Aspects to be considered for design of ozonation

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Joint Technical Workshop on "Ozonation for advanced wastewater treatment"
Tekniska Verken, Linköping, Sweden
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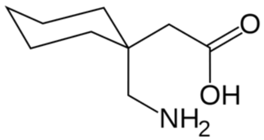
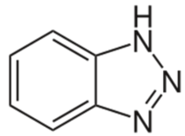
Why ozonation of secondary effluent?

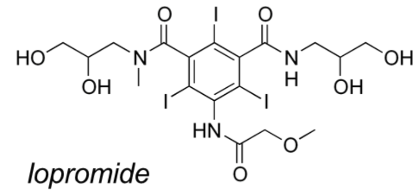
Elimination of trace organic compounds (TrOC)



Gabapentin

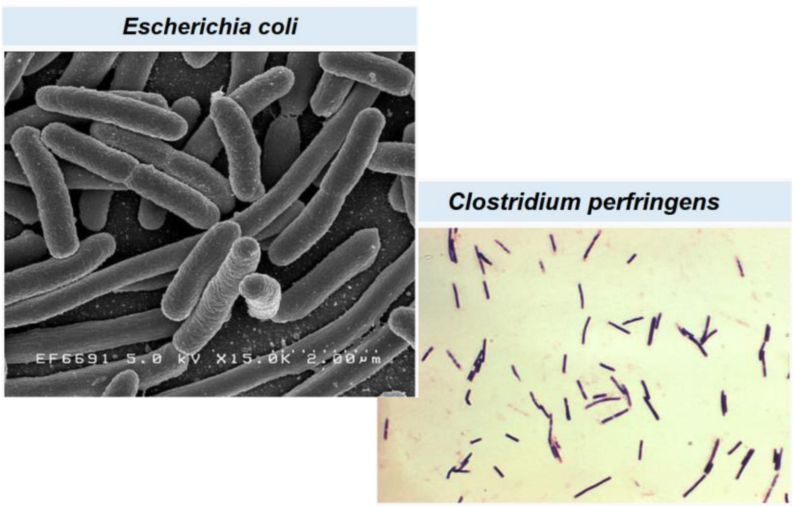


Benzotriazole



Iopromide

(Part)disinfection



Reduction of DOC, COD (with biological post- treatment)

Removal of odour, color

Figures left:
https://de.wikipedia.org/wiki/Escherichia_coli#/media/File:EscherichiaColi_NIAID.jpg; Credit: Rocky Mountain Laboratories, NIAID, NIH - NIAID:
https://de.wikipedia.org/wiki/Clostridium_perfringens#/media/File:Clostridium_perfringens.jpg; Content Providers(s): CDC/Don Stalons - This media comes from the Centers for Disease Control and Prevention's Public Health Image Library (PHIL), with identification number **#2995**.

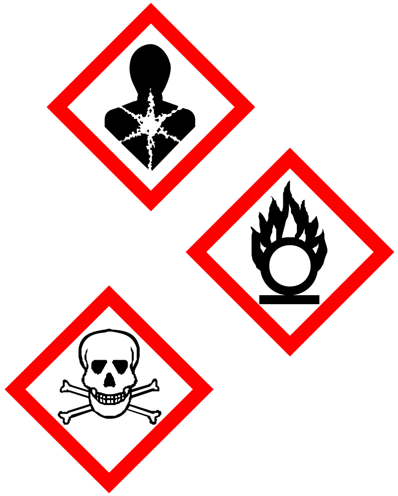
Properties of ozone

Ozone is:

- a strong oxidizing agent
- is not stable and must be produced on-site
- Highly toxic

