API removal with advanced wastewater treatment techniques

Ulf Miehe

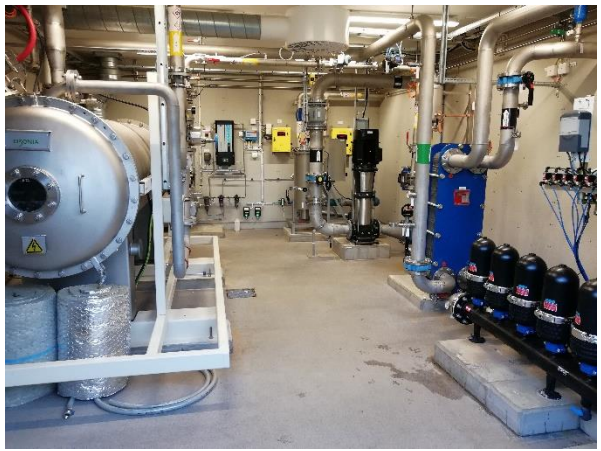
Berlin Centre of Competence for Water (KWB)

CWPharma project's final seminar, 18. 11. 2020

Advanced wastewater treatment for API elimination

- Focus of conventional WWTPs: C, N and P reduction
- Some active pharmaceutical ingredients (APIs) are biodegradable and, thus, are also removed at WWTPs (e.g. ibuprofen, metformin)
- Persistent APIs such as carbamazepine and diclofenac require an advanced wastewater treatment. Well known technical measures are:

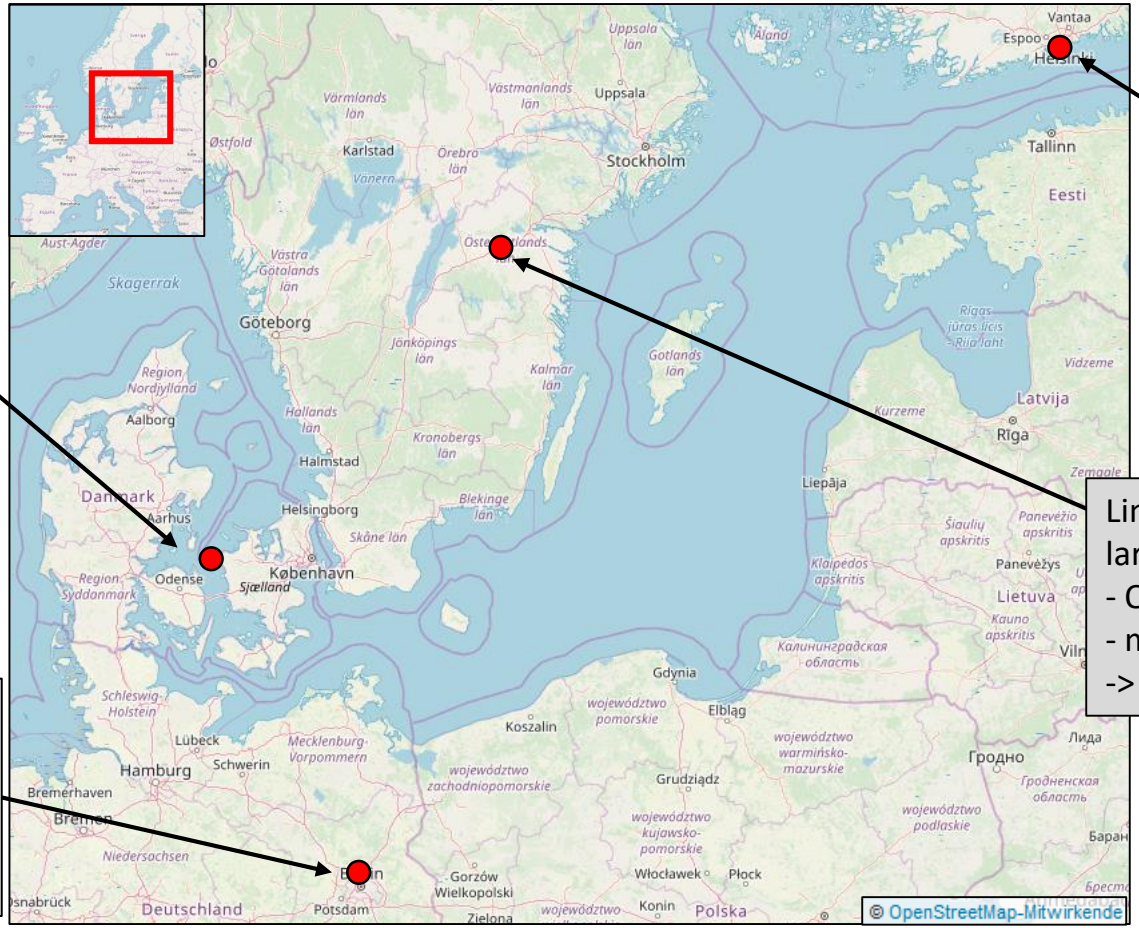
Ozonation



Powdered activated carbon (PAC)

Ganular activated carbon (PAC)

