University of Stuttgart
Institute for Modelling Hydraulic and Environmental Systems (IWS)
Research Facility for Subsurface Remediation (VEGAS)

Sorptive Treatment of Soils Contaminated with Per- and Polyfluoroalkyl Substances (PFASs)

Desorption Characteristics and Evaluation Strategies

Thomas Bierbaum

VEGAS Versuchseinrichtung zur Grundwasser- und Altlastensanierung

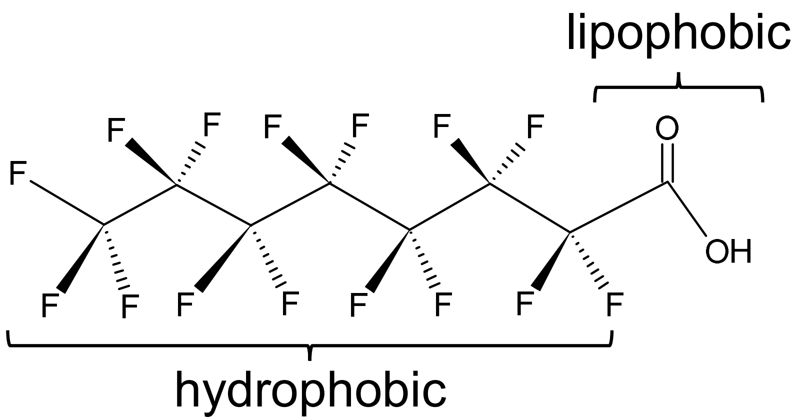
ENWAT International Doctoral Program

Contents

Introduction and Problem Definition

Per- and Polyfluoroalkyl Substances (PFASs)
Introduction

PFOA
(Perfluoro-
octanoic acid)



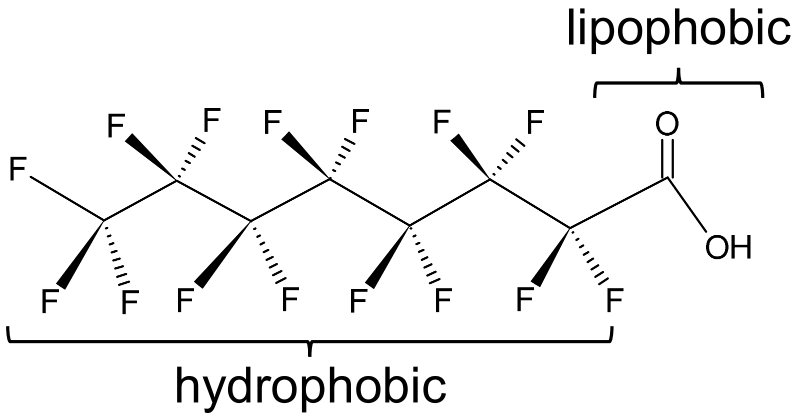
- Synthetic organic compounds with fluorinated carbons
- >4000 different PFASs

[1]

- Unique properties:
  chemically and thermally stable, water- and oil-repellent
- Problematic for the environment:
  persistency, mobility, bioaccumulative potential, toxicity
  → global enrichment in soil, water, animals, humans

Per- and Polyfluoroalkyl Substances
Introduction

PFOA
(Perfluoro-
octanoic acid)

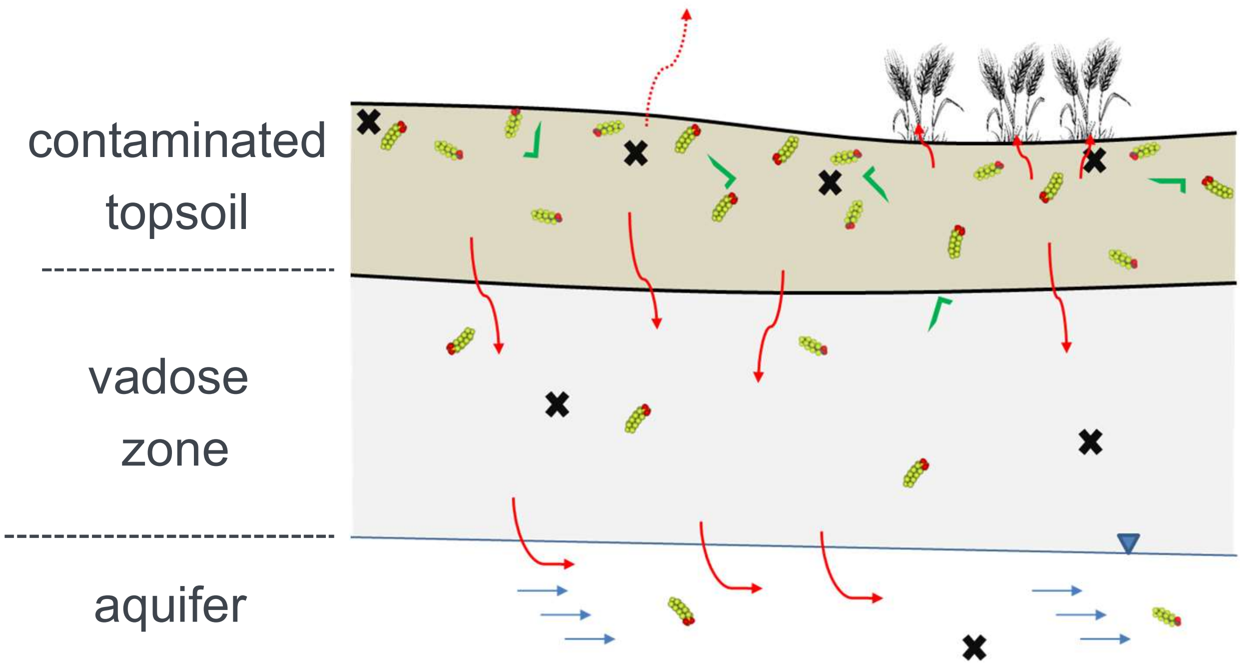


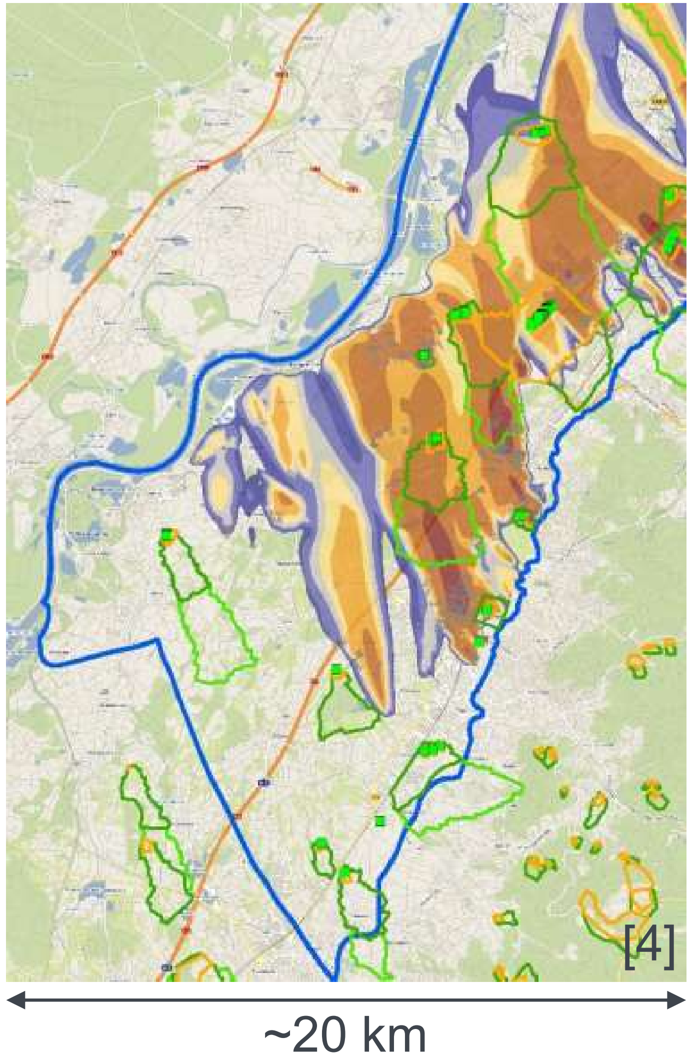
- Unique properties:
  chemically and thermally stable, water- and oil-repellent
- Problematic for the environment:
  persistency, mobility, bioaccumulative potential, toxicity
  → global enrichment in soil, water, animals, humans

Aqueous Film Forming Foam (AFFF)

PFASs on Contaminated Sites
Upper Rhine Valley

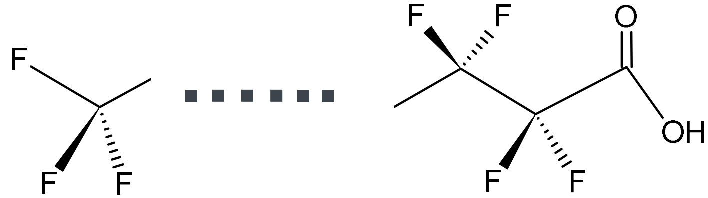
- Application of compost with paper-fibre biosolids
- Contamination of agricultural soil (>1000 ha)



