KONTRISOL

Approaches and technologies to treat membrane concentrates

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Outline

- KonTriSol at a glance
- Technical options for concentrate treatment
- Activated carbon treatment
  - Hybrid process powdered activated carbon / ultrafiltration
  - Granular activated carbon
- Oxidative water treatment
  - Sulfate radicals
  - Reaction kinetics
  - Degradation of antiscalants

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KonTriSol

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- **Concentrates from drinking water treatment** – Solutions for technical, legal and economic barriers for NF/RO-processes

www.kontrisol.de

- Funding

- 10 project partners
(09/19 – 08/22)

- Main research fields

Concentrate treatment	Antiscalants	Toxicological assessment	Approval process
- Technical options - Potential for removal of environmental contaminants	- Evaluation and effectiveness - Behavior during treatment - Alternatives / Minimization	- Eco toxicology - Human toxicology	- Identify regulatory barriers - Develop evaluation criteria

Technical Options

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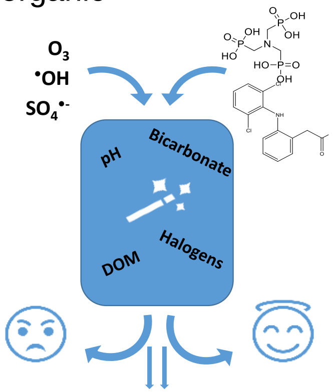
Activated carbon treatment

Removal of organic micropollutants

Source: TZW

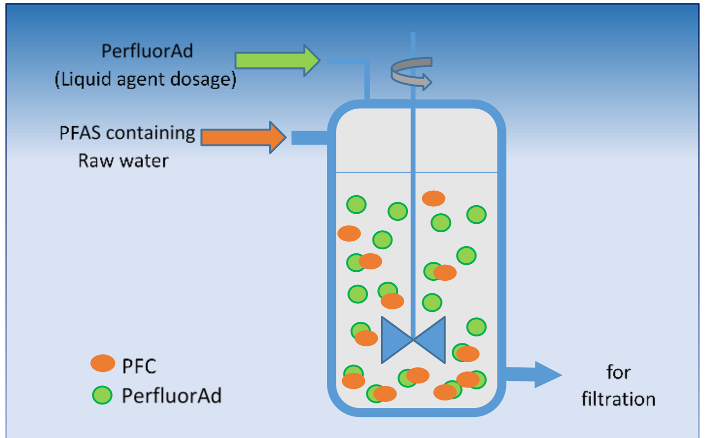
Oxidative treatment

Degradation of organic micropollutants



Chemical precipitation with PerfluorAd

Removal of PFAS



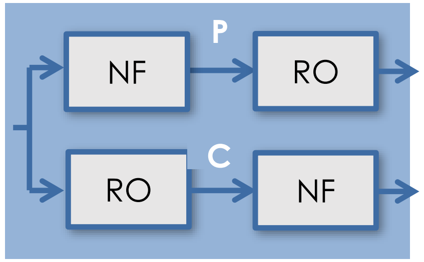
Source: Cornelsen Umwelttechnologie GmbH

Why concentrate treatment?

- Zero pollution: reduce or minimize release of unwanted substances into the environment
- Zero liquid discharge (ZLD): more efficient use of water resources

Further concentration

- Increase process recovery
- Salt-/ resource recovery



Source: TU Berlin

Recycling / Reuse of antiscalants

- High molecular polycarboxylates
- Separation via ultrafiltration
- Effectiveness in reuse?

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Activated carbon treatment

- **Powdered activated carbon (PAC)**
  - Coupled with ultrafiltration (UF)
  - PAC characteristics:
    - open-pored
    - small particle diameter
    - fast adsorption kinetics

Source: TZW

- **Granular activated carbon (GAC)**
  - GAC filtration in a filter vessel
  - Large-scale concentrate treatment

