

Zero PFAS
Roadshow 2024 &
EMPEREST
Workshop #1, 12.-
14.02.2024, Tartu



Micropollutants and PFAS removal in wastewater treatment plants with advanced treatment

German experiences

Prof. Dr.-Ing. Matthias Barjenbruch
Dr.-rer.-nat. Nikolaos Tzoupanos

TU Berlin,
Department Urban Water Management, Sekr. TIB 1B 16
Gustav-Meyer-Allee 25, D - 13355 Berlin

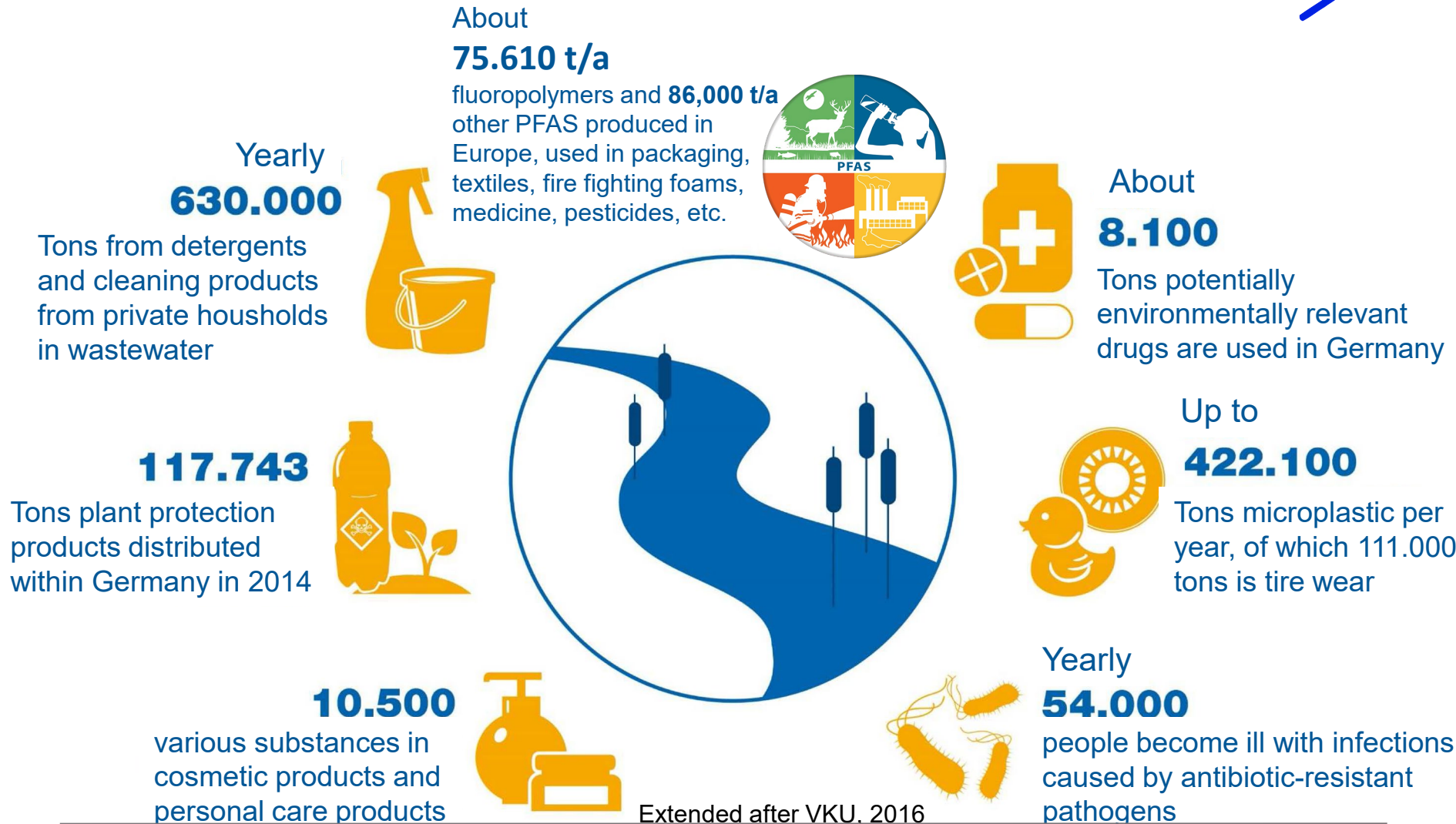
matthias.barjenbruch@tu-berlin.de

Definition

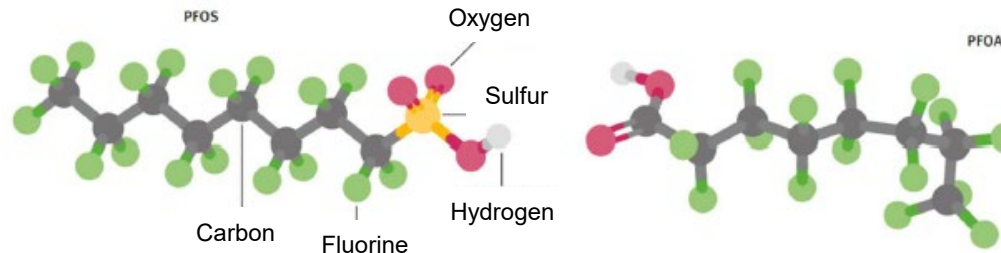
There is no official definition of micro-pollutants!