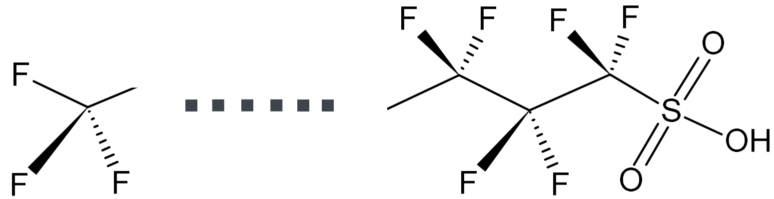


PFASs on Contaminated Sites
PFAS Species and Sorption

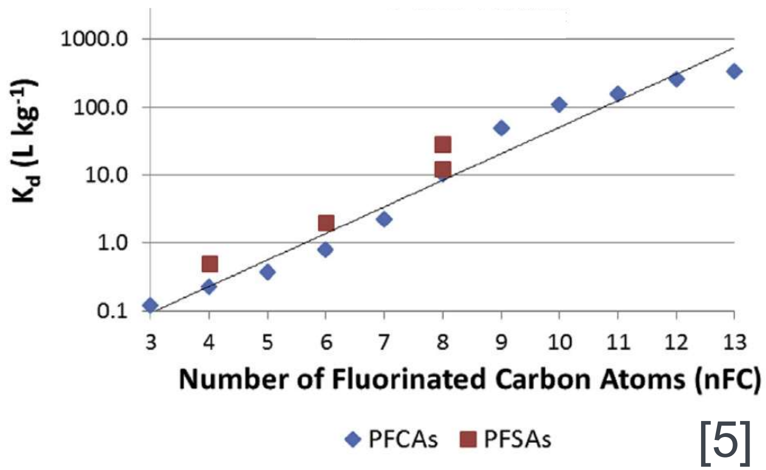
- Perfluoroalkyl carboxylic acids (**PFCAs**)



- Perfluoroalkyl sulfonic acids (**PFSAs**)

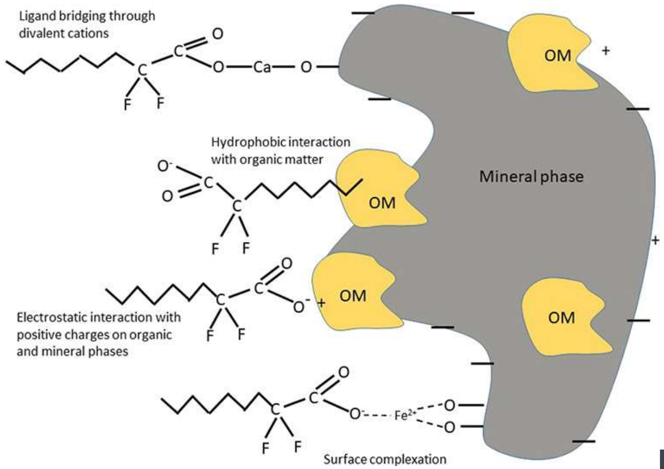


Soil-water distribution coefficient



[5]

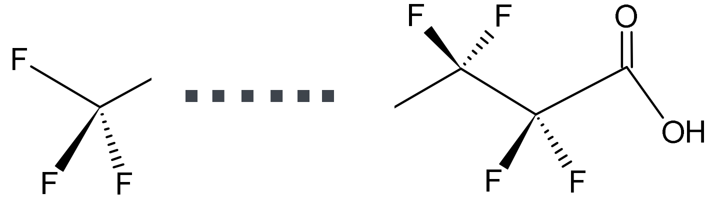
$$K_d = \frac{C_s}{C_w}$$



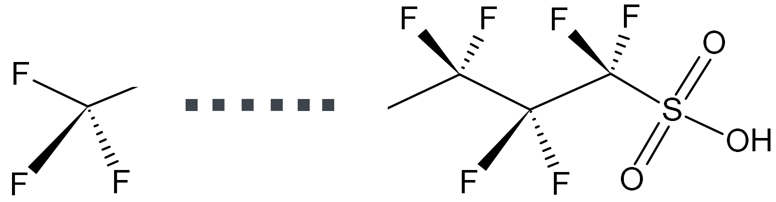
[6]

PFASs on Contaminated Sites
Precursors and Transformations (Upper Rhine Valley)

- Perfluoroalkyl carboxylic acids (**PFCAs**)



- Perfluoroalkyl sulfonic acids (**PFSAs**)



abiotic
and/or
biotic

„*Precursors*“: → source term

- Polyfluoroalkyl phosphate esters (**PAPs**)
  (6:2-/8:2-/10:2-monoPAP, 6:2-/8:2-/10:2-diPAP, …)

intermediates

- Perfluorooctane sulphonamido ethanol-based phosphate esters (**SAmPAPs**)
  (monoSAmPAP, diSAmPAP)

PFASs on Contaminated Sites

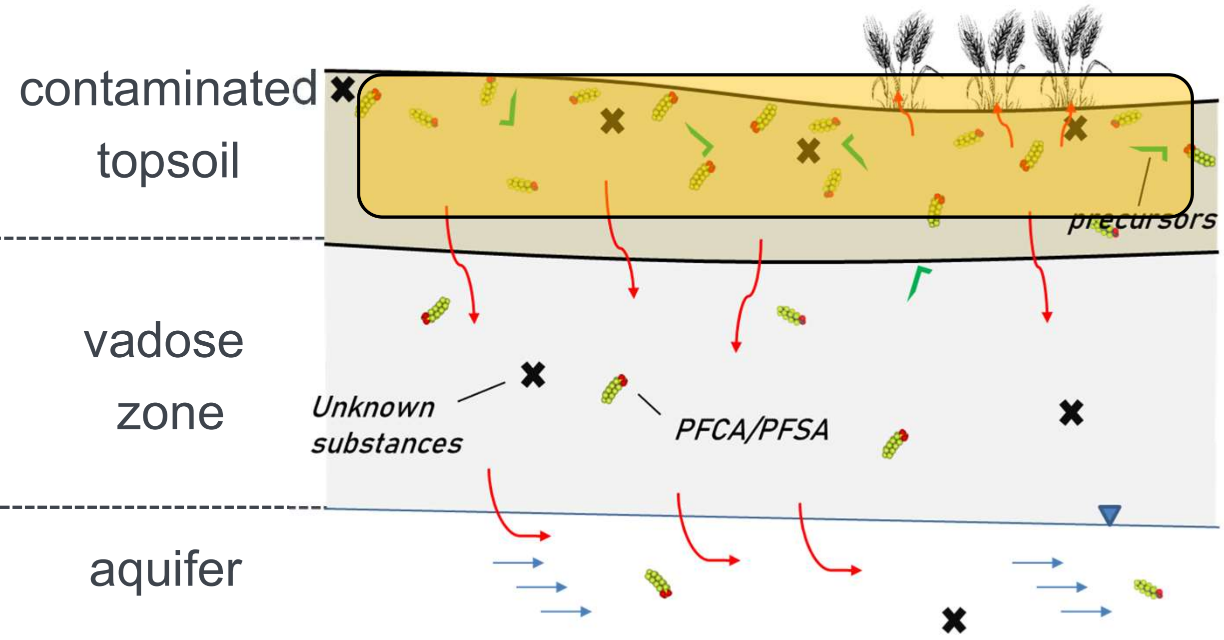
Analytical Challenge

- Target analytic: about 30 PFASs (mainly PFCAs and PFSAs) can be measured in chemical routine analysis (HPLC-MS-MS)

- Development of sum parameters:
  - extractable organic fluorine (EOF)
  - adsorbable organic fluorine (AOF)

- Total oxidisable precursor assay (TOP-Assay) → estimation of precursor content

Immobilisation of PFASs
A Discussed Strategy for Managing Contaminated Sites



Immobilisation

- goal: stop/reduce PFAS leaching
- treatment of contaminated soil with additives
  - to increase sorption capacity
  - to solidify soil material
- in-situ and ex-situ applications

Immobilisation of PFASs
State of Knowledge

Industry

- Few immobilisation products commercially available:
  - Soil mixing with adsorbent agents (activate-carbon based products)
  - Injection of colloidal active carbon
  - Soil stabilization and solidification
- Advertised as a feasible and cost-effective strategy

Scientific research

- Some immobilisation products were tested with common leaching tests (Hale et al., 2017; Barth et al., 2021; Kabiri et al., 2021; Bräunig et al., 2021)
- Few field applications/demonstrations with scientific monitoring (McDonough et al., 2022)

Research Objective

Research Objective

- Long-term stability of immobilisation not verified (especially in soils with precursors)
- Sorption mechanisms and processes not well understood
- Evaluation method to investigate/verify PFAS immobilisation not yet defined

