Simulating **PFAS** transport in **unsaturated soil**

Using the python interface to include **air-water-interfacial** retention

Camilla Jakobsen
caj@plen.ku.dk

UNIVERSITY OF COPENHAGEN

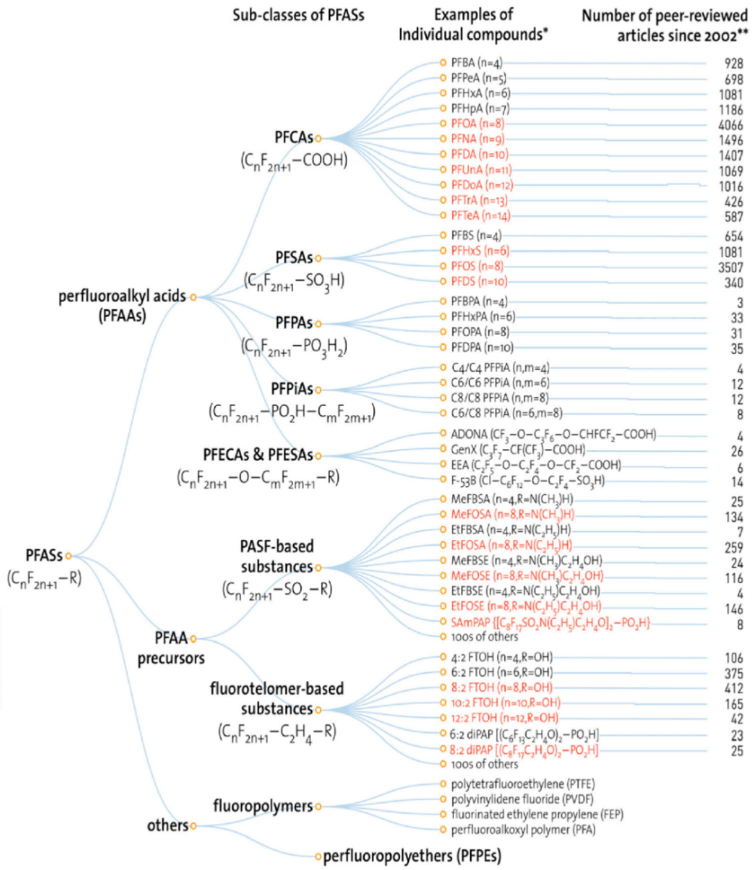
About me

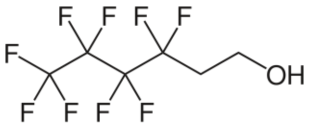
- **-2022:** Bachelor’s degree in Natural Resources, UCPH
- **-2024:** Master’s degree in Environmental Science (Chemistry, Toxicology and Health), UCPH
  - Thesis: **Sorption of PFAS in Zero Tillage Soil**
    - Supervisor: Bjarne W. Strobel
- **2024-** : Research Assistant at PLEN
  - Part of the Agrohydrology and Environmental Chemistry Group
  - Main work: Get to know and work with Daisy, continuing working with PFAS

Wang et al. (2021)

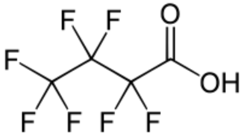
Introduction to PFAS

- **PFAS: P**er- and **P**oly**f**luoro**a**lkyl **S**ubstances
- Large group of **synthetic chemicals** used since the 1950 in a wide range of industrial and consumer products
- OECD Definition: any compound, with a few exceptions, containing at least one perfluorinated methyl group (-CF_3) or perfluorinated methylene group (-CF_2) (> 4700 PFAS)
- Length of fluorinated carbon chain highly control the physiochemical property, but functional groups are also important
- **C-F bond** is the strongest bond in organic chemistry
- PFAS are **very stable** molecules and **mobile**
- PFAS are found in water, air, biota, and soil worldwide
- Can **bioaccumulate** in humans and animals
- Some have been linked to increased risk of cancer, high cholesterol, reproductive disorders, hormonal disruption, weakening of the immune system

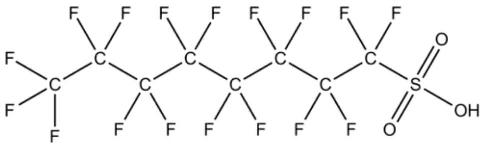




4:2 FTOH
Volatile (K_H = 0.3), precursor



PFBA
Very water-soluble, PM-bound



PFOS
Moderately water-soluble, increased Hydrophobicity, PM-bound

PFAS in soil

Direct use or via transformation of PFAS precursors

Point sources (high concentration)

