Non-Target-Analyse zur Bewertung von Kontaminanten im Trinkwasser-Verteilungssystem und bei Aufbereitungsverfahren

Selina Tisler, Victoria Eriksson, Tomas Diera,
Jan H. Christensen and many more..

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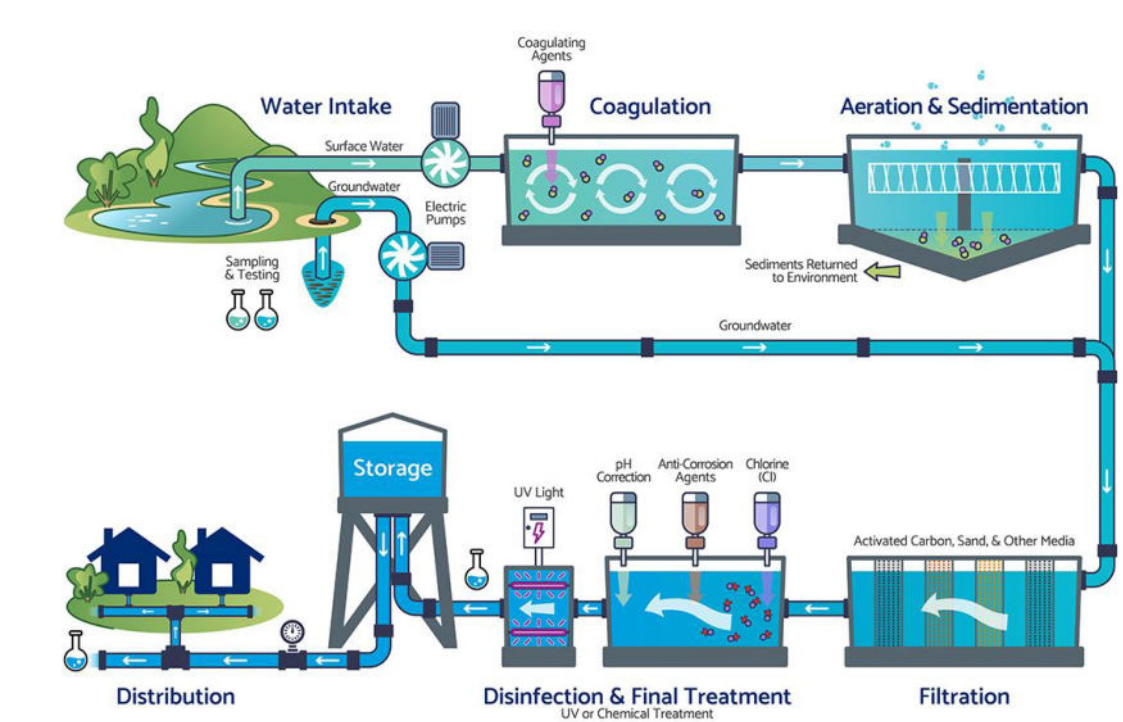


https://www.myutility.us/indiana/water-smart/utility-systems

Case 1

NTS for evaluation of activated carbon and resin filtration

Denmark: Groundwater based water supply

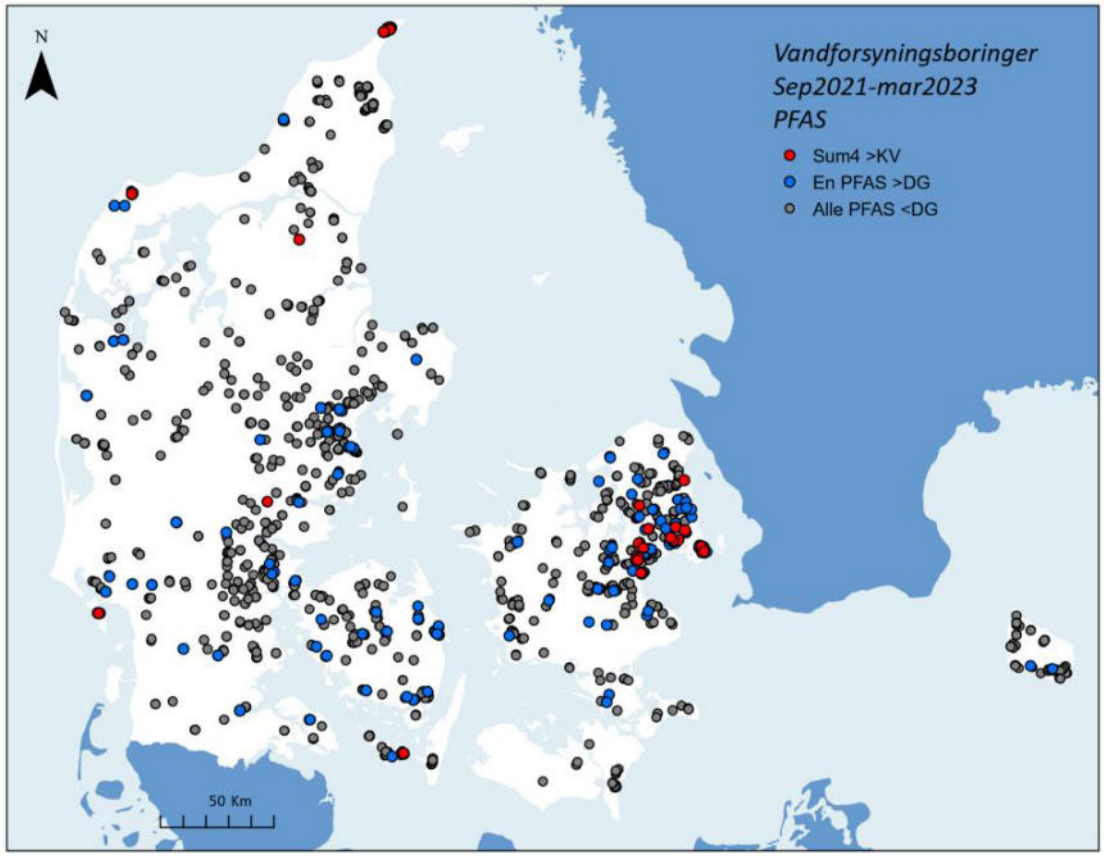
PFAS limit values in Denmark: Stricter as EU limits

Stofgruppe/sum-værdi	Stofnavn	Krav-værdi (KV, µg/l)
PFAS (4 styk)	PFHxS (perfluorhexansulfonsyre) PFOS (perfluoroctansulfonsyre) PFOA (perfluoroctansyre) PFNA (perfluornonansyre)	0,002
PFAS (12 styk)	Ovenstående fire +: PFBA (perfluorbutansyre) PFPeA (perfluorpentansyre) PFHxA (perfluorhexansyre) PFHpA (perfluorheptansyre) PFDA (perfluordecansyre) PFBS (perfluorbutansulfonsyre) PFOSA (perfluoroctansulfonamid 6:2 FTS (6:2 fluorotelomersulfonsyre)	0,1
PFAS (22 styk)	Ovenstående 12 +: PFUnDA (Perfluorundecansyre) PFDoDA (Perfluordodecansyre) PFTrDA (Perfluortridecansyre) PFPeS (Perfluorpentansulfonsyre) PFHpS (Perfluorheptansulfonsyre) PFNS (Perfluornonansulfonsyre) PFDS (Perfluordecansulfonsyre) PFUnDS (Perfluorundecansulfonsyre) PFDoDS (Perfluordodecansulfonsyre) PFTrDS (Perfluortridecansulfonsyre)	0,1
-	TFA (trifluoreddikesyre)	9

