DTU

Landfills with PFAS: Complexity and Longevity How can modelling help us?

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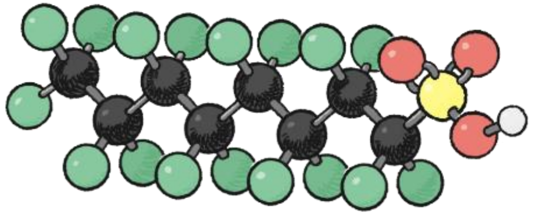
Landfills with PFAS

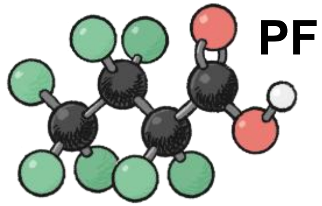
Landfills

- Potential **direct sources of PFAS** into surrounding groundwater and surface water
- **High PFAS concentrations** found in landfill leachates world-wide (years after landfill were operating)

- Highly **complex systems**
  - » chemical transformation
  - » heterogenous waste material
  - » landfill design & type
  - » leaching patterns of PFAS
  - » reduced environment, organic carbon

PFOS





PFBA

PFAS

- Highly complex and omnipresent group of anthropogenic chemicals → world-wide problem
- Many different PFAS = different behaviour at landfills

Objectives:

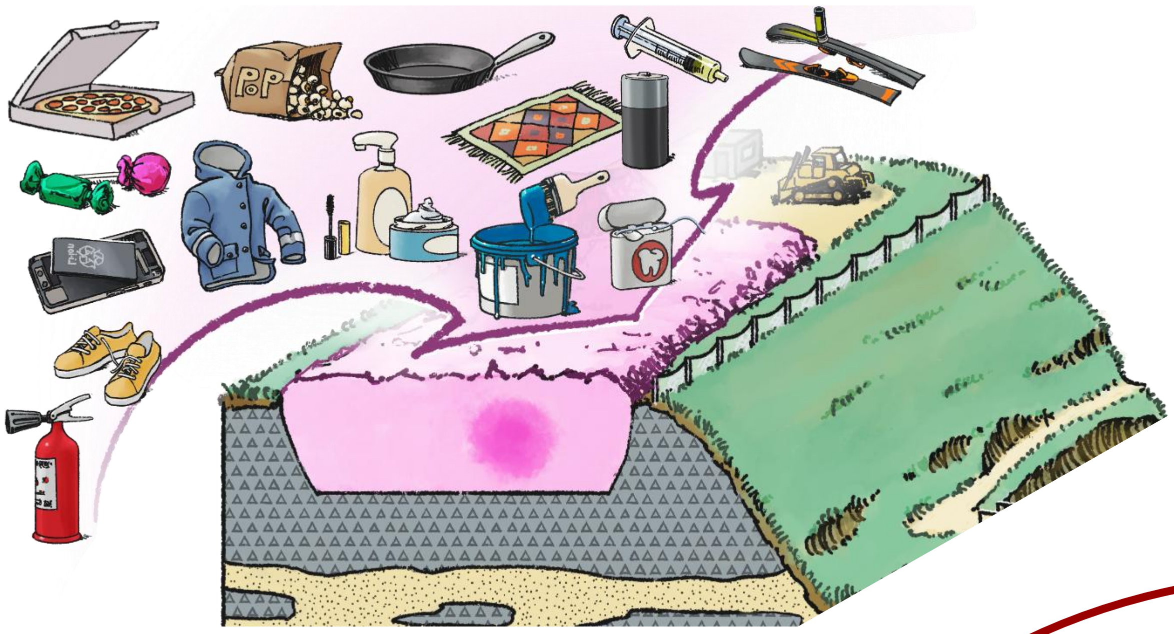
What to expect at different landfills with different conditions?

How to do investigations at different landfills with PFAS?

Risk for groundwater?

PFAS in waste products

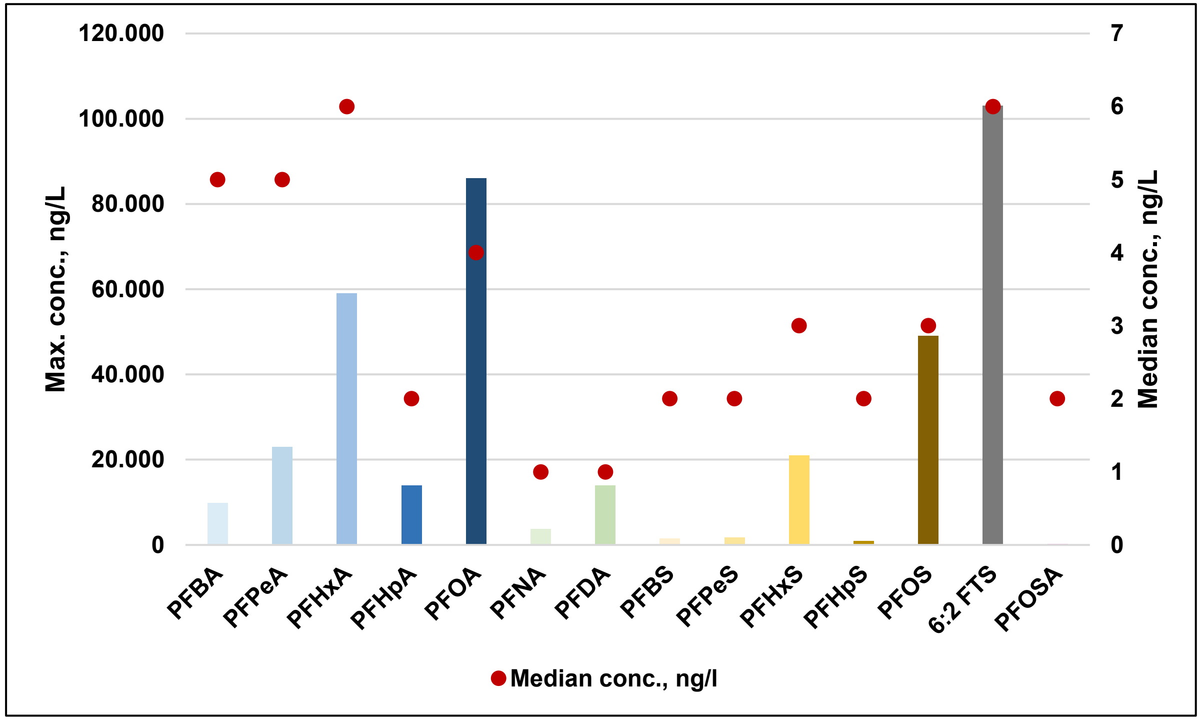
- Kotthoff et al., 2015, Lang et al., 2016, Pivato et al., 2024