- ▶ Micro-pollutants are chemical compounds, which appear in the environment in very small concentrations ($1\text{ }\mu\text{g/l}$ below 1 ng/l).
 - The focus lies on synthetically produced micro-pollutants
 - ▶ In the EU more than 100.000 chemicals are permitted.
 - 30.000 are produced in amounts larger than $> 1\text{ t/a}$
 - Only pharmaceuticals > 3.000 active agents, about 40.000 t/a
 - ▶ In the last decades: highly improved chemical analytics
 - More substances were detected in the environment.
 - In the past no one searched for those substances.
 - ▶ According to the actual state of knowledge, the measured concentrations of organic micro-pollutants in potable water are so low, that normally **no risk for humans must be feared.**
 - ▶ Selection of known effects in the environment:
 - Feminization of fishes by hormones
 - Vulture decease (ca. 10 Mio. animals) in India by diclofenac
 - Kidney, liver and gills malfunction of fishes
-

Emission of micro-pollutants and PFAS into water bodies



□ Per- und polyfluoroalkyl substances



- PFAS are stable, aliphatic substances, which contain the unit C_nF_{n+1}
 - > 4,700 known substances up to 100,000
 - All synthetic!
 - 1930s: Teflon.
 - 1950s: Manufacturing and commercial production in large scale.
 - 1970s: Health concerns.
 - 2000s: Development of analytical methods.
- Durable, resistant
 - Grease, dirt and water repellent
 - Bioaccumulative
 - Form aqueous, film-forming foam between surfaces/liquids and the fire zone
 - Toxic to reproduction
 - Carcinogenicity
 - Binders - Breathable clothing
 - Effects on the development of the unborn child
 - ...
- The high stability of PFAS results from the C-F bonds, which are neither chemically, physically nor biologically degradable under normal environmental conditions!

Legal frame -PFAS

► Amended UWWTD

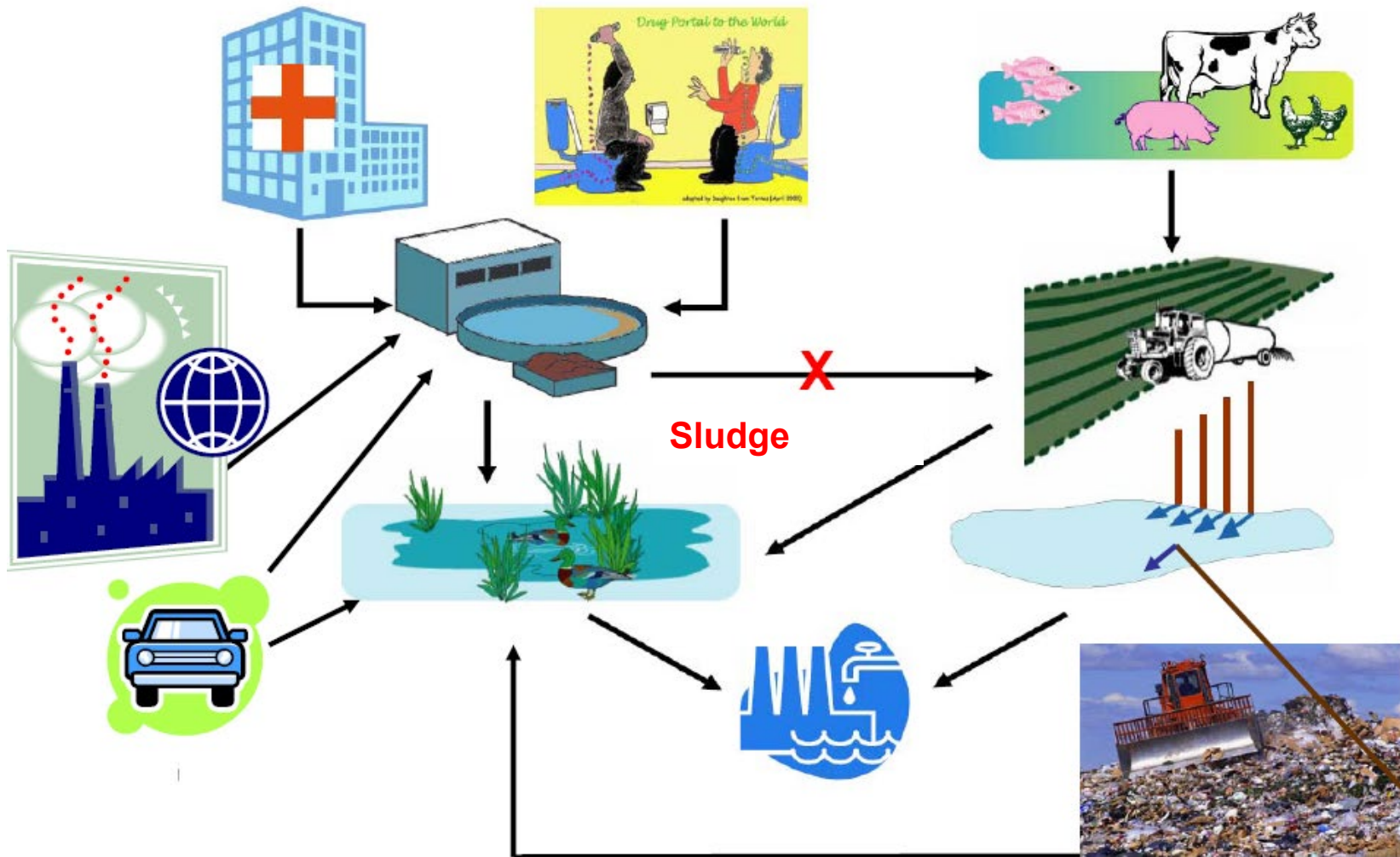
Besides pre-defined micro-pollutants also perfluorooctane sulfonic acid (PFOS) is mentioned in the newest draft of the UWWTD.

it is not sure whether they belong to the 80% reduction in all categories.