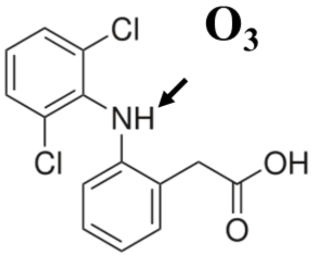
  > 0.1 ppm harmful to health

  > 10 ppm risk of death

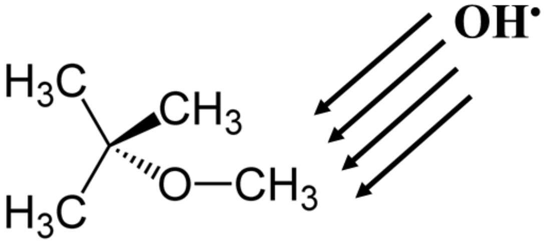


direct reaction (selective)

Diclofenac



reaction with OH-radicals (not selective)



MTBE

➔ No complete removal, but transformation of parent compound

Symbols: http://www.unece.org/trans/danger/publi/ghs/pictograms.html

Ozonation at municipal WWTPs

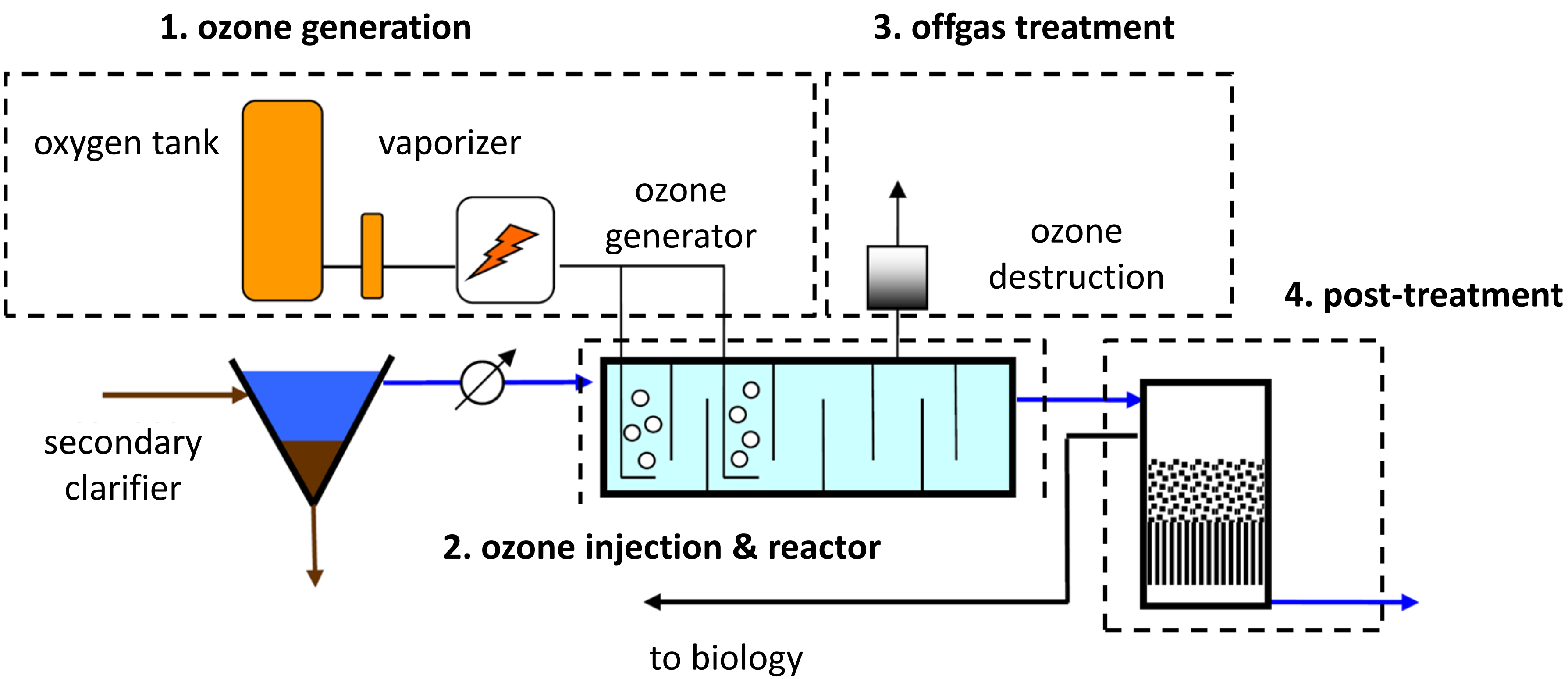


Figure based on:
Abegglen, C. und H. Siegrist, Mikroverunreinigungen aus kommunalem Abwasser. Verfahren zur weitergehenden Elimination auf Kläranlagen. 2012, Bundesamt für Umwelt (BAFU): Bern.

