# Fate and transport of per- and polyfluoroalkyl substances (PFAS) in the soil-groundwater system

Fritjof Fagerlund

Department of Earth Sciences, Uppsala University

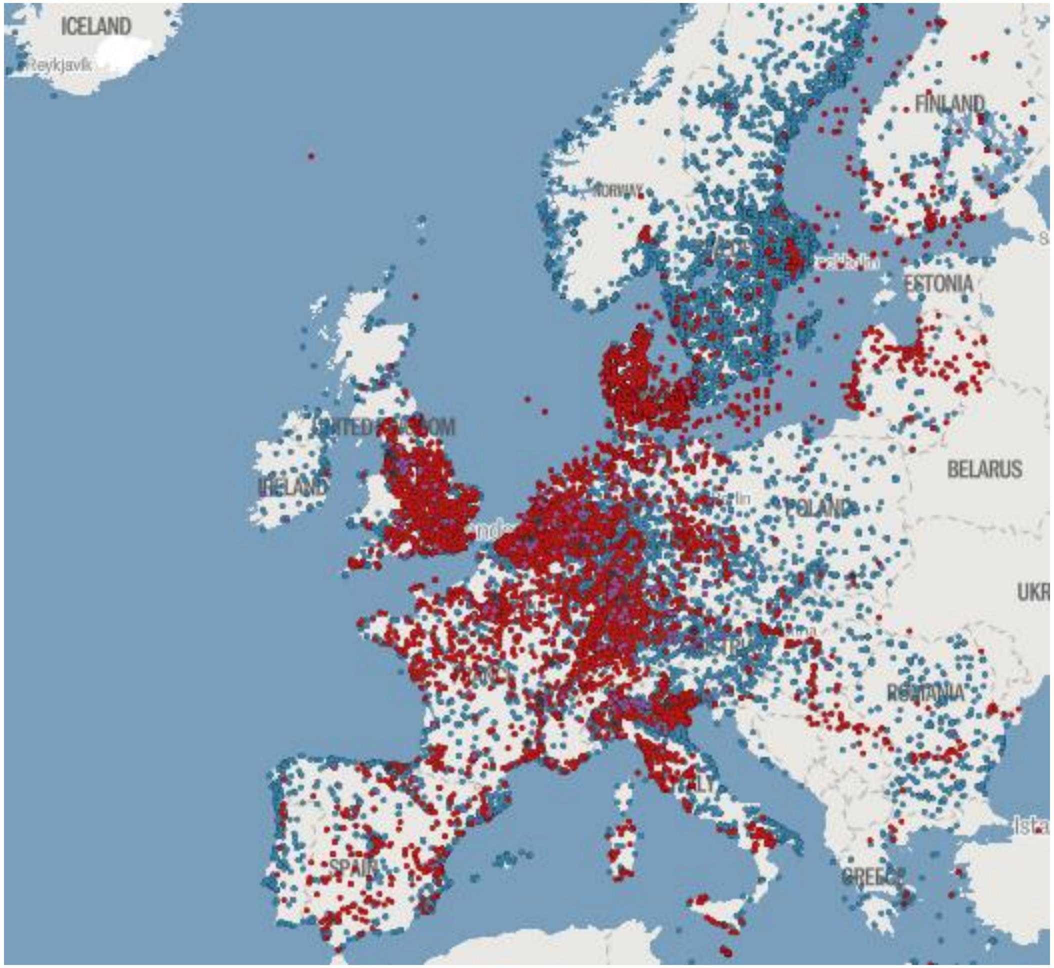
Photo: Regenesis

Photo: pixabay

Contributions from:
Georgios Niarchos (SLU), Robert Earon (SGI), Mamata Das (UU), Agnes Zuniga Ekeneberg (UU), Mason Johnson (UW), Nicola Messinger (UU), Lutz Ahrens (SLU), Dan Berggren Kleja (SLU, SGI)

# PFAS contaminated sites

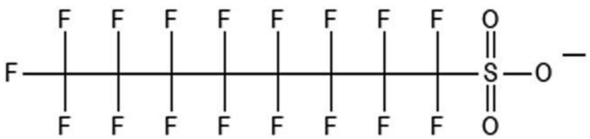
Le Monde Map of Forever Pollution in Europe



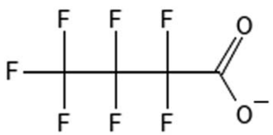

- **PFAS exist worldwide at fire training sites** and **airports** due to firefighting foams
- **Manufacturing sites** are quite few (8-12 in Europe), but bad
- Also **wastewater treatment plants, landfills** and **sludge application** to agriculture are sources for PFAS
- PFAS leach from **hotspots in soils** => **contaminate groundwater** and **surface water** resources
- Understanding PFAS **transport is essential**

# Complicated transport

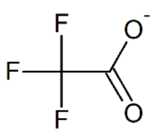
**Long chain**

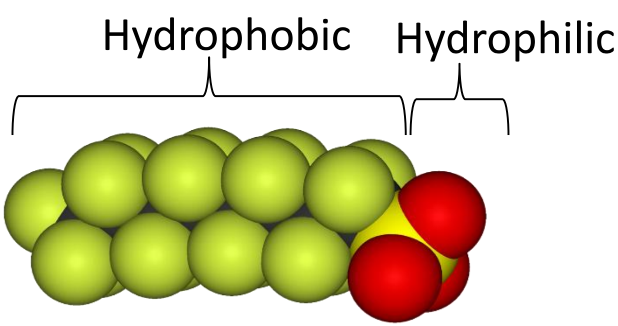


**Short chain**

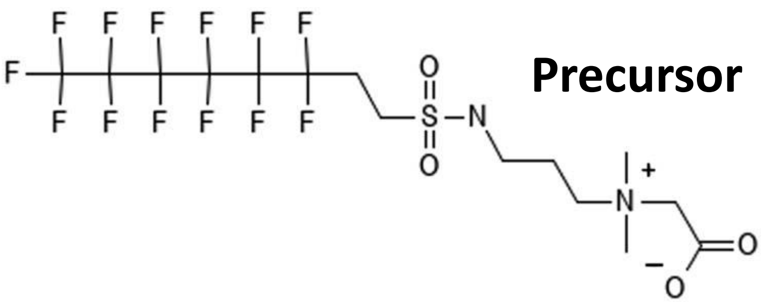


**Ultra short**



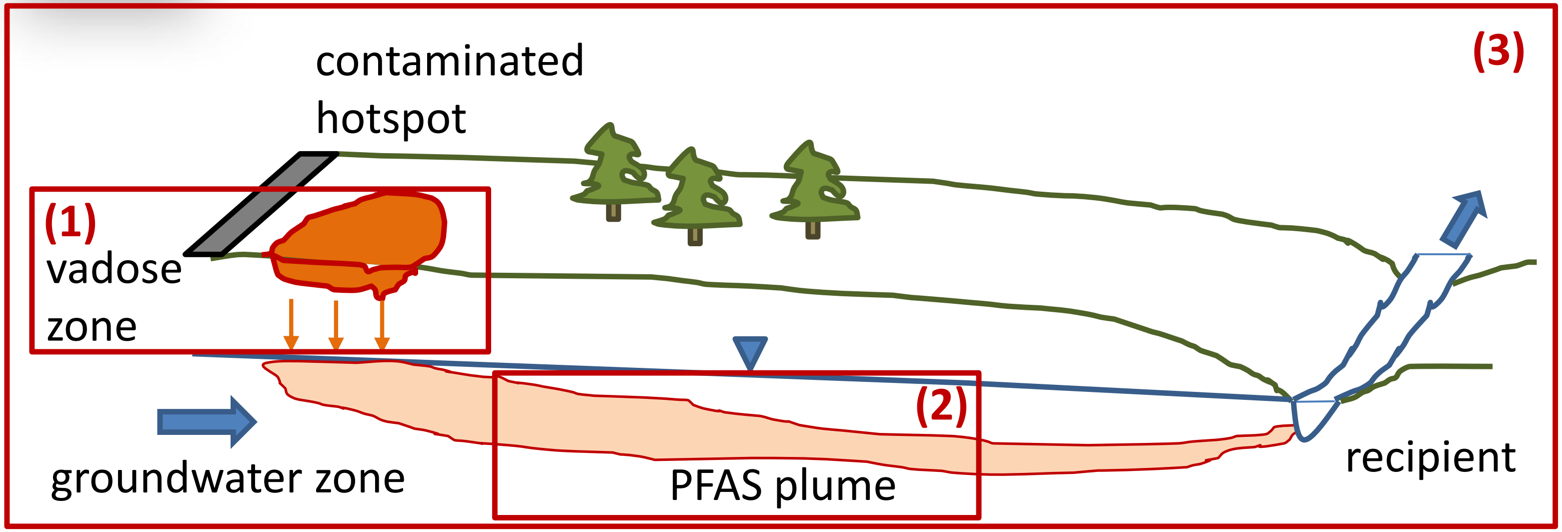



- > 10 000 PFAS
- Different characteristics:
  - length
  - functional group
  - charge
  - precursors etc.
- Many are surfactants
- Perfluoro-substances are extremely persistent



**Precursor**

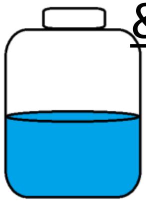
# PFAS fate and transport in the soil-groundwater system




1. Vadose zone:
    - adsorption of PFAS to air-water interfaces
    - transformation of precursors, competition effects, heterogeneity
2. Groundwater zone
    - Many PFAS with different transport properties, incl. precursors
    - complex sorption and competition for sorption sites
    - effects of DOC, heterogeneity
3. PFAS spreading at from source to recipient (watershed scale)