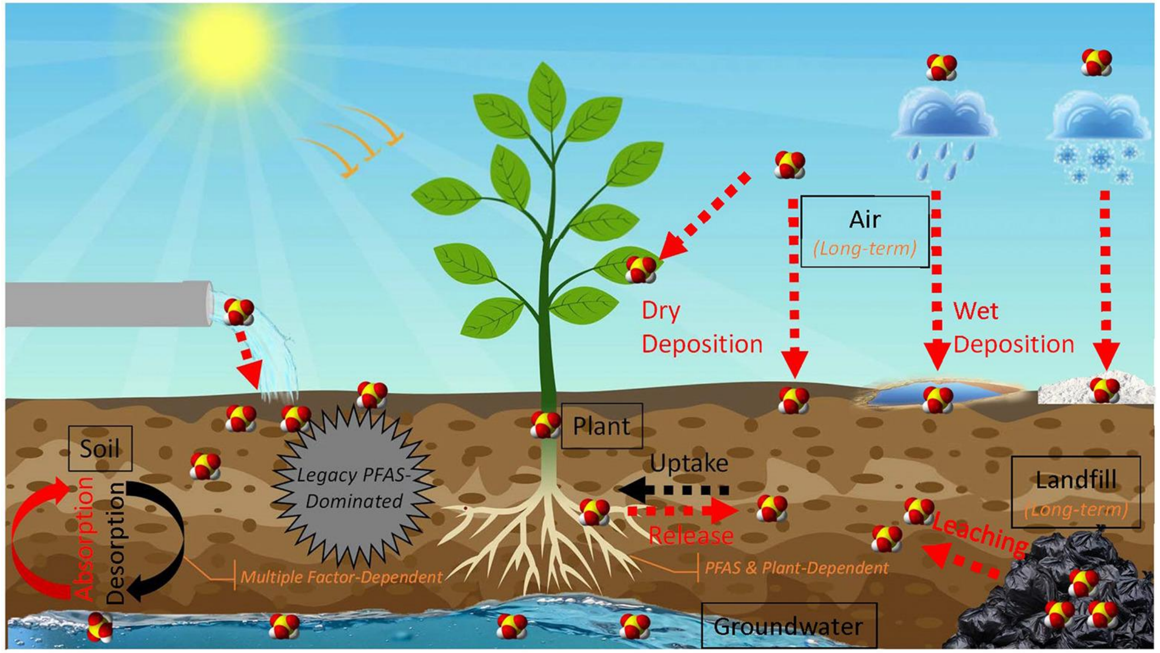
- Aqueous fire-fighting foam

Diffuse sources (low concentration)

- Atmospheric deposition (gas phase and/or on particles)
- Sewage sludge
- Sea spray aerosol

Limit values in soil (DK)