Thorling et al., 2024

Sum of 4 EFSA PFAS <2 ng/L

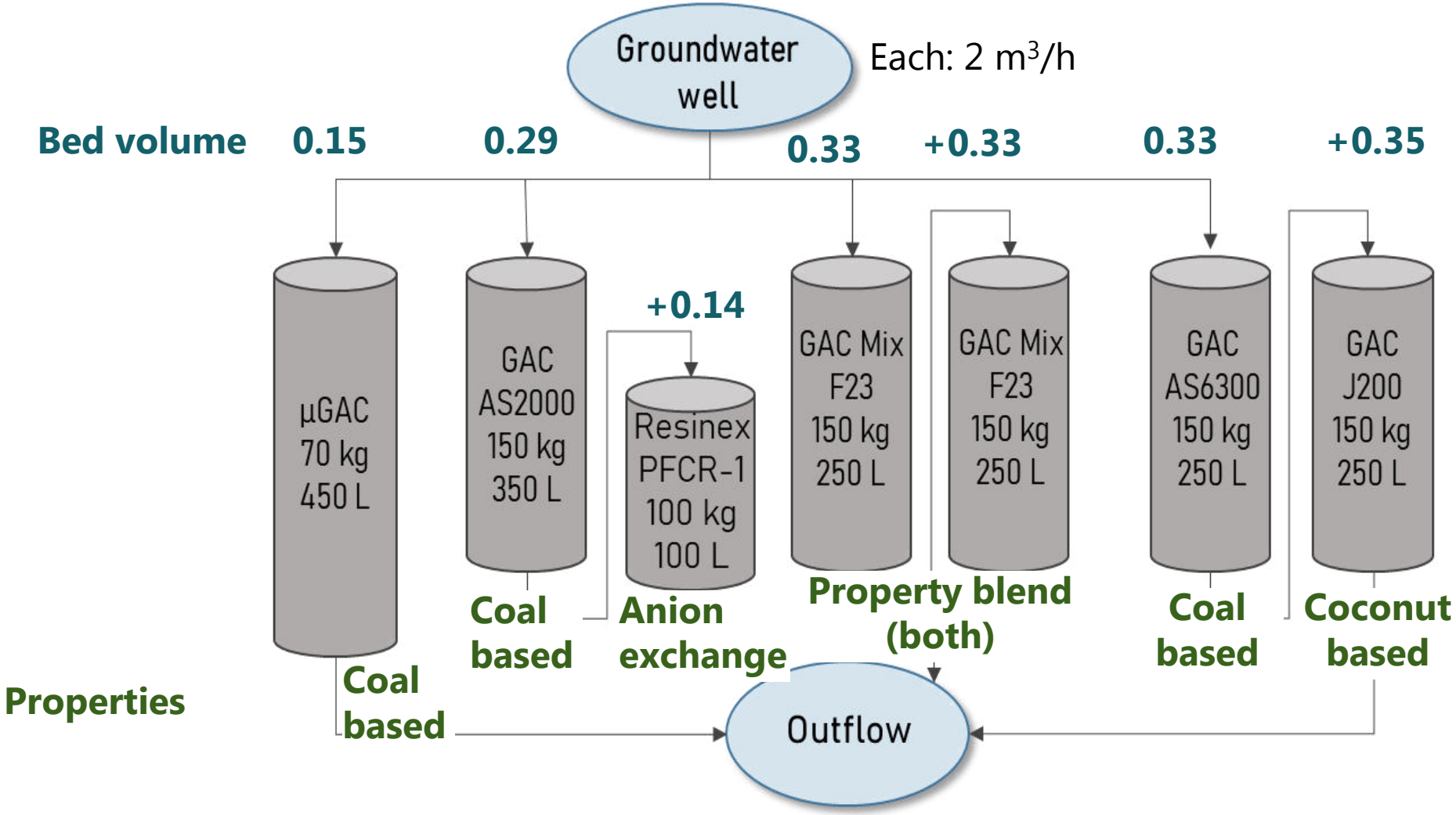
PFAS situation in Denmark:



Johnsen et al. (2023): GEUS, Rapport 2023/42

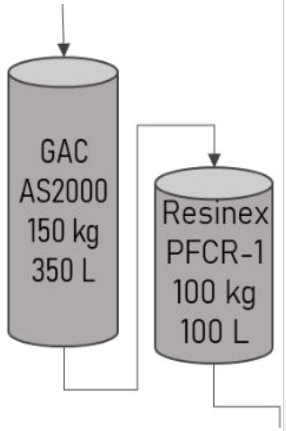
VUDP-Project: PFAS Removal in Copenhagen area

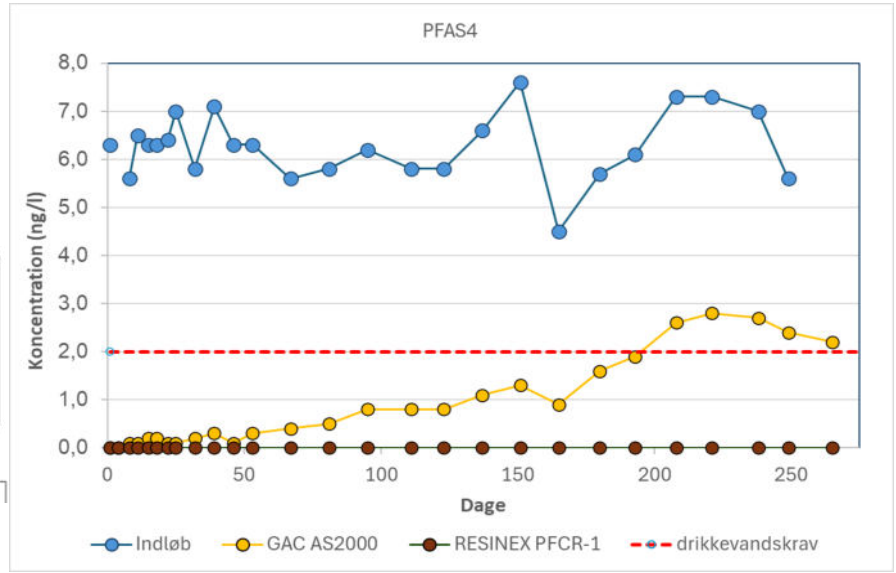
Aim of the project: finding treatment technologies to meet the Danish standard of <2 ng/L sum of the four EFSA PFAS in groundwater



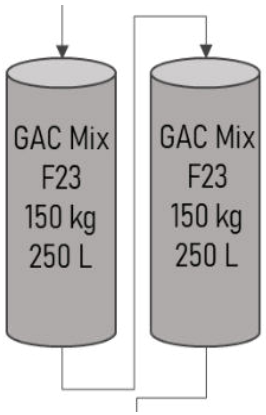
Removal of target 4 PFAS: after ~30k bed volumes