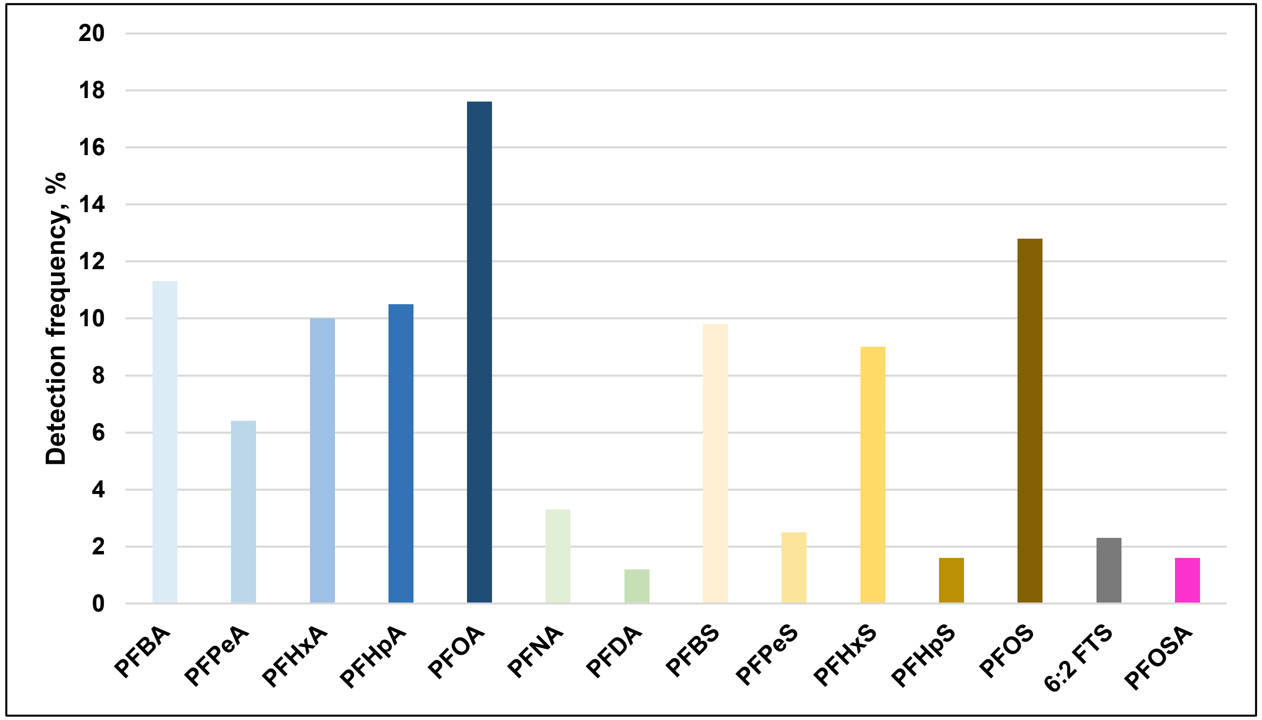
PFAS type	PFAS name	Typical products
Short chain	PFBA, PFBS	ski wax, leather
Long chain	PFOA, PFOS	carpets, outdoor textiles, metal, food packaging, plastic
Precursor	6:2 FTS	cleaning agents, outdoor clothes

Old Danish landfills - PFAS

Max. and median concentration - Groundwater



Most frequently detected PFAS - Groundwater



PFAS database, Danish Regions

Investigations at an old Danish old landfill

- Active in period 1987-1996
- Waste types: carpets, plastics, oil tanks, etc.
- Landfill with both an unsaturated zone below and directly in contact with GW
- Contaminants found at 2 waterworks located close to the landfill
- Investigation of potential groundwater and surface water contamination with PFAS

Thanks to Region Hovedstaden and WSP for data

Investigation at an old Danish old landfill

- Installed boreholes, GeoProbes and suction cells
- Flow field and head gradients
- Transect with depth discrete sampling
- Unsaturated zone measurements (pore water samples)
- Soil cores – A-rør

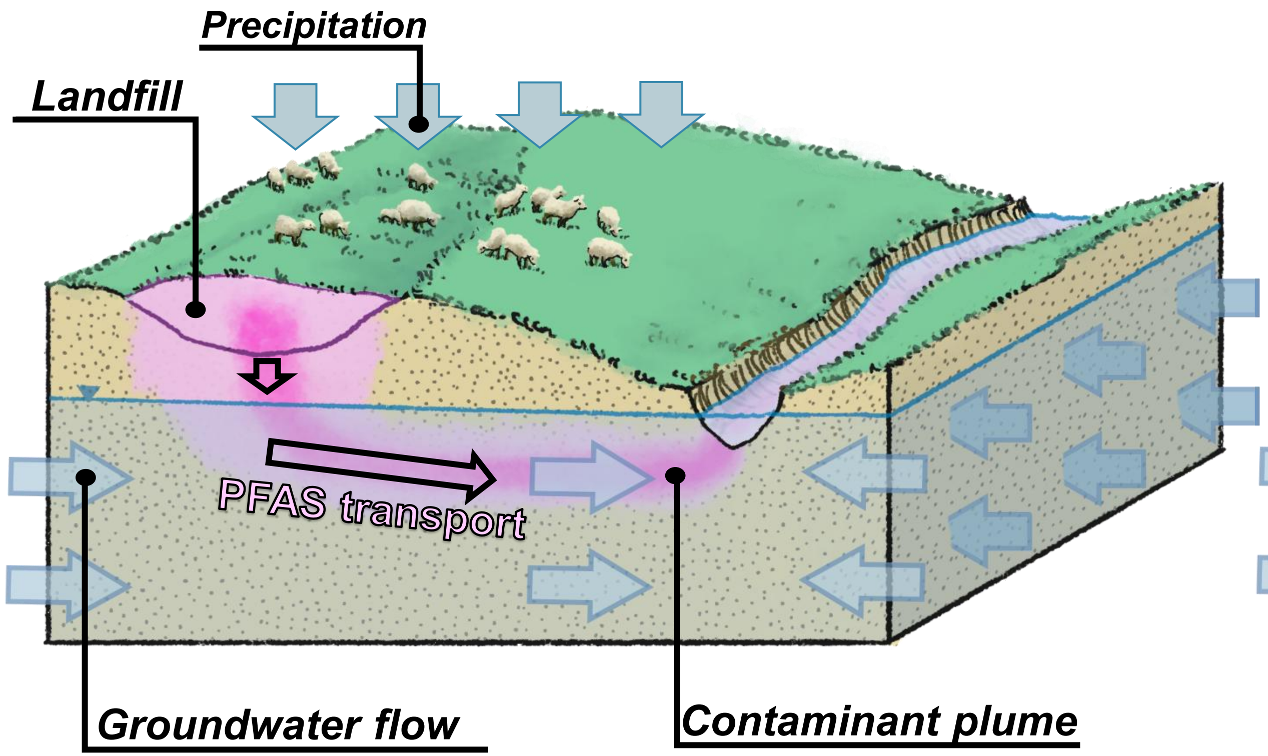
- **PFAS can have an impact on groundwater and surface water**

- Modelling helps in assessing the longevity of contamination

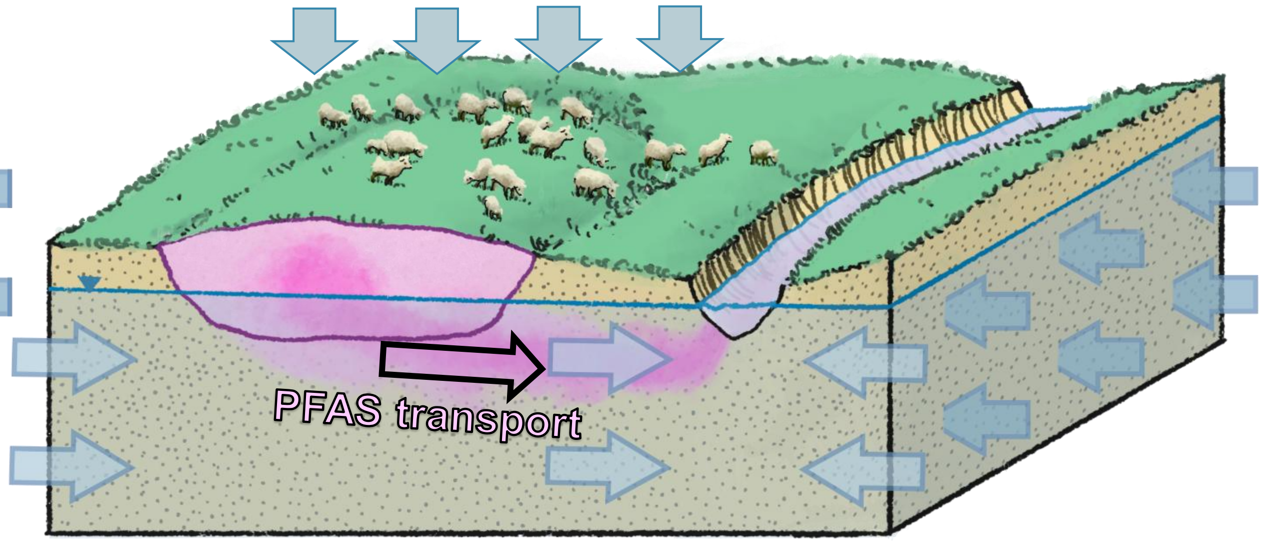
Thanks to Region Hovedstaden and WSP for data

