ELIMINATION OF MICRO POLLUTANTS OUT OF DRINKING WATER (PFAS)

INTERNATIONAL MEUSE SYMPOSIUM

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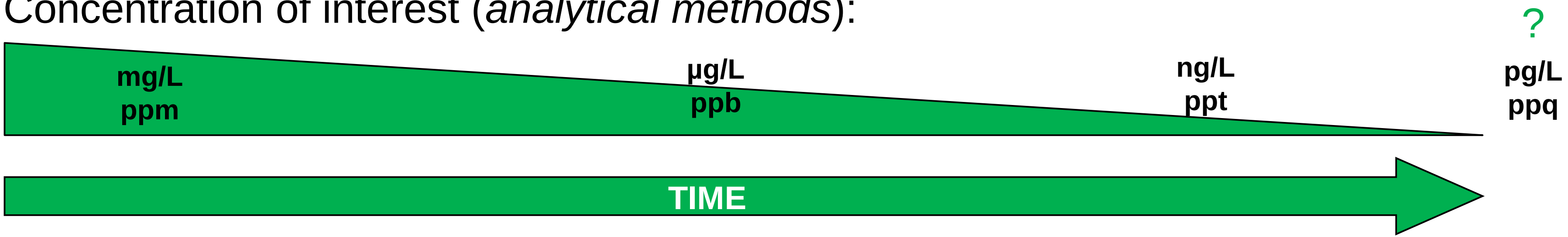
DVGW | TZW Technologiezentrum Wasser

MICRO POLLUTANTS

- Organic and anthropogenic
- Water sector‘s focus changes over time

Concentration of interest (*analytical methods*):