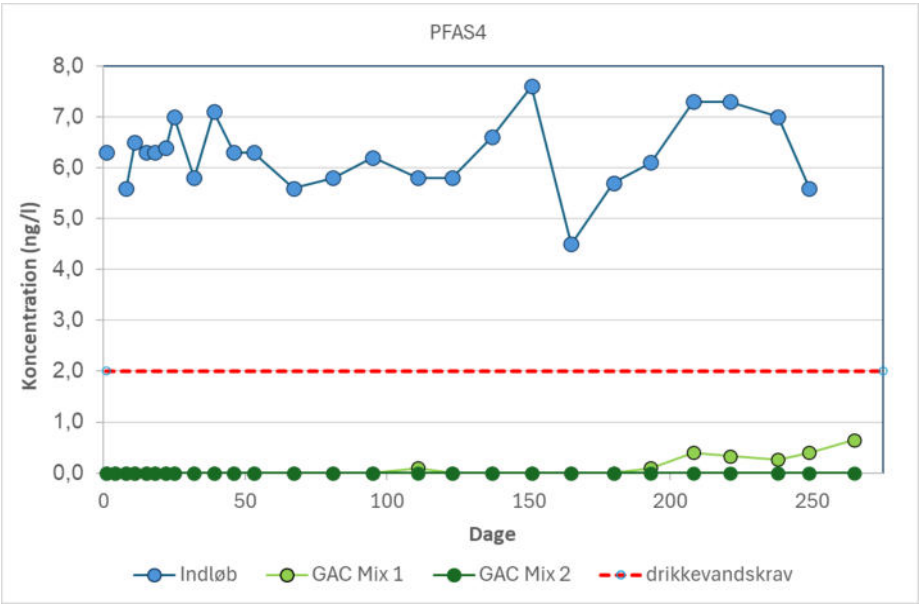
Filter 2





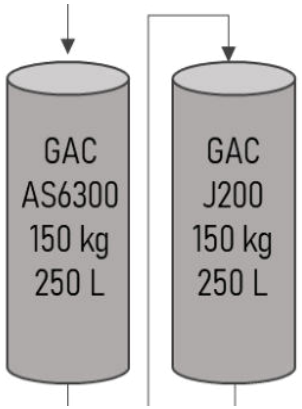
Filter 3

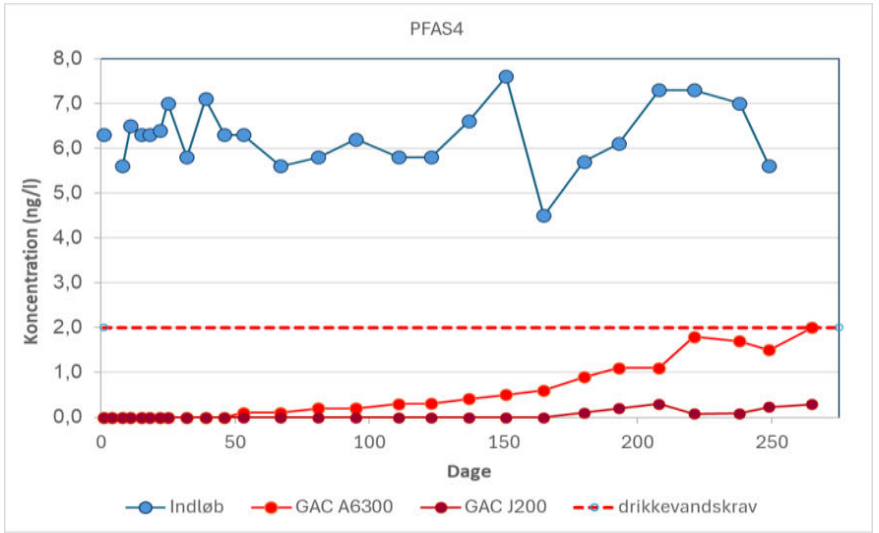




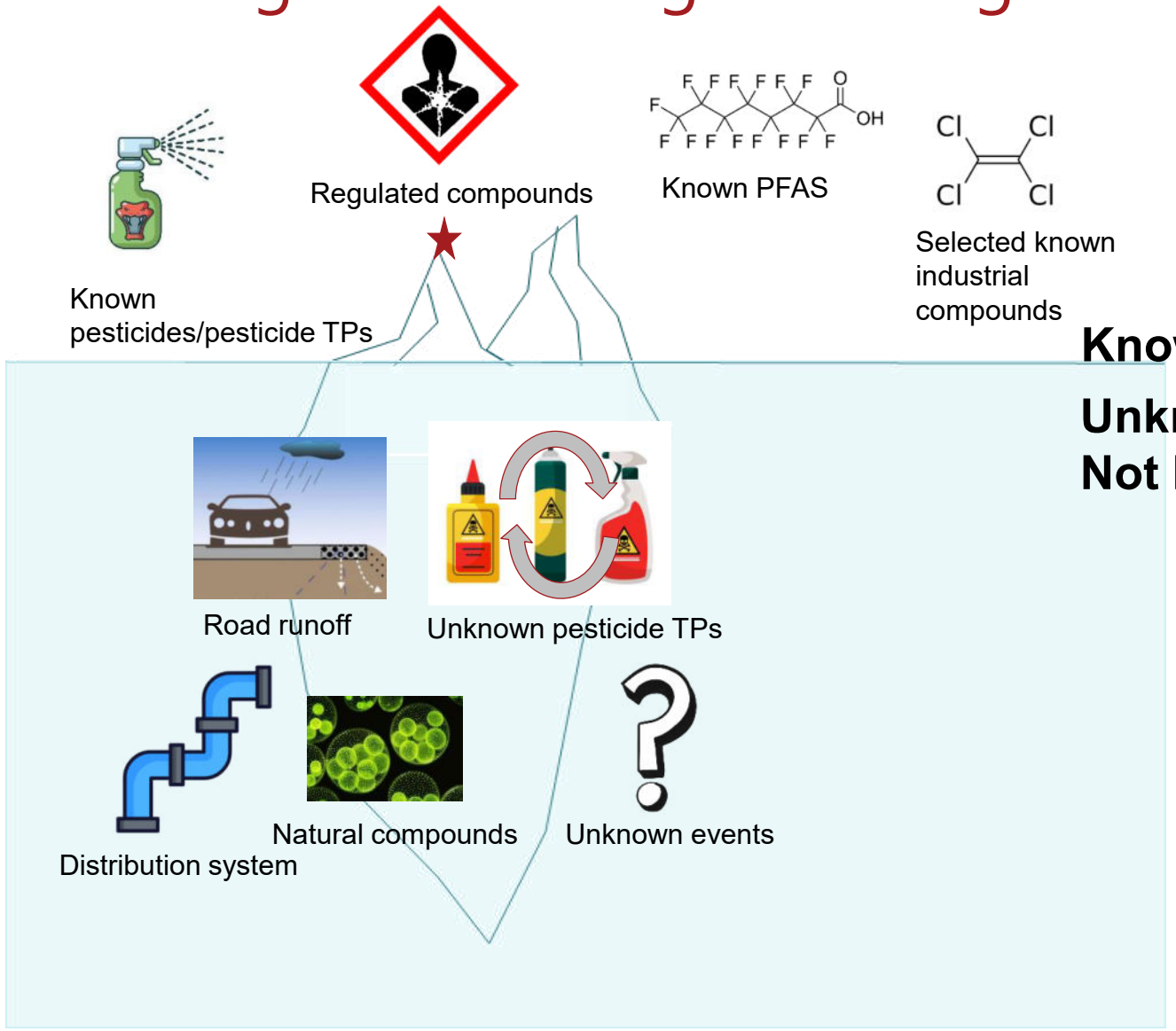
Shown: concentration of PFHxS, PFOS, PFOA, PFNA

Filter 4





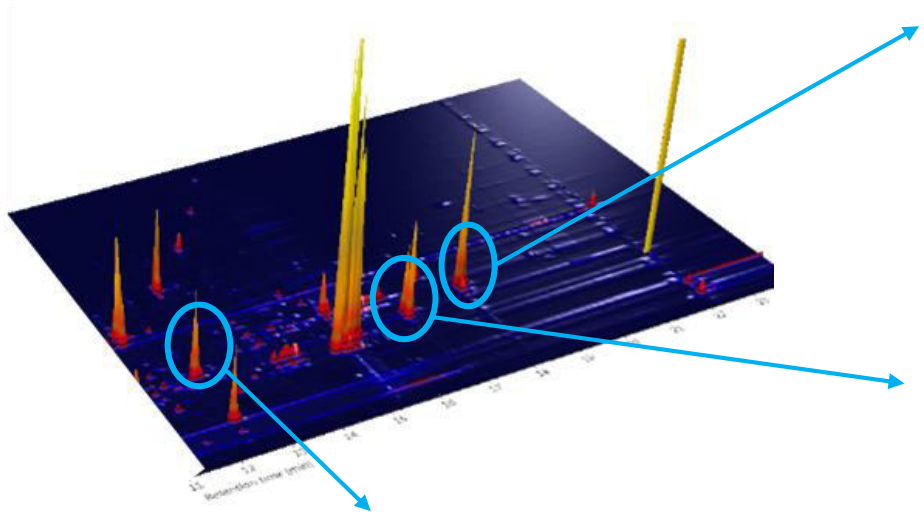
Non-Target Screening - Finding the unknowns…



Broader screening approaches are needed

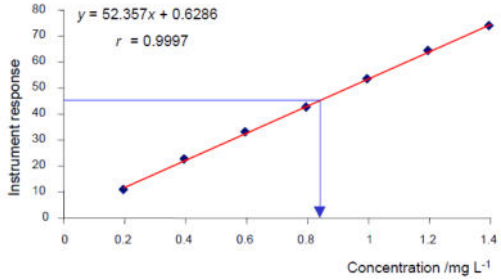
Method: Chemical fingerprinting

Liquid chromatography coupled to high resolution mass spectrometry



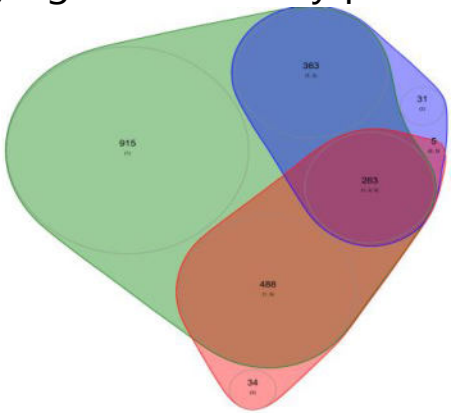
Target screening :

quantification of known chemicals



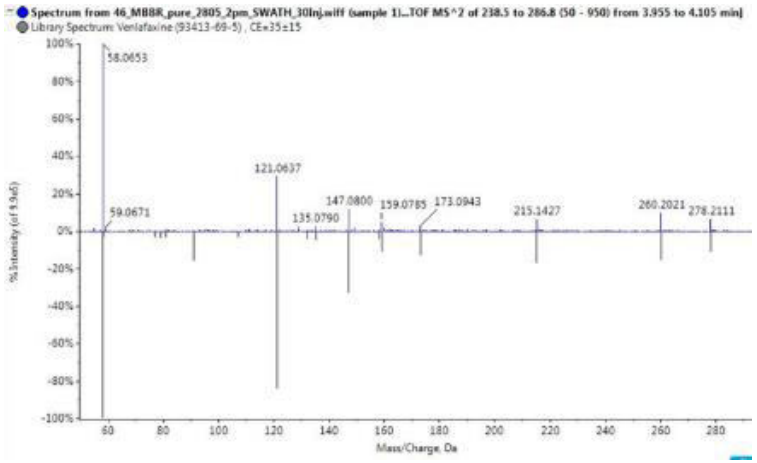
Non-target screening:

Identifying unknowns by prioritization



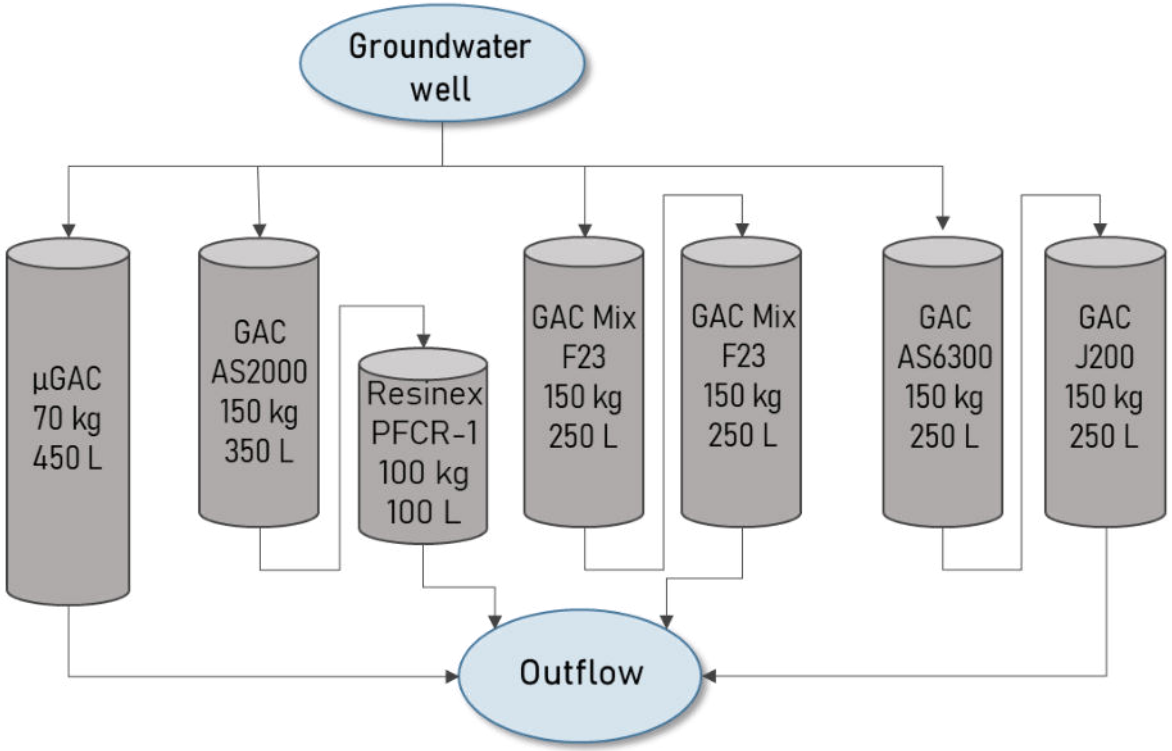
Suspect screening:

Identify compounds by comparison with databases



Non-target screening for treatment evaluation

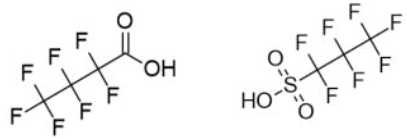
- Identifying unknown pollutants in groundwater
- Assessing the effectiveness of filter for other than target PFAS
- Assessing migration from pilot plant



Identification of compounds in the groundwater

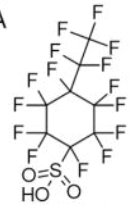
primarily used in aircraft hydraulic fluids and replacement of PFOS in various formulations.

PFAS



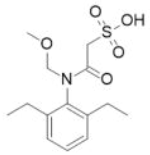
carboxylic acids
C4 to C8
PFBA
PFPeA
PFHxA
PFOA

sulfonic acids
C3 to C6
PFPrS
PFBS
PFPeS
PFHxS

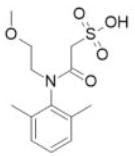


PFECHS

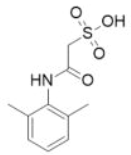
agricultural



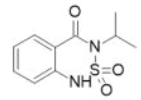
alachlor ESA



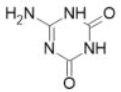
dimethachlor ESA



dimethachlor
CGA369873

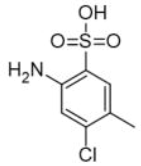


bentazone

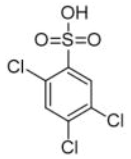


terbutylazine
metabolite MT23

diverse sources



2-amino-4-chloro-5-
methylbenzenesulfonic acid
(ACMBS)



2,4,5-trichloro-
benzenesulfonic acid
(2,4,5-TCBS)

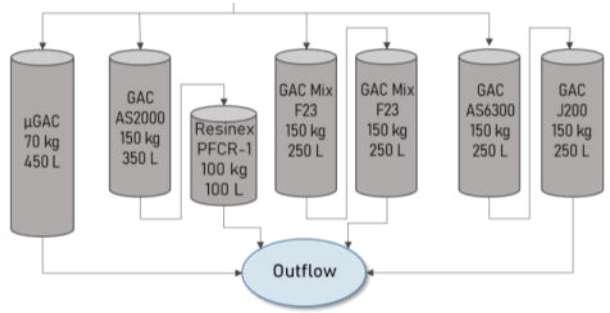
Pigment ACMBS: brilliant toning red amine, widely used in the synthesis of paint, rubber, and color inks. It is commonly used for plastic films in agricultural fields

Highest concentrations: **5 ng/L PFBA** **35 ng/L bentazone** **360 ng/L ACMBS**
35 ng/L 2,4,5-TCBS

Treatment of PFAS and the other identified compounds

Removal (%) after >10.000 m³ water

			1	2a	2b	3a	3b	4a	4b	
		Filter	µGAC	GAC AS2000	RESINEX	GAC MixA	GAC MixB	GAC AS6300	GAC J200	
		treated BV	**69k**	**36k**	**24k**	**31k**	**16k**	**31k**	**15k**	
Identified with	Name	Confidence level	Removal (%) in t2							inlet (ng/L)
SFC	PFBA	1	-2%	-16%	5%	-5%	20%	-13%	23%	5
SFC	PFPeA	1	-2%	7%	37%	12%	81%	5%	56%	2
SFC	PFPrS	1	12%	29%	96%	46%	95%	47%	89%	1
LC	PFBS	1	41%	58%	98%	83%	98%	70%	95%	2
SFC	PFHxA	1	24%	31%	91%	54%	91%	57%	87%	3
LC	PFPeS	1	58%	79%	99%	97%	99%	83%	98%	1
LC	PFHxS - lin	1	73%	84%	99%	99%	100%	93%	99%	2
LC	PFOA	1	45%	57%	98%	94%	99%	67%	99%	3
SFC	PFECHS	1	27%	23%	99%	62%	99%	44%	85%	1
SFC	Alachlor ESA	1	38%	60%	51%	79%	90%	55%	89%	4
LC	Dimethachlor ESA	1	36%	59%	51%	85%	98%	51%	94%	6
LC	Bentazon	2a	83%	93%	98%	99%	98%	96%	99%	35
SFC	Dimethachlor CGA369873	2a	59%	82%	75%	97%	98%	86%	98%	5*
SFC	Terbutylazine MT23	1	79%	90%	89%	98%	99%	93%	99%	4*
SFC	ACMBS	1	95%	92%	98%	100%	100%	99%	100%	360
LC	2,4,5-TCBS	2a	94%	94%	98%	98%	98%	98%	98%	35*



