Session: Per-and Polyfluoroalkl Substances (PFAS): a Persistent Challenge for the 21st Century Presentation Type: Platform Tuesday May 4<sup>th</sup>, 2021; 16:20 PM; Virtual Session Room: 3

# Investigating the Transfer of Polyfluorinated Phosphate Diesters (diPAPs) into Maize Plants

<u>René Lämmer</u><sup>1</sup>, Janine Kowalczyk<sup>2</sup>, Hildegard Just<sup>2</sup>, Jörn Breuer<sup>3</sup>, Bernd Göckener<sup>1</sup>, Kevin Severin<sup>1</sup>, Matthias Gaßmann<sup>4</sup>, Eva Weidemann<sup>4</sup>, Thorsten Stahl<sup>5</sup> and Mark Bücking<sup>1,6</sup>

 <sup>1</sup> Fraunhofer Institute for Molecular Biology and Applied Ecology IME, Auf dem Aberg 1, 57392 Schmallenberg, Germany
<sup>2</sup> German Federal Institute for Risk Assessment, Max-Dohrn-Str. 8-10, 10589 Berlin, Germany
<sup>3</sup> Agricultural Technology Centre Augustenberg, Neßlerstraße 23, 76227 Karlsruhe, Germany
<sup>4</sup> University Kassel, Kurt-Wolters-Str. 3, 34125 Kassel, Germany
<sup>5</sup> Chemisches und Veterinäruntersuchungsamt Münsterland-Emscher-Lippe (CVUA-MEL), Joseph-König-Str. 40, 48147 Münster, Germany
<sup>6</sup> School of Chemistry, Monash University, Box 23, Victoria 3800 Australia

E-mail contact: rene.laemmer@ime.fraunhofer.de

### 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a group of bioaccumulative, environmental persistent and often toxic substances, which can pose a risk to the human health [1]. The two main substances of this group are perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), which have already been intensively investigated [2]. As the production and use of both substances were heavily restricted [3, 4], alternative substances with similar properties are used more frequently. The environmental fate and pathways of these substitute PFAS are not yet fully understood.

The overall objective of the publicly funded project PROSPeCT is the development of scientific basics for the behaviour of PFAS based on a contamination site in Baden-Württemberg, a state in southwest Germany. In this specific study, the environmental behaviour of the substitute substances 6:2 polyfluoroalkyl phosphate diester (diPAP) and 8:2 diPAP was investigated in the pathway from the soil to maize plants. The PFAS analysis will focus on the diPAPs and different perfluorinated carboxylic acids (PFCAs) as their final degradation products in all relevant compartments.

### 2. Materials and methods

For the purpose of determining the fate of 6:2 diPAP and 8:2 diPAP, the two substances were mixed into PFAS free soils (1 mg/kg soil). Maize plants (*Zea mays*) were planted in Mitscherlich pots and grown under natural conditions regarding temperature and sunlight exposure. The plants were watered under regulated conditions without any impact of natural precipitation. After harvest, the homogenized maize compartments (root, stem, leaf, husk, cob and grain) and the soil were individually analyzed for PFAS concentration. The analysis was performed using isotope labeled standards and a solid-liquid-extraction method using tetrabutylammonium as an ion-pair reagent. The quantification was performed by ultra-high performance liquid chromatography coupled with high-resolution mass spectrometry (UHPLC-HRMS).

### 3. Results and discussion

After the vegetation period of 150 days, the primarily applied substances make up the majority of PFAS in the soil with around 15% (6:2 diPAP) and 47% (8:2 diPAP) of the initial concentration, respectively (Figure 1). Furthermore, perfluorinated carboxylic acids (PFCAs) are found in the soil although they were not initially applied. The soil applied with 6:2 diPAP contains small amounts of perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPA) and perfluorobexanoic acid (PFHxA), while the soil applied with 8:2 diPAP additionally contains perfluorobeptanoic acid (PFHA) and PFOA.

The roots contain lower diPAP levels and higher levels of multiple PFCAs in comparison with the determined PFCA-spectra in the soil. In all other plant compartments, solely PFCAs with chain lengths  $\leq$  C6 (6:2 diPAP application) or chain lengths  $\leq$  C8 (8:2 diPAP application) are detected. The highest levels of PFCAs occur in the leaves, whereas significantly lower concentrations are found in the cob and grain in particular. In addition, low levels of 6:2 diPAP and 8:2 diPAP are detected in the leaves.



Figure 1: PFAS concentrations in different compartments of maize plants grown on soil applied with 6:2 diPAP and 8:2 diPAP, respectively (1 mg/kg soil; mean and standard derivation; n=15).

# 4. Conclusions

The detection of PFCAs with chain lengths  $\leq$  C6 (6:2 diPAP application) or chain lengths  $\leq$  C8 (8:2 diPAP application) in the soil and in the plant compartments indicates the degradation of diPAPs into the persistent PFCAs in the environment. 6:2 diPAP and 8:2 diPAP themselves mainly remain in the soil or in the root system, whereas the plant takes up notable quantities of PFCAs. Especially leaves and husk accumulate short-chain PFCAs such as PFBA and PFPeA. This suggests a transport of small PFAS substances via the transpiration stream within the maize plant and an accumulation caused by evaporation of water from the leaves and shows the potential of diPAPs to contribute to the total PFCA contamination.

These results provide important insights into the transfer of PFAS from contaminated soil into plants. As maize plants in particular are used as animal feed, the uptake of PFAS from field soil displays an entry path into the food chain and thus may serve as a pathway for human exposure to PFAS.

# 5. References

- [1] Daniel Borg, Bert-Ove Lund, Nils-Gunnar Lindquist, Helen Håkansson. 2013. Cumulative health risk assessment of 17 perfluoroalkylated and polyfluoroalkylated substances (PFASs) in the Swedish population. Environment International 59:112-123.
- [2] Kurunthachalam Kannan. 2011. Perfluoroalkyl and polyfluoroalkyl substances: current and future perspectives. Environ. Chem. 8:333-338.
- [3] EU, Commission Regulation (EU) No 2017/1000 of 13 June 2017 amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards perfluorooctanoic acid (PFOA), its salts and PFOA-related substances. In Commission, T. E., Ed. 2017.
- [4] Stockholm Convention, Decision SC-4/17: Listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride. 2009.

#### Acknowledgements

The authors thank Carmen Bernhard and her team from Landesbetrieb Landwirtschaft Hessen for the cultivation of the maize plants.

The project "PROSPeCT" (PFAA and Precursors Soil Plant Contamination) is sponsered by the Umwelt- und Energieforschung des Landes Baden-Württemberg - Förderprogramm BWPLUS.