



HCR Syd 2.0

Quartinary step for cleaning pharmaceuticals

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Hillerød Forsyning

HCR Syd 2.0

Quartinary step : Cleaning for pharmaceuticals

1. Very short about HCR Syd
2. Examination in 2019
3. Decision 2020
4. CWPharma 2 Pilot plant in 2021
5. Control program in permission 2023
6. Proces choices
7. Architecture
8. Ozonation strategi based on Altenrhein



HCR SYD 2.0

Waste water treatment plant HCR Syd



Fully covered with Public acces

HCR Syd , a good daily operated plant

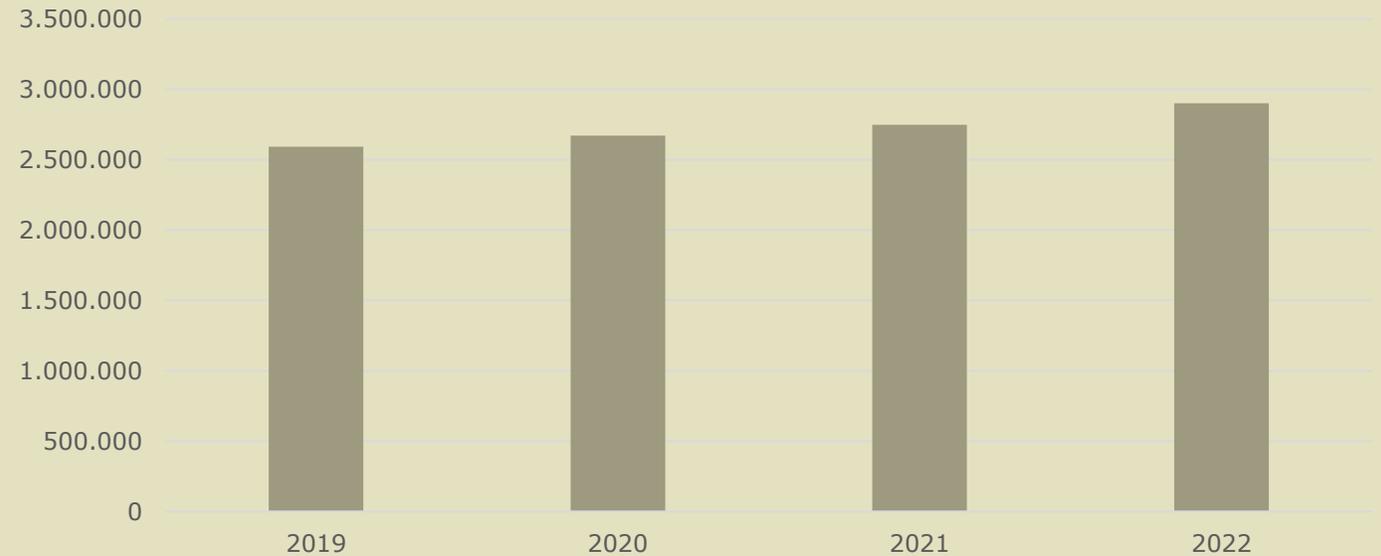
Results 2023

	New Demand	Results
Nitrogen	3,04 mg/l	1,58 mg/l
Phosphous	0,161 mg/l	0,13 mg/l

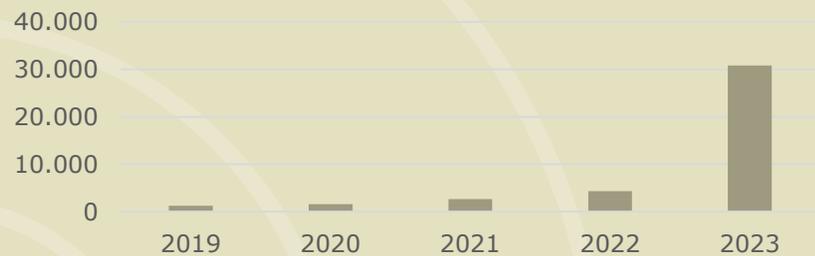
Sales of Pharmaceuticals in Denmark. www.Medstat.dk



Sold pharmaceuticals 2019-2022 i 1.000 DDD



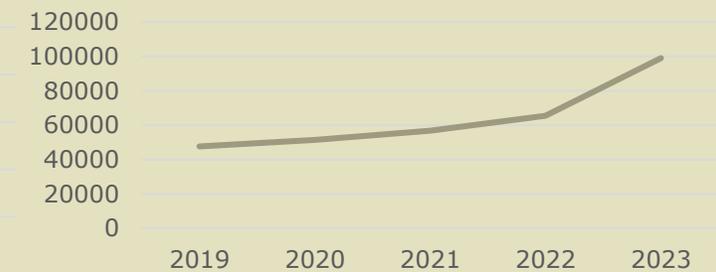
Weight-loss drugs i 1.000 DDD



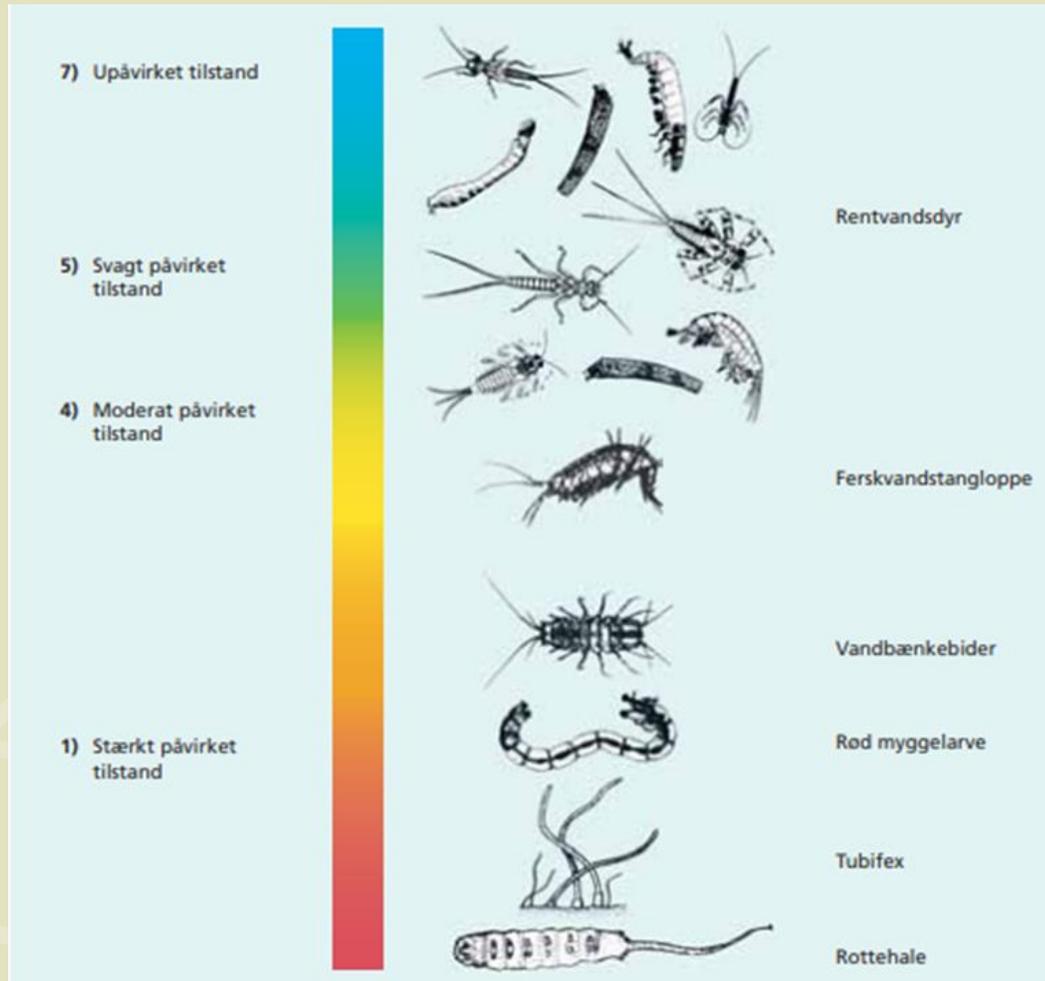
Paracetamol DDD



Pharmaceuticals Novo Nordic



Vision for HCR Syd



- The environment in Hillerød should be
- Good ecological quality
 - Outlet for the streams fulfill PNEC = (Predicted No Effect Concentrations)

Predicted Environmental Concentration (PEC) caused by the outlet (up to 90 % of stream flow)

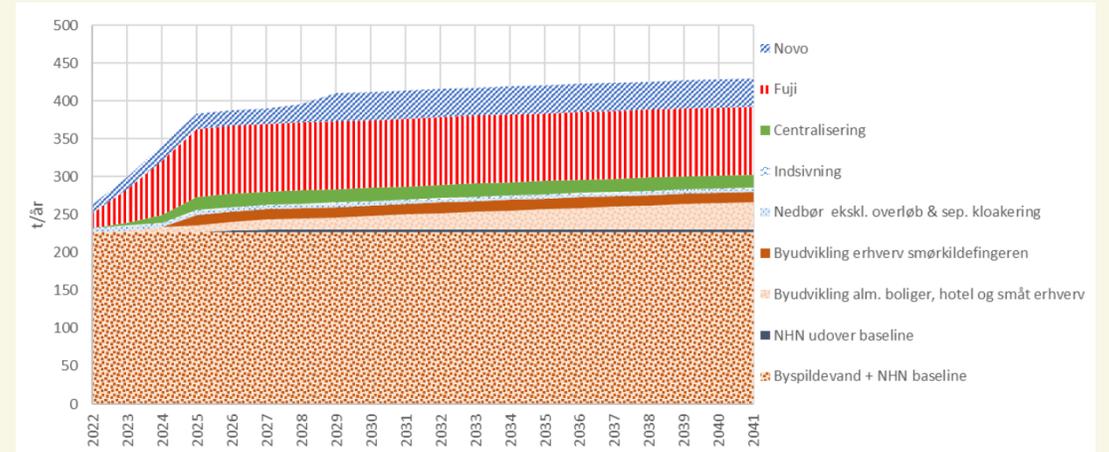


Pharmaceuticals found in 2021, which have the greatest environmental risk .
 Fx Sertralin (Fish on psychotropics).

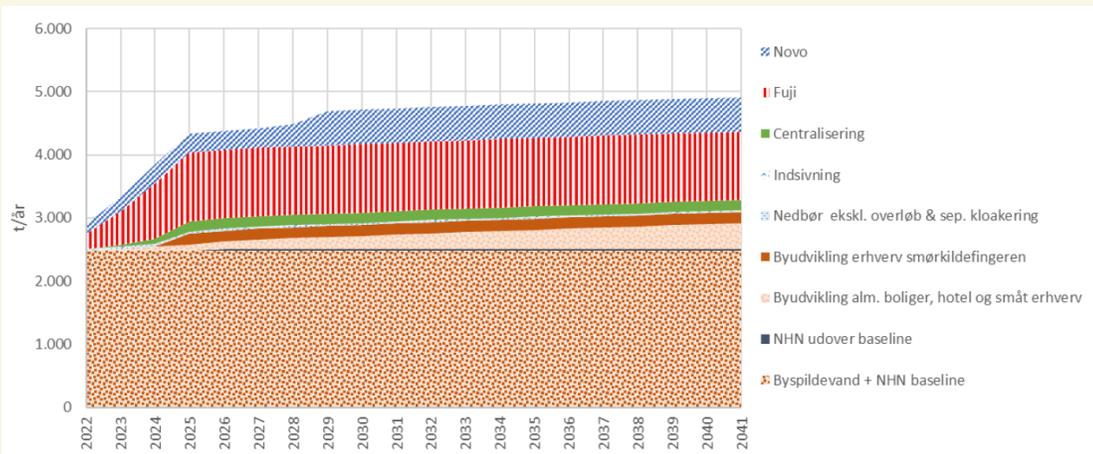
Environmental risk in order 2021 for pharmaceuticals in HCR Syd outlet.	outlet (PEC) HCR Syd 2021 mean [$\mu\text{g/l}$]	PNEC fresh water [$\mu\text{g/l}$]	Measured environmental risk outlet (PEC/PNEC)
Sertralin (antidepressant)	0,066	0,00052	127
Lidocaine (local anaesthetic)	0,296	0,00261	113,4
Oxazepam (fear and sleep)	0,184	0,0019	96,8
Venlafaxin (antidepressant)	0,634	0,1	6,3
Diclofenac (pain and rheumatism)	0,451	0,1	4,5
Clarithromycin (antibiotics)	0,151	0,06	2,5
Azithromycin (antibiotics)	0,279	0,09	3,1
Bicalutamid (prostatacancer)	0,251	0,1	2,5
Gemfibrozil (cholesterol)	0,249	0,15	1,66
Erythromycin (antibiotics)	0,024	0,02	1,2

Why?