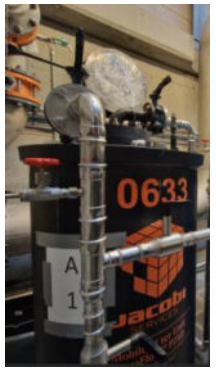
Breakthrough short chain PFAS

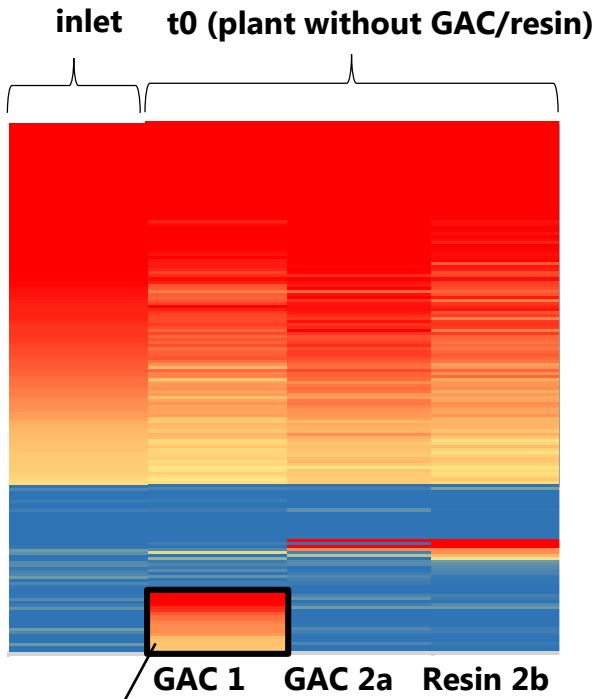
PFECHS: Less removal with coal and coconut based GAC

Many non-PFAS pollutants have low removal with Resin filter

*concentration predicted by qNTA according to Tisler et al. (2024); DOI: https://doi.org/10.1021/acs.analchem.3c03791

Non-target screening of treatment with new filters





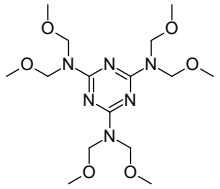
Peak intensity (260 peaks)

>6000

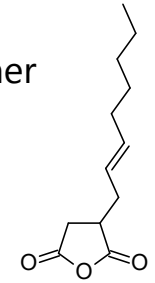
1000

<100

features migrating from container

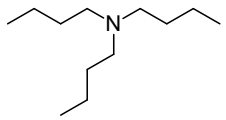


hexa(methoxymethyl)melamine

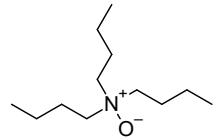


octenylsuccinic anhydride

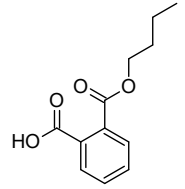
features migrating from resin



tributylamine derivatives

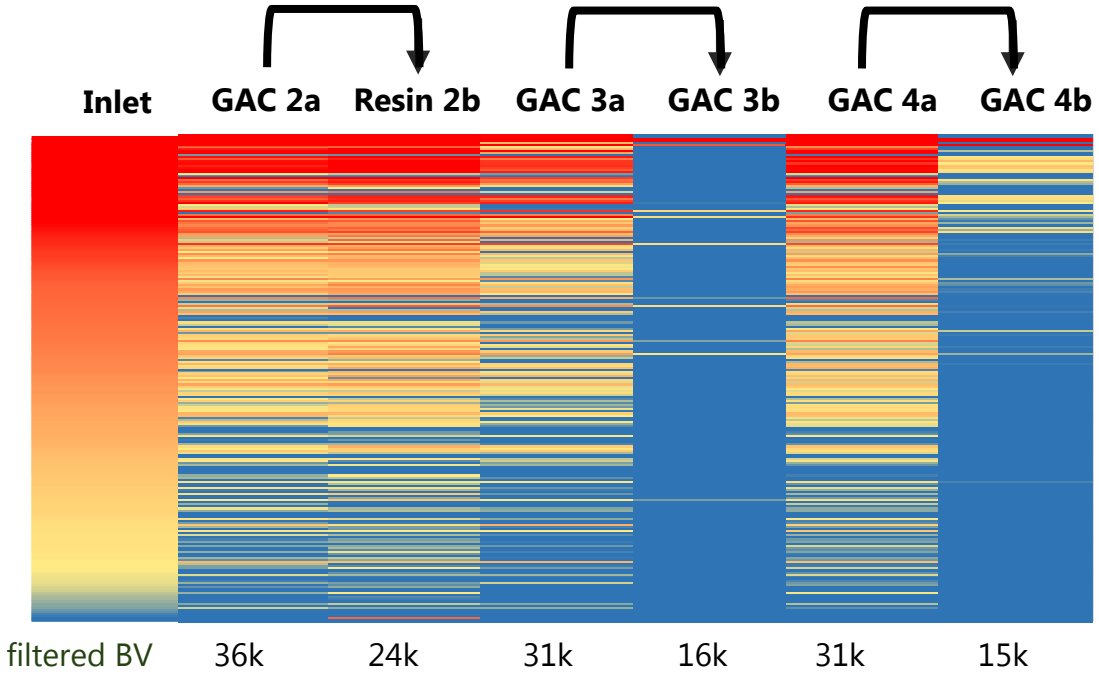


N-oxide tributylamine >800 ng/L!



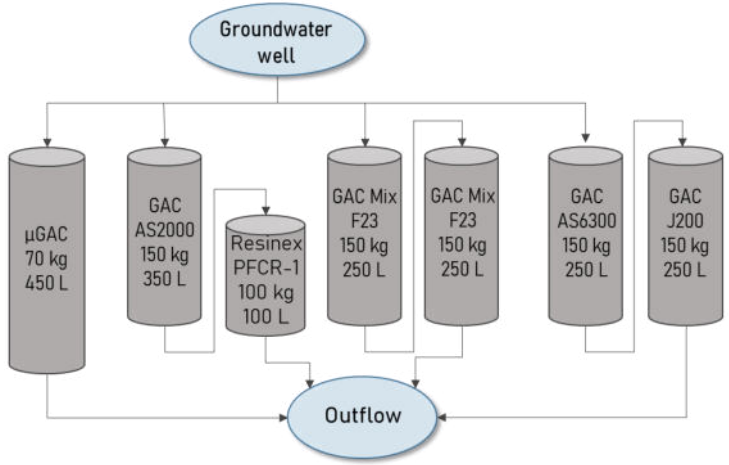
Monobutyl phthalate

Non-target screening after treatment of 10.000 m^3 water



SFC ESI+
Peak intensity

>6000
1000
<100



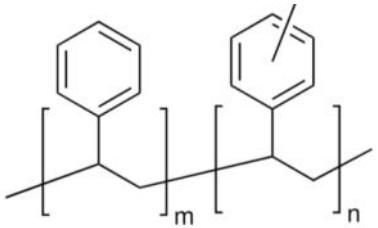
- ❑ Still more than 90 % removal for almost all compounds with GAC 3 and 4
- ❑ Resin with 50 % removal in ESI+ but 70 % removal in ESI-
- ❑ Still compounds are migrating from resin (e.g. Tributylamine (12 ng/L); N-oxide tributylamine (43 ng/L))

Resin migration study

Purofine PFA694E

Resinex PFCR-1

SW/DW



polymer structure polystyrene divinylbenzene with limited information on functional group