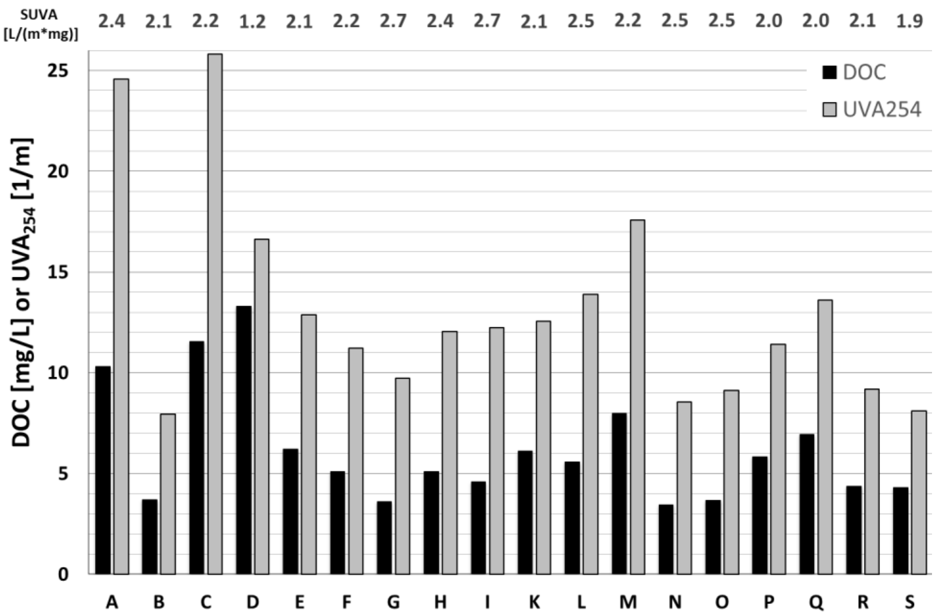
Water quality

- **Ammonia:** not affected by ozonation
- **Nitrite*:** fast oxidation to nitrate, consumes 3.4 mgO_3/mg-N
- **Nitrate**: increase in case of occurring nitrite, otherwise no effect
- **TSS:** at usual concentrations (< 10 mg/L) no relevant effect
- **Dissolved oxygen*:** strong increase up to 20 mg/L!
- **Phosphorous:** no significant impact
- **BOD_5:** slight increase
- **DOC*:** main reaction partner of ozone; decrease usually < 10%
- **COD:** decrease in the range of 10 - 20%
- **Bromide:** precursor for bromate formation,
  decrease depending on ozone dosage