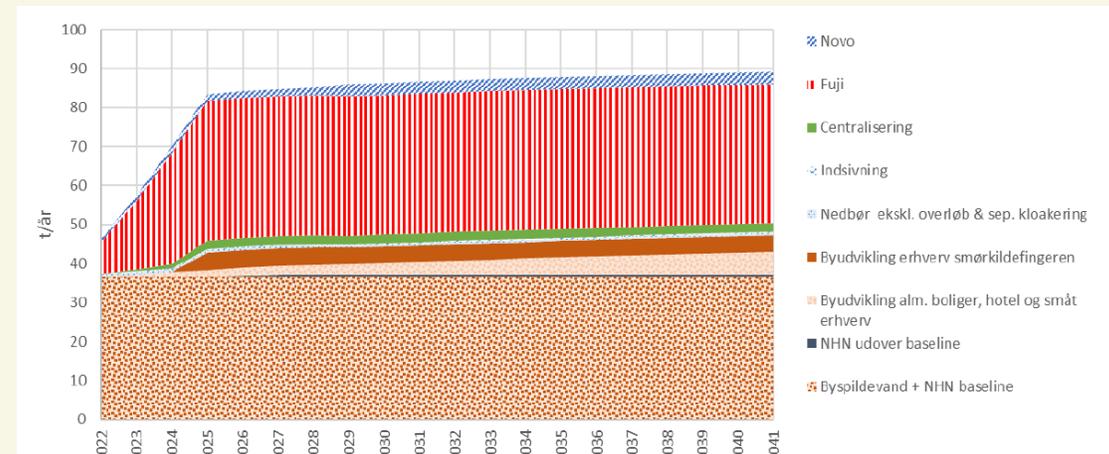
We get New hospital, pharmaceutical industries expands and the city grows



development in yearly load of TN to HCR Syd



development in yearly load of COD to HCR Syd



development in yearly load of TP to HCR Syd

Mapping of pharmaceuticals at HCR Syd in 2019. Over 1 µg/l

Pharmaceutical	inlet µg/l	outlet µg/l	Cleaning %
Iohexol (jod contrast)	53,4	2,34	96
Paracetamol (headache)	27,4	<0,01	100
Iomeprol (jod contrast)	22,4	0,3	99
Gabapentin (nerve pain)	14,2	1,77	88
Metformin (diabetes)	10,0	0,304	97
Tramadol (pain)	6,67	0,369	94
Losartan (blood pressure)	2,36	0,132	94
Cefuroxim (antibiotics)	2,02	0,516	74
Mycophenolsyre (anti-repulsion)	1,16	<0,02	100

Mapping of pharmaceuticals at HCR Syd i 2019. 0,1 til 1 µg/l

pharmaceutical	inlet µg/l	outlet µg/l	Cleaning %
Metoprolol (stress and fear)	0,724	0,562	22
10,11-Dihydro-10,11-dihydrocarbamazepin (NP)	0,588	0,418	29
Gemfibrozil (cholesterol)	0,516	0,080	84
Sulfapyridin (for animals)	0,375	0,141	62
Diclofenac (pain and rheumatism)	0,362	0,254	30
Valsartan (elevated blood pressure)	0,214	<0,01	100
Venlafaxin (antidepressant)	0,176	0,203	-15
Sulfamethoxazol (antibiotics)	0,173	0,05	71
Candesartan (blood pressure)	0,172	0,097	44
Clarithromycin (antibiotics)	0,169	0,190	-13
Bicalutamid (prostatacancer)	0,139	0,121	13
Ceftazidim (antibiotics)	0,134	0,098	27
Rosuvastatin (cholesterol)	0,119	0,003	98
Azithromycin (antibiotics)	0,104	0,128	-23
Guanyl-urea (NP-metformin)	0,104	3,52	-3285

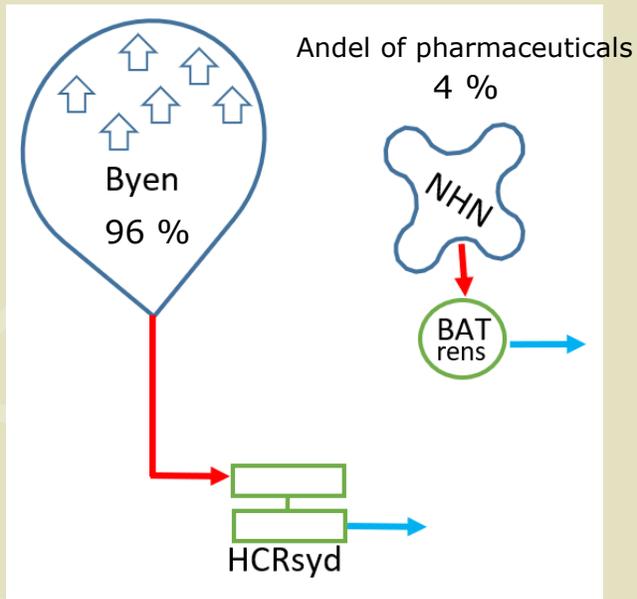
Mapping of pharmaceuticals i 2019. Under 0,1 µg/l

pharmaceutical	inlet µg/l	outlet µg/l	cleangrad
Roxithromycin (antibiotics)	0,095	0,096	-1
Erythromycin (antibiotics)	0,053	0,040	25
Metronidazol (antibiotics)	0,041	0,037	9
Trimethoprim (antibiotics)	0,038	0,048	-26
Ciprofloxacin (antibiotics)	0,037	0,016	57
Amoxicillin (antibiotics)	0,046	0,048	-7
Estron (sex hormone)	0,027	0,00094	97
Citalopram (antidepressant)	0,02	0,05	-111
Sertralin (antidepressant)	0,016	0,01	39

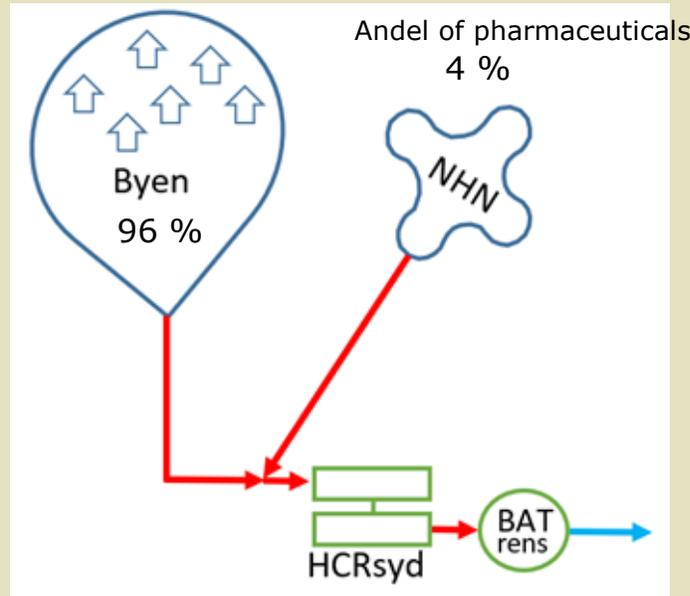
New hospital in Favrholm at Hillerød

The three scenarios in city council 24. juni 2020:

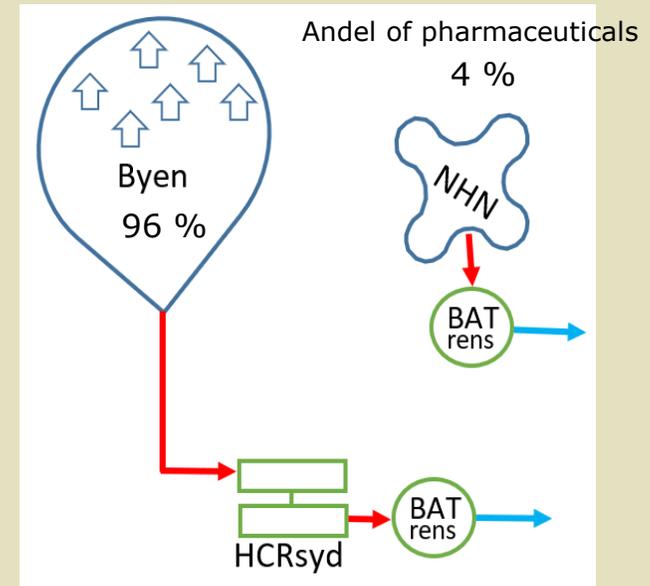
1. Cleaning at source (NHN)



