Investigating and modelling PFAS leaching from landfills to groundwater and surface water

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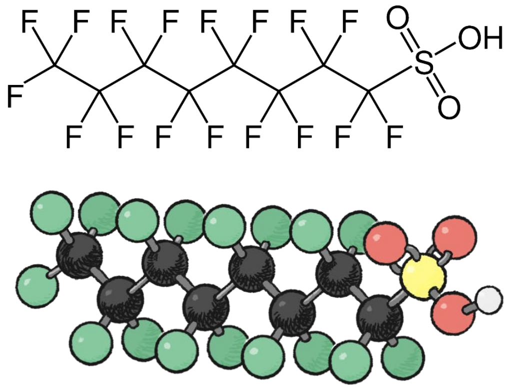
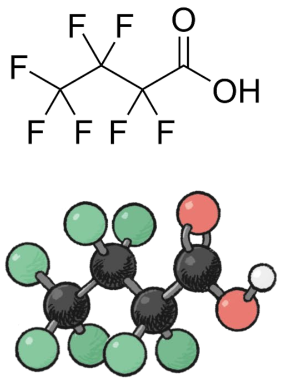
Introduction - PFAS

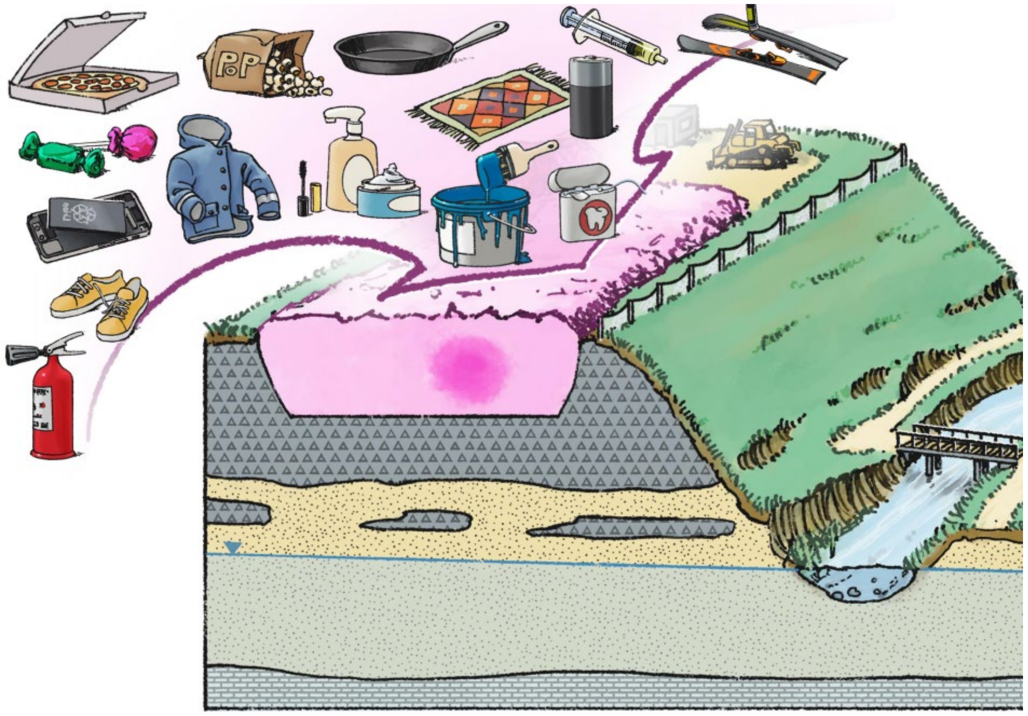
- Highly complex group of anthropogenic chemicals
- Present in water, air, food, wildlife and humans
- Most relevant and concerning 22 PFAS in Denmark
- World wide problem

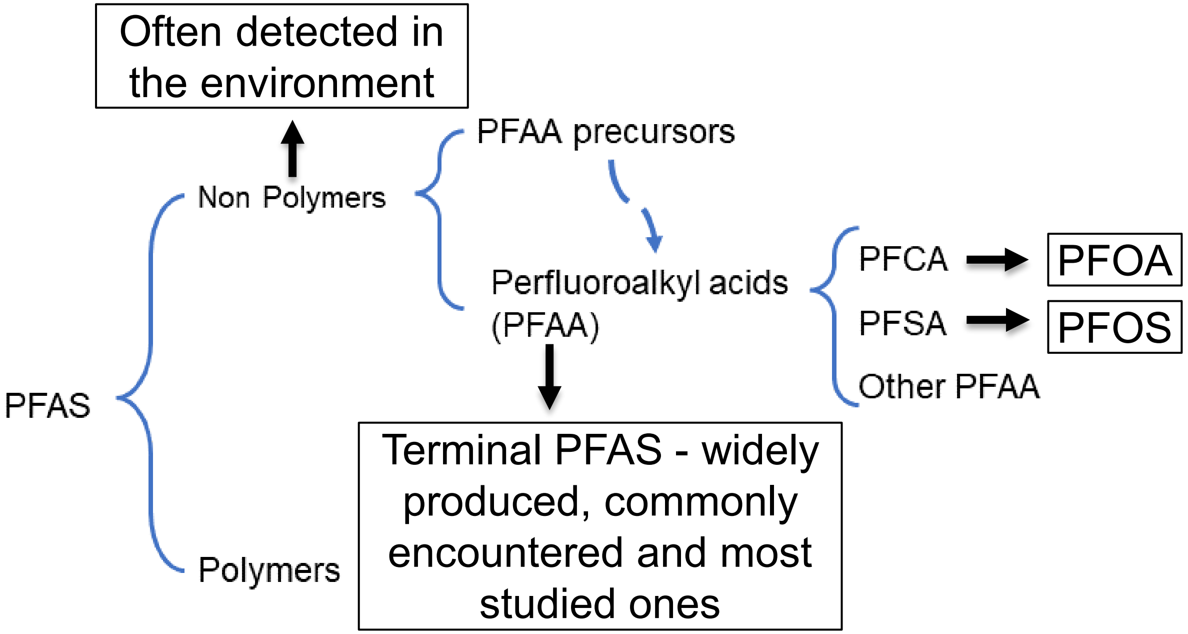
PFOS



PFBA







Landfills with PFAS

- Potential **direct sources of PFAS** into surrounding environment
- **High PFAS concentrations** found in landfill leachates world-wide
- Highly **complex systems**, not well understood

- Challenges:
  – Landfill specific processes – precursor transformation
  – Heterogenous waste material
  – Landfill design - old/engineered landfills, with/without liner, leachate collection
  – PFAS input function for landfills
  – Landfill environment - reduced environment, abundance of organic carbon, etc.

Landfills with PFAS – Global Concentrations

Global distribution of PFAS (PFAA) in landfill leachates (Wei et al. 2019)

Concentration, ng/L	Europe*	North America	Australia	China
∑PFCA	13 100	22 800	13 100	250 500
∑PFSA	4 700	8 700	3 800	48 100

*Germany, Denmark, Sweden, Finland, Norway

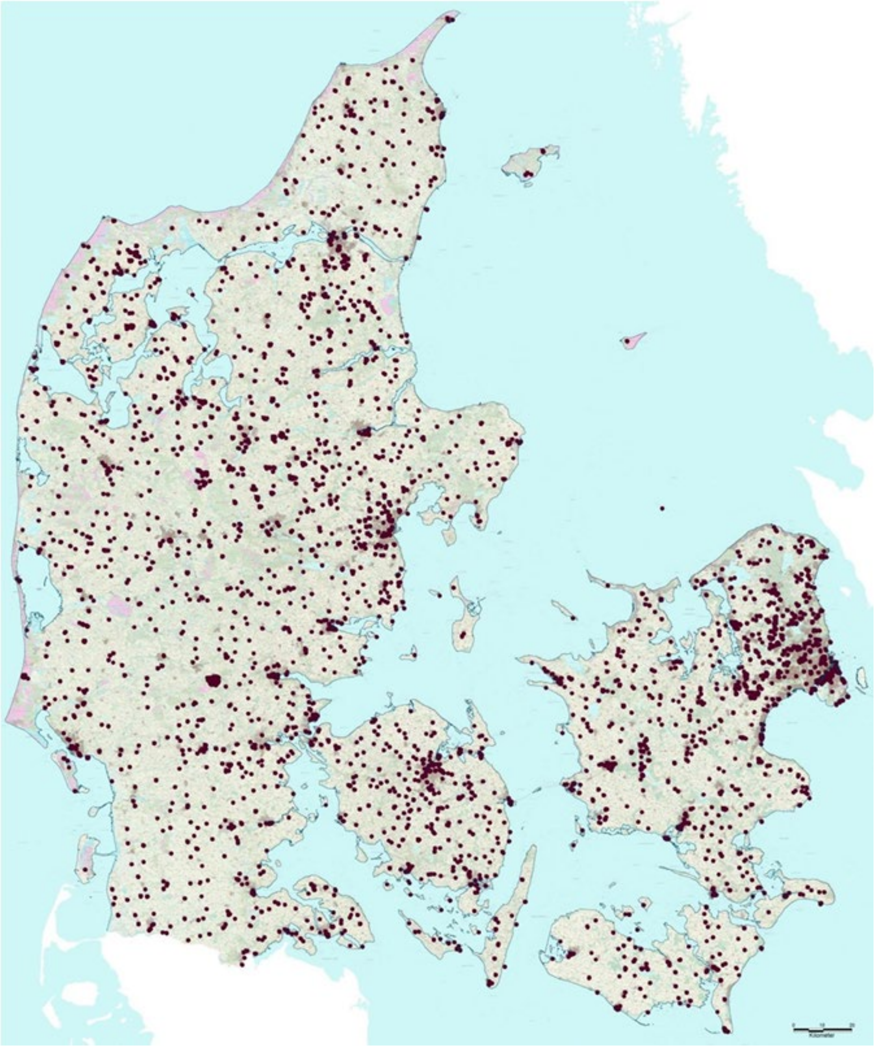
Individual PFAS (PFAA) compounds (Tang et al. 2024, Fuertes et al. 2017, Hamid et al. 2018)

- North America: PFHxA, PFHpA, PFBA, PFPeA, PFOA, PFOS, etc.
- Europe: PFOA, PFOS, PFHxS, PFHxA, PFBA, PFBS, etc.
- Australia: PFHxA, PFHxS, PFOS, PFOA
- China: PFBS, PFOA, PFPrA, PFBA, PFOS, etc.

