PERFLUORINATED COMPOUNDS AND ADONA IN BLOOD SAMPLES NEAR A FORMER PFOA PRODUCTION PLANT IN GERMANY

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Introduction

Perfluorinated or polyfluorinated compounds (PFAS) are anthropogenic substances consisting of an alkyl chain with hydrogen atoms replaced completely or partially by fluorine. These chemicals have been used in various products, applications, and industrial processes because of their chemical and thermal stability, low surface free energy and surface activity properties. There is evidence from numerous investigations that compounds such as perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are persistent in the environment and show different adverse effects especially to liver, development and immune system in experimental animals [1,2]. Again, epidemiological studies have found positive associations of blood levels and parameters of e.g. lipid metabolism, thyroid hormones, birth weight and immunity in the general population, especially in communities exposed through contaminated drinking water or in highly exposed workers [3-6]. Therefore these compounds are replaced. One PFOA substitute is 3H-perfluoro-3-[(3-methoxy-propoxy)propanoic acid] ammonium salt (ADONA) used in the study area in the production of fluoropolymers. Toxicological data for ADONA are limited, but seems to be less critical than those of PFOA[7,8].

The objective was to quantify the concentrations of eight PFAS and ADONA in subjects living next to a former PFOA production plant, where PFOA was used as an intermediate in the fluoropolymer production until 2008. Due to the contamination of soil and ground water, people were exposed over years via drinking water with higher levels of PFOA from 0.08 to 0.34 µg/l in contrast to a typical exposure of <0.001 µg/l in not contaminated drinking water facilities in the control region.

Materials and methods

Overall, 953 blood serum samples were collected on a voluntary basis in the contaminated area in 2018 from donors 3 months to 85 years old (median: 49 years). Additionally, 158 blood samples collected in 2016 in Munich served as a control group. Two times 200 µl of pooled human serum containing 2 ng/ml of every standard were injected using an online extraction LC-MS/MS system with a triple-stage quadrupole mass spectrometer. The limits of quantification (LOQ) were 0.25 µg/l for all target analytes.

Results and discussion:

The statistical parameters of the measurements are given in Table 1. We were able to quantify PFOA in all and PFOS in nearly all serum samples, while PFNA, PFHxS, and PFDA could be quantified in 93%, 83%, and 51% of the samples, respectively. ADONA were quantifiable only in three out of 953 samples with a maximum of 1.0 µg/l.

Figure 1 shows the single PFOA measurements in relation to sex. As expected, significant higher levels were found for male subjects compared to female for the five most abundant compounds (mean: PFOA 25.9 vs. 23.2 µg/l; PFOS: 2.7 vs. 2.1 µg/l).

In Figure 2 the mean values for each year of life and a smooth line using LOWESS (Locally Weighted Scatterplot Smoothing) correction were given. Higher levels were observed during infancy for children 1 to 8 years old and again an increasing tendency of PFOA means for subjects older than 40 years. Compared to our control region clearly higher levels were observed for PFOA. Whilst in the contaminated region medians and 95th percentiles of 19.9 µg/l and 57.5 µg/l PFOA were observed, respectively, in Munich the values were only 1.1 µg/l and 2.4 µg/l.

In Figure 3 the blood levels of subjects living in six drinking water distribution regions were given. Both within the six groups and compared to the control region subsequent differences were found. It could be concluded that small-scaled information of the contamination situation is essential for a proper exposure and risk assessment.

Based on the results of epidemiologic studies the German Human Biomonitoring Commission (HBM Commission), derived HBM I values of 2 µg PFOA/l and 5 µg PFOS/l blood plasma [9]. The HBM I value represents the concentration of a substance in human biological material below which no risk for adverse health effects over life time is expected. The HBM I value of 5 µg/l for PFOS was exceeded by approximately 8% in the contaminated sites and 7% in the control region. For PFOA 11% of the samples exceeded the HBM I value of 2 µg/l at the control site, while at the contaminated site A-F 99% of the samples exceeded the HBM I value of PFOA, respectively.

