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Investigation of the Feed to Egg Transfer of PFAS Including the Transformation of PFAA Precursors in Laying Hens

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Introduction

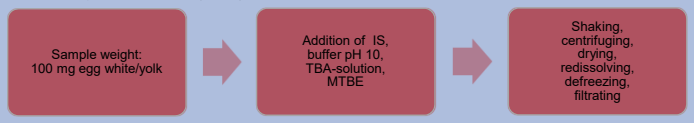
Per- and polyfluoroalkyl substances (PFAS) are chemicals that are used in a wide variety of consumer products for the everyday life due to their versatile application possibilities. Currently, according to the US EPA 5061 PFAS compounds are known [1]. In case of perfluoroalkyl carboxylic- (PFCAs) and –sulfonic acids (PFSAs), subgroups of PFAS, it is known that they accumulate in organisms and the environment. Additionally, those substances show high stability and are barely degradable because of the strong C-F bond [2]. Next to PFCA and PFSA also so-called precursors were found in food and environmental samples [3]. The high variety of PFAS compounds evokes problems for the analysis especially for the single compound determination. One possible solution to determine the overall PFAS exposure is the oxidation (Total Oxidizable Precursors, TOP method) of precursors to PFCA.

In a feeding study performed by the German Federal Institute for Risk Assessment (BfR) the transfer of PFCA and PFSA with a chain length of C4-C14 was investigated in chicken eggs. The uptake of PFAS took place by using contaminated feed containing amongst others barley and hay that were cultivated on PFAS contaminated soil. Afterwards, the concentration of different PFCAs and PFSAs were determined in different tissues and in the food product egg. The concentrations found in the egg yolk from the laying hens were quite high for some of the PFCAs and PFSAs. Noticeable is that the concentrations of PFHpS (C7), PFOS (C8) and PFNA (C9) were much higher in the egg yolk as could possibly ingested from the contaminated feed. One possible solution for these high concentrations could be the degradation of precursors in the feed to PFCAs and PFSAs. This hypothesis was investigated in a renewed analysis of the chicken eggs by analyzing not only PFCAs and PFSAs but also precursors.

Methods

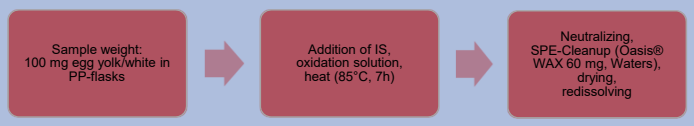
Egg Extraction

- Methyl-*tert*-butylether in alkaline solution with ion pair reagent tetrabutylammonium (TBA)



Oxidation method

- Direct oxidation of the egg white and egg yolk and the containing precursors in 200 mL oxidation solution (200 mM potassium persulfate, 500 mM sodium hydroxide)
  - (1) $S_2O_8^{2-} \xrightarrow{85\,°C,7\,h} 2\,SO_4^{-*}$
  - (2) $SO_4^{-*} + OH^- \longrightarrow SO_4^{2-} + OH^*$



Quantification:

- PFAS-Quantification by high-resolution mass spectrometry (Q Exactive Plus, Thermo Fisher)

Results:

Quantification before the oxidation: The extraction and measuring procedure used in this case confirmed the concentrations of PFCAs and PFSAs that were already determined in the feeding study. The precursors that were already determined in a preliminary test of the feed could also be quantified in the egg yolk. These precursors were perfluorooctane sulfonamide (FOSA), perfluorooctane sulfonamide acetic acid (FOSAA) as well as N-methyl- and N-ethyl-FOSAA. The concentrations of FOSAA and N-methyl-FOSAA were in some cases much higher as the concentrations of some of the PFCAs and PFSAs. Figure 1 shows the uptake of different PFCAs, PFSAs, and precursors over the time of the feeding study.

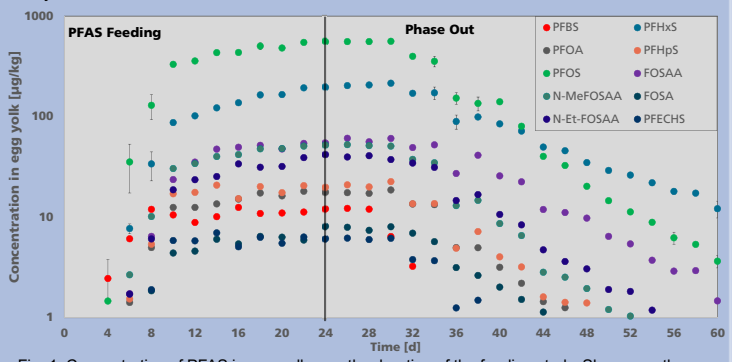


Fig. 1: Concentration of PFAS in egg yolk over the duration of the feeding study. Shown are the mean values of a double determination and their standard deviations as error.

Results:

Quantification after the Oxidation: The concentrations of PFCAs with a chain length between C5 and C8 increased especially for PFOA (C8) after the oxidation. C5-C7 were already determined before the oxidation but could not be quantified. The concentrations of the PFSAs were also increased especially for PFOS. For PFHxS (C6) the concentration is slightly increased whereas it stays the same for PFHpS (C7). Figure 2 shows the concentrations of PFCAs, PFSAs, and precursors from the day of the highest PFAS exposure (4 days after the PFAS feeding period with contaminated feed ended) before and after the oxidation. With a rate of 647 % PFOA shows the biggest increase in comparison of the concentration before and after the oxidation. Followed by PFOS with 140 % and PFHxS with 108 %. The increase of the C5-C7 PFCA and of the C6 PFSA implies that next to the identified C8 precursors also other precursors of a different chain length are contained in the chicken eggs.