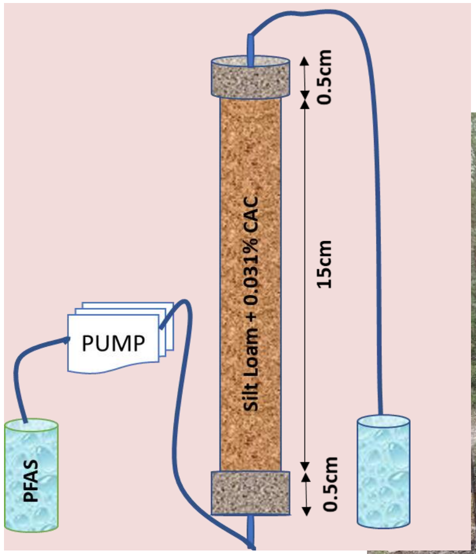
# Investigations at different scales

Batch experiments & incubations



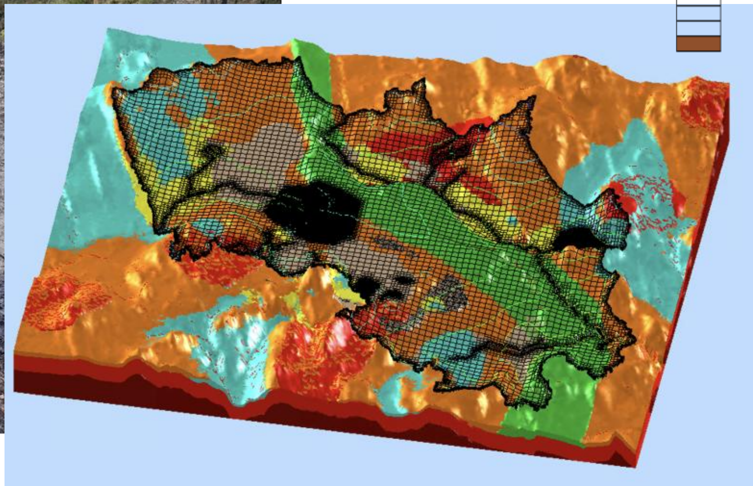
- Experimental and modelling studies over multiple scales are used to improve understanding of PFAS fate & transport processes

Columns

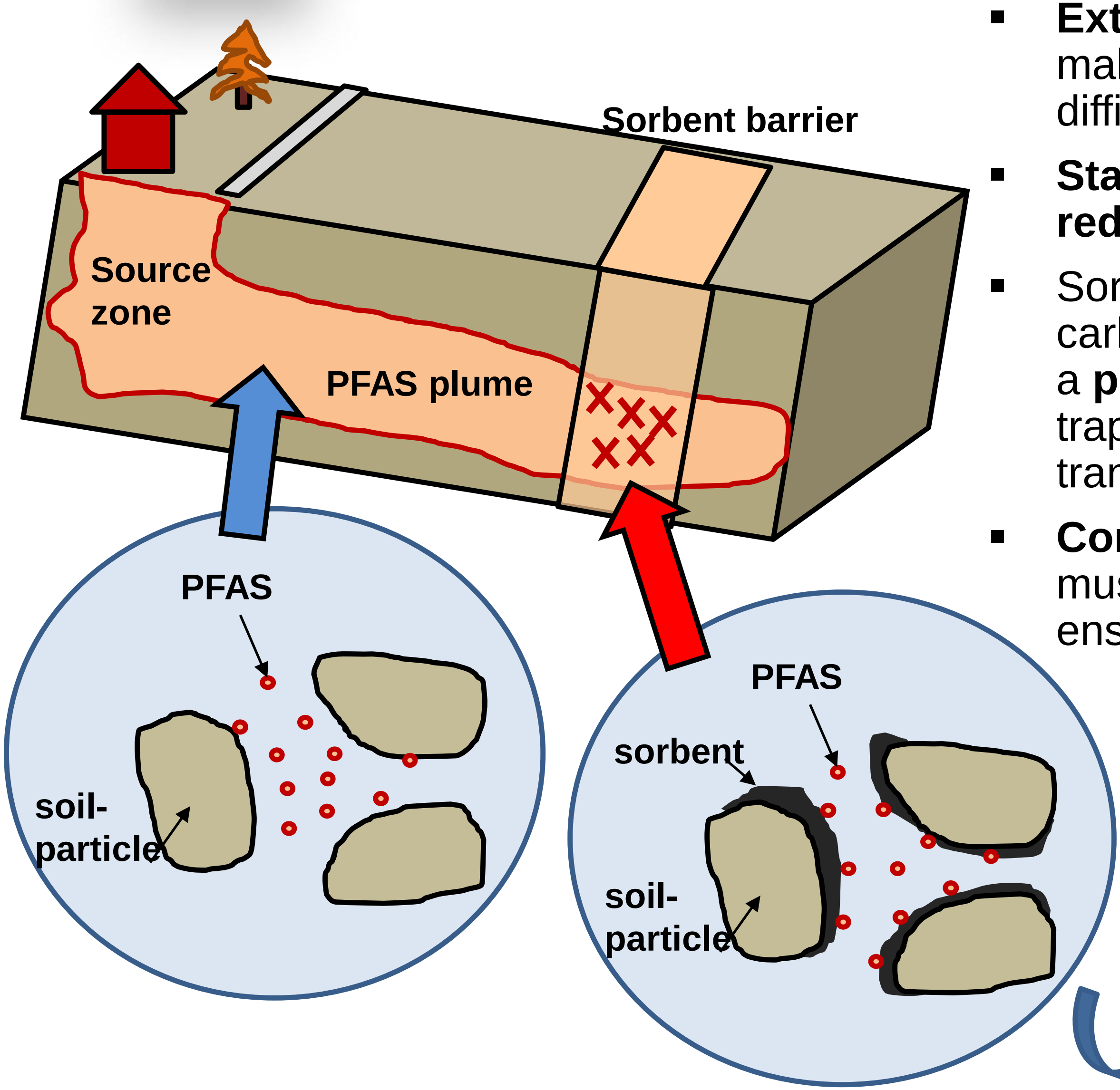



Pilot-scale filed studies

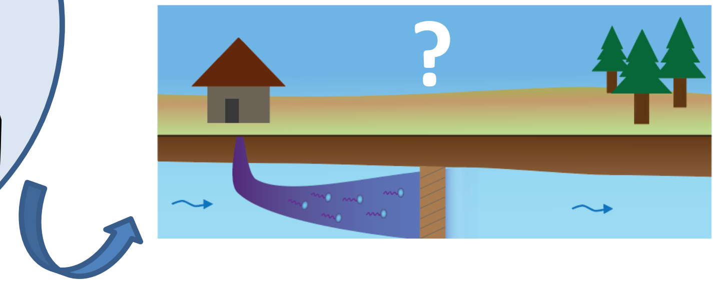
Small- and large scale modelling

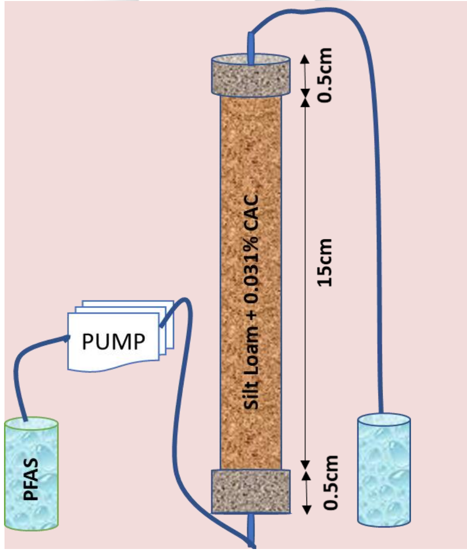


# Stabilization of PFASs using sorbents




- **Extreme persistence of PFAS** makes destructive methods very difficult
- **Stabilization** is an alternative that **reduces spreading from hotspots**
- Sorbents such as colloidal activated carbon (CAC) can be injected to form a **permeable reactive barrier**, trapping PFAS & slowing down the transport
- **Complex sorption behavior** of PFAS must be understood to predict and ensure **long term functioning**

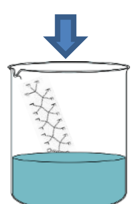


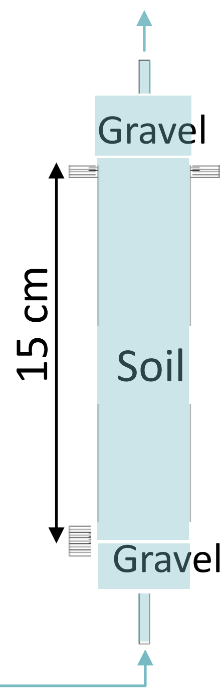


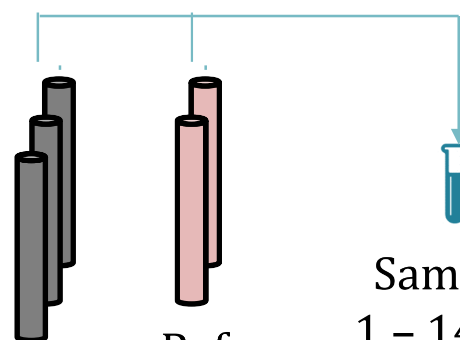

# Column experiments with colloidal activated carbon (CAC)

- Flow and breakthrough of PFAS in soils with CAC
- Artifial groundwater with spiked PFAS
- Artifial groundwater with spiked PFAS & DOC
- Real groundwater from contaminated site
- Soils with different CAC contents & reference soil

