Determination of Plant Uptake of Modified Polyfluorinated Substances and their Biodegradation Products in Soil and in Plants

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Introduction

Per- and polyfluorinated alkyl substances (PFAS) are a group of environmental persistent, bioaccumulative and often toxic substances, which pose a risk to the human health. The two lead substances of this group, namely perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), are intensively investigated and their hazards are being discussed. After the restriction for the production and use of PFOA and PFOS alternative substances with similar qualities were used more frequently. These substances are known as modified PFAS. An assessment of the toxicity, the environmental persistency and the ability to bioaccumulate is not possible because of a sparse data situation.

In this work, modified PFAS (6:2 FTOH [fluorotelomer alcohol], 8:2 FTOH, 10:2 FTOH, 6:2 FTS [fluorotelomer sulfonic acid], 6:2 monoPAP [monosubstituted polyfluoroalkyl phosphate], 8:2 monoPAP, 6:2 FTAC [fluorotelomer acrylate], 8:2 FTAC, 6:2 FTMAC [fluorotelomer methacrylate] and 8:2 FTMAC) were applied to soils and radishes (*Raphanus sativus var. sativus*) were grown on these soils. The contents of the applied substances and their degradation products were investigated, as well as the kinetic reduction of a fluorotelomer alcohol (8:2 FTOH) in soil over a time period of 18 days.

Methods

1. Preparatory works

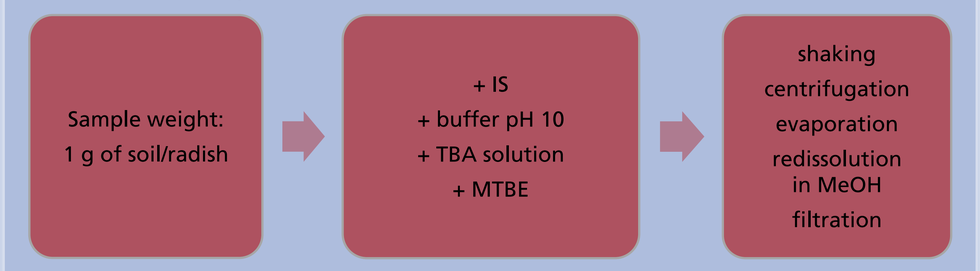
Mitscherlich pots were filled with 6.5 kg of two different soils (sand and clay) and analyte solutions (acrylates and non-acrylates) in different concentrations (0.64 – 4.69 mg/kg soil) were applied. Radishes were grown under natural conditions (sunlight and outdoor temperatures) and watered regularly. Radish and soil samples were taken after the vegetation period (8 weeks) and kept frozen until analysis.

2. Kinetic experiment

Ethanolic solutions of 8:2 FTOH (109 mg in 10 mL) were applied on two soil samples (350 g). While the first soil was kept dry over the experimental period, the second soil was watered regularly. Every couple of days soil samples were taken and kept frozen until analysis (TOP assay).

3. TBA extraction:

The ion pairing reagent tetrabutylammonium (TBA) forms an ion pair with the anionic target analytes. The target analytes include PFCA (perfluorocarboxylic acids), PFSA (perfluorosulfonic acids) and 6:2 FTS.

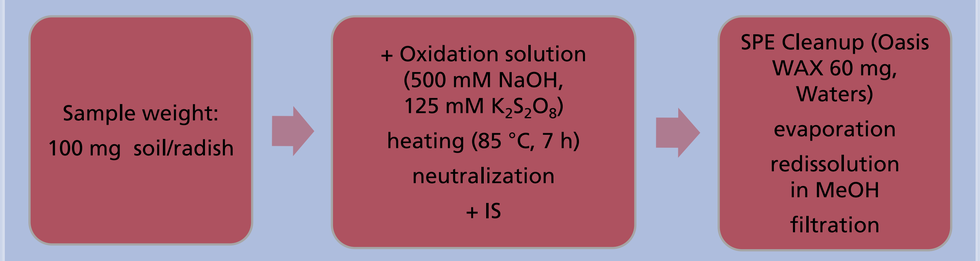


4. Total Oxidizable Precursor (TOP) assay:

Oxidizable PFAS are oxidized by hydroxide radicals.[1]

$$S_2O_8^{2-} \xrightarrow{85\,^{\circ}C,\ 7\ h} 2\ SO_4^{-*}$$

$$SO_4^{-*} + OH^- \longrightarrow SO_4^{2-} + OH^*$$



5. Analysis:

The quantification was performed by HPLC-MS (Q Exactive Plus, Thermo Fisher). The determined analytes contained PFCA and PFSA of different chain lengths as well as 6:2 FTS using isotope labeled internal standards (IS).

Results

PFCA of different chain lengths were identified as degradation products in the soil as well as in the radish compartments (root and leaves). PFSA and 6:2 FTS could not be detected.