Compounds	Value
Sum of 4 PFAS	10 µg/kg
Sum of 22 PFAS	400 µg/kg



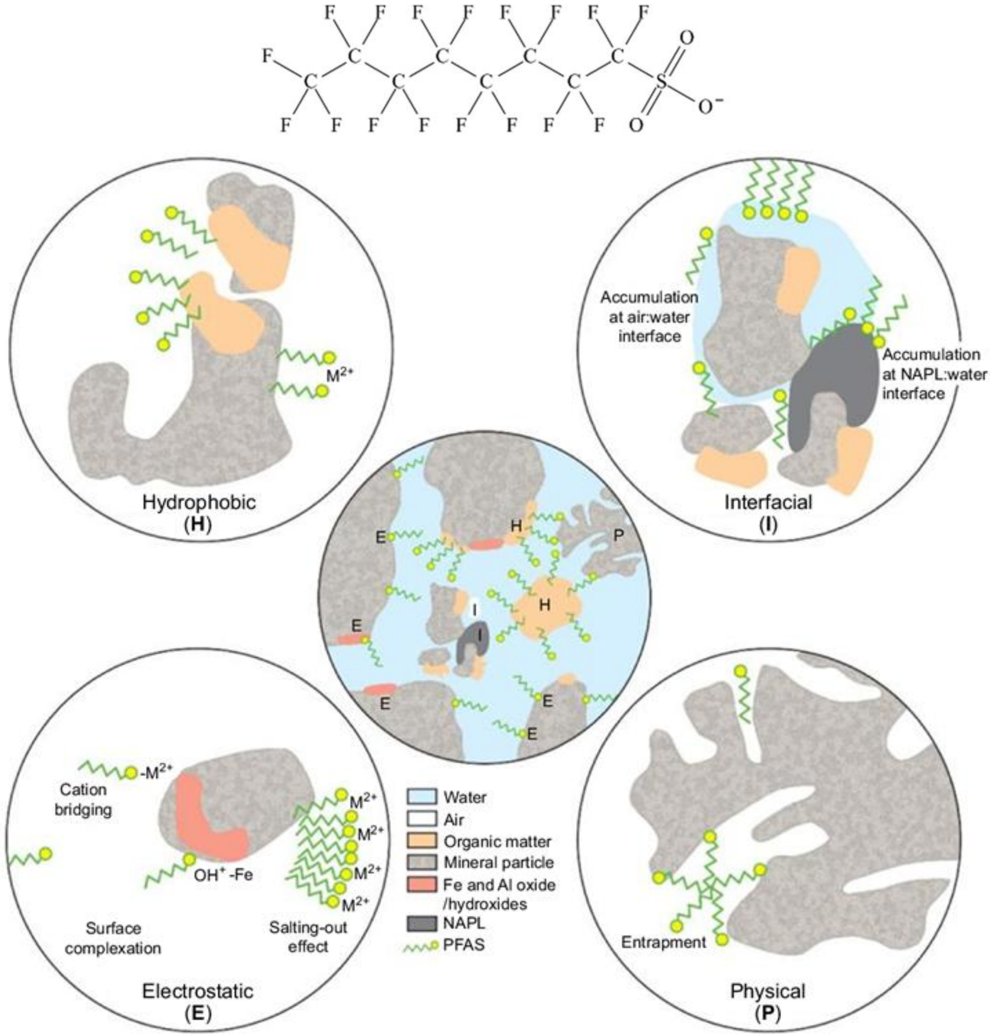
Wang et al (2023)

Key properties governing PFAS sorption in unsaturated soil

Perfluoroalkyl acids (PFAA):
- Permanent negative charge
- Surface active

Sorption to solid phase:
- Organic matter
- Clay minerals
    - pH dependent Al-, Fe-oxides, cation bridging

Adsorption air-water interface
- Surface active PFAS form films at fluid-fluid interfaces
    - Highly dependent of C-F chain length



Kookana et al. (2022)

Batch experiment: Sorption to soil

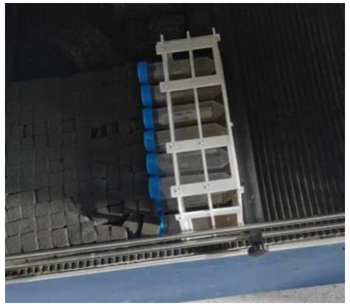
- From thesis: Batch experiment testing sorption of seven different PFAS in 11 different soils
- Individual linear isotherm:

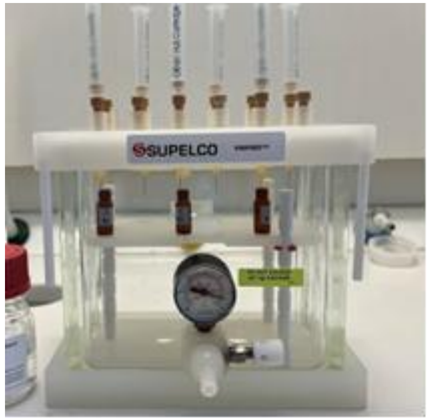
  $q = Kd \cdot c$

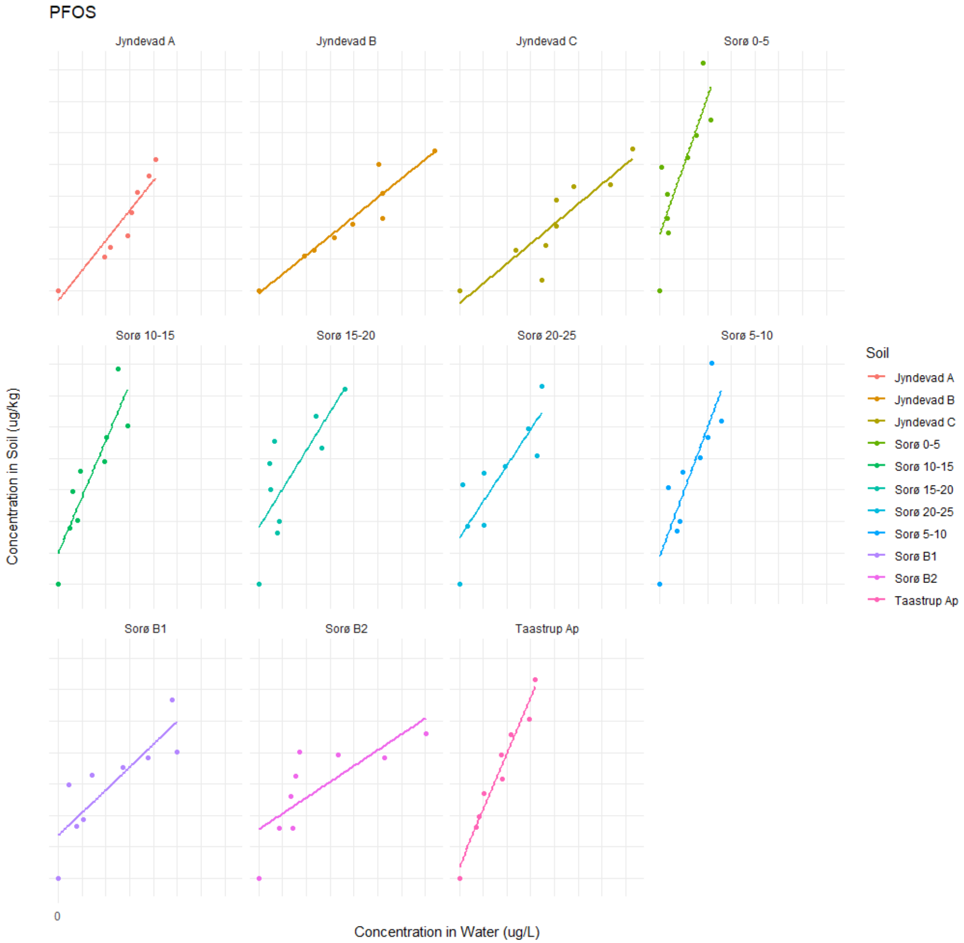
- Predicting Kd from soil parameters:

  $Kd = K_{OC} \cdot f_{OC} + K_{clay} \cdot f_{clay}$

  Using 'Excel Solver' to fit parameters (minimize SSR)

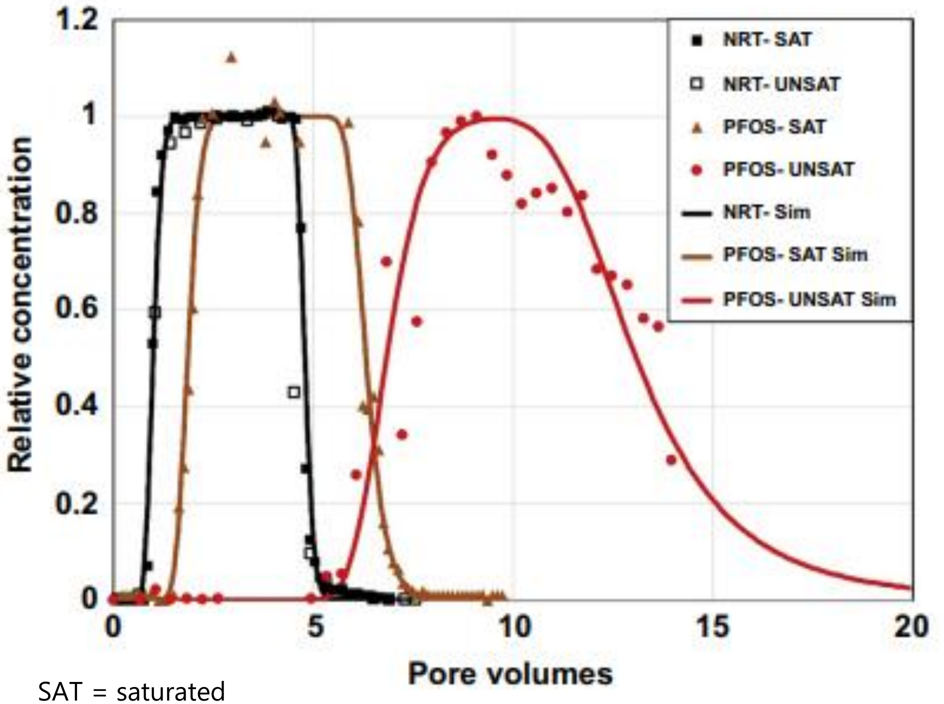






Retention in air-water interface: What other studies have found..

