# Monitoring of food in a region contaminated with PFAS

Radykewicz T, Schmitt M, Thoma K, Hansert F, Lippold R

State Institute for Chemical and Veterinary Analyses of Food, Bissierstrasse 5, 79114 Freiburg, Germany

**Introduction**

In the southwest of the state of Baden-Wuerttemberg (Germany) short chain perfluoroalkyl carboxylic acids (PFCAs) were detected during a routine investigation of groundwater in autumn 2013. Investigation identified bio solids containing coated paper as possible source of contamination. About 10 years ago these mixtures were used to improve the quality of the soil of farm land.

In 2014 a cooperation of different authorities was initiated to control levels of perfluoroalkyl substances (PFAS) in water, soil, plants, animals and food produced in the contaminated area [1]. The main goal was to ensure that no PFAS-contaminated samples were marketed.

**Materials and methods**

679 samples of vegetables, fruit and food of animal origin were collected between 2015 and 2016 from the market (see table 1). 35% of the samples were taken in the contaminated area and 65% from other agricultural areas (Germany and countries worldwide). The sampling was done within the scope of the official food control in the German state of Baden-Wuerttemberg.

**Table 1: Samples of food of plant and animal origin from the contaminated area and from other areas worldwide (BW: Baden-Wuerttemberg).**

| **from contaminated areas** | | |
|---|---|---|
| fruit | 39 | apple, berries, strawberry |
| vegetable | 90 | asparagus, cucumber, lettuce |
| food of animal origin | 16 | egg |
| | 6 | milk |
| | 57 | meat, liver, kidney (beef, pork, sheep) |
| | 29 | fish |

| **from other areas (55 % BW, 20 % Germany, 25 % worldwide)** | | |
|---|---|---|
| fruit | 38 | strawberry |
| vegetable | 112 | asparagus, baby food (cereals with milk), carrot, lettuce, tomato, cabbage |
| food of animal origin | 24 | egg |
| | 53 | milk |
| | 134 | meat, liver (beef, deer, pork, rabbit) |
| | 81 | fish |

Samples of fruit and vegetables were washed to remove attached soil and then homogenised. The PFAS were extracted in alkaline media with methyl tert-butyl ether (MTBE) and tetrabutylammonium hydrogen sulfate. After further concentration the extracts were analysed with LC-MSMS [2, 3].

Food samples of animal origin were homogenised and analysed after a liquid/liquid extraction with acetonitrile with LC-MSMS [2, 4].

The scope included short and long chain perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl carboxylic acids (PFSAs) (see table 2).

**Table 2: Food samples of plant and animal origin were analysed for these compounds.**

| | | | |
|---|---|---|---|
| PFBA | perfluorobutanoic acid | PFHxS | perfluorohexane sulfonate |
| PFBS | perfluorobutane sulfonate | PFNA | perfluorononanoic acid |
| PFDA | perfluorodecanoic acid | PFOA | perfluorooctanoic acid |
| PFDoDA | perfluorododecanoic acid | PFOS | perfluorooctane sulfonate |
| PFDS | perfluorodecane sulfonate | PFPeA | perfluoropentanoic acid |
| PFHpA | perfluoroheptanoic acid | PFTeDA | perfluorotetradecanoic acid |
| PFHpS | perfluoroheptane sulfonate | PFTrDA | perfluorotridecanoic acid |
| PFHxA | perfluorohexanoic acid | PFUnA | perfluoroundecanoic acid |

**Results and discussion**

*Comparison of pre-harvest plant samples and food samples from the contaminated area*

In plants grown on the contaminated soils mainly perfluoro-butanoic acid (PFBA), perfluoro-n-pentanoic acid (PFPeA) and perfluorohexanoic acid (PFHxA) were found. To ensure low concentrations of PFAS in food on the market a program to monitor levels of PFCAs in fruit and plants before harvest was started ([5], figure 1).

The pre-harvest tests are important for farmers and consumers. It can minimize the financial losses for farmers, for example, by avoiding additional labour costs for harvesting and it can increase the trust of the consumers in the safety of the products. For example asparagus and strawberries are often sold directly at the farms. The costumers from the region may be unsure about the PFAS contamination and will probably not buy the local products.

