PFAS research with industries and utilities:

Where and how acting to reduce PFAS risk

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2022 National Water and Wastewater Conference, Halifax

08th November, 2022

Presentation outline

PFAS

- **Q1 — WHAT?**
  - PFAS DESCRIPTION
- **Q2 — WHY?**
  - ENVIRONMENTAL BEHAVIOR
  - REGULATIONS
- **Q3 — HOW?**
  - HOW TO MANAGE PFAS IN THE WATER CYCLE?
- **Q4 — WHO?**
  - WHO SHOULD SEAT AT THE PFAS ROUNDTABLE?

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Q4 WHO?
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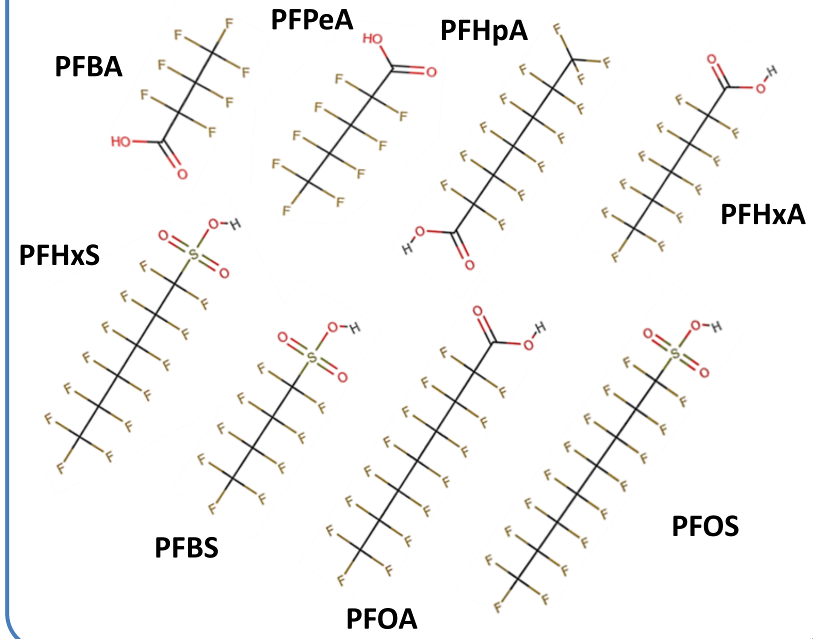
Main characteristics

- Anthropogenic compounds
- Fluorinated aliphatic carbon chains
- Highly thermal stability
- Hydrophobic and lipophobic



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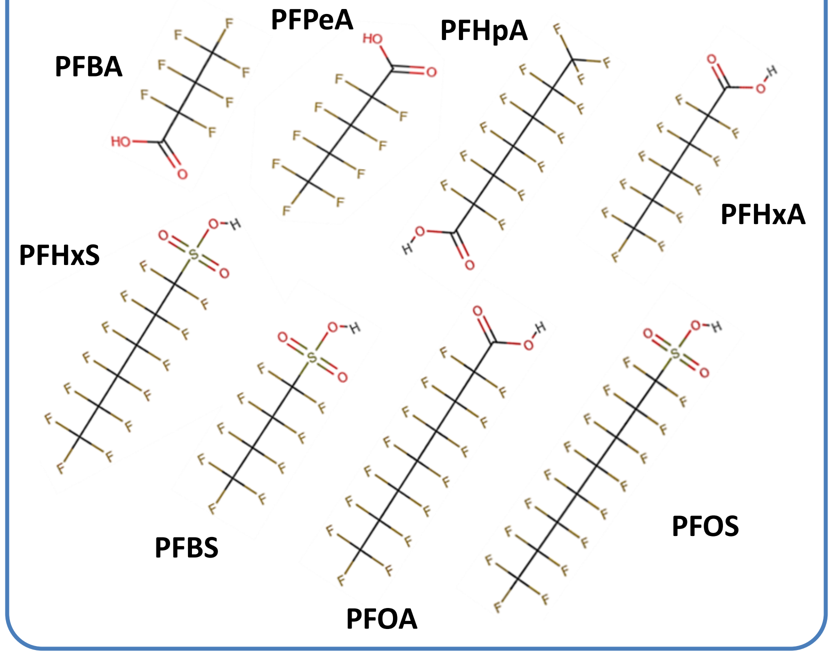

Uses

- Fluoropolymer coatings resistant to heat, oil, stain, grease, water
- Clothing manufacturing
- Electrical insulation
- Non-stick cooking surfaces
- Adhesives
- Food packaging

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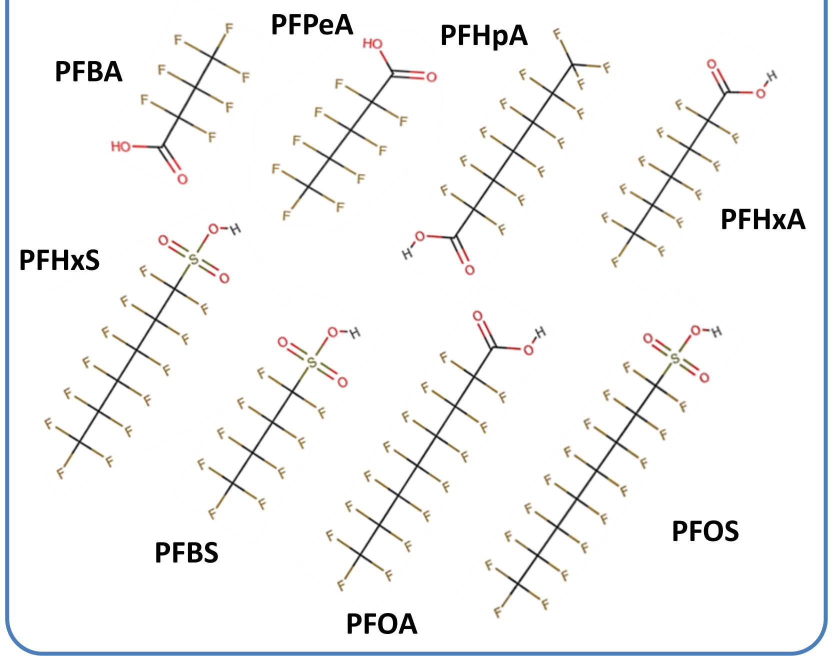

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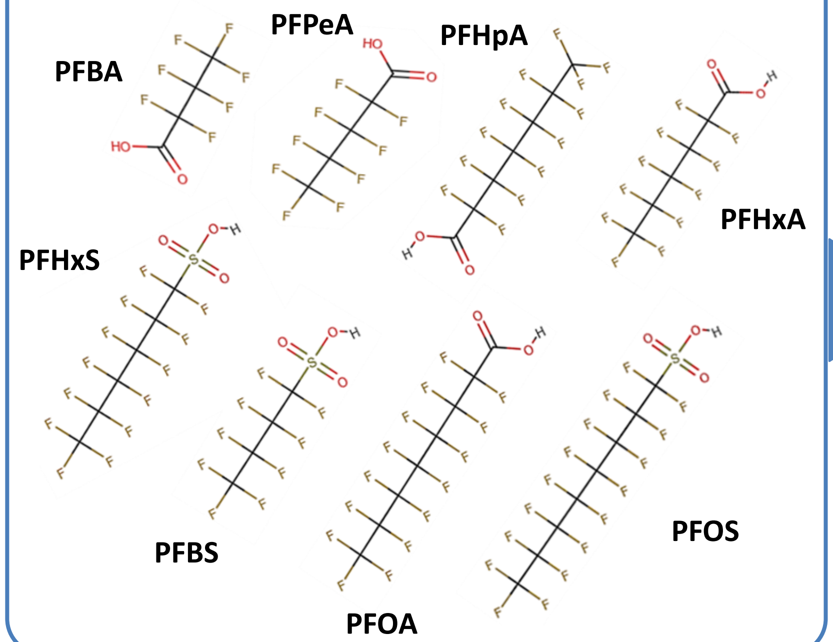

Uses

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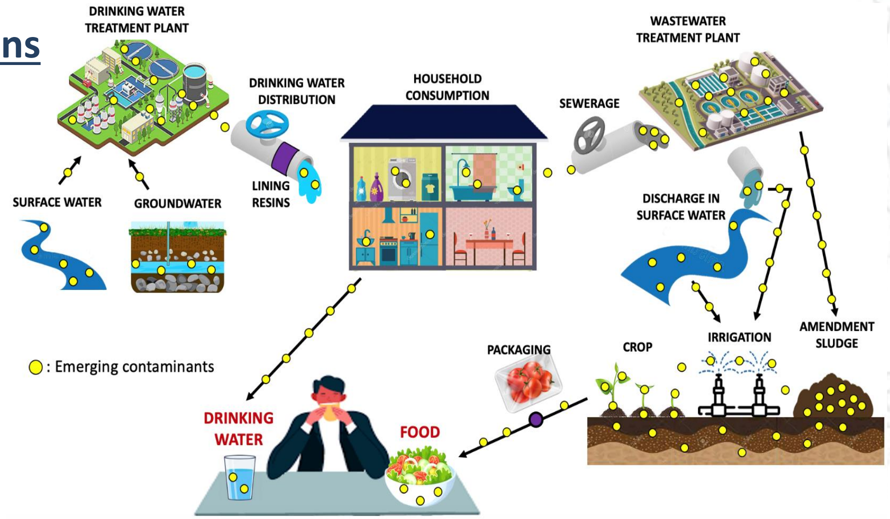
Environmental and health implications

- Ubiquitous in the environment
- "Forever Chemicals"
- Bioaccumulation
- Evidences of ecotoxicity
- Evidences of human toxicity on liver and reproductive system

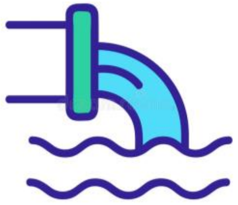


REGULATIONS ARE RAPIDLY EVOLVING

European PFAS banning or limitation in industrial products

Regulation	Included PFAS	Limit (if present)
Stockholm Convention on POPs – 2001 (POPs: Persistent Organic Pollutants) (http://chm.pops.int/TheConvention/ThePOPs/AllPOPs/tabid/2509/Default.aspx)	PFOA (Annex A) PFOS (Annex B)	Annex A: substances that you want to eliminate, so avoid their production and use. Annex B: substances to be restricted both in production and in use.
REACH 552/2009 (https://www.reach.gov.it/sites/default/files/allegati/regolamentoCE_552_22_06_2009.pdf)	PFOS	No placed on the market in semi-finished products, if the concentration of PFOS is equal or greater than 0.1% by weight.
Directive 2013/39/EU on priority substances (https://eur-lex.europa.eu/eli/dir/2013/39/oj/ita/pdf)	PFOS (Priority substance)	Environmental Quality standard (EQS): Surface water (0,65 ng/L); Marine-coastal surface water (0,13 ng/L); biota (9,1 µg/kg_{ww})
ZDHC (Zero Discharge Hazardous Chemicals Programme) (https://www.roadmaptozero.com/)	PFOS, PFOA, PFBS, PFHxA (2022: PFHxS, PFNA, PFBA, PFHpA)	Specific reference for the textile industry. This program aims to eliminate hazardous substances within the textile industry. Limit = 0,01 µg/L for PFOS, PFOA, PFBS, PFHxA

European Directive on PFAS **discharge in surface water** (under revision)



Compound	Concentration limit (µg/L)
PFOS	0.02 [0 – 36 month]; 0.00065 [after 36 months]
PFOA	0.3 [0 – 36 month]; 0.1 [after 36 months]
PFBA	7.0 [from the entry in force]
PFPeA, PFBS, other PFAS (C3-C6)	3.0 [from the entry in force]
PFHxA, PFHpA, PFHxS, PFNA, PFDeA, PFUnA, PFDoA, other PFAS (over C7)	1.0 [from the entry in force]
cC6O4	7.0 [13 – 24 month]; 3.5 [25 – 36 month]; 0.5 [> 36 months]
ADV	2.0 [13 – 24 month]; 0.5 [after 25 months]

PFAS limits or advisory levels in **drinking water** regulations worldwide

Standard limit	Country	Reference
0,3 µg/l (PFOS); 10 µg/l (PFOA)	UK	HPA UK, 2007
0,3 µg/l (PFOS+PFOA)	Germany	Roos et al., 2008
0,53 µg/l (PFOS); 0.0875 µg/l (PFOA)	Netherland	Schriks et al., 2010
0,3 µg/l (PFOS); 3 µg/l (PFOA)	EFSA	EFSA, 2018
0,1 µg/l (sum of 16 PFAS)	European Union	EU DW Directive 2020
0,02 ng/l (PFOS); 0.004 ng/l (PFOA); 10 ng/L (GenX); 2000 ng/L (PFBS)	USA	US EPA, 2022