PFAS at different landfill types

Landfill with unsaturated zone below



Landfill without unsaturated zone below



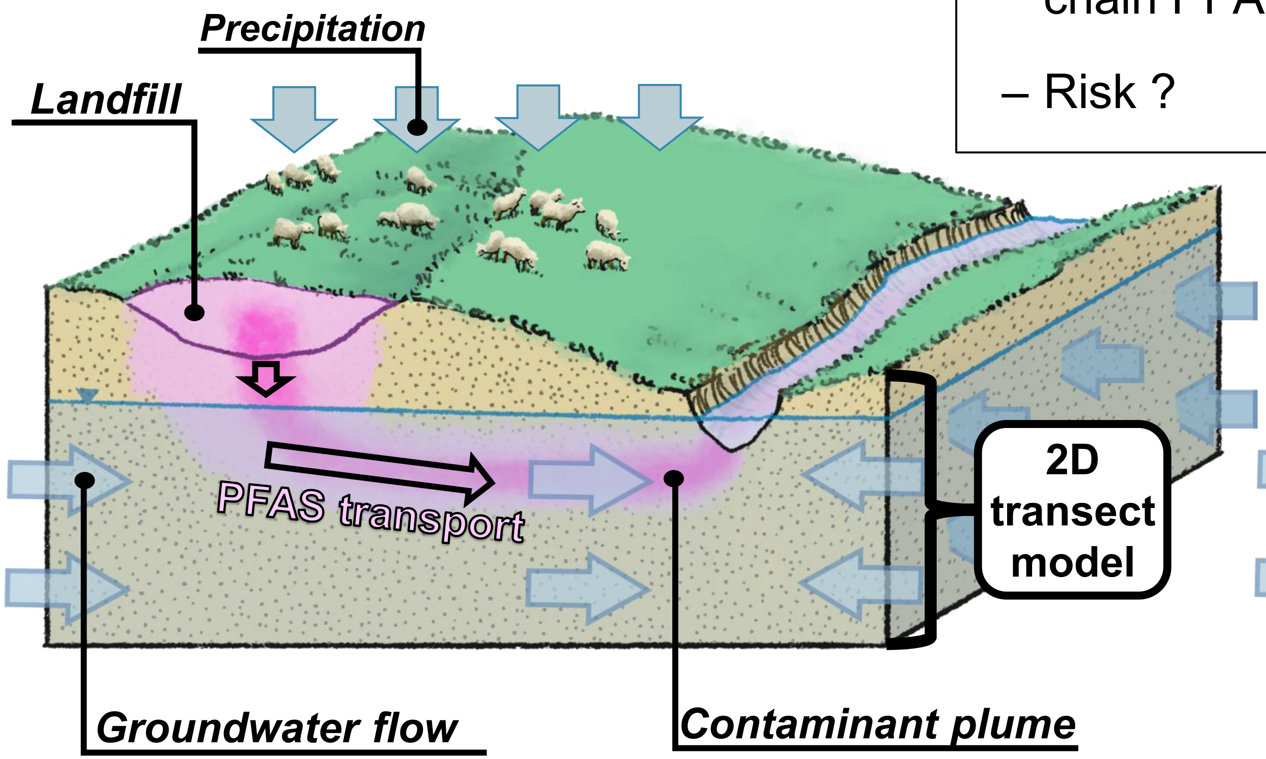
PFAS at different landfill types

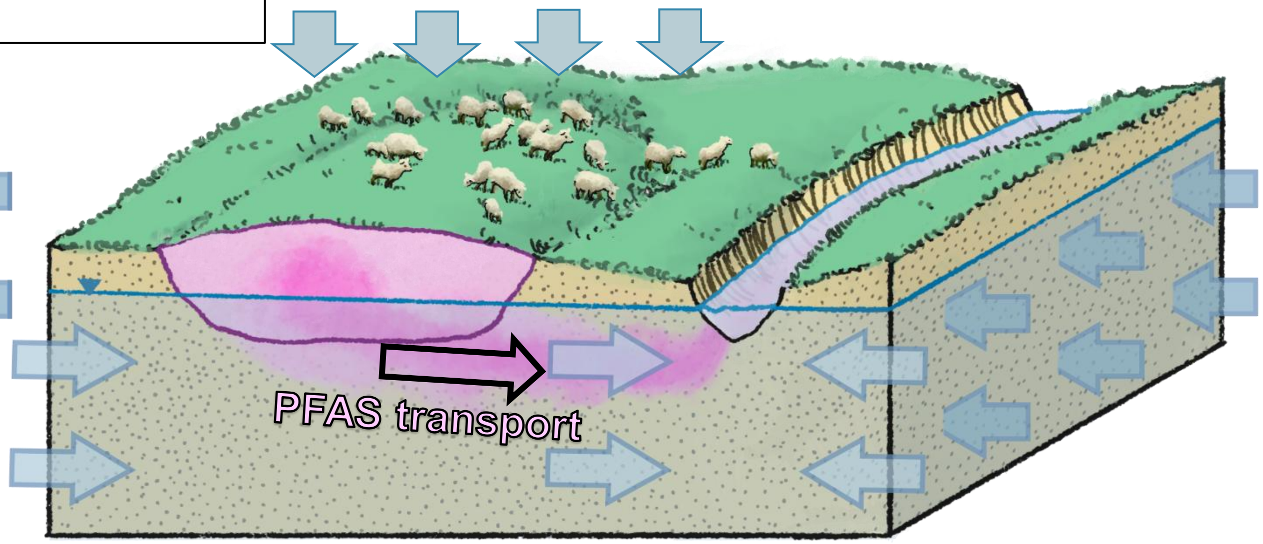
Landfill with unsaturated zone below

Differences:

- Water content
- Attenuation processes for long-chain PFAS
- Risk ?

