



CWPharma2
CLEAR WATERS FROM PHARMACEUTICALS

Interreg
Baltic Sea Region



EUROPEAN
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DEVELOPMENT
FUND



Feasibility and piloting of Pharmaceuticals removal at Hillerød WWTP

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The start



- CW Pharma guidelines focused on establishing a state of the art and describe how to get there
- HFORS was discussing expanded lists of target concentrations (PNEC) of relevant pharmaceuticals in Denmark with the authorities

-> 20 new analytes



Background

- Pharmaceutical removal triggered by new superhospital in Hillerød “industrial point source”
- Pharmaceutical removal should lead to no adverse effects present in Pøle Å and Havelse Å
- Use of CWPharma guideline
recommendation:
around 0.7 mgOzone/mg DOC (specific ozone dose)
20 min HRT in GAC



Background 2

- Pharmaceuticals with high potential for environmental risk were discussed between HFORS and authorities some of these were not tested in CW Pharma (original)
- CW Pharma recommendations were steered by ensuring well running of reactors not by reaching PNEC
- Metabolites and transformation products situation was a bit unclarified within CW Pharma and HFORS



Procedure

- Assess status in Hillerød
- Test ozonation efficiency/ozonation control
- Test GAC efficiency
- Assess whether PNECs can be reached
- Conclusions

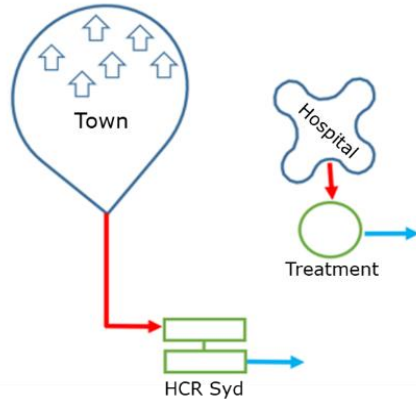


1) The status at Hillerød WWTP

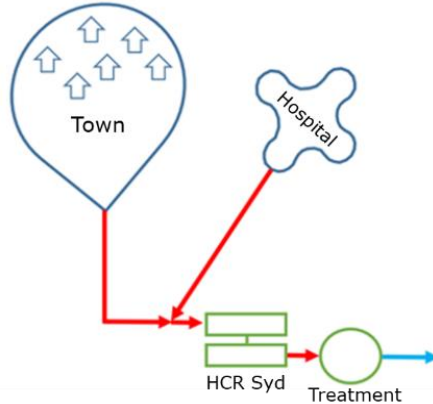


At source or central?

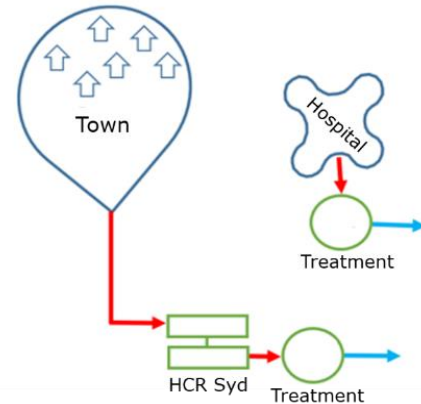
1. Treating at source



2. Treating at HCR Syd



3. Treating at source and at HCR Syd



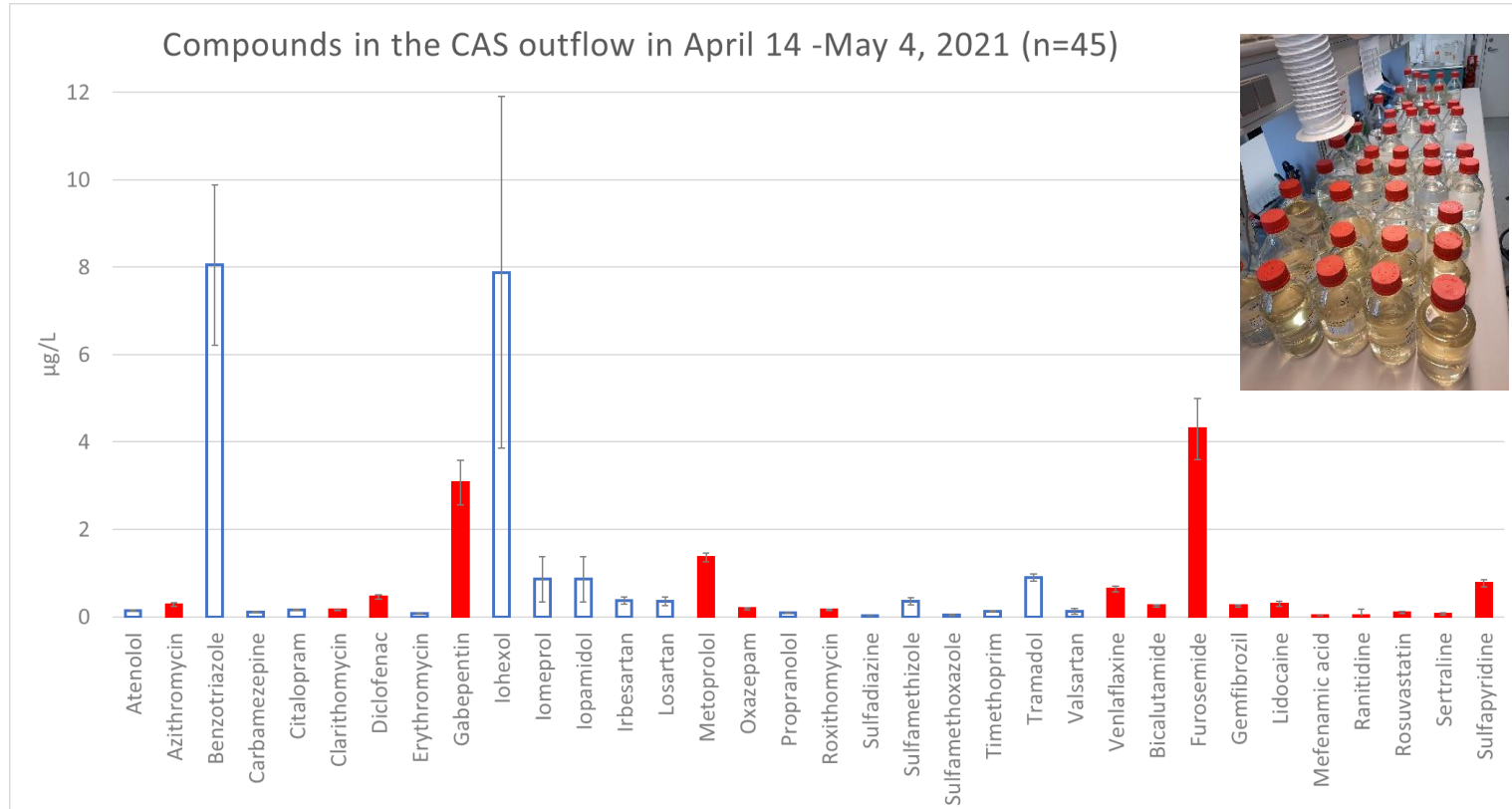
Selected PNEC values established at HFORS

Compound	Best guess PNEC fresh water [µg/L]	Reference
Amoxicillin	0,078	BEK nr 1625 af 19/12/2017
Ampicillin	0,00001	Orias & Perrodin 2013
Ampicillin	0,075	Mose Pedersen et al., 2007
Azithromycin	0,09	Fransen Krog et al., 2013
Benzotriazole	1.00	Ikke et lægemiddel ???
Bicalutamid	0,1	Biofos, 2013
Bicalutamid	1,0	Stuer-Lauridsen et al., 2013
Ceftazidime / Avibactam	0,10	Mose Pedersen et al., 2007
Candesartan	0,1	
Ciprofloxacin	0,0	
Ciprofloxacin	0,00	
Citalopram	0,000	
Citalopram	0,5	
Clarithromycin	0,0	
Clindamycin	0,01	
Clindamycin	0,5	
Codeine	0,0	
Diclofenac	0,1	
Erythromycin	0,02	Buus Kjær & Ulf Nielsen 2018
Erythromycin	0,04	Fransen Krog et al., 2013
Furosemid	31	Nielsen et al., 2013
Gabapentin	0,196	Orias & Perrodin, 2013
Gemfibrozil	0,15	Biofos's arbejdsgruppe 2013
Ibuprofen	4.0	Nielsen et al., 2013
Iohexol	1.000.000	Stuer-Lauridsen et al., 2013
Lidocain	0,0026	Orias & Perrodin, 2013

Compound	Best guess PNEC fresh water [µg/L]	Reference
Mefenamic acid	3,9	Orias & Perrodin, 2013
Metoprolol	0.10	Orias & Perrodin, 2013
Miconazol	-	Unknown PNEC
Mycophenolic acid	0.10	Nielsen et al., 2013
Oxazepam	0.019	Orias & Perrodin, 2013
		Buus Kjær, Ulf Nielsen 2018
		Orias & Perrodin 2013
		Nielsen et al., 2013
		Orias & Perrodin, 2013
		Ekengren et al., 2020
		Stuer-Lauridsen et al., 2013
		Mose Pedersen et al., 2007
		Unknown PNEC
		Mose Pedersen et al., 2007
		Biofos's arbejdsgruppe 2013
		BEK nr 1625 af 19/12/2017
Sulfamethizole	4	Orias & Perrodin, 2013
Sulfamethizole	12	Mose Pedersen et al., 2007
Sulfamethoxazole	0.12	Nielsen et al., 2013
Tramadol	2,25	Fransen Krog et al., 2013
Trimethoprim	10	BEK nr 1625 af 19/12/2017
Trimethoprim	0,0058	Orias & Perrodin, 2013
Venlafaxin	0.10	Biofos, 2013