Overview on CWPharma study sites



Helsinki (FI):
- Powdered activated carbon
- Small, pilot scale

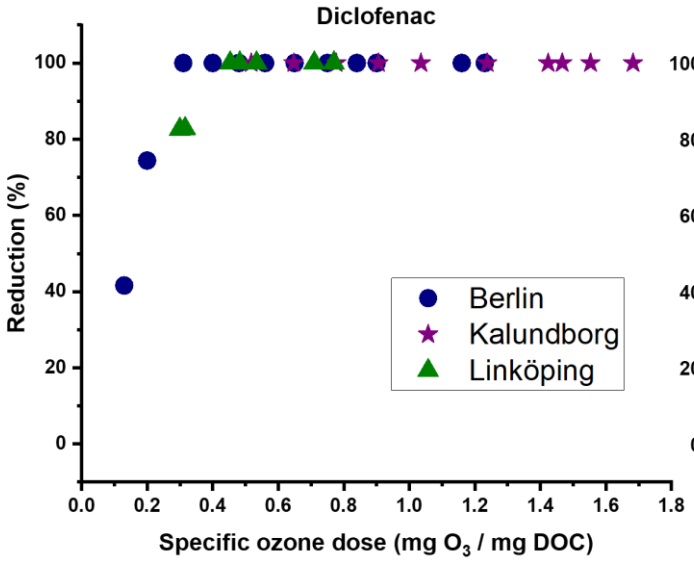
Kalundborg (DK):
large scale ozonation
- Q_{max} = 1200 m³/h
- $m_{O3,max}$ = 180 kgO_3/h
-> $D_{calc,Qmax}$ = 150 mgO_3/L

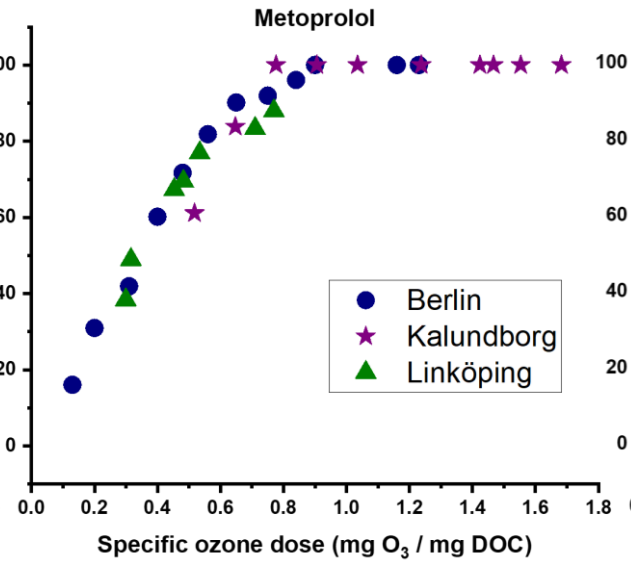
Linköping (SE):
large scale ozonation
- Q_{max} = 3000 m³/h
- $m_{O3,max}$ = 20 kgO_3/h
-> $D_{calc,Qmax}$ = 6.7 mgO_3/L

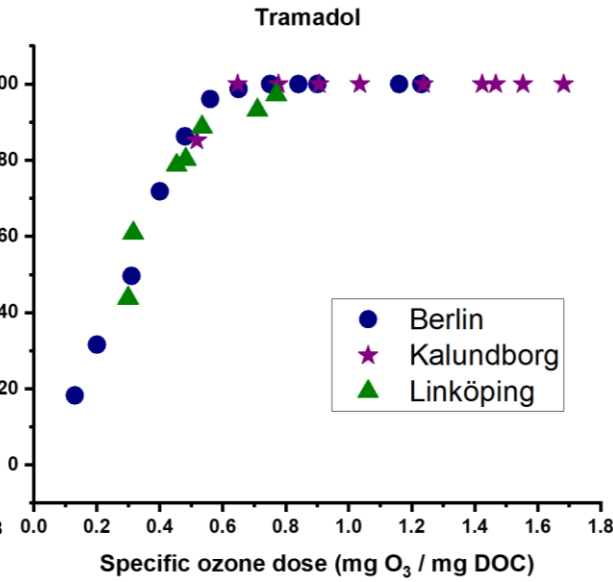
Berlin/Schönerlinde (DE):
Pilot scale ozonation
- Q_{max} = 15 m³/h
- $m_{O3,max}$ = 0.15 kgO_3/h
-> $D_{calc,Qmax}$ = 10 mgO_3/L