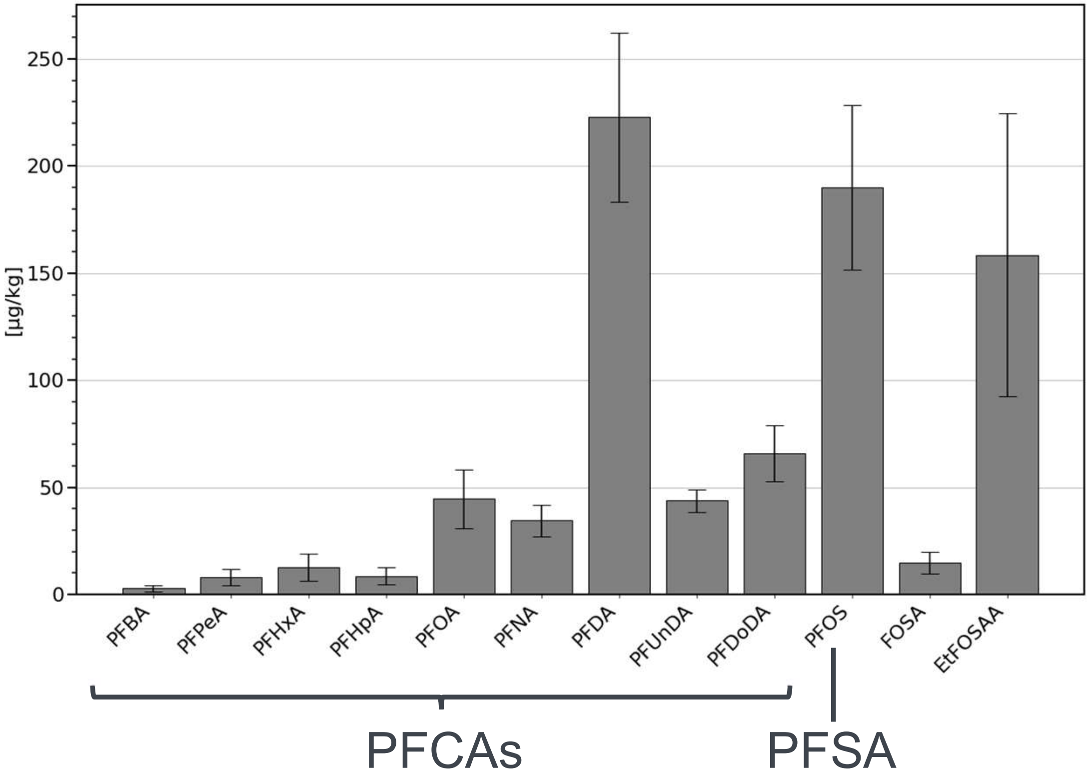
How to evaluate PFAS immobilisation in experiments and models?

- ➢ Application and critical evaluation of various experimental and analytical methods
- ➢ Numerical models for process understanding and for simulations of longer time periods
- ➢ Identification of the relevant processes → evaluation of leaching characteristics

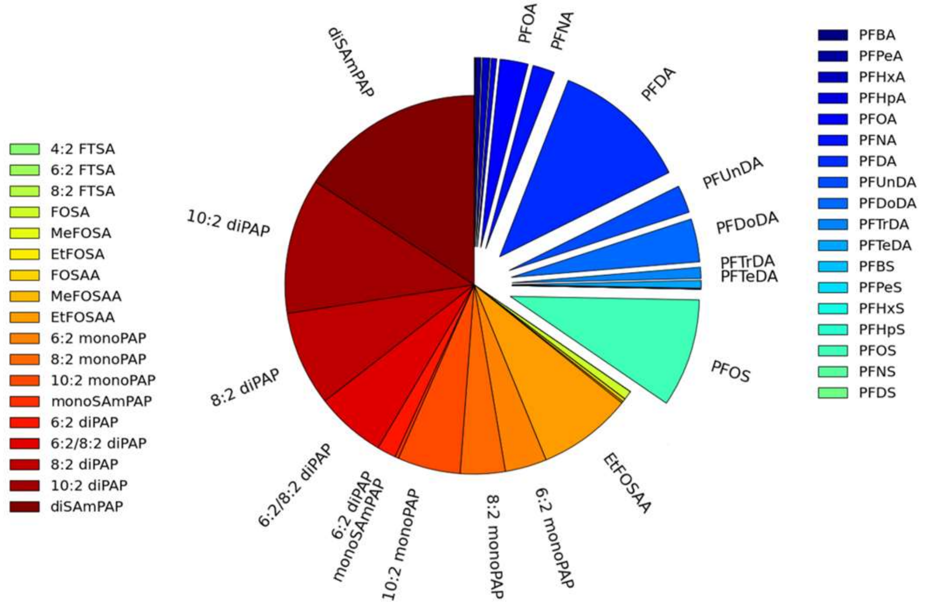
Methods

Contaminated Soil Material

PFAS concentrations in the studied soil (**N-1**)



Target analysis with some precursors



Soil Treatments
Immobilisation

Sorptive treatment:

- **R-1**: N-1 + 2.5 wt% powdered activated carbon
- **R-2**: N-1 + 2.5 wt% active-carbon based product (+ clay minerals, $AL(OH)_3$, …)

Soil stabilization:

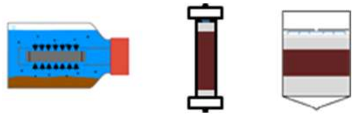
- **R-3**: N-1 + 7 wt% cement, bentonite, activated carbon

Application in concrete production:

- **R-4**: N-1 + 94 wt% concrete constituents

N-1 R-1 R-2 R-3 R-4

Original soil



Laboratory Experiments
Investigation of PFAS Immobilisation

How to evaluate PFAS immobilisation in experiments and models?

cm

Infinite Sink (IS) Experiment

dm

Column Experiment
(saturated)

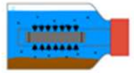
m

Lysimeter
(variably saturated)

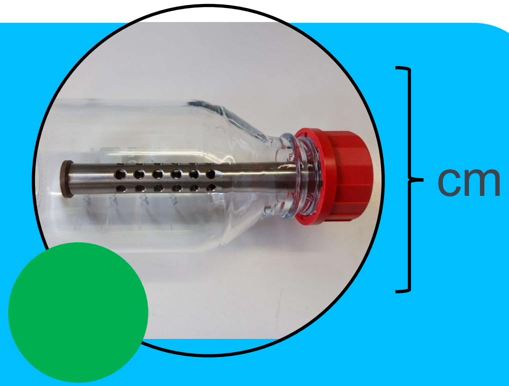
Analytical tools: target analysis, EOF, AOF, TOP-Assay

Laboratory Experiments

Investigation of PFAS Immobilisation



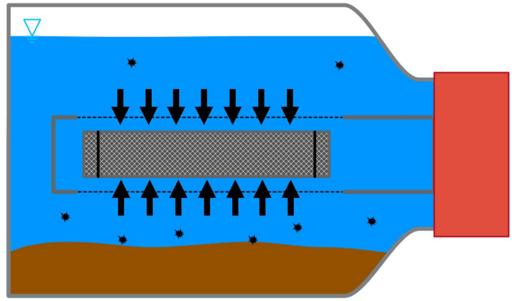
How to evaluate PFAS immobilisation in experiments and models?



Infinite Sink (IS) Experiment

[7]

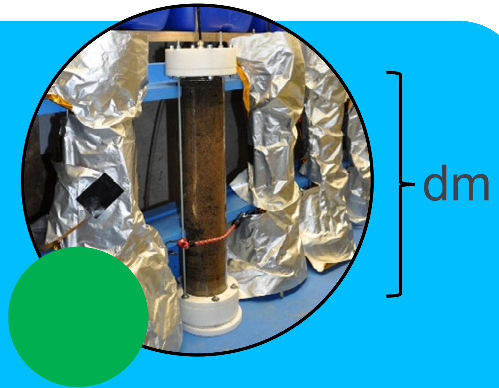
- Shaking test with 100g soil
- Sorbent (GAC) in contact with liquid phase
- Adsorption of PFASs onto sorbent → system not in equilibrium
- Repeated sampling of sorbent
- Hot extraction (4-fold, 105°C) prior to PFAS analysis



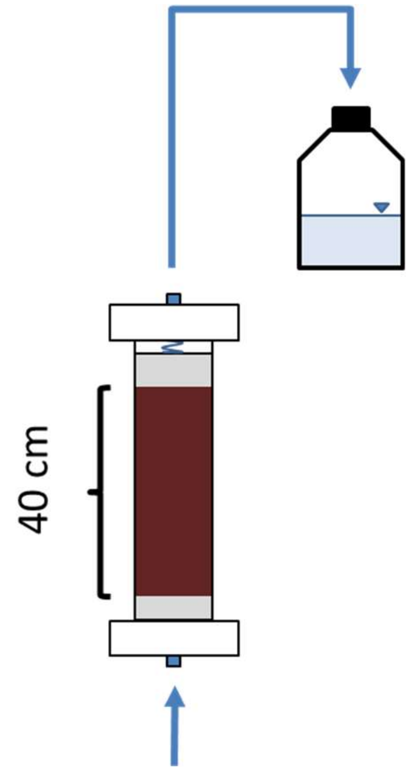
Laboratory Experiments
Investigation of PFAS Immobilisation

How to evaluate PFAS immobilisation in experiments and models?