The molar recovery rates of PFCA in soil in respect of the initially applied amount of substance were, depending on the experimental parameters, determined to be between 1.1 ± 0.1% and 8.5 ± 2.3%. A sum determination of all PFAS by usage of the TOP assay resulted in recovery rates of 1.6 ± 0.6% to 12.3 ± 1.5% (see Fig. 1). The determined molar contents of PFAS in the analyzed compartments are similar (soil: 346 ± 19 nmol/kg, root: 326 ± 46 nmol/kg, leaves: 527 ± 65 nmol/kg) to each other, the majority of the absolute PFAS mass however is still located in the soil.

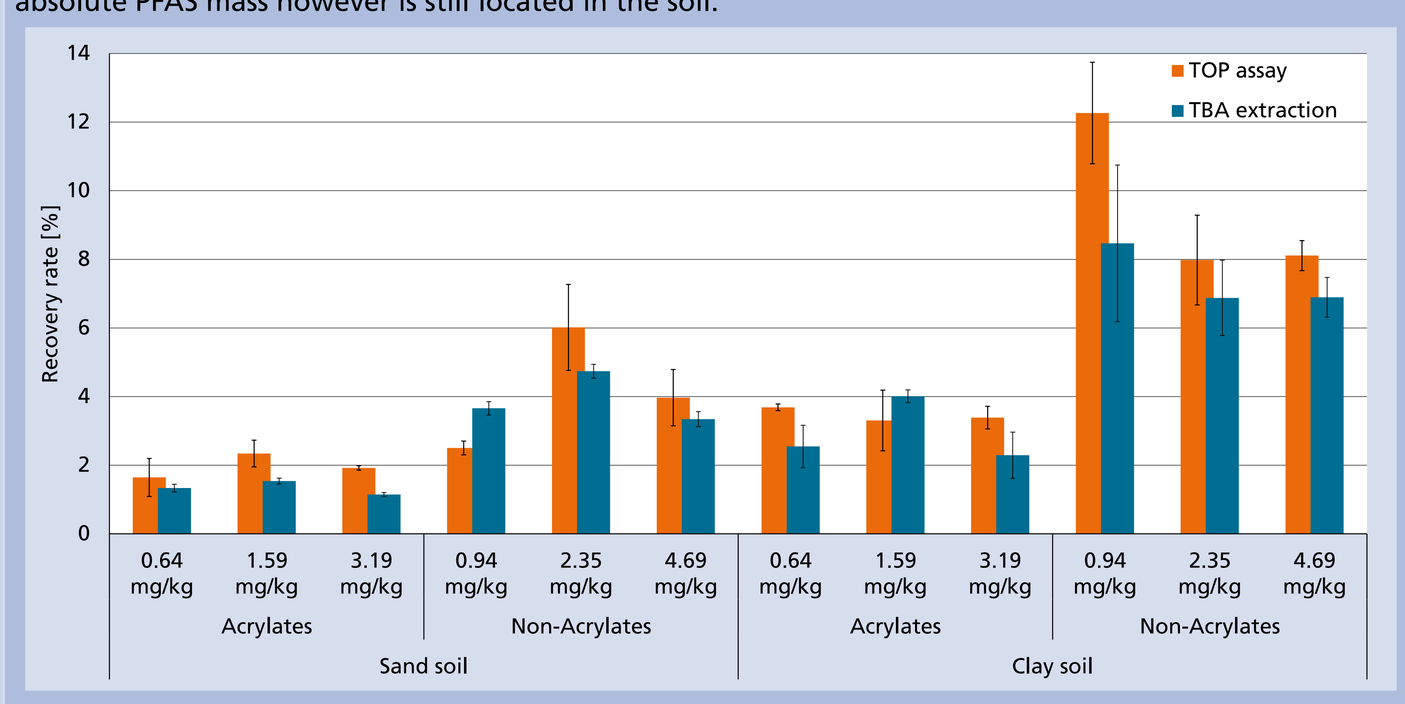


Fig. 1: Recovery rates of the determined PFCA contents in the sample soils depending on the application solution and the applied concentration (PFAS sum) after TOP assay (left; n = 2) and TBA extraction (right; n = 6). Shown are the mean values and their standard deviations as error.

The PFAS concentration in the wet soil of the kinetic experiment decreased exponentially during the 18 days (see Fig. 2), while the concentration in the dry soil hardly decreased. The half-life in wet soil could be determined to be 6.0 d.