2035: ‚Advanced treatment‘ all WWTP > 125,000 PE

Frame	Limiting values
Surface water (Priority substance list of Water Framework Directive (WFD), 2008/105/EC)	0.65 ng/L average yearly conc. and 36,000 ng/L max. conc. for inland surface waters and 0.13 ng/L and 7,200 ng/L respectively for transitional and coastal waters
Drinking water (Drinking water directive 2020/2184)	100 ng/L PFAS-20 (DE) 20 ng/l PFAS-4 (DE) 500 ng/L PFAS-total
Sewage sludge	100 µg/kg wet weight (PFOA & PFOS)
Biota / Fish (Priority substance list of WFD)	9.1 µg/kg wet weight (PFOS)
Human blood (Human Biomonitoring Commission of the German Environment Agency)	2 ng/mL (PFOA), 5 ng/mL (PFOS)

Pathways into the water courses



Stakeholder – strategy

German centre of micropollutants (UBA)

- Commission for determination of relevant micro-pollutants
 - Round table discussion with all stakeholder
 - Industry, trade, water companies, medicine sector, pharmacy, etc.
 - Common use oriented recommendations
 - Public campaigns
 - Education
 - Environmental friendly application
 -
 - Orientation guideline for advanced wastewater treatment
 - Relevant catchment, prioritisation of activity options, selection of WWTP
- **Aim: Reduction of water pollution**



Raising public awareness



Miehe 2020

Wastewater treatment

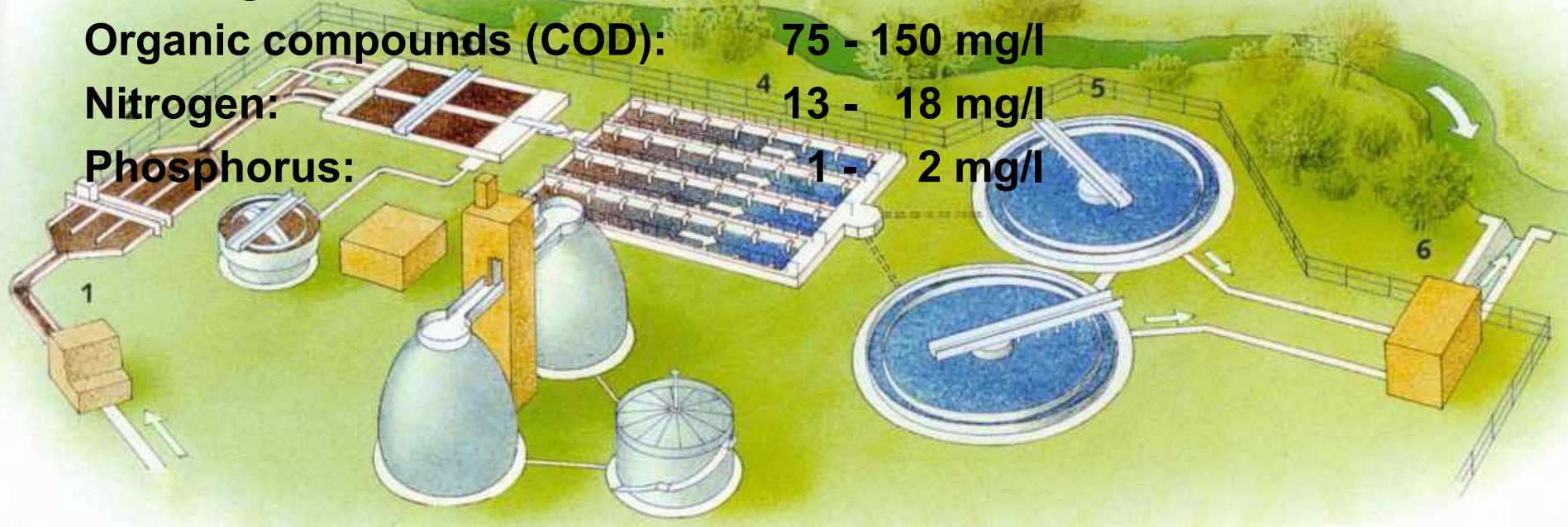
State of the art

- ▶ Actual regulations in Germany (Wastewater ordinance) according to the size of the WWTP:

Organic compounds (COD): 75 - 150 mg/l

Nitrogen: 13 - 18 mg/l

Phosphorus: 1 - 2 mg/l



- ▶ Results of DWA-survey of efficiency 2022 (Germany)

Organic substances (COD):	Inlet WWTP 601 mg/l	➔ outlet WWTP	26 mg/l
Nitrogen:	Inlet WWTP 55 mg/l	➔ outlet WWTP	8.7 mg/l
Phosphorus:	Inlet WWTP 8.2 mg/l	➔ outlet WWTP	0.53mg/l