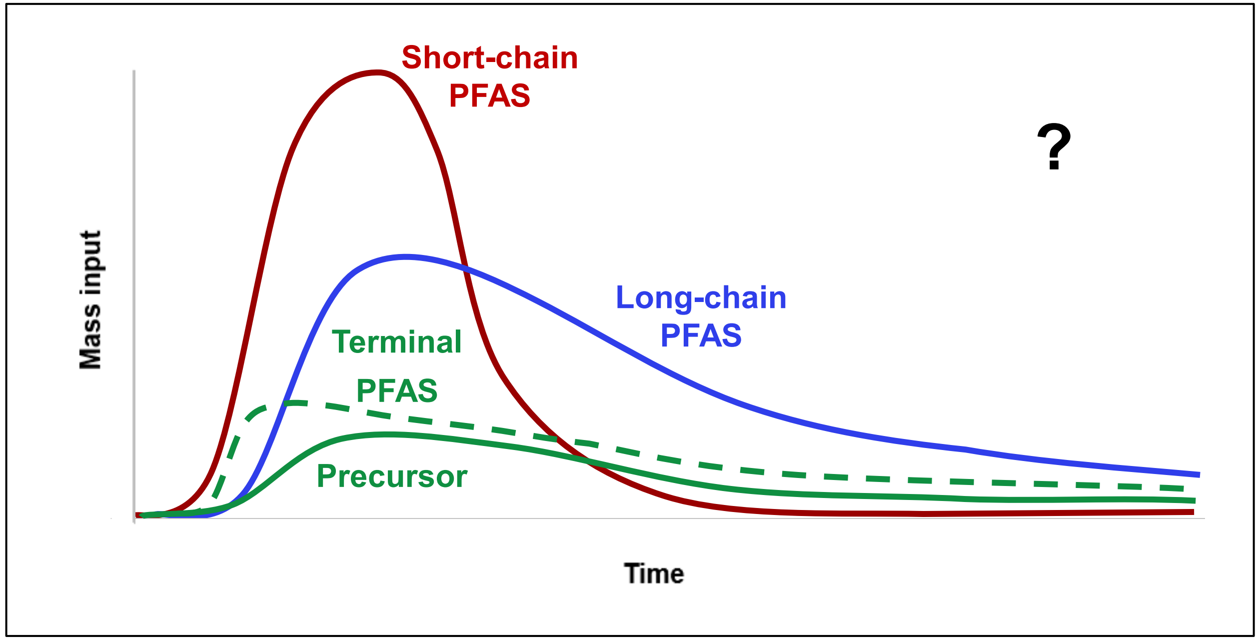
Landfill without unsaturated zone below





Development of PFAS leaching function

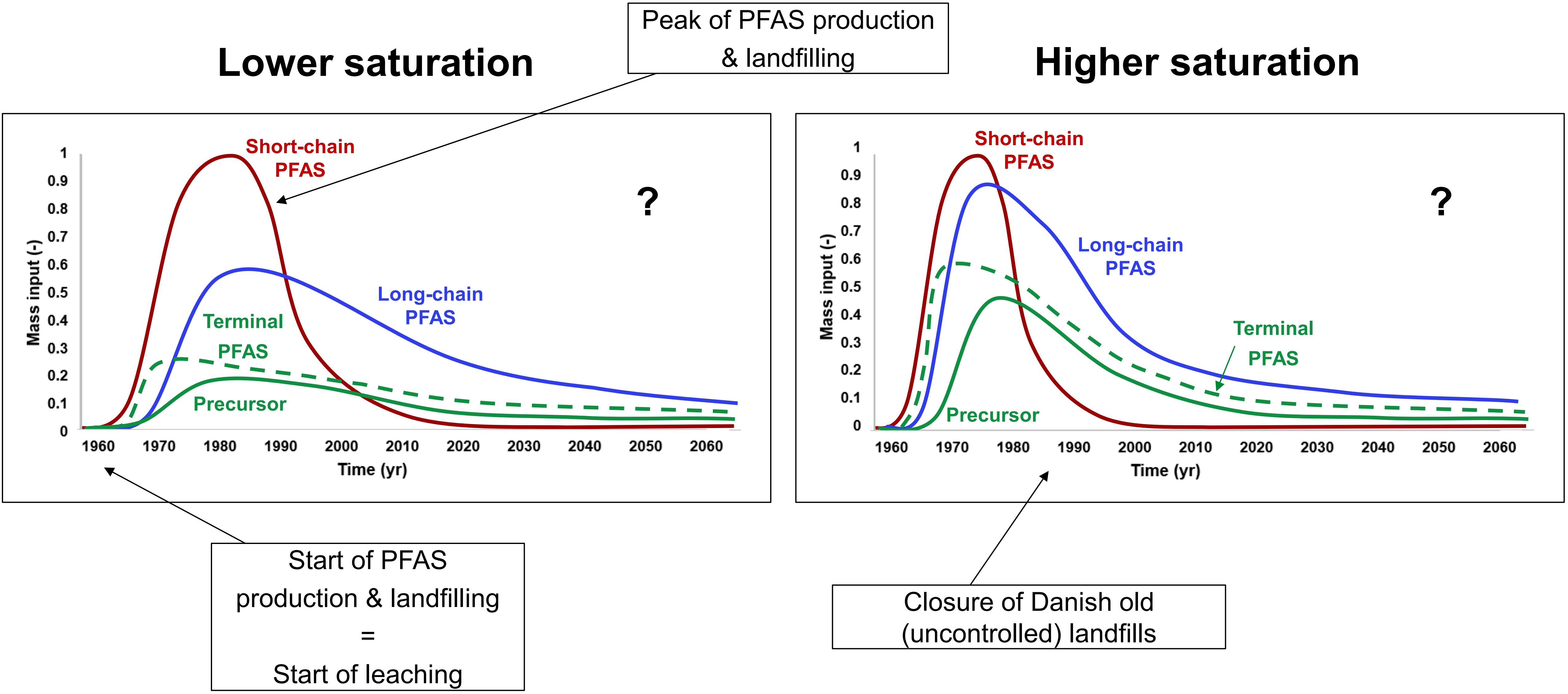
- Leaching function for PFAS from landfills



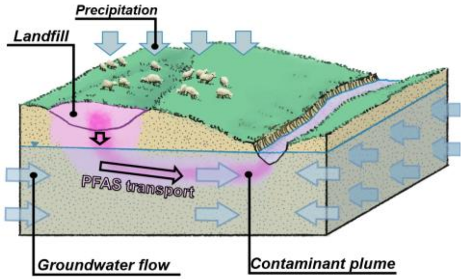
Leaching pattern

PFAS type	Start	Longevity	Specific PFAS
Short chain	Early	Short	PFBA, PFBS
Long chain	Delayed	Long	PFOA, PFOS
Precursor	Intermediate	Long	6:2 FTS
Terminal PFAS - formed	Intermediate	Long	PFBA

PFAS leaching patterns at old Danish landfills



Scenarios for old Danish landfills



- Flow & Transport 2D model for PFAS from landfills
- 2 landfill types + 2 leaching patterns = 4 leaching scenarios
- 4 terminal PFAS (Tang et al. 2024, Fuertes et al. 2017, Hamid et al. 2018)
  - PFCA C4 and C8: **PFBA**, **PFOA**
  - PFSA C4 and C8: **PFBS**, **PFOS**

What to expect at those 2 landfills types with 2 different saturations ?

Scenario	Landfill type	Saturation inside of a landfill	Result
1	Unsaturated zone	Low	?
2	Unsaturated zone	High	?
3	GW	Low	?
4	GW	High	?

Governing processes - Modelling framework

- Modelling approach by Brusseau and Guo

SORPTION TO SOLID PHASE | ADSORPTION TO AIR-WATER INTERFACE

$$R = 1 + \frac{K_d \cdot \rho_b}{\theta_w} + \frac{K_{ia} \cdot A_{ia}}{\theta_w}$$

R – Retardation factor [-]

K_d – Soil specific distribution coefficient [L/kg]

ρ_b – Bulk density [kg/L]

K_{ia} – Air-water interfacial adsorption coefficient [cm]

A_{ia} – Air-water interfacial area [1/cm]

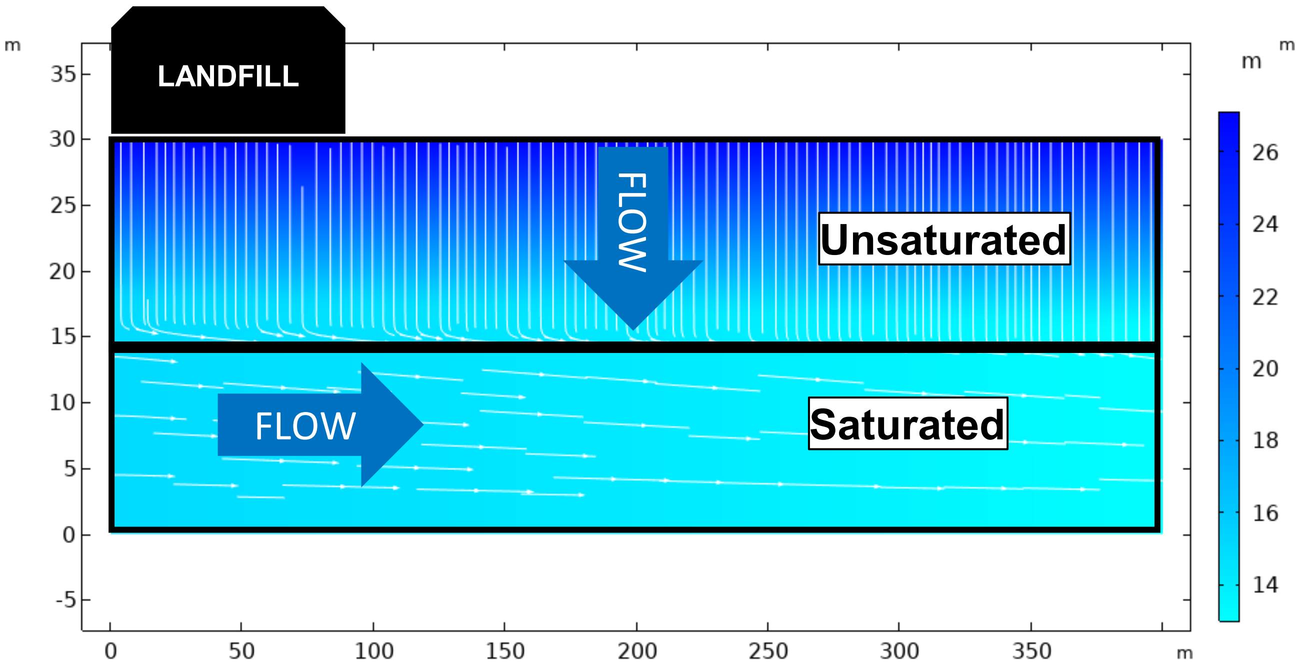
θ_w – Water content [-]