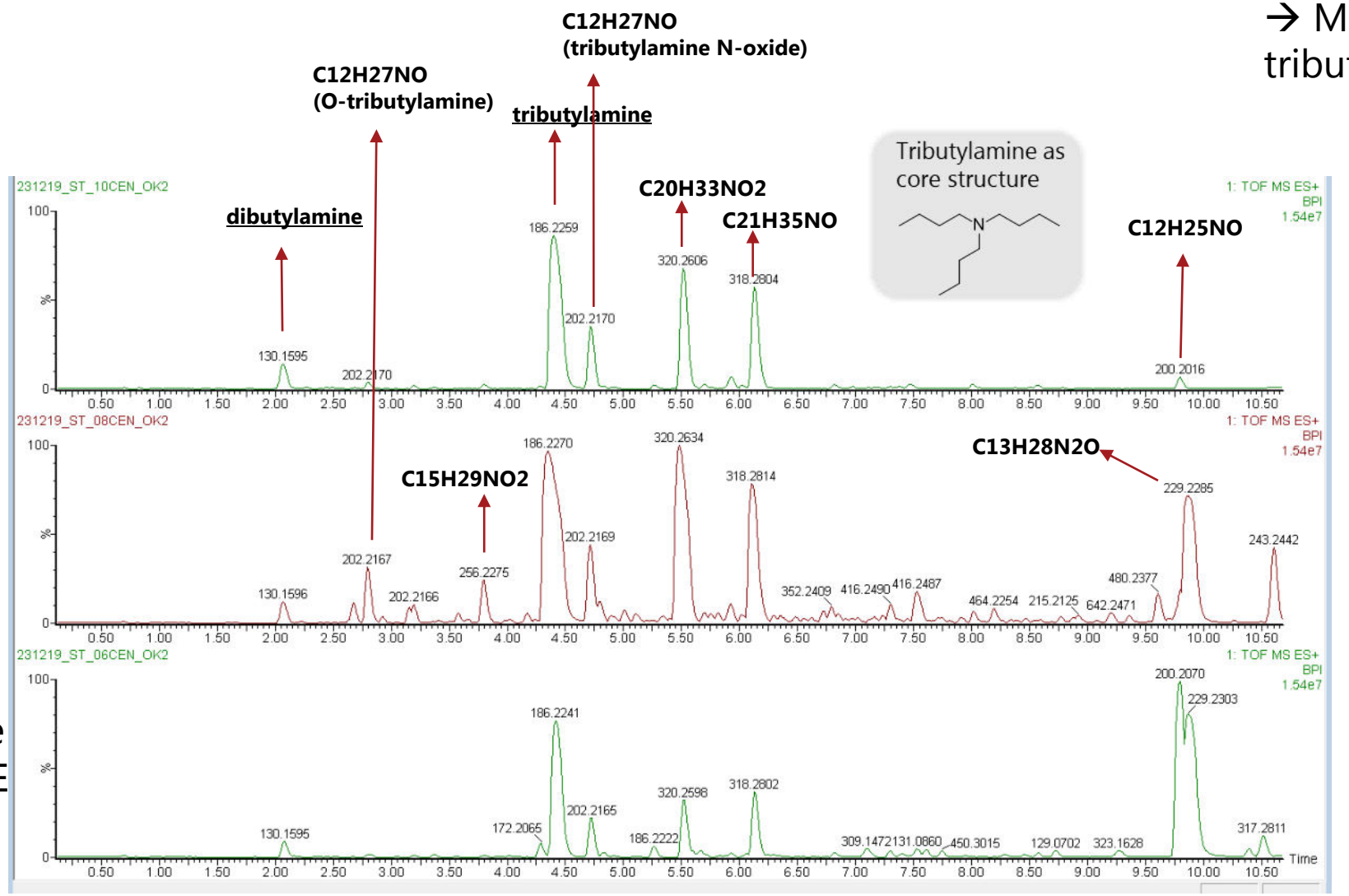
undisclosed

"complex amino"

tri-n-butylamine

Resin migration study- results

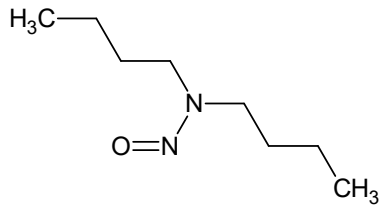
Tributylamine derivatives are very sensitive to in-source fragmentation
→ Most peaks were common tributylamine fragments



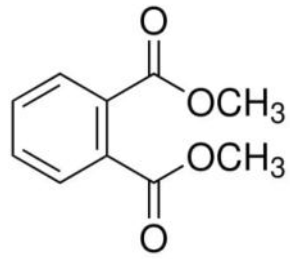
Resin migration study- results

Examples of other identified compounds:

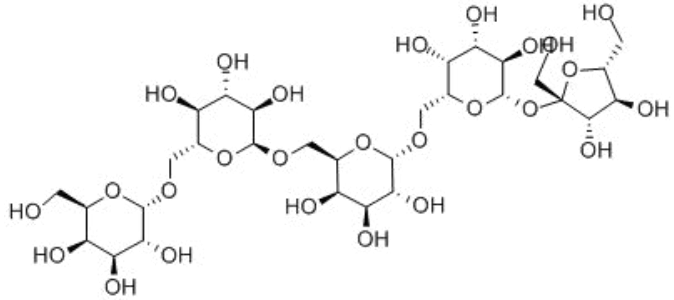
N-Nitrosodibutylamine (NDBA)



Monoethyl and dimethyl phthalate



Oligosaccharides



additional compounds (GC target method): dichlormethan, 1,2-dichlorethan and formaldehyde

Case 2

NTS for evaluation of concrete used for drinking water storage

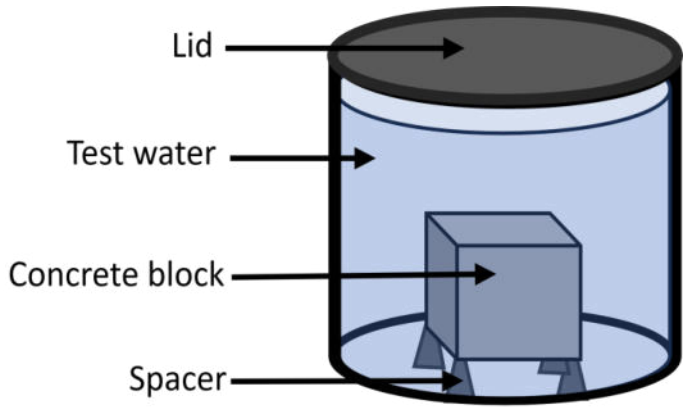
Research question based on EU Drinking Water Directive (2021)

All materials in contact with drinking water, including concrete, must be approved before installation by 2027→ **risk assessment at every stage, including risk by material leaching**

Three concretes for water storage tested

- ❑ Differences between concretes?
- ❑ Are the additives leaching from the concrete?
- ❑ What are the compounds leaching from concrete?

Migration experiment of concrete blocks

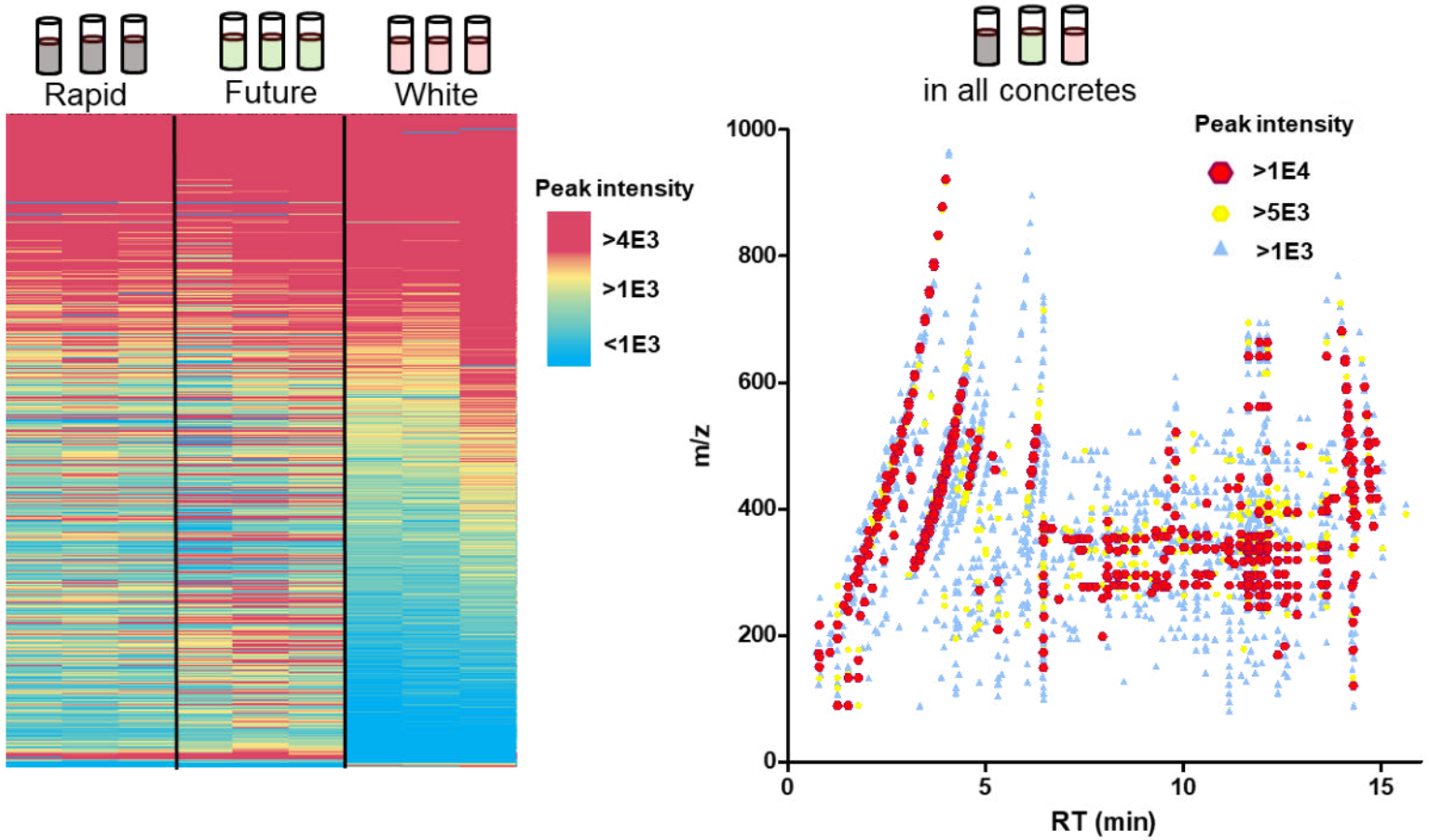


1. Precondition: 24 hours
2. Leaching period: 72 hours
3. pH adjustment to 6.5

Concrete blocks: 5x5x5 cm
Test water: MilliQ-water + salts (pH 7)

