Are PFAS mobilized in soil by biological processes? A one-year laboratory experiment provides clues

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Preliminary remark

The following article is a translation, the original can be found here, see page 25: https://www.hlnug.de/fileadmin/dokumente/altlasten/Boeden_Altlasten_Newsletter_2022_web_final.pdf

General

A group of fluorinated organic substances is referred to as PFC or PFAS, these substances are contained in numerous industrial and household products. In addition to the well-known applications as repellents and surfactants (e.g. in greaseproof food packaging, sunshades, awnings, special papers, stone floor care products) and as a component of special fire-extinguishing foams (AFFF foams), there are many other areas of application: latex and facade paints, heat transfer fluids, ski wax, dental floss, etc. [1]. The abbreviation PFC stands for per- and polyfluorinated chemicals. The term PFAS (per- and polyfluoroalkyl substances) has established itself in the scientific literature. Both terms can usually be used synonymously. The term PFAS is used below.

PFAS have both positives and negatives. PFAS have very attractive material properties, above all a very high resistance to environmental influences, so that PFAS products are very durable and the desired positive product properties last for a long time. The very stable Fluorine-Carbon bonds cause this persistence. The advantages mentioned turns out to be disadvantages when PFAS finds their way into the environment: with waste, in wastewater, as trace substances in water and soil, in drinking water and in food. They are extremely stable and accumulate in environmental media. Therefore, some of the PFAS are now banned (PFOS, PFOA). There are current publications that deal with the areas of application, analysis and evaluation of PFAS [2, 3].

The following is of particular relevance for the laboratory test "Degradation/mobilization of PFAS in soils" for:

- Instead of the previously used **per**fluorinated PFAS, **poly**fluorinated PFAS are now almost exclusively produced and used. There are several thousand **poly**fluorinated PFAS on the market.

- Currently the so-called fluorocarbon resins, which are a type of **poly**fluorinated PFAS, have a wide range of applications (see below).
- Although the analysis of perfluorinated PFAS is now established, many of the **poly**fluorinated PFAS can either not be detected or only with special analysis (TOP, AOF).
- The above fluorocarbon resins are not mobile. They cannot be detected with standard analysis. It is unclear whether fluorocarbon resins can be detected using specialized analysis methods such as the TOP method (see below).
- Concerning the persistence of the substances: **per**fluorinated chemicals are not degradable; although **poly**fluorinated chemicals are partially degradable, **per**fluorinated substances are formed as the final degradation product.
- Presumably, with the above referenced degradation, biological degradation processes are of particular importance. This can be caused by microorganisms in soil and water.
- The laboratory tests are intended to provide information as to whether the following scenario is plausible: polyfluorinated chemicals such as fluorocarbon resins are currently used and at least some of them end up in the environment. The polyfluorinated chemicals are neither mobile nor analyzable, so these substances remain undetected in the environment. However, degradation processes take place over time, converting the **poly**fluorinated chemicals into **per**fluorinated chemicals. These are usually both mobile and analyzable and can therefore be detected in soil, water and food.

Fluorocarbon Resins

Fluorocarbon resins are commonly used polyfluorinated chemicals. They are fluorine-containing macromolecules based on polyacrylates, polymethacrylates or polyurethanes, which have fluorine-containing side chains. Figure 1 shows an example of a fluorocarbon resin based on polyacrylate. The polyacrylate polymer forms a long carbon chain (main chain) shown as a horizontal zigzag line in the figure. The polymer chain has functional groups:

- Crosslinkers cause the polymer chain to cross-link with the material to be protected, such as paper or textiles.
- Ester bonds make the connections between the main chain and the side chains. The side chains are partly fluorinated (red line) and partly non-fluorinated (light blue line). The chemical properties of the fluorocarbon resins can be influenced by varying the chain lengths of the main and side chains, as can the ratio of fluorinated to non-fluorinated side chains.

In the laboratory test, fluorocarbon resins were examined which, according to the manufacturer's information, have fluorinated side chains with a length of six carbon atoms. Further details about the chemicals used are not known.

