

Investigating the Fate of Polyfluorinated Phosphate Diesters (diPAPs) in a Lysimeter System



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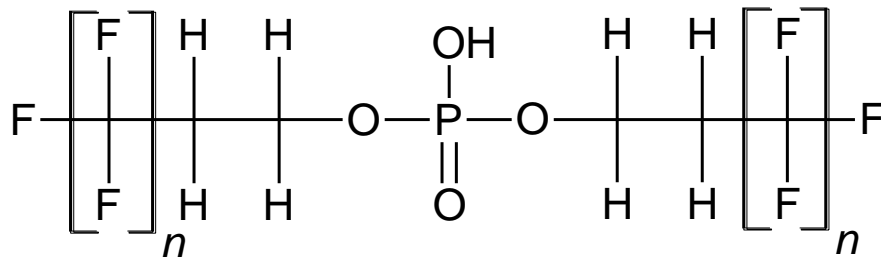
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Background

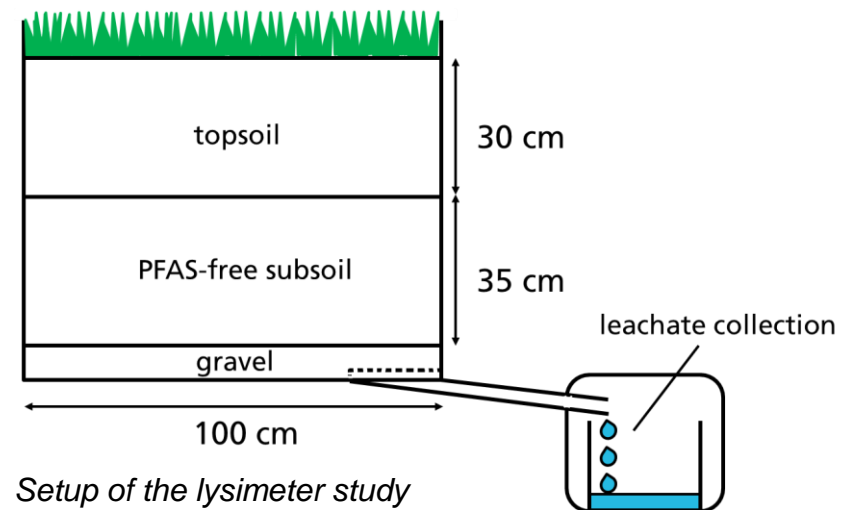
- Many PFAS proven to be hazardous
- PFOA and PFOS banned by the EU
- Several other PFAS were used, despite their ability to biodegrade into persistent shorter-chain PFCAs
- Environmental behavior of these precursors not yet fully understood



General chemical structure of symmetrical diPAPs (often $n = 6, 8, 10$)

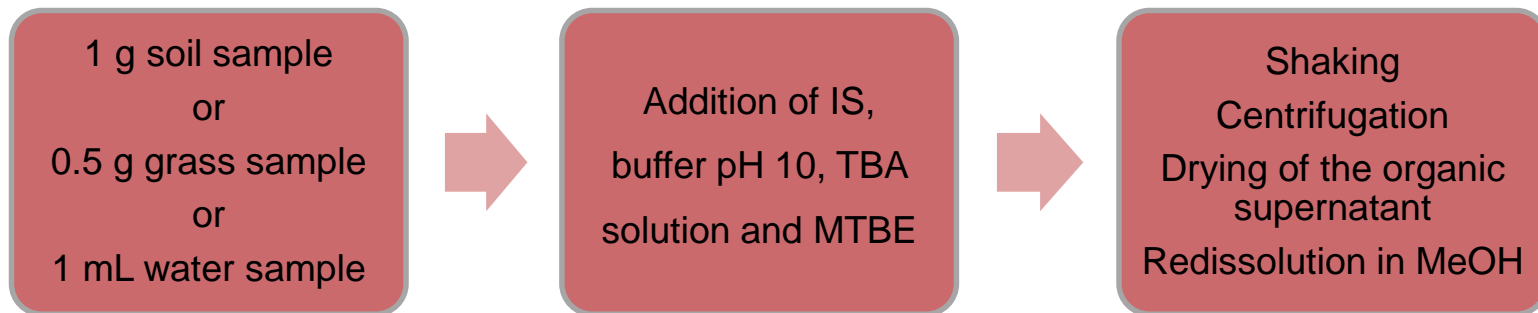
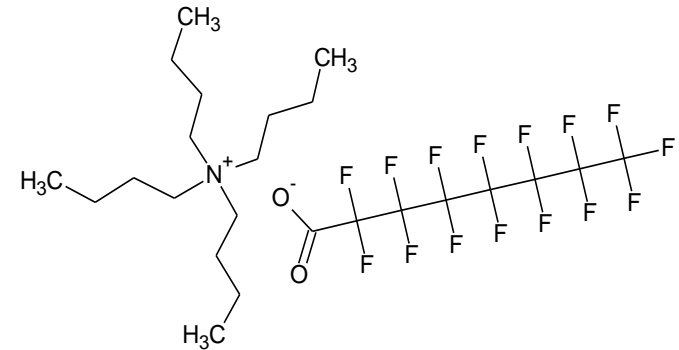
Experimental setup