Source: TZW

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PAC/UF hybrid process

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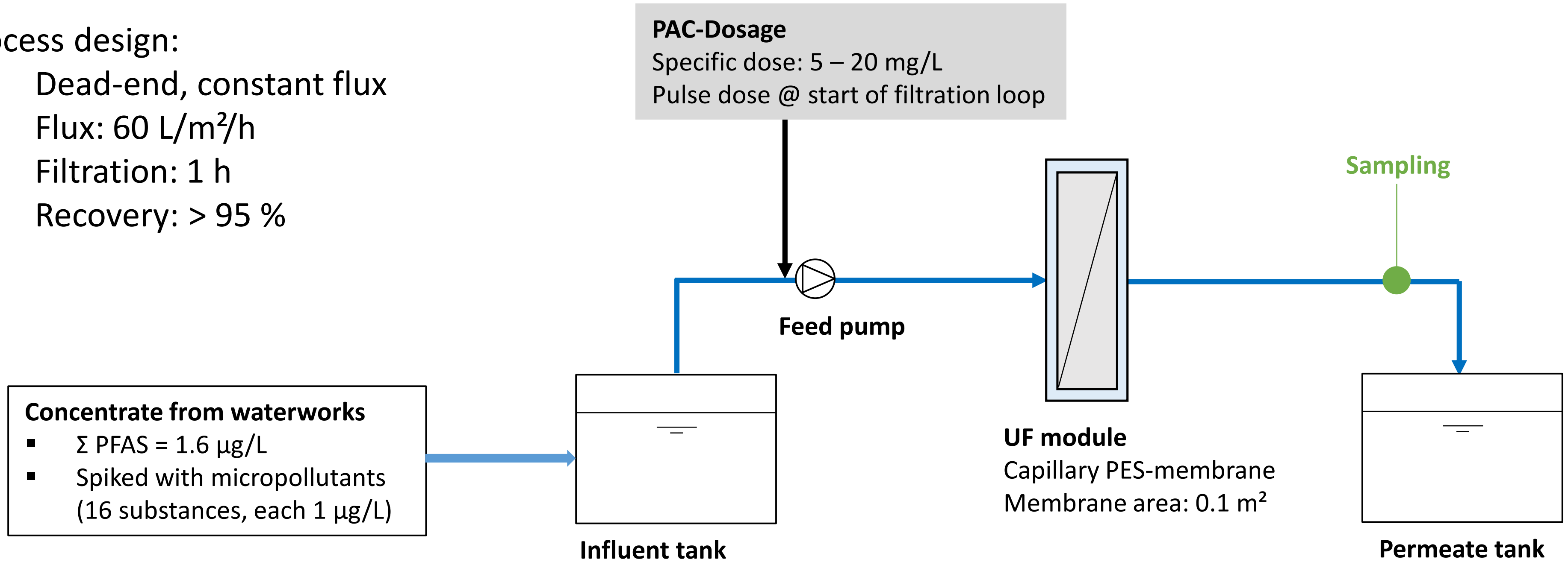
- Testing @ bench-scale plant
- Process design:
  - Dead-end, constant flux
  - Flux: 60 L/m²/h
  - Filtration: 1 h
  - Recovery: > 95 %



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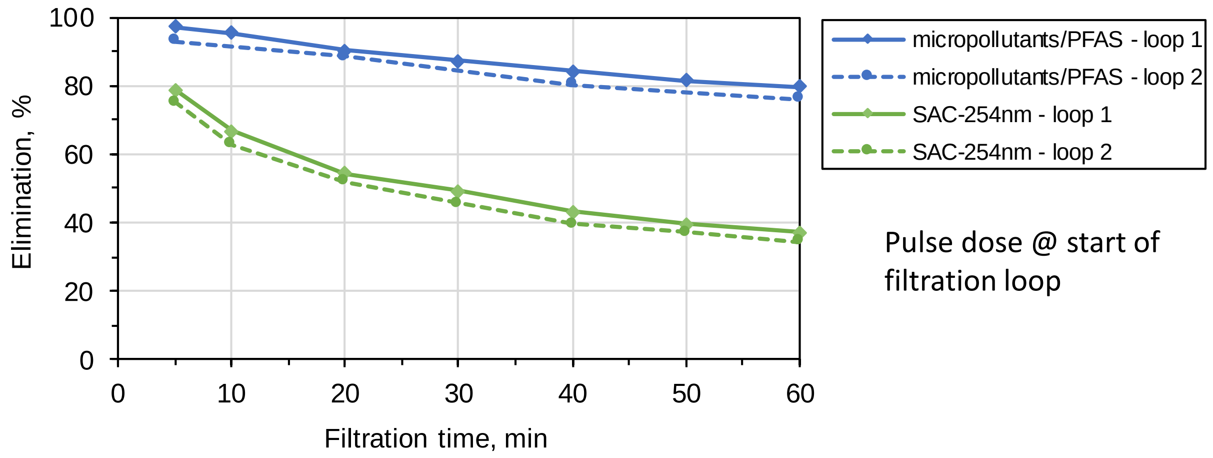
PAC/UF hybrid process