Concrete sample	Water pH after leaching	Amount additives	
		Superplasticizer (kg/m^3)	Retarder (kg/m^3)
Rapid	10.16	2.1	1.3
White	10.43	0.8	0.8
Future	9.84	3.0	-

Heatmap of all features detected in concrete leachates



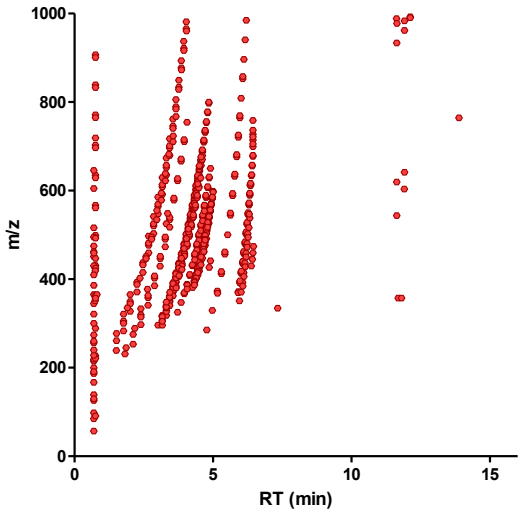
Similar leaching profiles for the three concrete types

→ „White“ leached in lowest concentrations and „Future“ in highest concentrations

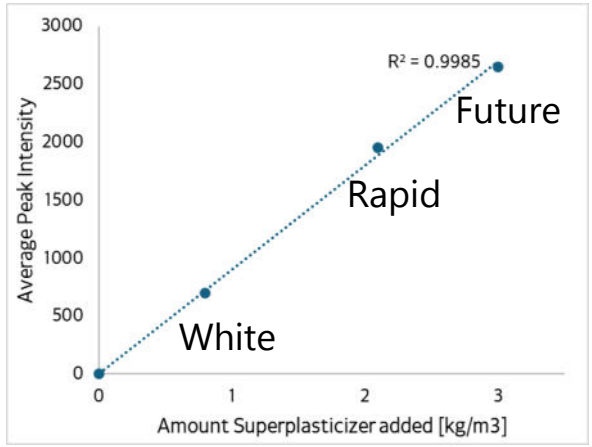
Leaching compounds

Superplasticizer determines the leaching

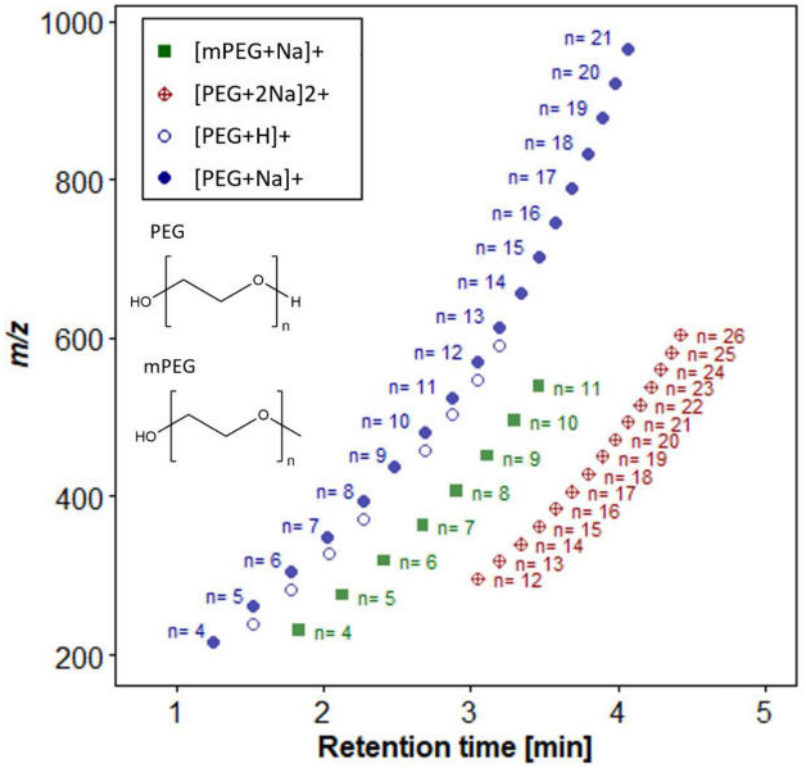
Compounds leaching from concrete and in superplasticizer



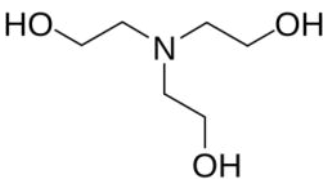
The more superplasticizer added, the higher leaching