- Lysimeters were filled with PFAS-free subsoil
 - + topsoil with 6:2 diPAP application (2 mg/kg) or
 - + topsoil with 8:2 diPAP application (2 mg/kg)
- Sowing of grass against erosion effects
- Watering only by natural rainfall
- Sampling according to leachate volume (~ 4 week intervals) for 2 years
- Grass cover mowed once per year
- Soil sampling in 5 depths at study end
- PFAS analysis of each compartment



Target Analysis

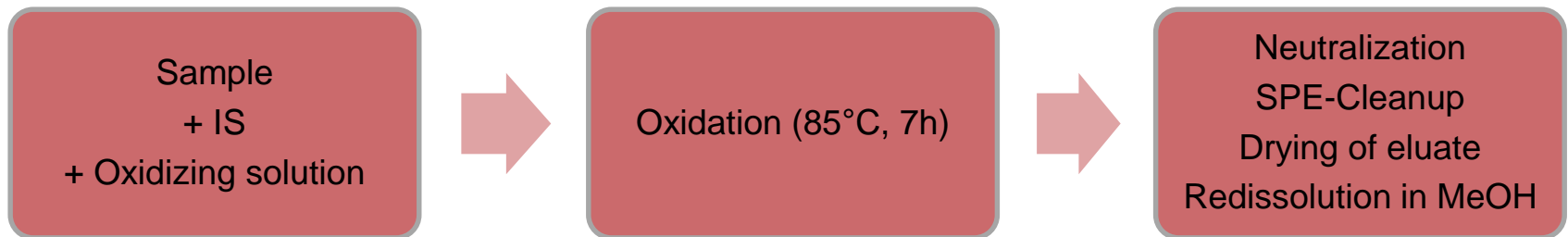
- Solid-liquid-liquid-extraction with MTBE
- Usage of isotope labeled internal standards (IS)
- Formation of ion pairs (TBA cations and PFAS anions)



- Analysis by UHPLC coupled with high-resolution MS

dTOP Assay

- dTOP Assay = direct Total Oxidizable Precursor Assay* as PFAS sum parameter
- Direct oxidation of all oxidizable PFAS precursors into measurable PFCAs without prior extraction step
- Oxidation solution: 200 mM $K_2S_2O_8$, 500 mM NaOH