Polycyclic aromatic hydrocarbon

Volatile halogenated hydrocarbons

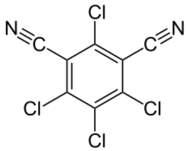
Pesticides

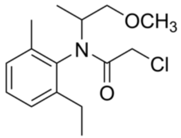
Pharma-ceuticals

Metabolites, Degradation products

PFAS
nrM ⇨ rM

Toxicological assessment: Metabolites of Chlorothalonil and S-Metolachlor





PATHWAYS INTO THE WATER CYCLE

- Depending on application

Pharmaceuticals
Sweeteners

Human body

Waste water
treatment plant

River

Pesticides

Ground Water River

Biological degradation,
Formation of metabolites

PATHWAYS INTO THE WATER CYCLE

- Depending on application

PFAS

↓ Fire fighting foams

Ground Water

↓ no biological degradation

River

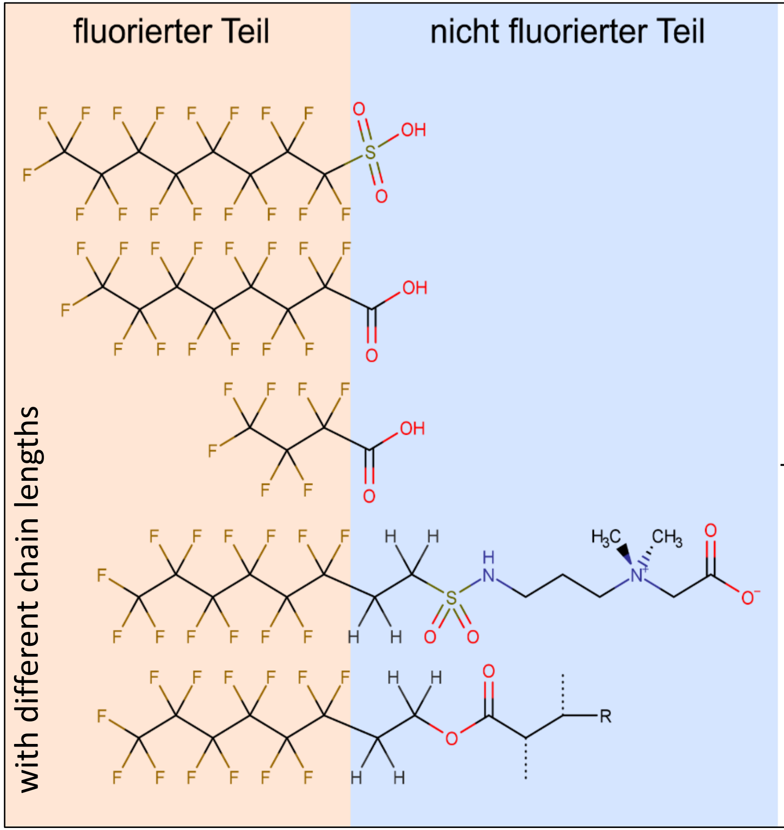
PFAS from the production site

↓ ↓

Ground Water River

PFAS: PER- AND POLYFLUOROALKYL SUBSTANCES

> 5,000 Substances



PFOS

PFOA

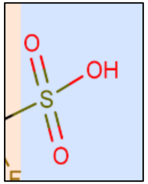
PFBA

Analysable single substances

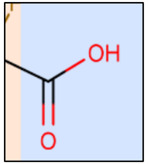
6:2 FTSA-Betain

6:2 FTAC

Precursors



Sulfonic Acids



Carboxylic Acids

Precursors can be degraded in nature to fluorinated sulfonic or carboxylic acids

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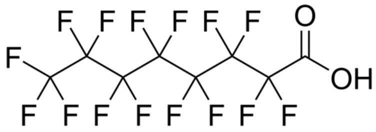
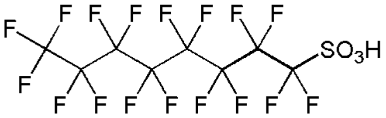
PFAS – DRINKING WATER THRESHOLD VALUES

∑ 20 PFAS:
0,1 µg/L

- 10 perfluorinated carboxylic acids + 10 perfluorinated sulphonic acids
- Each with chain lengths from C-4 to C-13

Carboxylic Acids 	PFBA	short chain
	PFPeA	
	PFHxA	
	PFHpA	
	PFOA	lc
	PFNA	
Sulfonic Acids 	PFBS	short
	PFPeS	
	PFHxS	long c.
	PFHpS	
	PFOS	

B	Butan	C-4
Pe	Pentan	C-5
Hx	Hexan	C-6
Hp	Heptan	C-7
O	Oktan	C-8
N	Nona	C-9

Based on EU DWD (Drinking Water Directive)

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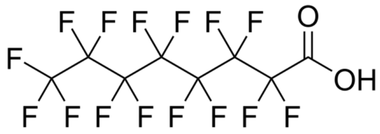
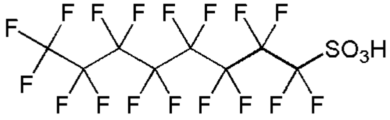
PFAS – DRINKING WATER THRESHOLD VALUES

∑ 20 PFAS:
0,1 µg/L

∑ 4 PFAS:

- DE: 0,02 µg/L (20 ng/L)
- Flanders: 0,004 µ/L (4 ng/L)
- DK: 0,002 µg/L (2 ng/L)
- SE: 0,004 µ/L (4 ng/L)

Carboxylic Acids 	PFBA	short chain
	PFPeA	short chain
	PFHxA	short chain
	PFHpA	short chain
	PFOA	lc
	PFNA	lc
Sulfonic Acids 	PFBS	short
	PFPeS	short
	PFHxS	long c.
	PFHpS	long c.
	PFOS	long c.

B	Butan	C-4
Pe	Pentan	C-5
Hx	Hexan	C-6
Hp	Heptan	C-7
O	Oktan	C-8
N	Nona	C-9

Based on the EFSA
(European Food Safety Authority)