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NEED FOR PFAS TREATMENT IN BOTH DRINKING WATER AND WASTEWATER

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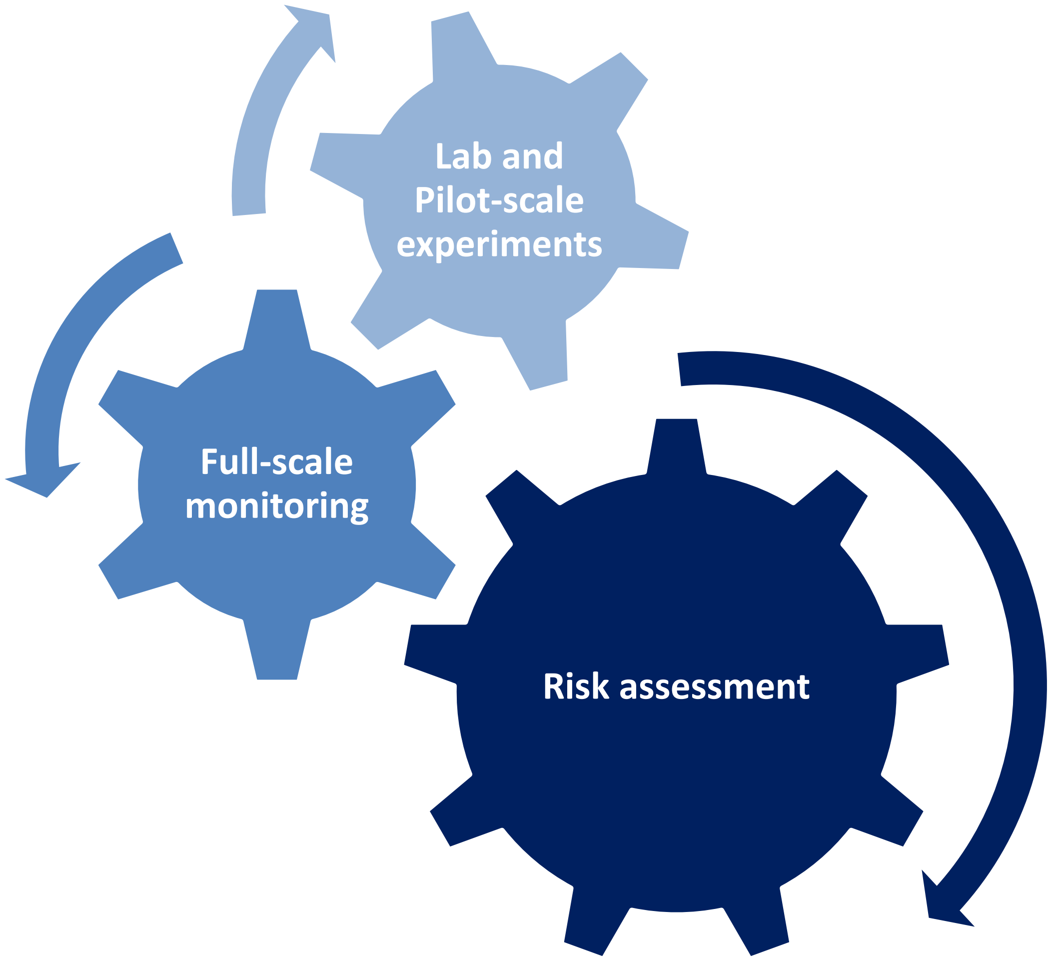
PFAS – HOW?

Development of an integrated framework for reliable treatment upgrade, design and planning to manage and minimize health risk related to PFAS



PFAS – HOW?

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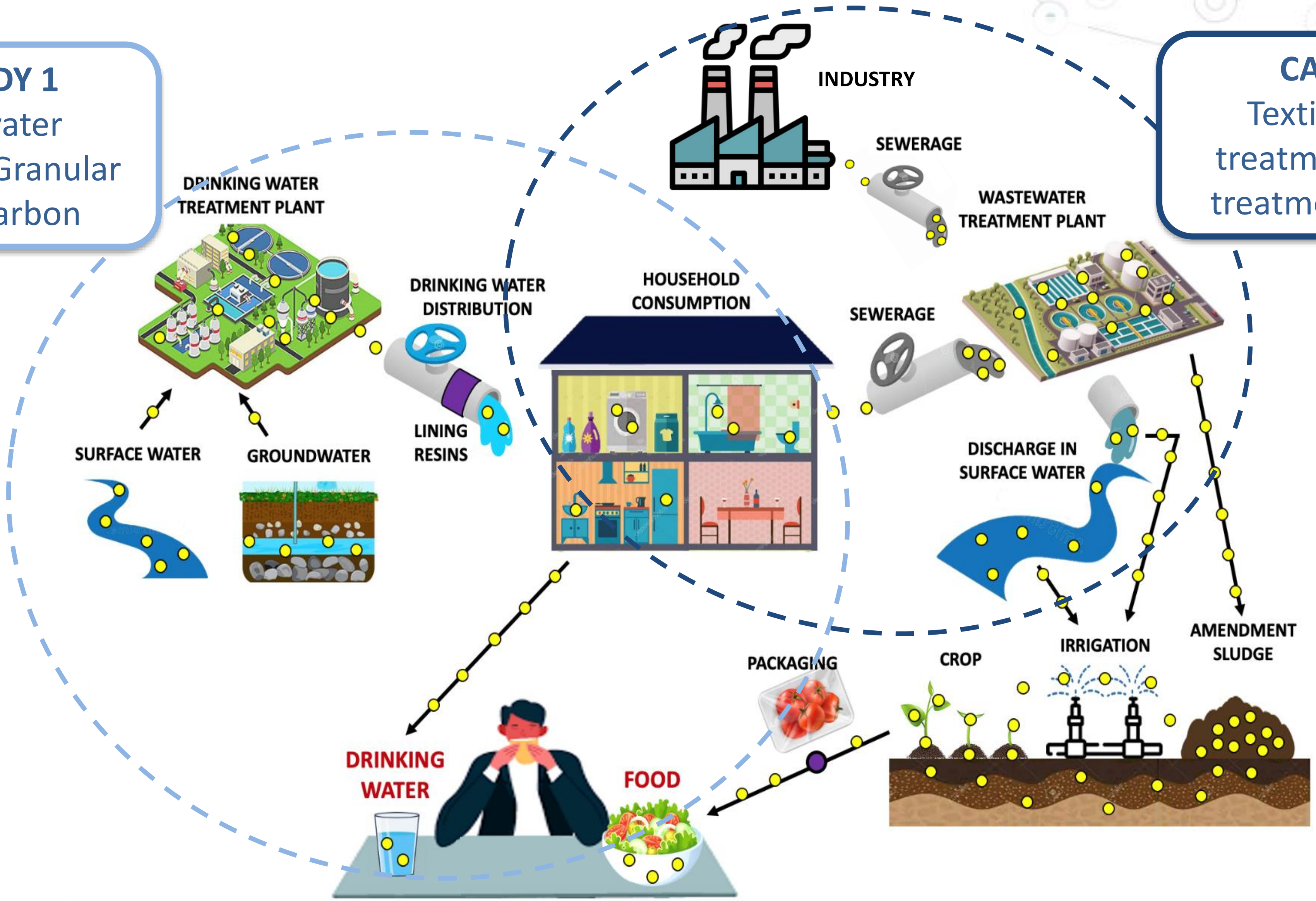
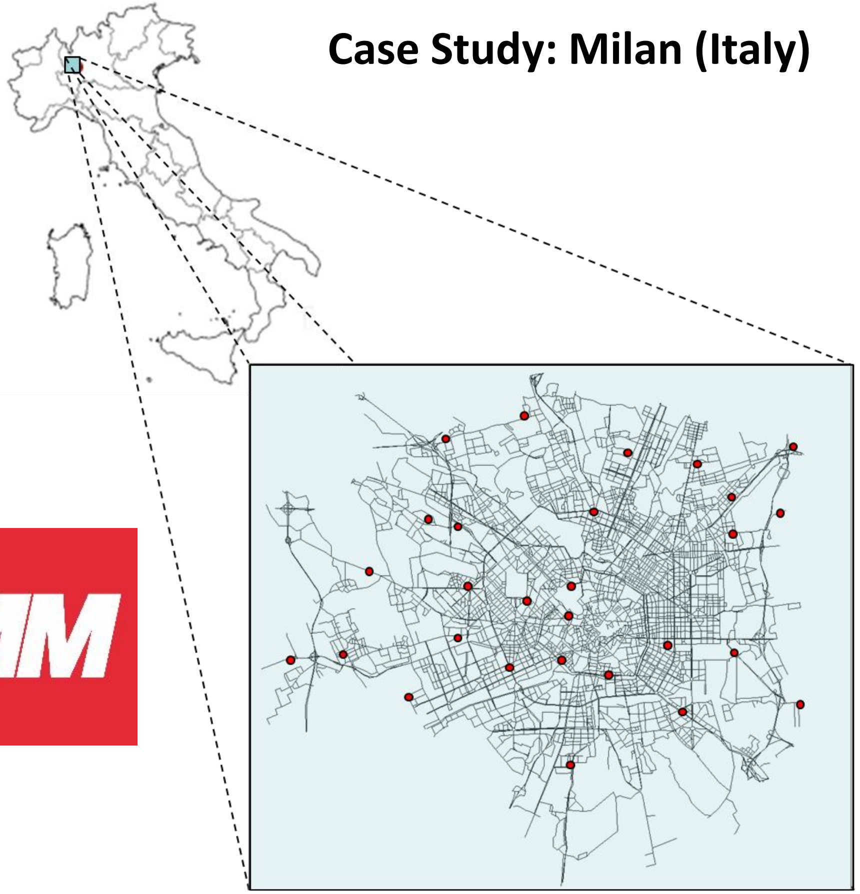
Drinking water treatment by Granular Activated Carbon

CASE STUDY 2
Textile wastewater treatment with several treatment technologies

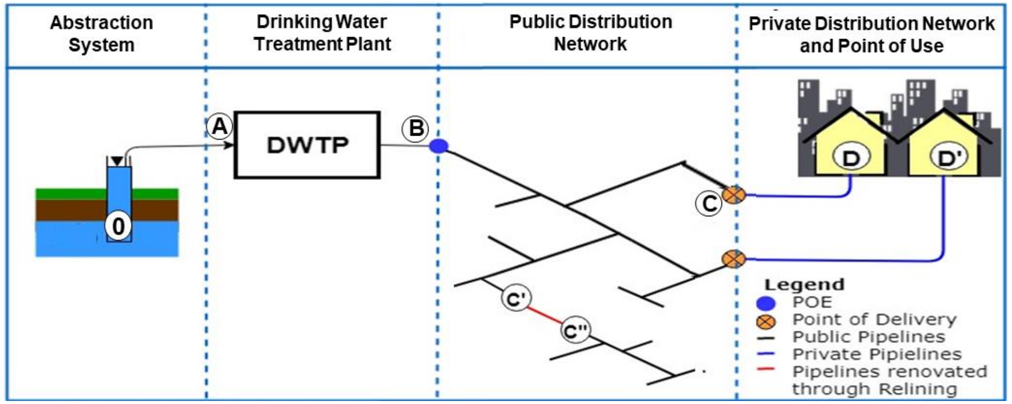


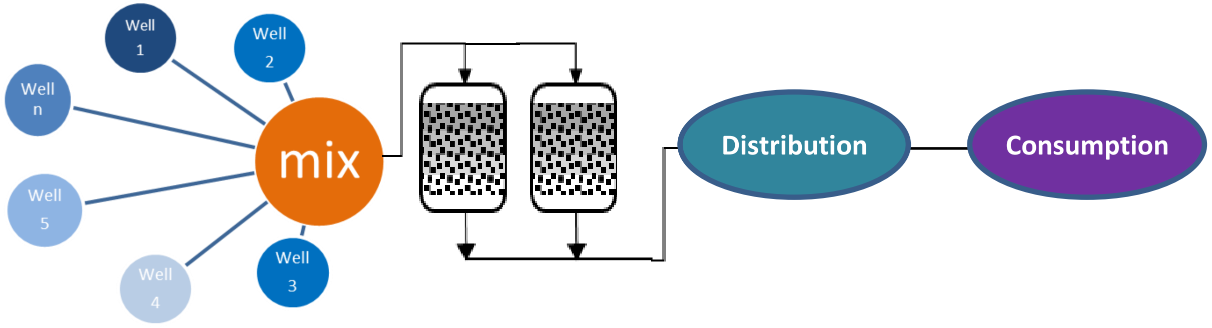
: PFAS

CASE STUDY 1: PFAS IN DRINKING WATER



Case Study: Milan (Italy)