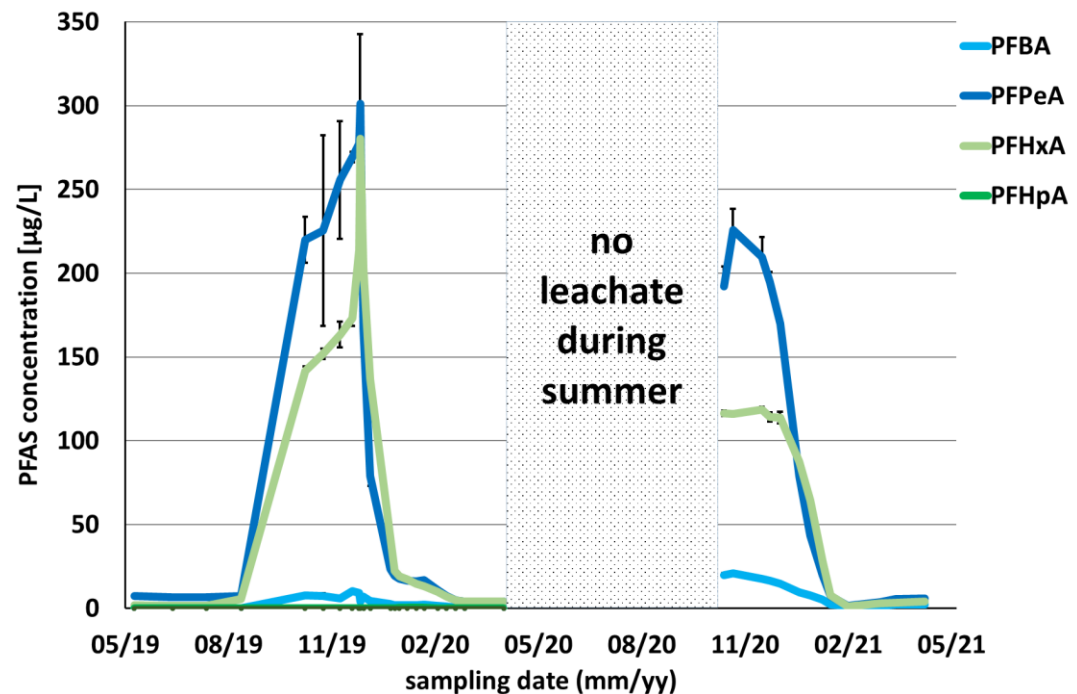


- Analysis by UHPLC coupled with high-resolution MS

* Published in: B. Göckener, *et al.*, Exploring Unknown Per- and Polyfluoroalkyl Substances in the German Environment – the Total Oxidizable Precursor Assay as Helpful Tool in Research and Regulation, Science of the Total Environment (2021)

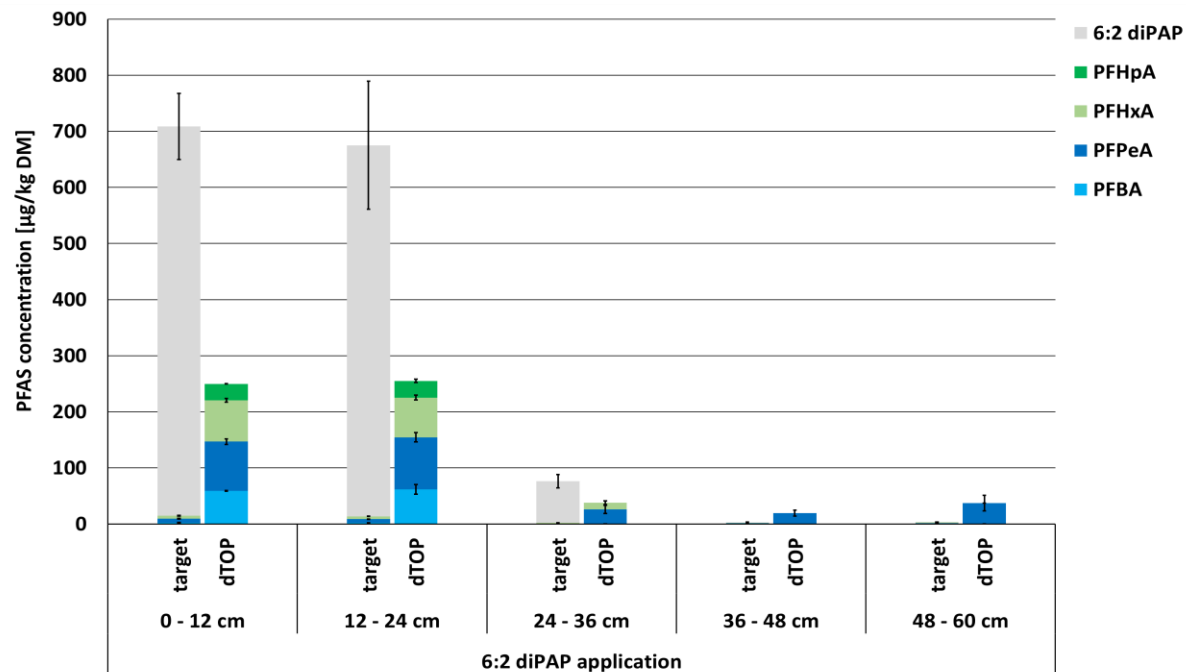
Results 6:2 diPAP application

- High concentrations of PFPeA and PFHxA during the first winter (main degradation products)
- Concentrations decrease to nearly zero in spring
- Concentrations increase after the summer period to lower levels compared to first year
- No known precursors detected in the leachate
- No further PFAS detected through dTOP assay