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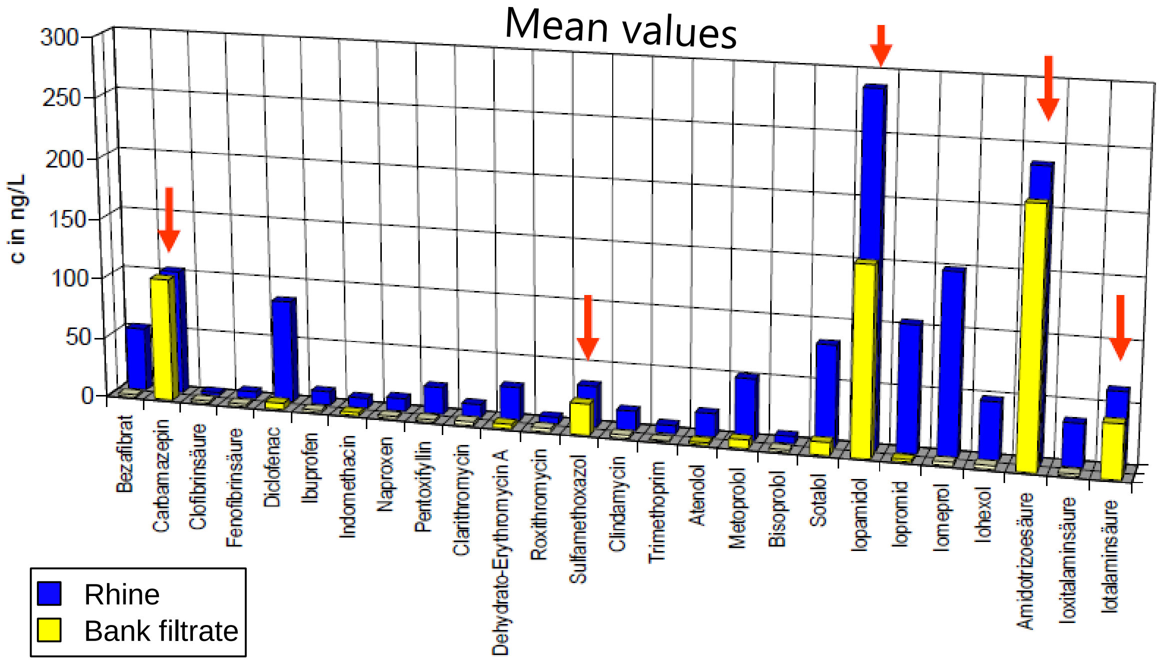
DRINKING WATER TREATMENT TECHNOLOGIES FOR MICRO POLLUTANTS

- **Biological Processes**
  bank filtration, sand filtration
- **Adsorption**
  Activated carbon, new adsorbents
- **Oxidation**
  Ozone, AOP
- **Membrane filtration**
  Nano filtration, reverse osmosis

BANK FILTRATION



- Effective barrier for many micro pollutants
- Stable substances are not degraded: X-ray contrast agent, PFAS

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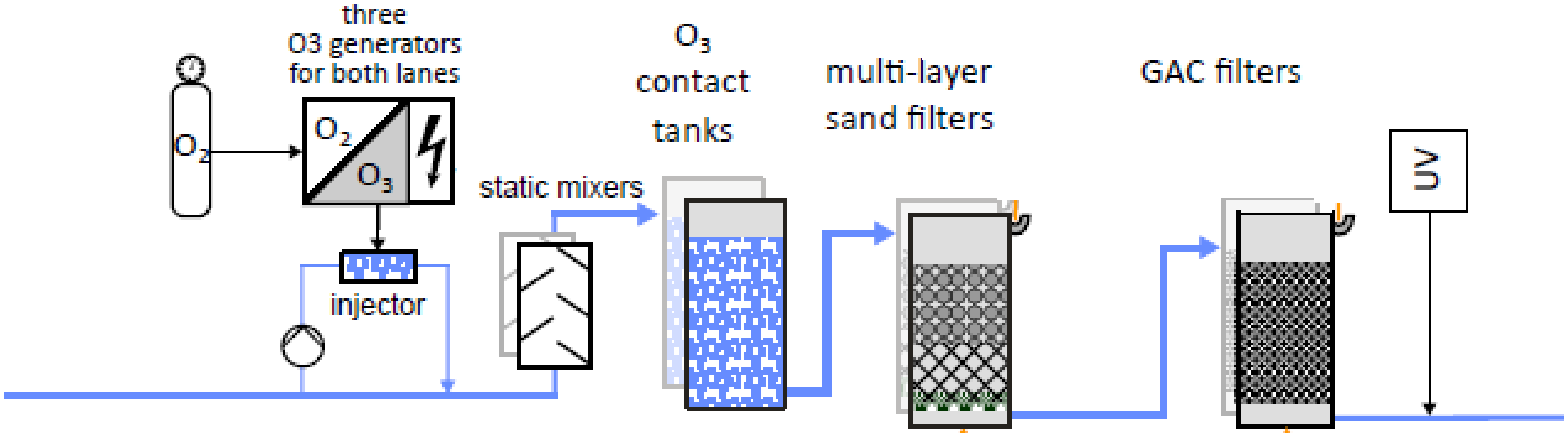
OXIDATION PROCESSES

- Most common: Ozonation
- Very often used for treatment of bank filtrate
- Always in combination with (sand) filtration (biological degradation)



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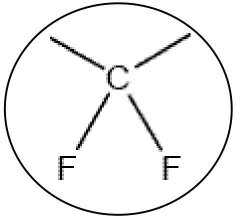
REMOVAL EFFECTIVENESS OF PHARMACEUTICALS

- “Removal” effectiveness = Destroying effectiveness
- Transformation products ?