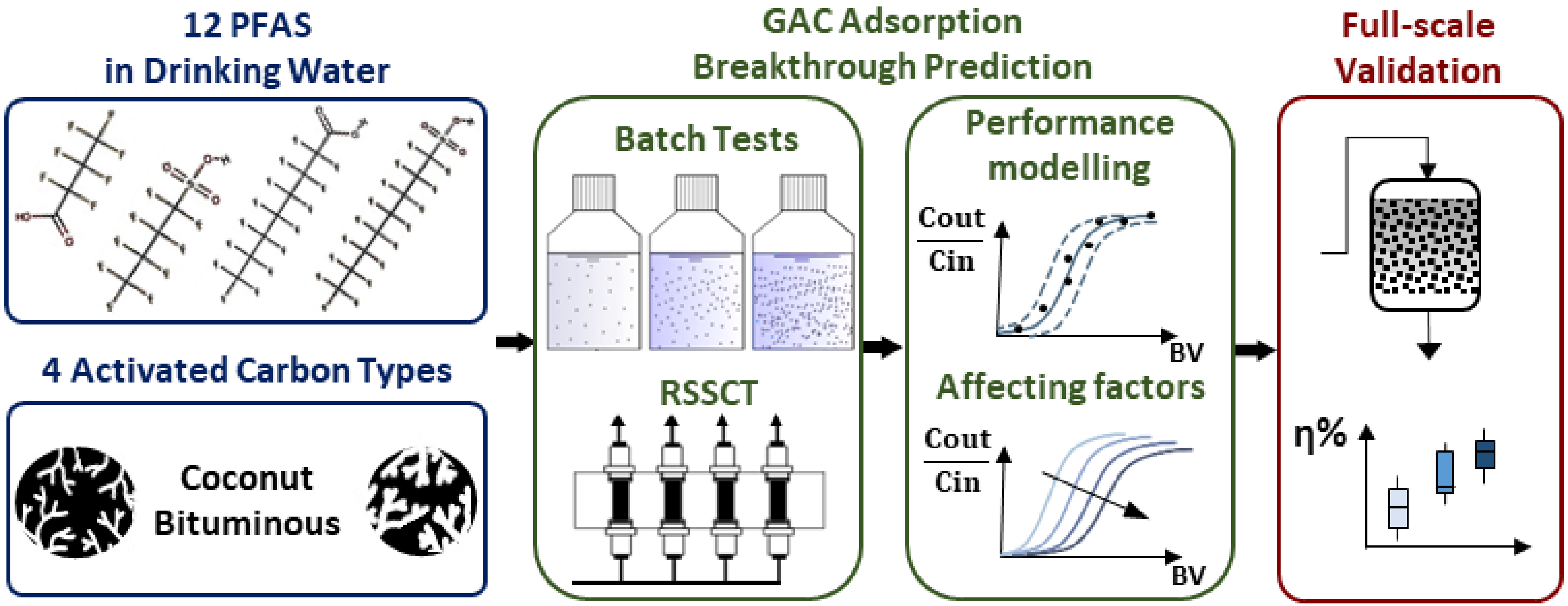


16 DWTPs with GAC filters

Designed and managed based on other **conventional micropollutants** (TCE, PCE, Chloroform, 2,6-dichlorobenzamide, 3,6-dichloropiridazine)

IS THE CURRENT GAC TREATMENT EFFICIENT ENOUGH? HOW WE SHOULD IMPROVE IT TO HANDLE PFAS?

DESIGN OF THE STUDY



Umwelt Bundesamt

TU berlin

MM

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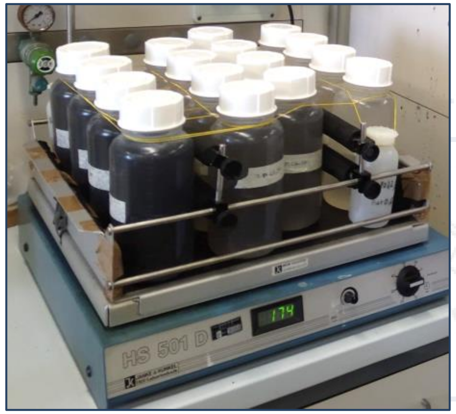
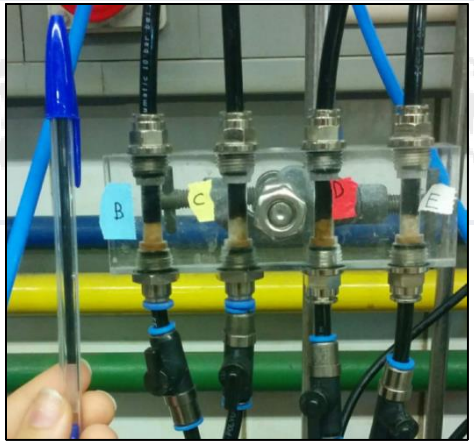
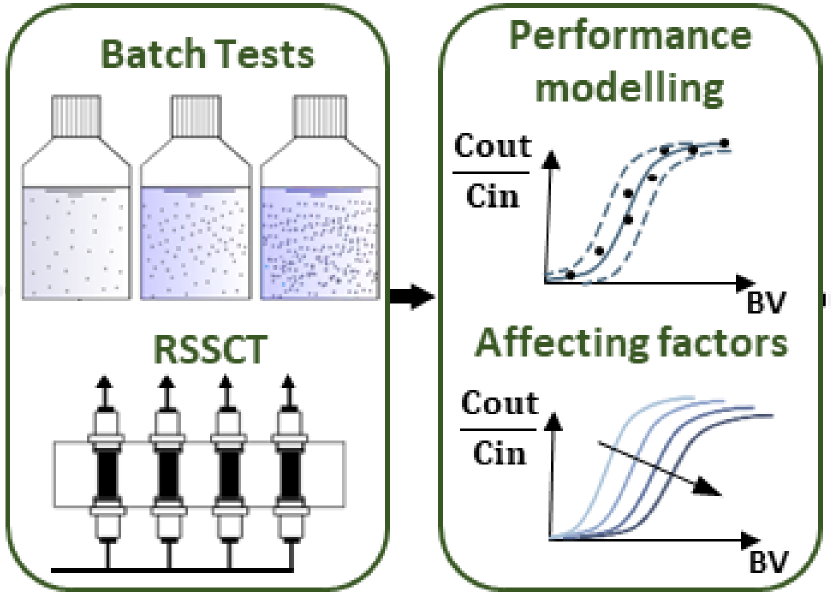




GAC Adsorption Breakthrough Prediction



Full scale

EBCT (average: 11 min)
$d_{p,LC}$ (average: 1200 um)

↓

Down-scaling method
Constant diffusivity equation:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]^2$$

↓

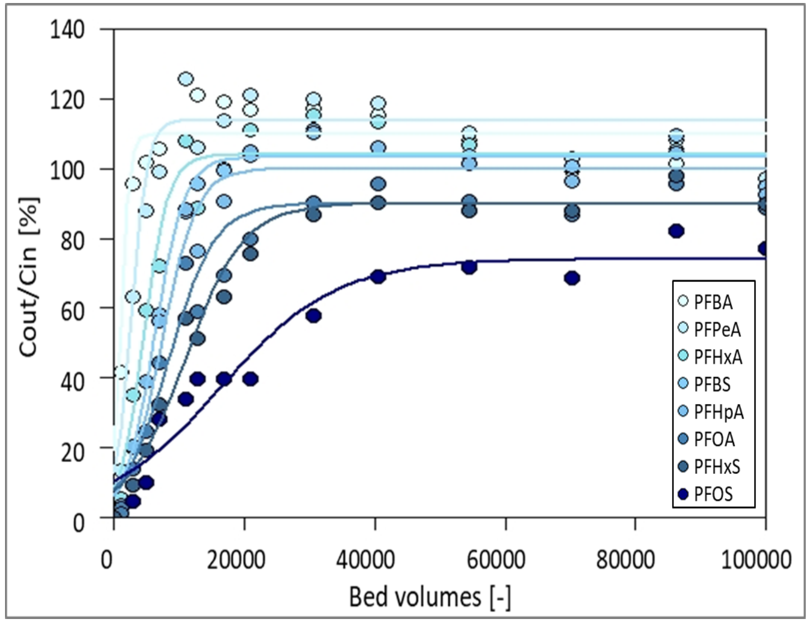
RSSCT

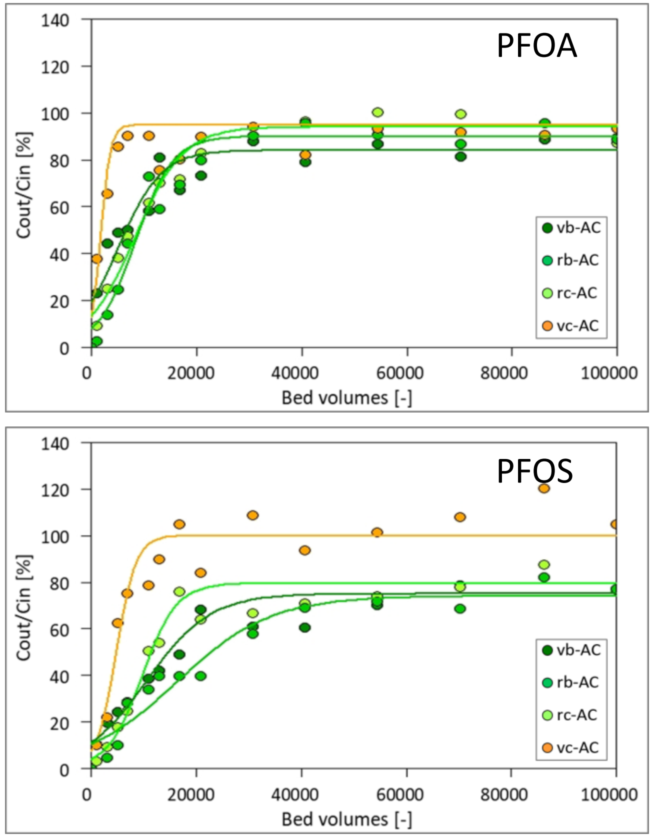
Milled and sieved ACs → $d_{p,\ RSSCT}$ (e.g. 110 um)
$EBCT_{RSSCT}$ (6.1 sec) → Flowrate (5.5 mL/min)

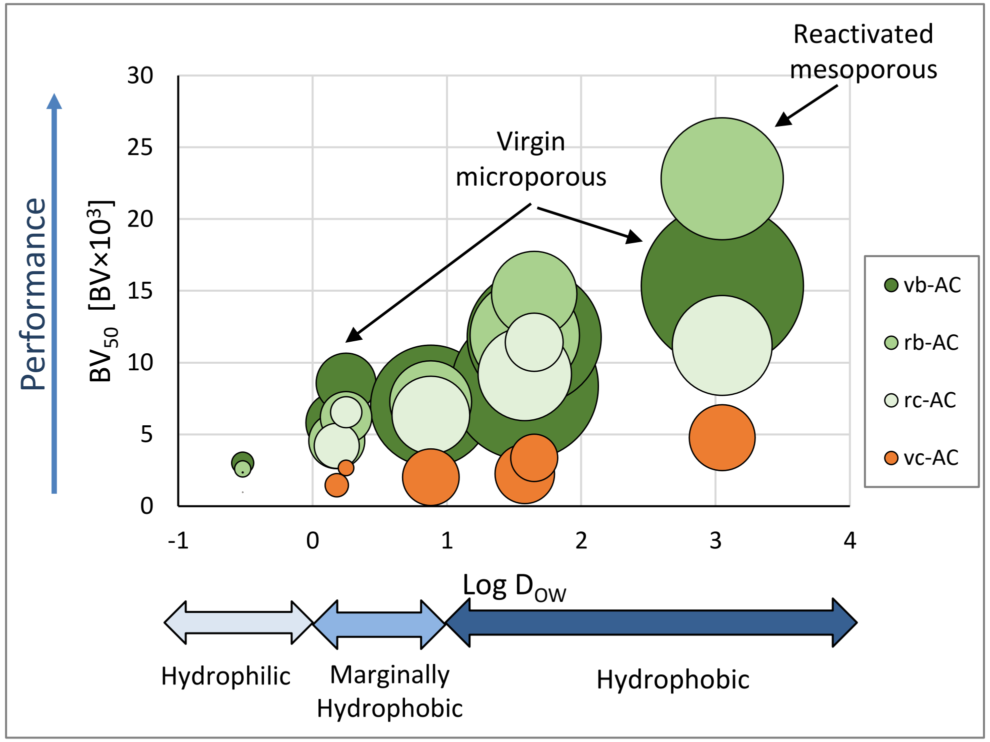
HIGHLIGHTS OF THE STUDY

Performance depends on:

- PFAS hydrophobicity (chain length, functional groups)
- Chromatographic effect
- GAC surface charge → Electrostatic interaction
- Interaction PFAS hydrophobicity - AC porosity