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

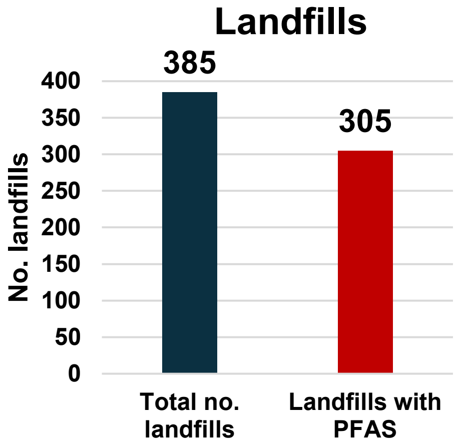
Landfills in databases of Danish Regions (registered until December 2012)



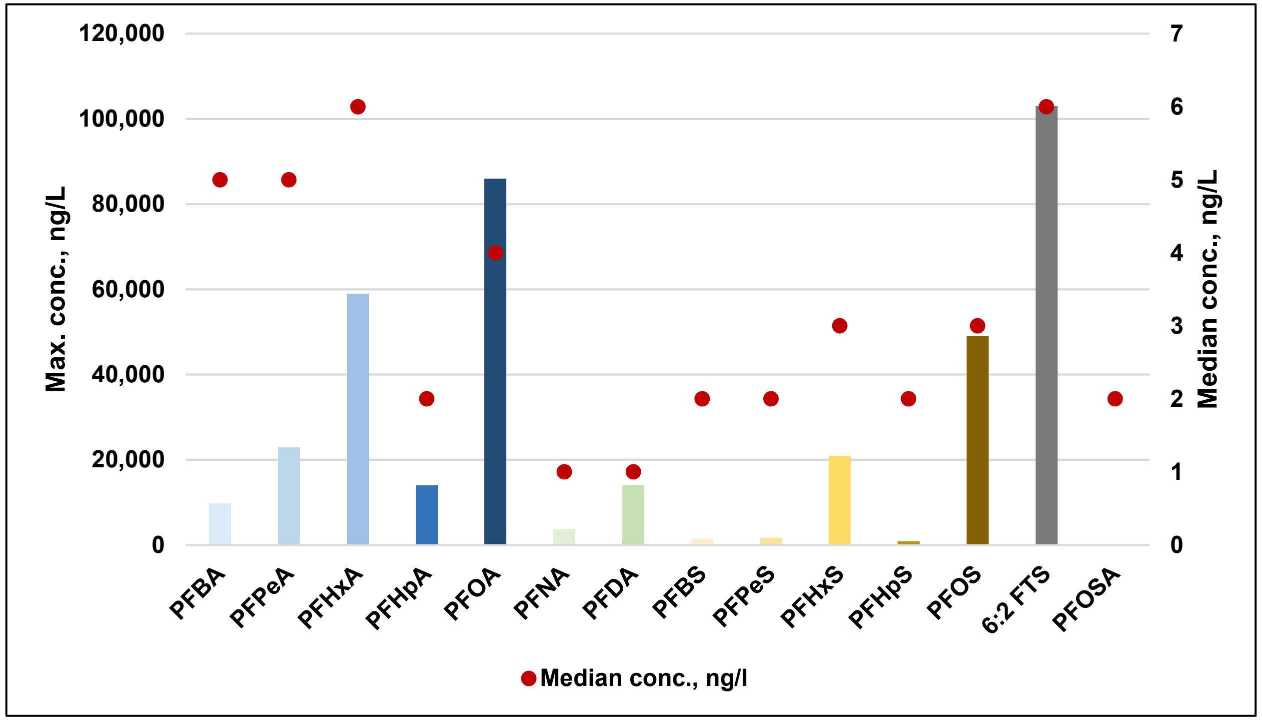
Bjerg et al., 2014

Danish old landfills - PFAS

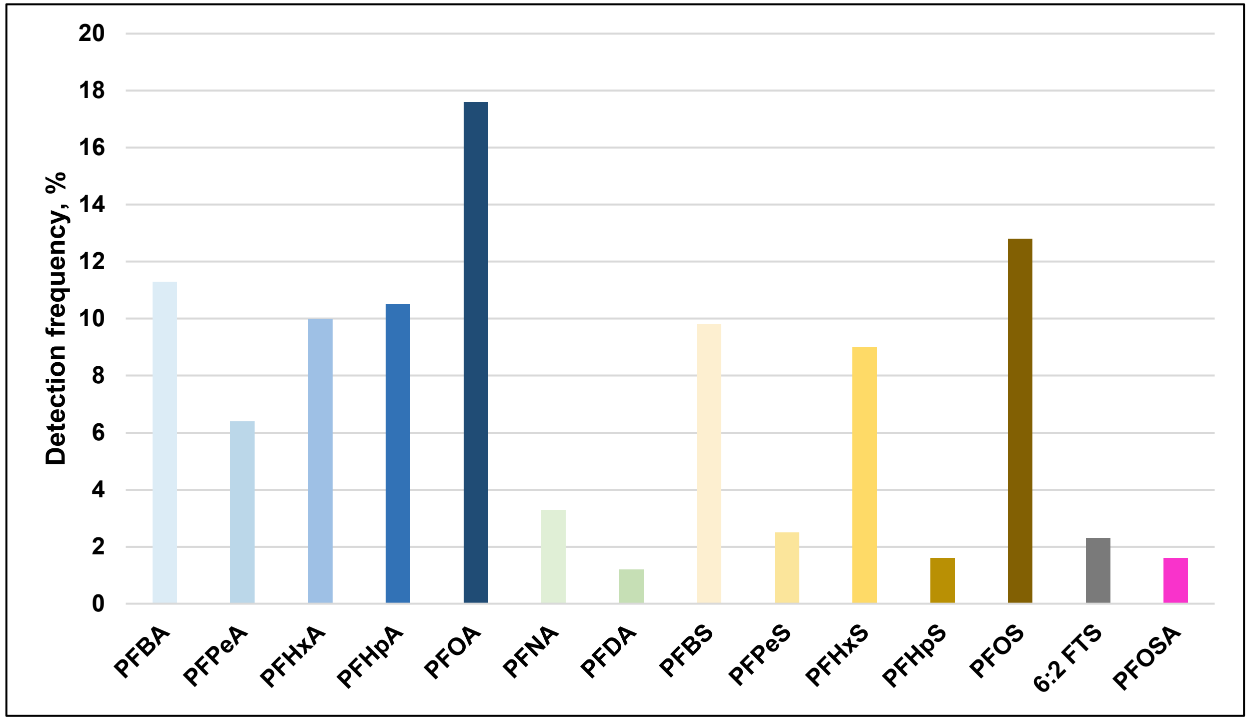
- PFAS database from Danish Regions, investigations 2014-2023
- One of the industries with the highest maximum and highest median concentrations for several PFAS



Max. and median concentration per compound - Groundwater



Most frequently detected PFAS - Groundwater



Research objectives

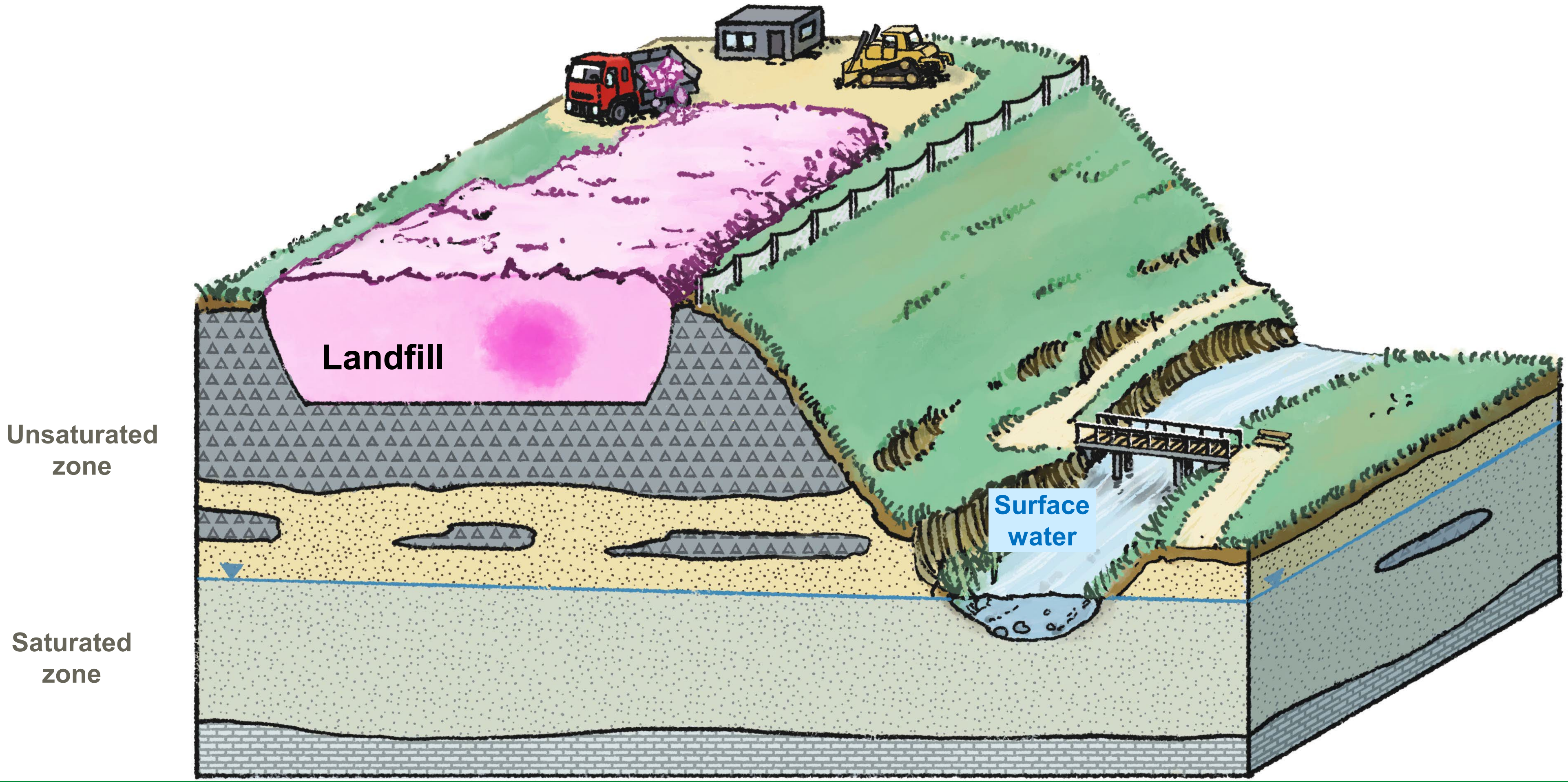
- PFAS specific behavior at landfill sites
- Transport model for PFAS leaching from landfills
- Quantify PFAS fluxes from landfills
- Controlling factors for PFAS at landfills