- PFAS-spiked artifical groundwater
- Real PFAS-cont. groundw.
- Added DOC



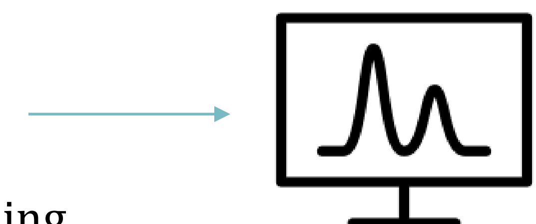


Soil + CAC
0.031%
0.10%
0.15%

Ref. soil

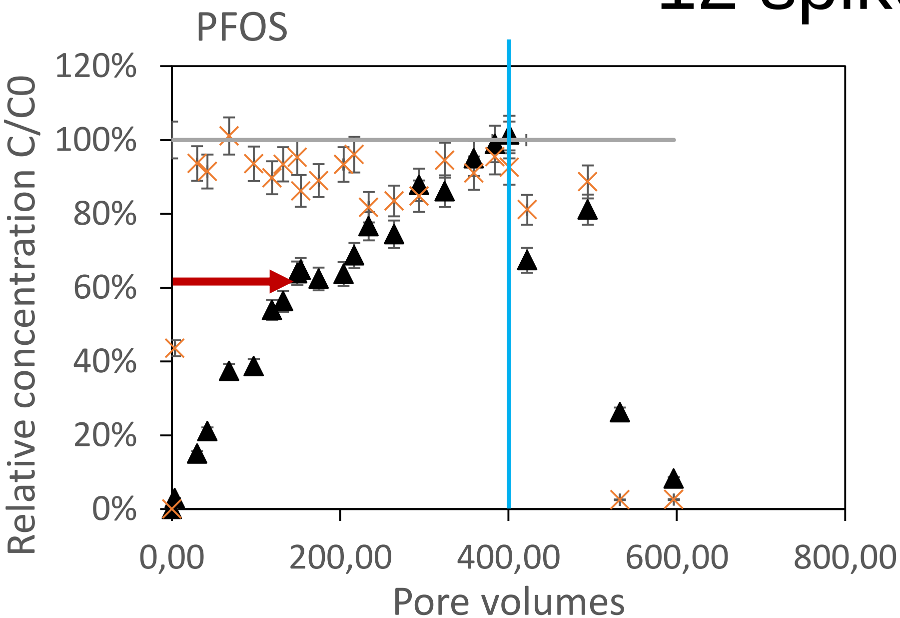
Sampling
1 – 14 days
intervals
total
duration up
6 months

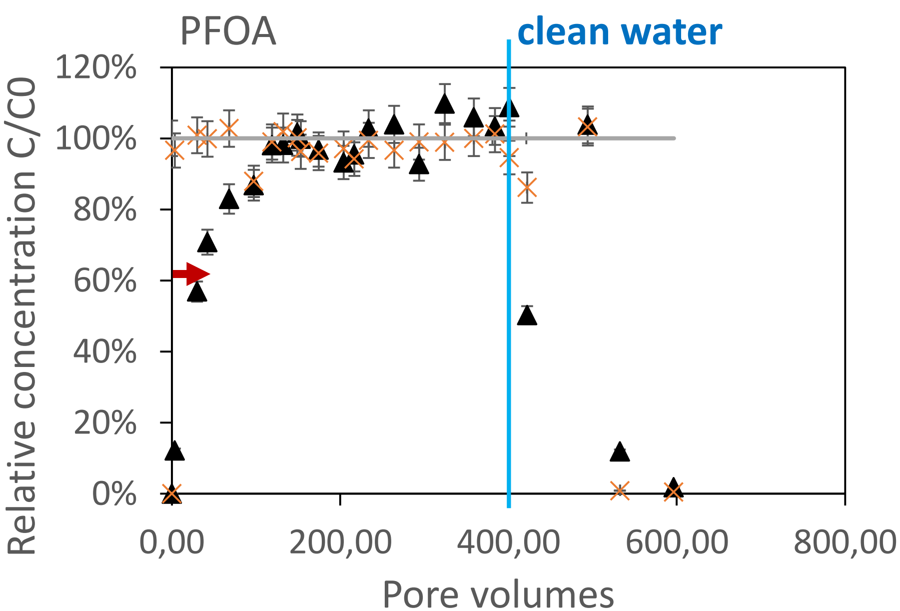


UHPLC-MS/MS

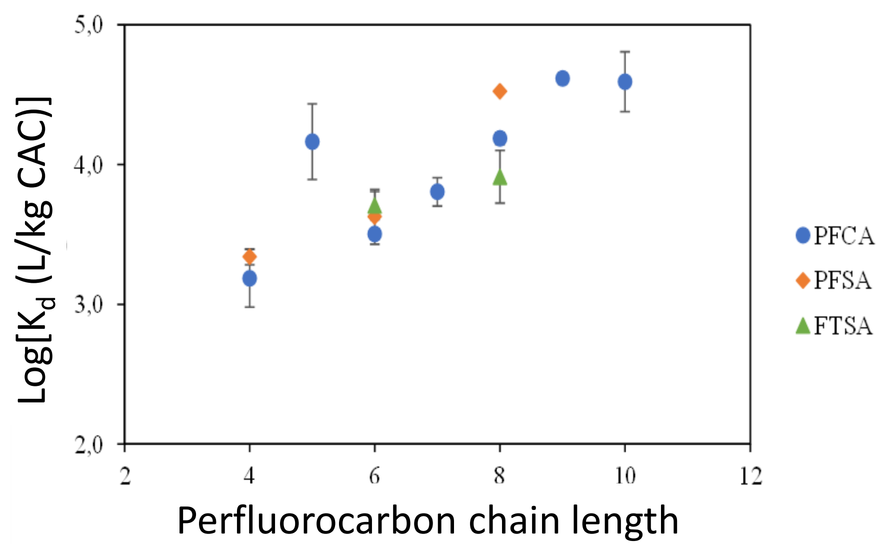
Niarchos et al., 2022. *Environmental Pollution* 308, 119667
Niarchos et al., 2025, *Submitted*
New experiments *in progress*

# 12 spiked PFAS, 0.031% CAC



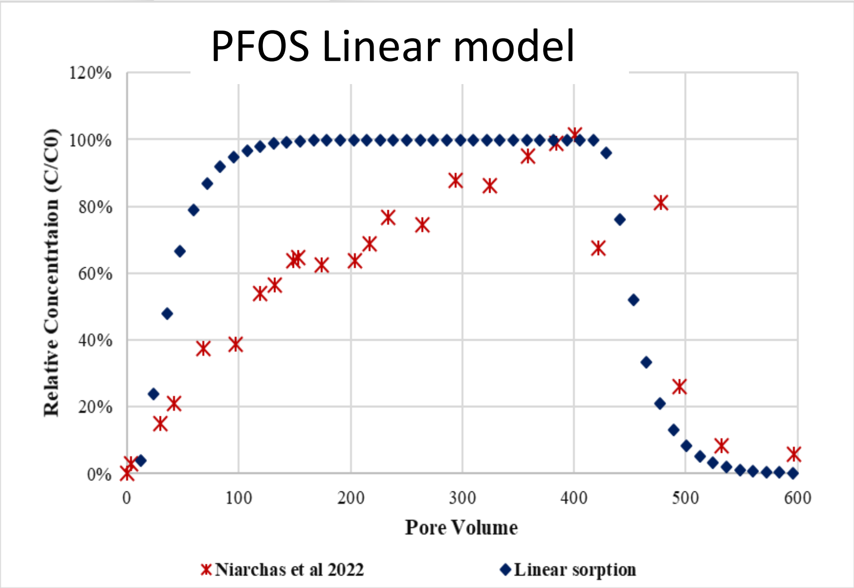




- Breakthrough with & without CAC for 12 different PFAS
- Retardation & linear Kd determined by comparing with ideal tracer
- Kd for CAC ~1000 to 60 000 L/kg for studied PFAS
- Kd increases with longer CF-chain
- Non-ideal breakthrough for many PFAS