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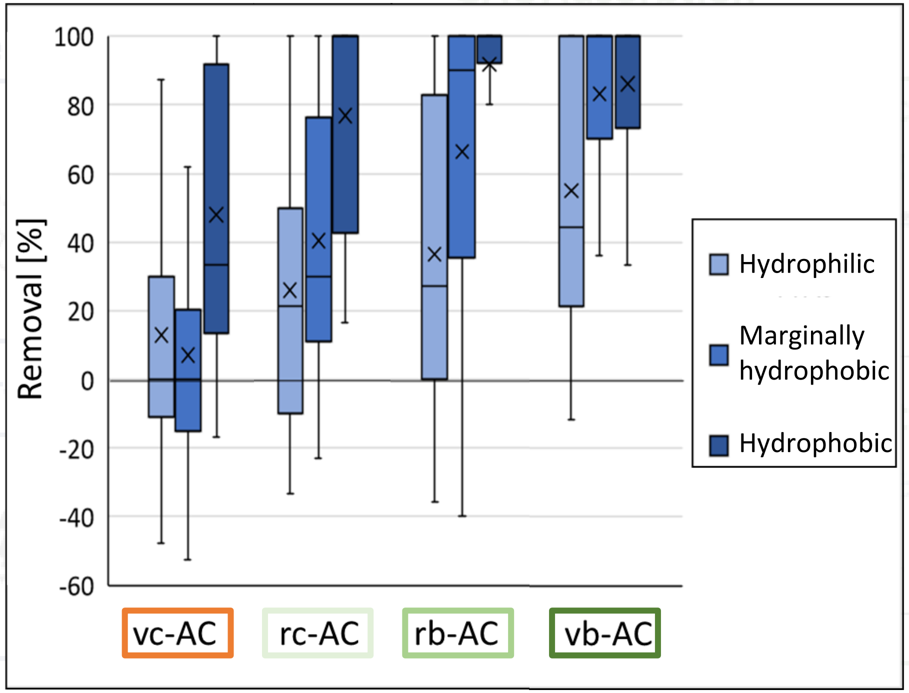
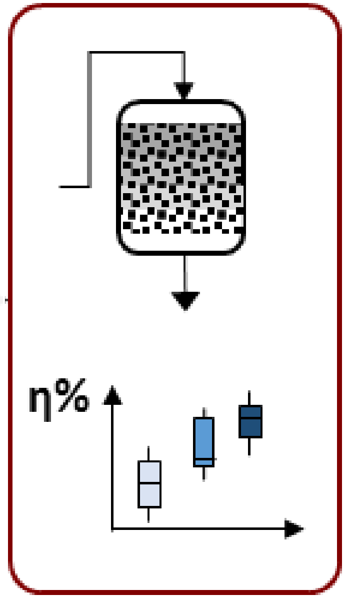
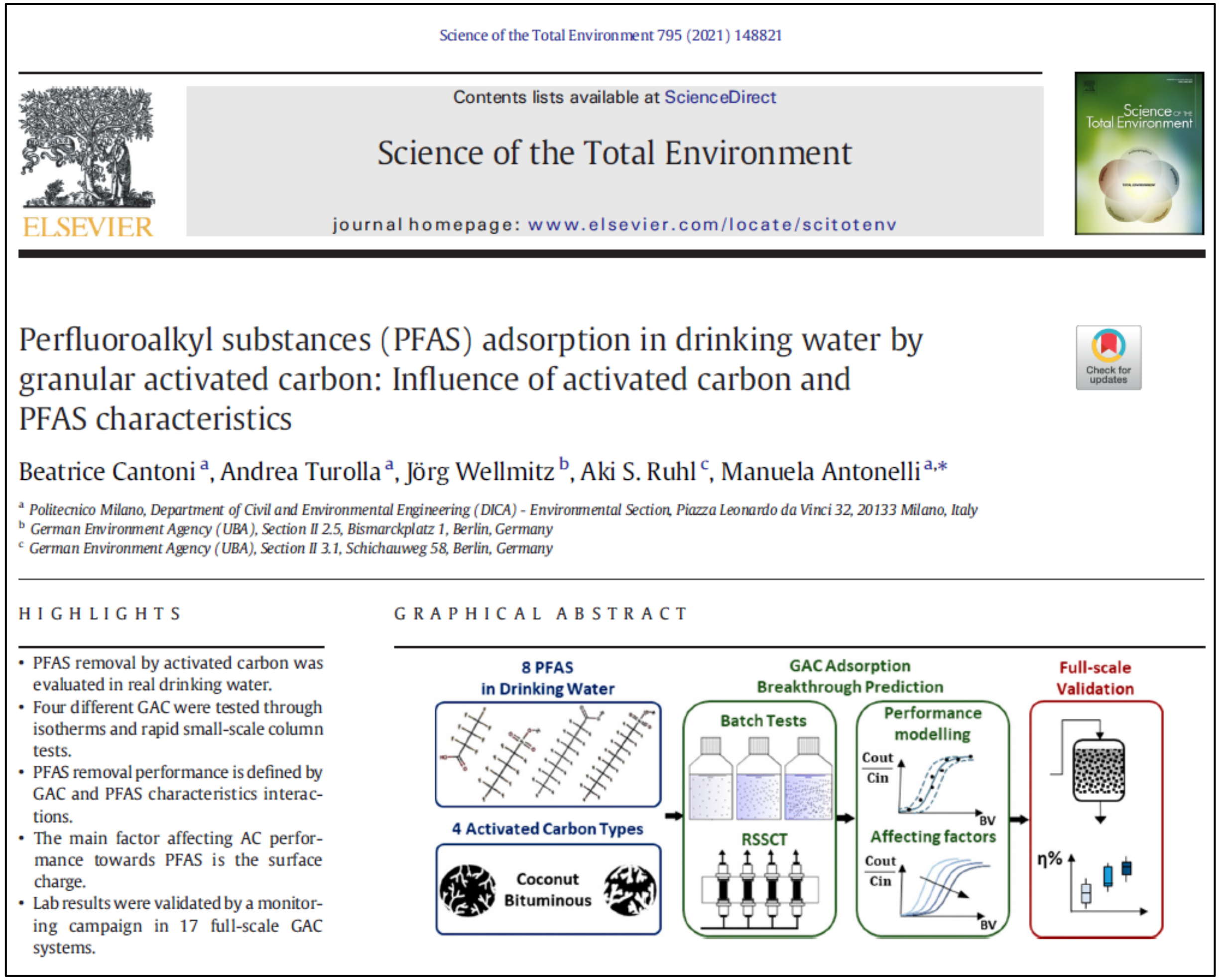
Validated with full-scale monitoring in 16 DWTPs using the same ACs

Sampling frequency: 2 weeks
Sampling period: Jan 2019 – Dec 2021



Full-scale Validation

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journal homepage: www.elsevier.com/locate/scitotenv

Perfluoroalkyl substances (PFAS) adsorption in drinking water by granular activated carbon: Influence of activated carbon and PFAS characteristics

Beatrice Cantoni [a], Andrea Turolla [a], Jörg Wellmitz [b], Aki S. Ruhl [c], Manuela Antonelli [a,*]

[a] Politecnico Milano, Department of Civil and Environmental Engineering (DICA) - Environmental Section, Piazza Leonardo da Vinci 32, 20133 Milano, Italy
[b] German Environment Agency (UBA), Section II 2.5, Bismarckplatz 1, Berlin, Germany
[c] German Environment Agency (UBA), Section II 3.1, Schichauweg 58, Berlin, Germany

HIGHLIGHTS

- PFAS removal by activated carbon was evaluated in real drinking water.
- Four different GAC were tested through isotherms and rapid small-scale column tests.
- PFAS removal performance is defined by GAC and PFAS characteristics interactions.
- The main factor affecting AC performance towards PFAS is the surface charge.
- Lab results were validated by a monitoring campaign in 17 full-scale GAC systems.

GRAPHICAL ABSTRACT

https://doi.org/10.1016/j.scitotenv.2021.148821

RISK ASSESSMENT FOR PFAS VS. CONVENTIONAL MICROPOLLUTANTS

Full-scale monitoring in 16 DWTPs

Sampling frequency: 2 weeks
Sampling period: Jan 2019 – Dec 2021

$$HQ_{out} = \frac{Cout}{Clim}$$

$$HI_{out} = \sum HQ_{out}$$

C_{lim} from the EU DW Directive (2020):

- Chloroform: 30 µg/l
- TCE + PCE: 10 µg/l
- 2,6-dichlorobenzammide: 0.1µg/l
- 3,6-dichloropiridazine: 0.1 µg/l
- Sum PFAS: 0.1 µg/l

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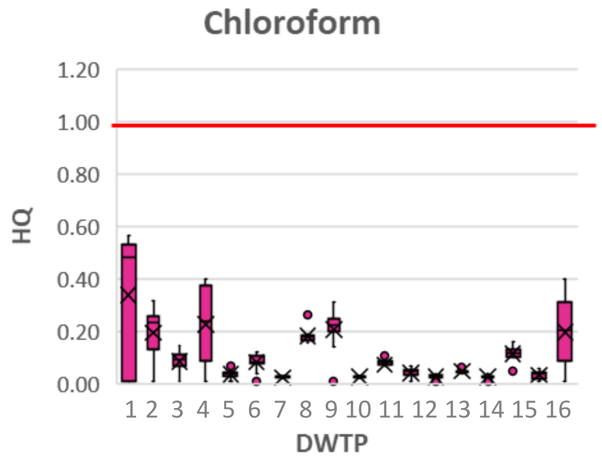

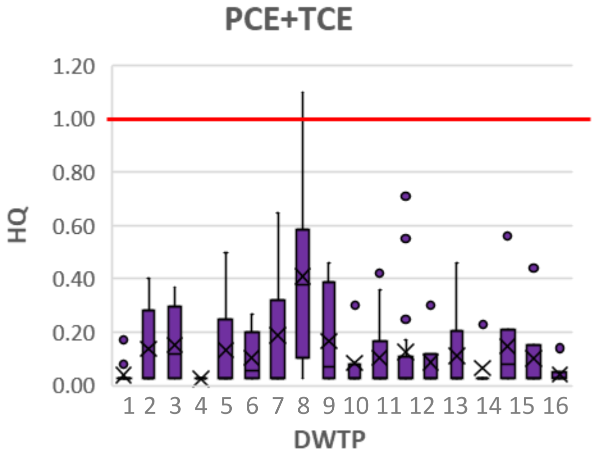

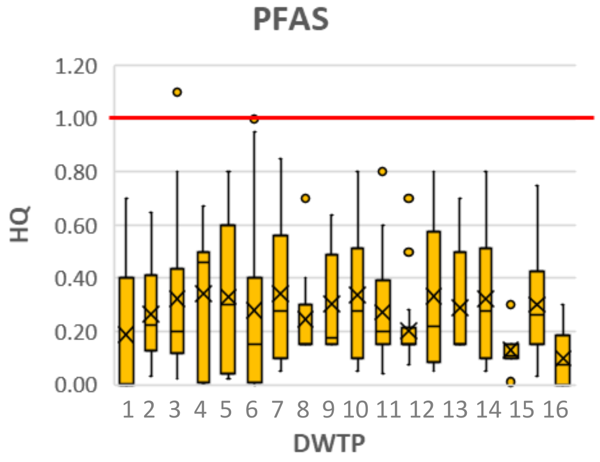

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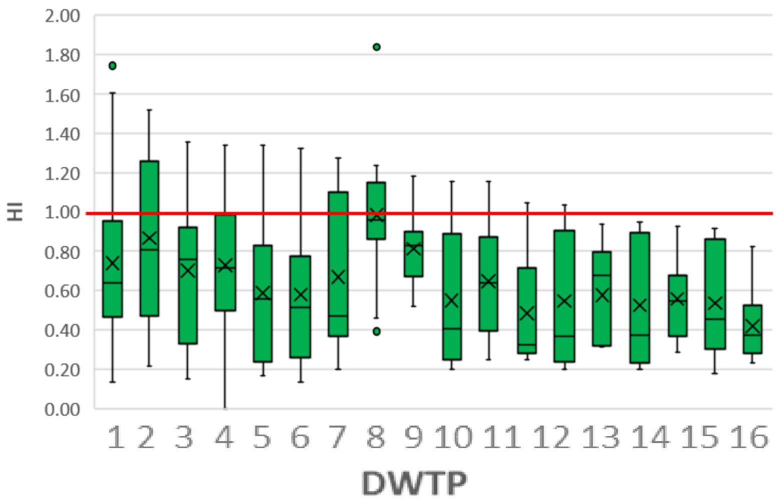
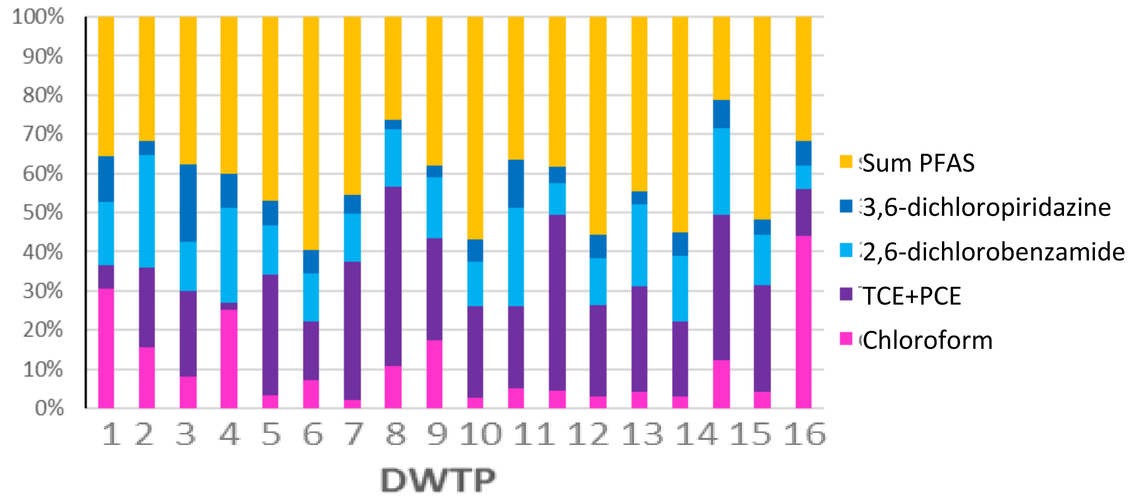
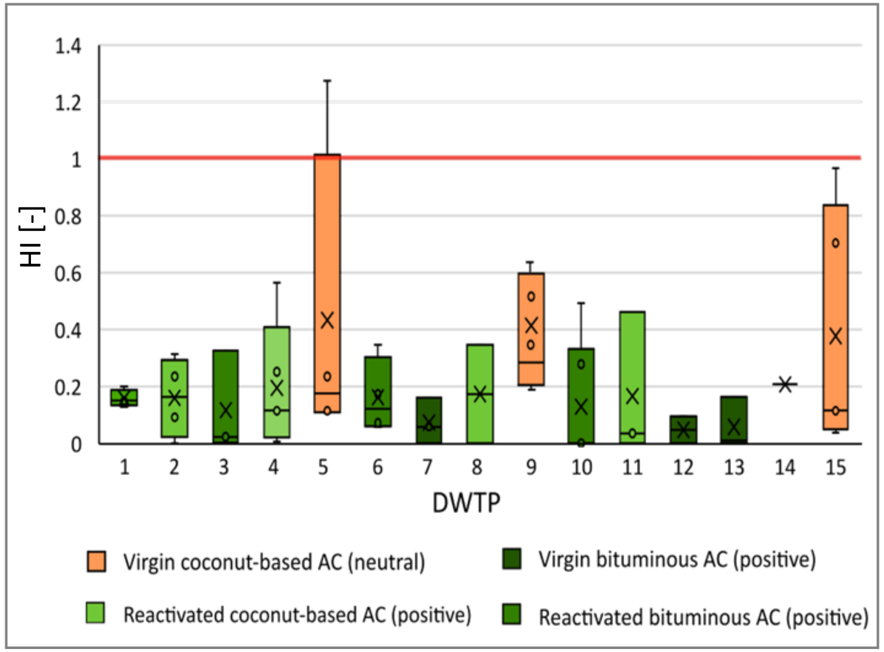