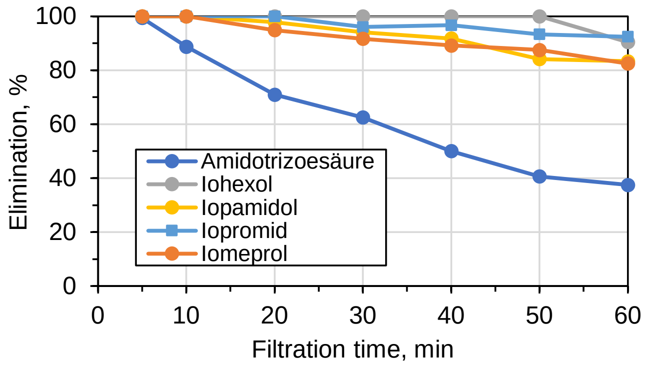
What elimination is attainable?

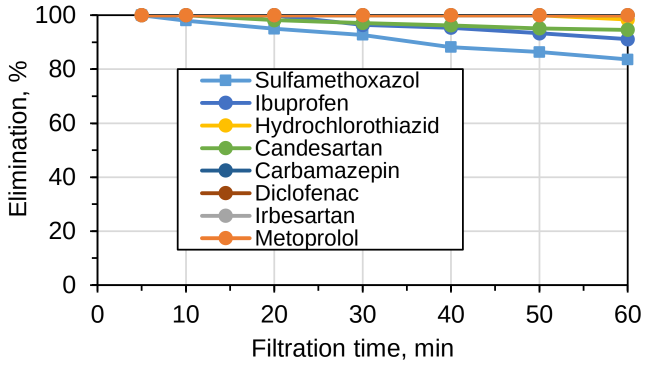
- Total elimination: 86 – 88 %
- Specific PAC-dose: 20 mg/L

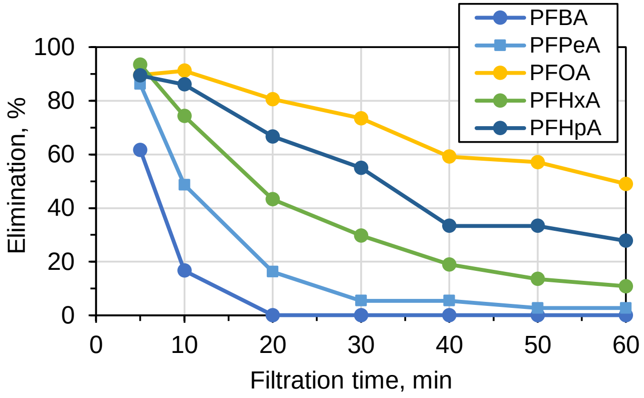


Pulse dose @ start of filtration loop

- Strong vs. weak adsorbable substances







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Activated carbon filtration

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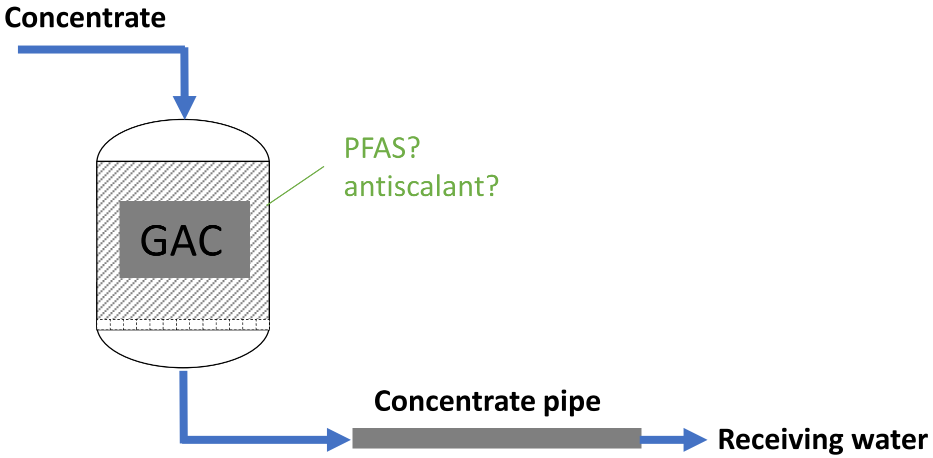
Large-scale concentrate treatment with granular activated carbon for removal of PFAS

- Background:
  - Water supplier operates RO plant for softening
  - Groundwater contamination with PFAS
  - Discharge into receiving water was only possible if target values for PFAS are met

- Monitoring of the plant:
  - How is the retention behavior for PFAS / antiscalant?
  - How often must the carbon be replaced?
  - How high is the operation and maintenance expanse?
  - Are there precipitations in the filter vessel?
  - How is the condition of the concentrate pipe (camera check)?