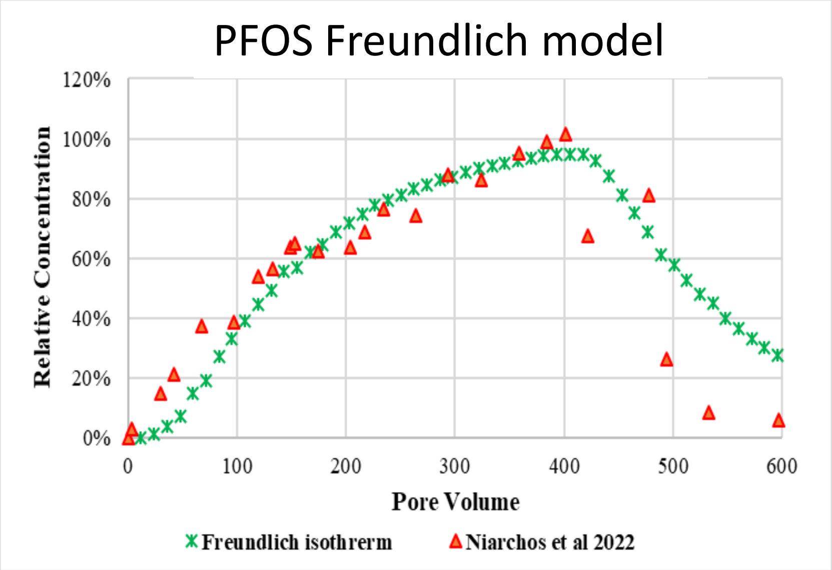


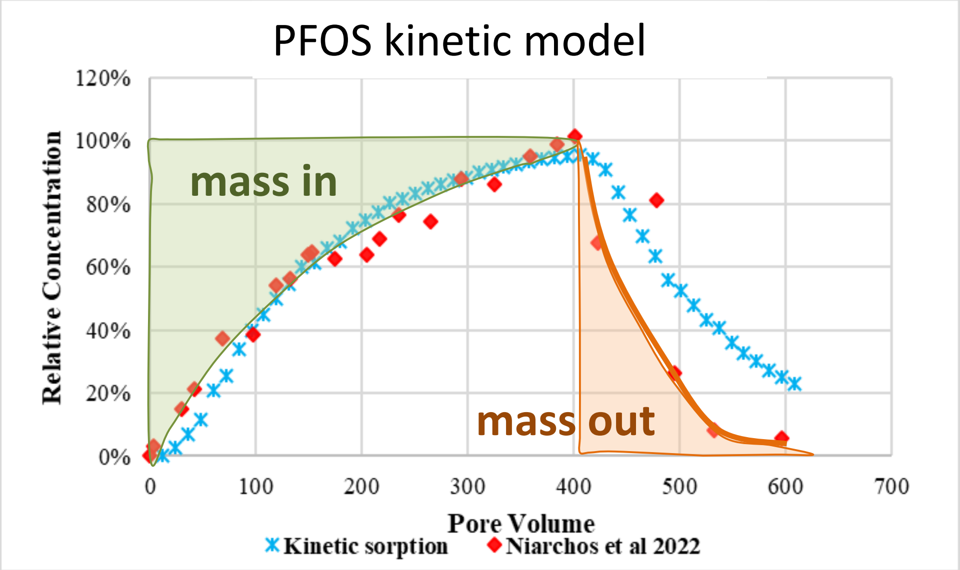
# Modelling with different sorption isotherms

UPPSALA UNIVERSITET



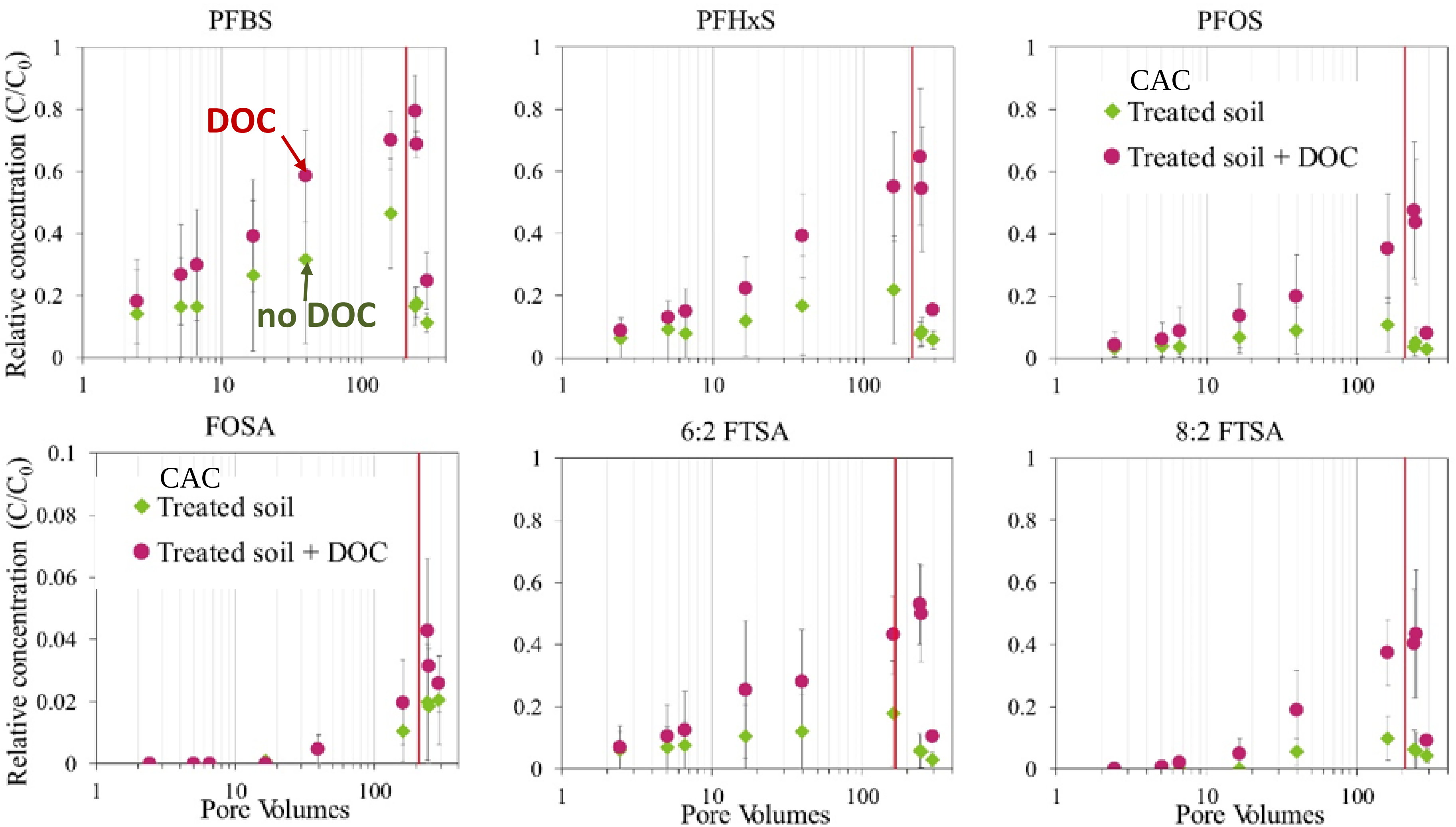

- Linear model cannot capture breakthrough in CAC-amended soil
- Both Freundlich and kinetic model capture sorption phase well
- Mass in > mass out => desorption is overpredicted for some PFAS
  - partly irreversible sorption?
  - slow desorption kinetics?



# Artificial groundwater with DOC in CAC-amended soil

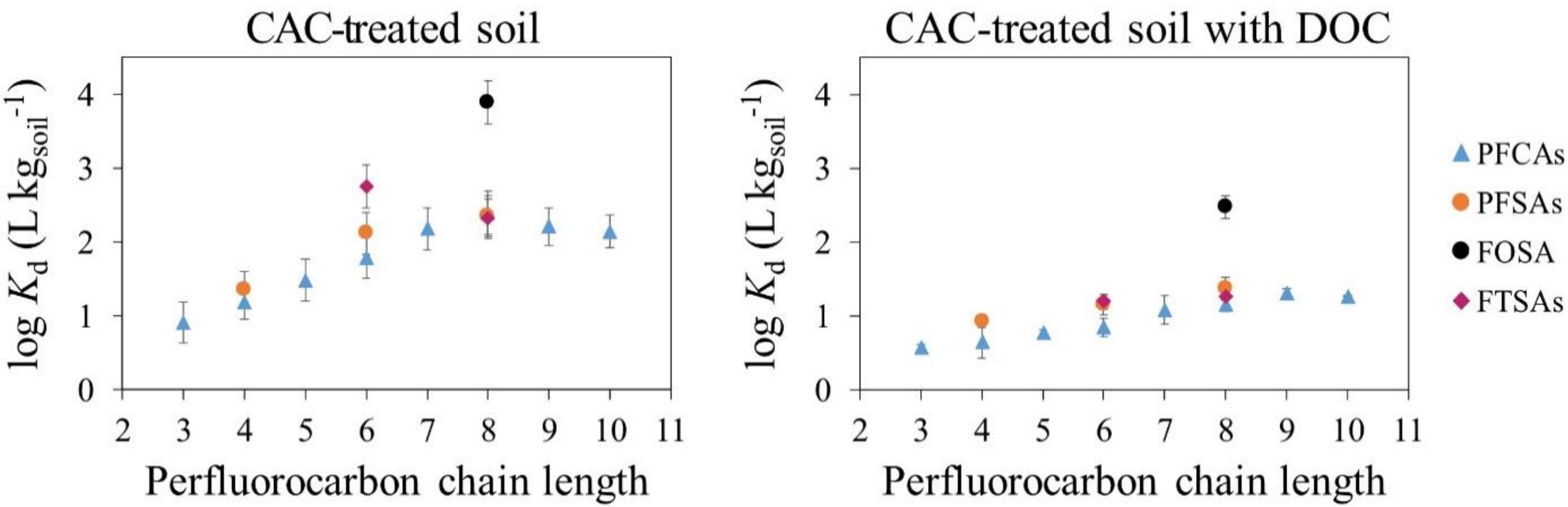
- Sorption & breakthrough is strongly affected by DOC in the water
  => **Less sorption with DOC**