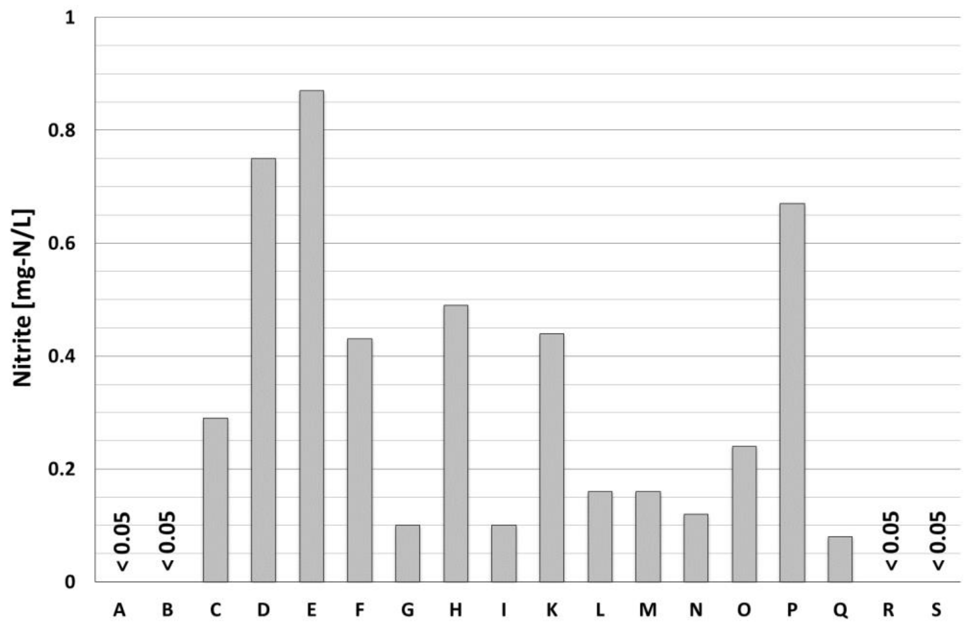
*Parameters with a relevant impact on ozonation or are affected by the ozonation

Water quality at WWTP effluents

DOC, UVA_{254}



Nitrite



In most cases, only on sample per WWTP (mixed or grab) -> values might is not necessarily representative

- DOC between 3,5 und 13,3 mg/L
- spec. UV-absorption (SUVA) was quite stable: 2.2 ± 0.3 L/(mg*m)

- Nitrite consumes ozone (3.43 mgO_3/mg-N)
- Big variations between WWTPs; concentrations measured up to 0.9 mg-N/L

Ozone generation

Basics:

- Principle: corona-discharge; O_2 bondings are split and then recombined to O_3
- only 10 – 15 M-% of the oxygen is converted into ozone
- about 90% of the energy is converted into heat -> cooling!

Required ozone production: $Q * D_{DOC} * C_{DOC}$

Q_{min} & Q_{max}!

DOC specific ozone dose:
0.3 – 0.9 mgO_3/mgDOC

D/A/CH: 5 – 13 mg/L

- Design flow in Germany often dry weather, in Switzerland rain weather
- Occurring nitrite can increase peak demand (3.43 mgO_3/mg-N) -> e.g. 0.5 mg-N/L -> 1.7 mgO_3/L

Oxygen supply

- Almost always liquid oxygen (LOX) is used
  -> usually most economic solution!

- Full scale (vacuum)-pressure-swing-adsorption units was planned at WWTP-Werdhölzli (CH), due to economic considerations
  (-> public subsidies!)

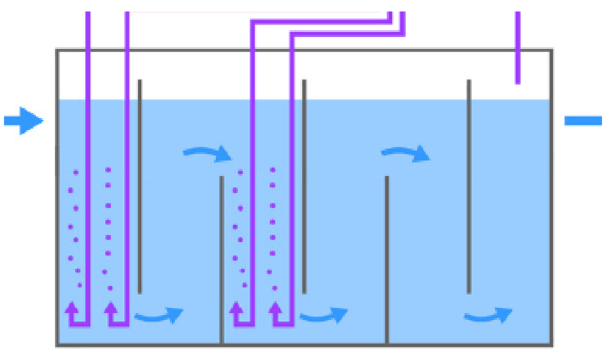
- Feed gas should contain 0,1 – 1 V-% N_2 to improve ozone generation
  -> addition of N_2 or pressurized air