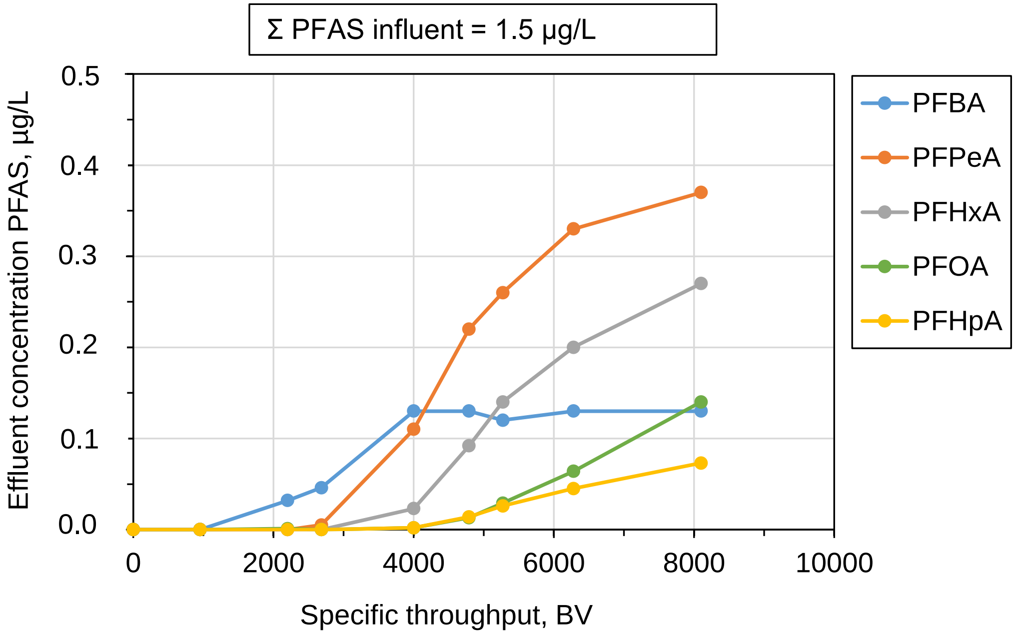
Activated carbon filtration

- PFAS removal:
  - Determination of breakthrough curves for PFAS
  - PFOA > 0.1 µg/L in effluent determines carbon replacement
  - Operation time: 7,000 – 8,000 BV
  - 6 month / 2 replacements per year

- Operational costs for GAC:
  - GAC supply/take-back: 1.6 €/kg
  - 0.10 €/m³ concentrate
  - 0.02 €/m³ drinking water

+ costs for analyses
+ costs for supervision
+ costs for maintenance

Environmental footprint?