2. Cleaning all at HCR Syd
Chosen solution

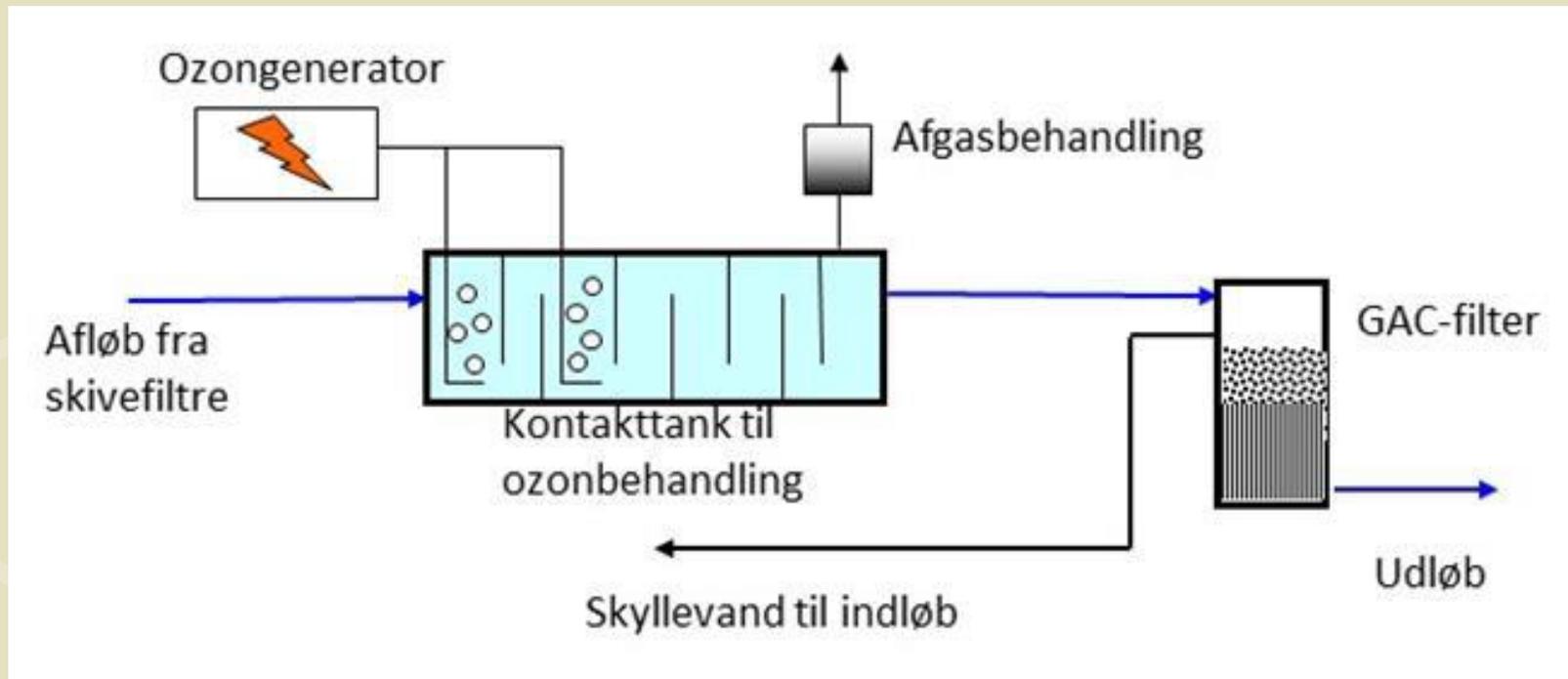


3. Cleaning at source and for the city



Marginal better cleaning around double cost

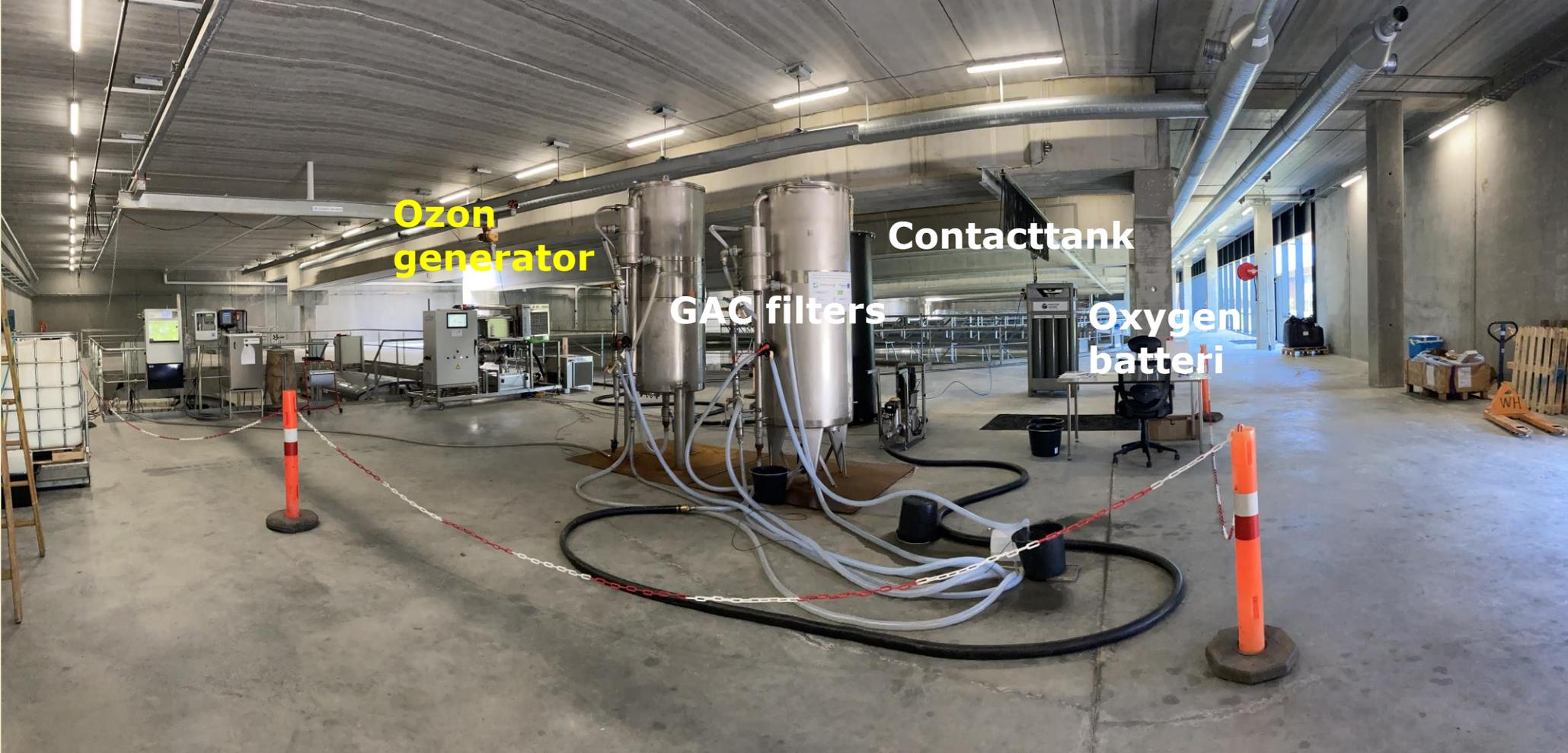
2020 Best Available Technology for Pharmaceuticals. Jes la Cour Jansen plus Kompetenzzentrum Wasser Berlin BAT is ozonation combined with active granular carbon (GAC)





Spring 2021. EU Interreg CWPharma 2 Pilot with ozonation and GAC filtration.

Pilot treatment plant in 2021



Analytical demand (mostly for ozonation)

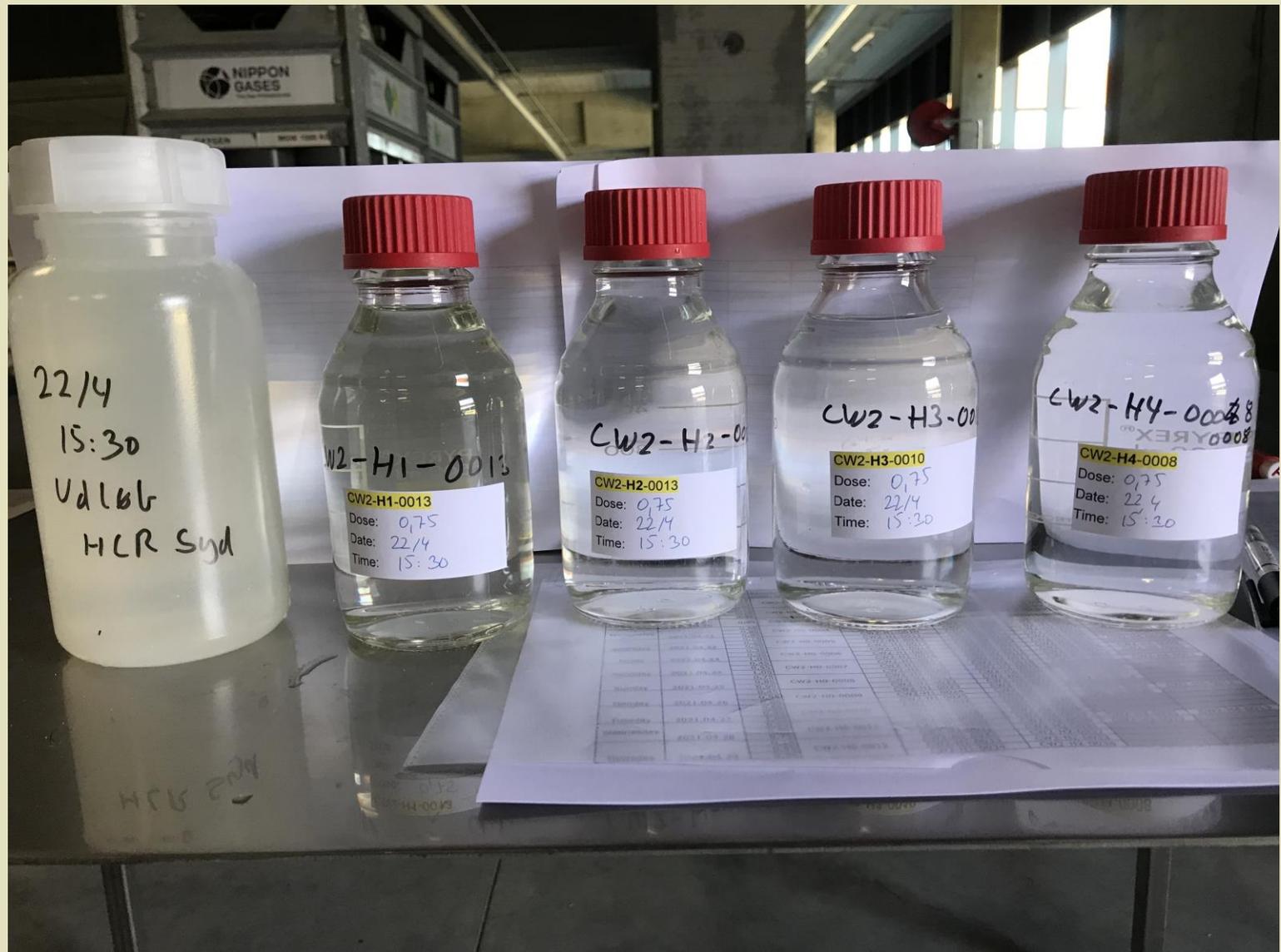
Controlling ozonation demand:

- Measurement of bromide. $\text{Br}^- + \text{O}_3 \rightarrow \text{BrO}_3$
- Measurement of NO_2^- . Nitrite consumes O_3
- Measurement of DOC/NVOC.
 - Controls demand of O_3
 - Ozon demand calculated as $\text{g O}_3 / \text{g DOC}$
 - Demand 0,3 – 0,7 $\text{g O}_3 / \text{g DOC}$

Spring 2021.

Measured for 53 selected pharmaceuticals:
15 not measured over detection limit in inlet
20 not measured over detection limit after biological treatment at HCR Syd.

45 tests with analysis rounds distributed over 10 Ozon dosing levels



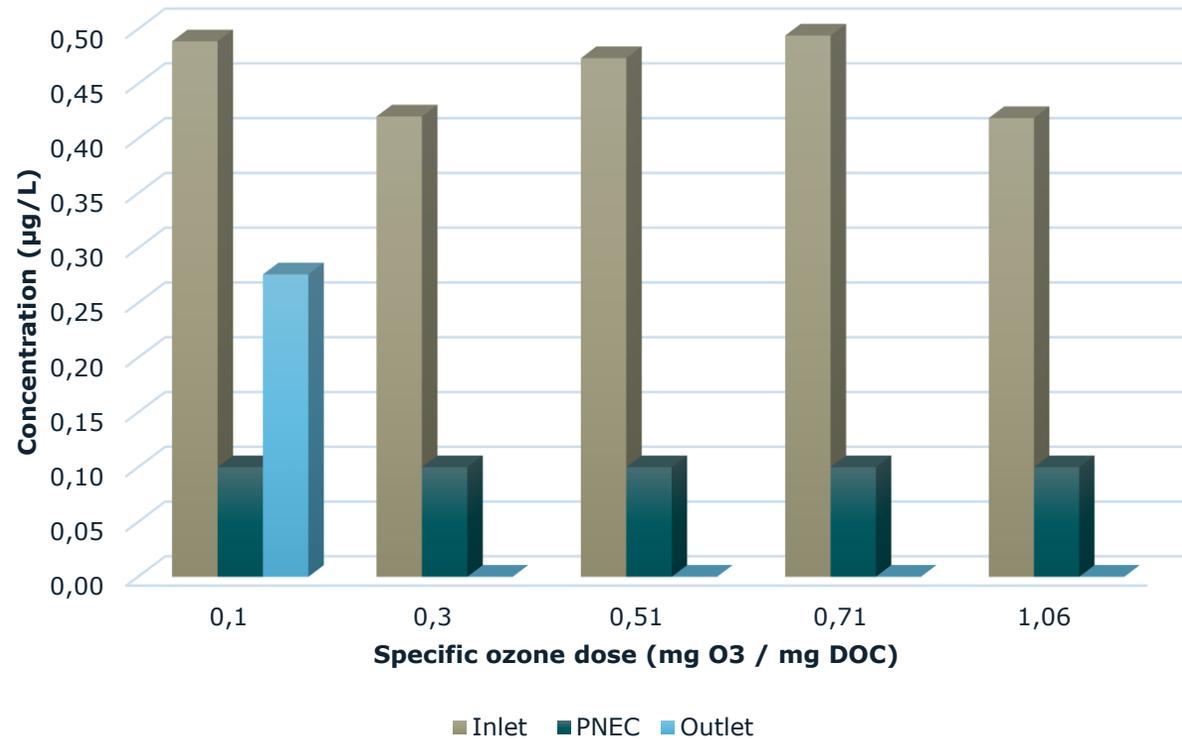
Overall Conclusions Pilot Spring 2021.

The yearly outlet (by 6 millioner m³ per year) of 33 Pharmaceuticals was reduced from 1.130 kg/year to 146 kg/year (or 87 %) **by biological treatment alone** at HCR Syd.

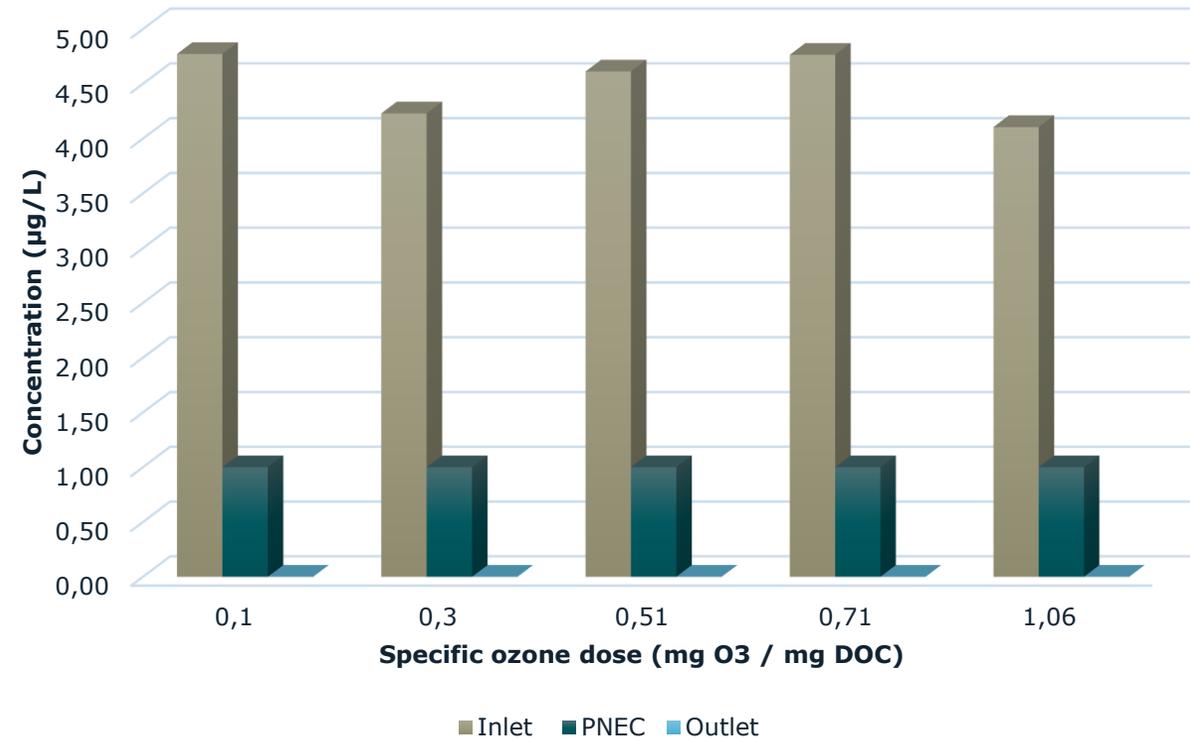
In pilot 4. step the yearly outlet of 33 Pharmaceuticals was reduced from 146 kg/year til under 1 kg/year (or 99 % more)