Pictures from WWTP Kalundborg

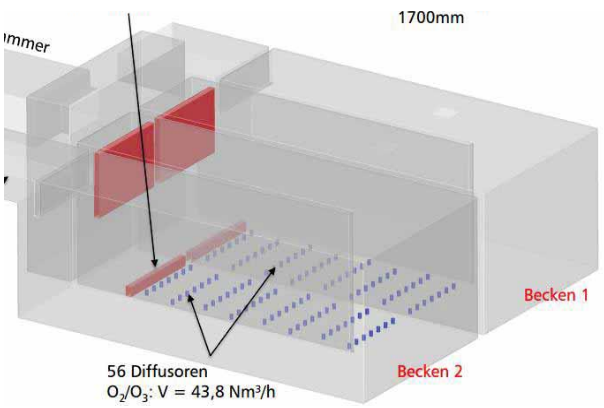
Reactor design

Reactor design should provide a sufficient reaction time, good mixing and no short-cuts.

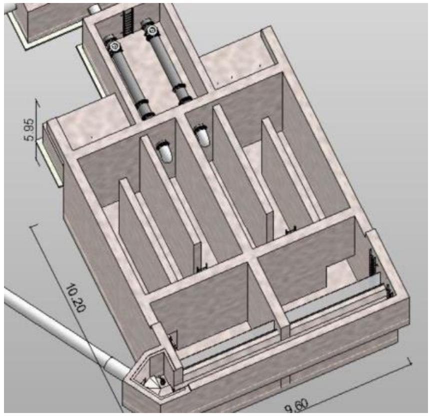
- no ozone at reactor effluent
- lab experiments, CFD modelling
- material resistant to ozone, gas-thight
- water level in reactor > 5 m (better gas-water-transfer)



WWTP Neugut (CH)



WWTP Aachen (DE)