Process	Equation
Flow in unsaturated zone (Richards' eq.)	$\frac{\partial \theta}{\partial t} + S_e S_p \left(-\frac{\partial \psi}{\partial t}\right) + \nabla \cdot \left(-K(\theta)\nabla(h+z)\right) = W$
Variable saturation (van Genuchten)	$\theta(\psi) = \begin{cases} \theta_r + \frac{\theta_s - \theta_r}{(1+(\alpha \cdot \psi)^n)^{1-1/n}} & \psi \geq 0 \\ \theta_s & \psi < 0 \end{cases}$
PFAS transport	$\frac{\partial(\theta c)}{\partial t} + \rho_b \frac{\partial c_s}{\partial t} + \frac{\partial c_{ia}}{\partial t} + \nabla \cdot (\theta c \vec{v}) + \nabla \cdot \left(-\theta \vec{D} \nabla c\right) = 0$
Solid phase sorption	$c_s = K_d \cdot c$
Air-water interface adsorption	$c_{ia} = A_{ia} \cdot K_{ia} \cdot c$
Air-water interfacial area	$A_{ia} = (-2.85 \cdot S_w + 3.6) \cdot ((1 - S_w) \cdot 3.9 \cdot d_g^{-1.2})$ (Brusseau, 2023)

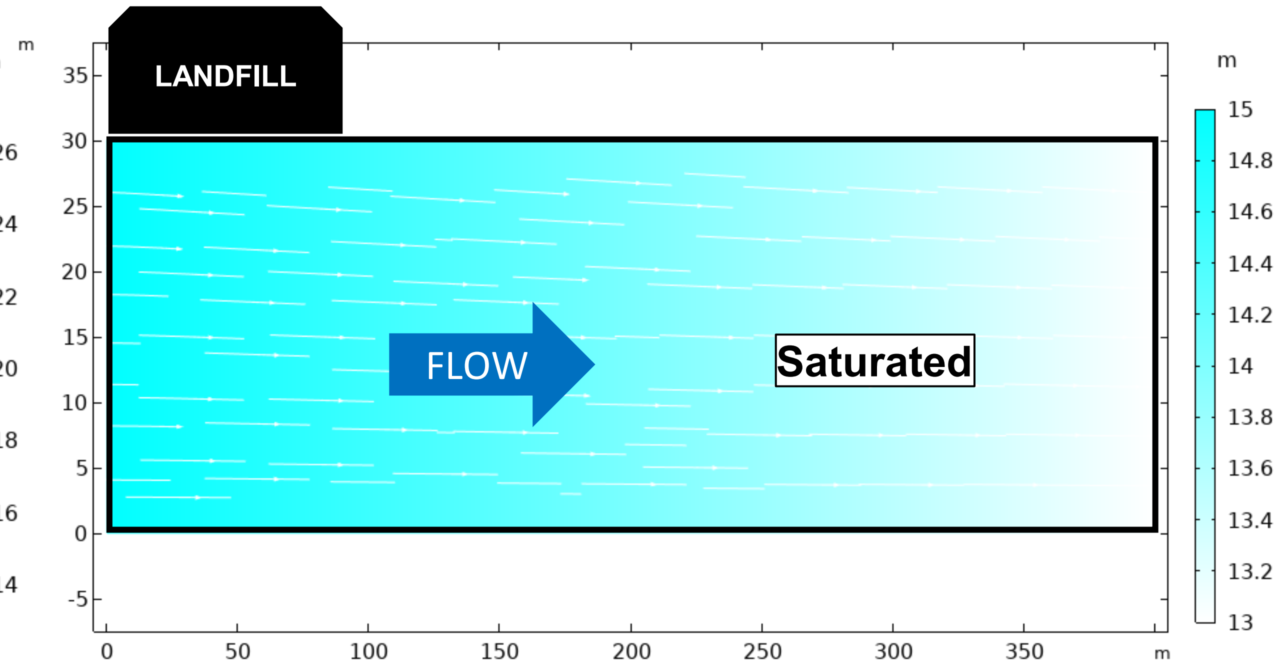
Specific parameters needed for modelling to assess longevity of fluxes and risks

Flow at different landfills

Landfill with unsaturated zone below



Landfill without unsaturated zone below

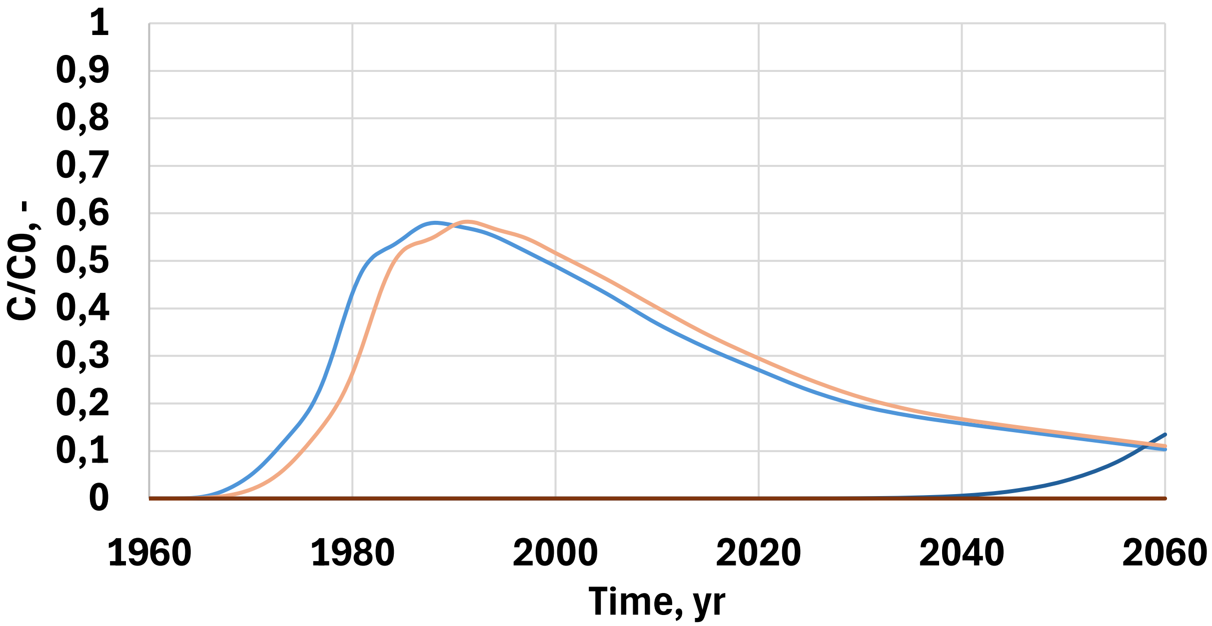


Do PFAS reach the groundwater?