	Entfernung in %				
	WW A	WW B	WW C	Labor	Labor
Bedingungen	-	O_3: 2 g/m³ 18 min	O_3: 0,5 g/m³ 15 min	O_3: 0,5 g/m³ 30 min	O_3: 1 g/m³ 30 min
Diclofenac	> 90	> 90		95	100
Ibuprofen	60				
Clofibrinsäure	40	> 50		15	35
Bezafibrat	50	> 80		10	35
Gemfibrizol	> 50	0			
Carbamazepin	> 90	> 90	> 90	95	100
Dehydrato-Erythromycin A		> 70	> 50		
Sulfamethoxazol			> 50		

OXIDATION EFFECTIVENESS OF PFAS

- No destruction of C-F bond under drinking water conditions
  ⇨ No PFAS destruction
- Transformation form precursors to PFAS end products



C-F-bond: very stable

Conc. in µg/L	River Rhine	Raw water	After Ozon	After Sand filtration
Trifluoracetat (TFA)	0,73	0,95	0,87	0,88
Perfluorpropionoat (PFPrA)	0,0066	0,0070	0,0068	0,0064
Perfluorbutanoat (PFBA)	0,0020	0,0028	0,0031	0,0035
Perfluorpentanoat (PFPeA)	0,0033	0,0023	0,0024	0,0023
Perfluorhexanoat (PFHxA)	0,0034	0,0018	0,0019	0,0019
Perfluorheptanoat (PFHpA)	0,0017	0,0013	0,0013	0,0013
Perfluoroctanoat (PFOA)	0,0025	0,0018	0,0020	0,0019
Perfluorbutansulfonat (PFBS)	0,0021	0,0024	0,0024	0,0025
Perfluorhexansulfonat (PFHxS)	0,0019	0,0016	0,0017	0,0016
Perfluoroctansulfonat (PFOS)	0,011	0,0069	0,0070	0,0067

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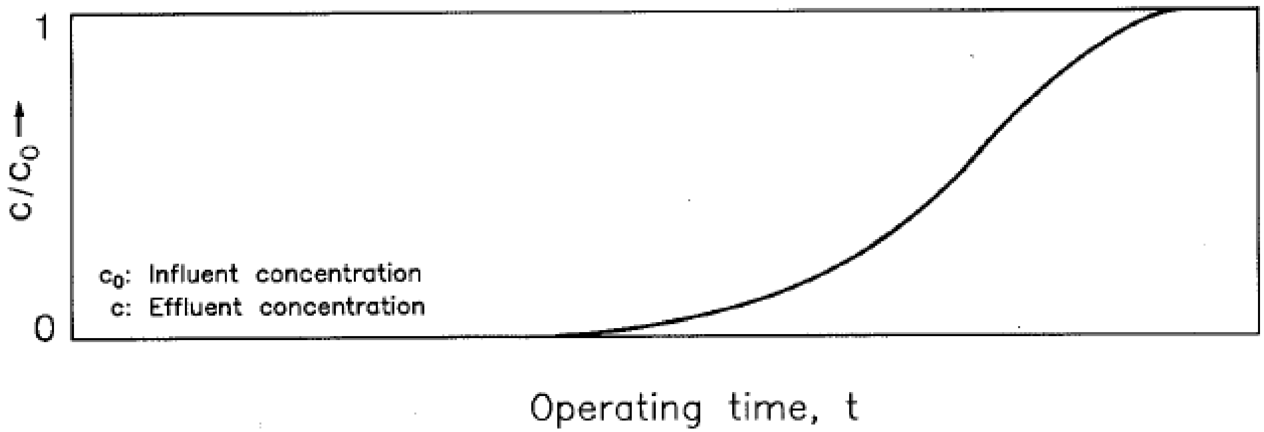
ADSORPTION: ACTIVATED CARBON FILTRATION

- Nearly every substance can be removed with activated carbon
  it is a question of runtime !!!