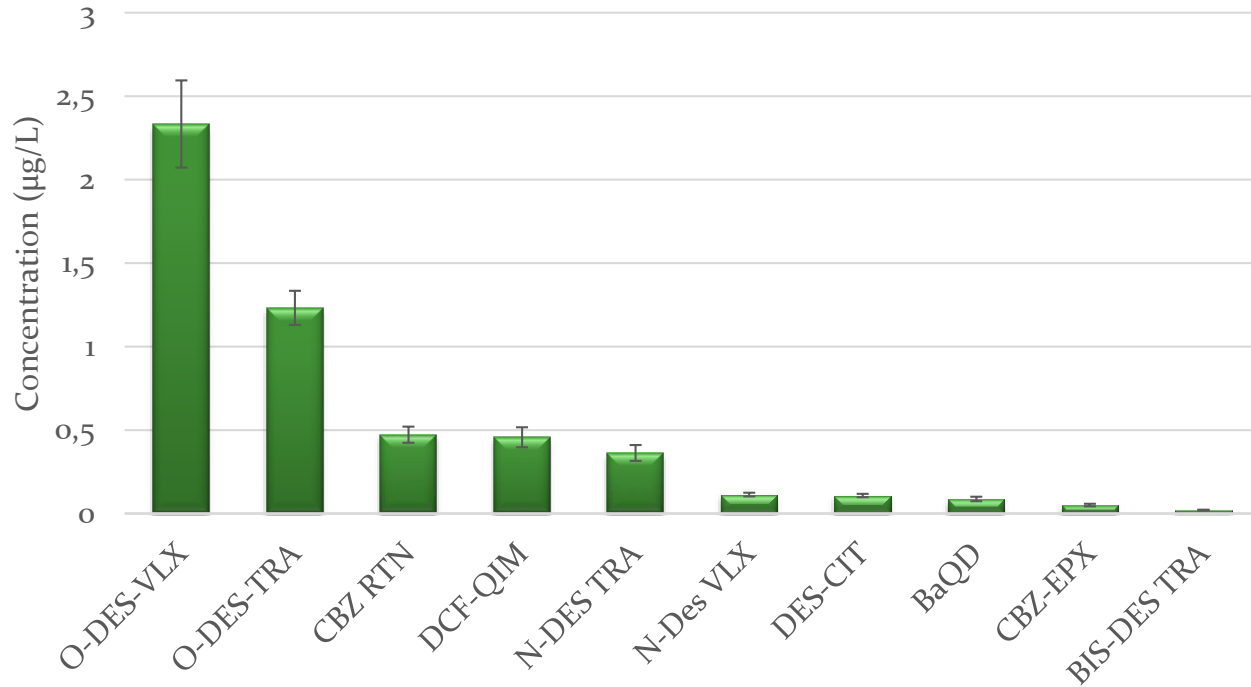
PNECs not in agreement with CWPharma PNECs

Pharmaceuticals concentration in effluent wastewater



- Short intensive monitoring of CAS effluent revealed the presence of 34 compounds (out of 53 measured)
- The average values 17 of the compounds exceeded their corresponding PNEC values (marked in **red**)
- The tertiary treatment options are discussed further in the presentation

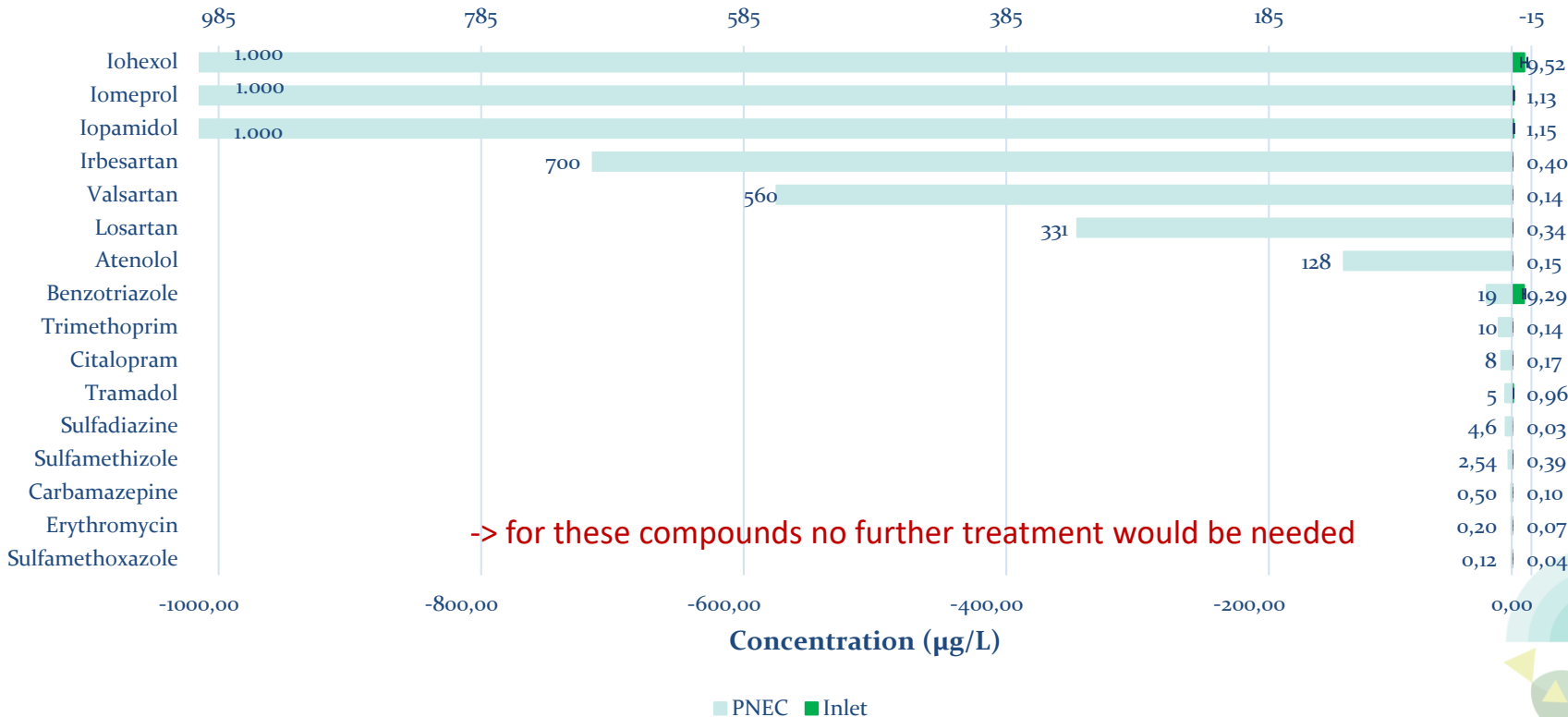
45 Pharmaceutical metabolites in effluent wastewater (highlights)



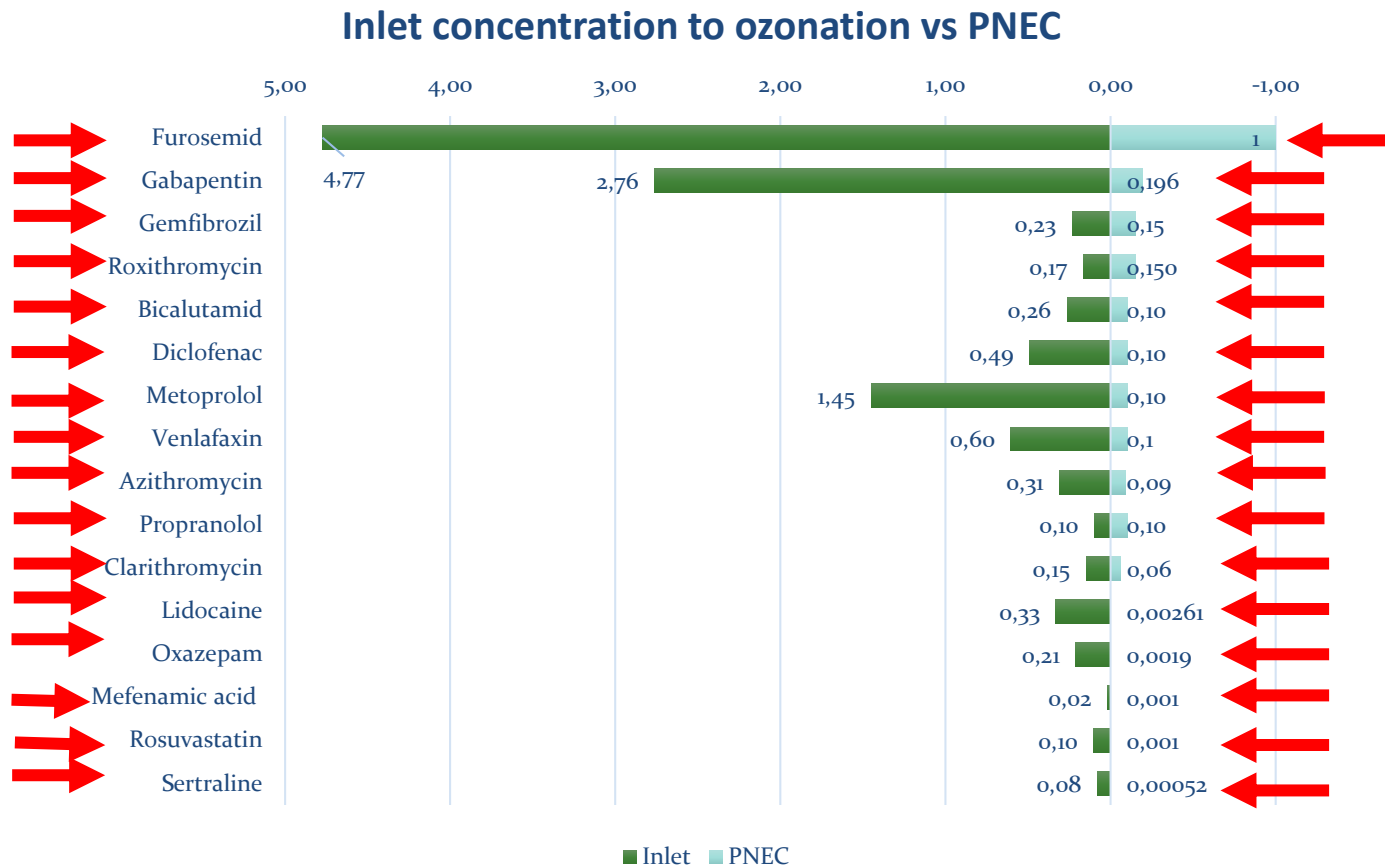
There are currently no targets discussed for transformation products