Removal of micro-pollutants by conventional biological treatment

	Stoffgruppe									
	Hormone und Xenohormone			Pharmazeutika					Röntgenkontrastmittel	
	Östron	17 β -Östradiol	17 α -Ethinylöstradiol	Carbamazepin	Diclofenac	Ibuprofen	Bezafibrat	Clofibrinsäure	Iopromid	Iopamidol
Conventional activated sludge										
COD removal t_{ds} 2 d	-- ³	--/+ ³	-- ³	-- ³	-- ³	--/+ ³	-- ³	-- ³	-- ³	-- ³
Nitrification (t_{ds} 10-15 d)	++ ³	++ ³	++ ³	-- ³	--/+ ³	++ ³	++ ³	-- ³	--/+ ³	-- ³
Sludge stabilization (t_{ds} 25-100 d)	++ ³	++ ³	++ ³	-- ³	--/+ ³	++ ³	++ ³	-- ³	--/+ ³	-- ³
Sludge stabilization (t_{ds} 100 - 200 d)			++ ¹	-- ¹	-- ¹	++ ¹	++ ¹			
MBR (Sludge age $t_{ds} \geq 22-25$ d)	++ ³	++ ³	++ ¹	-- ¹	-- ¹	++ ¹	++ ¹	-- ³	--/+ ³	-- ³
MBR (Sludge age $t_{ds} \geq 50$ d)			+ ¹	-- ¹	-- ¹	++ ¹	++ ¹			
Rotating disc without targeted nitrif.					++ ²	++ ²		--/+ ²		
Trickling filter without targeted nitrif.					--/+ ²	++ ²		--/+ ²		
Fixed bed reactor, nitrifying	++ ³	++ ³	++ ³	-- ³	--/+ ³			-- ³	--/+ ³	-- ³
-- Removal < 20% - 20% $\leq$ Removal < 40% -+ 40% $\leq$ Removal < 60% + 60% $\leq$ Removal < 80% ++ 80% $\leq$ Removal < 100% ... / ... from / till ¹ Clara, M. (2004). Das Verhalten ausgewählter organischer Spurenstoffe bei der biologischen Abwasserreinigung. Wien, Institut für Wassergüte und Abfallwirtschaft TU-Wien. ² Schrader, C., Krampe, J., et al. (2005). Untersuchung und Optimierung der Abwasserreinigung zur Eliminierung von organischen Spurenstoffen unter verfahrenstechnischen und ökonomischen Aspekten (Modul2). Universität Stuttgart - Institut für Siedlungswasserbau, Wassergüte- und Abfallwirtschaft. ³ Projekt POSEIDON (2005). Assessment of Technologies for the Removal of Pharmaceuticals and Personal Care Products in Sewage and Drinking Water Facilities to Improve the Indirect Potable Water Reuse. Final Report.										

Swiss study
Hunziker, 2008

PFAS in the effluent of conventional WWTPs in Germany

□ Effluent concentrations of PFAS-4

	Samples > LOQ (%)	Min	Max	Median	LOQ (ng/L)
PFOS	10 - 100	< LOQ – 10	6,1 – 5,700	< LOQ – 38	0.21 – 25
PFOA	5 - 100	< LOQ – 12,3	3 – 15,900	< LOQ – 34	0.12 – 25
PFHxS	1 - 89	< LOQ	1.4 – 921.9	< LOQ – 41	0.57 – 25
PFNA	0 - 100	< LOQ - 1	1.9 – 273.5	< LOQ – 2,3	0.12 - 25

Zhiteneva, V., et al., 2023; Tzoupanos, 2023

□ Sum parameter determination

Method	Samples > LOQ (%)	Min	Max	Median	LOQ (µg/L)
AOF	10 - 100	< 2	15	3.2 – 5	2 – 5

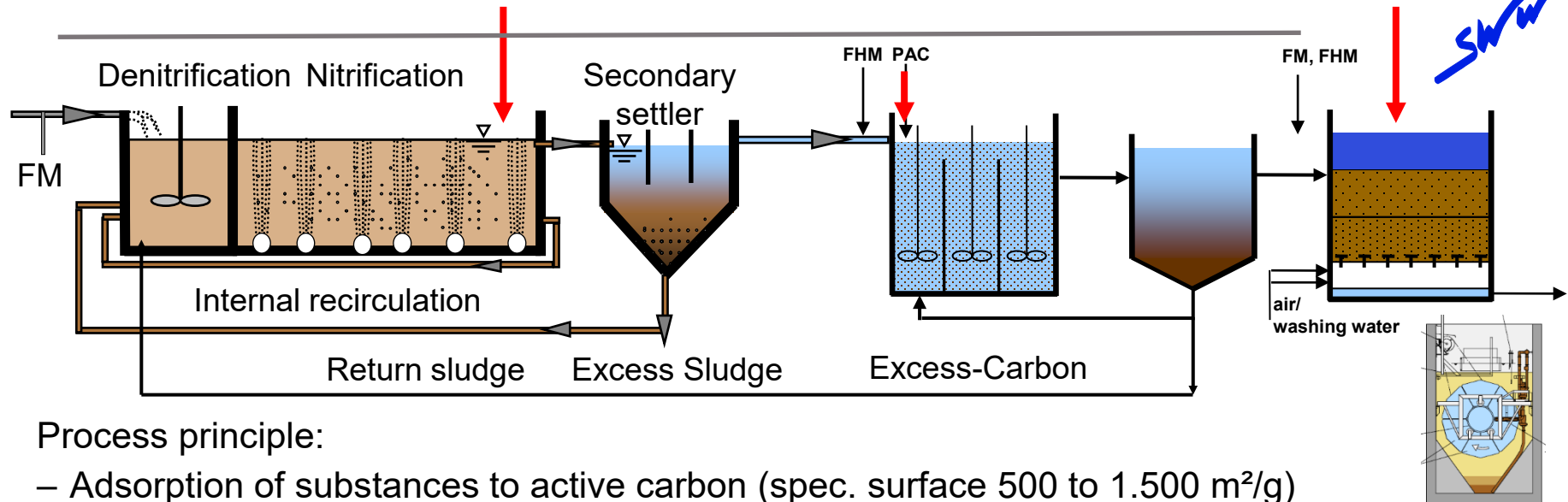
Abercron et al., 2019; Redeker et al., 2023