Concentration of pharmaceuticals at different ozone dose vs PNEC - rapidly reacting compounds

Diclofenac

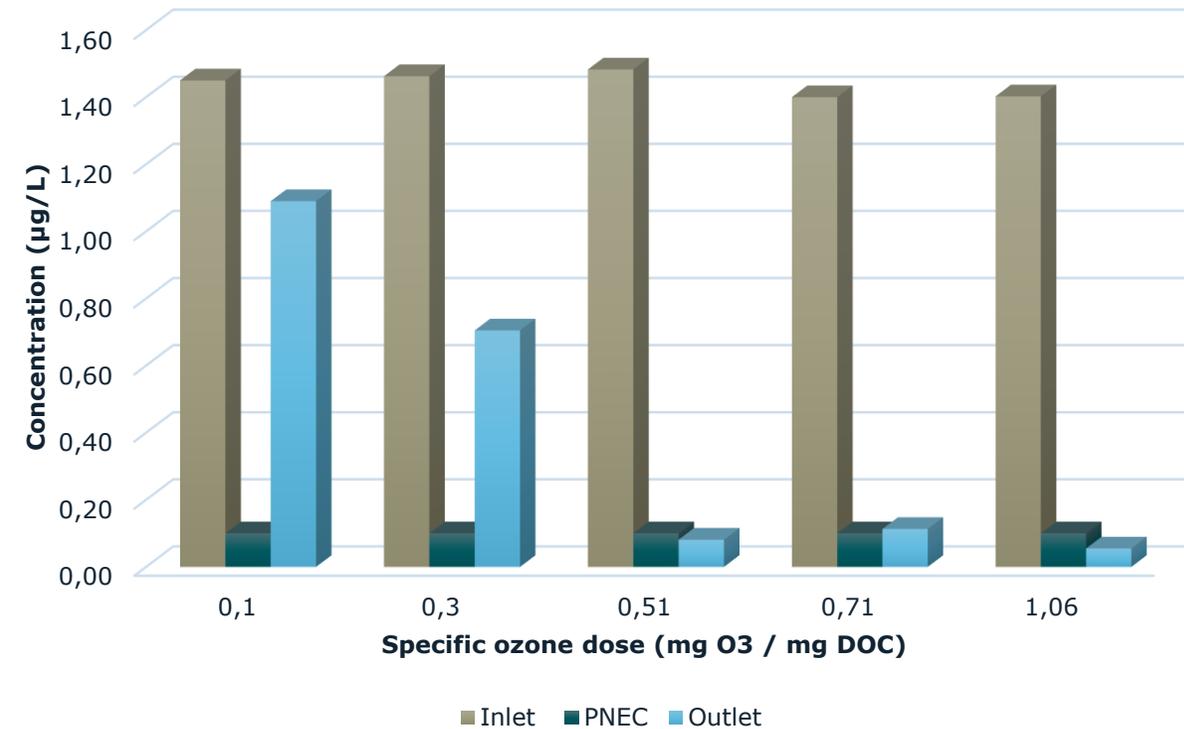


Furosemide

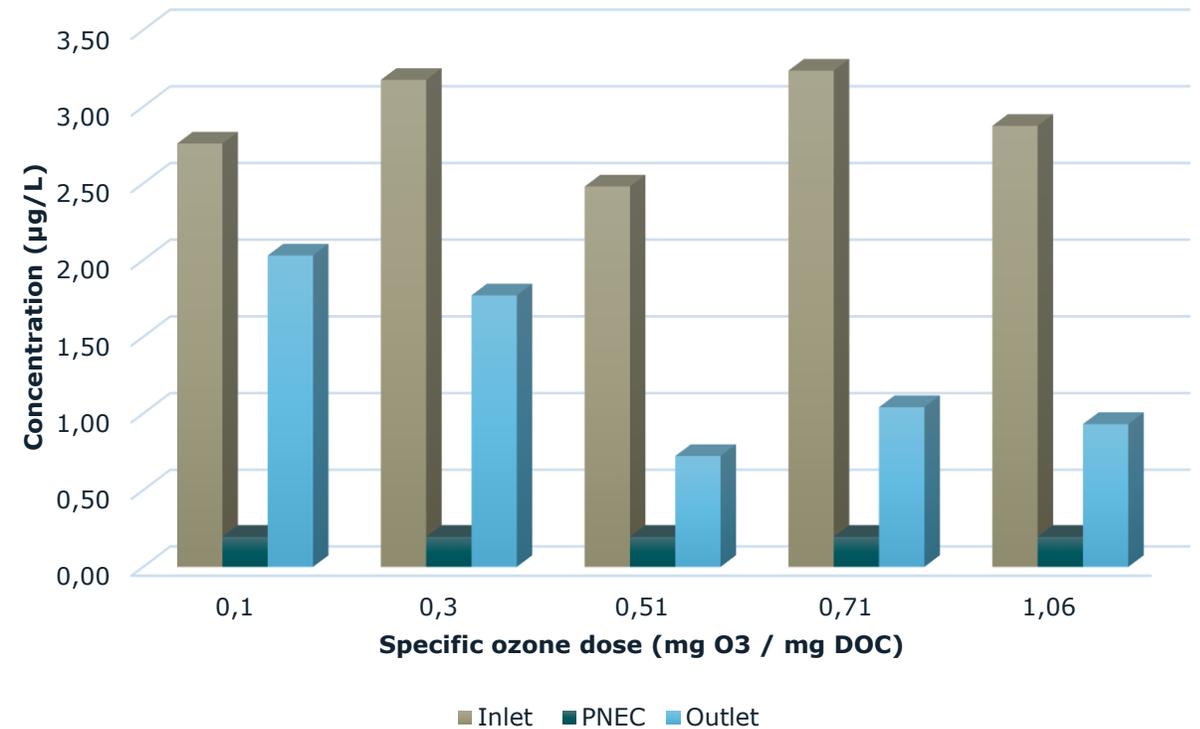


Concentration of pharmaceuticals at different ozone dose vs PNEC - intermediately reacting compounds

Metoprolol

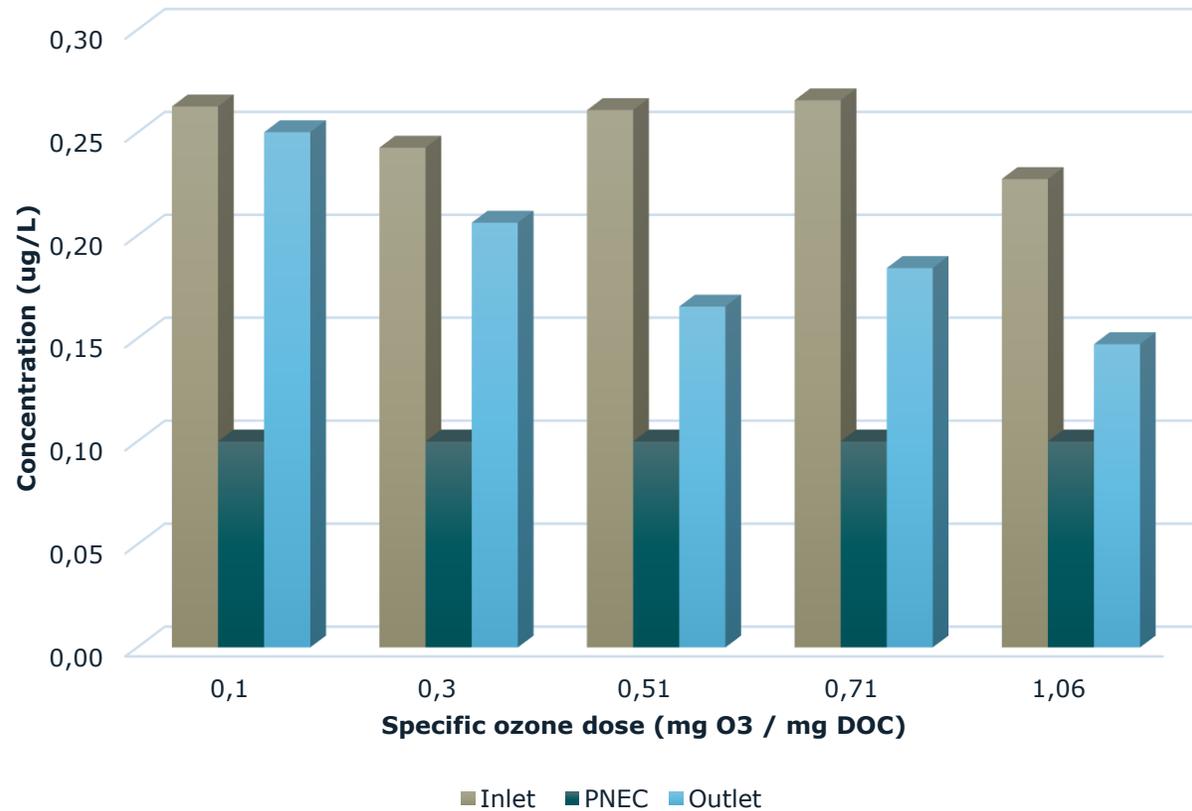


Gabapentin

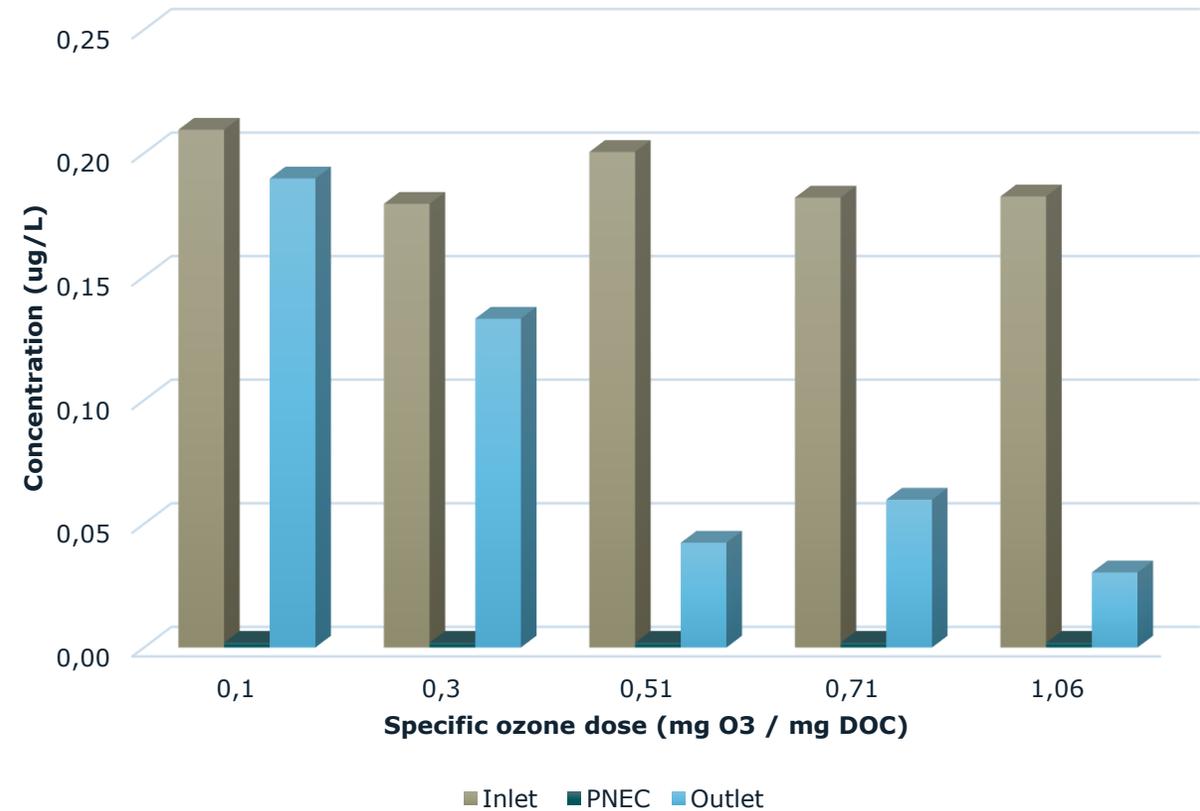


Concentration of pharmaceuticals at different ozone dose vs PNEC - slow reacting compounds

Bicalutamid



Oxazepam



Demands in the permit 2023 for 11 pharmaceuticals at HCR Syd

pharmaceuticals der anbefales, at indgå i et kontrolprogram for cleaning of pharmaceuticals at HCR Syd	PNEC fersk from bilag 1. [µg/l]	Opgivne Detektionsgrænser i [µg/l]	inlet HCR Syd april-maj 2021 mean [µg/l]	outlet HCR Syd april-maj 2021 mean [µg/l]	demand µg/l
Amisulprid (psykofarmicum)	0,17	0,01	0,02	0,02	0,17
Atorvastatin (cholesterol)	0,2	0,01	0,81*	0,08*	0,2
Candesartan (hblood pressure)	0,12	0,01	0,17*	0,10*	0,12
Citalopram (antidepressant)	0,51	0,003	0,23	0,16	0,51
Diclofenac (smerte og gigt)	0,1**	0,01	0,82	0,45	0,04
Erythromycin (antibiotics)	0,04	0,003	0,02	0,07	0,04
Carbamazepin (epilepsi)	0,50	0,01	0,078	0,105	0,5
Gemfibrozil (cholesterol)	0,15	0,01	0,52*	0,08*	0,15
Propranolol (hblood pressure)	0,1	0,01	0,10	0,09	0,1
Sulfamethoxazol (antibiotics)	0,12	0,01	0,20	0,05	0,12
Venlafloxin (antidepressant)	0,1	0,01	0,50	0,63	0,1

Purple is from EU's directive

* Data from 2019 **MST and EU adjust to 0,04 in latest proposal.