Map from https://www.openstreetmap.org/

Impact of ozonation on APIs







Ozonation process

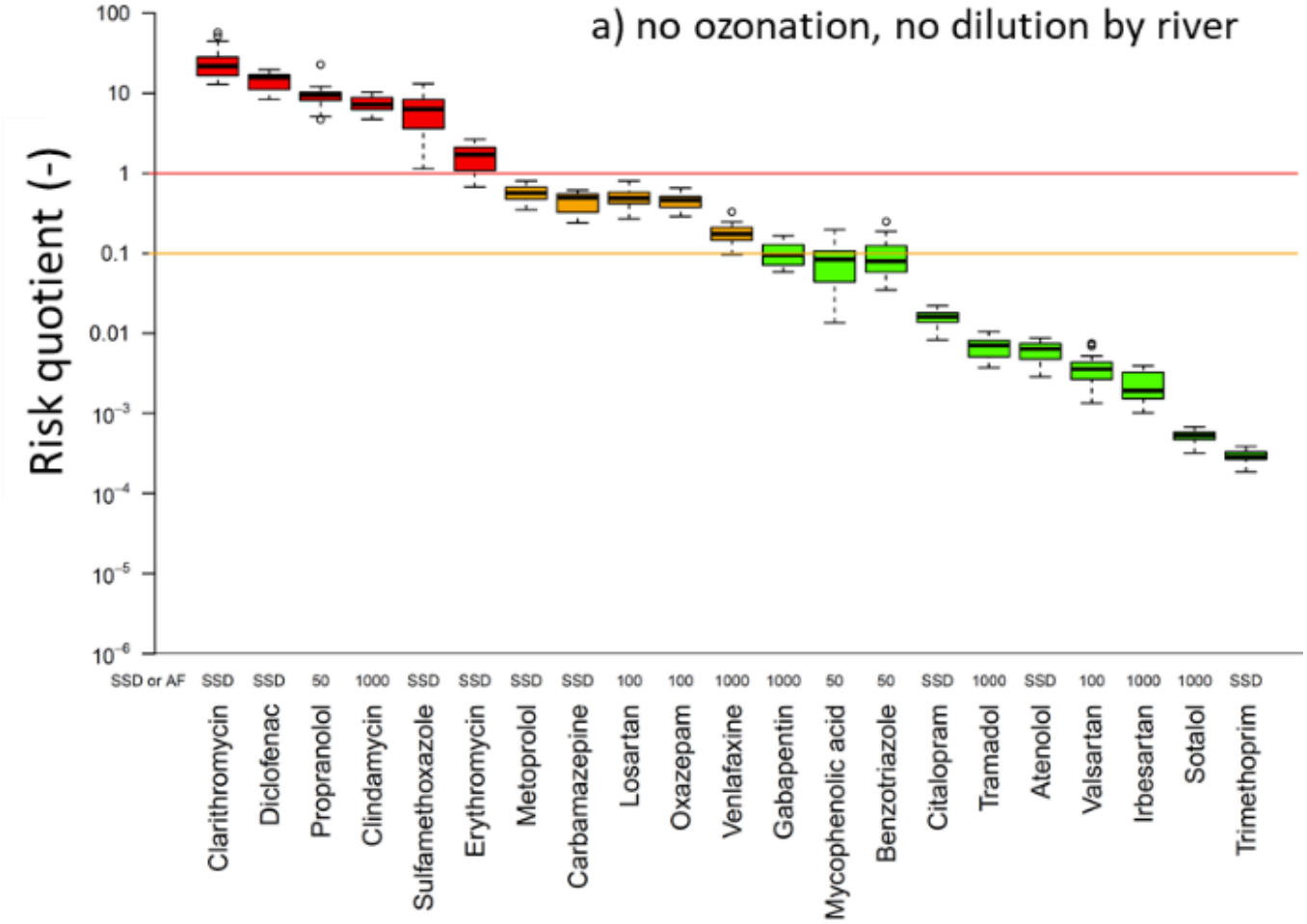
applied ozone dose (mgO_3/L)

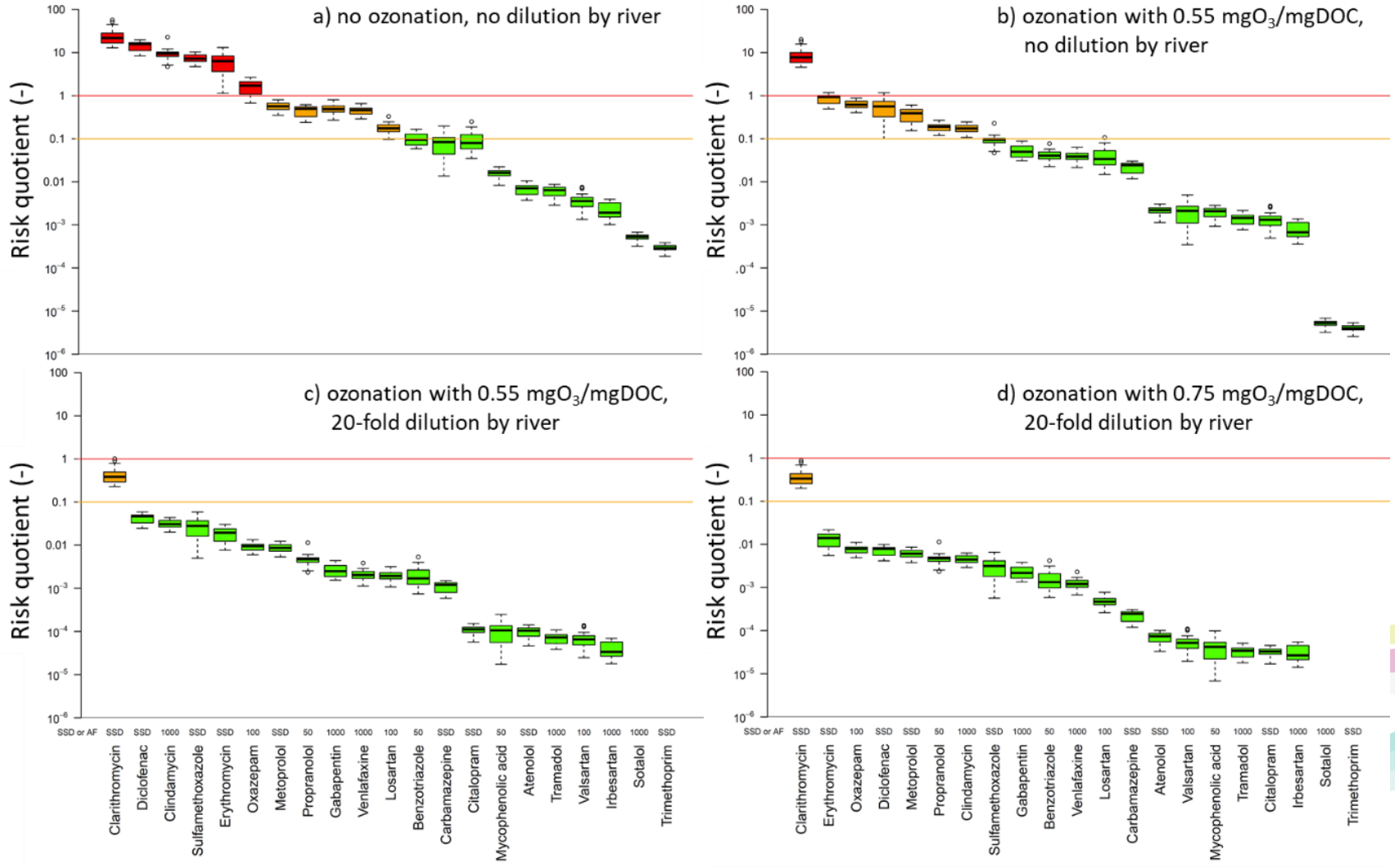
DOC (mg/L)