➤ Proportion of ,known‘ PFAS in AOF max. 17%!

Wastewater treatment processes for the specific removal of micro-pollutants and PFAS

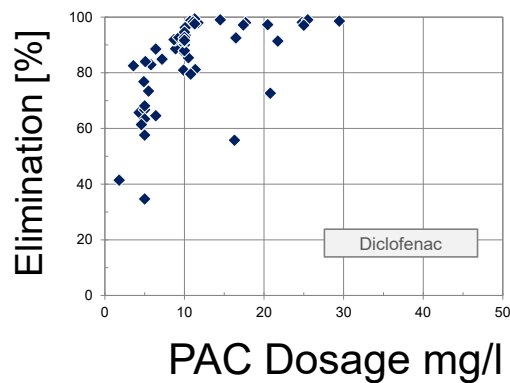
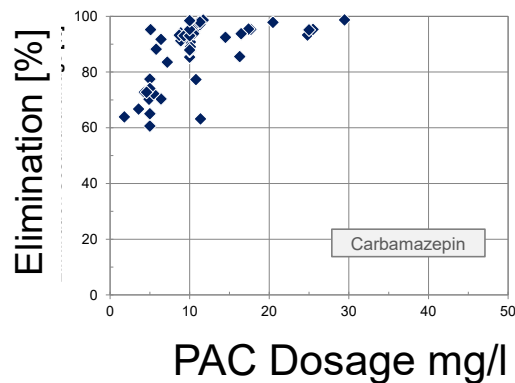
- Applied in large scale
 - ▶ Activated carbon adsorption
 - Powdered Activated Carbon (PAC) or Granulated Activated Carbon (GAC)
 - ▶ Oxidation with ozone
 - Biodegradable substances are produced (BOD)
 - Attention: **Transformations products** might be more persistent, more mobile and toxic compared to the original substances!
 - Ozone alone might not be suitable for breaking down all PFAS chemicals
 - ▶ Combinations, e.g. ozone + activated carbon
 - Under investigation (lab or pilot scale)
 - ▶ Anion exchange
 - ▶ Separation by membrane e.g. nanofiltration, reverse osmosis (not suitable)
 - .Disposal of the concentrate (15 - 30%), extremely high costs
 - ▶ Other (advanced) oxidation processes
 - e. g. ozonation and/or H_2O_2 + UV- irradiation, titan dioxide + UV-irradiation, plasma reactor, electrochemical oxidation, super critical water oxidation
- according Ahrens, 2023, modified

Powdered activated carbon (PAC)



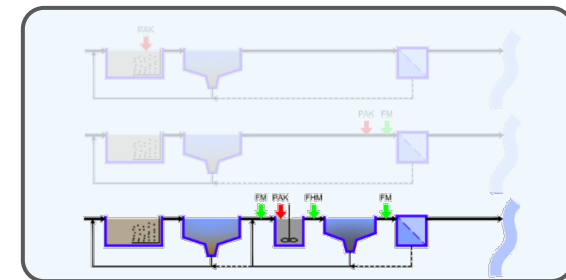
- ▶ Process principle:
 - Adsorption of substances to active carbon (spec. surface 500 to 1.500 m²/g)
 - Reduction efficiency depending on the properties of the micro-pollutants, broad band efficiency
 - No toxic by-products
 - Additional removal of DOC: 45-65% (threshold value)
- ▶ Contact reactor
 - Detention time about 0.5 h
- ▶ Demand of PAC ~ dosage rate: 10 or 20 mg PAC/l
- ▶ Excess coal increase amount of sludge
 - Additional adsorption in the activated sludge
 - DWA design leaf left DWA M 285

Removal efficiency with PAC



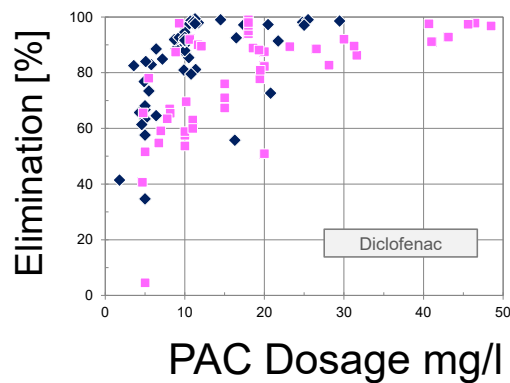
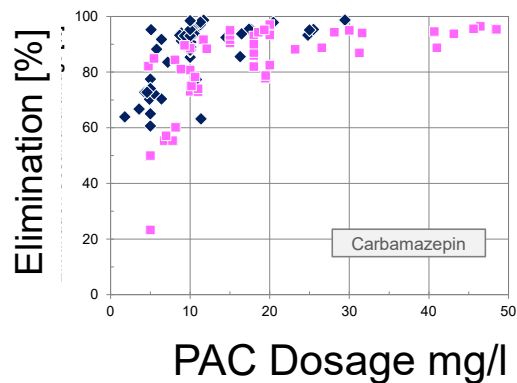
♦ Adsorption with dosage in separated reactor