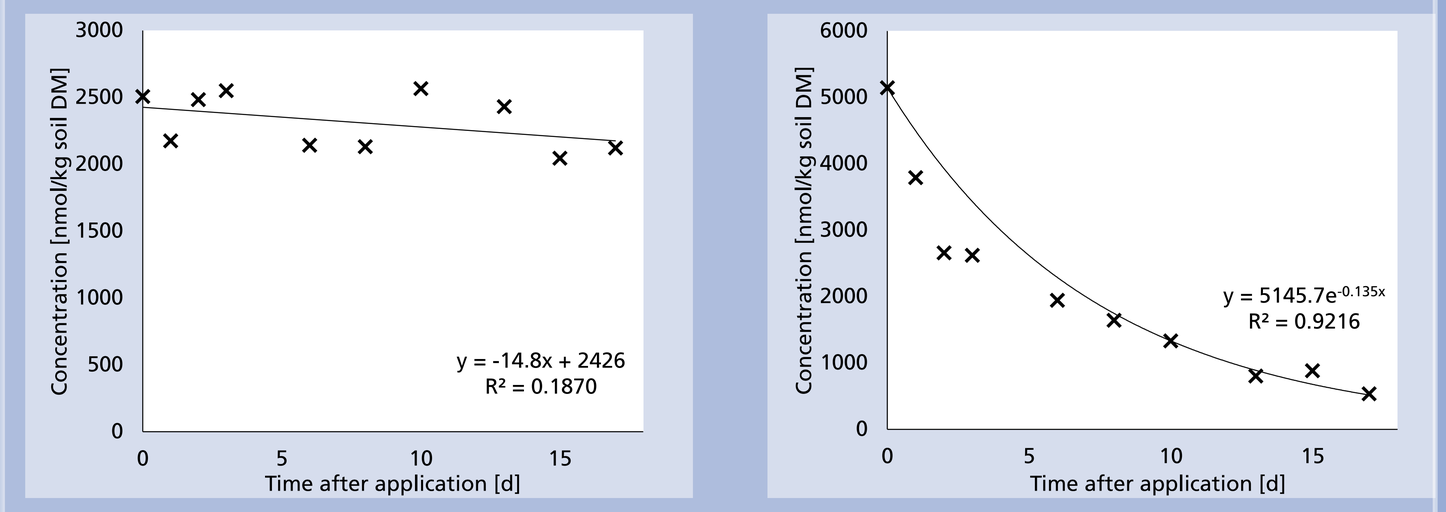


Fig. 2: Development of the PFAS concentration in dry soil (dry mass; left) and wet soil (dry mass; right) analyzed after oxidation (TOP assay) over time after 8:2 FTOH application (n = 1).

Discussion & Outlook

It was possible to show that the investigated modified PFAS were able to degrade into PFCA. The sum of the determined PFAS (TBA extraction; see Fig. 1) is slightly lower than the sum determination of all oxidizable PFAS (TOP assay). This indicates the existence of oxidizable but not determined PFAS. The overall recovery rates of less than 12.3% suggest that the majority of the applied fluorinated moieties left the system during the study duration. The kinetic experiment with 8:2 FTOH (see Fig. 2) supports this thesis. The results lead to the conclusion that certain PFAS degradation intermediates such as 8:2 FTOH can pass from soil into air. This represents a potential source of ubiquitous contamination. Further research is needed to examine the effects of these volatile species on the environment.

Reference:

[1] Houtz, E. F.; Sedlak, D. L., Oxidative conversion as a means of detecting precursors to perfluoroalkyl acids in urban runoff. *Environmental science & technology* **2012**, *46*, 9342-9.

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Determination of plant uptake of modified polyfluorinated substances and their biodegradation products in soil and in plants

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After the EU-wide statutory restriction of the production and use of perfluorinated substances (e.g. Perfluorooctanoic acid [PFOA] or Perfluorooctanoic sulfonic acid [PFOS]) due to their proven tendency to be bioaccumulative and persistent organic pollutants in 2006, polyfluorinated alkyl substances (PFAS), which are not covered by the legal guidelines, replaced many of these compounds. One replacement strategy is the use of polyfluorinated substances based on a fluorotelomeric structure modified with functional groups as phosphates, sulfates, alcohols and acrylates or methacrylates.

This investigation deals with different PFAS, namely 6:2 fluorotelomer alcohol (FTOH), 8:2 FTOH, 10:2 FTOH, 6:2 fluorotelomer sulfonate (FTS), 6:2 polyfluoroalkyl phosphate (PAP), 8:2 PAP, 6:2 fluorotelomer acrylate (FTAC), 8:2 FTAC, 6:2 fluorotelomer methacrylate (FTMAC) and 8:2 FTMAC.

The substances were applied on different types of soil (approx. 0.2 - 1 mg/kg soil) which was planted with radishes (*Raphanus sativus).* The grown period of radishes was 60 days. In first experiments investigating the content of PFAS in soil samples by using a methanol extraction and LC-MS/MS analysis method, several polyfluorinated carbon acids [perfluoropentanoic acid (C5) to perfluorodecanoic acid (C10)] were found in concentrations of approximately 1 – 30 µg/kg soil. As none of these acids was applied on the testing soils, it can be postulated that biodegradation processes formed them during the growth period of the radishes. In addition to that, in the soil samples the applied substances (PAPs, FTOHs and 6:2 FTS) were not found. For the determination of the FTOHs, FTACs and FTMACs as well as possible biodegradation intermediates, a GC-MS/MS method will be designed in the following experimental steps. Furthermore, the grown radishes will be analyzed to ascertain the amount of PFAS and their degradation products as well as the resorption capacity from soil to the radishes.