Nitrite (mg-N/L)

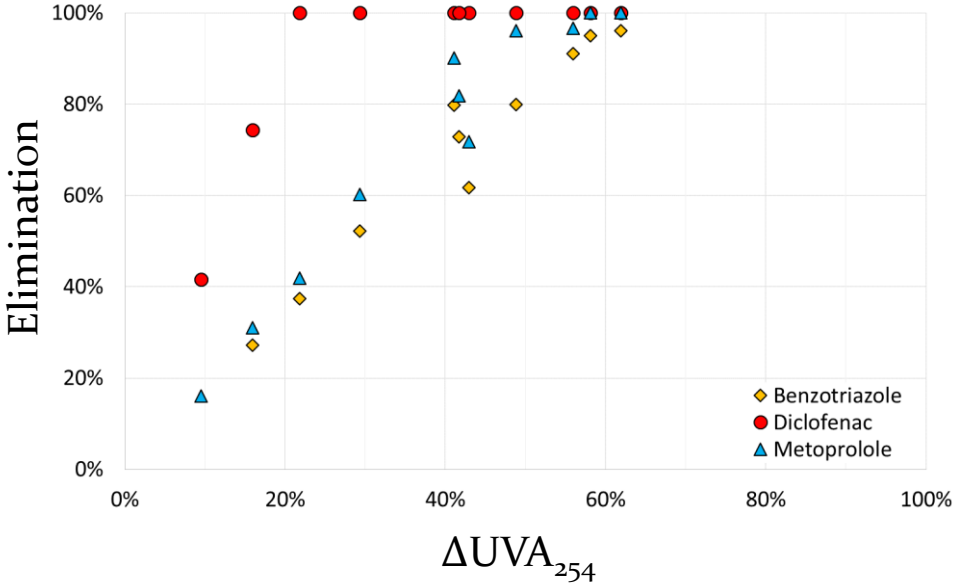
Water quality

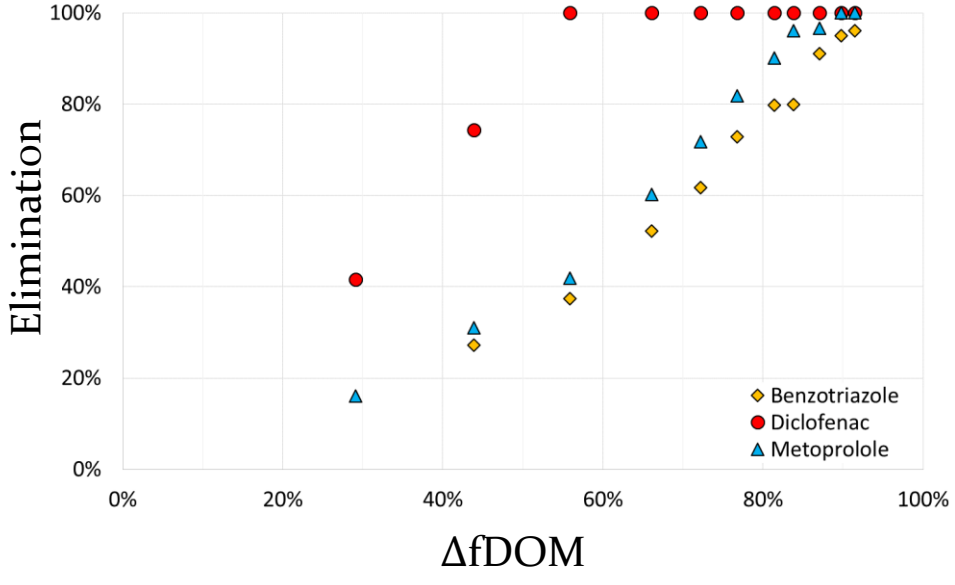
Impact of ozonation on risk quotient (WWTP Linköping)




a) no ozonation, no dilution by river
b) ozonation with 0.55 mgO3/mgDOC, no dilution by river
c) ozonation with 0.55 mgO3/mgDOC, 20-fold dilution by river
d) ozonation with 0.75 mgO3/mgDOC, 20-fold dilution by river
Risk quotient (-)
SSD or AF
Clarithromycin
Diclofenac
Clindamycin
Sulfamethoxazole
Erythromycin
Oxazepam
Metoprolol
Propranolol
Gabapentin
Venlafaxine
Losartan
Benzotriazole
Carbamazepine
Citalopram
Mycophenolic acid
Atenolol
Tramadol
Valsartan
Irbesartan
Sotalol
Trimethoprim