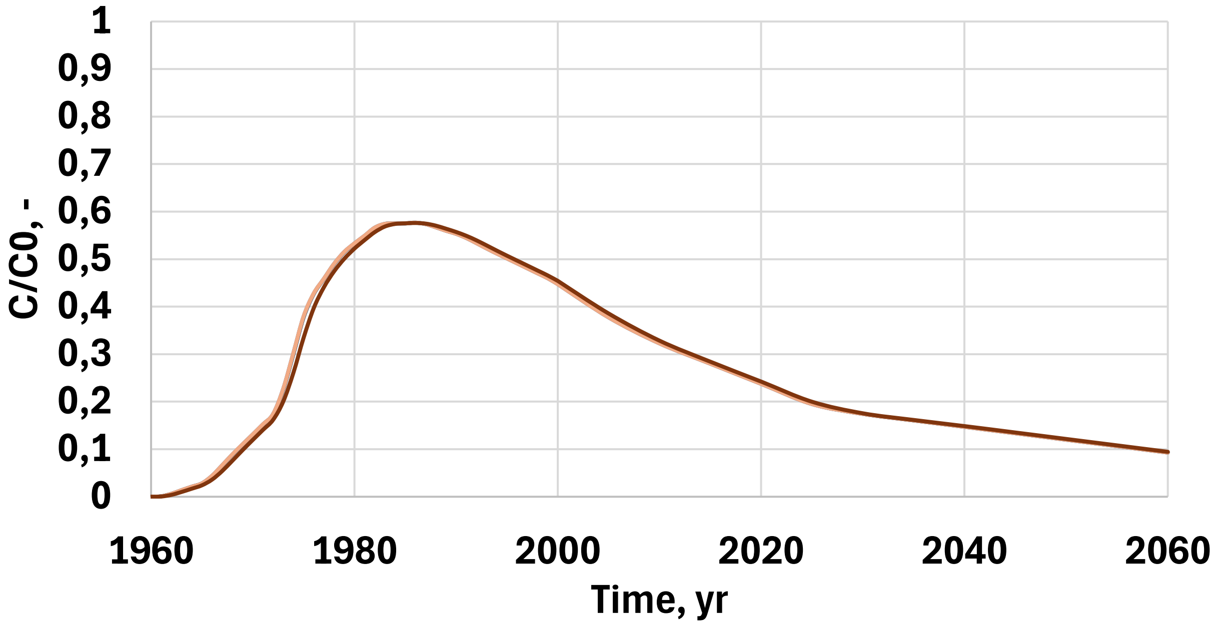
PFBA
PFOA
PFBS
PFOS

Lower landfill saturation

Landfill with unsaturated zone below



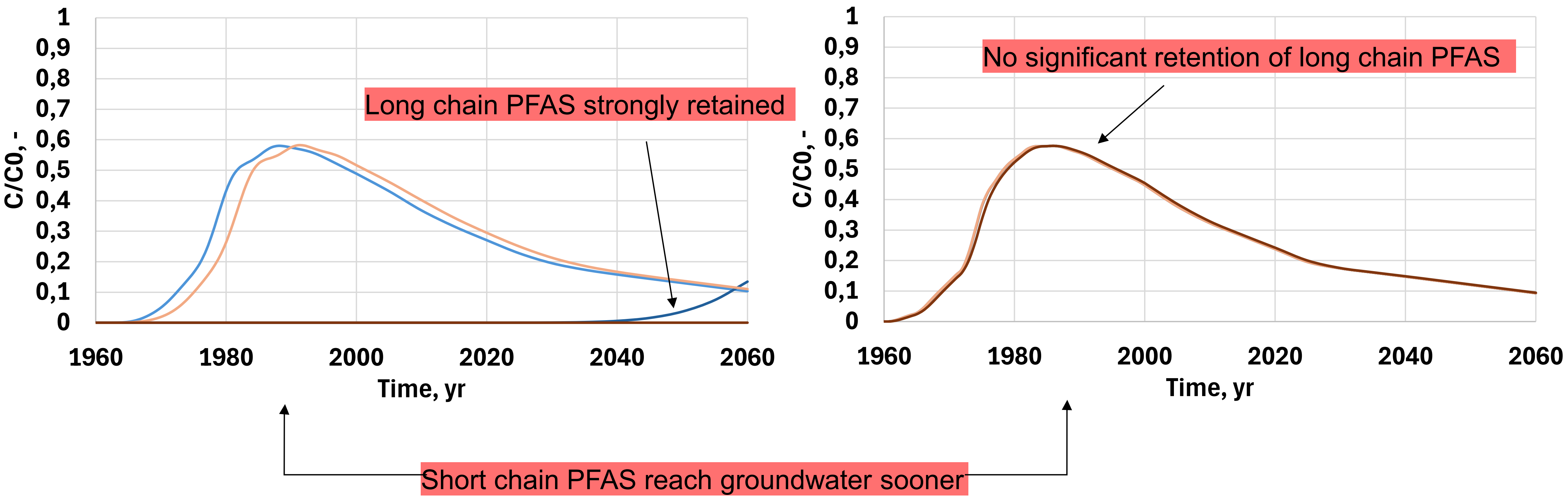
Landfill without unsaturated zone below



When will PFAS reach the groundwater?

Lower landfill saturation

Landfill with unsaturated zone below | **Landfill without unsaturated zone below**

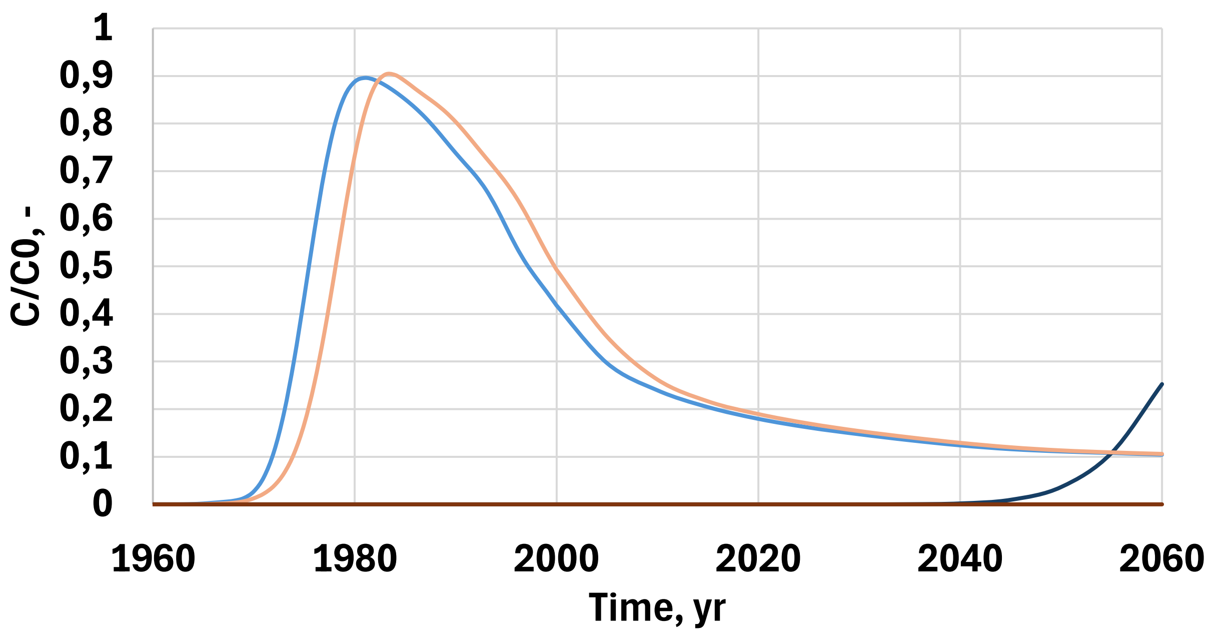


Do PFAS reach the groundwater?