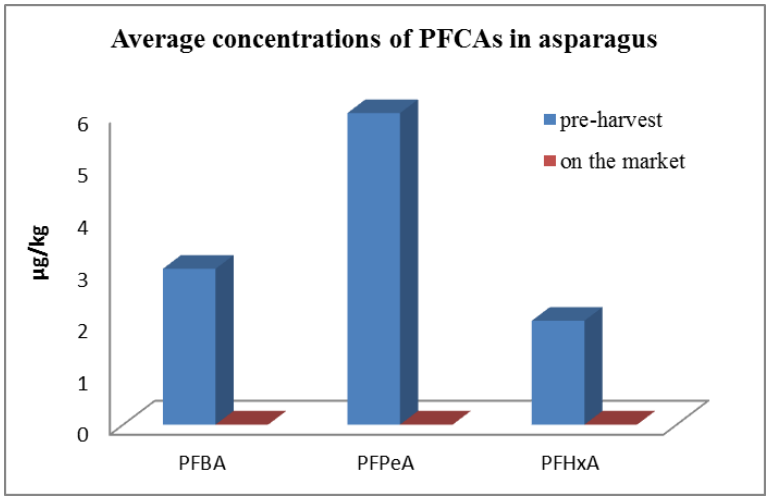


**Figure 1: Comparison of 38 pre-harvest asparagus and 37 food samples of asparagus from the contaminated area (pre-harvest data from Agriculture Center of Technologie Augustenberg - LTZ).**

Asparagus absorbs short chain PFCAs from contaminated water and/or soil. The results of the food monitoring show that the system of testing before harvesting works as the marketed food had only negligible concentrations of PFCAs. The combination of pre-harvest and food monitoring offers a high degree of safety for the public.

*Comparison of food samples from the contaminated area and other areas (Germany and other European countries)*
Since the contamination of short chain PFCAs was discovered in the south-western part of the state of Baden-Wuerttemberg, the question was whether it was only a regional or a worldwide problem. To clarify this question fruit and vegetables from other areas in Baden-Wuerttemberg, Germany and Europe were analysed.
There are no findings of elevated levels of short chain PFCAs from other area under cultivation in Germany and Europe. The contamination with short chain PFCAs is typical for the contamination incident in the south-western part of the state of Baden-Wuerttemberg.

*Comparison of food samples of animal origin from the contaminated area and other areas (Germany and other countries worldwide)*
The analysis of food of animal origin from the contaminated region should ensure that there was no incorporation of short chain PFCAs through contaminated feed or water. The analysis of PFCAs in meat, milk and eggs from the contaminated region showed no elevated levels. Fish from lakes in the contaminated area did not contain short chain PFCAs, although short chain PFCAs could be detected in the water. The findings of long chain PFAS in the fish were noticeable. Two lakes in the contaminated area showed higher contents of PFOS in fish (figure 3).