Concentration filter outlet



- Start of breakthrough depends on various factors,
  ⇨ mainly on **adsorption behaviour of the selected substance**

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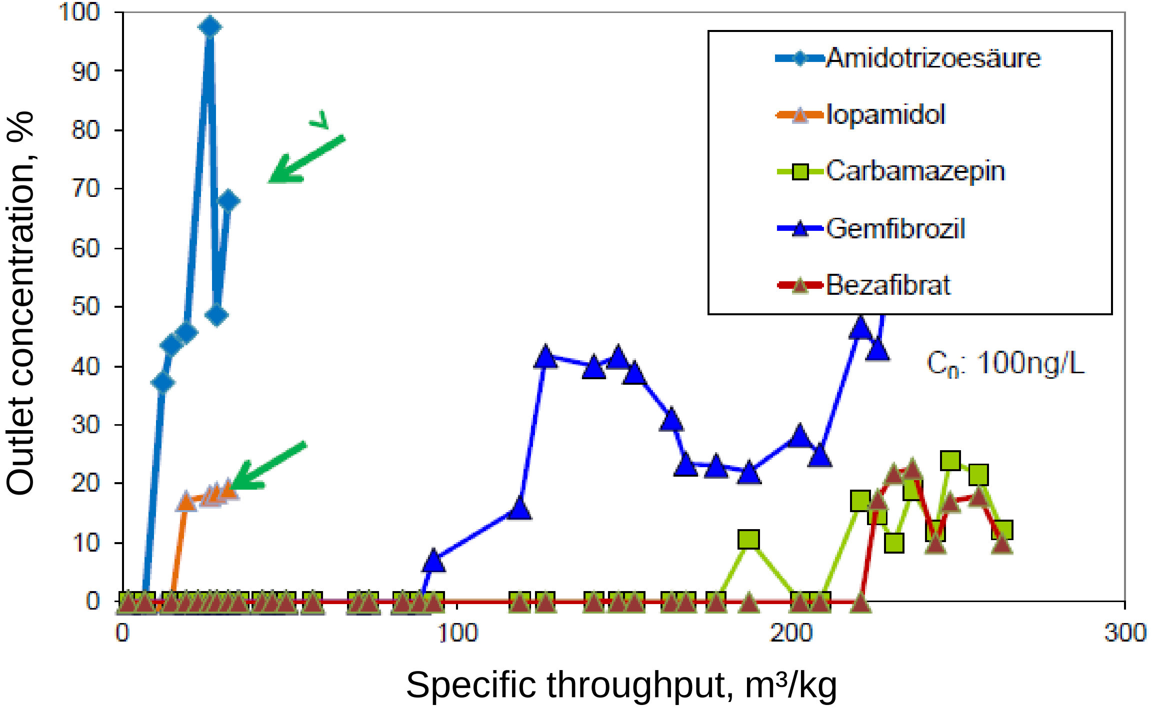
BREAKTHROUGH OF SOME MICRO POLLUTANTS



Unit: m³ Water / kg Adsorbent

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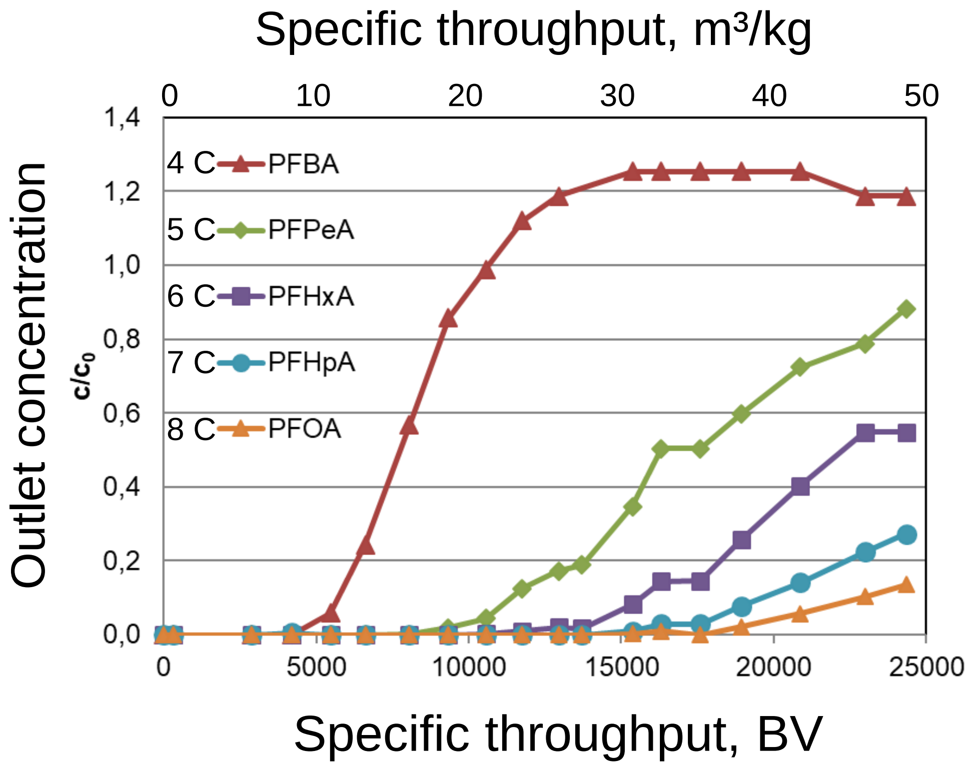
PFAS: DIFFERENT LEVELS OF ADSORBABILITY