Monitoring program in permit 2023 for 18 more pharmaceuticals at HCR Syd

Pharmaceuticals in indikatorprogram for cleaning of pharmaceuticals at HCR Syd	PNEC fersk from bilag 1. [$\mu\text{g}/\text{l}$]	Opgivne Detektionsgrænser i [$\mu\text{g}/\text{l}$]	inlet HCR Syd april-maj 2021 mean [$\mu\text{g}/\text{l}$]	outlet HCR Syd april-maj 2021 mean [$\mu\text{g}/\text{l}$]	demand $\mu\text{g}/\text{l}$
Indikator pharmaceuticals					No Demand
17α-Ethinylestradiol (hormone)	0,000075	0,0002	<0,02*	<0,0004*	Measure
17β-Estradiol (hormone)	0,0001	0,002	0,010*	<0,002*	Measure
Amoxicillin (antibiotics)	0,078	0,05	<0,05	<0,05	Measure
Azithromycin (antibiotics)	0,019***	0,01	0,27	0,28	Measure
Benzotriazol (not et pharmaceutical)	19,4***	0,05	24,7	8,2	Measure
Bicalutamid (cancer)	0,1	0,01	0,273	0,251	Measure
Clarithromycin (antibiotics)	0,06	0,01	0,107	0,151	Measure
Gabapentin (nervesmerter)	100**	0,03	23,12	3,073	Measure
Hydrochlorothiazid (vanddrivende)	200***	-	-	-	Measure
Metoprolol (stress og angst)	75	0,01	1,26	1,36	Measure
Ibuprofen (smerte og feber)	0,22***	0,01	11,2	n.d.	Measure
Iohexol (kontrastmiddel)	1.000.000	0,05	114	7,88	Measure
Irbesartan (elevated hblood pressure)	100	0,01	0,029	0,036	Measure
Sertralin (antidepressant)	0,00052	0,005	0,010	0,066	Measure
Sulfadiazin (antibiotics)	4,6	0,01	0,06	0,03	Measure
Trimethoprim (antibiotics)	10	0,01	0,21	0,13	Measure
Lidocain (lokalbedøvelse)	0,00261**	0,01	0,319	0,296	Measure
Oxazepam (angst og søvn)	0,0019**	0,01	0,215	0,184	Measure

Purple is from EU's Directive

*Data from 2019, **proposal ***PNEC efter EU's quality standard for fresh water.

Quartary step at HCR Syd. Unit operations

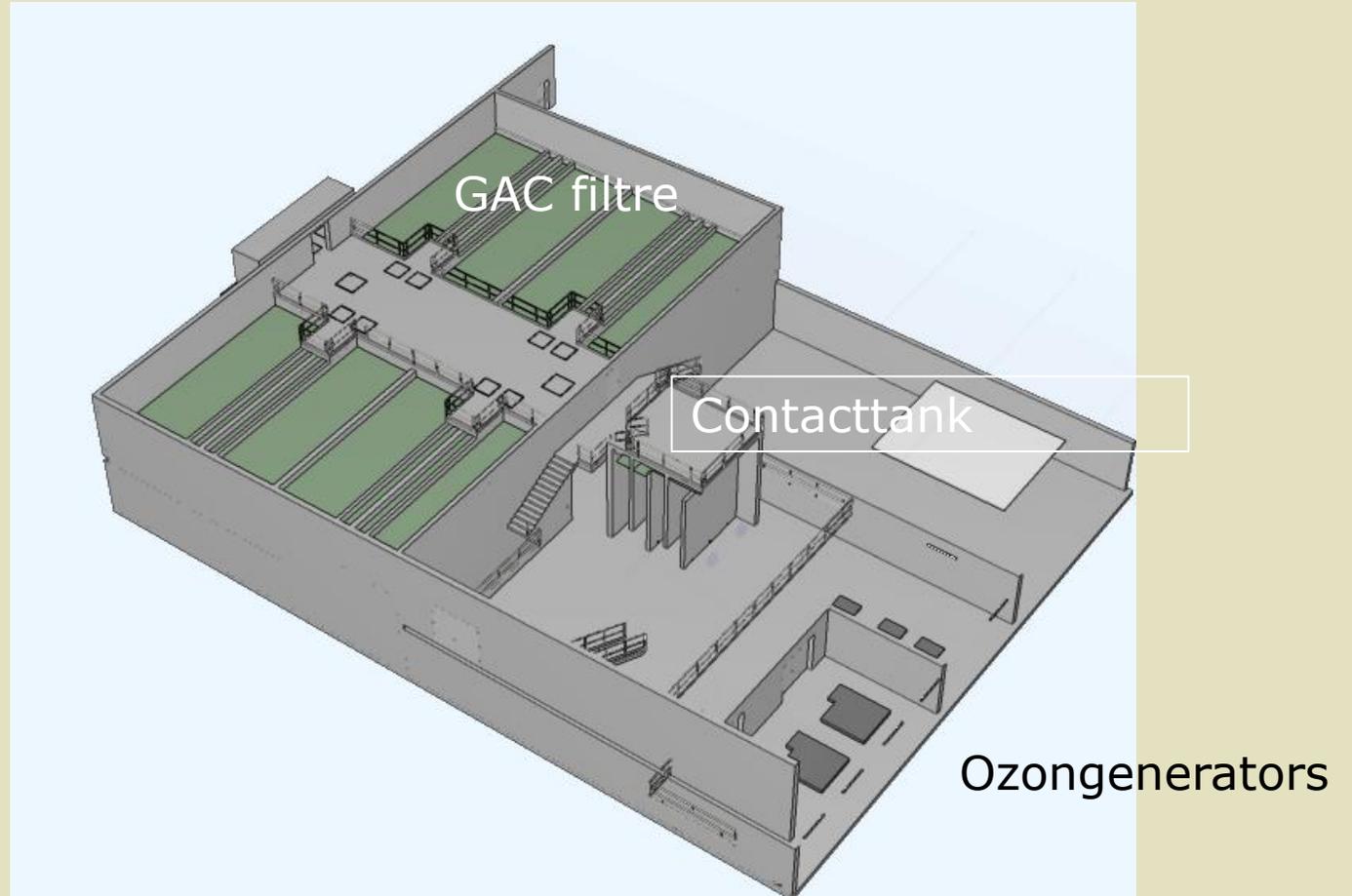
1. Extra filtration (with phosphorous precipitation)
2. Pure oxygen produced from LOX tank (Delivery of liquid oxygen)
3. Production of ozon (Wedeco Generator)
4. Mixing Ozon (and oxygen) in the waste stream (inline mixing)
5. Contacttank (2 minuts retention time)
6. Biological GAC filtration ala Altenrhein

Choice from 2020 Best Available Technology for Pharmaceuticals

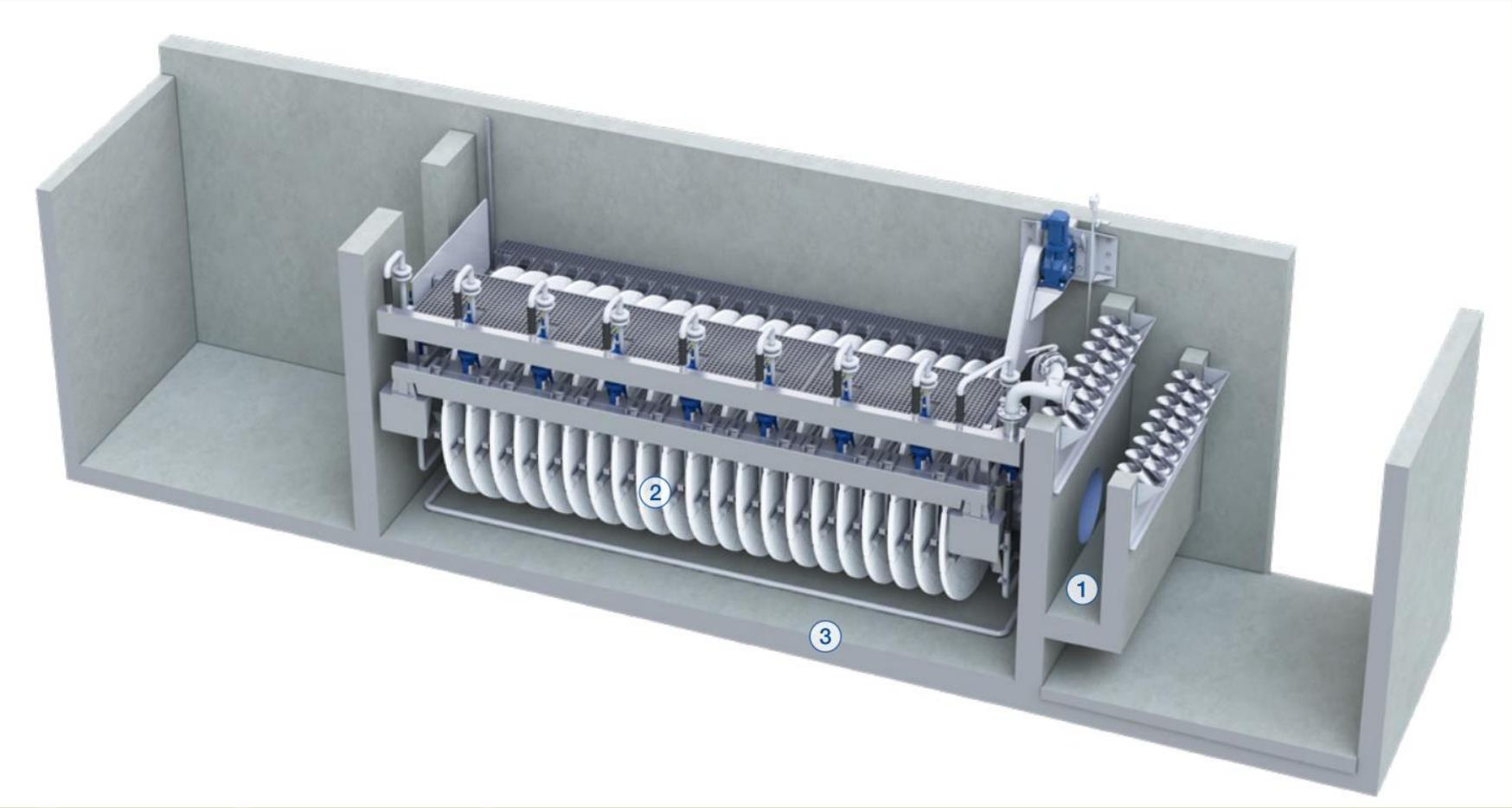
Jes la Cour Jansen and
Kompetenzzentrum Wasser Berlin:
BAT is ozonation combined with
active granular carbon (GAC)

Confirmed by pilot plant in 2021.