Collaboration

- SDC (Sino-Danish Center)
- The Capital Region of Denmark
- Possible input and discussion with other Danish regions, consulting companies, water utilities and other relevant partners in Denmark and China

Conceptualization – Transport of PFAS from landfills

- **Tool for risk assessment of landfill sites**



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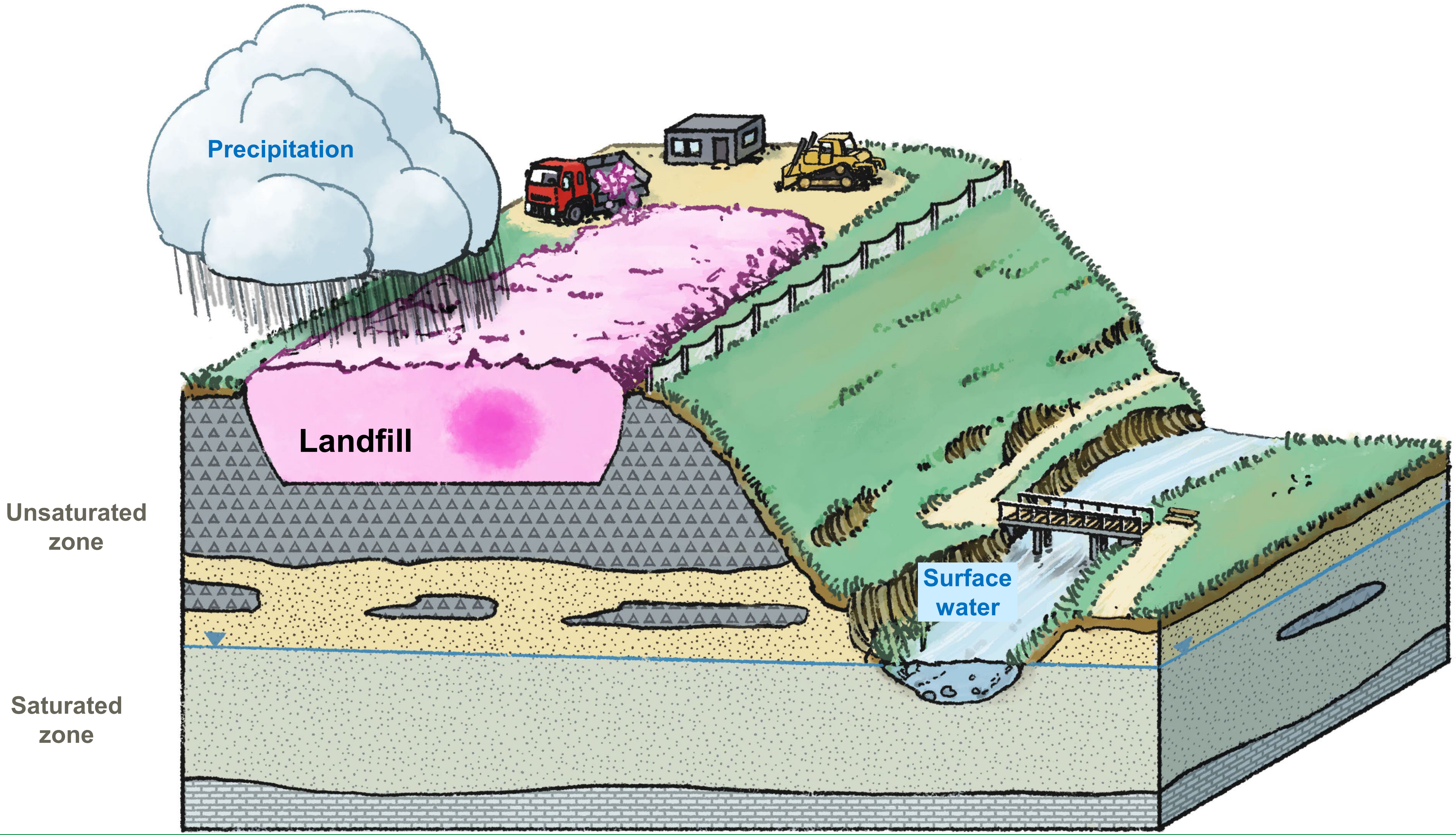

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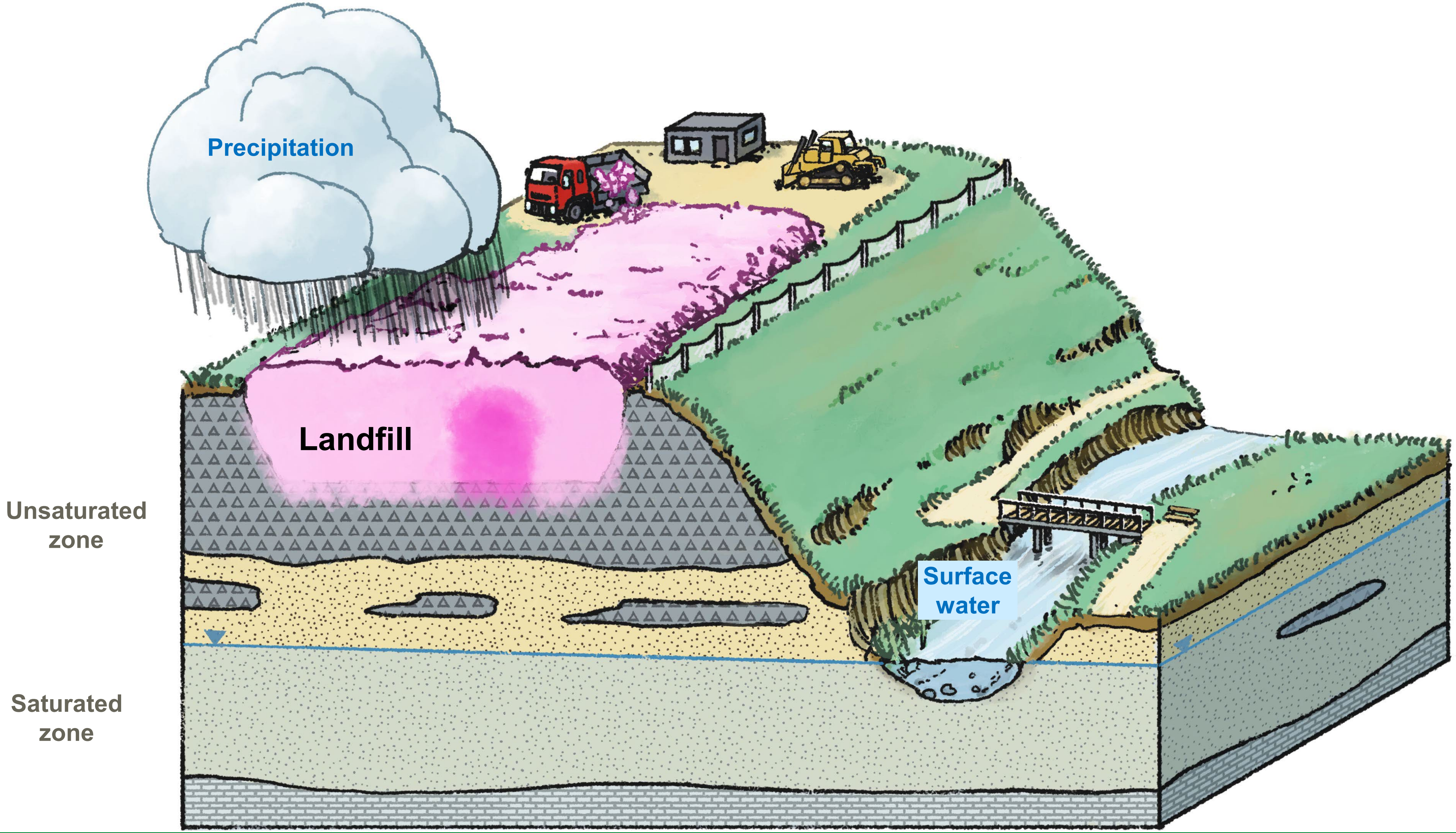