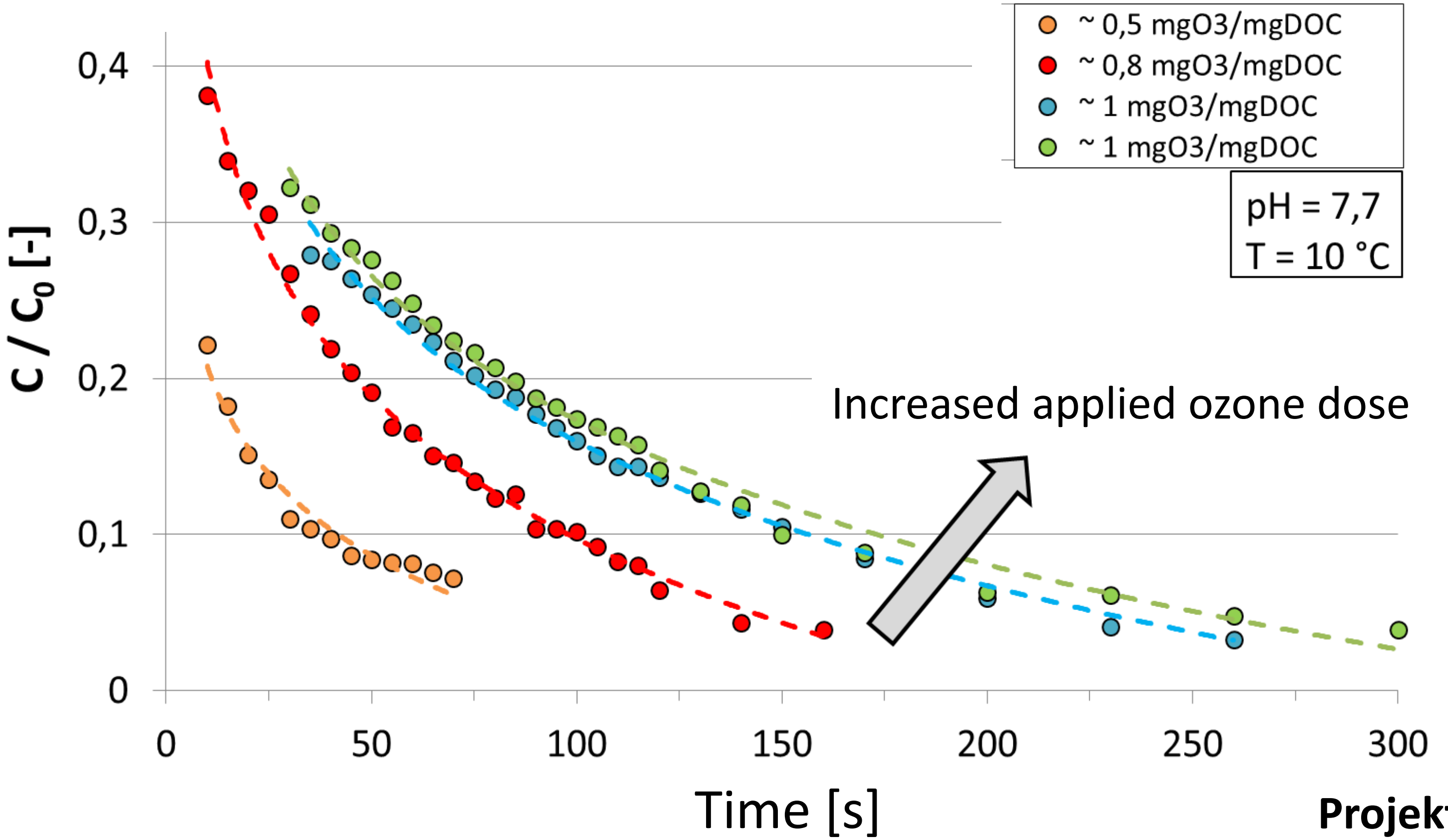


WWTP Warburg (DE)

Figure left: http://www.neugut.ch/scms/upload/Text/Ozonung/ARA_Factsheet10_2.pdf
Figure middle: Großtechnische Umsetzung einer Ozonung zur Vollstrombehandlung auf der Kläranlage Aachen-Soers; Ira Brückner, Wasserverbandes Eifel-Rur
Figure right: PLANUNG, BAU UND ERSTE ERGEBNISSE DER INBETRIEBNAHMEPHASE - OZONANLAGE WARBURG – Christian Maus // SWECO

Ozone depletion (1/2)

Ozone depletion can be determined at lab experiments by adding a ozone stock solution into a water sample and measuring the change of the dissolved ozone concentration.