Full scale 4. step is going to be
established in a new building
(39 X 35 X 7m):



Extra filtration. Dyna Cloth filter for SS (and P) removal:



Quartinary cleaning step. demand for ozonation

- Ozongeneratorer:

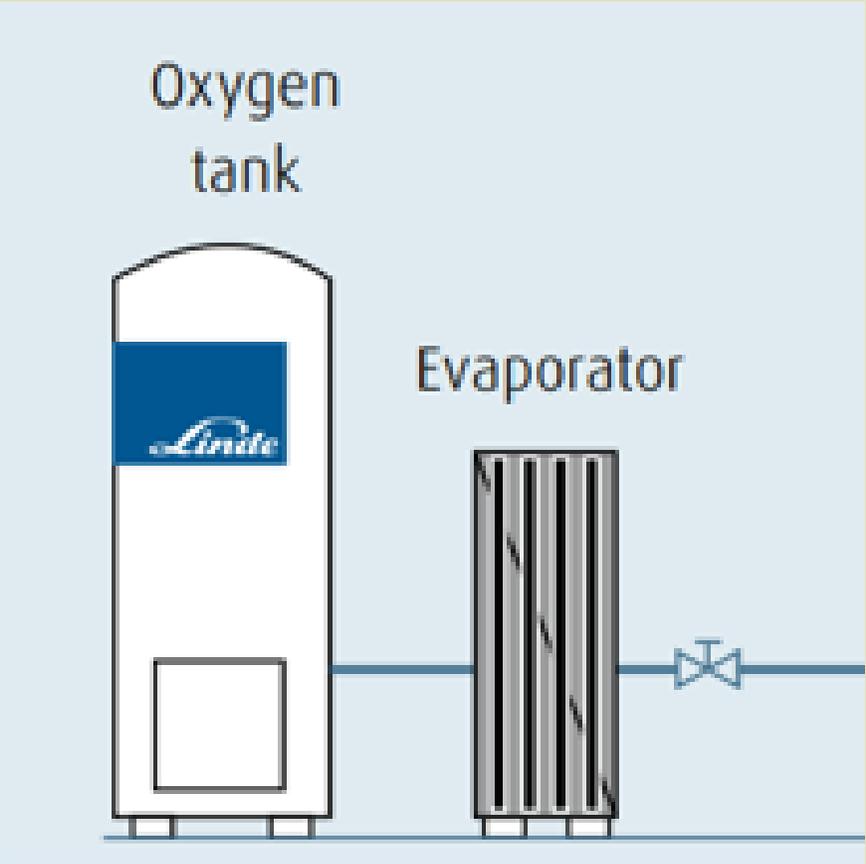
Maks. ozonproduktion: **6,0 kg O₃/time**

Min. ozonproduktion: **1,5 kg O₃/time**

- Redundans filosofi:

- Min. og Maks. Ozonproduction only needs 1 generator
- Automatic swift between generators
- Alternation

Oxygen for ozongenerator. LOX plant



2. Full scale O₂ og O₃ system at Stengården WWTP

Report C 538 – Evaluation of a full-scale tertiary treatment system for removal of pharmaceuticals and recovery of water at the WWTP Stengården in Simrishamn, Sweden



Figure 2.5 Full-scale installation of the ozonation system.

Wedeco Ozon generator “activates” the pure oxygen to a mix of O₂ og O₃.

O₃ will be about 10 % of the mix after the generator,

Energi consumption 8-12 kWh per kg O₃ eller ca. 1 kWh per kg O₂

OBS: the pure oxygen can also be made by Pressure Swing Adsorption (PSA) method from Oxymate in Helsingør. The method generates 95 % pure oxygen.

Ozongenerator from Wedeco.



Oxygen for Ozon generator is delivered from LOX tank and is by demand given traces of N_2

Designed for max. Flow 450 l/s.

$450 \text{ l/s} * 11 \text{ mg DOC/l} * 0,35 \text{ mgO}_3/\text{mg DOC}$
 $= 1.733 \text{ mgO}_3/\text{s} = 6,24 \text{ kg O}_3/\text{time}$

Or:

$10 \text{ kgO}_2/\text{kgO}_3 \rightarrow 62,37 \text{ kg O}_2/\text{time}$

Remark. 38,5 gram oxygen per m^3

Full scale Ozon mixing with wastewater.

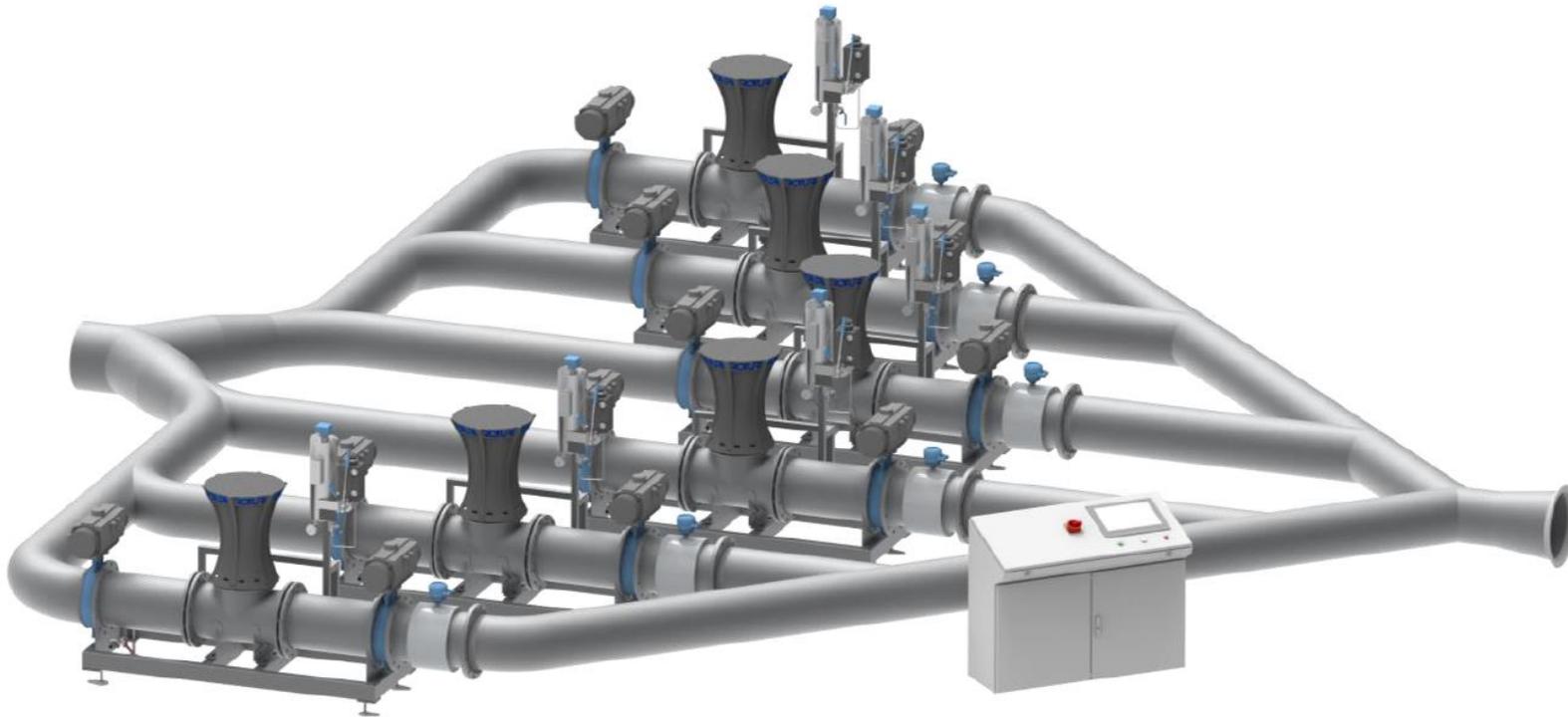


Figure 3: isometric view of a3op[®] skid for a flow of 1.620m³/h

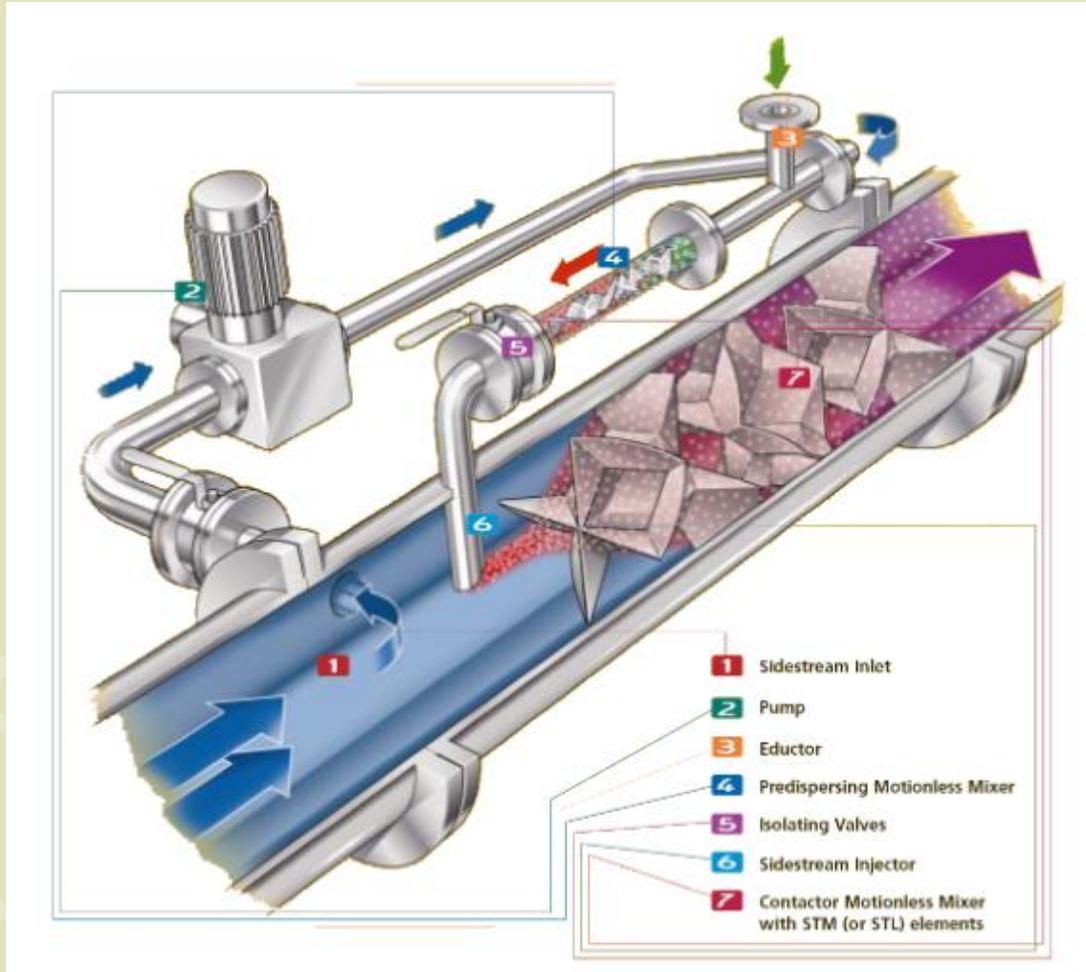
Mixing of Ozon gas and waste water can be done by diffusor or ejektor princip

In the pilot plant Roturi was used. A very efficient mixing-method.

Uses a rotating part and ultrasound.

Makes noise and uses energi

Chosen Statiflo Ozonmixing by sidestream-injection



The water is divided in two streams:

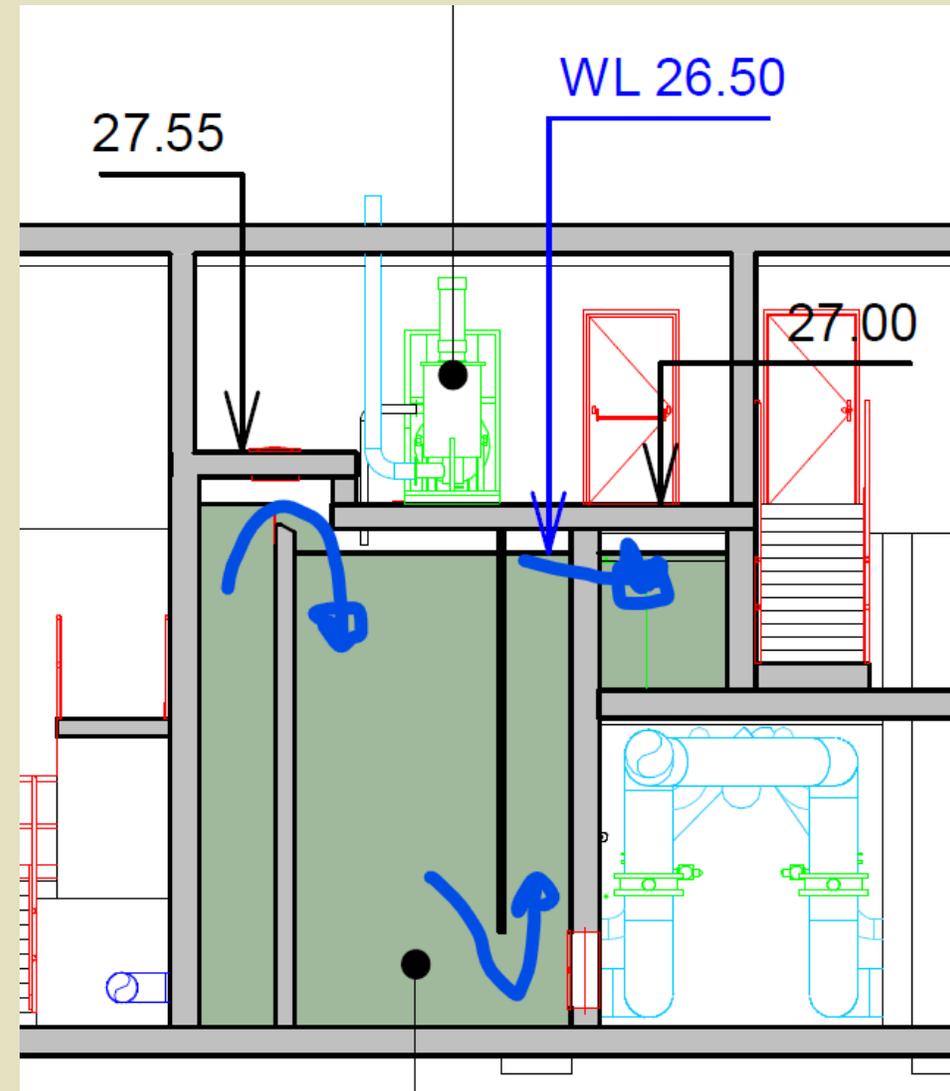
- *a static mixer (big diameter)
- *a static ozone dosing gasdispersionmixer (small diameter).