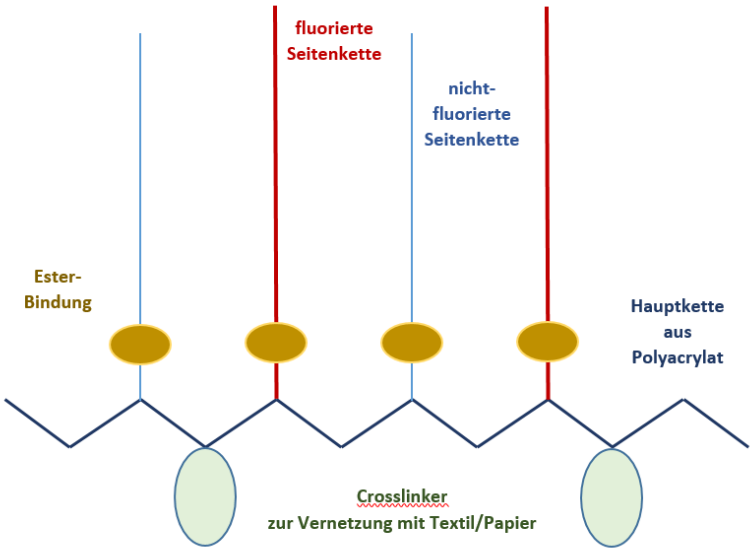

Figure 1: Chemical structure of a fluorocarbon resin (red line: fluorinated side chain)

Analytical Procedure

PFAS with short and medium chain lengths (max. six fluorinated carbon atoms) are relatively easily soluble in water. Since the PFAS determination limits are significantly higher in solids analysis than in aqueous media, it makes sense to elute PFAS-containing soil samples with water and measure the PFAS in the eluate. An elution process with a water-solid ratio of 2 to 1 was used in the laboratory tests (DIN 19529). A portion of each eluate sample was analyzed directly (native sample) and a portion after pretreatment using the TOP method (TOP sample).

In the TOP method (total oxidizable precursor), the sample is first subjected to strong oxidation, during which the **poly**fluorinated compounds (which cannot be analyzed using standard analysis) are converted into (analyzable) **per**fluorinated compounds. The analysis is then carried out analogously to the native sample according to DIN 38407-42. Then the results of the TOP sample and the native sample are compared. If the TOP sample contains significantly more PFAS than the native sample, this is evidence that the analyzed soil sample contains **poly**fluorinated PFAS.

Conception of the laboratory test "Degradation/mobilization of PFAS in soil"

The test setup was developed jointly by the DVGW Water Technology Center (TZW) and HLNUG. The laboratory tests were carried out at the TZW in Karlsruhe. The questions were: To what extent do biological degradation processes cause the release/mobilization of analytically detectable PFAS? Are fluorocarbon resins considered a relevant source of PFAS in soil, water and food?

Mixtures of sandy soil and 5% compost were mixed with PFAS-containing materials:

- Impregnation agent (fluorocarbon resin with fluorinated side chains of 6 carbon atoms)
- Textile, treated with the above mentioned impregnating agent
- Paper, treated with an impregnating agent similar to that mentioned above.

The soil-compost mixtures were moistened for almost a year to promote aerobic biodegradation processes. Subsamples were taken at the start of the tests and after 2.5, 4.5 and 11 months and analyzed as described above.

Results

The investigations of the three materials (impregnating agent, impregnated textile, impregnated paper) showed a similar release behavior. The results of the impregnating agent are shown as an example. Since the individual PFAS have different fluorine contents, it makes sense to state the molar fluorine concentration [µmol/l] in addition to the PFAS concentration.

In the native samples as well as in the TOP samples, three PFAS occur in particularly high concentrations (Fig. 2):

- PFBA perfluorobutanoic acid (perfluorinated triple chain)
- PFPeA perfluoropentanoic acid (perfluorinated 4-chain)
- PFHxA perfluorohexanoic acid (perfluorinated 5-chain)

This shows that the "fluorocarbon resin with fluorinated 6-side chains" does not contain any long-chain (and comparatively human-toxic) PFAS, i.e. no chain lengths of 7 or more. The **per**fluorinated carboxylic acids with the chain lengths 4 to 6 dominate. On the other hand, **per**fluorinated sulfonic acids only occur to a lesser extent. It is known from the literature that the chains in the TOP process are shortened as a result of oxidation (here: from a chain length of 6 to 5 or 4). Chain shortening also seems to play a role in biological processes.