Concentration of compounds with concentration below PNEC in the effluent of CAS /Inlet to pilot (n=5)



Concentration of pharmaceuticals in CAS effluent vs PNEC value



Results of status at Hillerød WWTP

- Some pharmaceutical's concentrations are exceeding the PNEC and will require removal
- No special reasons against any of the CW Pharma Technologies (no excessive Br^- , no high DOC, Sludge is incinerated)



Design of pilot Hillerød WWTP

Nippon Pure Oxygen batteri



Pure Oxygen

Ozone generator on a skid



O₂ + O₃

Ozone contact tank



Ozone Treated water

Feeding pump to GAC filter



GAC filters



Ozon + GAC Treated water

GAC Treated water

Back to plant inlet

CAS
effluent

Outlet
Discfilter



S2

S3

S1

S4

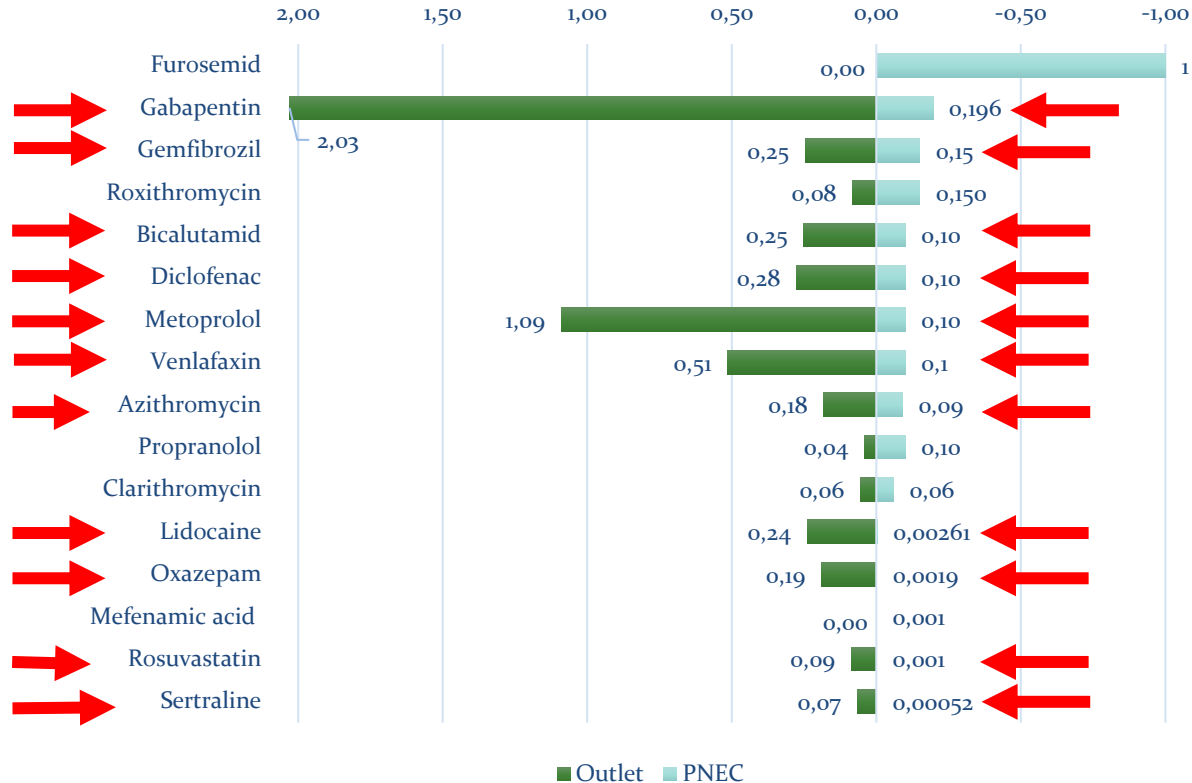


2) Test of Ozonation

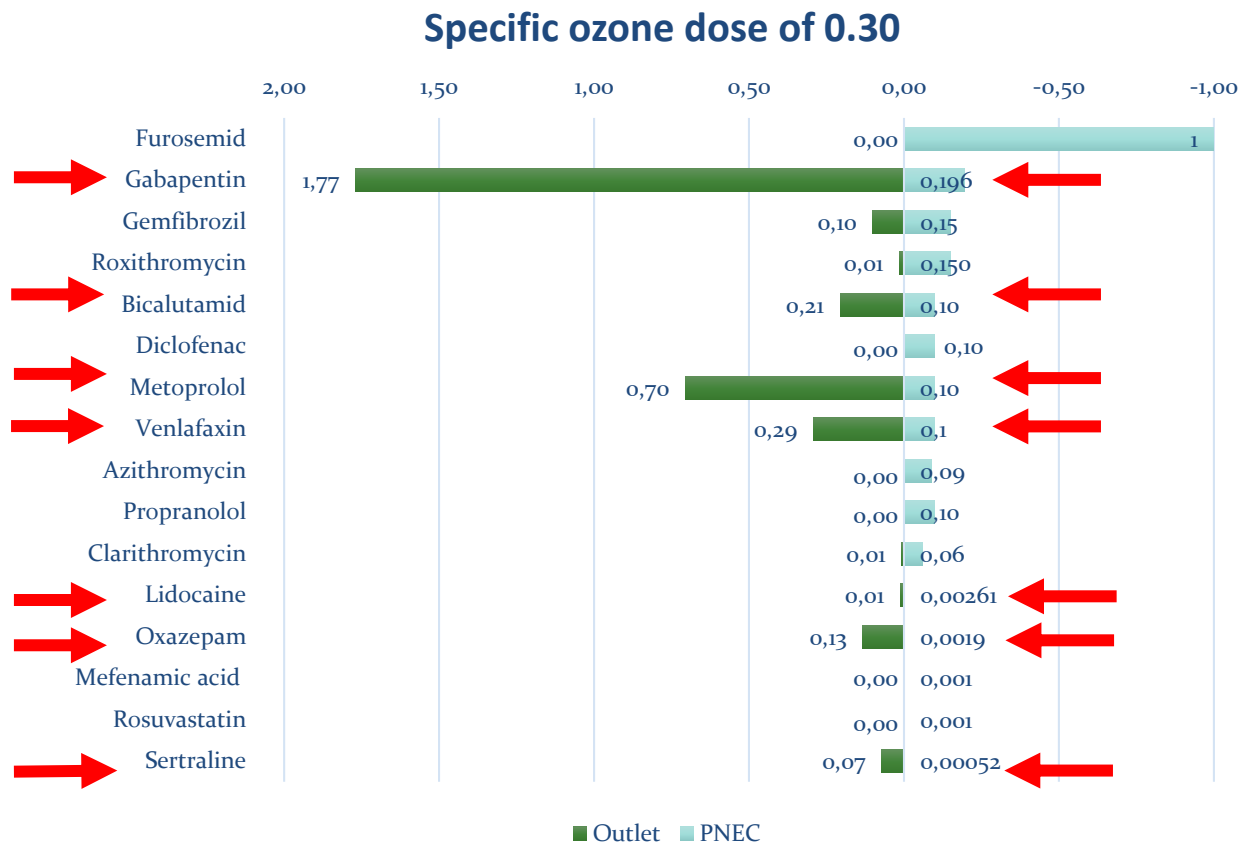


Concentrations after ozonation at specific ozone dose vs PNEC value

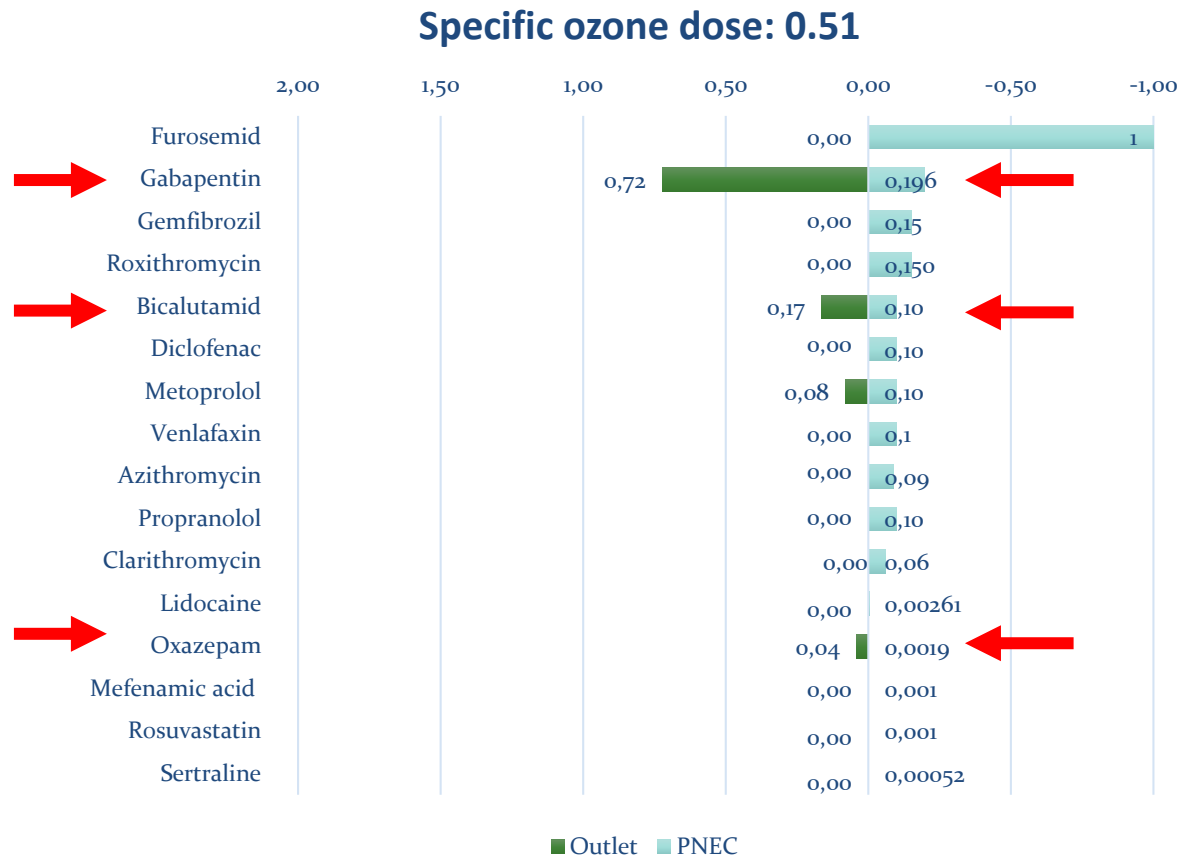
Specific ozone dose: 0.10



Concentrations after ozonation at specific ozone dose vs PNEC value

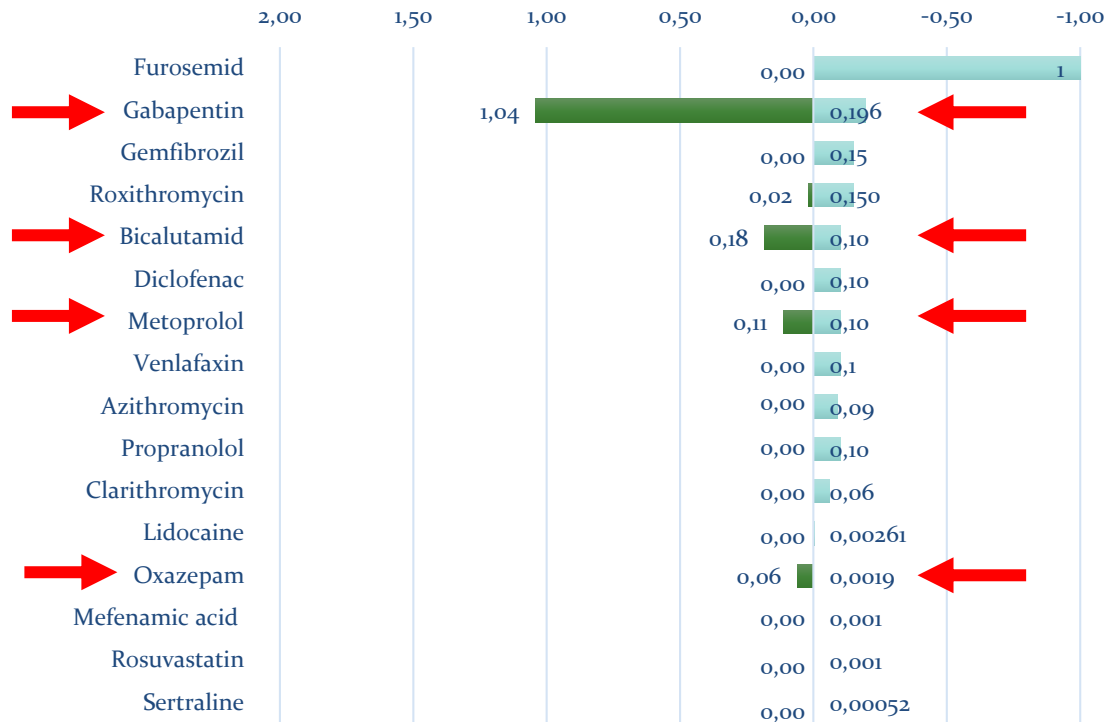


Concentrations after ozonation at specific ozone dose vs PNEC value



Concentrations after ozonation at specific ozone dose vs PNEC value

Specific ozone dose: 0.71

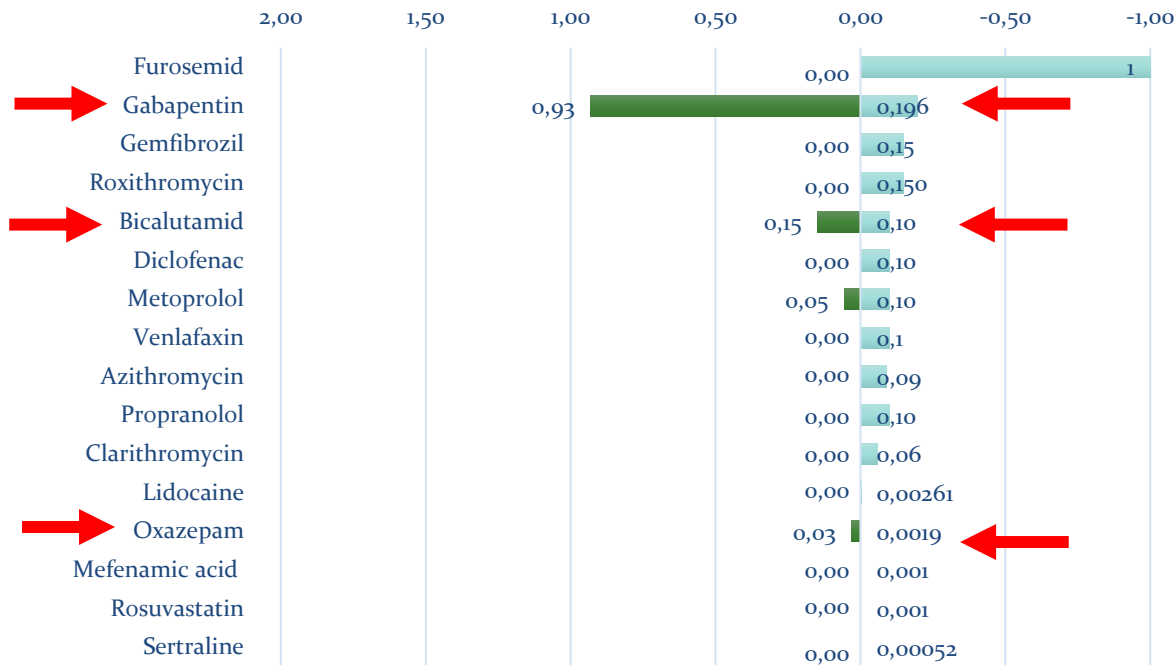


■ Outlet ■ PNEC



Concentrations after ozonation at specific ozone dose vs PNEC value

Specific ozone dose: 1.06



Concentration (µg/L)