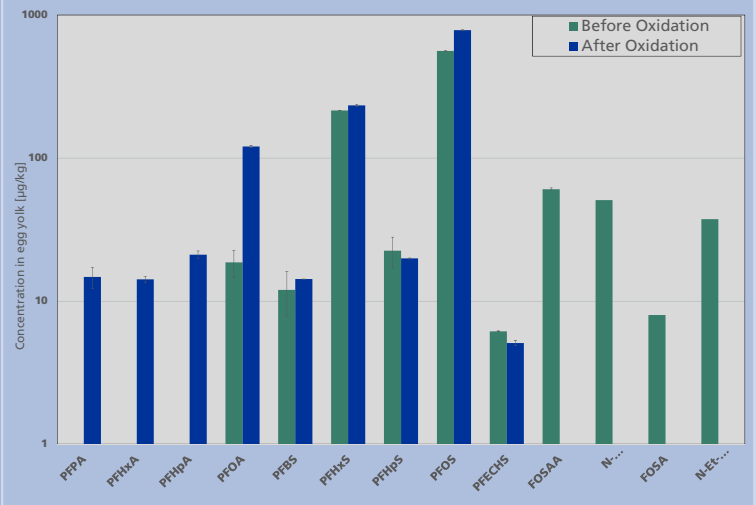


Fig. 2: Concentrations of PFAS in egg yolk before and after the oxidation. Shown are the mean values of a double determination and their standard deviations as error.

Discussion and Outlook:

The concentrations after the oxidation clearly show the importance of PFAS precursors to the total PFAS concentration in the chicken eggs. Therefore, it can be said that the sole quantification of PFCAs and PFSAs gives only partial insight into the overall PFAS burden. By comparing the PFAS concentrations in egg yolk before and after the oxidation it could be seen that this comparison can possibly result in a total overview of the complete PFAS spectrum as well as the possibility to draw conclusions on further unidentified precursors. The problem of identifying and quantifying those substances is the problem of the unavailability of standards for some substances or that those are highly expensive analytical standards. In future studies, it should be focused on the optimization of the TOP method to establish this method in the routine analysis of food monitoring. Furthermore, the kinetics and the toxicology of possible PFCAs and PFSAs precursors have to be investigated in further detail for a better estimation of the health risk for consumers.

Literatur:
[1] US EPA, PFAS Master List of PFAS Substances. Retrieved March 29, 2019, from https://comptox.epa.gov/dashboard/chemical_lists/pfasmaster
[2] Saez, M., P. de Voogt, and J.R. Parsons, Persistence *of perfluoroalkylated substances in closed bottle tests with municipal sewage sludge*. Environ Sci Pollut Res Int, 2008. **15**(6): p. 472-7.
[3] Gebbink, W.A., A. Bignert, and U. Berger, *Perfluoroalkyl Acids (PFAAs) and Selected Precursors in the Baltic Sea Environment: Do Precursors Play a Role in Food Web Accumulation of PFAAs?* Environmental Science & Technology, 2016. **50**(12): p. 6354-6362.

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Session: State of the Science on Emerging and Novel Poly- and Perfluoroalkyl Substances (PFASs) (P)
Poster, Exhibition Hall, ID TH070
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Per- and polyfluorinated alkyl substances (PFAS) are widely used in industry and in a wide range of consumer products due to their outstanding properties. Among the PFAS, the group of perfluoroalkyl acids (PFAA), which can be divided into perfluorocarboxylic (PFCA) and perfluorosulfonic acids (PFSA) depending on the functional group, is best characterized. Several PFAS are known precursors for PFAA which, due to their chemical stability, are persistent, bioaccumulative and toxic.

The distribution of PFAS is ubiquitous. They were detected in animal, water, plant and soil samples. Due to their detection in human samples and drinking water, investigations of PFAS and especially PFAA precursors also come into focus in terms of consumer protection.

In a feeding study conducted by the Federal Institute for Risk Assessment (BfR), chickens were fed PFAS-contaminated feed. The distribution of PFAA in the animals was investigated. The results of the transfer study showed that the animals excreted higher amounts of PFAA through the egg than was ingested with the feed. In investigations of the feed different precursor compounds could be identified. In addition, the eggs were investigated for their content of precursors. Chicken eggs play an important role in the human diet, therefore a valid analysis for this matrix is necessary. At the same time, the transfer of precursors from contaminated feed into eggs can be traced. For this purpose, a multimethod for the detection of more than 40 PFAS is adapted to the matrix chicken egg.

Using the Total Oxidizable Precursor (TOP) approach, precursors are degraded to their corresponding PFCA. By comparing the PFCA concentrations before and after the oxidation, it is possible to draw conclusions about the amount of precursors, and thus non-detected PFAS. This will provide an overview of the overall PFAS burden of egg samples obtained in the chickens transfer study.