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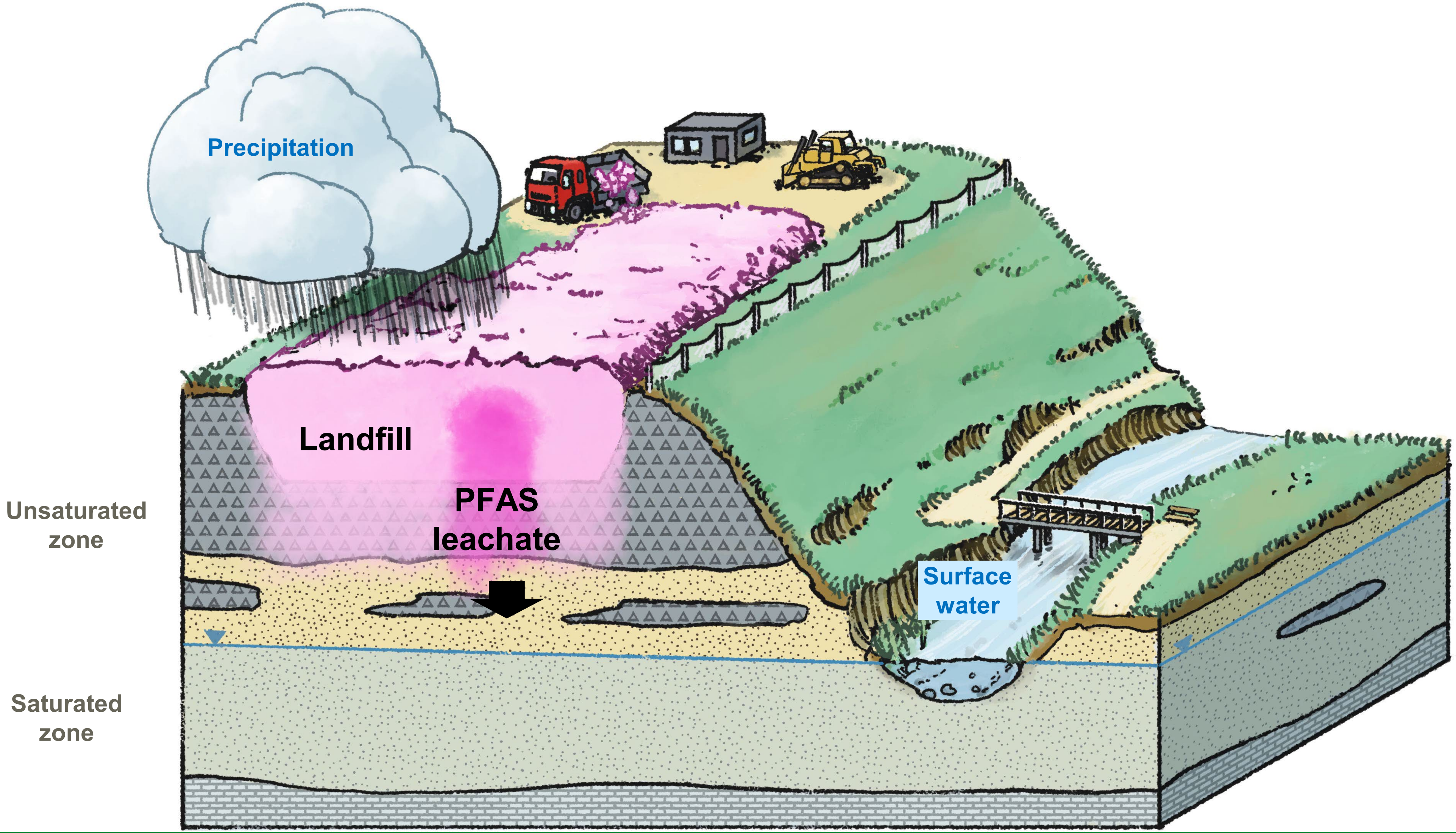

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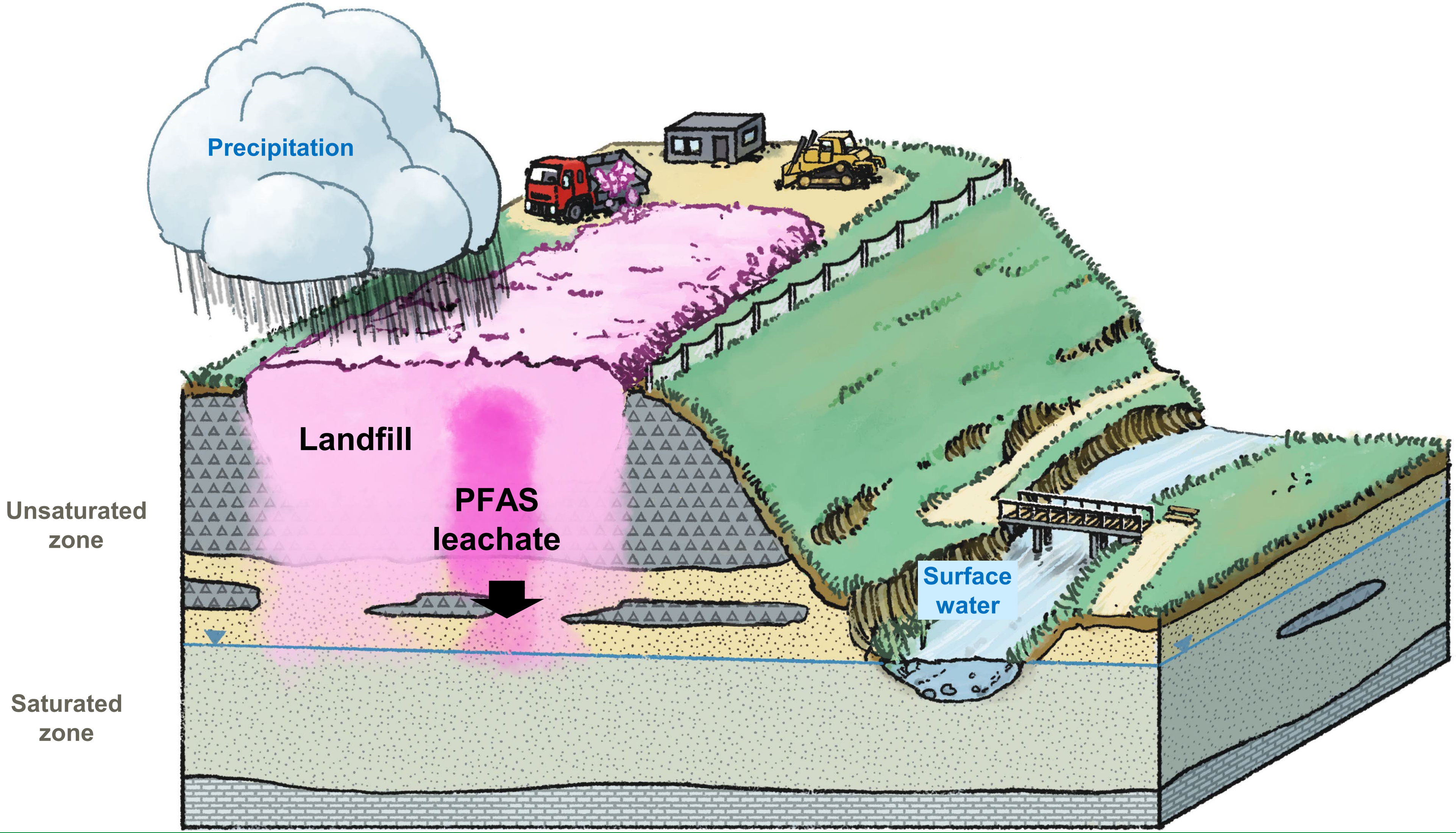

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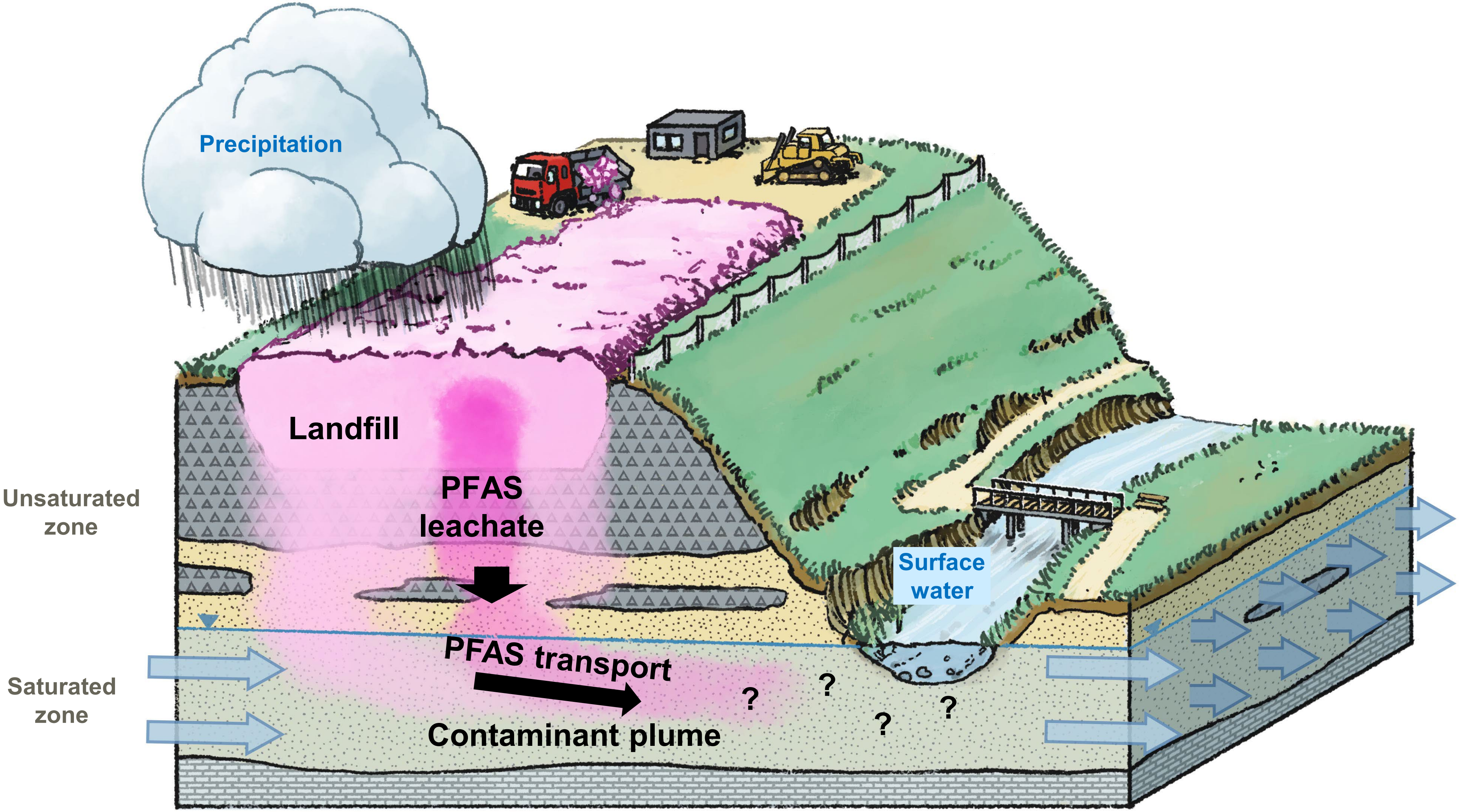