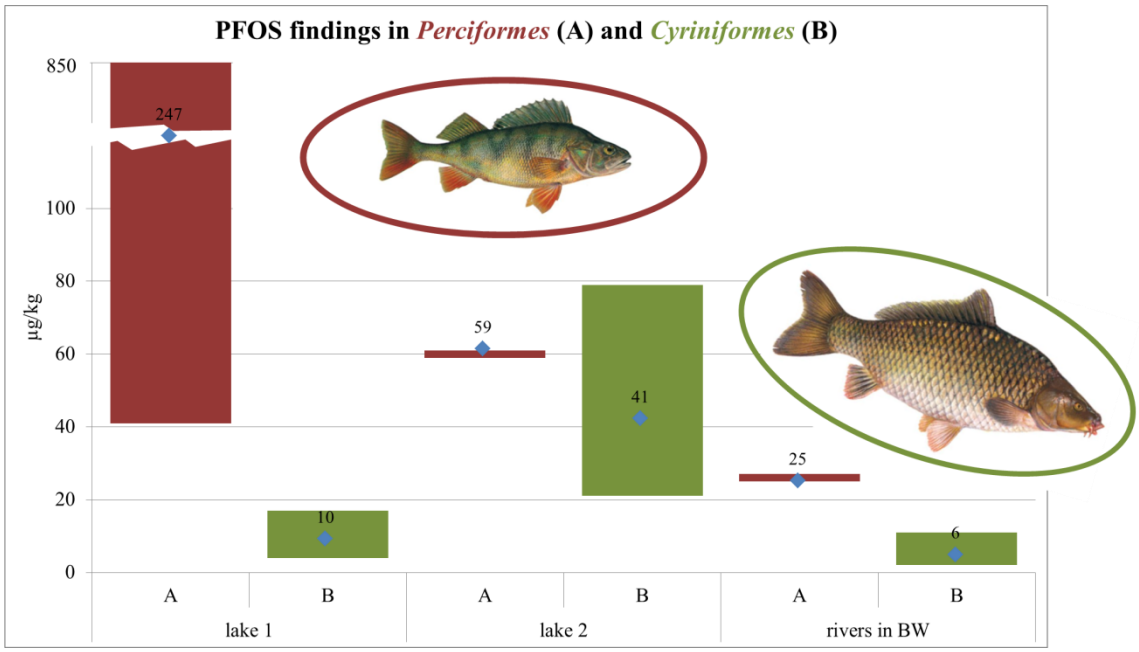


**Figure 3: PFOS findings (maximum, minima and average) in fish filet (order of *Cyriniformes* (20 samples) and *Perciformes* (11 samples), [6]) of different water bodies in Baden-Wuerttemberg (BW).**

There was no apparent correlation between the found concentrations of PFOS and the age/size of the fish, but between concentration of PFOS and the order of the fish (*Cyriniformes* and *Perciformes*). Comparative analyses of fish from other regions of Baden-Wuerttemberg showed lower levels of PFOS (< 30 µg/kg). Fish of the order of *Perciformes* showed very high concentrations (up to 850 µg/kg) in lake 1 and lower concentrations (< 60µg/kg) in lake 2 as well as rivers outside the contaminated area in Baden-Wuerttemberg. In contrast, the

fish of the order *Cyriniformes* show generally lower concentrations in the analysed samples (< 80 µg/kg). It is possible that the different diet of the two fish species have a strong influence on the contamination level. Fish of the order *Cyriniformes* are searching for food (plants, insects and zooplankton) at the ground of the see. Fish of the order Perciformes predominantly eat smaller fish. The higher concentration of PFOS in predatory fish may be related to a possible food-chain accumulation.
On the basis of the existing data, no conclusion can be drawn whether the high load of PFOS in this lake is associated with the contamination incident or whether an additional source of contamination is involved.

**Acknowledgements**
We would like to acknowledge the good cooperation of the colleagues from the following authorities in Baden-Wuerttemberg: Regierungspraesidium Karlsruhe; Landesanstalt für Umwelt, Messungen und Naturschutz Baden-Wuerttemberg; Lebensmittelueberwachung von Baden Baden, Mannheim und Rastatt; Landwirtschaftliches Technologiezentrum Augustenberg (LTZ) Chemisches und Veterinaeruntersuchungsamt Freiburg.

**References**
1. https://rp.baden-wuerttemberg.de/rpk/Abt5/Ref541/PFC/Seiten/default.aspx
2. Radykewicz T, Schmitt M, Thoma K, Hansert F, Lippold R (2016) chrom+food FORUM 09 32-34.
3. www.ua-bw.de/uploaddoc/cvuafr/lab31_PFAS_pflanz.pdf
4. www.ua-bw.de/uploaddoc/cvuafr/lab31_PFAS_tier.pdf
5. Radykewicz T, Lippold R, Steemann X, Nagel T, Breuer J, Zosak M (2016) Proceedings of Dioxin 2016 (Cod: S8.6006), http://www.eurl-freiburg.eu/dioxin/doc/PFAS_Florenz2016.pdf
6. Picture: wall chart – VDSF Verband Deutscher Sportfischer e.V.