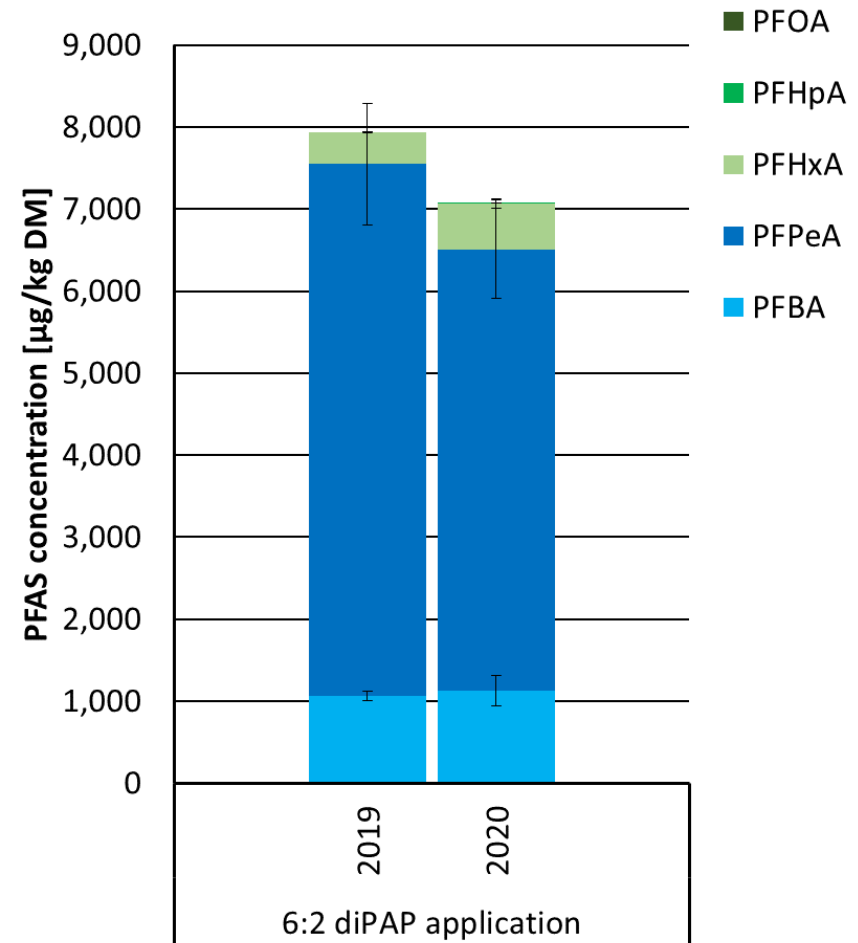
Results 6:2 diPAP application

- High concentrations of 6:2 diPAP in the top soil layers after two years
- Nearly no transfer of the diPAPs into deeper soil layers
- Only small amounts of PFCAs detected per target method
- dTOP assay reveals formation of PFCAs by oxidation (mass loss observable)