Usage of surrogats for process control and monitoring

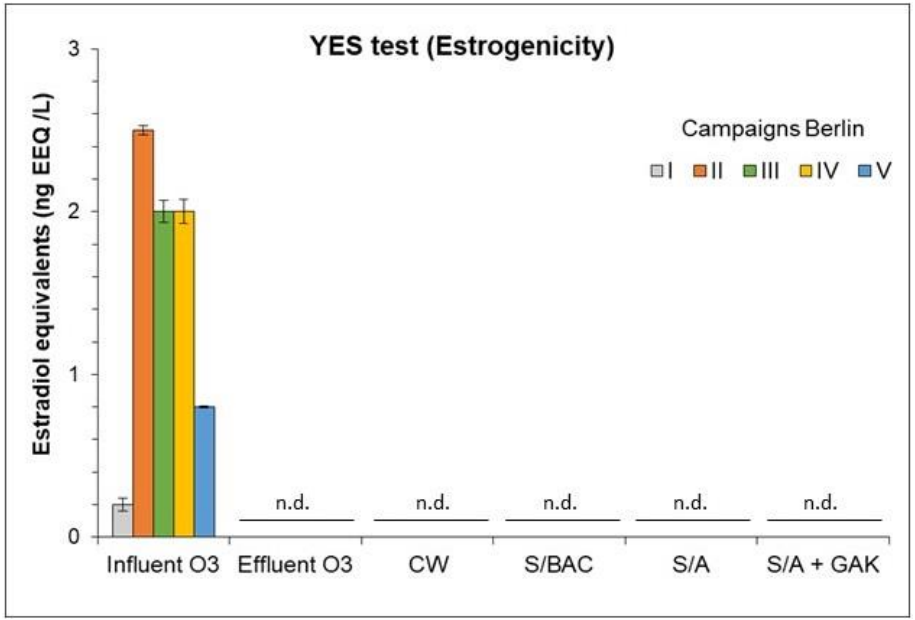


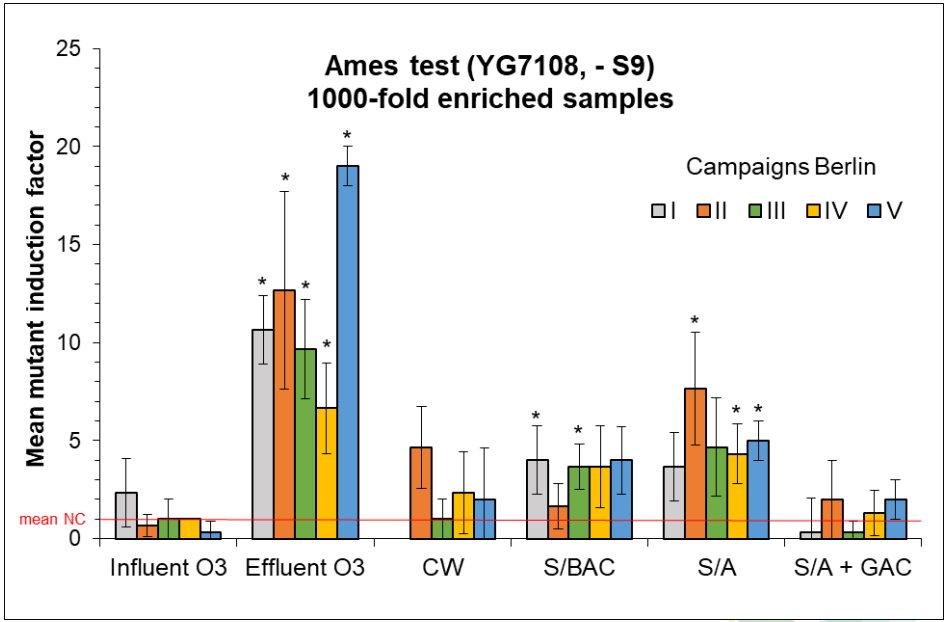


- API elimination can be monitored by using surrogate parameters (e.g. UVA_{254} reduction or fluorescence) – online or offline.
- Surrogate parameters can also be used for process control to adapt the dosage, but practical implementation sometimes tricky → local assessment of need vs. advantages

Usage of ecotoxicological test systems

17 ecotoxicological tests were performed by IOS (PL), LIAE (LV), and UBA (DE)
→ many of them showed no (systematic) effect at an enrichment factor of 10





Also positive impacts on *Aliivibrio fischeri* bioluminescence

➔ Biological post-treatment is needed

Impact of post-treatment

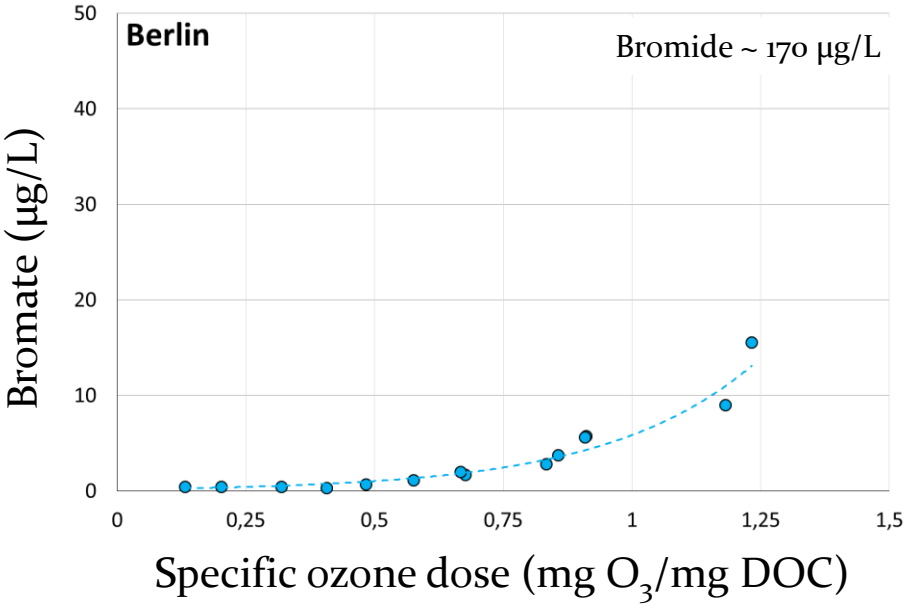
	WWTP Kalundborg		WWTP Berlin				
Mutagenicity	**Ozonation**	**MBBR**	**Ozonation**	**S/BAC**	**S/A**	**GAC**	**CW**
Ames (TA1535, -S9)	→ / ↑	→ / ↓	→	→ / ↓	→ / ↓	→ / ↓	→ / ↓
Ames (TA1535, +S9)	→ / ↓	→	→ / ↑	→ / ↓	→ / ↓	→ / ↓	→ / ↓
Ames (YG7108, -S9)	→	→	↑	↓	↓	↓	↓
APIs	**Ozonation**	**MBBR**	**Ozonation**	**S/BAC**	**S/A**	**GAC**	**CW**
Benzotriazol	↓	→	↓	↓	→	↓	→
Gabapentin	↓	→	↓	→	→	→	↑
Metoprolol	↓	→	↓	↓	→	↓	→
Transformation products	**Ozonation**	**MBBR**	**Ozonation**	**S/BAC**	**S/A**	**GAC**	**CW**
Diclofenac 2,5-Quinon imine	↑	↓[1]	↑	↓	↓	↓	→
Tramadol N-Oxid	↑	→	↑	→	→	↓	↓
Venlafaxin-N-Oxid	↑	→	↑	→	→	↓	↓