Projekt TestTools

Bundesministerium für Bildung und Forschung

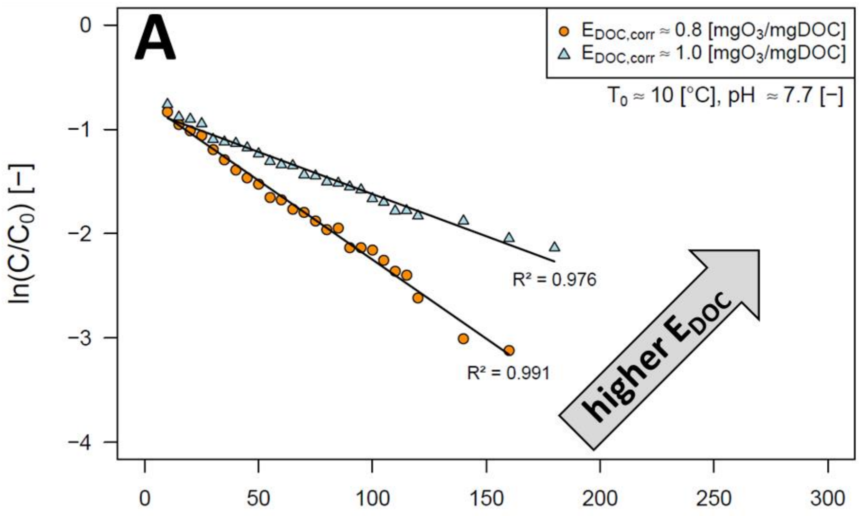
Berliner Wasserbetriebe

KOMPETENZZENTRUM Wasser Berlin

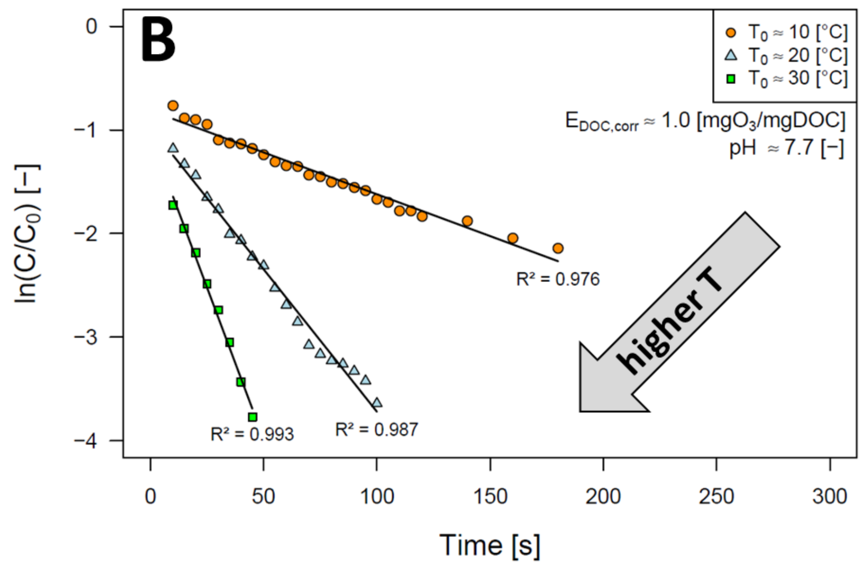
- rule of thumb: HRT = 3 x ozone depletion time
- flexibility during rain weather: reduction of ozone dose

Ozone depletion (2/2)

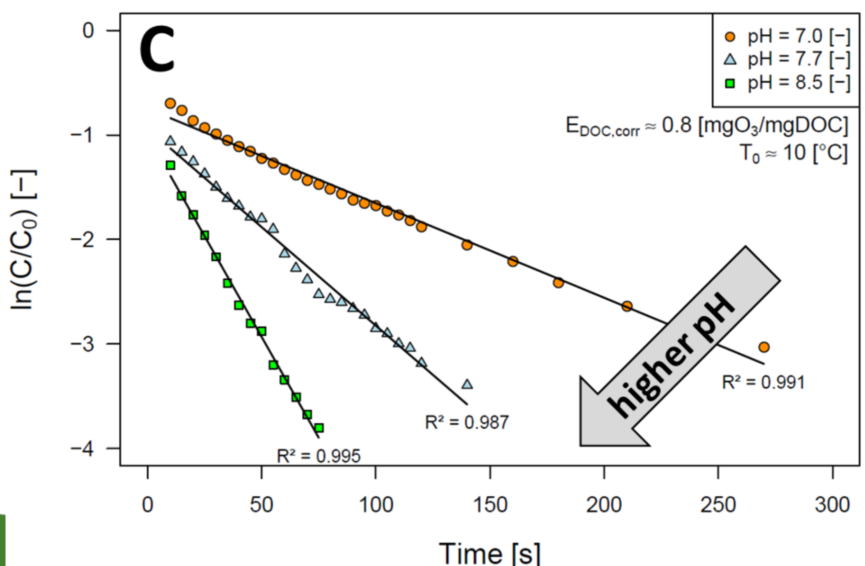
applied ozone dose



water temperature



pH



Time for complete ozone depletion increases at:

- high applied ozone dose
- low water temperature
- low pH

Projekt TestTools

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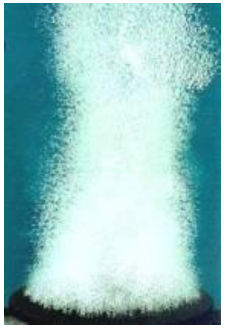
Ozone injection