- Percolation experiment under <u>saturated</u> conditions
- ~ 4 kg soil material
- Analysis of collective eluate samples
- Contact time approx. 11 h
- Water-to-solid ratio (WS) > 30 L/kg

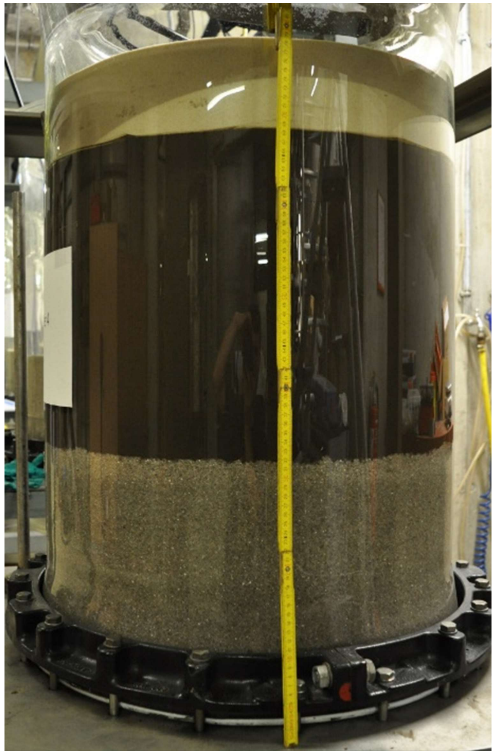


Column Experiment
(saturated)

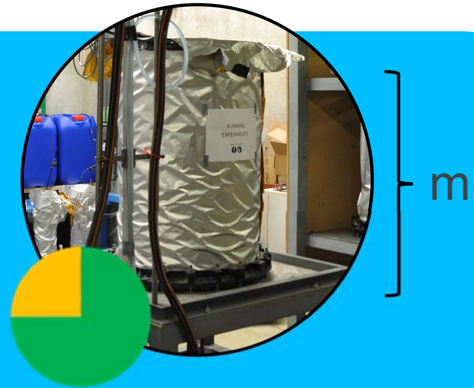


Laboratory Experiments
Investigation of PFAS Immobilisation

How to evaluate PFAS immobilisation in experiments and models?

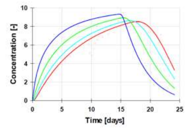


- Percolation experiment under variably saturated conditions
- ~180 kg soil material
- Analysis of collective eluate samples
- 400 mm/a < q_v < 1200 mm/a (field: 300 mm/a)

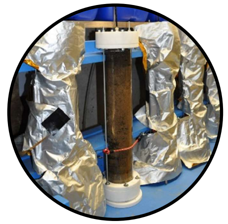


Lysimeter
(variably saturated)

Numerical Model

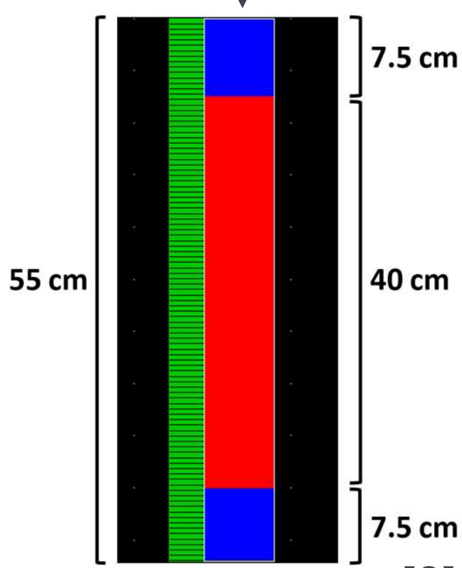


- Goals:
  - → identification of appropriate (sorption) model and calibration of parameters
  - → simulation of long-tailed elution
  - → simulation for longer time-periods
  - → process understanding



column

lysimeter

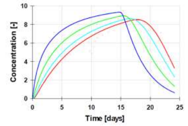


[8]

- Simulation of PFAS leaching observed in experiments for **PFBA** (C4), **PFOA** (C8), **PFOS** (C8)

- One-dimensional transport simulations in HYDRUS-1D

Numerical Model
HYDRUS-1D



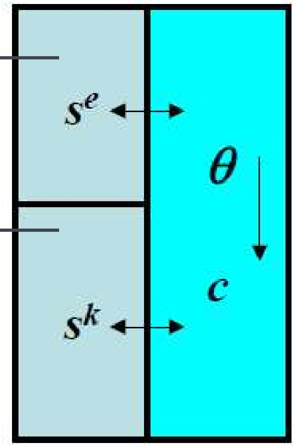
- Uniform one-dimensional flow (Richards equation): $$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[K\left(\frac{\partial h}{\partial x} + \cos\alpha\right)\right] - S$$
- Solute transport: $$\frac{\partial \theta c}{\partial t} + \rho \frac{\partial s}{\partial t} = \frac{\partial}{\partial x}\left(\theta D \frac{\partial c}{\partial x}\right) - \frac{\partial q c}{\partial x}$$
- Various flow and transport models exist (including physical and chemical non-equilibrium models)
- Tested until now:
  1. **equilibrium sorption** $$s = \frac{k_d c^\beta}{1 + \eta c^\beta}$$
  2. **two-site sorption**

two-site sorption

instantaneous

$$s_e = f\,s$$

kinetic



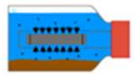
[8]

$$\frac{\partial s_e}{\partial t} = f \frac{\partial s}{\partial t}$$

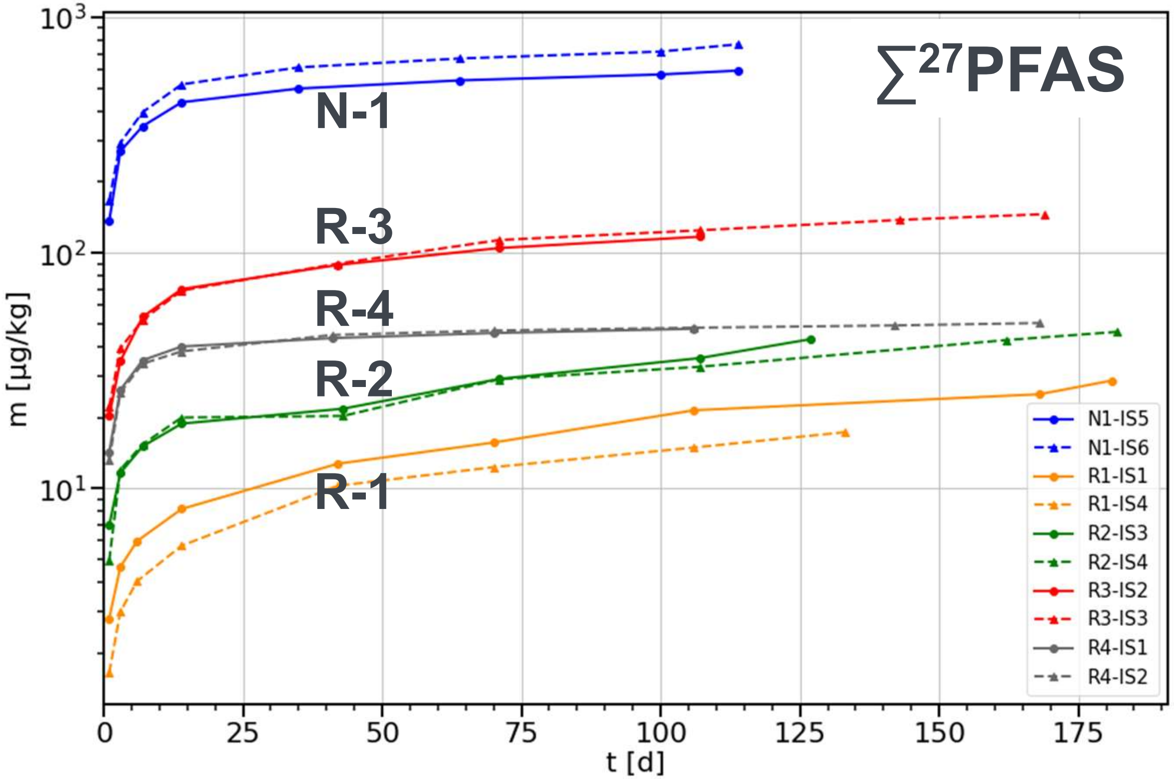
$$\frac{\partial s_k}{\partial t} = \omega\left[(1-f)\frac{k_d c^\beta}{1+\eta c^\beta} - s_k\right]$$

Results and Discussion

Laboratory Experiments
Infinite Sink (IS)