Datenquellen: KomS, 2017; Zöllig, 2017



Aktivkohleeinsatz auf Kläranlagen // Benstöm und Metzger // DWA Seminar: Weitergehende Abwasserreinigung, 07.11.19 Göttingen

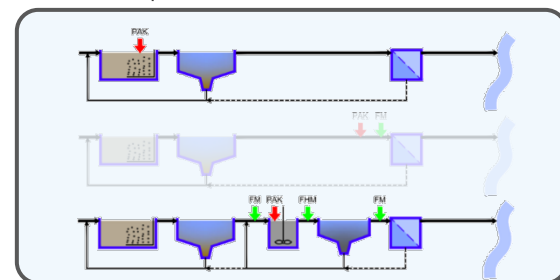
Removal efficiency with PAC



◆ Adsorption with dosage in separated reactor

■ Simultaneous dosage

Datenquellen: Böhler et al., 2012; Keyzers, 2016; KomS, 2017; Locher, 2016; Obrecht et al., 2015; Zöllig, 2017



Aktivkohleeinsatz auf Kläranlagen // Benstöm und Metzger // DWA Seminar: Weitergehende Abwasserreinigung, 07.11.19 Göttingen

PFAS elimination in WWTP with advanced treatment

15 WWTP in Baden-Württemberg

PFAS in the inlet and outlet of WWTP with PAC

	Before advanced treatment				With advanced treatment			
	Number of WWTPs	Elimination with biological treatment			Number of WWTPs	Total elimination		
		[%]				[%]		
		25 %-Quantil	Median	75 %-Quantil		25 %-Quantil	Median	75 %-Quantil
PFOS	12	5	28	39	4	53	79	92
PFOA	8	-2	2	40	3	31	63	77
PFBA	3	0	33	58	4	72	81	83
PFBS	4	7	10	16	2	41	58	75

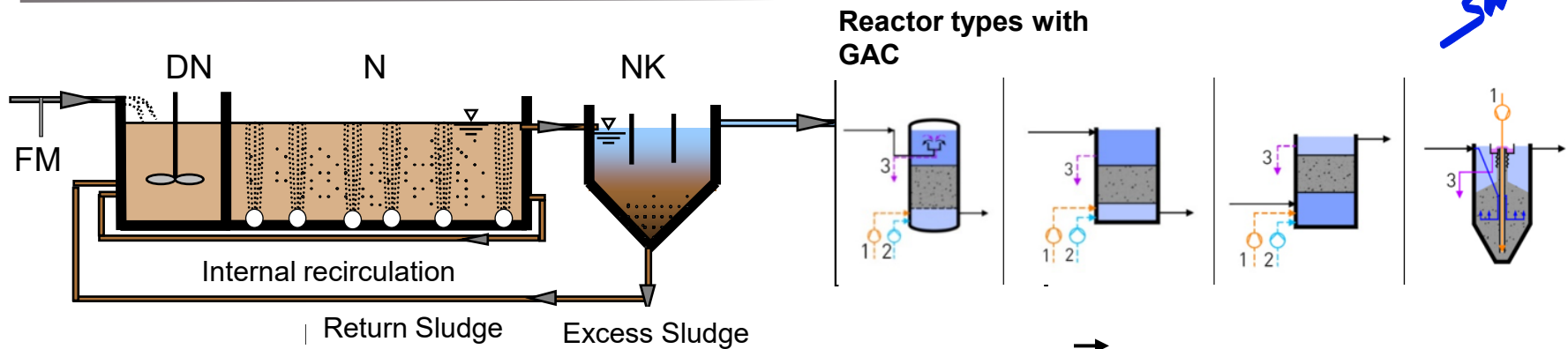
Quelle: A. Rößler, M. Launay, 2019, KomS BW, Kompetenzzentrum Spurenstoffe-BW

Removal of micropollutants

PAC-Process at the WWTP KA Ulm



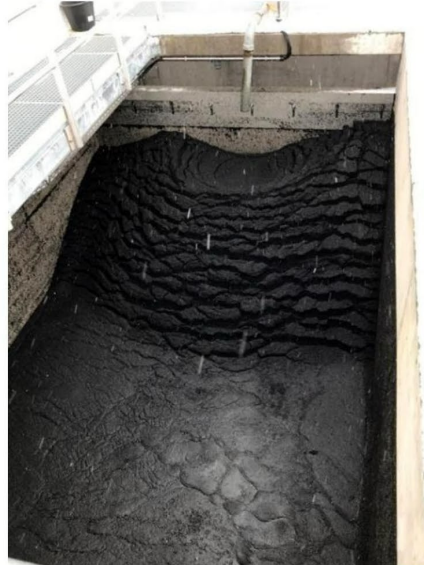
Process with granulated activated carbon