Q1 Q2 Q3 Q4

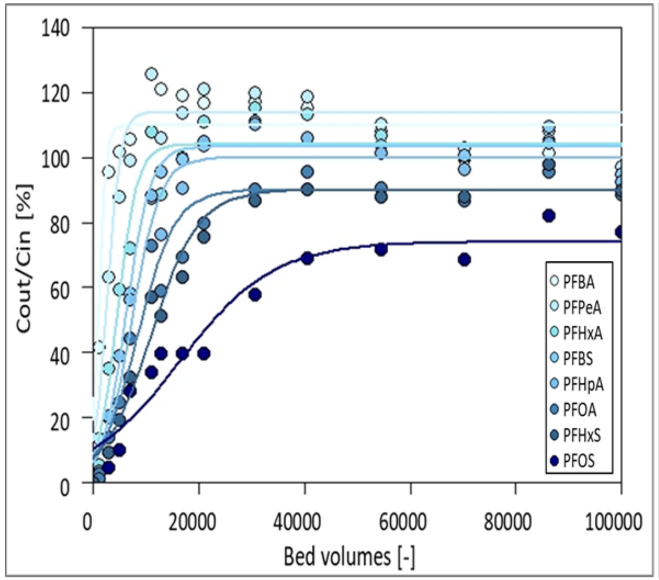
POSSIBLE INTERVENTION SCENARIOS

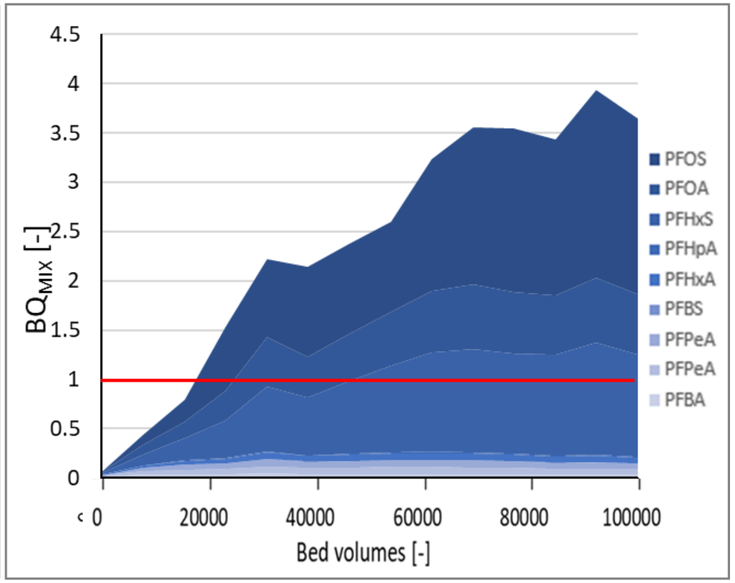
1) OPTIMAL GAC SELECTION



2) PROPER GAC FILTERS **MANAGEMENT AND REGENERATION**

based on risk breakthrough instead of single compounds breakthrough





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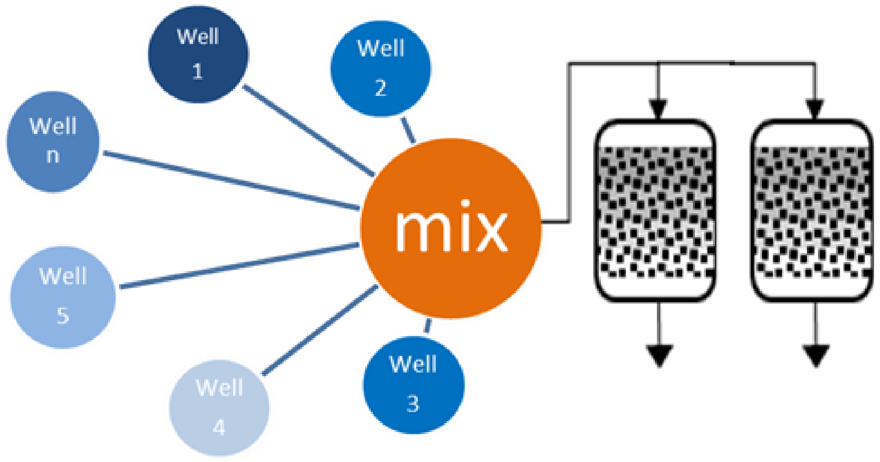


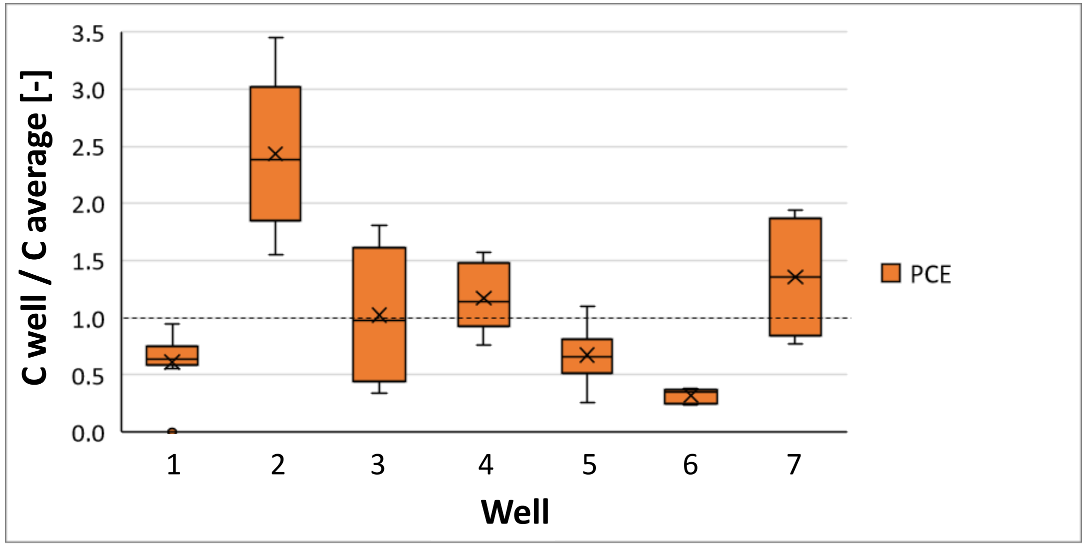
The optimization of abstraction wells management aims at minimizing the concentrations of target contaminants (conventional and emerging) entering the treatment plant

> **Abstraction flowrate** from wells < Target **compound concentration**

Boxplot is useful to compare the quality and variability of different water wells going into the mixed water entering the treatment

Compound i, Well j:

$$\frac{C_i\ (Well_j)}{C_i\ (average\ wells)}$$



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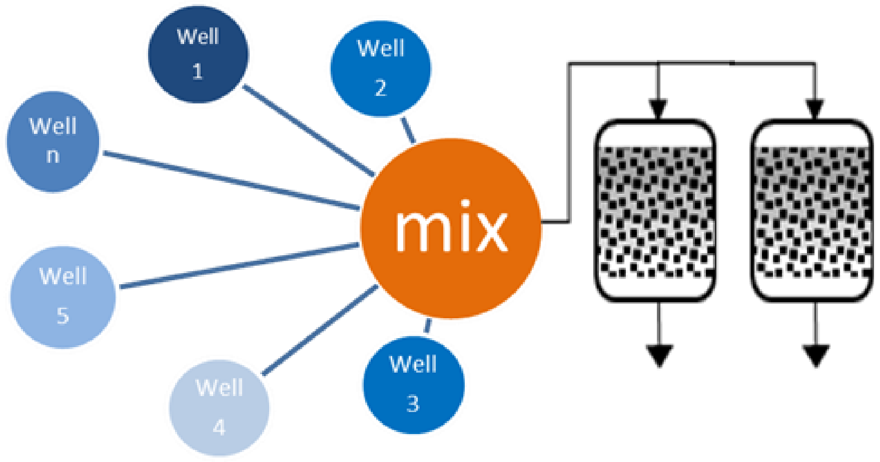

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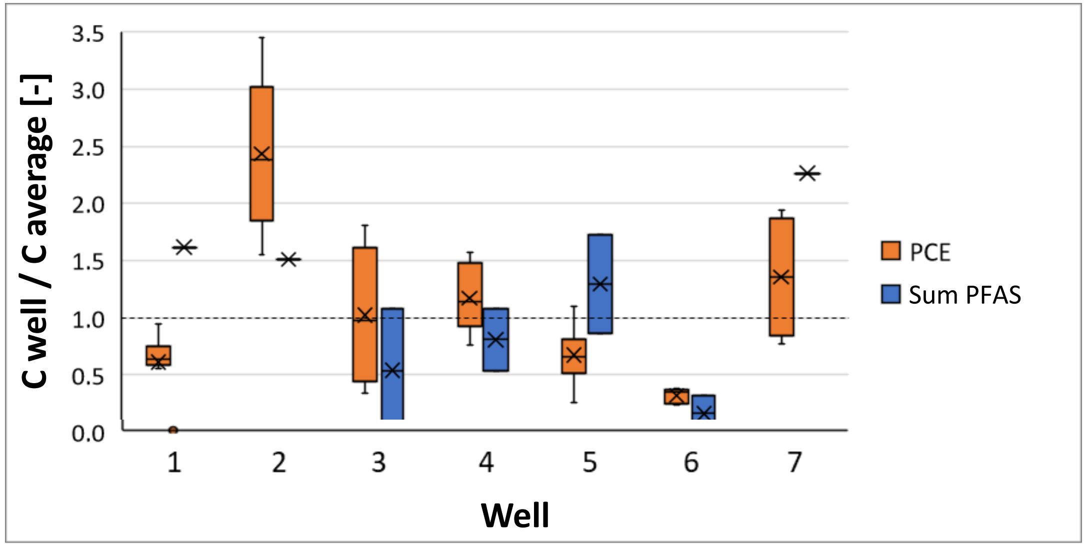

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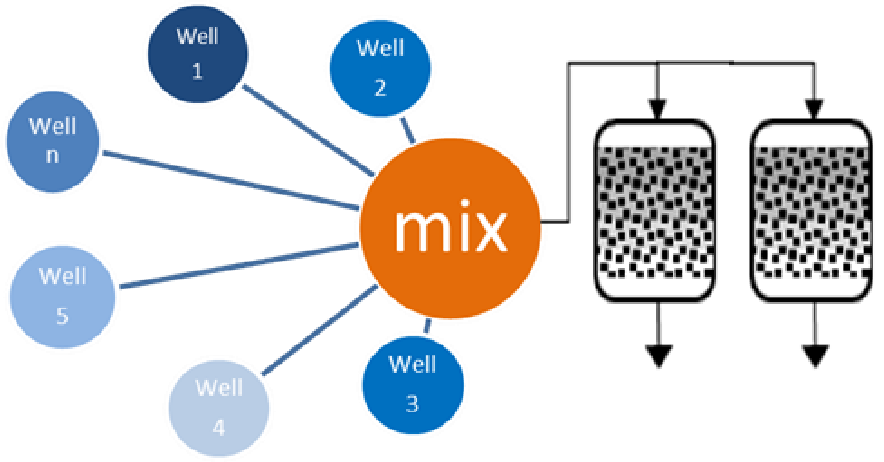