BV…Bed Volume = m³ Water / m³ Adsorbent

- Short chain carboxylic PFAS are much more difficult to remove

⇨ If short chain PFAS have to be removed, frequent AC changes are necessary

⇨ Type of PFAS contamination is important

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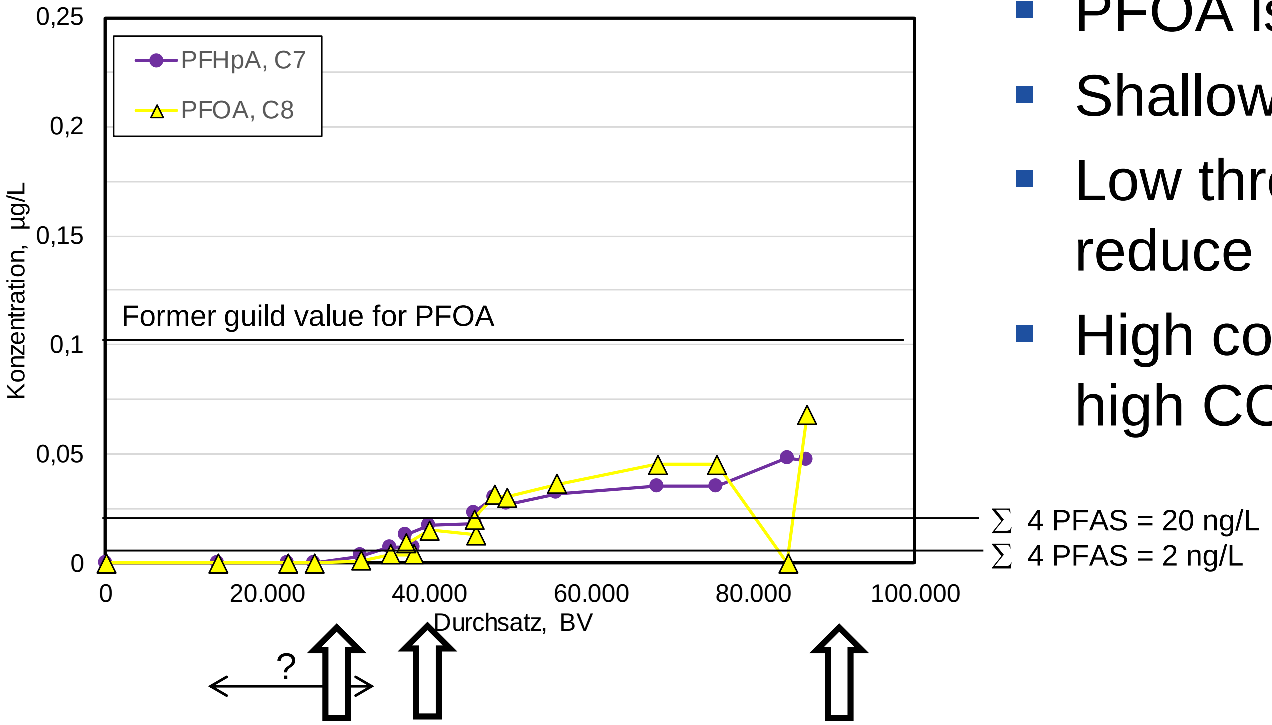
DIFFICULTY OF LOW THRESHOLD VALUES