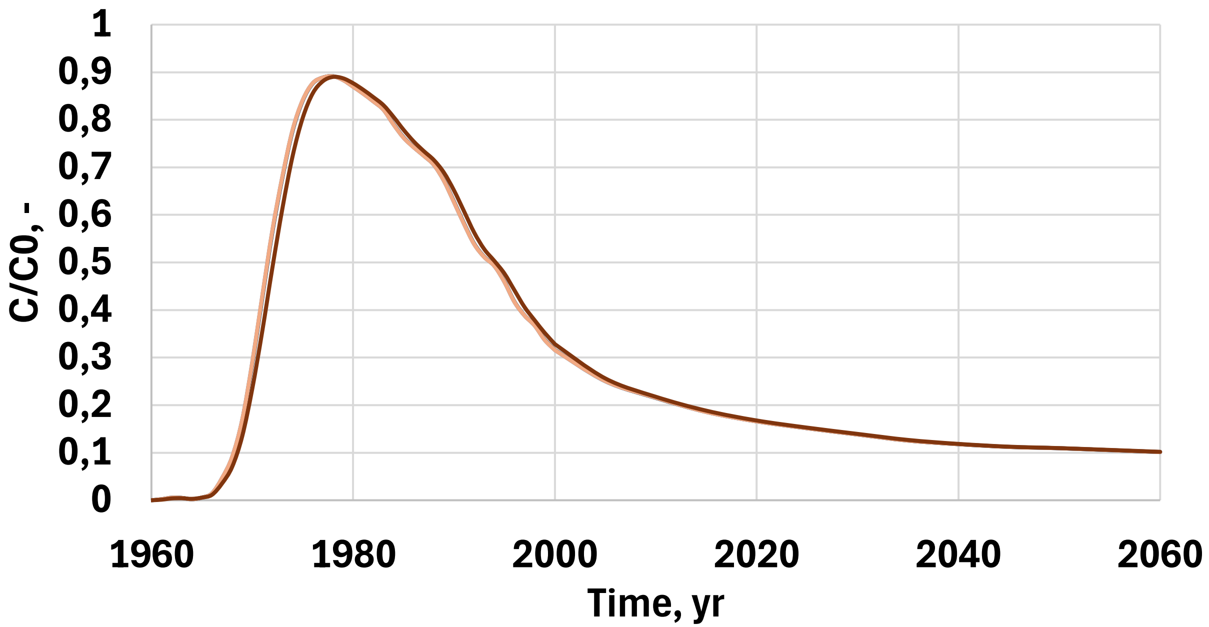
PFBA
PFOA
PFBS
PFOS

Higher landfill saturation

Landfill with unsaturated zone below



Landfill without unsaturated zone below



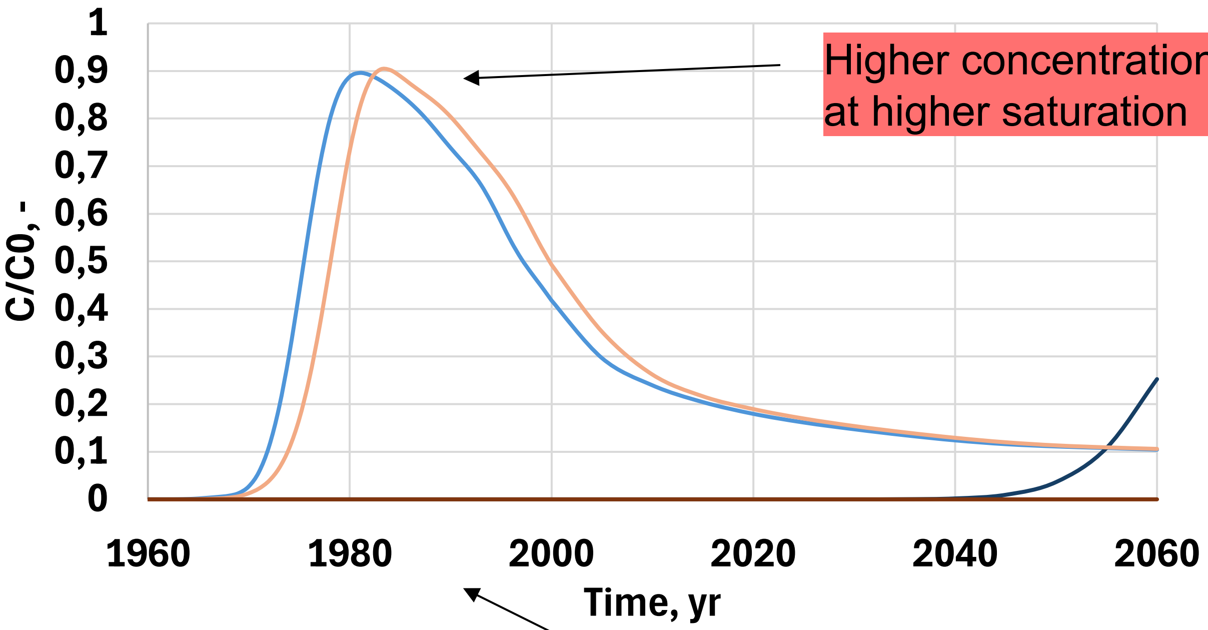
When will PFAS reach the groundwater?

PFBA
PFOA
PFBS
PFOS

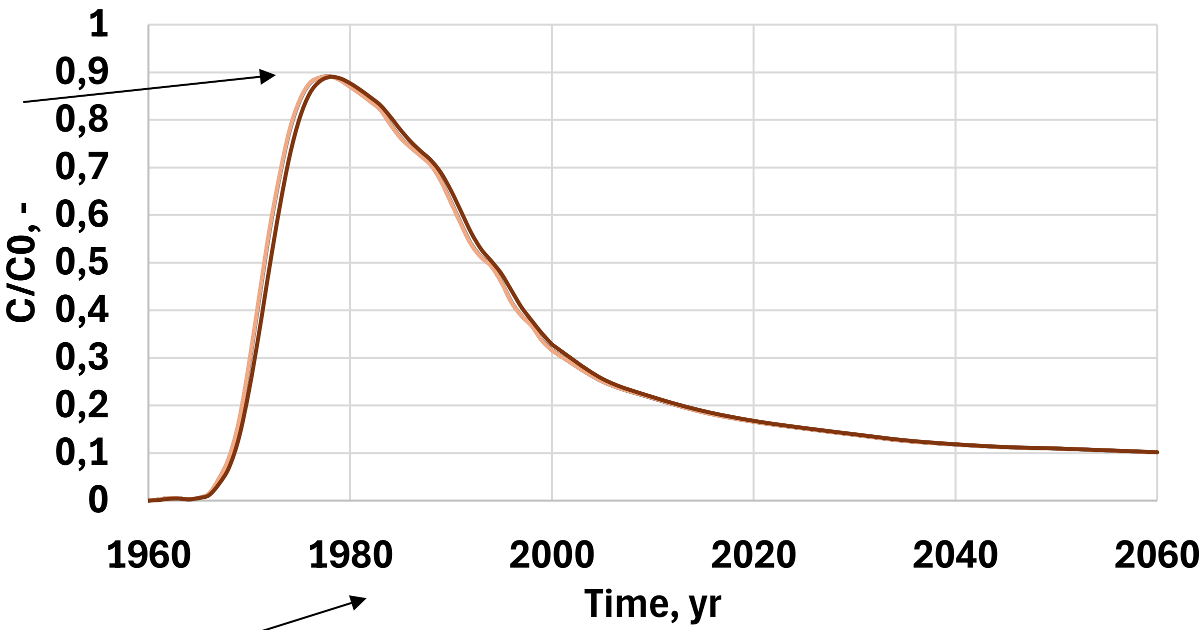
Higher landfill saturation

Landfill with unsaturated zone below

Landfill without unsaturated zone below



Higher concentration at higher saturation



Concentration peak occurs faster at higher saturation

Take home message:
Longevity of PFAS contamination

Scenario	Landfill type	Saturation inside of a landfill	Result
1	Unsaturated zone	Low	Long chain PFAS could leach for **decades** and **centuries**
2	Unsaturated zone	High	Long chain PFAS could leach for **decades** and **centuries**
3	GW	Low	Relatively shorter leaching time
4	GW	High	Relatively shorter leaching time

Continuous leaching is expected for a long time

Concentration levels could be significant

Shorter longevity expected for highly saturated landfills

Take home message:
What data is useful?

Unsaturated zone

-does it exist?

-location

-depth

-water content

-air-water interfacial area

-specific hydraulic parameters (van Genuchten)

Landfill

-historical data

-depth

-waste type

-waste location inside of landfill (hotspots)