Oxidative water treatment

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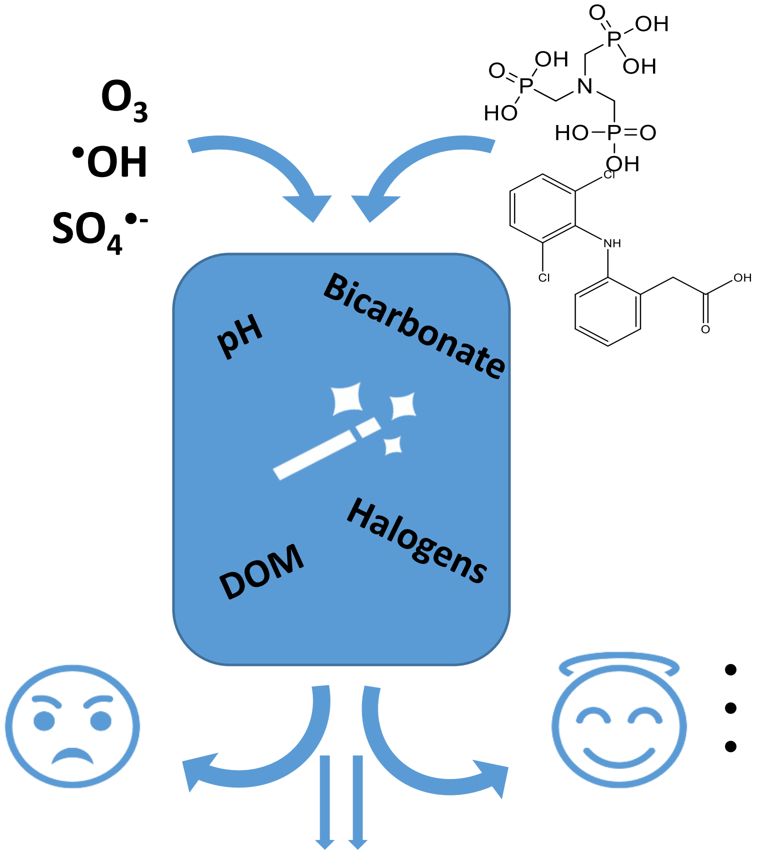
- Typical oxidants used in drinking water treatment: ozone, chlorine dioxide, chlorine
- Further oxidants used for water treatment: hydroxyl radicals and sulfate radicals

- **hazardous TPs (e.g., NDMA)**
- **oxidation by-products (e.g., bromate)**
- **increase toxicological potential**



- **Harmless TPs**
- **Complete mineralization**
- **Less toxicological potential**

Aim : disinfection and pollutant degradation

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Sulfate radical-based oxidation

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- Sulfate radical ($SO_4^{\bullet-}$) based processes have a high potential to remove organic pollutants
- Activation of persulfate ($S_2O_8^{2-}$) by heat, UV, base or metals generates $SO_4^{\bullet-}$

$$S_2O_8^{2-} \xrightarrow{heat/hv} 2\,SO_4^{\cdot-}$$

- Depending on pH hydroxyl radicals ($^{\bullet}OH$) are formed by chain reactions
- Advantages:
  - $SO_4^{\bullet-}$ and $^{\bullet}OH$ are strong oxidants
  - $SO_4^{\bullet-}$ has a high reactivity regards organic substances and a lower reactivity to natural organic matter
  - $SO_4^{\bullet-}$ can oxidize perfluorocarboxylic acids (PFAS)
- Application: mainly in the field of groundwater remediation (*In-Situ*-Chemical-Oxidation processes)

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Second-order reaction rate at pH 7

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- Ozone: great difference between *N*-containing and *N*-free organophosphonates
- Hydroxyl and sulfate radicals: Reactivity increase with number of phosphonate groups

Table 1: Second-order reaction rate constant of selected organophosphonates with ozone, •OH and $SO_4^{\bullet -}$ at *pH* 7

Substance	k_{O3} [$M^{-1} s^{-1}$]	$k_{\bullet OH}$ [$M^{-1} s^{-1}$]	$k_{SO4\bullet -}$ [$M^{-1} s^{-1}$]	Reference
HEDP	3,63 ± 0,12	$6,79 \pm 0,4 \times 10^{+8}$	$7,74 \pm 0,6 \times 10^{+7}$	This work
PBTC	$1,20 \times 10^{-1}$	$7,83 \times 10^{+8}$	-	Xu 2019
PBTC	$9,16 \pm 0,2 \times 10^{-1}$	$2,90 \pm 0,2 \times 10^{+8}$	$5,40 \pm 0,3 \times 10^{+7}$	This work
ATMP/ NTMP	-	$1,10 \times 10^{+8}$	$2,90 \times 10^{+7}$	Wang 2019
ATMP/ NTMP	$1,44 \pm 0,1 \times 10^{+5}$	$1,31 \pm 0,2 \times 10^{+9}$	$1,29 \pm 0,16 \times 10^{+8}$	This work
DTPMP	$1,16 \pm 0,05 \times 10^{+6}$	$2,89 \pm 0,4 \times 10^{+9}$	$1,15 \pm 0,22 \times 10^{+9}$	This work

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Degradation of antiscalants by ozone