- ▶ **Process principle /conditions:**
 - Adsorption to granulated activated carbon
 - Additional biological effects possible
 - No toxic by-products
 - Low solid content in the inlet required and background pollution must be regarded
 - Removal in dependence of abilities of the substances, broad band effects
- ▶ **Technical information**
 - Reachable run time/bed volume (only a few month)
 - High efforts for exchange of the GAC
 - Regeneration of loaded GAC possible
- ▶ **Experiences:**
 - Pilot-plant (e.g. Düren, Ober Lutter, Putzhagen, Wuppertal, Immendingen)
 - DWA design leaf left DWA M 285

Examples of operation with granulated carbon

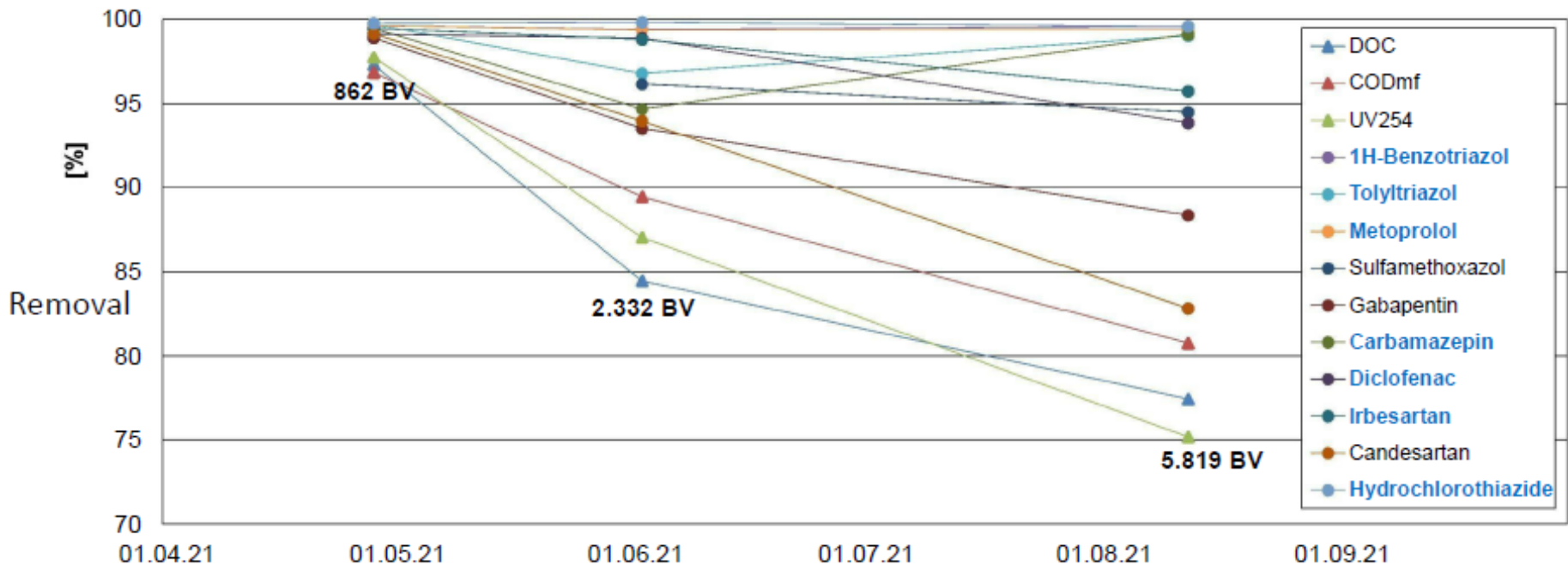
WWTP Immendingen, DE



control of backwashing



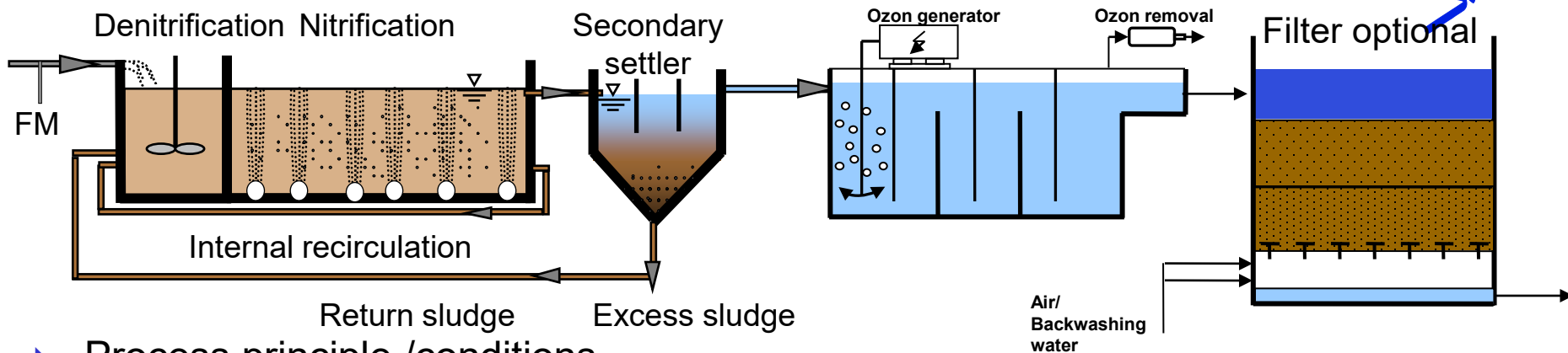
Removal of micropollutants by GAC, WWTP Immendingen, DE



Platz, 2023

Ozonation

(post-treatment)



► Process principle /conditions

- Strong oxidation agent reacts with lot of substances in the water
- Broad band effects of elimination of micro-pollutants
- Additional disinfectional effects
- Advanced removal of DOC; minor removal of PFAS
- Common dosages in wastewater: 5 - 15 mg O₃/l

► Development of reaction products

- Biological degradable substances (→ post treatment necessary)
- **Unknown conversion products** (transformation); → eventually toxic (bromate)?