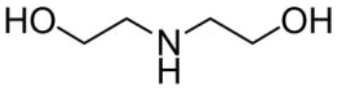
PEGs



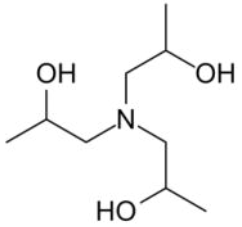
alkanolamines



Triethanolamine



Diethanolamine

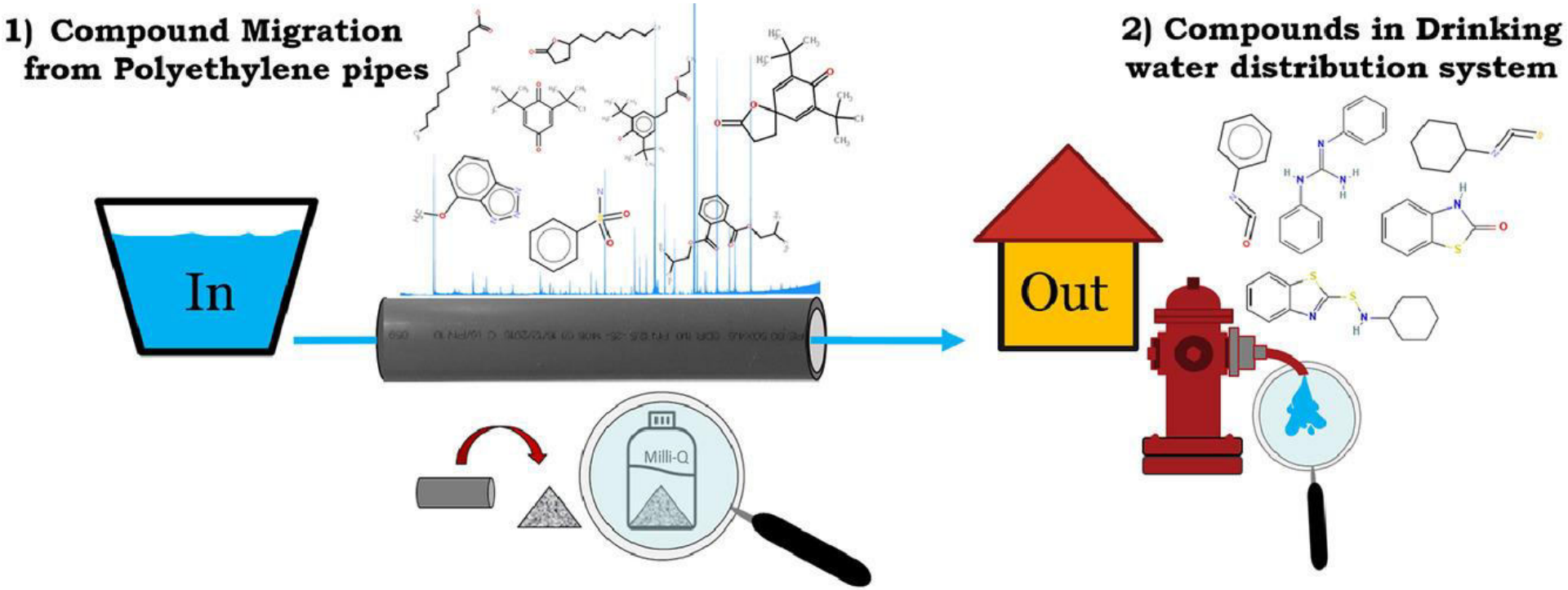


Triisopropanolamine

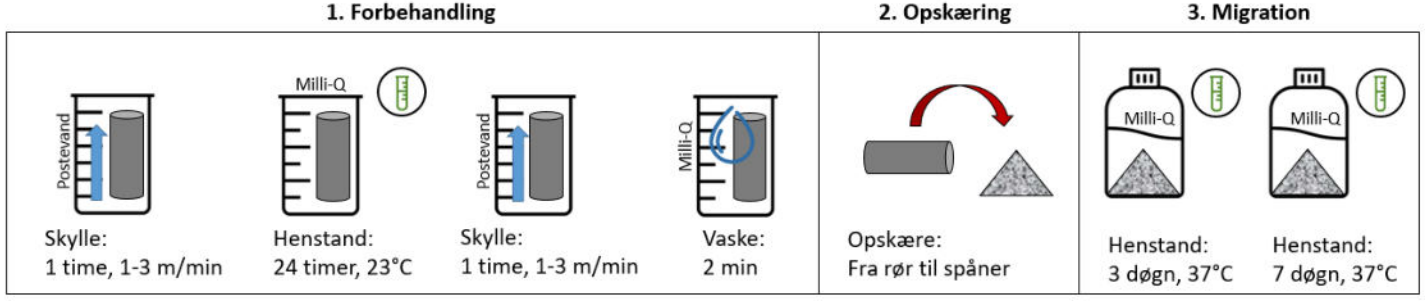
Case 3

NTS for evaluation of drinking water distribution system

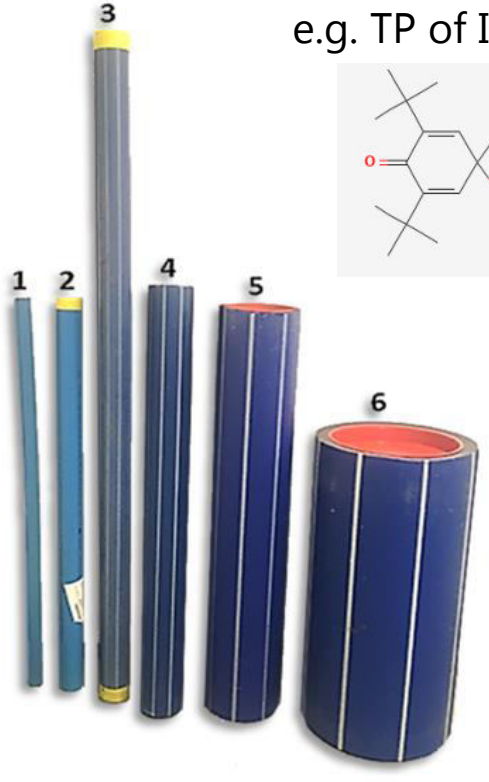
Which chemicals are leaching from the drinking water distribution system



Migration test of different materials approved for drinking water

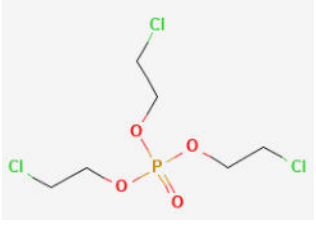


HDPE Pipes

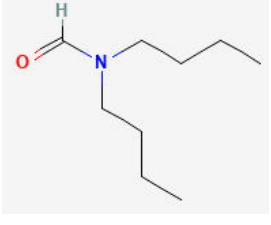


Antioxidant and TPs
e.g. TP of Irganox 1076

Plasticizer
e.g. TCPP

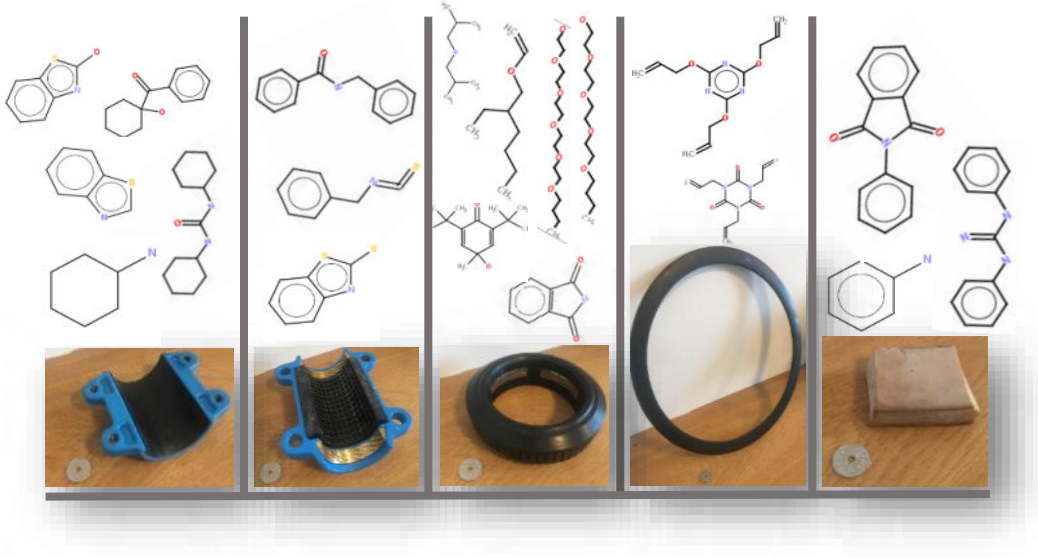


Other additives
(thermal stability)
e.g. N,N-dibutylformamide

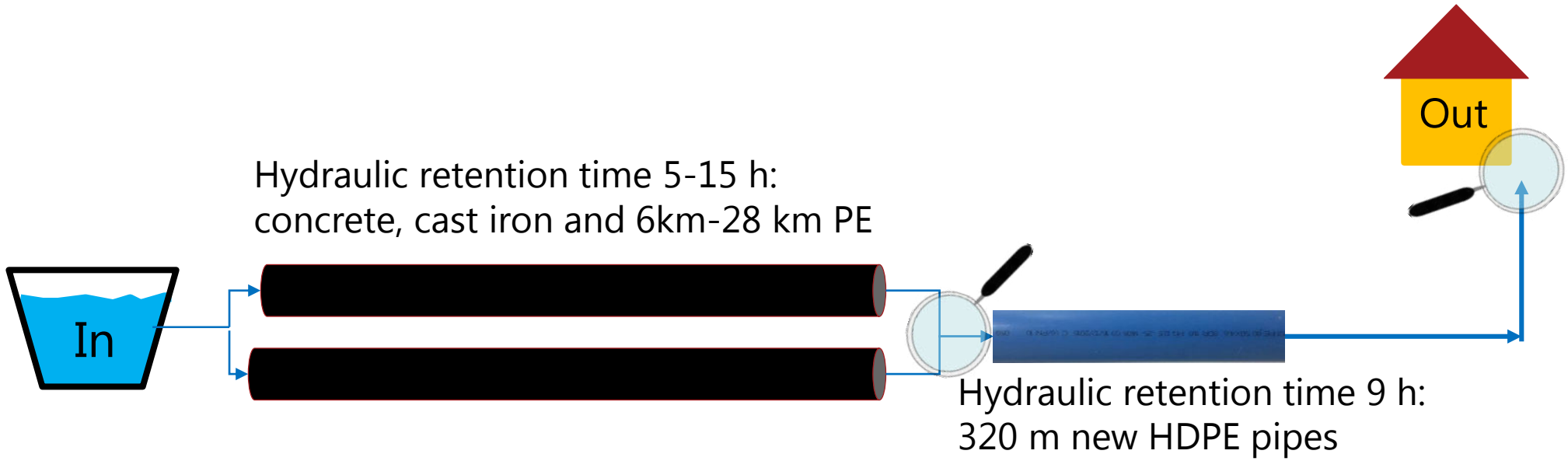


Rubber seals

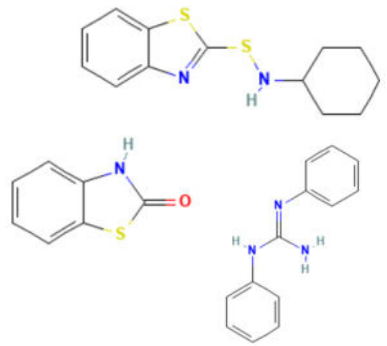
Similar compounds as migrating from car tires
→ benzothiazole, cyclohexyl isocyanate, amines and benzothiazolone



Which chemicals are detected in a real drinking water distribution system?



- No significant difference of any detected compounds before and after new HDPE pipe
- Rubber seals are more dominant in leaching as new HDPE pipes



Conclusion

- Combine target and non-target screening for better monitoring of organic compounds in drinking water
- Drinking water contamination is not only coming from the source!
- Filter material, construction materials and seals are leaching into the drinking water as well
- Non-target screening can help to point out so far neglected organic compounds → but hazard unknown

Acknowledgment

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