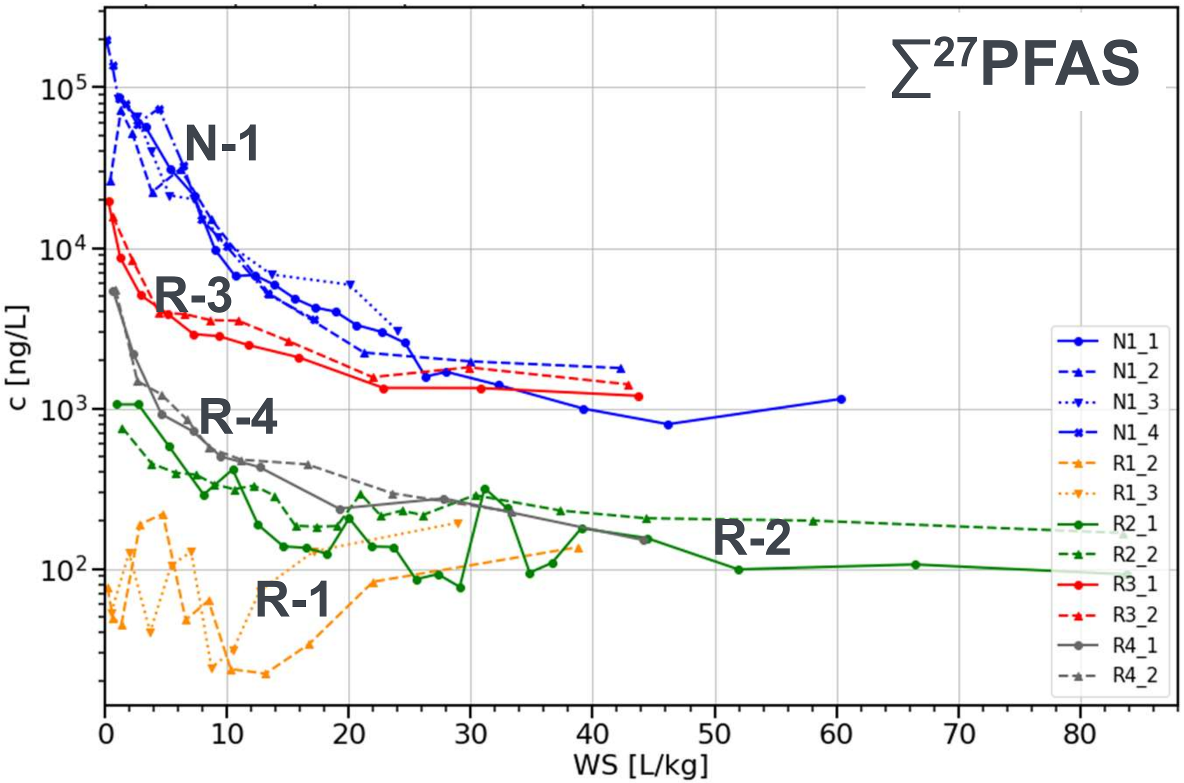
PFAS desorption (cumulative mass curves)



- PFAS desorption reduced in treated soils
- High desorption for t < 14 d
- Incomplete leaching process with different desorption rates for t > 14 d
- ➢ Continuous leaching?

Laboratory Experiments
Column Experiment

Eluate concentrations



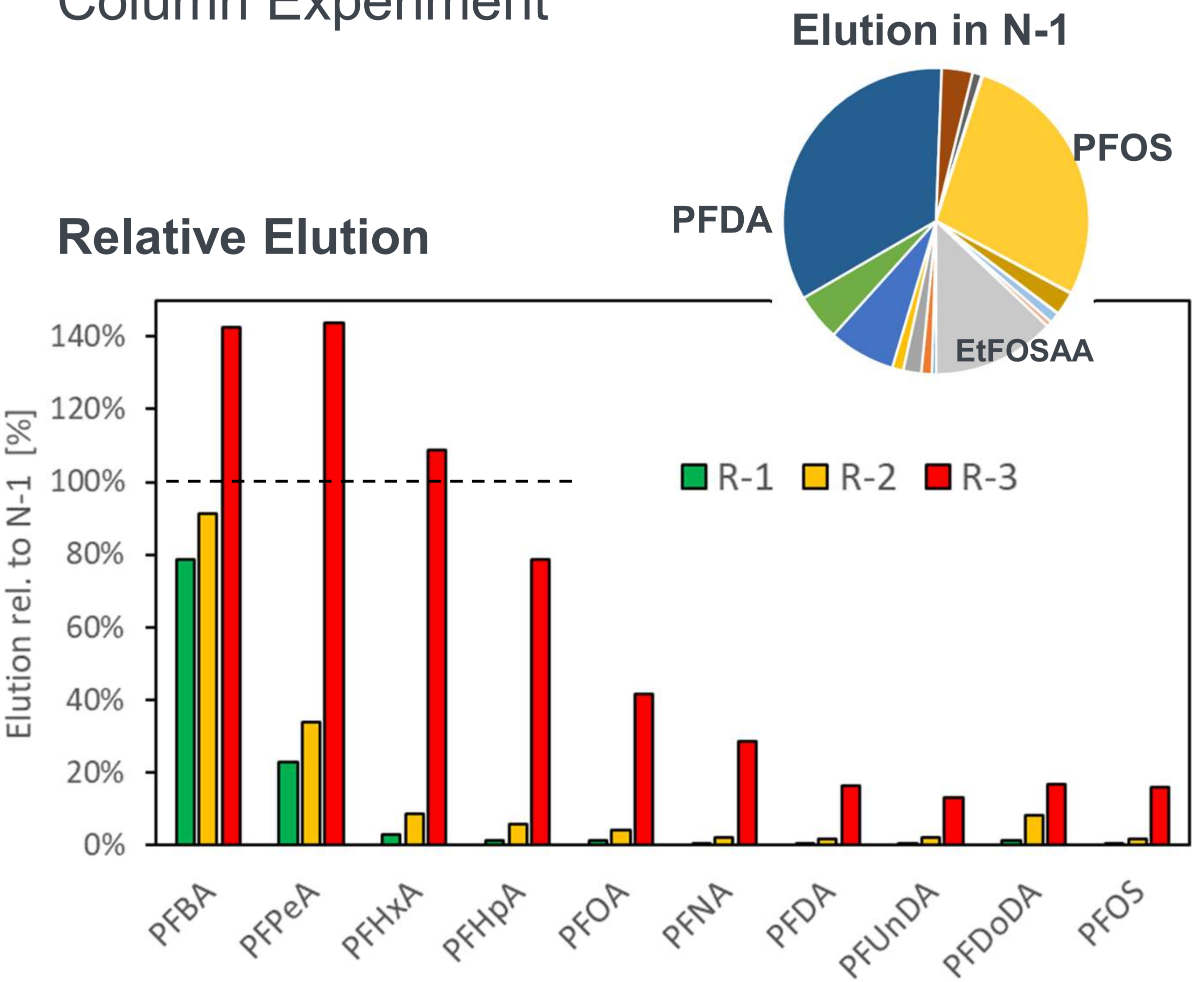
- Long elution process
- Similar immobilisation efficiencies in IS and columns:

	R-1	R-2	R-3	R-4
Infinite Sink	97 %	95 %	82 %	-6 %
Column Experiment	99 %	97 %	73 %	17 %

- $\sum^{27}$PFAS: effective reduction of PFAS desorption possible
  - ➢ Fate of single substances?