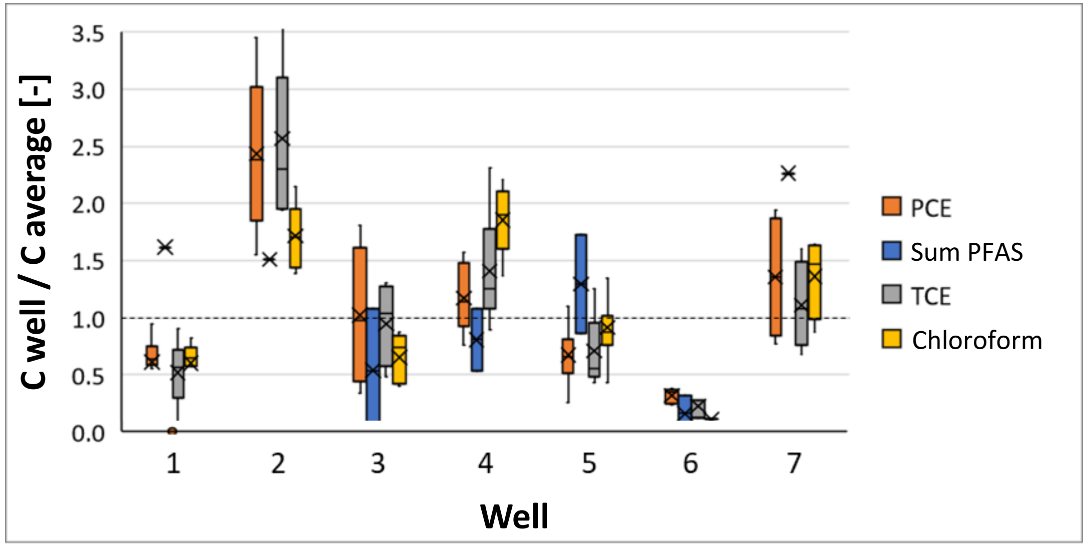

PFAS – HOW?

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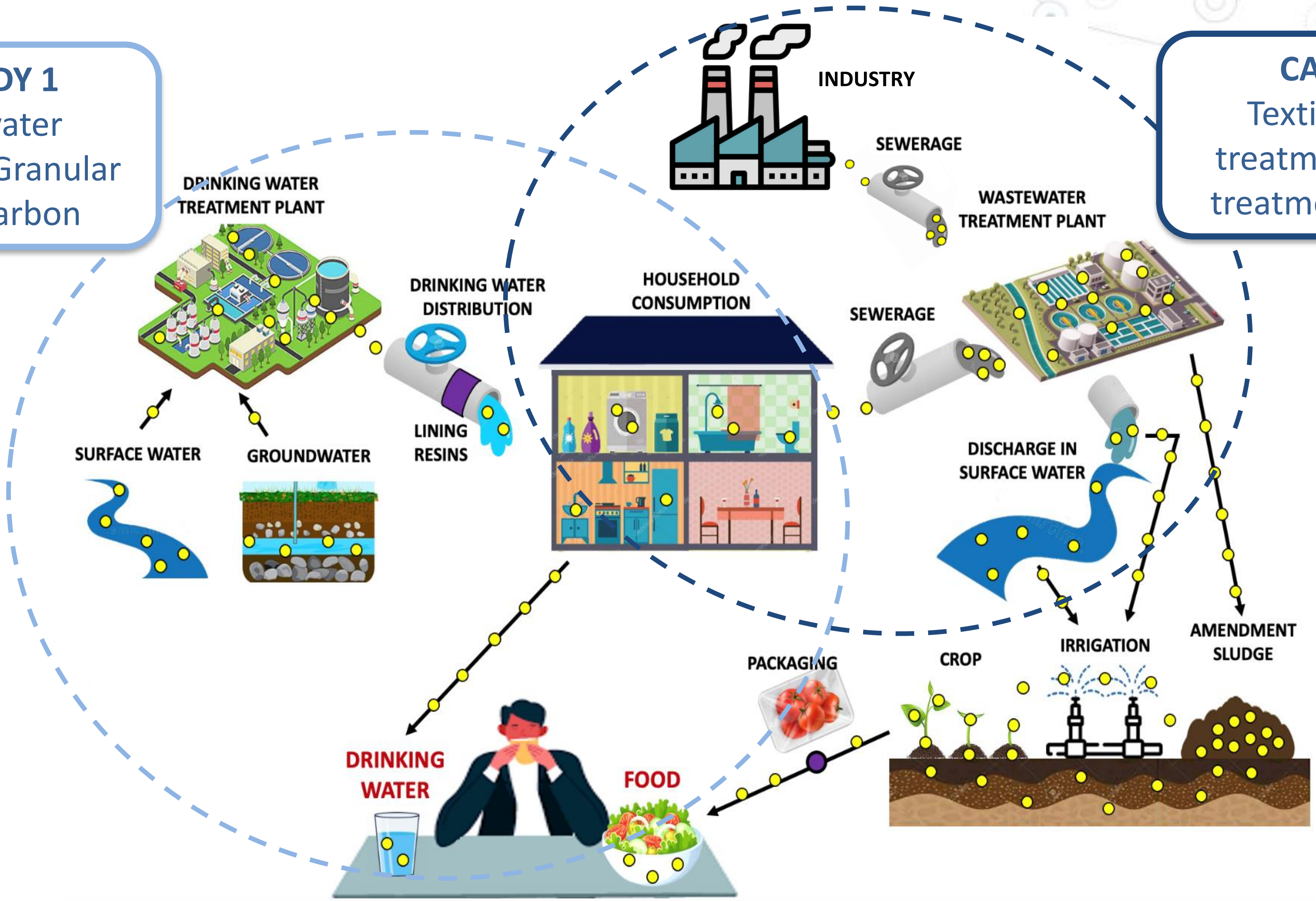
Drinking water treatment by Granular Activated Carbon

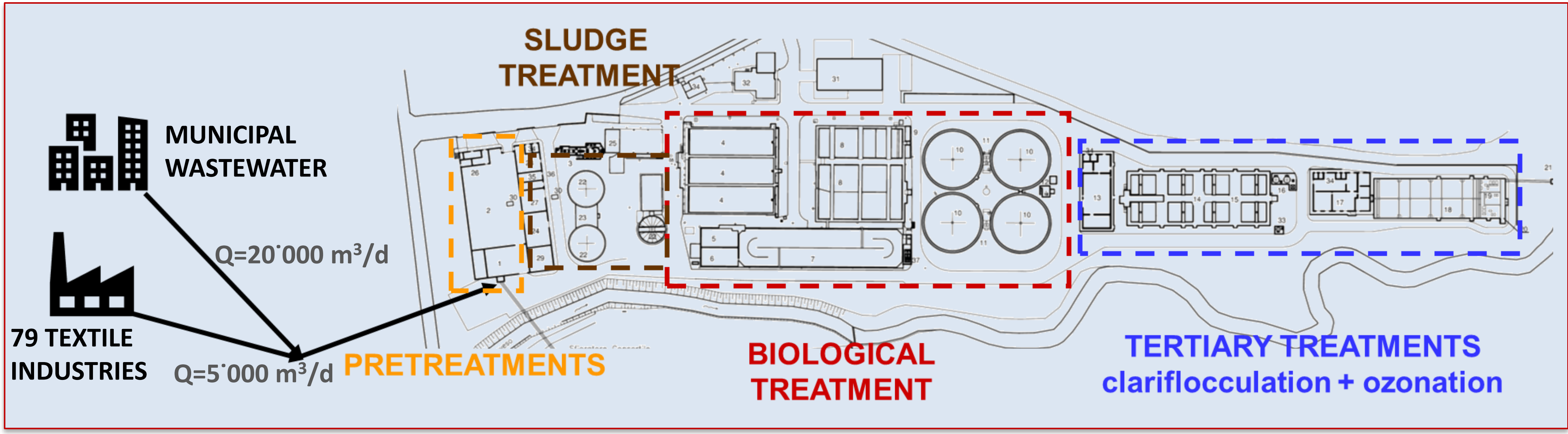
CASE STUDY 2
Textile wastewater treatment with several treatment technologies



: PFAS

CASE STUDY 2: PFAS IN TEXTILE WASTEWATER

LARIANA DEPUR

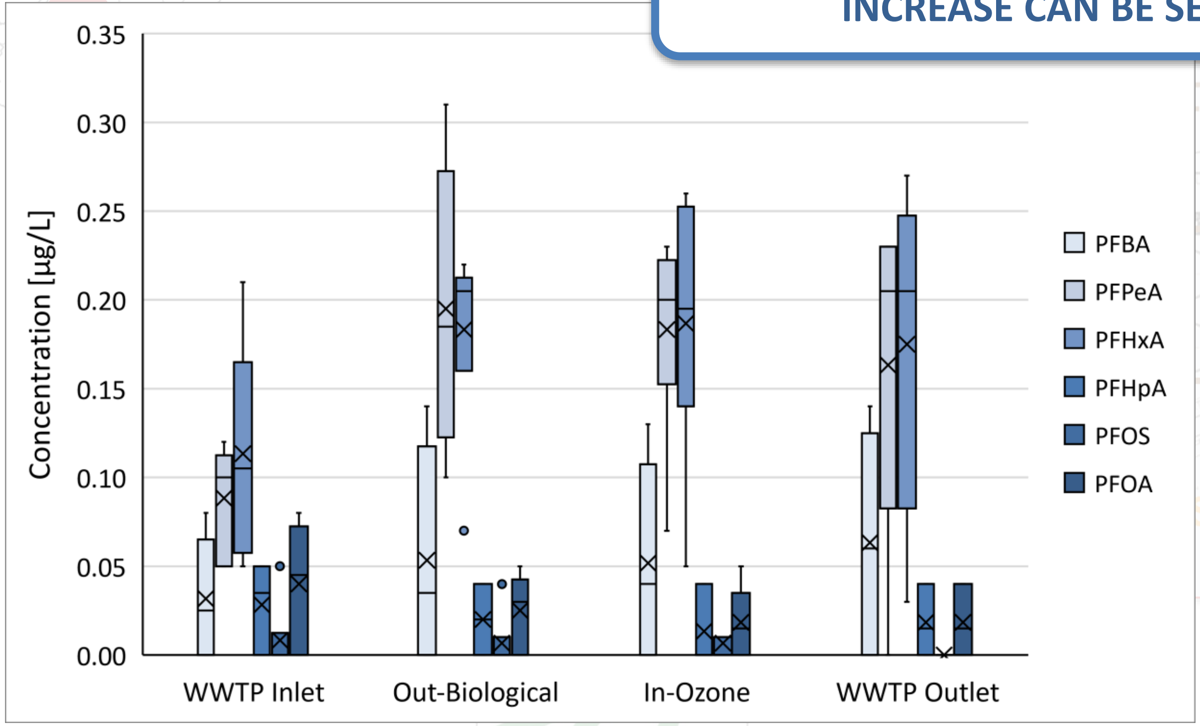


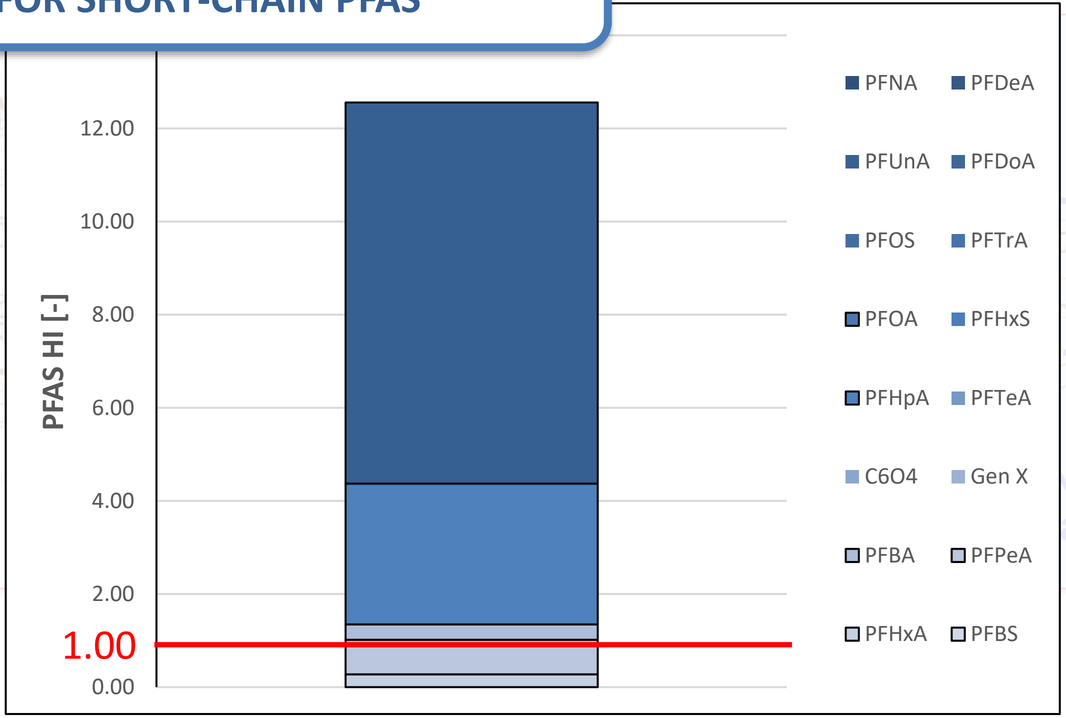
Centro Tessile Serico Sostenibile

IS THIS SYSTEM ABLE TO REDUCE PFAS DISCHARGE IN SURFACE WATER?