Niarchos et al., 2025. Submitted to *Environmental Pollution*

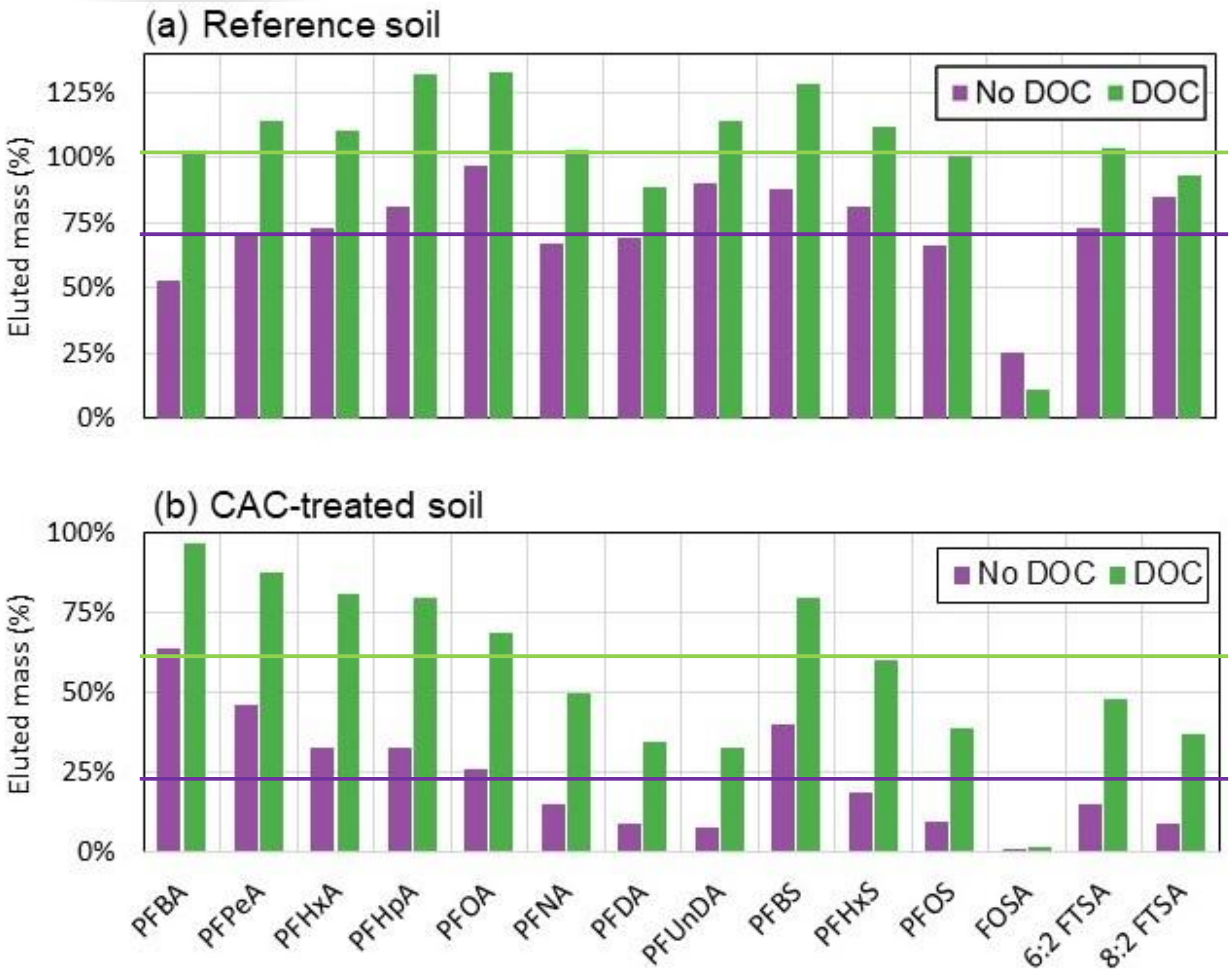
# Effect of DOC on Kd-values

- Soil with 0.1% by weight CAC – realistic for field application
- 20 mg/L Suwannee River fulvic acid => 10 mg/L DOC – high concentration
- Without DOC in water, soil Kd ~10 L/kg (PFBA) to couple 100s (PFOS, PFNA)
- With DOC, Kd decreases by an order of magnitude
    - Large effect on CAC-barrier performance




Niarchos et al., 2025. Submitted to *Environmental Pollution*

# Effect of DOC on eluted mass




Niarchos et al., 2025. Submitted to *Environmental Pollution*

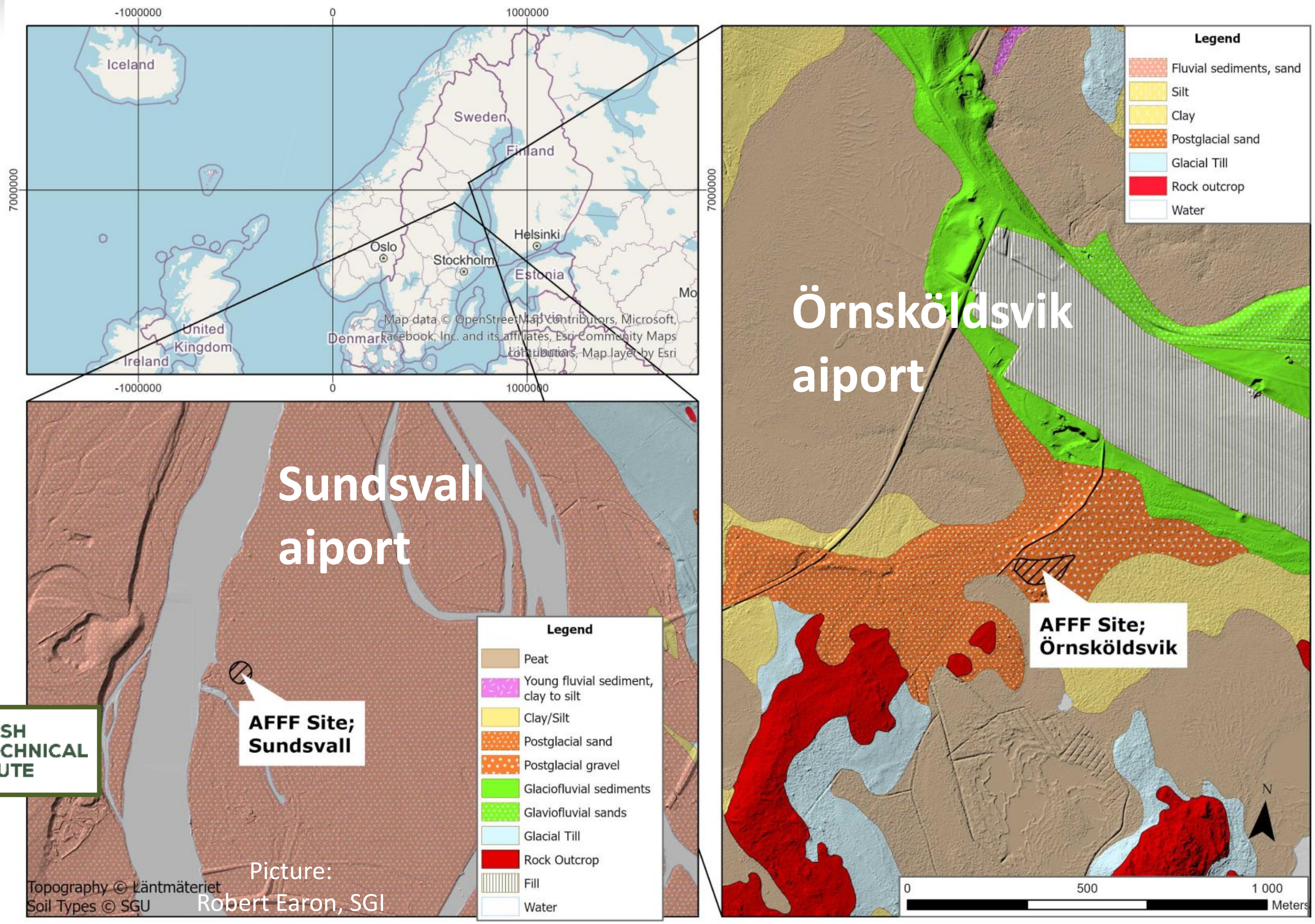
- Eluted compared to injected mass shows the amount of PFAS trapped in the columns
- More PFAS is trapped in CAC-amended soil
- DOC strongly reduces the amount of long-term trapping in both soils

# Conclusions, column experiments with CAC

- CAC significantly retards PFAS transport
- Sorption is nonlinear
  - Freundlich & kinetic models work well but may overestimate desorption
- Part of the sorption is irreversible or has very slow desorption kinetics
- DOC in groundwater can significantly reduce both PFAS retardation and long-term trapping in CAC-amended soil

# Pilot-scale field tests with sorbents for PFAS immobilisation

- Two airport sites in Northern Sweden
- Detailed collection of field data to understand fate and transport
- Tests run by Swedish Geotechnical Institute & Geological Survey