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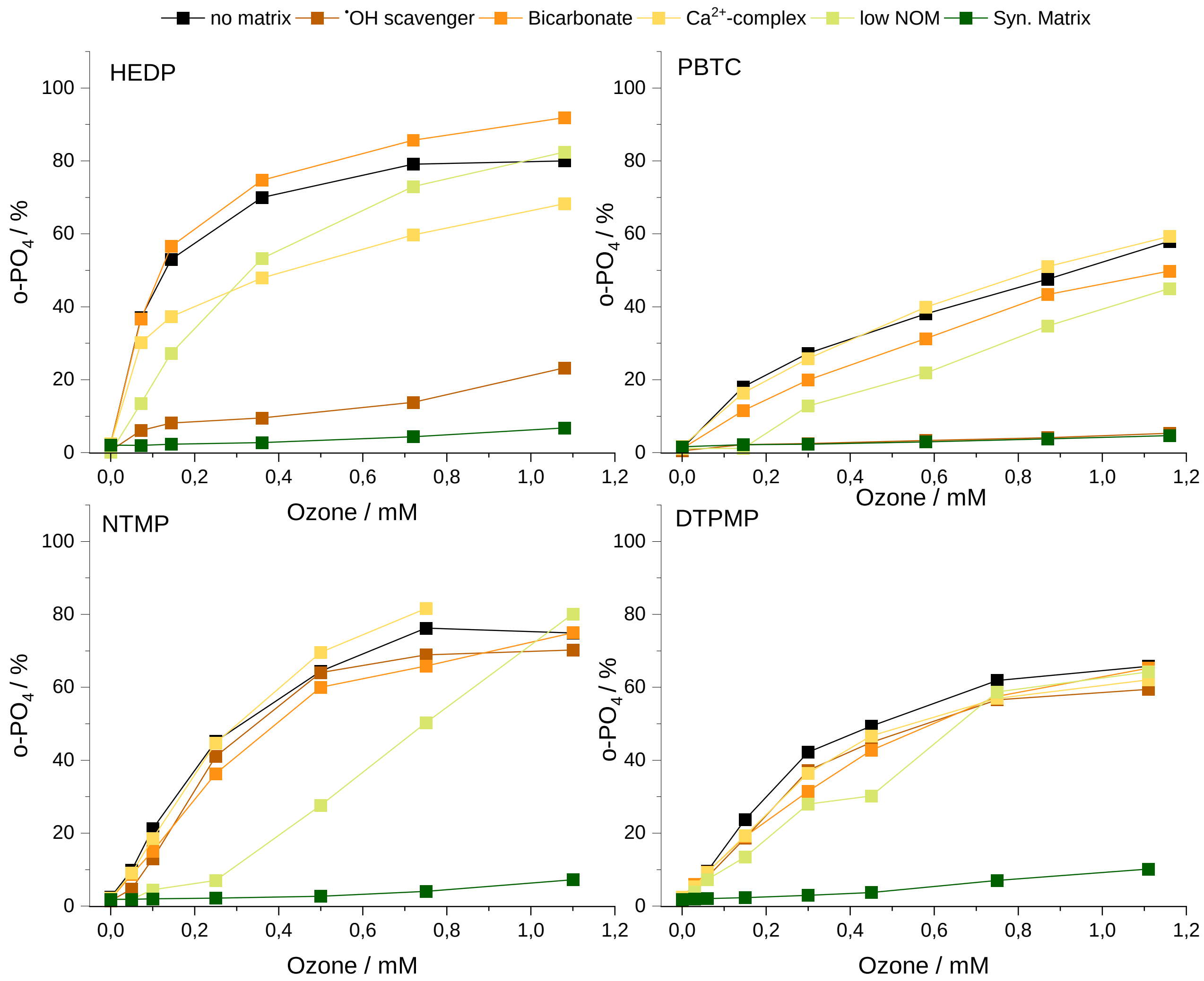

Figure 3: Degradation of antiscalants by ozone (0 – 1.1 mM) at pH 7.

- Antiscalants dosage equals 4.5 mg total Phosphorus/L (145 µM)
- Ozone dosage: 0 – 1.2 mM at pH 7 in borate buffer + matrix substituents
- Ozonation of HEDP and PBTC is mainly limited by •OH scavengers
- High ozone dosages are insufficient for a complete mineralization to o-PO_4
- Indication of formation of organic-phosphorus species

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Degradation of antiscalants by $SO_4^{\bullet-}$