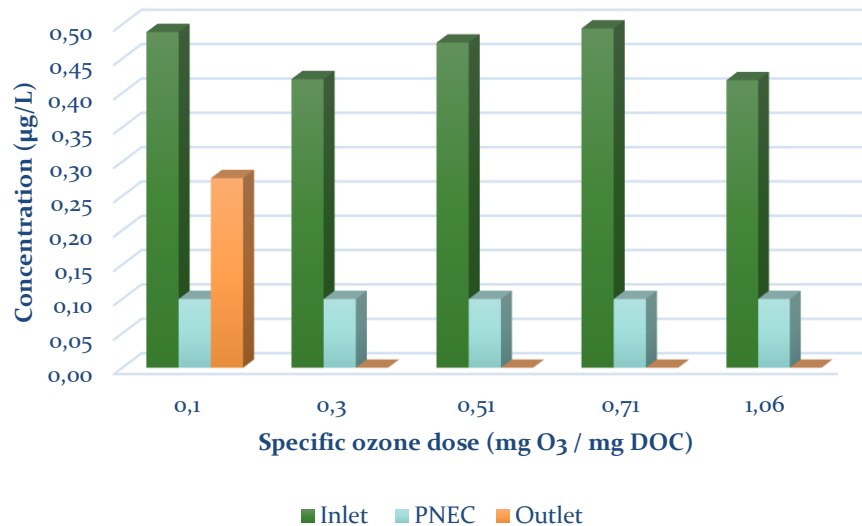
■ Outlet ■ PNEC



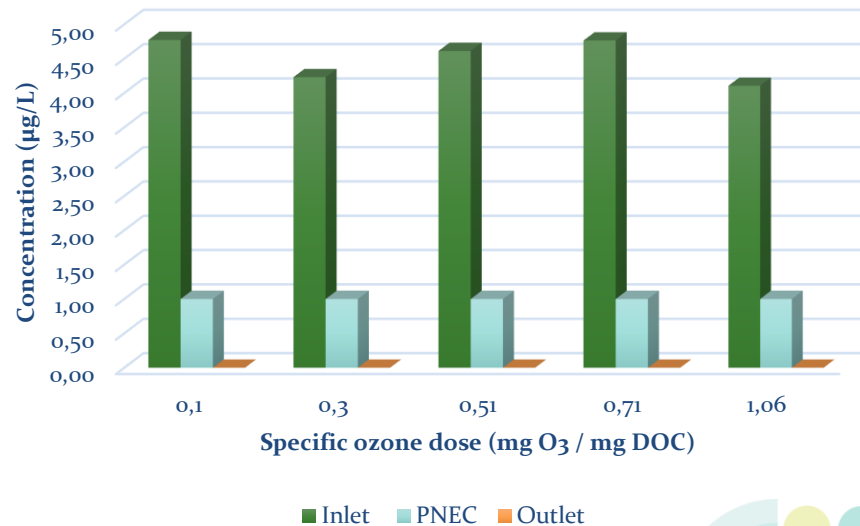
Concentration of pharmaceuticals at different ozone dose vs PNEC

- rapidly reacting compounds

Diclofenac



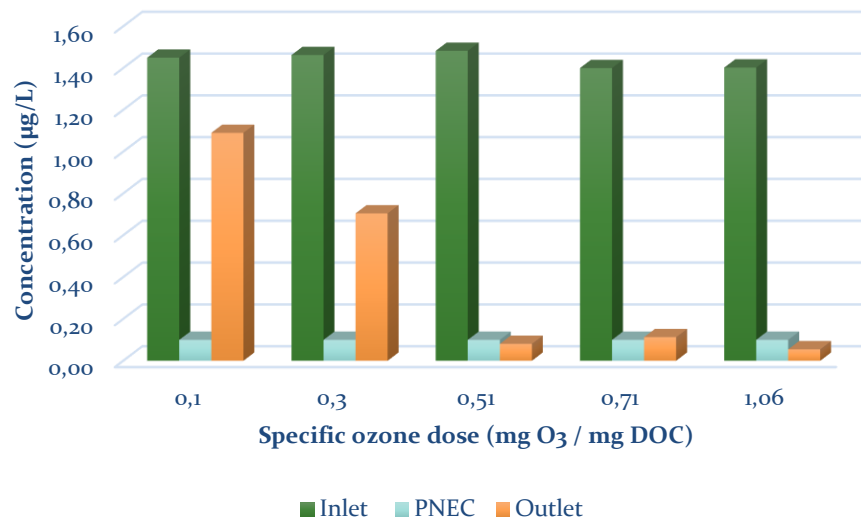
Furosemide



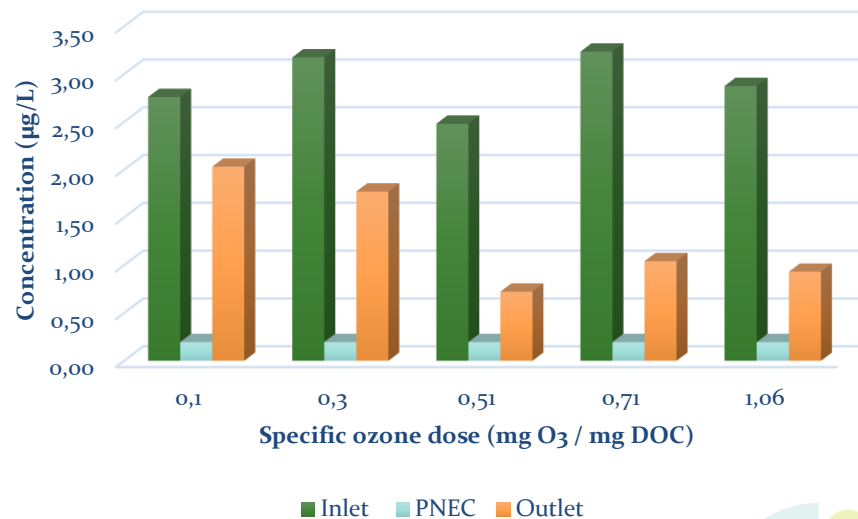
Concentration of pharmaceuticals at different ozone dose vs PNEC

- moderately reacting compounds

Metoprolol



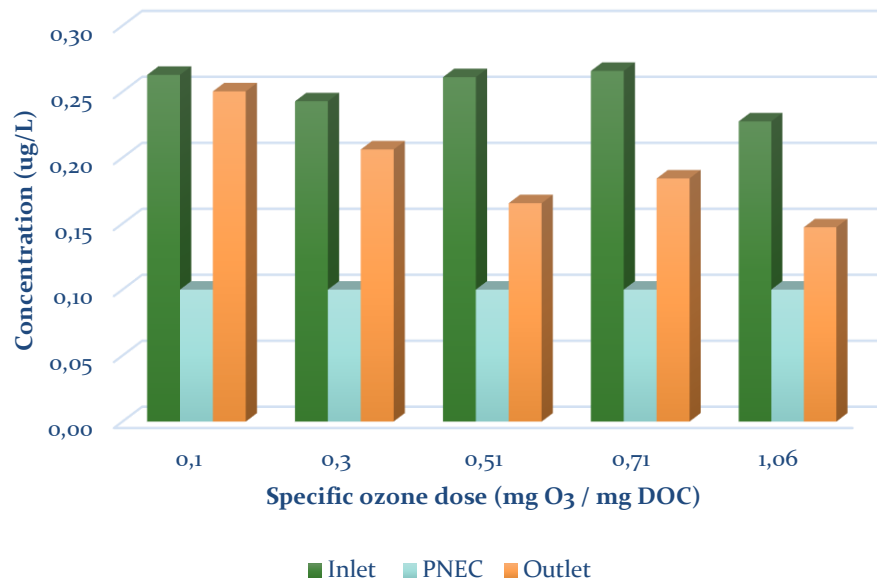
Gabapentin



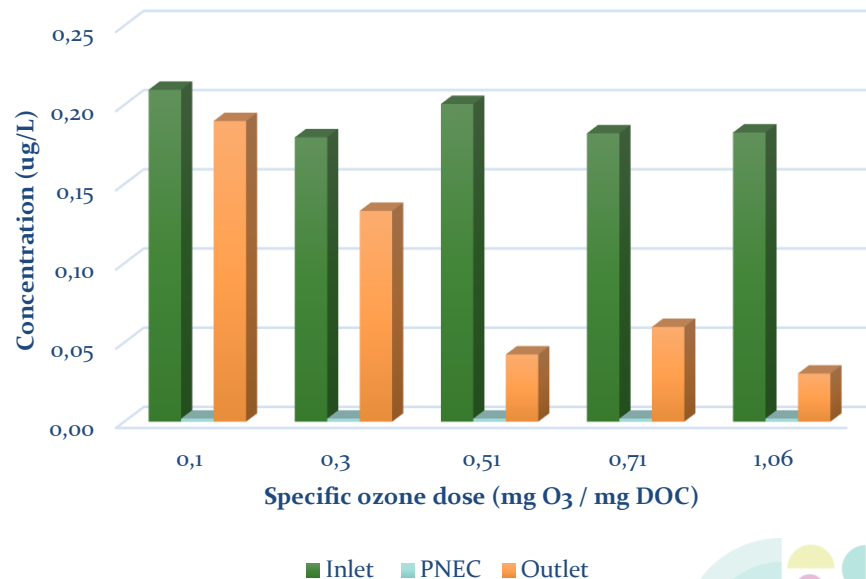
Concentration of pharmaceuticals at different ozone dose vs PNEC

- slowly reacting compounds

Bicalutamid



Oxazepam

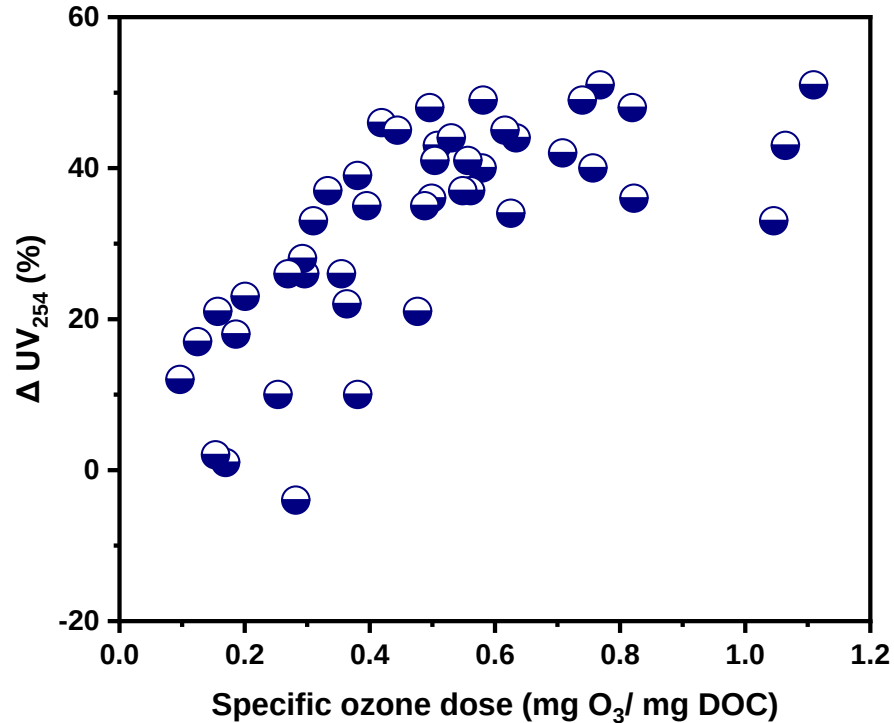


Can ozonation processes be controlled by UV detection ?