UPPSALA UNIVERSITET

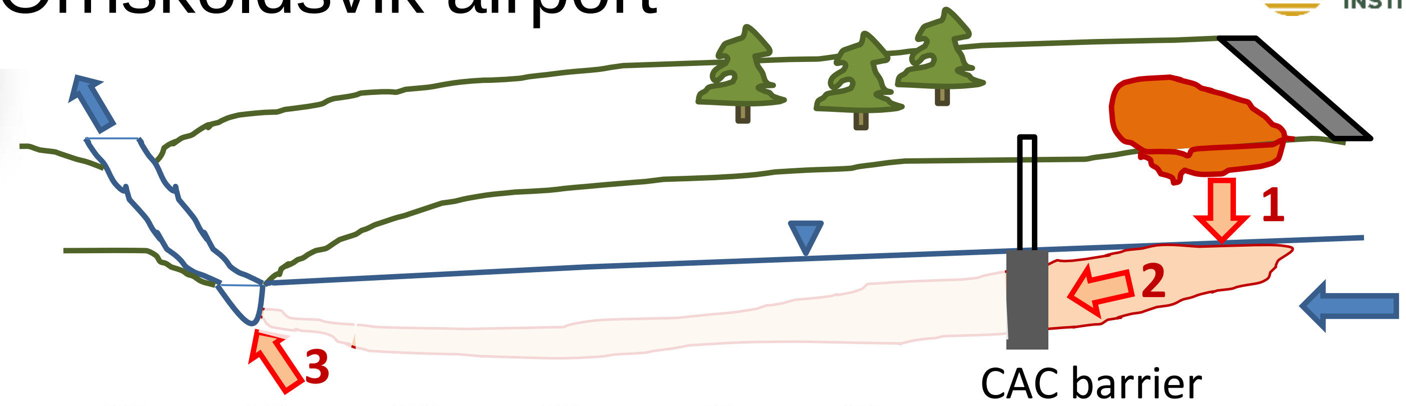
SWEDISH GEOTECHNICAL INSTITUTE

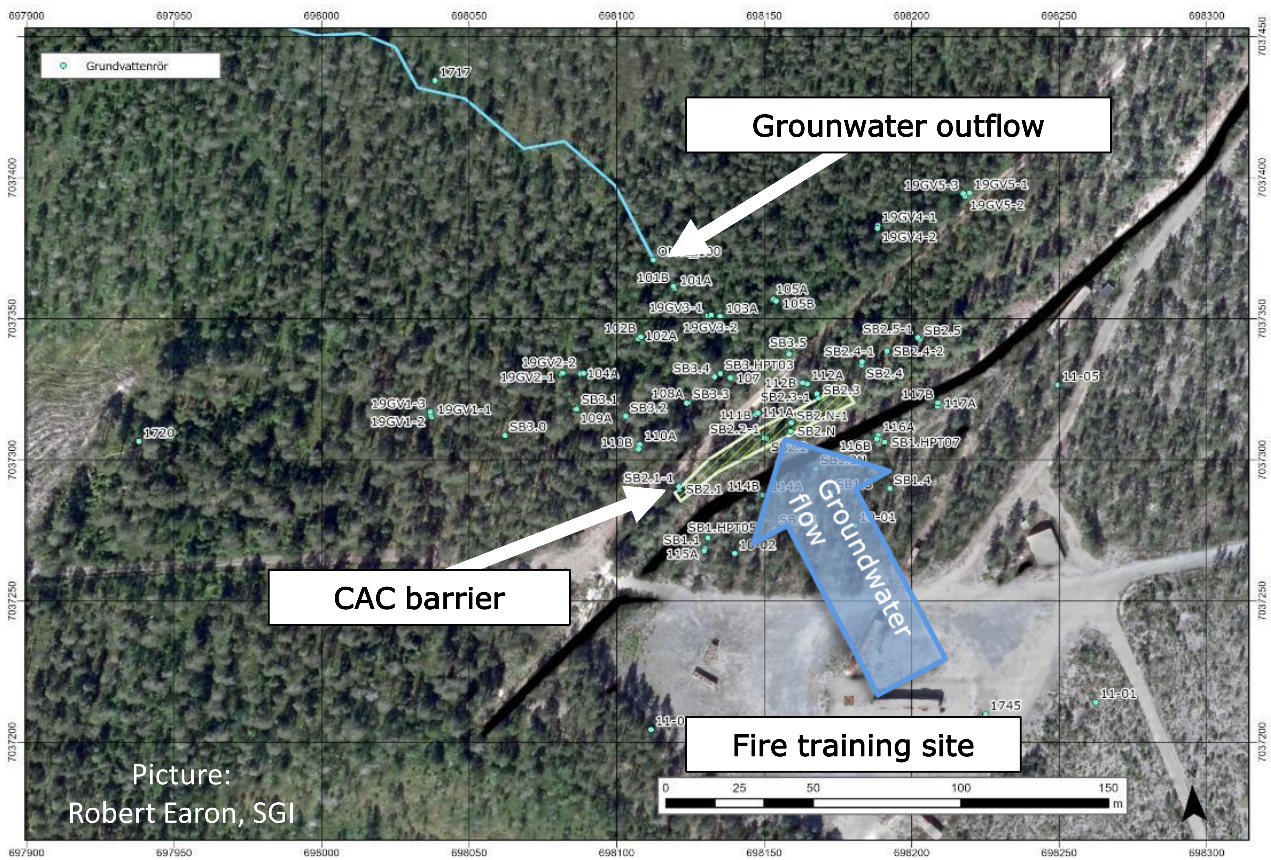
SGU Sveriges geologiska undersökning

# Pilot test with CAC barrier at Örnsköldsvik airport

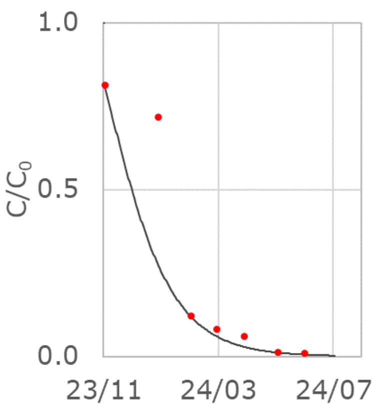
UPPSALA UNIVERSITET

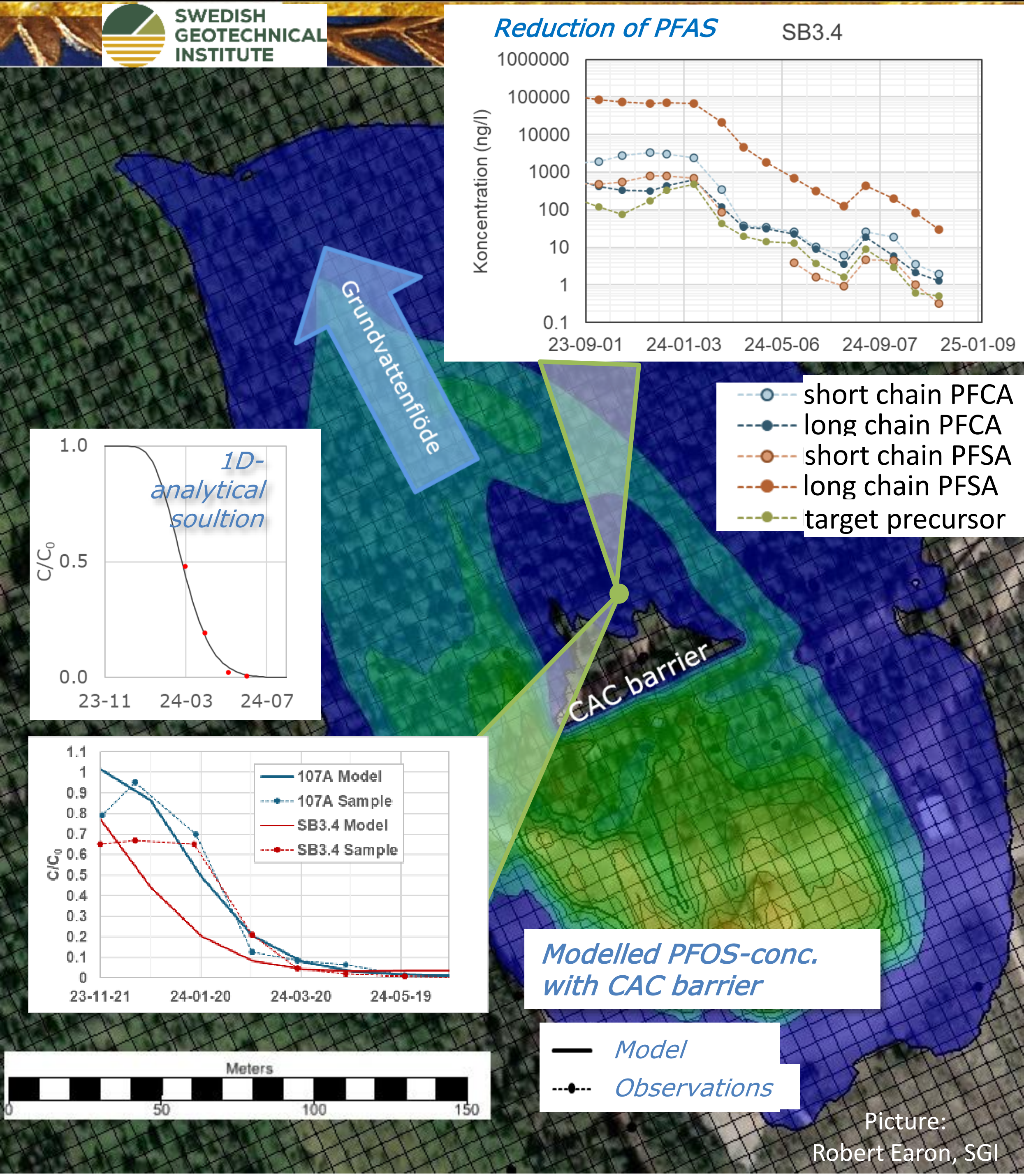
SWEDISH GEOTECHNICAL INSTITUTE




- A pilot-scale CAC barrier was injected Sep-Nov 2023
- Downstream the barrier PFAS conc. are decreasing