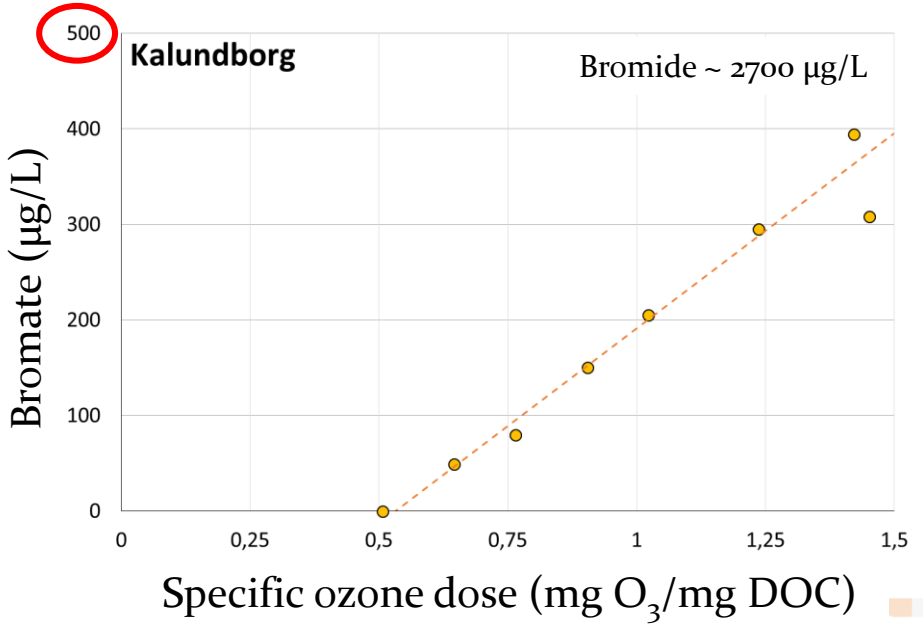
Legend for APIs and transformation products:
↑ = increase of concentration by more than 25%
→ = change of concentration less than 25%
↓ = decrease of concentration by more than 25%

[1] single measurement

Bromate formation by ozonation

Bromate drinking water limit (e.g. in Germany) = 10 µg/L
Proposed chronic quality standard for bromate = 50 µg/L[1]





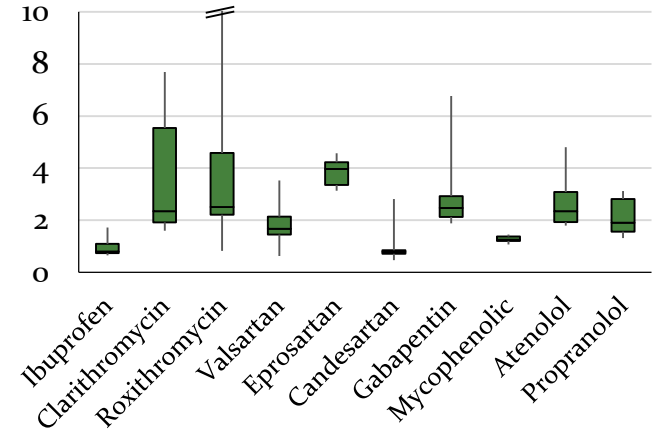
➔ Not critical

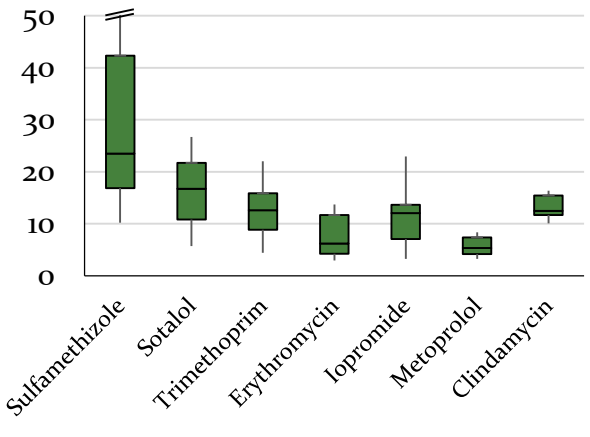
➔ High bromate formation due to elevated bromide level
➔ Relevant bromide sources: industrial wastewater and sea water intrusion into the canalisation