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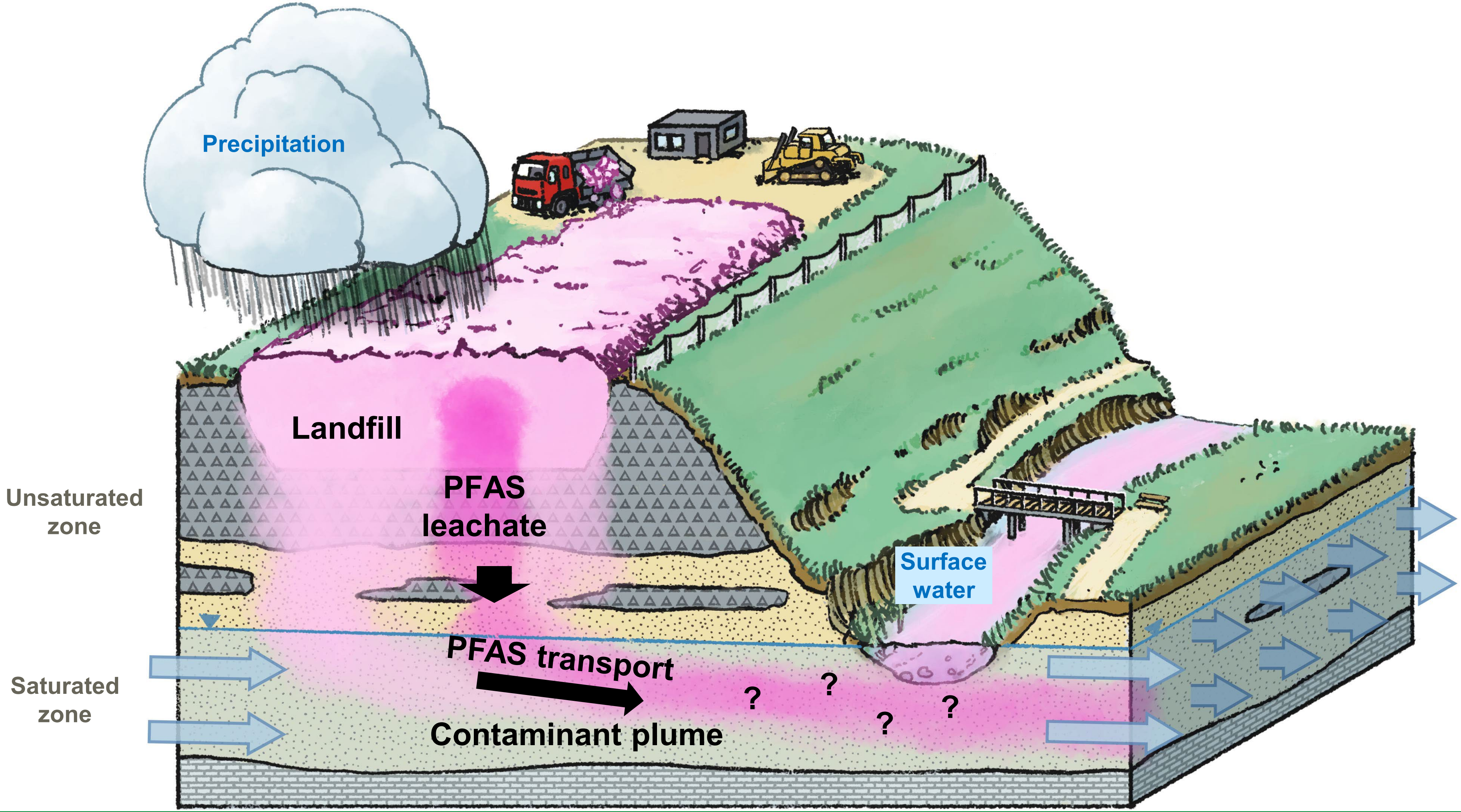

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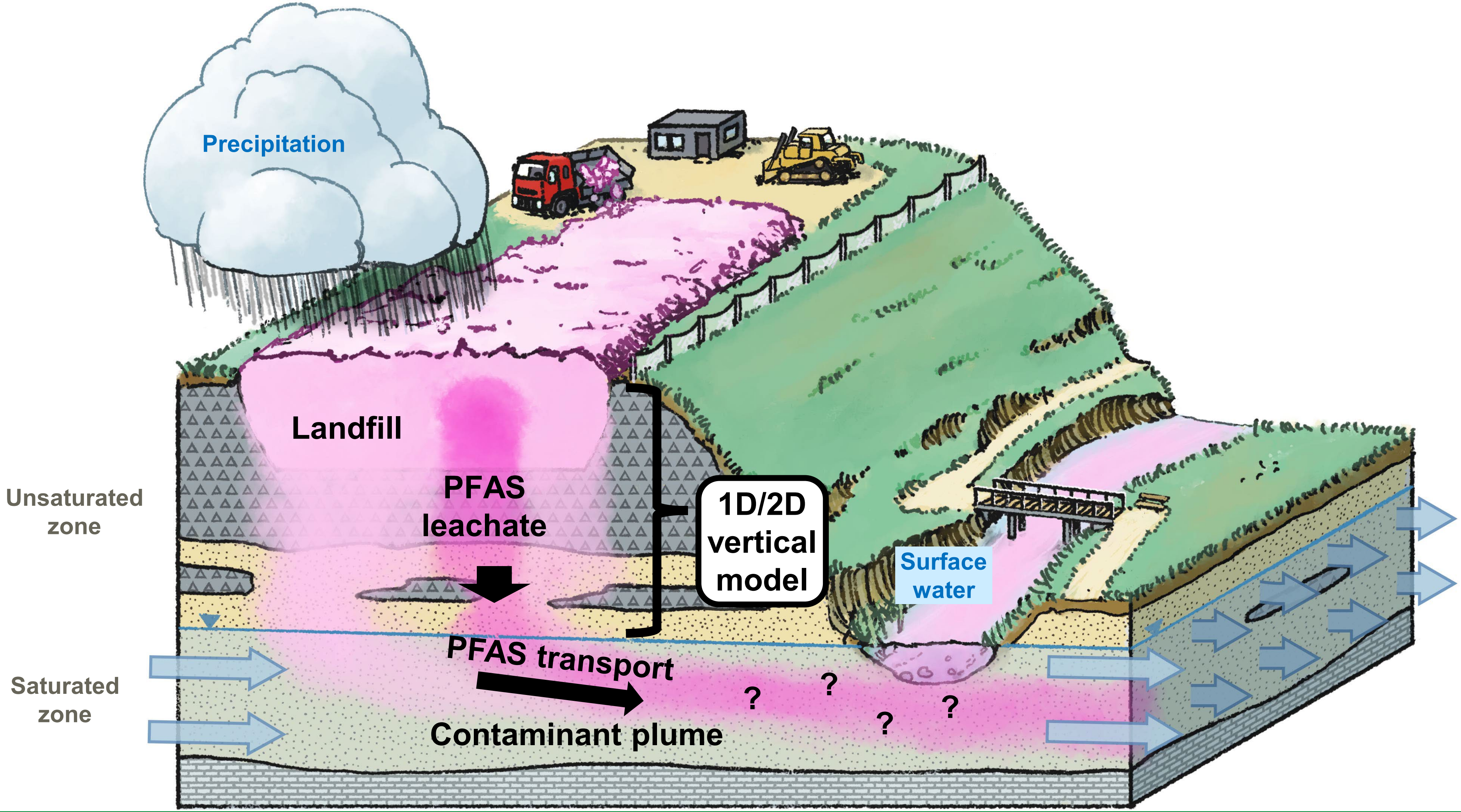