CASE STUDY 2: PFAS IN TEXTILE WASTEWATER

PFAS ARE NOT REMOVED BY THE WWTP AND CONCENTRATION INCREASE CAN BE SEEN FOR SHORT-CHAIN PFAS





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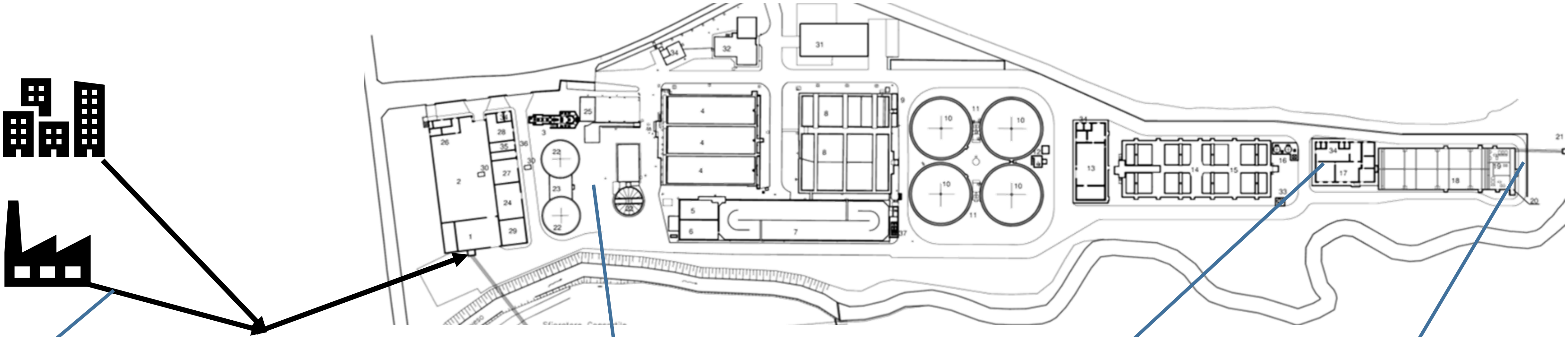


MIX TEXTILE WASTEWATERS

- Membrane separation (MF+NF)
- Adsorption on activated carbon
- Electro-coagulation (by external partner)

SLUDGE

- Anaerobic Digestion (AD)
- AD + Powder Activated Carbon

INLET OZONATION

FINAL DISCHARGE

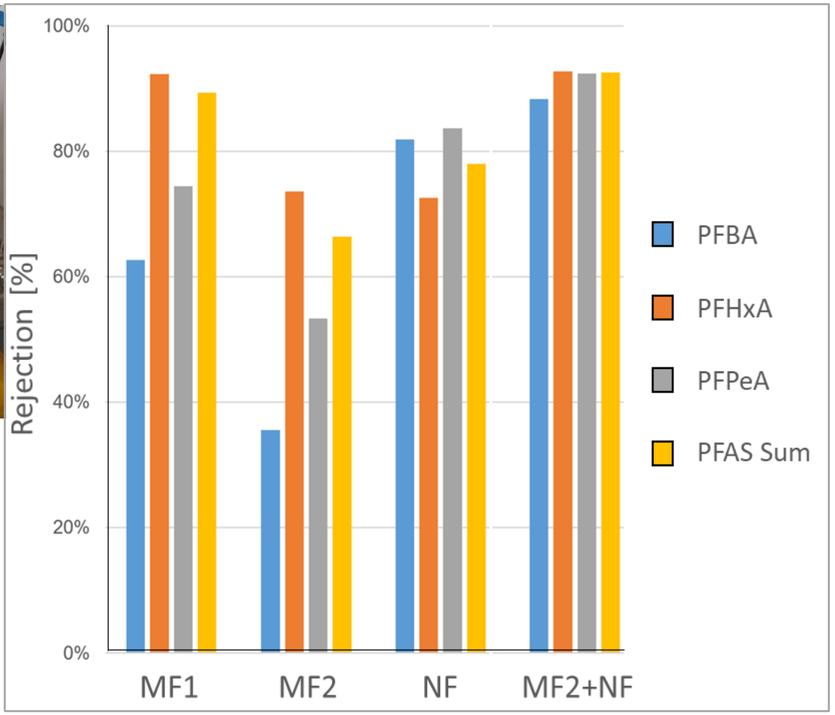
- Ozone + adsorption on activated carbon

WHERE AND HOW WE SHOULD ACT TO REDUCE PFAS DISCHARGE IN SURFACE WATER?

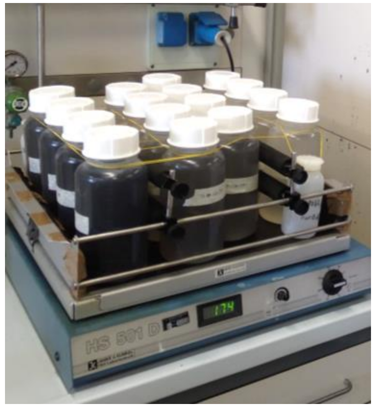
CASE STUDY 2: PFAS IN TEXTILE WASTEWATER

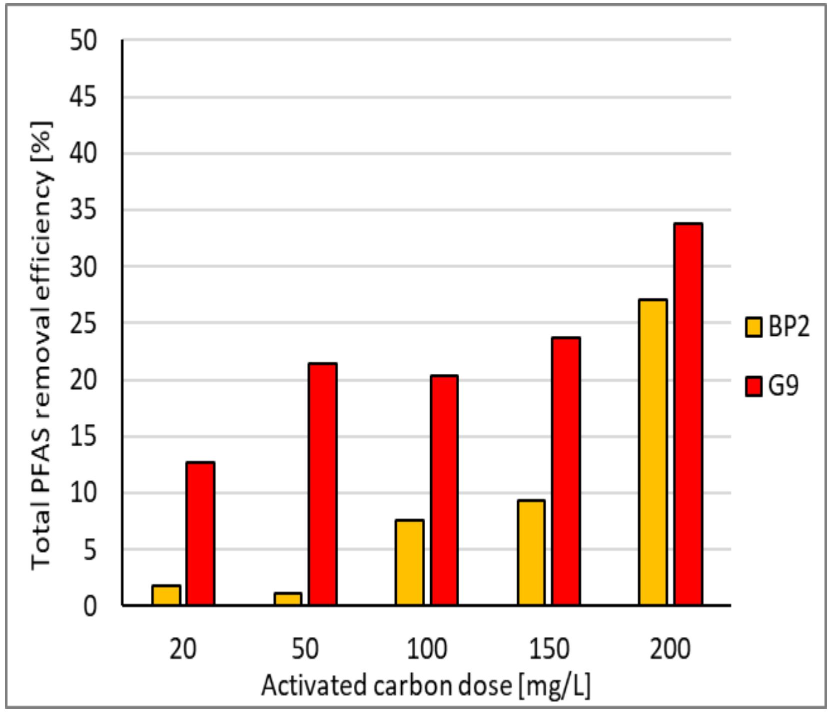
TEXTILE WASTEWATERS

Pressure-driven membrane separation

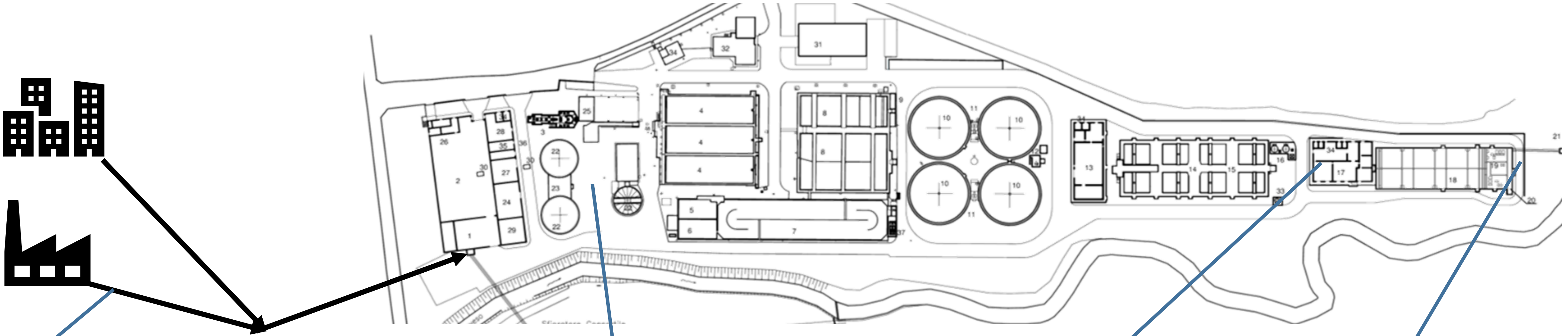


Powder activated carbon





CASE STUDY 2: PFAS IN TEXTILE WASTEWATER



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WHERE AND HOW WE SHOULD ACT TO REDUCE PFAS DISCHARGE IN SURFACE WATER?

CASE STUDY 2: PFAS IN TEXTILE WASTEWATER

Water collection at full-scale

Matrices

- WW from textile industries
- WW within the WWTP (IN-O_3 and OUT-O_3)

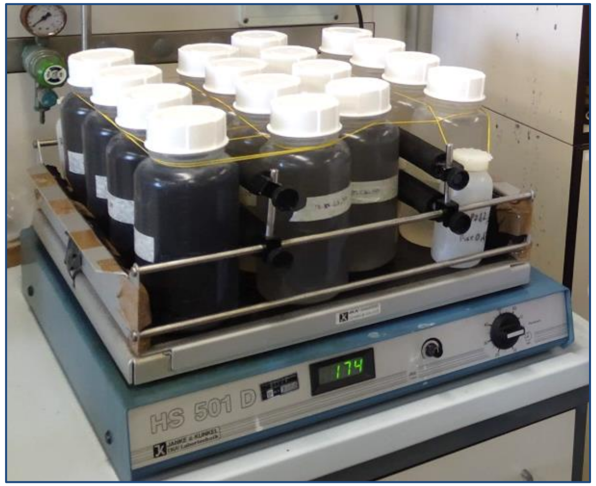
Politecnico di Milano - Environmental Engineering Lab

Adsorbent materials:

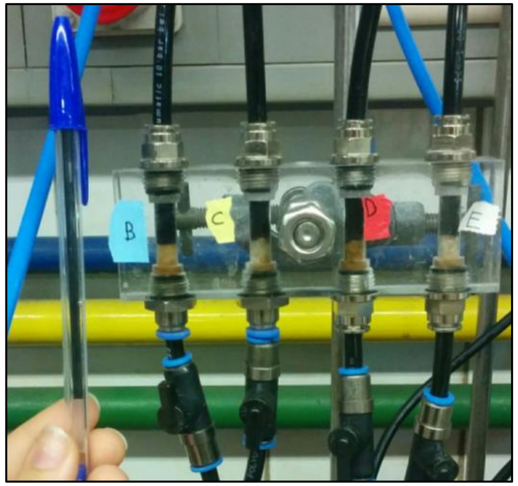
- 4 activated carbons
- 6 doses: 3 – 150 mg/L

Adsorbent	Origin	Porosity
CP1	Coconut	Micro
BP2	Bituminous	Meso
MP25	Bituminous	Meso / Macro
G9	Wood	Meso / Macro