Breakthrough curve of PFOS in sand column:



SAT = saturated
UNSAT = unsaturated conditions (0.66 saturation) during
NRT = non-reactive tracer
Reproduced from **Brusseau et al. (2019)**

PFOS was 4 times slower in unsaturated than in saturated sand

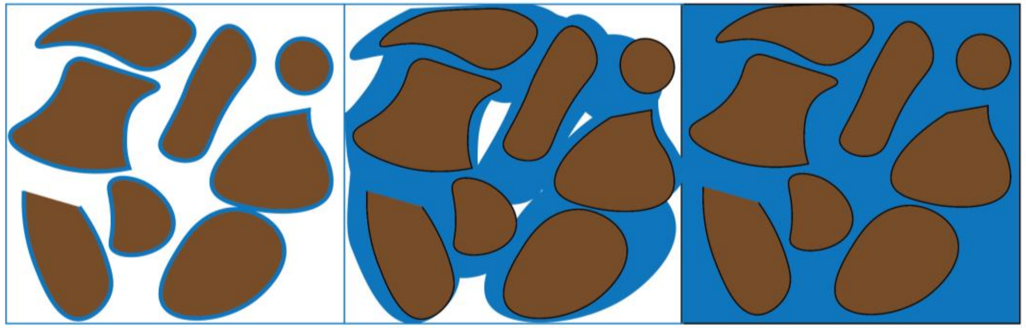
Effect on soil texture and grain size:

- Relative contribution of air-water interface in PFAS retention likely depends on soil properties:
  - **Lyu et al. (2018):** Grain size of sand affected PFOA movement:
    - In fine sand (average 0.35 mm) - big difference in retardation factor between saturated and unsaturated
    - Coarser sand (1.2 mm) - the difference in retardation factor was small due to the smaller Aaw
  - **Brusseau et al. (2019):** Despite soil having larger specific air-water interfacial area (A_{aw}) than sand, the relative contribution from A_{aw} was less in soil compared to sand, due to a higher sorption to the solid-phase in soil.

Estimating adsorption to air-water-interface

Empirical model estimating air-water interfacial areas (Brusseau, 2023)

$$A_{aw} = \left(-2.85 \cdot \frac{\theta}{\theta_{sat}} + 3.6\right)\left(1 - \frac{\theta}{\theta_{sat}} \cdot 3.9 \cdot {d_{50}}^{1.2}\right)$$



Air-water interfacial adsorption coefficient:

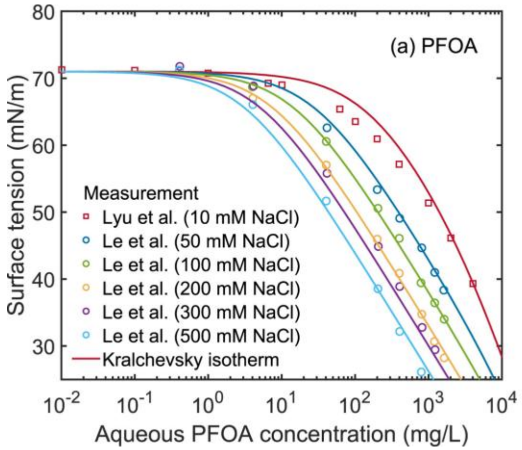
$$K_{aw} = \frac{\sigma_0 b}{RT(C + a)}$$ (Guo et al., 2020)

Concentration in air-water interface:

$$C_{aw} = A_{aw} \cdot K_{aw} \cdot C$$

a and b fitting parameters in Szyszkowski equation
Ionic strength dependent

AWI sorption parameters (Gao et al., 2020)		
PFAS	**a** ($\mu mol/cm^3$)	**b (-)**
PFOS	3.4e-3	0.107
PFOA	1.16e-2	0.033



(Zhang & Guo, 2024)

Python script (PFOS as example)