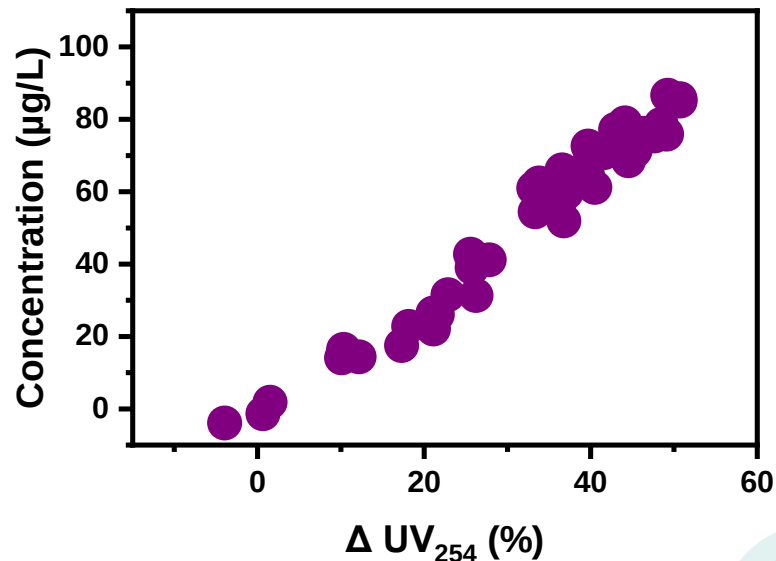
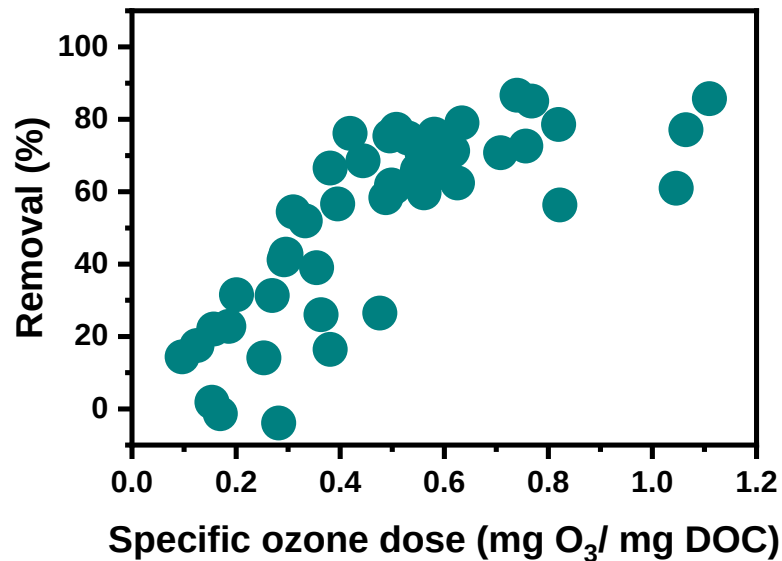
ΔUV_{254} as control parameter



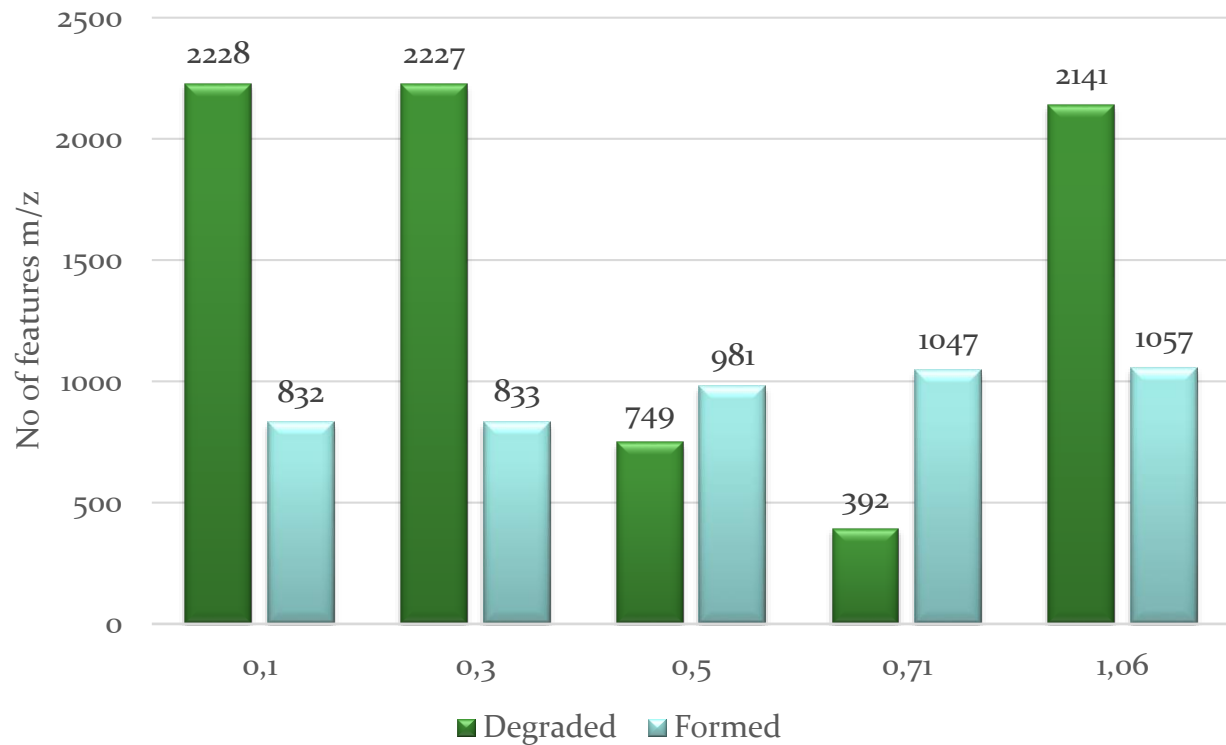
Delta UV vs specific ozone dose



Removal of a carbamazepine metabolite vs specific ozone dose / Delta UV



Non target screening at different specific ozone doses



Real challenges for ozonation



Conclusion of ozonation

- ✓ Ozonation removes most of the pharmaceuticals
- ✓ Gabapentin, Bicalutamid and Oxazepam concentration were
above PNEC value
- ✓ Post ozonation Delta UV can be used for process control



3) Test of GAC (Granulated Activated Carbon)



GAC-Pilot

- GAC installed in the WWTP is removing pharmaceuticals very well
 - removed 53 pharmaceuticals below limits of the quantitation
 - 49 of 53 below limits of detection*.
- Nevertheless, the GAC filter pilot was not exploited over commercially relevant times
- A small-scale GAC experiment was performed over 6 months at AU
 - Granules 0.4-1.7 mm *Brennsorb 1240* packed in 180 mL (40cm height) cylindric glass column
 - Operated with water-GAC contact time of 25 min (3.6 mL/min flowrate)
 - 25.6 EBV/day generated 4,500 EBVs per 6 months (EBV=empty bed volume)



* Traces of Iohexol, lomeprol, Iopromide and Erythromycin visible in selected post GAC samples

GAC Pilots worked well

...until there was a malfunctioning of the sludge settler in combination with an accidental bypass of the disc filter

GAC-covered by sludge with seriously decreased flow



GAC-Labscale

Test GAC over time (Capacity)