BATCH TESTS



RSSCT TESTS



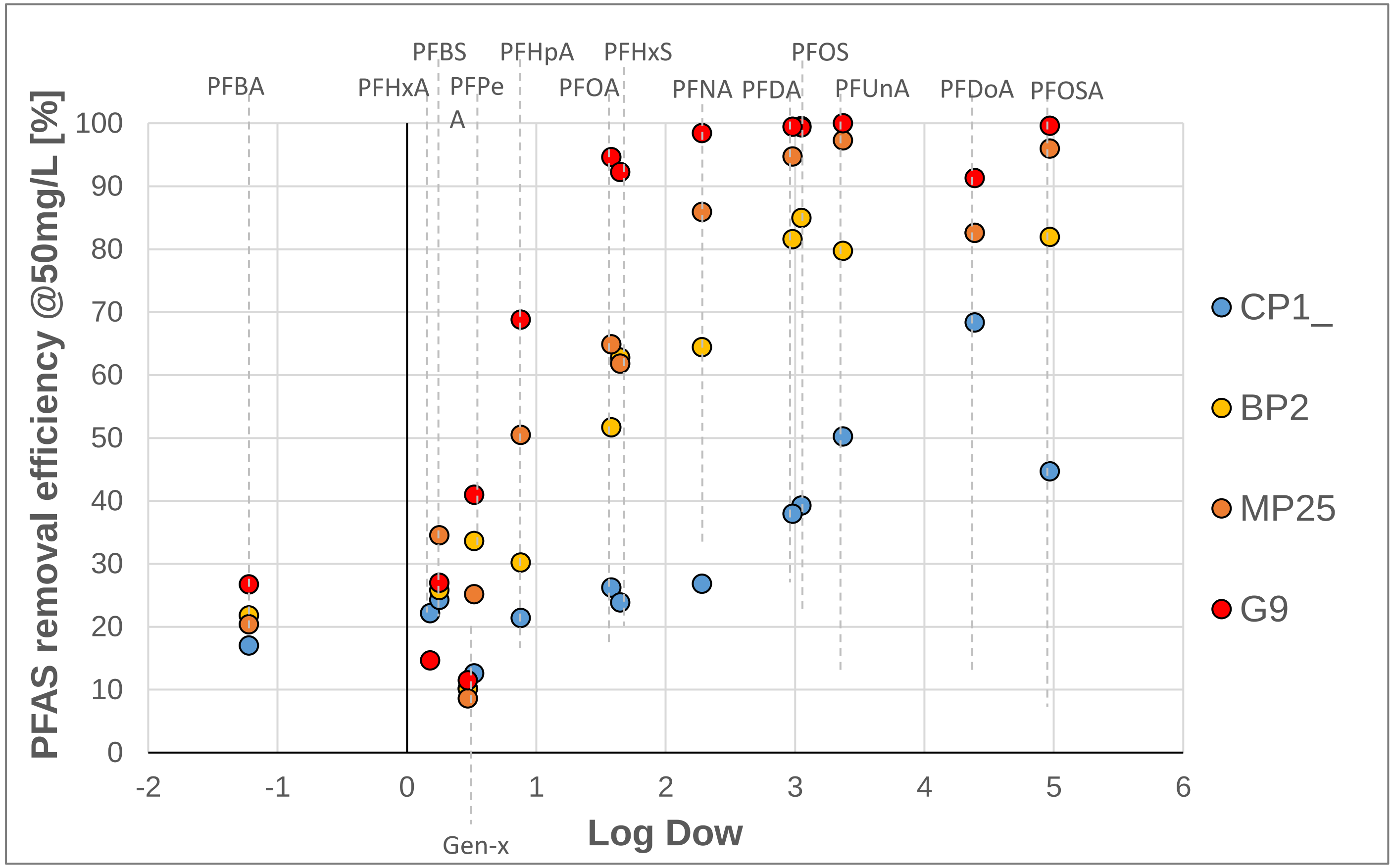
PILOT TESTS

Analyses

- 14 PFAS
- pH,conductivity
- COD
- UVA_{254}
- EEM fluorescence

CASE STUDY 2: PFAS IN TEXTILE WASTEWATER

PFAS removal in the pre-ozonation (Pre-O_3) matrix
For different adsorbent materials (@ 50 mg/L)



pH	-	7,7 ± 0,09
Conductivity	µS/cm	1332 ± 4,7
COD	mg/L	36 ± 1,2
UVA_{254}	m^{-1}	20,5 ± 0,42

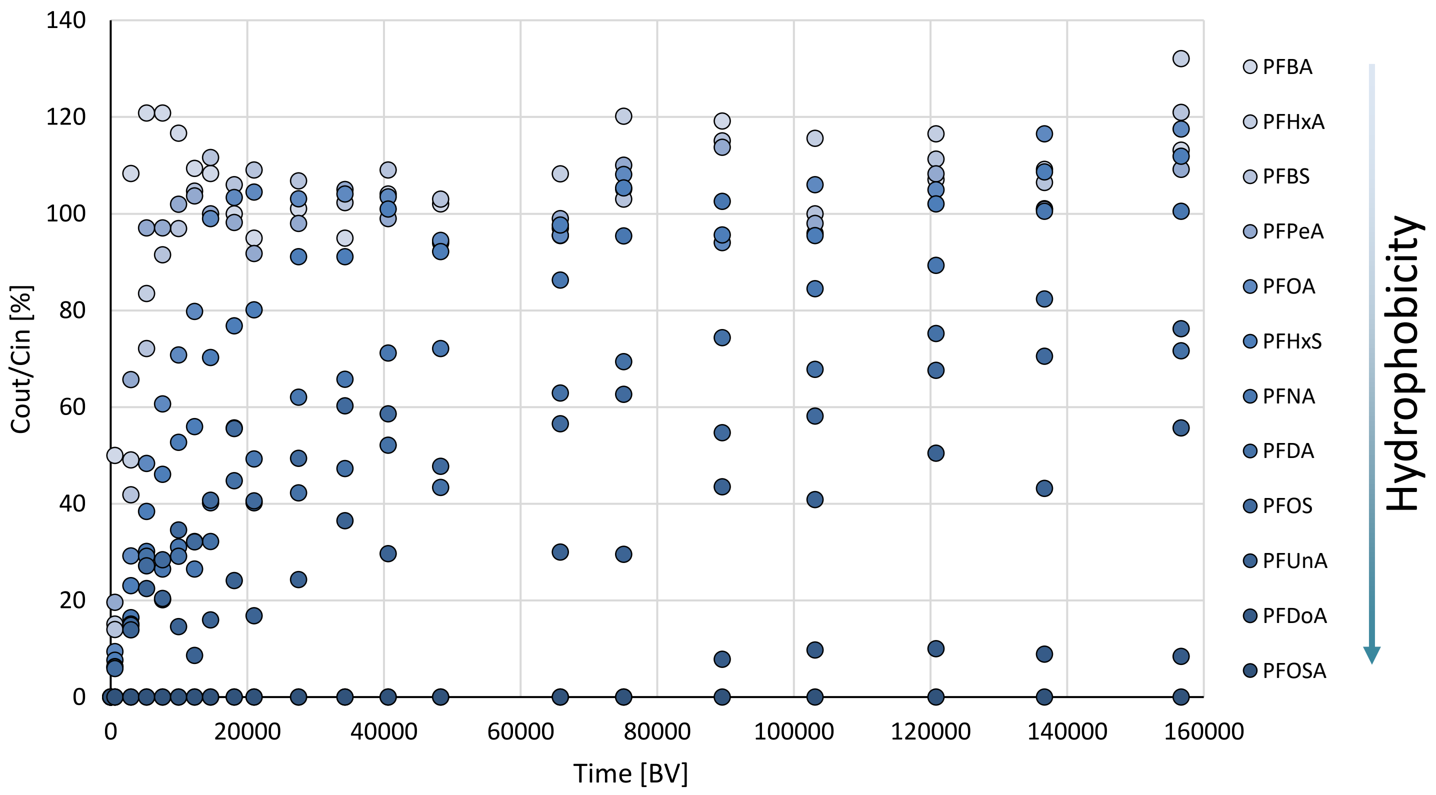
PFAS removal efficiency:

- Increases with PFAS hydrophobicity
- Hydrophilic: NS < ACs (no signif. differences)
- Hydrophobic: **NS** < **CP1** < **BP2** < **MP25** < **G9**
- Possible explanation: adsorbent surface charge → pH_{PZC}

Adsorbent	Origin	Activation	Iodin number (mg/g)	Porosity
NS	Cellulose	-	-	Micro / Nano
CP1	Coconut	Physical	1000	Micro
BP2	Bituminous	Physical	850	Meso
MP25	Bituminous	Physical	1000	Meso / Macro
G9	Wood	Physical	950	Meso / Macro

CASE STUDY 2: PFAS IN TEXTILE WASTEWATER

Breakthrough curves in test RSSCT
for 14 PFAS with MP25 activated carbon



The breakthrough slows down with PFAS hydrophobicity:

PFAS short-chain:

- 100% breakthrough at 3,000-15,000 BV
- Chromatographic effect (Cout > Cin) due to lower affinity with carbon compared to long-chain

PFAS long-chain:

- 100% breakthrough from 20,000 to >160,000 BV

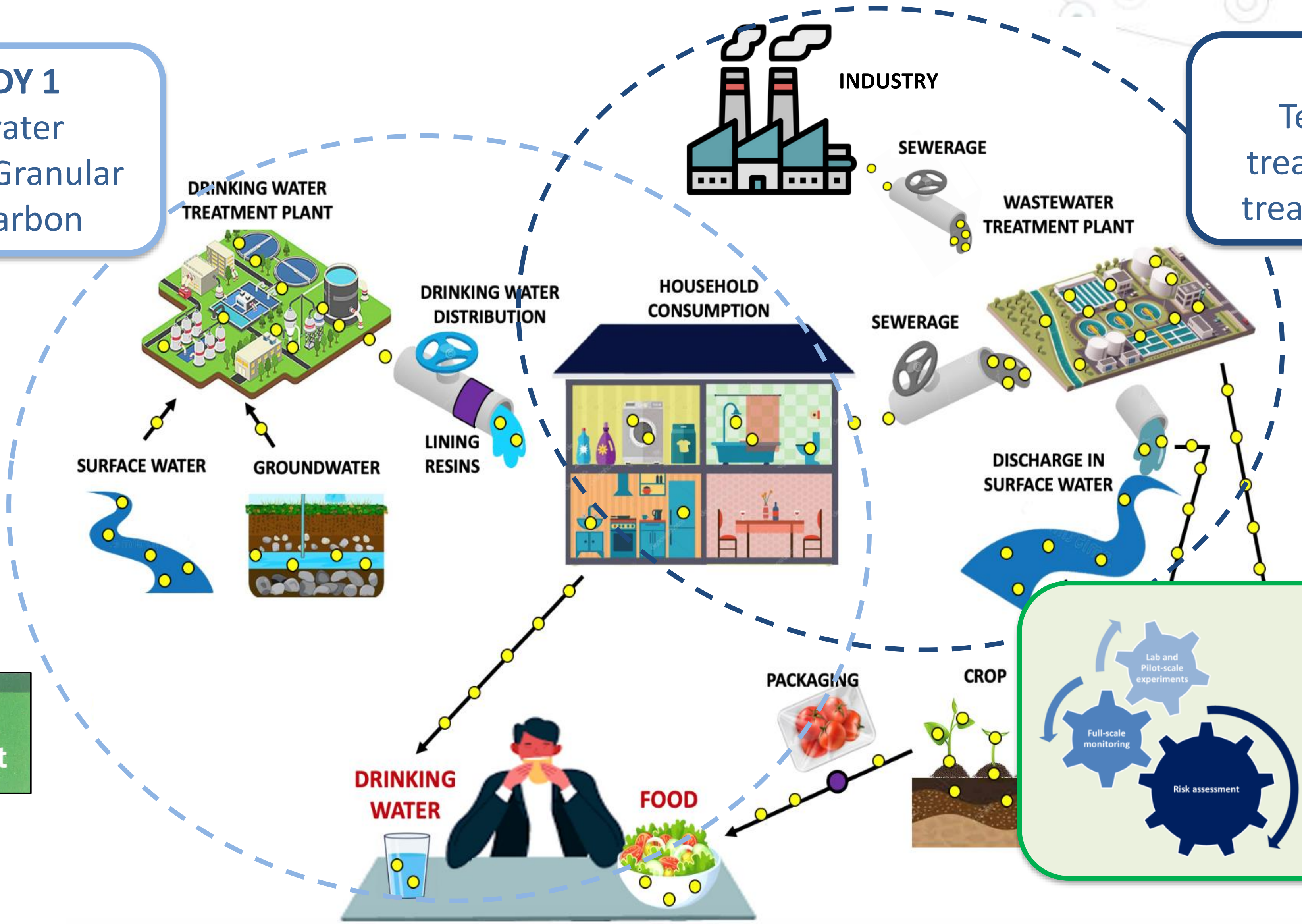
At the same chain length, sulphonated PFASs have slower perforations than carboxyl PFASs

PFAS – HOW?

Q1 Q2 Q3 Q4

CASE STUDY 1
Drinking water treatment by Granular Activated Carbon

CASE STUDY 2
Textile wastewater treatment with several treatment technologies



MM

TU berlin

Umwelt Bundesamt

LARIANA DEPUR

Centro Tessile Serico Sostenibile

EFFECTIVE TOOL TO DESIGN AND MANAGE THE WATER SYSTEM CONSIDERING THE WHOLE MIXTURE OF PFAS

● : PFAS

Presentation outline

PFAS

Q1	WHAT?	PFAS DESCRIPTION
Q2	WHY?	ENVIRONMENTAL BEHAVIOR REGULATIONS
Q3	HOW?	HOW TO MANAGE PFAS IN THE WATER CYCLE?
Q4	WHO?	WHO SHOULD SEAT AT THE PFAS ROUNDTABLE?

PFAS – WHO?

PFAS

RESEARCHERS
Analytical methods
Toxicology
Treatment processes

DECISION-MAKERS
Risk-assessment procedures
Prioritization

Technological advancement
Implementation
Limitations
WATER UTILITIES AND INDUSTRIES

Awareness
Behavioural change
SOCIETY

THANK YOU FOR YOUR ATTENTION!

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