Diffusor



- water level > 5 m
- ceramic diffusors
-> watch for min. & max. gas flow

Pump-injection-system

- high flexibility of gas flow
- easier to be maintained
- higher energy consumption (additional pump)

- Both methods are have their Pros and Cons, thus choice depends usually on economic and/or operational aspects.
- Adaption of ozone dose: first reduce gas flow, then ozone concentration in feed gas!
- If diffusors are turned off: water and particles can enter diffusor system!

Figures: https://www.ozonesolutions.com/info/venturi-vs-diffusers

Ozone destruction

As ozone is highly toxic, all gas leaving the ozone reactor need to be purged from ozone using a „residual ozone destructor“

Ozone destructor types:
1. thermal treatment (350°C for more than 2 s)
2. thermal/catalytic treatment (40 – 80°C, palladium or Cu/MnO)

- It is recommended to have a forced venting (e.g. low pressure after ozone destructor).
- Off-gas flow should be measured online for calculation of the ozone mass balance
- Offgas after ozone destructor is mainly oxygen and might be reused at CAS

WWTPs with full-scale ozonation

incl. planned ones, no claim to completeness

WB: MBBR
SF: sand filter
ST: polishing pond
GAK: GAC
BAK: BAC

	design capacity [1000 PE]	Start of operation	D_{DOC} [mgO$_3$/mgDOC]	treatment capacity	O_2	Ozone-injection	reactor depth [m]	reactor type	HRT [min]	Post-treatment
Aachen Soers*	458	2018	0.7 (DW) / 0.5 (RW)	RW	LOX	D	5	2 comp., horizontal	12 – 30	MBBR# + sand filter#
Bad Sassendorf*	13	2009	0.35	DW	LOX	D	5	4 comp.	12 – 40	polishing pond#
Duisburg-Vierlinden*	30	2011	0.3	DW	LOX	I	5	no comp. (1/3 NB)	> 30	MBBR
Espelkamp	33	2017	0.4 – 0.6		LOX					polishing pond#
Lemgo	98	Planned 2019	0.3 – 0.8	DW (83% YWW)	LOX	I	5.6	3 comp.	> 19	sand filter#
Schloß Holte-Stukenbrock	60	Planned 2018	0.7	DW	LOX	D	7	6 comp.	30	polishing pond#
Warburg	70	2016	0.7	DW (90% YWW)	LOX	D	5	3 comp., horizontal	> 20	MBBR
Weißenburg in Bayern*	35	2017		DW (85% YWW)	LOX	I	6	4 comp.	20 – 40	sand filter / BAC
Altenrhein	> 75	2018		2.5 * Q_{DW}	LOX	D		6 comp.		GAC
Neugut*	150	2014	0.33 – 0.5	RW	LOX	D	5.5	6 comp.	13 – 44	sand filter#
Werdhölzli, Zürich	670	2017	0.7 – 0.9	RW	VPSA+ LOX	D	5	8 comp.	> 12 26 (avg.)	sand filter#

* sites with (former) research activity
** expansion planned

allready existing

YWW: total anual volume of wastewater

What are we doing within CWPharma

Guideline for advanced API removal processes

- general guideline for operators, municipalities, and water authorities on how to plan, start, operate and control advanced wastewater systems
- optimized control of the ozone dosage for efficient and economic operation
- Recommendations for the removal of powdered activated carbon with a filtration process
- Three sites with ozonation plants:
  - WWTP Linköping (SE, full-scale)
  - WWTP Kalundborg (DK, full-scale)
  - WWTP Schönerlinde (DE, pilot-scale)

CWPharma
CLEAR WATERS FROM PHARMACEUTICALS

KOMPETENZZENTRUM Wasser Berlin

Interreg
Baltic Sea Region

EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND

Thanks for your attention!

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