- Same material as in Pilot
- Effluent water from HFORS

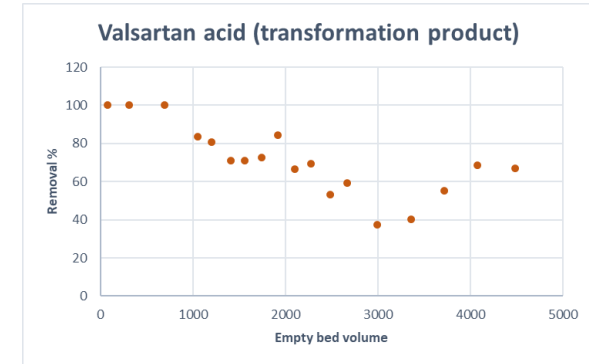
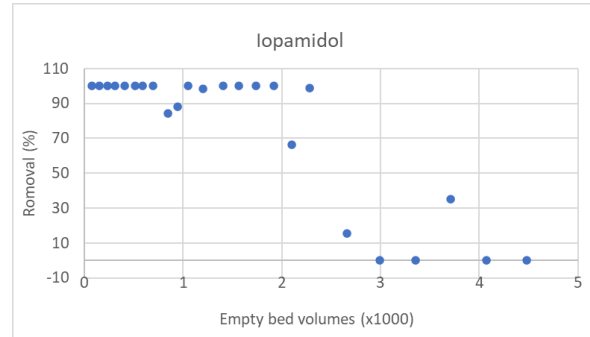
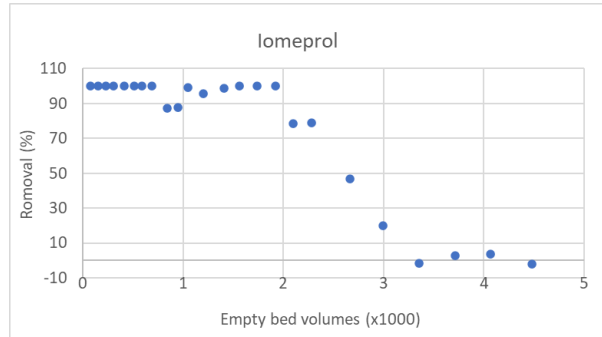
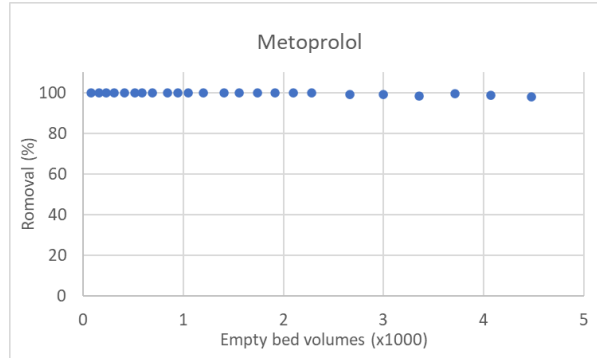
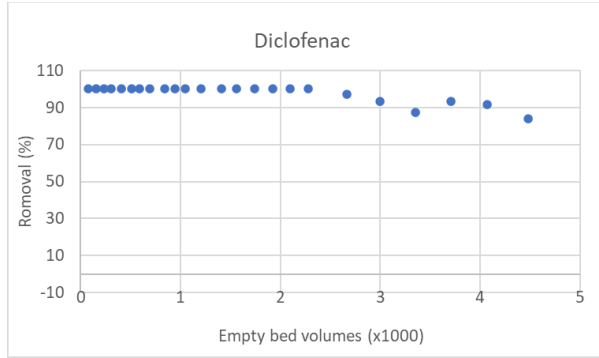
Long term target (used for cost assessments):
10.000-15.000 EBV (empty bed volumes)

Within this short term project we could reach
up to 4500 EBV

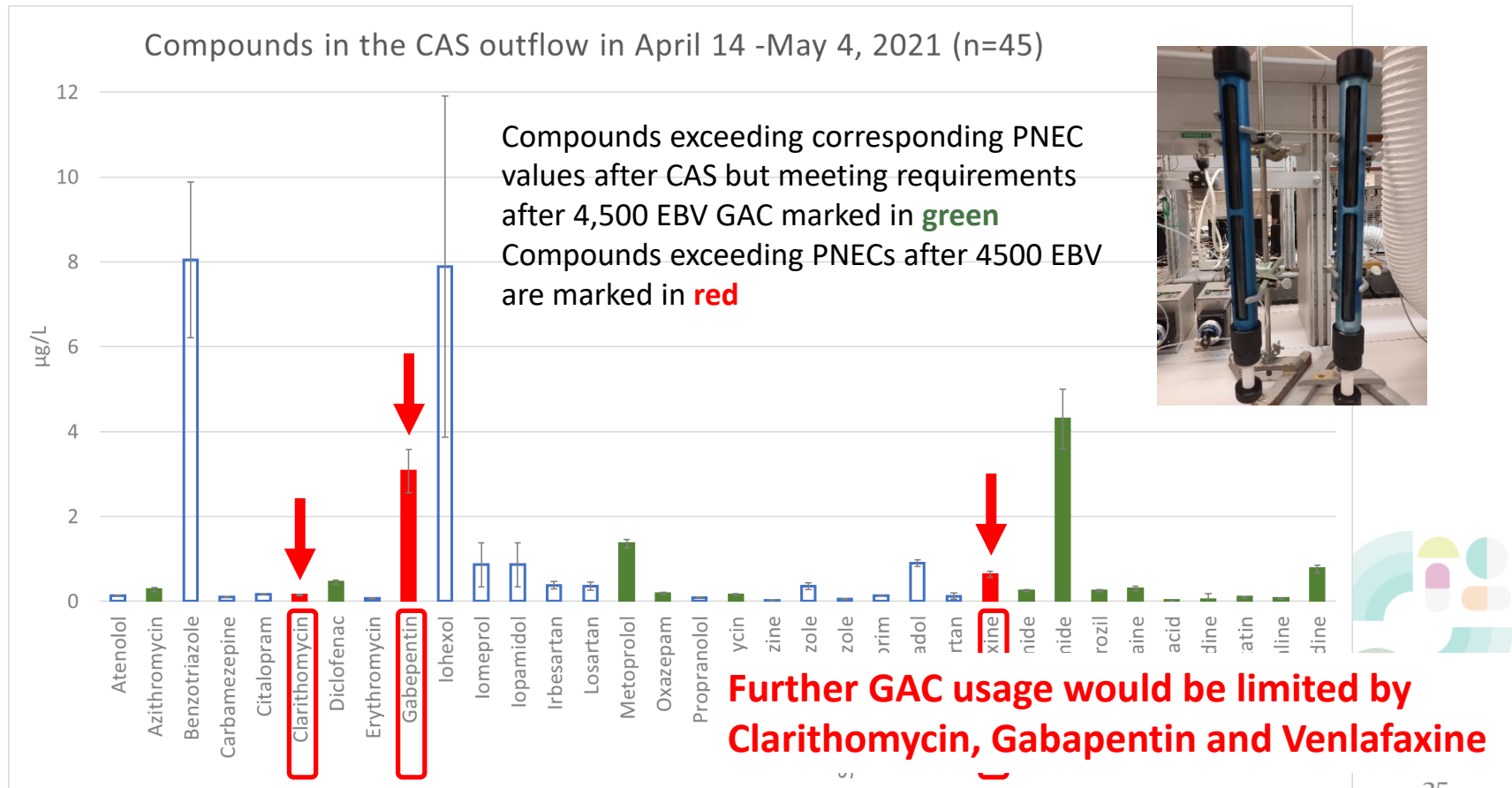
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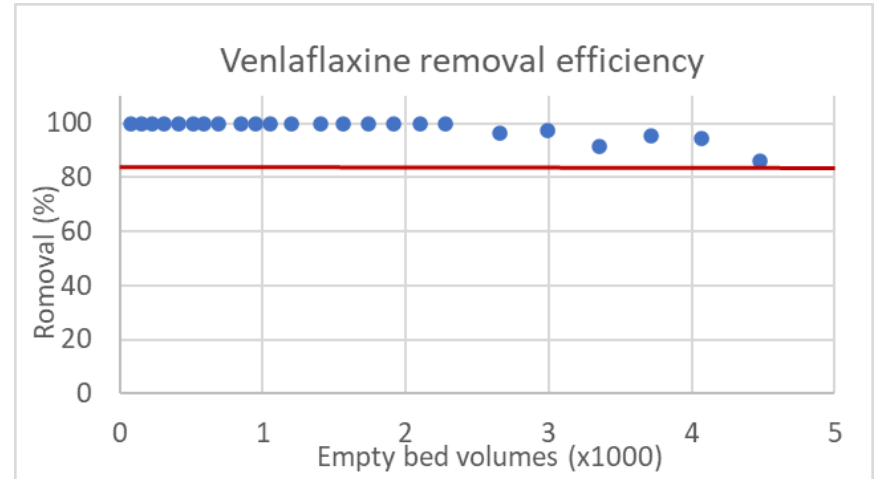
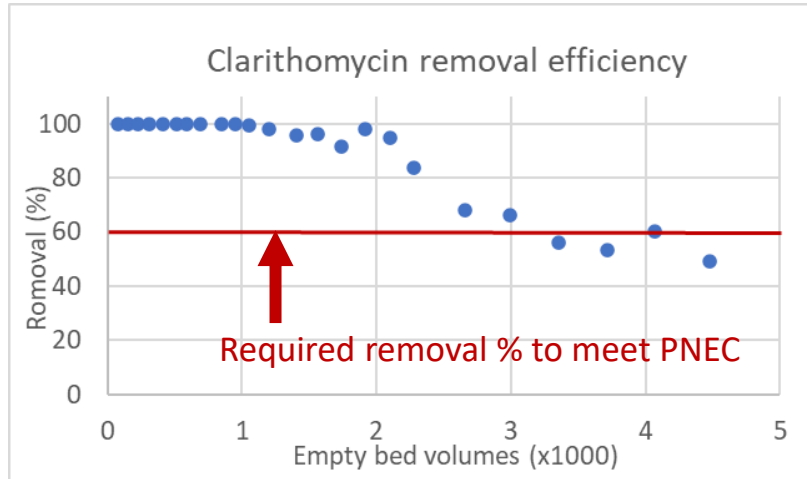
Removal of Pharmaceuticals with GAC over time