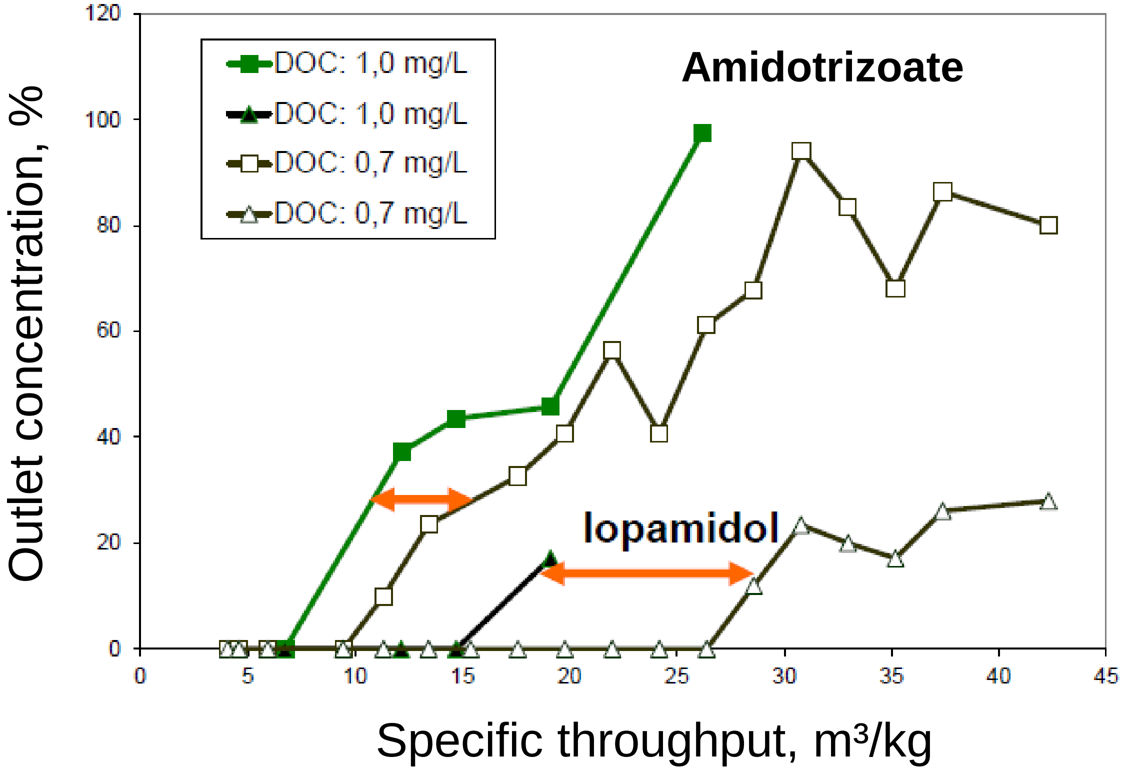
∑ 4 PFAS: 2 – 20 ng/L



- PFOA is well adsorbable
- Shallow breakthrough
- Low threshold values reduce operation time
- High costs, high CO_2 food print

Change of AC depends on threshold value

INFLUENCE OF THE WATER MATRIX



Organic Carbon (DOC) reduces the operation time (adsorption competitor)

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CHALLENGES IN ADSORPTIVE PFAS REMOVAL

- Some PFAS are very badly adsorbable
  (short-chain carboxylic acids like PFBA, PFPeA)
- Water matrix (DOC) impairs the adsorption
- Very low threshold values are difficult to reach

