
	*Lumbriculus variegatus*	reproduction	red	yellow	yellow
		biomass	red	yellow	yellow
	*Oncorhynchus mykiss* (FELST)	mortality	red	yellow	green
	*Dreissena polymorpha*	DNA damage	red	yellow	green

- Red: Significant negative effects compared to **E** (effluent final sedimentation)
- Yellow: No difference compared to **E**
- Green: Significant positive effects compared to **E**

Options for advanced wastewater treatment

		Energy (electrical/primary) kWh m^{-3}	Costs € m^{-3}	toxicological challenges
Full scale results	Ozonation/sand filter (3-10 mg/L O_3)	0.1–0.2 / 0.3–0.6	0.05 – 0.20	toxicology of by-products
Literature, lab scale	Reverse osmosis (RO) 20 to 60 bar	2–5 / 6–15 [1)]	0.7–1.5	up to 50% concentrated residue (brine)
Literature, lab scale	Nanofiltration 5 – 20 bar	1.5–3 / 4.5–9	0.2 – 0.50	concentrated residue
Literature, lab scale	Activated carbon (10-20 mg/L)+sand filter	0.05 / 0.4–0.7 [2)]	0.09 – 0.30	contaminated PAC

[1)] Busch and Mickols, Desalination, 2004
[2)] Primary energy consumption of PAC (no regeneration) 3.5 kg carbon needed for 1 kgPAC: 3.5kgC/kgPAC x 31MJ/kgC / 3.6MJ/kWh = 30kWh/kgPAC

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