Disse units work together for optimal gas/liquid-contact and effective mass transfer.

Contacttank after ozonation

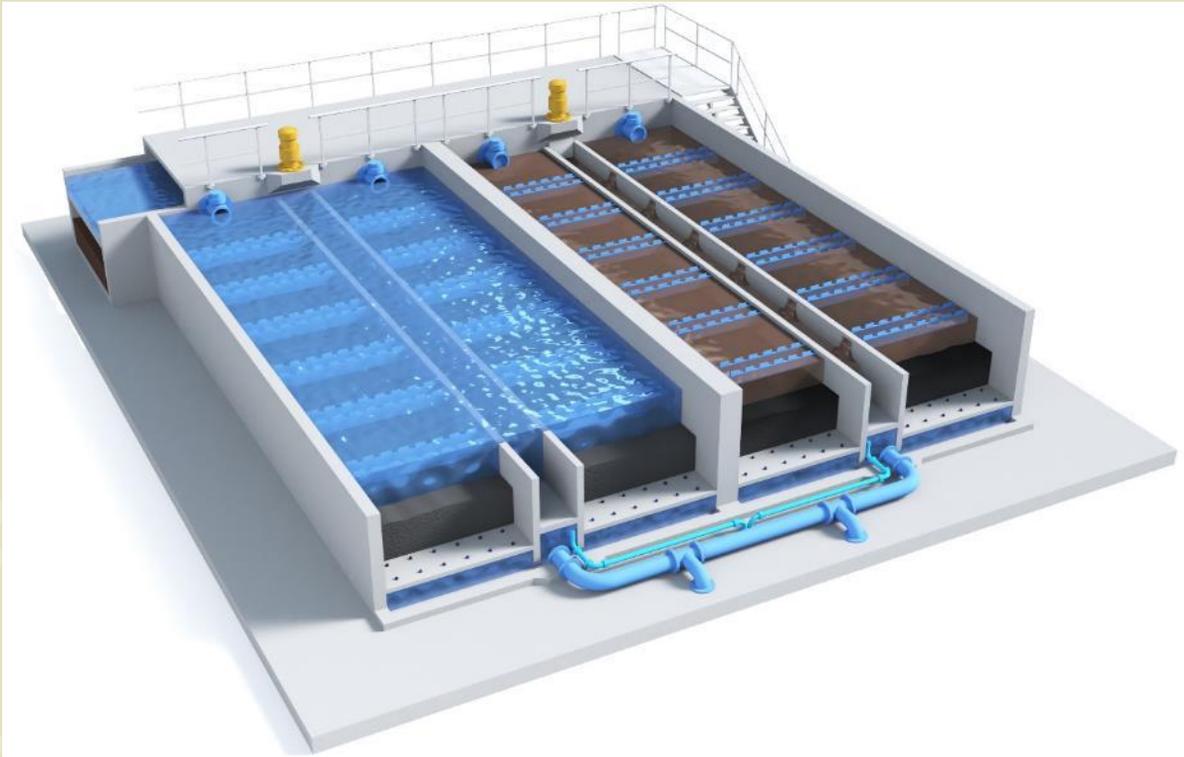
Contacttank dimensioned with 2 minutes retention time at max. flow at 450 l/sek.

Tanks are approx. 5 meter depth and 3,2 x times 3,7 m → 59,2 m³



GAC filter treatment plant. Design (Carbazur GH) Suez Water A/S

Carbazur GH - an open concrete GAC filters with a high-water head, efficient and secure



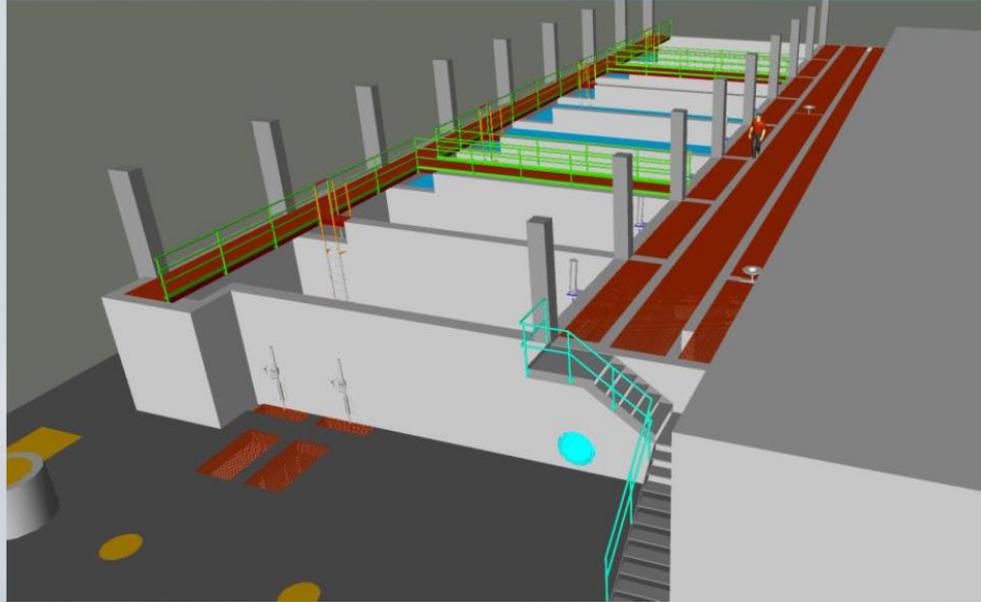
among our references

- La Thelle (France) - 240 m³/h
- Fabrègues (France) - 1,200 m³/h
- Les Moises (France) - 325 m³/h
- Mont-Valérien (France) - 4,000 m³/h
- Rabastens (France) - 840 m³/h
- Barentin (France) - 400 m³/h
- Rhône Sud (France) - 1,000 m³/h
- Morsang-sur-Seine (France) - 9,375 m³/h

Altenrhein. GAC filter i the Quartinary step:

Projekt Altenrhein

sustainable solutions. for a better life. 



Altenrhein. GAC filter treatment plant. Design a la a water work



The Quartinary step also cleans for COD etc.

Pilot plant results at HCR

Pilotanlæg	Foråret 2021			
4. trin HCR Syd				
HCR Syd udløb	COD	Tot-N	Tot-P	SS
Middelværdi	31,40	2,18	0,15	3,19
GAK udløb:				
Middelværdi	10,80	1,55	0,077	0,70
Renseeffekt 4. trin %	65,6	28,9	47,4	78,1

Ozonation also reduce E. coli down to 35 cfu/100 ml (250 cfu/100 ml is demand for bathing)

Pro's

What's in it for Hillerød ?:

1. Sure fullfilment of PNEC values for the pharmaceuticals demanded
2. Monitering at risk-pharmaceuticals
3. O_3 + GAC will reducere content of COD/BI5 samt N og P
4. Low load means good possibility for a Biological Active Carbonfilter (BAC)
5. Lifetime of GAC filter expected >5 years

Contra's

What's **not in it**:

1. Low cost cleaning
2. Cleaning for Zn^{2+} ions demands a 5. (unknown) step

Metal	Enhed	inlet HCR Syd	outlet HCR Syd	Qualitydemand
Barium (Ba)	µg/l	63	12	9,3
Kobber (Cu)	µg/l	50	2	1
Zink (Zn)	µg/l	150	25	7,8

Contra's *(continued)*

Ozonation is not cleaning for **PFAS**

- GAC cleans only for PFAS in 3 – 5.000 EBV.
- PFAS cleaning demands et 5. step
- Kan biological GAC biodegrade PFAS?
 - Future will tell (HFORS, Suez, Aarhus Universitet + ?)

**Henning Larsen
sketches for the
Quartary step:**



Henning Larsen sketches for the Quartinary step:



Henning Larsen sketches for the Quartinary step:

Full scale 4.
step.

Statiflo
mixers and
contacttank

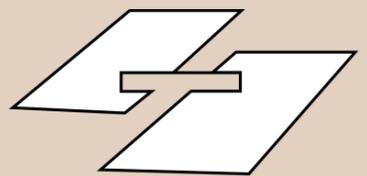


Henning Larsen sketches for the Quartinary step:



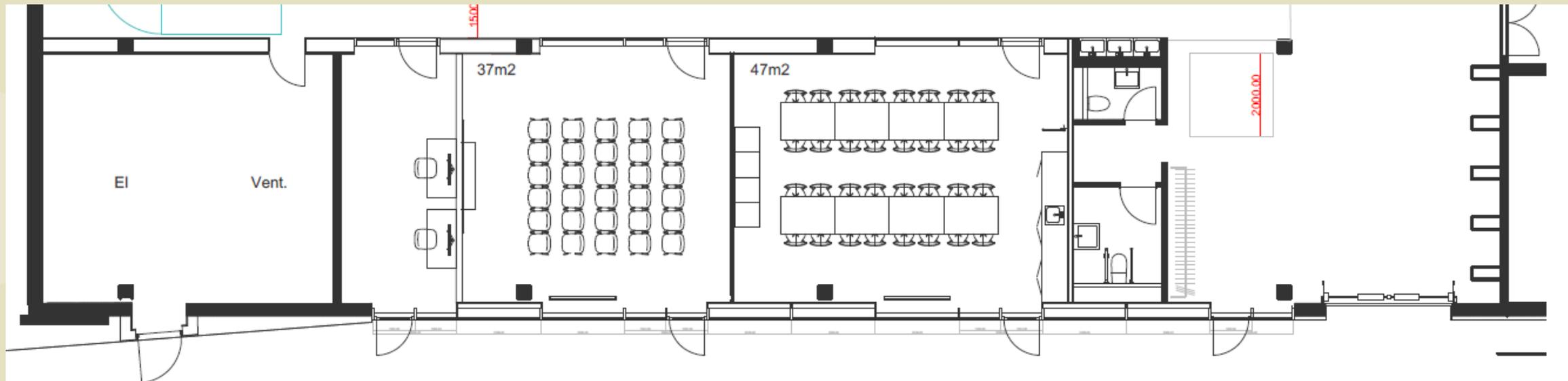
HCR SYD 2.0





HCR SYD 2.0

A communication room is put in the Quaternary step combined with possibilities of practical exercises with chemistry and physical processes that cleans for pharmaceuticals.





HCR SYD 2.0

communication room



HCR Syd 2.0
fullscale Quartinary
step.

Our Projectoffice

2024 to 2027

Visit: Contact me on
josk@hfors.dk



Extra from treatment plant Altenrhein in Switzerland

HFORS fullscale sister treatment plant in Switzerland.