⇨ Alternative technologies are required

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NEW ADSORPTION MATERIALS

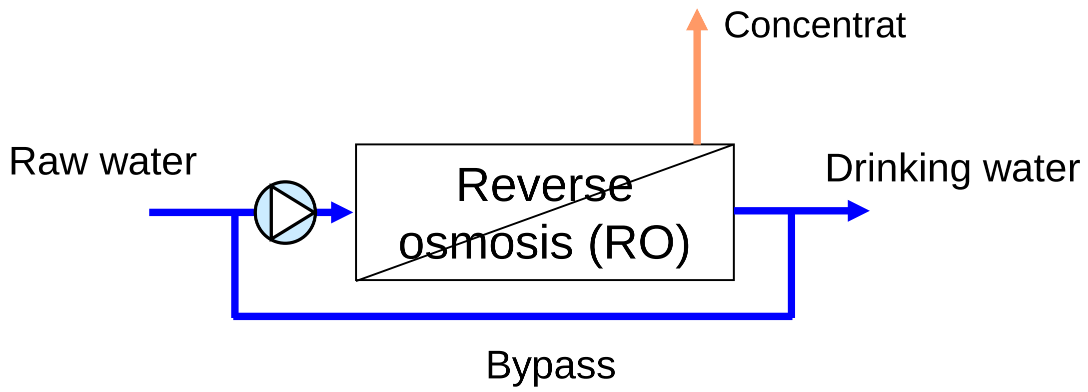
Adsorption materials for PFAS elimination :

- Activated carbon
- Ion exchangers
- Modified clay

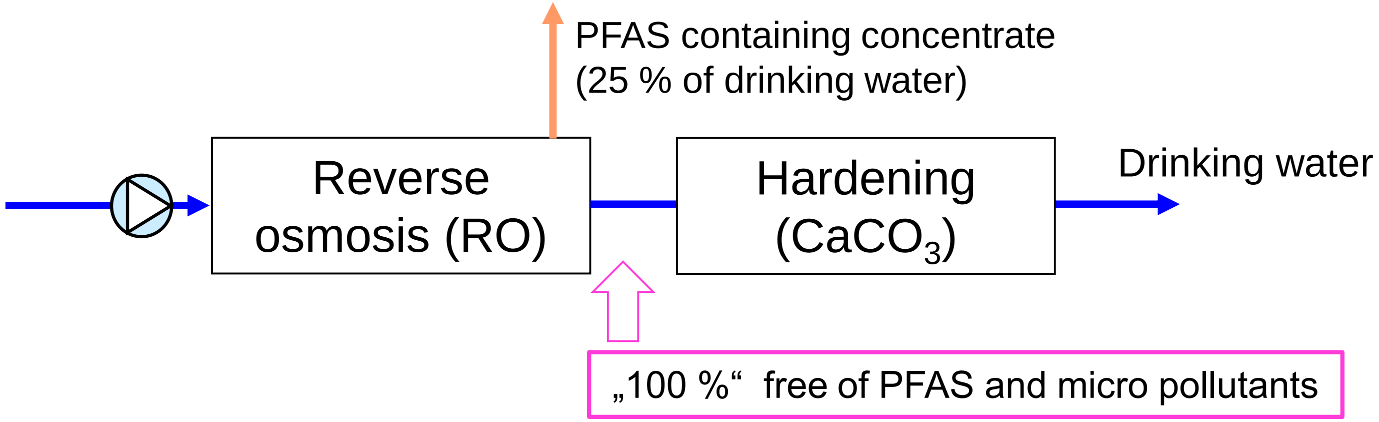
- Higher capacities for (most) PFAS
- Fast kinetics ⇨ smaller filter vessels ⇨ lower investment costs
- Material costs
  - Ion exchanger: more expensive than AC
  - Modified clax: comparable to AC
- Not yet allowed to be used in drinking water treatment (Germany: § 20 List)
- Available products in ≈ 2 years (?)

MICRO POLLUTANTS: REMOVAL WITH MEMBRANES

- Use of dense membranes (reverse osmosis, nano filtration) removes almost 100 % of PFAS
- But: normal use in drinking water treatment in by pass mode (reduction of hardness)



PFAS REMOVAL WITH LOW TREATMENT GOAL



- Much more water needed:
  - Climate change: water available?
  - Water rights: water available?
- High costs, energy intensive
  - Removal of all salts, dosing of salts
- PFAS are not destroyed, only concentrated ⇨ further treatment

CONCLUSIONS ON PFAS REMOVAL

- PFAS removal possible with
  - Activated carbon
  - Dense membranes
    - partly PFAS removal in by-pass mode
    - PFAS containing regenerate ⇨ new treatment technologies needed
- Activated carbon has technological limits
  - Poorly adsorbable single PFAS (PFBA , PFPeA)
  - High DOC
  - Very low threshold values
- New adsorption materials and new technology approaches should be developed to offer further treatment possibilities

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