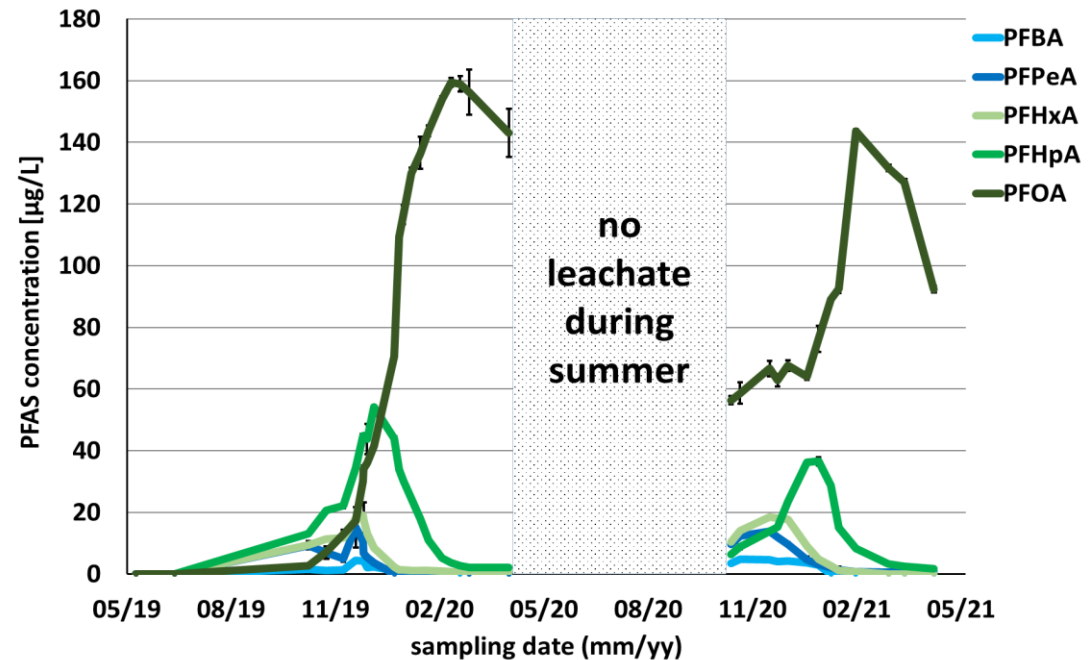
Results 6:2 diPAP application

- High concentrations of PFCAs in the grass cover
- PFPeA > PFBA > PFHxA
- No 6:2 diPAP transfer into the plant
- Small difference between the two harvests
- dTOP assay shows no additional formation of PFCAs
- Plant uptake makes up 0.1% of applied 6:2 diPAP amount per year



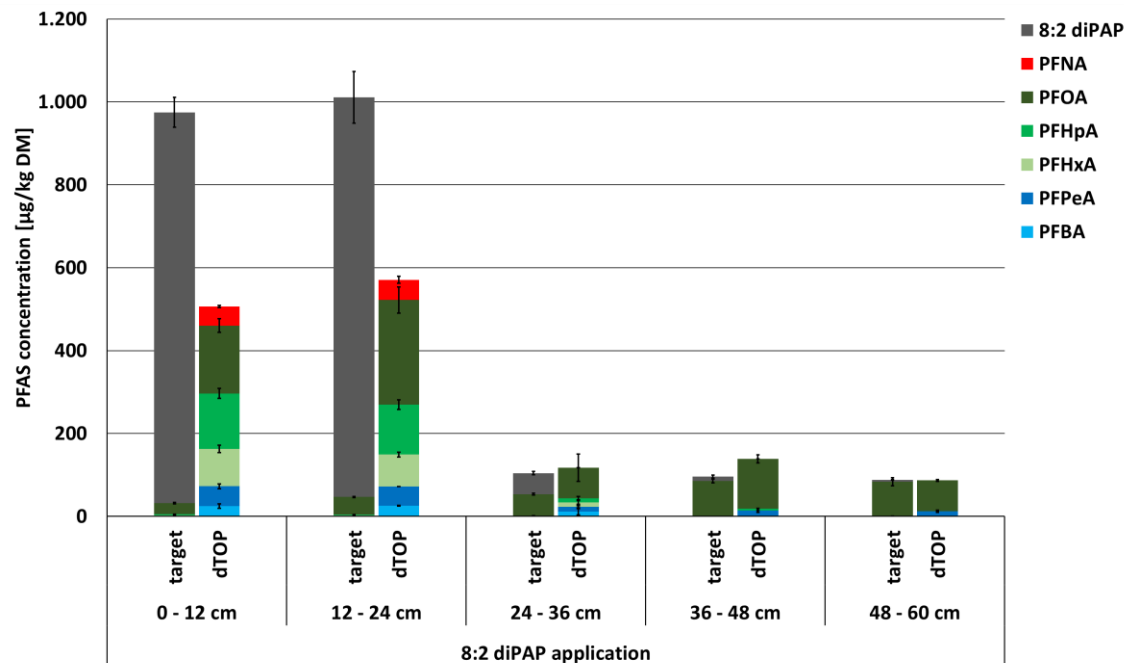
Results 8:2 diPAP application

- PFOA is the main degradation product, followed by PFHpA
- Low concentrations of PFBA, PFPeA and PFHxA
- All concentrations except PFOA decrease to nearly zero in spring
- Concentrations increase after the summer period to lower levels compared to first year
- No known precursors detected the leachate
- No further PFAS detected by dTOP assay