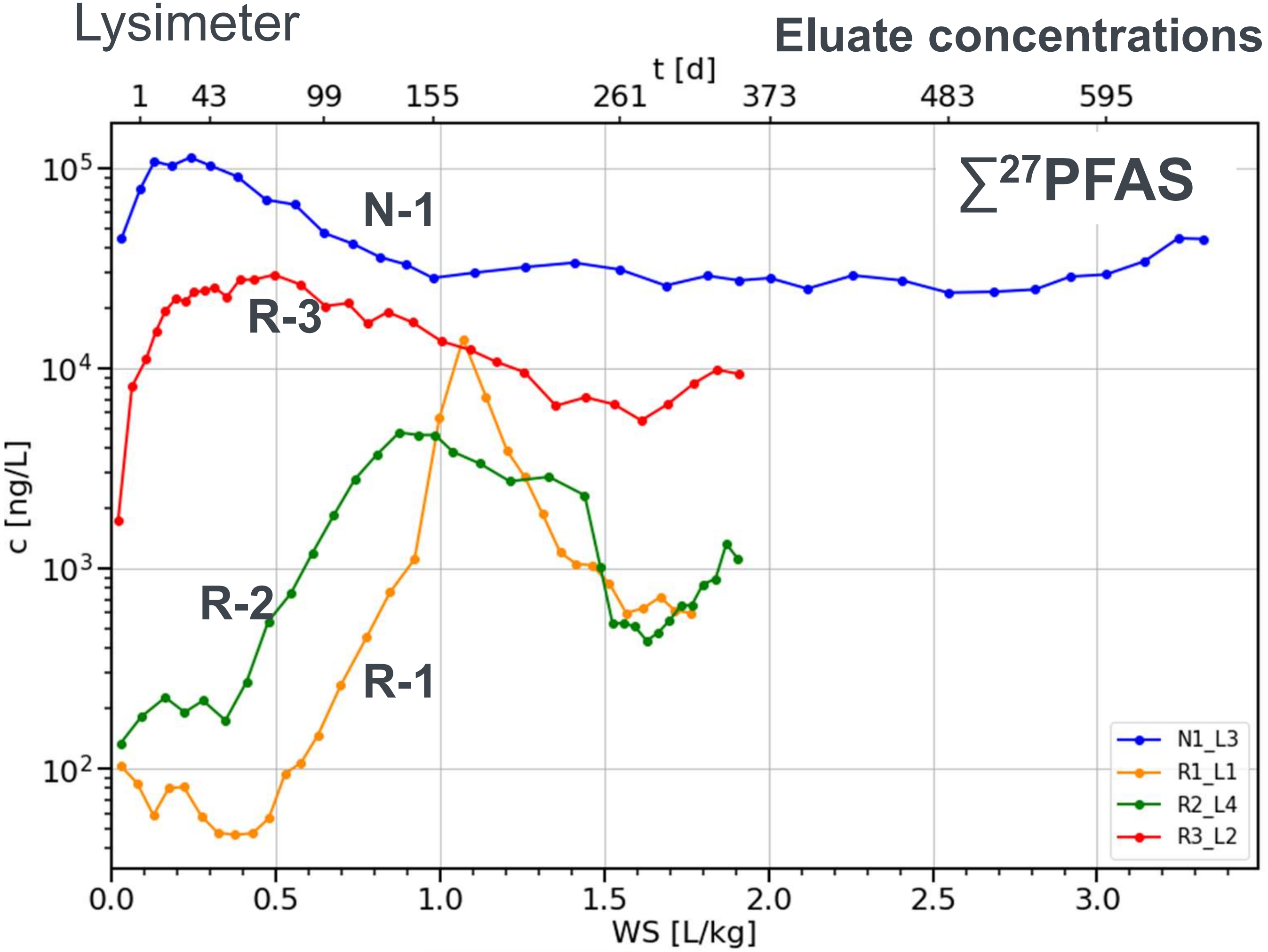
Laboratory Experiments
Column Experiment

Relative Elution



- Similar leached PFBA mass in treated soils
  - ➢ lower immobilisation efficiency for short-chain substances
- exceeding elution in R-3 (and R-4)
  - ➢ enhanced desorption
    + transformations (abiotic)

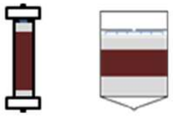
Laboratory Experiments
Lysimeter



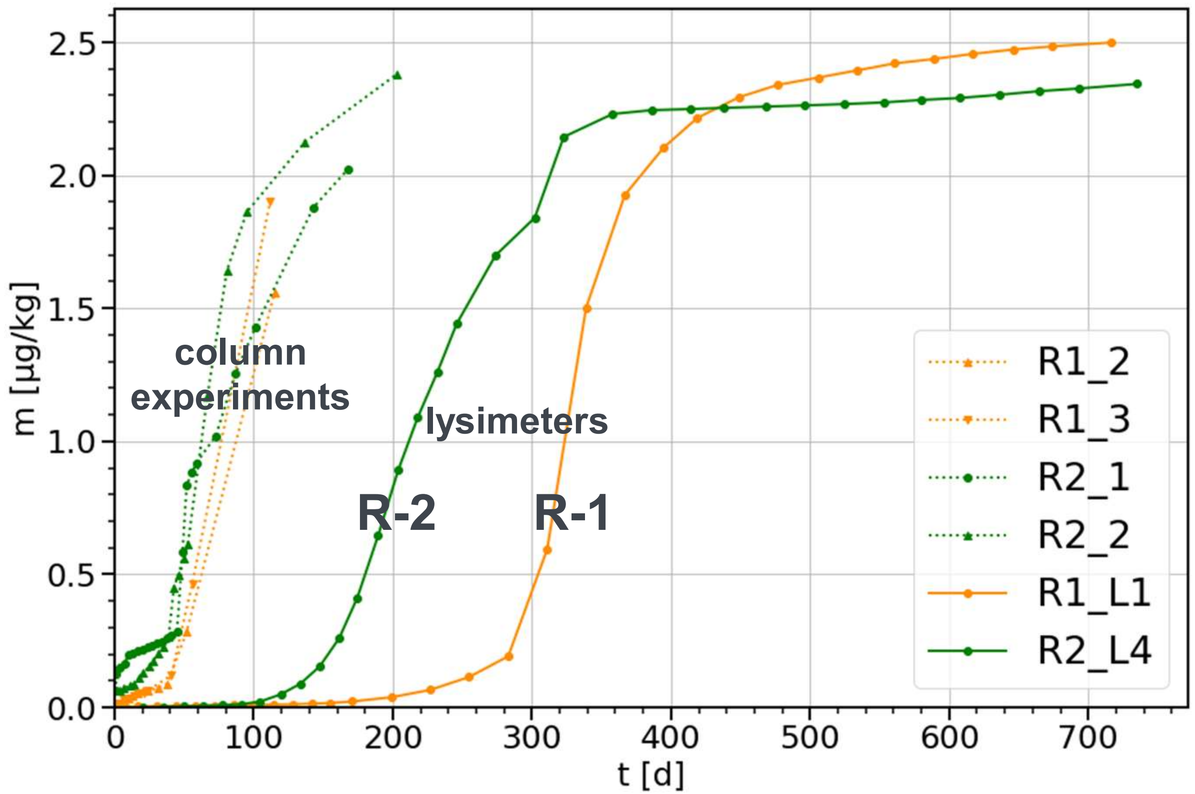
- Delayed leaching in R-1 and R-2
- Affects evaluation of long-term stability
- Indication of biotransformations
  - Production of PFBA?
  - Production of other substances and displacement of PFBA? (Gellrich et al., 2012)

Laboratory Experiments

Comparative Study: Column and Lysimeter Experiments



Leached PFBA mass (cumulative)

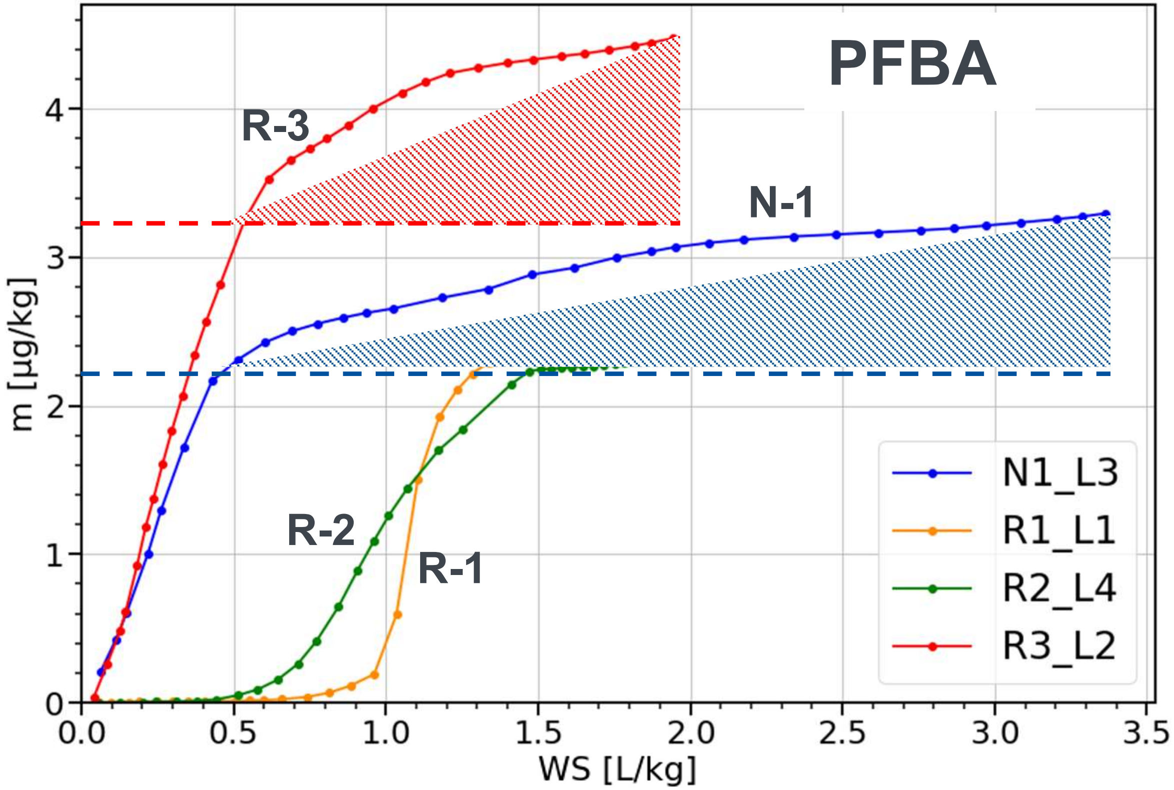


Leached PFBA mass in N-1 columns

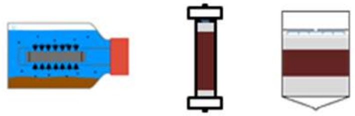
- Both in column and lysimeter experiments
- Similar elution rates in column and lysimeter experiments
- ➢ Indication of a process with a certain kinetic (time-dependency)
- Maximum level reached?