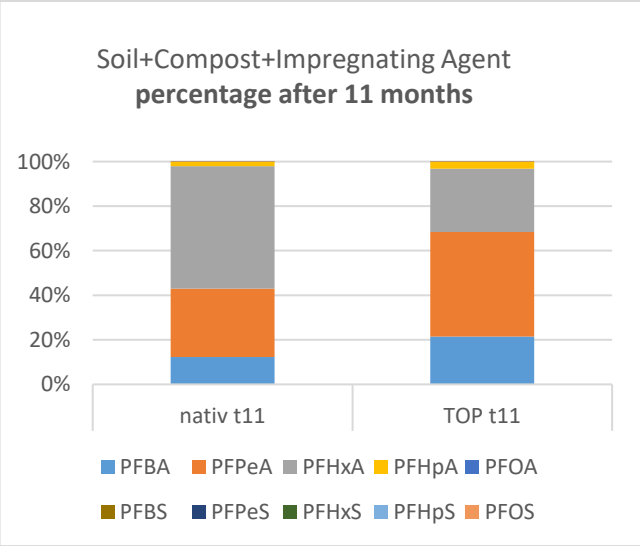

Figure 2: Percentages of individual PFAS in the "soil+compost+impregnating agent" samples after a test period of 11 months

In the case of the native samples, an almost linear increase in the PFAS concentrations can be seen as the duration of the test increases. After 11 months the concentrations increased by a factor of 6 (Fig. 3).

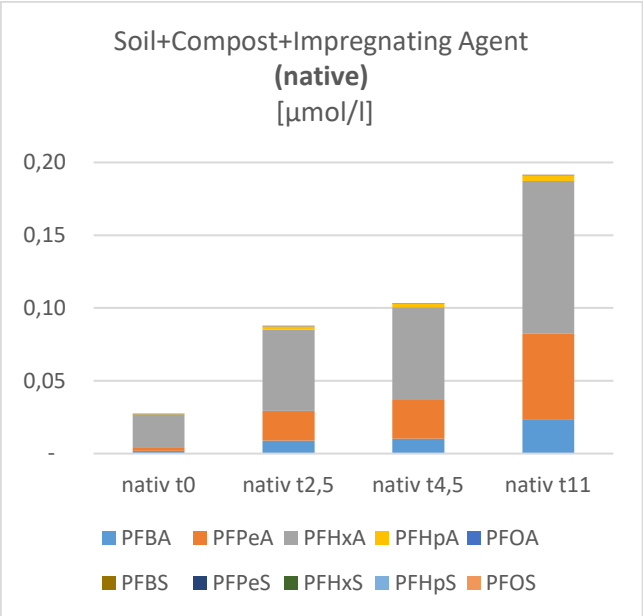

Figure 3: PFAS concentrations over the course of the experiment (11 months) in native samples

In contrast, no relevant increase in the PFAS concentrations can be seen in the TOP samples (Fig. 4). The TOP concentrations are about 4 times higher than in the native samples after an 11-month test period.

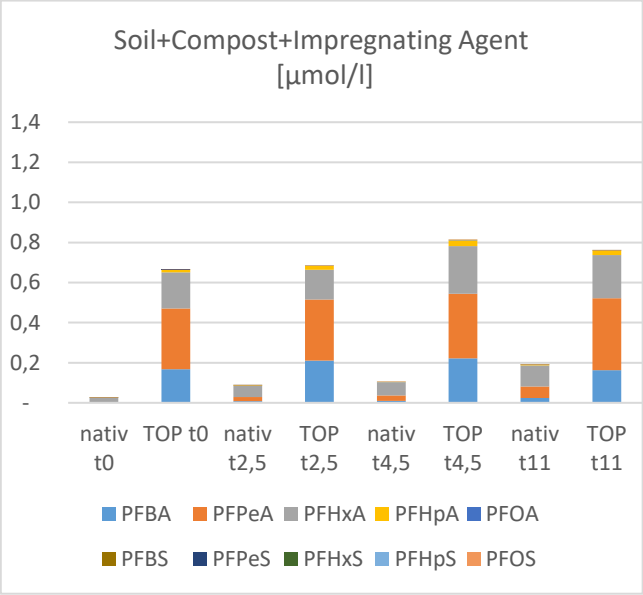

Figure 4: PFAS concentrations over the course of the experiment (11 months) in both native as well as TOP samples