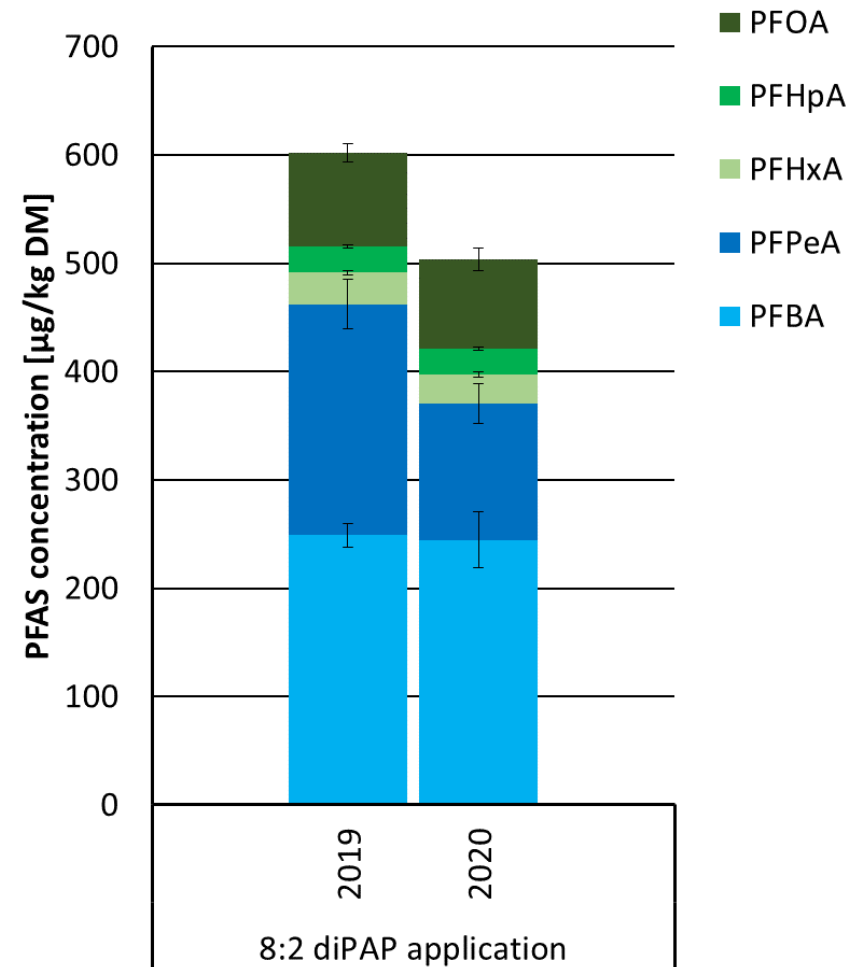
Results 8:2 diPAP application

- Higher concentrations of 8:2 diPAP in the top soil layers compared to 6:2 diPAP
- Nearly no transfer of diPAPs into deeper soil layers
- PFOA identified as main degradation product in the soil
- dTOP assay reveals formation of PFCAs by oxidation (mass loss observable)



Results 8:2 diPAP application

- Detection of PFCAs in the grass cover
- Lower uptake compared to 6:2 diPAP variant
- PFBA > PFPeA > PFOA > PFHxA > PFHpA
- No 8:2 diPAP transfer into the plant
- Small difference between the two harvests
- dTOP assay shows no additional formation of PFCAs
- Plant uptake makes up 0.01% of applied 8:2 diPAP amount per year

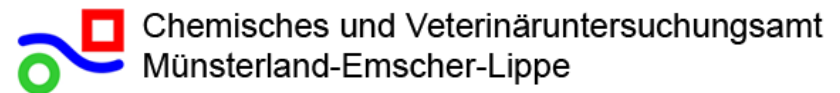


Conclusion

- Detection of diPAPs in top soil layers shows immobile behavior of both surveyed substances
 - DiPAPs form a reservoir with slow degradation into PFCAs
 - Transport of formed PFCAs into deeper soil layers with the leachate
 - Increased PFCA-concentrations in the leachate after the summer indicate diPAP degradation during summer period
 - Uptake of PFCAs with different chain lengths into grass cover
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- Potential pathway for PFAS into ground water and plants and therefore the food chain

Many thanks to all project partners:

U N I K A S S E L
V E R S I T Ä T



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THANK YOU FOR YOUR ATTENTION!



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