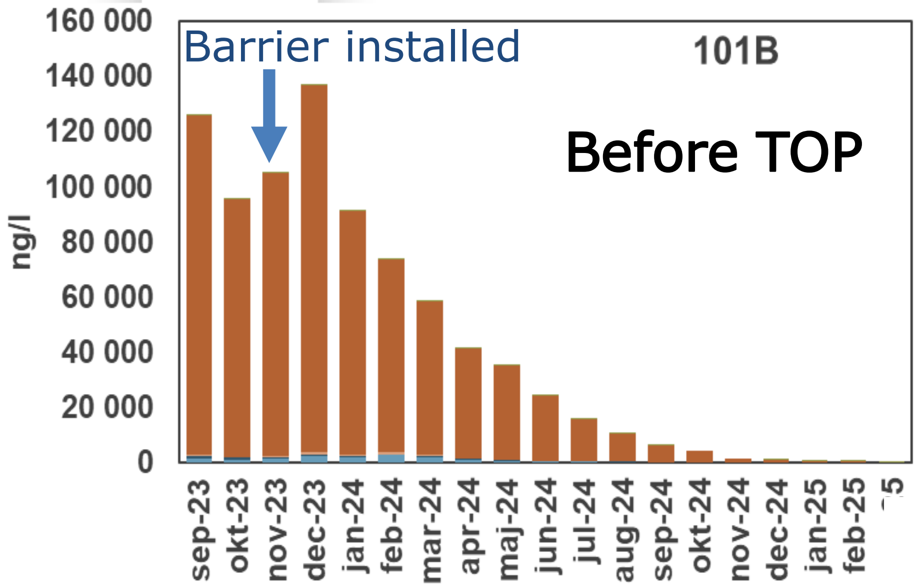


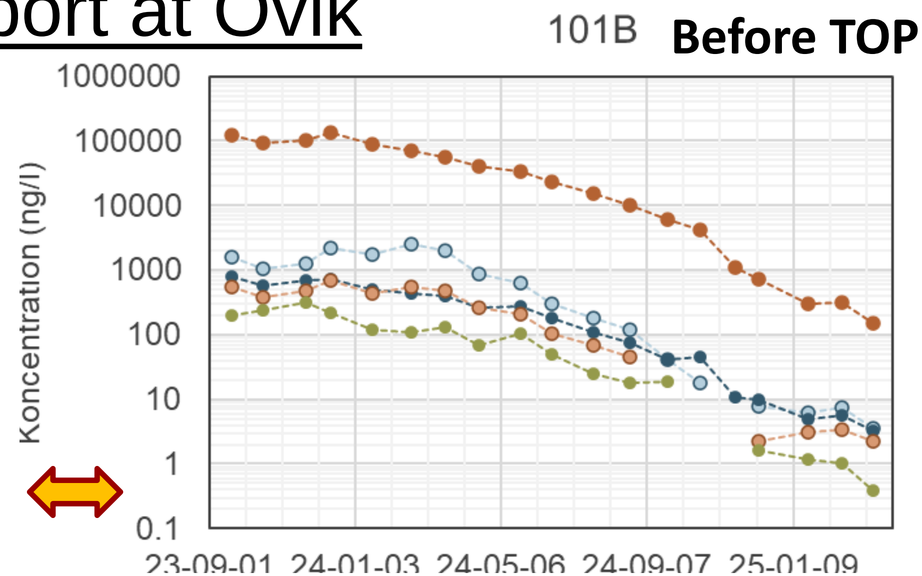


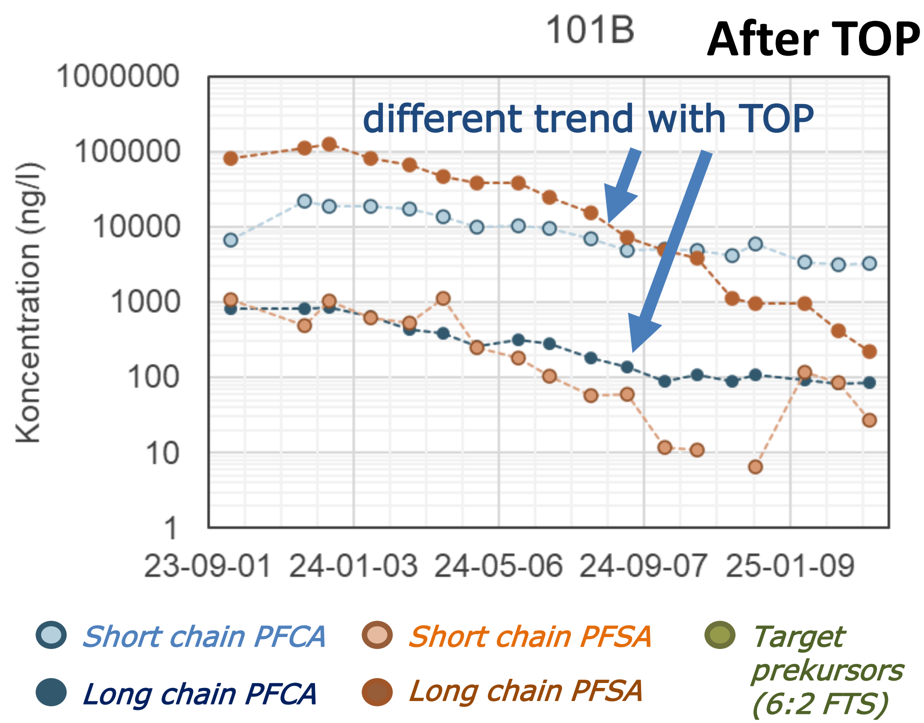

# Modelling the effect of the barrier

- Modelling is useful for understanding the effect of the CAC barrier
- Groundwater flow is essential for PFAS transport
- Fast reduction of PFAS downstream barrier shows both barrier efficency & minimal sorption in the absence of sorbents
- A key aspect is **how long** the barrier can **retard breakthrough** of different PFAS
- Remaining questions include: **precursors, competition effects**, **mass loading** from the **vadose zone**.

# Precursor transport at Övik

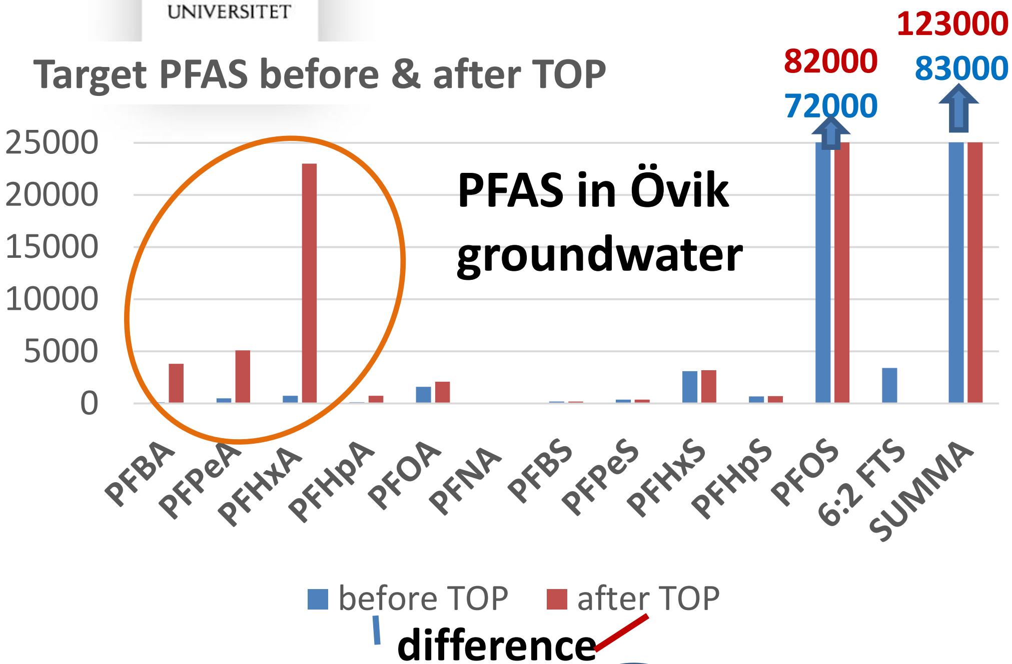


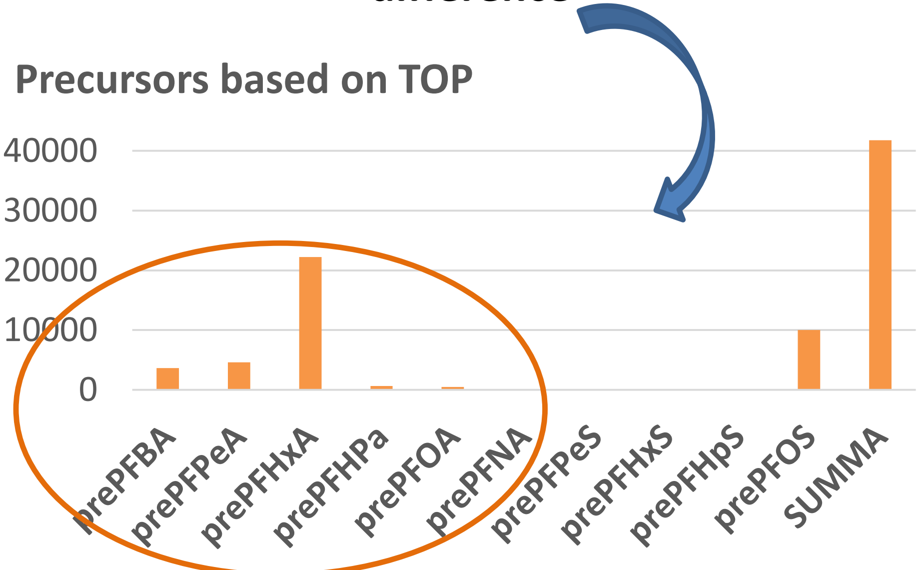



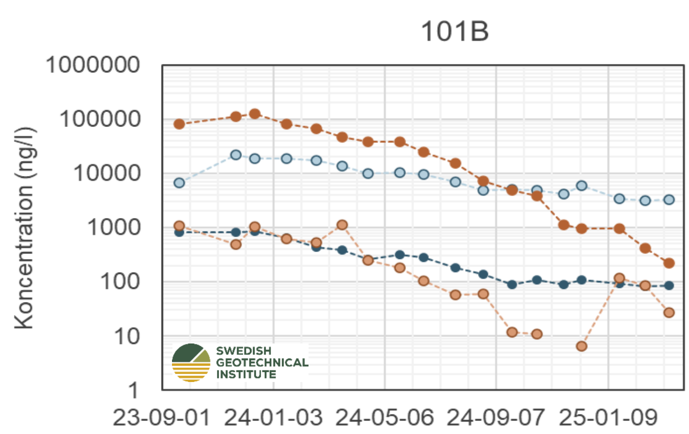

- Downstream barrier PFAS conc. decrease with time
- PFCA that are formed by oxidization (after TOP) have the slowest decreasing trend =>
  - slow precursor transport & kinetics
  - precursor transformation in barrier may be important