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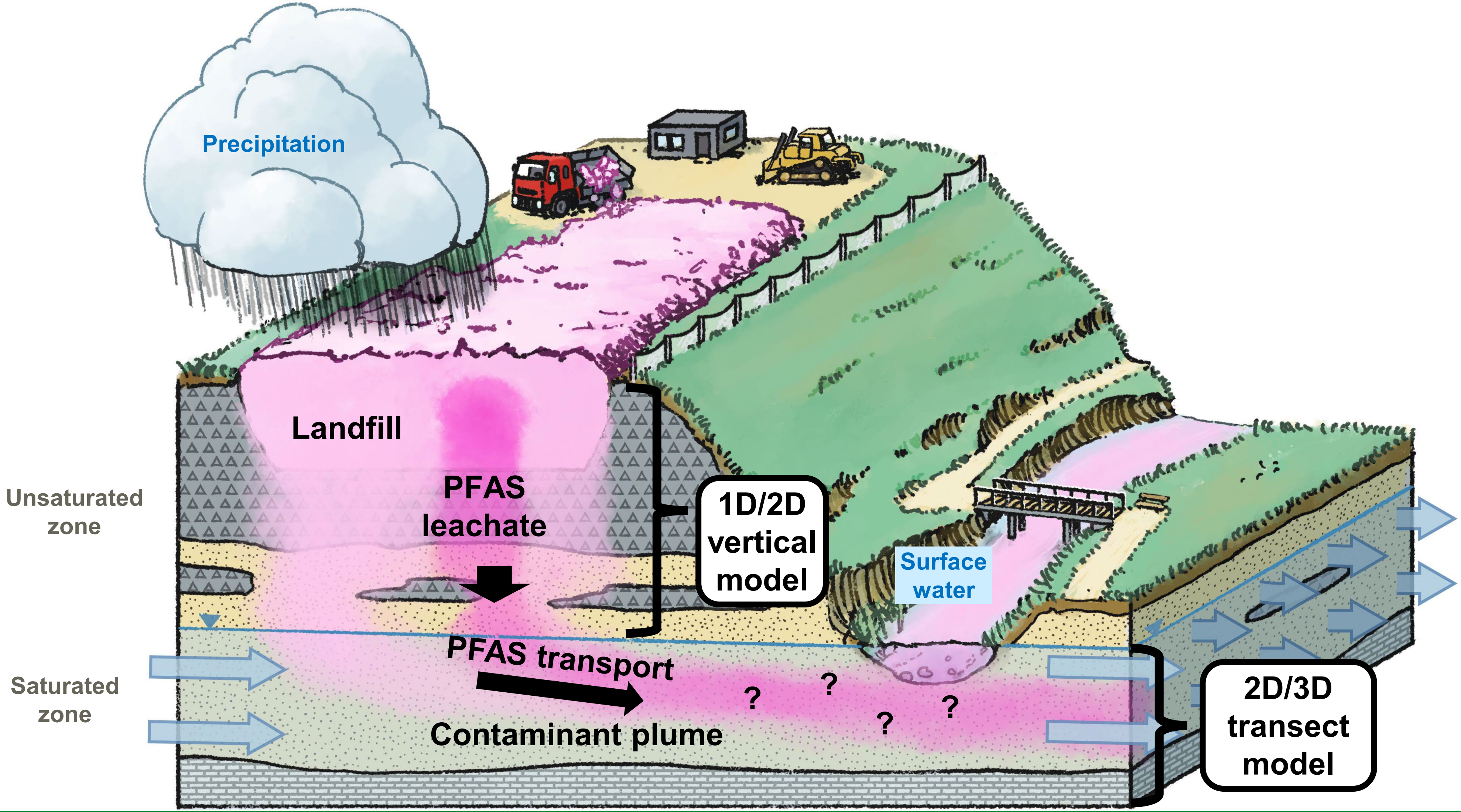

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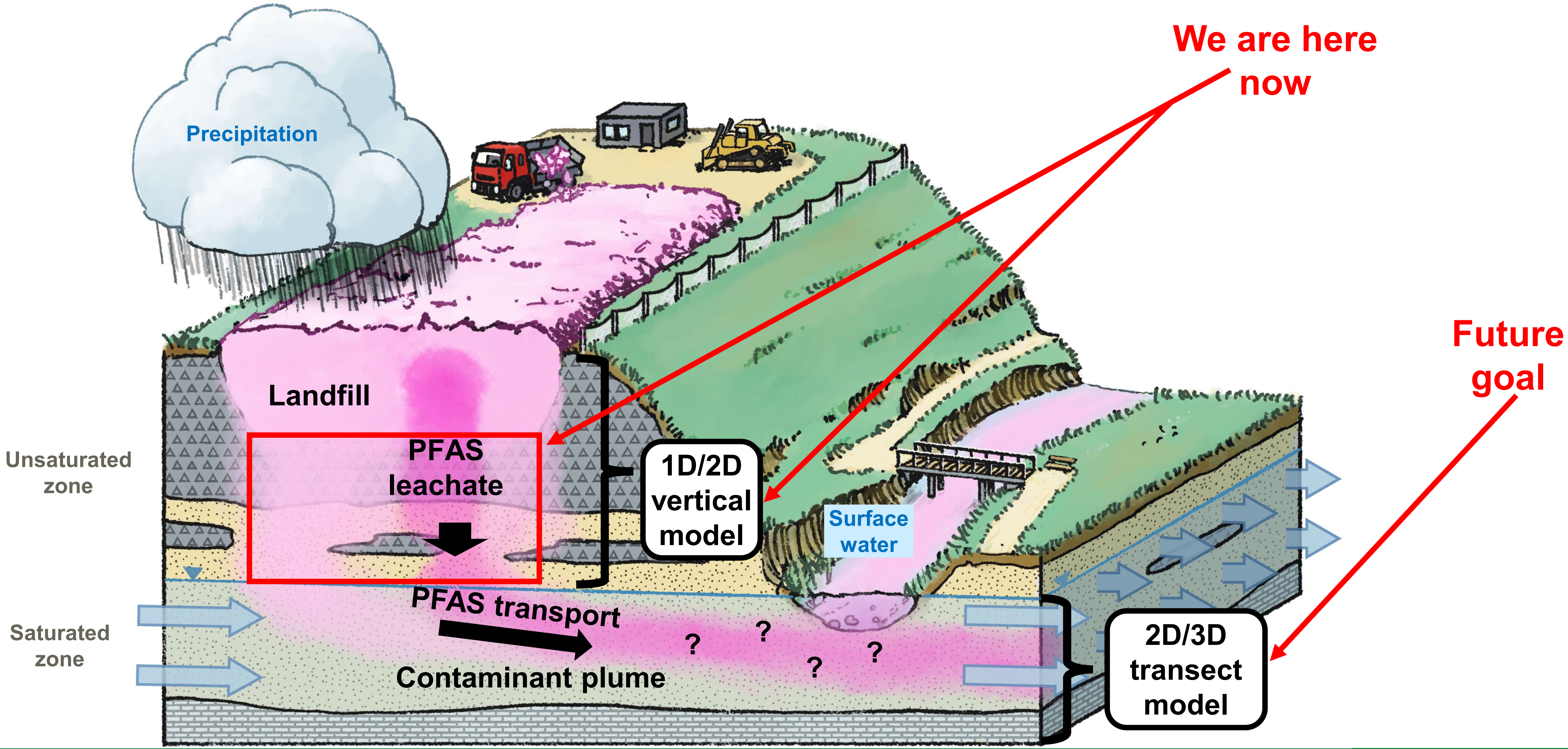
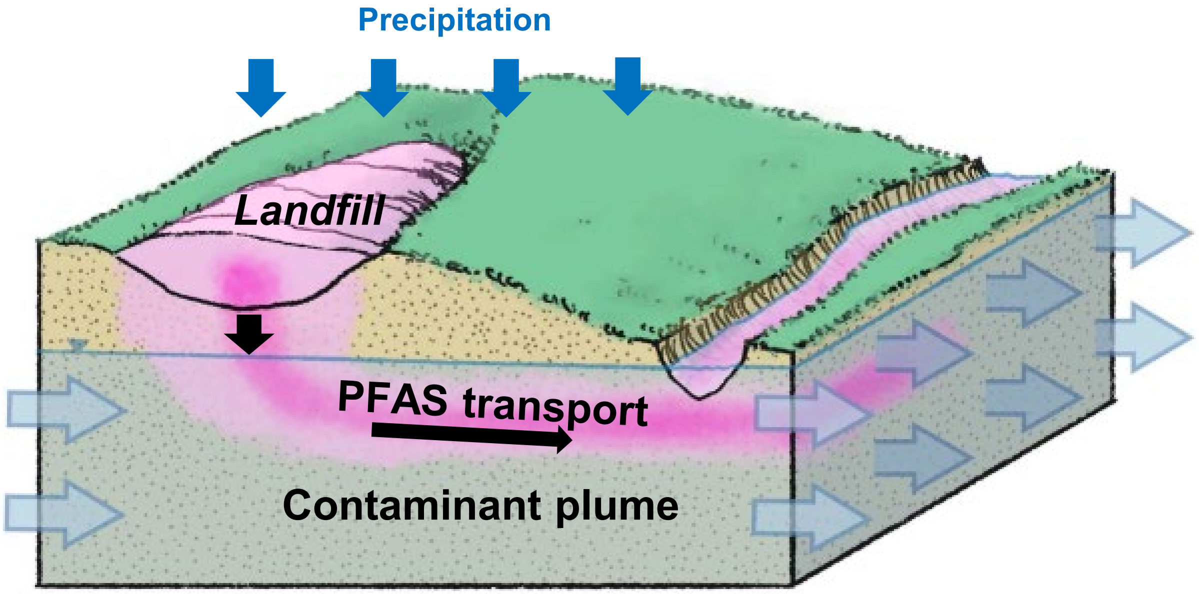


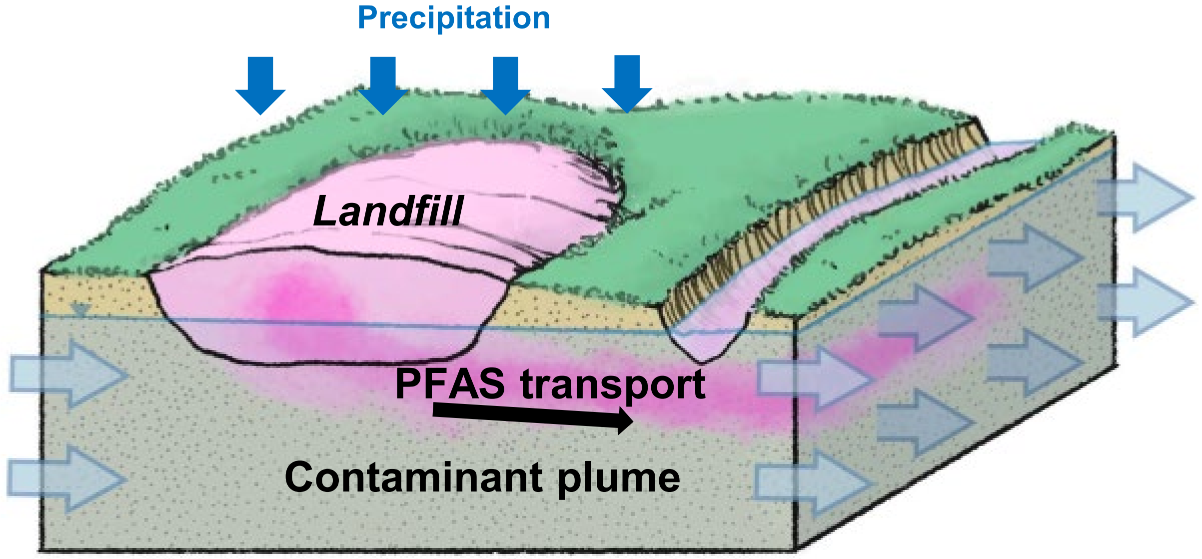
Conceptualization – Different landfill types

- Differences:
  - Water content
  - Attenuation processes for PFAS
  - Risk ?