Table 1: Statistical parameters of pefluorinated substances and ADONA in blood samples

	PFOS	PFOA	PFNA	PFDA	PFDoA	PFHxA	PFHxS	PFBS	ADONA
All (N: 953)									
N>LOQ	939	953	891	484	37	19	787	144	3
Mean	2.35	24.43	0.68	0.36	0.14	0.13	0.58	0.16	0.13
Median	1.76	19.90	0.53	0.25	0.13	0.13	0.49	0.13	0.13
95th percentile	6.07	57.53	1.46	1.05	0.13	0.13	1.27	0.35	0.13
Maximum	18.60	159.39	15.06	7.53	0.70	1.88	9.06	0.98	1.01
Female (N: 536)									
N>LOQ	527	536	490	256	18	8	392	72	1
Mean	2.06	23.23	0.59	0.33	0.13	0.13	0.42	0.15	0.13
Median	1.53	17.72	0.49	0.13	0.13	0.13	0.37	0.13	0.13
95th percentile	5.08	57.27	1.40	0.97	0.13	0.13	0.97	0.35	0.13
Maximum	15.00	128.61	4.14	4.76	0.68	1.47	2.32	0.76	1.01
Male (N: 417)									
N>LOQ	412	417	401	228	19	11	395	72	2
Mean	2.73	25.98	0.78	0.41	0.14	0.14	0.78	0.16	0.13
Median	1.99	20.99	0.60	0.27	0.13	0.13	0.69	0.13	0.13
95th percentile	7.41	57.77	1.61	1.23	0.13	0.13	1.56	0.33	0.13
Maximum	18.60	159.39	15.06	7.53	0.70	1.88	9.06	0.98	0.36