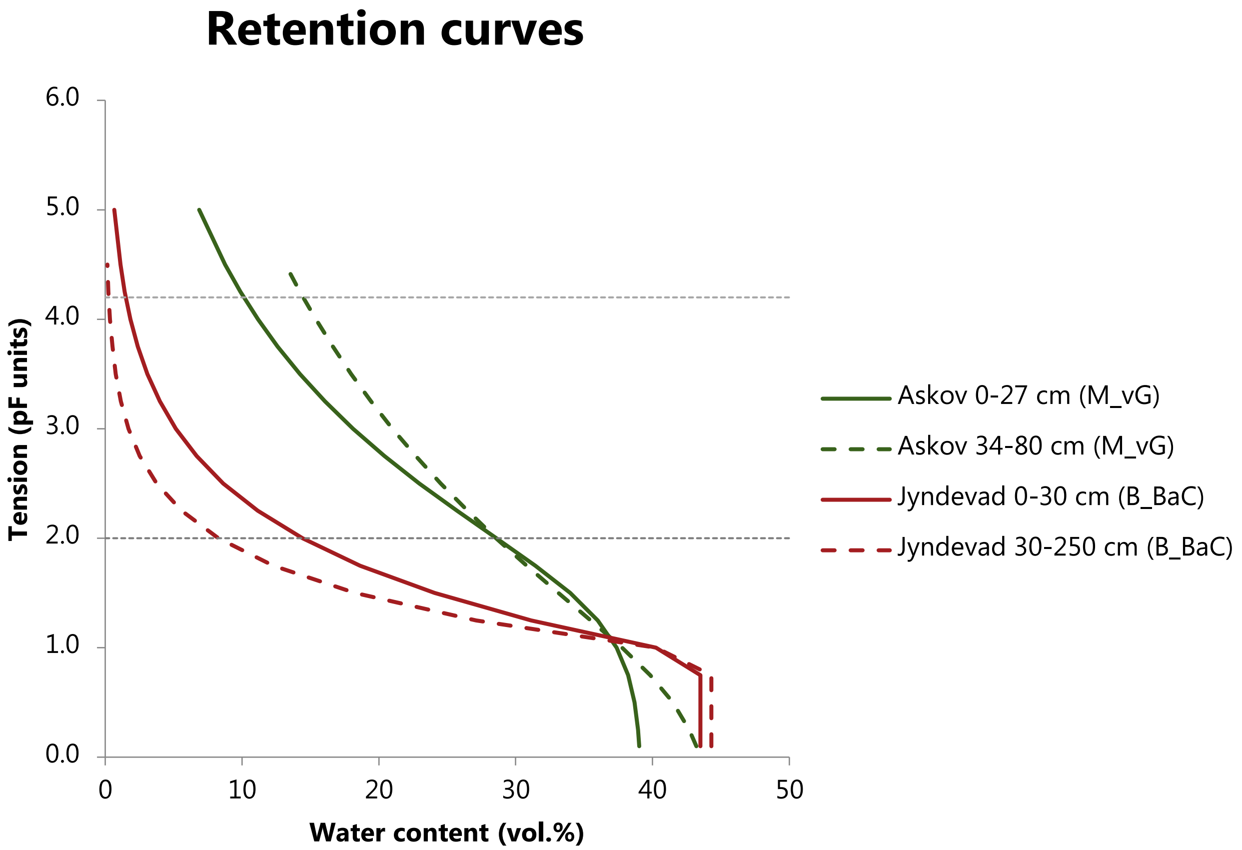
Daisy.py

```
def k_PFOS (f_OC, f_clay):
    k_OC = 445.1
    k_clay = 95.6
    return f_OC*k_OC + f_clay*k_clay

def a_aw (Theta, Theta_sat, d50):
    return (-2.85*(Theta/Theta_sat)+3.6)*((1-(Theta/Theta_sat))*3.9*d50**-1.2)

def K_aw_PFOS (C, T):
    a = 3.4e-03 # fitting parameter (mol/m3)
    b = 0.107 # fitting parameter (-)
    T = T + 273 # converting to Kelvin
    m_PFOS = 550 # molar mass of PFOS (g/mol)
    return (sigma*b)/(R*T*((C/m_PFOS)+a))

def C_to_M_PFOS (C, Theta_sat, Theta, rho_b, f_OC, f_clay, d50, T):
    d50 = d50/10000 # convert to cm
    k = k_PFOS(f_OC, f_clay)
    return rho_b*k*C + Theta*C + a_aw(Theta, Theta_sat, d50)*K_aw_PFOS(C, T)*C

def M_to_C_PFOS (C, Theta_sat, Theta, rho_b, f_OC, f_clay, d50, T):
  Numerical solution (bisection method)
```

Soils used in simulation

From the Daisy lib:

- Jyndevad
  - free drainage
- Askov
  - Biopores
  - Added a plow pan (layer below Ap with increased bulk density and low Ks)
  - Groundwater aquitard
  - Added drains (-120 cm)




```
(defhorizon "Askov Ap" ISSS4
  "Askov 10 & 30 cm soil. Data from O.H. Jacobsen (1989): Umættet
hydraulisk ledningsevne i nogle danske jorde. Beretning nr. S
2030. Statens Planteavlsforsøg."
  (clay 0.113)  (silt 0.277)
   (fine_sand 0.348) (coarse_sand 0.236)
  (humus 0.026) (C_per_N 11) (dry_bulk_density 1.55 [g/cm^3])
  (hydraulic M_vG (Theta_res 0.0)(Theta_sat 0.392)
             (alpha 0.0385)(n 1.211)(K_sat 7.52 [cm/h])))
```

```
(defhorizon "Jyndevad Ap" ISSS4
  "Jyndevad 15 cm soil. Data from O.H. Jacobsen (1989): Umættet
hydraulisk ledningsevne i nogle danske jorde. Beretning nr. S
2030. Statens Planteavlsforsøg."
  (clay 0.038)  (silt 0.072) (fine_sand 0.183) (coarse_sand 0.684)
  (humus 0.023) (C_per_N 13) (dry_bulk_density 1.472 [g/cm^3])
  (hydraulic "B_BaC"
             (Theta_res 0.036 []) (Theta_sat 0.435 [])
             (lambda 0.446 []) (h_b -8.4 [cm]) (K_sat 6.76e-5 [m/s])))
```

Simulations

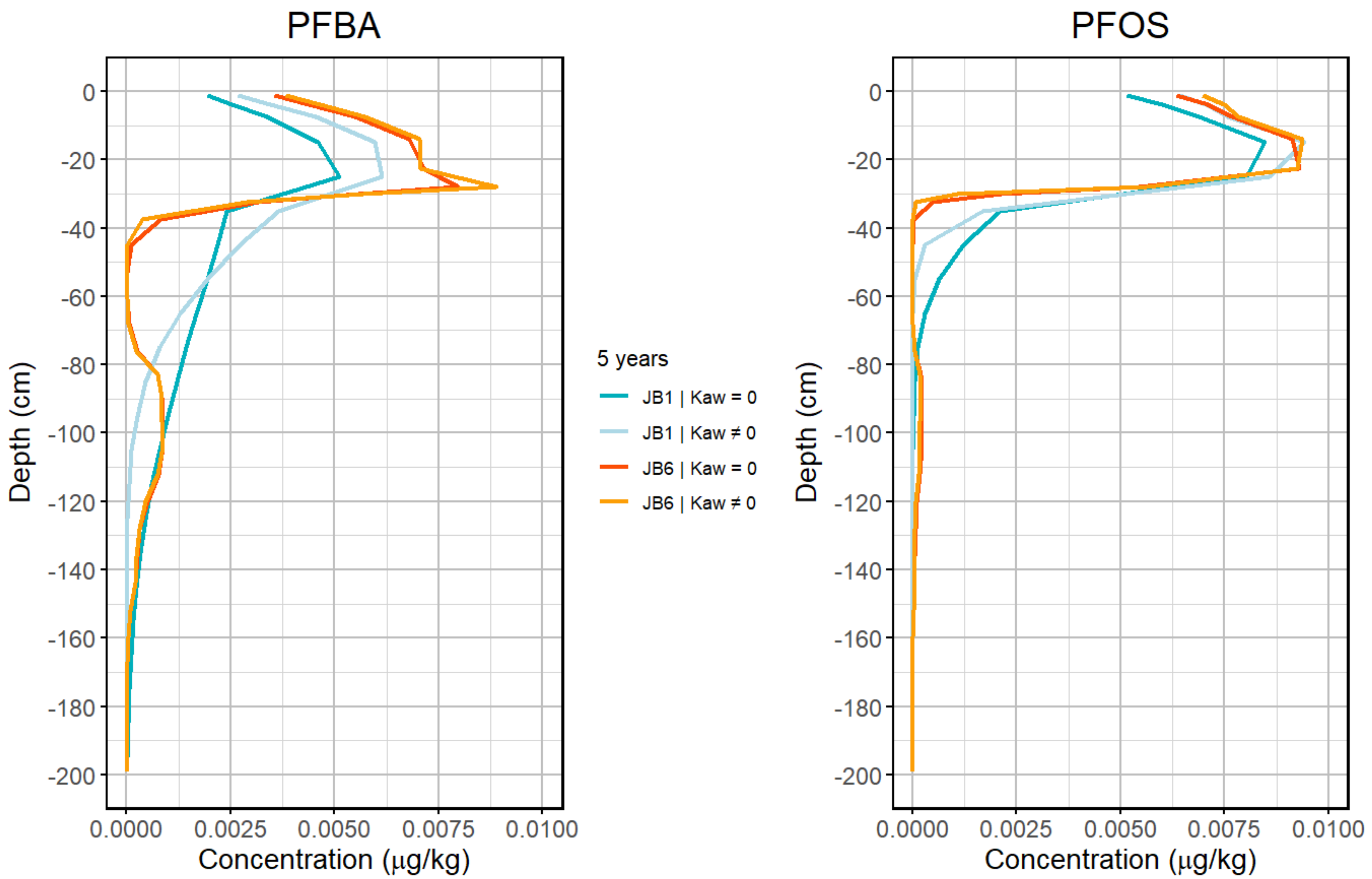
- **Soil:** Jyndevad and Askov
- **Management:** 5-year rotation (winter wheat, spring barley, winter wheat, spring barley, winter rape) (Vuaille et al., 2024)
- **Plant uptake:** No plant uptake
- **Weather:** Taastrup (hourly)
- **Simulation time:** 5 years (1997 to 2002)
- **PFAS:** PFOS and PFBA (strong vs weak sorption to soil)
- **PFAS input:** Based on PFAS content in precipitation (small study, only part of 1 year) (Bossi, 2024)