# Modelling precursor transport with TOP-data



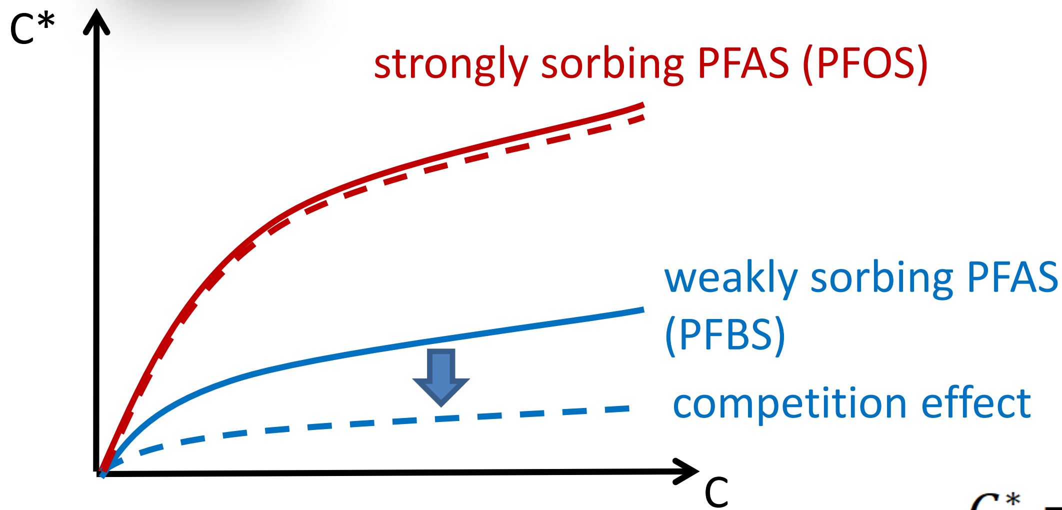



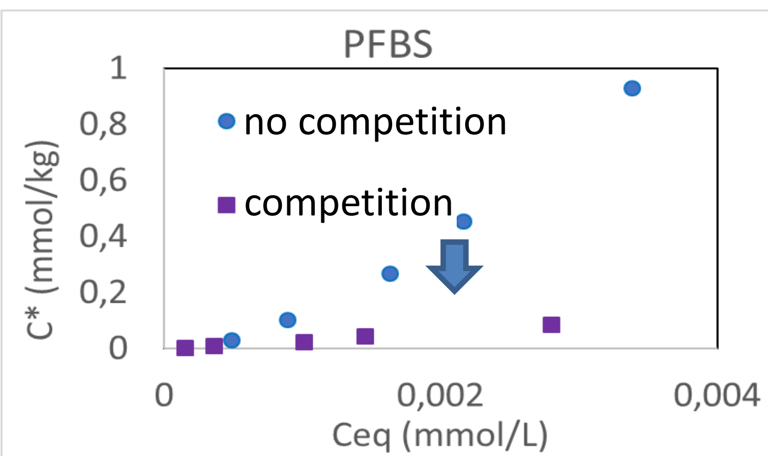

- Övik groundwater contains a large amount of unknown precursors
- Difference before & after TOP gives ***"pre-PFAS"** conc.*
- Detailed TOP data allows modelling of prePFAS transport
  - Assessment of sorption & transformation



UPPSALA UNIVERSITET

# Model for competition between PFAS during sorption




*Niarchos et al. (2023) Ecotox. & Environm. Safety*

## Freundlich isoterm

$$C_i^* = K_{f,i} C_i^{n_i}$$

## Freundlich w. competition

$$C_i^* = K_{f,i} C_i * \left(C_i + \sum_{j=1, j\neq i}^{Nc} \alpha_{ij} C_j\right)^{n_i - 1}$$

Interaction between PFASs: $\alpha_{ij} = \frac{K_{f,j} n_j}{K_{f,i} n_i}$

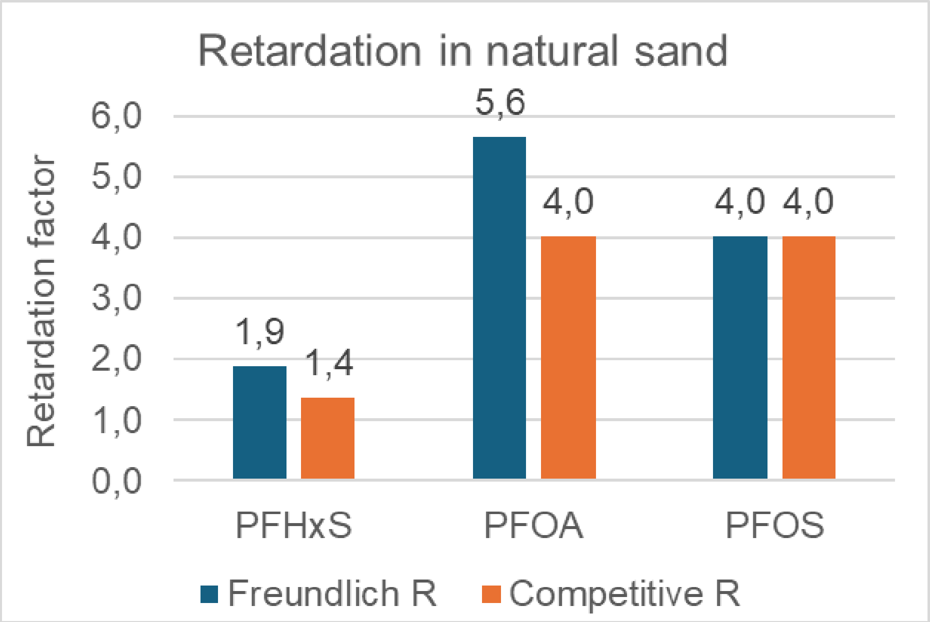
## Retardation influenced by competition

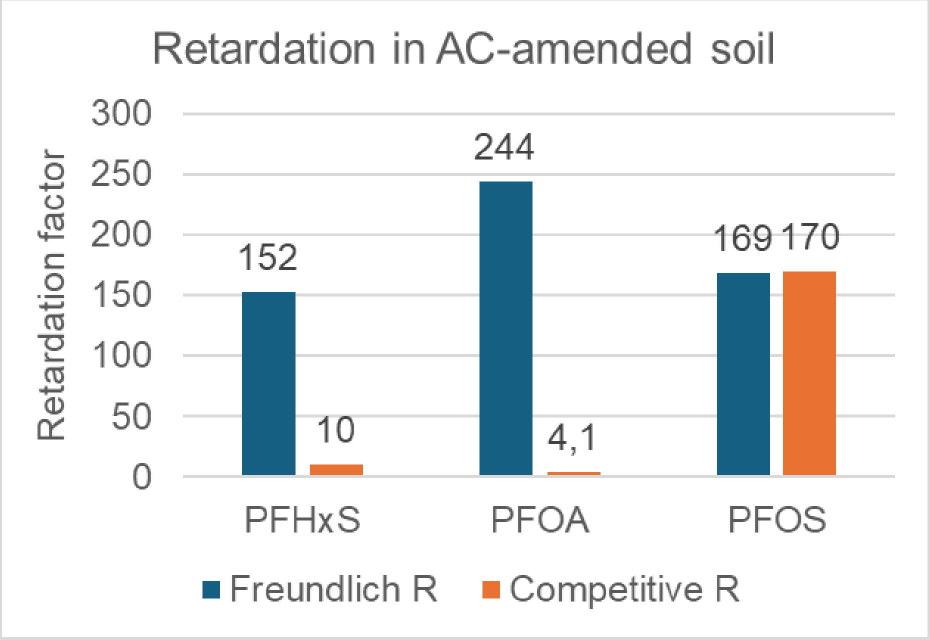
$$R = 1 + \frac{\rho_b}{\theta}\left(K_i \left(C_i + \sum \alpha_{ij} C_j\right)^{n_i - 2} \left(C_i n_i + \sum \alpha_{ij} C_j\right)\right)$$

*Sheindorf (1981) A Freundlich-type multicomponent isotherm. J. Colloid and Interface Sci, 136-142*

# Effect of competition on retardation, 3 PFAS

- In **natural sand**, the **effect of competition is small** for all 3 PFAS
- In sand **with CAC** the **effect of competition is large** for PFHxS och PFOA
- **Retardation depends also on concentration**
    - PFOA initially has high R due to low concentration
    - High PFOS conc. influences PFHxS & PFOA
- **Chromatographic effect**
    - PFOS competes only as far as it has migrated
- Model **needs validation against data**



# Conclusions

- Understanding PFAS fate and transport in the soil-groundwater system is critical for the protection of environment & water resources
- Sorbent amendments can help to reduce PFAS spreading from hotspots
- Complexities in PFAS sorption include: non-linear, kinetic and partly irreversible sorption as well as competition effects and precursors

## Thank you!

SLU

UPPSALA UNIVERSITET

SWEDISH GEOTECHNICAL INSTITUTE

SGU Sveriges geologiska undersökning

NATUR VÅRDS VERKET

*This work was supported by the Swedish Environmental Protection Agency grant 2023-00059, TUFFO – a research and innovation program on contaminated sites managed by the Swedish Geotechnical Institute (grant 1.1-1708- 0501). and the Government of Sweden's Grant no. 1:4 for remediation and restoration of contaminated sites. Presented material includes preliminary results from the Swedish Geotechnical Institute's and Geological Survey of Sweden's governmental assignment for PFAS.*