Laboratory Experiments
Comparative Study: Column and Lysimeter Experiments

Leached PFBA mass in Lysimeter (cumulative)



- Delayed in experiments with R-1 and R-2, but leached mass lower than in N-1
  - ➢ leached PFBA was not produced
- In lysimeter experiments increased PFBA elution in N-1 and R-3
  - ➢ Indication of transformation processes
- Similarly observed for other PFASs



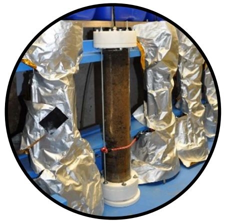
Laboratory Experiments
PFAS Desorption Characteristics

Intermediate findings:

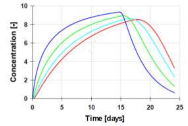
- Long leaching processes
- Diverse mobility of PFASs
- Transformation rate of precursors is low → difficult to identify in lab experiments

- Less effective immobilisation of short-chain PFASs
- Long-term stability questioned by delayed elution of short-chain PFASs
- Transformation of precursors may affect immobilisation efficiency

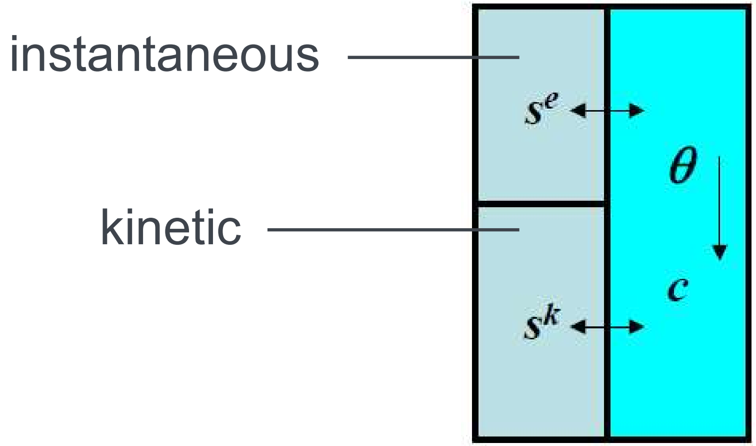
Numerical Model
Setup



column



- Contaminated soil, injection of fresh water
- Transient hydraulic boundary conditions (according to experiments)
- Initial concentrations:
  - s_0 derived from leached PFAS mass and soil analysis at end of experiment
    - ➢ One way to deal with incomplete or exceeding recoveries
  - Initial liquid concentration is calibrated → s_e according to sorption isotherm

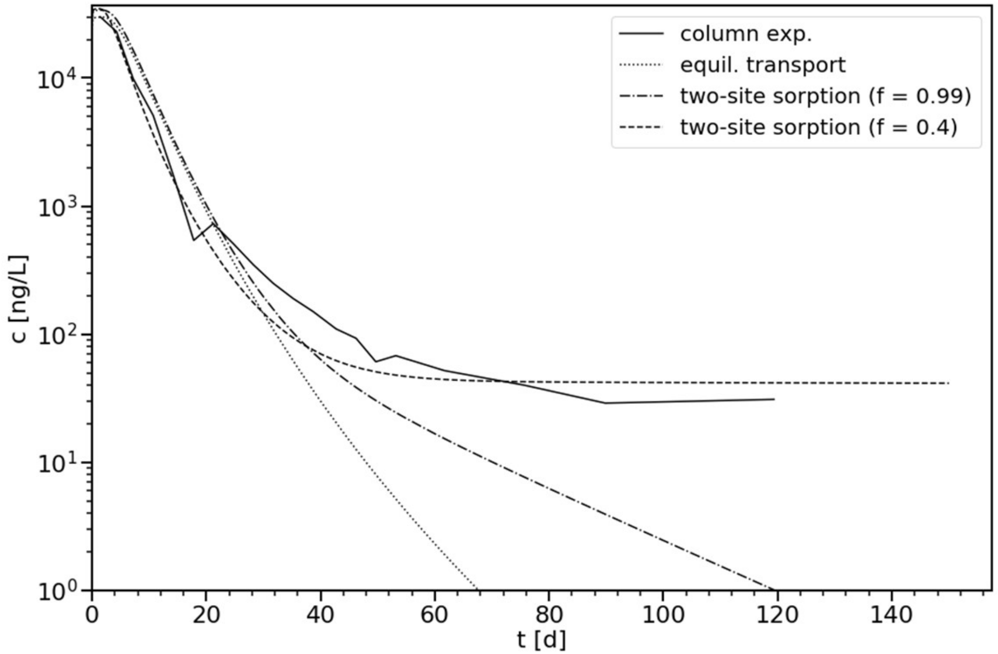


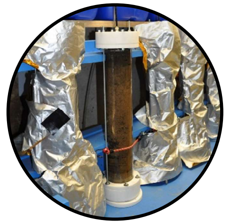
[8]

$$s_0 = \frac{m_{\text{leached}}}{m_{\text{soil}}} + s_{\text{end}} \quad \rightarrow \quad s_k = s_0 - s_e - c \cdot \frac{V_w}{m_{\text{soil}}}$$

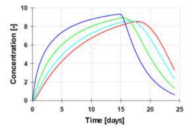
Numerical Model
Sorption models

Eluate concentrations (PFOS in N-1)





column



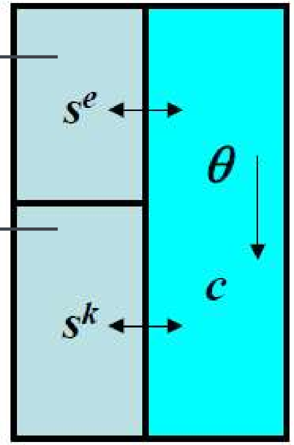
$$s = \frac{k_d c^\beta}{1 + \eta c^\beta}$$

instantaneous

$$\frac{\partial s_e}{\partial t} = f \frac{\partial s}{\partial t}$$

kinetic

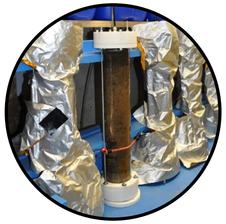
$$\frac{\partial s_k}{\partial t} = \omega \left[(1 - f) \frac{k_d c^\beta}{1 + \eta c^\beta} - s_k \right]$$

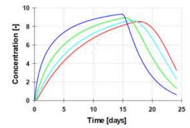


[8]

- Equilibrium sorption model not sufficient to reproduce observed concentration time-series (long tailing) → two-site sorption

Numerical Model
Calibration



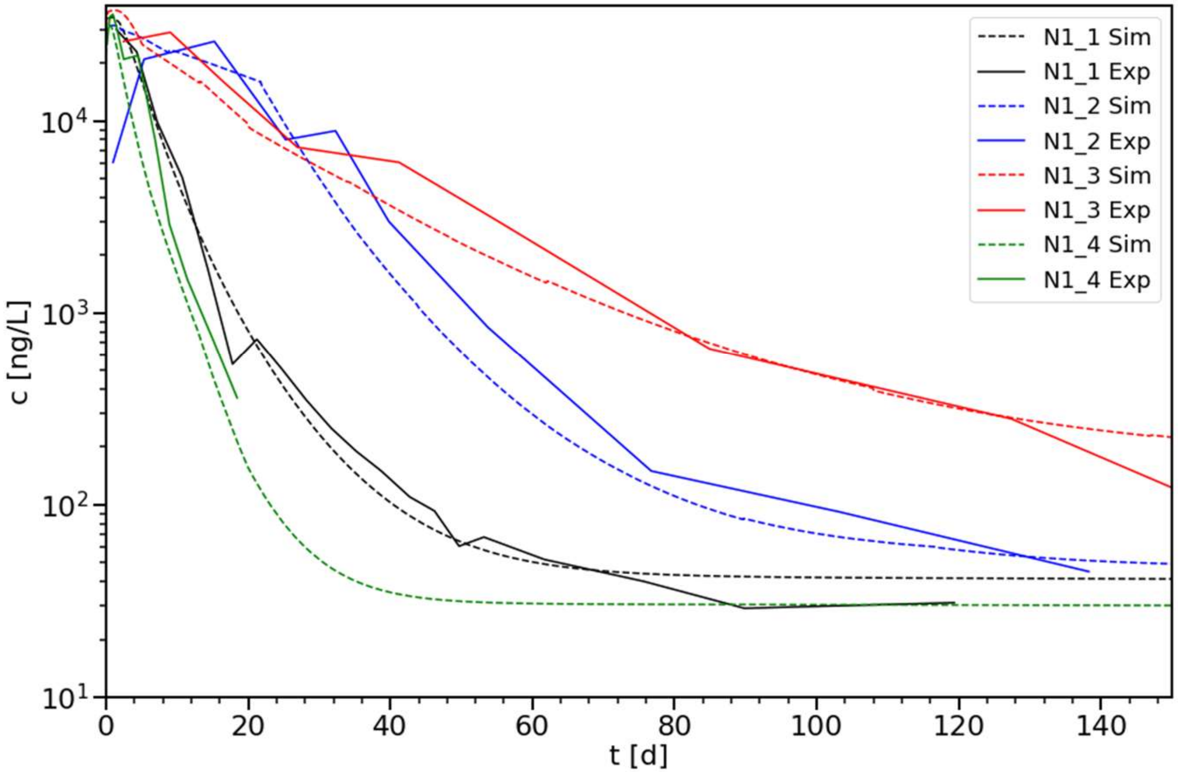


- Discretization of parameters
- Monte-Carlo simulations
- Determination of best-estimates:
  - Various error measures
    (squared error, squared log. error, weighted error)
  - Visualisation of long-tailed leaching on log. scale