4. step at ARA treatment plant in Altenrhein in Switzerland. 10.000.000 m³/year. Approximately 37 times 46 meter. Equal to : 1.700 m² . Ozonation based on LOX



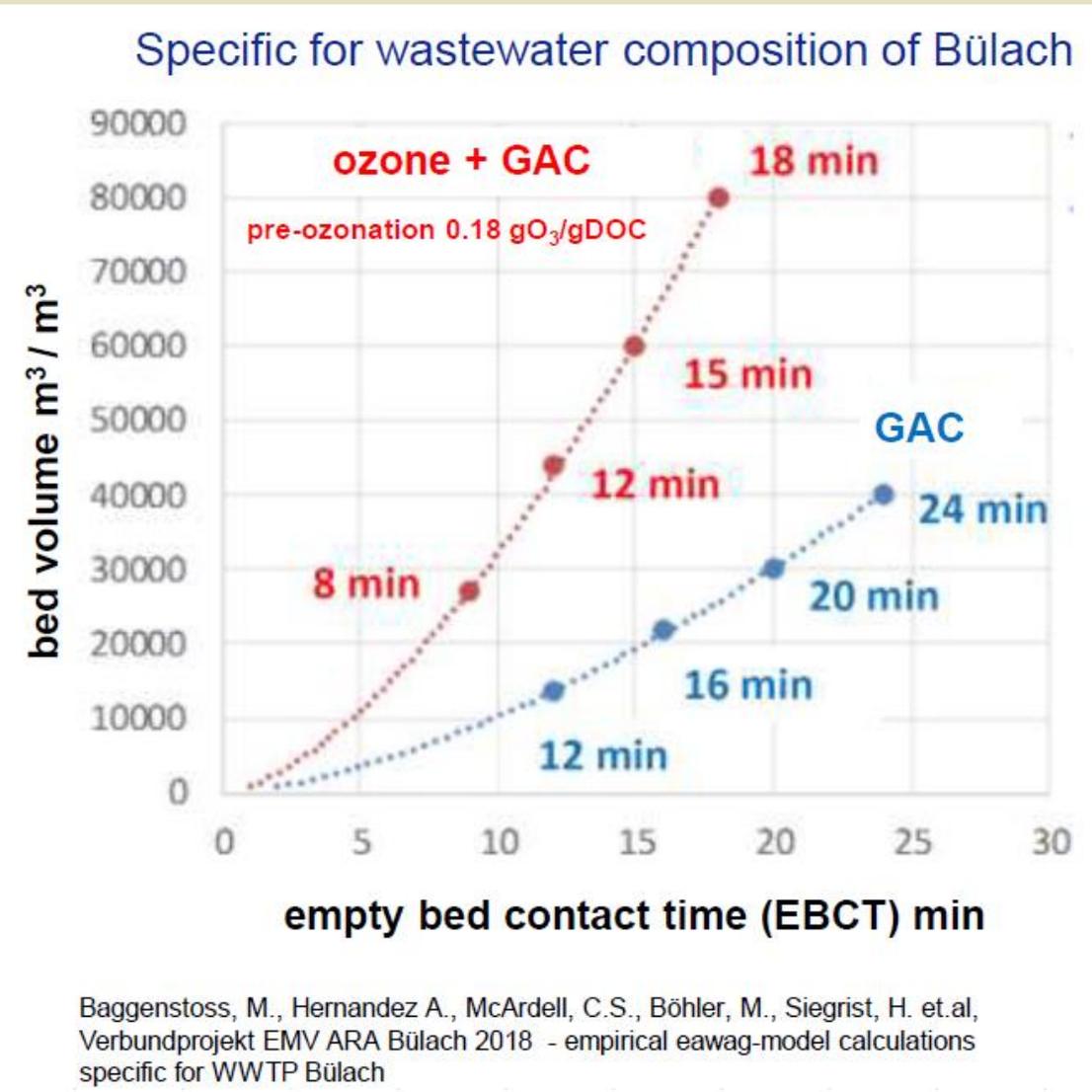
Ozon/GAC treatment plant.
(latest from Switzerland)

Biological activitet

With 6 for 8 millioner m³ waste water per year and a GAC filter of 810 m³ will be used:

$$6.000.000/810 = 7.407 \text{ EBCT per year}$$

$$8.000.000/810 = 9.876 \text{ EBCT per year}$$



Ozon/GAC treatment plant. (latest from Altenrhein i Switzerland)

Altenrhein treatment plant goes for costeffectivity,
and demand is **80 % cleaning for pharmaceuticals** in Switzerland.

Ozon dosis is regulated as:

2020: 0,3 mg O₃/mg DOC

2021: 0,2 mg O₃/mg DOC

2022: 0,1 mg O₃/mg DOC

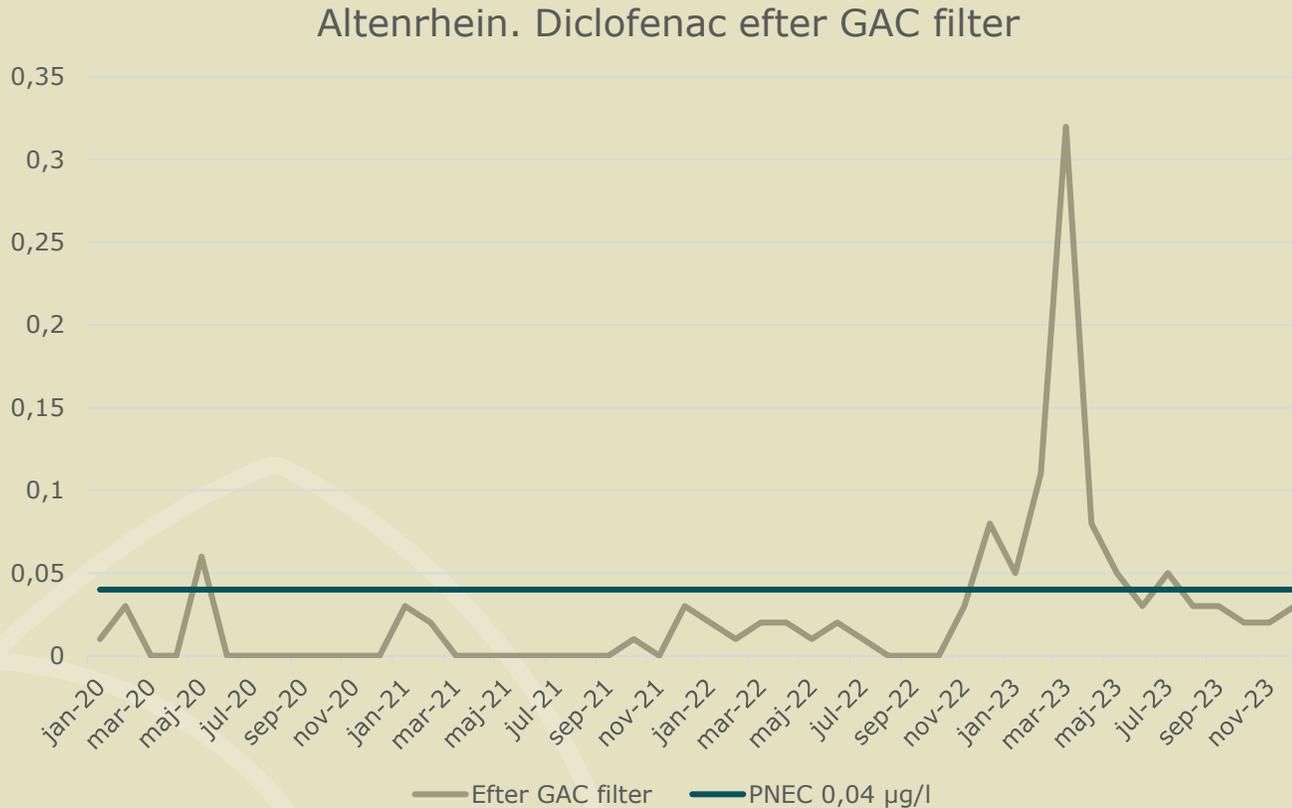
2023: 0,1 mg O₃/mg DOC

Ozon/GAC treatment plant. (latest from Altenrhein in Switzerland)

pharmaceuticals in controlprogram at Altenrhein	inlet Altenrhein 2023. mean [µg/l]	outlet Altenrhein 2023. mean [µg/l]	inlet HCR Syd 2021 mean [µg/l]	outlet HCR Syd 2021 mean [µg/l]	PNEC µg/l
Amisulprid (psykofarmicum)	0,48	0,03	0,02	0,02	0,17
Carbamazepin (epilepsi)	0,28	0,05	0,078	0,105	0,5
Citalopram (antidepressant)	0,14	0,01	0,23	0,16	0,51
Clarithromycin (antibiotics)	0,2	0,03	0,107	0,151	0,06
Diclofenac (smerte og gigt)	2,51	0,07	0,82	0,45	0,04
Hydrochlorothiazide	2,51	0,07		0,7*	?
Metoprolol (stress og angst)	0,13	0,01	1,26	1,36	75
Venlaflaxin (antidepressant)	0,31	0,02	0,50	0,63	0,1
Candesartan (hblood pressure)	1,11	0,45	0,17*	0,10*	0,12
Irbesartan (elevated blood pressure)	0,93	0,14	0,029	0,036	100
Benzotriazol	42,73	3,39			
Methylbenzotriazol	3,59	0,57			

*Data from 2019

Ozon/GAC treatment plant. (latest from Altenrhein in Switzerland)



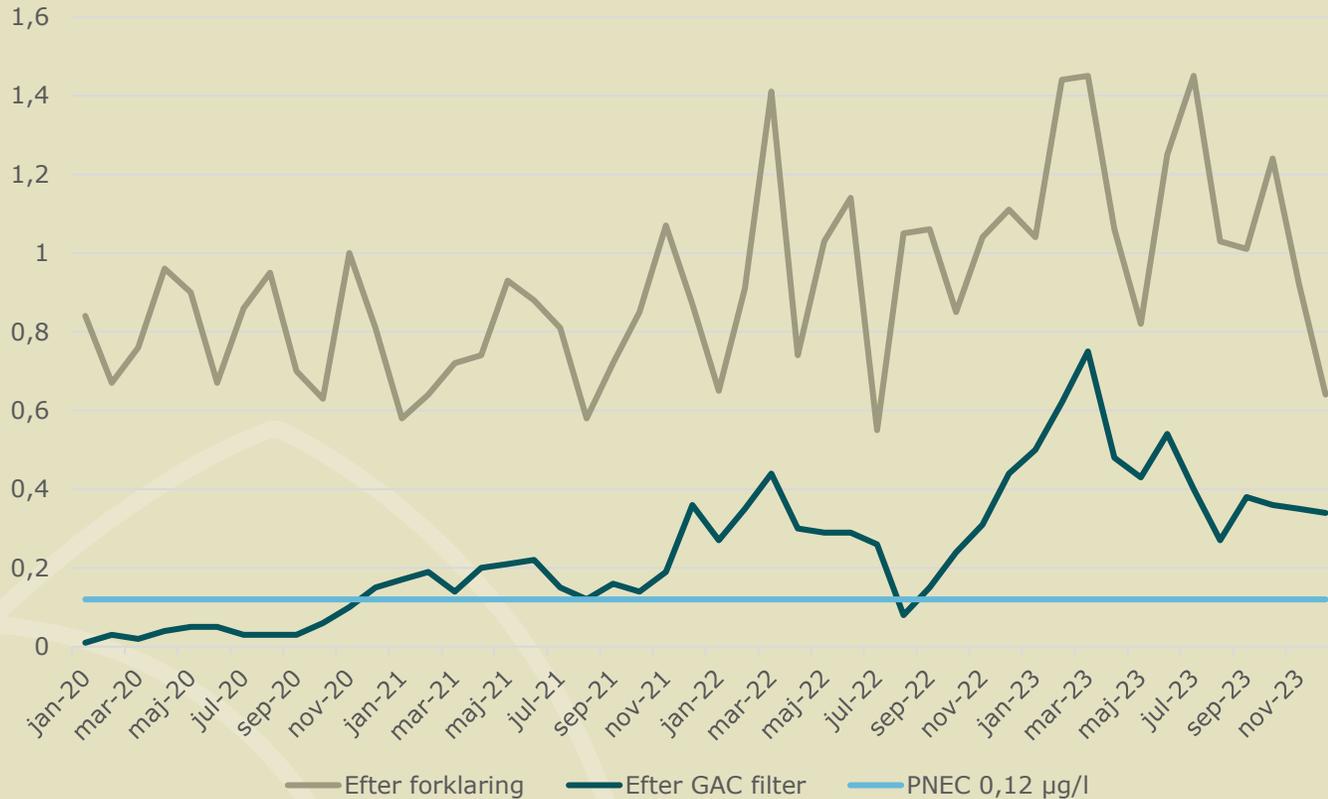
Diclofenac exceeds i en periode PNEC value in outlet from GAC filter approx. 1 year after, ozon dosing went down to 0,1 mg O₃/mg DOC.

Diclofenac is normally very easy to degrade with ozon, but 0,1 mg O₃/mg DOC is to low dosing for a stable result.

Don't go that low.

Ozon/GAC treatment plant. (latest from Altenrhein in Switzerland)

Altenrhein. Candesartan i µg/l før og efter GAC filter



Candesartan exceeds PNEC value at 0,12 µg/l in outlet from GAC filteret when ozon dosing was reduced from 0,3 to 0,2 mg O₃/mg DOC.

So maybe also 0,2 mg O₃/mg DOC is to low.

Ozon/GAC strategi HCR Syd 2.0 baseret at Altenrhein

Based on Altenrhein's results we go for trying a little more carefully:

HCR Syd 2.0 2026: Ozon dosis: 0,35 mg O₃/mg DOC

HCR Syd 2.0 2027: Ozon dosis: 0,30 mg O₃/mg DOC

HCR Syd 2.0 2028: Ozon dosis: 0,25 mg O₃/mg DOC