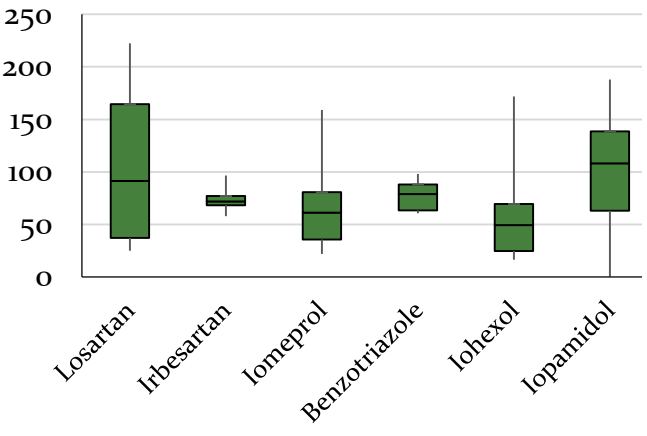
[1] https://www.oekotoxzentrum.ch/expertenservice/qualitaetskriterien/qualitaetskriterienvorschlaege-oekotoxzentrum/, visited at 13.11.2020

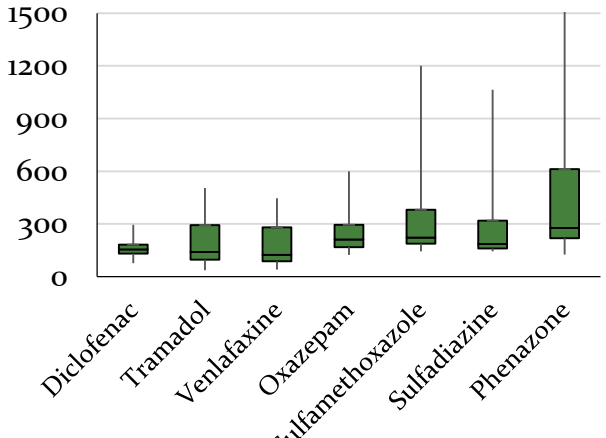
API elimination at moving bed biofilm reactors

half-life times (DT_{50} in hours, lab-scale tests)









Different MBBR feeding strategies were tested by AU:

- Intermittent feeding
- 12 different treatments
  - 2 days feast, 2-12 days famine
  - One reactor only on famine

Half-life times ≈ 1 - 100 hours

Impact of existing MBBRs is expected to be low for most APIs, due to low HRT (1 - 2 h)

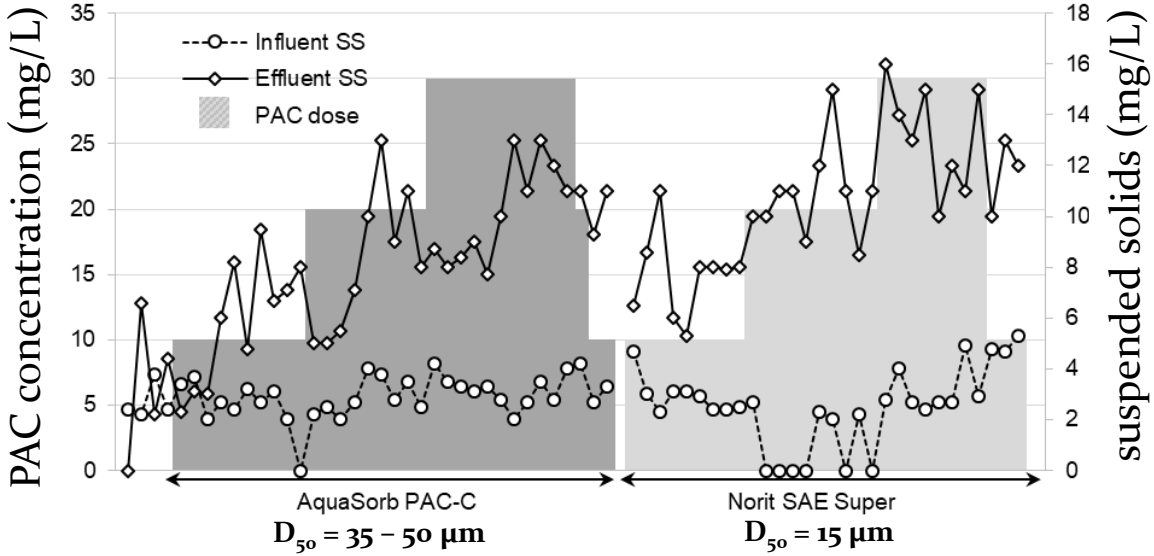
PAC-trials at WWTP Viikinmäki (FI)

➔ Focus: PAC retention from treated wastewater

Microsieve

Cloth filter

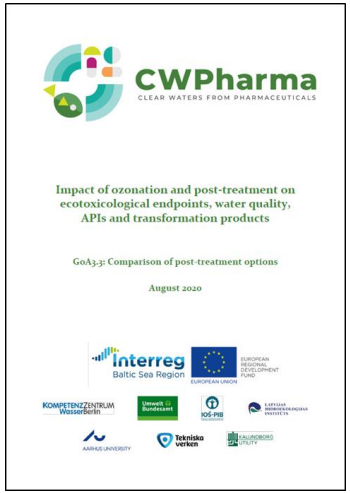
ACTIFLO® CARB

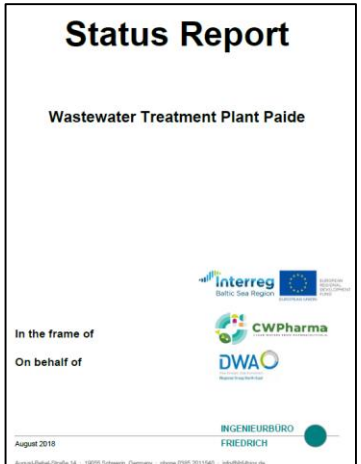


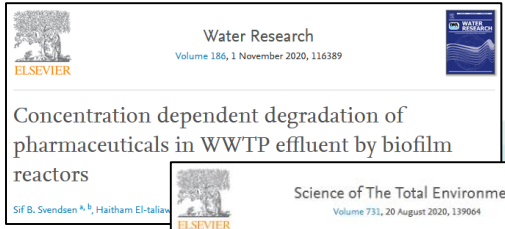
Insufficient PAC retention with microsieve
→ risk of PAC entry into aquatic environment