Landfill with unsaturated zone



Landfill without/ with shallow unsaturated zone



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]

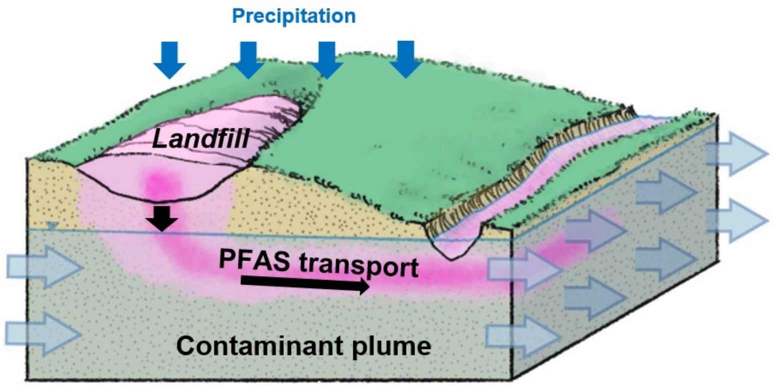
K_{ia} – Air-water interfacial adsorption coefficient [cm]

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

θ_w – Water content [-]

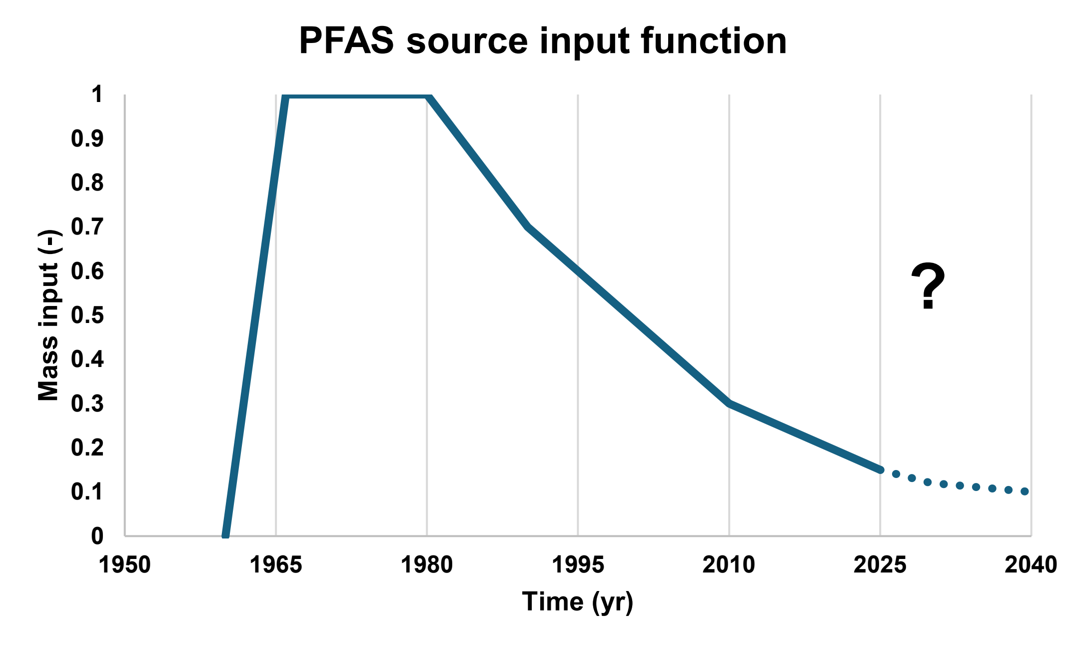
Process	Equation
Flow in unsaturated zone (Richards' eq.)	$\frac{\partial \theta}{\partial t} + S_e S_p \left(-\frac{\partial \psi}{\partial t}\right) + \nabla \cdot \left(-K(\theta)\nabla(h+z)\right) = W$
Variable saturation (van Genuchten)	$\theta(\psi) = \begin{cases} \theta_r + \frac{\theta_s - \theta_r}{(1+(\alpha \cdot \psi)^n)^{1-1/n}} & \psi \geq 0 \\ \theta_s & \psi < 0 \end{cases}$
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	$A_{ia} = (-2.85 \cdot S_w + 3.6) \cdot ((1 - S_w) \cdot 3.9 \cdot d_g^{-1.2})$

Model set up



- Flow + Transport vertical model in the unsaturated zone
- PFAS input function – old Danish landfills
- 4 PFAS
  - PFCA C4 and C8: **PFBA**, **PFOA**
  - PFSA C4 and C8: **PFBS**, **PFOS**
- Sandy soil
- Infiltration 200 mm/yr

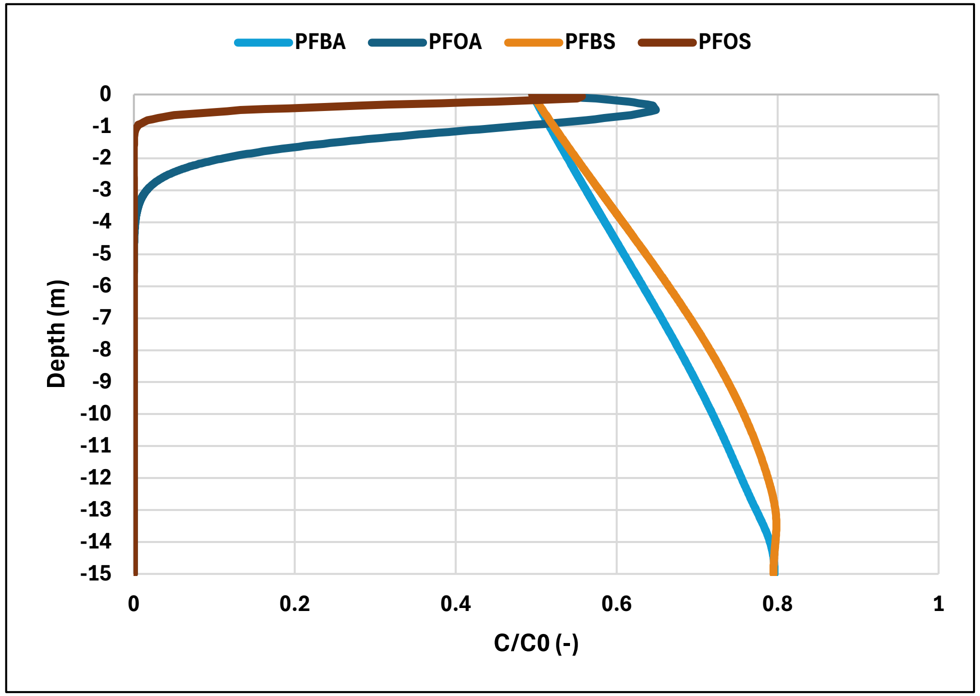
- 2 scenarios:
  - **Deep unsaturated zone**
    - » **h = 15 m**
  - **Shallow unsaturated zone**
    - » **h = 0.5 m**



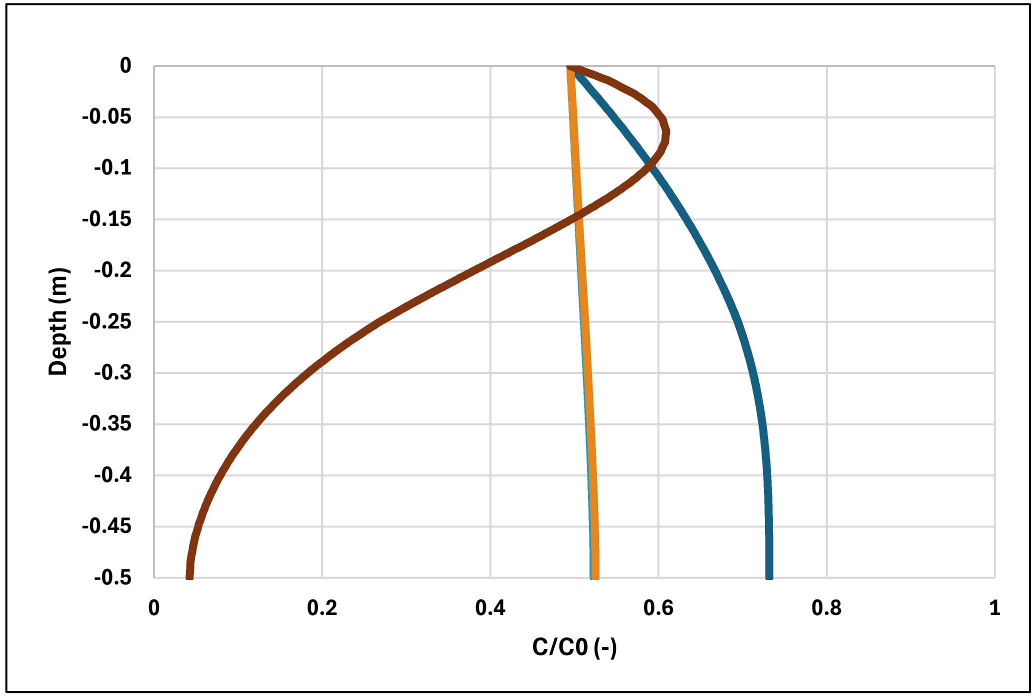
Vertical transport
t = 2000 yr (40 year after leaching started)

- Long-chain PFAS retained more than short-chained in general
- Less retention in landfill with shallow unsaturated zone