N: number; LOQ: limit of quantification

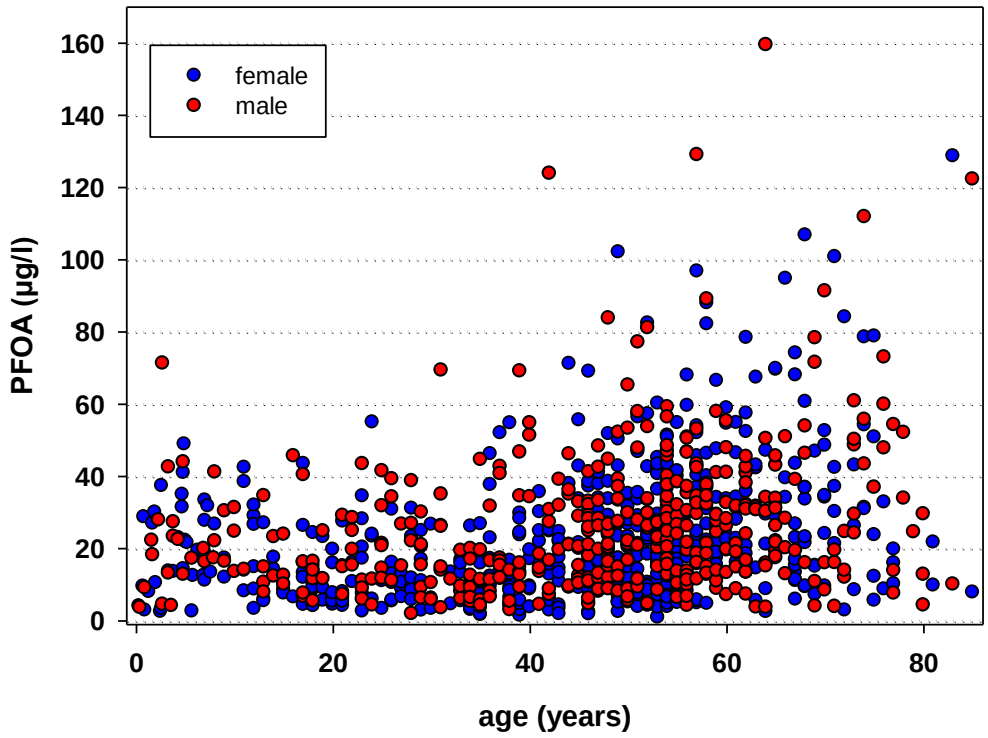

Figure 1: Single PFOA measurements

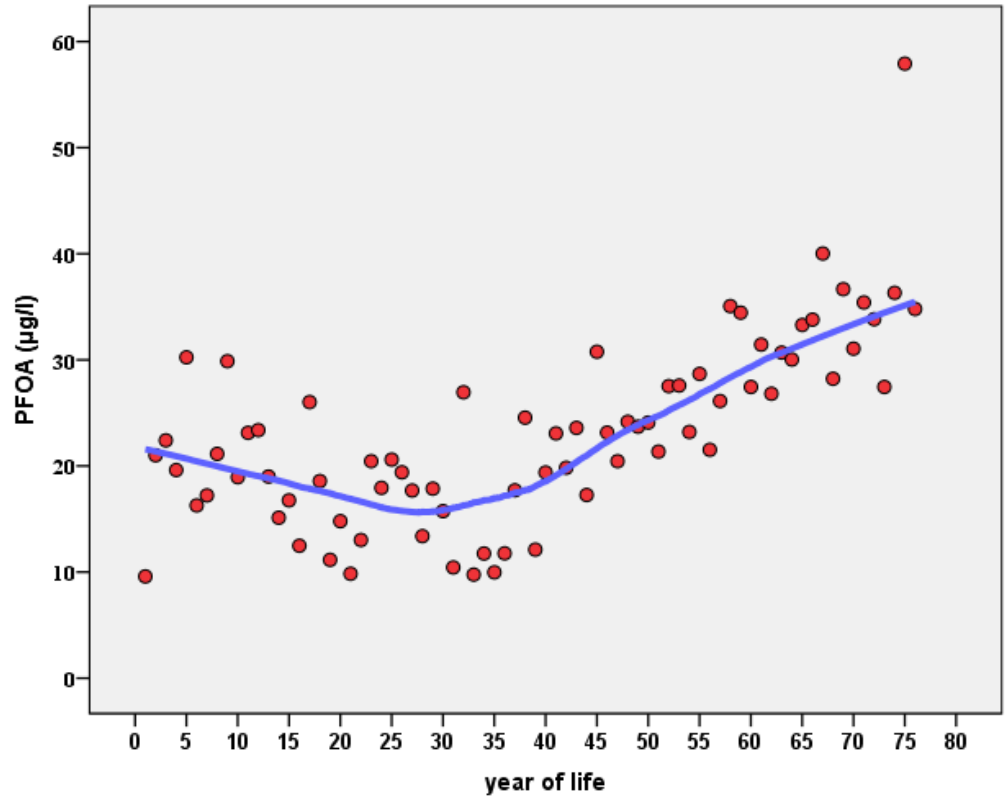

Figure 2: Mean values for each year of life (line prepared using lowess correction; values >75 years were transformed to one mean value)

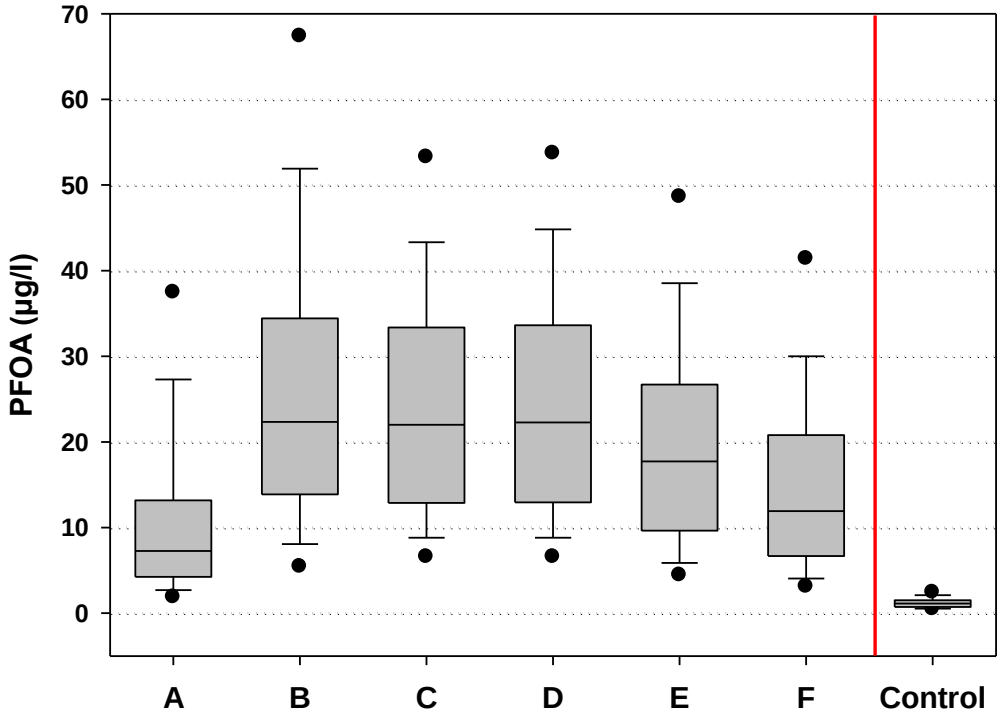

Figure 3: Box plots of PFOA in six drinking water distribution regions (A-F) in 2018 and in a control region in 2016 (5th, 10th, 25th, 50th, 75th, 90th, and 95th percentiles)

Acknowledgements:
The project was funded by a grant from the Bavarian State Ministry of Public Health and Care.

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