► Experiences

A lot of experience for potable water, (Bad Sassendorf, Aachen, pilot-plant for sewage)
New regulation from DWA

WWTP Zurich, CH



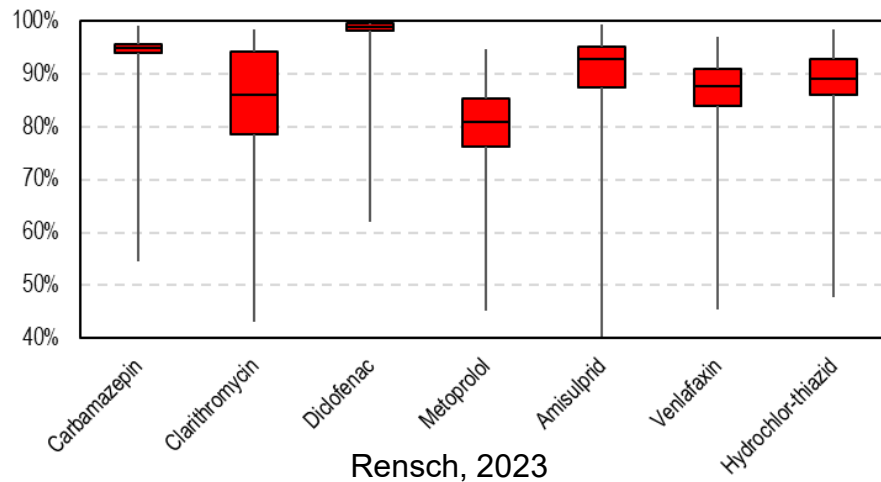
. 2011

Micropollutants and PFAS removal in WWTPs with advanced treatment
Zero PFAS Roadshow 2024 & EMPEREST Workshop #1, 12.-14.02.2024, Tartu

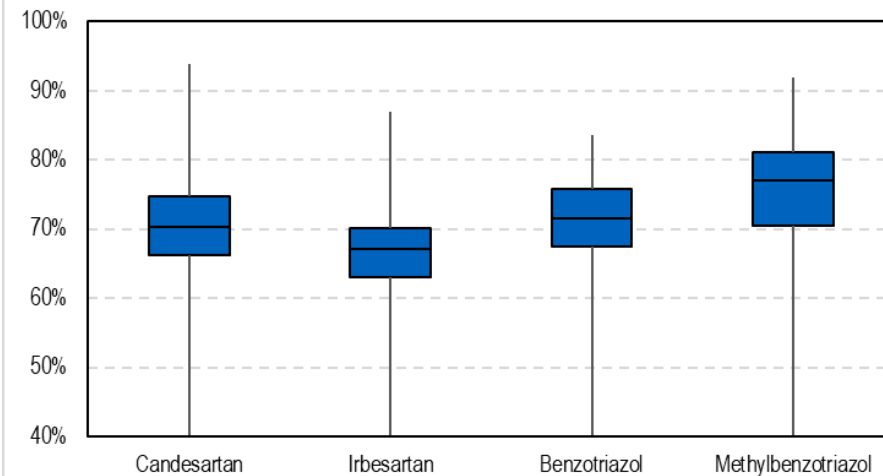
Matthias Barjenbruch | TU Berlin

Removal of micropollutants by ozonation, WWTP Zurich, CH

Single substance elimination



Single substance elimination



WWTP's with quaternary treatment for micropollutant removal - Germany



Barjenbruch et al., 2024

-
- Specific yearly costs €/m³
- Size of WWTP in PE
- $y = 13,408x^{-0,441}$
 $R^2 = 0,5078$

Matthias Barjenbruch | TU Berlin

Summary and outlook

- ▶ Anthropogenic micro-pollutants and PFAS can be detected in the water cycle in the range of μg and ng
- ▶ Measures and separation at the source:
 - Prohibition of substances, labeling of products → alternative substances
 - e.g. direct treatment of sewage in hospitals
- ▶ Conventional wastewater treatment is designed for:
 - COD-elimination, nutrient- and phosphorus removal
 - Respectable removal of micro-pollutants possible, but no specific treatment!
- ▶ Additional steps for the treatment of micro-pollutants and PFAS are necessary
 - Broad band efficiency ($> 80\%$) of ozonation (limited PFAS removal) and active carbon (GAC, PAC)
 - Partly flow treatment (e.g. upto 90% of inlet) has to be checked
- ▶ **In the future, a higher price will have to be paid than today for the preservation of our aquatic environment and our vital element water!**
 - Implementation of measures will be necessary according the new UWWTD

Thank you for your attention

Contacts

matthias.barjenbruch@tu-berlin.de

nikolaos.tzoupanos@tu-berlin.de

Department of Urban Water Management

Institute of Civil Engineering

Faculty VI Planning Building Environment

TECHNISCHE UNIVERSITÄT BERLIN

Sekr. TIB 1B 16

Gustav-Meyer-Allee 25

D - 13355 Berlin