PFAS	Yearly input	Solid phase sorption		AWI sorption parameter	
	"spray" (g/ha)	K_{OC} (ml/g)	K_{clay} (ml/g)	a (mol/cm^3)	b (-)
PFOS	0.01	445	96	3.4E-09	0.107
PFBA	0.01	61	26	1.6E-08*	0.033*

*Using PFOA AWI sorption parameters

Simulation results

Simulating 5 years with 0.01 g/ha yearly input



PFOS: Not a big difference in soil profile with or without retention in air-water interface (AWI)

PFBA: Higher retention when including AWI retention, especially in the sandy soil

- However, using AWI parameters for PFOA likely overestimates PFBA presence in AWI

Conclusion

- Higher retention of PFAS in topsoil was simulated when including air-water interface, especially in sandy soil.

- With a yearly input of 0.01 g/ha (estimated atmospheric deposition), the simulated soil concentration did not reach the limit value within the 5-year period.

References

Bossi (2024): Målinger af PFAS i luft og nedbør. Teknisk rapport fra DCE - Nationalt Center for Miljø og Energi nr. 313. ISBN: 978-87-7156-864-6

Brusseau et al. (2019): Comprehensive retention model for PFAS transport in subsurface systems. Water Research, 48, 41-50. https://doi.org/10.1016/j.watres.2018.10.035

Brusseau (2023): Determining air-water interfacial areas for the retention and transport of PFAS and other interfacially active solutes in unsaturated porous media, Science of the Total Environment, 884, 163730. https://doi.org/10.1016/j.scitotenv.2023.163730

Guo et al. (2020): A Mathematical Model for the Release, Transport, and Retention of Per- and Polyfluoroalkyl Substances (PFAS) in the Vadose Zone. *Water Resources Research*, 56(2). https://doi.org/10.1029/2019WR026667

Lyu & Brusseau (2020) The influence of solution chemistry on air-water interfacial adsorption and transport of PFOA in unsaturated porous media. *Science of the Total Environment,* 713, 136744. https://doi.org/10.1016/j.scitotenv.2020.136744

Kookana et al. (2022): Key properties governing sorption–desorption behaviour of poly- and perfluoroalkyl substances in saturated and unsaturated soils: a review. *Soil Research,* 61(2), 107-125 https://doi.org/10.1071/SR22183

Vuaille et al. (2024): Modelling pesticide degradation and leaching in conservation agriculture: Effect of no-till and mulching. Science of the total Environment, 929, 172559. https://doi.org/10.1016/j.scitotenv.2024.172559

Wang et al. (2021): Selectivity of Per- and Polyfluoroalkyl Substance Sensors and Sorbents in Water. *ACS Appl. Mater. Interfaces*, 13(51), 60789–60814. https://doi.org/10.1021/acsami.1c16517

Wang et al. (2023): Occurrence of per- and polyfluoroalkyl substances (PFAS) in soil: Sources, fate, and remediation. *Soil and Environmental Health*, 1(1), 100004. https://doi.org/10.1016/j.seh.2023.100004

Zang & Guo (2024): Anomalous Adsorption of PFAS at the Thin-Water-Film Air-Water Interface in Water-Unsaturated Porous Media. *Water Resources Research*, 60(3). https://doi.org/10.1029/2023WR035775