Landfill with deep unsaturated zone
h = 15 m



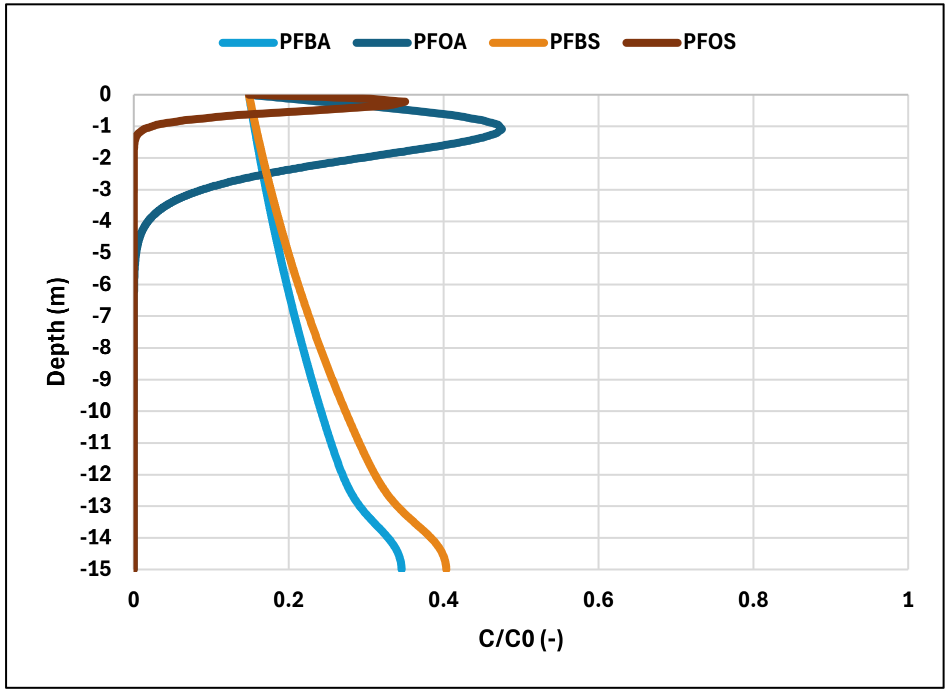
Landfill with shallow unsaturated zone
h = 0.5 m



Vertical transport
t = 2025 yr (65 year after leaching started)

- Stronger leaching for PFAS in landfill with shallow unsaturated zone
- Lower conc. of PFOA in shallow unsaturated zone
- Short chain PFAS reach the groundwater

Landfill with deep unsaturated zone
h = 15 m



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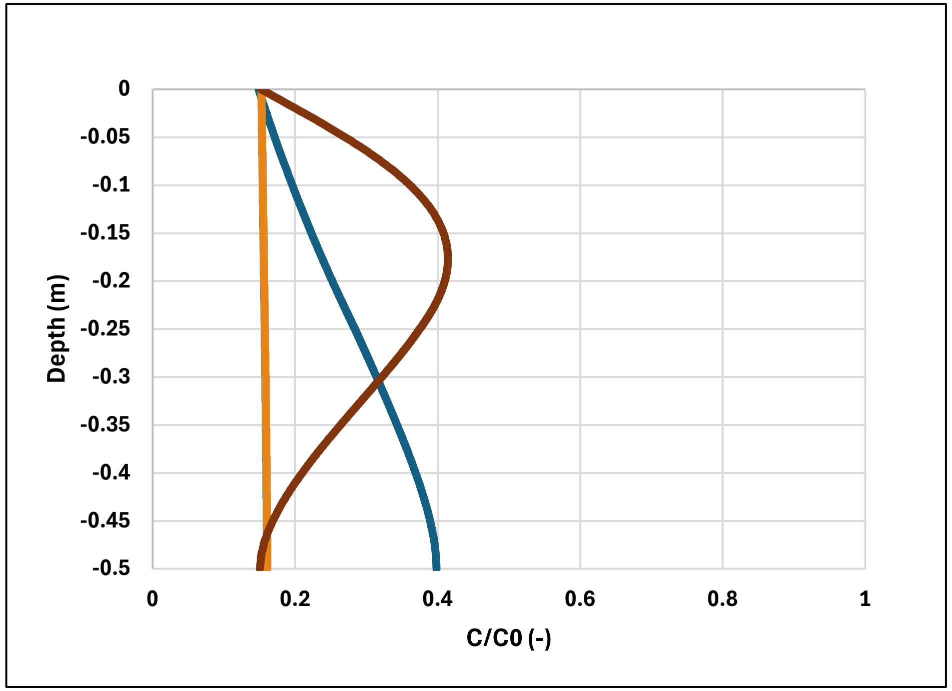
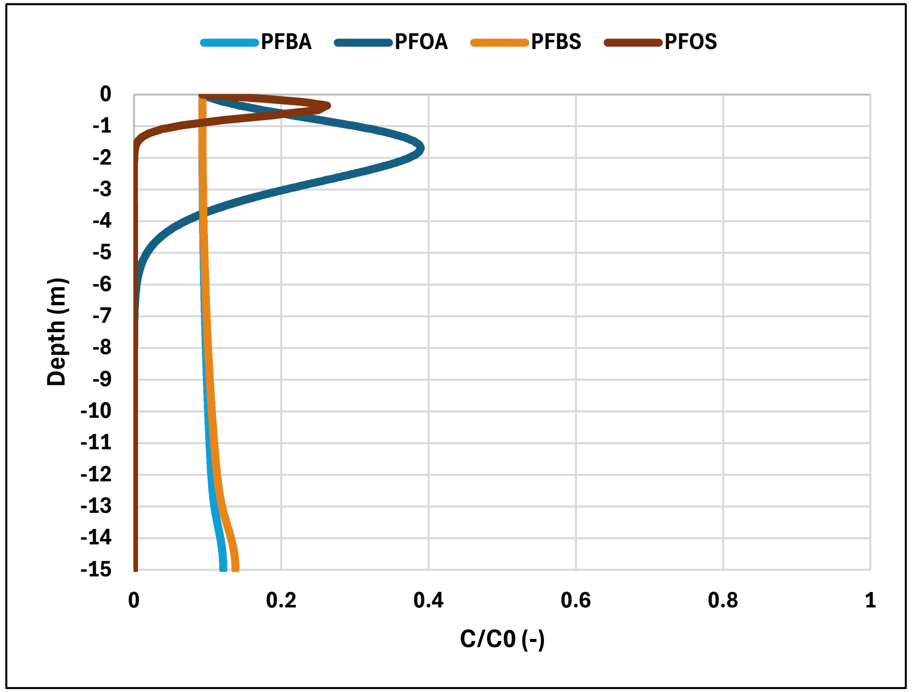


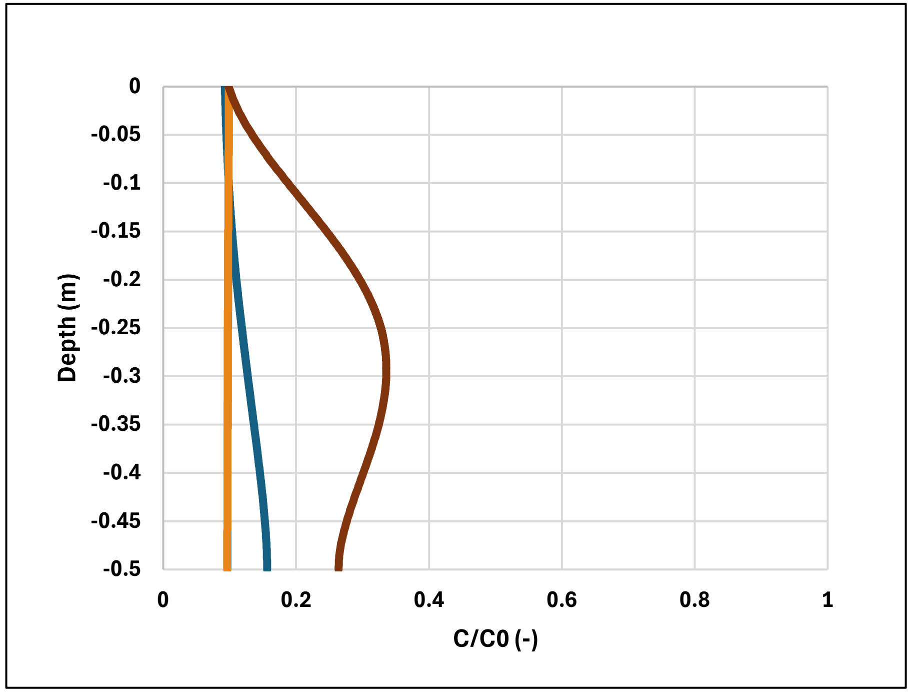
Vertical transport
t = 2050 yr (90 year after leaching started)

- Long chain PFAS in the top of the deep unsaturated zone – strongly retained

Landfill with deep unsaturated zone
h = 15 m



Landfill with shallow unsaturated zone
h = 0.5 m



Main Findings

- High concentrations of PFAS are found at landfills world-wide
- Terminal PFAS often found at landfills: PFAS C4-C8 from PFCA and PFSA
- Danish old landfills with PFAS – risk investigations needed

- The depth of the unsaturated zone influences PFAS leaching
- Long chain PFAS more retained than short chain PFAS
- Short chain and long chain PFAS have a faster transport through a shallow unsaturated zone than a deep unsaturated zone
  – Water saturation → adsorption to air-water interface
- PFAS input function crucial, but challenging to obtain

- Factors to consider at landfills: waste type, landfill design, landfill environment, etc.
- Modelling leads to improved quantitative predictions of PFAS fluxes from landfills – valuable for risk assessment of landfills

Future work

- Further development of the model for PFAS transport in unsaturated and saturated zone
- Further development of PFAS source input function
- Model applied as a risk assessment tool for a landfill site
- Sorption – pH, PFAS mixture ?
- Spatial distribution of PFAS at a landfill?

Thank you !

Questions ? ☺