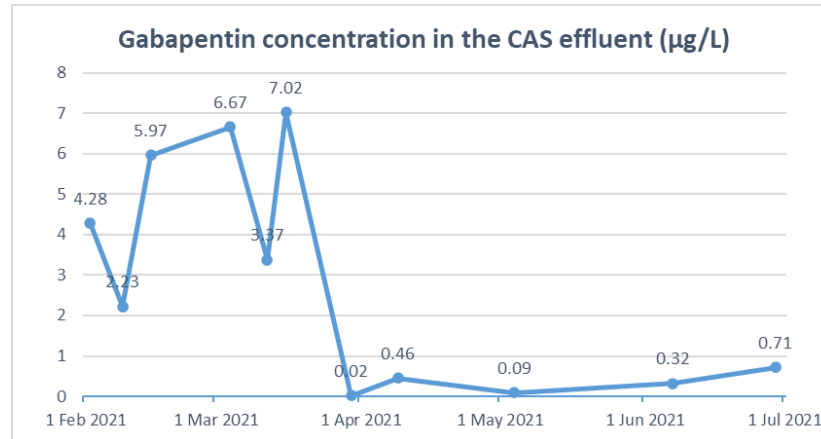
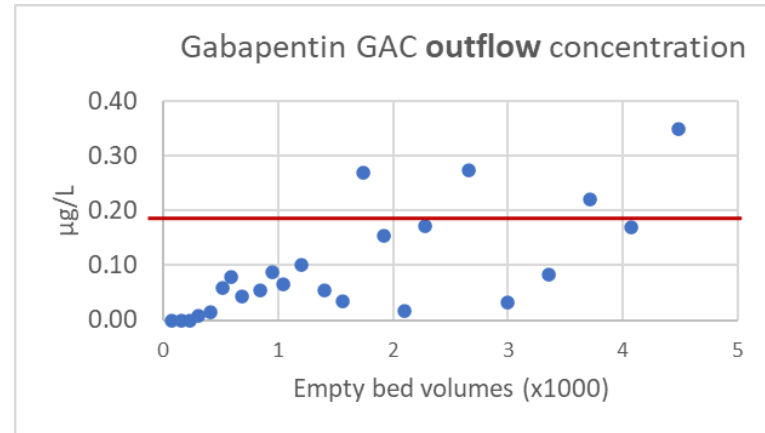
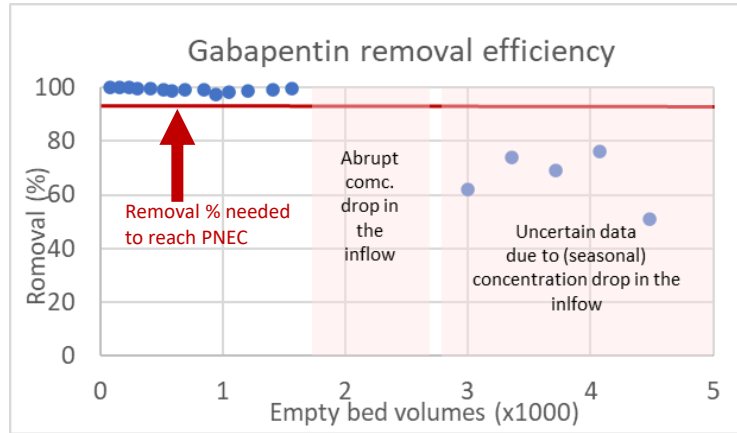
14 out of 17 PNEC-violating compounds were removed below PNEC value with 4,500 EBVs.



Compounds not removed to the required level by the GAC experiment



Determination of removal efficiency of Gabapentin hampered by temporal changes in conc.



Conclusions GAC

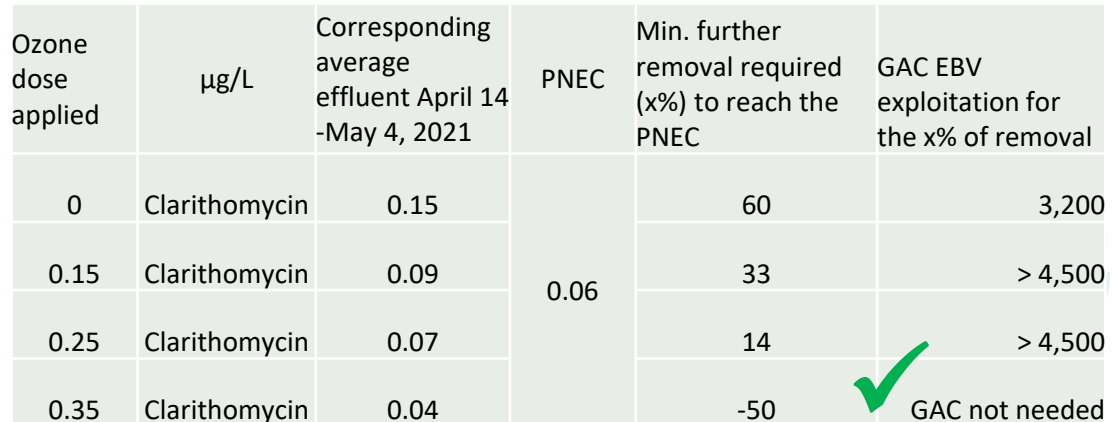
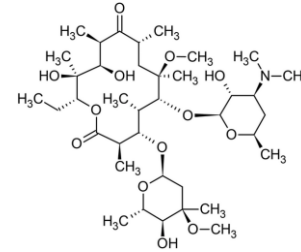
- ✓ Some compounds (e.g., X-ray contrast media) were poorly removed in GAC, but they were not concern regarding PNEC values without any tertiary treatment.
- ✓ 4,500 EBV GAC would totally remove or reduced below the PNEC values all the compounds of concern except Clarithomycin, Venlafaxine and (seasonally) Gabapentin.



4) Ozone and GAC combination



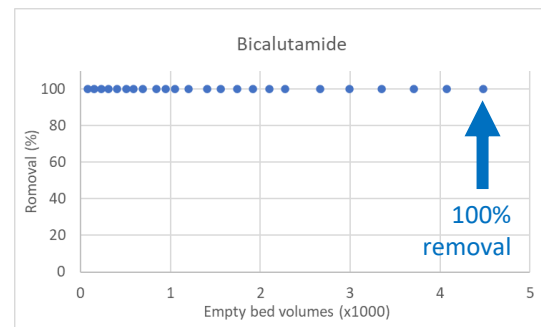
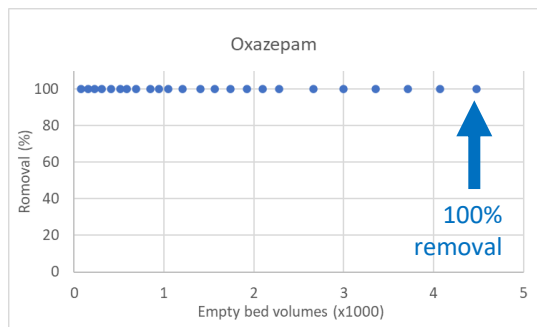
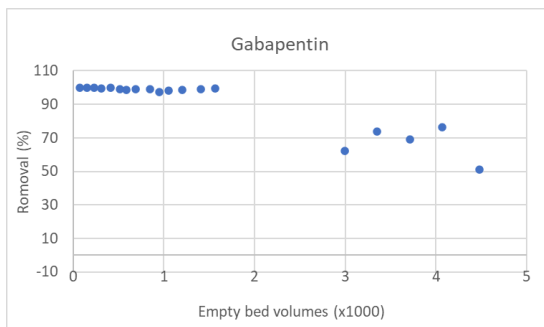
- Compound experimentally determined as limiting GAC exploitation: Clarithromycin



Conclusions Ozonation combined with GAC

- ✓ The compounds identified as limiting in the ozonation removal (Gabapentin, Oxazepam, Bicalutamide) could be further removed in GAC after the ozonation.

Gabapentin
Oxazepam
Bicalutamid



- ✓ Even though application of GAC-only or O_3 -only would be limited by several compounds, **all the compounds would be removed with the O_3 -GAC combination** (except possibly high/seasonal? concentrations of Gabapentin)



How valid is the Gabapentin PNEC in the “HFORS” dataset?

	Hfors PNEC	CW Pharma PNEC
Value	0.196 µg/L	100 µg/L
origin	Review, modelled with ECOSAR (2012)	Experimental data
	Legal but not preferred	Legal preferred

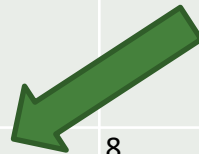


Result for Gabapentin from

ECOSAR 2.0 (17/11 2021)

Organism	Duration	End Point	Concentration (mg/L)	Max Log Kow	Flags
Fish	96h	LC50	53851.61	5	Chemical may not be soluble enough to measure this predicted effect. If the effect level exceeds the water solubility by 10X, typically no effects at saturation (NES) are reported
Daphnid	48h	LC50	4338.24	5	
Green Algae	96h	EC50	7771	6.4	
Fish		ChV	10350.03	8	
Daphnid		ChV	243.47	8	
Green Algae		ChV	1944.95	8	

The current version of ECOSAR would result in a PNEC of 243 µg/L which is about 1000 times higher than the one from the review used for Hfors (and very close to the CW Pharma PNEC)



Conclusions PNEC values

PNEC values need handling with care as intro data are often insecure.

When discussing big investments critical data should be double checked.

Generally PNEC values can be used to test motivation for treatment (several compounds have starting concentration exceeding PNEC considerably-> action).

It can be considered that all municipal WWTPs have effluent concentrations that exceed PNECs for multitude of compounds.



Conclusions:

All tested compounds reach targets ($<PNEC$) with the combination of ozone and GAC.

Full confirmation of CW Pharma guideline
(ozone dose can actually be decreased to $0.5 \text{ mgO}_3/\text{mg DOC}$ at HFORS).

GAC filters need protection from malfunctions in sludge management.

Transformation products need further clarification.



Acknowledgement



The whole CW Pharma 1 and 2 team