➢ **Parameter sets for N-1-experiments**

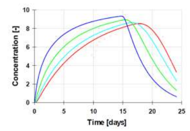
substance	k_d [L/kg]	β [-]	ω [d^{-1}]	f [-]
PFBA	0.7	0.9	0.01	0.6
PFOA	1.0	1.0	0.01	0.93
PFOS	4.5	0.98	0.005	0.93

Eluate concentrations in simulations and experiments
(PFOS in N-1 with various flow rates)



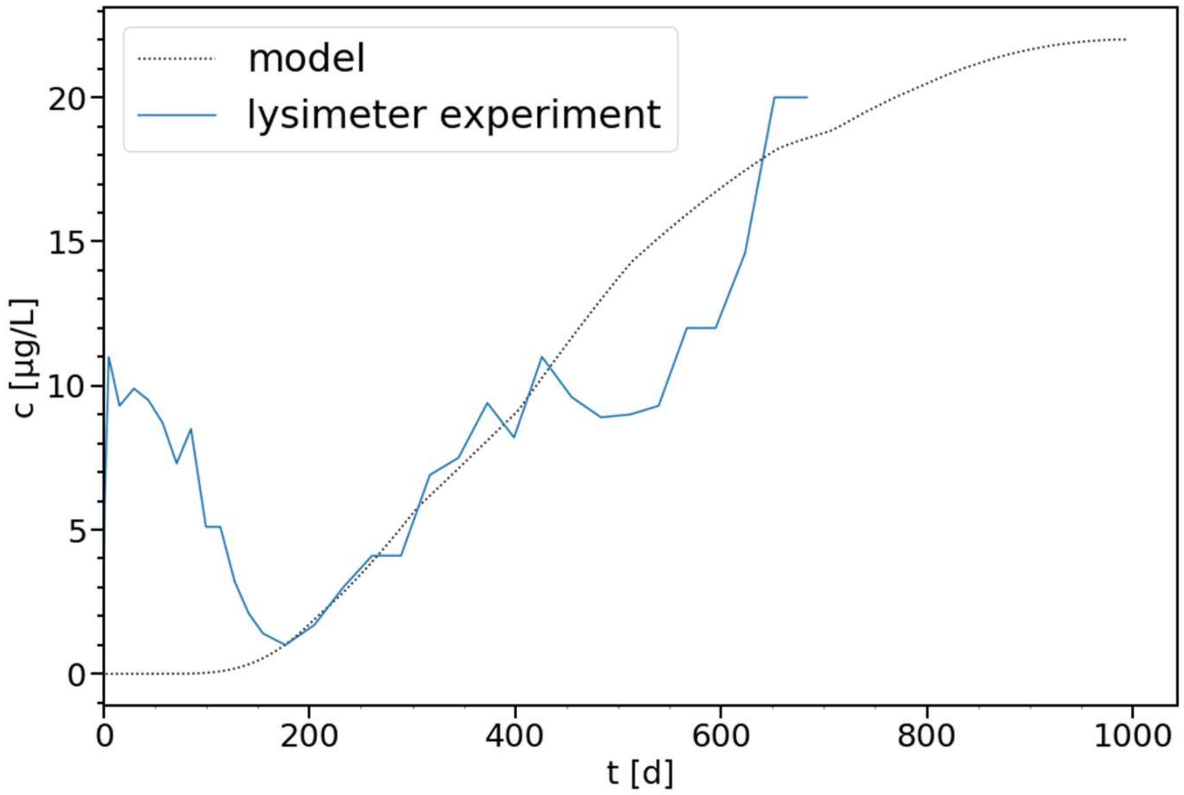
Numerical Model
Challenging leaching characteristics

lysimeter



- challenging leaching characteristics:
  - Fragmented leaching in lysimeter
    - ➢ Retardation in sand layer?
- Other models:
  - Dual-porosity / dual-permeability (macropores)
  - Reactive transport

PFOS in N-1 lysimeter



Conclusion and Outlook

Conclusion

- Typical **PFAS leaching behavior** observed → not fully understood
- Elution of **short-chain substances** indicate transformations
- **Transformation of precursors** may affect immobilisation efficiency and/or long-term stability
- **Several experiments** with different saturation conditions **necessary** for investigation of PFAS immobilisation
- Data-based **comparison of experimental methods** may help to identify dominant **processes**
- **Numerical simulations** may help to understand observed leaching behaviors
- **Long-term effects** challenging to assess in lab → other experiments and models necessary
- Contribution: **critical review** of available methods to investigate PFAS immobilisation

Outlook

- **Lysimeters**: end of experiment planned in May 2022 → soil analysis
- **Evaluation of experimental data**: Emphasis on non-conservative processes
  - Mass balances
  - Comparison of data from various experiments → **Critical evaluation** of methods
  - Process understanding
- Application of **various numerical models**
  - Physical non-equilibrium
  - Reactive transport
- Simulations for **longer time-scales** (lysimeter)
- **Sensitivity analysis**

References

[1]: PFAS Investigation and Management Programm. Australian Government, Department of Defence (last request: 24.02.2022) https://defence.gov.au/Environment/PFAS/pfas.asp

[2]: Scheringer, M.(2018): Highly toxic, extremely persistent and widely used. ETH Zürich. https://ethz.ch/en/news-and-events/eth-news/news/2018/10/martin-scheringer-pfas.html

[3]: Söhlmann: Untersuchung der Tiefenverlagerung von PFC und potentiellen Vorläufersubstanzen auf landwirtschaftlich genutzten Flächen im Raum Rastatt / Baden-Baden. Landkreis Rastatt, PFC-Geschäftsstelle, Bericht.

[4]: LUBW: Grundwassermodell Mittelbaden. Analyse und Prognose der PFC-Belastung im Raum Rastatt und Baden-Baden Stand Dezember 2017

[5]: McLachlan et al. (2019): Fate of a perfluoroalkyl acid mixture in an agricultural soil studied in lysimeters. *Chemosphere*, Vol. 223, 180-187

[6]: Li et al. (2018): A critical analysis of published data to discern the role of soil and sediment properties in determining sorption of per and polyfluoroalkyl substances (PFASs)

[7]: Wege, R. (2005): Untersuchungs- und Überwachungsmethoden für die Beurteilung natürlicher Selbstreinigungsprozesse im Grundwasser. University Stuttgart, IWS, Dissertation

[8]: Simunek (2013): The HYDRUS-1D Software Package for Simulating the One-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media. Department of Environmental Sciences, University of California, USA

Houtz et al. (2012): Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environmental Science and Technology*, Vol. 17, 9342-9349

Nürenberg et al. (2018): Nachweis von polyfluorierten Alkylphosphatestern (PAP) und Perfluoroktansulfonamidoethanol-basierten Phosphatestern (SAmPAP) in Böden. *Umweltchemie und Ökotoxikologie*

McDonough et al. (2022): Field-Scale Demonstration of PFAS Leachability Following In Situ Soil Stabilization. *ACS omega*, Vol. 7, 419-429

Gellrich et al. (2012): Behavior of perfluorinated compounds in soils during leaching experiments. *Chemosphere*, Vol. 9, 1052-1056

Kabiri et al. (2021): Durability of sorption of per- and polyfluorinated alkyl substances in soils immobilized using common adsorbents: 2. Effects of repeated leaching, temperature extremes, ionic strength and competing ions. *The Science of the total environment*

University of Stuttgart
Institute for Modelling Hydraulic and Environmental Systems (IWS)
Research Facility for Subsurface Remediation (VEGAS)

Thank you!

Thomas Bierbaum

e-mail thomas.bierbaum@iws.uni-stuttgart.de
phone +49 (0) 711 685-69171
www.vegasinfo.de

University of Stuttgart
Institute for Modelling Hydraulic and Environmental Systems (IWS)
Research Facility for Subsurface Remediation (VEGAS)
Pfaffenwaldring 61
70569 Stuttgart

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VEGAS
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