The amount of fluorine contained in the impregnating agent that was released and mobilized during the course of the test was balanced. It was shown that less than 0.5% of the fluorine present can be detected with the TOP method; in the case of the native samples, the proportion was only around 0.1%. Results for the impregnated paper and textile were comparable.

Interpretation and open questions

The laboratory tests "Degradation/mobilization of PFAS in soil" allow the following interpretations:

- If fluorocarbon resins get into soil or water, a release of perfluorinated PFAS can be assumed.

- After almost a year, the concentrations measured in the native samples were 6 times higher than at the beginning of the experiment. The increase in concentrations over the course of the experiment was almost linear. If the experiment lasts longer, it can be assumed that the concentrations will continue to rise. It is plausible that biological degradation processes are the main reason for the increase.
- Significantly higher concentrations were found in the TOP samples than in the native samples (approx. factor 4, after 11 months). Since no relevant increase in PFAS concentrations was evident during the course of the experiment, biological degradation processes appear to have only a minor influence on the TOP method.
- It is to be expected that the concentrations in the native samples and in the TOP samples will equalize over a longer period of time (several years). Therefore, with the TOP method, a "glimpse of the future" is possible.
- Even with the TOP method, approximately only 0.5% of the applied PFAS (fluorocarbon resins) can be detected. This indicates that over 99% of the PFAS (fluorocarbon resins) are still present in the soil, bound either to the original material (textile or paper) or to the soil grains.

Therefore, two scenarios are possible:

I. Non-mobile PFAS (here: fluorocarbon resins) are so stable that release of mobile PFAS into the environment occurs extremely slowly. Above all, product impurities are mobilized; these are fluorinated chains that are not attached to the main chain. Due to the very slow release, there is only a low risk for the soil-groundwater path. No statements can be made about other pathways (e.g. soil-crop-human).

II. Although non-mobile PFAS (here: fluorocarbon resins) are stable, relevant quantities of mobile PFAS will be released into the environment for the foreseeable future. Even if only low PFAS concentrations are found in the soil or soil eluate, non-mobile PFAS (here: fluorocarbon resins) can remain undetected and represent a significant source of long-term PFAS release/mobilization. The potential for release is therefore greatly underestimated.

Whether the optimistic scenario I. or the pessimistic scenario II. is correct should be clarified with further experiments. Until then, for environmental and precautionary reasons, it makes sense to assume scenario II. The ubiquitous pervasiveness of PFAS in the environment (blood, mother's milk, wild boar liver, etc.) shows that the concentrations of mobile PFAS are already too high.

Literature

[1] Hessisches Landesamt für Naturschutz, Umwelt und Geologie: PFC – Tausendundeine Verwendungsmöglichkeiten https://www.hlnug.de/fileadmin/dokumente/altlasten/PFC/Boeden_Altlasten_Newsletter_2021_PFC_210831_web.pdf

[2] Umweltbundesamt: UBA-Texte 137/2020 Sanierungsmanagement für lokale und flächenhafte PFAS-Kontaminationen https://www.umweltbundesamt.de/publikationen/sanierungsmanagement-fuer-lokale-flaechenhafte-pfas

[3] Bundesministerium für Umwelt, Naturschutz, nukleare Sicherheit und Verbraucherschutz: Leitfaden zur PFAS-Bewertung - Empfehlungen für die bundeseinheitliche Bewertung von Boden- und Gewässerverunreinigungen sowie für die Entsorgung PFAS-haltigen Bodenmaterials https://www.bmuv.de/download/leitfaden-zur-pfas-bewertung