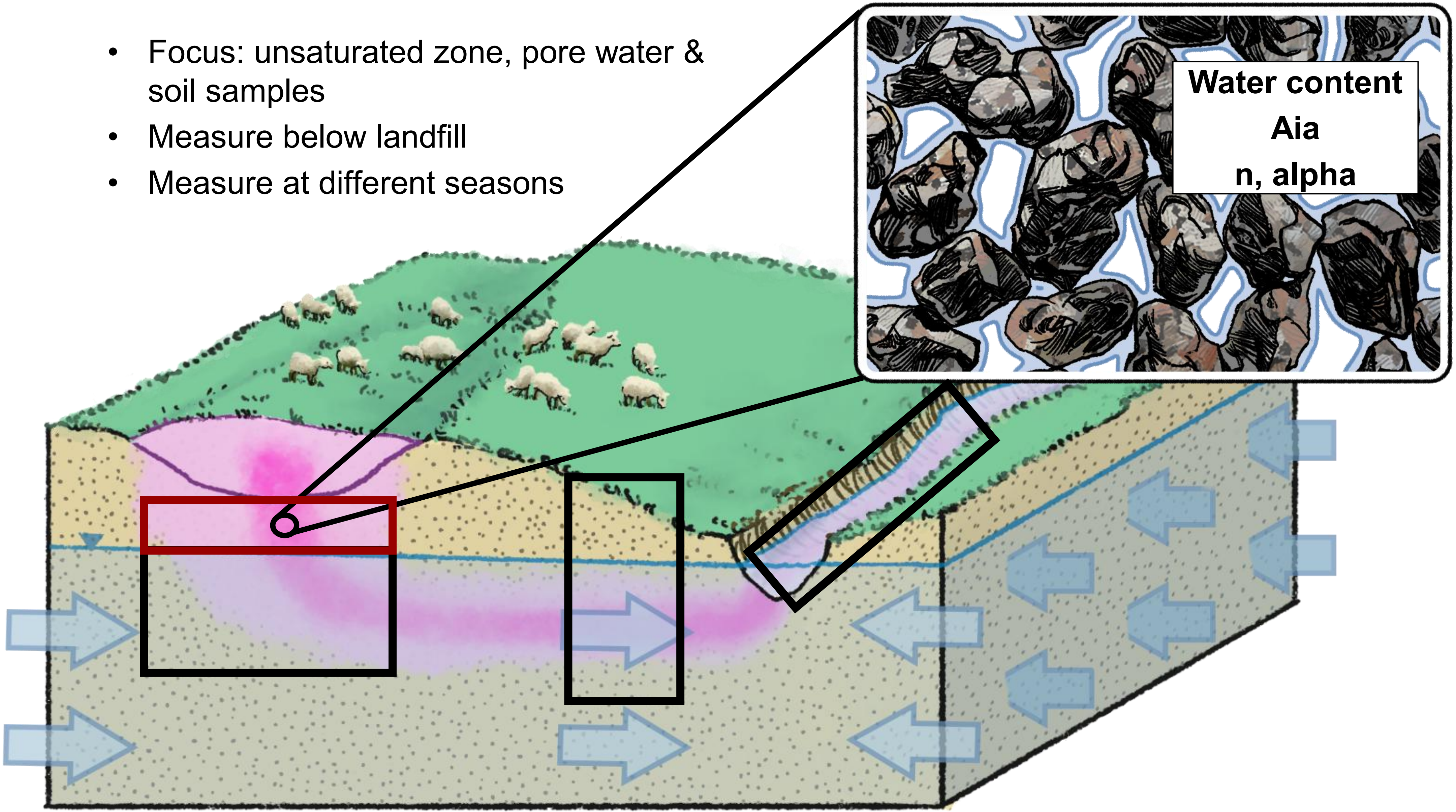
-landfill type

-duration of landfilling

-landfill saturation, leachate formation

Take home message:
Where to take samples/measurements?

- Focus: unsaturated zone, pore water & soil samples
- Measure below landfill
- Measure at different seasons



Acknowledgment

- SDC (Sino-Danish Center)
- The Capital Region of Denmark
- WSP

Thank you !

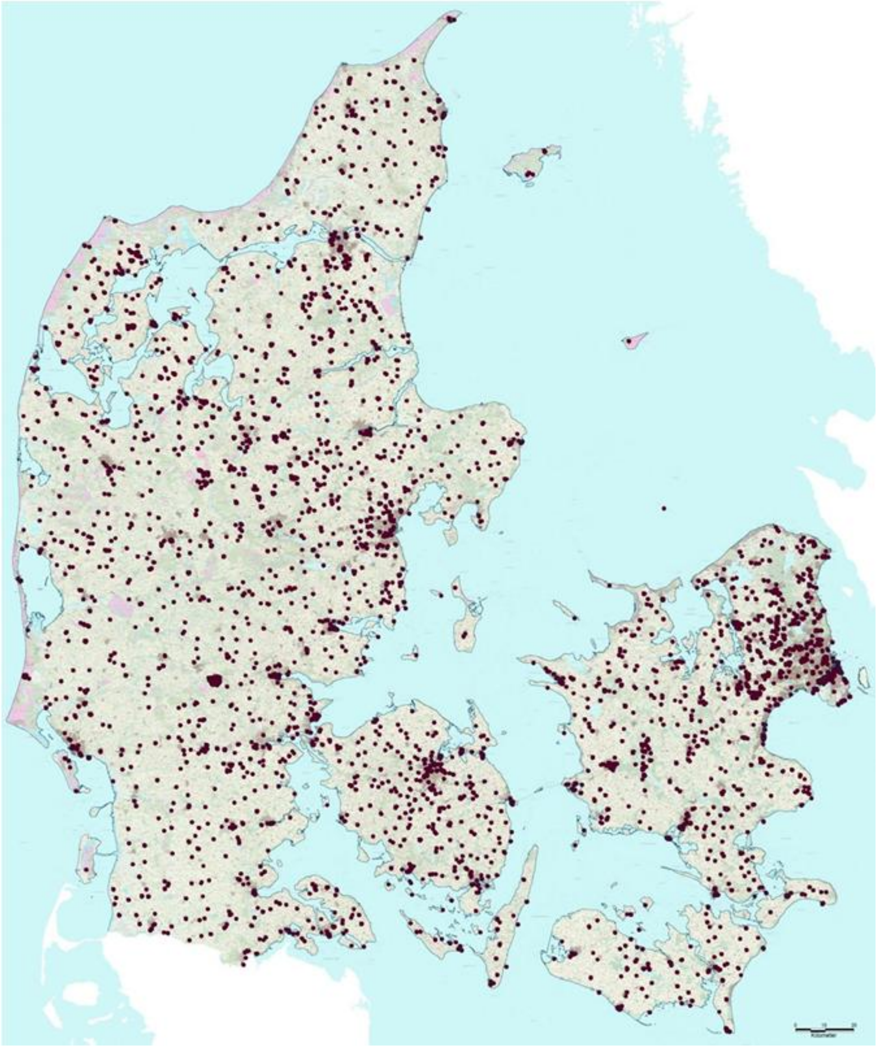
Questions ? ☺

Contact: nikb@dtu.dk

Danish old landfills

- Around 3000 old landfills
- Constructed before 1974
- Mixed waste landfills
- Uncontrolled landfills
  - No liners, no leachate collecting systems
  - Deposited in gravel pits, no compacting, no waste sorting, no control over the incoming material
- No regulations/policies
- Without measures for preventing groundwater and surface water pollution

Landfills in databases of Danish Regions (registered until December 2012)



Bjerg et al., 2014

Future work

- Further development of PFAS leaching function for landfills
- Fluctuating groundwater table
- Sorption – pH, PFAS mixture ?
- Spatial distribution of PFAS release at a landfill?
- Factors: precursor transformation, waste type, landfill environment ?

Parameters

Equation
$\frac{\partial \theta}{\partial t} + S_e S_p \left(-\frac{\partial \psi}{\partial t}\right) + \nabla \cdot \left(-K(\theta)\nabla(h+z)\right) = W$
$\theta(\psi) = \begin{cases} \theta_r + \frac{\theta_s - \theta_r}{(1+(\alpha \cdot \psi)^n)^{1-1/n}} & \psi \geq 0 \\ \theta_s & \psi < 0 \end{cases}$
$\frac{\partial(\theta c)}{\partial t} + \rho_b \frac{\partial c_s}{\partial t} + \frac{\partial c_{ia}}{\partial t} + \nabla \cdot (\theta c \vec{v}) + \nabla \cdot \left(-\theta \vec{D} \nabla c\right) = 0$
$c_s = K_d \cdot c$
$c_{ia} = A_{ia} \cdot K_{ia} \cdot c$
$A_{ia} = (-2.85 \cdot S_w + 3.6) \cdot ((1 - S_w) \cdot 3.9 \cdot d_g^{-1.2})$ (Brusseau, 2023)

θ_w – Water content [-]

S_e – Effective saturation [-]

S_p – Storage coefficient [1/Pa]

ψ – Capillary pressure [Pa]

K – Hydraulic conductivity [m/s]

h – Head [m]

W – Source/sink [m/s]

θ_r – Residual water content [-]

θ_s – Saturated water content [-]

α – Van Genuchten parameter [1/cm]

n – Van Genuchten parameter [-]

c – Concentration [ng/L]

ρ_b – Bulk density [kg/L]

$\vec{v}$ – Velocity [m/s]

$\vec{D}$ – Dispersion coefficient [cm^2/s]

K_d – Soil specific distribution coefficient [L/kg]

K_{ia} – Air-water interfacial adsorption coefficient [cm]

A_{ia} – Air-water interfacial area [1/cm]

S_w – Saturation [-]

d_g – Grain diameter [cm]