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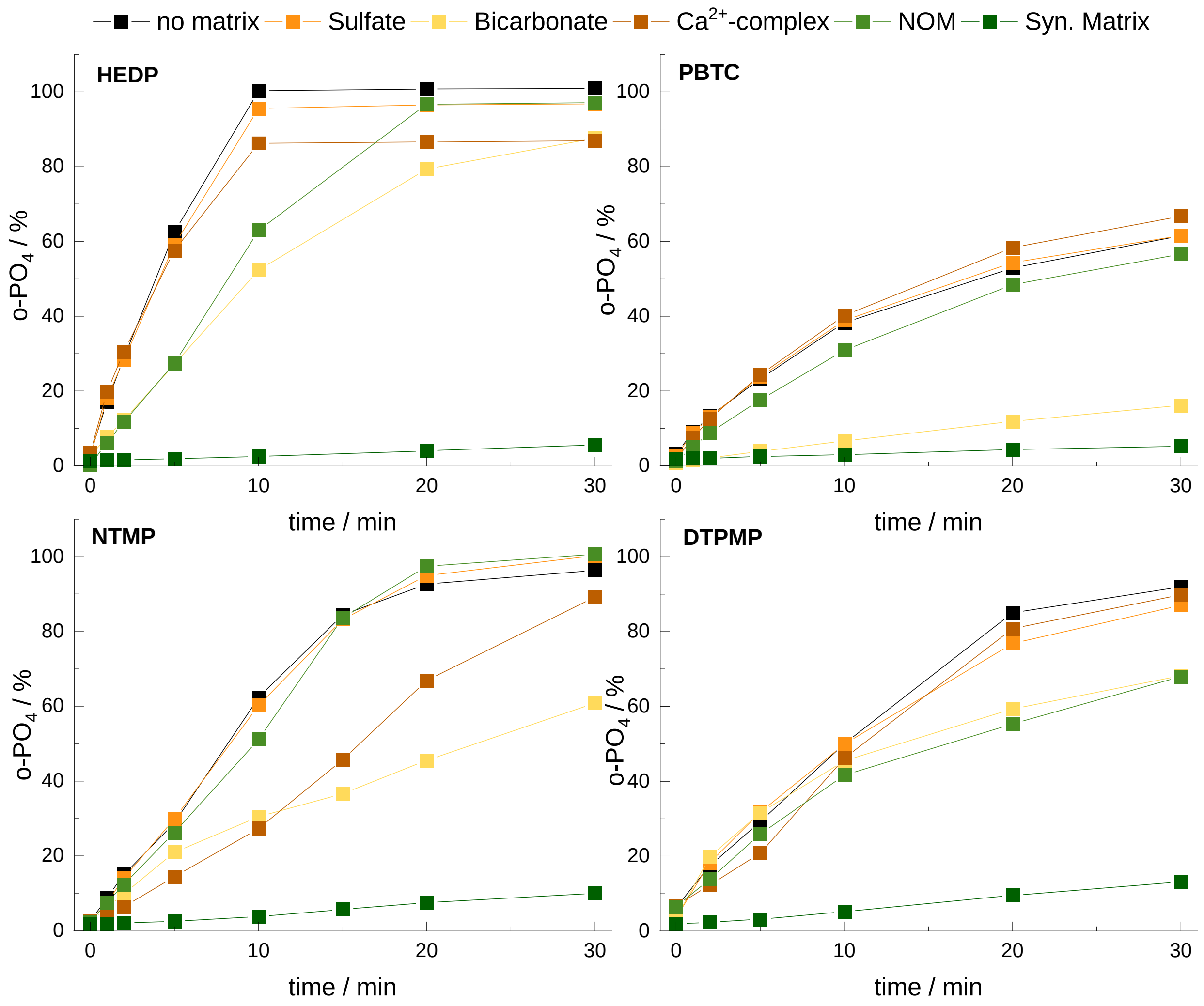

- Antiscalants dosage equals 4.5 mg total Phosphorus/L (145 µM)
- Generation of $SO_4^{\bullet-}$ by Persulfate/UV ([PS]=1mM)
- Radiation at 254 nm at 25°C
- HEDP: complete mineralization after 10 min
- PBTC : no complete degradation (max. 60%)
- NTMP: complete mineralization after 20 min
- DTPMP: only 90% mineralization within 30 min
- Bicarbonate/carbonate have the highest influence on the degradation
- Synthetic matrix combination of NOM and Carbonate reduce the degradation to max. 10%

Figure 3: Degradation of antiscalants by $SO_4^{\bullet-}$ generated via Persulfate/UV ([PS]=1mM) at 25°C at pH 7.

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Many thanks for your attention!

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