Read also publications from WP3

Reports are available at:
https://www.cwpharma.fi/en-US/Publications



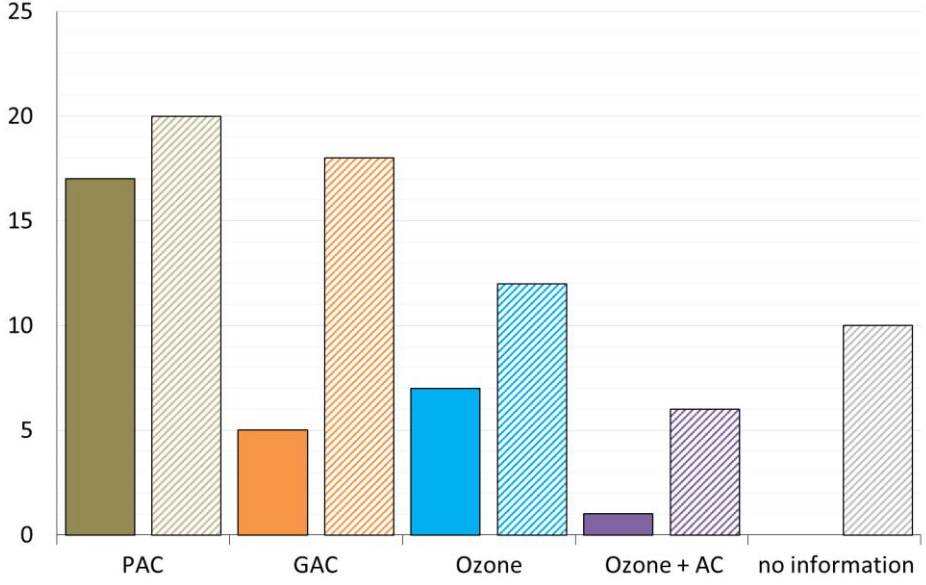




WWTPs with (planned) AWT in Germany and Switzerland

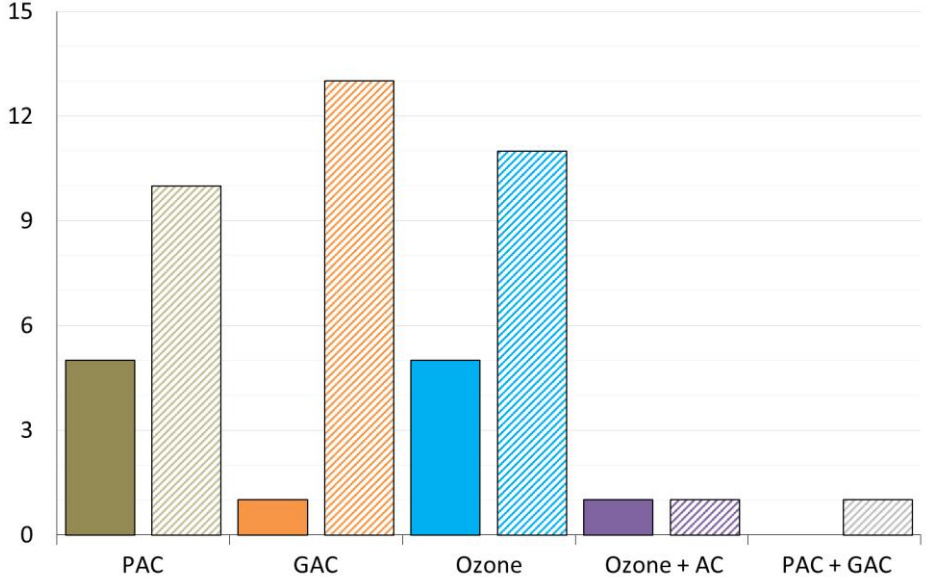
WWTPs with AWT in **Germany**

n = 96 (30 in operation, 66 in planning/construction)



WWTPs with AWT in **Switzerland**

n = 48 (12 in operation, 36 in planning/construction)



Full bars = in operation, shaded bars = in planning/construction

Data based on: Metzger, S., Barjenbruch, M., Beier, S., Miehe, U., & Nafo, I. (2020). Statusbericht „Spurenstoffentfernung auf kommunalen Kläranlagen in Deutschland“. *Korrespondenz Abwasser, Abfall, 67.*

Data based on: https://micropoll.ch/Mediathek/liste-der-aras-mit-mv-stufe/, status 02/09/2020

Summary

Know your water quality:

- Dosage of ozone and PAC has to be adapted to the organic background of the wastewater (DOC)
- Nitrite causes additional ozone demand (3.4 mgO_3/mg-N!)
- Be aware of bromide levels when you consider ozonation (sea side WWTPs!)

Monitor your process:

- API elimination can be monitored by using surrogate parameters (e.g. UVA_{254} reduction) – online or offline.
- Same surrogate parameters can also be used for process control to adapt the dosage, if necessary
- Ecotoxicological tests (e.g. mutagenicity, estrogenicity, *Aliivibrio fischeri* bioluminescence inhibition) can be used to evaluate the impact of the different treatment stages (enrichment factors 100 – 1000)

Project partners

EUROPEAN
REGIONAL
DEVELOPMENT
FUND